Selective conversion of furfural to cyclopentanone or cyclopentanol using different preparation methods of Cu–Co catalysts†

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Cu–Co catalysts, prepared by a co-precipitation method (CP) and an oxalate sol–gel method (OG), can selectively convert furfural (FFA) to cyclopentanone (CPO) or cyclopentanol (CPL), respectively. The conversion of FFA to CPO or CPL by Cu–Co catalysts were studied in aqueous solutions. We found that the product distribution was influenced by the catalyst support, Cu loading, calcination temperature, hydrogen pressure, the number of times the catalyst was reused and the preparation method of the catalyst. The surface morphology, surface area and composition of the catalysts were studied by XRD, XPS, BET, ICP-AES and TEM characterization. We found that there was a strong interaction between Cu and Co. Cu0, Cu2O and Co0 were the main active catalyst phases on the surfaces of the catalysts, but the amounts were different in the different catalysts. Cu2O, Co2 and Cu2O were the active hydrogenation species, and Cu2O also played the role of an electrophile or Lewis acid to polarize the C=O bond via lone pair electrons on the oxygen atom. According to XRD and XPS, the main phases on the surface of the CP catalysts were Cu0 and Cu2O. The hydrogenation activity of the CP catalyst was relatively weak and the main product was CPO. In contrast, the hydrogenation activity of the OG catalyst was high and the main product was the fully hydrogenated product CPL due to the main active phases of Co0 and Cu2O on the surface of the OG catalyst. At lower hydrogen pressure (2 MPa) and lower Cu loadings (2% for OG, 5% for CP), we obtained the highest yield of 67% CPO and 68% CPL, respectively.

1. Introduction

Efficient utilization of renewable biomass resources has become more and more attractive with the ever growing consumption of the non-recoverable fossil fuels. Biomass, as a unique renewable resource, can be converted into conventional liquids, solids, gases, fuels and other chemicals.1 Industrial applications of biomass are based on improving the competitiveness for biomass resources, developing preparation methods for inexpensive platform molecules and efficiently transferring platform molecules to fuels and chemicals.2

Furfural (FFA), an important platform molecule, can be obtained from hemicellulose in lignocellulosic biomass,3 and can be further transformed into a series of liquid fuels,4 fuel additives and other chemicals like furfuryl alcohol (FOL), tetrahydro-furfuryl alcohol (THFOL), 2-methyl tetrahydrofuran (MTHF),5 2-methyl furan (MF),6 isoprene, pentanediol, levulinic acid, etc. Currently, FFA is mainly used for the production of furfuryl alcohol, however its use in developing other downstream industrial products is limited. Thus, further research to expand the utilization of FFA is not only fundamentally important, but also practically necessary.

Cyclopentanone (CPO) and cyclopentanol (CPL) are fine chemical raw materials and have been widely used as solvents and starting materials for the synthesis of useful products (Scheme 1). For example, CPO and CPL have been used to prepare Jasmine family fragrances and drug materials. In addition, CPO has been widely used as a solvent in the electronics industry because it can easily solubilise various resins. Cyclopentyl methyl ether and cyclopentyl ethyl ether, which have high hydrophobicity characteristics, low latent heats of solvent evaporation, difficulties forming peroxides, are easy to dry, etc., have been used as solvents for Grignard reactions, coupling reactions and other important chemical reactions.7 The demand of CPO and CPL are a million tons per year.
Therefore, it would be highly valuable if CPO and CPL can be efficiently prepared from biomass-based FFA.

