Effects of Basic Promoters on the Catalytic Performance of Cu/SiO₂ in the Hydrogenation of Dimethyl Maleate

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Abstract: Continuous hydrogenation of dimethyl maleate (DMM) to γ-butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF) is a promising process in industry. In this study, Cu-M/SiO₂ catalysts modified by basic promoters (M = Mg, Ca, Sr, Ba, La) were prepared, and characterized by physical adsorption of N₂, in situ XRD, H₂-TPR, CO₂-TPD. With the addition of basic promoters, the basicity of Cu-M/SiO₂ catalysts was improved. The particle size of CuO on Cu-M/SiO₂ catalyst was increased after modified by Mg, Ca, Sr, Ba. However, the CuO particle was decreased on the Cu-La/SiO₂ catalyst. The series of Cu-M/SiO₂ catalyst was applied to the hydrogenation of DMM. The addition of basic promoters increased the selectivity of GBL during the hydrogenation for the basic promoters improved the dehydrogenation of BDO to GBL in alkaline sites. Furthermore, Cu-La/SiO₂ presented a higher activity in the hydrogenation of DMM, due to its higher dispersion of Cu.

Keywords: dimethyl maleate; hydrogenation; Cu/SiO₂; basic promoters

1. Introduction

Dimethyl maleate (DMM) as an important chemical intermediate is widely used in pharmaceutical, pesticide, chemical fiber, automobile and other industries [1–3]. Moreover, the hydrogenation products of DMM, such as γ-butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF) are all high value-added chemical intermediates (the reaction pathways of DMM as shown in Scheme 1) [4–7]. With the frequent breakthrough of the oxidation technology of n-butane to maleic anhydride and the decrease of production cost, it will be of significance for the development of the downstream products of maleic anhydride. Esterification of maleic anhydride and methanol to DMM, and then continuous hydrogenation to BDO, GBL and THF, are considered to be a very promising technology. The key to this process is the catalyst for hydrogenation of DMM.

The catalysts for the hydrogenation of esters mainly include Ru [8–11], Pt [12], Pd [13,14], Cu [15–18], and so on. The noble metal catalysts, such as Ru, Pt and Pd [19,20], have the advantages
of high activity, but their price is expensive. A supported Cu catalyst with a strong capacity for the adsorption, activation of C=O bond, and low hydrogenolysis activity of C–C bond, is cheap and easy to prepare—and then, it is widely used in ester hydrogenation reactions [21]. However, unmodified Cu catalyst has the disadvantage of poor activity and difficult to control the selectivity of hydrogenation products. Improving the preparation method of the supported Cu catalyst is the main way to enhance its catalytic performance. The preparation methods of supported Cu catalysts are as follows: Impregnation [22,23], ion exchange [24,25], sol-gel [26,27], deposition-precipitation [28], ammonia evaporation (AE) [29–31]. The AE method was invented by the Japanese Ube and used in the hydrogenation of esters [29]. It is a new method, based on ion exchange and deposition–precipitation: Copper ammonia complex ion is formed by ammonia and copper species precursor, followed by ion exchange with the hydroxyl on the surface of SiO$_2$, and the excess copper ammonia complex ions forming Cu(OH)$_2$ deposited on the surface of SiO$_2$ with the evaporation of ammonia. The dispersion of Cu in the Cu/SiO$_2$ catalyst prepared by the AE method is high, and it is difficult to sinter at high temperature. Moreover, there are two kinds of copper species: Cu$^+$ and CuO, both of which have been proved to have a synergistic effect, which can further improve the activity of ester hydrogenation. Therefore, the Cu/SiO$_2$ catalyst prepared by the AE method has the advantages of good dispersion and high activity, and has become a hot spot in recent years. Additives are an important factor affecting the catalyst activity, which changes the electronic structure of catalyst to improve the catalytic activity and selectivity, and also improve the dispersion of the active component and stability [32–36]. Yin et al. introduced NiO to improve the dispersion of metal Cu, and increased the TOF (turn of frequency) value; therefore, the introduction of NiO effectively improved the catalytic performance [32]. He et al. prepared Cu/SiO$_2$ catalysts promoted by different content of B, and found that the addition of an appropriate amount of B could improve the dispersion of Cu species and prevent the agglomeration of copper particles at high temperature [34]. With the increase of B content, the content of Cu$^+$ showed a rising trend, when Cu/B = 6.6, the content of Cu$^+$ was the highest, and the activity and stability of the Cu-B/SiO$_2$ catalyst was much higher than that of the conventional Cu/SiO$_2$ catalyst [34].

