HYDROGENATION OF DIMETHYL OXALATE TO ETHYLENE GLYCOL OVER SILICA SUPPORTED COPPER CATALYSTS

by

Xinbin Yu

Bachelor of Science
Ningxia University, 2012

Master of Science
Tianjin University, 2015

Submitted in Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy in
Chemical Engineering
College of Engineering and Computing
University of South Carolina

2020

Accepted by:
Christopher T. Williams, Major Professor
John R. Monnier, Committee Member
Andreas Heyden, Committee Member
Aaron K. Vannucci, Committee Member
Cheryl L. Addy, Vice Provost and Dean of the Graduate School
DEDICATION

I would like to dedicate this work to my family.
ACKNOWLEDGEMENTS

I would like to thank my family for encouraging and supporting me to pursue PhD degree abroad. I also would like to thank my advisor for giving me valuable suggestions in the research and thank national science foundation and industrial companies for sponsoring the research.

I would like to thank my committee members for giving me a lot of valuable help and inspiring feedbacks and attending my defense.

When I was doing research, I got numerous help from my friends. They help me reserve the instruments, repair the instruments, and lend me important parts. Thus, I would like to thank them for their help.

I would like to thank all the staffs in the department for their technical support.
ABSTRACT

Ethylene glycol is a bulk chemical and hydrogenation of dimethyl oxalate (DMO) on Cu/SiO$_2$ catalysts is the final reaction step in a growing industrial syngas to ethylene glycol (StEG) process. Efforts to improve the performance of the catalysts are still ongoing and the detailed catalytic mechanism remains controversial.

In the present work, a series of 10 wt% Cu/SiO$_2$ is prepared by urea hydrolysis method and indium species is introduced by incipient wetness impregnation. Reaction studies show that 0.25 wt%-0.5 wt% of indium species can dramatically enhance the performance of 10 wt% Cu/SiO$_2$ catalyst. Various characterizations reveal that indium species are partially reduced and have negligible effect on the content of Cu$^+$ species on the surface. Rather, the promotional effect likely originates from interactions between reduced indium species and Cu$^0$ species though enhanced ability of the latter to activate H$_2$.

Support materials and the synthesis parameters (AE temperature and copper loading) are also optimized to prepare Cu/SiO$_2$ catalysts as Cu$^+$ species for the activation of C=O group in the reaction comes from Cu species strongly interacted with SiO$_2$ during catalyst synthesis. KIT-6 supported copper catalysts are prepared via ammonia evaporation (AE) method. The mesoporous, interconnected channels of KIT-6 facilitate the dispersion of copper species. Reaction studies indicate that loading amount of copper species significantly influence the hydrogenation performance. Both AE temperature and loading amount of copper species influence the intrinsic activity. The hydrogenation of DMO to
EG is proposed to proceed via the synergy between Cu$^0$ and Cu$^+$ sites and catalysts with the highest surface Cu$^0$ content exhibit the highest intrinsic activity in the investigated range.

The adsorption DMO over Cu$^{2+}$/SiO$_2$ prepared by urea hydrolysis is studied via ATR-FTIR to know how C-O and/or C=O bond adsorb on the surface at room temperature. The results show that silica does not adsorb dimethyl oxalate and the primary intermediates over the surface of Cu$^{2+}$-containing sample are identified as adsorption of two C=O groups via bidentate mode (1606 cm$^{-1}$), acyl species (1357 cm$^{-1}$, 1315 cm$^{-1}$) and alkoxy C-O species (1045 cm$^{-1}$).
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{d}$</td>
<td>Average diameter of particles.</td>
</tr>
<tr>
<td>$d_i$</td>
<td>The diameter of $i$-th particle.</td>
</tr>
<tr>
<td>$n$</td>
<td>The total number of particles.</td>
</tr>
<tr>
<td>$N$</td>
<td>Mole.</td>
</tr>
<tr>
<td>$X_{DMO}$</td>
<td>Conversion of DMO in the reaction.</td>
</tr>
<tr>
<td>$S_{MG}$</td>
<td>Selectivity to methyl glycolate.</td>
</tr>
<tr>
<td>$S_{EG}$</td>
<td>Selectivity to ethylene glycol.</td>
</tr>
</tbody>
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### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>DMO</td>
<td>Dimethyl oxalate</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>IRE</td>
<td>Internal reflection element</td>
</tr>
<tr>
<td>MA</td>
<td>Methyl acetate</td>
</tr>
<tr>
<td>MCT</td>
<td>Mercury Cadmium Telluride</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MG</td>
<td>Methyl glycolate</td>
</tr>
<tr>
<td>PEG-PPG-PEG</td>
<td>Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)</td>
</tr>
<tr>
<td>SXAS</td>
<td>Small-angle X-ray scattering</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
</tbody>
</table>
TOF ................................................................................................................................. Turnover frequency

TPR ............................................................................................................................... Temperature programmed reduction

WHHSV ........................................................................................................................... Weight hourly space velocity

XRD ................................................................................................................................. X-ray powder diffraction

XPS ................................................................................................................................. X-ray photoelectron spectroscopy

XAES .............................................................................................................................. X-ray induced Auger electron spectroscopy

1,2-BDO .......................................................................................................................... 1,2-butanediol

1,2-PDO .......................................................................................................................... 1,2-propanediol
CHAPTER 1

LITERATURE REVIEW

1.1 TECHNIQUES FOR PRODUCING ETHYLENE GLYCOL

1.1.1 PROPERTIES AND APPLICATIONS OF ETHYLENE GLYCOL

Ethylene glycol (EG) is the simplest diol. It has unique applications due to a structure of two hydroxyl (OH) groups at adjacent positions along a hydrocarbon chain. The hydrocarbon chain of ethylene glycol can be bonded with suitable molecules to produce polyesters. The total demand of ethylene glycol in 2016 is 26.9 million tons (US$ 26 billion) with a compound annual growth rate of 5%-6%. It is widely used as antifreeze, coolant, solvent, desiccant, etc (Figure 1.1). The largest and most important use of ethylene glycol is the production of linear polyesters by reacting with dicarboxylic acids (1-1, 1-2, 1-3). [1]

Ethylene glycol is a odorless, colorless, and hygroscopic liquid of low volatility and viscosity. It is completely miscible with many polar solvents (water, alcohols, ketones, etc.) and only slightly soluble in non-polar solvents (benzene, pentane, dichloroethane, and chloroform, etc.). It becomes a highly viscous, super-cooled substance that eventually turns to a glass-like solid upon continuous cooling. Table 1.1 shows the detailed properties of ethylene glycol. [2]
Figure 1.1 Global demand of ethylene glycol by applications in 2016.

$$\text{HOOC-R-COOH} + \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{H}\left\{\text{OOC-R-COOCH}_2\text{CH}_2\right\}_n\text{OH} + \text{H}_2\text{O}$$

$$\text{HOOC-} + 2\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{HOH}_2\text{CH}_2\text{COOC-} + \text{COOCH}_2\text{CH}_2\text{OH}$$

$$\text{HOH}_2\text{CH}_2\text{COOC-} \rightarrow \text{H}\left\{\text{OOC-}\right\}_n + \text{HOCH}_2\text{CH}_2\text{OH}$$

Table 1.1 Physical properties of ethylene glycol

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS Registry Number</td>
<td>107-21-1</td>
</tr>
<tr>
<td>Auto-ignition temperature</td>
<td>427.0 °C</td>
</tr>
<tr>
<td>Boiling point at 101.3 kPa</td>
<td>197.6 °C</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>446.9 °C</td>
</tr>
<tr>
<td>Critical specific volume</td>
<td>$19.1 \times 10^{-2}$ L·mol$^{-1}$</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>6515.73 kPa</td>
</tr>
<tr>
<td>Compression factor, Z</td>
<td>0.2671</td>
</tr>
<tr>
<td>Cubic expansion coefficient at 20 °C</td>
<td>$6.2 \times 10^{-4}$ K$^{-1}$</td>
</tr>
</tbody>
</table>
Density at 20 °C  1113.5 × 10⁻⁹ g·m⁻³
Flash point, closed cup (Pensky-Martens closed cup ASTM D93)  126.7 °C
Flash point, open cup (Cleveland Open Cup ASTM D92)  137.8 °C
Heat of combustion at 25 °C  -1053.0 kJ·mol⁻¹
Heat of vaporization at 101.3 kPa  53.2 kJ·mol⁻¹
Heat of formation at 25°C  -392.878 kJ/mol
Heat of fusion  11.63 kJ/mol
Lower explosive limit  3.2 vol%
Molecular weight  62.1 g·mol⁻¹
Normal freezing point  -13.0 °C
Onset of initial decomposition  240.0 °C
Refractive index at 25 °C  143.0 × 10⁻²
Specific gravity (20/20 °C)  111.0 × 10⁻²
Solubility in water at 20 °C  100 wt%
Solubility of water in ethylene glycol at 20 °C  100 wt%
Surface tension at 25 °C  48.0 × 10⁻³ N·m⁻¹
Upper explosive limit  53.0 vol%
Vapor density (air = 1)  2.1
Vapor pressure at 20 °C  7.5 Pa
Viscosity at 20 °C  19.8 × 10⁻³ Pa·s

1.1.2 PREVIOUS SYNTHESIS METHODS OF ETHYLENE GLYCOL

Ethylene glycol was first prepared by a French chemist, Charles-Adolphe Wurtz, via hydrolysis of ethylene glycol diacetate in alkaline medium in 1859. [1] However, little interests in ethylene glycol existed due to no related applications at that time. The consumption of ethylene glycol soared during World War I because it substituted glycerol
to produce explosives in Germany. The growing interest in ethylene glycol compelled researchers to find a practical process to produce ethylene glycol. Lefort from Union Carbide Corporation (UCC) proposed the direct oxidation of ethylene to ethylene oxide followed by hydrolysis of ethylene oxide in 1937 (1-4). [3] It is still the major source of ethylene glycol nowadays. Ethylene is commercially produced by cracking petroleum and the oxidation of ethylene to ethylene oxide is catalyzed by silver catalysts. The hydrolysis of ethylene oxide is preferred to proceed in acid medium, in which ethylene oxide is activated by protonation and then reacts with water (Figure1.2(a)). Uncatalyzed hydrolysis in neutral medium and base-catalyzed hydrolysis either require excess amount of water at high temperature (200 °C) and pressure (1.5 - 2 MPa) to increase the selectivity to ethylene glycol or considerably decrease the selectivity to ethylene glycol due to the formation of oligomers such as diethylene glycol (Figure1.2(b)-(d)).[1, 4] The product purification process first remove water in multiple-effect evaporators and then remove by-products via vacuum distillation.[6]

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} + \text{H}_2\text{O} \\
\text{H}_2\text{C} & \quad \text{CH}_2
\end{align*}
\]
Figure 1.2 Mechanisms of hydration of ethylene oxide

Hydrolysis of ethylene carbonate with base (e.g. Na₂CO₃, 1-5) as catalyst can produce ethylene glycol as well. Ethylene carbonate is formed by reaction of ethylene oxide and CO₂ at 80-120 °C and 5.2 MPa (1-6) with alkali halides etc. as catalysts. The hydrolysis step requires high pressure which increases the cost of reactor. Ethylene carbonate can also undergo transesterification with methanol to produce ethylene glycol and dimethyl carbonate with a variety of compounds (e.g. zirconium and titanium compounds, acids, and bases) as catalysts (1-7). However, recycling homogeneous catalysts in the transesterification step is challenging.[5]
Ethylene glycol can also be produced from carbon monoxide and hydrogen (1-8, 1-9, 1-10, 1-11, 1-12). In this route, methanol is first produced from CO and H₂ on CuZnO/Al₂O₃ catalyst and then converted to formaldehyde via oxidative dehydrogenation over iron-molybdenum mixed oxide or silver-based catalysts.[7] Glycolic acid is produced from the reaction of formaldehyde, water, and carbon monoxide with acid as catalyst. Esterification of glycolic acid with methanol yields methyl glycolate. Subsequent catalytic hydrogenation of methyl glycolate produces ethylene glycol and methanol.

1.2 OVERVIEW OF HYDROGENATION OF DIMETHYL OXALATE TO ETHYLENE GLYCOL

Donald M. Fenton invented a method of preparing dimethyl oxalate by coupling of CO in 1965 (1-13). CO was introduced into an alcoholic solution of a platinum group metal salt and a soluble ferric or cupric salt. The salts were maintained in an oxidized state by introducing oxygen into the liquid medium. The reaction was performed in a substantially anhydrous medium at mild temperatures and relatively high pressures (> 2 MPa).[8] CO
The formation of alkyl nitride is an uncatalyzed reaction at 18-21 °C, 0.24-0.28 MPa in liquid phase (1-14). CO coupling with alkyl nitride proceeds over Pd/α-Al₂O₃ catalyst at 0.25-0.40 MPa, 100-140 °C (1-15) with high space time yield of dialkyl oxalate.

\[
\text{CO} + \text{CH}_3\text{OH} + 0.5\text{O}_2 \rightarrow (\text{COOCH}_3)_2 + \text{H}_2\text{O} \quad (1-13)
\]
\[
2\text{ROH} + 2\text{NO} + 0.5\text{O}_2 \rightarrow \text{RONO} + \text{H}_2\text{O} \quad (1-14)
\]
\[
2\text{CO} + 2\text{RONO} \xrightarrow{\text{Pd/α-Al}_2\text{O}_3} (\text{COOR})_2 + 2\text{NO} \quad (1-15)
\]

The hydrogenation of DMO to EG was first investigated in liquid phase. Matteoli \textit{et al.} found that the hydrogenation of dimethyl oxalate could form ethylene glycol (1-16) in the presence of ruthenium carbonyl carboxylates such as Ru₄(CO)₈(CH₃COO)₄(PBu₃)₂ and Ru₂(CO)₉(CH₃COO)₂(PBu₃) under 13.2 MPa of hydrogen at 180 °C with benzene as the solvent. Teunissen \textit{et al.} found that dimethyl oxalate could be efficiently hydrogenated to ethylene glycol under mild conditions (P(H₂) = 7 MPa, 100 °C) using a ruthenium catalyst based on Ru(acac)₃ and MeC(CH₂PPh₂)₃.[12-15]

\[
(\text{COOCH}_3)_2 + \text{H}_2 \rightarrow \text{HOCH}_2\text{COOCH}_3 + \text{HOCH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{OH} \quad (1-16)
\]

Chevron Research Company invented a process for hydrogenation of esters to alcohols in liquid phase. Ester was hydrogenated with hydrogen over a catalyst comprising cobalt, zinc, and copper under conditions of a temperature between 150 °C and 450 °C and a pressure of 3.5-69.0 MPa.[16] However, the liquid catalytic process has several drawbacks, such as very high pressure of H₂, difficult to separate catalysts and products. These problems stimulate the investigation of hydrogenation of DMO in heterogenous catalytic process.

