

Selective hydrogenation of furfural to cyclopentanone over Cu-Ni-Al hydrotalcite-based catalysts

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(Received 27 August 2013 • accepted 26 November 2013)

Abstract—A series of Cu-Ni-Al hydrotalcites derived oxides with a (Cu+Ni)/Al mole ratio of 3 with varied Cu/Ni mole ratio (from 0.017 to 0.5, with a Cu ratio of 0.0125 to 0.25) were prepared by co-precipitation method, then applied to the hydrogenation of furfural in aqueous. Their catalytic performance for liquid phase hydrogenation of furfural to prepare cyclopentanone was described in detail, considering reaction temperature, catalyst composition, reaction time and so on. The yield of cyclopentanone was influenced by the mole ratio of Cu-Ni-Al based heterogeneous catalyst and depended on the reaction conditions. The yield of cyclopentanone was up to 95.8% when the reaction was carried out under 413 K with H₂ pressure of 40 bar for 8 h. The catalysts were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM) and H₂ temperature-programmed reduction (H₂-TPR).

Keywords: Hydrotalcite-based Catalyst, Furfural, Cyclopentanone, Hydrogenation

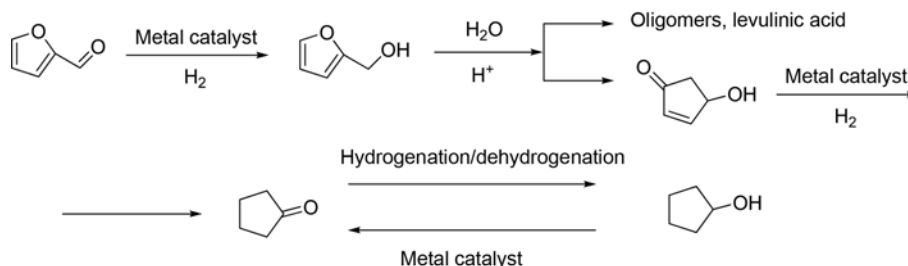
INTRODUCTION

Considering the decrease of petroleum reserves and increase of energy demand, as well as growing interest for application of renewable energy, it is imperative to develop economical and energy-efficient processes for chemical production to supplement or replace those derived from petroleum [1]. As a versatile raw material, biomass-derived furfural can be converted to many useful chemical products [2]. The main hydrogenation reaction of furfural is the reduction of the C=O group or the furan ring. Depending on different catalysts, vapor-phase hydrogenation or liquid-phase hydrogenation of furfural can give different kinds of products such as furfuryl alcohol, 2-methylfuran, tetrahydrofurfuryl alcohol and ring decomposition products, such as pentanols and pentanediols [3-6] catalyzed by Cu-Cr, nickel based catalysts, heteropolyacids or Pd, Pt, Ru modied with Cu, Fe, Ce [7-10].

Cyclopentanone, which used to be prepared by the liquid phase oxidation of cyclopentene with nitrous oxide or by the catalytic cyclization of 1,6-hexanediol or adipic esters [11-14], is an important

raw material, widely used for the synthesis of fungicides, pharmaceuticals, pesticides, rubber, chemicals, flavor and fragrance chemicals [15-21]. When water is used as solvent, the catalytic hydrogenation reaction of furfural can lead to unexpected and highly selective transformation to cyclopentanone [22]. Hronec et al. studied the effect of various solvents and different kinds of noble metal catalysts (e.g., Pt, Pd, Ru, Pt-Ru based catalysts) on the transformation of furfural to prepare cyclopentanone, with a yield up to 76.5%. They also reported one possible reaction pathway for furfural transformation to cyclopentanone (Scheme 1) [22]. However, to the best of our knowledge, there has been no report demonstrating the direct hydrogenation of furfural to prepare cyclopentanol using non-noble metal catalysts with satisfactory conversion and selectivity.

Herein, we report Cu-Ni-Al catalysts from hydrotalcite-like precursors, which are of high activity and good selectivity in the hydrogenation of furfural to produce cyclopentanone. The heterogeneous catalysts were prepared and their catalytic activities were investigated in the hydrogenation of furfural, and the yield of cyclopentanone was higher than 95% with good selectivity.



Scheme 1. The reaction pathways of furfural transformation to cyclopentanone.

