Nonoxidative Dehydrogenation of Methanol to Methyl Formate through Highly Stable and Reusable CuMgO-Based Catalysts

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ABSTRACT: Nonoxidative dehydrogenation of methanol to methyl formate over a CuMgO-based catalyst was investigated. Although the active site is metallic copper (Cu0), the best reaction conditions were obtained by tuning the ratio of Cu/Mg and doping the catalyst with 1 wt % of Pd to achieve a very specific activity for methyl formate synthesis. On the basis of the CO2 temperature-programmed desorption study, the basic strength of the catalyst plays a role in the efficient conversion of methanol to methyl formate via dehydrogenation. These CuMgO-based catalysts show excellent thermal stability during the reaction and the regeneration processes. Approx. 80% methanol conversion with constant selectivity to methyl formate was achieved even after 4 rounds of usage for a total reaction time exceeding 200 h, indicative of their potential for practical applications.

INTRODUCTION

Methyl formate (MF) is an essential reactive intermediate in C1 chemistry.1−3 It is widely used for the synthesis of numerous value-added products in the chemical industry, including ethylene glycol, N,N-dimethyl formamide, methyl glycolate, acetic acid, methyl propionate, and formamide. MF is also a highly valuable chemical that can directly be used as an antiseptic, solvent, and gasoline additive.4 Several modes of synthesis of MF have been reported in the literature. They involve the selective oxidation of methanol,5 dehydrogenation of methanol,6 hydrogenation of CO2 to MF,7 dimerization of formaldehyde,8 carbonylation of methanol,9 and esterification of methanol with formic acid,8 with the first two synthetic routes being the most popular for the commercial production. In comparison to the selective oxidation reaction, the nonoxidative dehydrogenation reaction not only avoids the addition of an oxidant, meaning that it is not only a safer reaction to lower the production costs, but it also produces hydrogen as a value-added byproduct that can be used as a fuel or reducing agent in various industries.

The direct dehydrogenation reaction of methanol to produce MF is described in details in Scheme 1. Although several homogeneous systems have been developed for dehydrogenative homocoupling of primary alcohols to the corresponding esters,10−16 the formyl group of MF from methanol tends to undergo further dehydrogenation reactions.17,18 On the other hand, for heterogeneous systems, the products obtained through dehydrogenation of methanol can be diverse, and many factors can influence the catalytic performance.19−21 For example, an acidic support leads to the increases in dehydration processes (e.g. dimethyl ether),22 and higher temperatures favor gaseous products such as CO or CO2.23 It has been demonstrated that copper was the active species for MF syntheses24−29 and previous studies30 also showed that metallic copper was the major active species for the methanol dehydrogenation reaction. Besides copper, there are other materials that can act as catalysts for this reaction, including palladium, nickel, and platinum.31 However, despite the high number of studies on the nonoxidative dehydrogenation of methanol to form MF, the formation rates of MF obtained so far are not sufficiently high for practical use, and a catalyst with a practically long lifetime still needs to be discovered.

Herein, we report that the formation rate of the MF can be enhanced by the addition of a basic material (MgO) and the catalytic performance can be improved by tuning the ratio of Cu/MgO. Compared to the traditional impregnated copper-based catalysts,4 the CuMgO-based catalysts show a significant improvement of methanol conversion (11.7−16.7%) and MF selectivity (62.5−88.1%). Furthermore, the incorporation of Pd to CuMgO was found to prevent the deactivation and

Scheme 1. Dehydrogenation of Methanol

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increase the stability of the catalyst for methanol dehydrogenation.

### RESULTS AND DISCUSSION

Characterization of Catalysts. Texture properties (Table 1) of the catalysts show that they all have similar Brunauer–Emmett–Teller (BET) surface areas (50.1–62.4 m²/g) and pore volumes (0.20–0.60 cm³/g), except the highest copper-containing catalyst (Cu₇MgO₃) which has a larger pore size. The N₂ adsorption–desorption isotherm plot shows that the adsorption amount increased slowly with increasing pressure during the initial stage, and after the pressure reached the saturated vapor pressure, the adsorption amount increased rapidly. These pores were all provided by the crystal stacking (type III, nonporous material). These results allow one to conclude that Cu₇MgO₃ produces the largest particles, resulting in a larger pore size. These large particles might be a result of copper aggregation, triggered by the higher copper loading. After the addition of palladium, the BET surface area and pore volume both decreased, because of the presence of the palladium heteroatom, as shown in 1Pd/Cu₃MgO₇ and 1Pd/Cu₅MgO₅.

