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Magnetic Co/Al₂O₃ catalyst derived from hydrotalcite for hydrogenation of levulinic acid to γ -valerolactone

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ABSTRACT

The efficient hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL) over a hydrotalcite-derived non-precious metal Co/Al₂O₃ catalyst was achieved. Its core-shell structure and a strong interaction between Co and Al species stabilized the Co particles against leaching and sintering. This magnetic non-precious metal catalyst showed a comparable catalytic performance to a commercial Ru/C for the liquid hydrogenation of LA. It was easily separated from the reaction medium with an external magnet. The catalyst exhibited excellent recyclability, complete LA conversion and >99% GVL selectivity, and would be useful in a large scale biorefinery.

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The hydrogenation of bio-derived levulinic acid (LA) and its esters [1–4] to γ -valerolactone (GVL) is a key reaction in sustainable biomass conversion because GVL can be widely used for fuel additive, food ingredient and as an intermediate for fine chemical production [5–8]. Both homogeneous and heterogeneous catalytic systems based on precious metal (Rh, Pd, Ir, Au, Ru) catalysts have been developed for efficient LA hydrogenation. Wright et al. [8] highlighted in their review that GVL production relied strongly on the use of noble metals, which could be an issue for the scale-up of the process due to their cost and the uncertain future availability. Although a few base metal heterogeneous catalysts have been successfully developed for this process [9–11], achieving a comparable activity and durability comparable with those of a low loading precious metal catalyst still remains a challenge due to their irreversible metal leaching and sintering, especially under liquid hydrogenation

conditions [12].

We recently reported an ordered mesoporous carbon supported Ru-Ni bimetallic nanoparticle catalyst for the efficient conversion of LA into GVL [13]. We described here that a supported Co catalyst can be a suitable alternative for this interesting transformation. Co is widespread in the Earth, and Co-based catalysts have found wide application in the well-known Fisher-Tropsch synthesis [14,15] and other hydrogenation reactions [16,17]. Hydrotalcite-like compounds can be suitable precursors for the preparation of uniformly dispersed metal catalysts due to their tunable composition and confinement effect endowed by the interlayer galleries [18–22]. In the present work, we utilized an easily fabricated Co/Al-hydrotalcite (HT), a hydrated Co-Al hydroxide with a lamellar structure, as the single precursor to prepare an Al₂O₃ supported Co particle catalyst (Co/Al₂O₃), which possessed a

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relatively high surface area and strong interaction between the Co and Al species. The catalyst had a unique core-shell structure with amorphous alumina dominating the shell. These outstanding characteristics gave this Co/Al₂O₃ catalyst a comparable catalytic efficiency and recyclability with those of the representative noble metal catalyst Ru/C (LA conversion 80%; GVL selectivity 90%) in the conversion of LA to GVL [6].

In the present work, we used M/Al-HT (M = Co, Fe, Cu, Ni) as the precursor to prepare Al₂O₃ supported transition metal particles. The 4Co/Al-HT ($n_{\text{Co}}/n_{\text{Al}} = 4$) catalyst was prepared by a constant pH co-precipitation by following a reported procedure with a modification [23,24], which included the dropwise addition of an aqueous solution (100 mL) of Co (II) and Al (III) nitrates (total concentration of cations was 0.5 mol/L with a Co/Al ratio of 4 into 200 mL solution of Na₂CO₃ ([Al³⁺] = [CO₃²⁻])). The suspension pH was kept at 10.0 by the addition of NaOH aqueous solution (1.0 mol/L). The slurry was vigorously stirred at 80 °C during the solution addition. After the solution of metal cations was completely added, the suspension was stirred at 80 °C for 1 h, then followed by the step of precipitate aging at the same temperature for 18 h without stirring. The prepared hydrotalcite sample (denoted as 4Co/Al-HT) was reduced under H₂ (50 mL/min) at 700 °C for 2.5 h, affording the Co particle supported catalyst denoted as 4Co/Al₂O₃. The other four catalysts (5Co/Al₂O₃, 3Co/Al₂O₃, 2Co/Al₂O₃, 1Co/Al₂O₃) were prepared following the same procedure but with the molar ratios of Co/Al = 5, 3, 2 and 1. The Fe/Al₂O₃, Cu/Al₂O₃ and Ni/Al₂O₃ catalysts were synthesized following a similar procedure but using Fe (III), Cu (II) or Ni (II) nitrate as the precursor. The Co₃O₄ supported on the γ -Al₂O₃ precursor (Co/Al = 4) prepared by incipient wetness impregnation was denoted as Co₃O₄/ γ -Al₂O₃, and the reduced catalyst 4Co/ γ -Al₂O₃ was prepared with the above reduction procedure. The 4Co/Al-HT hydrotalcite was first calcinated at 600 °C in air, then reduced under H₂ at 700 °C for 2.5 h. The sample was denoted as 4Co/Al₂O₃-CR.