Hronec et al. reported 81.32% total yield of CPO and CPL by using a 5% Pt/C catalyst at 433 K and 8 MPa H2 pressure. Later, Hronec et al. indicated that the key intermediate was 3-hydroxy-4-cyclopentenone. In 2013, Hronec et al. reported that the main reaction product was CPO, instead of the more stable CPL, due to oligomers on the surface of the catalyst at 448 K and 4 MPa H2. Additionally, Xu et al. obtained 62% yield of CPO by using a NiCu-50/SBA-15 catalyst at 433 K and 8 MPa H2. In contrast, the three key intermediates identified were furfuryl alcohol (FOL), 4-hydroxy-2-cyclopentenone and 2-cyclopentenone (2-CPEO). Nijhuis et al. obtained 16% CPO and 11% CPL by using Amberlyst-15 and Ru/C catalysts to catalyze the dehydration of xylose and the hydrogenation of FFA in a biphasic system. Hronec et al. then considered that there are two parallel reactions, including H+ ion catalysis generated by the decomposition of water and metal catalysis, in the rearrangement reaction. Xiao et al. reported 93.4% yield of CPL using a (Cu + Mg)/Al catalyst at 4 MPa H2 for 10 h, but the catalyst was severely deactivated after reusing it two times. Xiao et al. then used 30 wt% Ni/CNTs for the conversion of FFA to CPL. Ohyama et al. reported the conversion of 5-hydroxymethyl furfural to a cyclopentanone derivative by ring rearrangement over supported Au nanoparticles.

The rearrangement reactions of FFA to CPO and CPL still have many problems such as the use of expensive supported metals, high hydrogen pressures, long reaction times and low catalyst reusability. Cu catalysts are favorable for the selective hydrogenation of FFA to furfuryl alcohol due to their ability to strongly polarize the C=O bond whilst leaving the furan ring unaffected. It is well known that furfuryl alcohol is a key intermediate in the rearrangement reaction and its yield directly affects the yield of the final products. Co catalysts have a strong hydrogenation capability and a good ring closing ability in the synthesis of five membered rings. It is more attractive to use inexpensive Cu-Co catalysts than other supported noble metals.

Herein, we prepared a series of Cu–Co catalysts by different methods and found that CPO and CPL could be obtained selectively over CP catalysts and OG catalysts, respectively. We have studied the effects of different catalyst supports, Cu loadings, calcination temperatures, hydrogen pressures, the number of times the catalyst was reused and the preparation methods of the catalysts on the rearrangement reaction. The surface morphology, surface area and composition of the catalysts were studied by XRD, XPS, BET, ICP-AES and TEM characterization.

2. Experimental
2.1 Materials and reagents
Cu(NO3)2·3H2O (AR, >99%), Co(NO3)2·6H2O (AR, >99%), NaOH (AR, >96%), Na2CO3 (AR, >99.8%), anhydrous ethanol (AR, >99.7%), FFA (AR, >99%), furfuryl alcohol (CP, >98.5%), tetrahydrofurfuryl alcohol (CP, >98%), N,N-dimethylformamide (AR, >94%), CPL (CP, >97%) and CPO (CP, >97%) were purchased from Sinopharm group Co. Ltd. 2-Cyclopentenone (2-CPEO) was purchased from J&K Chemicals. Pure water was purchased from Wahaha, Hangzhou. FFA was used without further purification.

2.2 Catalyst preparation
A 20% Cu–Co-CP-500 catalyst was prepared by a co-precipitation method. 200 mL of an aqueous solution containing 4.78 g of sodium hydroxide and 6.34 g of sodium carbonate was slowly added into 200 mL of an aqueous solution containing 3.02 g of nitrate copper and 11.6 g of nitrate cobalt at room temperature until the pH of the solution was about 10–11. The catalyst was filtered after stirring at 353 K for 12 h. The precursors were then washed with water until pH = 7 and dried at 383 K overnight. The precursors were calcined at 773 K under air and the heating rate was 2 °C min⁻¹. The oxides were reduced at 473 K for 3 h and the gas composition was H2 : N2 (10 : 90), 100 mL min⁻¹. A similar method was used for preparing 5% Pd/Co3O4, 20% Ni/Co3O4, 5% Pd/MnOx, 30% Cu/ZrO2 and other Cu–Co-CP catalysts with different Cu loadings and calcination temperatures.