To better understand the effects of Pd and the Cu/MgO ratio, several techniques were employed to characterize the properties of the catalysts. In Figure 1a, the wide-angle X-ray diffraction (XRD) patterns show that the intensity of CuO peaks (35.6°, 38.8°, JCPDS card no. 01-073-6023) increased with increasing copper loading, whereas the peaks of MgO (36.8°, 42.7°, 61.9°, JCPDS card no. 1-071-1176) decreased. The spent catalysts all showed Cu (43.2°, 50.3°, JCPDS cards no. 00-004-0836) and MgO peaks but without those of CuO or Cu₂O (Figure 1b). These results indicate that the metallic state of copper species (Cu⁰) can be maintained after the dehydrogenation reaction and the catalysts were not oxidized during the catalytic test. The particle sizes of metallic copper increased with increasing copper loading because of the aggregation of copper species. Moreover, the addition of Pd likely inhibits the growth of copper crystal, as the Pd-containing catalyst shows smaller particle sizes than those of catalysts without Pd.

### Table 1. Textural Properties of Catalysts

| catalyst   | S_{BET} (m²/g) | V_p (cm³/g) | D_p (nm) | particle size of Cu (nm)* | H₂ up take (mmol/g-cat) | CO₂ up take (mmol/g-cat) |
|------------|----------------|-------------|----------|---------------------------|-------------------------|--------------------------|
| Cu₅MgO₅   | 50.1           | 132.1       | 0.54     |                           | 0.12                    | 0.81                     |
| Cu₆MgO₆   | 32.7           | 128.1       | 0.20     |                           | 0.33                    | 0.74                     |
| Cu₇MgO₇   | 49.6           | 129.4       | 0.75     | 9.46                      | 0.54                    | 0.59                     |
| 1Pd/Cu₃MgO₇ | 47.5           | 122.9       | 0.23     | 8.84                      | 0.61                    | 0.55                     |
| Cu₅MgO₅   | 67.4           | 152.6       | 0.68     | 11.88                     | 0.72                    | 0.21                     |
| 1Pd/Cu₅MgO₅ | 20.4           | 151.7       | 0.38     | 11.02                     | 0.78                    | 0.11                     |
| Cu₇MgO₃   | 62.4           | 330.0       | 0.60     | 23.63                     | 1.12                    | 0.07                     |

*Calculated by Scherrer equation.

![Figure 1. XRD patterns for: (a) fresh catalysts and (b) spent catalysts after the catalytic test for 20 h.](image1)

![Figure 2. TEM images for: (a) Cu₃MgO₇-fresh; (b) Cu₃MgO₇-spent; (c) 1Pd/Cu₃MgO₇-fresh; (d) 1Pd/Cu₃MgO₇-spent; (e) Cu₅MgO₅-fresh; (f) Cu₅MgO₅-spent; (g) 1Pd/Cu₅MgO₅-fresh; (h) 1Pd/Cu₅MgO₅-spent; (i) Cu₇MgO₃-fresh; and (j) Cu₇MgO₃-spent.](image2)
Transmission electron microscopy (TEM) images (Figure 2) show the significant differences in morphology between the high copper-containing and low copper-containing catalysts. The low copper-containing catalysts (Figure 2a,c,e,g) show a homogeneous mixture of copper nanoclusters and MgO with only small copper particles distributed on the MgO flakes. For the high copper-containing catalysts (Figure 2i), the small copper nanoparticles become larger copper cluster, consistent with the results from the XRD analysis. Moreover, the study of spent catalysts revealed that the catalysts with palladium (Figure 2d,g) showed less amorphous carbon coking layer compared to those without palladium doping (Figure 2b,f) after the catalytic test. These observations suggest that the addition of palladium may inhibit the coke formation.

Although XRD patterns and TEM images provide useful information about the catalysts’ surfaces, the X-ray photoelectron spectroscopy (XPS) measurement can offer more details about the high copper-containing catalysts, particularly Cu7MgO3. The Cu-LMM spectrum (Figure 3) shows a shoulder at approx. 572.2 eV, indicating that the Cu7MgO3 catalyst has a more complexed structure with larger copper clusters compared to others, further confirming the results in the XRD and TEM studies.

