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Highly Selective Hydrogenation of Diesters to Ethylene Glycol and Ethanol on Aluminum-Promoted CuAl/SiO₂ Catalysts

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Graphic Abstract

Highlights

- Aluminum modified silica sol was used to prepare CuAl/SiO2 catalysts by a hydrothermal method
- Al₂O₃ incorporation in silica enhanced the surface acidity and reduced the Cu crystalline size of CuAl/SiO₂ catalysts
- The moderate aluminum modification on SiO₂ in the form of =Si-OH-AI bond
- CuAl/SiO₂ exhibited high selectivity of ethanol (94%) and EG (95%) in DMO and EC hydrogenation

Abstract:

A highly selective CuAl/SiO₂ catalyst was investigated for the hydrogenation of dimethyl oxalate (DMO) and ethylene carbonate (EC) to ethylene glycol (EG) and ethanol. Aluminum modified silica sol was used to prepare CuAl/SiO₂ catalysts by a hydrothermal method. The catalytic performance of the CuAl/SiO₂ catalysts with varying aluminum content was investigated at the conditions of 280 °C and 2.5 MPa for DMO hydrogenation, while 180 °C and 3 MPa for EC hydrogenation. The results showed that the Cu1.0Al/SiO₂ catalyst exhibited the highest selectivity of ethanol (~94%) in the DMO hydrogenation, while the Cu0.5Al/SiO₂ catalyst exhibited the highest selectivity of EG (~95%) and methanol (65%) in the EC hydrogenation.

Characterizations (e.g., TPD, TPR and XANES) indicated that the moderate aluminum modification on SiO₂ in the form of \equiv Si-OH-Al bond could not only tune the support acidity to polarize the C=O bond of esters, but also intrinsically facilitate the dispersion of Cu active species to activate H₂, which thus facilitated the selective hydrogenation reaction to EG, ethanol and methanol.

Key Words: diester hydrogenation, copper-based catalysts, aluminum promoter, acidic sites

1. Introduction

The hydrogenation of diesters, including oxalate, carbonate, acetate and maleate, has drawn great attention as an efficient way to produce multiple kinds of chemicals, such as methanol, ethanol, dihydric alcohol and other pharmaceutical intermediates. However, the diesters generally possess multiple C=O or C-O bonds, their hydrogenation reactions generally include several cascade reactions. For instance, the dimethyl oxalate (DMO) hydrogenation reaction comprises several continuous reactions, including DMO hydrogenation to intermediate methyl glycolate (MG), MG hydrogenation to ethylene glycol (EG) and deep hydrogenation of EG to ethanol.^[1,2] Therefore, it is also would be a significant challenge for the selective hydrogenation to produce target products.

Copper-based catalysts were extensively investigated in the hydrogenation of esters due to the high activity of C-O and C=O bonds.^[1] In order to enhance hydrogenation reactivity and selectivity, the supports, such as MCM-41,^[2] SBA-15,^[4, 14]

^{9, 12]} KIT-6^[5] and HMS^[6, 7, 8] with orderly channels, were introduced to fabricate Cu⁰ and Cu⁺ sites to activate H₂ and polarize the C=O bond of esters, respectively. For instance, Deng et al. presented a series of Cu/MCM-41 catalysts by ammonia evaporation method, which significantly enhance the dispersion of the copper species compared with impregnation method.^[4] Nanoarrays Cu/SiO₂ catalysts were prepared with embedded active species in monolithic channels and exhibited excellent activity and promoted mass transfer efficiency.^[3, 4] Researchers also found that application of metal oxide promotor could change the crystalline size of Cu, and improve the dispersion of Cu, such as Cu-Au,^[9] Cu-Ag,^[10] Cu-Pd,^[11] and Cu-Pt,^[12] which enhanced their hydrogenation reactivity and thermal stability. Zhao et al. have reported a Ni containing Cu-Ni bimetallic nano-catalyst, achieving a moderate selectivity for ethanol (90%) under 2.5 MPa and 553 K.^[13] Le et al. have investigated the influence of dropping zinc and found that Zn has a significant influence on the texture and structure of the catalysts.^[14] Zheng et al. have found that catalyst with 1.0 wt% La loading exhibits the highest catalytic activity, which attributed to the formation of Cu-O-La bond enhancing the stability of Cu²⁺ under reductive atmosphere.^[15]

