Investigating The Influence Of Gold Nanoparticles On The Photocatalytic And Catalytic Reactivity Of Porous Tungsten Oxide Microparticles

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INVESTIGATING THE INFLUENCE OF GOLD NANOPARTICLES ON THE
PHOTOCATALYTIC AND CATALYTIC REACTIVITY OF
POROUS TUNGSTEN OXIDE MICROPARTICLES

A Dissertation Presented

by

Daniel P. DePuccio

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of

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ABSTRACT

Tungsten oxide (WO$_3$) is a semiconducting transition metal oxide with interesting electronic, structural, and chemical properties that have been exploited in applications including catalysis, gas sensing, electrochromic displays, and solar energy conversion. Nanocrystalline WO$_3$ can absorb visible light to catalyze heterogeneous photooxidation reactions. Also, the acidity of the WO$_3$ surface makes this oxide a good thermal catalyst in the dehydration of alcohols to various industrially relevant chemicals. This dissertation explores the photocatalytic and thermal catalytic reactivity of nanocrystalline porous WO$_3$ microparticles. Furthermore, investigations into the changes in WO$_3$ reactivity are carried out after modifying the porous WO$_3$ particles with gold nanoparticles (Au NPs). On their own, Au NPs are an important class of materials that have had a large impact in many fields such as catalysis, biomedical imaging, and drug delivery. When combined with WO$_3$, however, their influence as part of a composite Au/WO$_3$ catalyst has not been widely studied.

Porous WO$_3$ microparticles were first prepared using mesoporous silica (SiO$_2$) spheres as hard templates and the physical properties of these materials were fully characterized. A facile sonochemical method was used to deposit Au NPs on the WO$_3$ surface. Using methylene blue (MB) as a photocatalytic probe, the reaction products and the catalytic activity of WO$_3$ and Au/WO$_3$ catalysts were compared. Composite Au/WO$_3$ photocatalysts exhibited significantly greater rates of MB degradation compared to pure WO$_3$. Interestingly, the observed mechanism of MB degradation was not vastly different between the two types of catalysts.

The gas-phase photocatalytic oxidation of methanol (MeOH) was studied to further understand the role of WO$_3$ and Au NPs in these photocatalysts. Porous WO$_3$ showed greater photooxidation rates compared to bulk WO$_3$ because of its increased active surface area. Pure WO$_3$ and Au NPs on porous SiO$_2$ (SiO$_2$-Au) were both active MeOH photooxidation catalysts and were highly selective to formaldehyde (HCHO) and methyl formate (MF), respectively. Two different mechanisms, namely band gap excitation of WO$_3$ and surface plasmon resonance (SPR) on Au NPs, were responsible for this result. Again, the Au/WO$_3$ composite catalysts showed greater photocatalytic activity than WO$_3$, which increased with Au loading. This high activity led to the complete photooxidation of MeOH to carbon dioxide (CO$_2$) over Au/WO$_3$ catalysts.

Finally, the thermal catalytic transformation of MeOH under aerobic conditions was carried out to further characterize the acid and redox active sites of WO$_3$ and Au/WO$_3$ catalysts. Pure WO$_3$ was highly selective for MeOH dehydration to dimethyl ether (DME), whereas Au/WO$_3$ showed increased oxidation selectivity to products such as HCHO, FM, and CO$_x$. The Au NPs increased the reducibility of the WO$_3$ species, which made surface oxygen atoms more labile and reactive towards MeOH. Also, the WO$_3$ facilitated the formation of cationic Au (Au $\delta^+$) species. This combination of effects created through a strong Au/WO$_3$ interaction increased the activity of WO$_3$ species, but it decreased the activity of the Au NPs.
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<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>CMC</td>
<td>critical micelle concentration</td>
</tr>
<tr>
<td>CMK</td>
<td>Carbon Mesostructured by KAIST</td>
</tr>
<tr>
<td>CTAB</td>
<td>cetyltrimethyl ammonium bromide</td>
</tr>
<tr>
<td>DME</td>
<td>dimethyl ether</td>
</tr>
<tr>
<td>DMM</td>
<td>dimethoxymethane</td>
</tr>
<tr>
<td>$d_{\text{pore}}$</td>
<td>pore diameter</td>
</tr>
<tr>
<td>$d$-spacing</td>
<td>interplanar spacing</td>
</tr>
<tr>
<td>EDS</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EISA</td>
<td>evaporation-induced self-assembly</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>electrospray ionization mass spectrometry</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Name</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>FM</td>
<td>formaldehyde</td>
</tr>
<tr>
<td>HCHO</td>
<td>formaldehyde</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>high-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>KIT</td>
<td>Korea Advanced Institute of Science and Technology (KAIST)</td>
</tr>
<tr>
<td>m/z</td>
<td>mass to charge ratio</td>
</tr>
<tr>
<td>MB</td>
<td>methylene blue</td>
</tr>
<tr>
<td>MCM</td>
<td>Mobil Composition of Matter</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>MF</td>
<td>methyl formate</td>
</tr>
<tr>
<td>ROS</td>
<td>reactive oxygen species</td>
</tr>
<tr>
<td>SABET</td>
<td>BET surface area</td>
</tr>
<tr>
<td>SBA</td>
<td>Santa Barbara Amorphous</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SiO₂</td>
<td>silica</td>
</tr>
<tr>
<td>SPR</td>
<td>surface plasmon resonance</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TCD</td>
<td>thermal conductivity detector</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>tetraethoxysilane</td>
</tr>
<tr>
<td>Th</td>
<td>thionine</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>TMO</td>
<td>transition metal oxide</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature-programmed desorption</td>
</tr>
<tr>
<td>TPR</td>
<td>temperature-programmed reduction</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>$V_{pore}$</td>
<td>pore volume</td>
</tr>
<tr>
<td>W/F</td>
<td>contact time</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>tungsten oxide</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
CHAPTER 1: INTRODUCTION TO MESOPOROUS METAL OXIDE CATALYSTS

1.1. Porous Materials

Porous materials can exist in many different elemental compositions. These materials are primarily defined by the size of the pore openings contained within the nanoparticles. According to the International Union of Pure and Applied Chemistry (IUPAC), there are three classes of porous materials based on the size of the pore diameters: microporous (< 20 Å), mesoporous (20 – 500 Å), and macroporous (> 500 Å).\(^1\) Since the discovery of mesoporous silicates by researchers at Mobil in the early 1990s,\(^2\) these materials have been widely studied due to their unusual physical properties, such as large surface areas (> 1000 m\(^2\) g\(^{-1}\)) and large pore volumes compared to their microporous and dense counterparts. These features have driven the development of mesoporous materials for numerous applications including heterogeneous catalysis, separations, chemical sensing, and drug delivery. This dissertation will focus on the synthesis, characterization, and catalytic applications of mesoporous particles composed of silica (SiO\(_2\)), transition metal oxides, and noble metal nanoparticles.

1.2. Synthesizing Mesoporous Oxides

There are two main preparation methods to develop mesoporous oxides. Depending on the desired composition and properties of the materials, soft-templating or hard-templating strategies are used. Mesoporous silica is prepared using soft-
templating methods, and transition metal oxides are commonly prepared using hard-templating techniques.

1.2.1. Soft Templating of Mesoporous Silica

Soft templates are typically micelles formed by ionic\textsuperscript{3,4} or non-ionic\textsuperscript{5} organic surfactants, which control the pore morphology of the resulting mesoporous SiO\textsubscript{2} particles (that can be derived from various silicate precursors). Soft templating takes advantage of the simultaneous self-assembly and condensation of SiO\textsubscript{2} and surfactant species in either acidic or basic solution. Depending on the reaction conditions, electrostatic, hydrogen-bonding, or van der Waals interactions around the silica-surfactant interface control this process.\textsuperscript{5,6} As shown in Table 1-1, there are four proposed self-assembly pathways controlled by electrostatics, which involve cationic or anionic surfactants (S) and inorganic species (I). In some cases, counterions are necessary to mediate the interaction of similarly charged surfactants and inorganic species.\textsuperscript{7}

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Surfactant (S) Charge</th>
<th>Inorganic Species (I) Charge</th>
<th>Counterion Mediation\textsuperscript{a}</th>
<th>Ion Assembly</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S\textsuperscript{+}</td>
<td>\textit{I}</td>
<td>none</td>
<td>(S\textsuperscript{+} I)</td>
</tr>
<tr>
<td>2</td>
<td>S\textsuperscript{-}</td>
<td>I\textsuperscript{+}</td>
<td>none</td>
<td>(S I\textsuperscript{+})</td>
</tr>
<tr>
<td>3</td>
<td>S\textsuperscript{+}</td>
<td>I\textsuperscript{+}</td>
<td>X\textsuperscript{-}</td>
<td>(S\textsuperscript{+} X I\textsuperscript{+})</td>
</tr>
<tr>
<td>4</td>
<td>S\textsuperscript{-}</td>
<td>I</td>
<td>M\textsuperscript{+}</td>
<td>(S M\textsuperscript{+} I)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}X\textsuperscript{-} = Cl\textsuperscript{-} or Br\textsuperscript{-}; M\textsuperscript{+} = Na\textsuperscript{+} or K\textsuperscript{+}

The Mobil Composition of Matter (MCM) family of mesoporous molecular sieves was synthesized by pathway 1 using silicate or aluminosilicate gels (I) in a
concentrated solution of alkyltrimethylammonium ions (S\(^+\)) under basic conditions. Modifications of these preparation methods have produced the well-studied mesoporous MCM-41 and MCM-48, which have hexagonal and cubic pore structures, respectively (Figure 1-1).\(^8,9\) Although the pores are highly ordered in these examples, it is important to note that the pore walls of these materials are amorphous (i.e. the atomic-level ordering is non-crystalline).

![Figure 1-1. Pore structures of MCM-41 and MCM-48 mesoporous SiO\(_2\). Figure modified from reference 10.](image)

In this dissertation, mesoporous SiO\(_2\) possessing a disordered pore structure was prepared via pathway 3 under acidic conditions. Known as acid-prepared mesoporous spheres (APMS),\(^{11-14}\) these particles are synthesized using cationic cetyltrimethyl ammonium bromide (CTAB, \(\text{CH}_3(\text{CH}_2)_{15}\text{N(CH}_3)_2\text{Br}\)) and tetraethoxysilane (TEOS, Si(OEt)\(_4\)) as the surfactant and silicate source, respectively. When combined in aqueous solution with HCl, the silicate precursor readily hydrolyzes and the cationic SiO\(_2\) oligomers self-assemble with surfactant species by counterion mediation provided by Cl\(^-\). Further condensation of SiO\(_2\) around the surfactant yields mesostructured particles. The surfactant can then be removed via solvent extraction or high temperature calcination (> 500 °C) to create the accessible pore network (Figure 1-2).
Figure 1-2. APMS mesoporous structure formation via electrostatic self-assembly, SiO₂ condensation, and surfactant removal by calcination.

A combination of hydrogen bonding and electrostatics between non-ionic block copolymer surfactants and silica oligomers was utilized to develop the Santa Barbara Amorphous (SBA) class of mesoporous silica.⁵,¹⁵ Specifically, SBA-15 has been the most extensively researched phase. Its larger (50 – 300 Å) hexagonal pore structure and thicker pore walls compared to MCM-41 provide greater pore stability under high temperatures and pressures.

1.2.2. Soft Templating of Mesoporous Transition Metal Oxides

As shown above, the soft-templated formation of mesoporous SiO₂ can be carried out with great control of the self-assembly and SiO₂ condensation steps, leading to highly structured mesophases (Figure 1-3). Extension of these methods to other
compositions of mesoporous materials, including transition metal oxides (TMOs), has met with varying degrees of success, however. Initial studies involved water soluble TMO precursors like ammonium metatungstate ((NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$)) and potassium hexahydroxoantimonate (KSb(OH)$_6$) that self-assembled with low molecular weight ionic surfactants based on charge-matching principles.$^{7,16}$ Similar to SiO$_2$ materials, well-ordered TMO-surfactant phases were formed, but upon surfactant removal, many of these mesoporous TMOs were not stable and their pore structures collapsed. The instability of mesoporous TMOs originated from the changes in TMO crystallinity and/or redox reactions that occurred during the calcination of TMO precursors. Importantly, the pore walls of TMOs cannot usually withstand the curvature of the mesopores during recrystallization, resulting in bulk TMOs after the pores collapse.$^{17}$ Also, incomplete condensation of the TMO precursor during the self-assembly process led to unstable mesostructures. For mesoporous SiO$_2$ materials, no major structural changes occur after the silicate precursor polymerizes around the surfactant micelle. Thus, the SiO$_2$ pores are very stable during the template removal process.

![Figure 1-3](image.png)

**Figure 1-3.** Transmission electron micrograph of mesoporous SBA-15 SiO$_2$ with a hexagonal pore structure aligned (a) perpendicular to the page and (b) parallel to the page. Figure modified from reference 18.
Modified sol-gel\textsuperscript{19-21} processes were soon used to successfully create several mesoporous TMOs including TiO\textsubscript{2},\textsuperscript{22} ZrO\textsubscript{2},\textsuperscript{23} and Ta\textsubscript{2}O\textsubscript{5}.\textsuperscript{24} In a general sol-gel condensation mechanism, metal alkoxide TMO precursors readily hydrolyze in aqueous solutions (EQ.1) and then hydroxylated species condense with additional metal alkoxides to form polymers (EQ.2).\textsuperscript{21}

\[
\text{M—OR} + \text{H}_2\text{O} \rightarrow \text{M—OH} + \text{ROH}
\]

\[
\text{M—OH} + \text{RO—M} \rightarrow \text{M—O—M} + \text{ROH}
\]

These reactions are forms of nucleophilic substitutions between M(OR)\textsubscript{n} and mXOH species, where X = “H” for hydrolysis or “M” for condensation (Figure 1-4). Step 1 involves the nucleophilic addition of the HO\textsuperscript{δ−} moiety onto the M\textsuperscript{δ+} atom. The second step is a proton transfer to the OR group, which is then followed by the elimination of the ROH ligand from the metal oxide species in step 3. Most of these materials possessed non-crystalline frameworks and small pores (< 4 nm) upon surfactant removal.

**Figure 1-4.** Reaction mechanisms involved in the hydrolysis and condensation of metal alkoxide precursors. Definitions and reaction step descriptions found in text. Figure modified from reference 21.
Mesoporous TMOs with large, crystalline pore walls were developed by the evaporation-induced self-assembly (EISA) method (Figure 1-5). Surfactant and inorganic precursors in alcohol solutions are required for successful soft templating by EISA. Upon evaporation of the solvent, surfactant aggregates form at the critical micelle concentration (CMC), and with further drying, crystalline mesostructures form.25,26 Controlling the relative humidity during the drying of the mixture allows for modification of the mesostructure before the inorganic phase is completely condensed.27 Importantly, the rate of inorganic condensation dictates the final pore structure. When the rate of condensation is too fast, disordered pore structures are created, or precipitation of undesirable dense inorganic phases can occur.28

![Diagram](image.png)

**Figure 1-5.** Evaporation-induced self-assembly (EISA) of an inorganic mesoporous framework. Figure modified from reference 26.

The EISA method has produced several large pore mesoporous TMOs. Most notably, Stucky and coworkers29,30 used ethanol, metal chloride salts, and the block copolymer, Pluronic P123, which is a poly(ethylene) oxide – poly(propylene) oxide – poly(ethylene) oxide (PEO20-PPO70-PEO20) polymer with terminating primary hydroxyl groups. In the presence of Pluronic P123, this non-hydrolytic sol-gel route31-33
(Figure 1-6) was applied to TMOs with crystalline walls composed of TiO$_2$, ZrO$_2$, Nb$_2$O$_5$, WO$_3$, and SnO$_2$ and pore sizes from 3 – 7 nm.$^{30}$ In this case, the metal chloride (MCl) is reacted with an alcohol ligand, eliminating HCl, and then further condensation of the M—OR species with MCl leads to metal oxide polymerization.

![Figure 1-6. The non-hydrolytic sol-gel mechanism to produce metal oxide polymers. Figure modified from reference 32.](image)

The wide applicability of this method to several TMOs suggested a similar coordination and reaction mechanism for these materials. Metal ions can form crown ether-type complexes with the oxygen atoms on the polymer. Then, the hydrophilic PEO species become associated with the hydrolyzed metal oxide species (Figure 1-7) that further polymerize to form the inorganic-surfactant mesophase.

![Figure 1-7. Metal oxide species associated with hydrophilic poly(ethylene oxide) species of the block copolymer surfactant. Figure modified from reference 29.](image)
1.2.3. Hard Templating of Mesoporous Transition Metal Oxides

It is clear that the soft-templating techniques described above necessitate very careful control of the hydrolysis rate, the degree of inorganic cross-linking, the ratio of surfactant to inorganic oligomer, humidity, and evaporation conditions. These all have significant effects on the structure of the final mesostructure.\textsuperscript{34} For example, incomplete condensation of the inorganic framework, redox-unstable structures, or the inability of the pores to contain the newly crystallized metal oxide can lead to mass transfer and cause the collapse of the pore structure.\textsuperscript{17,35} Also, upon calcination treatments at temperatures $> 400 \, ^\circ\text{C}$, some soft-templated metal oxides lose their porosity because of changes in crystallinity and uncontrollable growth of metal oxide crystallites.\textsuperscript{36} It is advantageous for these materials to retain large porous structures to allow greater mass diffusion through the particles. Also, crystalline mesoporous TMOs exhibit intrinsic electronic functionality,\textsuperscript{17} which make these materials promising in catalysis,\textsuperscript{37} gas sensing,\textsuperscript{38} and electrochemistry.\textsuperscript{39} Photocatalysis, which is the major application studied in this dissertation, necessitates good charge transport through crystalline frameworks for favorable reactivity. Crystalline materials with fewer defects will enable diffusion of electrons and holes to the surface of the catalyst to initiate photochemical reactions.\textsuperscript{40} The lack of highly crystalline porous TMOs prepared via soft templating increases the need for alternative methods for improved mesoporous TMO crystallinity. This issue has been addressed mainly through a hard-templating route.

The hard-templating process, or nanocasting,\textsuperscript{34,35,41} was introduced by Ryoo and coworkers in 1999.\textsuperscript{42} This is a method that eliminates the difficulties of the soft-
templating techniques to form mesoporous and crystalline TMOs. Here, a pre-formed mesoporous hard template, usually composed of SiO$_2$ (i.e. MCM-41, MCM-48, SBA-15, KIT-6) or pyrolized carbon (i.e. CMK-3), is used to “cast” the mesoporous TMO of choice. The hard template can withstand high temperatures (> 500 °C) without losing mesoporosity, which facilitates the formation of crystalline metal oxides within the rigid pores. Typically, the resulting mesoporous TMO replicates the pore structure of the hard template. The porous template is first infiltrated with an aqueous or ethanolic solution of the TMO precursor salt. Upon evaporation of the solvent, the dry impregnated template undergoes a calcination treatment to convert the salt to the respective TMO. To improve the fidelity of the resulting pore structure, repeated impregnation and heat treatments are commonly used. Finally, hydrofluoric acid or hydroxide solutions are used to selectively remove the SiO$_2$ template from the SiO$_2$-TMO composite, which results in the pure mesoporous TMO replica (Figure 1-8).

**Figure 1-8.** Summary of the hard-templating process to form mesoporous transition metal oxides using (A) hexagonal and (B) cubic mesoporous silica templates. Figure taken from reference 43.
Mesoporous TMOs such as Fe$_2$O$_3$, MgO, Co$_3$O$_4$, MnO$_2$, In$_2$O$_3$, CeO$_2$, TiO$_2$, and SnO$_2$ have all been prepared using this general hard-templating process. Successful replication of the template, however, depends on variables such as the template pore structure, the TMO precursor interaction with the pore surface, and the infiltration technique.

The structure of the resulting porous TMO replica prepared through hard templating is greatly affected by the pore structure of the starting template. An interconnected pore structure is typically necessary for successful replication. For example, KIT-6 and SBA-15 possess 3D interconnected cubic and hexagonal pore channels, respectively. Replicated TMOs from these structures retain the morphology of the template pores because the TMO precursor can diffuse throughout the entire pore system of the nanoparticles during the impregnation step. Templates such as MCM-41 and SBA-15 synthesized at lower temperatures (80 °C) however, have 2D pore channels that are not connected to one another. Therefore, the resulting TMO may resemble individual rods after the template is removed from the composite (Figure 1-9).
Choosing a suitable TMO precursor and recognizing its interaction with the pore surface is crucial to the hard-templatting process. First, the TMO precursor needs to be highly soluble in solution or melt at a relatively low temperature. Aqueous or ethanolic solutions of metal salts such as nitrates are commonly used in nanocasting.\textsuperscript{55} Capillary forces at the nanometer scale drive the inclusion of the precursor solution into the template pores, which, in the case of SiO\textsubscript{2}, possess surface silanols (Si–OH) that can interact with the hydrophilic precursor solution via hydrogen bonding or electrostatics.\textsuperscript{56} Functionalization of the silica pore walls with amines and other coordinating moieties is a commonly used strategy to increase the degree of precursor pore filling in some nanocasting processes.\textsuperscript{57} Increased precursor adsorption due to these favorable interactions with the functionalized pores of the template can improve the replication by the metal oxide.

\textbf{Figure 1-9.} (A) High-resolution SEM image of porous Co\textsubscript{3}O\textsubscript{4} replicated from KIT-6 silica with interconnected pores\textsuperscript{47} and (B) TEM image of MoO\textsubscript{2} rods templated from SBA-15 with no pore interconnections.\textsuperscript{54} Figure created from those found in references 47 and 54.
Infiltration of the pores by the TMO precursor is followed by solvent evaporation, drying, and decomposition/conversion of the precursor species. During drying and heating, the precursor redistributes itself throughout the pore surfaces of the template particles. Heating decomposes the precursor salt and initiates the transformation to the final TMO structure. These drying, redistribution, and decomposition events are different depending on the TMO precursor, and have only recently gained attention in the hard-templatizing literature. For example, Smått and coworkers studied the impregnation of SBA-15 with ethanolic Ni(NO$_3$)$_2$ • 6H$_2$O via techniques such as X-ray diffraction, in-situ small-angle X-ray scattering, and nitrogen physisorption. After initial impregnation and drying of the precursor solution under vacuum, the Ni nitrate became slightly dehydrated and the species was present both inside and outside of the pores (Figure 1-10, step 1). Increasing the temperature induced the dissolution of the Ni nitrate precursor by waters of hydration and complete backfilling of the pores occurred through capillary forces (Figure 1-10, step 2). Dissolved dehydrated Ni nitrate then solidified, which stopped the backfilling of the pores. This left precursor species inside the pores and at the pore entrances (Figure 1-10, step 3). At temperatures of ~250 °C, the final NiO species formed and the significant volume contraction related to NiO formation led to completely filled pores and also completely empty pores (Figure 1-10, step 4). Thus, multiple impregnation steps were necessary to sufficiently fill the template pore structure. It is clear that the drying and decomposition temperatures play a large role in the final TMO crystallites location within the porous template. The composition of the gas and even the type of container used during these steps affect the mobility of the impregnated TMO
precursors. Therefore, much is still being learned about controlling these process parameters to optimize template pore filling.

![Diagram of the structural and chemical changes observed during the drying and conversion of Ni(NO₃)₂ • 6H₂O impregnated within SBA-15 pores.](image)

**Figure 1-10.** The structural and chemical changes observed during the drying and conversion of Ni(NO₃)₂ • 6H₂O impregnated within SBA-15 pores. Figure modified from reference 58.

Finally, once the SiO₂-TMO composite is created, the last step in acquiring a nanocast TMO involves the removal of the SiO₂ template. This etching process involves the selective dissolution of SiO₂ in HF or hydroxide solutions. It is important, however, that the TMO of interest is compatible with the acidic or basic medium and will not dissolve during this process. The hard-templating synthesis will primarily be used in the preparation of mesoporous tungsten oxide particles, which are the material of focus for this dissertation.

### 1.3. Tungsten Oxide (WO₃)

As discussed above, there are numerous transition metal oxides that can be developed with soft- and hard-templating strategies. This dissertation will focus on
tungsten oxide (WO$_3$), which is a transition-metal oxide studied in catalytic, electrochromic, gas sensing, and solar energy conversion applications.$^{59}$

Crystallites of WO$_3$ form through corner and edge sharing WO$_6$ octahedra in monoclinic, orthorhombic, tetragonal, triclinic, and cubic polymorphs. Corner sharing monoclinic (γ-WO$_3$) is the most stable phase at room temperature (Figure 1-11), with the other phases occurring from $<$ -43 °C to $>$ 740 °C.$^{60,61}$ In contrast to bulk WO$_3$, nanocrystals of WO$_3$ undergo phase transformations at lower temperatures$^{62}$ and can stabilize the orthorhombic phase at room temperature depending on the preparation method and the size and shape of the nanoparticles.$^{63}$

**Figure 1-11.** Unit cell representation of monoclinic tungsten oxide (γ-WO$_3$) composed of corner-sharing WO$_6$ octahedra. Space group $P2_1/n$; $Z = 8$; $a = 7.306$ Å, $b = 7.540$ Å, $c = 7.692$ Å; $\alpha = 90.00^\circ$, $\beta = 90.88^\circ$, $\gamma = 90.00^\circ$. Tungsten = blue spheres; oxygen = red spheres. Figure modified from reference 65.