ARCO developed a process for the preparation of ethylene glycol by the vapor phase hydrogenation of oxalate esters, such as a dibutyl oxalate, at elevated temperatures
and at relatively low hydrogen pressures.[17] The process can maximize the hydrogenation catalyst activity and minimize the hydrogenolysis of the glycol and other side reactions in the presence of a suitable hydrogenation catalyst, such as a copper chromite catalyst or copper zinc chromite catalyst. They also found the loss in catalyst activity might be poisoning by sulfur, halogen compounds the formation of copper salts (oxalates and glycolates), side products (e.g. hydrogenolysis of ethylene glycol and formation of polymeric esters) deposited on catalyst surface.

The detailed process for preparing ethylene glycol continuously from syngas was reported by UBE Industries in 1984.[18] The catalysts for the hydrogenation of DMO to EG are copper chromite, zinc copper chromite, and ammonium copper chromate as supported on an inert carrier such as active carbon, alumina, silica, diatomaceous earth, pumice, zeolite, or molecular sieve. Later they developed Cu-Cr-Mn catalyst for vapor phase or liquid phase hydrogenation of oxalates to EG. They also found oxalic acid diesters with small alkyl groups (e.g. dimethyl oxalate) are preferred raw material in vapor phase reaction and oxalic acid diesters with alcohol residue having relatively large carbon number (e.g. ≥4C) are preferred in liquid phase reaction.[19]

Union Carbide Corporation prepared copper-containing catalyst by contacting the support with an aqueous copper ammonium carbonate complex medium followed by reduction of oxidized copper species to active copper form.[20] The catalysts yielded improved activity in producing ethylene glycol without adversely affecting the ethylene glycol selectivity as compared to those prepared by conventional impregnation methods. The leachable iron (Fe$^{+2}$ and/or Fe$^{+3}$) content on the supports for hydrogenation of oxalates to EG should not exceed about 0.03%, by weight of the support.[21] They also investigated
the effect of physical properties of support such as (a) pore volume, (b) average pore diameter, (c) support geometry (the nominal external surface area and volume of the support), and (d) pore-size distribution on the vapor phase hydrogenation of oxalate to EG. The suitable pore volumes range from about 0.9 cm³/g to about 1.5 cm³/g and suitable average pore diameters range from about 12.5 to about 60 nm. The geometric shapes of the support (spheres, cylinders, cored tablets, stars, ribbed extrudates and saddles) as well as its size influence hydrogenation processes. The supports should be restricted to a minimum diameter to avoid too high drop in pressure across the catalyst bed.[22] The catalyst with a shape of an annular configuration with an open center core showed the best performance. The crush strength of the catalysts could be enhanced by adding up to about 50 wt% of milled glass fibers with little change in catalytic activity.[23]

As Cr⁶⁺ is toxic even at low concentration, interests in chromium-free copper-based catalysts grew. UBE Industries developed a method in which cupric nitrate was added to an aqueous solution of an alkali metal hydroxide such as sodium hydroxide or the like to precipitate a precipitate. This precipitate was subjected to reduction treatment before used in the hydrogenation of oxalate to EG in gas phase.[24] Later they applied ammonia as a precipitation reagent to deposit copper species onto silica. The obtained catalysts showed a high yield to ethylene glycol in hydrogenating oxalic acid diester, more particularly, ester of lower alcohol.[25] They also prepared copper catalysts on different supports (TiO₂, SiO₂, etc.) with ammonia evaporation method and tested the effect of promoters (e.g. Zn, Mo) on the catalytic performance.[26-28]
1.3 APPLICATIONS OF SILICA SUPPORTED COPPER CATALYSTS FOR HYDROGENATION OF DIMETHYL OXALATE TO ETHYLENE GLYCOL

Cu-based Cr-free catalysts have been widely used in efficient hydrogenation of DMO to EG due to its high reaction activity, low cost, and environment-friendly nature. Various supports (SiO$_2$, Al$_2$O$_3$, ZnO, La$_2$O$_3$) have been applied for preparing Cu-based catalysts.[24, 26-28, 30,31] Carlini et al. reported that strong acid sites of the support would catalyze the intermolecular dehydration of EG to ethanol, while strong basic sites promote the formation of C3 alcohol and C4 alcohol *via* dimerization of alcohol (Guerbet reaction).[32,33] Therefore, neutral support would be more preferred for the hydrogenation of DMO.[34] Zhu et al. compared the performance of Cu/SiO$_2$, Cu/ZrO$_2$ and Cu/Al$_2$O$_3$ in the hydrogenation of DMO to EG and found that Cu/SiO$_2$ showed the highest selectivity to EG.[35]

Two types of copper species, *i.e.* Cu$^0$ and Cu$^+$, are commonly detected by XPS after reduction on the surface of Cu/SiO$_2$ catalysts. Cu$^0$ species come from the reduction of CuO and Cu$^+$ species originate from the reduction of copper phyllosilicate and/or Cu-O-Si unit. Kohler *et al.* observed that two forms of Cu species on the calcined Cu/SiO$_2$ catalyst prepared by the ion-exchange method.[36] One was ascribed to Cu$^{2+}$ bonded with two silanol group of SiO$_2$. The other one was well-dispersed CuO species over the ion-exchanged Cu-O-Si layer, which originated from the calcination of copper species such as Cu(OH)$_2$. The formation of copper phyllosilicate was observed during the preparation of Cu/SiO$_2$ catalyst by the urea assisted deposition-precipitation method and by selective adsorption of Cu(NH$_3$)$_4$$^{2+}$ on SiO$_2$.[37] Certain amount of copper phyllosilicate decomposed during calcination and produced well dispersed CuO.[38,39] The
decomposition extent of copper phyllosilicate depended on the preparation conditions and the thermal pretreatment conditions. In some cases, large CuO particles attributed to the aggregation of some loose-bonding CuO species during calcination might exist as well.[37] Poels and Brands et al. suggested that during hydrogenation of methyl acetate, Cu\(^0\) dissociatively adsorbed H\(_2\), while Cu\(^+\) stabilized the methoxy and acyl species. [40] Chen et al. postulated that Cu\(^+\) could serve as electrophilic or Lewis acid sites to activate the C=O bond via the electron lone pair on oxygen.[37] The evolution of the catalytic activity with the Cu\(^0\) and Cu\(^+\) surface areas in hydrogenation of DMO to EG, indicating a cooperative effect existed between Cu\(^0\) and Cu\(^+\) which dissociated hydrogen and activated DMO, respectively. It is proposed that excellent catalytic performance could be achieved on catalysts with balanced amount of Cu\(^0\) and Cu\(^+\) sites, but it is still difficult to quantify the balanced of amount and predict the catalytic performance in terms of the measured surface information. Ma et al. prepared MCM-41 supported copper catalysts and attributed the best catalytic performance to high copper dispersion and large Cu\(^+\) surface area.[34] Yin et al. compared the performance of a series of HMS supported copper catalysts in the hydrogenation of DMO to EG.[41] They observed that the maximum ratio of Cu\(^0\)/Cu\(^+\) obtained via tuning the copper loading resulted in the highest DMO hydrogenation activity and EG selectivity.

Different methods are developed to disperse copper species well on the support. Deposition-precipitation method is most frequently used to prepare copper catalysts for hydrogenation of DMO to EG in vapor phase. With the help of reagents, such as ammonia, ammonia carbonate and urea, copper species can be deposited onto support. The universal precipitation reagent is ammonia, and the corresponding method is called ammonia
evaporation method. It involves the preparation of copper-ammonia complex solution with water-soluble copper salt such as cupric nitrate and the concentrated ammonia solution while maintaining the pH of the copper-ammonia complex solution ≥10. Then, colloidal silica sol was added to copper-ammonia complex solution and the mixture is agitated at room temperature or under heating to deposit copper species onto support. Samples containing copper species are obtained after drying the solution, washing the samples and calcination. When urea is used in the synthesis, the method is called urea hydrolysis and commonly used for depositing copper species onto silica sol. Other preparation methods are conventional impregnation method, sol-gel method, ion exchange, microemulsion techniques and selective leaching of Cu-containing alloy, etc.[41,42]

The effect of preparation variables on the catalytic performance has also been investigated. Chen et al. found that the texture, composition, and structure of the calcined and reduced Cu/SiO₂ catalysts were profoundly affected by the AE temperature.[37] Yin et al. found that the texture, surface composition and the surface structure of Cu/HMS catalysts prepared via ion exchange method were profoundly influenced by copper precursors and Cu–HMS catalysts using Cu(NH₃)₄(NO₃)₂ as the precursor showed the best catalytic performance.[43] Zhao et al. prepared mesoporous silica supported copper catalyst via ammonia evaporation method for dimethyl oxalate hydrogenation. They found appropriate pH value of the copper-ammonia solution could ensure the high dispersion of copper species.[44] Yin et al. prepared a series of Cu/HMS catalysts via ion exchange method at temperatures from 30 to 90 °C. They found surface and textural structure of the HMS support as well as the dispersion and nature of copper species depended strongly on the ion-exchange temperature.[45]
Various promoters are incorporated to enhance the performance of Cu/SiO$_2$ catalysts in the hydrogenation of DMO to EG. Wang et al. found that the performance of an SBA-15-supported Cu catalyst could be remarkably promoted with Au.[46] The formation of Cu-Au alloy nanoparticles could stabilize the active species and retard their agglomeration during the hydrogenation process. Huang et al. adopted one-step urea-assisted gelation method to prepare a SiO$_2$ supported CuAg catalysts. The interactions between the Cu and Ag species maintained a balanced Cu$^+$/Cu$^0$ ratio and prevented the transmigration of bimetallic nanoparticles in the reaction.[47] Yin et al. prepared Cu-Ni/SiO$_2$ via ammonia evaporation method and found that oxidative nickel species improved the dispersion of copper species because of the enrichment of copper on the surface of the nickel species. The selectivity to EG and MG could be tuned by modulating the chemical states of nickel species.[48] Zheng et al. prepared lanthanum oxide-modified Cu/SiO$_2$ (La-Cu/SiO$_2$) catalysts by urea-assisted gelation and found that strong interactions between La promoters and Cu species increased Cu metallic dispersion, improved ability for H$_2$ activation, elevated surface concentration of Cu$^+$ species, and enhanced stability of catalyst nanostructure.[49] Wang et al. prepared CuO-ZnO/SiO$_2$ catalysts with various Zn/Cu molar ratios by precipitation. The results showed that suitable zinc incorporation resulted in higher Cu$^+$ content on the surface of catalysts, better dispersion of Cu$^0$ particles and better sintering resistance.[50] He et al. prepared B–Cu–SiO$_2$ catalysts through urea-assisted gelation followed by post-impregnation with boric acid. Doping suitable amount of boric oxide could improve copper dispersion, Cu$^+$ content and retard the growth of copper particles in the reaction. Boric oxide could lower the reducibility of the Cu$^+$ species due to its relatively high affinity for electrons.[51] Ye et al. prepared dextrin-coated
Cu/SiO$_2$ via ammonia evaporation method. An appropriate amount of dextrin helps the formation of more compact nanosized crystalline copper structures with more Cu$^+$ species.[52]

Copper catalysts are found suitable for hydrogenation of C-O bonds, such as esters, ethers, furfural and carboxylic acids. The appropriate hydrogenation ability of copper catalysts allows the selective breaking of C-O bonds without cleaving C-C. However, the stability of copper catalysts remains to be a huge challenge which severely restricts their further industrial applications. Sintering of Cu nanoparticles in the reaction condition is the most important cause for the deactivation of copper catalysts. The Huttig temperature of Cu is only 134 °C which is much lower than the typical operation temperature (170 - 200 °C) leading to the mobilization of surface Cu atoms and subsequent aggregation of Cu particles to minimize the surface energy. Sintering directly causes the decrease in the amount and change in the distribution of surface Cu$^0$ and Cu$^+$ which contribute to the absorption and activation of reactants collaboratively. Besides, CO generated in the hydrogenation process may induce Ostwald ripening of Cu crystallites leading to the aggregation of Cu crystallites.[53,54] Other reasons for catalyst deactivation are carbon deposition, poisoning, leaching and mechanical damage.[55] Besides, the choice of solvent for DMO also influence the stability of catalysts. Wen et al. found that the loss of silica in the form of tetramethoxysilane from the support under the reaction conditions was one of the reasons responsible for the deactivation of the Cu/SiO$_2$ catalyst. The Cu/SiO$_2$ catalyst was more stable using EtOH as solvent than in the using MeOH as solvent.[56] Lin et al. also observed that the lifetime of a Cu/SiO$_2$ catalyst under DMO-ethanol feedstock was 20 times longer than that of the same catalyst under DMO-methanol feedstock. Ethanol tended
to stabilize active sites and slow down the agglomeration of copper particles in the reaction.[57]

One strategy to improve the stability of copper catalysts is incorporating a promoter. Au, Zn, La and B₂O₃ had been shown capable retard the sintering process. Another approach is embedding copper species into inorganic cavities or channels which not only help disperse copper species but also spatially restricted their growth (confinement effect).

Because of the low vapor pressure (0.3 kPa) of DMO at room temperature, the direct evidence of the adsorption of DMO molecules on the surface of reduced copper catalyst had not been reported yet. Instead, the information from the hydrogenolysis of esters with a similar structure but higher vapor pressure was often used as a model. Evans et al. studied the hydrogenolysis of aliphatic esters over Raney copper catalyst in the temperature range 210-280 °C.[58] They found that hydrogenolysis of ethyl acetate involved the surface reaction of adsorbed ethyl acetate or a dissociated fragment with adsorbed hydrogen. Isotopic labeling studies showed that the alkoxy fragment R'O" reacted quickly to form R'OH, while the adsorbed acyl group RCO" was more persistent. Sorum and Onsager et al. investigated the hydrogenolysis of methyl formate and proposed a mechanism whereby the formation of a hemiacetal intermediate was followed by dissociation into formaldehyde and methanol.[59] This was confirmed by Monti et al. using in situ infrared spectroscopy and labeled compounds.[60] Huang et al. studied the hydrogenation of methyl acetate (MA) to ethanol over Cu/SiO₂ catalyst.[61] It was found that MA was predominantly adsorbed in a molecular form under higher MA partial pressure, differing from the dissociative adsorption at lower MA partial pressure. Poels and Brands et al. postulated that during hydrogenation of methyl acetate, Cu⁰ dissociatively adsorbed
H₂, while Cu⁺ stabilized the methoxy and acyl species.[40] From the kinetics of hydrogenolysis of diethyl oxalate over copper-based catalysts, Thomas et al. suggested that the reaction proceeded via dissociative adsorption of diethyl oxalate on the copper surface.[62] This in turn led to the formation of ethanol and ethyl glycolate intermediate that further reacted via an analogous mechanism to form a second ethanol molecule and ethylene glycol. Li et al. screened 34 kinetics models and proposed that the hydrogenation of DMO depended on the synergistic effect of Cu⁰ and Cu⁺ sites, wherein hydrogen and the ester were adsorbed via dissociative states, respectively.[63] The dissociative adsorption of the ester was the rate-controlling step in the hydrogenation of DMO over Cu/SiO₂ catalyst prepared by ammonia-evaporation method. Wang et al. prepared a series of highly comparable Cu/SiO₂ catalysts and postulated that the Cu⁺ sites adsorbed the methoxy and acyl species, while the Cu⁰ facilitated the H₂ decomposition.[64] Overall, it is still unclear whether DMO adsorbs on the surface of the reduced catalyst dissociatively and/or in molecular form, and how reactive the resulting adsorbed species are towards hydrogen.

