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An Alternative Synthetic Approach for Efficient Catalytic Conversion of Syngas to Ethanol

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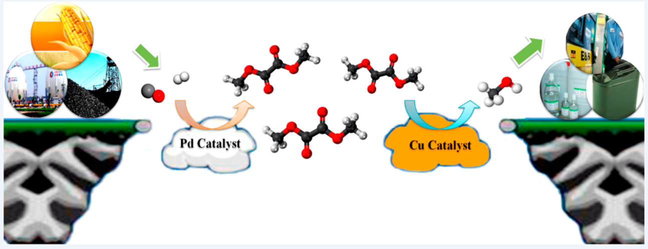

CONSPECTUS: Ethanol is an attractive end product and a versatile feedstock because a widespread market exists for its commercial use as a fuel additive or a potential substitute for gasoline. Currently, ethanol is produced primarily by fermentation of biomass-derived sugars, particularly those containing six carbons, but coproducts 5-carbon sugars and lignin remain unusable. Another major process for commercial production of ethanol is hydration of ethylene over solid acidic catalysts, yet not sustainable considering the depletion of fossil fuels. Catalytic conversion of synthetic gas ($CO + H_2$) could produce ethanol in large quantities. However, the direct catalytic conversion of synthetic gas to ethanol remains challenging, and no commercial process exists as of today although the research has been ongoing for the past 90 years, since such the process suffers from low yield and poor selectivity due to slow kinetics of the initial C−C bond formation and fast chain growth of the C_2 intermediates.

This Account describes recent developments in an alternative approach for the synthesis of ethanol via synthetic gas. This process is an integrated technology consisting of the coupling of CO with methanol to form dimethyl oxalate and the subsequent hydrogenation to yield ethanol. The byproduct of the second step (methanol) can be separated and used in circulation as the feedstock for the coupling step. The coupling reaction of carbon monoxide for producing dimethyl oxalate takes place under moderate reaction conditions with high selectivity (~95%), which ideally leads to a self-closing, nonwaste, catalytic cycling process. This Account also summarizes the progress on the development of copper-based catalysts for the hydrogenation reaction with remarkable efficiencies and stability. The unique lamellar structure and the cooperative effect between surface Cu^0 and Cu^+ species are responsible for the activity of the catalyst with high yield of ethanol (~91%). The understanding of nature of valence states of Cu could also guide the rational design of Cu-based catalysts for other similar reactions, particularly for hydrogenation catalytic systems. In addition, by regulating the reaction condition and the surface structure of the catalysts, the products in the hydrogenation steps, such as ethanol, methyl glycolate, and ethylene glycol, could be tuned efficiently. This synthetic approach enables a more sustainable ethanol, methyl glycolate, and ethylene glycol synthesis in industry and greatly reduces the dependence on petroleum resources and the emission of the greenhouse gas.

1. INTRODUCTION

Synthetic gas (syngas) is indispensable in chemical, oil, and, energy industries. They are important building blocks and serve as feedstocks for the production of chemicals such as methanol, gasoline, and dimethyl ether. In the energy field, recent developments in integrated gasification combined cycle (IGCC) and fuel cell technologies have generated a need to convert the conventional fuels such as coal (particularly in China), natural gas, or biomass to either pure hydrogen or syngas for efficient power generation.[1] In addition, the dwindling supply of crude oil and rising demand for clean transportation fuels led to intensive research and development (R&D) efforts for alternative sources of fuels through various conversion technologies, including gas-to-liquid (GTL), coal-to-liquid (CTL), and biomass-to-liquid (BTL), which involve syngas as a key component.

Ethanol—frequently used as a additive to power fuel cells and diesel—has received much attention primarily because of its environmental and long-term economical advantages over conventional fossil fuels.[2] In 2012, worldwide ethanol fuel production reached 28.3 billion gallons (*Renewable Fuels Association, F.O. Lichts*). The primary approach (Scheme 1) for ethanol production is based on the fermentation of agricultural feedstocks, such as sugar cane, potato, manioc, and corn.[3] The technology for conversion of cellulosic materials is promising for the use of all kinds of wood and other biomass feed-stocks for ethanol production,[4] but still requires considerable R&D efforts for commercial scale. From an agronomic perspective, the arable land for crops now provides, with some shortfalls, food for 6 billion people and will need to feed 9 billion by 2050, which is an enormous challenge to increase food production during the next 40 years.[3] Recently, a direct synthesis of ethanol from syngas over supported metal nanoclusters attracts regenerated worldwide interest.[1,5] However, this heterogeneous catalytic process suffers from low yield

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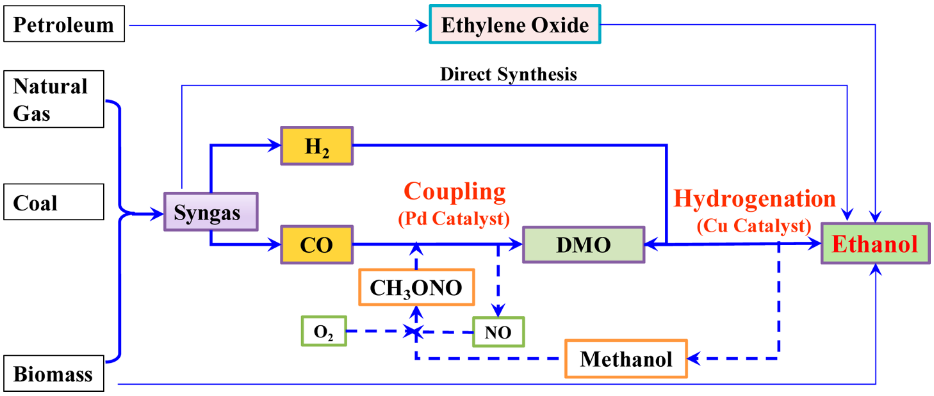
Scheme 1. Production of Ethanol from Biomass and Fossil-Based Resources



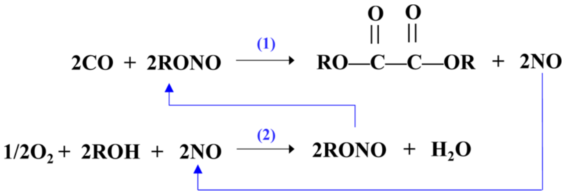
and poor selectivity due to slow kinetics of the initial C−C bond formation and fast chain growth of the C_2 intermediate.[5,6] Alternatively, an indirect approach for the synthesis of ethanol via syngas has been developed,[7] which is an integrated technology consisting of the coupling of CO with methanol to form dimethyl oxalate (DMO) and subsequent hydrogenation to yield ethanol (Scheme 1). In comparison with the one-step direct synthetic process, this route needs one mole more hydrogen and produces an extra mole of water, but presents reasonable advantages of high efficiency and accessibility in industry. Since the first step was successfully scaled up into commercial production in 2010, we can envisage the production of ethanol via this process with promising prospects. Moreover, the products of the hydrogenation reaction can be tuned efficiently to produce ethanol, ethylene glycol (EG) and methyl glycolate (MG), which thereby will greatly reduce the dependence on petroleum resources.