A 30% Cu–Co-OG-500 catalyst was prepared by a sol–gel method. 5.4 g of cobalt nitrate, 2.4 g of copper nitrate and 100 mL of ethanol were added into a 500 mL beaker. Then 100 mL of ethanol containing 4.3 g of dissolved oxalic acid was added under rapid stirring. The reaction liquid was left overnight after stirring for 4 h at room temperature. The precipitate was filtered, washed with ethanol several times and dried at 383 K overnight. The precursors were calcined at 773 K under air and the heating rate was 2 °C min⁻¹. The oxides were reduced at 473 K for 3 h and the gas composition was H2 : N2 (10:90), 100 mL min⁻¹. A similar method was used for preparing 30% Cu/ZrO2 and other Cu–Co-OG catalysts with different Cu loadings and calcination temperatures.

Cu/HZSM-5 was prepared by an impregnation method. 3.8 g of copper nitrate was dissolved in 5 mL of water. Then 9 g of HZSM-5 (Si/Al = 50) were added in batches under stirring. The precursors were calcined at 823 K for 6 h after drying for 8 h. The oxides were reduced at 553 K for 4 h and the gas composition was H2 : N2 (10 : 90), 100 mL min⁻¹.
2.3 Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) surface area analysis, transmission electron microscopy (TEM) and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.4 Typical experiment and product analysis

Studies on the rearrangement reaction were performed in a 25 mL autoclave (Hastelloy, Parr Instrument). In a typical experiment, 2 mmol of furfural, 50 mg of catalyst and 10 mL of H$_2$O were added into the autoclave. The autoclave was sealed, purged with H$_2$ four times, and then pressurized with H$_2$ to the required pressure. The autoclave was heated to the required temperature and the reaction was left for the required time (Fig. S6, ESI†). After the required time, the reactor was cooled and the solution was transferred with 20 mL of ethanol. A certain amount of N,N-dimethylformamide (DMF) was then added as an internal standard substance. The samples were analyzed by GC (Shimadzu GC-2-14C, FID) with a DM-WAX column (30 m × 0.32 mm × 0.25 µm) and GC-MS (Thermal Trace GC Ultra with a Polaris Q ion trap mass spectrometer equipped with a TR-5MS capillary column). The conversion of FFA and the yield of products were calculated using the following formula:

\[ \text{Conv} \, (\%) = \left( \frac{n_{\text{FFA}} - n'_{\text{FFA}}} {n_{\text{FFA}}} \right) \times 100\% \]

\[ Y(\%) = \left( \frac{\text{mole of product}} {n_{\text{FFA}}} \right) \times 100\% \]

where $n_{\text{FFA}}$ is the number of moles of FFA before the reaction, and $n'_{\text{FFA}}$ is the number of moles of FFA after the reaction.

3. Results and discussion

We firstly studied the effects of different metal centers and supports on the conversion of FFA to CPO and CPL. The main products of THFOL, FOL, 2-CPEO, CPO and CPL were determined and are presented in Table 1. The conversion of FFA was almost 100% for all samples except for entry 4 (86%). This may be due to oligomers, formed by the oligomerization of furfuryl alcohol under acidic conditions (HZSM-5), on the surface of the catalyst, which reduced the activity of the catalyst.$^{15,19}$ This resulted in a lower conversion rate of FFA and lowered the total yield of CPO and CPL. The main product was THFOL over supported Pd catalysts (entries 1 and 3). This is attributed to the high hydrogenation activity of Pd metal. Due to the unaffected furan ring and the easier hydrogenation of the aldehyde C==O bond to an alcohol, the total yield of CPO and CPL was higher using the supported Cu catalysts (entries 5–8) compared to the other samples.$^{20}$ Improving the selectivity of FOL is helpful for improving the yield of the final products. The product selectivity was not high over the Cu/ZrO$_2$ catalysts (entries 5 and 6). CPO and CPL can be obtained selectively over the Cu–Co catalysts prepared by the co-precipitation method and the sol–gel method, respectively. Monometallic Cu or Co as the catalyst for the hydrogenation conversion of FFA were also tested (Table S2†). The results show that the yield and selectivity of the products were less satisfactory when using a single metal as the catalyst compared to using Cu–Co catalysts. This indicates that the strong interaction between Cu and Co is the cause of the high selectivity.