1.4 SCOPE OF RESEARCH

Cu/SiO₂ catalysts have been proved efficient for the hydrogenation of DMO to EG in vapor phase. However, several problems still exist, such as the agglomeration of copper particles and valence transition of copper species in the reaction. Besides, although it is proposed that excellent performance could be achieved on catalysts with balanced amount of Cu⁰ and Cu⁺ sites, it is still controversial what kind of surface parameters could be correlated with the intrinsic activity.
Thus, the present research will focus on the following topics. First, a variety of promoters has been discovered for improving the performance of Cu/SiO$_2$ in the hydrogenation of DMO to EG and the effect of most promoters is attributed to favor the formation of Cu$^+$ species on the catalysts. New promoters are still highly desired as it is an efficient way to upgrade Cu/SiO$_2$ catalysts. Thus, the present research will explore the possibility of applying promoters for Cu/SiO$_2$ catalysts based on the existing knowledge about Cu/SiO$_2$ catalysts and promoters. The details about how the promoters interact with copper species and subsequently influence the catalytic performance will be studied as well.

Second, novel silica supports are necessary as they not only help disperse copper species but also react with certain amount of copper species to form copper phyllosilicate and/or Cu-O-Si unit. The sintering of copper particles is currently the most significant problems of Cu/SiO$_2$ catalysts and previous studies show that confinement effect could be used for alleviating the problem of particle agglomeration. Thus, the present research will employ novel ordered mesoporous silica as support for Cu/SiO$_2$ catalysts in the hydrogenation of DMO to EG.

Third, ammonia evaporation method is frequently used to fabricate Cu/SiO$_2$ catalysts. However, the effect of the preparation parameters on the performance and especially, the intrinsic activity of Cu/SiO$_2$ catalysts is not well studied. Thus, the present research will investigate several preparation parameters of ammonia evaporation method for the optimization of Cu/SiO$_2$ catalysts and elucidate how these parameters influence the surface properties and the following catalytic behaviors.

Fourth, DMO molecules are proposed to adsorb on actives sites before undergoing further reaction. However, information about how DMO molecules adsorb on the catalysts
are still scarce because the melting temperature of DMO is high and it hard to investigate the adsorption of DMO on catalysts via conventional methods. Thus, the present research will apply ATR-FTIR to investigate the adsorption of DMO on catalysts. The approach will be developed and can be extended to the adsorption of chemicals on other catalysts.
CHAPTER 2
EXPERIMENTAL TECHNIQUES

2.1 MATERIALS

All the reagents are commercially available and used without further purification. Copper (II) nitrate trihydrate (99%, Acros Organics), Indium (III) nitrate hydrate (99.99%, Alfa Aesar), 40 wt % Ludox AS-40 colloidal silica (Sigma-Aldrich), dimethyl oxalate (99%, Sigma-Aldrich), concentrated nitric acid (68-70%, BDH), urea (99.7%, Fisher Chemical), ammonia aqueous solution (BDH, 28%), Pluronic® P-123 (average Mn ~5,800, Sigma-Aldrich), n-butanol (99.5%, ACROS), HCl (37%, Sigma-Aldrich), tetraethyl orthosilicate (TEOS, 99.9%, Alfa Aesar), dichloromethane (99.9%, Sigma-Aldrich) are used as received. H₂ (UHP), He (UHP), Ar (UHP), N₂ (UHP), 0.5 vol.% O₂/He (UHP), 0.5 vol.% O₂/N₂ (UHP) and air (Zero grade) are supplied by Praxair or Airgas. Deionized water (18 MΩ) is obtained by using a Milli-Q water system with Barnant B-pure filter.

2.2 CATALYSTS PREPARATION

10 wt% Cu/SiO₂ catalyst is prepared by urea hydrolysis. Briefly, 2.03 g of Cu(NO₃)₂·3H₂O, 3.5 ml of ammonia aqueous solution is dissolved in 96.5 mL of DI water in a round-bottom flask. Subsequently, 3 g of urea is added before slowly dropping 12 g of 40 wt % Ludox AS-40 colloidal silica under stirring. The mixture is vigorously stirred and aged at 80 °C in water bath for 4 hours. The obtained light blue precipitate is filtrated, washed three times with deionized water, dried overnight at 120 °C in an oven. Copper-indium bimetallic catalysts are prepared by incipient wetness impregnation. For example,
to prepare the sample with 0.5 wt% of In, 5 g of oven-dried 10 wt% Cu/SiO₂ is mixed with 6.5 ml solution containing 0.0777 g indium nitrate. The slurry is dried at room temperature for 48 hours and then at 120 °C for 12 hours. Finally, all samples are calcined at 400 °C for 3 h in air.

1 wt% In/SiO₂ is prepared with incipient wetness impregnation to determine if metallic indium species consumes N₂O during N₂O titration process as urea hydrolysis does not work for depositing indium species on colloidal silica. 40 wt % Ludox AS-40 colloidal silica is first dried to remove water, grinded to fine particles and then mixed with a certain amount of aqueous solution containing indium nitrate. The slurry is dried at room temperature for 48 hours and then at 120 °C for 12 hours. Finally, the sample is calcined at 400 °C for 3 h in air.

KIT-6 is prepared according to the reported method.[65, 66] 13.5 g of PEG-PPG-PEG (Pluronic® P123) is mixed with 487.5 g of DI water and 26.1 g of HCl (37%) and stirred for 1 h. 13.5 g of n-butanol is added at 35 °C followed by 1 h of stirring at 35 °C in a silicone oil bath. Then 29 g of TEOS is added and the mixture is stirred for 24 h at 35 °C. Subsequently, hydrothermal treatment is carried out at 95 °C for 24 h. The white powder is collected by filtration and washed with adequate amount of DI water to remove Cl⁻ (tested with 0.1 M of AgNO₃ solution). Then the powder is dried overnight at 110 °C and calcined for 6 h at 550 °C.

Cu/KIT-6 catalysts are prepared by ammonia evaporation (AE) method. For example, to prepare 10 wt% Cu/KIT-6, 3.8 g of Cu(NO₃)₂·3H₂O is dissolved in a mixture of 100 ml of DI water and 16 ml of NH₃·H₂O (28%) and stirred for 1 h. The pH of the solution is adjusted to 11. Then 9 g of KIT-6 is added and the pH is kept at 11. The
suspension was stirred overnight and then heated in a silicone oil bath at 70 °C to remove NH₃ until the pH was less than 7. The mixture is filtrated, washed three times with deionized water and dried overnight at 110 °C in an oven. Finally, the obtained powder is calcined at 400 °C for 3 h in air, denoted as 10Cu-70 where 10 is weight percent loading of Cu on KIT-6 and 70 is AE temperature. Samples with various copper loading (5 wt% and 20 wt%) and different AE temperature (80 °C, 90 °C and 100 °C) are prepared in the same method.

Cu/SiO₂ catalysts are prepared by ammonia evaporation (AE) method. For example, to prepare 30 wt% Cu/SiO₂, 26.07 g of Cu(NO₃)₂·3H₂O is dissolved in a mixture of 100 ml of DI water and 47.75 ml of NH₃·H₂O (28%) and stirred for 1 h. The pH of the solution is adjusted to 11. Then 40 g of Ludox AS40 colloidal silica is added and the pH is kept at 11. The suspension was stirred overnight and then heated in a silicone oil bath at 90 °C to remove NH₃ until the pH was less than 7. The mixture is filtrated, washed three times with deionized water and dried overnight at 110 °C in an oven. Finally, the obtained powder is calcined at 400 °C for 3 h in air, denoted as 30Cu-11.0 where 30 is weight percent loading of Cu on SiO₂ and 11.0 is pH value of the mixture before starting ammonia evaporation. 15 wt%, 20 wt% and 25 wt% Cu/SiO₂ at pH = 11.0 and 30 wt% Cu/SiO₂ at pH = 11.2 and 11.6 are prepared by the same method.

20wt% Cu/SiO₂ catalyst for spectroscopic research is prepared by urea hydrolysis as previously described. 7.6 g of Cu(NO₃)₂·3H₂O and 13.2 ml of ammonia aqueous solution (28%) is dissolved in 100 mL of DI water in a round-bottom flask. Subsequently, 3.4 g of urea is added before slowly dropping 20.0 g of 40 wt% Ludox AS-40 colloidal silica under stirring. The mixture is vigorously stirred and aged at 70 °C in water bath
overnight. The obtained light blue precipitate is separated, washed three times with deionized water, dried overnight at 120 °C, and calcined at 400 °C for 4 h in air.

2.2 CATALYSTS CHARACTERIZATIONS

Nitrogen adsorption-desorption isotherms at -196 °C are measured with a Micromeritics ASAP 2020 surface area and pore size analyzer. Samples are degassed at 120 °C for 1.5 hours to remove physically adsorbed impurities before each measurement. The specific surface areas are calculated following the Brunauer-Emmett-Teller (BET) method. Pore size distribution is calculated by Barrett-Joyner-Halenda method (BJH) method using the adsorption or desorption isotherm branch.

The actual metallic contents of catalysts are analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Perkin Elmer Avio 200 instrument. The surface area of copper on catalysts are measured by pulsed N₂O titration method at 60 °C. The generation of N₂ is detected by TCD and the specific area of metallic copper is calculated from the total amount of N₂O consumption assuming 1.46 × 10¹⁹ copper atoms/m². The result from N₂O titration on 1 wt% In/SiO₂ shows that metallic indium does not consume N₂O.

H₂ temperature-programmed reduction (H₂-TPR) is performed on a Micromeritics Autochem II 2920 instrument. For H₂-TPR, 100 mg of a calcined sample is loaded into the U-shape quartz tube. The sample is reduced with 10% H₂/Ar flowing at 40 mL/min at a ramping rate of 10 °C/min from RT to 600 °C. TCD is used to monitor the consumption of H₂.

The Fourier-transform infrared (FT-IR) spectra of calcined sample are collected on Perkin Elmer Spectrum 100 FT-IR spectrometer with 4 scans for each spectrum at room
temperature. The spectrometer is equipped with a diamond internal reflection element (IRE) and operated in ATR mode. Sample powders are spread on the IRE and tightened by an alumina cylinder to ensure a close contact with IRE.

Small angle X-ray diffraction pattern is obtained on a SAXSLab Ganesha instrument. A Xenocs GeniX3D microfocus source is used with a Cu target to generate a monochromatic beam with a 0.154 nm wavelength. The instrument is calibrated using National Institute of Standards and Technology (NIST) reference material 640c silicon powder with the peak position at $2\theta = 28.44^\circ$ where $2\theta$ is the total scattering angle. The sample is scanned from 0.18 to 4 degree at a speed of 0.2 degree/min at room temperature.

X-ray diffraction (XRD) patterns of catalysts are collected on a Rigaku SmartLab SE X-ray diffractometer using Cu K\(\lambda\) radiation ($\lambda = 0.15418$ nm) with a scanning angle ($2\theta$) range of 10° to 90°. The tube voltage and current are 40 kV and 44 mA, respectively. The XRD patterns for calcined samples are scanned at a speed of 15°/min. For in situ XRD measurement, 10 wt%Cu/SiO$_2$ and CuIn/SiO$_2$ catalysts are reduced in an in-situ reactor with 20% H$_2$-80% N$_2$ mixture (100 mL/min) at 350 °C for 2 h and Cu/KIT-6 and Cu/SBA-16 catalysts are reduced in an in-situ reactor with 10% H$_2$-90% N$_2$ mixture (100 mL/min) at 350 °C for 2 h. XRD patterns are collected when the temperature is held at 350 °C or decreases to 190 °C at a scanning speed of 5 °/min. The Cu crystallite size is calculated according to Scherrer equation using the full width at half-maximum (FWHM) of the Cu(111) diffraction peak at $2\theta = 43.2^\circ$.

Transmission electron microscopy (TEM) images are obtained on a Hitachi HT7800 transmission electron microscope operating at an acceleration voltage of 100 kV. Reduced powders of 10 wt%Cu/SiO$_2$ and CuIn/SiO$_2$ catalysts are passivated with 0.5 vol.%
O₂/He and reduced powders of Cu/KIT-6 and Cu/SBA-16 catalysts are passivated with 0.5 vol.% O₂/N₂ (100ml/min) at RT for 12 hours. The passivated samples are first grinded to fine particles and then ultrasonically dispersed in ethanol at RT for 1 hour. The solution is dipped onto carbon-coated copper grid (300 mesh) and evaporating the solvent before it is loaded into the chamber. More than 300 particles are counted for the distribution of particle size. The mean diameter of particles is calculated with the following formula:

\[
\overline{d} = \frac{\sum d_i}{n}
\]

where \(d_i\) is the diameter of \(i\)-th particle and \(n\) is the total number of particles.

X-ray photoelectron spectroscopy measurements are performed using a Kratos AXIS Ultra DLD XPS system, with a monochromatic Al Kα source, operated at 15 keV and 150W and a hemispherical energy analyzer. The X-rays are incident at an angle of 45° with respect to the surface normal and analysis is performed at a pressure of 1x10⁻⁹ mbar. High resolution core level spectra are measured with a pass energy of 40 eV and survey scans with a pass energy of 160 eV. The \textit{in situ} reduction of the catalysts is performed in a reaction cell (Model: ES-009R01) directly attached to the XPS chamber, which allows the sample to be treated at H₂ flow conditions. The samples are transferred inside the reaction cell and back to the analysis chamber without exposure to the atmosphere. Since the SiO₂ support is an insulator, a charge neutralizer is used to compensate the substrate charge during XPS measurements. Calcined samples are reduced at 350 °C in an \textit{in situ} cell for 1.5 h. XPS analysis is conducted on the same instrument after the sample cooling down to RT. All spectra are corrected using 284.8 eV as a reference for C1s binding energy (BE).
2.3 CATALYSTS EVALUATION

Catalytic evaluation of vapor-phase DMO hydrogenation is conducted in a stainless-steel tubular reactor. In a typical run, 0.6 g of calcined samples (40-60 mesh) is placed in the center of the reactor (9.4 mm internal diameter), and the top and bottom side of the catalyst bed are packed with adequate amount of quartz powder (20-40 and 40-60 meshes). The calcined sample is activated in a flow of 20% H\textsubscript{2}-80% N\textsubscript{2} stream (75 mL/min) controlled by mass flow controllers at 350 °C and ambient pressure for 4 h with a ramping rate of 2 °C/min. The system pressure is increased and precisely controlled at 2.5 MPa with a back-pressure regulator when the reactor is cooled to the target reaction temperature (190 °C). A 10 wt% DMO solution (in methanol) is pumped into the reactor using an ISCO pump (Teledyne ISCO). The products are collected after the reaction reaches steady state and analyzed on a gas chromatograph (Agilent 5890) equipped with a flame ionization detector and RTX-Wax capillary column (30 m × 0.25 mm ×0.25 μm). The calculation of the conversion of DMO and selectivity to various products (methyl glycolate and ethylene glycol) follows formula below:

\[ X_{DMO} = \frac{N_{DMO,in} - N_{DMO,out}}{N_{DMO,in}} \times 100 \]

\[ S_{MG} = \frac{N_{MG}}{N_{DMO,in} - N_{DMO,out}} \times 100 \]

\[ S_{EG} = \frac{N_{EG}}{N_{DMO,in} - N_{DMO,out}} \times 100 \]

The selectivity to other products including ethanol, 1,2-butanediol (1,2-BDO) and 1,2-propanediol (1,2-PDO) is negligible.
Turnover frequency (TOF, mol\textsubscript{DMO}/(mol\textsubscript{Cu on the surface} × h) or h\textsuperscript{-1}) of the reaction is measured based on the number of surface Cu\textsuperscript{0} atoms determined by N\textsubscript{2}O chemisorption method.