In industry, BDO, GBL and THF are co-produced by the hydrogenation of DMM with the yield of THF the highest [31], and the yield of different products was controlled by varying the reaction conditions according to the market. How to further improve the activity of supported Cu catalyst and regulate the selectivity of DMM hydrogenation products controllably is a hot research topic. Guo et al. used Cu–B/γ-Al$_2$O$_3$ catalysts to obtain 100% DMM conversion at 533 K, 5 Mpa, H$_2$/(DMM 120 and LHSV (Liquid hourly space velocity) 0.36 h$^{-1}$ [7]. Wang et al. enhanced the DMM conversion through adsorption precipitation compared to impregnation [37]. What is more, Chen et al. reported that Cu/SBA-15 could reach 100% DMM conversion in dimethyl maleate hydrogenation [38]. However, the study on the catalytic performance of Cu/SiO$_2$ catalyst modified with alkaline additives in DMM hydrogenation is quite incomplete. In this paper, the basicity of the SiO$_2$ vector was modulated by adding the basic additives (Mg, Ca, Sr, Ba, La), and the effect of different alkali metals on the dispersion of Cu in Cu/SiO$_2$ catalyst prepared by the AE method was explored. Furthermore, the effects of Cu dispersion and the basicity of the supports on the catalytic performance of hydrogenation of DMM were studied.

2. Results and Discussion

2.1. Catalysts Characterization

To begin, 25 wt% Cu/SiO$_2$ and 25 wt% Cu-5 wt% M/SiO$_2$ were characterized by N$_2$ physical adsorption, in situ XRD, H$_2$-TPR and CO$_2$-TPD.

The surface area, pore volume and pore size of SiO$_2$, Cu/SiO$_2$ and Cu-M/SiO$_2$ were characterized by N$_2$ physical adsorption, as shown in Table 1. After loading active component Cu and metal promoter M, the surface area and pore volume of SiO$_2$ were decreased, due to the large loading amount of Cu and M. However, the average pore diameters of Cu/SiO$_2$ and Cu-M/SiO$_2$ were both larger than that of...
pure supporter SiO₂, which should be due to the preparation method (AE) of Cu/SiO₂ and Cu-M/SiO₂ for the dissolution of partial SiO₂ during the preparation under high temperature (363 K) and basic condition. Then, Si(OH)₄ formed by the dissolution of SiO₂ in the basic solution was further reacted with neutral Cu(OH)₂(H₂O)₄ in solution to form phyllosilicate [31,39].

| Sample       | Surface Area (m²/g) | Pore Volume (cm³/g) | Average Pore Size (nm) | Elemental Composition (wt%) |
|--------------|---------------------|---------------------|------------------------|-----------------------------|
|              |                     |                     |                        | Cu | M               |
| SiO₂         | 167                 | 0.50                | 11.8                   | 0  | 0               |
| Cu/SiO₂      | 117                 | 0.42                | 14.4                   | 19.8 | 0               |
| Cu-Mg/SiO₂   | 108                 | 0.39                | 14.3                   | 18.8 | 3.2             |
| Cu-Ca/SiO₂   | 95                  | 0.33                | 13.9                   | 19.0 | 3.1             |
| Cu-Sr/SiO₂   | 102                 | 0.36                | 14.1                   | 18.9 | 2.9             |
| Cu-Ba/SiO₂   | 99                  | 0.35                | 14.0                   | 19.1 | 2.8             |
| Cu-La/SiO₂   | 112                 | 0.40                | 14.4                   | 18.9 | 3.0             |

In order to investigate the effect of adding alkaline additives on the dispersion of Cu species on the catalyst, in situ XRD characterizations of the calcined catalysts were carried out, and the result was shown in Figure 1. The peak at 2θ = 22.5° is attributed to the amorphous SiO₂, and the peaks at about 2θ = 43.2° and 50.5° are attributed to Cu. By comparing in situ XRD patterns of Cu-M/SiO₂ and Cu/SiO₂, it was found that the peaks of CuO of Cu-M/SiO₂ (M selected from Mg, Ca, Sr or Ba) at 2θ = 43.2° and 50.5° were much sharper than the peaks of Cu/SiO₂ with no alkaline additives, which indicated that adding alkaline additives as Mg, Ca, Sr or Ba led to much larger Cu particles. However, there was no obvious Cu diffraction peaks at 2θ = 43.2° and 50.5° in the in situ XRD patterns of Cu-La/SiO₂ modified by La, suggesting the Cu particles were too small to detect by in situ XRD. This conclusion is consistent with the result of Cu-M/SiO₂ samples detected by XRD in Figure S1. We think that the effect of the reduction process has little effect on the dispersion of Cu/SiO₂ catalyst. Therefore, the Cu dispersion of Cu-La/SiO₂ is higher than that of unmodified Cu/SiO₂. The addition of La increased the dispersion of Cu species on SiO₂, resulting in an increase in the active Cu species per unit area.

