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Cite this: DOI: 10.1039/c0xx00000x

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PAPER

Selective conversion of furfural to cyclopentanone and cyclopentanol by different preparation methods of Cu-Co catalysts†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

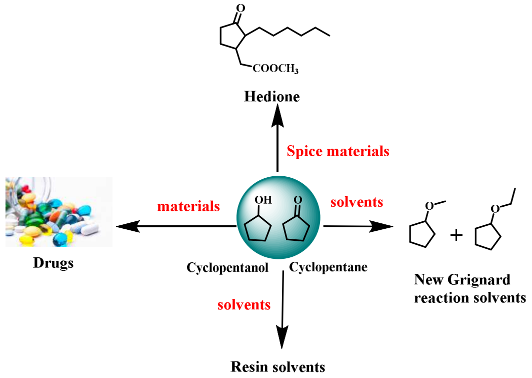
Cu-Co catalysts, prepared by co-precipitation method (CP) and oxalate sol-gel method (OG), can selectively convert furfural (FFA) to cyclopentanone (CPO) and cyclopentanol (CPL), respectively. The conversion of FFA to CPO and CPL by Cu-Co catalysts was studied in aqueous solution. We found that product distribution was influenced by different catalyst supports, Cu loadings, calcination temperature, reused times, hydrogen pressure and the preparation methods of catalyst. The surface morphology, surface area and composition of catalysts were studied by XRD, XPS, BET and ICP-AES and TEM characterization. We found that there was a strong interaction between Cu and Co. Cu^0, Cu_2O and Co^0 were the main active catalyst phases on the surface of catalysts, but the content of them were different in different catalysts. Cu^0, Co^0, Cu_2O were active hydrogenation ingredients, Cu_2O also played an electrophile or Lewis acid sites to polarize C-O bond via lone pair electrons on oxygen. According to XRD and XPS, the main phases on the surface of CP catalysts were Cu^0 and Cu_2O. The hydrogenation activity of CP catalysts was relatively weak and the main product was CPO. In contrast, the hydrogenation activity of OG catalysts was high. And the main product was full hydrogenation product CPL due to the main active phases Co^0 and Cu_2O on the surface of OG catalysts. 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 becomes more and more attractive with the evergrowing consumption of the non-recoverable fossil fuels. Biomass as unique renewable resources could be converted to conventional liquids, solids, gases, fuels and other chemicals. [1] The industry applications of biomass are based on improving the competitiveness for biomass resources, developing preparation methods for inexpensive platform molecules and efficiently transferring platform molecule to fuels and chemicals. [2]

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

Cyclopentanone (CPO) and cyclopentanol (CPL), as fine chemical raw materials, have been wildly used as solvents and starting materials for synhtesis 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 solvent in the electronics industry because of its good solubility of various resins. Cyclopentyl methyl ether and cyclopentyl ethyl ether, which have characteristics of high hydrophobicity, low latent heat of solvent evaporation, difficultly forming peroxides, easily drying, etc., have been used as solvents for Grignard reactions, coupling reactions and other important chemical reactions. [7] The demand of CPO and CPL are million tons per year. Therefore, it will be highly valuable if CPO and CPL can be efficiently prepared from biomass-based FFA. [8]



Scheme 1. Applications of cyclopentanone and cyclopentanol

Hronec *et al.* reported 81.32% total yield of CPO and CPL by using 5% Pt/C catalyst at 433 K and 8 MPa H_2 pressure.[9] Later, Hronec *et al.* indicated that the key intermediate was 3-hydroxy-4-cyclopentenone.[10] 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 catalyst at 448 K and 8 MPa H_2.[11] Additionally, Xu *et al.* obtained 62% yield of CPO by using NiCu-50/SBA-15 catalyst at 433 K and 4 MPa H_2. Differently, the identified three key intermediates were furfuryl alcohol (FOL), 4-hydroxy-2-cyclopen-tenone and 2-cyclopentenone (2-CPEO).[12] Nijhuis *et al.* obtained 16% CPO and 11% CPL by using Amberlyst-15 and Ru/C catalysts catalyzed dehydration of xylose and hydrogenation of FFA in biphasic system.[13] Then Hronec *et al.* considered that there are two parallel reactions, including H^+ ions catalysis generated by decomposition of water and the metal catalysis in rearrangement reaction.[14] Xiao *et al.* reported 93.4% yield of CPL by (Cu+Mg)/Al catalyst at 4 MPa H_2 for 10 h, but the catalyst is severe deactivation after reused two times.[15] Then Xiao *et al.* used 30 wt.% Ni/CNTs for the conversion of FFA to CPL.[16] Ohyama *et al.* reported the conversion of 5-hydroxymethyl furfural to a cyclopentanone derivative by ring rearrangement over supported Au nanoparticles.[17] Recently, the rearrangement of FFA to CPO and CPL still have many problems, like the expensive supported metals, the higher reaction hydrogen pressure, the longer reaction time and the lower catalyst reused times. Cu catalysts were favorable for selective hydrogenation of FFA to furfuryl alcohol due to their strong polarization of C=O bond and the exclusion of furan ring. It was known that furfuryl alcohol was a key intermediate in rearrangement reaction and its yield directly affected the yield of final products. Co catalysts had a strong capability of hydrogenation and good closing ring ability in the synthesis of five membered ring.[18] It was more attractive for 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 temperature, reused times, hydrogen pressure and preparation methods of catalysts in rearrangement reaction. The surface morphology, surface area and composition of catalysts were studied by XRD, XPS, BET and ICP-AES and TEM characterization.