2.4 FILM PREPARATION AND ATR-FTIR STUDY

Finely grinded calcined sample of 20wt% Cu/SiO\textsubscript{2} is dispersed in water with a mass ratio of sample:water of 0.0025. Then the solution is sonicated for 1 h at room temperature resulting in a slurry. About 1.4 mL of the slurry is deposited onto the ZnSe internal reflection element (45°, 80 mm × 10 mm × 3 mm, Simplex) to form a uniform liquid layer and dried out under room condition (25 °C, 1 atm air). The thickness of the film is about 8 microns measured by Leica microscope equipped with CCD camera (figure 2.1). This thickness is above the penetration depth (1-3 microns) of the evanescent wave ensuring that the infrared electric field will be attenuated within the thin film. Then the internal reflection element is mounted into the ATR flow cell (Simplex) and the resulting films were stable on the ZnSe element in the presence of solvent (CH\textsubscript{2}Cl\textsubscript{2}) for at least 24 h in the flow cell.
DMO/CH₂Cl₂ solution and pure solvent are stored in different three-neck round-bottom flasks with magnetic stirrers. Teflon tubing is used due to chemical resistance to both the solvent and reactants/products. The flow cell with a chamber of 1.1 cm³ for the flow of fluids is gasket-sealed with a Viton O-ring. The liquids are pumped with a flow rate of 0.1 ml/s into the flow cell with a scheduled time-concentration profile using Labview software (figure 2.2). The schematic of the flow cell accessories and ATR-IR system is displayed in the supporting information.
In situ ATR-IR spectra are obtained by using a Nicolet 670 Fourier transform infrared spectrometer with a liquid nitrogen-cooled MCT detector. Before collection, pure solvent is flowed through the flow cell for at least 9h to remove any contaminants and let the system reach a stable signal. The background is then collected in the pure CH$_2$Cl$_2$ solvent flow. Spectra consisting of 128 scans with 4 cm$^{-1}$ resolution are recorded every two minutes. All experiments are performed at room temperature (20 °C). The flow of DMO solution and solvent through the cell are controlled by switching the valves in the system. For the present study, the thin film (support or calcined sample) is exposed to a standard DMO concentration-time step profile. Every step lasts 1 h to obtain enough data (ca. 22 spectra per step) to facilitate spectral analysis. The last spectra obtained in each step is typically chosen for curve fitting analysis.
CHAPTER 3

ENHANCED HYDROGENATION OF DIMETHYL OXALATE TO
ETHYLENE GLYCOL ON INDIUM PROMOTED COPPER
CATALYSTS

3.1 INTRODUCTION

The hydrogenation of dimethyl oxalate (DMO) has attracted attention because it can bridge the gap between synthesis gas and methyl glycolate (MG), ethylene glycol (EG) and ethanol, etc.\cite{2,67,68} EG is widely used as a solvent and anti-freezing agent, and in the production of polyester fiber, among many other applications.\cite{2} As a versatile building block, synthesis gas can be readily produced from coal, natural gas and biomass, making the DMO-to-EG process more economically and technologically feasible (2-1, 2-2).\cite{37}

\[ \text{H}_3\text{COOC-COOCH}_3 + 2\text{H}_2 \rightarrow \text{H}_3\text{COOC-CH}_2\text{OH} + \text{CH}_3\text{OH} \quad (2-1) \]

\[ \text{H}_3\text{COOC-CH}_2\text{OH} + 2\text{H}_2 \rightarrow \text{HOH}_2\text{C-CH}_2\text{OH} + \text{CH}_3\text{OH} \quad (2-2) \]

Various catalytic materials have been designed to facilitate the efficient hydrogenation of DMO to EG. The most widely used catalyst in industry is the well-established copper-chromium, which exhibits excellent activity and stability.\cite{17,19} However, the hazardous Cr\textsuperscript{6+} motivates exploration of other effective and yet more environmentally friendly alternatives. Silica supported copper catalysts have
been found to be active in this process due to a unique Cu-O-Si structure that balances the concentration of surface Cu$^+$ and Cu$^0$ species. The former species facilitates the activation of ester group in DMO, while the latter serves to activate and dissociate H$_2$ molecules. Different preparation methods (e.g., ammonia evaporation, sol-gel, precipitation-deposition, impregnation), silica supports (e.g., MCM-41, SBA-15, HMS), and process variables (e.g., pH, temperature) have been explored to prepare catalysts with high metallic dispersion and moderate interaction between copper and silica.[34,37,50,55,69-71]

Such catalytic systems suffer from inherent issues such as susceptibility to Cu agglomeration due to its low Hüttig temperature, and loss of Cu$^+$ species by valence transition during the reaction.[72] These problems cause diminution of active sites, collapse of the synergistic effect between Cu$^0$ and Cu$^+$ species, and eventually the degradation of catalytic performance. One strategy to address these issues is through modification of the properties of silica supported copper catalyst with appropriate promoters. A variety of species (e.g., Au, Ag, Ni, La, Zn, B$_2$O$_3$, etc.) have been found to improve the catalytic performance of silica supported copper catalysts by increasing the dispersion and/or enhancing the stability of Cu$^0$ and/or Cu$^+$ species.[48-52, 73] The forms of promoters and their specific role in enhancing catalytic performance are a topic still under intense investigation.

Here we report the promotional effect of indium species on the performance of hydrogenation of DMO to EG on silica supported copper catalysts. The highly dispersed catalysts are synthesized in a simple, robust method with a low amount of the cheap, non-toxic promoter. The effect of weight hourly space velocity (WHSV) and pressure on the catalytic performance and the stability of catalysts are studied in detail. Various
characterization methods are conducted to elucidate the role of indium species to establish the structure-performance correlation and reveal how the size distribution of promoter and the interaction between two metals modify the properties of main catalytic components.

3.2 RESULTS AND DISCUSSION

The hydrogenation performance DMO over silica supported copper and copper-indium catalysts was investigated in a fixed bed reactor. Figure 3.1(a) shows the effect of weight percentage of In on the performance at 190 °C. Further increasing the amount of In above 0.5 wt% decreases both the conversion and EG selectivity, which may result from covering active sites by excess amount of indium species.

The effect of WHSV on the catalytic performance (10Cu/SiO₂ and 10Cu0.5In/SiO₂) was investigated to measure the production capacity on different catalysts. Figure 3.1 (b, c) shows that the performance in terms of conversion and selectivity to EG decreases on both catalysts with the increasing WHSV due to the shortening of contact time of the reactant with catalysts.[74] However, the performance of 10Cu0.5In/SiO₂ is better than that obtained with 10Cu/SiO₂ catalyst under different WHSV, confirming the advantage of bimetallic catalyst in this case. The results show that incorporation of an appropriate amount of In can improve the performance of 10 wt% Cu/SiO₂.

The effect of H₂ pressure on the performance of catalysts was also examined. As shown in Figure 3.1 (d, e), the selectivity to EG increased with H₂ pressure, possibly arising from the increased concentration of surface absorbed H₂ species.[75] However, the performance of hydrogenation of DMO on 10Cu0.5In/SiO₂ is much less influenced than that on 10Cu/SiO₂ in the low-pressure range showing a potential to decrease the operating pressure in industry.
Turnover frequency is calculated according to the DMO conversion data (less than 20% at 190 °C) and the surface amount of Cu$^0$ sites determined by N$_2$O titration method. Diffusion limitations are ruled out evidenced by Table 3.1. As shown in Table 3.2, the TOF value has a volcano shape with respect to the increasing amount of In content. The value is larger on bimetallic catalysts when the In content is not higher than 1 wt%, reaching a maximum (70.3±5.9 h$^{-1}$) at 0.25 wt% In doping.

Table 3.1 Evidence of ruling out diffusion problems

<table>
<thead>
<tr>
<th>Conversion/%</th>
<th>WHSV=4.8 h$^{-1}$</th>
<th>WHSV=4.8 h$^{-1}$</th>
<th>WHSV=4.8 h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Cu0.25In/SiO$_2$</td>
<td>19</td>
<td>18</td>
<td>17</td>
</tr>
</tbody>
</table>

The comparison of stability is performed on 10Cu0.5In/SiO$_2$ and 10Cu/SiO$_2$ catalyst (Figure 3.1 (f)) over a 100h run test. While both catalysts are stable, the activity of 10Cu0.5In/SiO$_2$ and its selectivity to EG are much higher than the monometallic Cu counterpart.
Various characterization methods have been conducted to reveal why an appropriate amount of indium species can promote the performance of Cu/SiO₂ in the hydrogenation of DMO to EG. The chemical compositions and textural properties of all catalysts are summarized in Table 3.2 ICP-OES proves the effectiveness of the preparation method which can deposit most of the copper and indium species onto the silica support. The N₂ physisorption measurement shows that all the calcined samples exhibit type IV isotherms with mesopores with pore diameter of ~20 nm and certain amount of micropores (Figure 3.2). The BET surface areas of samples with low In loading amount (0-1 wt%) are all close to each other. The exception is the material with 2 wt% loading of indium species.
which shows a 23% decrease in the BET surface area compare with monometallic Cu catalyst, possibly arising due to pore blockage by indium oxide particles at such high loading. Indeed, the introduction of indium species decreases the pore volume by about 10-15% when compared with the pore volume of monometallic Cu catalyst.

Table 3.2 Physicochemical and catalytic properties of Cu/SiO$_2$ catalyst with different In loading amount

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu content,$^a$ (wt %)</th>
<th>In content,$^a$ (wt %)</th>
<th>$S_{\text{BET}},^b$ /m$^2$·g$^{-1}$</th>
<th>$V_p,^c$ /cm$^3$·g$^{-1}$</th>
<th>$S_{\text{Cu}},^d$ /m$^2$·g$^{-1}$</th>
<th>$d_p,^e$ /nm</th>
<th>$d_p,^f$ /nm</th>
<th>TOF,$^g$ /h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Cu/SiO$_2$</td>
<td>11.4</td>
<td>0</td>
<td>256</td>
<td>0.81</td>
<td>3.9</td>
<td>4.6</td>
<td>2.9</td>
<td>38.8±4.6</td>
</tr>
<tr>
<td>10Cu0.25In/SiO$_2$</td>
<td>10.6</td>
<td>0.30</td>
<td>242</td>
<td>0.74</td>
<td>4.5</td>
<td>4.2</td>
<td>3.3</td>
<td>70.3±5.9</td>
</tr>
<tr>
<td>10Cu0.5In/SiO$_2$</td>
<td>10.2</td>
<td>0.53</td>
<td>256</td>
<td>0.71</td>
<td>4.7</td>
<td>4.4</td>
<td>3.4</td>
<td>64.2±2.4</td>
</tr>
<tr>
<td>10Cu1In/SiO$_2$</td>
<td>10.5</td>
<td>1.04</td>
<td>244</td>
<td>0.73</td>
<td>4.3</td>
<td>4.2</td>
<td>3.4</td>
<td>54.3±2.3</td>
</tr>
<tr>
<td>10Cu2In/SiO$_2$</td>
<td>9.9</td>
<td>1.93</td>
<td>198</td>
<td>0.70</td>
<td>4.8</td>
<td>4.5</td>
<td>3.3</td>
<td>14.6±0.3</td>
</tr>
</tbody>
</table>

$^a$ Determined by ICP-OES analysis. $^b$ BET specific surface area. $^c$ Pore volume that obtained from $P/P_0 = 0.99$. $^d$ Cu metallic surface area per gram of catalyst determined by N$_2$O titration method. $^e$ Average particle size determined by TEM images. $^f$ Average particle size determined by Cu(111) peak from in situ XRD patterns at 190 °C. $^g$ TOF value calculated according to surface number of Cu$^0$ atoms from N$_2$O titration method.
Figure 3.2 (A) N₂ adsorption-desorption isotherms and (B) BJH pore size distribution of the calcined catalysts of different copper loadings. a. 10Cu/SiO₂, b.10Cu0.25In/SiO₂, c. 10Cu0.5In/SiO₂, d. 10Cu1In/SiO₂, e. 10Cu2In/SiO₂.

H₂-TPR was conducted to understand the reducibility of the catalysts and to elucidate surface chemical information such as the distribution of metal species and the interaction between them. Figure 3.3 shows the H₂-TPR profiles of 10 wt% Cu/SiO₂ with different amounts of In. For 10 wt% Cu/SiO₂, the peak centered at 192 °C is assigned to the collective reduction of Cu²⁺ species to Cu⁰/Cu⁺. The reduction of bulk cupric oxide usually occurs at much higher temperatures of around 243-255 °C.[49,51] Thus, the low reduction temperature of 10 wt% Cu/SiO₂ indicates a high dispersion of copper species on silica which is further supported by TEM measurements and a weak interaction between certain amount of copper species (e.g. CuO) with SiO₂. Interestingly, the reduction temperature gradually increases with the amount of indium species as listed in the inset except for the sample with 0.25 wt% In. The gradual shift of reduction temperature suggests the existence of an interaction between copper and indium species. Thus, the incorporation of In hinders the reduction of 10 wt% Cu/SiO₂, which is similar to modification of copper catalysts with other promoters.[49-51,76]
Figure 3.3 H2-TPR profile, a. 10Cu/SiO2, b.10Cu0.25In/SiO2, c. 10Cu0.5In/SiO2, d. 10Cu1In/SiO2, e. 10Cu2In/SiO2.