The conversion of levulinic acid to GVL was carried out in a 100 mL stainless steel autoclave equipped with a mechanical stirrer (Dalian Sanlin Instrument Co., China). A typical procedure was the following: LA 2.32 g (0.02 mol), catalyst Co/LA = 1.5% (molar ratio), solvent 30 mL, H₂ 5 MPa, 180 °C, stirring rate 1000 r/min, 3 h. The liquid product was analyzed by a gas chromatograph (Agilent GC-7890A) equipped with a capillary

Table 1

Catalytic performance of the base metal catalysts for the conversion of LA.

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	2Fe/Al ₂ O ₃	0.5	>99
2	2Cu/Al ₂ O ₃	2	>99
3	2Ni/Al ₂ O ₃	39	>99
4	2Co/Al ₂ O ₃	43	>99
5	1Co/Al ₂ O ₃	46	>99
6	3Co/Al ₂ O ₃	43	>99
7	4Co/Al ₂ O ₃	100	>99
8	5Co/Al ₂ O ₃	93	>99
9	4Co/ γ -Al ₂ O ₃	29	>99
10	4Co/Al ₂ O ₃ -CR	69	>99
11	γ -Al ₂ O ₃	—	—
12	Blank	—	—
13 ^a	4Co/Al ₂ O ₃	6	>99
14 ^b	Ru/C	100	>99

Reaction conditions: LA 0.02 mol, catalyst Co/LA = 1.5% (molar ratio), 1,4-dioxane 30 mL, agitation rate 1000 r/min, H₂ 5 MPa, 180 °C, 3 h.

^a Water used as solvent. ^b Ru/LA = 1.5% (molar ratio).

column AT-SE-54 (60 m × 0.32 mm × 0.1 μ m) and FID detector using diethylene glycol dimethyl ether as an internal standard. The qualitative identification of the products was achieved by GC-MS (Agilent 5975C/7890A).

The results of the hydrogenation of LA to GVL over the HT-derived Co, Fe, Ni, Cu catalysts are summarized in Table 1. The 2Fe/Al₂O₃ and 2Cu/Al₂O₃ catalysts were almost inactive for LA hydrogenation. 2Ni/Al₂O₃ showed moderate hydrogenation activity with 39% LA conversion. 2Co/Al₂O₃ gave higher conversion (43%) of LA with >99% selectivity for GVL under the same reaction conditions, with no other hydrogenation product being detected in the product. Then we tested a series of HT-derived Co catalysts in which the Co/Al ratio was varied in the range of 1–5 (entries 5–8). The catalytic performance of the HT-derived Co catalyst was strongly dependent on the Co/Al ratio. The 4Co/Al₂O₃ catalyst exhibited by far the highest catalytic activity (100% conversion) with a low catalyst loading (1.5% molar ratio of LA) and short time (3 h). Also, the selectivity to GVL remained >99%. Notably, the reference catalyst, Co supported on γ -Al₂O₃ prepared by impregnation with a Co/Al ratio of 4 only gave 29% of LA conversion (entry 9), suggesting that the catalyst preparation protocol greatly affected

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Fig. 1. Procedure for catalyst separation. (a) Mixture of catalyst and reaction solution; (b) magnetic catalyst was separated from the mixture by a magnet; (c) catalyst was suspended in water when the magnet was removed.

the catalytic performance. Furthermore, 4Co/Al₂O₃-CR showed a lower LA conversion (69%) than 4Co/Al₂O₃ in the hydrogenation reaction (entry 10), so we prepared the catalyst sample by directly reducing the hydrotalcite without the calcination step. The possible reason for this phenomenon is discussed below together with Fig. 7. GVL was not formed when pure γ -Al₂O₃ or no Co-catalyst was used in the reaction (entries 11 and 12), which confirmed that the presence of dispersed Co particles was essential for the high activity in the hydrogenation of LA. In particular, the conversion of LA dropped to 6% when water was used as the solvent (entry 13). The commercial Ru/C catalyst used in the hydrogenation of LA achieved excellent LA conversion and GVL selectivity (entry 14). By comparison, 4Co/Al₂O₃ showed comparable catalytic performance with Ru/C in the liquid hydrogenative transformation to GVL.

