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ORIGINAL PAPER

Promotion effect of nickel for Cu–Ni/γ-Al_2O_3 catalysts in the transfer dehydrogenation of primary aliphatic alcohols

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Abstract Cu–Ni/γ-Al_2O_3 bimetallic catalysts were developed for anaerobic dehydrogenation of non-activated primary aliphatic alcohols to aldehydes. Systematic investigation about the promotion effect of nickel on the catalytic performance was carried out. Hydrogenation of C=C bond rather than C=O bond, was significantly improved over Cu–Ni/γ-Al_2O_3 catalyst by introducing nickel, which interprets the good conversion of primary aliphatic alcohols. This work would contribute to design new catalysts for dehydrogenation of primary aliphatic alcohols.

Keywords Heterogeneous catalysis · Alcohols · Dehydrogenation

Introduction

The selective oxidation of non-activated primary aliphatic alcohols is one of the most challenging reactions. Stoichiometric oxidizing agents such as chromium and manganese salts are traditionally used which often result in large amount of toxic wastes. Development of catalytic aerobic oxidation of alcohols attracts much attention for both environmental and economic reasons [1–10]. However, it is rather challenging to obtain high selectivity toward aldehydes because of facile oxidation of aldehydes into acids in presence of molecular oxygen and transitional metal catalysts [1–3, 11–13]. Catalytic dehydrogenation of alcohols is an attractive method [14] in which further oxidation of aldehydes into acids is limited under an inert atmosphere. Although various monometallic catalysts including Ag [15, 16], Co [17] and Cu [18–21] have been reported for efficient liquid-phase dehydrogenation of secondary aliphatic alcohols, catalytic dehydrogenation of non-activated primary aliphatic alcohols into aldehydes is rather difficult.

In catalytic transfer dehydrogenation of alcohols, a readily available unsaturated organic compound is often used as hydrogen acceptor [22, 23]. Generally, both dehydrogenation of alcohols and hydrogenation of carbonyl product would occur simultaneously, and an equilibrium would be temporarily established without hydrogen acceptor (unsaturated organic compounds). The competitive hydrogenation of hydrogen acceptor with C=O bond of aldehydes would be crucial in catalytic transfer dehydrogenation of primary aliphatic alcohols. To obtain high yield of aliphatic aldehydes, a catalyst is desired with preference for catalytic hydrogenation of hydrogen acceptor rather than aliphatic aldehyde.

Monometallic copper catalysts exhibit good performance on catalytic dehydrogenation of alcohols [18–21, 24–27]. Enhancing the catalytic activity on hydrogenation of hydrogen acceptor would be favorable for production of aliphatic aldehydes for copper catalysts. Considering the high C=C bond hydrogenation activity and selectivity of nickel [28–31], and similar lattice parameters between copper and nickel [32–35], a copper–nickel bimetallic catalyst had been explored by our group [36]. Hydrogenation of hydrogen acceptor (styrene) would be accelerated when the nickel was introduced into the copper catalyst,

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and formation of aliphatic aldehydes would be enhanced. In this work, we present systemic and specific evidence to understand the promotion effect of nickel for Cu–Ni/γ-Al_2O_3 catalysts in the transfer dehydrogenation of primary aliphatic alcohols into aldehydes.

Experimental section

Materials

Deionized water used in all experiments was purified by a Milli-Q system (Millipore). γ-Al_2O_3, $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and ammonia solution (25 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. 3,3-Dimethyl-1-butanol, styrene and mesitylene were of analytic grade and obtained from Aladdin Chemical Reagent Corporation.

Preparation of Cu/γ-Al_2O_3 and Cu–Ni/γ-Al_2O_3 catalysts

Cu/γ-Al_2O_3 was prepared with a reported method [18, 19]. $Cu(NO_3)_2 \cdot 3H_2O$ (7.6 g) was dissolved in 100 mL of deionized water, and the pH value of the solution was adjusted to 9 using ammonia solution (25 %). Then, the solution was transferred into an ice-water bath. After that, γ-Al_2O_3 (20.0 g) was added to the above solution. After stirring for 20 min, the suspension was diluted by a large quantity of water. The solid was separated from the suspension by filtration and washed with deionized water for three times. Finally, the solid was dried at 110 °C overnight and calcined at 400 °C for 4 h in air. Cu loading of Cu/γ-Al_2O_3 was 6.6 wt% determined by XRF.

A series of Cu–Ni bimetallic catalysts with varying Cu/Ni ratios supported on γ-Al_2O_3 were prepared through introducing nickel to the above Cu/γ-Al_2O_3 by incipient wetness impregnation. Firstly, calculated amount of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in deionized water (1.4 mL). Then, Cu/γ-Al_2O_3 (2.0 g) was added to the solution. After stirring for 3 h, the slurry was dried at 80 °C for 8 h and calcined at 400 °C for 4 h in air. Before used in catalytic reactions, all the as-prepared materials were reduced in an atmosphere of H_2 at 500 °C for 5 h unless stated otherwise. We denoted the Cu–Ni bimetallic catalyst as *x*Cu–*y*Ni/γ-Al_2O_3, where *x* and *y* were denoted as the weight percent of Cu and Ni relative to γ-Al_2O_3.