The surface acidity of catalysts is also an important factor to improve the selectivity of the products in the ester hydrogenation, since the acidic sites could polarize the C=O bond via the electron lone pair in oxygen, thus improving the reactivity of the ester group. The metal oxides, such as B₂O₃, and ZrO₂, have been used as promoters to controllably tune the surface acidity of catalysts, which further

improve the selectivity of desirable product.^[16, 17, 18] Our previous work has introduced B₂O₃ species by impregnation into Cu/SiO₂ catalysts with improved selectivity and stability, which could be ascribed to the suitable acid sites and high dispersion of copper species by B₂O₃ doping.^[18, 19, 20] Tian et al. prepared Cu_x-Mg_y-Zr_z/SiO₂ catalysts, also showing better catalytic performance after doping with MgO and ZrO₂ due to the change of surface acidity.^[21] Alumina and zirconia supported Cu catalysts were both appeared to exhibit high activity and hydrothermal stability, which were frequently used in CO and CO₂ hydrogenation.^[22, 23, 24] In the reaction of CO₂ hydrogenation to product methanol, the modification of Al₂O₃ can provide modest acidity sites as well as decrease copper cluster size.^[24] The modification of aluminum on silica surface such as SBA-15^[25] and MCM-41^[26] also illuminated that it could strengthen the acidity and the interaction of copper species with the supports. Therefore, metal oxides as promoters may controllably tune the acidity of catalysts and enhance the interaction of copper species with the supports, which further improve the catalytic performance of esters hydrogenation.

However, the reported work primarily used the surface doping or impregnation to introduce metal oxides as promoters on the supports and catalysts. The incorporation of the metal oxides in to the silica framework may facilitate the dispersion and stability of promoters. Herein, the silica precursor (silica sol) was first modified with aluminum salts and was used to prepare CuAl/SiO₂ catalysts by a hydrothermal method. The aluminum content in the silica sol was controlled to investigate the effect on hydrogenation of diesters (e.g., DMO and EC) to selectively

produce EG and ethanol. All the catalysts were systematically characterized for a better understanding of the structures and surface chemistry of the catalysts and the catalytic performance. The role of aluminum promotion on the catalytic performances was discussed through correlating surface concentration of moderate-intensity acidic sites with the selectivity of EG, ethanol and methanol in the DMO and EC hydrogenation reaction, respectively.

2. Experiment

2.1 Materials

Dimethyl oxalate was purchased from Aladdin (Shanghai) Biochemical Technology Co., Ltd. Ethylene carbonate was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Methanol, 1,4-Diocan, ammonia aqueous solution, Cu(NO₃)₂·3H₂O (> 99%) and Al(NO₃)₃·9H₂O (> 99%) were bought from Kelong Chemical Co., Ltd. 30 wt% colloidal silica was from Qingdao Yijida Chemical Co. Ltd.; Hydrogen gas (99.99%) was from Tianyi Gas Co., Ltd. All the chemicals above were used as received and without any purification.

2.2 Catalysts preparation

The colloidal silica solution (30 wt%) was first added with Al(NO₃)₃·9H₂O with the Al/SiO₂ weight content of 0.5%~2%. The Cu/SiO₂ and CuxAl/SiO₂ catalysts were synthesized by a hydrothermal method. Firstly, 2.8 mmol of Cu(NO₃)₂·H₂O was dissolved in 240 mL of deionized water and then added with 24 mL of 25% ammonia aqueous solution. 1.72 g of Al containing colloidal silica solution were added to the

solution. After vigorous stirring for 30 min, the slurry was transferred into the Teflonlined autoclaves for hydrothermal synthesis. After heating in an oven at 413 K for 10 h, the products were washed with deionized water and ethanol to pH=7. Finally, the catalysts were dried and calcined at 723 K for 4 h. The calcined samples were denoted as Cu/SiO_2 and $CuxAl/SiO_2$ catalysts, where x represents the weight content of Al/SiO_2 (0.5, 1.0, 1.5 and 2.0%).

