



Short Communication

Hydrogenation of glucose over reduced Ni/Cu/Al hydrotalcite precursors



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ABSTRACT

Ni/Cu/Al hydrotalcite precursors were synthesized by a co-precipitation method. The activity of the reduced precursors for hydrogenation of glucose to sorbitol was tested. The effects of preparation methods and activation treatment on the performance of the obtained catalysts were investigated in detail. XRD and XPS tests provided the essential properties of the precursors and prepared catalysts. The properly high reduction temperature could obviously enhance catalyst activity. The conversion of glucose and selectivity to sorbitol on Ni_{1.85}Cu₁Al_{1.15} catalyst at 398 K were 78.4 and 93.4 %, respectively.

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1. Introduction

Sorbitol, generally produced by glucose hydrogenation and cellulose hydrogenolysis, is known as one of the 12 important target chemicals that US-DOE selected in their biomass program [1]. Most importantly, sorbitol can be further degraded into polyols that are the downstream products in petrochemical industry. It also can be used for the synthesis of lactic acid under alkaline hydrothermal condition [2]. Recent studies show that the structure and catalytic performance of some catalysts would be apparently improved when little sorbitol was added during catalyst preparation [3,4]. Due to its widespread applications, it is meaningful to do much more research on sorbitol production.

In recent years, Raney-type nickel and ruthenium catalysts are mainly applied in sorbitol production, especially Ru-based catalysts. For example, Hoffer et al. [5] studied selective hydrogenation of glucose by carbon supported Ru catalyst by comparison with Raney-type Ni. It was found that Ru/C displayed nearly 100% selectivity to sorbitol, and the catalyst activity was proportional to Ru surface area and was independent of preparation methods. The Ni in Raney-type Ni catalyst could be easily leached into the solution. Notably, catalytic activity of supported Ru catalysts partially depended on the organic promoters, precursors (ruthenium acetate [6] and ruthenium trichloride [7]) and carriers (activated carbon, [5] Al₂O₃, [8] and MCM-41 [9]). In spite of the great performance of Ru catalysts, the cost was too high that limited their application in industry. Therefore, a considerable effort is still necessary to develop some other cheap and efficient catalysts for the hydrogenation of glucose.

Hydrotalcite-like compounds (HTLcs) were used as precursors for the preparation of hydrogenation catalysts for the first time early in the 1970s [10]. The catalysts prepared from HTLcs exhibited exciting activity for merits of smaller crystal size, higher surface area and acidic/basic surface. The catalytic applications of HTLcs in hydrogenation reactions as well as many other reactions, such as oxidation reactions, aldol condensation, and polymerization, are reviewed in the literature [11]. For hydrogenation reactions, this needs the precursors to be reduced under high temperature at H₂ atmosphere, only in this way can the existing Ni or Cu element shows excellent catalytic activity. Meanwhile, it is worth noting that the preparation cost of HTLcs is lower when compared to that of Ru catalysts.

In this work, a series of hydrogenation catalysts were prepared from Ni/Cu/Al hydrotalcite precursors. The catalytic performance of obtained catalysts in the hydrogenation of glucose to sorbitol was investigated. The effects of various parameters on the catalytic performance of the prepared catalysts were also studied in detail.

2. Experimental

2.1. Catalysts preparation

A series of Ni/Cu/Al hydrotalcite precursors with different Ni:Cu:Al atomic ratios was synthesized by a co-precipitation method [12]. An aqueous solution (150 mL) containing appropriate amount of Cu(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O with cation concentration of 1 mol/L was added dropwise with vigorous stirring into 150 mL of NaOH and Na₂CO₃ solutions ([OH⁻] = 2 ([Cu²⁺] + [Ni²⁺] + [Al³⁺]), [CO₃²⁻] = 0.5 [Al³⁺]). The addition took about 0.5 h. The pH was kept between 8.5 and 10. The resulting slurry was aged at 333 K for 10 h. The precipitate was filtered, washed thoroughly with distilled water and then dried at 353 K for 24 h.

