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Communication

Dehydrogenation of primary aliphatic alcohols to aldehydes over Cu-Ni bimetallic catalysts

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ABSTRACT

The catalytic conversion of non-activated primary aliphatic alcohols to aldehydes is a challenge, and monometallic Cu-based catalysts loaded on different supports have often been used for these reactions. Cu-Ni/ γ -Al₂O₃ bimetallic catalysts were prepared and used for anaerobic dehydrogenation of 3,3-dimethyl-1-butanol to 3,3-dimethyl-1-butanal. These catalysts exhibited higher activity than Cu/ γ -Al₂O₃ under the same reaction conditions, and a wide range of primary aliphatic alcohols were efficiently converted to the corresponding aldehydes over Cu-Ni/ γ -Al₂O₃ under mild conditions.

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The selective transformation of alcohols to aldehydes is of great importance in both academia and industry [1]. In particular, the conversion of non-activated primary aliphatic alcohols is a challenge. For both environmental and economic reasons, catalytic aerobic alcohol oxidation, in which water is usually released as a by-product, has been developed as a substitute for the use of stoichiometric oxidants [1–3]. However, further oxidation of aldehydes to acids easily occurs under aerobic conditions, especially in the presence of transition metals [1,4], and water gradually deactivates some metal catalysts. Catalytic dehydrogenation under anaerobic conditions circumvents these problems [5,6]. Recently, Cu catalysts have attracted much attention for the efficient liquid-phase dehydrogenation of alcohols [6–11]. For example, a cheap and simple Cu/Al₂O₃ catalyst was reported by Ravasio and coworkers [6] for the conversion of secondary aliphatic alcohols. However, the development of new catalysts for efficient dehydrogenation of

non-activated primary aliphatic alcohols to aldehydes remains a challenge.

Monometallic Cu nanoparticles on different supports, including Al₂O₃, SiO₂, MgO, TiO₂, hydrotalcite (HT), La₂O₂CO₃, and La₂O₃, have been studied for catalytic dehydrogenation [6–11]. The development of bimetallic catalysts for liquid-phase dehydrogenation is necessary because introduction of a second metal is an important approach to tailoring the catalytic activity of Cu-based catalysts [12]. In Cu-catalyzed alcohol dehydrogenation, unsaturated organic compounds such as styrene are usually used as hydrogen acceptors. Hydrogen removed from the alcohol is transferred via hydrogenation of a hydrogen acceptor, which favors alcohol dehydrogenation. Catalysts with both dehydrogenation and hydrogenation activity are therefore required. As described in previous reports, Ni catalysts show high activity and selectivity in C=C bond hydrogenation [13]. Cu and Ni have face-centered cubic structures with similar lattice

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Fig. 1. XRD patterns of samples reduced using H₂ at 500 °C. (1) γ -Al₂O₃; (2) 6.6Ni/ γ -Al₂O₃; (3) 6.6Cu/ γ -Al₂O₃; (4) 6.6Cu-2Ni/ γ -Al₂O₃.

parameters, and Cu-Ni interactions occur easily [14]. The introduction of Ni into Cu/ γ -Al₂O₃ catalysts accelerates styrene C=C bond hydrogenation and promotes formation of aliphatic aldehydes. Here, the catalytic dehydrogenation of primary aliphatic alcohols to aldehydes using Cu-Ni/ γ -Al₂O₃ under anaerobic conditions is described.

Cu/ γ -Al₂O₃ was prepared using a known method [6], and Cu-Ni/ γ -Al₂O₃ was prepared via introducing Ni into Cu/ γ -Al₂O₃ by incipient wetness impregnation. The Cu-Ni bimetallic catalysts are denoted by xCu-yNi/ γ -Al₂O₃, where x (%) and y (%) are the mass percentages of Cu and Ni relative to γ -Al₂O₃, respectively. Before use in catalytic reactions, the as-prepared material was reduced in a H₂ atmosphere at 500 °C for 5 h unless otherwise stated.