2.3 Catalytic characterization

Textural properties were measured at 77 K by N₂-physisorption using a Micromeritics ASAP 2460 instrument. The specific surface areas were calculated from the isotherms using Brunauer-Emmett-Teller (BET) method, and pore size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method. The actual copper and aluminum contents were tested though inductively coupling plasma optical emission spectrometry (ICP-OES). X-ray diffraction (XRD) spectra were implemented by the Empyrean diffraction meter using Cu k α radiation (λ =1.5406Å) at 40 kV and 35 mA, and the copper species particle sizes were calculated by the Scherrer equation.

The H₂ temperature-programmed reduction (H₂-TPR) was determined by Micromeritics AutoChem II 2920 instrument. After pretreated in argon atmosphere at 393 K for 1 h, approximately 50 mg catalysts were reduced in 10 vol% H₂-Ar (30 mL·min⁻¹) with temperature increased from 323 K to 1073 K (heating rate 10 K·min⁻¹). The TCD was employed to determine the amount of hydrogen consumption during this process.

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Fourier transform infrared spectroscopy (FT-IR) was carried out on a FTIR spectrometer (Nicolet, iS50). The materials were finely dried in oven and grounded before dispersed in KBr powder. The spectra range was started from 4000 cm⁻¹ to 400 cm⁻¹ with resolution ratio of 0.5 cm⁻¹.

The CO₂ and NH₃ temperature-programmed desorption (TPD) was carried out on Micromeritics AutoChem II 2920 instrument. For qualified evaluation of basic sites or acid sites, 100 mg catalysts were placed in a quartz U tube and reduced in 10 vol% H₂-Ar (30 mL·min⁻¹) at 623 K for 4 h before the gas switched to CO₂ or NH₃, which passed through the U tube for 1 h to reach adsorption saturation. After weak adsorption was removed by argon sweeping, the temperature was increase from room temperature to 973 K at a heating rate of 10 K·min⁻¹ under argon atmosphere.

The specific surface area of metallic copper species was qualified by dissociative N₂O adsorption and H₂-TPR reverse titration. Typically, after pretreated in Ar at 473 K for 2 h, 50 mg of catalysts were reduced with temperature from 323 K to 973 K (this process was defined as total TPR). Then switched to 10 vol%N₂O-Ar mixture under room temperature and pulse titrated for 2 h, which oxidized copper species to higher valence states. Finally, the reduction process repeated while temperature inclined to 573 K (this process was defined as Surface TPR). The dispersion (D_{Cu}), specific surface area (S_{Cu}) and diameter of copper species (d_{Cu}) were calculated by following formula:

$$D_{Cu}(\%) = \frac{2 \times H_{2 \text{ consumption (Surface TPR)}}}{H_{2 \text{ consumption (Total TPR)}}} \times 100\%$$
(1)

$$S_{Cu^0}(m^2 g^{-1} Cu) = \frac{D_{Cu} \times N_{av}}{M_{Cu} \times 1.46 \times c} \approx 649 \times D_{Cu}$$
(2)

$$d_{Cu}(nm) = \frac{6}{S_{Cu} \times \rho_{Cu}} \approx \frac{1.0}{D_{Cu}}$$
(3)

Where assumed Cu species are sphere and contains 1.46x10¹⁹ individual each square meter.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were performed at the XAFS station in the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) operating at about 150 mA and 2.2 GeV. The absorption spectra of the Cu K-edge of the samples and reference compounds were recorded at room temperature in transition mode. The harmonic content in monochrome beamline was reduced with a Si(111) double-crystal monochromator. The back-subtracted EXAFS function was converted to k-space and weighted by k³ to compensate for the diminishing amplitude. The Fourier transforming of k³-weighted EXAFS data was performed in the range of k =3-11 Å⁻¹, using a Hanning function window.

2.4 Catalytic performance

The vapor-phase hydrogenation of DMO and EC was tested in a fixed-bed tubular reactor (length of 50 cm, inner diameter of 0.8 cm and external diameter of 1.6 cm). Typically, 0.4 g of catalyst (40-60 mesh) was placed in the middle section of reactor. After reduced in H₂ atmosphere at 623 K for 4 h and cooled to the reaction temperature of 553 K, DMO (15wt% dissolved in methanol) was injected to the reactor. The H₂/DMO molar ratio, reaction pressure and weight hour space velocity (WHSV) were 200, 2.5 MPa and 0.2 h⁻¹, respectively. Same reduction condition was

applied to the hydrogenation of EC, while the reaction temperature is 453 K and the raw material is 10wt% EC dissolved in 1,4-diocan. In this case, the H₂/EC molar ratio, reaction pressure and WHSV were 200, 3 MPa and 0.2 h⁻¹, respectively. The reaction products were analyzed by GC SP-2100A equipped with flame ionization detector (FID) and a DB-WAX capillary column (Agilent Technologies Company, 30 m×0.250 mm). All experimental data were averaged from three to six separate GC samples to ensure repeatability of catalysts.