Additionally, the H2-temperature-programmed reduction (TPR) measurement (Figure 4) shows that the low copper-containing catalysts (Cu1MgO9 and Cu2MgO8) possess no reactivity in the reduction reaction. The amount of H2 consumption increased with the increasing copper loading, but the reduction temperature almost stayed the same (250 °C); these findings suggest that our preparation processes using the coprecipitation method can successfully enhance the amount of surface copper, and all the copper-based catalysts have similar reduction sites with different amounts of H2 consumption (Table 1). The H2-TPR measurement also reveals the effects of the addition of palladium. The reduction peak slightly shifted to higher temperatures to approx. 350 °C, presumably because of the interaction of the small palladium particles with hydrogen, which enhances the reduction ability of the copper oxide through the dissociation of H2 on palladium followed by the spillover on the copper oxide phase.

In the CO2 temperature-programmed desorption (TPD) study, the strength of basic sites was found to increase with the magnesium content (Figure 5). The high copper-containing (low magnesium) catalysts only showed a weak basic site (100–150 °C), and the Cu7MgO3-CP catalyst showed almost no basic sites. Both Cu5MgO5-CP and Cu2MgO8-CP, however, afforded medium-strong basic sites. The addition of palladium heteroatoms can reduce the amount of medium-strong basic sites as well as the total amount of basic sites (Table 1), and these findings are directly correlated to the activity of the catalysts in the methanol dehydrogenation reaction.

Activity Test. In the catalyst screening, the dramatic influence of the Cu/MgO ratio on the catalytic performance was observed. Table 2 and Figure 6a show that a specific ratio of Cu/MgO is necessary for a methanol dehydrogenation to occur. Although a higher copper ratio can improve the conversion, the excess amount of copper harms the catalytic performance, presumably because of the fact that the high copper concentration may lead to bigger copper clusters, whereas lower copper loading favors the formation of smaller copper nanoparticles. Higher copper-containing catalysts, such as Cu3MgO5 and Cu3MgO7 also displayed a higher CO selectivity compared to those of the low copper-containing catalysts. According to the recent work by Yang et al., the higher amount of CO2 byproduct could be a result from the C−H and C−O bond cleavage mechanism, which is mostly related to the presence of larger copper clusters in high copper-containing catalysts (entries 5–7). The conversion decreased as the reaction time increased, and this deactivation is likely related to the coke formation. The coke species may hinder the
active sites, leading to the decrease of conversion. Nevertheless, the selectivity for MF formation remains high. As the copper loading increased, the lifetime became longer but only up to the Cu/MgO ratio of 1. The catalyst lifetime then decreased for those of Cu/MgO ratios higher than 1 (Figure 6b). Again, these observations suggest that the larger copper clusters were formed in the high copper loading rather than copper nanoparticles, thus offering less active sites. In addition to the copper effect, an insufficient MgO content provides almost no basic sites (CO$_2$-TPD, Figure 5), and resulted in the decrease of the catalytic performance. Excess MgO, which offers more medium-strong basic sites, also harms the catalytic performance because the stronger basic sites can facilitate other side reactions such as polymerisations and formation of polycyclic aromatics. These side reactions may form more coke and deactivate the catalyst faster.

The addition of palladium can improve the performance and stability of the catalyst because palladium inhibits the medium-strong basic sites (Figure 5) and extends the lifetime of the catalyst. The excessed medium-strong basic sites in high MgO-containing catalysts promote more side reactions to form the coke to deactivate the catalyst. Moreover, the addition of palladium also decreased the reduction ability of the catalyst to lower the selectivity toward gaseous products (such as CO and CO$_2$) and to enhance MF selectivity (Table 2, entries 3−6). As shown in Figure 7, the low copper-containing catalysts (Cu$_3$MgO$_7$ and 1Pd/Cu$_3$MgO$_7$) showed significant differences in the catalytic activity (methanol conversion = 6.1 and 15.0%), and Cu$_5$MgO$_5$ and 1Pd/Cu$_5$MgO$_5$ catalysts provided a similar methanol conversion (16.7 and 14.9%) and MF selectivity (88.1 and 93.3%). The long-term test showed that 1Pd/Cu$_5$MgO$_5$ can maintain 80% of the original activity over the course of reaction time of 100 h (Figure 8, 79.2% of methanol conversion and 80.0% MF formation rate), whereas the activity of the Cu$_5$MgO$_5$ catalyst was dropped by approx.