The X-ray diffraction (XRD) patterns of γ -Al₂O₃, 6.6Cu/ γ -Al₂O₃, 6.6Ni/ γ -Al₂O₃, and 6.6Cu-2Ni/ γ -Al₂O₃ reduced using H₂ at 500 °C are displayed in Fig. 1. γ -Al₂O₃ showed the typical diffraction peaks of a cubic structure. 6.6Ni/ γ -Al₂O₃ exhibited peaks at $2\theta = 44.5^\circ$, 51.9° , and 76.4° , corresponding to reflections from the (111), (200), and (220) planes, respectively, of cubic Ni⁰; no significant NiO diffraction peak was observed. For 6.6Cu/ γ -Al₂O₃, diffraction peaks at $2\theta = 43.3^\circ$, 50.5° , and 74.2° appeared and were ascribed to reflections from the (111), (200), and (220) planes, respectively, of cubic Cu⁰. For 6.6Cu-2Ni/ γ -Al₂O₃ after H₂ reduction, peaks were observed, but

Fig. 2. H₂-TPR profiles of 6.6Cu/ γ -Al₂O₃, 6.6Cu-2Ni/ γ -Al₂O₃, and 6.6Ni/ γ -Al₂O₃.

those from Ni⁰ were absent. The absence of characteristic Ni⁰ peaks in 6.6Cu-2Ni/ γ -Al₂O₃ indicates that it was highly dispersed or the particles were too small to be detected.

H₂ temperature-programmed reduction (H₂-TPR) experiments were also performed (Fig. 2). The Cu monometallic catalyst gave one peak at ca. 193 °C, ascribed to the reduction of CuO. For 6.6Ni/ γ -Al₂O₃, the H₂ consumption peaks in the region 400–800 °C were ascribed to the reduction of NiO. On introduction of Ni into the Cu-based catalyst, the H₂ consumption peak corresponding to CuO reduction shifted to a higher temperature, and that of NiO shifted to a lower temperature. A similar phenomenon was described in a previous report [15]; it indicates Cu-Ni interactions. The presence of shoulder peaks at around 200 °C for the bimetallic catalysts also suggests Cu-Ni interactions [12,15].

Fig. 3 shows the transmission electron microscopy (TEM) images of the samples reduced under H₂ at 500 °C. The diameter of the Cu particles in 6.6Cu/ γ -Al₂O₃ was larger than 100 nm. When Ni was introduced into Cu/ γ -Al₂O₃, the metal particle size decreased significantly; for example, the sizes of most metal particles in 6.6Cu-2Ni/ γ -Al₂O₃ were in the range 5–10 nm. The Ni particles in 6.6Ni/ γ -Al₂O₃ were much smaller (< 5 nm) than the Cu particles in 6.6Cu/ γ -Al₂O₃. This is consistent with the XRD results. The diffraction peaks of Ni⁰ in 6.6Ni/ γ -Al₂O₃ were very weak because the Ni⁰ particles were small, whereas

Fig. 3. TEM images of samples reduced at 500 °C. (a) 6.6Cu/ γ -Al₂O₃; (b) 6.6Cu-2Ni/ γ -Al₂O₃; (c) 6.6Ni/ γ -Al₂O₃.

Table 1

Dehydrogenation of 3,3-dimethyl-1-butanol to 3,3-dimethyl-1-butanal over different catalysts.

Entry	Catalyst	Time (h)	Conv. (%)	Select. (%)
1	None	5	—	—
2	6.6Ni/ γ -Al ₂ O ₃	5	<1	>99
3	6.6Cu/ γ -Al ₂ O ₃	5	11	>99
4	6.6Cu/ γ -Al ₂ O ₃ + 6.6Ni/ γ -Al ₂ O ₃ ^b	5	14	>99
5	6.6Cu-2Ni/ γ -Al ₂ O ₃	5	25	>99
6	6.6Cu-2Ni/ γ -Al ₂ O ₃	24	52	>99
7 ^a	6.6Cu-2Ni/ γ -Al ₂ O ₃	24	93	>99

Reaction conditions: 3,3-dimethyl-1-butanol 2 mmol, catalyst 0.20 g, styrene 4 mmol, mesitylene 2 mL, $T = 130\text{ }^{\circ}\text{C}$, N₂ atmosphere.^a Catalyst 0.40 g, styrene 8 mmol, $T = 150\text{ }^{\circ}\text{C}$.^b Mechanical mixture of 6.6Cu/ γ -Al₂O₃ and 6.6Ni/ γ -Al₂O₃.

the peaks in 6.6Cu/ γ -Al₂O₃ were very strong because the Cu⁰ particles were large and highly crystalline (Fig. 1(2) and (3)).