2. Experimental

2.1 Materials and reagents

Cu $(NO_3)_2 \cdot 3H_2O$ (AR, >99%), Co $(NO_3)_2 \cdot 6H_2O$ (AR, >99%), NaOH (AR, >96%), Na_2CO_3 (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%), 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

20% Cu-Co-CP-500 catalyst was prepared by co-precipitation method. 200 mL aqueous solution containing 4.78 g sodium hydroxide and 6.34 g sodium carbonate was slowly added into 200 mL aqueous solution containing 3.02 g nitrate copper and 11.6 g nitrate cobalt at room temperature until the pH of solution was about 10~11. The catalysts were filtered after stirring at 353 K for 12 h. Then the precursors were 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. The oxides were reduced at 473 K for 3 h and the gas composition was H_2: N_2 (10:90), 100 mL/min. The similar method for preparing 5% Pd/Co_3O_4, 20% Ni/Co_3O_4, 5% Pd/MnOx, 30% Cu/ZrO_2 and other Cu-Co-CP catalysts with different Cu loadings and calcination temperature.

30% Cu-Co-OG-500 catalyst was prepared by sol-gel method. 5.4 g cobalt nitrate, 2.4 g copper nitrate, 100 mL ethanol were added into 500 mL beaker. Then 100 mL ethanol dissolving 4.3 g oxalic acid was added under rapid stirring. The reaction liquid was placed overnight after stirring for 4 h at room temperature. The precipitates were 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. The oxides were reduced at 473 K for 3 h and the gas composition was H_2: N_2 (10:90), 100 mL/min. The similar method for preparing 30% Cu/ZrO_2 and other Cu-Co-OG catalysts with different Cu loadings and calcination temperature.

Cu/HZSM-5 was prepared by impregnation method. 3.8 g copper nitrate was dissolved into 5 mL water. Then 9 g HZSM-5 (Si/Al = 50) were added in batches under stirring. The precursors were calcined at 823 K for 6 h after dried for 8 h. The oxides were reduced at 553 K for 4 h and the gas composition was H_2: N_2 (10:90), 100 mL/min.

2.3 Catalyst characterization

Catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Barrett-Emmet-Taller (BET) transmission electron spectroscopy (TEM) and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.4 Typical experiment and product analysis

Studies on 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_2O were added into autoclave. Then the autoclave was sealed, purged with H_2 four times, and then pressurized with H_2 to a required pressure. The autoclave was heated to a required temperature and reacted for a required time (Fig. S6). After reaction, the reactor was cooled and the solution was transferred with 20 mL ethanol. Then a certain amount of N,N-dimethylformamide (DMF) was 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 by following formula:

$$\text{Conv}/\ \% = \frac{(n_{FFA} - n_{FFA}')}{n_{FFA}} \times 100\%$$

$$\text{Y}/\ \% = \frac{(\text{mole of product})}{n_{FFA}} \times 100\%$$

n_{FFA} : mole of FFA before reaction
n_{FFA}' : mole of FFA after reaction

3. Results and discussion

Table 1 Product distribution for hydrogenation rearrangement of FFA with various catalysts

Entry	Cat.	C-FFA/%	Yield/%						
			MTHF	THFOL	FOL	2-CPEO	CPO	CPL	CPO+CPL
1	5% Pd/Co_3O_4	100	1	82	0	0	0	3	3
2	20% Ni/Co_3O_4	100	0	7	1	0	24	29	53
3	5% Pd/MnOx	100	0	81	0	0	0	14	14
4	Cu/HZSM-5	86	0	0	1	14	9	1	10
5	30% Cu/ZrO_2	100	0	0	0	0	25	40	65
6	30% Cu/ZrO_2 [a]	100	0	0	0	0	24	26	50
7	30% Cu/Co_3O_4 [a]	100	0	0	0	0	10	58	68
8	20% Cu/Co_3O_4	100	0	0	0	0	46	7	53

(Reaction conditions: 2 mmol FFA, 0.1 g catalyst, 10 mL H_2O, 6 h, 423 K, 4 MPa H_2, mole yield. [a]. catalysts were prepared by sol-gel method.)

