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Efficient Hydrogenation of Alkyl Formate to Methanol over Nanocomposite Copper/Alumina Catalysts

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The production of methanol, an important fuel and chemical feedstock, from carbon dioxide is an important process for CO_2 utilization. We describe herein a mild and efficient method for the indirect hydrogenation of carbon dioxide to methanol via a CO_2-derived formate ester intermediate by using a simple heterogeneous catalyst system comprising Cu highly dispersed in an alumina matrix under solvent-free conditions. This catalyst is also effective for the hydrogenation of other formate esters, such as ethyl formate, propyl formate, and butyl formate.

Carbon dioxide levels in the atmosphere have reached approximately 400 ppm for the first time in recorded history as a consequence of human activities.[1a] Converting CO_2 into useful feedstock chemicals and fuels is an important strategy for removing CO_2 from the atmosphere and for reducing dependence on petrochemicals.[1] Among the products derived from CO_2, methanol is an extremely important basic energy chemical, as it is a feedstock for the production of formaldehyde, olefins, dimethyl ether, methyl *tert*-butyl ether, acetic acid, and a wide variety of other products.[2] In 2005, Olah and co-workers initiated a "methanol economy" concept.[3] According to this proposal, methanol can serve as an efficient energy-storage chemical and a fuel substitute. For example, methanol can be converted into gasoline (MTG process), aromatics (MTA process), ethylene and propylene in the MTO (methanol to olefins) process, as well as other useful petrochemicals.[4] Therefore, the synthesis of methanol from CO_2 hydrogenation can reduce the dependence on fossil fuels and control greenhouse gas emissions in the future. Currently, much work in this area has focused on the direct hydrogenation of CO_2 into CH_3OH on Cu–Zn oxide based catalysts.[5] However, these process require high operating temperatures (200–250 °C), which limits the theoretical yield of methanol, as the CO_2 hydrogenation reaction is thermodynamically favored at low temperature. So, it is desirable to find a new strategy for the efficient conversion of CO_2 into methanol at a relatively low reaction temperature.

Very recently, Milstein and co-workers developed an alternative, indirect approach from CO_2 to methanol through hydrogenation of CO_2-derived organic carbonates, carbamates, and formates by using Ru-based homogeneous catalysts under mild conditions.[6] In their experiments, the formation of methanol is almost quantitative through hydrogenation of the above-mentioned CO_2 derivatives under relatively mild conditions (1.0–6.0 MPa H_2, 110–145 °C). In particular, the hydrogenation of formate ester has been established as a desirable approach from CO_2 to methanol, as efficient transformation of CO_2 into formic acid and its derivatives [e.g., methyl formate (MF)] is known and well investigated.[7] Later on, Huff and Sanford also reported the hydrogenation of MF to methanol catalyzed by a Ru-based molecular catalyst system in a cascade catalysis for the homogeneous hydrogenation of CO_2 to methanol.[8] From synthetic and economic point of views, these systems are not practically useful because of the inherent problems of non-reusability, the processing cost, as well as additional handling problems. Hence, the successful development of an excellent reusable solid catalyst would represent a significant advancement in the hydrogenation of formate ester to methanol.

Heterogeneous catalyst systems reported for the hydrogenation of formate esters to methanol have mainly focused on copper-based catalysts. Wainwright et al. reported the gas-phase hydrogenation of methyl formate to methanol over a copper chromite catalyst in a U-tube reactor to give >90% conversion to MF at 200 °C.[9] However, the selectivity to methanol reached only 70% because of the formation of 30% CO as a byproduct. Then, their group reported the liquid-phase hydrogenation of MF in a three-phase slurry reactor by using a copper chromite catalyst. Measurements at 170 °C showed very high selectivity to methanol.[10] Upon evaluating Raney copper as a catalyst for the transformation, a similar yield of methanol was achieved at 110–160 °C under a hydrogen pressure of 5.2 MPa.[11] MF hydrogenation has also been studied over heterogeneous rhenium catalysts to give 46.1% conversion with 90% selectivity to methanol under severe conditions of temperature and pressure (200 °C and 10 MPa H_2).[12] Recently, Iwasa reported the hydrogenation of MF over various supported Pd and Pt catalysts.[13] The Pd/ZnO catalyst exhibited