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Modified Ni/Cu/Al hydrotalcite precursors were prepared with the addition of nitrates of Mg, Zn, Co, Cr and Fe according to the above method. The theoretical molar ratios of Mg/Cu, Zn/Cu, Co/Cu, Cr/Al, and Fe/Al were 1:1. Before the test, the samples were reduced in a H₂ flow for 3 h. In particular, these calcined catalysts were treated at 773 K in air for 4 h before reduction treatment. The chemical composition of hydrotalcite precursors and specific names of the obtained catalysts were shown in Table 1.

2.2. Catalytic reaction procedure

The conversion of glucose into sorbitol was performed with high pressure reactor (PARR 5500). For each run, glucose, catalysts, and deionized water were put into the reactor, then the reaction was carried out at 398 K and 3 MPa H₂ with a stirring rate of 600 rpm. After reaction, the stirring stopped and the reactor was cooled down to room temperature with ice water. The liquid products were collected by filtration and stored in the refrigerator. The samples were analyzed by IC (Dionex ICS-3000) with CarboPac™ PA1 column. The eluents were NaOH and H₂O with a flow rate of 0.25 mL/min. The column temperature was 303 K.

Glucose conversion, yields of main products and corresponding product selectivity (i.e., sorbitol and mannitol) were calculated as follows:

$$\text{Glucose conversion (wt.\%)} = \frac{[(\text{mass of starting glucose}) - (\text{mass of glucose after reaction})]}{(\text{mass of starting glucose})} * 100\%$$

$$\text{Product yield (wt.\%)} = \frac{(\text{mass of the product})}{(\text{mass of starting glucose})} * 100\%$$

$$\text{Product selectivity (\%)} = \frac{(\text{product yield})}{(\text{glucose conversion})} * 100\%$$

2.3. Catalysts characterization

Chemical analyses were carried out on a Thermo Elemental ICP-AES spectrometer after dissolution of the solid sample in a HNO₃ solution. Powder X-ray powder diffraction (XRD) was performed in a Bruker D8 Advance diffractometer using Cu K α radiation. The operating voltage and current were 40 kV and 40 mA respectively. The step length was 0.02° with scanning rate of 2°/min. The crystallite size was calculated by XRD-line broadening using the Scherrer equation [13]. X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Ultra system employing an Al K α radiation source. The binding energies for each spectrum were calibrated with a C1s spectrum of 284.6 eV. Survey spectra for each sample over a binding energy range of 0–1100 eV were recorded at pass energy of 160 eV and resolution of 1 eV per step. High-resolution spectra of Cu 2p and Ni 2p were recorded at

pass energy of 40 eV and resolution of 0.1 eV per step, for quantitative measurements of binding energy.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD test

Phase identification of the prepared samples was performed by XRD, as given in Figs. 1 and 2. The XRD patterns of HTLcs (Fig. 1) exhibited sharp and symmetrical reflections for (003), (006) and (113) planes and broad and asymmetric reflections for (012), (015) and (018) planes, characteristic of a well-crystallized HT in carbonate form [14,15]. The peaks at 11.7, 23.3, 35.0, 39.0, 47.2 and 61.6° could be assigned to the (003), (006), (012), (015), (018) and (113) diffractions of HTLcs respectively. It was found that the intensity of the diffraction lines slightly decreased by the addition of Ni cations in sample C4 as compared to C1, especially in (003), (006), (012), and (113) planes, indicating that the crystallinity of the HT phase in the Ni-containing precursors became lower with the increase in Ni content [16]. Furthermore, an obvious decrease in the intensity of the diffraction lines was observed in Co, Cr and Fe modified Ni/Cu/Al HTLcs. It may be caused by the interaction among metallic ions (Ni²⁺, Cu²⁺, Co²⁺, Fe³⁺, Cr³⁺, Al³⁺) and anions (OH⁻ and CO₃²⁻).