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EXPERIMENTAL

1. Chemicals

Furfural was purchased from Shanghai Jinshanting New Chemical Reagent Factory Co., Ltd. $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were purchased from Guangdong Guanghua Chemical Factory Co., Ltd.. NaOH was purchased from Nanjing Ningshi Chemical Reagent Co., Ltd. Na_2CO_3 was purchased from Shanghai Lingfeng Chemical Reagent Factory Co., Ltd.

2. Catalyst Preparation

The Cu-Ni-Al hydrotalcite-like precursors were prepared by co-precipitation method. Solution A (100 ml) contained $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (total 0.12 mol), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.04 mol), while solution B (80 ml) contained NaOH (0.28 mol) and Na_2CO_3 (0.20 mol). Both solutions were synchronously dropped into 20 ml 333 K deionized water slowly, accompanied with vigorous mechanical stirring, maintaining the pH between 9 and 11. The mixture was held at 333 K while keeping stirred vigorously for 2.5 h. Then the mixture was filtered and washed with deionized water until the pH value of filtrate was about 7. The precipitate was dried at 338 K over night and calcined at 773 K for 4 h. Cu-Ni-Al catalyst was obtained after reduction in H_2 at 673 K for 3 h.

3. Catalytic Characterization

Catalysts were characterized by powder X-ray diffraction (XRD) and scanning electron microscope (SEM) to verify its structure. XRD measurements were performed on a Rigaku D/max-A instrument with a Cu K radiation at 40 kV and 20 mA and a scan speed of 0.02°/min.

H_2 temperature-programmed reduction (H_2 -TPR) studies were carried out in a quartz tube reactor. Fifty milligrams of catalyst was pretreated in a flow of helium (30 ml/min) at 400 °C for 1 h to remove undesirable physisorbed species, and after cooling to 100 °C, the sample was heated in a flow of 10% H_2 /90% N_2 (40 ml/min) from 50 to 800 °C at a heating rate of 20 °C/min.

4. Hydrogenation of Furfural

All the aqueous-phase catalytic hydrogenations of furfural were carried out in a 200 ml stainless autoclave equipped with an electromagnetically driven stirrer. For each run, 95 ml of water, 5 ml of furfural and 1.5 g catalyst were added to the reactor vessel. After displacing the air, the hydrogen pressure was raised to a certain value. Then the reactor was heated to the desired temperature and the stirring speed was fixed to 600 rpm to eliminate diffusion effects [23]. Finally, the reactor was quickly cooled and the reaction products were separated from the catalysts by centrifugation. The aqueous phase was analyzed by gas chromatography (Ouhua GC 9160) equipped with an SE-54 capillary column (30 m×0.32 mm×0.5 μm), with a flame ionization detector (FID). The vaporization temperature was 300 °C, the detector temperature was 280 °C, and the oven temperature was 130 °C.

RESULTS AND DISCUSSION

1. Catalyst Characterization

Fig. 1 shows the XRD patterns of Cu-Ni-Al hydroxides with different mole ratio of Cu/Ni/Al. All samples had the characteristic reflections of layered double hydroxides. No diffraction peak of separated Cu-containing oxide or Ni-containing oxide was observed.

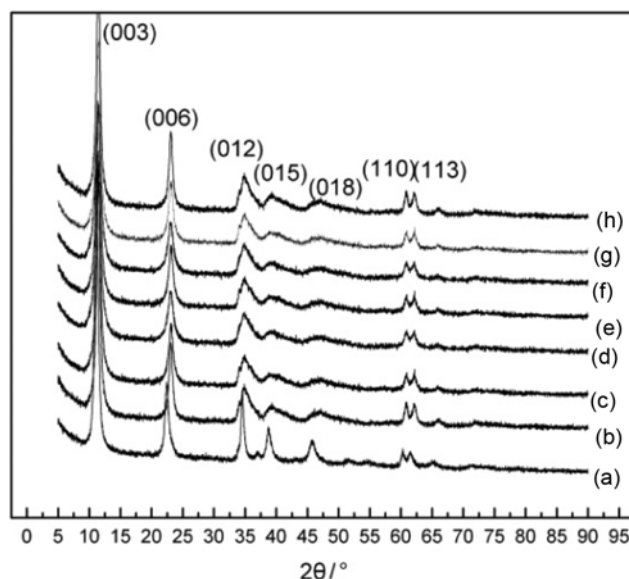


Fig. 1. XRD patterns of the Cu-Ni-Al hydroxides with different mole ratio of Cu : Ni : Al, (a) (1 : 59 : 20), (b) (1 : 29 : 10), (c) (3 : 57 : 20), (d) (1 : 14 : 5), (e) (3 : 27 : 10), (f) (2 : 13 : 5), (g) (1 : 5 : 2), (h) (1 : 2 : 1).