3,3-Dimethyl-1-butanol is a key intermediate in the preparation of neotame, which is a high-intensity sweetener [16]. The conversion of 3,3-dimethyl-1-butanol to 3,3-dimethyl-1-butanal was selected as a model reaction (Table 1). Initially, the transformation was performed in mesitylene under N₂, and styrene was used as the hydrogen acceptor. At $130\text{ }^{\circ}\text{C}$, 3,3-dimethyl-1-butanol conversion was less than 1% within 5 h when 6.6Ni/ γ -Al₂O₃ was used as the catalyst (Table 1, entry 2). Although 6.6Cu/ γ -Al₂O₃ exhibited much higher activity than 6.6Ni/ γ -Al₂O₃ under the same reaction conditions, the 3,3-dimethyl-1-butanol conversion was only 11%, which is roughly in line with previous reports [6] (Table 1, entry 3). The activity of 6.6Cu-2Ni/ γ -Al₂O₃ was higher than that of 6.6Cu/ γ -Al₂O₃ and 6.6Ni/ γ -Al₂O₃. 3,3-Dimethyl-1-butanol conversion of 25% was observed, which was about twice that achieved using 6.6Cu/ γ -Al₂O₃ (Table 1, entry 5). When a mechanical mixture of 6.6Cu/ γ -Al₂O₃ and 6.6Ni/ γ -Al₂O₃ was used as the catalyst (the Cu/Ni ratio was the same as that in entry 5), a much lower conversion of 3,3-dimethyl-1-butanol was achieved than with 6.6Cu-2Ni/ γ -Al₂O₃ (Table 1, entry 4). The Cu-Ni bimetallic catalyst therefore showed excellent catalytic activity in 3,3-dimethyl-1-butanol dehydrogenation. After systematic optimization of the reaction conditions, 93% conversion of 3,3-dimethyl-1-butanol with 99% selectivity for 3,3-dimethyl-1-butanal was achieved at $150\text{ }^{\circ}\text{C}$ after 24 h (Table 1, entry 7).

We explored the substrate scope over 6.6Cu-2Ni/ γ -Al₂O₃ using alcohols other than 3,3-dimethyl-1-butanol (Table 2). The dehydrogenation of primary aliphatic alcohols such as isoamyl alcohol, *n*-amyl alcohol, and *n*-hexyl alcohol produced the corresponding aldehydes with 89%, 91%, and 91% conversions, respectively, and selectivity for the corresponding aldehydes of more than 99% (Table 2, entries 1–3). *n*-Octanol and iso-octanol, which have higher carbon numbers, were more difficult to convert. Nevertheless, 98% and 92% conversions were achieved for *n*-octanol and iso-octanol, respectively, when the reaction time was prolonged to 40 h (Table 2, entries 4 and 6). Conversely, only 38% of *n*-octanol was converted under the same conditions when 6.6Cu/ γ -Al₂O₃ was used (Table 2, entry

Table 2Dehydrogenation of various alcohols over 6.6Cu-2Ni/ γ -Al₂O₃ catalyst.

Entry	Substrate	Product	Conv. (%)	Select. (%)
1			89	>99
2			91	>99
3			91	>99
4 ^a			98	>99
5 ^{a,b}			38	>99
6 ^a			92	>99
7 ^c			>99	>99
8 ^c			>99	>99
9 ^c			>99	>99
10			93	>99
11			37	>99

Reaction conditions: substrate 2 mmol, 6.6Cu-2Ni/ γ -Al₂O₃ 0.40 g, styrene 8 mmol, mesitylene 2 mL, $T = 150\text{ }^{\circ}\text{C}$, $t = 24\text{ h}$, N₂ atmosphere.^a $t = 40\text{ h}$. ^b The catalyst was 6.6Cu/ γ -Al₂O₃. ^c $T = 130\text{ }^{\circ}\text{C}$.

5); this is roughly in agreement with previous results [6]. As expected, 6.6Cu-2Ni/ γ -Al₂O₃ also showed high catalytic activity for the dehydrogenation of secondary aliphatic alcohols to the corresponding ketones. Conversions higher than 99% were easily obtained when the substrate was 2-octanol, cyclopentanol, or cyclohexanol (Table 2, entries 7–9), even when the reaction temperature was as low as $130\text{ }^{\circ}\text{C}$. It was previously reported that when Cu/Al₂O₃ was used in catalytic dehydrogenation, primary benzylic alcohols such as benzyl alcohol and 2-phenylethanol were difficult to convert [6]. In this work, 93% of benzyl alcohol was converted over 6.6Cu-2Ni/ γ -Al₂O₃, and 37% conversion of 2-phenylethanol was achieved. To the best of our knowledge, this is the first report of Cu-Ni/ γ -Al₂O₃-catalyzed dehydrogenation of aliphatic alcohols, and a wide range of non-activated primary aliphatic alcohols were successfully converted to the corresponding aldehydes with high conversions.