Fig. 2 shows the XRD patterns of prepared C1–C4 catalysts. Peak corresponding to planes (200) at 2 θ of 50.8° in Fig. 2(A) and (B) was clearly observed. It coincided with those in files JCPDS 4-836, which corresponded to metallic copper (Cu⁰) in a face-centered cubic structure. The peaks at 2 θ of 37.3° (planes 110) and 2 θ of 63.1° (planes 220) demonstrated the presence of NiO. Besides, peaks corresponding to planes (111) at 2 θ of 43.8° and planes (220) at 2 θ of 75.3° indicated the formation of the Cu–Ni solid solution. The results were in line with those reported by Rao et al. and Wu et al., in relation to the peak positions in the XRD diagram of Cu–Ni alloy [17–19]. For calcined C4 catalyst, the peaks at 2 θ of 35.7 and 38.6° demonstrated the existence of monoclinic CuO with planes of (111) (JCPDS 80-1917). In calcined C2 sample, an obvious peak at 2 θ of 23.5° could be assigned to the phase of α -Al₂O₃ [20]. Meanwhile, due to the effect of sintering, the crystallite size of calcined C2 increased from 4.3 to 5.1 nm as compared with non-calcined sample. It can be found that the peak intensity decreased obviously with increasing Ni/Cu molar ratio, as seen in the XRD test of calcined samples (C1–C4).

3.1.2. XPS analysis

The main reason for conducting XPS analysis was to obtain information regarding chemical environment presented in C2 samples. High-resolution scans of the XPS spectra of Cu 2p and Ni 2p with

Table 1
Chemical composition of hydrotalcite precursors and names of the catalysts.

Chemical analysis (wt.%)			Catalyst precursors	Reduced samples ^a (reduction: H ₂ , 3 h)
Ni	Cu	Al		
18.34	21.39	5.77	Ni _{0.92} Cu ₁ Al _{0.63} (OH) _{5.1} (CO ₃) _{0.315}	C1 (Ni _{0.92} Cu ₁ Al _{0.63})
25.31	14.75	7.20	Ni _{1.85} Cu ₁ Al _{1.15} (OH) ₈ (CO ₃) _{0.575}	C2 (Ni _{1.85} Cu ₁ Al _{1.15})
29.21	11.42	7.25	Ni _{2.75} Cu ₁ Al _{1.49} (OH) _{10.48} (CO ₃) _{0.745}	C3 (Ni _{2.75} Cu ₁ Al _{1.49})
30.83	7.31	7.50	Ni _{4.54} Cu ₁ Al _{2.41} (OH) _{15.9} (CO ₃) _{1.205}	C4 (Ni _{4.54} Cu ₁ Al _{2.41})
23.34	14.10	6.64	Ni _{1.78} Cu ₁ Mg _{1.29} Al _{1.11} (OH) _{10.36} (CO ₃) _{0.555} ^b	C5 (Ni _{1.78} Cu ₁ Mg _{1.29} Al _{1.11})
21.28	13.50	5.59	Ni _{1.70} Cu ₁ Zn _{0.99} Al _{0.97} (OH) _{9.32} (CO ₃) _{0.485} ^c	C6 (Ni _{1.70} Cu ₁ Zn _{0.99} Al _{0.97})
20.41	12.91	4.96	Ni _{1.70} Cu ₁ Co _{0.84} Al _{0.90} (OH) _{8.88} (CO ₃) _{0.45} ^d	C7 (Ni _{1.70} Cu ₁ Co _{0.84} Al _{0.90})
25.39	14.64	6.19	Ni _{1.87} Cu ₁ Al _{0.99} Cr _{0.51} (OH) _{8.74} (CO ₃) _{0.75} ^e	C8 (Ni _{1.87} Cu ₁ Al _{0.99} Cr _{0.51})
26.62	15.31	4.16	Ni _{1.87} Cu ₁ Al _{0.64} Fe _{0.57} (OH) _{8.16} (CO ₃) _{0.605} ^f	C9 (Ni _{1.87} Cu ₁ Al _{0.64} Fe _{0.57})

^a Denoted with the molar ratio of metals.

^b Mg: 6.88 wt.%.

^c Zn: 13.68 wt.%.