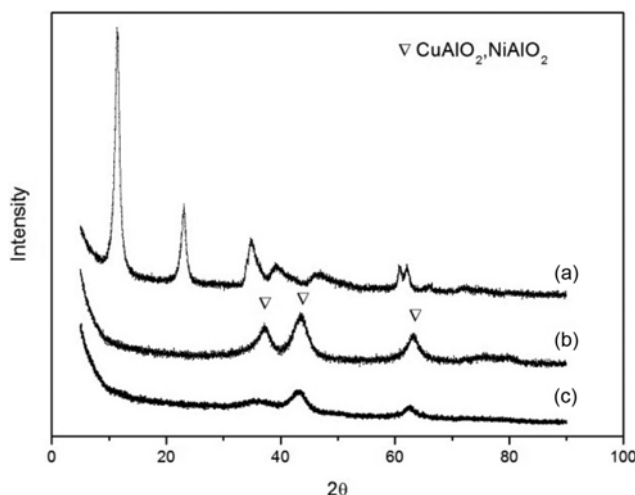


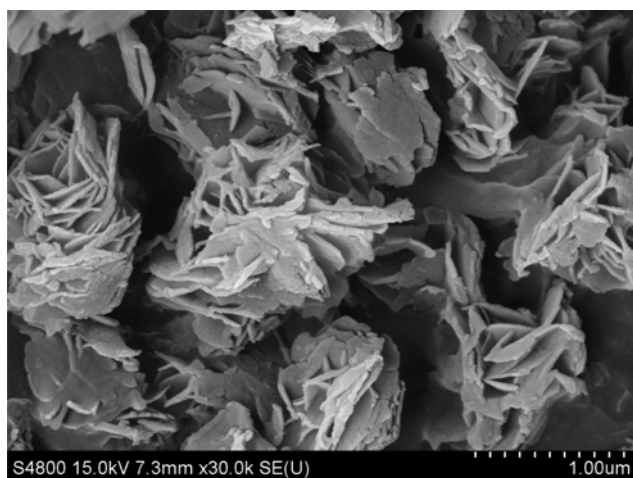
Fig. 2. XRD patterns of the uncalcined Cu-Ni-Al (1 : 14 : 5) hydroxides (a), reduced Cu-Ni-Al catalysts (b), reduced Cu-Ni-Al hydroxides (c), calcined Cu-Ni-Al hydroxides.

Sharp and symmetrical reflections at 11.7°, 23.2°, 60.6° and 61.8° are designated to diffraction of (003), (006), (110) and (113) plane in layered structure.

Fig. 2 describes the XRD patterns of Cu-Ni-Al metal oxides derived from hydrotalcite precursors. After calcination, the typical hydrotalcite phase disappeared as shown in Fig. 2. The sharp and symmetrical reflections at 11.7°, 23.2° disappeared when hydrotalcites were calcined. What's more, the sharp diffraction peak at 35.5° changed to be broad and flat, which illustrated that the layered structure of hydrotalcite was stable. It still remained a portion of the hydrotalcite structure after calcination at 773 K for 4 h, which might be conducive to the increase of furfural conversion and cyclopentanone selectivity, when connected with the Table 1. XRD of reduced Cu-Ni-Al

Table 1. Effect of Cu, Ni and Al mole ratio on cyclopentanone yield, cycloentanol yield and furfural conversion