3. Results and discussion

3.1 Catalytic activity of DMO and EC hydrogenation over the Cu/SiO₂ and CuAl/SiO₂ catalysts

The catalytic performance over the Cu/SiO₂ and CuxAl/SiO₂ catalysts was investigated to understand their catalytic activity of DMO and EC hydrogenation. As shown in Fig. 1(a), all the catalysts exhibited a 100% DMO conversion. The yield of ethanol raised while the yield of C₃-C₄ products (including n-propanol, ethylene glycol monomethyl ether and diethyl ether) declined with the increase of Al content on the catalysts. The optimal ethanol yield of 94.35% was achieved over the Cu1.0Al/SiO₂ catalyst at a WHSV of 0.2 h⁻¹.

The catalytic performance of the EC hydrogenation over the CuxAl/SiO₂ catalysts was shown in Fig. 1(b). The EC hydrogenation reaction involved several cascade reactions, including hydrogenating EC to methanol and EG and further hydrogenating EG to ethanol.^[27] All the catalysts obtained approximately 100%

conversion toward EC. With the increase of the Al amounts, the yield of EG and ethanol fluctuated slightly, while the yield of another primary product, methanol, showed a noticeable change. Minor amount of aluminum enhanced the yield of methanol, which inclined from 45% to 64%, but further doping inhibited this phenomenon. This can be resulted in the copper crystal were enlaged which suppressed the production of methanol. The optimal methanol yield of 64.48% and EG yield of 95.37% were achieved over the Cu0.5Al/SiO₂ catalyst at a WHSV of 0.2 h^{-1} .

3.2 Physical-chemical properties of the Cu/SiO2 and CuxAl/SiO2 catalysts

3.2.1 Textural properties

The textural properties of the Cu/SiO_2 and $CuxAl/SiO_2$ catalysts are vital for the catalytic performance. The effects of aluminum additive on the physical properties of catalysts are shown in Fig.2 and Table 1.

All the samples displayed reversible Langmuir type IV isotherms in Fig. 2(a) with H1-type hysteresis loops, which illustrated that the catalysts prepared by hydrothermal method possess large-pore mesopores. The introduction of aluminum didn't significantly change the pore structures. The board hysteresis loops in the isotherms of all the catalysts indicated the wide distribution of pore diameter, which were consist with the pore size distribution curves in Fig. 2(b). As displayed in Table 1, the BET surface area, pore volume and pore diameter of Cu/SiO₂ were 483.01 m^2/g , 0.89 cm³/g and 6.29 nm, respectively. With the increase the content of

aluminum, the S_{BET} slightly decreased from 369.08 to 278.94 m²/g as well as the decline of D_{pore} (from 5.77 to 4.03 nm). Meanwhile, the decrease of V_{pore} from 0.61 to 0.24 cm^3 /g could be attributed to the aluminum oxide particles entered in the mesopores of the SiO₂, but not leading to the destruction of pore structures.

The ICP-OES results in Table1 showed that the copper contents of all catalysts were consistent, and the aluminum contents of all samples were similar to the target value when the content was lower than 1.5%. High aluminum content led to a clear deviation, which may be resulted from the breakaway of the excessive and unstable aluminum oxide on the support.

The N₂O pulse titration results illustrated that the existence of aluminum oxide could appreciably enhance the surface area (from 20.5 to 26.3 m²/g) and dispersion of copper species (from 28.9 to 37.0%), respectively. Excessive incorporation in the silica would impair this benefit but still better than original Cu/SiO₂ catalyst. Associated with the result in FT-IR test, it could be proposed that part of the copper species strongly bonded with SiO₂ were replaced by aluminum. The copper could further effuse on the surface of the support and form much smaller copper nanoparticles, and thus caused the decrease of particle sizes of copper and enhanced the Cu dispersion.