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 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 oligomerization of furfuryl alcohol under acidic conditions (HZSM-5), on the surface of catalysts reduced the activity of catalysts. [11,19] The results slowed down the conversion rate of FFA and lowered the total yield of CPO and CPL. The main product was THFOL over supported Pd catalysts (Entry 1 and Entry 3). It was attributed to the high hydrogenation activity of Pd metal. Because the exclusion of furan ring and the easier hydrogenation of aldehyde C=O bond to alcohol, the total yield of CPO and CPL were higher by using supported Cu catalysts (Entry 5-8) than other samples. [20] Improving the selectivity of FOL was helpful to improve the yield of final products. The selectivity of products was not high over Cu/ZrO_2 catalysts (Entry 5 and Entry 6). CPO and CPL can be obtained selectively over Cu-Co catalysts prepared by co-precipitation method and sol-gel method, respectively. The monometallic Cu or Co as catalyst for the hydrogenation conversion of FFA were also proceeded (Table S2). The results showed that the yield and selectivity of products were less satisfaction by using single metal as catalyst than that of Cu-Co catalysts. This indicated that the strong interaction between Cu and Co was the cause of high selectivity.

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

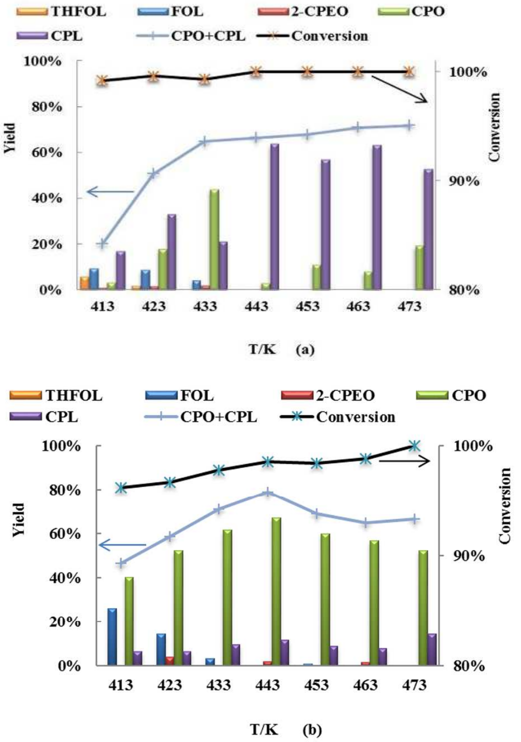


Fig. 1 Effect of reaction temperature (a. 5% Cu-Co-OG-500 catalyst; b. 5% Cu-Co-CP-500 catalyst) on product distribution. Reaction conditions: 2 mmol FFA, 50 mg catalyst, 10 mL H_2O, 2 MPa H_2, 1 h, mole yield.

3.1 Effect of reaction temperature

The effect of reaction temperature on product distribution for the hydrogenation rearrangement of FFA over 5% Cu-Co-OG-500 catalyst was determined and presented in Fig. 1(a). Under reaction conditions, the conversion of FFA for all samples was greater than 98%. The major products were FOL, CPO, CPL and THFOL. The highest 64% CPL was obtained while only 3% CPO was observed at 443 K, 1 h, 2 MPa H_2. 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 high temperature and produced from water dissociation. H^+ ions played a key role in protonation of FOL and this was a key step in rearrangement of FFA. [9] We found that the yield of CPO was increased again when the temperature over 443 K. Oligomers attached on the surface of catalyst reduced the hydrogenation activity of catalyst may bring about this result. [11] 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 subject to further research.

Compared to Fig. 1(a), Fig. 1(b) was the effect of temperature on product distribution by using 5% Cu-Co-CP-500 catalyst. FFA converted almost completely at all temperatures. The main products were FOL and CPO at lower temperature and the yield of CPO was only 40%. About 26% FOL were detected at 413K. This suggested that H^+ ions, prepared by dissociation of water, were too weak to protonate FOL at lower temperature. [21] The highest yield of CPO (67%) was achieved at 443 K. The yield of CPO decreased followed with increasing temperature from 443 K to 473 K. The formation of oligomers may be the main reason for the yield of CPO increased primarily and decreased afterwards. [11,] The corresponding BET results of the two catalysts were showed in Table S4 and Fig S5.