Crystalline WO$_3$ is a semiconducting metal oxide that possesses filled O 2p orbitals in the valence band and empty W 5d orbitals in the conduction band. The bandgap (E$_g$) of this material is defined as the difference in energy between the valence
band (HOMO) and the conduction band (LUMO) and is approximately 2.62 eV for monoclinic WO$_3$, but can vary depending on structure and crystal size.$^{66}$ This energy difference corresponds to the energy of UV and blue visible light. Upon absorption of light with sufficient energy to excite the WO$_3$ bandgap, electrons (e$^-$) are promoted into the conduction band, leaving holes (h$^+$) in the valence band. These e$^-$/h$^+$ pairs are the basis of photocatalysis reactions on semiconductor surfaces, which are discussed below. Several types of semiconductors and their respective bandgaps are shown in Figure 1-12.

![Figure 1-12](image.png)

**Figure 1-12.** Valence band (green), conduction band (dark red), and bandgap energies (in eV) for various semiconductor. Figure taken from reference 67.
1.4. Photocatalysis on Metal Oxide Semiconductor Surfaces

Exciton formation across the HOMO-LUMO energy gap of a semiconductor is initiated by UV-visible light absorption at the crystallite surfaces. These energetic $e^-$ in the conduction band (CB) and $h^+$ species in the valence band (VB) are responsible for various photocatalytic reactions, especially environmental decontamination and solar energy production.\textsuperscript{68,69} As an example, a schematic for photocatalytic water splitting to form H$_2$ and O$_2$ is shown in Figure 1-13.\textsuperscript{70,71} After light absorption, a major problem that affects all photocatalysts is the unproductive recombination of $e^-/h^+$ pairs. This is a very rapid and favorable process that occurs within a nanosecond on TiO$_2$.\textsuperscript{68} Therefore, $e^-/h^+$ separation must be enhanced for the desired reaction between excitons and surface adsorbates to occur. Addition of a cocatalyst on the semiconductor surface can increase the photocatalytic activity of a material, increasing the $e^-/h^+$ pair separation lifetime by trapping these energetic species. Cocatalysts are usually nanoparticulate noble metals such as Au, Ru, or Pt, oxidized forms of these metals, chalcogenides, or metal complexes adsorbed on the surface.\textsuperscript{72} In general, the excited electrons in the CB perform reduction half-reactions, while the holes carry out oxidation half-reactions. These reactions occur at both the semiconductor surface and at the cocatalyst (Figure 1-13). It is important to note that the conduction band potential for WO$_3$ is not sufficiently negative (energetically too low) to reduce water to H$_2$. However, the valence band holes are good oxidizers (i.e. high oxidation potential, low energy) for the conversion of water to O$_2$. 

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1.4.1. Photocatalytic Oxidation of Organic Compounds

Many studies have applied photocatalysis towards the degradation of organic pollutants adsorbed on semiconductor surfaces, especially in aqueous conditions.\textsuperscript{69} Oxidizing holes and reactive oxygen species (ROS) formed during photocatalysis are responsible for the transformation of organics to oxidized species or mineralization to CO\textsubscript{2}. Photoexcited electrons reduce O\textsubscript{2} in air to form superoxide radicals, O\textsubscript{2}•\textsuperscript{-} that consequently form H\textsubscript{2}O\textsubscript{2} through a second electron reduction in the presence of protons. Hydrogen peroxide can react with electrons or additional O\textsubscript{2}•\textsuperscript{-} to create...
hydroxyl radicals (\(\bullet\)OH). It is clear from these mechanisms that other ROS species including HOO\(^{\bullet}\), HOO\(^{-}\), and OH\(^{-}\) are also formed (Figure 1-14).\(^{69}\) Hydroxyl radicals are also created from the reaction of holes with adsorbed water or surface hydroxyl groups (M–OH, such as Ti–OH). The \(\bullet\)OH reacts with adsorbed organic scavengers, which form a variety of organic radicals that subsequently oxidize under O\(_2\) in the presence of ROS.\(^{69}\)

\[
\begin{align*}
O_2 + e^{-}_{CB} & \rightarrow O_2^{-} \\
O_2^{-}, 
H_2O & \rightarrow O_2 + HO_2^{\bullet} + OH^{-} \\
O_2^{\bullet}, 
H^+ & \rightarrow O_2 + HO_2^{\bullet} + OH^{-} \\
H_2O_2 & \rightarrow O_2 + HO_2^{\bullet} \quad \text{(electrons from CB)} \\
& \rightarrow O_2 + H_2O_2 \quad \text{(electrons from CB)} \\
& \rightarrow e^{-}, 
H^+ \quad \text{(electrons from CB)} \\
& \rightarrow \bullet OH + OH^{-} \\
& \rightarrow O_2 + HO_2^{\bullet} \quad \text{(electrons from CB)} \\
& \rightarrow \bullet OH + OH^{-} + O_2
\end{align*}
\]

**Figure 1-14.** Reaction pathways of reactive oxygen species (ROS) production initiated by O\(_2\) reduction via photoexcited electrons in the semiconductor conduction band. Figure modified from reference 69.

Importantly, the energies of the valence and conduction bands within a given semiconductor determine the types of ROS that evolve after photoexcitation. As an example, zinc oxide (ZnO) has VB and CB energies that are sufficient for the oxidation of H\(_2\)O to \(\bullet\)OH and the reduction of O\(_2\) to O\(_2^{\bullet}\), respectively.\(^{73}\) Gold nanoparticles have been used as a cocatalyst for ZnO in the photocatalytic degradation of organic compounds.\(^{73}\) The Au serves as an electron trap and effectively prevents \(e^{-}/h^{+}\) recombination. This source of electrons generates more ROS such as O\(_2^{\bullet}\), and thus, increases the photocatalytic rates of converting organic substrates. Also, due to the
increased exciton separation, h\(^+\) reactions with H\(_2\)O and O\(_2\)\(^-\) are observed to create \(\cdot \)OH and singlet oxygen (O\(_2\))\(^1\)), respectively (\textbf{Figure 1-15}).

\textbf{Figure 1-15.} (a) Energy diagram of ZnO valence band and conduction bands along with redox potentials of H\(_2\)O/\(\cdot \)OH and O\(_2\)/O\(_2\)\(^-\). (b) ROS formation and photocatalytic enhancement mechanisms over Au-ZnO. Figure taken from reference 73.

1.5. Characterizing Porous Catalyst Nanoparticles

1.5.1. Powder X-ray Diffraction (XRD)

The crystallinity of nanostructured TMOs plays a large role in their observed catalytic properties, especially photocatalysis. Powder X-ray diffraction (XRD) is the primary tool used to understand the bulk structure of nanoparticulate materials that, due to their small crystallite sizes, cannot be analyzed via single-crystal XRD. Experimentally, the crystalline sample is in the form of a dry powder that is pressed into a sample holder until a smooth, flat surface is obtained. X-rays are generated at a metal anode that is bombarded with electrons from a heated filament. The wavelength
of emitted X-rays depends on the metal used as the source, which is typically copper. Copper is the most common metal used and has a characteristic wavelength of 1.5418 Å (Kα). During analysis, the sample stage is continuously tilted at θ angles relative to the incident X-rays and the diffracted X-rays are detected at 2θ angles relative to the incident beam at the goniometer (Figure 1-16).

![Figure 1-16. Simplified schematic of a powder X-ray diffractometer.](image)

Upon impact with the sample, X-rays are scattered and reflected in various directions out of phase with the incident beam. Detection of diffraction planes occurs only when two parallel X-ray beams constructively interfere and satisfy Bragg’s Law (EQ.3).

\[ n\lambda = 2d \sin \theta \]  

(3)
In this equation, $n$ is the order of diffraction and is an integer, $\lambda$ is the wavelength of the incident X-rays, which for Cu = 1.5418 Å (K$_\alpha$), $d$ is the interplanar spacing between atomic diffraction planes, and $\theta$ is the angle between the incident and the diffracted radiation. The right hand of \textbf{EQ.3} ($d \sin \theta$) is equal to the extra distance that the second incident X-ray beam travels to the second atomic layer. Using trigonometry and solving for $x$ (\textbf{EQ.4} – \textbf{6}): 

\begin{equation}
\sin \theta = \frac{\text{opposite}}{\text{hypotenuse}} \tag{4}
\end{equation}

\begin{equation}
\sin \theta = \frac{x}{d} \tag{5}
\end{equation}

\begin{equation}
d \sin \theta = x \tag{6}
\end{equation}

this extra distance is multiplied by 2 because the diffracted beam must travel the same distance as the incident (\textbf{Figure 1-17}).
Figure 1-17. Representation of Bragg’s Law as two incident X-ray beams are diffracted in phase from two atomic planes separated by an interplanar spacing, $d$. The lower beam travels a total extra distance of $2d \sin \theta$ compared to the upper beam.

The positions of the peaks in an X-ray diffraction pattern (Figure 1-18A) provide information on the dimensions of a crystal unit cell. The unit cell is defined by lattice constants $a$, $b$, and $c$ and angles $\alpha$, $\beta$, and $\gamma$, which vary depending on the symmetry of the crystal system. For instance, copper(I) oxide possesses simple isometric cubic symmetry with equal lattice constants ($a = b = c$) and angles ($\alpha = \beta = \gamma = 90^\circ$). The Miller indices $h$, $k$, and $l$, are the reciprocal distance from the origin to the intercept of a given plane along $a$, $b$, and $c$ within a unit cell. As an example, Figure 1-18B depicts the $(110)$ plane in a cubic unit cell. Calculation of lattice constants for the $(110)$ plane in a cubic symmetry is done by using the experimentally determined interplanar spacing, $d_{hkl}$ and solving for $a$ using the following equation (EQ.7):

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} = d_{110} \sqrt{1^2 + 1^2 + 0^2} = d_{110} \sqrt{2}$$  \hspace{1cm} (7)
This equation will differ depending on the crystal system of the unit cell. For the most common crystal system, monoclinic \((a \neq b \neq c, \text{ and } \alpha = \gamma = 90^\circ, \beta \neq 90^\circ)\), the lattice constants can be determined using EQ.8:

\[
\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)
\]

\[(8)\]

Figure 1-18. (A) Powder XRD pattern of cubic copper(I) oxide (Cu\(_2\)O) with Miller indices of the unit cell referenced above each peak [taken from reference 74] and (B) an illustration of a cubic unit cell with lattice constants \(a, b,\) and \(c,\) and angles \(\alpha, \beta,\) and \(\gamma.\) The \((110)\) diffraction plane is highlighted.

1.5.2. Nitrogen Physisorption

Increased surface areas relative to their bulk counterparts make porous TMOs more favorable materials for catalysis and separation applications. Nitrogen physisorption is utilized to measure the pore diameter, pore volume, and surface area of porous materials. Samples are dosed with increasing amounts of gaseous N\(_2\) at liquid N\(_2\) temperatures (77 K) and the volume of gaseous N\(_2\) adsorbed on the surface of a
sample is measured as a function of increasing N\textsubscript{2} partial pressure, \(P/P_o\), where \(P\) is a given pressure below the experimentally determined saturation pressure, \(P_o\) (i.e. the pressure at which N\textsubscript{2} condenses). This results in a N\textsubscript{2} physisorption isotherm that describes the sample’s pore characteristics. Gas-solid interactions involved in physisorption include van der Waals, dispersion, and intermolecular repulsion forces.\textsuperscript{75}

These forces and the strength of fluid-wall and fluid-fluid interactions within confined pore spaces determine the shape of the isotherm.

Adsorption in mesopores (> 2 nm) occurs first through the development of a monolayer of N\textsubscript{2} molecules on the pore surfaces. The N\textsubscript{2} adsorbates are randomly distributed on the surface and it is assumed that there are no lateral interactions between them.\textsuperscript{76} At partial pressures of 0.05 – 0.2, the monolayer capacity, \(V_m\), can be calculated at known \(P/P_o\) by the theory of Brunauer, Emmett, and Teller\textsuperscript{77} using the BET equation (EQ.9):

\[
\frac{1}{V \left( \frac{P_o}{P} \right) - 1} = \left( \frac{1}{V_m} \right) C + \left( \frac{C - 1}{V_mC} \right) \left( \frac{P}{P_o} \right)
\]

where \(V\) is the volume of adsorbed N\textsubscript{2} and \(C\) is a constant that describes the strength of attractive gas-surface interactions. A linear BET plot of 1/[\(V(P_o/P)\)-1] vs \(P/P_o\) yields \((C-1)/V_mC\) and \((1/V_m)C\) as the slope and y-intercept, respectively. After obtaining \(V_m\), the BET surface area (\(S_A\text{BET}\)) is then given in units of area per gram of sample (EQ.10):

\[
S_A\text{BET} = \frac{V_m N \sigma (\frac{1}{a})}{M_V}
\]
where \( N \) is Avogadro’s number, \( \sigma \) is the cross sectional area of \( \text{N}_2 \) (0.162 nm\(^2\)), \( 75 M_V \) is the molar volume of \( \text{N}_2 \), and \( a \) is the mass of the sample being analyzed.

As increasing amounts of \( \text{N}_2 \) (\( P/P_o > 0.2 \)) are dosed onto the pore surfaces, multilayer adsorption occurs. Depending on the gas-surface interactions dictated by the pore size and geometry and gas-gas interactions, these additional layers reach a critical point where no further gas layers can be stabilized. The gaseous layers then undergo a phase transformation to the liquid state, which is known as capillary condensation, and \( \text{N}_2 \) adsorption rapidly increases. This process is described by a modified Kelvin equation\(^{75,78} \) that relates pore diameter to the capillary condensation pressure, and shows that condensation occurs at higher partial pressures as the pore diameter increases. Using this model of pore filling, the Barrett, Joyner, Halenda (BJH) method\(^{79,80} \) determines the pore sizes (EQ.11):

\[
r(P/P_o) = \frac{2\gamma V_L}{RT \ln([P/P_o])}
\]

where \( r \) is the pore radius, \( \gamma \) and \( V_L \) are the surface tension and molar volume of the liquid adsorbate, respectively, \( R \) is the universal gas constant, and \( T \) is the absolute temperature.

The adsorption isotherm is completed at \( P/P_o = 1.0 \) and it is in this \( P/P_o \) region of approximately 0.95 – 1.0 that the total pore volume of the sample is determined. Here, it is assumed that liquid \( \text{N}_2 \) completely fills all of the pores within the sample. Desorption of \( \text{N}_2 \) then begins as the partial pressure at the sample is reduced and the desorption isotherm is measured. For porous samples with larger pores, usually in
excess of 50 Å, removal of N$_2$ from the pores does not occur at the same partial pressures as in the adsorption process. The curvature of the pore walls leads to the condensation of liquid N$_2$ inside the pores at higher partial pressures, which is known as capillary condensation. A greater energy potential (i.e. lower pressures during desorption) is necessary to remove N$_2$ from this more thermodynamically stable state. This irreversibility causes hysteresis loops in the region of multilayer adsorption. The pore geometry and the behavior of the liquid condensate removal from inside of the pores govern the shape of the hysteresis.$^{75,81}$ Figure 1-19 shows a typical N$_2$ physisorption isotherm for a mesoporous SBA-15 sample and highlights the information one can gain from the various portions of the isotherm.

![Figure 1-19](image_url)

Figure 1-19. Nitrogen physisorption isotherm of SBA-15 silica showing both adsorption (black) and desorption (red) curves. Regions of interest with regard to pore characteristics are labeled.
1.5.3. Scanning Electron Microscopy (SEM)

Electron microscopic techniques allow for higher resolution imaging compared to optical microscopes, and they are used heavily to probe the morphology and size of nanoparticulate materials. Scanning electron microscopes (SEM) direct a focused beam of electrons through a series of lenses and apertures towards a specimen in a sample chamber (Figure 1-20). Samples are usually coated in a conductive metal alloy such as Au/Pd prior to analysis to reduce charge build up at the sample surface. The accelerating voltage at the electron source determines the penetration depth of the electrons through the sample. The objective lens determines the diameter of the focused electron probe, or spot size, on the specimen. Initial interactions between the electron beam and the specimen include scattering within the sample. Electrons from the source may interact with both the nucleus and the electrons composing the sample surface and produce multiple signals such as backscattered electrons, secondary electrons, X-rays, and Auger electrons. Secondary electrons are produced when the source electrons interact with a valence electron in the sample, and a transfer of energy to this valence electron causes its emission from its valence shell. Due to their low energy (< 50 eV), only secondary electrons produced at the surface are able to escape from the specimen. Electrons generated deeper in the sample volume are reabsorbed (i.e. not detected). Therefore secondary electron detection is sensitive to the surface topography and sample thickness.
1.5.4. Energy-Dispersive X-ray Spectroscopy (EDS)

An energy dispersive X-ray spectrometer (EDS) detects the characteristic X-rays that are emitted when a material comes into contact with the incident electron beam in an electron microscope (Figure 1-20). First, the incident electron beam ionizes the 1s core electrons (K shell) of the sample. Then, X-rays are emitted when this core vacancy is filled by electrons from the 2p (L shell) or 3p (M shell). The energy of the emitted X-rays is element-specific; therefore, this technique provides an elemental analysis of the sample surface. With samples composed of various elements, EDS can...
ideally be used to quantify the relative amount of each element comprising the specimen. Also, depending on the spot size of the electron beam as it comes into contact with the sample, elemental distributions within defined sample regions may be analyzed.

1.5.5. Transmission Electron Microscopy (TEM)

In contrast to SEM, if the accelerating voltage is large enough (~100 kV), incident electrons may also pass through the sample in an electron microscope. Detection of these focused electrons is the basis of transmission electron microscopy (TEM). As expected, the sample thickness plays a large role in the successful imaging of materials, especially those composed of heavier elements. Sample preparation typically includes preparing a thin slice of the specimen. For powdered materials, a diluted suspension of particles is deposited onto a copper grid and the sample can be imaged after solvent evaporation. Nanoparticle size distributions are commonly determined by TEM and surface features are observed at higher resolutions compared to SEM. High-resolution TEM (HR-TEM) allows for direct imaging of atomic crystallinity that complements X-ray diffraction data. To obtain these higher resolution images, the accelerating voltage must increase considerably (from ~120 to ~200 kV). In addition, the contrast of the imaged sample depends on the atomic number of the elements composing the sample. Heavier elements appear darker in TEM images, which is useful in imaging areas with different elemental composition in a composite material (Figure 1-21).
1.5.6. Temperature-Programmed Reduction (TPR)

Transition metal oxides are some of the most commonly used catalysts in transformations such as selective oxidation,\textsuperscript{85} hydrodesulfurization (HDS),\textsuperscript{86} Fischer-Tropsch synthesis of hydrocarbons from synthesis gas (H\textsubscript{2} + CO),\textsuperscript{87} and selective catalytic reduction (SCR) of NO by NH\textsubscript{3}.\textsuperscript{88} In these reactions, the oxidation states and the reducibility of the catalysts are related to the observed reaction mechanisms and activity. Temperature-programmed reduction (TPR) is used to characterize reducible components in heterogeneous catalysts. In a typical experiment, the oxidized form of the catalyst is loaded into a reaction tube that is enclosed within a programmable oven.

Figure 1.21. (a and b) TEM images of Pt nanocubes synthesized within SBA-15 pores; (c) HR-TEM of individual Pt nanocube and fast Fourier transform of crystalline Pt lattice (inset); (d) Pt size distribution plot showing an average Pt size of 4.8 ± 0.8 nm. Figure taken from reference 84.
The catalyst is then subjected to a continuous flow of reducing gas, usually H\textsubscript{2}, and the temperature of the oven is increased at a known rate. Over the course of the temperature ramp, H\textsubscript{2} is consumed by the catalyst as a function of temperature. This H\textsubscript{2} consumption changes the thermal conductivity of the gas downstream from the catalyst relative to the initial feed, thus resulting in an observed peak in the TPR trace. Initially, reduction occurs at the surface sites of the catalyst\textsuperscript{89,90}. At a temperature sufficient to overcome the reduction potential of the oxide, dissociated H atoms react with surface O atoms and remove them from the lattice. Electrons resulting from this oxygen vacancy migrate to the bulk of the catalyst as water desorbs from the surface (Figure 1-22). Ideally, reduction continues at higher temperatures to convert the bulk of the catalyst to its metallic form.

![Figure 1-22. Reduction of surface WO\textsubscript{3} sites by H\textsubscript{2} gas (1) that dissociates at the Au/WO\textsubscript{3} interface (2) and reacts with surface lattice O to form water and an O vacancy (3); the O vacancy migrates to the bulk (4) and H\textsubscript{2}O is desorbed from the surface. Figure modified from reference 59.](image)
The temperature at which peaks occur during TPR is a qualitative indication of the reducibility of an oxide species. In general, the observation of peaks at lower temperatures is an indication of a facile reduction event, while peaks at higher temperatures indicate a more difficult reduction event. Multiple features in a TPR profile indicate that intermediate reduced oxide species exist in the catalyst. Some catalysts, however, cannot stabilize reduced intermediates and show only a single reduction event (Figure 1-23). The peak area provides quantitative information of the amount of H\textsubscript{2} consumed by the catalyst. In order to determine these quantities, a known amount of a reference material such as Ag\textsubscript{2}O is analyzed\textsuperscript{91} and its reduction peak integration is used to calibrate the detector response of the catalyst.

**Figure 1-23.** H\textsubscript{2}-TPR of nanowire (NW) and mesoporous (meso) manganese oxide (MnO\textsubscript{2}) materials. Note the shifts of the MnO\textsubscript{2} reduction peaks to lower temperatures in the presence of Au nanoparticles. Figure taken from reference 92.
1.5.7. Temperature-Programmed Desorption (TPD)

The adsorption energy of a molecule on a catalyst surface is characteristic of the reactivity of surface active sites. For example, Lewis basic probe molecules such as ammonia and pyridine are commonly used to characterize the acid site strength of solid catalysts.\textsuperscript{93,94} Temperature-programmed desorption (TPD) determines the strength of the adsorbate-adsorbent interaction at the surface. Catalysts are subjected to a flow of the gaseous probe molecule at low temperature to saturate the surface sites. Following the removal of weakly bound physisorbed molecules, the sample is heated at a constant rate while a downstream detector quantifies the amount of desorbed species as a function of temperature. At a certain temperature, the activation energy of the adsorbate-adsorbent bond is reached and the chemisorbed probe molecule desorbs from the surface. Therefore, weaker bonds are broken at lower temperatures and stronger bonds at higher temperatures. This makes it possible to characterize the various active sites on the same catalyst (Figure 1-24). Also, titrants may be adsorbed on the catalyst surface to selectively block certain active sites. For example, propylamine may be used to block Brønsted acid (H\textsuperscript{+}) sites in order to characterize Lewis acid sites on a zeolite catalyst.\textsuperscript{95}
Figure 1-24. Ammonia TPD of zeolite H-SSZ-13 after saturation with NH$_3$ at 323 K. Two acid sites are observed: a weak acid site with NH$_3$ desorption at 429 K and a strong acid site with desorption at approximately 700 K. Figure taken from reference 95.