3.2.2 XRD patterns

XRD patterns, which helpful to understand the structure change and activity sites evolution, are depicted in Fig. 3. Fig. 3(a) showed that no significant CuO

diffraction peaks were observed on the fresh Cu/SiO₂ catalyst. The main peaks centered at $2\theta = 20.04$, 30.61, 36.07, 56.17, and 62.15° can be indexed to the CuSiO₃·2 H₂O phase (JCPDS NO. 11- 0322).^[28] During the hydrothermal process, the $[Cu(NH_3)_4]^{2+}$ in the solution vigorously reacted with the surface hydroxyl groups of the silica support, and then the copper silicate was formed. With the addition of Al on the catalysts, these broadening peaks still maintained until the amount of aluminum was up to 2%, which could be concluded that the aluminum introduction doesn't affect the stable structures of copper silicate. After the reduction and reaction, great differences were observed over the used catalysts in Fig. 3(b). The peaks of copper silicates were replaced by a wide diffraction peak of amorphous silica at approximately 23°. Meanwhile, several obvious diffraction peaks at around 43.3°, 50.4° and 74.1° emerged, which are indexed to the (111), (200), (220) crystal plans of Cu (JCPDS 04-0836), respectively. In addition, the peak at 36.5° belongs to the (111) crystal plans of Cu₂O (JCPDS 05-0667). There were no obvious CuO observed on the used samples, suggesting that CuO particles were either completely reduced or highly dispersed on the support. The coexistence of Cu and Cu₂O could be regarded as the reduction of CuO and copper silicates species during reduction process, since the strong interaction between silica and copper species for the copper silicates hampered the further reduction of Cu₂O to metallic Cu.

The particle sizes of copper for the used catalysts were calculated and listed in Table 1. The results showed that the moderate amount of aluminum suppressed the agglomeration of copper species during the reaction, while surplus aluminum on the

catalysts could not obviously suppress the agglomeration.

3.2.3 NH₃-TPD and CO₂-TPD results

In order to evaluate the strength and quantities of acidic and basic sites on catalysts with the introduction of aluminum, NH₃-TPD and CO₂-TPD were employed and the results were depicted in Fig. 4 and Table 2. As shown in Fig. 4(a), all the catalysts showed three similar peaks. The peak in low temperature could be interpreted by desorption of ammonia with weak adsorption on Si-OH.^[29, 30] The peak at 500-600 K was associated with the ammonia adsorbed on the acidic hydroxide group of \equiv Si-OH-Al, which was agree with the result reported by Hidalgo *et al.*^[31] The third peak at high temperature might be concluded to ammonia adsorbed on copper species.^[32]

The CO₂-TPD profiles showed all the samples with two peaks. The lowtemperature peak at 400 K could be ascribed to the weak CO_2 adsorption on the catalysts. The second peak at approximate 780 K could be attributed to the adsorption CO_2 on the surface basic sites with intense interaction.^[33]

Depending the NH₃-TPD and CO₂-TPD profiles, the amounts of acid sites and basic sites with different strength of acidity and basicity were calculated and shown in Table 2. It was easy to find that the amount of total acid sites increased with the aluminum concentration. With the increase of the aluminum content, the amount of weak acid sites fluctuated slightly while the amount of strong acid sites increased from 0.44 to 0.49 mmol/g. Meanwhile, a slight of Al (e.g., 0.5wt%), could

significantly increase the acid sites in medium strength area, indicating the formation of acidic hydroxide group of \equiv Si-OH-Al. In addition, the induction of aluminum led to a notably reduction of total basic sites from 0.36 to 0.19 mmol/g, indicating a successful suppression of the basicity of catalysts. High content of Al doping increased both the basic and acidic sites at the same time, which could be due to amphoteric properties of the Al₂O₃.