3.2 Effect of hydrogen pressure

The product distribution by using 5% Cu-Co-OG-500 catalyst was determined and 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 H_2). A mixture of CPO and CPL were obtained at 1 MPa H_2. Further increasing pressure, the yield of CPL increased firstly and then decreased. This was considered that the intermediates and products further hydrogenated into other products at higher hydrogen pressure. This speculation could 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 H_2.

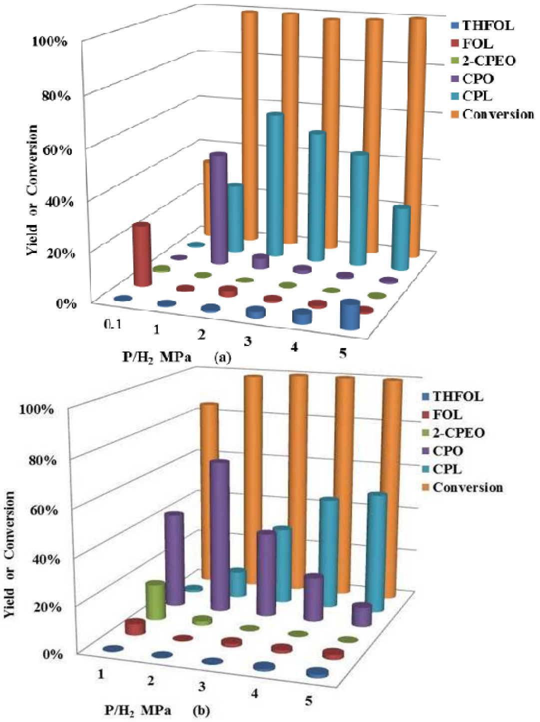


Fig. 2 Effect of hydrogen pressure (a. 5% Cu-Co-OG-500 catalyst, b. 5% Cu-Co-CP-500 catalyst) on product distribution. Reaction conditions: 2 mmol FFA, 50 mg catalyst, 10 mL H_2O, 443 K, 1 h, mole yield.

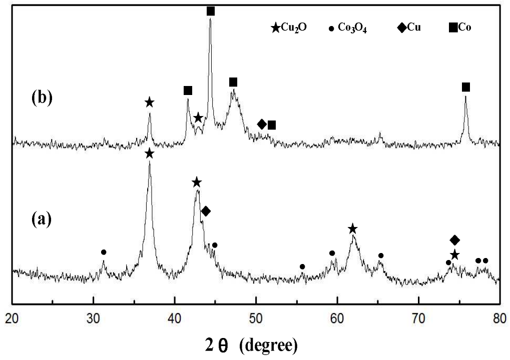
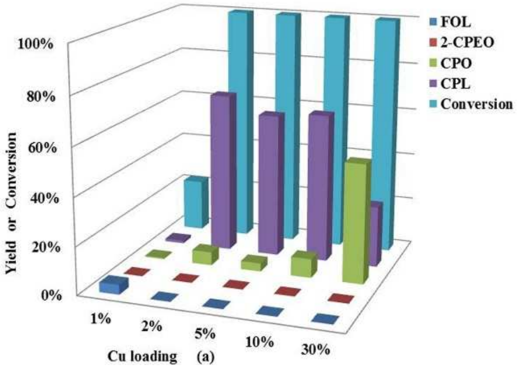


Fig. 3 XRD. (a). 5% Cu-Co-CP-500; (b). 5% Cu-Co-OG-500.

Fig. 2(b) was the product distribution by using 5% Cu-Co-CP-500 catalyst. The main products were CPO, FOL and 2-CPEO at 1 MPa H_2. The highest yield of CPO (67%) occurred in 2 MPa H_2. Then the yield was decrease. For all hydrogen pressures, FFA converted completely except for 1 MPa H_2. It also illustrated that hydrogen pressure had a certain promoting effect on the reaction rate. Comparing the product distribution by using the two catalysts at same conditions, we found that catalyst activity of 5% Cu-Co-OG-500 catalyst was higher than that of 5% Cu-Co-CP-500 catalyst, especially for the hydrogenation step. In order to study the structure of the prepared catalysts and the correlation with their catalytic properties, we conducted X-ray diffraction analysis. Fig. 3 showed the XRD patterns of the prepared two kinds of catalysts. In 5% Cu-Co-OG-500 catalyst, the distinct diffraction peaks of Co^0 appeared due to the interaction between Cu and Co (Fig. 3b). [23, 24] The existence of excessive hydrogenation product THFOL and the decreased yield of CPL along with increasing hydrogen pressure were derived from the higher hydrogenation activity of Co^0 and the interaction between Cu and Co. [25] Cu^0 and Cu_2O were the obvious phases in XRD of 5% Cu-Co-CP-500 catalyst (Fig. 3a). Cu_2O had a strong polarization for C=O and the relative lack of hydrogenation ability. [26-28] The total yield of CPO and CPL changed little while the yield of CPL increased. So we could suggest that the yield of CPL was improved by further hydrogenation of CPO and the side reactions occurred rarely. The results for hydrogenation reaction of CPO can also support this speculation (Table S1). The complete conversion of CPO but the yield of CPL was only 88% under 5% Cu-Co-OG-500 catalyst indicated that there were about 10% byproducts. The total yield of CPO and CPL was 99% by using 5% Cu-Co-CP-500 catalyst for hydrogenation of CPO. The results showed that excessive hydrogenation products and side reactions did not existence. It also explained the different hydrogenation ability between the two catalysts.