Characterization

X-ray diffraction analysis was performed using Rigaku D/Max 2500/PC powder diffractometer with Cu-Kα radiation (λ = 0.15418 nm) at 40 kV and 200 mA with a scanning rate of 5° min^{-1}. Transmission electron microscopy (TEM) images were obtained on FEI Tecnai G^2 Spirit electron microscope at an accelerating voltage of 120 kV. Temperature-programmed reduction (TPR) of the samples was conducted at a heating rate of 10 °C min^{-1} in an H_2/Ar atmosphere at a flowing rate of 50 mL min^{-1}. Before measurements, sample of the catalyst was degassed at 150 °C in an atmosphere of Ar for 0.5 h. Sample weight was about 0.10 g, and the consumption of H_2 was monitored by TCD detector. X-ray fluorescence (XRF) was performed on a Philips Margix X-ray fluorescence spectrometer. N_2 adsorption–desorption isotherms were measured with a Quantachrome Autosorb using N_2 as adsorbate at 77 K. Samples were outgassed at 423 K for 2 h before measurements. The surface area was calculated according to Barrett–Emmet–Taller (BET) method. The physical parameters of the samples are shown in Table 1.

Table 1 Physical properties of different catalysts

Catalyst	Cu/Ni[a]	S^{b}_{BET} (m^2 g^{-1})	V^{c}_{pore} (mL g^{-1})
γ-Al_2O_3	–	201.2	0.31
6.6Cu/γ-Al_2O_3	–	170.3	0.32
6.6Ni/γ-Al_2O_3	–	166.5	0.31
6.6Cu–1Ni/γ-Al_2O_3	6.6	180.3	0.35
6.6Cu–1.3Ni/γ-Al_2O_3	5.0	214.0	0.38
6.6Cu–2Ni/γ-Al_2O_3	3.3	150.2	0.30
6.6Cu–4Ni/γ-Al_2O_3	1.7	161.9	0.28

[a] Mass ratio of Cu/Ni

[b] Surface area was determined by the BET method at a relative pressure of 0.05–0.30

[c] Total pore volume

Typical procedure for catalytic dehydrogenation

Typically, the dehydrogenation reactions were performed in a stainless steel autoclave equipped with an automatic temperature controller, a thermocouple, a magnetic stirrer and a pressure gauge. Taking catalytic dehydrogenation of 3,3-dimethyl-1-butanol as an example: 3,3-dimethyl-1-butanol (2 mmol), 6.6Cu–2Ni/γ-Al_2O_3 (0.4 g), styrene (8 mmol) and mesitylene (2 mL) were added to the autoclave. After the autoclave was sealed, N_2 was charged to replace the air. Then, the autoclave was heated to 150 °C under magnetic stirring within 20 min. After 24 h, the reactor was cooled down to room temperature. The liquid reaction mixture was diluted and analyzed.

Product analysis

The reaction mixture was analyzed by gas chromatography (GC) method. Gas chromatography measurements were performed on an Agilent 7890A GC with an DB-225

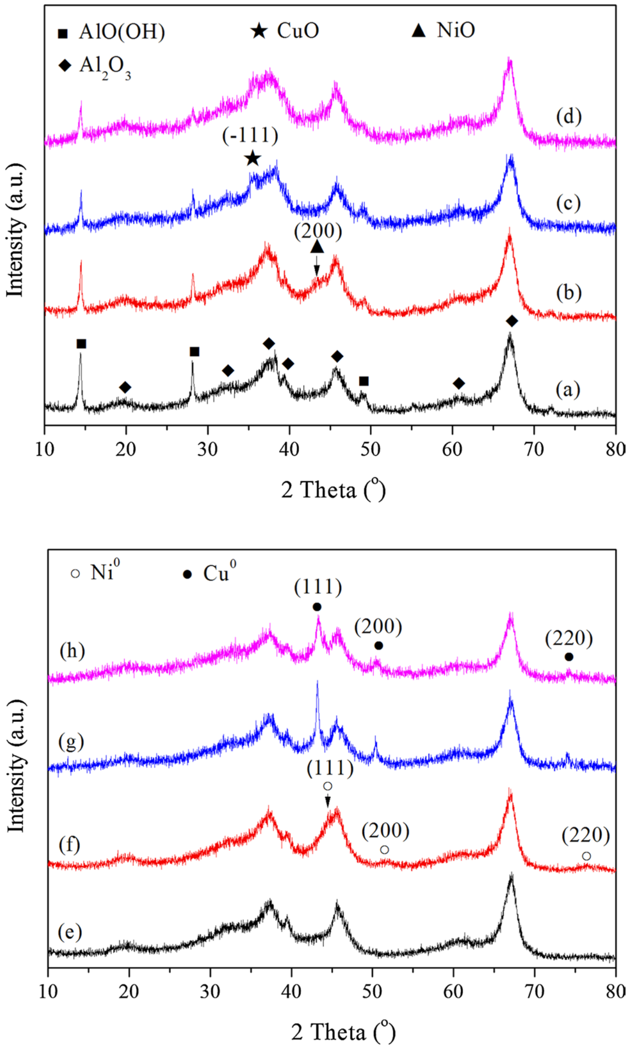


Fig. 1 XRD patterns of samples without reduction: **a** γ-Al_2O_3; **b** 6.6Ni/γ-Al_2O_3; **c** 6.6Cu/γ-Al_2O_3; **d** 6.6Cu–2Ni/γ-Al_2O_3 and reduced by H_2 at 500 °C: **e** γ-Al_2O_3; **f** 6.6Ni/γ-Al_2O_3; **g** 6.6Cu/γ-Al_2O_3; **h** 6.6Cu–2Ni/γ-Al_2O_3

capillary column and a flame ionization detector. Conversion and selectivity were determined by the area normalization method. Products were identified by using Agilent 6890 N GC/5973MS and the comparison with authentic samples.