1.6. Dissertation Objectives

The aims of this work include the preparation, characterization, and application of porous WO$_3$ materials for various catalytic reactions. First, the porous WO$_3$ materials are synthesized using spherical particles of porous SiO$_2$ as hard templates in a nanocasting approach. Further surface modification of the WO$_3$ structures with gold nanoparticles (Au NPs) is carried out through a facile sonochemical deposition method. Complete characterization of these materials with techniques such as XRD, N$_2$ physisorption, SEM, TEM, and inductively coupled plasma optical emission spectroscopy (ICP-OES) are used to understand the structure, morphology, and composition of these pure and Au-modified catalysts. Chapters 2 and 3 explore the use
of WO₃ and Au-loaded WO₃ as photocatalysts in the adsorption and degradation of methylene blue (MB) in water (Chapter 2), and the gas-phase oxidation of methanol in a homemade continuous-flow reactor (Chapter 3). Specifically, the objectives of these studies were to increase the visible light photocatalytic activity of porous WO₃ by modifying these materials with Au NPs. Also, porous WO₃ is compared to bulk WO₃ to highlight the positive influence of porosity in photocatalytic reactions. Also, the mechanisms of photocatalytic reactions over pure WO₃ and Au-WO₃ are compared to study the selectivity effects of modifying WO₃ with Au NPs. Finally, Chapter 4 studies the active sites of pure WO₃ and Au-modified WO₃ catalysts by using the thermal catalytic transformation of methanol as a characterization tool. The product distribution of this reaction, in particular, is indicative of the major reaction pathways occurring over different catalyst active sites. Furthermore, H₂-TPR is used to analyze the electronic effects that deposited Au NPs impart on the porous WO₃ catalysts.
1.7. References


2.1. Introduction

Tungsten oxide (WO$_3$) is an n-type semiconductor that has been extensively studied for applications in gas sensing, catalysis, solar energy conversion, and electrochromic displays.$^{1-6}$ With a small band gap of 2.4 – 2.8 eV, WO$_3$ is more effective than TiO$_2$ at absorbing visible light. Indeed, WO$_3$ has been studied as a visible light photocatalyst.$^7,8$ It is resistant to degradation due to photocorrosion,$^9$ which can lead to the formation of metal ions and decrease catalytic activity. Importantly, a deep lying valence band (+3.1 eV) favors oxidation reactions on the WO$_3$ surface.$^9,10$ These attributes make WO$_3$ a promising alternative to TiO$_2$, which needs to be modified in order to absorb visible light.

In addition to favorable photocatalytic attributes, WO$_3$ surfaces possess highly negative surface charges that are ideal for adsorption applications, especially for cationic dyes such as methylene blue (MB). Negative charges on the surface of WO$_3$ are a result of the oxide’s low isoelectric point (IEP = 0.2 – 1). Studies using other WO$_3$ nanostructures have also taken advantage of this strong electrostatic interaction between MB and WO$_3$.$^{11-13}$ The combination of high adsorption capacity for MB and the photocatalytic nature of the WO$_3$ surface makes this oxide a strong candidate for subsequent conversion of adsorbed MB in aqueous systems.

Modifying WO$_3$ with Au nanoparticles has proven to be beneficial in improving the gas sensing,$^{14-16}$ photochromic, and electrochromic$^{17,18}$ properties of the pure oxide.
Since Haruta’s authoritative review of catalysis performed by supported gold nanoparticles, numerous studies have been conducted to further study and optimize these systems in various chemical transformations. More recently, Au nanoparticles have been explored in photocatalysis applications, with Au/TiO$_2$ being one of the most frequently studied systems. The preparation and application of Au-loaded WO$_3$ visible light photocatalysts have not been thoroughly explored, however. It is expected that Au nanoparticles will facilitate better photocatalytic activity on the surface of WO$_3$ compared to pure WO$_3$. Enhancement of photocatalytic activity has been demonstrated with different Au-WO$_3$ systems. The increased photocatalytic ability of Au-WO$_3$ originates from the trapping of excited conduction band electrons in WO$_3$ by Au nanoparticles and increased e$^-$/h$^+$ (exciton) separation. Valence band holes (h$^+$) of WO$_3$ can be used for the oxidation of adsorbed molecules. Alternatively, h$^+$ can oxidize surface H$_2$O to form reactive $\bullet$OH, which can subsequently oxidize adsorbed organics. Improving the exciton separation on the WO$_3$ surface with Au nanoparticles will ultimately enhance photoreactivity toward adsorbed molecules.

Synthetically, there is still a great need for a facile and reliable method to deposit well-dispersed Au nanoparticles on the surface of WO$_3$. Due to the low IEP of WO$_3$, the simple deposition-precipitation (DP) technique is generally poor in creating small Au nanoparticles on this oxide and others that possess an IEP $< 5$. Furthermore, physical methods to deposit Au nanoparticles on WO$_3$ such as pulsed laser deposition (PLD), magnetron sputtering, and aerosol assisted chemical vapor deposition (AACVD) include expensive instrumentation, evacuated environments, and are not readily accessible in most laboratories.
Sonochemical deposition serves as a promising chemical route to overcome these shortcomings in order to easily prepare small Au nanoparticles on metal oxides. Previous work by Chen\textsuperscript{39,40} and Gedanken\textsuperscript{41} demonstrated the effectiveness of this method in the deposition of small (< 5 nm) Au nanoparticles on silica. Most recently, Lin and co-workers\textsuperscript{42} have used the sonochemical approach to deposit Au nanoparticles on the (001) and (101) facets of anatase TiO\textsubscript{2} to facilitate the plasmon-induced photocatalytic degradation of 2,4-dichlorophenol under visible light. The Au nanoparticles in that study possessed a mean diameter of 10 – 11 nm, but the thermal stability of the nanoparticles and the surface areas of the catalysts were not assessed. We predict that a porous SiO\textsubscript{2}-WO\textsubscript{3} composite will serve as a suitable substrate for the sonochemical deposition of small Au nanoparticles, which will increase the visible light photocatalytic activity of these porous powders.

In the studies described here, a sonochemical approach is developed to deposit Au nanoparticles within the pores of acid-prepared mesoporous spheres (APMS) of silica previously impregnated with crystalline WO\textsubscript{3} (SiO\textsubscript{2}-WO\textsubscript{3}) to form Au-SiO\textsubscript{2}-WO\textsubscript{3}. Similar to the nanocasting technique, Au-SiO\textsubscript{2}-WO\textsubscript{3} is selectively etched to form porous Au-WO\textsubscript{3}. Porous Au-WO\textsubscript{3} particles have not been thoroughly developed for photocatalytic applications. This facile method avoids the problem of large Au NP deposition on WO\textsubscript{3} when using the traditional DP method. To the best of our knowledge, this combination of sonochemical and nanocasting techniques has not been previously studied for the deposition of Au nanoparticles on metal oxides. Herein, the Au nanoparticles are deposited without an organic stabilizer such as polyvinylpyrrolidone (PVP), which can negatively affect the Au-WO\textsubscript{3} interactions upon
removal.\textsuperscript{28} Lastly, solutions containing methylene blue (MB) are used to probe both the adsorption capacity and the visible light photocatalytic activity of Au-loaded and nonloaded oxides, and mass spectrometry is used to study the mechanism of MB photocatalytic conversion.

2.2. Results and Discussion

2.2.1. Synthesis and Characterization of Materials

Mesoporous WO\textsubscript{3} and SiO\textsubscript{2}-WO\textsubscript{3} microparticles with a spherical morphology were prepared as described in the Experimental Section. This process used a nanocasting procedure in which (NH\textsubscript{4})\textsubscript{6}H\textsubscript{2}W\textsubscript{12}O\textsubscript{40}, ammonium metatungstate or AMT, was impregnated into mesoporous silica spheres in several stages, followed by calcination at each stage to produce SiO\textsubscript{2}-WO\textsubscript{3} microparticles with the same spherical morphology as the silica template. For some experiments, this material was etched with HF to dissolve the SiO\textsubscript{2}, leaving pure WO\textsubscript{3} mesoporous microparticles with diameters of 1 – 3 μm, as confirmed by energy-dispersive X-ray spectroscopy and scanning electron microscopy (\textbf{Figure 2-1}). Purity of the WO\textsubscript{3} catalysts was further supported by elemental analysis (ICP-OES, see below).
Figure 2-1. SEM micrographs (top) and corresponding EDS spectra (bottom) of spherical WO₃ (A) and Au-WO₃ (B). EDS confirmed the complete removal of SiO₂ from (A) and (B). Also, the presence of Au throughout sample (B) was confirmed.

Sonication of silica in aqueous solutions containing HAuCl₄ and NH₃, followed by calcination at 500 °C, has been shown to produce Au nanoparticles on the silica surface.⁴¹ It is thought that the purpose of NH₃ is to activate silanol groups on the surface of SiO₂. Powerful jets formed during sonication then provide the necessary energy to propel Au species toward the SiO₂ surface, and upon impact, the Au reacts with free silanols or Si-O-Si species, resulting in the formation of Au-O-Si bonds. In previous research, the nature of Au-silanol bonds was indirectly characterized by Fourier transform infrared (FT-IR) measurements, which showed a disappearance of the isolated silanol stretching band when Au was deposited on the surface.⁴¹ Here, this
procedure was adapted for SiO$_2$-WO$_3$ to produce Au-SiO$_2$-WO$_3$. Although WO$_3$ dissolved to produce water-soluble tungstate ions (WO$_4^{2-}$) at the pH of the sonication (10.5),$^{43,44}$ we found that enough of the WO$_3$ remained to allow us to prepare Au-SiO$_2$-WO$_3$ by the sonication/calcination procedure with retention of the overall structural integrity of the nanocomposite. Attempts to use this sonication procedure on pure WO$_3$ to afford Au-WO$_3$ catalysts were unsuccessful. Excessive dissolution and degradation of WO$_3$ particles in the basic solution, as well as poor dispersion of Au nanoparticles, was observed when using pure WO$_3$ as the starting material. Therefore, SiO$_2$ in the initial substrate was necessary for successful Au deposition. Previous research suggested that sonication produces H• radicals in solution that reduce surface-bound Au$^{3+}$ in AuCl$_4^-$ to Au$^{0}$. In this study, however, the yellow color of the as-prepared samples before calcination indicated that Au$^{3+}$ reduction did not occur in solution during sonication. After calcination of Au-SiO$_2$-WO$_3$, small, well-dispersed Au nanoparticles were found at low loadings, and the sample took on the characteristic red-purple color signifying Au reduction. This suggests that the main role of sonication in this synthesis is to facilitate bonding between the Au precursor and the SiO$_2$ surface. Finally, Au-WO$_3$ was then formed by removing the SiO$_2$ from Au-SiO$_2$-WO$_3$ by etching with HF. Elemental analysis confirmed complete removal of SiO$_2$ from both WO$_3$ and Au-WO$_3$. During the washing steps after this final HF treatment, the supernatant was dark purple after centrifugation. We attribute this to the loss of Au and smaller Au-WO$_3$ nanoparticles that are not retained on the spherical Au-WO$_3$ microparticles during etching. Elemental analysis data suggested that WO$_3$ was removed to a greater extent than Au during HF etching of Au-SiO$_2$-WO$_3$ (ICP-OES, see
below). The dark red-purple color of Au-WO$_3$ and further direct analyses indicated that crystalline Au nanoparticles remained on WO$_3$. A schematic summarizing the synthetic procedures is shown in Figure 2-2.

![Figure 2-2. Summary of synthesis procedures used to prepare the materials in these experiments. “AMT” = ammonium metatungstate. Complete synthetic details are in the Experimental Section.](image)

The crystallinity of the materials was analyzed by powder X-ray diffraction (Figure 2-3). Mesoporous materials showed a broad peak at low angles due to pore-to-pore scattering. Materials containing WO$_3$ (composites and pure WO$_3$) displayed high angle diffraction peaks corresponding to monoclinic WO$_3$. All WO$_3$-containing samples exhibited peak broadening due to the nanocrystalline nature of the metal oxide. On the basis of Scherrer equation$^{45}$ calculations, nanoparticles of WO$_3$ ranged in sizes from 6 to 15 nm. These small WO$_3$ nanoparticles are aggregated and make up the spherical microparticles observed by SEM. It was clear that the sonochemical deposition of Au nanoparticles did not significantly alter the crystallinity of the WO$_3$. Au-SiO$_2$-WO$_3$ and
Au-WO₃ showed an additional broad, weak intensity peak at 38° due to the Au(111) diffraction plane, which was used to estimate the crystallite diameter of the Au contained in those samples. X-ray diffraction data revealed Au nanoparticles with a diameter of 5 and 10 nm in Au-SiO₂-WO₃ and Au-WO₃, respectively. Transmission electron microscopy (TEM) was also used to characterize the nature of the deposited Au nanoparticles (Figure 2-3). Well dispersed Au nanoparticles with diameters of 3 – 5 and 10 nm for Au-SiO₂-WO₃ and Au-WO₃, respectively, were confirmed by TEM. These nanoparticle sizes are in agreement with the XRD data. The presence of only larger (~10 nm) Au nanoparticles in Au-WO₃ meant that the smallest nanoparticles are removed during the etching of the SiO₂ matrix.

**Figure 2-3.** (A) Powder XRD patterns of materials prepared for catalytic experiments. Miller indices for monoclinic WO₃ (ICDD: 043-1035) are shown above relevant peaks. The asterisk denotes the Au(111) peak. TEM images of (B) Au-SiO₂-WO₃ and (C) Au-WO₃. Arrows indicate Au nanoparticles.
The Au nanoparticles within Au-SiO$_2$-WO$_3$ were further characterized by EDS and high-resolution TEM (HR-TEM). A TEM image and corresponding EDS spectra at several locations within this region are shown in Figure 2-4. The EDS peak for Si (1.74 keV) is known to overlap with the adjacent W peak (1.78 keV), and in region 3 within this TEM image, the combined Si/W peak was clearly shifted to lower energies as compared to regions 1 and 2, signifying the presence of Si in region 3. Au was found both in areas containing pure WO$_3$ as well as those with combined SiO$_2$-WO$_3$. Thus, it appeared that the Au nanoparticles were in contact with all regions of the sample, not only those containing SiO$_2$. Figure 2-4 also shows a HR-TEM image of an isolated Au nanoparticle in contact with a WO$_3$ surface within the composite. Of note is the fact that this nanoparticle is slightly larger (~10 nm) than the diameter calculated from XRD data (5 nm).

There is some evidence to suggest that the Au nanoparticles in contact with the WO$_3$ portions of the composite should be larger than those in contact with SiO$_2$, based on the difference in isoelectric point values of the two materials (WO$_3$ = 0.2 – 1; SiO$_2$ = 2). Another factor is the error associated with estimation of particle diameters from XRD data. However, it seems clear that the Au nanoparticles within Au-SiO$_2$-WO$_3$ were between 3 and 10 nm, depending on their location. In any case, the Au nanoparticles appeared to be uniformly deposited, hemispherical in shape, and highly crystalline. Measurements of the Au lattice fringes yielded a $d$-spacing of 0.23 nm, corresponding to the Au(111) plane, which is consistent with the XRD pattern. The measured $d$-spacing of 0.30 nm for the WO$_3$ corresponded to the (112) plane of monoclinic WO$_3$. 

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Figure 2-4. Structural characterization of Au-SiO$_2$-WO$_3$. (A) TEM image and (B) associated EDS of selected regions within Au-SiO$_2$-WO$_3$. Numbers in panel B correspond to sites identified in panel A. (C) HR-TEM image of an Au nanoparticle on an area of WO$_3$.

Sintering of Au nanoparticles is a common problem for catalysts during industrial catalytic reactions, as small Au nanoparticles tend to sinter at temperatures above 400 °C.$^{46-49}$ To observe the thermal stability of Au in our materials, Au-SiO$_2$-WO$_3$ was subjected to four heating cycles during which the samples were heated to 450 °C and held at that temperature for 3 h, cooling to room temperature between cycles. TEM showed that the particle size of the Au nanoparticles did not change significantly after this experiment (Figure 2-5), indicating that the SiO$_2$-WO$_3$ composite is a good support for thermally stable Au nanoparticles.
Figure 2-5. TEM micrographs of (A) as-prepared Au-SiO$_2$-WO$_3$, and Au-SiO$_2$-WO$_3$ following (B) 1, (C) 2, and (D) 4 calcinations at 450 °C for 3 h. During these treatments, the size of the deposited gold nanoparticles remained in the range of 3-5 nm with most still possessing sizes < 10 nm.

The porosity of the materials was examined using N$_2$ physisorption (Table 2-1, Figure 2-6). The mesoporous silica substrate had only a moderate surface area (463 m$^2$ g$^{-1}$), consistent with its relatively large average pore diameter (78 Å). We found in previous studies that a large pore diameter was required for successful nanocasting that retained the particle morphology of the silica template. The surface areas of the SiO$_2$-WO$_3$ composite and the WO$_3$ product were consistent with a moderately porous material, given the increased mass of W relative to Si, and are also consistent with
porous WO$_3$ from the literature. The decreased pore diameter of the SiO$_2$-WO$_3$ composite (47 Å) relative to the SiO$_2$ template showed that a significant portion of the SiO$_2$ pore surfaces had been modified with WO$_3$. Elemental analysis and the determined Si/W ratio of SiO$_2$-WO$_3$ showed that WO$_3$ was incorporated throughout the sample (Table 2-1). On the other hand, upon etching, the pore diameter increased significantly due to increased porosity of the material after removal of SiO$_2$. Importantly, the pure WO$_3$ sample had the same, if not slightly higher surface area than similar materials reported previously.$^{50,51}$

Further changes in porosity were found for Au-loaded materials. While the surface area of Au-SiO$_2$-WO$_3$ decreased compared to SiO$_2$-WO$_3$, the pore diameter increased and was larger than expected based on the characterization of the SiO$_2$-WO$_3$ composite with no Au. This indicated that the pore surfaces had been modified during sonication and Au deposition and confirmed that some of the WO$_3$ dissolved in the basic aqueous solution used for sonication. It also showed that the effect of SiO$_2$ and WO$_3$ dissolution (pore expansion) played a greater role than Au nanoparticle deposition (pore blockage) in the resulting porosity of the Au-SiO$_2$-WO$_3$ composite. A decrease in the Si/W mole ratio of Au-SiO$_2$-WO$_3$ in relation to SiO$_2$-WO$_3$ provided evidence of greater SiO$_2$ dissolution compared to WO$_3$ during the sonochemical deposition of Au nanoparticles. As mentioned above, this data also indicated a loss of Au (in the form of <10 nm nanoparticles) and WO$_3$ during the etching of Au-SiO$_2$-WO$_3$ to form Au-WO$_3$. Indeed, the decrease in the W/Au mole ratio signified that the loss of WO$_3$ was greater than that of Au. The pore diameter of Au-WO$_3$ was larger than the unetched composite (Au-SiO$_2$-WO$_3$), as found for the material not loaded with Au. Overall, Au-SiO$_2$-WO$_3$,
Au-WO₃, and WO₃ had somewhat larger surface areas than similar materials from the literature; this, with the nanocrystallinity observed by TEM and XRD, made them desirable for adsorption and visible light photocatalysis,

Table 2-1. Summary of elemental analysis, Au nanoparticle sizes, and N₂ physisorption data for the porous Au-loaded and nonloaded oxides discussed in this work.

<table>
<thead>
<tr>
<th>sample</th>
<th>W (wt%)</th>
<th>Au (wt%)</th>
<th>Si/W (mole ratio)</th>
<th>W/Au (mole ratio)</th>
<th>Au diameter (nm)</th>
<th>SABET (m² g⁻¹)</th>
<th>Vpore (cm³ g⁻¹)</th>
<th>dpore (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>463</td>
<td>0.95</td>
<td>78</td>
</tr>
<tr>
<td>SiO₂-WO₃</td>
<td>54.6</td>
<td>--</td>
<td>1.68</td>
<td>--</td>
<td>--</td>
<td>65</td>
<td>0.12</td>
<td>47</td>
</tr>
<tr>
<td>WO₃</td>
<td>79.9</td>
<td>--</td>
<td>0.0099</td>
<td>--</td>
<td>--</td>
<td>53</td>
<td>0.20</td>
<td>101</td>
</tr>
<tr>
<td>Au-SiO₂-WO₃</td>
<td>56.8</td>
<td>3.74</td>
<td>1.24</td>
<td>16.3</td>
<td>3-5⁶</td>
<td>55</td>
<td>0.17</td>
<td>74</td>
</tr>
<tr>
<td>Au-WO₃</td>
<td>73.8</td>
<td>5.95</td>
<td>0.0113</td>
<td>13.3</td>
<td>~10⁶</td>
<td>66</td>
<td>0.24</td>
<td>135</td>
</tr>
</tbody>
</table>

⁶Weight percent and mole ratios determined by ICP-OES
⁷Measured by TEM and XRD
2.2.2. Adsorption and Photocatalytic Degradation of Methylene Blue

Photocatalysis is widely used in environmental remediation; often the goal in this application is to degrade environmental contaminants under ambient conditions,
that is, in aqueous solutions using the solar spectrum. The removal and subsequent photocatalytic degradation of pollutants from aqueous systems has been demonstrated in the presence of semiconducting metal oxides capable of absorbing UV and/or visible light, such as TiO$_2$ or modified TiO$_2$. Methylene blue (MB) is a dye that is commonly used to probe the photoactivity of metal oxides, and this molecule was the basis of our own photocatalysis studies using SiO$_2$-WO$_3$, WO$_3$, and the Au nanoparticle-loaded versions of these materials. In this work, we took advantage of the highly negative charges on the WO$_3$ surface to synthesize an excellent adsorbant for MB. By incorporating Au nanoparticles into WO$_3$-containing catalysts, we also increased the photoactivity of these materials under visible light irradiation.

Photocatalytic experiments were performed by adding materials to an aqueous MB solution, equilibrating the resulting suspensions in the dark for 120 min, and then irradiating the suspensions with visible light for 300 min. A halogen lamp (72 W, 1520 lm) was used for visible light exposures; the UV portion of the spectrum was specifically excluded by passing the light through a UV filter. Electrospray ionization mass spectrometry (ESI-MS) is an effective method to determine byproducts of MB photodegradation in solution$^{54-56}$ and this technique was used in our initial experiments to identify degradation products, using Au-SiO$_2$-WO$_3$, Au-WO$_3$, and WO$_3$. Preliminary analysis of MB by ESI-MS showed a major peak at m/z = 284 due to MB, and a second small peak at m/z = 270 due to contamination with azure B, a monodemethylated product of MB. There were no peaks at higher m/z ratios, indicating that the ESI-MS technique did not cause any further degradation or polymerization of MB.
We found that degradation of MB on our materials proceeded primarily through demethylation (Figure 2-7) and polymerization, although oxidized products were also observed after irradiation. The addition of MB over 120 min in the dark by Au-SiO₂-WO₃ led to the formation of the fully demethylated product thionine with m/z = 228 (Figure 2-8), although MB remained the most abundant species. Major MS peaks were also observed at m/z = 340, 358, 402, 453, 680, and 702 due to polymerization of demethylated products.

**Figure 2-7.** Methylene blue and the demethylated derivatives found by ESI-MS after adsorption and photocatalytic degradation.
Figure 2-8. ESI-MS spectra of MB and MB degradation products using Au-SiO$_2$-WO$_3$, Au-WO$_3$, and WO$_3$ before and after exposure to visible light (300 min). AA, AB, and AC = azure A, B, and C, respectively; Th = thionine. Y-axes are in arbitrary intensity units. Note: When present, the highest intensity m/z = 114 peak is truncated so that other peaks can be easily distinguished.

There are several significant peaks identified throughout the series of mass spectra worth mentioning. The peaks at m/z = 453 and 680 were identified as the thionine dimer and trimer, respectively, which was supported by further analyses of these peaks using tandem MS-MS (MS2, Figure 2-9). The +2-charged tetramer of thionine could also be contributing to the peak at m/z = 453 because a small peak at m/z = 906 due to the singly charged thionine tetramer was also observed. The peak at m/z = 340 was identified as the +2-charged thionine trimer from isotope ratio and MS2 analysis. Doubly charged NH$_4^+$ and 3ACN+2H (ACN = acetonitrile) adducts of the thionine trimer were responsible for the peaks at m/z = 358 and 402, respectively.\textsuperscript{57} and
the peak at m/z = 702 was due to the Na\(^+\) adduct of the thionine trimer. Other, smaller peaks in the complicated ESI-MS spectrum could be due to several other stable degradation products or adducts of MB and demethylated aggregates at higher m/z values.

**Figure 2-9.** ESI tandem MS-MS spectra of m/z = 453 (♦) and m/z = 680 (◇). The peak at m/z = 226 m/z (●) in both spectra was attributed to the thionine monomer, thus confirming m/z = 453 m/z as the thionine dimer and m/z = 680 as the thionine trimer.
During the dark adsorption period, it appeared that MB degradation occurred on the surfaces of Au-SiO$_2$-WO$_3$, Au-WO$_3$, and WO$_3$ (Figure 2-8). The ESI-MS data indicated that prior to visible light irradiation, MB remained the major component, but degradation occurred primarily through demethylation to azures A, B, and C and thionine, and polymerization of these products to form dimers and trimers. This correlated with previous reports that used spectrophotometric techniques to characterize MB and thionine polymerization on WO$_3$ nanocolloids$^{58}$ and MB aggregates on amorphous WO$_3$.\textsuperscript{12} Importantly, Au nanoparticles did not affect the types of products observed during adsorption of MB under dark conditions. Also, oxidation of MB was not apparent over Au-SiO$_2$-WO$_3$ and WO$_3$ during this time. However, in the presence of Au-WO$_3$, a substantial m/z = 319 peak was observed under dark conditions, which could be attributed to the ring-opened MB sulfone. Upon further MS2 analysis, this peak could also be assigned to the Na$^+$ adduct of an unidentified compound with m/z = 296, which is a potential MB degradation intermediate.