3.3 Effect of Cu loadings

The product distribution by using Cu-Co-OG-300 catalyst with different Cu loadings were determined and presented in Fig. 4(a). As we could see from the chart, the conversion of FFA was very low (20%) and only a small amounts of CPO and CPL were obtained when the Cu loading was 1%. Weaker interaction between Cu and Co made the reduction of Co oxides too little to produce more products at 1% Cu loading. As the Cu loading increased to 2%, the yield of CPL increased to 68% and the



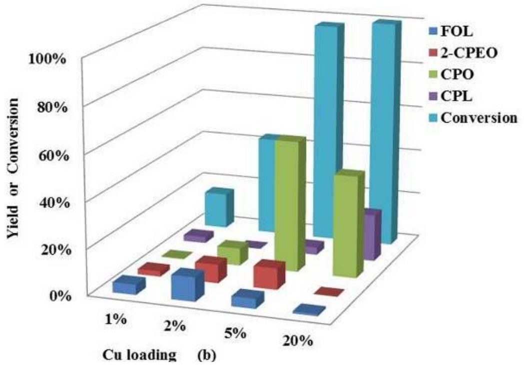


Fig. 4 Effect of Cu loadings (a. Cu-Co-OG-300 catalyst, b. Cu-Co-CP-600 catalyst) on product distribution. Reaction conditions: 2 mmol FFA, 50 mg catalyst, 10 mL H_2O, 443 K, 1 h, 2 MPa H_2, mole yield.

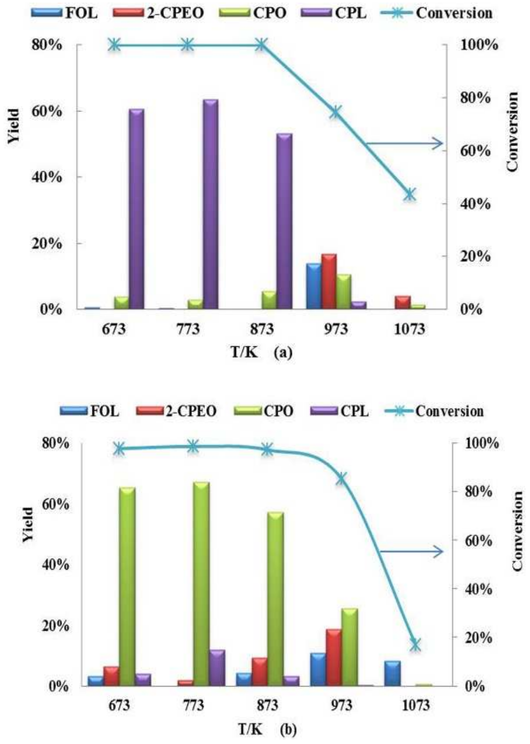


Fig. 5 Effect of calcination temperature (a. 5% Cu-Co-OG catalyst; b. 5% Cu-Co-CP catalyst) on product distribution. Reaction conditions: 2 mmol FFA, 50 mg catalyst, 10 mL H_2O, 443 K, 1 h, 2 MPa H_2, mole yield.