We also investigated the influence of experimental conditions on the product distribution over different Cu–Co catalysts.

### 3.1 Effect of reaction temperature

The effect of reaction temperature on the product distribution for the hydrogenation rearrangement of FFA over the 5% Cu–Co-OG-500 catalyst was determined and is presented in Fig. 1(a). Under the reaction conditions, the conversion of FFA for all samples was greater than 98%. The major products were FOL, CPO, CPL and THFOL. The highest yield of CPL (64%) was obtained with only 3% CPO using the reaction conditions of 443 K, 1 h and 2 MPa H$_2$. The total yield of CPO and CPL persisted to increase along with the increased temperature, especially from 413 K to 433 K. The reason may be due to the H$^+$ ions, which were promoted by the high temperature and were produced from water dissociation. H$^+$ ions play a key role in the protonation of FOL and this is a key step in the rearrangement of FFA.$^9$ We found that the yield of CPO

<table>
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<th>Cat.</th>
<th>C-FFA/%</th>
<th>Yield/%</th>
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<tr>
<td></td>
<td></td>
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<td>8</td>
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*Reaction conditions: 2 mmol FFA, 0.1 g catalyst, 10 mL H$_2$O, 6 h, 423 K, 4 MPa H$_2$, mole yield. *Catalysts were prepared by the sol–gel method.
increased again when the temperature was over 443 K. Oligomers attached on the surface of the catalyst reduce the hydrogenation activity of the catalyst and this may bring about this result. The yield of CPL increased and then reduced when the temperature increased from 433 K to 453 K. Continuing to increase the temperature from 453 K to 473 K, the yield of CPL reduced and then increased. The reasons for this are subject to further research.

Compared to Fig. 1(a), Fig. 1(b) shows the effect of temperature on the product distribution using the 5% Cu–Co-CP-500 catalyst. FFA converted almost completely at all temperatures. The main products were FOL and CPO at lower temperatures and the yield of CPO was only 40%. About 26% FOL was detected at 413 K. This suggests that H⁺ ions, generated by the dissociation of water, were too weak to protonate FOL at lower temperatures. The highest yield of CPO (67%) was achieved at 443 K. The yield of CPO decreased with increasing temperature from 443 K to 473 K, the yield of CPL reduced and then increased. The reasons for this are subject to further research.

3.2 Effect of hydrogen pressure

The product distributions using the 5% Cu–Co-OG-500 catalyst at varying hydrogen pressures were determined and are presented in Fig. 2(a). The conversion of FFA was low (only 33%) and the main product was FOL at atmospheric pressure of hydrogen (0.1 MPa H₂). A mixture of CPO and CPL was obtained at 1 MPa H₂. By further increasing the pressure, the yield of CPL increased and then decreased. We considered that the intermediates and products further hydrogenated into other products at higher hydrogen pressure. This speculation can be partly proved through the increased yield of THFOL. Incidentally, the conversion of FFA was more than 97% under all pressures except for 0.1 MPa. The highest yield of CPL was 64% at 2 MPa H₂.

Fig. 2(b) shows the product distribution using the 5% Cu–Co-CP-500 catalyst at varying hydrogen pressures. The main products were CPO, FOL and 2-CPEO at 1 MPa H₂. The highest yield of CPO (67%) occurred at 2 MPa H₂. The yield then decreased at higher pressures. For all hydrogen pressures, FFA converted completely except for at 1 MPa H₂. The results also illustrate that the hydrogen pressure has a certain promoting effect on the reaction rate. Comparing the product distributions using the two catalysts under the same conditions, we found that the catalyst activity of the 5% Cu–Co-OG-500 catalyst was higher than that of the 5% Cu–Co-CP-500 catalyst, especially for the hydrogenation step.