Results and discussion

Characterization

X-ray diffraction patterns (XRD) of the samples are displayed in Fig. 1. Crude γ-Al_2O_3 without reduction showed diffraction peaks of cubic Al_2O_3 and orthorhombic AlO(OH) (Fig. 1a), as AlO(OH) (Al_2O_3·H_2O) was the precursor of γ-Al_2O_3. Thus, after H_2 reduction at 500 °C, diffraction peaks of AlO(OH) disappeared completely (Fig. 1e). The 6.6Ni/γ-Al_2O_3 without reduction exhibited a weak diffraction peak of NiO, and this peak corresponded to the reflection from (2 0 0) plane of the monoclinic NiO (Fig. 1b). When 6.6Ni/γ-Al_2O_3 was exposed to hydrogen at 500 °C for 5 h, the diffraction peak of NiO disappeared and characteristic peaks at $2\theta = 44.5°$, 51.9° and 76.4° were observed (Fig. 1f). These peaks corresponded to the reflection from (1 1 1), (2 0 0) and (2 2 0) planes of the cubic Ni^0. The changes between Fig. 1b, f indicated that the NiO species was reduced to Ni^0 by H_2 reduction at 500 °C. The 6.6Cu/γ-Al_2O_3 sample without reduction showed a diffraction peak at $2\theta = 35.7°$ which was ascribed to the reflection from (−1 1 1) plane of the monoclinic CuO (Fig. 1c). After reduction under H_2 at 500 °C, the characteristic line of CuO disappeared and diffraction peaks at $2\theta = 43.3°$, 50.5° and 74.2° appeared (Fig. 1g). These peaks were ascribed to the reflection from (1 1 1), (2 0 0) and (2 2 0) planes of the cubic Cu^0. Thus, the CuO species could also be converted to Cu^0 after H_2 reduction at 500 °C. The 6.6Cu–2Ni/γ-Al_2O_3 sample without reduction showed the characteristic peak of CuO, and the diffraction peak of NiO was not observed (Fig. 1d). After reduction, peaks of Cu^0 appeared and that of Ni^0 were absent (Fig. 1h). The absence of NiO and Ni^0 in 6.6Cu–2Ni/γ-Al_2O_3 indicates that they were highly dispersed or too small to be detected. Figure 2 shows the H_2-TPR profiles of the samples. When Ni was introduced into the Cu-based catalyst, the H_2 consumption peak corresponding to CuO reduction shifted to a higher temperature, and the H_2 consumption peak corresponding to NiO reduction shifted to a lower temperature, which indicates an interaction between Cu and Ni.

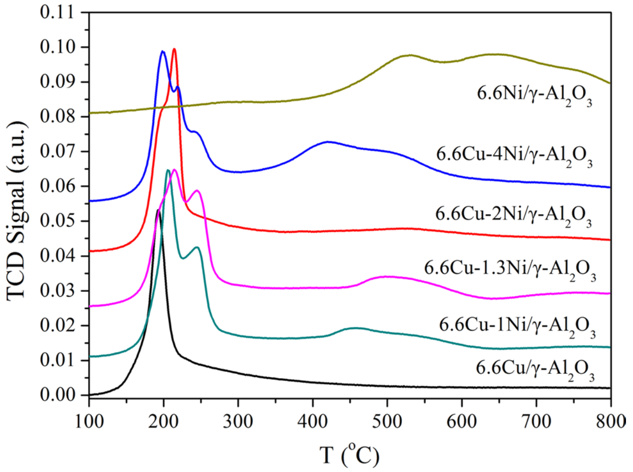


Fig. 2 H_2-TPR profiles of 6.6Cu/γ-Al_2O_3, 6.6Cu–1Ni/γ-Al_2O_3, 6.6Cu–1.3Ni/γ-Al_2O_3, 6.6Cu–2Ni/γ-Al_2O_3, 6.6Cu–4Ni/γ-Al_2O_3 and 6.6Ni/γ-Al_2O_3

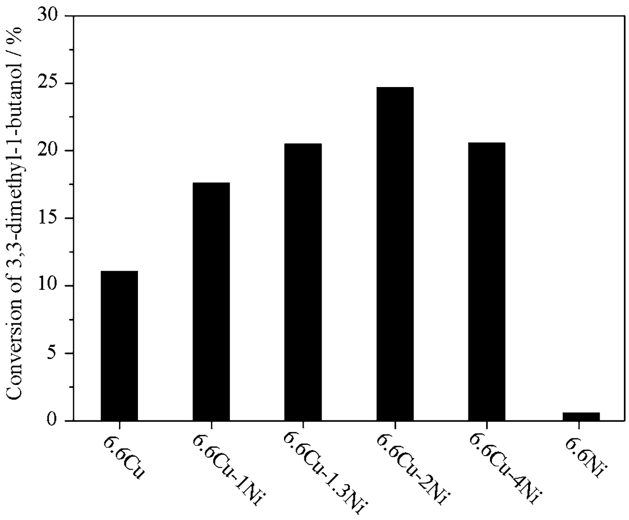


Fig. 3 Effect of Cu/Ni mass ratio on catalytic activity of different catalysts on dehydrogenation of 3,3-dimethyl-1-butanol. Reaction conditions: 3,3-dimethyl-1-butanol (2 mmol), catalyst (0.20 g), styrene (4 mmol), mesitylene (2 mL), $T = 130$ °C, $t = 5$ h, N_2 atmosphere