This Account describes our recent efforts regarding the development of this indirect conversion of syngas to ethanol with a focus on catalyst design and exploration of reaction mechanism. We will discuss a number of relevant subreactions in the scheme. The relationship between catalytic performance and nature of active sites of the catalysts will also be presented.

2. THE CO COUPLING REACTION

CO coupling with alcohols in the present of an oxidizer (O_2) for dialkyl oxalate synthesis was originally discovered in 1974.[8] Subsequently, this oxidative coupling reaction has been widespread for the synthesis of dialkyl oxalate. The CO coupling process using alkyl nitrites (RONO) as efficient reoxidizing agents involves two reactions shown in Scheme 2.[9] Particularly, nitrogen oxide obtained from the coupling reaction participates in a regeneration reaction with oxygen and alcohols to form dialkyl nitrite, which is then recycled to the coupling reaction.[9] This process is also practical since both subreactions take place under moderate reaction conditions (e.g., atmospheric pressure, 120 °C).[10,11]

Scheme 2. CO Oxidative Coupling Reaction for the Synthesis of Dialkyl Oxalate



$$2CO + 2RONO \xrightarrow{(1)} RO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OR + 2NO$$

$$1/2O_2 + 2ROH + 2NO \xrightarrow{(2)} 2RONO + H_2O$$

2.1. The Coupling Reaction Mechanisms

Understanding of the reaction mechanism at a molecular level could help optimize the formula of catalysts and thus increase reactivity. As for the gas-phase CO coupling reaction over Pd-based catalysts, in situ diffuse reflectance infrared spectroscopy (DRIRS) combined with X-ray photoelectron spectroscopy measurements were generally used to probe the surface state of the catalyst, the redox process of the active component, Pd^0, and surface intermediates.[12,13] Specifically, in the presence of methyl nitrite, the behavior of carbomethoxypalladium complex has been identified,[12] indicating the absorbable CO molecule inserts in Pd(II) alkoxyl compound to form the carbomethoxypalladium complex (DCPC). In general, the linear-adsorption of palladium atom is weaker compared to the bridge-adsorption state, which benefits the carbon−carbon bond formation. Consequently, the intermolecular coupling-elimination reaction of the intermediate DCPC leads to the formation of DMO and the reduction of Pd(II) to Pd(0).

Therefore, the CO coupling reaction over palladium active sites in the presence of methyl nitrite is a redox process (proposed mechanism shown in Scheme 3).[12,14] The methyl nitrite plays a role in oxidizing Pd^0 to Pd^{2+} to form an intermediate, $CH_3O-Pd(II)-OCH_3$, and providing negative alkoxyl ions. Then, the linearly adsorbed CO inserts palladium ion-alkoxyl bond to form DCPC. Finally, the intramolecular

Scheme 3. Proposed Catalytic Mechanism of CO Oxidative Coupling to DMO over Pd Catalyst

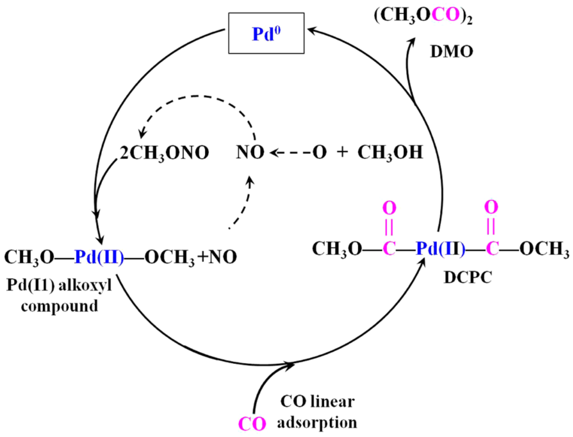


Table 1. Representative Catalytic Systems for CO Coupling Reactions

catalyst	reaction conditions	rate of DMO formation	ref
1%Pd(O)/AC	120 °C, 0.3 MPa, GHSV = 4000 h^{-1}, CO/CH_3ONO = 2, N_2 base	161.8 g/h L-cat	15
1%Pd−Cl/AC		11.8 g/h L-cat	
1.2%Cu−Cl/AC		0 g/h L-cat	
1%Pd−1.2%Cu−Cl/AC		29.5 g/h L-cat	
1%Pd−1.2%Cu−Br/AC		39.0 g/h L-cat	
1%Pd−1.2%Cu−AcO/AC		222.0 g/h L-cat	
1%Pd−1.2%Cu−NO_3/AC		257.4 g/h L-cat	
1%Pd/Al_2O_3	90 °C, CO/CH_3ONO = 2	conversion of CH_3ONO = 57.1%	10
1%Pd−0.8%CeO_2/α-Al_2O_3	140 °C, CO/CH_3ONO = 16/13	conversion of CH_3ONO = 80%	
1%Pd−0.5%Fe/Al_2O_3	90 °C, contact time = 0.91 s, CO/CH_3ONO = 2	79.8g/h L-cat	12
Pd NPH/α-Al_2O_3[a]	130 °C, 0.1 MPa, GHSV = 3000 h^{-1}, CO/CH_3ONO = 2	642 g/h L-cat	14
Pd NC/α-Al_2O_3[b]		79 g/h L-cat	

[a] NPHs: Monodisperse Pd nanopolyhedrons. [b] NCs: nanocubes.

coupling elimination reaction of DCPC leads to the formation of DMO and the reduction of Pd(II) to Pd(0).