The growing peak with respect to increasing indium content at 270 °C is ascribed to the partial reduction of indium species, which is further confirmed by XPS (see below). As indium species are very difficult to be well dispersed on silica, the size distribution is broad with a certain amount of large grains. [77,78] The reduction behavior of indium species is highly dependent on the particle size, with small grains able to be reduced below 300 °C and large grains being reduced only at very high temperatures.[77,78] The reduction of indium species could also be initiated by the neighboring copper species when they are in close contact. We also cannot rule out that part of the reduction profile of indium species with small particle size may be overlapped with the reduction profile of copper species, given the low loading of indium species in this study.
XRD patterns of the calcined samples and the \textit{in situ} reduced catalysts were collected to understand the existing phase and crystallite sizes within the catalysts. The XRD patterns of calcined samples (Figure 3.4(A)) do not exhibit noticeable peaks belonging to metal oxides implying their high dispersion and amorphous character. After \textit{in situ} reduction at 350 °C, the peaks (Figure 3.4(B, C)) at 43.5° and 74.4° can be ascribed to Cu\textsuperscript{0}(111) and Cu\textsuperscript{0}(220). The average particle size of Cu crystallite is calculated in terms of Scherrer equation and listed in Table 1. The crystallite sizes for all the samples are around 3 nm, which shows that the metallic species are well-dispersed after reduction.
Figure 3.4 (A) XRD patterns of calcined sample at room temperature and (B) *in situ* XRD patterns of reduced sample at 350 °C, (C) *in situ* XRD patterns of reduced sample at 190 °C, a. blank XRD reactor, b. 10Cu/SiO$_2$, c. 10Cu0.25In /SiO$_2$, d. 10Cu0. 5In /SiO$_2$, e. 10Cu1ln /SiO$_2$, f. 10Cu2In /SiO$_2$.

ATR-FTIR was utilized to reveal structural information for the calcined samples shown in Figure 3.5. The band at 1118 cm$^{-1}$ is ascribed to asymmetric stretching vibration
band ($v_{SiO}$) of SiO$_2$. The deformation band ($\delta_{OH}$) of OH at 670 cm$^{-1}$ and asymmetric stretching vibration band ($v_{SiO}$) of Si-O at 1045 cm$^{-1}$ in the FTIR spectra prove the existence of cupric phyllosilicate (Cu$_2$Si$_2$O$_5$(OH)$_2$), suggesting the existence of Cu$^+$ during the reduction.[41,49] The relative content of cupric phyllosilicate in each sample can be estimated using the intensity ratio of the deformation band ($\delta_{OH}$) of cupric phyllosilicate at 670 cm$^{-1}$ and the symmetric stretching vibration band ($v_{SiO}$) of silica at 800 cm$^{-1}$, denoted as $I_{670}/I_{800}$. [79] However, the $I_{670}/I_{800}$ ratio only gives a qualitative estimation of the content of cupric phyllosilicate as the extinction coefficients of the corresponding IR bands are not known. Nevertheless, cupric phyllosilicate exists in all the catalyst samples.

![Figure 3.5 FT-IR spectra of calcined samples, a. 10Cu/SiO$_2$, b.10Cu0.25In/SiO$_2$, c. 10Cu0.5In/SiO$_2$, d. 10Cu1In/SiO$_2$, e. 10Cu2In/SiO$_2$, f. SiO$_2$.](image)

TEM images (Figure 3.6) of reduced catalysts were obtained to reveal the distribution of particle sizes in the catalysts. The histograms of particle size (inset) exhibit a very narrow distribution with the mean particle diameter about 4 nm for all the samples.
Thus, copper species are highly dispersed on silica, which is consistent with the results of H$_2$-TPR and in situ XRD measurements.

![Figure 3.6 TEM images of reduced catalysts, a.10Cu/SiO$_2$, b.10Cu0.25In/SiO$_2$, c. 10Cu0.5In/SiO$_2$, d. 10Cu1In/SiO$_2$, e. 10Cu2In/SiO$_2$.](image)

Surface properties of reduced catalysts were investigated by XPS and with X-ray induced Auger electron spectroscopy (XAES). Figure 3.7 shows the Cu 2$p$ XPS spectra of calcined samples. The peak at around 936 eV is assigned to Cu$^{2+}$ which is confirmed by the characteristic satellite peak of Cu$^{2+}$ species at 945 eV. No peaks belonging to Cu$^0$ or Cu$^+$ are observed suggesting that copper exists as Cu$^{2+}$ species in the calcined sample. After reduction, only two peaks at 932.1 and 951.9 eV are observed (Figure 3.8(A)), attributed to Cu 2$p$3/2 and Cu 2$p$1/2, respectively.[34,49] Furthermore, the satellite peak and the peak with Cu 2$p$ binding energy of 936 eV assigned to Cu$^{2+}$ species are absent. These results show that Cu$^{2+}$ species on the surface are reduced to Cu$^0$ and/or Cu$^+$ species which is consistent with H$_2$-TPR result. The binding energy for Cu 2$p$3/2 in 10Cu0.5In/SiO$_2$ is lower (0.4 eV) than that in 10Cu/SiO$_2$ indicating an electron transfer from reduced In species to
copper species. This is reasonable since the Pauling electronegativity of copper (1.90) is higher than that of indium (1.78). Thus, an interaction between a certain amount of copper and reduced indium species, possibly by alloying, may exist in the bimetallic samples.

![Cu 2p XPS spectra](image)

Figure 3.7 Cu 2p XPS spectra of fresh samples, a. 10Cu/SiO₂, b. 10Cu0.25In/SiO₂, c. 10Cu0.5In/SiO₂, d. 10Cu1In/SiO₂, e. 10Cu2In/SiO₂.

As the difference in Cu 2p3/2 and Cu 2p1/2 binding energies between Cu⁺ and Cu⁰ are negligible, Cu LMM XAES was recorded to discriminate these peaks.[34,49,70] Two peaks with Auger kinetic energy of 914 eV and 917 eV are observed for the reduced catalysts (Figure 3.8(B)), confirming the simultaneous existence of Cu⁰ and Cu⁺ species on these catalysts.[49,71-73,80]
Figure 3.8 (A) Cu 2p XPS spectra and (B) Cu LMM XAES spectra of reduced catalysts, a. 10Cu/SiO₂, b. 10Cu0.25In /SiO₂, c. 10Cu0.5In/SiO₂, d. 10Cu1In /SiO₂, e. 10Cu2In/SiO₂, (C) In 3d XPS spectra of calcined and reduced bimetallic samples, a. 10Cu0.25In/SiO₂, b. 10Cu0.5In/SiO₂, c. 10Cu1In /SiO₂, d. 10Cu2In/SiO₂, i. calcined samples, ii. reduced samples.

Deconvolution results (Table 3.3) show that the near-surface content of Cu⁺ species for all samples with various In loading amounts is almost the same. The high content of
Cu⁺ species further confirms the assumption of well-dispersed copper species on silica and the existence of interaction between copper species and SiO₂ as indicated by H₂-TPR and TEM.

Figure 3.8(C) shows In 3d XPS spectra of calcined and reduced 10Cu0.5In/SiO₂. The peaks at approx. 446 eV and 453.6 eV are assigned to In 3d₅/₂ and In 3d₃/₂, indicating that the indium species in the calcined sample are in oxide form.[78,81] However, two new peaks located at 444.1 eV and 451.7 eV attributed to metallic indium species emerge after reduction.[82-85] The result shows that indium species are partially reduced to metallic form after reduction consistent with the analysis in H₂-TPR test.

High metal dispersion is generally acknowledged to enhance the hydrogenation activity of Cu/SiO₂ catalysts by promoting the formation of Cu⁺ species for the cooperation between Cu⁰ and Cu⁺ sites.[86,87] It is proposed that Cu⁰ species adsorb and dissociate hydrogen molecules, while the Cu⁺ species stabilize the methoxy and acyl species from the activated ester molecules.[47,49,51] An excellent hydrogenation performance could be achieved via the synergetic effect of balanced Cu⁰ and Cu⁺ sites on the surface, which can explain the superior performance of 10Cu/SiO₂ in our case. The amount of Cu⁺ sites has been proposed previously to be directly related to the selectivity to EG and the effect of promoters is usually ascribed to the increase in the content of Cu⁺ species.[47,49,51] However, XPS results show that the near-surface amount of Cu⁺ for the catalysts in our case (at least prior to reaction) is roughly the same.
Table 3.3 Deconvolution Results of XPS and Cu LMM XAES of Reduced Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>KE, a eV</th>
<th>AP, b eV</th>
<th>Cu 2p3/2 BE, eV</th>
<th>X_{Cu^+} % c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu⁺</td>
<td>Cu⁰</td>
<td>Cu⁺</td>
<td>Cu⁰</td>
</tr>
<tr>
<td>10Cu/SiO₂</td>
<td>914.1</td>
<td>917.5</td>
<td>1846.9</td>
<td>1850.3</td>
</tr>
<tr>
<td>10Cu0.25In/SiO₂</td>
<td>913.8</td>
<td>917.8</td>
<td>1846.6</td>
<td>1850.6</td>
</tr>
<tr>
<td>10Cu0.5In/SiO₂</td>
<td>914.1</td>
<td>917.8</td>
<td>1846.5</td>
<td>1850.2</td>
</tr>
<tr>
<td>10Cu1In/SiO₂</td>
<td>913.8</td>
<td>917.5</td>
<td>1846.8</td>
<td>1850.5</td>
</tr>
<tr>
<td>10Cu2In/SiO₂</td>
<td>914.1</td>
<td>917.7</td>
<td>1846.8</td>
<td>1850.4</td>
</tr>
</tbody>
</table>

a. Kinetic energy, b. Auger parameter, c. Ratio of peak areas between Cu⁺ and (Cu⁺ + Cu⁰) by deconvolution of Cu LMM XAES spectra under the assumption that the Cu⁺ ions and Cu⁰ atoms occupy identical areas and have identical atomic sensitivity factors.

Furthermore, N₂O titration results reveal that doping indium species (0.25-2 wt%) can slightly increase the surface amount of Cu⁰ sites which might be another evidence for the existence of the interaction between copper species and indium species. However, the performance of bimetallic samples with low loading of indium species (10Cu0.25In/SiO₂ and 10Cu0.5In/SiO₂) are significantly improved over that of 10Cu/SiO₂. We propose that the increased performance of these In promoted samples might be attributed to the enhanced ability of adsorption and activation of H₂ on bimetallic surface sites.

Indeed, the estimated TOF value of bimetallic catalysts (10Cu0.2In/SiO₂ and 10Cu0.5In/SiO₂) based on Cu⁰ content, are much higher than the TOF of 10Cu/SiO₂ which indicates the nature of the active sites are significantly different. Thus, a new active phase attributed to the modification of Cu⁰ crystallites with In⁰ species is created on the surface. Wang et al. find that when the accessible metallic Cu surface area is below a certain value(approximately 20 m²/g in their case), the catalytic activity of hydrogenation of DMO
on silica supported copper catalysts linearly increases with increasing Cu\(^0\) surface area as the insufficient H\(_2\) decomposition limits the reaction rates.[64] Considering that the majority of copper species are Cu\(^+\) species and the surface area of Cu\(^0\) for all the samples is very low in our case, it is likely that the incorporation of In\(^0\) with Cu\(^0\) clusters forming bimetallic sites promotes the dissociation of H\(_2\). The TOF value of 10Cu2In/SiO\(_2\) is much smaller than the TOF value of 10Cu/SiO\(_2\) even though they have similar Cu\(^+\) content and the bimetallic catalyst has ~22\% higher amount of Cu\(^0\) sites. It is generally accepted that the dispersion of metal oxides on support decreases with the increasing loading amount of metal oxides. The absolute amount of unreduced In\(_2\)O\(_3\) species tends to increase with the incremental amount of indium species on the catalysts as indium species are hard to be well dispersed on silica and only small In\(_2\)O\(_3\) particles and/or In\(_2\)O\(_3\) particles close to Cu\(^0\) sites can be reduced. Moreover, the generation of excess amount of In\(^0\) species on bimetallic catalysts with high loading of indium species might also be a factor for deteriorating the catalytic activity. This significant decrease in TOF from overpromotion of In is likely a result of disruption of the balance between Cu\(^0\) and Cu\(^+\) sites on the surface by In\(_2\)O\(_3\) species and/or excess In\(^0\) species (e.g. covering sites with high activity and separating metallic sites from Cu\(^+\) sites). Thus, incorporating only an appropriate amount of indium species offering a balance between the amount of In\(^0\) species and In\(_2\)O\(_3\) species can improve the intrinsic activity of 10Cu/SiO\(_2\).

The detailed reaction pathways in the hydrogenation of DMO on Cu/SiO\(_2\) catalysts are given in Figure 3.9. Figure 3.10 depicts the role of indium species in the hydrogenation of DMO to EG. The reduction of cupric phyllosilicate (Cu\(_2\)Si\(_2\)O\(_5\)(OH)\(_2\)) and copper oxide (CuO) can yield Cu\(^+\) and Cu\(^0\) sites, respectively. The reduction of indium species can be
initiated by In$_2$O$_3$ particles with small crystallite size and the intimate contact with neighboring Cu$^0$ species. The reduced indium species interacts with the Cu$^0$, possibly by alloying, to form a new type of metallic sites. These sites enhance the adsorption and activation of H$_2$, resulting in the efficient refilling of activated H$_2$ species consumed in the reaction and thus enhancing the number of turnover.

![Chemical Reaction Diagram](image)

Figure 3.9 Reaction pathways in the hydrogenation of DMO on Cu/SiO$_2$ catalysts.
Figure 3.10 Schematic illustration of promotional effect of indium species on 10 wt% Cu/SiO$_2$ in the hydrogenation of DMO to EG.

3.3 CONCLUSION

Silica supported Cu-In bimetallic catalysts are successfully prepared via urea-assisted gelation followed by incipient wetness impregnation. The incorporation of a low amount (less than 1 wt% in this study) of cheap, nontoxic indium species dramatically enhances the intrinsic activity of Cu/SiO$_2$ for the conversion of DMO to EG. Two types of indium species, In$^0$ and In$^{3+}$, are observed after reduction via XPS. An interaction among copper species and indium species are confirmed by H$_2$-TPR, N$_2$O titration and XPS. However, the surface content of Cu$^+$ which is related to the activation of ester group is not significantly affected by indium species. Instead, In$^0$ species might be alloyed with Cu$^0$ species to form a new type of metallic sites with enhanced ability to dissociate H$_2$ which might account for the observed increase in the intrinsic activity of bimetallic catalysts.
CHAPTER 4

HYDROGENATION OF DIMETHYL OXALATE TO ETHYLENE GLYCOL ON KIT-6 SUPPORTED COPPER CATALYSTS

4.1 INTRODUCTION

Ethylene glycol (EG) is a commodity widely consumed as a solvent, building block of polyester fibers, anti-freezing agent, alkyd resin and so forth [2] Traditionally, EG is synthesized by hydration of ethylene oxide derived from petroleum feedstocks.[88] However, due to non-uniform global distribution of petroleum resources, the synthesis of EG from syngas is emerging as a rapidly growing technology, especially in Eastern Asia.[2,37] The process consists of producing syngas from coal, coupling of CO by methyl nitride on Pd/α-Al₂O₃ to form dimethyl oxalate (DMO), and subsequent hydrogenation of DMO to EG. This process has already been implemented on an industrial scale.[51]

The choice of catalysts is vital to the hydrogenation reaction, with CuCr catalysts having been found applicable to have excellent activity and stability.[17,19] However, the Cr⁶⁺ is a known health hazard and environmental pollutant, which motivates research for alternative, environmentally friendly catalysts. Along these lines, Cu/SiO₂ catalysts have proved effective for this reaction, due to the coexistence of surface Cu⁰ and Cu⁺ species that are proposed as sites for the activation of H₂ and C=O, respectively.[37,51] The Cu⁰ species originate primarily from the reduction of CuO, while Cu⁺ species come from
the reduction of copper phyllosilicate (Cu$_2$Si$_2$O$_5$(OH)$_2$) and/or Cu-O-Si unit, which are the products of copper precursor species reacting with silica during the preparation of catalyst. Excellent performance of hydrogenation of DMO to EG can be achieved over Cu/SiO$_2$ by adjusting the balance of Cu$^0$ and Cu$^+$ sites.