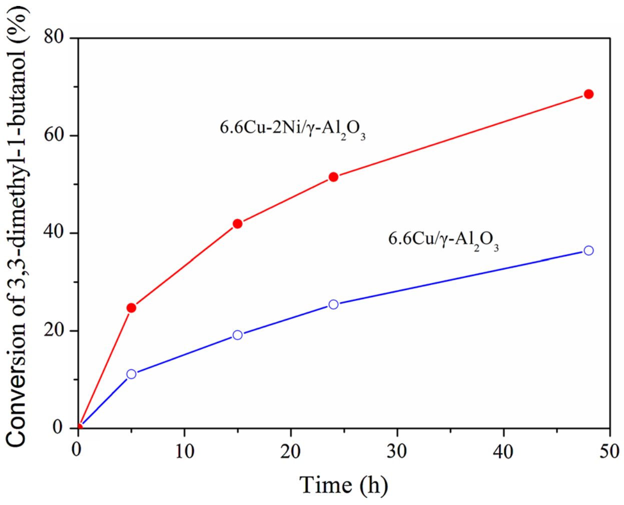


Fig. 4 Time courses of 3,3-dimethyl-1-butanol dehydrogenation over 6.6Cu/γ-Al_2O_3 and 6.6Cu–2Ni/γ-Al_2O_3 catalysts. Reaction conditions: 3,3-dimethyl-1-butanol (2 mmol), catalyst (0.20 g), styrene (4 mmol), mesitylene (2 mL), $T = 130$ °C, N_2 atmosphere

Effect of Cu/Ni mass ratio

Catalytic performance of the prepared catalysts was tested in the dehydrogenation of 3,3-dimethyl-1-butanol to 3,3-dimethyl-1-butanal which is a key intermediate for synthesis of the novel high-intensity sweetener of neotame [37]. Figure 3 shows the effect of the Cu/Ni mass ratio on the catalytic activity of Cu–Ni/γ-Al_2O_3 in the dehydrogenation of 3,3-dimethyl-1-butanol. The conversion was controlled below 30 %. As expected, monometallic catalyst of 6.6Cu/γ-Al_2O_3 and 6.6Ni/γ-Al_2O_3 showed lower catalytic activity than the bimetallic Cu–Ni/γ-Al_2O_3 catalysts. Only 11 and 1 % of 3,3-dimethyl-1-butanol can be converted to 3,3-dimethyl-1-butanal over monometallic 6.6Cu/γ-Al_2O_3 and 6.6Ni/γ-Al_2O_3,respectively. For bimetallic Cu–Ni/γ-Al_2O_3 catalysts, when the content of nickel was raised from zero to 2 %, conversion of 3,3-dimethyl-1-butanol increased from 11 to 25 %; however, higher nickel content (6.6Cu–4Ni/γ-Al_2O_3) afforded lower conversion of 3,3-dimethyl-1-butanol than that of 6.6Cu–2Ni/γ-Al_2O_3. Introduction of the nickel into Cu–Ni/γ-Al_2O_3 catalysts promoted the dehydrogenation activity obviously. All the selectivities of 3,3-dimethyl-1-butanal for the reaction mentioned above were higher than 99 %.

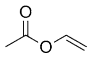
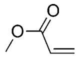
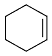
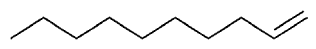
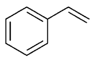
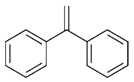
Time courses of the dehydrogenation of 3,3-dimethyl-1-butanol over 6.6Cu/γ-Al_2O_3 and 6.6Cu–2Ni/γ-Al_2O_3

Time courses of the dehydrogenation of 3,3-dimethyl-1-butanol over 6.6Cu/γ-Al_2O_3 and 6.6Cu–2Ni/γ-Al_2O_3 are shown in Fig. 4. 6.6Cu–2Ni/γ-Al_2O_3 showed much higher conversion than 6.6Cu/γ-Al_2O_3 under the same reaction conditions. Even when the reaction time was prolonged to 48 h, 36 and 69 %, conversions of 3,3-dimethyl-1-butanol were obtained using 6.6Cu/γ-Al_2O_3 and 6.6Cu–2Ni/γ-Al_2O_3 as catalyst, respectively. Above results further confirmed the promotion effect of nickel for the 6.6Cu–2Ni/γ-Al_2O_3 catalyst in the dehydrogenation of 3,3-dimethyl-1-butanol. Selectivities of 3,3-dimethyl-1-butanal for the dehydrogenation reactions mentioned above were all >99 %.

