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Short Communication

Effect of carbon and chlorine on the performance of carbon-covered alumina supported Ru catalyst for ammonia synthesis

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ABSTRACT

Uniformly carbon-covered alumina (CCA), which was prepared by pyrolysis of sucrose, was used as support of ruthenium catalyst. Carbon did not significantly influence on the ammonia synthesis activities of Ru catalysts by changing their Ru particle sizes or Ru $3d_{5/2}$ binding energies. Residual chlorine severely suppressed ammonia synthesis by decreasing the amount of hydrogen with the desorption peak at medium temperatures. Carbon also inhibited the adsorption of this hydrogen species for chlorine-free Ru catalysts, but did not change their activities. On the other hand, carbon can increase the ammonia synthesis activities of containing-chlorine Ru catalysts by decreasing the disadvantageous effect of chlorine on H_2 adsorption.

1. Introduction

Supported ruthenium catalyst represents the next generation of catalyst for ammonia synthesis after the iron-based catalyst [1–4]. Ru catalysts supported on the thermally modified active carbon have been proved to be much more active than fused iron catalysts [5,6]. However, the unavoidable methanation of carbon support in Ru catalyst under the ammonia synthesis condition [5,6] is still a problem for its extensive use in industry. It is thus desirable to develop a stable Ru catalyst that overcomes these issues, and oxides supported ruthenium catalysts have been investigated frequently. Aika et al. [1] claimed that the rate of ammonia synthesis was relative with the basicity of support materials (Ru/CaO>RuMgO>Ru/BeO>Raney Ru>Ru/$A1_2O_3$>Ru powder>Ru/AC) because basic supports can donate electrons to Ru atoms. This idea has been used widely for accounting for the difference in ammonia synthesis activities for Ru catalysts supported on various oxides [7–9], and thus Al_2O_3 was not considered to be an ideal support material for Ru catalyst because of the acidic nature of alumina [1]. Rao et al. [10,11] prepared carbon coated alumina by pyrolysis of an alkene on Al_2O_3. They claimed that this carbon coated alumina not only can eliminate the disadvantages of the low strength of carbon and the acidity of Al_2O_3, but also offered the advantages of the electron withdrawing capacity of carbon and the stability of alumina, therefore, the high activity for supported Ru catalyst can be obtained.

However, recently the high efficient Ru catalysts supported on Al_2O_3 have been prepared by some appropriate methods. Miyazaki et al. [12] found that the ammonia formation rate of Ru/Al_2O_3 catalyst obtained from a metal colloid with ethylene glycol as reducing agent was about 12 times higher than those of non-promoted Ru/Al_2O_3 catalysts prepared by conventional methods. Seetharamulu et al. [13] presented this polyol reduction method can be used for preparing the highly active Ru catalysts supported on Al_2O_3, MgO or Mg-Al hydrotalcite. Furthermore, they found that the activity of Cs promoted Ru/Al_2O_3 with hydrogen reduction was higher than that of Cs-Ru/MgO. Miyazaki et al. [12] and Seetharamulu et al. [13] claimed that the high dispersion of Ru nano-particles was the main reason for the high activity of the catalysts with polyol reduction. We also have successfully prepared chlorine-free Ru/Al_2O_3 catalysts with high catalytic activity by hydrazine reduction [14,15] or precipitation method [16]. We found that residual chlorine inhibited CO chemisorption, and then Ru particle sizes based on CO chemisorption would be overestimated. Transmission Electron Microscopy (TEM) study showed the average metal particle sizes of chlorine-containing Ru/Al_2O_3 catalysts were close to the values of chlorine-free samples, which can rule out the possibility that the change of the activity was mainly depended on the difference in Ru dispersion. The hydrogen temperature-programmed desorption study (H_2-TPD) for Ru catalyst showed that residual chlorine inhibited the hydrogen desorption peaks at medium temperature. Previously, these peaks have been temporarily assigned to hydrogen adsorbed at sites at the metal-support interface, and then it can be assumed the interaction between Ru particles and alumina surface exerts a strong influence on hydrogen adsorption and catalytic activity.

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It can be expected that the presence of carbon on alumina surface would change the interaction between Ru and alumina, herein CCA was used as support material for Ru catalyst to further understand the relationship among ruthenium particles, support material and chlorine. The samples were characterized by X-ray fluorescence (XRF), CO chemisorption, X-ray diffraction (XRD), TEM, X-ray photoelectron spectroscopy (XPS) and H_2-TPD. The aim of this work was also to further confirm the influence of chlorine on hydrogen adsorption and the catalytic activity of Ru catalysts. The influence of carbon on the performance of Ru catalyst supported on CCA for ammonia synthesis also has been reconsidered.

2. Experimental

2.1. Preparation of CCA and ruthenium catalysts

Uniformly CCA was prepared according to the procedure described by Lin et al. [17,18], briefly, γ-Al_2O_3 (WYA-251, 175 m^2/g, Wenzhou Jingjing Alumina Co., Ltd.) was sieved into 12–16 meshes, baked at 500 °C for 4 h and impregnated with aqueous solutions of sucrose. After dried at 120 °C for 1 h, the samples were heated at 600 °C in N_2 (100 ml/min) for 0.5 h. The weight ratios of sucrose to alumina for CCA3 and CCA6 were 0.3 and 0.6, respectively. The carbon content was estimated by burning the organic deposit in the oven at 800 °C for 4 h.