To confirm that crystalline WO$_3$ was responsible for the extensive polymerization of dye molecules, the pure porous SiO$_2$ starting material was added to a solution of MB and equilibrated for 120 min under the same conditions. On the basis of ESI-MS data, no significant high m/z peaks are observed, and azure B remains as the secondary peak to MB (Figure 2-10). It was clear that SiO$_2$ did not demethylate MB or aggregate the converted products to any significant extent. Therefore, the addition of acidic WO$_3$ species to these materials caused extensive demethylation and polymerization of dye molecules to occur during the initial adsorption period. In fact, it
has also been observed in different materials that the incorporation of strongly acidic W-sites favors dealkylation and polymerization processes.\textsuperscript{59}

Figure 2-10. ESI-MS spectrum of the observed products after 120 min of dark MB adsorption with SiO$_2$. The major peak was MB monomers, with very minor demethylation and polymerization peaks.

After exposure of the catalyst suspensions to visible light for 300 min, the ESI-MS spectra showed significant changes. A more complicated mass spectrum indicated that a wider variety of products was observed as a result of photodegradation. Importantly, similar photocatalytic selectivity was observed over the three studied catalysts, regardless of their composition (Figure 2-8). Similar to the spectra measured after dark adsorption, MB demethylation products and aggregates of these products remained as the major components, and their abundance at the expense of monomeric MB (small peak at m/z = 284) indicated that MB was almost completely converted.
New peaks at m/z = 242 and 256 were attributed to the partial demethylation of MB to form azure C and azure A, respectively. Adducts of partially demethylated products, such as the NH$_4^+$ adduct of azure B (m/z = 288) were also observed. Major peaks at m/z = 114 and 150 were assigned to stable fragments of MB or demethylated products. Aggregates of thionine, the fully demethylated compound, were still the major products. Continued polymerization of partially demethylated products was shown by the peaks at m/z = 730, 774, and 818, corresponding to the trimers of azure C, azure A, and azure B, respectively. The peak at m/z = 906 was assigned as the thionine tetramer. Similar to the dark equilibration period, Au-loaded and nonloaded materials show similar selectivity toward this photocatalytic reaction.

In addition to demethylation products, the ESI-MS spectra showed evidence of photo-oxidation in the presence of each catalyst. A small peak at m/z = 319 was assigned to the ring-opened sulfone oxidation product of MB during photoirradiation. However, the sulfoxide (m/z = 303) could not be clearly identified in these tests. Depending on the catalyst, the m/z = 319 peak had varying intensities, with Au-WO$_3$ showing the most significant peak. It has been accepted that ring sulfur atoms of adsorbed MB are oxidized to the sulfoxide, causing ring opening, and then further oxidized to the sulfone.$^{52,60}$ Here, we conclude that demethylation is the primary mode of MB photodegradation, but oxidation may also proceed as a secondary photodegradation pathway. Also, this oxidation pathway may be more facile over Au-loaded catalysts (i.e., Au-WO$_3$). As highlighted below, Au-loaded catalysts also showed a substantial increase in MB photodegradation activity compared to their nonloaded counterparts. Current experiments are being performed on the interaction of
adsorbed MB with the surface, to examine the effect of this strong interaction on the photodegradation process.

After preliminary identification of MB degradation products with ESI-MS, we used UV-visible spectroscopy to quantify the removal of MB over time. A representative series of UV-vis spectra, for Au-SiO₂-WO₃, are shown in Figure 2-11. The major peak at 664 nm is due to monomeric MB, whereas the shoulder at 619 nm is due to the MB dimer. It is clear that a portion of MB was adsorbed by the solid during the initial period in the dark, and that some of the dimer was adsorbed as well. During the 300 min of visible light irradiation, a hypsochromic shift of the peak at 664 nm was observed due to polymerization and demethylation of MB, which is consistent with the compounds identified by ESI-MS (Figure 2-8). Similar spectra and hypsochromic shifts were observed in all UV-vis experiments (Figure 2-12).

Figure 2-11. UV-visible spectra of MB in an aqueous solution containing Au-SiO₂-WO₃ during irradiation with visible light. Inset: spectrum of MB in solution (no solid or irradiation).
Figure 2-12. UV-Vis spectra showing adsorption and visible light photodegradation of MB in the presence of SiO$_2$-WO$_3$, WO$_3$, and Au-WO$_3$ catalysts.
Utilizing the absorbance at 664 nm, we measured the ratios of the remaining MB concentration vs the initial MB concentration ($C/C_0$) before and during visible light irradiation with each catalyst (Figure 2-13A). Prior to irradiation, Au-WO$_3$ and WO$_3$ both had a significantly greater affinity for MB than Au-SiO$_2$-WO$_3$ and SiO$_2$-WO$_3$ and were able to adsorb nearly all of the MB from solution. Pure SiO$_2$ adsorbed an amount of MB (not shown, $C/C_0 = 0.88$) that was comparable to that for Au-SiO$_2$-WO$_3$. The large surface area of this sample (~450 m$^2$/g) accounted for the facile MB adsorption. Visible light irradiation of the MB/catalyst suspension followed the dark equilibration over the course of 300 min. Irradiation of MB in the absence of any porous solid did not produce any change in concentration. Also, there was no MB degradation with Au-SiO$_2$-WO$_3$ after 300 min in the dark following the initial adsorption period. This indicated the need for photoexcitation of the catalyst in order for MB degradation to proceed. It is clear from our data that Au-WO$_3$ and WO$_3$ behaved similarly, adsorbing most of the MB from solution during the 120 min adsorption period, and converting the remainder during visible light exposure. To compare reaction rates, the photodegradation data was fitted to first-order reaction kinetics, and the observed rate constant ($k_{obs}$) was calculated as the slope of the linear fit (Figure 2-13B). Importantly, Au-WO$_3$ had a faster rate of photodegradation than WO$_3$ under visible light irradiation. It also appeared that essentially all MB was degraded over Au-WO$_3$ before 300 min. Thus, it seemed that porous Au-WO$_3$ was, overall, the best material for total MB removal and degradation. As discussed above, Au-WO$_3$ did not contain smaller (< 10 nm) Au nanoparticles, as they were lost during the etching of Au-SiO$_2$-WO$_3$, which could negatively affect the photocatalytic performance of this material. Among the
SiO₂-containing materials, Au-SiO₂-WO₃ was slightly better than SiO₂-WO₃ at adsorbing MB, but was significantly better at degrading MB during the visible light exposure. Consistent with the pure WO₃ materials, the rate of MB conversion over Au-SiO₂-WO₃ was much greater than SiO₂-WO₃. We attributed this to the presence of small (3-5 nm) Au nanoparticles dispersed throughout the Au-SiO₂-WO₃ catalyst. Almost all of the MB was photocatalytically degraded in the presence of Au-SiO₂-WO₃ (93% conversion), while only 51% conversion was achieved with SiO₂-WO₃ after 300 min. Comparing $k_{obs}$ among the various materials, catalysts not containing SiO₂ showed faster rates of photodegradation than the SiO₂-containing catalysts. The rate of photodegradation was much faster for Au-WO₃ than Au-SiO₂-WO₃, but the difference was not as significant when WO₃ was compared to SiO₂-WO₃. This suggested that the presence of SiO₂ in these materials might hinder the rate of photocatalysis.
Figure 2-13. (A) Plot of MB remaining in solution (C/C₀, measured by the absorbance at 664 nm) as a function of photoirradiation time in the presence of various catalysts. The dashed line signifies the start of photoirradiation. (B) First-order reaction kinetics for data shown in panel A; respective $k_{obs}$ are listed to the right of each linear fit. Correlation coefficients ($R^2$) for each fit in panel B can be found in Table 2-2.

Table 2-2. Correlation coefficients ($R^2$) for each first-order linear fit in Figure 2-13B.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-WO₃</td>
<td>0.9482</td>
</tr>
<tr>
<td>WO₃</td>
<td>0.8633</td>
</tr>
<tr>
<td>Au-SiO₂-WO₃</td>
<td>0.9990</td>
</tr>
<tr>
<td>SiO₂-WO₃</td>
<td>0.9603</td>
</tr>
</tbody>
</table>

Importantly, this more clearly showed the benefit of depositing Au nanoparticles on these catalysts to enhance the rate of photocatalytic degradation of the remaining portion of MB. The improved photocatalytic activity of Au-loaded materials was attributed to the more efficient separation of $e^-/h^+$ pairs after WO₃ band gap
excitation. Upon photoexcitation, the electrons in the WO$_3$ conduction band (+0.2 eV vs NHE)$^{61}$ transfer to Au, which has a lower Fermi level (+0.5 eV vs NHE)$^{27,62}$.

Photoexcited h$^+$ can lead to direct oxidative degradation of adsorbed MB, or these excitons can oxidize adsorbed water to create reactive •OH. The latter mechanism has been proposed by Houas et al.$^{60}$ and further accepted by Steiner and Eder$^{52}$ for MB photo-oxidation over mesoporous WO$_3$. A scheme that relates the proposed photodegradation pathways to the relevant energy levels of the materials involved is shown in Figure 2-14. At this time, other mechanisms for the photocatalytic enhancements due to Au cannot be excluded, however. For instance, nanoparticulate Au deposited on WO$_3$ catalysts may also benefit from surface plasmon resonance (SPR) that could improve the rate of photocatalysis.$^{28}$ In summary, pure WO$_3$ adsorbed the greatest amount of MB and Au-loaded materials possessed enhanced photocatalytic activity compared to their nonloaded counterparts. Future studies will focus on altering Au loadings to optimize these photocatalysts.
Figure 2.14. Proposed photodegradation mechanisms of MB over Au-WO$_3$ catalysts. The heights of the valence band (VB) and conduction band (CB) of WO$_3$, and the Fermi level of Au on the schematic correspond to the energy scale on the left.

2.3. Conclusions

Porous Au-loaded SiO$_2$-WO$_3$ and WO$_3$ catalysts have been synthesized using a combined sonochemical and nanocasting process. Gold nanoparticles were found to be highly dispersed within the SiO$_2$ and WO$_3$ matrices. Also, the size of the deposited Au nanoparticles depended on the substrate composition, and ranged from 3 to 10 nm. Thermally stable Au nanoparticles resisted sintering after repeated high temperature (450 °C) treatments when combined in the SiO$_2$-WO$_3$ composite. We have prepared a porous Au-WO$_3$ photocatalyst simply by etching the Au-SiO$_2$-WO$_3$ composite. Mass spectral data in combination with UV-vis spectroscopy confirmed demethylation and polymerization of MB as the major degradation pathways during adsorption and visible light irradiation over Au-SiO$_2$-WO$_3$, Au-WO$_3$, and WO$_3$. Photo-oxidation of the MB ring sulfur also occurred as a secondary degradation pathway. The WO$_3$ contained in
these samples was responsible for the extensive polymerization of dye molecules. In addition, samples of pure WO$_3$ adsorb significantly more MB than SiO$_2$-WO$_3$ composites. Finally, we have shown clear photocatalytic benefits in loading SiO$_2$-WO$_3$ and WO$_3$ materials with Au nanoparticles. Gold nanoparticles did not alter the selectivity of MB photodegradation over these catalysts, but the Au-loaded catalysts photocatalytically degraded MB at a greater rate than their nonloaded counterparts. Enhanced exciton (e$^-$/h$^+$) separation within Au-loaded catalysts greatly improved the visible light photocatalytic activity of these materials, which may serve as promising environmental remediation photocatalysts.

2.4. Experimental Section

2.4.1. Materials Characterization

Nitrogen physisorption was carried out at 77 K on a Micromeritics TriStar 3000 surface area and porosity analyzer. Surface areas and pore size distributions were calculated using the BET and BJH methods, respectively. Powder X-ray diffraction (XRD) was performed on a Rigaku MiniFlex II diffractometer using Cu Kα radiation generated with a tube output voltage and current of 30 kV and 15 mA, respectively. The diffractometer was equipped with a water-cooled Scintillator detector that was used at a continuous rate of 0.5° (2θ) per minute. Scanning electron micrographs were recorded with a JEOL JSM-6060 SEM instrument. Dry samples were dispersed on carbon tape and sputter coated with Au/Pd prior to imaging. Sputter coating was omitted for samples containing Au. Transmission electron micrographs were recorded with a JEOL JEM-1400 TEM instrument operating at 120 kV. In some cases, samples
were embedded in Spurrs epoxy resin at 70 °C overnight and then micromted in order to analyze the interior surfaces of the porous particles. Others were dispersed in ethanol and then dropped onto copper grids. High-resolution transmission electron micrographs were recorded with a JEOL JEM 2100F microscope operating at 200 kV. Samples were dispersed in methyl chloride and transferred to carbon coated copper grids prior to analysis. Energy dispersive X-ray spectroscopy (EDS) elemental analysis of samples was done with an Oxford INCA system attached to the same microscope. Elemental analysis by ICP-OES was completed on a PerkinElmer Optima 7000DV ICP optical emission spectrometer (OES) with a CCD array detector, a PerkinElmer S10 autosampler, and WinLab32 software. Samples were first dried at 100 °C in air for several hours or overnight. Additionally, etched samples were calcined at 500 °C for 3 h in air to remove residual ethanol that was adsorbed during the washing step. Samples were first digested by adding 0.020 g of material to 1 mL of 2 M NaOH in a 1.5 mL Eppendorf tube followed by approximately 25 min of ultrasonication. Mixtures were left to shake vigorously for several hours or overnight to completely dissolve SiO₂ and WO₃ components. Samples containing Au NPs were allowed to settle overnight before subsequent centrifugation (14800 rpm, 5 min) and separation. The Au pellet was washed with 1 mL of H₂O then centrifuged. The supernatants were added to the initial digest solution of SiO₂ and/or WO₃. Three total H₂O washings were performed, and then the digest solution was adjusted to 0.1 M NaOH with H₂O. Diluted digest solutions of SiO₂ and WO₃ were prepared with 0.1 M NaOH in 100 mL volumetric flasks. Gold nanoparticles were transferred in water via pipet to a vial and then evaporated to near dryness on a hot plate. The Au NP residue was then digested in aqua
regia and then heated to evaporate solution to near dryness. To the Au/aqua regia residue, approximately 2 mL of 0.5 M HCl was added, swirled, and then evaporated by heating until residue remained. This washing/evaporation step was repeated a second time before transferring the Au solution to a 25 mL volumetric flask and diluting to mark with 0.5 M HCl. Concentrations of Au, Si, and W were determined by calibration curves. A PerkinElmer Lambda 35 UV/vis spectrometer with PerkinElmer UV Winlab software was used for the measurement of methylene blue in solution. Samples were analyzed in a quartz cuvette with a path length of 1 cm. Electrospray ionization mass spectrometry (ESI-MS) analysis of samples were conducted on an AB Sciex 4000 QTrap (AB Sciex, Framingham, MA) hybrid triple quadrupole/linear ion trap liquid chromatograph-mass spectrometer operating in single quadrupole mode, scanning from 100 to 1000 Da. Positive electrospray ionization (ESI) was used as the ionization source. Source temperature was maintained at 350 °C. Nitrogen was used as the sheath gas (GS1, flow = 30, arbitrary units), auxiliary gas (GS2, flow = 40) and curtain gas (flow = 30). The declustering potential was set to 60. Tandem MS (MS2) spectra were obtained using nitrogen as the collision gas. The accelerating voltage (collision energy) into the collision cell was optimized for each precursor ion to maximize the intensity of product ions. Samples were directly infused at 1 µL/min into an isocratic (50% H₂O and 50% acetonitrile with 0.1% formic acid) mobile phase flow from a Shimadzu Prominence high performance liquid chromatography (HPLC) system (Shimadzu Scientific Instruments, Columbia, MD). Mobile phase flow was maintained at 100 µL/min. Concentrated ammonium hydroxide (29 wt%) was obtained from Fisher
Scientific. All other chemicals were obtained from Sigma-Aldrich. All chemicals were used as received.

2.4.2. Synthesis of APMS Mesoporous Template

APMS are disordered mesoporous silica microparticles that can be synthesized very rapidly with good control of porosity and spherical morphology.\textsuperscript{63-65} In a typical synthesis, cetyltrimethylammonium bromide (CTAB, 9.0 g, 24.7 mmol) was dissolved in deionized H\textsubscript{2}O (198.0 g, 11 mol), EtOH (95\%, 55.5 g, 1.14 mol), and concentrated HCl (37 wt\%, 22.0 g, 223.0 mmol) at room temperature with vigorous stirring. Tetraethoxysilane (TEOS, 20.0 g, 96.0 mmol) was then added and stirring was continued for 5 min, after which time sodium fluoride (0.5 M, 23.8 g, 11.9 mmol) was added. The solution became turbid in 83 s and was immediately transferred to a polypropylene bottle that was sealed and placed in an oven at 373 K for 160 min. The bottle was then removed from the oven and cooled at room temperature for 20 min before collection of the product by filtration. The filtered precipitate was washed with water and ethanol. After air drying, the product was calcined using the following program: heat from 298 K to 723 K at 2 K min\textsuperscript{-1}, hold at 723 K for 240 min, heat to 823 K at 10 K min\textsuperscript{-1}, and finally hold at 823 K for 480 min before cooling rapidly to room temperature.

2.4.3. Nanocast Synthesis of Mesoporous WO\textsubscript{3} Microspheres

Ammonium metatungstate hydrate (AMT, 3.75 g, 1.26 mmol) was mixed with deionized H\textsubscript{2}O (2.5 mL, 0.14 mol) to create a 1.5 g AMT/mL solution. The sealed vial
was placed in a 373 K oven for 1 min to completely dissolve the WO$_3$ precursor. To a small crucible, APMS (0.5 g) was added and then impregnated with the AMT precursor by incipient wetness. More specifically, the volume of the precursor matched the pore volume of the hard template as determined by N$_2$ physisorption experiments. About half of the precursor was added dropwise into the template using an adjustable Eppendorf pipette and then stirred manually with a spatula for a few seconds. The rest of the precursor was then added and the mixture was stirred for approximately 10 min. During this time, the mixture became damp and aggregated. The mixture was then allowed to dry at room temperature for 3-4.5 h with periodic manual stirring. Once dried, the powder was then calcined in a box furnace (Lindberg Blue M/BF51866A) with chamber dimensions (width x depth x height) of 15.2 cm x 22.8 cm x 15.2 cm under flowing air with the following program: ramping from 298 K to 423 K, holding at 423 K for 180 min, ramping to 523 K, holding at 523 K for 180 min, ramping to 823 K, and finally holding at 823 K for 300 min. All temperature ramps proceeded at 1 K min$^{-1}$. Samples were loaded twice with AMT by repeating the above impregnation procedure. The resulting SiO$_2$-WO$_3$ composites were etched by gently shaking the greenish-yellow powder in a 15 mL centrifuge tube loaded with an aqueous solution of 10% (v/v) HF (10 mL) on an orbital shaker for 4 h and then centrifuged. The pale greenish-yellow product was washed three times with deionized H$_2$O (10 mL) and once with EtOH (10 mL) for 5 min each. The washed product was then dried at 348 K overnight. The dry product was a pale green powder. It is noteworthy to mention that this synthesis has been successfully scaled up to use an initial APMS weight of 3.0 g.
2.4.4. Sonochemical Deposition of Au Nanoparticles on SiO$_2$-WO$_3$ Spheres

A sonochemical method adapted from Gedanken and co-workers$^{41}$ was used to deposit Au nanoparticles on SiO$_2$-WO$_3$ spheres at room temperature. In a typical synthesis, 300 mL (16.67 mol) of deionized H$_2$O was added to a 500 mL round-bottom flask. Then, 0.6 g of SiO$_2$-WO$_3$ (APMS previously impregnated twice with ammonium metatungstate, AMT), and 3.088 mL chloroauric acid trihydrate (1 g HAuCl$_4$$\cdot$3H$_2$O in 100 mL of H$_2$O, 15.4 mg of Au, 0.078 mmol Au) were added with stirring. The nominal weight loading of Au was 2.5 wt % based on SiO$_2$-WO$_3$. After 30-40 min of stirring, the flask was submerged in a water bath-type sonicator (Branson 2510, 40 kHz, 130 W). During sonication, 19.5 mL of aqueous ammonium hydroxide (14.8 wt %, 8.7 M, 0.170 mol NH$_3$) was added dropwise in several installments throughout the total sonication time of 45 min. The suspension was then centrifuged for 15 min at 15000g, and then the liquid was decanted. The solid was washed twice with deionized water. The damp, yellow-colored solid was dried overnight under vacuum at room temperature. The dry powder was then calcined with the following program: ramp from 298 to 773 K at 0.95 K min$^{-1}$ followed by a 3 h hold at 773 K. The resulting product was a dark wine-colored powder.

2.4.5. Synthesis of Mesoporous Au-WO$_3$ Microspheres

Au-WO$_3$ microspheres were created by etching the Au-SiO$_2$-WO$_3$ composite material in 10% HF in a similar manner to the SiO$_2$-WO$_3$ composite above.
2.4.6. Visible Light Photocatalytic Degradation of Methylene Blue

Photocatalytic methylene blue (MB) degradation experiments were adapted from Steiner and Eder. In a typical experiment, MB in deionized H₂O (50 mL, 4.9 mg MB L⁻¹, 0.015 mM MB) was stirred in a foil-wrapped 100 mL beaker for several minutes. The appropriate photocatalyst powder (0.010 g) was then added and the mixture was left stirring in the dark for 2 h at room temperature to allow for adsorption equilibrium between the dye and the catalyst. After, the mixture was subjected to visible light irradiation (halogen lamp, white light, 72 W, 1520 lm) that was passed through a UV filter (Ru UV filter-001). The light source was positioned approximately 7 cm from the top of the beaker, which was fan-cooled during the experiment. At the appropriate time point, an aliquot was removed from the beaker and passed through a 22 mm syringe filter with a 0.2 μm nylon membrane (VWR International) before analysis by UV-vis spectroscopy and liquid chromatography (LC-MS). Filtration of the reaction solution was necessary to avoid artificial results due to light scattering from catalyst particles during spectroscopic measurements.
2.5. References


CHAPTER 3: PHOTOCATALYTIC OXIDATION OF METHANOL USING POROUS Au/WO₃ AND VISIBLE LIGHT

3.1. Introduction

Photocatalytic oxidation of organic molecules to CO₂, as well as more selective oxidation to other useful products, has been widely studied.¹⁻⁴ Titania (TiO₂) is the most commonly used photocatalyst⁵,⁶ because of its availability and its stability under various reaction conditions. However, a major disadvantage of TiO₂ is that it is only activated with UV radiation. Photocatalysts responsive to visible light, allowing lower energy sources and solar radiation to be used are of particular interest. Tungsten oxide (WO₃) has a band gap energy of ~2.4 – 2.8 eV, allowing it to be photoactivated with blue light (λ < 500 nm) and to serve as a viable alternative photocatalyst to TiO₂.

As is the case with all photocatalysts, there is a need to improve upon the charge separation of electrons and holes to increase catalytic rates. Metal oxide photocatalysts such as WO₃⁷,⁸ and TiO₂ absorb light of sufficient energy to induce band gap excitation and the formation of reactive electrons (e⁻) and holes (h⁺) that are responsible for catalytic reactions.⁹ For pure WO₃, the highly oxidizing holes in the O 2p valence band (VB = +3.1 V_NHE) will rapidly recombine with electrons in the W 5d conduction band (CB = +0.5 V_NHE) after band gap excitation. This significantly inhibits productive photooxidation at the catalyst surface. Also, the WO₃ conduction band is not sufficiently negative enough for the single electron reduction of O₂ to O₂⁻ (−0.284 V_NHE) or O₂ + H⁺ to HO₂ (−0.046 V_NHE), which are facile processes over TiO₂ because of its more negative CB potential. There have been observations of O₂⁻ over WO₃ photocatalysts,¹⁰ however, due to the reduction of O₂. Thus, the exact mechanism of
WO$_3$ CB electrons is still not completely understood. A second photocatalytic component is usually added to WO$_3$ to effectively trap electrons near the CB and serves as an electron pool that promotes O$_2$ reduction. Unlike the single electron reduction process, O$_2$ readily proceeds through multielectron reductions at more positive potentials over WO$_3$ photocatalysts (e.g., O$_2$ + 2H$^+$ + 2e$^-$ → H$_2$O$_2$, +0.682 V$_{NHE}$; O$_2$ + 4H$^+$ + 4e$^-$ → 2H$_2$O, +1.23 V$_{NHE}$). Therefore, these multielectron reactions can effectively utilize CB electrons given long exciton separation times. To achieve this goal, WO$_3$ has been coupled with various secondary oxides$^{11}$ and metal nanoparticles$^{4,7}$ that serve as cocatalysts. Commonly, metal nanoparticles such as Au and Ag are deposited on the metal oxide surface and form Schottky barriers that promote extended e$^-$ and h$^+$ separation.$^{12,13}$ With these composite systems, oxidation reactions involving alcohols can rapidly occur over WO$_3$ photocatalysts.