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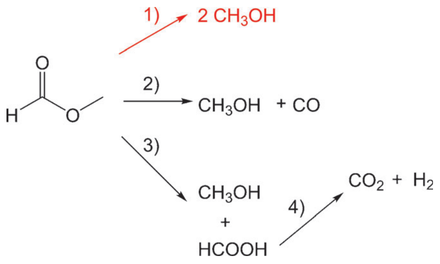
high selectivity (≈95%) for methanol formation with 10% conversion at 150 °C because of the formation of Pd–Zn alloys.

Taken together, the copper chromite catalyst shows effective catalytic activity for formate ester hydrogenation to methanol. However, a drawback of chromium-containing catalysts is the toxicity of the chromium compounds.[14] Alumina has been widely identified as a promising support material for many metal catalysts, especially for catalysts used in liquid-phase hydrogenation reactions, because of its textural properties and acid/base characteristics.[15] In this work, we show that a nanocomposite Cu/Al_2O_3-OG catalyst prepared by the oxalate–gel (OG) coprecipitation method is an active and highly selective heterogeneous catalyst for the hydrogenation of formate ester to methanol under mild conditions (100–150 °C). To the best of our knowledge, this Cu/Al_2O_3-OG catalyst represents the most efficient, simple, and ecofriendly catalytic system for the convenient and controlled synthesis of methanol from formate esters to date.



Scheme 1. Simplified pathway for the hydrogenation of MF.

At the start of our work, a series of copper-based catalysts (see the Supporting Information for the preparation of the catalysts) were applied to the selective hydrogenation of MF to methanol in the absence of solvent. The problem of this particular transformation is the large variety of reduction products that can possibly be formed (Scheme 1). Besides methanol, carbon monoxide and carbon dioxide are also typical products formed in the hydrogenation process.[16] As one of the main requisites for subsequent technical applications is methanol, the key point in MF hydrogenolysis would be to avoid the formation of CO and CO_2 byproducts. We first tested Cu-Al_2O_3-OG catalysts with different loadings, which were prepared by an oxalate–gel coprecipitation method. Prior to the reaction, the copper-based catalysts were reduced by a flow of 5% hydrogen in argon at 300 °C for 2 h and successively passivated by 2% oxygen diluted with helium (see the Supporting Information for the experimental details). Table 1 demonstrates that selective production of methanol in 57% yield could be achieved if 50 wt% Cu/Al_2O_3-OG was used (Table 1, entry 1). A decrease in the Cu loading to 40 or 30% significantly increased the yield of methanol (Table 1, entries 2 and 3). The highest product yield was 92%, which was obtained by using the Cu/Al_2O_3-OG catalyst containing 20 wt% copper (20-Cu/Al_2O_3-OG; Table 1, entry 4). However, a further decrease in the Cu loading to 10 wt% led to a clear decrease in the yield of methanol (Table 1, entry 5). We also tested the repeated use of the 20-Cu/Al_2O_3-OG catalyst for MF hydrogenation. Much to our delight, MF conversion and methanol yield decreased only slightly after three repeated uses (Table 1, entry 6); inductively coupled plasma (ICP) analysis showed that no Cu was present in the filtrate, and this is indicative of its high stability and reusability. It is noted that the total turnover number (TON) based on three successive runs was as high as 1092, and this is the highest TON ever reported for the hydrogenation of MF to methanol by using a heterogeneous catalyst (see Table S1, Supporting Information).