One of the major issues for supported metal catalysts in the hydrogenation conversion of carboxylic acids in the liquid phase is their deactivation due to metal leaching and/or sintering, which are serious for the non-precious metal catalysts. Since carbonyl groups adsorb on metal nanoparticles, aggregation or even the formation of soluble metal-carbonyl complexes can occur especially when the interaction between the metal and support is not strong enough. To examine the stability of the optimal 4Co/Al₂O₃ catalyst for GVL production, the reusability experiment of 4Co/Al₂O₃ was carried out. To recycle the magnetic catalyst, a simple separation method was designed

Fig. 2. Reusability of 4Co/Al₂O₃ at 50% LA conversion. Reaction conditions: LA 0.06 mol, Co/LA = 0.4% (molar ratio), 1,4-dioxane 30 mL, agitation rate 1000 r/min, H₂ 5 MPa, 180 °C, 3 h.

shown in Fig. 1, where a glass tube equipped with a permanent magnet was used. The spent 4Co/Al₂O₃ was easily separated from the reaction mixture by the magnet. Since the surface of a Co nanoparticle was easily oxidized to cobalt oxide in air during the catalyst separation, before each run the separated catalyst was washed with distilled water and then reduced under H₂ flow (50 mL/min) at 700 °C for 1 h. After this treatment, the activity of the recovered catalyst was almost the same as in the first run (Fig. 2). The concentration of leached Co ion in the filtrate was measured as 8 ppm by ICP-AES, indicating that the Co/Al₂O₃ catalyst was stable enough in the liquid phase reaction and did not suffer severe deactivation under the relatively harsh conditions.

The HT-derived Co catalysts were characterized by N₂ adsorption isotherm, inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray photoelectron spectroscopy (XPS), NH₃ temperature programmed desorption (NH₃-TPD), powder X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR), and transmission electron microscopy (TEM) to elucidate the origin of their high LA hydrogenation activity and stability. Typical data of the BET surface area, Co/Al ratio, acid amount, Co loading, and mean particle size are summarized in Table 2.

It can be seen that there was no apparent relationship between the BET surface area or total acid sites and the catalytic performance of the Co/Al₂O₃ samples, indicating the activity of the HT-derived samples was less associated with the external texture and acidity. However, associating the bulk and surface Co/Al ratio in Table 2 showed a good correlation between the

Table 2

Physicochemical properties of the Co/Al₂O₃ catalysts.

Sample	<i>A</i> _{BET} (m ² /g)	Bulk Co/Al ^a (molar ratio)	Surface Co/Al ^b (molar ratio)	Total acid sites ^c (mmol/g)	Co loading ^d (%)	Co particle size ^e (nm)
1Co/Al ₂ O ₃	120.4	1.72	0.27	0.031	53.6	25.1
2Co/Al ₂ O ₃	86.7	2.07	0.31	0.020	69.8	25.4
3Co/Al ₂ O ₃	88.7	3.06	0.33	0.023	77.6	25.1
4Co/Al ₂ O ₃	74.9	4.04	0.72	0.021	82.4	25.5
5Co/Al ₂ O ₃	89.2	4.60	0.35	0.027	85.3	27.3

^a Calculated by ICP-AES. ^b Determined from XPS. ^c Determined from NH₃-TPD. ^d Calculated by ICP-AES. ^e Calculated from TEM image.

Co content and the catalytic performance of the $\text{Co}/\text{Al}_2\text{O}_3$ catalysts. The surface Co/Al ratio of each sample was less than the corresponding bulk value, suggesting the catalyst surface was enriched in Al. The fact that the specific composition of the $4\text{Co}/\text{Al}_2\text{O}_3$ sample maximized the exposure of active Co species (highest surface Co/Al ratio) was crucial for achieving a high efficiency in the LA hydrogenation.

As for the five Co/Al -HT precursors, the XRD patterns showed the characteristic peaks of the hydrotalcite structure [Fig. 3] [25,26]. All samples have sharp diffraction peaks at 11.7° , 23.5° , 34.8° , 39.4° , 47.2° , 60.2° , 61.6° , which were indexed to the (003), (006), (009), (015), (018), (110), and (113) lattice planes of hydrotalcite, respectively. For the samples with the higher Co/Al molar ratio (5,4,3, and 2), only the hydrotalcite crystal phase was observed, suggesting the high purity of the hydrotalcite. However, there were both the hydrotalcite phase and Bayerite phase in the sample with the Co/Al molar ratio of 1, due to that the excess Al ions precipitated as an additional Bayerite phase [27,28].