Gold nanoparticles (Au NPs) are a type of metal cocatalyst that can be deposited onto WO$_3$ catalysts, and they also have interesting optical properties of their own. Gold nanoparticles themselves exhibit surface plasmon resonance (SPR)$^{2,14-16}$ when irradiated by visible light that equals the frequency of d-electron dipole oscillations. These induced dipoles enhance the local electromagnetic field at the Au NP surface, and also increase the temperature at the nanoparticle to drive catalytic reactions.$^2$ The absorption energy is approximately 450 – 600 nm, but it strongly depends on the size and shape of the Au NPs. Recently, Kominami and coworkers$^{17}$ prepared a WO$_3$ photocatalyst coupled with Au and Pt nanoparticles for H$_2$ and O$_2$ formation using sacrificial glycerin in aqueous solutions. Action spectra showed that both band gap excitation of WO$_3$ and SPR of Au were necessary for significant H$_2$
formation. Platinum nanoparticles served as sites for $\text{H}^+$ reduction. Therefore, it is of interest to study the two different modes of photocatalysis on Au/WO$_3$ and observe differences in activity and product distributions depending on the catalyst composition. Other cocatalysts have also been used in conjunction with WO$_3$ for photooxidation reactions. For example, the partial oxidation of 2-propanol to acetone in aqueous solutions containing O$_2$ with WO$_3$/PdO$_x$ photocatalysts was studied by Abe and coworkers. $^4$ Although Au/TiO$_2$ photocatalytic oxidation of methanol (MeOH)$^{18}$ and other alcohols$^{19}$ has been well established using UV irradiation, Au/WO$_3$ systems using visible light have not been the focus of much research. Many electrocatalytic$^{20-23}$ and photoelectrocatalytic$^{24-26}$ studies of methanol (MeOH) oxidation have been performed. But the gas-phase photocatalytic oxidation of this molecule over WO$_3$ has been less studied, and in particular the behavior of Au/WO$_3$ photocatalysts in a continuous flow system in the gas phase is of specific interest to understand the influence of the catalyst surface composition on its reactivity and observe the cooperativity between WO$_3$ and Au NPs.

With this background in mind, we prepared porous WO$_3$ photocatalysts through a hard-templating approach and characterized with various physical and chemical techniques. These materials were then studied in the visible light photocatalytic oxidation of MeOH in a continuous flow gas-phase reactor under aerobic conditions at atmospheric pressure. The influence of the porous WO$_3$ structure on MeOH conversion rates was analyzed by comparing the porous particles to bulk WO$_3$ powder. Modification of WO$_3$ with SPR-active Au NPs was performed and the effects of Au
3.2. Results and Discussion

3.2.1. Characterization of Photocatalysts

Powder X-ray diffraction (XRD) was performed to analyze the crystallinity of the various photocatalysts (Figure 3-1). The broad WO₃ diffraction peaks were a reflection of the nanocrystalline nature of these materials. Tungsten oxide crystallite sizes ranged from 9 – 11 nm based on Scherrer calculations using the most intense peak at approximately 23°. On the basis of similar calculations, Au NP sizes were determined from the Au(111) peak at 38° for the WO₃-Au catalysts. The Au NP sizes were approximately 6 to 10 nm depending on the catalyst. Therefore, at various loadings, Au NPs of similar sizes remained on the porous WO₃ catalysts after sonochemical deposition and subsequent SiO₂ etching. It is expected that there was variability in the Au NP sizes, but these results are consistent with those observed in our previous work.²⁷,²⁸ SiO₂-Au possessed Au NPs with diameters of 4 nm. Bulk WO₃ ((B)-WO₃) prepared by the calcination of ammonium metatungstate and porous TiO₂ was also characterized by XRD (Figure 3-2). Based on XRD peak widths, it was clear that (B)-WO₃ was composed of larger crystallites (28 – 37 nm) than the porous WO₃ samples. Nanocrystalline anatase TiO₂ was the only observed phase for the porous TiO₂ material.
**Figure 3-1.** XRD patterns of porous WO$_3$ and WO$_3$-Au catalysts at various Au wt% loadings. Miller indices of the monoclinic WO$_3$ phase (ICDD: 043-1035) are notated above relevant peaks. The shaded section designates the Au(111) peak observed with Au-modified materials. The Au(200) peak at 45° is only visible in the SiO$_2$-Au sample.

**Figure 3-2.** XRD patterns of (B)-WO$_3$ and porous TiO$_2$. Monoclinic WO$_3$ and anatase TiO$_2$ (JCPDS: 84-1286) are the only observed crystalline phases for these samples.
The porous nature of the WO$_3$ catalysts provided these materials with increased surface areas relative to (B)-WO$_3$ as shown by N$_2$ physisorption experiments (Table 3-1, Figure 3-3, Figure 3-4). Hard templating using mesoporous SiO$_2$ afforded porous WO$_3$ with a BET surface area of 76 m$^2$ g$^{-1}$ after SiO$_2$ removal, which is consistent with other similar preparations of porous WO$_3$. The porosity of WO$_3$-Au was not substantially different from WO$_3$, regardless of the amount of Au loading. Au wt%, W/Au ratios, and the complete removal of the SiO$_2$ template were confirmed by ICP-OES (Table 3-1). Thus, the combination of XRD, N$_2$ physisorption, and ICP-OES data supported the synthesis of pure and Au-modified porous nanocrystalline WO$_3$ catalysts, similar to those prepared in our previous studies.$^{27,28}$

Table 3-1. Summary of elemental analysis, Au nanoparticle sizes, and porosity data for the catalysts studied in this work.

<table>
<thead>
<tr>
<th>sample</th>
<th>W (wt%)$^a$</th>
<th>Au (wt%)$^a$</th>
<th>W/Au (mole ratio)$^a$</th>
<th>Si/W (mole ratio)$^a$</th>
<th>Au size (nm)$^b$</th>
<th>$S_A_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{pore}$ (cm$^3$ g$^{-1}$)</th>
<th>$d_{pore}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>500</td>
<td>1.00</td>
<td>93</td>
</tr>
<tr>
<td>SiO$_2$-Au</td>
<td>---</td>
<td>1.07</td>
<td>---</td>
<td>---</td>
<td>4</td>
<td>500</td>
<td>0.58</td>
<td>43</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>78.2</td>
<td>---</td>
<td>---</td>
<td>0.0044</td>
<td>---</td>
<td>76</td>
<td>0.18</td>
<td>29</td>
</tr>
<tr>
<td>(B)-WO$_3$</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1</td>
<td>0.004</td>
<td>36</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>70</td>
<td>0.06</td>
<td>29</td>
</tr>
<tr>
<td>WO$_3$-Au(1)$^c$</td>
<td>74.8</td>
<td>1.98</td>
<td>40.4</td>
<td>0.0024</td>
<td>10</td>
<td>76</td>
<td>0.21</td>
<td>28</td>
</tr>
<tr>
<td>WO$_3$-Au(3)$^c$</td>
<td>74.2</td>
<td>4.03</td>
<td>19.7</td>
<td>0.0042</td>
<td>6</td>
<td>75</td>
<td>0.19</td>
<td>26</td>
</tr>
</tbody>
</table>

$^a$ Determined by ICP-OES. $^b$ Measured by XRD. $^c$ Nominal Au wt% loading
Figure 3.3. N$_2$ physisorption isotherms and pore size distributions (insets) for catalysts not modified with Au NPs.
3.2.2. Photocatalytic Oxidation of Methanol in a Continuous Gas-Phase Flow Reactor

A continuous gas-phase flow reactor was designed to evaluate the porous WO$_3$ materials in the visible light photocatalytic oxidation of MeOH. Details concerning the photoreactor set-up used in this work are described in the Experimental Section. The feed composition (MeOH, N$_2$, and air) and flow rate, and the lamp intensity were optimized to obtain significant MeOH conversions for the porous catalysts.
The emission spectrum (380 – 950 nm) of the Xe arc lamp after passing through the UV filter, the hot mirror, and the water jacket of the photoreactor was measured (Figure 3-5). It was clear that, although efforts were made to reduce heating radiation, a significant portion of IR (> 800 nm) radiation relative to visible light was emitted by the Xe arc lamp and irradiating the surface of the photocatalysts. Visible light from 400 – 500 nm was another major component of the Xe arc lamp emission and was useful to both WO$_3$ and Au NPs. The lamp intensity at the reactor (800 mW cm$^{-2}$) was sufficient to photocatalytically convert MeOH under continuous-flow conditions. Importantly, this Xe arc source increased the temperature at the outer surface of the reactor to ~90 – 100 °C at the spot of irradiation. However, the water cooled jacket surrounding the reactor minimized potential thermal reactions at the catalyst. Future studies will focus on modifying the current photoreactor to better address heating issues.

Figure 3-5. Emission spectra of the 125 W Xe arc lamp used in this study. IR radiation > 800 nm comprises a significant portion of the Xe arc lamp output spectrum.
Figure 3-6 compares the visible light photocatalytic conversion of MeOH over various catalysts as a function of irradiation time. Steady-state MeOH conversions were observed in about 0.5 h and decreased slightly with increasing time. Control experiments with porous SiO$_2$, porous TiO$_2$, and a reactor with no catalyst were performed under similar conditions. As expected, porous SiO$_2$ was not active in this visible light photocatalytic reaction because of its insulating properties. Porous TiO$_2$ was also inactive, which confirmed that the reaction is occurring under visible light irradiation. Photocatalytic MeOH conversion would be expected if significant UV radiation was incident on the sample. To test this hypothesis, an experiment with porous TiO$_2$ was performed without the UV filter used in the other tests. Indeed, the UV photooxidation of MeOH was observed over TiO$_2$ with a maximum MeOH conversion of 19%. Notably, the TiO$_2$ UV photocatalyst was less active than porous WO$_3$ under visible light. This result also meant that the UV filter was effective at removing higher energy UV wavelengths. Also, there was no appreciable MeOH photolysis in the absence of a catalyst. Clearly, the photocatalytic conversion of MeOH was successful only in the presence of WO$_3$ and/or Au NP visible light photocatalysts. The porous WO$_3$ catalyst exhibited significantly greater conversions (~30%) than (B)-WO$_3$ (< 1%), which showed negligible activity under the studied reaction conditions. This result highlighted the significant benefit of introducing porosity to the WO$_3$ catalysts. Notably, the color of the WO$_3$ catalyst changed from its initial greenish yellow to blue-green during photocatalysis. This indicated that the WO$_3$ was reduced during the reaction and that the reoxidation of WO$_3$ was a slow process, which was also observed by Sayama and coworkers in the photocatalytic oxidation of acetaldehyde.$^{29}$
This reduction of WO$_3$ during irradiation, however, did not have a significant influence on the photocatalytic activity, as shown by the steady conversion over 2 h of reaction.

![Graph showing photocatalytic conversion of methanol as a function of irradiation time for various catalysts under flow-type reaction conditions.

Figure 3-6. Photocatalytic conversion of methanol as a function of irradiation time for various catalysts under flow-type reaction conditions.]

Supported Au NPs alone are active photooxidation catalysts in the presence of air. The large surface area of the porous SiO$_2$ support also provided abundant reaction sites. Gold-modified SiO$_2$ (SiO$_2$-Au) was also an active catalyst that reached a maximum MeOH conversion of 43%. Porous WO$_3$ modified with Au NPs (WO$_3$-Au) were significantly more active than the pure metal oxide and activity increased with Au loading. Visible light photocatalysis over both pure WO$_3$ and SiO$_2$-Au indicated that band gap excitation and SPR, respectively, are the observed mechanisms for these two catalysts under these reaction conditions. Initial attempts to isolate the band gap excitation (with a blue LED) and the SPR effect (with a green LED) were unsuccessful with our current reactor design, due to the low power of the LEDs. Future experiments...
will focus on studying the individual photocatalytic mechanisms on these composite catalysts.

To better compare the reactivities of these catalysts, the normalized rates of MeOH conversion (µmol min⁻¹) were calculated per unit of irradiated surface area (cm²), per gram of catalyst (g_{cat}⁻¹), per unit of catalyst surface area (m²), and per gram of Au in the catalyst (g_{Au}⁻¹) (Table 3-2). Photocatalytic rates normalized to the irradiated surface area and per gram of catalyst are similar for both SiO₂·Au and WO₃, which showed, in this case, that SPR and band gap excitation provided similar activities. When normalized to the surface area of the catalyst (as determined by N₂ physisorption), the WO₃ catalyst is more active than SiO₂. This can be explained by the physical and chemical nature of the catalysts. For instance, SiO₂·Au is composed of mostly insulating SiO₂, which is not an active photocatalyst, as shown above. Porous WO₃, however, is comprised entirely of nanocrystalline WO₃ that is photocatalytically active under visible light irradiation. Therefore, WO₃ has a greater percentage of active surface area compared to SiO₂·Au, which is only active at Au sites.

Table 3-2. Photocatalytic methanol conversion rates for the active catalysts studied in this work.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>conversionᵃ</th>
<th>MeOH conversion rate (µmol min⁻¹)</th>
<th>cm⁻²</th>
<th>g_{cat}⁻¹</th>
<th>m²·cat⁻¹</th>
<th>g_{Au}⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂·Au</td>
<td>43%</td>
<td>1.27</td>
<td>78.6</td>
<td>0.157</td>
<td>7350</td>
<td></td>
</tr>
<tr>
<td>WO₃</td>
<td>35%</td>
<td>1.43</td>
<td>81.3</td>
<td>1.07</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>WO₃·Au(1)</td>
<td>60%</td>
<td>2.06</td>
<td>120</td>
<td>1.57</td>
<td>6040</td>
<td></td>
</tr>
<tr>
<td>WO₃·Au(3)</td>
<td>90%</td>
<td>3.65</td>
<td>205</td>
<td>2.74</td>
<td>5100</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Equilibrium MeOH conversion at approximately 40 min.
ᵇ Irradiated catalyst surface = 3.08 cm²
ᶜ Calculated using the total surface area of catalyst
As shown previously, the deposition of Au NPs onto metal oxides can positively influence the rate of photocatalysis for several different reactions.\textsuperscript{30,31} Indeed, WO\textsubscript{3}-Au was more active than WO\textsubscript{3}. Also, the activity of WO\textsubscript{3}-Au increased with Au loading, with WO\textsubscript{3}-Au(3) being the most active catalyst studied. The WO\textsubscript{3}-Au catalysts were more active than pure WO\textsubscript{3} due to the combined band gap excitation of nanocrystalline WO\textsubscript{3} and the SPR absorption of Au NPs. When combined, the SPR effect of Au NPs significantly enhanced the separation of photoexcited valence band holes and conduction band electrons in WO\textsubscript{3}, leading to increased photocatalytic activity. Also, it was expected that the WO\textsubscript{3}-Au(3) catalyst was the most active per unit of irradiated area, as a greater percentage of the catalyst surface was covered with Au NPs. Initial studies showed that SiO\textsubscript{2}-Au activity also increased at higher Au wt% loadings. Therefore, it is important to emphasize that Au NPs are clearly responsible for the increased photocatalytic activity of these materials. We predict that Au loading plays an important role in the observed rates.

Observations of the catalytic rates per gram of Au were used to better compare the SiO\textsubscript{2} and WO\textsubscript{3} catalysts, which have different Au loadings. These rates showed that the activity of the Au NPs was greater when deposited on SiO\textsubscript{2} compared to WO\textsubscript{3}. Thus, the metal – support interaction influenced the reactivity of the Au NPs. The data suggested that WO\textsubscript{3} has a negative effect on the Au NP photocatalytic activity. One explanation for the decreased Au NP activity when deposited on WO\textsubscript{3} may be revealed through X-ray photoelectron spectroscopy (XPS) studies. Compared to SiO\textsubscript{2}-Au, WO\textsubscript{3}-Au clearly exhibited higher energy Au 4f bands.\textsuperscript{28} Shifts of these bands to higher energies indicated a strong Au/WO\textsubscript{3} interaction. Also, this showed that the Au NPs on
WO₃ possessed slightly cationic (Au δ⁺) character, while SiO₂-Au possessed mainly Au⁰ species. Therefore, oxidized Au species on WO₃ may be detrimental to the photocatalytic activity of Au NPs. Stronger electronic interactions between Au and WO₃ are expected for this metal – semiconductor combination compared to the SiO₂-Au (insulator – metal) material.

In addition to catalytic rates, the steady-state photocatalytic product distributions were monitored by GC-TCD for WO₃ catalysts with and without Au NP modification and for SiO₂-Au (Figure 3-7). Analysis of product distributions provided information on the mechanisms of photocatalytic reactivity for each catalyst. Pure porous WO₃ (Figure 3-7A) was selective mainly towards the oxidation of MeOH to formaldehyde (HCHO, ~60%). This could be due to the formation of hydroxyl radicals (•OH) from the reaction of adsorbed H₂O with oxidizing h⁺, which could then selectively oxidize MeOH to HCHO. Adsorbed methoxy groups (–OCH₃) could also be present on the catalyst surface after MeOH dissociation, and direct oxidation of these groups³²,³³ to HCHO through reaction with h⁺ is also expected.³²-³⁴

It was also apparent that water was a major product of this photocatalytic reaction. As mentioned above, WO₃ is capable of a 4-electron reduction of O₂ to H₂O under visible light irradiation due to the sufficiently negative potential of the WO₃ conduction band. Therefore, H₂O formation is expected under these aerobic reaction conditions. Oxidative removal of adsorbed H atoms by O₂ from the feed gas may also be a source of H₂O.³⁵ Finally, surface hydroxyls can react with adsorbed H atoms to release H₂O, with dissociated oxygen atoms filling the resulting vacancies.³⁴
Separate from HCHO and H₂O, other products were found in smaller amounts. Importantly, CO₂ formation was negligible when WO₃ was used as a catalyst. This result illustrates the highly selective nature of this catalyst to primarily one oxidation product of MeOH even with a high O₂ content in the feed (20%). Also, this means that the photocatalytic oxidation of MeOH to HCHO and the desorption of HCHO occurred at a greater rate than the formation of CO₂. Methyl formate (MF) resulted from the photocatalytic oxidative coupling of HCHO and surface-adsorbed methoxy species that were present after the dissociative adsorption of MeOH. The dimerization of photocatalytically generated HCHO has also been reported as another mechanism for MF production over TiO₂ UV photocatalysts. Other mechanisms for photocatalytic MF formation have also been proposed, which were less likely to occur in our system particularly when pure WO₃ was the catalyst. Minor thermal catalytic reactions involving WO₃ and MeOH were observed in the form of dimethyl ether (DME) production at approximately 5 – 6% selectivity. As mentioned above, by using the current photoreactor configuration, we were unable to completely remove all heating effects of the Xe arc lamp. In our previous work, DME formed during the catalytic dehydration of MeOH over nanocrystalline WO₃ acid sites under thermal conditions. Also, MF was not observed in thermal catalytic reactions over WO₃, which further supported the photocatalytic formation of this minor product in the current study.
Figure 3-7. Product selectivity as a function of irradiation time during the photocatalytic oxidation of MeOH over (A) WO₃, (B) SiO₂-Au, (C) WO₃-Au(1), and (D) WO₃-Au(3). The reacted e⁻/h⁺ ratio is shown for each catalyst.

A markedly different product distribution was observed when SiO₂-Au was used as the catalyst (Figure 3-7B). Water was the major product (42%) at earlier irradiation times. Again, this could be a result of O₂ reduction by photoexcited electrons in Au NPs after SPR absorption. However, dissociation of MeOH to methoxy species and H atoms is facile over Au surfaces, and similar mechanisms for H₂O formation as described above for WO₃ are possible. Methanol oxidation to HCHO was also a major reaction pathway. Total oxidation to CO₂ also occurred in 5% selectivity, which indicated that more complete oxidation was facilitated by Au NPs compared to WO₃. Interestingly, as irradiation time increased, the selectivity to MF
also increased to 42% at the expense of decreasing HCHO selectivity. This led to two conclusions: first, that there were greater amounts of adsorbed methoxy groups and HCHO (as shown by the decreasing amount of HCHO in the product effluent) on SiO$_2$-Au compared to WO$_3$; second, that MF formation was rapid over Au NPs. As shown above, the formation and desorption of HCHO was fast on WO$_3$, but longer residence times of HCHO and methoxy groups on SiO$_2$-Au led to higher MF selectivity. An explanation for the increasing trend towards MF selectivity may be due to changes in methoxy surface coverage during irradiation. Also, at longer irradiation times, SPR absorption by Au NPs may rapidly heat the particles and facilitate oxidation reactions.$^{2,39}$ The SPR effect over silver nanoparticles supported on SiO$_2$ was similarly shown to be responsible for the selective formation of MF in the liquid phase oxidation of MeOH.$^{40}$ During SPR absorption, MeOH oxidation occurs at the positive (h$^+$ rich) dipole and O$_2$ reduction at the negative dipole (e$^-$ rich) of the Au NPs.$^{41}$ Interestingly, this selectivity towards MF is similar to the thermal catalysis selectivity shown by SiO$_2$-Au in the aerobic transformation of MeOH.$^{28}$ Overall, the different product distributions at similar MeOH conversions (35 – 43%) over WO$_3$ and SiO$_2$-Au indicated that different MeOH oxidation reaction mechanisms were in operation in each system.

The combination of WO$_3$ and Au NPs led to further changes in the product distribution. Formaldehyde (32 – 40%) was the major oxidation product for WO$_3$-Au(1) (Figure 3-7C), but CO$_2$ was the major product (39%) for WO$_3$-Au(3) (Figure 3-7D). Therefore, WO$_3$-Au(1) behaved similarly to WO$_3$, although there was slightly higher selectivity to MF and CO$_2$, which is attributed to the activity of the Au NPs on the WO$_3$
surface. Oxygen dissociation at the Au surface increased as gold content increased (i.e., from WO$_3$-Au(1) to WO$_3$-Au(3)), facilitating the deep oxidation of adsorbed methoxy groups and HCHO to CO$_2$. On the basis of our previous work, it is also possible that Au NPs increased the lability of WO$_3$ lattice oxygen to oxidize MeOH and HCHO to CO$_2$. The higher activity and higher MeOH conversions achieved over the WO$_3$-Au(3) catalyst also decreased the density of adsorbed methoxy groups and HCHO, which led to unfavorable MF formation. The rates of methoxy group and HCHO oxidation were faster than their desorption, which was not observed over WO$_3$ alone. Therefore, Au NPs clearly increased the oxidizing activity of these WO$_3$ photocatalysts.

The reacted $e^-/h^+$ ratio is a measure of the efficiency of the reduction and oxidation reactions that were observed over the studied catalysts (Figure 3-7). This ratio was the greatest for WO$_3$-Au(3) ($e^-/h^+ = 1.15$), which indicated that the number of reacted electrons relative to reacted holes was greatest for this catalyst. Enhanced separation of $e^-/h^+$ pairs in the presence of Au NPs led to high H$_2$O production. Also, the reduction reaction became more efficient with increased Au loading. In contrast, $e^-/h^+ = 0.44$ for the WO$_3$ catalyst. Thus, electrons were more efficiently utilized in the presence of Au NPs. The low $e^-/h^+$ ratio for WO$_3$ agreed with the high oxidation selectivity for this catalyst, which meant that reactions with surface $h^+$ were more favored on the pure WO$_3$ catalyst than those modified with Au NPs.

3.3. Conclusions

Active porous WO$_3$ photocatalysts were prepared using a facile hard-templating approach and modified with dispersed Au NPs using a sonochemical method. The
increased surface area of the porous WO$_3$ catalyst led to enhanced visible light photooxidation activity relative to bulk WO$_3$. Our findings are summarized in Figure 3-8, which shows the three different photocatalytic mechanisms observed over the different catalysts. In the photooxidation of MeOH, WO$_3$ was highly selective to HCHO, and produced negligible CO$_2$ (Figure 3-8A). Gold nanoparticles on porous SiO$_2$ oxidized MeOH to HCHO, which rapidly coupled with adsorbed methoxy species at longer irradiation times to produce methyl formate (Figure 3-8B). The single component photocatalysts (WO$_3$ and SiO$_2$-Au) were highly selective catalysts on their own. Sonochemically deposited Au NPs significantly increased the oxidation activity of the WO$_3$ catalysts due to simultaneous WO$_3$ band gap excitation and Au nanoparticle SPR absorption, which improved e$^-$/h$^+$ separation (Figure 3-8C). At lower Au loadings, WO$_3$-Au(1) behaved similarly to WO$_3$ in that HCHO was the major oxidation product. The increased oxidation activity of WO$_3$-Au(3), however, led to greater production of CO$_2$ at the expense of decreased selectivity to HCHO.
Figure 3-8. (A) Thermally driven formation of methoxy groups over WO₃ surfaces followed by the photocatalytic oxidation to HCHO via valence band h⁺; (B) photocatalytic MF formation over SPR-active Au NPs on SiO₂-Au; (C) simultaneous band gap excitation and SPR on WO₃-Au, leading to increased CO₂ production at higher loadings.