![Figure 1](image_url)
H₂-TPR tests of Cu-M/SiO₂ and Cu/SiO₂ were carried out to investigate the changes in the interaction between the active Cu species and the support forces upon the addition of alkaline additives (Figure 2). After the basic additive (except La) was added, the reduction peak of Cu-M/SiO₂ was shifted slightly towards the low temperature. According to the results of in situ XRD analysis, the addition of basic additives (except La) decreased the dispersity of Cu species and increased its particle size, which also reduced the interaction between the Cu particles and the SiO₂ support, leading to a decrease in the reduction temperature of the catalyst when the alkaline additive (except La) was added. However, for Cu-La/SiO₂ catalyst with La additive, the reduction temperature of H₂-TPR was slightly higher than that of unmodified Cu/SiO₂, which suggested that the addition of La enhanced the interaction of Cu species with the SiO₂ support, thus making Cu species more difficult to be reduced. However, for Cu-La/SiO₂ with La promoter, the reduction temperature of H₂-TPR was slightly higher than that of unmodified Cu/SiO₂, which indicated that the addition of La enhanced the interaction between Cu species and carriers and made the Cu species more difficult to be reduced. Similar phenomena have also been found in La modified Cu/SiO₂ investigated by Zheng et al., due to the formation of a Cu-O-La bond at the interface between LaOₓ and Cu species, which improved the stability of the catalyst [40]. In addition, with the characterization of in situ XRD, smaller CuO particles in Cu-La/SiO₂ were detected, and this also led to the stronger interaction between Cu and the carrier, thus increasing the reduction temperature of Cu-La/SiO₂. What is more, the ratio of different catalysts’ peak area is 1.11:0.98:0.94:1.02:1.07:1 for Cu/SiO₂, Cu-La/SiO₂, Cu-Sr/SiO₂, Cu-Mg/SiO₂, Cu-Ca/SiO₂ and Cu-Ba/SiO₂. It means the H₂ consumptions of catalysts are similar.

![Figure 2](image_url)

**Figure 2.** H₂-TPR profiles of the calcined catalysts: (a) Cu/SiO₂; (b) Cu-Mg/SiO₂; (c) Cu-Ca/SiO₂; (d) Cu-Sr/SiO₂; (e) Cu-Ba/SiO₂; (f) Cu-La/SiO₂.

In order to further explore the acid-base property of the catalyst surface after adding basic promoters, the CO₂-TPD of Cu/SiO₂ and Cu-M/SiO₂ catalysts were studied. As shown in Figure 3, both Cu/SiO₂ and Cu-M/SiO₂ catalysts have a significant CO₂ desorption peak at 400–500 K in the CO₂-TPD profiles, and the position and intensity of the desorption peak are very close. However, a CO₂ desorption peak of the Cu-M/SiO₂ catalyst is observed at 500–580 K, and the intensity of the peak is less than that of the main desorption peak at 400–500 K. In CO₂-TPD, the higher the temperature of
desorption peak of CO₂ means the stronger the basicity of the catalyst; therefore, the addition of basic additives really increased the basicity of the catalyst surface. It is also found that the desorption peak of CO₂ from (b) to (f) catalyst shifts slightly towards low temperature, indicating that the basicity of the catalyst surface is Cu-Mg/SiO₂ > Cu-Ca/SiO₂ > Cu-Sr/SiO₂ > Cu-Ba/SiO₂ > Cu-La/SiO₂. The actual order of basicity of the oxides is: MgO < CaO < SrO < BaO < La₂O₃ [41], which is contrary to the basicity of the catalyst surface. The reason should be the basic promoters in the calcined Cu-M/SiO₂ not only exist in the form of oxides, but also may exist in some form similar to Cu-O-M or M-O-Si [42].

![Figure 3. CO₂-TPD profiles of the calcined catalysts: (a) Cu/SiO₂; (b) Cu-Mg/SiO₂; (c) Cu-Ca/SiO₂; (d) Cu-Sr/SiO₂; (e) Cu-Ba/SiO₂; (f) Cu-La/SiO₂.](image)

2.2. Hydrogenation of DMM

The hydrogenation of DMM was carried out in a fixed bed reactor over unmodified Cu/SiO₂ and basic metal modified Cu-M/SiO₂ (M = Mg, Ca, Sr, Ba, La) to evaluate the influence of basic promoters to the catalytic performance of Cu-M/SiO₂ catalysts. The conversion of DMM and the selectivity of the products were shown in Table 2.

| Catalysts         | LHSV (h⁻¹) | DMM Conversion/% | GBL  | BDO  | THF  |
|-------------------|------------|------------------|------|------|------|
| Cu/SiO₂           | 0.3        | 100              | 0    | 0    | 100  |
| Cu/SiO₂           | 0.6        | 100              | 0    | 0    | 100  |
| Cu/SiO₂           | 0.9        | 83.65            | 0    | 0    | 100  |
| Cu-Mg/SiO₂        | 0.3        | 84.21            | 24.43| 4.82 | 70.75|
| Cu-Ca/SiO₂        | 0.3        | 88.38            | 27.42| 0    | 72.58|
| Cu-Sr/SiO₂        | 0.3        | 83.17            | 32.17| 3.43 | 64.40|
| Cu-Ba/SiO₂        | 0.3        | 64.21            | 25.43| 5.01 | 69.56|
| Cu-La/SiO₂        | 0.3        | 100              | 24.54| 4.29 | 71.17|

Reaction conditions: T = 513 K, p = 5 MPa, and H₂/ester = 50.