After the reduction at 700°C , the characteristic diffraction peaks of the hydrotalcite structure disappeared. Meanwhile, the major diffraction peaks with 2θ values of 44.3° , 51.6° and 76.1° (JCPDS 01-1255) ascribed to metal Co appeared (Fig. 4), indicating that the Co ions were reduced to metallic Co. During the catalyst screening, we found $4\text{Co}/\text{Al}_2\text{O}_3$ was the most efficient catalyst in the hydrogenation reaction of LA, so we looked for the explanation for its superior performance. When comparing the XRD patterns from these five $\text{Co}/\text{Al}_2\text{O}_3$ catalysts, obvious and wide diffraction peaks ascribed to the Co(100) and Co(101) planes were clearly observed in $4\text{Co}/\text{Al}_2\text{O}_3$. These results indicated that the Co(100) and Co(101) planes were highly active in the hydrogenation reaction, and the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst exposed more of these two planes when the molar ratio of Co/Al = 4. We found that the used $4\text{Co}/\text{Al}_2\text{O}_3$ catalyst also maintained the Co and CoAl_2O_4 phases, which further con-

Fig. 3. XRD patterns of Co/Al -HT precursors. (1) $5\text{Co}/\text{Al}$ -HT; (2) $4\text{Co}/\text{Al}$ -HT; (3) $3\text{Co}/\text{Al}$ -HT; (4) $2\text{Co}/\text{Al}$ -HT; (5) $1\text{Co}/\text{Al}$ -HT.

Fig. 4. XRD patterns of samples reduced with H_2 . (1) $5\text{Co}/\text{Al}_2\text{O}_3$; (2) $4\text{Co}/\text{Al}_2\text{O}_3$; (3) $3\text{Co}/\text{Al}_2\text{O}_3$; (4) $2\text{Co}/\text{Al}_2\text{O}_3$; (5) $1\text{Co}/\text{Al}_2\text{O}_3$; (6) spent $4\text{Co}/\text{Al}_2\text{O}_3$.

firmed the catalyst was stable under the reaction conditions.

The micro-structure and particle size distribution of the fresh and spent Co-based catalysts were characterized by TEM. As displayed in Fig. 5, the HT-derived Co catalysts showed the well dispersed nature of the Co nanoparticles. All of the fresh catalysts had particle sizes in the range of 25–30 nm (Table 2), indicating that the particle size of Co was not affected by its amount. However, the average Co particle size of $4\text{Co}/\gamma\text{-Al}_2\text{O}_3$ was larger than 200 nm (Fig. 5(e)). In view of the similar Co content in $4\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and $4\text{Co}/\text{Al}_2\text{O}_3$, it was deduced that the

Fig. 5. TEM images of $1\text{Co}/\text{Al}_2\text{O}_3$ -HT (a), $2\text{Co}/\text{Al}_2\text{O}_3$ -HT (b), $3\text{Co}/\text{Al}_2\text{O}_3$ -HT (c), $5\text{Co}/\text{Al}_2\text{O}_3$ -HT (d), $4\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (e), used $4\text{Co}/\text{Al}_2\text{O}_3$ -HT (f).

difference in Co particle size was caused by the different preparation procedures. The remarkable difference in the microstructure between the 4Co/Al₂O₃ and 4Co/ γ -Al₂O₃ catalysts manifested that the hydrotalcite was a good precursor for preparing well dispersed Co with a high loading. The TEM image of the used 4Co/Al₂O₃ catalyst is shown in Fig. 5(f), and the mean particle size was calculated to be 25.6 nm, demonstrating no significant aggregation of Co particles occurred under the reaction conditions.

The structure of the most efficient 4Co/Al₂O₃ catalyst was studied in detail to investigate its activity and stability (Fig. 6). It was clear that the Co particles have a core-shell structure (Figs. 6(a) and (b)). In the high resolution TEM (HRTEM) image, a dark core was surrounded by a light shell. The fast Fourier transform (FFT) patterns of the core are displayed in Fig. 6(d). It is common that the surface of the reduced Co nanoparticle is quickly oxidized to Co₃O₄ in air at room temperature. As for 4Co/Al₂O₃, the surface composition also changed during the TEM sample preparation, and the corresponding FFT patterns are in good accordance with the Co₃O₄ (400), (222), and (331) planes (JCPDS 43-1003). In addition, no FFT dot was observed in the shell area, indicating that the shell was dominated by amorphous Al₂O₃. The composition of the Co/Al₂O₃ core-shell