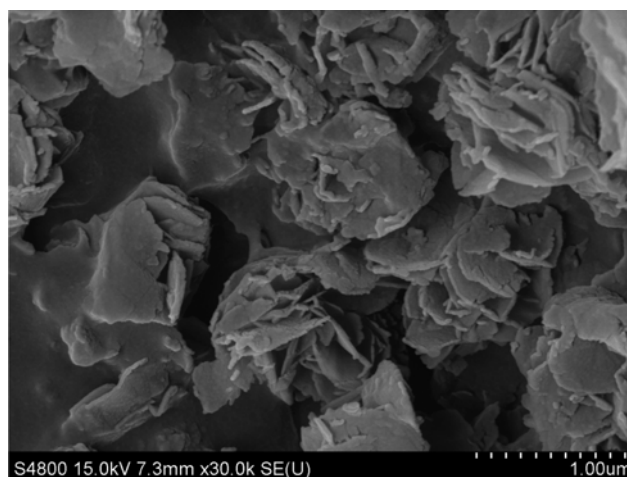
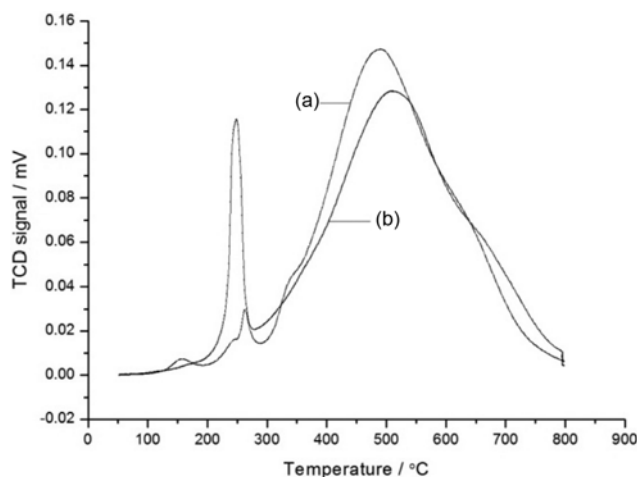
Cu : Ni : Al Mole ratio	Conversion (%)	Yield (%)	
		Cy _{PON}	Cy _{POL}
1 : 59 : 20	98.2	52.5	32.1
1 : 29 : 10	98.5	63.2	16.9
3 : 57 : 20	99.8	81.3	14.9
1 : 14 : 5	100	95.8	3.0
3 : 27 : 10	100	77.7	21.3
2 : 13 : 5	98.6	69.1	24.0
1 : 5 : 2	97.8	57.4	26.2
1 : 2 : 1	97.1	46.7	31.4

**Fig. 3. SEM of Cu-Ni-Al HTLCs, Cu, Ni and Al mole ratio of this hydrotalcite was: 1 : 14 : 5.**

catalysts are shown in Fig. 2. It can be found that the intensity improved obviously, and the XRD patterns of reduced catalyst clearly indicated the formation of spinel species such as CuAlO_2 or NiAlO_2 [24].

As we can see from the SEM image in Fig. 3, the layer structure of the Cu-Ni-Al hydroxides was clear with dense particles and some sand rose morphology characteristics. Cu, Ni and Al mole ratio of this hydrotalcite was 1 : 14 : 5. Connected with the Table 1, it can be inferred that the ordered arrangement of these layered solid lamellars brought the interlayer space and slit pores between lamellars, which can be regarded as the source of mesopores. These mesopores could enhance the access of reactants to active sites, which would contribute significantly to the increase of furfural conversion and cyclopentanone selectivity. SEM images of the Cu-Ni-Al hydroxides (Fig. 4) indicated that the orderliness of these layered double hydrotalcite crystals decreased with increasing amount of Cu. Consequently, it would cause the decrease in surface area of the catalyst.

Cu^0 species were considered as the catalytic active sites for the hydrogenation of FFR over the Cu-containing catalysts [10,25]. The H_2 -TPR results of catalysts (see Fig. 5) show that Cu-Ni-Al based catalysts give a relatively intensive H_2 consumption peak at about 250–300 °C with the increase of Cu amount in the catalysts. The sharp peak at lower temperature was ascribed to the reduction of Cu^{2+} species, and the broad peak was assigned to the reduction of Ni^{2+} species [24].

**Fig. 4. SEM of Cu-Ni-Al HTLCs, Cu, Ni and Al mole ratio of this hydrotalcite was: 1 : 2 : 1.****Fig. 5. H_2 -TPR of Cu-Ni-Al catalysts with different mole ratio: (a) Cu : Ni : Al (1 : 14 : 5), (b) (1 : 59 : 20).**

2. Influence of Metal Composition in Catalysts

Cu-Ni-Al based catalysts of different metal mole ratio were prepared and the reaction results of which are presented in Table 1. As can be seen, the furfural conversion was over 97% with varied cyclopentanone yield changed from 46.7% to 95.8%. The yield of cyclopentanone increased first when the Cu content increased, then began to decrease, because in a reaction the increased amount of active ingredient would inevitably lead to the increase of product yield. However, when the Cu content continued to increase, some byproducts such as cyclopentanol or pentanol began to appear, which were due to the further hydrogenation products of cyclopentanone under the combined effect of the exceeded active ingredient and hydrogen. Additionally, continued increase in active ingredient would lead to the particle accumulation (seen in Fig. 3 and Fig. 4), which would lead to the decrease of catalyst surface area, then affect the reaction selectivity and the catalytic activity. So, for the preparation of catalyst with high reaction activity, a Cu/Ni/Al mole ratio of 1 : 14 : 5 was chosen considering the conversion and reaction selectivity.