Effect of hydrogen acceptor

In transfer dehydrogenation, unsaturated organic compounds are usually used as hydrogen acceptor to facilitate the reaction [22, 23]. In this study, various olefins were selected as hydrogen acceptors and the results are summarized in Table 2. Without a hydrogen acceptor, the conversion of 3,3-dimethyl-1-butanol was only 2 % in 24 h. When vinyl acetate and methyl acrylate were used as hydrogen acceptor, no promotion effect was observed. Cyclohexene, 1-decene, styrene and diphenylethylene could accelerate the dehydrogenation of 3,3-dimethyl-1-butanol, and the reactivity order is styrene > 1-decene > diphenylethylene > cyclohexene. Delocalization effect of benzene ring made C=C bond in styrene more reactive to be hydrogenated. That is why the highest conversion was obtained when styrene was used as hydrogen acceptor. However, lower conversion was observed when diphenylethylene was applied as hydrogen acceptor. This might be related to its bigger molecular size which made it difficult to contact with the active site for hydrogenation on catalyst.

Table 2 Dehydrogenation of 3,3-dimethyl-1-butanol with different hydrogen acceptor over 6.6Cu–2Ni/γ-Al_2O_3 catalyst

Entry	Hydrogen acceptor	Conversion of 3,3-dimethyl-1-butanol (%)	Selectivity of 3,3-dimethyl-1-butanal (%)
1	None	2	>99
2		2	>99
3		3	>99
4		8	>99
5		28	>99
6		52	>99
7		17	>99

Reaction conditions: 3,3-dimethyl-1-butanol (2 mmol), 6.6Cu–2Ni/γ-Al_2O_3 (0.20 g), hydrogen acceptor (4 mmol), mesitylene (2 mL), $T = 130$ °C, $t = 24$ h, N_2 atmosphere

Effect of reaction conditions

The influence of reaction time, reaction temperature, amount of catalyst and styrene on the dehydrogenation of 3,3-dimethyl-1-butanol over 6.6Cu–2Ni/γ-Al_2O_3 is illustrated in Table 3. When the reaction time was prolonged from 5 to 24 h, conversion of 3,3-dimethyl-1-butanol was increased from 25 to 52 % (Table 3, entries 1, 2 and 3). Then, elevating the reaction temperature to 150 °C, 79 % conversion was obtained (Table 3, entry 5). The catalytic performance of 6.6Cu–2Ni/γ-Al_2O_3 also improved when the amount of catalyst and styrene was increased (Table 3, entries 4, 6 and 7). After optimization of reaction conditions, 93 % conversion of 3,3-dimethyl-1-butanol with 99 % selectivity of 3,3-dimethyl-1-butanal can be obtained at 150 °C after 24 h (Table 3, entry 8). Under the optimized reaction conditions

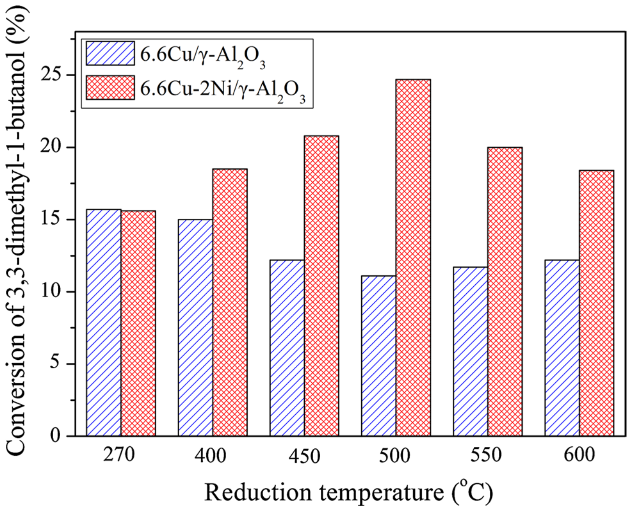


Fig. 5 Effect of reduction temperature of 6.6Cu/γ-Al_2O_3 and 6.6Cu–2Ni/γ-Al_2O_3. Reaction conditions: 3,3-dimethyl-1-butanol (2 mmol), catalyst (0.20 g), styrene (4 mmol), mesitylene (2 mL), $T = 130$ °C, $t = 5$ h, N_2 atmosphere

Table 3 Dehydrogenation of 3,3-dimethyl-1-butanol over 6.6Cu–2Ni/γ-Al_2O_3 under different reaction conditions

Entry	Amount of catalyst (g)	Reaction temperature (°C)	Reaction time (h)	Conversion (%)
1	0.2	130	5	25
2	0.2	130	15	42
3	0.2	130	24	52
4	0.1	130	24	37
5	0.4	130	24	70
6	0.2	150	24	79
7	0.4	150	24	84
8[a]	0.4	150	24	93

Reaction conditions: 3,3-dimethyl-1-butanol (2 mmol), styrene (4 mmol), mesitylene (2 mL), N_2 atmosphere. Selectivity of 3,3-dimethyl-1-butanal >99 % for all entries