structure was further supported by that no impurity was observed in the energy dispersive X-ray (EDX) analysis (Fig. 6(f)). The above observations were consistent with the reported core-shell structure of Co₄N-Al₂O₃-HT, which also could be prepared with a high metal loading [29]. The surface Co/Al ratio of each sample (Table 2) was less than the corresponding bulk value, suggesting the catalyst surface was enriched in Al. Therefore, it was deduced that the particle core was composed of metal Co species while the shell was made up of amorphous Al₂O₃. This special core-shell structure prevented the sintering and leaching of the Co particles and resulted in the small particle sizes. In addition, compared with the fresh 4Co/Al₂O₃, the XRD pattern (Fig. 4(f)) and TEM image (Fig. 5(f)) of the used catalyst did not show any obvious change. Therefore, both the core-shell structure and strong interaction of Co and Al species were responsible for the stability of the catalyst.

As discussed above with Table 1, entries 7 and 10, 4Co/Al₂O₃-CR showed lower activity than 4Co/Al₂O₃ in the hydrogenation of LA. TEM was used to compare their microstructure. The Co particle of 4Co/Al₂O₃ was embedded in the Al shell and the average particle size was 25 nm (Fig. 7(a)). However, 4Co/Al₂O₃-CR showed no core-shell structure, and the Co particle size was 54 nm (Fig. 7(b)). So we propose that the high activity for the reduced 4Co/Al₂O₃ catalyst sample can be ascribed to its unique core-shell structure and small particle size.

To gain a deeper insight into the interaction between the supported phase and the carrier, H₂-TPR analysis was performed to observe the oxide reduction process. Figure 8 shows the H₂-TPR profiles of the Co₃O₄/ γ -Al₂O₃ and Co/Al-HT catalyst precursors with different Co/Al ratios. Two sharp peaks ($T_{\max}$ = 220 and 311 °C) were observed with Co₃O₄/ γ -Al₂O₃. Since Al₂O₃ cannot be reduced in this temperature range, the reduction peaks were due to the reduction of Co species. Co₃O₄/ γ -Al₂O₃ was reduced in two steps at 220 and 311 °C yielding CoO and Co⁰, respectively [30,31]. However, all the HT-derived samples showed one or two broad peaks from 500 to 700 °C. The $T_{\max}$ of the Co/Al-HT samples were located at 551, 605, 620, 631 and 647 °C for 5CoAl-HT, 4CoAl-HT, 3CoAl-HT, 2CoAl-HT, 1CoAl-HT, respectively. The shift to higher temperature revealed that the increase in Al amount in the samples hampered the reduction of Co ions [25]. In other words, there was a strong interaction between the Co ions and Al ions, which would prevent the sintering and leaching of Co nanoparticles.

The TPR results also reflected the strong interaction between Co and Al species in that the reduction temperature of 4Co/ γ -Al₂O₃ was below 350 °C, while those of the HT-derived Co catalysts were higher than 550 °C. From these observations,

Fig. 6. TEM images of 4Co/Al₂O₃. (a), (b) low magnification image, (c) HRTEM image, (d) FFT pattern of the red framed area in (c), (e) FFT pattern of the blue framed area in (c), (f) EDX image.

Fig. 7. TEM images of 4Co/Al₂O₃ (a) and 4Co/Al₂O₃-CR (b).

Fig. 8. H_2 -TPR profiles of the Co/Al-HT precursors. (1) 5Co/Al-HT; (2) 4Co/Al-HT; (3) 3Co/Al-HT; (4) 2Co/Al-HT; (5) 1Co/Al-HT; (6) $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$.

during the thermal treatment of the precursor under H_2 flow, the reduction of Co and the formation of the Co/Al core-shell structure simultaneously occurred. Consequently, the embedded Co nanoparticle is more difficult to reduce, so a broad TPR peak appeared at higher temperatures.

In summary, we developed an inexpensive and magnetic recyclable Co-based catalyst for the hydrogenation of LA to GVL. A unique core-shell Co/ Al_2O_3 catalyst derived from hydrotalcite with a high Co loading was fabricated. The core-shell structure and strong interaction between Co and Al made the Co-based catalyst stable under the reaction conditions. These results also shed light on the rational design of efficient non-precious metal alternatives as heterogeneous catalysts.