^d Co: 10.13 wt.%.

^e Cr: 6.12.

^f Fe: 7.72 wt.%.

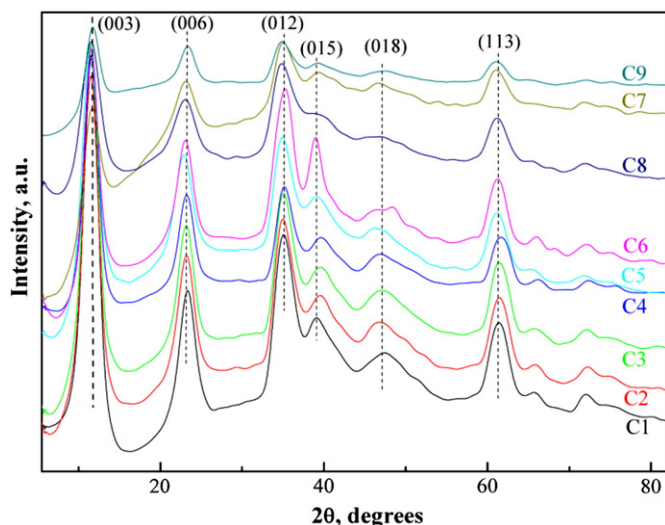


Fig. 1. Powder XRD patterns of HTlcs precursors (C1–C9).

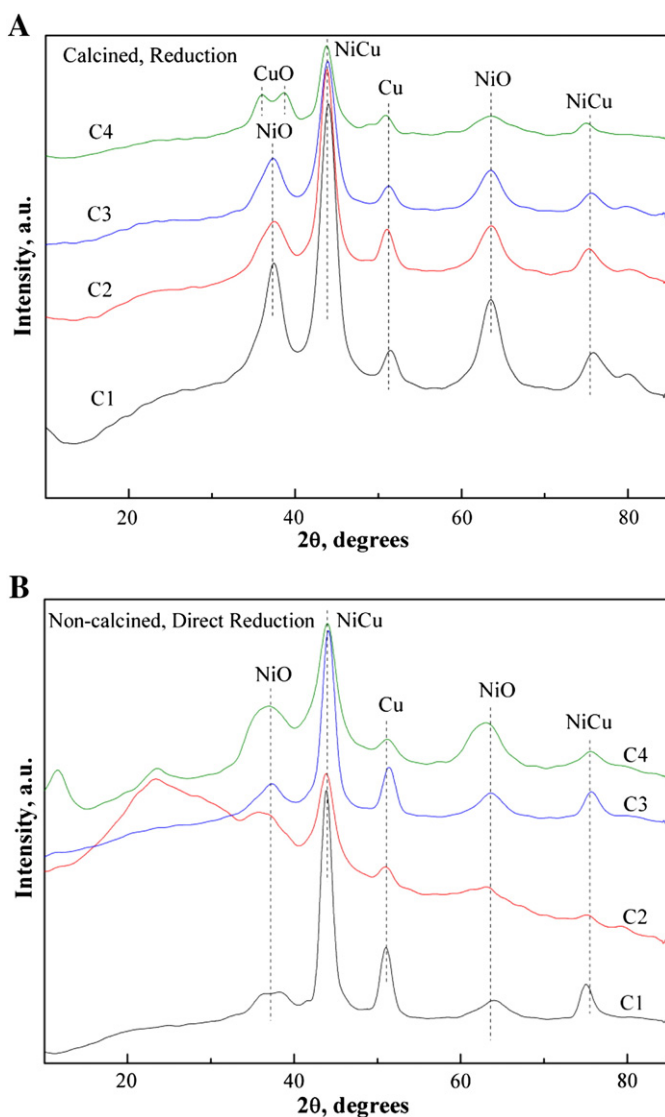


Fig. 2. Powder XRD patterns of reduced C1–C4 samples: (A) calcined – 773 K, 4 h, reduction – 773 K, 3 h and (B) non-calcined, direct reduction – 773 K, 3 h.