2.2. The Catalytic Reaction Systems

The coupling reaction can be carried out in both liquid- and gas-phase systems over base- and noble-metal catalysts, such as Pd, Cu, Ce, and Fe.[9−11] A list of representative catalytic systems for CO coupling reactions to DMO is shown in Table 1.

Pd-based catalysts have been intensively examined for liquid-phase systems. Fenton et al. first reported the synthesis of dialkyl oxalate by oxidative carbonylation in the presence of $PdCl_2$−$CuCl_2$ catalyst in a liquid phase.[8] A supported chlorine-free Pd catalyst was also used in this system, which is relatively stable in the presence of water and could be repeatedly used.[15] However, these systems suffer from facile deactivation of the catalysts due to leaching or poisoning of active metal sites and from separation of the catalysts.[9,15]

Accordingly, the synthesis of dialkyl oxalate by CO coupling reaction in gas−solid phase systems has been developed, particularly over palladium-based catalysts. Numerous efforts have been exerted to understand the nature of active sites,[12,14] catalyst structure,[13] support effect,[10] operating conditions and process,[16] kinetics,[12] and reaction mechanism[12,13] of the supported Pd catalysts. From Table 1, we note that Pd- or bimetallic Pd-based (e.g., Pd−Fe, Pd−Ce) nanoclusters supported on α-Al_2O_3 exhibited excellent catalytic performance. Specifically, an appropriate surface area and larger pores of the α-Al_2O_3 were required to supply sufficient reactant molecules.[12] To understand the correlation between the surface structure and catalytic performance of Pd nanocatalysts, Guo et al. synthesized monodisperse Pd nanocrystals with exposed (111) and (100) facets through preferentially oriented facet growth (Figure 1).[14] They found that the (111) facets of Pd nanocrystals were active planes for CO oxidative coupling to DMO, and the shape and size of Pd nanocatalysts (2−3 nm) were vital to the catalytic performance.

Another important issue for the CO oxidative coupling is the enhancement of the efficiency of the Pd catalysts. Recently, Pd-based monolithic catalysts (with the loading of Pd as low as 1.0 wt %) prepared by a dip-coating method exhibited a remarkable yield of 650g/(L·h) for DMO under mild reaction conditions (20%CO−15%RONO−65%N_2, GHSV = 2500 h^{-1}, 0.1 MPa and 393 K).[11] These monolithic catalysts offer several advantages over the traditional pellet catalysts, such as the high efficiency of mass transportation, low pressure drop, less diffusion limitations. Notably, Peng et al. further developed a Pd/α-Al_2O_3 nanocatalyst with ultralow Pd loading (0.13%) by a Cu^{2+}-assisted in situ reduction method at room temperature.[17] This catalyst exhibited high activity and stability for CO oxidative coupling to DMO, ascribing to the small size and high dispersion of Pd nanoparticles (NPs) facilitated by Cu^{2+} ions.

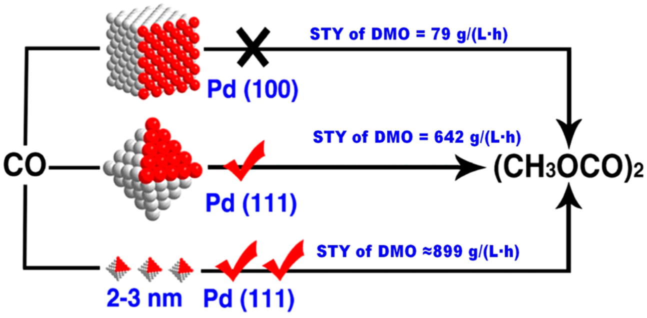


Figure 1. Pd nanocrystals with exposed (111) and (100) facets for CO oxidative coupling to DMO. Reaction conditions: 200 mg of catalyst, 3000 h^{-1} of GHSV, 0.1 MPa, 130 °C. Reproduced with permission from ref 14. Copyright 2012 American Chemical Society.

3. THE DMO HYDROGENATION REACTION

The DMO hydrogenation reaction is one of the key steps in the synthesis of ethanol from syngas.[7,18−20] Since a number of side reactions could occur in the hydrogenation reaction, efforts focused on this process were made primarily on developing highly efficient catalysts for selective hydrogenation to ethanol. Several transition metals or oxides, such as Cu-, Co-, Ni-, Ag- and Au-based catalysts, were reported as promising catalysts. For instance, Ni/SiO_2 and Co/SiO_2 were found to be active for the hydrogenation reaction, but suffered from low ethanol selectivity due to alcohol decomposition to form CO and subsequent methanation of CO to methane. Comparatively, copper-based catalysts possessed a higher yield of ethanol for hydrogenation reactions, since the copper sites account for the selective hydrogenation of carbon−oxygen bonds and are relatively inactive for the hydrogenolysis of carbon−carbon bonds.[7]

3.1. Reaction Mechanism

3.1.1. Active Sites of Copper-Based Catalysts for C═O Hydrogenation. Copper-based catalysts are the primary catalytic systems for hydrogenation of DMO to ethanol. With regard to the nature of active species of copper-based catalysts, there is still debate regarding the precise role of the Cu^0 and

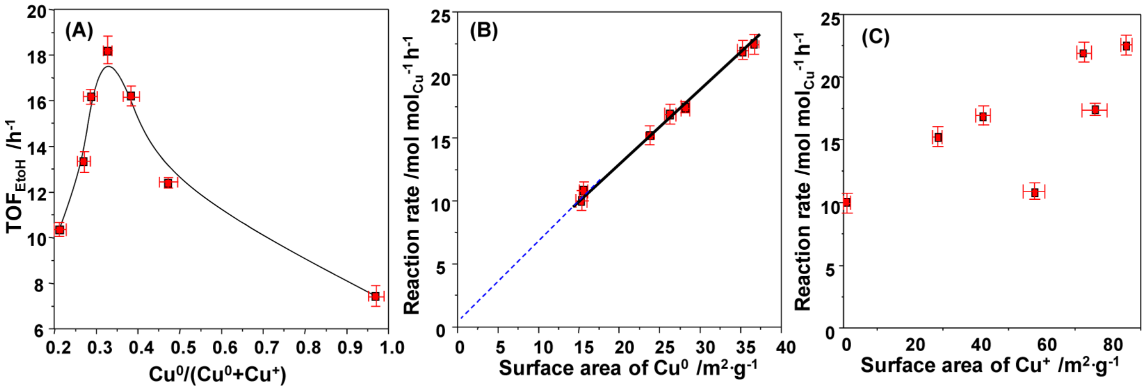


Figure 2. (A) Correlation of the TOF of ethanol with $Cu^0/(Cu^0 + Cu^+)$, reaction rate as a function of (B) Cu^0 and (C) Cu^+. The reaction rate was calculated as moles of EtOH and $C_3{\sim}C_4OH$ produced in the initial 1h per mole of surface metal. Reproduced with permission from ref 7. Copyright 2012 American Chemical Society.