The conversion rate of DMM reached 100% over the unmodified Cu/SiO₂ catalyst showed its good activity, and THF as the only hydrogenated product was observed for the weak alkalinity of the Cu/SiO₂ surface. What is more, when Cu/SiO₂ exhibits low activity in high LHSV, the THF selectivity...
still maintains 100%. Therefore, we think high LHSV has little effect on selectivity. After the basic additive (except La) was added to Cu/SiO₂ catalyst, the catalytic activity decreased significantly for the conversion of DMM over Cu-M/SiO₂ (M = Mg, Ca, Sr, Ba) did not reach 100%, especially the conversion over Cu-Ba/SiO₂ just 64.21%. However, the catalytic activity of La modified Cu-La/SiO₂ was higher, and the conversion rate of DMM was also 100%.

The activity of Cu-M/SiO₂ (M = Mg, Ca, Sr, Ba, La) in the hydrogenation of DMM should be related to the dispersion of Cu on the surface of Cu-M/SiO₂. The higher dispersion of Cu on Cu-La/SiO₂ led to the higher catalytic activity for the hydrogenation of DMM, and the other Cu-M/SiO₂ (M = Mg, Ca, Sr, Ba) with the lower dispersion of Cu than that of unmodified Cu/SiO₂ catalyst caused that DMM had not been completely converted under the same reaction condition. The addition of basic promoter to Cu/SiO₂ catalyst varied the selectivity of the hydrogenation products. There was just THF as the only product during the hydrogenation of DMM over the unmodified Cu/SiO₂. After modified by basic promoter, the selectivity of THF decreased, and more GBL was obtained. In addition, a small amount of BDO was generated. One possible reason for the low selectivity of THF over modified catalysts was the covering of the part of the acid sites on the surface of SiO₂ by the basic additives leading to the weakening of the dehydration of BDO to THF under acidic conditions. Moreover, we have tested the Cu-La/SiO₂ catalyst for 100 h stability test. As shown in Table 3, We found the catalyst still maintain stable activity and selectivity.

Table 3. The influence of time on the Cu-La/SiO₂ catalytic performance.

| Reaction Time (h) | DMM Conversion (%) | GBL (%) | BDO (%) | THF (%) |
|------------------|--------------------|---------|---------|---------|
| 0                | 100                | 24.54   | 4.29    | 71.17   |
| 5                | 100                | 25.12   | 4.04    | 70.84   |
| 10               | 100                | 24.98   | 4.16    | 70.86   |
| 15               | 100                | 24.67   | 4.28    | 70.05   |
| 20               | 100                | 24.38   | 4.35    | 71.27   |
| 25               | 100                | 24.87   | 4.31    | 70.82   |
| 30               | 100                | 25.22   | 4.17    | 70.61   |
| 35               | 100                | 25.16   | 4.42    | 70.42   |
| 40               | 100                | 24.45   | 4.55    | 71      |
| 45               | 100                | 24.23   | 4.26    | 71.51   |
| 50               | 100                | 24.79   | 4.13    | 71.08   |
| 55               | 100                | 25.72   | 4.59    | 69.69   |
| 60               | 100                | 25.48   | 4.26    | 70.26   |
| 65               | 100                | 25.56   | 4.37    | 70.07   |
| 70               | 100                | 24.94   | 4.14    | 70.92   |
| 75               | 100                | 24.42   | 4.3     | 71.28   |
| 80               | 100                | 24.1    | 4.17    | 71.73   |
| 85               | 100                | 23.87   | 4.46    | 71.67   |
| 90               | 100                | 24.71   | 4.58    | 70.71   |
| 95               | 100                | 25.66   | 4.27    | 70.07   |
| 100              | 100                | 25.34   | 4.33    | 70.33   |

Reaction conditions: T = 513 K, p = 5 MPa, LHSV = 0.3 h⁻¹ and H₂/ester = 50.

3. Experimental

3.1. Catalysts Preparation

Preparation of Cu/SiO₂: 3.78 g Cu(NO₃)₂·3H₂O was dissolved in 40 mL deionized water, and stirred at room temperature for 10 min until it is completely dissolved, then 11.5 mL ammonia (28 wt%) was added to obtain the solution of copper ammonia with stirring for 30 min. Added 4 g SiO₂ into the solution and stirred for 240 min. The mixture was quickly moved to the oil bath at 363 K to evaporate ammonia until the pH to 6.5, and then it was cooled to room temperature and filtered. The filter
cake was washed by deionized water for three times followed with drying at 393 K for 480 min and calcination at 723 K for 240 min. The final catalyst was denoted as 25 wt% Cu/SiO₂.