different intensity scales as ordinate are shown in Fig. S1. As seen in Fig. S1 (A), four obvious peaks in the diagram of Cu 2p were detected in the reduced C2 samples, representing various valence states of Cu element. Two shake-up lines appeared at 940.6 and 960.7 eV separately. The binding energies of Cu 2p_{3/2} and 2p_{1/2} were around 932.3 and 953.2 eV respectively, which were very close to that of Cu⁰. This demonstrated that the Cu²⁺ was essentially reduced to metallic copper (Cu⁰). Notably, the binding energies of metallic Cu are around 932.6 and 953.8 eV [21,22]. It was inferred that the reduction temperature required for converting Cu²⁺ to Cu⁰ was low, and the reduction of Cu²⁺ could be easily completed at a temperature of 623 K under H₂ atmosphere.

For Ni element, the obtained binding energies were around 852.8 and 869.9 eV, indicating the presence of Ni 2p_{3/2} and 2p_{1/2} respectively. The binding energy of Ni 2p_{3/2} in pure NiO is 854.5 eV while for NiAl₂O₄ spinel it appears at 856 eV [23]. With regard to reduced C2 sample, two peaks were observed at binding energies of about 853.5 and 871.0 eV that were among that of Ni⁰ and Ni²⁺, demonstrating the existing of metallic Ni and NiO species. As the samples were not calcined under high temperature in air, which were prepared by direct reduction in hydrogen atmosphere, the structure of NiAl₂O₄ spinel was not found in the reduced catalysts according to the resulting binding energies. Furthermore, it can be seen from Fig. S1 (B) that two satellites at binding energies of about 860.0 and 878.0 eV were observed. With increasing reduction temperature to 873 K, there was still little NiO in reduced C2 catalyst. This showed that the Ni²⁺ was hard to be totally reduced to metallic Ni (Ni⁰), and higher temperature may be required for this reduction process to obtain Ni⁰.

3.2. Catalytic performance for the conversion of glucose

3.2.1. Influence of preparation methods and activation treatment on catalyst performance

The effect of preparation methods on the catalytic activity of C1–C4 catalysts was investigated in detail. As shown in Table 2, the glucose conversions for non-calcined samples were generally higher than those calcined ones, which reached to around 80% in C2 and C3 samples. It was proposed that the calcined samples had larger crystallite size due to the effect of sintering and the factual contact area became lower in calcined samples, so the reactant might not make a good contact with catalyst. In order to simplify preparation process and lower cost, the catalysts were prepared by direct reduction without calcination treatment. With increasing Ni/Cu molar ratio, the yield and selectivity of sorbitol also increased obviously at first. When further increasing Ni content, an obvious decrease in the yield and selectivity of sorbitol could be found. Because the hydrogenation ability of C3–C4 catalysts would be partly weakened due to the decrease in Cu content, much more Ni²⁺

Table 2
Effect of preparation methods on the catalytic activity of obtained catalysts.

Catalysts	Sorbitol yield, %	Glucose conversion, %	Sorbitol selectivity, %
C1 (non-calcined)	40.3	63.9	63.0
C1 (calcined)	45.0	80.4	56.0
C2 (non-calcined)	69.2	80.0	86.5
C2 (calcined)	60.6	68.7	88.2
C3 (non-calcined)	62.8	81.7	76.9
C3 (calcined)	65.0	72.2	90.0
C4 (non-calcined)	46.3	76.9	60.2
C4 (calcined)	42.2	71.3	59.2
C5 (non-calcined)	53.2	94.7	56.2
C6 (non-calcined)	26.3	70.9	37.1
C7 (non-calcined)	51.3	67.1	76.4
C8 (non-calcined)	48.8	59.2	82.4
C9 (non-calcined)	59.0	82.9	71.1

Reaction conditions: 2.0 g glucose, 0.4 g catalysts (reduction temperature: 873 K), 40 mL aqueous solution, 398 K, 600 rpm, 3 h and 3 MPa H₂.

in C3–C4 samples could not be easily reduced into Ni⁰ based on the results of XPS analysis. The highest level of 69.2 and 86.5% in the yield and selectivity of sorbitol was achieved using non-calcined C2 catalyst.