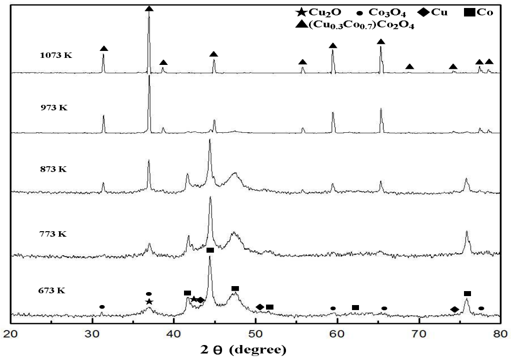


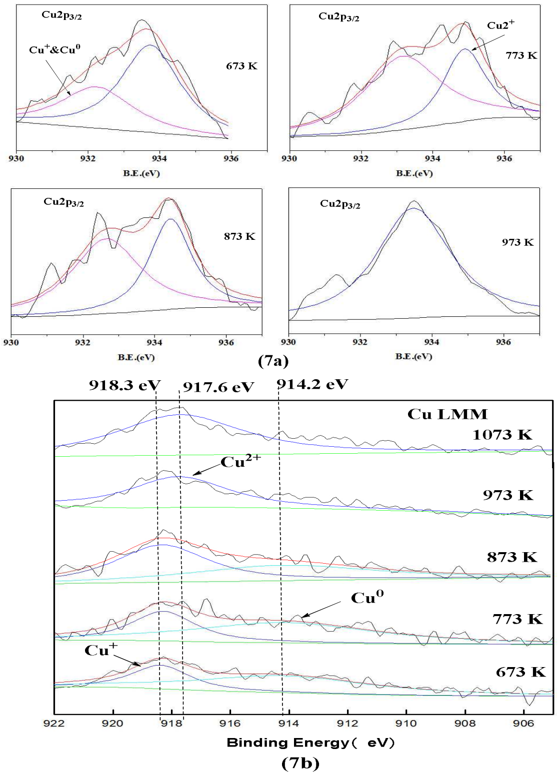
Fig. 6 The XRD diffraction peaks for 5% Cu-Co-OG catalysts under different calcination temperature

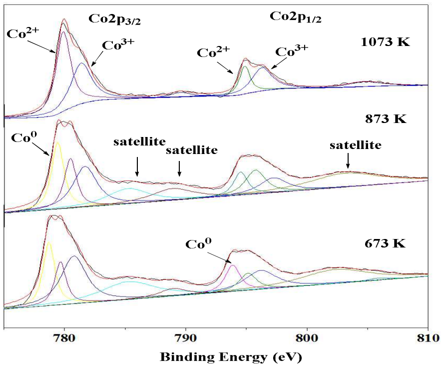
highest yield of CPL was obtained. FFA were converted completely over 2% Cu loadings. Further increasing the Cu loading over 5%, the interaction between Cu and Co enhanced and the selectivity of products reduced. [23] To further increase the Cu loading, the selectivity of product reduced obviously due to the reunion of active metals and the possible formation of solid solution between Cu and Co. [29] The TEM microphotographs for 5% Cu-Co-OG-500 and 10% Cu-Co-OG-400 were showed in Fig. S1(a, b).

Similar to Fig. 4(a) at 1% Cu loading, the conversion of FFA was too low (15%) and the products were FOL and 2-CPEO by using CP catalyst (Fig. 4b). [19] The highest yield of CPO was obtained at 5% Cu loading with complete conversion of FFA. Increasing Cu loading to 20%, the total yield of CPO and CPL was increased and the proportion of CPL was increased significantly, but the selectivity of products was poor. This may suggest that the proportion of active phases was changed along with the increased Cu loadings.

3.4 Effect of calcination temperature

Fig. 5(a) was the result of product distribution by using 5% Cu-Co-OG catalysts with different calcination temperature. Results showed that catalysts had high activity below 873 K. The highest yield of CPL (64%) was obtained at 773 K. With 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 fully hydrogenated product CPL was obtained indicated serious deactivation of catalysts. Fig. 6 showed the XRD diffraction peaks for 5% Cu-Co-OG catalysts under different calcination temperature. The distinct diffraction peaks of Co^0 and Cu_2O appeared led to the high catalytic activity and high product yield below 873 K. [24, 30] Increasing the calcination temperature to 973 K and 1073 K, the diffraction peaks of Co^0 and Cu_2O decreased dramatically and the distinct phases on XRD became (Cu0.3Co0.7) Co_2O_4 spinel (JCPDS: 25-





(7c)

Fig.7 XPS spectra for 5% Cu-Co-OG catalysts under different calcination temperature. (a): Cu2 $p_{3/2}$; (b): Cu LMM; (c): Co2 p.

0270). The large particles of spinel were showed in TEM (Fig. S1c). Due to the strong interaction of atoms, spinel was difficult to be restored. [31] The corresponding analysis of Cu2 $p_{3/2}$, Cu LMM and Co2 p spectra were showed in Fig. 7. In the Cu2 $p_{3/2}$ spectra (Fig. 7a), the distinct peaks with electron binding energy among 932 eV to 933.4 eV were belonged to Cu^+ and Cu^0. [26] Because of the contiguous binding energy of Cu^+ and Cu^0, the Cu LMM spectra were required. The distinct peaks with electron binding energy of 918.3 eV and 914.2 eV were observed and can be respectively attributed to Cu^+ and Cu^0 in Cu LMM spectra below 873 K (Fig. 7b). [26, 32] Shen *et al.* have reported that when copper is highly dispersed and in intimated contact with the supports, Cu Auger parameters may deviate significantly from the corresponding bulk values. [32] This was consistent with our observation. Increasing the calcination temperature to 973 K and 1073 K, only the distinct peak at 917.6 eV ascribed to Cu^{2+} can be observed. [32] The change of Cu species has played a certain influence on the activity of catalysts and the yield of products. Co2 p spectra showed the changes of the Co species (Fig 7c). [29, 32] The existent peak of Co^0 (778.8 eV) disappeared when the calcination temperature was above 873 K. Common disappearance of Cu^+ and Co^0 eventually led to the collapse of the catalyst activity and the product yield.