3.4. Experimental Section

3.4.1. Materials and Characterization Methods

Nitrogen physisorption was carried out at 77 K on a Micromeritics TriStar 3000 surface area and porosity analyzer. Surface areas and pore size distributions were calculated using the BET and BJH methods, respectively. Powder X-ray diffraction (XRD) was performed on a Rigaku MiniFlex II diffractometer using Cu Kα radiation generated with a tube output voltage and current of 30 kV and 15 mA, respectively. The diffractometer was equipped with a water-cooled Scintillator detector that was used at a continuous rate of 0.5° (2θ) per minute. Elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) was completed on a PerkinElmer Optima 7000DV ICP optical emission spectrometer with a CCD array.
detector, a PerkinElmer S10 autosampler, and WinLab32 software. Concentrated ammonium hydroxide (29 wt%) was obtained from Fisher Scientific. Chloroauric acid trihydrate (HAuCl₄•₃H₂O, ACS reagent, 99.99%) was purchased from Alfa Aesar. All other chemicals were obtained from Sigma-Aldrich. All chemicals were used as received.

3.4.2. Synthesis of Acid-Prepared Mesoporous Spheres (SiO₂)

Cetyltrimethyl ammonium bromide (CTAB, 9.0 g, 24.7 mmol) was dissolved in a solution of deionized water (198 g, 11 mol), ethanol (200 proof, 55.5 g, 1.20 mol), and concentrated HCl (37 wt%, 22.0 g, 223.0 mmol) at room temperature with vigorous stirring. Tetraethoxysilane (TEOS, 20.0 g, 96.0 mmol) was then added and stirring was continued for 5 min, after which a solution of NaF (0.5M, 23.8 g, 11.9 mmol) was added. The solution became turbid in about 83 s and was immediately transferred to a Teflon bottle that was sealed and placed in an oven at 373 K for 160 min. The bottle was then removed from the oven and cooled at room temperature for 60 min before filtration of the product and washing with water and ethanol. Following air drying of the product at room temperature, the material was calcined under flowing air with the following heating program: ramp from 298 K to 723 K at 2 K min⁻¹, hold at 723 K for 240 min, ramp to 823 K at 10 K min⁻¹, and hold at 823 K for 480 min before cooling to room temperature. This sample is denoted as SiO₂.
3.4.3. Sonochemical Deposition of Au NPs onto APMS (SiO$_2$-Au)

Calcined APMS was dried at 100 °C overnight (1.0 g) before being dispersed in 150 mL H$_2$O in a 250 mL round-bottom flask with stir bar and then stirred for 10 min. Brief sonication of the flask (water bath-type sonicator, Branson 2510, 40 kHz, 130 W) was done to break up aggregates of SiO$_2$. A solution of chloroauric acid (0.0255 M HAuCl$_4$•3H$_2$O, 1.366 mL, 0.0372 mmol Au) was then added and stirring continued for 30 – 40 min. Sonication of the mixture began as above, during which, concentrated aqueous ammonium hydroxide (29 wt% NH$_3$, 4 mL, 61.3 mmol NH$_3$) was added dropwise over the course of the entire sonication period (45 min). The NH$_3$ : Au mole ratio was 1648 : 1, and the reaction mixture pH = 10.91. The product was filtered, washed with 250 mL water, dried under vacuum air at room temperature overnight, and calcined under air flow at 773 K for 3 h (ramp rate = 0.95 K min$^{-1}$) yielding a red colored product. This sample is denoted as SiO$_2$-Au.

3.4.4. Incipient-Wetness Impregnation of SiO$_2$ with Ammonium Metatungstate and Etching of SiO$_2$ to Yield WO$_3$

About 3 g SiO$_2$ was added to a crucible and then an aqueous solution of ammonium metatungstate (AMT, 1.5 g AMT/mL H$_2$O) was added dropwise to the dry powder via incipient wetness (2.992 cm$^3$ g$^{-1}$ = total pore volume of SiO$_2$). The damp mixture was manually stirred for 10 min, and then the mixture was left to dry at room temperature in air for 4.5 h. The dry powder was then calcined under air flow with the following program: ramp from 298 K to 423 K, hold at 423 K for 3 h, ramp to 523 K, hold at 523 K for 3 h, ramp to 823 K, hold at 823 K for 5 h. All ramp rates were 1 K
min\(^{-1}\). The impregnation, drying, and calcination steps were repeated a second time. This yielded a yellowish-green colored SiO\(_2\)-WO\(_3\) composite powder.

To remove the silica template, the SiO\(_2\)-WO\(_3\) composite (1.0 g) was added to 11 mL of 10% HF in H\(_2\)O (1 mL concentrated HF with 9 mL H\(_2\)O) contained in a 15 mL plastic centrifuge tubes. Caution: HF is extremely toxic and corrosive, it is imperative that researchers wear appropriate personal protective equipment while using this acid. The sealed tubes were placed on orbital shakers to mix gently for approximately 4 h. The solids were then centrifuged and the supernatant disposed of appropriately. The particles were washed three times with 11 mL H\(_2\)O and then once with 11 mL ethanol. The washed samples were left to dry in the centrifuge tube under air in an oven at 353 K overnight. The resulting sample is denoted as WO\(_3\). Similar WO\(_3\) materials have been prepared in our previous studies.\(^{27,28}\)

### 3.4.5. Bulk WO\(_3\) Preparation ((B)-WO\(_3\))

Ammonium metatungstate hydrate (AMT, (NH\(_4\))\(_6\)H\(_2\)W\(_{12}\)O\(_{40}\) \(\cdot\) xH\(_2\)O, 4.3 g) was ground into a fine powder and then calcined in the same way as the SiO\(_2\)-WO\(_3\) composite above.

### 3.4.6. Porous TiO\(_2\) Preparation (TiO\(_2\))

Porous TiO\(_2\) was prepared using an adapted procedure from Leitner and coworkers.\(^{45}\) In a beaker, 2.0 g SiO\(_2\) was mixed with 40 mL of a 50/50 (v/v) solution of ethanol and titanium isopropoxide (Ti(iPrO)\(_4\)). Brief sonication was utilized to disperse the powder, and then stirring continued for 20 h. The mixture was then centrifuged and
the supernatant was removed. The product was left to dry over night at 90 °C. The dry powder was mixed with another 40 mL ethanol and was added to yield 40 mL 50/50 (v/v) solution of Ti(iPrO)$_4$ and ethanol, then dried at 80 °C. A 20 mL Ti(iPrO)$_4$/ethanol solution was mixed with the powder followed by centrifugation, decantation of the supernatant and then drying at 60 °C. Hydrolysis of the Ti(iPrO)$_4$ precursor loaded inside the pores of SiO$_2$ was completed with a 40 mL 50/50 (v/v) solution of water and ethanol for 3 h. After evaporation of the solvent at 60 °C, the sample was calcined with the same program as used for SiO$_2$, to yield SiO$_2$-TiO$_2$.

The SiO$_2$-TiO$_2$ composite was added to 2M NaOH in a plastic centrifuge tube and shaken for about 3 h to remove the silica portion of the composite. Following centrifugation and removal of the supernatant, the material was added to a fresh solution of 2M NaOH for a second and then a third time. The final material was dried at 60 °C overnight. This sample is denoted as TiO$_2$.

3.4.7. Sonochemical Deposition of Au NPs onto SiO$_2$-WO$_3$ Followed by SiO$_2$ Removal (WO$_3$-Au)

The SiO$_2$-WO$_3$ composite (1.3 g) was first dried at 100 °C overnight and then added to 195 mL H$_2$O in a 250 mL round-bottom flask with stir bar and then stirred for 10 min. Brief sonication was used to break up aggregates of SiO$_2$-WO$_3$. Different volumes of chloroauric acid (0.0255 M HAuCl$_4$•3H$_2$O) were added to the suspension depending on the desired nominal wt% loading of Au NPs. For 1 wt% Au (based on the mass of SiO$_2$-WO$_3$), 2.521 mL (0.0687 mmol Au) were used, and for 3 wt% Au, 7.873 mL (0.215 mmol Au) were used. The suspension was stirred for 30 – 40 min.
Sonication of the mixture began as above, during which, concentrated aqueous ammonium hydroxide (29 wt% NH₃, 5.2 mL, 79.7 mmol NH₃) was added dropwise over the course of the entire sonication period (45 min). The NH₃ : Au mole ratio (and pH) was 1160 : 1 (pH = 10.45) and 371 : 1 (pH = 10.76 ) for the 1 wt% Au sample and the 3 wt% sample, respectively. After filtration, washing, drying, and calcination as done with SiO₂-Au above, dark, wine purple-colored SiO₂-WO₃-Au powders were obtained. The SiO₂ portion of the SiO₂-WO₃-Au product was removed with 10% HF as described above. Some Au NPs are lost during this process as confirmed by the purple colored supernatant observed during washes. The samples are denoted as WO₃-Au(1) and WO₃-Au(3), where the number in parentheses is the nominal Au wt% (based on SiO₂-WO₃ mass) used in the synthesis.

3.4.8. ICP-OES Sample Preparation Procedures

Samples were first dried at 100 °C in air for several hours. Additionally, samples that were previously etched (free of SiO₂) were calcined at 500 °C for 3 h in air to remove residual ethanol that was adsorbed during the washing step. Samples were first digested by adding 0.020 g of material to 1 mL of 2 M NaOH in a 1.5 mL Eppendorf tube followed by approximately 30 min of ultrasonication. Mixtures were left to shake vigorously for several hours to completely dissolve SiO₂ and WO₃ components. Samples containing Au NPs were allowed to settle overnight before subsequent centrifugation (15,000 rpm, 2 min) and separation. The Au pellet was washed with 1 mL H₂O then centrifuged. The supernatants were added to the initial digest solution of SiO₂ and/or WO₃. Three total H₂O washings were performed, and
then the digest solution was adjusted to 0.1 M NaOH with H₂O. Diluted digest solutions of SiO₂ and WO₃ were prepared with 0.1 M NaOH in 100 mL volumetric flasks. Gold nanoparticles were quantitatively transferred via pipet from the Eppendorf tube with water to a vial and then evaporated to near dryness on a hot plate. The Au NP residue was then digested in aqua regia and then heated to evaporate solution to near dryness. To the Au/aqua regia residue, approximately 2 mL 0.5 M HCl was added, swirled, and then evaporated by heating until residue remained. This washing/evaporation step was repeated a twice before transferring the Au solution to a 25 mL volumetric flask and diluting to mark with 0.5 M HCl. Concentrations of Au, Si, and W were quantified by calibration curves using emission wavelengths of 267.599 nm, 251.611 nm, and 207.912 nm, respectively.

3.4.9. Continuous-Flow Photocatalytic Oxidation of Methanol

Photocatalytic methanol (MeOH) oxidation studies were carried out under aerobic conditions at atmospheric pressure in a horizontal continuous flow reactor. Photographs and diagrams of the catalysis setup and the reactor itself are shown in Figure 3-9.
Figure 3-9. (A, C) Schematics and (B, D) photographs of the photocatalysis rig and the Pyrex glass photoreactor in which the catalyst coated borosilicate plate was inserted. The UV filter is the optic closer to the Xe arc lamp and the hot mirror is closer to the reactor as shown in (D).

The catalysts were fixed on a borosilicate glass slide with dimensions of 2.2 cm x 1.4 cm (length x width) by dropping an ethanolic suspension of particles (0.05 g) on the slide and evaporating the solvent at room temperature in air. When dry, the coated slide was placed in an oven at 100 °C overnight to dry further. The coated slide was seated inside the Pyrex reactor and the reactor chamber was sealed with a Viton O-ring and clamp. Nitrogen was bubbled through a methanol saturator at 1 mL min⁻¹ at 26 °C and combined downstream with flowing air (24 – 26 mL min⁻¹) at a mixing valve. The
flow rate of the combined feed gas was 26 – 27 mL min\(^{-1}\). Flow rates were controlled with variable area flow meters (Cole-Parmer) and measured with a bubble meter. The combined feed gas molar composition was 1% MeOH : 20% O\(_2\) : 79% N\(_2\), which is equivalent to a MeOH concentration of approximately 10,000 ppm. The feed gas was allowed to pass through the reactor loaded with the catalyst for 1.5 h to achieve equilibration of the feed gas and adsorption/desorption with the catalyst surface as determined by GC peak integrations. Transfer lines were heated at 110 °C to avoid condensation of reactant and product gases. A fan-cooled 125 W Xe arc lamp (Ushio) was positioned perpendicular to the catalyst surface, 11.5 cm away from the midpoint of the reactor. Radiation from the Xe arc lamp was first passed through a UV filter (EMF, Optivex) and then a hot mirror (Edmunds Optics) that removed heating radiation to isolate visible light wavelengths. Experiments were carried out at room temperature with a water-cooled outer Pyrex jacket surrounding the reactor to maintain a consistent temperature at the reactor. The reaction mixture was sampled online with an autosampling valve connected to a gas chromatograph (Agilent 6890) equipped with a Carboxen\(^{\text{TM}}\) 1006-PLOT column (length = 30 m, i.d. = 0.53 mm, film thickness = 30 \(\mu\)m) and a thermal conductivity detector (TCD). Methanol conversions (\(X\)) were calculated by dividing the total sum of the TCD peak areas of products (\(\sum\text{products}\)) by the total sum of the TCD peak areas of methanol (MeOH) and products (\(\sum\text{MeOH}+\text{products}\)) at specified irradiation times (EQ.1). Corrections for water and formaldehyde (HCHO) impurities in the reactant feed gas were made by subtracting, from each irradiation time, the average background conversion (~2% conversion, \(n = 3\) or 4) after the 1.5 h dark equilibration period prior to irradiation.
Catalytic selectivity was determined by dividing the peak area of a single product (y) by the sum of the peak areas for all products ($\sum_{\text{products}}$) at specified irradiation times (\textbf{EQ.2}). Products were identified based on retention time matching of manually injected pure substances.

\[
selectivity(\%) = \left( \frac{y}{\sum_{\text{products}}} \right) \times 100
\]  \hfill (2)

The reacted $e^-/h^+$ ratio was estimated using the ratio of reduction product selectivity ($% \text{H}_2\text{O}$) and oxidation product selectivity ($% \text{HCHO} + % \text{MF} + % \text{CO}_2$) for each catalyst at the final analyzed time point (\textbf{EQ.3}). When comparing different catalyst compositions, this ratio indicates the relative efficiency of the observed reduction and oxidation reactions.$^{42-44}$

\[
\frac{e^-}{h^+} = \frac{\text{reduction}}{\text{oxidation}} = \frac{(%\text{H}_2\text{O})}{(%\text{HCHO} + (%\text{MF} + (%\text{CO}_2))}
\]  \hfill (3)
Photocatalytic rates (mol$_{\text{MeOH}}$ min$^{-1}$) were calculated based on the MeOH flow rate, $F$ (mol$_{\text{MeOH}}$ min$^{-1}$), and MeOH conversion ($X$) as shown in (EQ.4). Catalytic rates were normalized to mass of catalyst (g$_{\text{cat}}^{-1}$), irradiated surface (cm$^2$), catalyst surface area (m$^2$) from BET measurements, and mass of Au in the catalyst (g$_{\text{Au}}^{-1}$) as determined by ICP-OES.

$$rate = F\left(\frac{X}{100}\right) \quad (4)$$
3.5. References


CHAPTER 4: INVESTIGATING THE INFLUENCE OF Au NANOPARTICLES ON POROUS SiO₂-WO₃ AND WO₃ METHANOL TRANSFORMATION CATALYSTS

4.1. Introduction

Supported tungsten oxide (WO₃) materials are highly efficient dehydration catalysts, and they have been mainly studied as dispersed monomers, oligomers, and clusters on various supports.¹⁻¹¹ These previous studies have established a good understanding of the performance of these catalysts as a function of WO₃ domain size and support effects. The acid site reactivity of WO₃ catalysts is commonly probed using the selective transformation of methanol (MeOH) to dimethyl ether (DME).¹² Unlike dispersed WO₃ catalysts, crystalline nanoparticles of WO₃ have received little attention as an acid catalyst.¹³,¹⁴ The bulk particles behave similarly to their dispersed counterparts, with dehydration serving as the major reaction pathway. The MeOH dehydration reaction to yield DME is very appealing due to the potential widespread use of DME as an alternative fuel to help meet our future energy needs.¹⁵⁻¹⁸ Industrially, this reaction is usually carried out over γ-Al₂O₃ or zeolites such as ZSM-5,¹⁹,²⁰ which possess strong acid sites that are prone to rapid deactivation. Weaker acid sites on WO₃ are expected to have lower rates of deactivation at the expense of lower activities compared to these industrial catalysts. Some studies suggest, however, that crystalline WO₃ catalysts may perform better than WO₃ dispersed on MCM-41 in the dehydration of 1-butanol.¹⁴

In addition, selective oxidations are also desirable over transition metal oxide catalysts. For example, oxidations of aryl alcohols in the liquid phase have been
recently studied with V$_2$O$_5$/WO$_3$ composite catalysts with *tert*-butyl hydrogen peroxide being used as the oxidant.$^{21}$ Baeck and coworkers used mixed oxide V$_2$O$_5$-WO$_3$ catalysts in the partial oxidation of ethanol in the gas phase.$^{22}$ The highest activity and good selectivity to acetaldehyde were observed when the catalyst composition was 95% V$_2$O$_5$ – 5% WO$_3$. Interestingly, the catalysts containing mostly WO$_3$ performed the worst. Oxidations of olefins to epoxides are also readily accessible in the presence of WO$_3$ catalysts and peroxide,$^{23-26}$ and semiconducting WO$_3$ serves as a very efficient catalyst in photochemical and electrochemical oxidation reactions.$^{27-29}$

Despite success in these applications, catalysts containing mostly WO$_3$ have been limited in gas-phase thermal oxidations of alcohols with O$_2$ or air as the only oxidant. The poor alcohol oxidation reactivity of pure WO$_3$ may be attributed to the non-labile lattice oxygen atoms of WO$_3$ under catalytic conditions that favor dehydration. Once formed, however, oxygen-deficient tungsten oxide (WO$_{3-x}$) can stabilize various reduced states with differing amounts of oxygen vacancies.$^{29,30}$ Recently, DFT calculations and experimental data have shown that reduced tungsten oxides are very active for hydrogenation reactions, and that there is a linear relationship between hydrogenation activity and oxygen vacancy concentration.$^{30}$ Therefore, it is expected that increasing the reducibility of WO$_3$ will increase the reactivity of the surface lattice oxygen species, highlighting an opportunity to use modified WO$_3$ catalysts for thermal gas-phase oxidations. Blackman and coworkers synthesized Au nanoparticles ("Au NPs") supported on WO$_3$ nanostructures by using an aerosol assisted chemical vapor deposition (AACVD) method using a gold-phosphine complex.$^{31}$ The catalytic activity of these materials was studied in the solution-phase
oxidation of benzyl alcohol to benzaldehyde with *tert*-butyl hydrogen peroxide. Energy-dispersive X-ray spectroscopy and XPS experiments revealed reduced tungsten species in Au-modified WO₃, which explained the increase in catalyst activity compared to pure WO₃ with respect to the entire catalyst (Au and WO₃). However, the selectivity to benzaldehyde was similar for Au-modified WO₃ (100%) and pure WO₃ (94%), which suggests a similar mechanism over both catalysts.

Interactions at the metal nanoparticle – metal oxide interface can have a major influence on the redox properties of a catalyst. Hydrogen temperature-programmed reduction (H₂-TPR) has been used to characterize the reducibility of oxides in the presence of Au NPs. Several studies have analyzed systems such as Au/Fe₂O₃ and Au/CeO₂ using this method, but to the best of our knowledge, the redox behavior of WO₃ in the presence of Au NPs has not been thoroughly explored by H₂-TPR. Gold nanoparticles can weaken metal – oxygen bonds, causing more facile reduction of the oxide. The extent of this effect depends on the preparation method of the Au-oxide catalyst and the concentration of nanoparticles within the oxide.

In this study, we sought to explore the reducibility of WO₃ with Au NPs, using the transformation of MeOH as a probe reaction. This reaction serves as a good catalytic characterization tool to better understand acid and redox catalysts. A combined sonochemical and hard-templating method was used to prepare crystalline porous WO₃ catalysts loaded with monodisperse Au NPs in order to modify the reducibility of WO₃. Various characterization techniques were performed to evaluate the effects of Au NPs on the WO₃ structure and reactivity. The acidic nature of the WO₃ catalysts was confirmed by temperature-programmed desorption (TPD). Also,
differences in WO$_3$ reducibility were probed by TPR in the presence and absence of deposited Au NPs and the oxidation state of Au was analyzed by XPS. Finally, the gas-phase MeOH transformation reaction was carried out under aerobic conditions with Au-modified and non-modified catalysts. Comparisons between the two types of materials were made to learn more about the role of Au NPs in tuning the activity and redox properties of these WO$_3$ catalysts.

4.2. Results and Discussion

4.2.1. Catalyst Synthesis and Characterization

The preparation of porous Au-loaded and non-loaded WO$_3$ catalysts were carried out as described in our recently published work,$^{36}$ with minor adjustments (Figure 4-1). Starting with acid-prepared mesoporous spheres (APMS) of silica, well-dispersed gold nanoparticles (Au NPs) were sonochemically deposited within the porous SiO$_2$ particles to yield SiO$_2$-Au. Tungsten oxide (WO$_3$) and Au NPs were added to APMS in a two-step process: first, APMS was twice impregnated with ammonium metatungstate (AMT) via incipient wetness and calcined to crystallize WO$_3$, and then Au NPs were sonochemically deposited to form SiO$_2$-WO$_3$-Au catalysts. For catalysts not containing Au NPs (i.e. SiO$_2$-WO$_3$ and WO$_3$), APMS was subjected to a sonochemical treatment in the absence of HAuCl$_4$•3H$_2$O and then calcined at 500 °C before continuing with WO$_3$ incorporation. In some cases, catalysts with lower loadings of Au NPs were prepared and characterized (designated SiO$_2$-Au$^L$ and SiO$_2$-WO$_3$-Au$^L$). Etching of SiO$_2$-WO$_3$ and SiO$_2$-WO$_3$-Au composites with HF led to pure WO$_3$ and WO$_3$-Au catalysts, respectively, as confirmed by ICP-OES.
Figure 4-1. Synthesis scheme for the various porous materials studied in this work.

Powder X-ray diffraction (Figure 4-2) was used to study the crystallinity of the prepared catalysts after calcination. It was apparent that all catalysts containing WO$_3$ were nanocrystalline in nature, which was expected due to ammonium metatungstate decomposition during calcination to form monoclinic WO$_3$ (ICDD No. 00-043-1035).
Figure 4-2. Powder X-ray diffraction patterns of (A) catalysts containing only Au NPs or WO$_3$ and (B) catalysts loaded with both Au NPs and WO$_3$. Monoclinic WO$_3$ (ICDD No. 00-043-1035) phases are indicated in (A).

Scherrer calculations of the broadened diffraction peaks yielded WO$_3$ crystallite sizes of 6 – 12 nm; combined with the larger crystallite sizes observed by TEM (see
below), this was an indication of the polycrystalline nature of the WO₃ aggregates. An additional broad feature at 38° assigned to the Au(111) plane was evidence of crystalline Au nanoparticles loaded within the different catalysts. It was clear that the sonochemical deposition of Au NPs onto SiO₂-WO₃ did not have a significant effect on the crystallinity of WO₃. Gold nanoparticle sizes of 5 – 12 nm were determined by XRD depending on the substrate on which the Au NPs were deposited. The larger Au NPs found in SiO₂-WO₃-Au¹ as compared to SiO₂-WO₃-Au can be explained by the differences in the synthesis pH of these catalysts. A consistent NH₃ : Au mole ratio of 250 : 1 was used during the preparation of SiO₂-WO₃-Au and SiO₂-WO₃-Au¹. Therefore, lower concentrations of both NH₃ and HAuCl₄•3H₂O were used during the synthesis of SiO₂-WO₃-Au¹, which decreased the pH relative to SiO₂-WO₃-Au. Although the nominal Au wt% loading was lower for SiO₂-WO₃-Au¹, this lower synthesis pH (pH = 8.97) yielded larger Au NPs of (12 nm) compared to SiO₂-WO₃-Au, which was prepared at pH = 9.89. In contrast, the higher pH during the preparation of SiO₂-WO₃-Au favored deposition of 7 nm Au NPs even at a higher wt% loading.³⁷ Future work will address these size differences by focusing on maintaining similar pH conditions with changing Au loadings.