We examined the recyclability of the 6.6Cu-2Ni/ γ -Al₂O₃ catalyst in the dehydrogenation of 3,3-dimethyl-1-butanol. After the first run, the solid catalyst was separated from the reaction mixture by centrifugation and washed with mesitylene. The catalyst was then used for the next run. The conversion of 3,3-dimethyl-1-butanol in the second run was 85%. Although the catalyst was reused without any reactivation, 74% conversion of 3,3-dimethyl-1-butanol was still observed after the fourth run, and the selectivity for 3,3-dimethyl-1-butanal was more than 99% (Fig. 4).

Graphical Abstract

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Dehydrogenation of primary aliphatic alcohols to aldehydes over Cu-Ni bimetallic catalysts

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Cu-Ni/ γ - Al_2O_3 bimetallic catalysts were developed for anaerobic dehydrogenation in the presence of styrene, and a wide range of primary aliphatic alcohols were smoothly converted to the corresponding aldehydes under mild conditions.

Fig. 4. Reuse tests for 6.6Cu-2Ni/ γ - Al_2O_3 in dehydrogenation of 3,3-dimethyl-1-butanol. Reaction conditions: 3,3-dimethyl-1-butanol 2 mmol, 6.6Cu-2Ni/ γ - Al_2O_3 0.4 g, styrene 8 mmol, mesitylene 2 mL, $T = 150^\circ\text{C}$, $t = 24$ h, N_2 atmosphere.

In summary, Cu-Ni bimetallic catalysts for selective dehydrogenation of 3,3-dimethyl-1-butanol in the liquid phase were developed. The catalytic activity was higher than that of a monometallic Cu catalyst under the same reaction conditions. A wide range of primary aliphatic alcohols were converted to the corresponding aldehydes in the presence of styrene (hydrogen acceptor). This study will contribute to the development of new catalysts for the dehydrogenation of non-activated primary aliphatic alcohols.

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Cu-Ni双金属催化剂催化脂肪伯醇脱氢制备醛

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摘要: 脂肪伯醇催化转化制备相应的醛是具有挑战性的课题, 目前多采用负载的单金属铜基催化剂。本文报道了双金属催化剂Cu-Ni/ γ - Al_2O_3 催化3,3-二甲基-1-丁醇脱氢制备相应的醛, 在相同反应条件下, Cu-Ni/ γ - Al_2O_3 比单金属催化剂Cu/ γ - Al_2O_3 表现出更高的催化活性, 能将一系列脂肪伯醇高选择性转化为相应的醛。

关键词: 脂肪伯醇; 醛; 铜-镍; 催化; 脱氢

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醇类选择氧化制醛具有重要的科学意义和工业应用价值^[1], 尤其是不活泼的脂肪伯醇的选择氧化更具挑战性. 采用分子氧为氧化剂的催化氧化法具有经济和环境友好优势, 近年来取得很大进展并逐渐取代传统计量氧化法^[1–3]. 然而, 在分子氧和过渡金属催化剂存在条件下, 醛基容易进一步氧化转化为酸^[1,4], 并且水作为副产物容易造成过渡金属催化剂失活. 为了解决上述问题, 研究者们发展了无氧条件下催化脱氢的方法将脂肪醇选择氧化为相应的醛^[5,6]. 在液相催化醇类脱氢反应中, Cu基催化剂是一类重要的催化剂, 受到众多研究者关注. 例如, Ravasio课题组^[6]利用Cu/ γ -Al₂O₃为催化剂, 有效实现了二级脂肪醇选择氧化. 然而, 该催化剂对脂肪伯醇转化的效果并不理想. 目前, 催化脂肪伯醇脱氢制备相应的醛仍面临极大挑战, 有待设计和开发新的催化剂^[6–11].