3. Influence of Reaction Condition

As seen in Fig. 6(a), reaction time was of great importance to

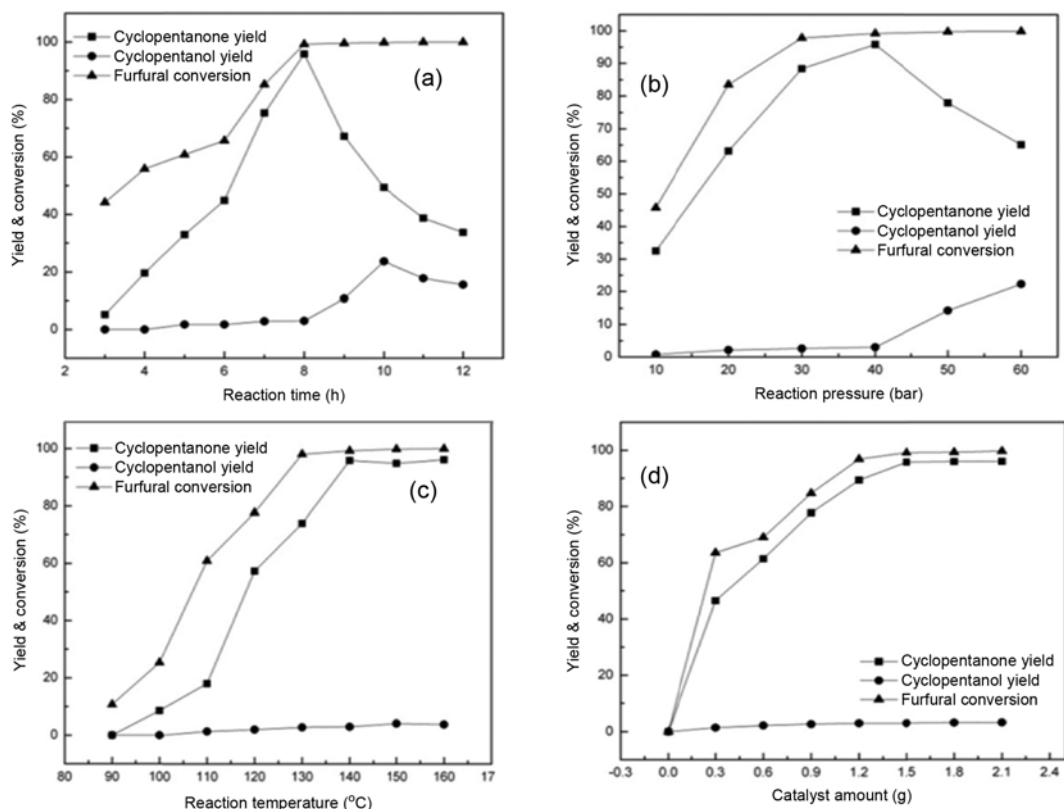


Fig. 6. Effect of different influencing factors: (a) reaction time; (b) H_2 pressure; (c) reaction temperature; (d) catalyst amount.

the distribution of hydrogenation products of furfural. Obviously, the prolongation of the reaction time increased the yield of cyclopentanone. However, when the reaction time exceeded 8 h, the yield of cyclopentanone tapered off and the yield of cyclopentanol proportionally increased within a certain period of time. Here cyclopentanol was a further hydrogenation product due to the prolongation of reaction time, the catalyst used, and the existence of excess hydrogen. When the reaction exceeded 10 h, another byproduct, pentanol, began to appear as the further hydrogenation product of cyclopentanol [23]. So in the reaction, 8 h was finally selected as the reaction time to get better yield toward cyclopentanone.

Fig. 6(b) shows that high yield of cyclopentanone was obtained over the same reaction time at relatively lower hydrogen pressure, which was in accordance with the result in Fig. 6(a). For example, when the hydrogen pressure was 40 bar, the yield of cyclopentanone could obtain over 95%, which was much higher than the results at high hydrogen pressure. This result was probably caused by the right amount of hydrogen dissolved in the liquid phase, which was all consumed for the furan ring rearrangement rather than for the consecutive hydrogenation of primarily formed cyclopentanone.