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were used to provide further details of the crystalline nature of the catalysts loaded with WO₃ and Au (Figure 4-3). Highly dispersed Au NPs were observed throughout the catalysts after calcination, and the approximate sizes of the Au NPs were in agreement with the XRD data. It was clear from the micrograph of SiO₂-Au¹ that 5 – 6 nm Au were deposited evenly throughout the larger spherical SiO₂
particles. These Au NP sizes were also found in SiO₂-Au (not shown). TEM measurements showed that SiO₂-WO₃-Au possessed Au NPs with average diameters of 5 nm, which were similar to SiO₂-Au. Regions of smaller Au NP clusters (1 – 2 nm) could also be observed, as well as slightly larger Au NPs that had sizes in agreement with the Scherrer calculations from the XRD data of SiO₂-WO₃-Au. Less favorable interactions between Au NPs and WO₃ crystallites with low surface isoelectric points (IEP) are thought to cause Au NP growth during the calcination treatment. The overall spherical morphology of the SiO₂-WO₃-Au microparticles was also confirmed by TEM. Large crystallites of WO₃ were present on the outer surface of the microparticles, which made it clear that some WO₃ was not incorporated inside the pores of the porous silica (Figure 4-4). However, energy dispersive X-ray spectroscopy (EDS) analysis of the spherical SiO₂-WO₃-Au catalyst (Figure 4-5) revealed that Au NPs were present in both SiO₂ and WO₃ matrices within the composite microparticles, which was in accordance with our previous studies of similar materials. The nanocrystalline nature of the catalysts was studied further with high-resolution TEM; as an example, HR-TEM of WO₃-Au is shown in Figure 4-3. The d-values between lattice fringes within WO₃ nanoparticles were 0.30 nm, which corresponded to the monoclinic WO₃(112) plane. Likewise, the 0.23 nm spacing of Au(111) planes were apparent in highly crystalline Au NPs that were slightly larger than 5 nm. These d-spacing measurements matched the values obtained from the peaks for WO₃ and Au observed in the XRD data.
Figure 4-3. (A) Dark-field STEM micrograph of SiO$_2$-Au$^1$, (B) bright-field STEM micrograph of SiO$_2$-WO$_3$-Au, and (C) HR-TEM of WO$_3$-Au. Arrows denote individual Au nanoparticles. The white circle highlights a region containing smaller (1-2 nm) Au nanoparticle clusters in SiO$_2$-WO$_3$-Au.

Figure 4-4. TEM micrograph of SiO$_2$-WO$_3$-Au catalyst microparticles possessing spherical morphology. Large crystallites of WO$_3$ are clearly visible on the outer surfaces of the spherical particles.
Figure 4-5. Dark-field STEM micrograph of SiO$_2$-WO$_3$-Au catalyst accompanied by the respective EDS analyses for Si, W, and Au within the microparticle.

The 4f Au XPS spectra for SiO$_2$-Au and WO$_3$-Au are shown in Figure 4-6. Both catalysts showed the Au 4f$_{5/2}$ and Au 4f$_{7/2}$ doublet for Au$^0$ species. Although formal spectral features of Au$^+$ and Au$^{3+}$ were not observed, the energy of the Au 4f$_{7/2}$ peak for SiO$_2$-Au was 83.2 eV, while the corresponding peak for WO$_3$-Au was shifted to higher energies (83.8 eV). This same trend was observed for the Au 4f$_{5/2}$ peak, which appeared at 86.7 eV and 87.5 eV for SiO$_2$-Au and WO$_3$-Au, respectively. This energy
shift of approximately 0.6 – 0.8 eV was consistent with the presence of some Au$^+$ on WO$_3$.\textsuperscript{38,39} Cationic Au indicated a stronger electronic interaction between Au/WO$_3$ than Au/SiO$_2$. The Si/W, W/Au, and Au/Si atomic ratios determined by XPS for various catalysts are summarized in Table 4-1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Au_4f_XPS_spectra.png}
\caption{Au 4f XPS spectra of WO$_3$-Au and SiO$_2$-Au catalysts. The dotted lines are shown to highlight the shift in the Au 4f$_{7/2}$ and Au 4f$_{5/2}$ bands when comparing the two catalysts.}
\end{figure}

Table 4-1. XPS atomic ratios for various samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XPS (atomic ratios)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si/W</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>---</td>
</tr>
<tr>
<td>SiO$_2$-WO$_3$</td>
<td>NA*</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>NA</td>
</tr>
<tr>
<td>SiO$_2$-Au</td>
<td>---</td>
</tr>
<tr>
<td>SiO$_2$-Au$^+$</td>
<td>---</td>
</tr>
<tr>
<td>SiO$_2$-WO$_3$-Au</td>
<td>9.9</td>
</tr>
<tr>
<td>SiO$_2$-WO$_3$-Au$^+$</td>
<td>21.3</td>
</tr>
<tr>
<td>WO$_3$-Au</td>
<td>---</td>
</tr>
</tbody>
</table>

*NA = not analyzed by XPS
Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to study the catalyst composition at various stages of preparation (Table 4-2). The incorporation of crystalline WO$_3$ was supported by the expected increase in W (wt%), and etching of the SiO$_2$ template was shown by the significantly lower Si/W ratio for WO$_3$ compared to SiO$_2$-WO$_3$. Using this sonochemical method, fairly high loadings of Au (> 3.5 wt%) were obtained in the Au NP modified catalysts. The slight increase in the Si/W ratio from SiO$_2$-WO$_3$ to SiO$_2$-WO$_3$-Au meant that WO$_3$ dissolved to a greater extent than SiO$_2$ during the sonochemical deposition of Au NPs under basic conditions. In the end, it was clear that a large amount of WO$_3$ was preserved in the Au-loaded catalysts after deposition of Au NPs, even in solutions containing NH$_3$. Similar to SiO$_2$-WO$_3$ described above, the HF treatment of SiO$_2$-WO$_3$-Au was successful in removing the SiO$_2$ portion of this material to afford WO$_3$-Au (Si/W = 0.02).

**Table 4-2.** Summary of elemental analysis, gold nanoparticle size, and N$_2$ physisorption data of the catalysts studied in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>W (wt%)</th>
<th>Au (wt%)</th>
<th>Si/W (mole ratio)</th>
<th>W/Au (mole ratio)</th>
<th>Au size (nm)</th>
<th>$S_{BET}^A$ (m$^2$ g$^{-1}$)</th>
<th>$V_{pore}$ (cm$^3$ g$^{-1}$)</th>
<th>$d_{pore}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>494</td>
<td>0.66</td>
<td>58</td>
</tr>
<tr>
<td>SiO$_2$-WO$_3$</td>
<td>56.7</td>
<td>---</td>
<td>1.54</td>
<td>---</td>
<td>---</td>
<td>81</td>
<td>0.09</td>
<td>36</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>78.4</td>
<td>---</td>
<td>0.02</td>
<td>---</td>
<td>---</td>
<td>62</td>
<td>0.15</td>
<td>64</td>
</tr>
<tr>
<td>SiO$_2$-Au</td>
<td>---</td>
<td>3.74</td>
<td>---</td>
<td>---</td>
<td>5 $^a$</td>
<td>478</td>
<td>0.69</td>
<td>57</td>
</tr>
<tr>
<td>SiO$_2$-Au$^b$</td>
<td>---</td>
<td>0.55</td>
<td>---</td>
<td>---</td>
<td>5 – 6 $^{a,b}$</td>
<td>489</td>
<td>0.80</td>
<td>72</td>
</tr>
<tr>
<td>SiO$_2$-WO$_3$-Au</td>
<td>54.4</td>
<td>3.53</td>
<td>1.63</td>
<td>16.5</td>
<td>87</td>
<td>143</td>
<td>0.14</td>
<td>43</td>
</tr>
<tr>
<td>SiO$_2$-WO$_3$-Au$^b$</td>
<td>52.0</td>
<td>0.62</td>
<td>2.03</td>
<td>89.3</td>
<td>12 $^a$</td>
<td>122</td>
<td>0.17</td>
<td>43</td>
</tr>
<tr>
<td>WO$_3$-Au</td>
<td>74.5</td>
<td>4.74</td>
<td>0.02</td>
<td>16.8</td>
<td>8 $^a$</td>
<td>73</td>
<td>0.21</td>
<td>28</td>
</tr>
</tbody>
</table>

$^a$ Measured by XRD. $^b$ Measured by TEM. $^c$ Lower Au wt% loading.

The porosity of the studied catalysts was probed by N$_2$ physisorption, and the results are summarized in Table 4-2. Associated physisorption isotherms (Figure 4-7)
and pore size distributions (Figure 4-8) are also shown. The mesoporous SiO$_2$ particles contained large pores, which made them a suitable template for WO$_3$ incorporation. As expected, filling of the pores with high loadings of crystalline WO$_3$ decreased the porosity of this material. Removal of the SiO$_2$ template from SiO$_2$-WO$_3$ led to pure porous WO$_3$ catalysts, which had larger pores than the composite. It is relevant to note the very broad external pore size distributions for these catalysts. Irregular voids between the aggregated WO$_3$ crystallites forming the pores in porous WO$_3$ caused pore distributions to be non-uniform in all cases. The reported pore diameters are the observed maxima in these distributions, but it was apparent that the pore sizes varied widely over 100 – 200 Å and showed multiple features depending on the material. Comparing SiO$_2$-WO$_3$ and SiO$_2$-WO$_3$-Au, a significant broadening of the pore size distribution was observed after Au loading. A combination of SiO$_2$ and WO$_3$ dissolution during this process led to the formation of larger irregular pores, whereas Au deposition had a lesser effect on the porosity of SiO$_2$-WO$_3$-Au.
Figure 4-7. N$_2$ physisorption isotherms for catalysts discussed in this work.
Figure 4-8. Pore size distributions for catalysts discussed in this work.
4.2.2. Catalyst Acid Site Characterization

Ammonia temperature-programmed desorption (NH$_3$-TPD) is a commonly used method to analyze the surface acidity of various catalysts.$^{5,40-42}$ Figure 4-9 shows the NH$_3$-TPD traces of several representative catalysts containing WO$_3$. Pure mesoporous SiO$_2$ (not shown) showed a weak feature at 120 °C that corresponded to the desorption of weakly bound NH$_3$ over weakly acidic SiO$_2$.\textsuperscript{5} The broad feature at 200 °C in SiO$_2$- and WO$_3$-containing composites (solid lines) signified the introduction of different, slightly stronger acid sites on these catalysts compared to SiO$_2$. These new features may correspond to substitution of W in the amorphous SiO$_2$ framework. Higher temperature (> 500 °C) features indicated desorption of NH$_3$ from strong acid sites on these composite SiO$_2$-WO$_3$ catalysts. Desorption of H$_2$O from surface dehydroxylation at temperatures above the calcination temperature (500 °C) may also explain this observation. After removal of the SiO$_2$ template, it was clear that pure WO$_3$ catalysts possessed moderate acidity. Two resolved features at 170 °C and 260 °C suggested that there may be both weak and medium strength acid sites on these catalysts,$^{40}$ which were not affected by the presence of Au NPs. Strong acidity was not observed over pure WO$_3$ catalysts as shown by the absence of peaks at temperatures > 500 °C. From this data, it was expected that these acidic WO$_3$ catalysts would be beneficial in the selective dehydration of methanol to dimethyl ether.$^{14,15,40}$
4.2.3. Catalyst Reducibility Characterization by H$_2$-TPR

The reducibility of the catalysts was monitored by H$_2$ temperature-programmed reduction (H$_2$-TPR). The oxide reducibility can be informative in regards to describing the relative reactivity of the SiO$_2$-WO$_3$ and WO$_3$ catalysts. In general, peaks appearing at lower temperatures in a TPR profile indicate more facile reduction events occurring within the metal oxide. The TPR profiles of various Au-modified and non-modified catalysts are shown in Figure 4-10. A control sample, SiO$_2$-Au, did not show any reduction events. Silica is a non-reducible oxide in this temperature range, and Au was in its fully reduced metallic state as Au$^0$ NPs, in agreement with the XRD, XPS, and TEM data.

Figure 4-9. NH$_3$-TPD traces for Au-modified and non-modified catalysts in the composite (SiO$_2$-WO$_3$, solid lines) and pure (WO$_3$, dashed lines) forms.
Materials containing WO₃, however, displayed multiple reduction events up to 1000 °C. The position and resolution of the peaks for the various catalysts depended on the stability of the reduced WOₓ species within the materials. In the non-modified SiO₂-WO₃ composite and pure WO₃, three major regions of reduction were observed. The peak near 500 – 550 °C can be attributed to the reduction of surface oxygens on WO₃ to form substoichiometric WO₂.₉ surface species. This was followed by a bulk reduction step from WO₂.₉ to WO₂ from 700 – 900 °C, and then a final reduction of WO₂ to W⁰ near 1000 °C.¹⁴,⁴³

Clearly, WO₃ catalysts not loaded with Au NPs displayed different TPR profiles than those loaded with Au NPs. Initial WO₃ surface reduction (WO₃ → WO₂.₉) was more facile for SiO₂-WO₃-Au and SiO₂-WO₃-Au¹ than SiO₂-WO₃ (Figure 4-10A, inset). It appeared that this WO₃ reduction event shifted to lower temperatures and resolved into two separate features in the temperature range of 100 – 250 °C in the presence of Au NPs. This result suggested that there were significant Au—O—W interactions on the surface of these catalysts, which led to weakened surface W—O bonds.³³,⁴⁴ The formation of two separate reduction events indicated the presence of two stable WOₓ species during reduction in this temperature range. Increased Au NP loading caused the features to shift to lower temperatures, which meant increased oxygen reducibility.³³ However, the larger Au NPs of SiO₂-WO₃-Au¹ may also affect the WO₃ reducibility differently than smaller Au NPs. As shown in the inset of Figure 4-10B, similar behavior was seen in WO₃-Au, which has increased surface oxygen reducibility compared to WO₃. Dissociation of H₂ over Au NPs or reduced WO₃-x³⁰ and other electronic effects increased the reducibility of the surface oxygen of WO₃, which
led to oxygen vacancies at the catalyst surface.⁷ This result was expected to have implications on the reactivity of the Au-loaded WO₃ catalysts in methanol transformation reactions. Specifically, facile removal of lattice oxygen from the WO₃ surface will introduce oxidation reactivity to these Au-loaded catalysts as will be discussed below.

![H₂-TPR traces of (A) SiO₂-WO₃ and (B) WO₃ catalysts both with and without loaded Au NPs. Insets are zoomed-in regions from 0 – 600 °C.](image)

**Figure 4-10.** H₂-TPR traces of (A) SiO₂-WO₃ and (B) WO₃ catalysts both with and without loaded Au NPs. Insets are zoomed-in regions from 0 – 600 °C.

The bulk reduction events of WO₃ were also impacted by Au NPs loaded on the surface of the catalysts. Interestingly, this observation is in contrast to reports of Au/CeO₂, in which Au NPs only affected the reduction surface ceria species, but not the bulk.⁴⁴,⁴⁵ In the presence of Au NPs, the WO₃ species were generally more reducible than without Au NPs, as shown by the shifting of reduction events to lower temperatures. Complete reduction to W⁰ was shown at temperatures below 1000 °C for
Au-loaded catalysts, but SiO$_2$-WO$_3$ and WO$_3$ were not completely reduced up to 1000 °C. Also, there were significant changes in the TPR profile shapes when comparing Au-loaded and non-loaded catalysts. SiO$_2$-WO$_3$-Au and SiO$_2$-WO$_3$-Au$^{L}$ showed a single broad reduction event in the 800 – 900 °C region, while pure WO$_3$ and WO$_3$-Au catalysts showed resolved features and at slightly lower temperatures (700 – 800 °C). The increased peak resolution in the bulk region of pure WO$_3$ catalysts may indicate increased stabilization of tungsten oxides with intermediate oxidation states. Overall, it was apparent that Au NPs loaded on the surface of these catalysts led to more easily reduced surface and bulk WO$_3$ species.

4.2.4. Methanol Transformation Activity Studies

Catalytic gas-phase methanol transformation reactions were conducted under aerobic conditions in the presence of various Au-loaded and non-loaded catalysts. Pure SiO$_2$ does not possess significant acid or redox sites, and thus the activity of this material was negligible, which agreed with the NH$_3$-TPD and H$_2$-TPR data. However, SiO$_2$-Au was very reactive, showing increasing activity as the loading of Au increased. Considering equal contact times between all catalysts, the Au-loaded catalysts showed greater conversions at lower temperatures than the non-loaded catalysts (Figure 4-11). These results showed the significant role that Au NPs played in converting MeOH at lower temperatures. The SiO$_2$-WO$_3$-Au$^{L}$ catalyst was an exception to this trend, however. The lower activity of this catalyst is most likely attributed to the lower Au loading, the larger Au NP sizes (~12 nm), and the greater W/Au mole ratio associated
with this material. Therefore, it seemed beneficial to use catalysts that possess smaller dispersed Au NPs for this catalytic reaction.

![Graph](image)

**Figure 4-11.** Methanol conversion as a function of reaction temperature for (A) SiO$_2$-Au, (B) SiO$_2$-WO$_3$, and (C) WO$_3$ catalysts. *W/F for SiO$_2$-Au = 3.4 g$_{\text{cat}}$ h (mol$_{\text{MeOH}}$)$^{-1}$; all other catalysts W/F = 6.7 g$_{\text{cat}}$ h (mol$_{\text{MeOH}}$)$^{-1}$.

To compare the activity of Au-loaded and non-loaded catalysts, the rates of MeOH conversion were determined for several catalysts at similar temperatures (234 – 247 °C) and contact times (**Table 4-3**). To make more complete comparisons between the WO$_3$ and WO$_3$-Au catalysts, additional MeOH conversion rates were determined at lower reaction temperatures (**Table 4-4**). The catalytic rates and the selectivity distributions (**vide infra**) were compared using slightly different temperatures and conversions because of the exothermic nature of this reaction and the high reactivity of the studied catalysts. For these reasons, large temperature gradients at the catalyst were observed.
Table 4-3. Rates of methanol (MeOH) conversion for Au-loaded and non-loaded catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (°C)</th>
<th>X_{MeOH} (%)</th>
<th>rate MeOH conversion (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>mmol_{MeOH} h^{-1} g_{cat}^{-1}</td>
</tr>
<tr>
<td>SiO_{2}-Au</td>
<td>241</td>
<td>47.0</td>
<td>138</td>
</tr>
<tr>
<td>SiO_{2}-WO_{3}-Au</td>
<td>234</td>
<td>17.3</td>
<td>25.8</td>
</tr>
<tr>
<td>SiO_{2}-WO_{3}-Au</td>
<td>247</td>
<td>3.5</td>
<td>5.22</td>
</tr>
<tr>
<td>SiO_{2}-WO_{3}</td>
<td>239</td>
<td>9.2</td>
<td>13.7</td>
</tr>
<tr>
<td>WO_{3}-Au</td>
<td>246</td>
<td>66.9</td>
<td>99.9</td>
</tr>
<tr>
<td>WO_{3}</td>
<td>239</td>
<td>12.6</td>
<td>18.8</td>
</tr>
</tbody>
</table>

(a) Contact time (W/F) = 6.7 g_{cat} h (mol_{MeOH})^{-1} for all catalysts except for sample SiO_{2}-Au (W/F = 3.4 g_{cat} h (mol_{MeOH})^{-1})

(b) Calculated using the surface area of catalyst

Table 4-4. Methanol conversion rates for WO_{3} and WO_{3}-Au at lower reaction temperatures.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (°C)</th>
<th>X_{MeOH} (%)</th>
<th>rate MeOH conversion (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>mmol_{MeOH} h^{-1} g_{cat}^{-1}</td>
</tr>
<tr>
<td>WO_{3}-Au</td>
<td>213</td>
<td>22.8</td>
<td>34.0</td>
</tr>
<tr>
<td>WO_{3}</td>
<td>220</td>
<td>6.8</td>
<td>10.1</td>
</tr>
</tbody>
</table>

(a) Contact time (W/F) = 6.7 g_{cat} h (mol_{MeOH})^{-1} for all catalysts

(b) Calculated using the surface area of catalyst

The SiO_{2}-Au sample was clearly the most active catalyst, which indicated that Au NPs are responsible for increased reaction rates at lower temperatures. Comparisons of SiO_{2}-Au and SiO_{2}-WO_{3} reaction rates exhibited the greater activity of Au NPs relative to WO_{3} nanocrystals. Also, the greater surface area and accessible porosity of SiO_{2}-Au better facilitated MeOH conversion compared to SiO_{2}-WO_{3} catalysts. When WO_{3} and Au NPs were added to the SiO_{2} support (SiO_{2}-WO_{3}-Au), the rate per g Au
and per \( m^2_{\text{cat}} \) decreased, illustrating that \( \text{WO}_3 \) had a negative effect on Au NP activity. This result may be related to the observed XPS shifts in Au 4f band energies for \( \text{SiO}_2\)-Au and \( \text{WO}_3\)-Au shown in Figure 4-6, indicating that a more fully reduced Au species is favorable for the MeOH reaction. On the other hand, a significant increase in the rate of conversion per gram of W showed that Au NPs increased the activity of \( \text{WO}_3 \) species, especially at higher loadings. These more active Au-modified \( \text{WO}_3 \) species agreed with the more easily reduced \( \text{WO}_3 \) species observed on \( \text{SiO}_2\)-\( \text{WO}_3\)-Au via \( \text{H}_2\)-TPR (Figure 4-10).

Among \( \text{SiO}_2\)-\( \text{WO}_3 \) composite catalysts, the rate of MeOH conversion per gram of total catalyst (\( g_{\text{cat}}^{-1} \)), per gram of tungsten (\( g_{\text{W}}^{-1} \)), and per unit surface area (\( m^2 \)) was the greatest for \( \text{SiO}_2\)-\( \text{WO}_3\)-Au. For the pure \( \text{WO}_3 \) catalysts, MeOH conversion rates confirmed that \( \text{WO}_3\)-Au was more active than \( \text{WO}_3 \), which agreed with the results for the \( \text{SiO}_2\)-\( \text{WO}_3 \) composites. Overall, the features of \( \text{WO}_3\)-Au made it the most active catalyst containing \( \text{WO}_3 \). Au NPs clearly increased the activity of all \( \text{WO}_3 \)-containing catalysts.

We sought to further explore the interaction between \( \text{WO}_3 \) and Au by testing a physical mixture of \( \text{SiO}_2\)-Au and \( \text{SiO}_2\)-\( \text{WO}_3 \). The results of this experiment showed that the activity of the physical mixture mirrored that of \( \text{SiO}_2\)-Au alone (Figure 4-12). This supported the hypothesis that the negative effects of the \( \text{WO}_3 \) species on Au NPs originate from the interaction between the two when both are in intimate contact through synthesis.
4.2.5. Methanol Dehydration to DME Over Catalysts Without Au NPs

Analysis of the MeOH transformation product selectivity was carried out for the various catalysts. Figure 4-13 shows the product distributions for the SiO$_2$-WO$_3$ and WO$_3$ catalysts at both low and high methanol conversions. Very high selectivity (> 60%) to dimethyl ether (DME) was observed over both types of catalysts at all studied conversions. Minor redox products such as formaldehyde (FM), methyl formate (MF), and dimethoxymethane (DMM) were observed. Also, non-selective carbon oxides (CO + CO$_2$) formation was low (< 18% selectivity) up to 300 – 350 °C. The dehydration reactivity of these catalysts confirmed the moderate acidity of the crystalline WO$_3$ species, which was supported by the NH$_3$-TPD data. As with non-crystalline WO$_3$ and
tungsten Keggin heteropoly acid (HPA) catalysts found throughout the literature,\textsuperscript{1-4,6,12} these crystalline SiO$_2$-WO$_3$ and WO$_3$ catalysts were very selective to DME, with no significant oxidation reactivity.

![Figure 4-13. Percent selectivity for the methanol transformation reaction over SiO$_2$-WO$_3$ and WO$_3$ catalysts at (left) low methanol conversions and (right) high methanol conversions. Percent conversions ($X_{\text{MeOH}}$) for each catalyst are shown at top of graphs. See text for abbreviation definitions.]

4.2.6. Methanol Aerobic Transformation Over Au-Loaded Catalysts

The oxidative MeOH transformation on Au-modified catalysts showed significant differences compared to their non-modified counterparts. It was clear that once Au NPs were loaded in the catalysts, MeOH dehydration selectivity decreased at the expense of increased oxidation selectivity. Figure 4-14A shows the product distributions of various Au-loaded catalysts at low MeOH conversions (7 – 13%). Gold
nanoparticles on porous SiO₂ (SiO₂-Au) led to mainly MF production, which is in accordance with the literature on Au catalysts.⁴⁵,⁴⁶ Moreover, dimethyl ether selectivity was not observed in this case.