3.2.4 H₂-TPR results

The H₂-TPR was implemented to investigate the reducibility of the catalysts. As shown in Fig. 5, the reduction profiles of all the samples exhibited a reduction peak at 535K. With the increase of the aluminum content, the reduction peaks were slightly changed, indicating the Cu dispersion and the interaction between metal and support were improved after Al incorporation in silica. Our previous work showed that the copper silicates reduced to Cu⁺ occurred at around 510 K (the further reduction to Cu⁰ at a tough condition of 873 K), which is overlapped with the temperature for the reduction of well-dispersed CuO to Cu⁰ at around 515 K.^[34,35,36] Therefore, the single peak at approximately 535 K for the catalysts in this work was a result of combined reduction of highly dispersed CuO to Cu⁰ and copper silicates to Cu⁺. The higher reduction temperatures of the Cu/SiO₂ and CuxAl/SiO₂ catalysts here (~535 K) than that of Cu/SiO₂ catalysts in other literatures (~510 K) could be attributed to the strong metal support interaction of copper silicates species prepared by hydrothermal method. And the increased reduction temperatures in CuxAl/SiO₂ catalysts in Fig. 5

are probably due to the altered interaction between Cu and SiO₂ caused by Al addition.

3.2.5 FT-IR results

To further investigate the influence of aluminum doping on the surface group information of the copper-based catalysts, FT-IR spectra of the catalysts with different contents of Al were collected and shown in Fig. 6. The peaks at 1106 cm⁻¹, 800 cm⁻¹ and 475 cm⁻¹ appeared in all the samples, which were aroused from the asymmetric stretching vibration, symmetric stretching vibration and bending mode of Si-O-Si bonds in the amorphous silica, respectively.^[37] Similarly, the characteristic δ_{OH} vibration bond of 674 cm⁻¹ and the shoulder peak at 1042 cm⁻¹ were observed over all the catalysts, indicating copper silicates component were successfully formed during the hydrothermal process. It should be noted that the v_{SiO} band of SiO₂ at 800 cm⁻¹ was moved to the lower frequency side with the increase of Al content. According to FKS regulation,^[38] due to the higher length of Al-O bond (1.75 Å) compared with Si-O bond (1.61 Å) and the less electronegativity of Al, it can be suggested that this moving trend indicated the forming of Al-O bond. This bond substituted the preceding the trace amount of copper silicates' structure, further cause the effusion of copper species. This could be evidenced by the increase of dispersion. But excess replacement with aluminum will cause aggregation due to the surfeit detached copper formed larger cluster. This result was in accordance with the NH₃-TPD profiles and N₂O titration results.

3.2.6 Cu K-edge XANES and EXAFS

To gain further insights into the change of local coordination structures, we performed the XAFS experiments including XANES and EXAFS (Fig. 7). Obviously, the adsorption edge and white line feature of the Cu K-edge XANES spectra of the CuxAl/SiO₂ catalysts are similar with those of Cu/SiO₂ in Fig. 7(a), suggesting that the valence state and coordination environment of Cu are slightly changed after the decoration of Al. The radial structure functions (RSFs) of Cu K-edge derived from EXAFS spectra of used catalysts are shown in Fig. 7(b). The first coordination shell at ~0.15 nm (without phase-scattering shift correction) is attributed to the scattering pathway of the Cu-O bond, and the shell at ~0.27 nm can be ascribed to the Cu-Cu coordination. Notably, the amplitudes of both the Cu-O and Cu-Cu shell, associated with the coordination number, firstly lower and then increase as the Al increases. This indicated that the addition of Al can beneficial to the Cu dispersion, and the Cu0.5Al/SiO₂ exhibits the highest Cu dispersion, which is in accordance with the N₂O titration results in Table 1. Thus, the Al is not decorated on the surface of the catalyst, but definitely incorporated in the local structures of silica to regulate the physiochemical properties.

3.3 Discussions

3.3.1 The role of aluminum on the acidic sites and catalytic performance

During the hydrothermal process, the $Cu(NO_3)_2$ reacted with ammonia to form complexes ($[Cu(NO_3)_4]^{2+}$), which further clung or reacted on the silica to generate the

CuO and Cu silicates.^[39] According to the above experimental results, the generation of acidic sites were according to the following paths: Al(NO₃)₃ grafted on the SiO₂ support and then formed Al₂O₃ through calcination. Meanwhile, some aluminum species interacted with the surface Si-O bond during the deposition-precipitation process, which formed \equiv Si-OH-Al bond and further influenced the yield of products. Moreover, the formed \equiv Si-OH-Al is also a Lewis acidic site, that has been proved to polarize the C=O/C-O bond in DMO or EC via the electron lone pair in oxygen, which absolutely promote the catalytic performance in hydrogenation reaction.