Table 2. Catalyst Screen

| entry | catalyst     | rate (g$_\text{MeOH}$/g$_\text{cat.}$ h) | conversion (%) | selectivity (%) | MF | CO | CO$_2$ | carbon balance (%) | coking wt (%) |
|-------|--------------|-----------------------------------------|----------------|----------------|----|----|-------|-------------------|--------------|
| 1     | Cu$_1$MgO$_9$| 22.0                                     | 100            |                | 93.8| 1.2| 2.4   | 97.4              | 26.5         |
| 2     | Cu$_2$MgO$_8$| 1.3                                      | 1.6            | 91.3           | 2.4| 2.5| 96.2  | 30.6              |
| 3     | Cu$_3$MgO$_7$| 4.9                                      | 6.1            | 93.1           | 1.6| 1.6| 96.3  | 19.1              |
| 4     | 1Pd/Cu$_3$MgO$_7$ | 12.4                                  | 15.0           | 88.1           | 5.5| 2.4| 96.0  | 15.9              |
| 5     | Cu$_4$MgO$_6$| 13.1                                     | 16.7           | 93.3           | 4.1| <0.5| 97.4  | 11.0              |
| 6     | 1Pd/Cu$_4$MgO$_6$ | 12.4                                  | 14.9           | 92.3           | 5.2| <0.5| 97.5  | 25.6              |
| 7     | Cu$_5$MgO$_5$| 3.6                                      | 4.3            | 93.3           | 4.1| <0.5| 97.4  | 11.0              |

*Reaction condition: $T$ = 250 °C, carrier gas flow (N$_2$) = 50 mL/min, feedstock (liquid methanol) = 0.1 mL/min, catalyst = 100 mg, WHSV$_\text{MeOH}$ = 47.4 h$^{-1}$, 30 h.

Figure 6. Effect of the Cu/MgO ratio on: (a) catalytic reaction and (b) deterioration rate.

Figure 7. Palladium (Pd) effect on the catalytic reaction: (a) methanol conversion (b) MF selectivity (c) formation rate of MF. Reaction conditions: $T$ = 250 °C, carrier gas flow (N$_2$) = 50 mL/min, feedstock (liquid methanol) = 0.1 mL/min, catalyst = 100 mg, and WHSV$_\text{MeOH}$ = 47.4 h$^{-1}$, 30 h.
40% (56.9% of methanol conversion and 57.5% of MF formation rate).

**Reuse Test.** Results of the reuse test on the Cu5MgO5 catalyst indicated that after 4-round usage, the catalyst still maintained 80.1% of activity in the MF formation rate (Figure 9). The activity test after the second round led to the similar results (MF formation rate = 9.9, 9.6, and 9.7 gMF/gcat·h); however, the performance was slightly lower than those obtained for the first round, suggesting that a few active sites might be poisoned after the first round and cannot be regenerated effectively. The weight loss of the spent catalyst (Figure 10) suggests that some of the coke cannot be removed under 600 °C and this unremovable hard coke might cause the deactivation of the regenerated catalysts.

**CONCLUSIONS**

Our study reveals that an optimized value of the Cu/MgO ratio is essential to facilitate the methanol dehydrogenation reaction. The excessive copper loading forms larger copper clusters rather than copper nanoparticles, which lower the MF selectivity. On the other hand, the excess MgO leads to the increase of coke formation because of the higher medium-strong basic sites. These two effects both harm the catalytic performance (i.e. methanol conversion and lifetime of the catalyst). The Cu/MgO ratio of 1 provides the best catalytic performance. In addition, Pd also plays a critical role to prolong the lifetime of the catalyst by decreasing the amount of medium-strong basic sites. The addition of Pd not only modifies the catalyst’s basic property with a smaller amount of medium-strong basic sites but also enhance the reduction ability of copper oxide to improve the catalytic activity and stability. The reuse test demonstrated that the Cu5MgO5 catalyst can be efficiently regenerated and reused for at least 4 rounds. After the regeneration process (through calcination), at least 80% methanol conversion and constant MF selectivity can be achieved, suggesting a great potential for practical applications in a low-cost process for the MF production.

**EXPERIMENTAL SECTION**

**Catalyst Preparation.** CuMgO catalysts were prepared by the coprecipitation method. Certain amounts (Cu/MgO weight ratio = 1:9, 2:8, 3:7, 1:1, 7:3) of Cu(NO3)2·3H2O (Sigma-Aldrich, ≥99%) and Mg(NO3)2·6H2O (Sigma-Aldrich, ≥99%) were dissolved in 100 mL of deionized (DI) water, and a 0.6 M K2CO3 (Sigma-Aldrich, ≥99%) solution was then added dropwise under vigorous stirring at 70 °C for 3 h. The blue solid coprecipitates were filtered and washed with DI water and then dried overnight at 90 °C and finally calcined at 400 °C for 3 h (these catalysts were labeled as Cu_xMgO_y, where the x/y is the weight ratio of Cu/MgO).