[a] Mole ratio of styrene/substrate = 4

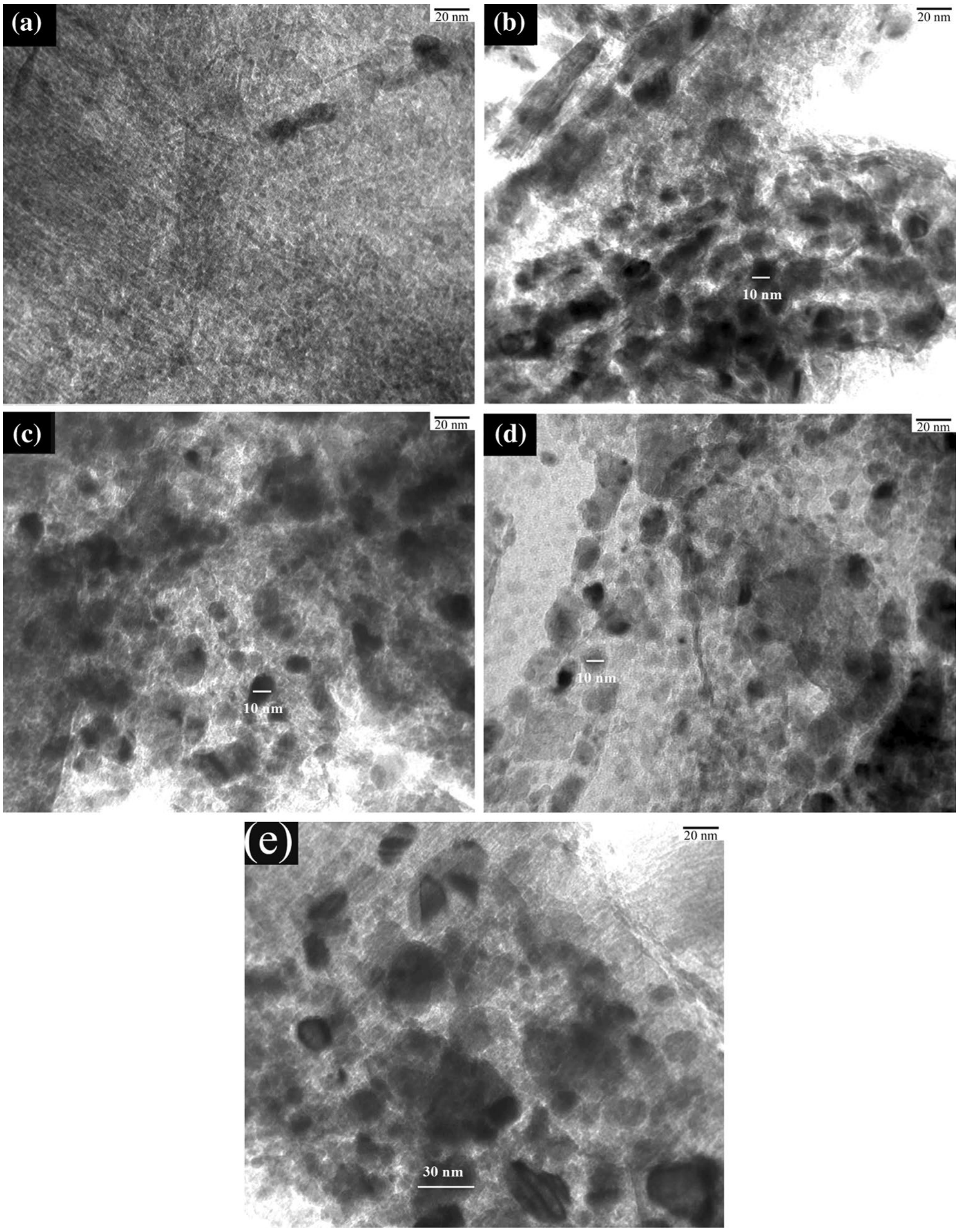
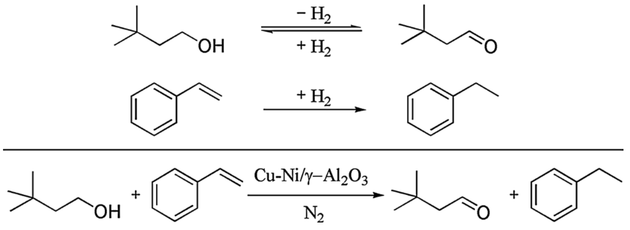


Fig. 6 TEM images of 6.6Cu–2Ni/γ-Al_2O_3: **a** without reduction; **b** reduced at 270 °C; **c** reduced at 400 °C; **d** reduced at 500 °C; **e** reduced at 600 °C

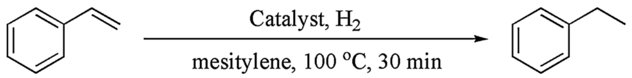
(same as Table 3, entry 8), dehydrogenation of some other primary aliphatic alcohols including isoamyl alcohol, *n*-amyl alcohol and *n*-hexyl alcohol was carried out. 89, 91 and 91 % conversions of isoamyl alcohol, *n*-amyl alcohol and *n*-hexyl alcohol were obtained, respectively, and all the selectivity of the corresponding aldehydes was more than 99 %.