The yield of cyclopentanone obtained over various reaction temperature is shown in Fig. 6(c). As can be observed, the higher the reaction temperature was, the less change of cyclopentanone yield was observed, when the reaction temperature was over 413 K. Therefore, the reaction temperature played a small effect on the transformation of furfural to cyclopentanone.

The distributions of final products for the hydrogenation of furfural carried out over various amount of catalyst are shown in Fig. 6(d). As can be seen, better yield toward cyclopentanone could be

obtained with the increase of catalyst dosage, because increasing the catalyst amount would lead to the increase of contact opportunity between the catalyst and the reactants, which would definitely accelerate the reaction speed, and then improve the conversion and yield. However, there seems no obvious improvement in conversion and yield when the catalyst amount used exceeds 1.5 g. Therefore, 1.5 g was chosen as the optimal catalyst amount for the hydrogenation of furfural. On the whole, the optimal reaction condition was as follows: Cu/Ni/Al mole ratio-1 : 14 : 5, reaction time-8 h, hydrogen pressure-40 bar, reaction temperature-413 K, catalyst amount-1.5 g.

4. Catalyst Recyclability

To investigate the recyclability of catalysts, a batch of Cu-Ni-Al-HT (Cu/Ni/Al=1 : 14 : 5) originated catalysts was used repeatedly for the catalytic hydrogenation of furfural at 413 K in water. All the used catalysts were washed, dried, calcined and reduced in H_2 before the next run for hydrogenation of furfural. As shown in Table 2, conversion and yield slightly decreased due to the loss of

Table 2. Results of repeated use of Cu-Ni-Al-HT-originated catalysts

Catalyst (mole ratio)	Hydrogenation pressure (bar)	Entry	Con./%	Yield % C-PON
Cu-Ni-Al (1 : 14 : 5)	40 bar	1	100	95.8
		2	91.2	85.9
		3	85.2	74.5

Reaction conditions: 1.5 g catalyst, 5 ml FFR, 95 ml water; reaction temperature 413 K; reaction time 8 h

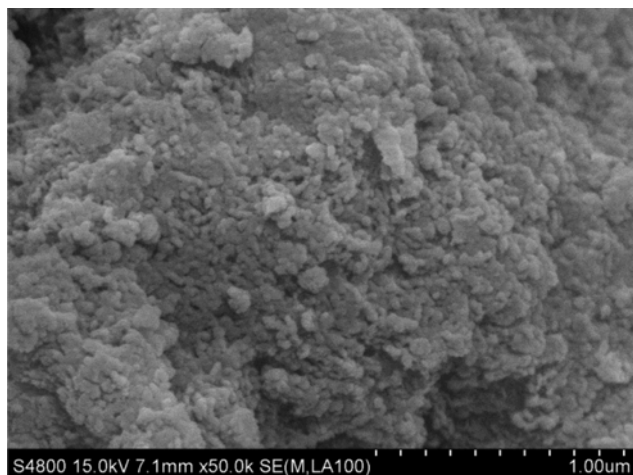


Fig. 7. SEM of reused catalyst (Cu/Ni/Al=1 : 14 : 5).

catalyst activity after the catalysts were reused twice, which might be caused by catalyst agglomeration in the catalytic hydrogenation process of furfural, and calcination over and over again. It was found in Fig. 7 that catalyst agglomerated seriously after repeated calcination and hydrogenation reaction. As for the reaction time, here 8 h was selected, for prolonged reaction time did not do any good to the conversion and yield.

CONCLUSIONS

Cu-Ni-Al hydrotalcite-based catalysts were prepared by co-precipitation method. Furfural could be converted to cyclopentanone with the yield up to 95.8% under 413 K, the initial H_2 pressure of 40 bar and reaction time for 8 h, catalyzed by catalyst with a Cu/Ni/Al mole ratio of 1 : 14 : 5. The catalyst processes have advantages such as high catalytic activity, easy separation of the catalyst by simple centrifugation and application of non-toxic and inexpensive chemicals. Furthermore, so prepared Cu-Ni-Al hydrotalcite-based catalysts could be repeatedly used with little decrease in selectivity and yield. The new route provides a feasible approach for the upgrading of bio-oil via furans platform.

ACKNOWLEDGEMENT

The authors are grateful for the financial support from the National Hi-tech Research and Development Program of China (863Program) (2012AA051801) and the National Basic Research Program of China (973 Program) (2010CB732206).

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