To investigate the origin of the catalytic activity of the Cu/Al_2O_3-OG catalysts, the present Cu/Al_2O_3-OG catalysts with loadings of 10–50 wt% were characterized. Typical data such as metal loadings, BET surface areas, and Cu metal surface areas (determined from chemical N_2O titration) are summarized in Table 2. It can be seen that there is only a weak relationship between the BET surface area or the Cu particle sizes and the performance of the Cu/Al_2O_3-OG samples; this indicates that the external texture is not a key factor in determining the cata-

Table 1. Hydrogenation of MF to methanol with various catalysts.[a]

Entry	Catalyst	Metal loading [wt%]	Conv.[b] [%]	Selectivity[b] [%] Methanol	CO_2+CO
1	Cu/Al_2O_3-OG	50	57	>99	<1
2	Cu/Al_2O_3-OG	40	76	>99	<1
3	Cu/Al_2O_3-OG	30	85	>99	<1
4	Cu/Al_2O_3-OG	20	92	>99	<1
5	Cu/Al_2O_3-OG	10	79	>99	<1
6[c]	Cu/Al_2O_3-OG	20	90	>99	<1
7[d]	Cu/Al_2O_3-CP	20	60	>99	<1
8[e]	Cu/Al_2O_3-IMP	20	14	>99	<1
9	Cu/ZnO-OG	20	8	>99	<1
10	Cu/ZnO–Al_2O_3	50	12	>99	<1
11	Cu/ZrO_2-OG	20	39	>99	<1
12	Cu/Cr_2O_3	30	51	98	2

[a] Reaction conditions: MF (162 mmol), $n_{MF}/n_{metal}=54$, H_2 (3 MPa), 130 °C, 6 h. [b] Conversion and selectivity were determined by GC and GC–MS. [c] Results for the third run for the Cu/Al_2O_3 catalyst recycled under the reaction conditions described in entry 4. [d] Cu/Al_2O_3-CP prepared by coprecipitation with Na_2CO_3. [e] Cu/Al_2O_3-IMP prepared by impregnation.

Table 2. Physicochemical properties of the Cu/Al_2O_3 catalysts with different Cu loadings and preparation methods.[a]

Entry	Catalyst	Cu loading [%]	S_{BET} [$m^2 g_{cat}^{-1}$]	S_{Cu}[b] [$m^2 g_{cat}^{-1}$]	S_{Cu}[b] [$m^2 g_{Cu}^{-1}$]	D_{Cu} [%]	d_{Cu}[c] [nm]
1	Cu/Al_2O_3-OG	10	44	6.0	60.0	9.2	–
2	Cu/Al_2O_3-OG	20	43	17.8	89.0	13.5	14.3
3	Cu/Al_2O_3-OG	30	32	19.7	65.6	10.1	15.2
4	Cu/Al_2O_3-OG	40	29	21.2	53.0	8.2	21.3
5	Cu/Al_2O_3-OG	50	27	24.1	48.2	7.5	27.8
6	Cu/Al_2O_3-CP	30	19	6.8	22.6	4.1	45.1
7	Cu/Al_2O_3-IMP	30	18	1.0	3.3	0.5	80.6

[a] S_{BET} = BET surface area, S_{Cu} = Cu metal surface area, D_{Cu} = copper dispersion, d_{Cu} = size of copper metallic particles. [b] Determined by N_2O titration method. [c] Estimated by the Scherrer equation from the diffraction peaks of Cu in the XRD patterns.

lytic activity of the present samples prepared by oxalate–gel coprecipitation. However, by careful correlation of the Cu dispersion data included in Table 2, it was found that there is a good relationship between the metallic copper dispersion and the performance of the Cu/Al_2O_3-OG catalysts with various Cu loadings. Notably, the data of the metallic Cu surface area as measured by N_2O titration demonstrate clearly that the 20-Cu/Al_2O_3-OG catalyst exhibits the highest copper dispersion of all the samples. Therefore, the fact that the specific composition of the 20-Cu/Al_2O_3-OG sample can substantially maximize the exposure of the fraction of catalytically active species at the catalyst surface is crucial for achieving high activity in MF hydrogenation, which is in line with the large amount of literature documenting the structure–activity relationship for supported copper catalysts.[17]