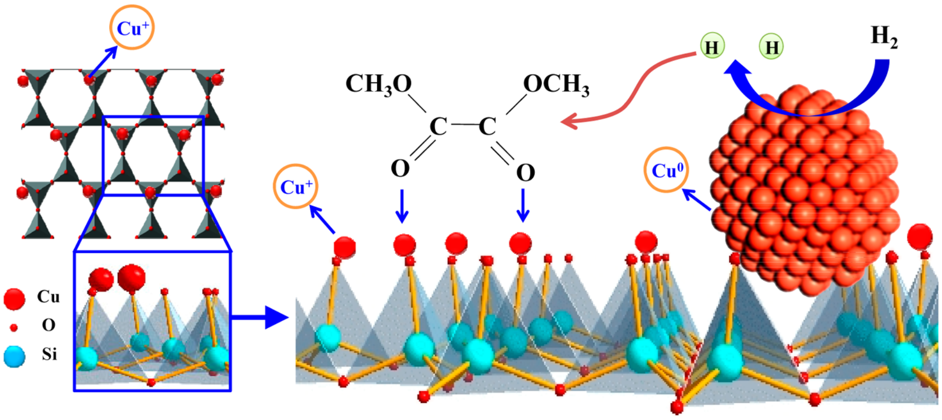


Figure 3. Schematic model of the reaction mechanisms over Cu/SiO_2 catalyst for hydrogenation of DMO.

Cu^+ species for the DMO hydrogenation reaction. Metallic copper was believed to be an active phase for hydrogen dissociation because the activity was frequently found to be proportional to copper-surface area.[21] However, earlier work has failed to establish a linear correlation between activity and cuprous surface area relationship, suggesting that a synergy between copper and the oxide components also influence activity.

To gain insight into the effect of the Cu active species on the hydrogenation of DMO, the turnover frequency (TOF) of ethanol and reaction rate were examined as a function of the surface valence states (Figure 2).[7,22] The highest TOF of ethanol is located at an appropriate $Cu^0/(Cu^0 + Cu^+)$ (~0.33) (Cu^0 surface area determined by N_2O titration and Cu^+ surface area determined from irreversible CO adsorption isotherms). The strong correlation between the surface Cu^0 site density and the formation rates, and the intercept of the trend line imply that the catalytic activity primarily depend on the number of Cu^0 sites. Therefore, the optimal TOF of ethanol on the copper catalyst lies in the high surface Cu^0 site density and the cooperative effect of Cu^0 and Cu^+.

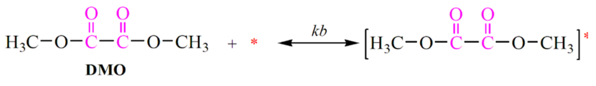
Accordingly, a surface model of the Cu/SiO_2 catalyst for catalytic hydrogenation of DMO is shown in Figure 3. Specifically, Cu^0 sites could not only activate H_2, but also adsorb the intermediates (e.g., EG and methanol) through the hydroxyl group to facilitate the dehydration reaction. The Cu^+ species acts as the stabilizer of the methoxy and acyl species, which are intermediates in DMO hydrogenation. They could also function as electrophilic or Lewis acidic sites to polarize the C═O bond via the electron lone pair in oxygen, thus improving the reactivity of the ester group in DMO.

3.1.2. Reaction Pathway.

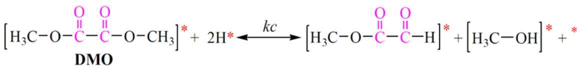
The C═O and C–O bond cleavage of DMO in the hydrogenation reaction over Cu-base catalyst were based on the consecutive reaction pathway (where the red asterisk (*) indicates the active site).[23] First, the hydrogen molecules are dissociatively adsorbed on the Cu active site.

$$\mathrm{H{-}H} + 2^* \xrightleftharpoons{ka} 2\mathrm{H}^* \qquad (1)$$

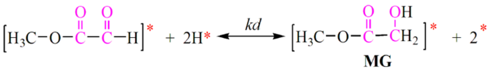
The dissociated hydrogen atoms (2H*) facilitate the adsorption of DMO molecules. An ester radical (C–O bond) of adsorbed DMO is reduced by hydrogenolysis, and the unsaturated link (C═O) is saturated. DMO is then converted to MG.



$$\underset{\textbf{DMO}}{\mathrm{H_3C{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_3}} + {}^* \xrightleftharpoons{kb} \left[\mathrm{H_3C{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_3}\right]^* \qquad (2)$$

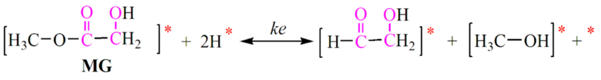


$$\underset{\textbf{DMO}}{\left[\mathrm{H_3C{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_3}\right]^*} + 2\mathrm{H}^* \xrightleftharpoons{kc} \left[\mathrm{H_3C{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H}\right]^* + \left[\mathrm{H_3C{-}OH}\right]^* + {}^* \qquad (3)$$



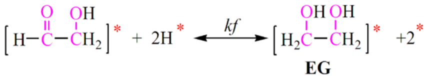
$$\left[\mathrm{H_3C{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H}\right]^* + 2\mathrm{H}^* \xrightleftharpoons{kd} \underset{\textbf{MG}}{\left[\mathrm{H_3C{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{OH}{CH_2}}\right]^*} + 2^* \qquad (4)$$

Another ester radical of MG is further hydrogenolyzed to form intermediate EG. Finally, ethanol is generated via deep hydrogenation of the C−O bond of EG molecule.