To gain a better understanding of the corresponding-relationship between the amount of aluminum and the catalytic activities, the moderate-intensity acidic amounts and the yield of EtOH and MeOH in different reactions as functions of weight content of Al are illustrated in Fig. 8. In Fig. 8(a) the Cu1.0Al/SiO₂ catalysts exhibited the highest EtOH yield in the hydrogenation of DMO. As we all known, ethanol is the product of deep hydrogenation, which is dependent on the dissociation rate of H₂ in DMO hydrogenation. As reported^[40, 41], Lewis acidic sites could polarize the C=O/C-O bond via the electron lone pair in oxygen, while the Cu⁰ sites can activate H₂. In our system, the amounts of \equiv Si-OH-Al, a medium and Lewis acidic site that can improve the reactivity of DMO, increased with the elevated Al content (Fig. 8(a)). But from Table 1, the surface Cu⁰ first increased and then decreased with the Al doping. Combined these two points, the selectivity of ethanol increased first and then decreased with the increase of the doping amount of Al. In Fig. 8(b) Cu0.5Al/SiO₂ exhibited the highest MeOH yield in the hydrogenation of EC. Trace

amount of aluminum can enhance the performance by regulate the copper grain scale and the acidic density of catalysts. However, abundant aluminum oxide will promote the side reaction as well as destroy the primary structures of the Cu/SiO₂ catalysts. On the basis of the characterization of textural properties, the calculated of the size of copper species and the quantitative analysis of acidic sites and basic sites during different temperature ranges and the catalytic performance, we can summarize that the combined effect of the textural structure, the particle size of copper and the acidic sites co-operation played a vital role in the optimal catalytic activity of the CuAl/SiO₂ catalysts in the hydrogenation of esters.

3.3.2 The role of aluminum incorporation on the catalytic stability

The catalytic stability of catalysts is of great significant for the hydrogenation of DMO to ethanol from the viewpoint of further industrialization. The Cu/SiO₂ and Cu1.0Al/SiO₂ catalysts were selected to test the long-term stability, which could also survey the influence of doping aluminum. As shown in Fig. 9, both the two catalysts exhibited complete conversion of DMO, while the yield of target product, ethanol, proved different trend. The Cu1.0Al/SiO₂ presented stable yield of ethanol (92%~94%), after 40-h reaction period. However, this yield dropped from 85% to 78% on the Cu/SiO₂ without aluminum. The Cu1.0Al/SiO₂ catalyst with \equiv Si-OH-Al exhibited superior catalytic stability than the Cu/SiO₂ catalyst, implying the \equiv Si-OH-Al bond can enhance the catalytic stability for hydrogenation.

The activity decrease over copper-based catalysts is generally caused by the

aggregation of copper species, which declined in copper dispersion as well as changed the valence of Cu active species, during the long-term hydrogenation reaction.^[42] Previous researches illustrated the doping of acid oxides can also promoted the stability of catalysts due to the inhibition of agglomeration.^[18, 23] As pictured in Fig. 3(b) and Table 1, it can be concluded that the moderate amount of Al can decrease the degree of aggregation, which can maintain the excellent selectivity of ethanol and restrain the by-reaction after the long time reaction.

4. Conclusions

The CuAl/SiO₂ catalyst was prepared using the aluminum modified silica sol as the support by a hydrothermal method. The catalysts were investigated for the hydrogenation of dimethyl oxalate (DMO) and ethylene carbonate (EC) to ethylene glycol (EG) and ethanol. The results showed that the incorporation of Al₂O₃ in the silica could tune the surface acidity, intrinsically reduce the Cu crystalline size of the catalysts and alter the textural properties of catalysts thus facilitated the esters hydrogenation. The Cu1.0Al/SiO₂ catalysts exhibited the highest selectivity of ethanol (94%) in the DMO hydrogenation, while Cu0.5Al/SiO₂ exhibited the highest selectivity of EG (~95%) and methanol (65%) in the EC hydrogenation. This study delivered an easy and accessible way to prepare CuAl/SiO₂ catalysts with high activity and selectivity in esters hydrogenation reactions.

Author Contributions

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G.Q.S, K.M, H.R.Y and B.L. conceived and designed the experiments, analyzed the results and participated in writing the manuscript. All authors contributed to the discussions of the results in this manuscript.

Conflict of interest

The authors declare no competing financial interest.