Various promoters (B, Ni, Zn, La, Ag, Au, In, etc.) have been studied in detail to reveal how the surface content of Cu$^0$ and Cu$^+$ sites can be tuned for the optimal catalytic performance.[46-51,70,73] However, supports also play an important role as they not only help disperse the active species but also react with certain copper species to form copper phyllosilicate and/or Cu-O-Si unit. Ordered mesoporous silicas (e.g. MCM-41, SBA-15, and HMS) with tuneable mesopores, easily accessible internal surface, and high specific surface areas have been successfully applied as supports for metal catalysts in many reactions.[89,90] The spatial confinement exerted by channels on active species exhibits interesting phenomena, such as inhibiting particle growth and modifying product distribution. However, most of the studied mesoporous silicas for hydrogenation of DMO only have one- or two-dimensional pores.[34,44,69,70,73] These structures may suffer from problems such as inefficient utilization of active species due to blocked channels by particles (during preparation and reaction), coke and collapsed wall and inferior mass transfer kinetics.[34,44] Silicas with three dimensional, interconnected mesopores like KIT-6 would be a good choice to address these problems, and have not yet been explored as a support for the hydrogenation of DMO over copper catalysts.

Ammonia evaporation (AE) method is typically employed to deposit copper species onto silica supports like colloidal silica and mesoporous silicas.[37,70] As copper phyllosilicate and/or Cu-O-Si unit are generated by the reaction between copper-ammonia
complexes and silica at the preparation stage, their content and the attendant change in the catalytic properties may be regulated by parameters such as ammonia evaporation temperature, pH, types of copper precursors, concentration of copper, calcination temperature, etc. Chen et al. found that ammonia evaporation temperature significantly influenced the deposited copper amount, relative content of Cu$^+$ and surface area of Cu$^0$ of reduced Cu/SiO$_2$ catalysts and the optimal temperature was 90 °C.[37] Yin et al. found that the surface ratio of Cu$^0$/Cu$^+$ could be adjusted by the copper loading, which then influenced both DMO hydrogenation activity and selectivity to EG.[41]

In the present work, ordered mesoporous silica with interconnected channels, KIT-6, is facilely synthesized by soft-templating method and then employed as support for copper catalysts prepared by ammonia evaporation method. The effect of AE temperature and copper loading on the performance and intrinsic activity of catalysts has been studied in detail. The catalysts are extensively characterized to investigate how the changes in surface properties (i.e. specific surface area of Cu$^0$ and surface ratio of Cu$^0$/Cu$^+$) induced by AE temperature and copper loading influence the catalytic performance.

4.2 RESULTS AND DISCUSSION

The hydrogenation of DMO over KIT-6 supported copper catalysts was investigated in a flow reactor. The reaction proceeds via DMO to MG and then MG to EG, with further dehydration of EG producing other by-products like ethanol.

Figure 4.1(A) shows the effect of AE temperature on the hydrogenation performance at 190 °C. The AE temperature only slightly influence the hydrogenation performance. However, Figure 4.1(B) and Figure 4.2 show that the loading amount of copper species has a dramatic effect on the hydrogenation performance in terms of conversion of DMO and selectivity to EG, which is consistent with other reports.[34,41,44]
Figure 4.1 (A). Effect of temperature of evaporating NH$_3$ on hydrogenation of DMO over 10wt% Cu/KIT-6, (B). Effect of copper weight percentage on hydrogenation of DMO over Cu-70, reaction condition: T = 190 °C and 195 °C for 5Cu-70, P(H$_2$) = 2.5 MPa, H$_2$/DMO molar ratio = 95, WHSV = 0.66 h$^{-1}$.

Figure 4.2 S(MG)-X(DMO) for different catalysts, reaction condition: T = 190 °C, P(H$_2$) = 2.5 MPa, H$_2$/DMO molar ratio = 95.

Figure 4.3 shows the stability of hydrogenation of DMO over 20 wt% Cu/KIT-6 prepared at 70 °C. The catalyst does not show any deactivation after 221 h on stream.
4.3 Material characterizations

Several characterizations have been performed to gain an insight into the effect of AE temperature and loading amount of Cu on the structure of Cu/KIT-6 catalysts. Figure 4.4 shows the structural characterizations of bare KIT-6. The pattern (Figure 4.4(A)) exhibits peaks at 0.92° (211), 1.01° (220) and 1.75° (420), indicating that the support has cubic Ia3d symmetry with interconnected channels.[66] The TEM image (Figure 4.4(B)), N₂ adsorption-desorption isotherm pattern (Figure 4.4(C)) and BJH pore size distribution analysis (Figure 4.4(D)) confirm that the support has mesopore structure with mesopore diameter of 6.6 nm. Moreover, a certain amount of pores in the micropore/small mesopore range is observed, which is attributed to the secondary pore system in the framework walls (i.e., intra-wall pores) providing interconnections for adjacent mesopores (Figure 4.4D).[91-95]
The bulk properties and compositions of representative catalysts are summarized in Table 4.1. ICP-OES confirms that the real deposited amount of copper species on KIT-6 via ammonia evaporation method is close to the target weight percentage in the investigated range. All the calcined samples exhibit type IV isotherms revealed by N2 physisorption (Figure 4.5(A)). The pore diameter distribution plot shows that all the samples have mesopores with pore diameter of ~6 nm with a certain amount of pores in the micropore/small mesopore range, similar to mesopore diameter of bare support (Figure 4.5(B)). The BET measurement of bare KIT-6 support has a specific surface area of 703 m²/g. The specific surface area decreases to 305 m²/g upon the loading of 5 wt% of copper species. However, the specific surface area does not change significantly for samples with 10 wt% and 20 wt% of copper species. Besides, only small change (~10%) in pore volume exists when comparing 5Cu-70 sample with bare support. Based on these observations, we think that copper species are deposited on the external surface, in intra-wall pores and mesopores and more mesopore volume is occupied when the deposited amount of copper is higher (e.g. 20 wt%). Similar analysis has been reported by other researchers.[41,93]
Figure 4.4 Structural characterizations of KIT-6, (A). SAXS pattern (B). TEM image, (C). N₂ adsorption-desorption isotherm, (D). BJH pore size distribution.
Figure 4.5 (A) N$_2$ adsorption-desorption isotherms and (B) BJH pore size distribution of the calcined catalysts of different copper loadings, a. 5Cu-70, b. 10Cu-70, c. 10Cu-80, d. 10Cu-90, e. 10Cu-100, f. 20Cu-70.

Table 4.1 Physicochemical and catalytic properties of Cu/KIT-6 catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu content, a /wt%</th>
<th>S$_{\text{BET}}$, b /m$^2$.g$^{-1}$</th>
<th>V$_p$, c /cm$^3$.g$^{-1}$</th>
<th>S$_{\text{Cu}}$, d /m$^2$.g$^{-1}$</th>
<th>d$_p$, e /nm</th>
<th>TOF, f /h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KIT-6</td>
<td>0</td>
<td>703</td>
<td>1.03</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>5Cu-70</td>
<td>5.7</td>
<td>305</td>
<td>0.90</td>
<td>~</td>
<td>2.1</td>
<td>~</td>
</tr>
<tr>
<td>10Cu-70</td>
<td>10.4</td>
<td>294</td>
<td>0.84</td>
<td>2.8</td>
<td>2.8</td>
<td>63.3 ± 4.5</td>
</tr>
<tr>
<td>10Cu-80</td>
<td>10.3</td>
<td>294</td>
<td>0.84</td>
<td>2.93</td>
<td>~</td>
<td>49.9 ± 6.9</td>
</tr>
<tr>
<td>10Cu-90</td>
<td>11.3</td>
<td>290</td>
<td>0.85</td>
<td>2.84</td>
<td>~</td>
<td>87.8 ± 0.5</td>
</tr>
<tr>
<td>10Cu-100</td>
<td>10.5</td>
<td>280</td>
<td>0.85</td>
<td>2.47</td>
<td>~</td>
<td>58.5 ± 6.5</td>
</tr>
<tr>
<td>20Cu-70</td>
<td>19.7</td>
<td>268</td>
<td>0.69</td>
<td>4.55</td>
<td>3.2</td>
<td>99.4 ± 10.4</td>
</tr>
</tbody>
</table>

a. Determined by ICP-OES analysis, b. BET specific surface area, c. Pore volume at P/P$_0$ = 0.99, d. Surface area of Cu$^0$ per gram of catalyst measured by N$_2$O titration method, e. Average crystallite size measured in terms of Cu(1 1 1) peak at 190 °C, f. TOF value calculated in terms of specific surface area of Cu$^0$ from N$_2$O titration results.
Figure 4.6 FT-IR spectra of different calcined samples, a. KIT-6, b. 5Cu-70, c. 10Cu-70, d. 10Cu-80, e. 10Cu-90, f. 10Cu-100, g. 20Cu-70.

Figure 4.6 shows the FT-IR spectra of calcined KIT-6 and Cu-containing samples to gain an insight into the existing copper species on the calcined samples. It is observed that copper could form copper phyllosilicate and/or Cu-O-Si unit with silica at the preparation stage. The absence of the peak at 670 cm\(^{-1}\) attributed to the \(\delta_{OH}\) band of copper phyllosilicate indicates that copper phyllosilicate may not exist on the Cu-containing samples.[34, 41] The peaks located at 800 cm\(^{-1}\) and 1061 cm\(^{-1}\) are assigned to the symmetric and asymmetric \(\nu_{SiO}\) band of amorphous silica, respectively. The peaks at 1643 cm\(^{-1}\) are ascribed to the bending mode of OH groups of adsorbed water. No peaks at 690 cm\(^{-1}\) belonging to the bending absorption of the Cu-OH bond exist confirming the absence of copper hydroxide on the calcined samples. The ratio of peak intensities at 970 cm\(^{-1}\) and 800 cm\(^{-1}\) (I\(_{970}/I_{800}\)) is calculated to estimate the amount of incorporated copper as the peak at 800 cm\(^{-1}\) represents the symmetric \(\nu_{SiO}\) band of KIT-6 and the change in the intensity of peak at 970 cm\(^{-1}\) originates from incorporated copper.[34] The gradual increase in I\(_{970}/I_{800}\)
when elevating the loading amount of copper as listed in Figure 4.6 suggests that a certain amount of copper is incorporating into the framework of KIT-6. No copper hydroxide or copper phyllosilicates exist over the calcined Cu/KiT-6 samples, unlike Cu/SiO$_2$ prepared with colloidal silica as silica source.[48,49]

![H$_2$-TPR profiles of different catalysts.](image)

Figure 4.7 shows the H$_2$-TPR profiles of different catalysts to reveal their reducibility. All the profiles exhibit a single peak centered at different temperature, attributed to the collective reduction of Cu$^{2+}$ and Cu$^+$ species (see XPS section) to Cu$^0$ and/or Cu$^+$. The reduction temperature (185 °C-206 °C) in our case is significantly lower than the typical reduction temperature of Cu/SiO$_2$ catalysts (243-270 °C) reported in literature, implying that copper species are well dispersed on KIT-6.[34,37,44,69,96] This is correlated well with TEM and XRD measurements. Comparing the peak positions reveals that the peak gradually shifts to higher temperature when increasing the loading amount of Cu. It has been reported that supported CuO with smaller crystallites is much more facile to be reduced than bulk CuO.[37,97] In situ XRD results reveal that elevating the
loading amount of Cu causes an increase in average size of crystallites. Thus, the shift is attributed to increasing copper particle sizes and decrease in the dispersion.

The existing copper species on the calcined samples can be a mixture of Cu\(^+\) species, CuO with different dispersions and Cu–O–Si structures, although the profile only shows one reduction peak for every sample. Van der Grift et al. and Marchi et al. found that the reduction of the copper phyllosilicate and ion-exchanged Cu–O–Si species to Cu\(^+\) could overlap with the reduction of well dispersed CuO to Cu\(^0\).[98,99] FT-IR spectra shows that Cu–O–Si structure rather than copper phyllosilicate is present on the Cu-containing samples, in accordance with others reports with ordered mesoporous silica as support.[34, 41] \(\text{H}_2\)-TPR might not differentiate different copper species present on the calcined samples due to their difference in the amount and reducibility. XPS results show that both Cu\(^0\) and Cu\(^+\) species exist on the surface of samples reduced at 350 °C, which suggests that not only one type of copper species exist on the calcined samples. Further reduction of Cu\(^+\) species originating from Cu–O–Si structure may require a much higher temperature to destroy their stable structures.[98,99]
Figure 4.8 (A). XRD patterns of calcined samples at room temperature, (B) In situ XRD patterns of reduced catalysts at 350 °C, (C) In situ XRD patterns of reduced catalysts at 190 °C, a. a blank XRD reactor, b. 5Cu-70, c. 10Cu-70, d. 20Cu-70.

Wide-angle powder XRD patterns of the calcined and reduced samples were obtained to differentiate the existing phases and calculate crystallite sizes. No noticeable peaks assigned to metal oxides exhibit on calcined samples (Figure 4.8(A)) implying that copper species are highly dispersed on the support. Two peaks (Figure 4.8(B)) at 43.5° and 74.4° attributed to Cu⁰(111) and Cu⁰(220) emerge after in situ reduction at 350 °C.[34,76,100] The peaks become more intense and sharper as the loading amount of copper species increase, implying the growth in particle size. The average particle sizes are
calculated according to Scherrer equation (Table 4.1). It shows the average particle sizes grow with the increase in the loading amount of copper as it becomes more difficult to disperse metal oxides well on the support when elevating their loading amount.\cite{74,75} The average particle sizes are all around 3 nm, confirming that the copper species are highly dispersed on the catalysts. The Cu particles sizes in our case are also smaller than Cu particles supported over other ordered mesoporous silica.\cite{34,41,96}

Figure 4.9 TEM images of (A) 5Cu-70, (B) 10Cu-70, (C) 20Cu-70, (D) 20Cu-70 after stability test.