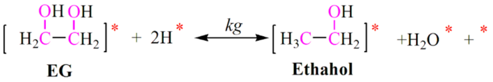


$$\left[H_3C-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH_2}\right]^* + 2H^* \xleftrightarrow{ke} \left[H-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH_2}\right]^* + \left[H_3C-OH\right]^* + {}^* \quad (5)$$

$$\underset{MG}{}$$



$$\left[H-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH_2}\right]^* + 2H^* \xleftrightarrow{kf} \underset{EG}{\left[H_2\overset{\overset{OH}{|}}{C}-\overset{\overset{OH}{|}}{CH_2}\right]^*} + 2^* \quad (6)$$



$$\underset{EG}{\left[H_2\overset{\overset{OH}{|}}{C}-\overset{\overset{OH}{|}}{CH_2}\right]^*} + 2H^* \xleftrightarrow{kg} \underset{Ethahol}{\left[H_3C-\overset{\overset{OH}{|}}{CH_2}\right]^*} + H_2O^* + {}^* \quad (7)$$

Along with main reactions, a couple of side reactions also occur in the presence of acidic/basic sites species over the catalysts. The reaction network of DMO hydrogenation is summarized in Scheme 4. The strong acidic sites over the catalysts induce the intermolecular dehydration of ethylene glycol to ethanol, whereas strong basic sites catalyze the Guerbet reaction leading to the formation of 1,2-butanediol (1, 2-BDO) and 1,2-propanediol (1,2-PDO). These two reactions lead to the primary byproducts of the 1, 2-BDO and 1,2-PDO with a yield of ∼10−15%. In addition, MG can also be deeply hydrogenated to methyl acetate, and can react with methanol to methyl methoxyacetate.

3.2. Performance of Copper-Based Catalysts

A number of novel nanoreactors, surface modified, as well as conventional copper-based catalysts have been developed to catalyze the DMO hydrogenation to ethanol. Representative catalytic systems are shown in Figure 4.

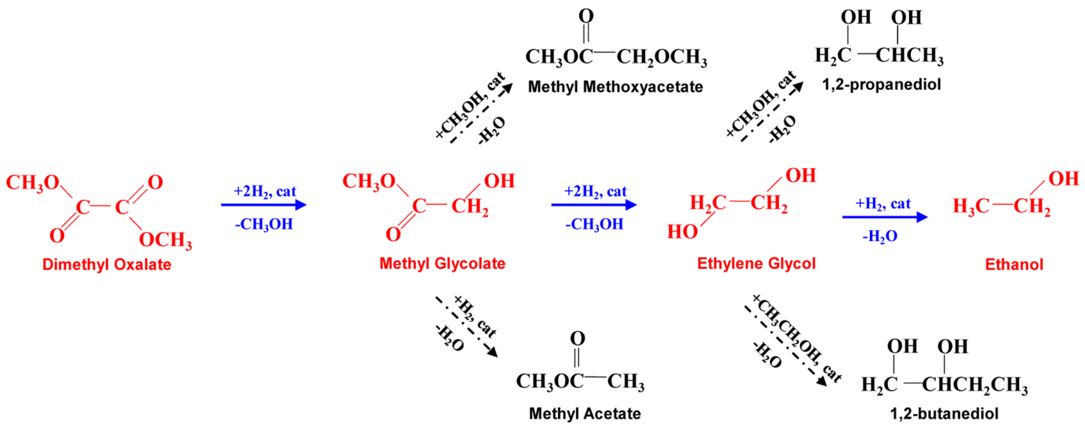
Supported copper-based catalysts are extensively investigated for hydrogenation of DMO. Indeed, conversion of DMO is largely dependent on the copper active sites,[7] copper dispersion and the surface chemistry,[19] whereas the valence states of copper and properties of the carriers (e.g., acidic/basic and textural properties) affect the selectivity of products.[21] Al_2O_3 was chosen as a representative acidic oxide support, and ZrO_2 (or TiO_2) and SiO_2 were selected as weakly amphoteric and neutral oxides to support Cu NPs.[7] From the catalytic performance of the catalysts (Figure 4), we note that Cu/TiO_2, Cu/Al_2O_3, and Cu/ZrO_2 catalysts afforded the lower yields of ethanol than the Cu/SiO_2 catalyst. It could be ascribed to high Cu dispersion and large surface areas of the Cu/SiO_2 catalyst. In addition, strong acid sites induce the intermolecular dehydration of ethanol and/or ethylene glycol to ether, whereas strong basic sites catalyze the Guerbet reaction into the formation of 1,2-butanediol (1,2-BDO),[18,24] both of which diminish the selectivity of ethanol. Therefore, copper catalysts for this reaction are generally supported on neutral or weak acid/alkaline carriers, such as SiO_2, hexagonal mesoporous silica (HMS), SBA.[25−27]

The methodology for preparation of Cu/SiO_2 catalysts is also significant since it could affect the dispersion of copper species and metal−support interactions,[24,28,29] which includes deposition−precipitation (DP), incipient wet impregnation (IWI), ion-exchange (IE) and ammonia evaporation (AE). Among them, we have shown recently the ammonia evaporation hydrothermal (AEH) method leads to significantly high dispersion and strong metal−support interactions due to the formation of copper phyllosilicate [$Cu_2SiO_5(OH)_2$] phases as well as controllable lamellar or tubular structures (the formation mechanism shown in Scheme 5). These unique phyllosilicate structures could highly disperse the Cu NPs in the structure to hamper the sintering of the Cu NPs, and thus enhance the activity and stability.

Another important issue regarding the catalytic activity of the DMO hydrogenation is the mass-transfer resistances, particularly for the internal mass-transfer of the large-grained industrial catalyst.[30] Calculations based on the Wheeler-Weisz group[24] indicated that the internal mass transfer could be the main reason for their lower activity of the large-grained catalysts. A structured catalytic reactor consisting of Cu supported on silica-coated monoliths was introduced to reduce the influence of internal diffusion (Figure 5).[24] This novel structure guarantees high dispersion of copper species within the mesopores of silica matrix in the form of copper phyllosilicate, which renders the catalyst with high activity and stability for the DMO hydrogenation reaction. The shorter diffusion paths in the monolith wash-coat could facilitate the diffusion of reactants and formed ethanol more readily on and out of the catalytic sites. The calculated and experimental results indicated the mass-transfer resistances could be negligible over the monolithic catalysts.