In order to study the structures of the prepared catalysts and the correlation with their catalytic properties, we conducted X-ray diffraction analysis. Fig. 3 shows the XRD patterns of the two kinds of prepared catalysts. For the 5% Cu–Co-OG-500 catalyst, the distinct diffraction peaks of Co⁶⁺ appear.
due to the interaction between Cu and Co (Fig. 3b).\textsuperscript{23,24} The existence of the excessive hydrogenation product THFOL and the decreased yield of CPL with increasing hydrogen pressure result from the higher hydrogenation activity of Co\textsuperscript{0} and the interaction between Cu and Co.\textsuperscript{25} Cu\textsubscript{2}O can strongly polarize C\textsubscript{O} and result in a relatively low hydrogenation ability.\textsuperscript{26–28} The total yield of CPO and CPL changed only slightly, while the yield of CPL increased. Therefore we could suggest that the yield of CPL was improved by further hydrogenation of CPO and the side reactions rarely occurred. The results of the hydrogenation reaction of CPO can also support this speculation (Table S1, ESI\textsuperscript{†}). The complete conversion of CPO with a CPL yield of only 88% under the 5% Cu–Co-OG-500 catalyst indicates that there were about 10% byproducts. The total yield of CPO and CPL was 99% using the 5% Cu–Co-CP-500 catalyst for the hydrogenation of CPO. The results show that excessive hydrogenation products and side reactions did not exist. This also explains the different hydrogenation abilities of the two catalysts.

3.3 Effect of Cu loadings

The product distributions using the Cu–Co-OG-300 catalyst with different Cu loadings were determined and are presented in Fig. 4(a). As shown in the chart, the conversion of FFA was very low (20%) and only small amounts of CPO and CPL were obtained when the Cu loading was 1%. The weaker interaction between Cu and Co makes the reduction of Co oxides too difficult to produce more products at 1% Cu loading. As the Cu loading increased to 2%, the yield of CPL increased to 68% and the highest yield of CPL was obtained. FFA was converted completely using over 2% Cu loadings. By further increasing the Cu loading to over 5%, the interaction between Cu and Co was enhanced and the selectivity of the products was reduced.\textsuperscript{21} Further increasing the Cu loading resulted in a significant reduction in the selectivity of the products due to the reunion of the active metals and the possible formation of a solid solution between Cu and Co.\textsuperscript{29} The TEM microphotographs for the 5% Cu–Co-OG-500 and 10% Cu–Co-OG-400 catalysts are shown in Fig. S1(a and b), ESI\textsuperscript{†}

Similar to the 1% Cu loading results in Fig. 4(a), the conversion of FFA was also low (15%) and the products were FOL and 2-CPEO by using the CP catalyst (Fig. 4b).\textsuperscript{19} The highest yield of CPO was obtained at 5% Cu loading with complete conversion of FFA. By increasing the Cu loading to 20%, the total yield of CPO and CPL increased and the proportion of CPL increased significantly. However the selectivity of the products was poor. This may suggest that the proportion of active phases changed with the increased Cu loadings.

3.4 Effect of calcination temperature

Fig. 5(a) shows the product distributions using the 5% Cu–Co-OG catalyst with different calcination temperatures. The results show that the catalyst had a high activity below 873 K. The highest yield of CPL (64%) was obtained at 773 K. By increasing the temperature from 973 K to 1073 K, the conversion of FFA decreased significantly and the main products were FOL, 2-CPEO and CPO. Almost none of the fully hydrogenated product CPL was obtained indicating serious deactivation of the catalyst. Fig. 6 shows the XRD diffraction peaks for the 5% Cu–Co-OG catalyst under different calcination temperatures. The distinct diffraction peaks of Co\textsuperscript{0} and Cu\textsubscript{2}O correlate to high catalytic activity and high product yield below 873 K.\textsuperscript{24,30} When the calcination temperature was increased to 973 K and 1073 K, the diffraction peaks of Co\textsuperscript{0} and Cu\textsubscript{2}O decreased dramatically and the distinct phases in
the XRD pattern were (Cu0.3Co0.7)Co2O4 spinel (JCPDS: 25-0270). The large particles of spinel are shown in the TEM microphotograph (Fig. S1c, ESI†). Due to the strong interactions between the atoms, spinel was difficult to restore.31 The corresponding analysis of the Cu2p3/2, Cu LMM and Co2p XPS spectra are shown in Fig. 7. In the Cu2p3/2 spectra (Fig. 7a), the distinct peaks with electron binding energies between 932 eV and 933.4 eV belong to Cu+ and Cu0.26 Due to the contiguous binding energies of Cu+ and Cu0, the Cu LMM spectra were required. Distinct peaks with electron binding energies of 918.3 eV and 914.2 eV were observed and can be respectively attributed to Cu+ and Cu0 in the Cu LMM spectra below 873 K (Fig. 7b).26,32 Shen et al. have reported that when copper is highly dispersed and in close contact with supports, the Cu Auger parameters may deviate significantly from the corresponding bulk values.32 This is consistent with our observation. When the calcination temperature was increased to 973 K and 1073 K, only the distinct peak at 917.6 eV ascribed to Cu2+ can be observed.32 The change of Cu species plays a