Figure 4.9 shows the TEM images of representative Cu/KIT-6 catalysts. All the catalysts maintain the characteristics of the mesoporous structure, and the copper species
are clearly well-dispersed along the channel, substantiating the analysis in H$_2$-TPR and XRD sections. Furthermore, the uniform distribution of copper species along the channel suggests that the high specific surface area, interconnected mesoporous channels, and intra-wall pores of the support may facilitate the Cu dispersion compared with similar catalysts employing ordered mesoporous silicas as support.[34,41,44] The copper species distributed on KIT-6 are not in the form of typical spherical particles which makes us unable to calculate the average particle sizes from TEM images.

The specific surface area of Cu$^0$ was measured by N$_2$O titration method as listed in Table 4.1. The specific surface area of Cu$^0$ for all the samples with 10 wt% Cu is roughly the same and it increases significantly when elevating the loading amount of copper species.
XPS measurements and with X-ray induced Auger electron spectroscopy (XAES) were conducted to reveal chemical states of copper species and their relative content on calcined samples and reduced catalysts. For Cu 2p XPS spectra of calcined samples (Figure 4.10(A)), the peak at around 934.7 eV is assigned to Cu$^{2+}$ species, confirmed by the characteristic satellite peak at 943 eV.[37,48] The peak at around 932.8 eV is attributed to Cu$^{+}$ species. The Cu$^{+}$ might be generated by thermally removing oxygen atom from CuO lattice during the calcination stage as Cu$_2$O species are more thermodynamically stable
than CuO species at high temperature. Only reduced copper species are present on the surface after reduction, evidenced by the existence of two peaks at 932.8 eV and 953.0 eV (Figure 4.10(B)), assigned to Cu 2p3/2 and Cu 2p1/2 of reduced copper species, respectively.[37,48] Consistent with these assignments, the satellite peaks with Cu 2p binding energy of 943 eV assigned to Cu2+ species are absent. The XPS results confirm that surface Cu2+ species are reduced to Cu0 and/or Cu+ species.

Table 4.2 Deconvolution Results of XPS and Cu LMM XAES of Reduced Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>KE,a eV</th>
<th>AP,b eV</th>
<th>Cu 2p3/2 BE, eV</th>
<th>XCu+, c %</th>
<th>Cu0/Cu+, d</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Cu-70</td>
<td>913.7</td>
<td>917.6</td>
<td>1846.6</td>
<td>932.9</td>
<td>86</td>
</tr>
<tr>
<td>10Cu-70</td>
<td>913.8</td>
<td>917.6</td>
<td>1846.7</td>
<td>932.9</td>
<td>68</td>
</tr>
<tr>
<td>10Cu-80</td>
<td>914.0</td>
<td>917.7</td>
<td>1846.8</td>
<td>932.8</td>
<td>65</td>
</tr>
<tr>
<td>10Cu-90</td>
<td>913.7</td>
<td>917.5</td>
<td>1846.4</td>
<td>932.7</td>
<td>56</td>
</tr>
<tr>
<td>10Cu-100</td>
<td>913.7</td>
<td>917.7</td>
<td>1846.6</td>
<td>932.9</td>
<td>68</td>
</tr>
<tr>
<td>20Cu-70</td>
<td>913.7</td>
<td>917.6</td>
<td>1846.6</td>
<td>932.9</td>
<td>50</td>
</tr>
</tbody>
</table>

a. Kinetic energy, b. Auger parameter, c. Ratio of peak areas between Cu+ and (Cu+ + Cu0) by deconvolution of Cu LMM XAES spectra under the assumption that the Cu+ ions and Cu0 atoms occupy identical areas and have identical atomic sensitivity factors, d. Cu0/Cu+ is calculated by (1 - XCu+)/ XCu+.  

Cu LMM XAES was obtained to further distinguish the chemical states of copper species (Cu0 and Cu+) present on the reduced surface by the difference in their kinetic energies. The co-existence of Cu0 and Cu+ species on reduced samples is proved by two visible peaks with Auger kinetic energy of 913.5 eV and 917.5 eV (Fig.4.10(C)).[37,48] Peak deconvolution is employed to calculate the relative content of near-surface Cu0 and Cu+ species. The results (Table 4.2) show that the surface content of Cu+ species for
samples prepared at 70 °C (5 wt%, 10 wt% and 20 wt%) decreases with the increasing loading amount of Cu. This might be explained by the increased difficulty to disperse copper species at higher loadings. Interestingly, 10 wt%Cu/KIT-6 prepared at 90 °C shows lower Cu\(^+\) content than other 10 wt%Cu/KIT-6 samples prepared at 70 °C, 80 °C, 100 °C, which might be attributed to the effect of temperature on the growth of different copper species.

Table 4.3 Evidence of ruling out diffusion problems

<table>
<thead>
<tr>
<th></th>
<th>40-60 mesh,</th>
<th>40-60 mesh,</th>
<th>60-80 mesh,</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion/%</td>
<td>100 mg, WHSV=5.1 h(^{-1})</td>
<td>128mg, WHSV=5.1 h(^{-1})</td>
<td>100mg, WHSV=5.1 h(^{-1})</td>
</tr>
<tr>
<td>20Cu-70</td>
<td>28</td>
<td>29</td>
<td>27</td>
</tr>
</tbody>
</table>

4.4 Discussion

The optimization of Cu/SiO\(_2\) catalysts for the hydrogenation of DMO to EG has been intensively studied in terms of promoters for copper species and mophologies of supports. With respect to the support, it not only disperses active species, but also can react with a certain amount of copper species to generate the precusor of Cu\(^+\) species. In addition, effective supports should help inhibit the growth of copper particles, since the Hütting temperature of copper is low and sintering is actually the most significant problem for Cu/SiO\(_2\) catalysts. Thus, ordered mesoporous silicas with high specific surface area and well-defined pore structure have been utilized for the hydrogenation of DMO. Yin et al. prepared hexagonal mesoporous silica (HMS) support copper catalysts by an impregnation method.[96] They found that HMS supports with large pore diameters and specific surface areas facilitated the dispersion of the active copper species and exhibited large copper surface areas, which then improved the performance of DMO hydrogenation. Ma et al.
fabricated mesoporous MCM-41 supported copper catalysts for hydrogenation of DMO to EG, and attributed the excellent performance to the high dispersion of copper species and large specific surface areas of copper.[34] As high metal dispersion is one of the keys to enhance the hydrogenation activity of Cu/SiO₂ catalysts, ordered mesoporous silicas with high specific surface area, interconnected mesoporous channels, and intra-wall pores would be an excellent choice because they may facilitate the homogenous deposition of copper species during the preparation stage. Characterizations (XRD, TEM and H₂-TPR) confirm that the KIT-6 supported copper catalysts exhibit excellent dispersions of copper. TEM measurements shows that 20Cu-70 catalyst still maintains a good dispersion of copper species along the channels after 221 h stability test.

As the AE method is widely used to prepare Cu/SiO₂ catalysts, it is worthwhile to consider the effect of various preparation parameters (e.g. loading amount of Cu and pH) on both the absolute amount and relative content of Cu⁺ and Cu⁰ species on the surface and the resulting change in the performance and intrinsic activity of the catalysts. However, most of the related research focuses on catalysts with support from colloidal silica. Yin et. al. found that the initial precipitation temperature significantly influenced the textural properties of Cu/SiO₂ catalysts and surface content of copper species.[101] The observed enhancement in the catalytic performance was attributed to the high dispersion of copper species and suitable ratio of Cu⁰/Cu⁺. Zhao et. al. studied hydrogenation of DMO over ordered mesoporous silica (OMS) supported copper catalysts.[44] They found that appropriate pH value of the mixture of [Cu(NH₃)₄]²⁺ and OMS could preserve the mesoporous structure and proper loading amount of copper species could facilitate the dispersion of copper. The sample with high surface areas of Cu⁰ and Cu⁺, and the highest
ratio of $\text{Cu}^+/(\text{Cu}^0 + \text{Cu}^+)$. showed the best performance. In the present case, the loading amount of copper species exhibits a more significant effect on the performance of 10 wt% Cu/KIT-6 in terms of conversion of DMO and selectivity to EG than AE temperature in the investigated range. It is explained by that more active sites will be available when increasing the loading amount of copper.

It is often proposed that hydrogenation of DMO to EG happens via a synergism between balanced amount of $\text{Cu}^0$ and $\text{Cu}^+$ species.[37,40,54,64,102] Poels et al. studied the hydrogenation of methyl acetate and suggested that $\text{Cu}^0$ species were sites for the activation of hydrogen molecules and the $\text{Cu}^+$ species were active sites for adsorption of the methoxy and acyl species.[40] In this case, the two distinct peaks of the Cu LMM XAES spectra confirm that both $\text{Cu}^0$ and $\text{Cu}^+$ species exist on the surface of all the reduced Cu/KIT-6 catalysts. For Cu/SiO$_2$ catalysts with colloidal silica as support, copper phyllosilicate is observed over the calcined samples which account for the $\text{Cu}^+$ species over the reduced catalysts. However, our study and the results from other groups indicate that copper phyllosilicate is not present over the calcined Cu/SiO$_2$ samples with ordered mesoporous silcia as the support and the $\text{Cu}^+$ species over the reduced catalysts are proposed to originate from the reduction of Cu-O-Si unit.[34,41] The results suggest the types of silica influence the formation of copper phyllosilicate. As $\text{Cu}^+$ species are Lewis acid sites, Yin et al. proposed that the activation of C=O bond might be facilitated on $\text{Cu}^+$ species via the electron lone pair on oxygen atom in the hydrogenation of DMO to EG.[41] Although catalysts with balanced amount of $\text{Cu}^0$ and $\text{Cu}^+$ sites on the surface could exhibit excellent performance, it is still not clear what ratio of $\text{Cu}^+/(\text{Cu}^+ + \text{Cu}^0)$ is best for the catalysts and whether the surface should be $\text{Cu}^0$-rich or $\text{Cu}^+$-rich to achieve high intrinsic activity. For
Cu/SiO$_2$ catalysts with colloidal silica and some types of ordered mesoporous silica as support, the best performance is usually achieved on catalysts with the highest Cu$^+$/\(\text{Cu}^+ + \text{Cu}^0\)). However, Yin et. al. found that Cu/HMS catalysts with the highest ratio of Cu$^0$/Cu$^+$ were most active for DMO hydrogenation and exhibited the highest selectivity to EG.[41] Zhao et. al. suggested that surface area of Cu$^0$ species might be the key parameter for the DMO hydrogenation on Cu/OMS catalysts.[44] The diffusion limitations are ruled evidenced by Table 4.3. In our case, all the 10Cu/KIT-6 samples exhibit roughly the same Cu$^0$ surface area but the highest turnover frequency is achieved on10Cu-90 with lowest surface Cu$^+$ content. It is substantiated by 20Cu-70 sample with high surface Cu$^0$/Cu$^+$ ratio which also shows very high intrinsic activity. Thus, surface Cu$^0$/Cu$^+$ ratio is decisive to the intrinsic activity of hydrogenation of DMO on Cu/KIT-6 catalysts.

4.5 Conclusions

KIT-6 supported copper catalysts are prepared via ammonia evaporation (AE) method. The high specific surface area, inter-connected mesoporous channels, and intra-wall pores of the support facilitate the dispersion of copper species along the channel. The particles still maintain a high dispersion even after nine days during the stability test. The effect of AE temperature and loading amount of copper are studied to optimize the performance of DMO hydrogenation on Cu/KIT-6 catalysts. AE temperature does not influence the hydrogenation performance achieved over 10 wt%/KIT-6 significantly, but it has a noticeable effect on the intrinsic activity. The loading amount of copper species influences both the hydrogenation performance and intrinsic activity. The effect of AE temperature and loading amount of copper species on intrinsic activity is attributed to
induced change in the ratio of Cu\(^0\)/Cu\(^+\) on the surface and high Cu\(^0\)/Cu\(^+\) ratio on the surface favors the hydrogenation of dimethyl oxalate in this case.
CHAPTER 5
ATR-IR STUDY OF THE ADSORPTION OF DIMETHYL OXALATE ON SILICA AND SILICA SUPPORTED COPPER CATALYSTS

5.1 INTRODUCTION

C-O and C=O bond extensively exist in the structure of numerous organic molecules, such as esters, carboxylic acids, ethers, alcohols, aldehydes and ketones.[103-105] The selective cleavage of C-O and C=O bond in these molecules can produce a lot of chemicals with practical applications. A representative example is the hydrogenation of C-O and C=O bond of dimethyl oxalate (DMO) which is a key step in the process of producing ethylene glycol from syngas in industry.[2,37,68] Ethylene glycol is heavily consumed for manufacturing polyesters, coolants, anti-freezing agent and so on.[34,49]

Many catalytic processes are developed to facilitate the cleavage of C-O and C=O bond. Among the catalysts designed for these processes, copper based heterogenous catalysts are widely used as they can efficiently break C-O and C=O bond and avoid the rupture of other bonds, such as C-C bond.[2,37,68] It is postulated that the selective cleavage of C-O and C=O bond on the surface of heterogenous catalysts involves the adsorption and activation of C-O and C=O bond on the active sites.[68,103-105] Thus, the determination of adsorption mode of C-O and C=O bond and the induced adsorbed species on the catalytic surface is important to the elucidation of catalytic mechanisms and optimization of catalysts. In the case of hydrogenation of DMO, the direct evidence of the
adsorption of DMO molecules on the surface of copper catalyst had rarely been reported yet because of the low vapor pressure (0.3 kPa) of DMO at room temperature.

Instead, the information from the hydrogenolysis of esters with a similar structure but higher vapor pressure is often used as a model. Evans et al. studied the hydrogenolysis of aliphatic esters over Raney copper catalyst in the temperature range 210-280 °C. They found that hydrogenolysis of ethyl acetate involved the surface reaction of adsorbed ethyl acetate or a dissociated fragment with adsorbed hydrogen. Isotopic labeling studies showed that the alkoxy fragment R'O" reacted quickly to form R'OH, while the adsorbed acyl group RCO" was more persistent. Huang et al. studied the hydrogenation of methyl acetate (MA) to ethanol over Cu/SiO₂ catalyst and found that MA was predominantly adsorbed in a molecular form under higher MA partial pressure, differing from the dissociative adsorption at lower MA partial pressure. Poels and Brands et al. postulated that during hydrogenation of methyl acetate, Cu⁰ dissociatively adsorbed H₂, while Cu⁺ stabilized the methoxy and acyl species.

However, the problem can be alleviated by using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy in which DMO is first dissolved in a suitable solvent and delivered into the FTIR cell for measurement. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is one of the most powerful tools available currently for study of solid-liquid interfaces and has been developed in heterogenous catalysis since the late 1980s. ATR-FTIR provided a method of examining the solid sample without changing the characteristics of the surface. This most attractive feature allowed in-situ investigation of the sample at the interface while avoiding (or at least diminishing) the signal from bulk liquid. Thus, it can provide valuable information of
high signal-to-noise ratio about chemical forces between atoms and vibrational frequencies of molecules.