In situ XRD measurements were used to provide further insight into the genesis of the active phases in the 20-Cu/Al_2O_3-OG catalyst. The calcined catalyst was reduced by passing 5 vol% H_2 in argon while increasing the temperature with simultaneous XRD analysis. As shown in Figure 1, for the sample calcined at 400 °C, two peaks exist at $2\theta = 35.5$ and 38.8°, which correspond to the (002) and (111) characteristic peaks of CuO. No peaks of Al_2O_3 are observed, which can be ascribed to particles that are too fine to be detected.[18] If the reduction temperature was increased to 200 °C, a clear peak positioned at $2\theta = 43.3°$ appeared, which was ascribed to the (111) lattice plane of metal Cu. Along with a continuous increase in the reduction temperature to 300 °C, the intensity of the Cu peak increased gradually and no diffraction features of CuO could be identified; this indicates that CuO was completely reduced into metallic Cu. The average size of the resultant Cu particles was estimated to be approximately 14 nm on the basis of the Scherrer equation. High-resolution transmission electron microscopy (HRTEM) investigation of the reduced catalysts showed that Cu nanoparticles approximately 14 nm in size were observed (Figure 2), which is consistent with the XRD results. An ordered lattice fringe with an interplanar spacing of 0.209 nm is clearly seen at the crystal edge, which can be ascribed to the (111) crystal plane of Cu with a face-centered cubic structure. The structure of Cu at 20-Cu/Al_2O_3-OG was further investigated by collecting the X-ray absorption fine structure (XAFS) data at the Cu K edge. Both the X-ray absorption near-edge structure (XANES) region, used to determine the oxidation state of the Cu species, and the extended X-ray absorption fine structure (EXAFS) region of the data were analyzed. The XANES region of the Cu K edge (Figure 3) shows a clear pre-edge peak maximum at 8982.2 eV, which is characteristic of a 1s-to-3d transition in the Cu^0 compound. This can be further confirmed by the presence of a main peak at 2.22 Å in the Fourier transform EXAFS region, which can be attributed to the Cu–Cu metal bond (Figure S4). This scenario can be further corroborated by transmission electron microscopy (TEM), XRD, and temperature-programmed reduction (TPR) analyses (see Figure S1–S3).

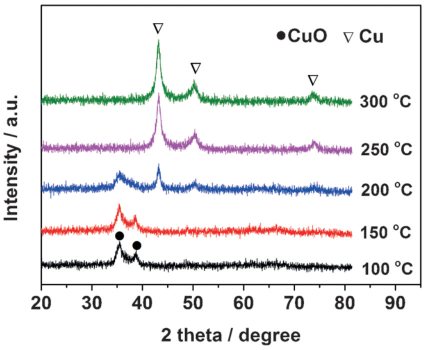


Figure 1. In situ XRD patterns of the 20-Cu/Al_2O_3-OG catalyst taken during reduction of the calcined Cu/Al_2O_3 oxide precursors in 5% H_2/Ar.

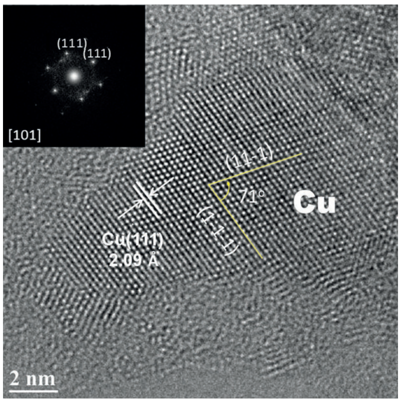


Figure 2. HRTEM images of Cu particles in the reduced 20-Cu/Al_2O_3-OG catalyst.