Effect of reduction temperature

Figure 5 shows the effect of reduction temperature on the catalytic activity of 6.6Cu/γ-Al_2O_3 and 6.6Cu–2Ni/γ-Al_2O_3. 6.6Cu/γ-Al_2O_3 and 6.6Cu–2Ni/γ-Al_2O_3 showed comparable activity after H_2 reduction at 270 °C. When the reduction temperature was between 270 and 500 °C, an increase in the conversion of 3,3-dimethyl-1-butanol was observed over 6.6Cu–2Ni/γ-Al_2O_3 and a decrease in conversion was obtained over 6.6Cu/γ-Al_2O_3. Lower activity of 6.6Cu/γ-Al_2O_3 reduced at 500 °C was obtained than 270 °C which might be related to the bigger Cu particle size. However, 6.6Cu–2Ni/γ-Al_2O_3 reduced at 270, 400 and 500 °C showed similar metal particle size (Fig. 6). Thus, particle size was not the only factor affecting the activity of 6.6Cu–2Ni/γ-Al_2O_3



Scheme 1 Proposed reaction pathways in the transfer dehydrogenation of 3,3-dimethyl-1-butanol over Cu–Ni/γ-Al_2O_3 catalyst



Catalyst	Conversion
6.6Cu/γ-Al_2O_3	28%
6.6Ni/γ-Al_2O_3	40%
6.6Cu-2Ni/γ-Al_2O_3	80%

Scheme 2 Hydrogenation of styrene over different catalysts. Reaction conditions: styrene (4 mmol), catalyst (0.2 g), mesitylene (8 mL), H_2 (0.6 MPa)

in range of 270–500 °C. Figure 2 shows that CuO species could be reduced to Cu^0 under H_2 at 270 °C completely, however, reduction of NiO occured at higher temperature. The presence of Ni^0 might be important for the high activity of 6.6Cu–2Ni/γ-Al_2O_3.

Figure 6 shows the TEM images of the 6.6Cu–2Ni/γ-Al_2O_3 reduced by H_2 at different temperatures. Most particles in the 6.6Cu–2Ni/γ-Al_2O_3 samples reduced at 270, 400 and 500 °C exhibited similar particle size ranges (5–15 nm) (Fig. 6a–d). However, higher temperature (600 °C) led to larger particle size (Fig. 6e). These results indicate that metal particle size was not affected significantly by reduction temperature in a broad range (270–500 °C) when Ni was introduced into the Cu–Ni/γ-Al_2O_3 catalyst. This might be related to the interaction between copper and nickel which was also observed in the H_2-TPR results (Fig. 2).

Promotion effect of nickel in Cu–Ni bimetallic catalyst on hydrogenation of styrene

On the basis of the previous work [18–21, 24–27], we proposed reaction pathways in transfer dehydrogenation of 3,3-dimethyl-1-butanol over Cu–Ni/γ-Al_2O_3 catalyst in this study (Scheme 1): (1) conversion of 3,3-dimethyl-1-butanol into 3,3-dimethyl-1-butanal directly by dehydrogenation; (2) rehydrogenation of 3,3-dimethyl-1-butanal; (3) hydrogenation of the styrene. An equilibrium would be temporarily established between reactions (1) and (2) without styrene (take styrene as an example). The immediate transfer of hydrogen would affect the equilibrium significantly. Hydrogenation of hydrogen acceptor like styrene would be one of the key steps in the transfer dehydrogenation of 3,3-dimethyl-1-butanol.

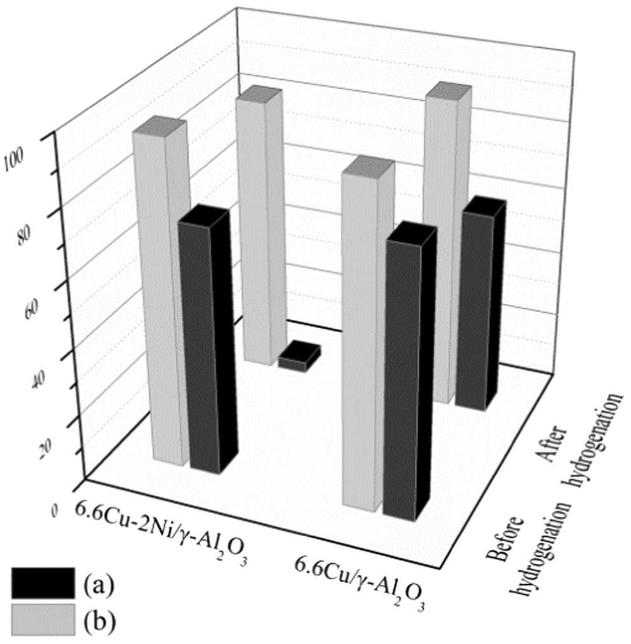


Fig. 7 Hydrogenation of mixture of 3,3-dimethyl-1-butanol, 3,3-dimethyl-1-butanal, styrene and ethylbenzene over 6.6Cu–2Ni/γ-Al_2O_3 and 6.6Cu/γ-Al_2O_3. **a**, **b** were denoted as below: **a** amount of styrene/(amount of styrene and ethylbenzene) × 100; **b** amount of 3,3-dimethyl-1-butanal/(amount of 3,3-dimethyl-1-butanal and 3,3-dimethyl-1-butanol) × 100. Reaction conditions: 3,3-dimethyl-1-butanal (2 mmol), catalyst (0.4 g), mesitylene (10 mL), $T = 100$ °C, $t = 30$ min, H_2 (0.6 MPa)

As mentioned above, the catalytic activity of 6.6Cu/γ-Al_2O_3 in dehydrogenation of 3,3-dimethyl-1-butanol was significantly enhanced by introduction of nickel. We are interested in the role of nickel during the transfer dehydrogenation reaction. Hydrogenation of styrene over different catalysts was carried out (Scheme 2). Conversion of styrene on 6.6Cu/γ-Al_2O_3 and 6.6Ni/γ-Al_2O_3 was 28 and 40 % in 30 min at 100 °C, respectively, indicating that 6.6Ni/γ-Al_2O_3 was more active than 6.6Cu/γ-Al_2O_3 in the catalytic hydrogenation of styrene. Moreover, conversion of styrene over 6.6Cu–2Ni/γ-Al_2O_3 catalyst increased significantly to 80 %, which was much higher than that over 6.6Cu/γ-Al_2O_3 or 6.6Ni/γ-Al_2O_3. This result suggests that introduction of nickel enhanced the hydrogenation activity of 6.6Cu–2Ni/γ-Al_2O_3 dramatically. The literature also reported that the catalytic activity of nickel was much higher than that of copper for hydrogenation of styrene [38].