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Catalysts	M _{Cu} (%) ^[a]	M _{Al} (%) ^[a]	$\frac{S_{BET}}{(m^2\!/g)^{[b]}}$	V _{pore} (cm ³ /g) ^[c]	D _{pore} (nm) ^[c]	$\frac{S_{Cu}{}^{0}}{(m^{2}\!/g)^{[d]}}$	D _{cu} (%) ^[d]	d _{Cu} (nm) ^[d]	d _{Cu} (nm) ^[e]
Cu/SiO ₂	25.9	/	483.01	0.8860	6.29	20.5	28.9	3.5	7.9
$Cu0.5Al/SiO_2$	24.3	0.48	369.08	0.6064	5.77	26.3	37.0	2.7	4.9
Cu1.0Al/SiO ₂	25.8	1.01	337.01	0.5736	5.81	24.1	35.5	2.8	5.4
Cu1.5Al /SiO2	27.8	1.44	296.46	0.3781	4.87	22.5	32.3	3.1	6.4
Cu2.0Al/SiO ₂	26.5	1.76	278.93	0.2434	4.03	21.0	30.8	3.3	7.2

Table1 Physical properties of the Cu/SiO2 and CuxAl/SiO2 catalysts

[a] Al and Cu content determined by ICP-OES analysis.

[b] S_{BET} determined by the Brunauer-Emmett-Teller (BET) equation.

[c] Pore volume and pore diameter determined by the BJH method from N_2 desorption

[d] Surface area of $Cu^0(S_{Cu}^0)$, Cu dispersion (D_{cu}) and Cu diameter (d_{Cu}) determined by the N₂O titration

[e] Metal Cu sizes (d_{Cu}) of used catalysts calculated from the XRD data based on the Scherrer equation

Catalysts Acidic sites Amounts (mmol/g) Basic sites Amounts (mmol/g) Weak Total Strong Weak Total Medium Strong Cu/SiO₂ / 0.9378 0.5842 0.3533 0.0179 0.3427 0.3605 $Cu0.5Al/SiO_2\\$ 0.5515 0.1958 0.4365 1.1838 0.0268 0.1705 0.1973 Cu1.0Al/SiO2 0.5421 0.2368 0.4245 1.2034 0.0248 0.1691 0.1939 Cu1.5Al/SiO2 0.5192 0.2423 0.4416 1.2030 0.0253 0.2162 0.2415 0.4921 Cu2.0Al/SiO₂ 0.5241 0.2677 1.2839 0.0181 0.2305 0.2486

Table 2 Amounts of Acidic sites and Basic sites over the Cu/SiO2 and CuxAl/SiO2 catalysts

Figure 1 Catalytic Performance of DMO and EC hydrogenation over the Cu/SiO₂ and Cu xAl/SiO₂. (a) WHSV = $0.2 h^{-1}$, H₂/DMO = 200 (mol/mol), T= 553 K, P=2.5 MPa; (b) WHSV = $0.2 h^{-1}$, H₂/EC = 200(mol/mol), T= 453 K, P=3 MPa

Figure 2 (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of Cu/SiO₂ and CuxAl/SiO₂ catalysts

Figure 3 XRD patterns of the fresh (a) and used (b) Cu/SiO_2 and $CuxA1/SiO_2$ catalysts.

Figure 4 (a) NH₃-TPD and (b) CO₂-TPD of Cu/SiO₂ and CuxAl/SiO₂ catalysts.

Figure 5 H₂-TPR profiles of the Cu/SiO₂ and CuxAl/SiO₂ catalysts.

Figure 6 FT-IR spectra of Cu/SiO_2 and $CuxAl/SiO_2$ catalysts.

Figure 7 (a) XANES spectra of Cu K-edge and (b) Fourier transform of k^3 -weighted EXAFS spectra for Cu/SiO₂ and CuxAl/SiO₂ catalysts.

Figure 8 (a) Yield of ethanol in the hydrogenation of DMO and (b) Yield of methanol in the hydrogenation of EC and medium acidic sites amount by weight content of aluminum.

Figure 9 Stability test of the Cu/SiO₂ and Cu1.0Al /SiO₂ catalysts. Conditions: WHSV = 0.2 h^{-1} , H₂/ DMO = 200 (mol/mol), T= 553 K, P= 2.5 MPa.