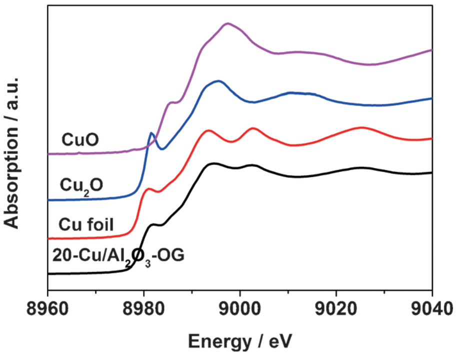


Figure 3. XANES at the Cu K absorption edge of the 20-Cu/Al_2O_3-OG catalyst, Cu foil, Cu_2O, and CuO.

In a comparison of other Cu/Al_2O_3 catalysts with identical Cu loadings prepared by conventional coprecipitation and impregnation methods, it was observed that the Cu/Al_2O_3-OG catalyst featuring a higher component dispersion prepared by the oxalate–gel coprecipitation method had the best MF hydrogenation activity (Table 1, entries 6–8). The hydrogenation reaction did not occur in the absence of the catalysts and $<2\%$ methanol was formed upon using Al_2O_3, Cu, Cu_2O, or a mixture of Cu–Al_2O_3 and Cu_2O–Al_2O_3 as catalysts directly (Table S2). Therefore, the stronger interaction between copper and the alumina support generated during catalyst preparation by using oxalate–gel coprecipitation should be the major reason for its high activity.[19] As the choice of the support plays an important role in metal catalysis, we also evaluated copper supported on other supports prepared by the oxalate–gel coprecipitation method and commercial copper-based catalysts. Conventional Cu/ZnO-OG and industrial Cu/ZnO–Al_2O_3 methanol synthesis catalysts gave low activity (Table 1, entries 9 and 10). Upon using the Cu/ZrO_2-OG catalyst, the yield of methanol was approximately as high as 39%. Considering that Cu/Cr_2O_3 is widely used in the hydrogenation of MF to methanol, we also tested its catalytic activity. The use of this commercial catalyst resulted in the formation of the desired methanol product in moderate yield (Table 1, entry 12). Among the different supported copper catalysts examined, the Cu/Al_2O_3-OG catalyst exhibited the best catalytic performance. To clarify the origin of the enhanced activity of the catalyst towards MF conversion upon using Al_2O_3 as a support, $HCOOCH_3$ temperature-programmed desorption ($HCOOCH_3$-TPD) measurements were conducted over different supported copper catalysts. These measurements revealed that a significantly greater amount of MF was desorbed from the Cu/Al_2O_3-OG catalyst relative to that desorbed from other catalysts (Figure 4), which implies that the high adsorption capacity of MF associated with the Cu/Al_2O_3-OG catalyst was responsible for its superior performance in the transformation of MF into methanol.

Having established that 20-Cu/Al_2O_3-OG was the best catalyst for the hydrogenation of MF to methanol, our attention shifted toward optimization of the reaction parameters by varying the reaction temperature and pressure (see Figure S5 and S6). First, the effect of the reaction temperature was investigated at a hydrogenation pressure of 3.0 MPa. An increase in reaction temperature from 100 to 130 °C led to a dramatic increase in the MF conversion from 25 to 92% after a reaction time of 6 h. As the temperature was further increased to 140 °C, complete MF conversion was obtained within 6 h. Moreover, studies on the effect of the hydrogen pressure (pH_2) in the range from 1 to 3 MPa at 130 °C revealed that the reaction proceeded much more rapidly at higher pressures. Building upon these results, we started to examine the scope of the hydrogenation of formate esters with 20-Cu/Al_2O_3-OG. Table 3 presents the results for the synthesis of methanol from different formate esters under liquid-phase conditions. For example, ethyl formate, propyl formate, and butyl formate were selectively hydrogenated to methanol, and the corresponding alcohols were obtained in high yields (Table 3, entries 2–4).