Selective hydrogenation of C=C bond over Cu–Ni/γ-Al_2O_3 catalyst

Generally, hydrogenation of hydrogen acceptor like styrene is supposed to compete with that of aldehyde in

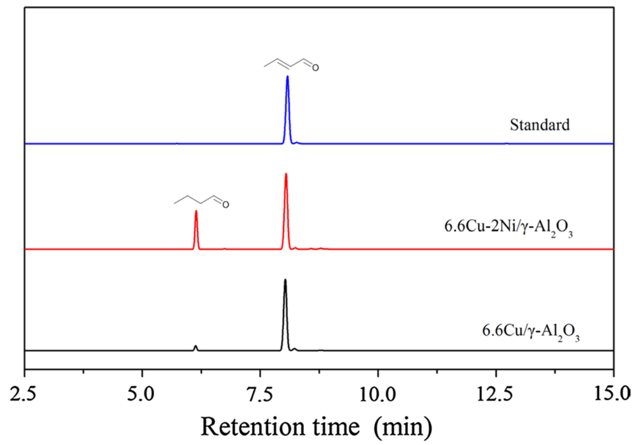


Fig. 8 GC traces for hydrogenation of crotonaldehyde over 6.6Cu–2Ni/γ-Al_2O_3 and 6.6Cu/γ-Al_2O_3. The retention times correspond to the following compounds: 6.14 min (*n*-butanal), 8.05 min (crotonaldehyde), 8.24 min (crotyl alcohol), and 8.56 min (*n*-butanol). Reaction conditions: crotonaldehyde (4 mmol), catalyst (0.30 g), mesitylene (10 mL), $T = 90$ °C, $t = 1$ h, H_2 (1.5 MPa)

transfer dehydrogenation of alcohols. We carried out a control experiment to test and verify the assumption. Firstly, 3,3-dimethyl-1-butanol was dehydrogenated with moderate conversion over 6.6Cu–2Ni/γ-Al_2O_3 in presence of styrene. After separation of catalyst, extra styrene was added to the reaction solution. Then, a mixture of 3,3-dimethyl-1-butanol, 3,3-dimethyl-1-butanal, styrene and ethylbenzene was obtained. The mixture was hydrogenated by H_2 over 6.6Cu–2Ni/γ-Al_2O_3 and 6.6Cu/γ-Al_2O_3, respectively (Fig. 7). When 6.6Cu–2Ni/γ-Al_2O_3 was employed as catalyst, 95 % of styrene was hydrogenated to ethylbenzene, and 13 % of 3,3-dimethyl-1-butanal was converted to 3,3-dimethyl-1-butanol. Moreover, when 6.6Cu/γ-Al_2O_3 was applied as catalyst, only 22 % styrene was hydrogenated compared to 6.6Cu–2Ni/γ-Al_2O_3. Thus, 6.6Cu–2Ni/γ-Al_2O_3 showed prior hydrogenation of C=C bond (styrene) to C=O bond (primary aliphatic aldehyde). Similar observation was described in our recent report [39], and this result was also in good agreement with that in Scheme 1.

Furthermore, we carried out hydrogenation of crotonaldehyde (Fig. 8). Compared to 6.6Cu/γ-Al_2O_3, much more crotonaldehyde was converted into *n*-butanal when 6.6Cu–2Ni/γ-Al_2O_3 was used as catalyst. In particular, only C=C bond in crotonaldehyde was hydrogenated. It was also reported that nickel catalysts were selective in hydrogenation of C=C bond versus C=O bond [28–31].

Thus, the introduction of nickel into the Cu–Ni/γ-Al_2O_3 improved the catalytic activity for styrene hydrogenation. Since hydrogenation of 3,3-dimethyl-1-butanal and styrene is competitive, equilibrium in Scheme 1 should shift to the right, when hydrogenation of styrene was significantly enhanced over Cu–Ni/γ-Al_2O_3 catalyst. As a result, rehydrogenation of 3,3-dimethyl-1-butanal would be impeded and the formation of 3,3-dimethyl-1-butanal was promoted.

Conclusions

In summary, we report Cu–Ni bimetallic catalysts for high selective dehydrogenation of 3,3-dimethyl-1-butanol in liquid phase, which exhibited higher activity than that of monometallic copper catalyst under the same reaction conditions. Selective hydrogenation of C=C bond, rather than C=O bond, was significantly improved over Cu–Ni/γ-Al_2O_3 catalyst by introducing nickel, which accounted for the enhanced activity in catalytic dehydrogenation of primary aliphatic alcohols.

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