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**Fig. 5** Effect of calcination temperature (a: 5% Cu–Co-OG catalyst; b: 5% Cu–Co-CP catalyst) on the product distribution. Reaction conditions: 2 mmol FFA, 50 mg catalyst, 10 ml H2O, 443 K, 1 h, 2 MPa H2, mole yield.

**Fig. 6** The XRD diffraction patterns for the 5% Cu–Co-OG catalyst under different calcination temperatures.

**Fig. 7** XPS spectra for the 5% Cu–Co-OG catalyst under different calcination temperatures: (a) Cu2p3/2; (b): Cu LMM; (c): Co2p.
certain influence on the activity of the catalysts and the yields of the products. The Co2p spectra show the changes in the Co species (Fig. 7c). The peak of Co\(^{0}\) (778.8 eV) disappears when the calcination temperature is above 873 K. The disappearance of Cu\(^{+}\) and Co\(^{0}\) eventually leads to the collapse of the catalyst activity and the product yield.

The product distributions of the 5% Cu–Co-CP catalyst with different calcination temperatures were determined and are presented in Fig. 5(b). CPO was obtained selectively when the calcination temperature was between 673 K and 873 K, and the yields were 65% (673 K), 67% (773 K) and 57% (873 K). FFA converted completely over the catalyst at these temperatures. When the calcination temperature was 973 K, the conversion of FFA decreased to about 80%, the yield of CPO dropped to only 26%, and 11% FOL and 18% 2-CPEO were obtained. The composition of products was similar to that of the OG catalyst at this temperature. Further increasing the calcination temperature to 1073 K resulted in the conversion of FFA declining sharply to only about 17% and the products observed were only 8% FOL and 1% CPO. The formed spinel and the disappearance of the active phases contributed to the reduced product yield.

### 3.5 Reusability of the catalyst

The result of reusing the 5% Cu–Co-OG-500 catalyst was determined and is presented in Fig. 8(a). The yield of CPL hardly changed and the conversion of FFA was complete even after reusing the catalyst five times. The yield of CPO increased continuously, but the total yield of CPO and CPL was essentially unchanged. Deposited carbon on the surface of the catalyst, enrichment of oligomers and loss of metal may be the main reasons for the reduction in the hydrogenation activity of the catalysts. The Co and Cu metal contents in the fresh catalyst were 84.75% and 7.19%, respectively, as determined by ICP-AES. After reusing the catalyst five times, the Co and Cu metal contents were 84.07% and 6.92%, respectively. These results indicate that Cu and Co were partly lost after use. The results show a gradual weakening in the hydrogenation ability of the catalyst and a gradual increase in the yield of CPO.

Fig. 8(b) shows the result of reusing the 5% Cu–Co-CP-500 catalyst. The yield of CPO hardly changed even after reusing the catalyst five times. FFA converted completely every time. We identified that the selectivity and yield of CPO and CPL were almost unchanged after reusing both catalysts five times.