Preparation of Cu-M/SiO₂: A certain amount of M nitrate (M selected from Mg, Ca, Sr, Ba, or La) containing M 0.2 g was dissolved in 40 mL deionized water. 4 g SiO₂ was added into the solution. The mixture was filtered after had been stirred for 600 min, followed by drying at 393 K for 480 min and calcination at 723 K for 240 min. The modified carrier was denoted as M/SiO₂. 3.78 g Cu(NO₃)₂·3H₂O was dissolved in 40 mL deionized water, and stirred at room temperature for 10 min until it is completely dissolved, then 11.5 mL ammonia (28 wt%) was added to obtain the solution of copper ammonia with stirring for 30 min. Added the above made M/SiO₂ into the solution and stirred for 240 min. The mixture was quickly moved to the oil bath at 363 K to evaporate ammonia until the pH to 6.5, and then it was cooled to room temperature and filtered. The filter cake was washed by deionized water for three times followed with drying at 393 K for 480 min and baking at 723 K for 240 min. The final catalyst was denoted as 25wt% Cu-5wt% M/SiO₂.

3.2. Catalyst Characterization

N₂ physical adsorption: The surface area, pore volume and pore diameter of the catalyst were determined by N₂ physical adsorption at 77 K using Micromeritics ASAP 2020 (Micromeritics, Hangzhou, China). Firstly, the sample was heated to 573 K under vacuum condition for 6 h to remove the adsorbed species, and then N₂ physical adsorption isotherm was performed. The surface area of the sample was calculated by the BET equation, and the pore volume and pore size distribution of the catalyst were obtained by BJH theory.

In situ XRD: X-ray powder diffraction patterns of the samples were obtained in the scanning angle (2θ) range of 10–80° under H₂/Ar atmosphere at 573 K on a Thermo ARL SCINTAG X-TRA (Thermo, Hangzhou, China) using Cu Kα1 radiation (λ = 1.5406 Å) operated at 40 kV and 40 mA. Because of the in situ measurement system, the peak positions had some fluctuations compared with Standard XRD patterns.

The elemental content of the catalysts was detected using XRF (Thermo ARL ADVANT’X, Thermo, Hangzhou, China).

H₂ temperature-programed reduction (H₂-TPR)—0.1 g calcined catalyst was loaded into a quartz tube, and then a mixture of 5% H₂/Ar was passed into the tube with the flow rate at 30 mL/min, while the exhaust gas was detected by a thermal conductivity detector (TCD). After the baseline was stable, the following heating program was carried out: retaining at 303 K for 10 min, and then rising to 1123 K for 82 min.

CO₂ temperature-programed desorption (CO₂-TPD)—0.1 g calcined catalyst was loaded into a U-tube, and treated at 723 K for 1 h in an Ar atmosphere to remove the adsorbed species. Then the temperature dropped to 373 K, and CO₂ was passed into the U-tube. After CO₂ adsorbed at 373 K for 30 min, the atmosphere was switched to Ar, and the exhaust gas was detected by a mass spectrum (MS). After the baseline was stable, the following heating program was carried out: rising to 773 K from 373 K for 40 min, and then retaining at 773 K for 10 min.

3.3. Hydrogenation Reaction

The hydrogenation reaction was carried out in a fixed bed reactor (Tianjin Pengxiang Technology Co. Ltd., Tianjin, China) with the diameter of 10 mm and the length of 500 mm and the constant temperature zone length ≥100 mm. The catalyst (20–40 mesh) was loaded into the middle of the constant temperature zone, and activated at 573 K with H₂ (30 mL/min) for 240 min. Then the temperature dropped to 513 K. H₂ was introduced up to the desired pressure for 5 MPa and the raw material (20 vol% DMM in methanol) was pumped into a vaporizer using a high-pressure pump (Series II), and then reacted with H₂. The reaction products were quantitatively analyzed by gas chromatography (Agilent, GC, 7890A, Santa Clara, CA, USA) with DB-1 chromatographic column and FID (flame ionization detector) detector. In the reaction, methane and methol are also generated. However, methane was not
detected in the reaction products, and therefore, the methoxy groups of DMM were probably converted to methanol. However, quantification of methanol was not possible because methanol was used as a solvent.