在醇类脱氢反应研究中, 所用Cu基催化剂主要为不同载体负载的单组分催化剂, 如Cu/Al₂O₃, Cu/SiO₂, Cu/MgO, Cu/TiO₂, Cu/HT, Cu/La₂O₂CO₃和Cu/La₂O₃等. 引入第二组分是有效调变催化剂催化性能的重要策略, 有待开发双组分Cu基催化剂用于催化醇类脱氢反应^[12]. 在Cu基催化剂催化醇类脱氢反应中, 通常采用不饱和有机化合物(如苯乙烯)作为氢接受体. 氢接受体通过加氢反应将醇中脱除的氢转移, 以利于醇脱氢反应进行. 因此, 理想的催化脂肪伯醇脱氢的催化剂应同时具备优异的脱氢和加氢活性. 已有研究表明, Ni基催化剂在C=C双键加氢反应中表现出优异的催化活性和选择性^[13]. 而且, Ni和Cu具有相同的面心立方结构和相似的晶胞参数, 两者间容易产生相互作用^[14]. 因此, 在Cu/ γ -Al₂O₃中引入Ni, 可能会有助于苯乙烯加氢, 从而有利于脂肪伯醇脱氢氧化制备醛. 本文报道了无氧条件下Cu-Ni/ γ -Al₂O₃催化脂肪伯醇脱氢制备相应的醛.

采用文献报道的方法制备Cu/ γ -Al₂O₃催化剂^[6], 并利用浸渍法在Cu/ γ -Al₂O₃催化剂中引入Ni, 得到Cu-Ni/ γ -Al₂O₃催化剂. 催化剂标记为xCu-yNi/ γ -Al₂O₃, x(%)和y(%)分别表示Cu和Ni相对于 γ -Al₂O₃的质量分数. 使用前, 催化剂在500 °C下H₂气氛中还原5 h.

图1为500 °C下H₂还原后 γ -Al₂O₃, 6.6Cu/ γ -Al₂O₃, 6.6Ni/ γ -Al₂O₃和6.6Cu-2Ni/ γ -Al₂O₃的X射线衍射(XRD)

图谱. γ -Al₂O₃的特征衍射峰表明其为立方结构. 6.6Ni/ γ -Al₂O₃中没有明显的NiO衍射峰出现, 但在 $2\theta = 44.5^\circ$, 51.9° 和 76.4° 处观察到三个特征衍射峰, 分别归属于立方Ni⁰的(111), (200)和(220)晶面衍射. 6.6Cu/ γ -Al₂O₃在 $2\theta = 43.3^\circ$, 50.5° 和 74.2° 处出现三个特征衍射峰, 分别对应于立方Cu⁰的(111), (200)和(220)晶面衍射. 样品6.6Cu-2Ni/ γ -Al₂O₃中仅观察到Cu⁰的特征衍射峰, 没有观察到Ni⁰的特征峰出现, 推测是因为Ni⁰的分散度较高或者颗粒较小.

对样品H₂还原过程进行了研究, 结果如图2所示. 6.6Cu/ γ -Al₂O₃在193 °C左右出现一个还原峰, 归属为CuO的还原. 6.6Ni/ γ -Al₂O₃在400–800 °C的还原峰则为NiO的还原. 对于6.6Cu-2Ni/ γ -Al₂O₃, 随着Ni的引入, 对应于CuO的还原峰向高温区移动, 而NiO的还原峰向低温区移动. 类似现象在文献^[15]中也有报道. 上述现象表明, Cu和Ni之间发生了相互作用. 而且, 样品6.6Cu-2Ni/ γ -Al₂O₃在200 °C左右出现的肩峰进一步证实了Cu和Ni之间存在相互作用^[12,15].

图3为样品经500 °C下H₂还原后的透射电镜(TEM)照片. 可以看出, 6.6Cu/ γ -Al₂O₃中Cu颗粒直径大于100 nm. 引入Ni后, Cu-Ni/ γ -Al₂O₃中金属颗粒直径显著减小, 金属颗粒直径主要在5–10 nm. 6.6Ni/ γ -Al₂O₃中Ni颗粒直径非常小(<5 nm). TEM结果证实了上述基于XRD结果的推测, 6.6Ni/ γ -Al₂O₃中Ni⁰的衍射峰较弱主要是因为Ni⁰的颗粒较小, 6.6Cu/ γ -Al₂O₃中Cu⁰的衍射峰较强则是Cu⁰的颗粒较大所致.