Pd-containing catalysts were prepared by the incipient wetness impregnation method. CuMgO catalysts were impregnated with a given amount (1 wt % of Pd to CuMgO) of Pd(NO3)2·2H2O (Aldrich, ~40% Pd basis) precursor in an aqueous solution at 60 °C, and stirred for 3 h. After impregnation, the samples were dried at 90 °C overnight and then calcined at 300 °C for 4 h.

**Characterization.** CO2-TPD and H2-TPR were performed using the apparatus Altamira AMI 200 Ip (Altamira Instruments, Inc.) and detected by a Hiden HPR 20 mass spectrometer (Hiden Analytical, Inc.), 30 mg of each catalyst was used for measurement. CO2-TPD samples were pretreated 120 min at 250 °C under argon (50 mL/min) and then treated in a flux of 1% of CO2 in helium (25 mL/min) for 60 min at room temperature, followed by helium flush for 1 h at 50 °C.
The temperature of the calorimeter furnace was then programmed with a heating rate of 10 °C/min and at a helium flow rate of 50 mL/min. Samples of H2-TPR were pretreated 120 min at 250 °C under argon (50 mL/min), and then cooled to room temperature for 60 min. Once the catalysts were stabilized, they underwent a reduction process in the calorimeter furnace with a heating rate of 10 °C/min and at 5% H2 in Ar at 30 mL/min.

Samples were imaged using Titan CT (FEI Company) operating at 300 kV and equipped with a 4K × 4K charge-coupled device camera (Gatan Inc., Pleasanton, CA). They were placed on a 300 mesh copper grid precoated with a holey amorphous carbon film.

XRD spectra of the catalysts were obtained using D8 ADVANCE XRD (Bruker) at 40 kV and 40 mA, with Cu Kα (1.54184 Å) as the X-ray source. Diffraction patterns were recorded between 10° and 70° (2θ), by incremental steps of 0.02° at 10°/min.

Textural properties (e.g., specific surface areas, pore size, and pore volume) of the catalysts were determined using the single-point BET method, by adsorption of N2 at its liquid temperature and subsequent desorption at room temperature. The ASAP 2420 apparatus (Micromeritics) was used in the experiments. Samples were degassed at 673 K for 10 h, prior to analysis.

XPS experiments were performed using a Kratos AXIS Ultra DLD instrument equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) operated at a power of 150 W and under ultrahigh vacuum conditions in the range of ∼10−9 mbar. All spectra were recorded in the hybrid mode using electrostatic and magnetic lenses and an aperture slot of 300 μm × 700 μm. The survey and high-resolution spectra were acquired at fixed analyzer pass energies of 160 and 20 eV, respectively. The samples were mounted in the floating mode in order to avoid differential charging. Therefore, XPS spectra were acquired using charge neutralization.

The thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/differential scanning calorimetry instrument equipped with a GC 200 Gas Controller and an auto-sampler. The sample was first subjected to an isothermal treatment of 150 °C for 30 min, and under flowing N2 (99.9999% purity) with a flow rate of 50 mL/min. It was subsequently heated to 1000 °C (10 °C/min).

**Catalytic Reaction.** The methanol dehydrogenation reaction was carried out with a fixed-bed reactor. Prior to the reaction, 100 mg of catalyst was placed in the reactor and reduced by dilute hydrogen (H2/N2 = 30 mL/min:20 mL/min) at 250 °C for 3 h. After pretreatment, a stream of pure methanol solution was first fed (0.1 mL/min) into the reactor, and then the methanol vapor was carried into the reactor by N2 (50 mL/min). Reaction products were analyzed using an online GC system (Varian GC-450) connected with two channels, A and B. Channel A is consisted of a set of three packed columns, "HayeSep” Q (CP81073), "HayeSep” T (CP81072), and "MolSieve” 13X (CP81073), connected with a TCD detector to monitor CO and CO2. Channel B uses a CP wax 52CB column (CP7668) and was connected with a flame ionization detector to monitor MF and other oxygenates. After a reaction time of 50 h, the spent catalyst was regenerated by calcination for 3 h at 400 °C, under an air atmosphere, to remove the coking. Once regenerated, the catalyst was reduced by dilute H2 before undergoing the next round of the catalytic test as previously described.

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**Notes**

The authors declare the following competing financial interest(s): A U.S. Provisional Application was filed by King Abdullah University of Science and Technology.

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