Mg 促进的 Ru-Ba/AC 高效氨合成催化剂

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摘要: 通过 X 射线衍射、CO 化学吸附、X 射线光电子能谱和氨合成活性测试等手段, 研究了 Mg 助剂对 Ru/AC 催化剂组分分布和活性的影响。结果显示, 适量 Mg 的添加有利于 Ba 和金属 Ru 粒子在活性炭表面的均匀分布, 从而提高了催化剂活性。

关键词: 钡; 活性炭; 镁; 钌; 氨合成

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Highly Efficient Ru-Ba/AC Catalyst Promoted by Magnesium for Ammonia Synthesis

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Abstract: The effect of alkaline-earth oxides as promoters on Ru/AC (AC = activated carbon) catalysts was explored. Alkaline-earth metal oxides can reduce the agglomeration of ruthenium particles at high temperatures, which increases the amount of available ruthenium. The influence of the Mg promoter on the distribution and activity of the Ru/AC catalyst were investigated by CO chemisorption, X-ray diffraction, and energy dispersive spectrometry and by an activity test for ammonia synthesis. The results show that a specific quantity of magnesium significantly promotes the uniform distribution of Ba and Ru on the surface of AC, which enhances catalytic activity. The introduction of Mg significantly improved the size of the Ru particles and increased the Ru surface area. The distribution and interaction were improved greatly for the Ba promoter and the Ru precursor on the surface of the AC because of the addition of the Mg promoter. The introduction of magnesium to Ru-Ba-K/AC significantly improved the utilization ratio of the noble metals and the performance-price ratio.

Key words: barium; activated carbon; magnesium; ruthenium; ammonia synthesis

Ruthenium catalysts are considered as the second generation catalysts for ammonia synthesis following iron catalysts [1–3]. Ruthenium catalysts have an unparalleled advantage in the reduction of energy consumption and increased yields of ammonia at low temperatures and low pressures are obtained compared with the iron-based catalysts for ammonia synthesis [4–7]. However, because it is a precious metal, Ru resources are scarce and expensive and the high content required in the catalysts results in high cost and this impedes its promotion and application. Therefore, the development of a catalyst with lower Ru content is very important for the economic use of Ru catalysts for ammonia synthesis.

Numerous studies have shown that the so-called B₅ active sites increase in number when the size of the Ru nanoparticles is around 2 nm in the Ru/AC (AC = activated carbon) catalyst used for ammonia synthesis [5,8–10]. Therefore, a highly uniform dispersion of Ru over the surface of the AC is an important feature for a low content Ru catalyst with a higher activity for ammonia synthesis. Earlier studies focused on the modification of the texture and the surface of the AC to obtain a higher dispersion of Ru [11–16]. However, after impregnating with a ruthenium precursor (such as ruthenium chloride) controlling the agglomeration behavior of the Ru particles has rarely been considered for the subsequent catalyst reduction process to produce catalysts with

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high activity and low precious metal content for ammonia synthesis.

Metal oxides could be used to stabilize and anchor the nanoparticles to reduce the agglomeration of nanoparticles [17–19]. For the Ru/AC catalyst to be used in ammonia synthesis, alkaline earth or rare earth metal oxides can play an important role in the dispersion of ruthenium nanoparticles and in their promotion. We thus investigated the effect of alkaline earth oxides as promoters on Ru/AC catalysts, and tried to find a catalyst with a low content of ruthenium, and with high activity at low temperature.

1 Experimental

1.1 Catalyst preparation

Graphitic activated carbon was ground and sieved to retain the 12–16 mesh fractions. The graphitic activated carbon was then impregnated with magnesium nitrate and RuCl_3 followed by barium nitrate in an aqueous solution at ambient temperature. The nominal Ru loading on AC was 4.5% or 5%. The solvent was evaporated after impregnation by drying under infrared light. The sample was reduced in a stream of mixed 75% H_2 -25% N_2 gas at 450 °C for 6 h. The K promoter was then introduced by impregnating with an aqueous solution of KOH, and the sample was evaporated under infrared light.

1.2 Characterization of the catalysts

CO chemisorption was carried out using an AutoChem 2910 instrument. Ru dispersion was calculated from the cumulative volume of CO adsorbed during the pulse, assuming a chemisorption stoichiometry $\text{CO}/\text{Ru} = 1:1$. N_2 physisorption was measured using a gas adsorption instrument (Nova Win2). The component distribution was studied by energy dispersive spectrometry (EDS) using scanning electron microscopy (SEM, JSM-6700F). The crystal structure was determined by powder X-ray diffraction (XRD, Philips, X' Pert MPD, $\text{Cu } K_{\alpha}$, $\lambda = 0.15418 \text{ nm}$).