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Graphical Abstract

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Magnetic Co/ Al_2O_3 catalyst derived from hydrotalcite for hydrogenation of levulinic acid to γ -valerolactone

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A non-precious metal Co/ Al_2O_3 catalyst prepared by reduction of a hydrotalcite precursor hydrogenated levulinic acid to γ -valerolactone with high efficiency and stability.

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水滑石基磁性Co/Al₂O₃催化剂在乙酰丙酸加氢制备γ-戊内酯反应中的应用

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摘要: γ-戊内酯广泛应用于食品添加剂、燃料添加剂、溶剂、汽油、柴油以及多种化工中间体的合成, 由于其上游原料乙酰丙酸是重要的生物质基平台化合物已实现了工业化生产, 因此发展其高效、可循环使用的催化合成新体系是近年来生物质催化转化的研究热点之一。目前使用的多相催化剂体系主要是浸渍法制备的负载型金属纳米颗粒催化剂, 活性金属主要有Ru, Pd, Pt, Au, Cu, Ni等。由于乙酰丙酸制备γ-戊内酯反应是一个酸性的含水体系, 在高温、高压条件下, 使用浸渍法得到的催化剂特别是非贵金属催化剂容易发生活性金属的聚集、流失, 从而使得催化剂重复使用的效果不佳。

从非贵金属替代贵金属和提高催化剂稳定性这两点入手, 本论文以水滑石为合成催化剂的单一前驱体, 将非贵金属(Cu, Ni, Fe, Co)掺入到水滑石的结构骨架中, 通过直接氢气焙烧还原制得了高负载量的负载型金属纳米颗粒多相催化剂。将制得的催化剂应用于乙酰丙酸加氢反应, 其催化活性顺序为: Co>Ni>Cu>Fe。制备出了5种不同Co/Al比的Co基催化剂, 其中4Co/Al₂O₃催化剂在H₂ (5 MPa)、180 °C条件下, 显示出了类似贵金属钌催化剂的活性和选择性, 乙酰丙酸在3 h内完全转化, γ-戊内酯的选择性高达99%。

为了进一步了解催化剂的结构与其活性和稳定性之间的关系, 我们采用X射线粉末衍射仪(XRD), 氢气程序升温还原(H₂-TPR), X射线光电子能谱(XPS), 透射电子显微镜(TEM)等表征手段研究了催化剂的形貌和结构。TEM结果表明, 以水滑石为前驱体制备的Co催化剂中负载的Co纳米颗粒的平均粒径在25–30 nm, 而用浸渍法制备的相同负载量的Co催化剂的Co纳米颗粒粒径大于150 nm。相应的催化反应结果表明, 前者的催化活性要远好于后者。水滑石前驱体的H₂-TPR实验结果表明, 随着Co/Al比增加, 其还原峰向低温方向位移。这是由于Al含量的减少, 导致金属Co离子周围键合的Al离子数量减少, 从而使得Co与Al之间的作用力减弱, Co更加容易被还原。表现在还原温度上, 即为还原温度降低, 说明了Co纳米颗粒与载体之间具有一种强相互作用。结合TEM测试结果, 正是这种强相互作用限制了Co纳米颗粒的长大, 使其要远小于用浸渍法制得的Co纳米颗粒。HRTEM测试结果显示在4Co/Al₂O₃催化剂结构中, Co金属纳米颗粒与载体Al₂O₃之间存在一种核壳结构的关系, Co纳米颗粒被包埋于载体Al₂O₃中形成核壳结构。这种结构同样也保证了活性金属与载体之间较强的相互作用, 有效地避免Co纳米颗粒在强水热、酸性条件下的聚集和流失, 从而使该催化剂在循环使用四次时仍能保持优异的活性和选择性。我们进一步研究了该核壳结构形成的原因。发现催化剂在制备过程中如果先用空气高温焙烧, 再用氢气还原, 得到的催化剂中则没有明显的核壳结构, 且Co纳米颗粒粒径在55 nm左右。相应的催化反应结果也要差于直接氢气焙烧还原得到的4Co/Al₂O₃催化剂。这也从侧面说明了以水滑石为前驱体制备负载型金属纳米颗粒催化剂时, 其原位的限制效应在控制金属纳米颗粒的大小、稳定性方面的优越性。此外, 由于该Co催化剂具有磁性特征, 很容易通过磁性回收实现催化剂与反应液的分离, 大大简化了催化剂的回收及产物分离过程。

关键词: 生物质转化; 乙酰丙酸; γ-戊内酯; 稳定碱金属催化剂; 核壳结构; 钴

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