4. Conclusions

By comparing our previous work, Cu-M/SiO\(_2\) catalysts were modified by basic promoters (M = Mg, Ca, Sr, Ba, La) to improve the basicity of the surface of catalysts. After modification of the basic promoters, such as Mg, Ca, Sr and Ba, the diameter of CuO particles on the Cu-M/SiO\(_2\) catalyst increased, that is, the dispersion of Cu was reduced. On the contrary, adding La promoter reduced the CuO particle and improved the dispersion of CuO on SiO\(_2\). The selectivity of the hydrogenation products was modified during the continuous hydrogenation of DMM over Cu-M/SiO\(_2\) catalysts, due to the addition of basic promoters, which accelerated the dehydrogenation of BDO to more GBL in the basic active sites.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/9/704/s1, Figure S1: X-ray diffraction patterns of the calcined catalysts: (a) Cu/SiO\(_2\); (b) Cu-Mg/SiO\(_2\); (c) Cu-Ca/SiO\(_2\); (d) Cu-Sr/SiO\(_2\); (e) Cu-Ba/SiO\(_2\); (f) Cu-La/SiO\(_2\).

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References

1. Muller, S.P.; Kucher, M.; Ohlinger, C.; Kraushaar-Czarnetzki, B. Extrusion of Cu/ZnO catalysts for the single-stage gas-phase processing of dimethyl maleate to tetrahydrofuran. J. Catal. 2003, 218, 419–426. [CrossRef]
2. Ohlinger, C.; Kraushaar-Czarnetzki, B. Improved processing stability in the hydrogenation of dimethyl maleate to gamma-butyrolactone, 1,4-butanediol and tetrahydrofuran. Chem. Eng. Sci. 2003, 58, 1453–1461. [CrossRef]
3. Zellmer, D.; Niewa, R.; Kreher, R.P. A functionalized dimethyl maleate (maleic acid dimethyl ester). Acta Cryst. 2014, 55, 823–825. [CrossRef]
4. Emig, G.; Martin, F. Economics of maleic anhydride production from C-4 feedstocks. Catal. Today 1987, 1, 477–498. [CrossRef]
5. Centi, G.; Trifiro, F.; Ebner, J.R.; Franchetti, V.M. Mechanistic aspects of maleic anhydride synthesis from C4 hydrocarbons over phosphorus vanadium oxide. Chem. Rev. 1988, 88, 55–80. [CrossRef]
6. Wang, L.; Abudukelimu, N.; Ma, Y.B.; Qing, S.; Gao, Z.; Wumanjiang, E. Catalytic performance of Fe-modified Ru/Al\(_2\)O\(_3\) in the hydrogenation of dimethyl maleate. J. Fuel Chem. Technol. 2014, 42, 839–844.
7. Guo, P.J.; Chen, L.F.; Yan, S.R.; Dai, W.L.; Qiao, M.H.; Xu, H.L.; Fan, K.N. One-step hydrogenolysis of dimethyl maleate to tetrahydrofuran over chromium-modified Cu-B/γ-Al\(_2\)O\(_3\) catalysts. J. Mol. Catal. A Chem. 2006, 256, 164–170. [CrossRef]
8. Pritchard, J.; Filonenko, G.A.; van Putten, R.; Hensen, E.J.M.; Pidko, E.A. Heterogeneous and homogeneous catalysis for the hydrogenation of carboxylic acid derivatives: History, advances and future directions. Chem. Soc. Rev. 2015, 44, 3808–3833. [CrossRef] [PubMed]
9. Luo, Z.C.; Bing, Q.M.; Kong, J.C.; Liu, J.Y.; Zhao, C. Mechanism of supported Ru3Sn7 nanocluster-catalyzed selective hydrogenation of coconut oil to fatty alcohols. Catal. Sci. Technol. 2018, 8, 1322–1332. [CrossRef]
10. Kuwahara, Y.; Kaburagi, W.; Fujitani, T. Catalytic transfer hydrogenation of levulinate esters to gamma-valerolactone over supported ruthenium hydroxide catalysts. RSC Adv. 2014, 4, 45848–45855. [CrossRef]
11. Fang, X.L.; Zhang, C.Y.; Chen, J.; Zhu, H.P.; Yuan, Y.Z. Synthesis and catalytic performance of ruthenium complexes ligated with rigid o-(diphenylphosphino)aniline for chemoselective hydrogenation of dimethyl oxalate. RSC Adv. 2016, 6, 45512–45518. [CrossRef]
12. Stathis, P.; Stavroulaki, D.; Kaika, N.; Krommyda, K.; Papadogianakis, G. Low trans-isomers formation in the aqueous-phase Pt/TPPTS-catalyzed partial hydrogenation of methyl esters of linseed oil. *Appl. Catal. B Environ.* 2017, 209, 579–590. [CrossRef]

13. Numwong, N.; Luengnaruemitchai, A.; Chollacoop, N.; Yoshimura, Y. Partial hydrogenation of polyunsaturated fatty acid methyl esters over Pd/activated carbon: Effect of type of reactor. *Chem. Eng. J.* 2012, 210, 173–181. [CrossRef]