The DMO hydrogenation reaction is highly exothermic, and the calculated corresponding adiabatic temperature (DT) for the synthesis of ethanol at 553 K is about 50−80 K dependent on the hourly space velocity.[19,24] The favorable temperature for hydrogenation of DMO to ethanol is at the range of 503−553

Scheme 4. Reaction Network of DMO Hydrogenation



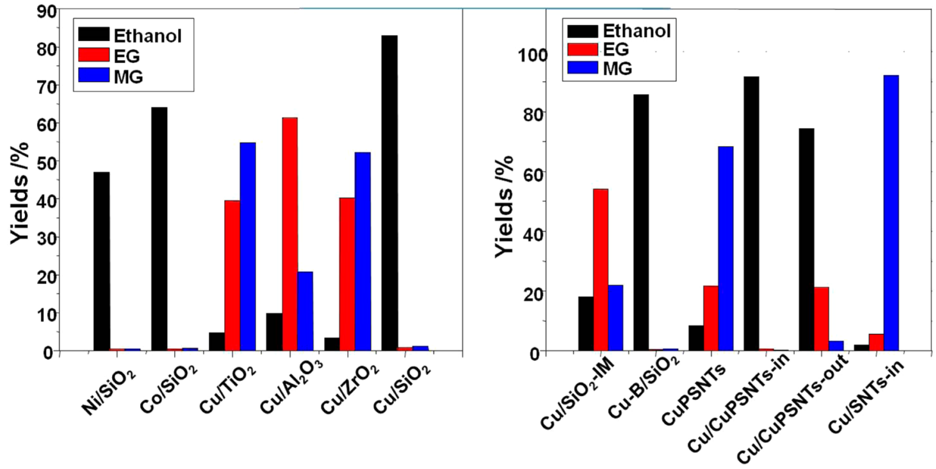
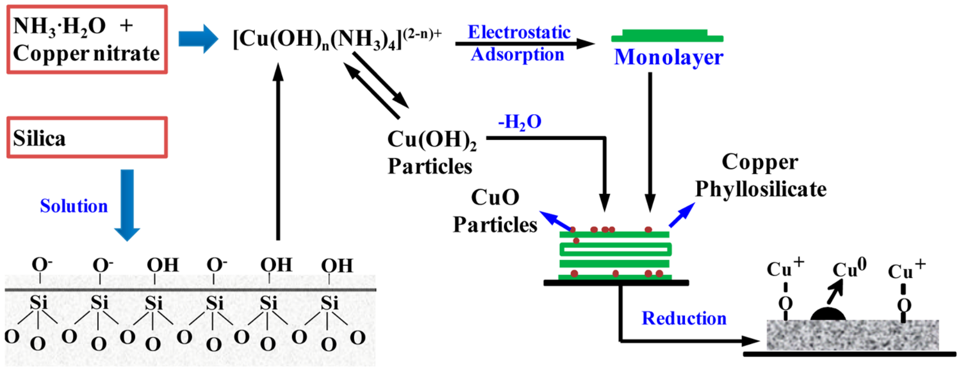


Figure 4. Catalytic performances of copper-, nickel-, and cobalt-based catalysts. Cu/SiO_2–IM: Cu/SiO_2 catalyst prepared by the impregnation method. Cu–B/SiO_2: Cu/SiO_2 catalyst modified with B_2O_3. CuPSNTs: copper phyllosilicate nanotube catalyst. Cu/CuPSNTs-in and Cu/CuPSNTs-out: copper filled in and out CuPSNTs, respectively. Cu/SNTs: copper supported on SiO_2 nanotubes. Reaction conditions: LHSV of 2.0 h^{-1}, 553 K, H_2/DMO of 200 (mol/mol).

Scheme 5. Schematic Procedure for the Synthesis of Cu/SiO_2 Catalysts by the Ammonia Evaporation Hydrothermal Method



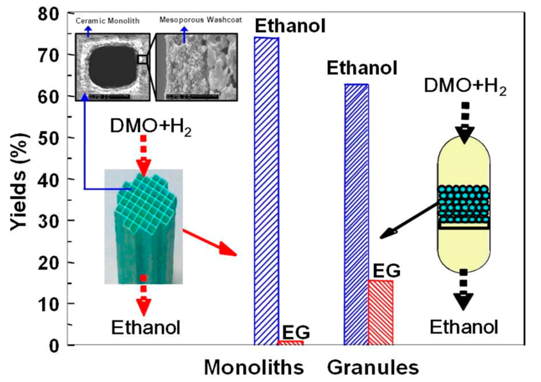


Figure 5. Yields of ethanol over monolithic and granular Cu/SiO_2 catalysts.

K, which is higher than the Hüttig temperature of metallic Cu (407 K). Notably, these lead to the tendency of copper NPs to grow into larger crystallites through migration and coalescence of particles. Therefore, poor lifespan and thermal stability are the major drawbacks for silica supported copper catalysts because they are the impediments to stable performance.

Novel nanostructured catalysts (e.g., core–shell and core–sheath) with the encapsulation of individual metallic NPs in morphologically well-defined inorganic shells or tubes are the efficient approach to enhance the thermal and chemical stabilities in catalysis.[31,32] We have developed a simple and efficient approach for the fabrication of a core–sheath nanoreactor with a copper-phyllosilicate nanotube (CuPSNT) sheath, selectively immobilizing copper NPs inside the cavity, and stable and balanced Cu active species.[22] This nanocatalyst exhibited a superior reactivity for DMO hydrogenolysis with high efficiency (an ethanol yield of 91%) and steady performance (>300 h at 553 K) (Figure 6). The originality of the enhanced hydrogenation activity and thermal stability of the nanoreactor was described as follows. First, the high surface Cu^0 site density and the cooperative effect of Cu^0 and Cu^+ account for the optimal TOF of ethanol. Second, the spatial restriction on copper NPs provided by the nanosized channels of CuPSNTs can hamper the aggregation of Cu NPs (5–8 nm) after catalytic test for 300 h and thermal treatment, which led to a steady performance. Additionally, the confinement inside the sheath nanochannels (inner diameter of 6–15 nm and a length of 100–500 nm) could prolong the contact time of reactants and reaction intermediates with the active sites, which favors the deep hydrogenation reaction and leads to a higher selectivity of ethanol.