1.3 Measurement of activity for ammonia synthesis

The catalytic activity for ammonia synthesis was measured in a stainless steel reactor. Before testing, the catalysts were activated in a flowing gas mixture of 75% H_2 and 25% N_2 from ambient temperature to 500 °C at 1 °C/min (kept at 200, 300, 400, 450, and 500 °C for 2 h) and then stabilized under the chosen reaction conditions (i.e., 10 MPa, 673 °C, 10000 h^{-1} , and a H_2/N_2 molar ratio of 3) for more than 2 h. The ammonia concentration in the effluent was determined by chemical titration [20].

2 Results and discussion

2.1 Effect of the Mg promoter on the component distribution

As shown in Table 1, the catalyst promoted by magnesium has a lower specific surface area and smaller pore volume, but its pore radius is larger. The results suggest that magnesium was adsorbed preferentially in the micropores. The decrease in pore volume is mainly due to the adsorption of magnesium in the micropores. This is similar to that found for the adsorption of citric acid in the micropores of AC [21]. From Table 1 the pore volume and specific surface area of the catalyst decreases obviously because of the addition of the Mg promoter. The specific surface area decreases rapidly by about 10% even when the loading of magnesium is only 1.4%, which suggests that a small loading of magnesium influences the texture of the AC greatly. The distribution of Ru and Ba also has an influence. Micropore blockage is favorable for the Ru/AC catalysts. Partially formed Ru particles must be located in the small mesopores and micropores as ultrafine particles, and are probably poorly organized nanoparticles [22]. These ultrafine Ru nanoparticles (< 1.5 nm) only have a few active sites [8]. Therefore, micropore blockage decreases the Ru content in the micropores, which is favorable for increased ruthenium activity.

Table 1 Effect of the Mg promoter on the texture of the Ru/AC catalyst

Sample	$A_{\text{BET}}/$ (m^2/g)	$A_{\text{micro}}/$ (m^2/g)	$A_{\text{meso}}/$ (m^2/g)	$V_{\text{pore}}/$ (cm^3/g)	$R_{\text{pore}}/$ nm
4.5%Ru-4%Ba/AC	752.2	482.5	205.9	0.62	1.65
1.4%Mg-4.5%Ru-4%Ba/AC	683.2	412.4	207.0	0.58	1.70

CO chemisorption shows that the dispersion of Ru improved for the catalyst containing the Mg promoter, as shown in Table 2. The particle size of Ru decreased from 2.40 nm to 1.94 nm, and the surface area of Ru per gram increased from 201.39 m^2/g to 249.19 m^2/g . The increase in this ratio was thus 23.88%. This remarkable improvement showed that the addition of magnesium promotes the distribution of Ru nanoparticles by reducing agglomeration and increasing the dispersion of the Ru nanoparticles on the surface of the AC. This remarkable improvement could also result from the magnesium nitrate with low melting point (95 °C), which forms hydroxynitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 4\text{Mg}(\text{OH})_2$) before the reduction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$. The interaction of hydroxynitrate and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ before reduction could lead to $\text{Ru}(\text{OH})_3$, which decreases the agglomeration of Ru by the interaction of hydroxyls with $\text{Mg}(\text{NO}_3)_2 \cdot 4\text{Mg}(\text{OH})_2$ and $\text{Ru}(\text{OH})_3$ at the high reduction temperature. The melting point of $\text{Ba}(\text{NO}_3)_2$ (592 °C) is higher than the

Table 2 Effect of the Mg promoter on the Ru dispersion of the catalyst

Sample	Ru dispersion (%)	Ru surface area (m ²)		Ru diameter (nm)	TOF (s ⁻¹)
		Per gram of sample	Per gram of metal		
4.5%Ru-4%Ba/AC	55.27	9.08	201.39	2.40	0.22
1.4%Mg-4.5%Ru-4%Ba/AC	68.21	11.21	249.19	1.94	0.21

reduction temperature. Hydroxynitrate forms with difficulty at low reduction temperatures. Ba decreases the amount of Ru agglomeration in the reductive nanoparticles [23,24], but the Mg promoter decreases the amount of agglomeration before the reduction. The interaction between Ba and Mg leads to a significant increase in Ru dispersion.