14. Pérez-Cadenas, A.F.; Kapteijn, F.; Zievelink, M.M.P.; Moulijn, J.A. Selective hydrogenation of fatty acid methyl esters over palladium on carbon-based monoliths: Structural control of activity and selectivity. *Catal. Today* 2007, 128, 13–17. [CrossRef]

15. Li, F.; Lu, C.S.; Li, X.N. The effect of the amount of ammonia on the Cu$^0$/Cu$^+$ ratio of Cu/SiO$_2$ catalyst for the hydrogenation of dimethyl oxalate to ethylene glycol. *Chin. Chem. Lett.* 2014, 25, 1461–1465. [CrossRef]

16. Huang, H.; Cao, G.; Wang, S. An evaluation of alkylthiols and dialkyl disulfides on deactivation of Cu/Zn catalyst in hydrogenation of dodecyl methyl ester to dodecanol. *J. Ind. Eng. Chem.* 2014, 20, 988–993. [CrossRef]

17. Gong, J.; Yue, H.; Zhao, Y.; Zhao, S.; Zhao, L.; Lv, J.; Wang, S.; Ma, X. Synthesis of Ethanol via Syngas on Cu/SiO$_2$ Catalysts with Balanced Cu$^0$–Cu$^+$ Sites. *J. Am. Chem. Soc.* 2012, 134, 13922–13925. [CrossRef]

18. Ma, X.; Yang, Z.; Liu, X.; Tan, X.; Ge, Q. Dynamic redox cycle of Cu$^0$ and Cu$^+$ over Cu/SiO$_2$ catalyst in ester hydrogenation. *RSC Adv.* 2015, 5, 37581–37584. [CrossRef]

19. Zhang, Q.; Li, K.; Xiang, Y.; Zhou, Y.; Wang, Q.; Guo, L.; Ma, L.; Xu, X.; Lu, C.; Feng, F.; et al. Sulfur-doped porous carbon supported palladium catalyst for high selective o-chloronitrobenzene hydrogenation. *Appl. Catal. A Gen.* 2019, 581, 74–81. [CrossRef]

20. Sadjadi, S. Palladium nanoparticles immobilized on cyclodextrin-decorated halloysite nanotubes: Efficient heterogeneous catalyst for promoting copper- and ligand-free Sonogashira reaction in water–ethanol mixture. *Appl. Organomet. Chem.* 2018, 32. [CrossRef]

21. Brands, D.S.; Poels, E.K.; Bliek, A. Ester hydrogenolysis over promoted Cu/SiO$_2$ catalysts. *Appl. Catal. A Gen.* 1999, 184, 279–289. [CrossRef]

22. Toupanece, P.; Kermarec, M.; Louis, C. Metal Particle Size in Silica-Supported Copper Catalysts. Influence of the Conditions of Preparation and of Thermal Pretreatments. *J. Phys. Chem. B* 2004, 108, 965–972. [CrossRef]

23. Munnik, P.; Wolters, M.; Gabrielson, A.; Pollington, S.D.; Headock, G.; Bitter, J.H.; de Jongh, P.E.; de Jong, K.P. Copper Nitrate Redispersion To Arrive at Highly Active Silica-Supported Copper Catalysts. *J. Phys. Chem. C* 2011, 115, 14698–14706. [CrossRef]

24. Shimokawabe, M.; Takezawa, N.; Kobayashi, H. Characterization of copper-silica catalysts prepared by ion exchange. *Appl. Catal. B* 1992, 2, 379–387. [CrossRef]

25. Kohler, M.A.; Curry-Hyde, H.E.; Hughes, A.E.; Sexton, B.A.; Cant, N.W. The structure of CuSiO$_2$ catalysts prepared by the ion-exchange technique. *J. Catal.* 1987, 108, 323–333. [CrossRef]

26. Shi, L.; Zeng, C.; Jin, Y.; Wang, T.; Tsubaki, N. A sol–gel auto-combustion method to prepare Cu/ZnO catalysts for low-temperature methanol synthesis. *Catal. Sci. Technol.* 2012, 2, 2569–2577. [CrossRef]

27. Ye, R.P.; Lin, L.; Chen, C.C.; Yang, J.X.; Li, F.; Zhang, X.; Li, D.J.; Qin, Y.Y.; Zhou, Z.; Yao, Y.G. Synthesis of Robust MOF-Derived Cu/SiO$_2$ Catalyst with Low Copper Loading via Sol–Gel Method for the Dimethyl Oxalate Hydrogenation Reaction. *ACS Catal.* 2018, 8, 3382–3394. [CrossRef]

28. Kasinathana, P.; Hwang, D.W.; Lee, U.H.; Hwang, Y.K.; Chang, J.S. Effect of Cu particle size on hydrogenation of dimethyl succininate over Cu-SiO$_2$ nanocomposite. *Catal. Commun.* 2013, 41, 17–20. [CrossRef]

29. Miyazaki, H.; Hirai, K.; Uda, T.; Nakamura, Y.; Ikezawa, H.; Tsuchie, T. Process for Producing Ethylene Glycol and/or Glycolic Acid Ester, Catalyst Composition Used Therefor, and Process for the Production of This Composition. Patent EP0064241A1, 4 September 1985.