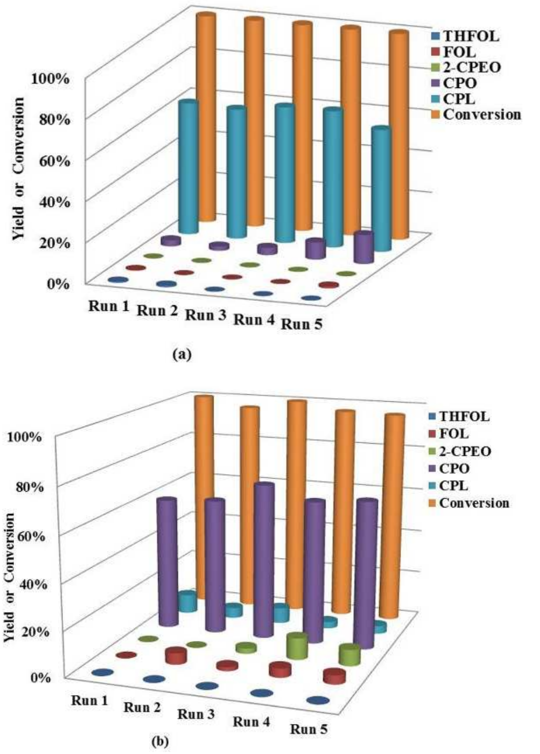
The product distribution of 5% Cu-Co-CP catalysts with different calcination temperature were determined and presented in Fig. 5(b). CPO was obtained selectively while the calcination temperature increased from 673 K to 873 K and the yields were 65%, 67% and 57%, respectively. FFA converted completely over these catalysts. 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 OG catalysts at this temperature. Further increasing the calcination temperature to 1073 K, the conversion of FFA declined sharply to only about 17% and the products were observed only 8% FOL and 1% CPO. The formed spinel and the disappeared activity phases were contributed to the reduced product yield.

3.5 Reusability of catalyst

The result of reusing 5% Cu-Co-OG-500 catalyst was determined and presented in Fig. 8(a). The yield of CPL changed little and the conversion of FFA was complete even after reusing five times. The yield of CPO was increased continuously, but the total yield of CPO and CPL was essentially unchanged. The deposition carbon on the surface of catalyst, the enrichment of oligomers and the loss of metal may be the main reasons to reduce the hydrogenation activity of catalysts. Detected by the ICP-AES, the metal content of Co and Cu in fresh catalyst were 84.75%, 7.19%, respectively. After reused five times, the metal content of Co and Cu were 84.07%, 6.92%, respectively. The results indicated that Cu and Co were part of loss after reuse. The results led to the gradually weakened hydrogenation ability of catalysts and the gradually increased yield of CPO.

Fig. 8(b) was the reuse of 5% Cu-Co-CP-500 catalyst. The yield of CPO changed little even after reused five times. FFA converted completely every time.

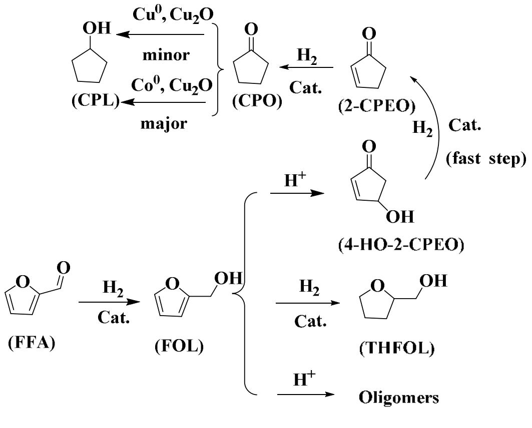
So here we identified that the selectivity and yield of CPO and CPL were almost no changed after reused five times over the two different preparation methods of catalysts, respectively.



(a)

(b)

Fig. 8 Effect of reuse times (a. 5% Cu-Co-OG-500 catalyst; b. 5% Cu-Co-CP-500 catalyst) on product distribution. Reaction conditions: 2 mmol FFA, 50 mg catalyst, 10 mL H_2O, 443 K, 1 h, 2 MPa H_2, mole yield.