**Figure 4-14.** Percent selectivity for the methanol transformation reaction over Au-loaded catalysts at (A) low methanol conversions and (B) high methanol conversions. Percent conversions (X_{MeOH}) for each catalyst are shown at top of each graph. See text for abbreviation definitions.

The product distribution of the SiO₂-WO₃-Au¹ catalyst was different than that of SiO₂-WO₃, but the major reaction product was still DME (73.9%) at low methanol conversion. This indicated that the amount of Au in this sample was insufficient to be reactive and have a major impact on the WO₃ acid sites. Indeed, simply altering the loading of Au NPs on these catalysts modulated the reactivity of these catalysts. The
Au-modified composite catalyst (SiO$_2$-WO$_3$-Au) showed a greater variety of oxidation products compared to SiO$_2$-Au. In addition to MF, FM was observed from the primary oxidation of MeOH, and dimethoxymethane (DMM) was produced from the secondary HCHO-CH$_3$OH acetalization reaction over WO$_3$ acid sites. Deep oxidation to CO$_x$ was also more facile with Au NPs coupled to WO$_3$ as more labile surface oxygen atoms from the WO$_3$ support reacted with MeOH. In this way, the WO$_3$-Au showed higher CO$_x$ formation, with a distribution of FM, MF and DMM similar to that observed for sample SiO$_2$-WO$_3$-Au suggesting that, in both cases, Au NPs were interacting with WO$_3$ crystallites.

The SiO$_2$-Au/SiO$_2$-WO$_3$ physical mixture strongly favored MF production and minor DMM formation, which was different from the reactivity observed over SiO$_2$-WO$_3$-Au. The DMM selectivity originated from the secondary oxidation product of FM in the presence of WO$_3$ acid sites. This indicated that the SiO$_2$-Au reactivity was more accessible and facile than the SiO$_2$-WO$_3$ reaction pathway, especially because no DME was observed. Therefore, WO$_3$ crystallites significantly affected the reactivity of Au NPs when the two species were in intimate contact through synthesis, which agreed with the MeOH conversion results of the physical mixture. Similar product distributions between SiO$_2$-WO$_3$-Au and WO$_3$-Au meant that at low conversions, these two catalysts behaved nearly the same. This oxidation activity was attributed to Au NPs, which had two major effects: the Au NPs (1) activated O$_2$ in the feed gas and (2) induced more reactive WO$_3$ surface redox sites, which were confirmed by H$_2$-TPR. Secondary HCHO-CH$_3$OH acetalization reactions led to intermediates that can either convert to DMM on acid sites or dehydrogenate to form MF over redox sites on the
support. This was evidence that the composition of the catalyst support played a major role in the oxidation reactions initiated by the Au NPs. Slightly higher selectivity to CO\textsubscript{x} over WO\textsubscript{3}-Au compared to SiO\textsubscript{2}-WO\textsubscript{3}-Au was due to the higher oxidation activity of this catalyst.

At higher MeOH conversions, further changes in the reaction selectivity were observed (Figure 4-14B). Two general differences in selectivity occurred at the higher reaction temperatures used to obtain higher MeOH conversions. First, the production of CO\textsubscript{x} increased for most of the catalysts, which was favored at high temperatures under aerobic reaction conditions. Second, DMM was not significantly produced (only a small quantity was detected in the physical mixture catalyst). At higher temperatures, the acidic surface hydroxyl groups on SiO\textsubscript{2}-WO\textsubscript{3} and WO\textsubscript{3} became less stable, which led to increasing non-selective oxidation reactions to CO\textsubscript{x} in the presence of abundant Au NPs. In addition, primary oxidation of MeOH to FM may be quickly followed by desorption of FM from the catalyst surface or further oxidation to CO\textsubscript{x}, whereas further coupling with MeOH to form DMM is less likely at higher MeOH conversions. The exception to this trend was SiO\textsubscript{2}-WO\textsubscript{3}-Au\textsuperscript{L}, which showed 78.1% DME selectivity at 48.6% MeOH conversion. This suggested that WO\textsubscript{3} acid sites dominated the MeOH catalysis at lower loadings of Au NPs, as was the case at low MeOH conversions.

In terms of selective oxidation products, FM was favored over the WO\textsubscript{3}-containing catalysts, with only small amounts of MF formed. Stabilization of FM species on WO\textsubscript{3} Brønsted acid sites\textsuperscript{50} may have prevented further oxidative coupling with MeOH to form MF. Subsequent desorption of FM or further oxidation to CO\textsubscript{x} seemed to be favored under these high temperatures and aerobic reaction conditions.
Selectivity comparisons between SiO$_2$-WO$_3$-Au and WO$_3$-Au suggested that the pure WO$_3$ support may have had stronger interactions with surface-bound FM than SiO$_2$-WO$_3$ and more abundant active O* from the WO$_3$ lattice. Thus, the stabilized FM molecules were converted primarily to total oxidation products (CO$_x$) over the WO$_3$-Au catalyst. Interestingly, SiO$_2$-Au remained highly selective to MF, highlighting the unique reactivity of Au NPs on inert supports. Overall, FM was only observed in the presence of Au NPs and WO$_3$, which can be correlated to the presence of more reducible WO$_3$ species as shown by H$_2$-TPR.

Figure 4-15 displays the possible reaction pathways observed in this study. It was clear that the catalyst composition could be tuned to alter the activity and selectivity towards MeOH transformations. Over acid sites, MeOH was dehydrated to DME over all catalysts that contained WO$_3$ and low loadings of Au NPs. Increasing the Au wt% loading caused MeOH oxidation to occur more favorably at the expense of dehydration reactivity. At low conversions and in the presence of acidic WO$_3$, DMM was favored, but at high conversions, FM was the major oxidation product. A combination of strongly adsorbed FM, less stable acid sites, and high MeOH conversions effectively diminished the oxidative coupling (MF) and non-oxidative condensation (DMM) pathways. Therefore, primary oxidation to FM and total oxidation to CO$_x$ were observed in the presence of excess O* (both labile lattice O and activated O from the feed gas) and high temperatures. Methanol oxidation can be seen as a three step process that involves (1) the dissociation of MeOH to methoxy on the metal oxide surface, (2) the activation of the methoxy species by lattice oxygen, which causes oxygen vacancy formation and subsequent reduction of the oxide, and (3) the re-
oxidation of the catalyst by O$_2$ in the feed.$^{47,51}$ In theory, the combination of increased lattice oxygen reactivity and the acidic nature of the catalyst surface could be further optimized for these materials, which makes them very interesting as selective oxidation catalysts in future studies.

![Possible catalytic reaction pathways for the aerobic methanol transformation reaction described in this paper. Modified from reference 48.](image)

**Figure 4-15.** Possible catalytic reaction pathways for the aerobic methanol transformation reaction described in this paper. Modified from reference 48.

### 4.3. Conclusions

Porous nanocrystalline WO$_3$-containing catalysts were prepared by a hard-templating process and further modified with Au nanoparticles through a sonochemical approach. The acidic WO$_3$ species in catalysts without Au nanoparticles allowed for highly selective methanol dehydration reactivity while minimizing oxidation pathways at higher temperatures and conversions. Catalysts with Au nanoparticles at higher Au wt% loadings displayed greater catalytic activity in the aerobic transformation of methanol. No differences in WO$_3$ structure and acidity were observed when comparing Au-loaded and non-loaded catalysts. Changes in catalyst redox properties were
confirmed by TPR and showed that Au nanoparticles directly affected the reducibility of crystalline WO$_3$. Specifically, the WO$_3$ species are more easily reduced with increasing Au loadings. However, WO$_3$ species decreased the reactivity of supported Au NPs possibly through an electron-withdrawing effect to form oxidized surface Au. Oxidation of methanol to formaldehyde, methyl formate, dimethoxymethane, and CO$_x$ over Au-loaded catalysts agreed with the observation of more labile lattice oxygen from easily reduced WO$_3$. The Au loading and the temperature of reaction had significant effects on the oxidation product distribution.

4.4. Experimental Section

4.4.1. Synthesis of WO$_3$- and Au-Containing Catalysts

Porous catalysts containing WO$_3$ were prepared via a hard-templating technique using ammonium metatungstate as the WO$_3$ precursor and porous SiO$_2$ spheres as hard templates. The sonochemical deposition of Au NPs on SiO$_2$-WO$_3$ composites was carried out to modify these WO$_3$-containing materials with metal nanoparticles. Selective removal of SiO$_2$ templates with HF afforded pure WO$_3$ catalysts. Synthetic details for all catalysts in this study can be found below.

4.4.2. Synthesis of Acid-Prepared Mesoporous Spheres (APMS)

Cetyltrimethyl ammonium bromide (CTAB, 9.0 g, 24.7 mmol) was dissolved in a solution of deionized water (198 g, 11 mol), ethanol (200 proof, 55.5 g, 1.20 mol), and concentrated HCl (37 wt%, 22.0 g, 223.0 mmol) at room temperature with vigorous stirring. Tetraethoxysilane (TEOS, 20.0 g, 96.0 mmol) was then added and stirring was
continued for 5 min, after which a solution of NaF (0.5M, 23.8 g, 11.9 mmol) was added. The solution became turbid in about 83 s and was immediately transferred to a Teflon bottle that was sealed and placed in an oven at 373 K for 160 min. The bottle was then removed from the oven and cooled at room temperature for 20 min before filtration of the product and washing with water and ethanol. Following air drying of the product at room temperature, the material was calcined under flowing air with the following heating program: ramp from 298 K to 723 K at 2 K min\(^{-1}\), hold at 723 K for 240 min, ramp to 823 K at 10 K min\(^{-1}\), and hold at 823 K for 480 min before cooling to room temperature.

### 4.4.3. Sonochemical Treatment of APMS to Yield SiO\(_2\) Material

Calcined APMS (1.0 g) was dispersed in 150 mL H\(_2\)O in a 250 mL round-bottom flask with stir bar and stirred for 45 min. The flask was then submerged in a water bath-type sonicator (Branson 2510, 40 kHz, 130 W). After 2 min of sonication, concentrated aqueous ammonium hydroxide (29 wt\% NH\(_3\), 0.359 mL, 5.51 mmol NH\(_3\)) was added dropwise during sonication. The flask was swirled periodically to mix the solution during the 45 min sonication treatment. The product was then filtered, washed with water, and dried under vacuum at room temperature overnight. The dried white powder was then calcined under air flow at 773 K for 3 h (ramp rate = 0.95 K min\(^{-1}\)). This sample is denoted as SiO\(_2\).
4.4.4. Sonochemical Deposition of Au NPs onto SiO$_2$ (SiO$_2$-Au)

Calcined APMS (1.0 g) was dispersed in 150 mL H$_2$O in a 250 mL round-bottom flask with stir bar and then stirred for 10 min. A solution of chloroauric acid (0.0255 M HAuCl$_4$$\cdot$3H$_2$O, 5.202 mL, 0.133 mmol Au) was then added and stirring continued for 30 – 40 min. Sonication of the mixture began as above, during which, concentrated aqueous ammonium hydroxide (29 wt% NH$_3$, 2.151 mL, 33.0 mmol NH$_3$) was added dropwise over the course of the entire sonication period (45 min). The NH$_3$ : Au mole ratio was 248 : 1. The product was filtered, washed, dried, and calcined as above for SiO$_2$ yielding a purplish-red colored product. This sample is denoted as SiO$_2$-Au.

A sample with a lower Au wt% loading (SiO$_2$-Au$^{1}$) was prepared in a similar fashion, but instead using 0.867 mL chloroauric acid (0.0255 M HAuCl$_4$$\cdot$3H$_2$O, 0.0221 mmol Au) and 0.359 mL concentrated aqueous ammonium hydroxide (29 wt%, 5.51 mmol NH$_3$) in a NH$_3$ : Au mole ratio of 249 : 1.

4.4.5. Incipient-Wetness Impregnation of SiO$_2$ with WO$_3$ (SiO$_2$-WO$_3$)

About 0.9 g SiO$_2$ was added to a crucible and then an aqueous solution of ammonium metatungstate (AMT, 1.5 g AMT/mL H$_2$O) was added dropwise to the dry powder (1 mL AMT solution per gram of SiO$_2$). The damp mixture was manually stirred for 10 min, and then the mixture was left to dry at room temperature in air for 4 – 5 h. The dry powder was then calcined as above for SiO$_2$ (773 K, 3 h). The impregnation, drying, and calcination steps were repeated a second time. This yielded a yellowish-green colored powder denoted as SiO$_2$-WO$_3$. 

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4.4.6. Two-Step Impregnation of APMS with WO₃ and Sonochemical Deposition of Au NPs (SiO₂-WO₃-Au)

About 0.6 g APMS was subjected to two cycles of AMT impregnation (1 mL AMT solution per gram APMS) and calcination at 773 K similar to above. The resulting composite material loaded with WO₃ (1.0 g) was sonochemically treated in the presence of chloroauric acid (0.0273 M HAuCl₄•3H₂O, 4.847 mL, 0.132 mmol Au) and concentrated NH₃(aq) (29 wt% NH₃, 2.151 mL, 33.0 mmol NH₃) as described above. The NH₃ : Au mole ratio was 250 : 1. After filtration, washing, drying, and calcination similar to SiO₂-Au above, a dark, wine purple-colored powder was obtained, denoted as SiO₂-WO₃-Au.

A sample with a lower loading of Au (SiO₂-WO₃-Au₁) was prepared sonochemically in a similar manner, but with 0.8 g of composite material, 125 mL H₂O, 0.778 mL chloroauric acid (0.0273 M HAuCl₄•3H₂O, 0.0212 mmol Au), and 0.346 mL concentrated NH₃(aq) (29 wt% NH₃, 5.31 mmol NH₃) in a NH₃ : Au mole ratio of 250 : 1. Filtration, washing, drying, and calcination of this material led to a dark, wine purple-colored powder.


To remove the silica template in the Au-loaded (SiO₂-WO₃-Au) and non-loaded (SiO₂-WO₃) samples containing WO₃, the materials were added to 11 mL of 10% HF in H₂O contained in separate 15 mL plastic centrifuge tubes. Caution: HF is extremely toxic and corrosive, wear appropriate personal protective equipment while using this
acid. The sealed tubes were placed on orbital shakers to mix gently for approximately 4 h. The solids were then centrifuged and the supernatant disposed of appropriately. It is important to note that some Au NPs are lost during this process as confirmed by the purple-colored supernatant. The particles were washed three times with 11 mL H$_2$O and then once with 11 mL ethanol. The washed samples were left to dry in the centrifuge tube under air in an oven at 348 K overnight. The resulting Au-loaded and non-loaded samples are denoted $\text{WO}_3$-$\text{Au}$ and $\text{WO}_3$, respectively.

4.4.8. Materials Characterization

Nitrogen physisorption was carried out at 77 K on a Micromeritics TriStar 3000 surface area and porosity analyzer. Surface areas and pore size distributions were calculated using the BET and BJH methods, respectively. Powder X-ray diffraction (XRD) was performed on a Rigaku MiniFlex II diffractometer using Cu K$_\alpha$ radiation generated with a tube output voltage and current of 30 kV and 15 mA, respectively. The diffractometer was equipped with a water-cooled Scintillator detector that was used at a continuous rate of 0.5° (2θ) per minute. High-resolution transmission electron micrographs were recorded with a JEOL JEM 2100F microscope operating at 200 kV. Samples were dispersed in methylchloride and transferred to carbon coated copper grids prior to analysis. Energy dispersive X-ray spectroscopy (EDS) elemental analysis of samples was done with an Oxford INCA system attached to the same microscope. X-ray photoelectron spectroscopy (XPS) was carried out using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg K$_\alpha$ radiation (300 W, 15 kV, 1253.6 eV) for the analysis of photoelectronic signals of C 1s, O 1s, Si 2p, Au 4f and W 4f.
with a multi-channel detector. Additional experimental details regarding the XPS analyses can be found in reference 52. Elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) was completed on a PerkinElmer Optima 7000DV ICP optical emission spectrometer with a CCD array detector, a PerkinElmer S10 autosampler, and WinLab32 software. Concentrated ammonium hydroxide (29 wt%) was obtained from Fisher Scientific. Chloroauric acid trihydrate (HAuCl₄•3H₂O, ACS reagent, 99.99%) was purchased from Alfa Aesar. All other chemicals were obtained from Sigma-Aldrich. All chemicals were used as received.

### 4.4.9. ICP-OES Sample Preparation Procedures

Samples were first dried at 100 °C in air for several hours or overnight. Additionally, samples that were previously etched (free of SiO₂) were calcined at 500 °C for 3 h in air to remove residual ethanol that was adsorbed during the washing step. Samples were first digested by adding 0.020 g of material to 1 mL of 2 M NaOH in a 1.5 mL Eppendorf tube followed by approximately 25 min of ultrasonication. Mixtures were left to shake vigorously for several hours or overnight to completely dissolve SiO₂ and WO₃ components. Samples containing Au NPs were allowed to settle overnight before subsequent centrifugation (14,800 rpm, 5 min) and separation. The Au pellet was washed with 1 mL H₂O then centrifuged. The supernatants were added to the initial digest solution of SiO₂ and/or WO₃. Three total H₂O washings were performed, and then the digest solution was adjusted to 0.1 M NaOH with H₂O. Diluted digest solutions of SiO₂ and WO₃ were prepared with 0.1 M NaOH in 100 mL volumetric flasks. Gold nanoparticles were transferred in water via pipet to a vial and then
evaporated to near dryness on a hot plate. The Au NP residue was then digested in aqua regia and then heated to evaporate solution to near dryness. To the Au/aqua regia residue, approximately 2 mL 0.5 M HCl was added, swirled, and then evaporated by heating until residue remained. This washing/evaporation step was repeated a second time before transferring the Au solution to a 25 mL volumetric flask and diluting to mark with 0.5 M HCl. Concentrations of Au, Si, and W were quantified by calibration curves using emission wavelengths of 267.599 nm, 251.611 nm, and 207.912 nm, respectively.

4.4.10. Ammonia Temperature-Programmed Desorption (NH3-TPD)

Experiments were conducted on a Micromeritics Chemisorb 2720 chemisorption analyzer equipped with a thermal conductivity detector (TCD) and a ChemiSoft TPx system for temperature control and data analysis. Samples were analyzed as powders positioned between two beds of quartz wool in a U-shaped quartz tube. Catalysts (0.05 g) were pretreated under N₂ flow at 733 K for 2 h and then cooled to 373 K under the same flow. Pretreated samples were then exposed to anhydrous NH₃ at 373 K for 1 h followed by a flow of N₂ at the same temperature for 1 h to desorb weakly physisorbed NH₃. The temperature was then increased from 373 K to 873 K at 10 K min⁻¹ while monitoring desorbed NH₃. All gas flow rates were 30 cm³ min⁻¹.

4.4.11. Hydrogen Temperature-Programmed Reduction (H₂-TPR)

Tests were carried out on powdered samples using the same analyzer as in NH₃-TPD experiments (see above). Catalysts (0.05 g) were pretreated under N₂ flow at 403
K for 2 h and then cooled to 323 K under the same flow. Pretreated samples were then reduced with 10% H$_2$/Ar at a heating ramp of 10 K min$^{-1}$ to 1273 K while monitoring H$_2$ consumption. Water vapor was collected downstream of the quartz tube reactor using a NaCl/ice bath upstream from the TCD. All gas flow rates were 30 cm$^3$ min$^{-1}$.

### 4.4.12. Methanol Aerobic Transformation Catalysis

Catalytic methanol transformation tests were carried out under aerobic conditions at atmospheric pressure in a fixed bed quartz tube reactor (i.d. 12 mm, length 400 mm). Catalyst samples (0.1 g, 0.25 – 0.60 mm particle size) were mixed with 2 g of silicon carbide (0.75 mm particle size) to maintain a constant volume within the catalyst bed. The feed gas consisted of a mixture of methanol/oxygen/nitrogen in a 6:13:81 molar ratio. The flow rate was 100 cm$^3$ min$^{-1}$. Experiments were carried out from 381 – 648 K to obtain the greatest conversion of methanol. Reactants and reaction products were characterized online with gas chromatography using Rt®-U-BOND (fused silica PLOT, length 30 m, i.d. 0.53 mm) and HP-Molesieve (length 30 m, i.d. 0.53 mm) columns.
4.5. References


CHAPTER 5: CONCLUSION

5.1. Summary of Research

In this dissertation, active porous tungsten oxide (WO$_3$) catalysts were prepared using a hard-templating technique with porous silica (SiO$_2$) templates, and they were further modified with gold nanoparticles (Au NPs) with sizes of 3 to 10 nm using a simple sonochemical method. A primary goal of this work was to increase the visible light photocatalytic activity of the WO$_3$ materials with Au NPs deposited on the surface. The mechanisms of liquid-phase and gas-phase photocatalytic reactions over WO$_3$ and Au-WO$_3$ were also studied. Complete characterization of the Au-modified materials was sought to provide a better understanding of the electronic and chemical effects that Au NPs had on WO$_3$ materials. It was clear that Au NPs significantly altered the reactivity of pure WO$_3$ catalysts.

In Chapter 2, highly dispersed and thermally stable (up to 450 °C) Au NPs were deposited onto a SiO$_2$-WO$_3$ composite, which was etched with HF to afford pure Au-WO$_3$ photocatalysts. These materials were successfully applied in the adsorption and photocatalytic degradation of methylene blue (MB) dye in aqueous solutions. Mass spectral and UV-vis spectroscopy data confirmed demethylation and polymerization of MB as the major degradation pathways during visible light irradiation. Pure WO$_3$ catalysts adsorbed more MB than the SiO$_2$-WO$_3$ composites. Finally, Au-modified photocatalysts showed greater rates of MB degradation than their non-modified counterparts, which was due to the enhanced e$^-$/h$^+$ pair separation of these materials.

Chapter 3 described the use of these WO$_3$ catalysts in the gas-phase photocatalytic oxidation of methanol (MeOH) under continuous-flow conditions using
a homemade photocatalysis rig. Importantly, it was shown that porous WO$_3$ photocatalysts were significantly more active than bulk WO$_3$ and porous titania (TiO$_2$). This highlighted the positive effect of using porous catalysts with higher surface areas in photocatalytic applications. Pure WO$_3$ was also highly selective to formaldehyde (FM) and produced negligible CO$_2$. Gold nanoparticles on SiO$_2$ (SiO$_2$-Au) were also very active photocatalysts due to the surface plasmon resonance (SPR) effect and oxidized MeOH to methyl formate (MF). Again, Au NPs on WO$_3$ greatly increased the photocatalytic activity of the porous WO$_3$ materials, and this effect was directly related to the Au loading. The combined mechanisms of band gap excitation on WO$_3$ and SPR on Au NPs improved $e^-$/$h^+$ pair separation. At lower Au loadings, WO$_3$-Au catalysts behaved more similarly to pure WO$_3$, whereas at higher Au loadings, these catalysts were very active to the complete oxidation of MeOH to CO$_2$.

The active site characterization of WO$_3$ and Au-modified WO$_3$ catalysts were the focus of Chapter 4. The thermal transformation of MeOH in the gas-phase was used as a test reaction. It was shown that WO$_3$ alone has moderate acidity, which was confirmed by NH$_3$-TPD studies. The Brønsted acidic hydroxyl (–OH) surface groups made these catalysts highly selective to dimethylether (DME) via MeOH dehydration. Upon modification with higher loadings of Au NPs, these catalysts showed greater catalytic activity than pure WO$_3$. Interestingly, the product selectivity shifted to a variety of oxidation products such as FM, MF, and dimethoxymethane due to changes in the redox properties of WO$_3$, which were induced by the surface Au NPs. Specifically, Au NPs increased the reducibility of WO$_3$ species, which was confirmed by H$_2$-TPR. In contrast, the activity of Au NPs decreased when deposited on WO$_3$. 

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compared to SiO$_2$, and some cationic Au$^+$ were observed on WO$_3$ via X-ray photoelectron spectroscopy. Overall, the Au NPs modified the reactivity of WO$_3$ and the loading of Au and reaction temperature had a large influence on the observed oxidation selectivity.

5.2. Future Directions

The studies described in this dissertation can certainly evolve into other interesting works. For example, new synthetic methods to develop porous metal oxide materials are still very desirable in order to control their structure, which is beneficial in various applications. Also, modifying these materials with other metal nanoparticles or substituting metal cations in the porous oxide lattice can impart new functionality and reactivity to transition-metal oxides.

Catalytic applications directly related to energy conversion could potentially be of interest, specifically to modified WO$_3$ materials. Water splitting to form H$_2$ and O$_2$ is a process that is favorable over WO$_3$, which is an active water oxidation catalyst, in conjunction with another cocatalyst such as Pt. Using visible light irradiation to drive this and other processes is more desirable compared to using high temperature and high pressure conditions that are commonly used in industrial settings.
Comprehensive Bibliography


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