### 3.6 Probable reaction pathway

The probable reaction pathway for the conversion of FFA to CPO and CPL over the Cu–Co catalysts is shown in Scheme 2. Several main compounds (2-CPEO, FOL, CPO, CPL and THFOL) were detected through the optimization of the reaction conditions (Fig. 2b). We propose a possible reaction pathway with the analysis of products and characterization. First is the hydrogenation of FFA to FOL in aqueous solution. We found that the Cu loading and hydrogen pressure affected the conversion of FFA. Further reactions of FOL are competitive. One is the catalysis reaction by H\(^{+}\) ions. This reaction obtains 4-hydroxy-2-cyclopentenone (4-HO-2-CPEO), which is another key intermediate in the rearrangement of FFA. Other reactions include the excessive hydrogenation of FOL to THFOL and oligomeric reactions under acidic conditions to obtain oligomers. The carbon-loss mainly comes from the hardly detected oligomers and this is attributed to the inherent properties of FFA and FOL. The oligomers are formed inevitably by the resification of FFA and reaction intermediates in high-temperature water.
is lower at high hydrogen pressure and Cu loading (Fig. 2 and 4). The high hydrogen pressure may promote the oligomerization of FFA. The increased Cu loading led to increased metal sites, and unexpected side reactions occurred and several hardly detected byproducts were obtained. The yield of 4-HO-2-CPEO directly influenced the yield of the final products. Then the dehydration of 4-HO-2-CPEO to 2-CPEO occurs, followed by the hydrogenation of 2-CPEO to CPL in the presence of the catalyst. Production of CPL is dependent on the reaction conditions used. The different active phases on the surface of the two catalysts are shown in the XRD patterns (Fig. 3). Under the experimental conditions, CPL converts almost completely and gives about 88% CPL over the 5% Cu–Co-OG-500 catalyst, while there was still 61% yield of unreacted CPO over the 5% Cu–Co-CP-500 catalyst. This indicates that the hydrogenation activity of the 5% Cu–Co-OG-500 catalyst is higher than that of the 5% Cu–Co-CP-500 catalyst. The different active phases on the surface of the two catalysts are shown in the XRD patterns (Fig. 3). We found that the major phases on the surface of the 5% Cu–Co-OG-500 catalyst were Cu2O and CoO. CoO has a higher hydrogenation activity of the catalyst. We suggest that the hydrogenation activity of Cu0 and Cu2O are relatively weaker than the phases on the surface of the 5% Cu–Co-OG-500 catalyst. The major active phases were Cu2O on the surface of the 5% Cu–Co-CP-500 catalyst. The hydrogenation activity of Cu2O is higher than that of the surface of the 5% Cu–Co-OG-500 catalyst. The different active phases on the surface of the two catalysts are shown in the XRD patterns (Fig. 3). We found that the major phases on the surface of the 5% Cu–Co-OG-500 catalyst were Cu2O and CoO. CoO has a higher hydrogenation activity. In contrast, the main phases were CuO and Cu2O on the surface of the 5% Cu–Co-CP-500 catalyst. The hydrogenation activity of Cu2O and CuO are relatively weaker than the phases on the surface of the 5% Cu–Co-OG-500 catalyst. Therefore, the major product was not the fully hydrogenated product CPL but CPL over the CP catalyst under the reaction conditions used. The different interactions and the different contents of the phases in the catalysts cause the different selectivity of the final products. Further studies on the detailed mechanism are necessary.

4. Conclusions

In summary, we can selectively convert FFA to CPL or CPL using Cu–Co catalysts prepared by a co-precipitation method or a sol–gel method, respectively. The product distribution was influenced by the catalyst support, Cu loading, calcination temperature, hydrogen pressure, the number of times the catalyst was reused and the preparation method of the catalyst. There were obvious interactions between Cu and Co according to the characterization. The major active phases were Cu2O and CoO in the OG catalyst, while the major active phases were CuO and Cu2O in the CP catalyst. The different interactions and the different contents of the phases in the catalysts caused the different selectivity of the final products.

Acknowledgements

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