Surface modification of the catalysts is another practical solution to enhance catalytic stability since it could result in a strong metal–support interaction and high metal dispersion for the high-temperature hydrogenation reaction. The studies of the B_2O_3-modified copper catalysts exhibited enhanced DMO

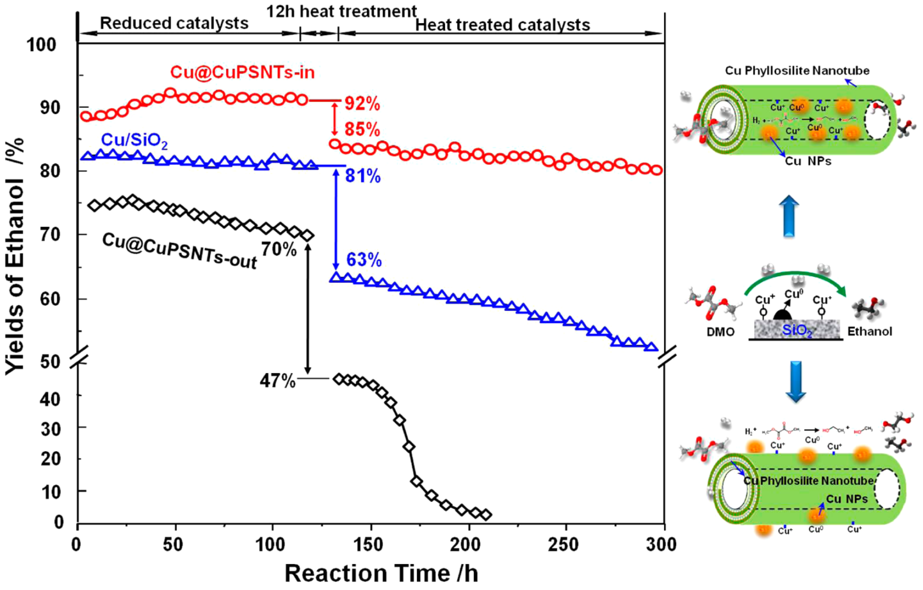


Figure 6. Catalytic performance and stabilities of the Cu@CuPSNT-in, and Cu@CuPSNT-out, and the supported Cu/SiO_2 catalysts. Reaction conditions: LHSV = 2.0 h^{-1}, H_2/DMO = 200, T = 553 K. Reproduced with permission from ref 22. Copyright 2013, Nature Publishing Group.

conversion, ethanol selectivity, and stability.[19] Because boron has higher electronegativity than silicon, the strong interaction between boric oxide and surface copper species retards the transmigration of copper NPs and stabilizes the metal NPs. In addition, boron is easily gathered on copper clusters, which could diminish the grains of heterogeneous nuclei and modifiers and suppress the growth of copper particles during the high-temperature reaction.

4. SELECTIVE SYNTHESIS OF ETHANOL, EG, AND MG

We also need to mention that EG and MG are the byproducts in the hydrogenation of DMO. Indeed, EG is an important chemical used in a variety of industrial applications, such as antifreeze, polyester, H_2 energy, and fuel cells.[18,33] At present, the technology of ethylene oxidation/hydration accounts for the major share of the EG market. As ethylene oxide is commercially produced from ethylene via petroleum cracking, and the global market demand for EG always surpasses its production capacity, increasing efforts have been devoted to exploring alternative processes. Similarly, MG is also an important fine chemical intermediate with wide applications. Another interesting feature of this paradigm is that principally the selectivity of ethanol, MG, and EG can be tuned efficiently by regulating the catalytic systems (e.g., Cu, Au, and Ag) and the reaction conditions (e.g., temperature and residence time).

4.1. The Origin of Tunable Selectivity

The DMO hydrogenation reaction pathway shows that MG could be obtained in the first hydrogenation step. However, the thermodynamic constant of the first hydrogenation step is 2 orders of magnitude smaller than that of the subsequent hydrogenation step;[34] thus, it is difficult to suppress the further hydrogenation of MG to other products. According to the element intrinsic dynamic model, the hydrogenation reaction follows the Langmuir–Hinshelwood mechanisms; hydrogen takes part in the surface dissociative adsorption site on the catalyst, and both the main and side reaction rate are controlled by the surface reaction.[23] Therefore, control of the dissociative hydrogen adsorbed on the active sites may moderate the second hydrogenation step and tune the MG from the first step.

Silver surfaces, compared to Cu, generally lack affinity toward H_2 dissociation due to the filled d-band of silver, and could benefit to the selective hydrogenation of DMO to the corresponding alcohols.[35] Therefore, a Ag-based catalyst were investigated in the hydrogenation of DMO for tunable synthesis of MG and EG, with yields of 92% and 96% on the 15Ag/SiO_2 catalyst, respectively (Figure 7).[34] Zheng et al. also developed the Au promoted Ag-based catalysts supported on SBA-15 for the DMO hydrogenation at a low temperature (418 K), with the highest selectivity of MG (99.5%).[36] They proposed a synergistic effect between Au and Ag. The Au sites activated DMO molecules and the Ag sites contributed to H_2 molecule activation by chemisorptions, whereas and the Au–Ag alloy promoted charge transfer between Au and Ag.

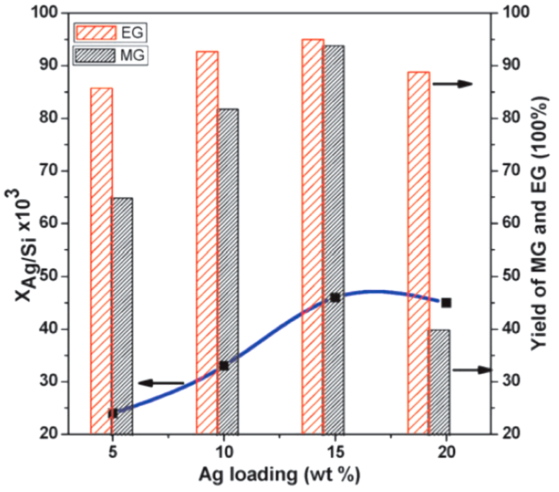
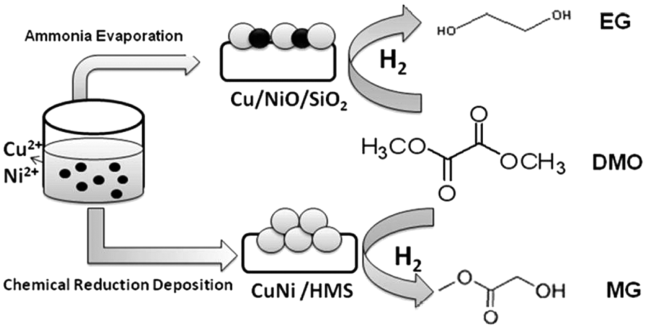


Figure 7. Yield of EG/MG and surface Ag dispersion (XAg/Si) calculated by XPS results vs the Ag loading. Reproduced from ref 34. Copyright 2010 Royal Society of Chemistry.