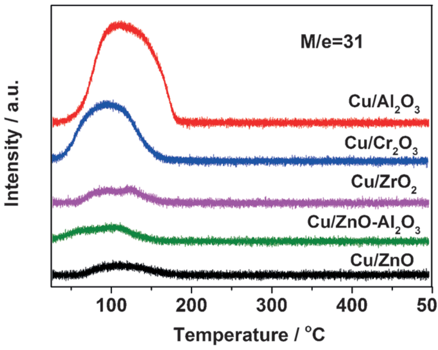


Figure 4. $HCOOCH_3$ TPD profiles for Cu catalysts supported on different supports.

Table 3. Selective hydrogenation of various formate esters into methanol over a fresh 20-Cu/Al_2O_3-OG catalyst.[a]

Entry	Substrate	T [°C]	t [h]	Conv. [%]	Methanol yield[b] [%]
1	methyl formate	130	8	100	99
2	ethyl formate	130	10	98	92
3	propyl formate	150	10	97	91
4	butyl formate	150	12	95	91

[a] Reaction conditions: MF (162 mmol), $n_{MF}/n_{metal}=54$, H_2 (3 MPa). [b] Yield determined by GC and GC–MS.

In summary, we demonstrated that a simple heterogeneous catalyst system comprising Cu highly dispersed in an alumina matrix can efficiently catalyze the selective hydrogenation of CO_2-derived formate esters into methanol under solvent-free conditions. The sequence of catalytic activity for the synthesis of methanol from the hydrogenation of methyl formate is in good agreement with the results of the physicochemical properties; the 20-Cu/Al_2O_3-OG catalyst with the highest copper dispersion prepared by the oxalate–gel coprecipitation method exhibited the highest activity. The observation that the copper-based metal oxide catalyst could be reused suggests that this catalyst is compatible with a high yield and continuous operation, which thus paves a new way toward a renewable chemical industry. The findings in this work could inspire the development of new efficient heterogeneous catalysts for the conversion of CO_2 into methanol through indirect synthetic methodology.

Experimental Section

Preparation of Cu/Al_2O_3-OG catalysts

A series of Cu/Al_2O_3-OG catalysts were prepared by the oxalate–gel coprecipitation method following the reported procedure.[17] A mixed alcoholic solution (each 0.1 M) of copper nitrate and aluminum nitrate was injected rapidly into an alcoholic solution of a 20% excess amount of oxalic acid at room temperature under vigorous stirring. The resultant gel-like precipitates were separated by centrifugation followed by drying at 110 °C overnight. Then, calcination of the as-obtained materials was performed in a muffle oven at 400 °C for 4 h. Following calcination, the catalysts were reduced at 300 °C under 5 vol% H_2/Ar atmosphere for 2 h. After reduction, the catalysts were allowed to cool to room temperature and were then passivated in flowing 2% oxygen in helium for 3 h.

Hydrogenation of MF

The hydrogenation of MF was performed in a 50 mL high-pressure Parr reactor. First, MF (162 mmol) was added into the autoclave. The prereduced copper-based catalyst was quickly added into the reactor after replacing the air in the autoclave with approximately

1 MPa H_2 (5×) After introduction of hydrogen with a certain pressure (typically, 3 MPa), the reaction was started by heating the mixture up to a reaction temperature (typically, 130 °C). Samples were taken periodically during the reaction. After the reaction, the liquid products were analyzed by using an Agilent 7820 A gas chromatograph equipped with a capillary column INNOWAX (30 m× 0.25 mm) and a flame ionization detector. The identification of the products was performed by using a GC–MS spectrometer. Gas-phase products were collected in a gas bag and were analyzed by using an Agilent GC (7820A) equipped with a Porapak Q and 5A packed column and a thermal conductivity detector.

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Keywords: carbon dioxide · copper · formate esters · hydrogenation · methanol

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