In the following work, the C2 catalyst was modified with various metallic elements such as Mg, Zn, Co, Cr and Fe, with the aim of enhancing hydrogenation reactivity. It can be seen from Table 2 (non-calcined C5–C9 samples) that the Mg and Fe modified C2 catalysts exhibited great glucose conversion, while the corresponding selectivities towards sorbitol were lower. Note that the Zn modified C2 catalyst showed poor activity compared to other modified catalysts. Through the comparison and analysis, the hydrogenation activity of those added metals was not greater when compared to active Ni and Cu catalysts, which were hardly applied in hydrogenation reactions. On the other hand, it was inferred that these metals did not apparently promote the activation of the C=O in glucose molecules, thus leading to the decrease in the yield and selectivity of sorbitol.

Subsequently, the influence of reduction temperature on the activity of C2 catalyst was studied. As seen in Table S1, the catalyst activity was greatly improved by increasing reduction temperature from 623 to 873 K. For Cu element, it could be easily reduced from Cu²⁺ to Cu⁰ in the precursors, because the reduction of Cu²⁺ was completed at 623 K under hydrogen atmosphere according to XPS analysis. However, reduction of Ni element needed to be carried out under higher temperature. Due to limitation of reduction equipment, the maximum temperature was conducted at 873 K. With increasing temperature to 873 K, much more Ni in samples was reduced and it would facilitate the sorbitol hydrogenation, even though there was still little NiO in reduced catalyst. By comparison with temperature of 623 K, the corresponding yield and selectivity increased from 60.0 to 73.2% and 78.2 to 93.4% respectively.

3.2.2. Influence of reaction solution on yield and selectivity of sorbitol

It was known that the glucose was converted into sorbitol via isomerization and hydrogenation. However, the specific environment of the medium plays a great part in glucose isomerization, which will affect the subsequent hydrogenation process. In this section, various reaction solutions were employed for the conversion of glucose. As shown in Table 3, both acidic and alkaline conditions were not conducive to the conversion of glucose into sorbitol. A reasonable explanation is that little 5-HMF and LA could be formed by glucose dehydration under acidic medium [24]. While the alkaline condition favored both the procedures of glucose isomerization and sorbitol hydrogenolysis, 19.4% mannitol and much lower alcohols such as ethylene glycol and propanediol would be produced at high glucose conversion (84.9 %) [25]. Therefore the sorbitol selectivity became lower when the reaction was conducted under conditions of 15 mmol/L H₂SO₄ (78.6%) and 15 mmol/L NaOH (49.7%), especially in alkaline solution. With all these observations considered together, deionized water was chosen as the most suitable medium for sorbitol production.

4. Conclusions

Cu/Ni/Al hydrotalcites with different compositions were prepared by a coprecipitation method. XRD results of the precursors suggested the formation of hydrotalcite structure. The XRD and XPS tests of reduced catalysts indicated that the Cu²⁺ was completely reduced to

Cu⁰ and little unreduced NiO was found in the reduced samples. The C2 catalyst prepared without calcination showed higher activity for glucose hydrogenation when compared to that of calcined sample. The acidic or alkaline medium did not favor sorbitol production. The desired yield and selectivity of sorbitol on C2 catalyst were 73.2 and 93.4 % at reaction temperature and time of 398 K and 3 h with catalyst dosage of 20 %.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2013.01.017>.

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Table 3

Effect of reaction mediums on the hydrogenation of glucose.

Medium	15 mmol/L H ₂ SO ₄	Deionized water	15 mmol/L NaOH
Sorbitol yield, %	52.1	73.2	42.2
Glucose conversion, %	66.3	78.4	84.9
Sorbitol selectivity, %	78.6	93.4	49.7

Reaction conditions: 2.0 g glucose, 0.4 g non-calcined C2 catalyst (reduction temperature: 873 K), 40 mL reaction medium, 398 K, 600 rpm, 3 h and 3 MPa H₂.