3,3-二甲基-1-丁醛是制备新型强力甜味剂纽甜的重要中间体^[16], 本研究选取3,3-二甲基-1-丁醇脱氢制3,3-二甲基-1-丁醛为模型反应, 研究了催化剂的催化脱氢性能(表1). 反应在N₂气氛下进行, 选择苯乙烯作为氢接受体. 当以6.6Ni/ γ -Al₂O₃为催化剂时, 130 °C下反应5 h, 3,3-二甲基-1-丁醇的转化率小于1%(表1, 反应2). 在相同反应条件下, 6.6Cu/ γ -Al₂O₃的活性虽远远高于6.6Ni/ γ -Al₂O₃, 但3,3-二甲基-1-丁醇的转化率仍仅有11%(表1, 反应3). 6.6Cu/ γ -Al₂O₃的催化活性基本上与文献[6]报道的脂肪伯醇脱氢催化剂活性相当. 令人欣喜的是, 将6.6Cu-2Ni/ γ -Al₂O₃用于催化3,3-二甲基-1-丁醇转化, 在相同反应条件下, 3,3-二甲基-1-丁醇的转化率可达25%,

6.6Cu-2Ni/ γ -Al₂O₃的催化活性远远优于6.6Cu/ γ -Al₂O₃和6.6Ni/ γ -Al₂O₃(表1, 反应5)。有趣的是, 将6.6Cu/ γ -Al₂O₃和6.6Ni/ γ -Al₂O₃机械混合(Cu/Ni比与反应5相同)作为催化剂时, 其催化活性远低于6.6Cu-2Ni/ γ -Al₂O₃(表1, 反应4)。因此, 引入Ni后, 双金属Cu-Ni催化剂催化3,3-二甲基-1-丁醇脱氢的活性显著提高。采用6.6Cu-2Ni/ γ -Al₂O₃作为催化剂, 优化反应条件后, 3,3-二甲基-1-丁醇转化率可达93%, 3,3-二甲基-1-丁醛的选择性大于99%(表1, 反应7)。

我们进一步研究了6.6Cu-2Ni/ γ -Al₂O₃催化剂催化其他醇类脱氢反应活性, 结果如表2所示。可以看到, 6.6Cu-2Ni/ γ -Al₂O₃能够催化一系列脂肪伯醇脱氢高选择性生成相应的醛。例如, 6.6Cu-2Ni/ γ -Al₂O₃催化异戊醇、正戊醇和正己醇脱氢, 转化率分别为89%, 91%和91%, 得到异戊醛、正戊醛和正己醛的选择性均大于99%(表2, 反应1–3)。碳数较高的正辛醇和异辛醇等脂肪醇不易转化; 然而, 当反应时间延长至40 h, 正辛醇和异辛醇转化率分别可达98%和92%(表2, 反应4和6)。相比之下, 以6.6Cu/ γ -Al₂O₃为催化剂时, 相同反应条件下, 正辛醇转化率仅为38%, 与文献[6]报道结果一致。6.6Cu-2Ni/ γ -Al₂O₃对二级醇脱氢制备相应的酮表现出优异的催化活性, 即使反应温度降低至130 °C, 仲辛醇, 环戊醇和环己醇转化

率仍大于99%(表2, 反应7–9)。文献[6]报道, Cu/ γ -Al₂O₃作为催化剂时, 苯甲醇和苯乙醇等苄醇难以转化。然而, 当采用6.6Cu-2Ni/ γ -Al₂O₃为催化剂时, 苯甲醇转化率可达93%, 苯乙醇转化率也达到37%。综上所述, 本研究首次将Cu-Ni/ γ -Al₂O₃催化剂用于催化脂肪醇脱氢, 并实现了多种脂肪伯醇高转化率高选择性转化制备相应的醛。

进一步研究了6.6Cu-2Ni/ γ -Al₂O₃催化剂催化3,3-二甲基-1-丁醇脱氢的循环使用情况, 催化剂首次使用后通过离心的方法从反应液中分离出来, 用均三甲苯洗涤后用于下一次反应。催化剂第二次重复使用时, 3,3-二甲基-1-丁醇转化率为85%。6.6Cu-2Ni/ γ -Al₂O₃催化剂在重复使用过程中, 无需任何再活化过程, 催化剂重复使用4次, 3,3-二甲基-1-丁醇转化率依然可达74%, 3,3-二甲基-1-丁醛选择性高于99%(图4)。

总之, 本研究报道了Cu-Ni/ γ -Al₂O₃双金属催化剂液相催化3,3-二甲基-1-丁醇选择性脱氢制备相应的醛。相同反应条件下, 该催化剂活性高于单金属Cu/ γ -Al₂O₃催化剂。在Cu-Ni/ γ -Al₂O₃催化作用下, 以苯乙烯为氢接受体, 可实现多种脂肪伯醇脱氢制备相应的醛。本工作可为脂肪伯醇脱氢新催化剂的开发和设计提供借鉴和参考。