The bimetallic catalysts in presence of 3d transitional metal on the surface play a crucial role in selective C=O hydrogenation reaction due to different binding energies and bonding morphologies with the adsorbed substrate. Dai et al. reported Ni–Cu bimetallic catalysts could offer decent activity, with an 86% yield of MG and a 98% yield of EG over CuNi/HMS and Cu/NiO/HMS, respectively (Scheme 6).[37] The high activities were ascribed to the enhanced dispersion of copper species and the synergetic effects of the metallic copper and nickel species, while the selectivity might result from the chemical states of the nickel species.

Scheme 6. Selective Synthesis of MG and EG via DMO Hydrogenation over Ni–Cu Bimetallic Catalyst[a]



[a]Reproduced with permission from ref 37. Copyright 2013 Elsevier.

4.2. The Effect of the Reaction Temperature

The selective synthesis of EG from the DMO hydrogenation is primarily affected by the reaction temperature. From thermodynamic perspective, the enthalpy change of the DMO hydrogenation reaction for the formation of ethanol (ΔH = 145.93 kJ/mol) is greater than that of EG (ΔH = 58.73 kJ/mol),[24] which leads to the synthesis of ethanol thermodynamically favorable at high temperatures. Therefore, the formation of EG is favorable at relatively low temperatures (e.g., 473K, yield of ca. 95%) (in Figure 8), whereas elevated temperatures (e.g., 553 K, yield of 83%) induce the intramolecular dehydration of EG to form ethanol and intermolecular dehydrogenation of ethanol and methanol with EG to form C_3–C_4 diols (e.g., 1,2-BDO and 1,2-PDO).[7] The thermodynamic analysis also indicated the dependence of the equilibrium yield of ethylene glycol on the reaction pressure above 1.0 MPa and the H_2/DMO ratio above 30/1 are favorable for the formation of EG.[23]

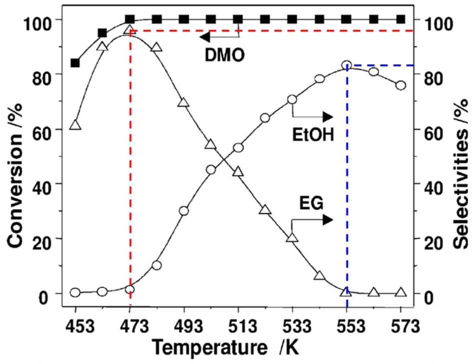


Figure 8. Selective synthesis of EG and ethanol over the $20Cu/SiO_2$ catalyst in hydrogenation of DMO. Reaction conditions: LHSV = 2.0 h^{-1}, H_2/DMO = 200 (mol/mol), 2.5 MPa. Reproduced with permission from ref 7. Copyright 2012 American Chemical Society.

4.3. The Role of the Properties of Supports

The acidic or basic properties of the supports could induce dehydration reactions, which plays vital roles in selective synthesis of EG and ethanol. Zhu et al. reported the Cu-based catalysts supported on Al_2O_3 and ZrO_2 with surface coordinatively unsaturated $Al^{3+}$and $Zr^{4+}O^{2-}$cationic Lewis acid sites for the DMO hydrogenation reaction.[38] The results showed a better stability and selectivity for EG synthesis over Cu/ZrO_2 catalyst, while an excellent ethanol selectivity over Cu/Al_2O_3catalyst. On the base of the NH_3-TPD, the intermolecular dehydration reactions on the acidic centers were confirmed to be the main active sites for selective hydrogenolysis to EG and ethanol.

5. CONCLUSIONS AND PROSPECTS

The coupling of CO with methanol to form oxalates and subsequent hydrogenation to produce ethanol opens a new avenue for the sustainable production of bulk chemicals or fuels from syngas. This cascade reaction requires multifunctional catalysts over which coupling of CO, cleavage of C=O and C–O bonds and hydrogenation of DMO and intermediate MG/EG should cooperate well. Palladium-based catalysts prove to be highly active, selective, and probably unique for the synthesis of diethyl oxalate via gas-phase CO coupling reaction. Particularly the monolithic Pd catalysts possess higher yield of oxalate and save almost 80% of noble-metal Pd. The copper catalysts with an excellent catalytic performance for the hydrogenation require intrinsic high surface of stable Cu^0 and Cu^+, optimal $Cu^0/(Cu^0+Cu^+)$, neutral or weak acid/alkaline surface chemistry to avoid the side reactions, and unique morphologies for confinement of both the active phase and the reactants to aim products. Another interesting feature is that the products—ethanol, MG and EG—can be tuned efficiently by regulating the reaction condition, and the chemistry of the catalysts in this reaction system. Therefore, this process has the potential to enable a more sustainable MG and EG synthesis in industry. The major disadvantage of this synthetic route compared to direct synthesis of ethanol via syngas is the relatively complicated reaction scheme.

Although great progresses have been made in this indirect process conversion of syngas to ethanol, there are still a number of grand challenges that should be faced and addressed. Potential exists for breakthroughs in the development of more efficient technology and optimal catalytic systems that allow the rational synthesis of ethanol form syngas. Future research should be encouraged in the following aspects: (i) integration of the coupling and hydrogenation steps with high energy and reaction efficiency for possible industrialization; (ii) the exact role of Cu^0 or Cu^+ for hydrogenation reaction that has not been fully understood and the structures of active sites need to be elucidated, which needs development of powerful in situ characterization techniques such as X-ray adsorption and environmental electron miscrscopy adaptable to explore the mechanistic understanding at a molecular level; (iii) design of cheaper but more efficient CO coupling catalysts, and green, long-life DMO hydrogenation catalysts based on aggressive advancement in materials science and theoretical calculations; and (iv) developments of advanced technology for separation and purification of ethanol/EG/MG from side products and to intensify the process for efficient use of energy.

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Notes

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