Consider a two-phase system containing an interface, where one side was an internal reflection element (IRE) with higher refractive index (n₁) and the other side a thin film contacting the crystal element with a lower refractive index (n₂). In ATR-FTIR, an infrared beam was passed through the IRE with an angle that was at or greater than the critical angle, θₖ, where

\[
\sin(\theta_c) = \frac{n_1}{n_2}
\]

With this arrangement, the beam would undergo total reflection at the interface. Every time that the IR beam reflected from the interface, an evanescent electric field (radiation) was produced at that spot and penetrated the sample, decaying exponentially with distance into rarer medium. The radiation was absorbed within the sample and an absorption spectrum of the sample was obtained.

The goal of ATR-FTIR was to measure a catalyst sample at the interface and avoid (or decrease) signal from the pure bulk liquid. To accomplish this, the sample should be thicker than at least three times the penetration depth (dₚ), which was defined as the depth at which the strength of electric field decayed to e⁻¹ (37%) of its value at the surface. The penetration depth (dₚ) was always on the order of one micrometer.

\[
d_p = \frac{\lambda}{\sqrt{2 \times \pi \times (\sin^2 \theta - n_{21}^2)}}
\]

\(\lambda\): the wavelength of the IR beam,

\(n_{21}\): the ratio of \(n_2\) over \(n_1\),

\(\theta\): incident angle (\(\theta > \theta_c\)).
Thus, penetration depth \((d_p)\) of a system could therefore be controlled by either changing the incidence angle \((\theta)\) or the composition of the crystal element. Typical crystals for ATR-IR were made of zinc selenide (ZnSe), germanium (Ge), zinc sulfide (ZnS), silicon (Si) and diamond (C), etc. with various refractive indices. In this proposed research, ZnSe was chosen because of its excellent property at elevated temperature.

ATR-IR was currently one of the few available techniques that allowed for \textit{in-situ} investigation of solid-liquid interfacial process and phenomena. Information about the nature of adsorbed species could be readily acquired with the details of the orientation of adsorbates, adsorption/desorption equilibrium and kinetics.[110,111] Figure 5.1 depicted the IR beam route within the IRE.

\[
E = E_0 e^{-(z/d_p)}
\]

![Diagram of IR beam route within IRE](image)

Figure. 5.1 Description of the beam route within IRE.

Here we apply ATR-FTIR spectroscopy to study the adsorption of DMO on the surface of SiO\(_2\) and CuO/SiO\(_2\). The method we reported can be adapted for investigation of adsorption of chemical bonds or chemicals on other catalysts.
5.2 RESULTS AND DISCUSSION

Figure 5.2 shows the stacked ATR-IR spectra acquired during alternating pure solvent/DMO solution flow on a bare ZnSe IRE to investigate whether DMO adsorb on the bare ZnSe IRE. Two noticeable peaks located at 1745 cm\(^{-1}\) and 1768 cm\(^{-1}\) emerge when introducing 30 mM DMO/CH\(_2\)Cl\(_2\) solution into the flowcell. The intensities of these peaks grow when increasing the concentration of DMO/CH\(_2\)Cl\(_2\) solution to 100 mM and then decrease when lowering the concentration of DMO/CH\(_2\)Cl\(_2\) solution to 60 mM. These two peaks are attributed to the interaction of DMO in the liquid phase on the surface of ZnSe IRE. The change in intensities of peaks at 1745 cm\(^{-1}\) and 1768 cm\(^{-1}\) reflect the concentration of DMO/CH\(_2\)Cl\(_2\) solution in the flowcell. As DMO has two C=O groups, it is likely that only one C=O group interacts with the surface of ZnSe via a unidentate coordination while the other C=O group remain in a free mode. Similar phenomenon has been reported by other researchers over the surface of MgO, ZnAl\(_2\)O\(_4\), \(\gamma\)-Al\(_2\)O\(_3\), SiO\(_2\) and \(\alpha\)-Al\(_2\)O\(_3\).[112] The peak at 1768 cm\(^{-1}\) is ascribed to the asymmetric vibration of free C=O group and the peak
at 1745 cm\(^{-1}\) is assigned to C=O bond interacted with the surface of ZnSe.\cite{113, 114} The assignment of peaks at 1267 cm\(^{-1}\) could not be done with confidence due to the interference of the Viton O-ring in the flowcell. The peaks at 1207 cm\(^{-1}\) and 1145 cm\(^{-1}\) was attributed to the symmetric vibration of C-O and vibration of C-O-C, respectively.\cite{112} However, all these peaks disappear after flushing ZnSe IRE with pure solvent, demonstrating these species are the physically adsorbed species on the ZnSe IRE and ZnSe does not have the capability to chemisorb DMO.

![Figure 5.3](image)

Figure 5.3 Stacked ATR-IR spectra acquired during alternating pure solvent/DMO solution flow on SiO\(_2\).

Pure silica support is deposited onto ZnSe IRE to investigate the adsorption of DMO on silica and the results are shown in Figure 5.3. Peaks located at 1745 cm\(^{-1}\), 1768 cm\(^{-1}\), 1027 cm\(^{-1}\) and 1155 cm\(^{-1}\) appear when flowing DMO/CH\(_2\)Cl\(_2\) with various concentrations into the flowcell. The assignment of these peaks is similar to the discussion of DMO adsorption over bare ZnSe IRE. All the peaks do not exist when flowing pure CH\(_2\)Cl\(_2\) into the flowcell except the peaks around 1267 cm\(^{-1}\) coming from the interference of Viton O-ring. The change in the intensities of peaks at 1745 cm\(^{-1}\) and 1768 cm\(^{-1}\) also
reflects the concentration of DMO/CH$_2$Cl$_2$ solution. The results indicate that pure silica support does not adsorb DMO at the investigation condition. Zaki et al. found that the C=O group of acetone molecules was weakly bonded to surface hydroxyl groups could be removed easily.[115] Similarly, Millar et al. found that the adsorption of formic acid on the silica support was very weak.[116] Thus, C=O bond does not have to tendency to chemisorb over silica in this case.

![Figure 5.4 Stacked ATR-IR spectra acquired during alternating pure solvent/DMO solution flow on a CuO/SiO$_2$.](image)

Figure 5.4 shows the stacked ATR-IR spectra acquired during alternating pure solvent/DMO solution flow on a Cu$^{2+}$/SiO$_2$ sample. As bare ZnSe IRE and SiO$_2$ support, any detected peaks originate from the adsorption of DMO over Cu$^{2+}$ species on the sample. Peaks at 1770 cm$^{-1}$, 1745 cm$^{-1}$, 1606 cm$^{-1}$, 1357 cm$^{-1}$, 1315 cm$^{-1}$ and 1045 cm$^{-1}$ are present when flowing DMO/CH$_2$Cl$_2$ solutions into the flowcell. Peaks at 1770 cm$^{-1}$ and 1745 cm$^{-1}$ are attributed to asymmetric vibration of free C=O group and C=O group physically interacted with the surface, respectively. The change in the concentration of DMO/CH$_2$Cl$_2$ solution also influences the intensities of peaks at 1745 cm$^{-1}$ and 1768 cm$^{-1}$. These two
peaks disappear when flowing pure CH₂Cl₂ into the flowcell which indicates that they are not the chemisorbed species on the surface. Only peaks at 1606 cm⁻¹, 1357 cm⁻¹, 1315 cm⁻¹ and 1045 cm⁻¹ remain on the surface after flushing the flowcell with pure CH₂Cl₂. Moreover, the intensities of these peaks grow when switching the concentration of DMO/CH₂Cl₂ solution from 30 mM to 100 mM. However, their intensities do not decrease when changing the concentration of DMO/CH₂Cl₂ solution from 100 mM to 80 mM, suggesting that the existence of stable, saturated adsorption of surface species. The peak at 1606 cm⁻¹ is assigned to the adsorption of two C=O groups of DMO over Cu²⁺ species via bidentate mode.[117] The peak at 1045 cm⁻¹ is the characteristic adsorption of alkoxy C-O (O-CH₃ in this case). Peaks at 1357 cm⁻¹ and 1315 cm⁻¹ are attributed to acyl C-O rather than sp³ C-H bend because these peaks are not very strong and no other peaks belonging to sp³ C-H (such as stretching) are observed at higher wavenumbers.[115,116]

Poels and Brands et al. postulated that during hydrogenation of methyl acetate, Cu⁰ dissociatively adsorbed H₂, while Cu⁺ stabilized the methoxy and acyl species.[40] From the kinetics of hydrogenolysis of diethyl oxalate over copper-based catalysts, Thomas et al. suggested that the reaction proceeded via dissociative adsorption of diethyl oxalate on the copper surface.[62] For the hydrogenation of DMO over copper catalysts, Chen et al. postulated that Cu⁺ might function as electrophilic or Lewis acid sites to polarize the C=O bond via the electron lone pair on oxygen.[37] As it is very difficult to obtain silica supported pure Cu⁺ and Cu⁰-containing samples in liquid phase, the adsorption of DMO over Cu²⁺/SiO₂ might provide useful information about how DMO molecules interact with Lewis acid sites. Figure 5.5 lists the structure of reactant and expected adsorbed intermediates during adsorption of DMO on Cu²⁺/SiO₂ sample. Based on the ATR-FTIR
results, the adsorption of DMO over Cu$^{2+}$/SiO$_2$ proceeds in a dissociative way with diacyl, acyl and methoxy as the surface adsorbed species.

\[
\begin{align*}
\text{DMO} & \quad \text{acyl} & \quad \text{diacyl} \\
\text{CH}_3\text{O} & \quad \text{M} & \quad \text{R} & \quad \text{COO} & \quad \text{M}_x \\
\text{methoxy} & \quad \text{carboxylates}
\end{align*}
\]

Figure 5.5 Reactant and expected adsorbed intermediates during adsorption of DMO on Cu$^{2+}$/SiO$_2$ sample.

5.3 CONCLUSION

The adsorption of DMO over unreduced Cu/SiO$_2$ sample is studied via ATR-FTIR in liquid phase at room temperature and atmospheric pressure. Dissolving DMO in CH$_2$Cl$_2$ overcomes challenge of introducing DMO with high melting point and low vapor pressure into the FTIR cell. Copper species exist in Cu$^{2+}$ state as the sample is not reduced. Two peaks located at 1770 cm$^{-1}$, 1745 cm$^{-1}$ are attributed to the two C=O bonds of DMO and their intensities are positively related to the concentration of DMO in the solution. Both ZnSe IRE and silica support show no adsorption of DMO on the surface at the investigated conditions. The adsorption of DMO over Cu$^{2+}$/SiO$_2$ produced stable surface species located at 1606 cm$^{-1}$ (adsorption of two C=O groups via bidentate mode), 1357 cm$^{-1}$, 1315 cm$^{-1}$ (acyl species) and 1045 cm$^{-1}$ (alkoxy C-O species). The method demonstrates that ATR-FTIR is a powerful tool for investigation of adsorption phenomenon of organic chemicals at the liquid-solid interface, especially for substances with high melting point which are difficult to be studied via other FTIR methods.
CHAPTER 6

CONCLUSIONS

In this work, the hydrogenation of dimethyl oxalate to ethylene glycol over Cu/SiO₂ catalysts are investigated in a flow reactor. Promoters are screened to enhance the performance of Cu/SiO₂ catalysts. Silica supported Cu-In bimetallic catalysts are successfully prepared via urea hydrolysis followed by incipient wetness impregnation. The incorporation of a low amount (less than 1 wt% in this study) of cheap, nontoxic indium species dramatically enhances the intrinsic activity of Cu/SiO₂ for the conversion of DMO to EG. Two types of indium species, In⁰ and In³⁺, are observed after reduction via XPS. An interaction among copper species and indium species are confirmed by H₂-TPR, N₂O titration and XPS. However, the surface content of Cu⁺ which is related to the activation of ester group is not significantly affected by indium species. Instead, In⁰ species might be alloyed with Cu⁰ species to form a new type of metallic sites with enhanced ability to dissociate H₂ which might account for the observed increase in the intrinsic activity of bimetallic catalysts.

Silica support is also very important to Cu/SiO₂ catalysts as the precursors of Cu⁺ species (copper phyllosilicate and/or Cu-O-Si unit) are products of reaction between Cu²⁺ species and support during catalyst preparation stage. Besides, the absolute amount and relative content of Cu⁺ and Cu⁰ are influenced by the distributions of precursors of Cu⁺ and Cu⁰ species, which might be influenced by preparation parameters, such as AE temperature and copper loading. KIT-6 supported copper catalysts are prepared via
ammonia evaporation (AE) method. The high specific surface area, inter-connected mesoporous channels, and intra-wall pores of the support facilitate the dispersion of copper species along the channel. The particles still maintain a high dispersion even after nine days during the stability test. The effect of AE temperature and loading amount of copper are studied to optimize the performance of DMO hydrogenation on Cu/KIT-6 catalysts. AE temperature does not influence the hydrogenation performance achieved over 10 wt% KIT-6 significantly, but it has a noticeable effect on the intrinsic activity. The loading amount of copper species influences both the hydrogenation performance and intrinsic activity. The effect of AE temperature and loading amount of copper species on intrinsic activity is attributed to induced change in the ratio of Cu0/Cu+ on the surface and high Cu0/Cu+ ratio on the surface favors the hydrogenation of dimethyl oxalate in this case.

The adsorption of DMO over unreduced Cu/SiO2 sample is studied via ATR-FTIR in liquid phase at room temperature and atmospheric pressure. Dissolving DMO in CH2Cl2 overcomes challenge of introducing DMO with high melting point and low vapor pressure into the FTIR cell. Copper species exist in Cu2+ state as the sample is not reduced. Two peaks located at 1770 cm\(^{-1}\), 1745 cm\(^{-1}\) are attributed to the two C=O bonds of DMO and their intensities are positively related to the concentration of DMO in the solution. Both ZnSe IRE and silica support show no adsorption of DMO on the surface at the investigated conditions. The adsorption of DMO over Cu2+/SiO2 produced stable surface species located at 1606 cm\(^{-1}\) (adsorption of two C=O groups via bidentate mode), 1357 cm\(^{-1}\), 1315 cm\(^{-1}\) (acyl species) and 1045 cm\(^{-1}\) (alkoxy C-O species). The method demonstrates that ATR-FTIR is a powerful tool for investigation of adsorption phenomenon of organic
chemicals at the liquid-solid interface, especially for substances with high melting point which are difficult to be studied via other FTIR methods.
REFERENCES


[32] C. Carlini, M. Di Girolamo, A. Macinai, M. Marchionna, M. Noviello,


[85] A. C. Parry-Jones, P. Weightman, P. T. Andrews, The M\textsubscript{4,5}N\textsubscript{4,5}N\textsubscript{4,5} Auger spectra of Ag, Cd, In and Sn, *J. Phys. C.*, 1979, 12, 1587-1600.