Table 2 shows that the Ru surface area increases remarkably and the TOF decreases slightly with a decrease in Ru size, which indicates that an increase in the size of Ru from 2.40 nm to 1.94 nm leads to a remarkable increase in the amount of B₅ active sites for the 1.4%Mg-4.5%Ru-4%Ba/AC catalyst compared with the 4.5%Ru-4%Ba/AC catalyst. This significant increase in the number of B₅ sites leads to a significant increase in activity for ammonia synthesis. However, there is no direct correlation between the activity of Ru and dispersion from the CO chemisorption data [8,25–27].

Figure 1(a) shows XRD patterns of the unreduced catalyst. The main crystal phase is Ba(NO₃)₂ (JCPDS 04-0773) without the diffraction maximum of magnesium nitrate. The diffraction maxima in Fig. 1(a)(2), Fig. 1(b)(1), and Fig. 1(b)(2) are characteristic AC peaks without the characteristic nitrates or oxides of Ba, Mg, or Ru. This shows that a preferential adsorption of magnesium nitrate in the micropores decreases the extent of Ba(NO₃)₂ dispersion in the unreduced catalyst. However, more surface area was exposed to the Ba promoter, which improved the distribution of Ba after reduction at high temperature. Therefore, the Mg promoter influences the dispersion of the Ru precursor and also the Ba promoter. The stronger interactions of Mg, Ru, and Ba during preparation and reduction significantly improved the distribution of the precursors and the promoters,

Fig. 1. XRD patterns of the unreduced (a) and reduced (b) catalysts. (1) 1.4%Mg-4.5%Ru-4%Ba/AC; (2) 4.5%Ru-4%Ba/AC.

followed by higher activity for ammonia synthesis.

Figure 2 shows that the distribution of the barium promoter and ruthenium are more uniform and similar for the 1.4%Mg-4.5%Ru-4%Ba/AC catalyst containing the magnesium promoter compared with the 4.5%Ru-4%Ba/AC catalyst. Magnesium, as a structural promoter, could play multiple roles in promoting the uniform distribution of barium

Fig. 2. EDS spectra of the Ru-Ba/AC catalyst with or without the Mg promoter. (a) 4.5%Ru-4%Ba/AC; (b) 1.4%Mg-4.5%Ru-4%Ba/AC. Red: Ru; blue: Mg; green: Ba.

and ruthenium, which increases the contact area of barium and ruthenium and decreases the agglomeration of ruthenium etc.

2.2 Catalytic activity for ammonia synthesis

Ba is the best structural and electronic promoter for the Ru/AC catalyst for use in ammonia synthesis. The K promoter was introduced to significantly improve the activity of ammonia synthesis at lower temperatures [24]. The introduction of K is necessary to confirm the significant influence of the Mg promoter. The Mg promoter significantly improved the catalytic activity of the Ru-Ba/AC catalyst. The increase in ammonia was 0.77 vol% for 1.4%Mg-4.5%Ru-4%Ba/AC and 1.77 vol% for 1.4%Mg-5%Ru-4%Ba/AC compared with the homologous Ru-Ba/AC catalyst without Mg promoter at 10 MPa, 10000 h⁻¹, and 400 °C from Table 3. This could result from the Mg promoter significantly improving the distribution and interaction of Ru and Ba. The activity increase at 375 or 425 °C for the catalysts promoted with Mg and Ba was lower than the increase at 400 °C. This decrease is mainly influenced by the equilibrium ammonia concentrations at 425 °C. The activity at 375 °C was far below that at 400 °C, which could be correlated to the activation of nitrogen. These mechanisms need to be further investigated.

Table 3 Effect of Mg promoter on the activity of the Ru-Ba/AC catalysts for ammonia synthesis

Catalyst [*]	NH ₃ concentration (vol%)		
	375 °C	400 °C	425 °C
4.5%Ru-4%Ba/AC	10.76	16.63	18.36
5%Ru-4%Ba/AC	11.77	19.20	19.66
1.4%Mg-4.5%Ru-4%Ba/AC	11.43	17.40	19.04
1.4%Mg-5%Ru-4%Ba/AC	12.91	20.97	20.45

Reaction conditions: 10 MPa, 10000 h⁻¹. ^{*}KOH content: 18%.

3 Conclusions

Magnesium was introduced into the Ru/AC catalyst as a promoter. Magnesium was adsorbed preferentially in micropores, which significantly improved the size of Ru and increased its surface area. The distribution and interaction improved remarkably for the Ba promoter and the Ru precursor on the surface of the AC because of the addition of the Mg promoter. The introduction of magnesium to Ru-Ba/AC significantly improved the utilization ratio of the noble metal and its catalytic efficiency for ammonia synthesis.

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