30. Chen, L.F.; Guo, P.J.; Qiao, M.H.; Yan, S.R.; Li, H.X.; Shen, W.; Xu, H.L.; Fan, K.N. Cu/SiO$_2$ catalysts prepared by the ammonia-evaporation method: Texture, structure, and catalytic performance in hydrogenation of dimethyl oxalate to ethylene glycol. *J. Catal.* 2008, 257, 172–180. [CrossRef]

31. Han, X.Q.; Zhang, Q.F.; Feng, F.; Lu, C.S.; Ma, L.; Li, X.N. Selective hydrogenation of dimethyl maleate to tetrahydrofuran over Cu/SiO$_2$ catalyst: Effect of Cu$^+$ on the catalytic performance. *Chin. Chem. Lett.* 2015, 26, 1150–1154. [CrossRef]

32. Yin, A.; Wen, C.; Guo, X.; Dai, W.L.; Fan, K. Influence of Ni species on the structural evolution of Cu/SiO$_2$ catalyst for the chemoselective hydrogenation of dimethyl oxalate. *J. Catal.* 2011, 280, 77–88. [CrossRef]
33. Ungureanu, A.; Dragoi, B.; Chirieac, A.; Royer, S.; Duprez, D.; Dumitriu, E. Synthesis of highly thermostable copper-nickel nanoparticles confined in the channels of ordered mesoporous SBA-15 silica. *J. Mater. Chem.* 2011, 21, 12529–12541. [CrossRef]

34. He, Z.; Lin, H.; He, P.; Yuan, Y. Effect of boric oxide doping on the stability and activity of a Cu–SiO$_2$ catalyst for vapor-phase hydrogenation of dimethyl oxalate to ethylene glycol. *J. Catal.* 2011, 277, 54–63. [CrossRef]

35. Zhao, S.; Yue, H.; Zhao, Y.; Wang, B.; Geng, Y.; Lv, J.; Wang, S.; Gong, J.; Ma, X. Chemoselective synthesis of ethanol via hydrogenation of dimethyl oxalate on Cu/SiO$_2$: Enhanced stability with boron dopant. *J. Catal.* 2013, 297, 142–150. [CrossRef]

36. Zhu, S.; Gao, X.; Zhu, Y.L.; Zhu, Y.F.; Zheng, H.; Li, Y. Promoting effect of boron oxide on Cu/SiO$_2$ catalyst for glycerol hydrogenolysis to 1,2-propanediol. *J. Catal.* 2013, 277, 54–63. [CrossRef]

37. Wang, L.; Abudukelimu, N.; Ma, Y.; Qing, S.; Gao, Z.; Eli, W. Enhanced Ru/Alumina catalyst via the adsorption-precipitation (AP) method for the hydrogenation of dimethyl maleate. *React. Kinet. Mech. Catal.* 2014, 112, 117–129. [CrossRef]

38. Chen, L.; Guo, P.; Zhu, L.; Qiao, M.; Shen, W.; Xu, H.; Fan, K. Preparation of Cu/SBA-15 catalysts by different methods for the hydrogenolysis of dimethyl maleate to 1,4-butanediol. *Appl. Catal. A Gen.* 2009, 356, 129–136. [CrossRef]

39. Van Der Grift, C.J.G.; Elberse, P.A.; Mulder, A.; Geus, J.W. Preparation of silica-supported copper catalysts by means of deposition-precipitation. *Appl. Catal.* 1990, 59, 275–289. [CrossRef]

40. Zheng, X.; Lin, H.; Zheng, J.; Duan, X.; Yuan, Y. Lanthanum Oxide-Modified Cu/SiO$_2$ as a High-Performance Catalyst for Chemoselective Hydrogenation of Dimethyl Oxalate to Ethylene Glycol. *ACS Catal.* 2013, 3, 2738–2749. [CrossRef]

41. Zhang, G.; Hattori, H.; Tanabe, K. Aldol Addition of Acetone, Catalyzed by Solid Base Catalysts: Magnesium Oxide, Calcium Oxide, Strontium Oxide, Barium Oxide, Lanthanum (III) Oxide and Zirconium Oxide. *Appl. Catal.* 1988, 36, 189–197. [CrossRef]

42. Zhang, B.; Zhu, Y.; Ding, G.; Zheng, H.; Li, Y. Modification of the supported Cu/SiO$_2$ catalyst by alkaline earth metals in the selective conversion of 1,4-butanediol to γ-butyrolactone. *Appl. Catal. A Gen.* 2012, 443–444, 191–201. [CrossRef]