Scheme 2. Probable Reaction Pathway

3.6 Probable reaction pathway

The probable reaction pathway for the conversion of FFA to CPO and CPL over Cu-Co catalysts was shown in Scheme 2. Several main compounds of 2-CPEO, FOL, CPO, CPL and THFOL were detected through the optimization of reaction conditions (Fig. 2b). We proposed a possible reaction pathway with the analysis of products and characterization.[9, 12, 22] First was the hydrogenation of FFA to FOL in aqueous solution. We found that the Cu loadings and hydrogen pressure affected the conversion of FFA. Further reactions of FOL were competitive.[13] One was the catalysis reaction by H^+ ions . This reaction obtained 4-hydroxy-2-cyclopentenone (4-HO-2-CPEO) which was another key intermediate for the rearrangement of FFA.[10] Other reactions were the excessive hydrogenation of FOL to THFOL and the oligomeric reactions under acidic conditions obtained oligomers. The carbon-loss mainly came from the hardly detected oligomers and this was attributed to the inherent properties of FFA and FOL. The oligomers formed inevitably by the resinification of FFA and reaction intermediates in high-temperature water.[9, 10, 12] The C-balance was lower at high hydrogen pressure and Cu loadings (Fig. 2 and Fig. 4). The high hydrogen pressure may promote the oligomerization of FFA. The increased Cu loadings led to an increased metal sites, the unexpected side reactions occurred and several hardly detected byproducts were obtained. The yield of 4-HO-2-CPEO directly influenced the yield of final products. Then the dehydration of 4-HO-2-CPEO to 2-CPEO occurred followed by the hydrogenation of 2-CPEO to CPO in the presence of catalyst. Production of CPL was depended on the hydrogenation activity of catalysts. We suggested that the selectivity of final products were caused by the different hydrogenation activity of CPO over different catalysts. Therefore, 5% Cu-Co-OG-500 catalyst and 5% Cu-Co-CP-500 catalyst were used for the hydrogenation of CPO to verify this speculation (Table S1). Under the experimental conditions, CPO converted almost completely and gave about 88% CPL over 5% Cu-Co-OG-500 catalyst while there was still 61% yield of unreacted CPO over 5% Cu-Co-CP-500 catalyst. This indicated that the hydrogenation activity of 5% Cu-Co-OG-500 catalyst was higher than that of 5% Cu-Co-CP-500 catalyst. The different active phases on the surface of the two catalysts also showed in XRD (Fig. 3). We found that the major phases on the surface of 5% Cu-Co-OG-500 catalyst were Cu_2O and Co^0. Co^0 had higher hydrogenation activity.[25] But the main phases were Cu^0 and Cu_2O on the surface of 5% Cu-Co-CP-500 catalyst. The hydrogenation activity of Cu^0 and Cu_2O were relatively weaker than that of 5% Cu-Co-OG-500 catalyst. Therefore, the major product was not the fully hydrogenated product CPL but CPO over CP catalysts under reaction conditions. The different interaction and the different content of phases in catalysts caused the different selectivity of final products. Further studies on the detailed mechanism were necessary.

4. Conclusions

In summary, we can selective conversion of FFA to CPO and CPL by Cu-Co catalysts which were prepared by co-precipitation method and sol-gel method, respectively. The product distribution was influenced by catalyst supports, Cu loadings, calcination temperature, reused times, hydrogen pressure and the preparation methods of catalysts. There was obvious interaction between Cu and Co according to the characterization. The major active phases were Cu_2O and Co^0 in OG catalysts while the major active phases were Cu^0 and Cu_2O in CP catalysts. The different interaction and the different content of phases in catalysts caused the different selectivity of final products.

Acknowledgements

This work was supported by the 973 Program (2012CB215305, 2013CB228103), NSFC (21402181, 21472033, 21325208, 21272050, 21172209), CAS (KJCX2-EW-J02), FRFCU (WK2060190025, WK2060190033), CPSF(2014M561835) and NCET-11-0627.

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† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

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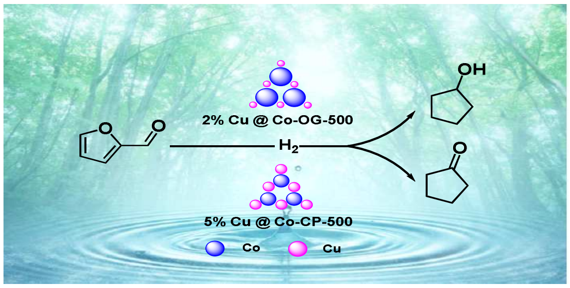

Different Cu-Co catalysts have been developed for the hydrogenation-rearrangement of furfural to cyclopentanone or cyclopentanol.