Ru catalysts (about 0.04 g Ru metal per gram of alumina) were prepared by impregnating aqueous of $RuCl_3 \cdot nH_2O$ (37 wt.% Ru, Sino-Platinum Metals Co. Ltd.) on CCAx. One part of the impregnated solids was treated by precipitation method [16]. After washing until no chlorine ions were detected ($AgNO_3$ titration), the sample was heated in hydrogen gas at 450 °C for 6 h. Sm was introduced to the as-obtained Ru/CCAx by incipient wet impregnation method with an aqueous solution of samarium nitrate, and the weight ratio of Sm to Al_2O_3 was ca. 20%. The catalyst was labeled as SmRu/CCAx. Another part of the sample was treated with only hydrogen reduction, and Sm promoted catalyst was named as SmRu/CCAx-H.

2.2. Catalyst characterization

N_2 physisorption measurements were performed on an ASAP 2020 apparatus (Micromeritics, USA). The surface area was calculated by means of the Brunauer–Emmett–Teller (BET) method. The total pore volume was obtained from the amount of adsorbed N_2 at a relative pressure of 0.98. The pore size distribution curves were determined from the N_2 desorption isotherms using the Barrett–Joyner–Halenda (BJH) method. The micropore volume and micropore surface area were calculated by t-plot method.

The composition concentrations of catalyst were obtained using a PANalytical Axios XRF spectrometer under a vacuum atmosphere. The result was reported based on a calibration curves. The surface morphology was examined with a field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800). TEM was performed on a FEI Tecnai G2 F20 field emission transmission electron microscope operated at 200 kV. XPS analysis was performed on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific) at 3.0×10^{-10} mbar using Al Kα X-ray beam (1486.6 eV). XPS peak fitting were performed with XPSPEAK software (version 4.1, Raymund WM Kwok). The C1s peak at 284.6 eV was selected as an inner standard calibration peak. A Shirley background and an 20:80 Lorentzian/Gaussian peak shape were assumed. H_2-TPD and CO chemisorption were performed on an AutoChem 2910 instrument (Micromeritics), according to the procedure from Lin et al. [16].

2.3. Activity studies

Ammonia synthesis was measured in a stainless steel reactor. Before activity testing, the catalysts (2 ml) were activated in a stoichiometric H_2 and N_2 mixture (3:1) at different temperatures (200, 300, 400, 450 and 500 °C) for 2 h. The ammonia concentration in the effluent was determined by neutralizing a known amount of diluted H_2SO_4 with Congo red as indicator after the catalysts were stabilized under the reaction conditions (i.e. 10 MPa, 10000 h^{-1}, 450 °C) [19].

3. Results and discussion

The carbon content and the texture properties of Al_2O_3, CCA3 and CCA6 are listed in Table 1. Fig. 1 presents the adsorption-desorption nitrogen isotherms and pore size distribution curves of Al_2O_3, CCA3 and CCA6. XRD study shows the patterns of Al_2O_3, CCA3 and CCA6 were similar (see Fig. S1 in Supplementary material), indicating that carbon was highly dispersed on Al_2O_3 or the deposited carbon was amorphous. As can be seen in Table 1, the double sucrose loading led to the double increase of carbon content, which agrees well with the result of Lin et al. [18]. CCA3 had lower surface area (S_{BET}) than that of Al_2O_3, while CCA6 showed highest specific surface area. Obviously, the increase of carbon content led to the decrease of total pore volume and pore size, but increased the micropore surface and micropore volume. The results were due to the change of the pore structures after the introduction of carbon. The presence of carbon would cover the surface of alumina and fill in the mesopores of alumina, which have been proved by pore size distributions of samples (Fig. 1) and SEM images (Fig. S2), and then decreased its surface area, total pore volume and pore size. However, a new step at a lower partial pressure, 0.4–0.7 can be clearly observed in the nitrogen adsorption/desorption isotherms of CCA6, and a new peak at a pore diameter of 3–4 nm also appeared in its pore size distribution curve. Obviously, the presence of larger amount of carbon decreased the total pore volume and pore size, but were advantageous to the generation of micropore, and thus the micropore volume and micropore surface area both increased. CCA6 even showed much higher value of specific surface area than that of Al_2O_3 as a result of large amounts of micropores. SEM images of samples (see Fig. S2) also show that the morphologies of carbon were quite different with those of CNTs [20], indicating that the as-obtained samples obtained by pyrolysis of sucrose mainly were amorphous carbon.

The compositions, CO uptake, Ru metal dispersion and particle size of the Sm-promoted Ru catalysts are collected in Table 2. Rather large number of chlorine remained on the Ru catalysts with only hydrogen reduction, while only trace of chlorine was detected in samples with precipitation method. This observation is good accordance with our previous result [16]. The presence of chlorine severely decreased the values of particle size based on CO chemisorption. However, TEM images with particle size distribution histograms (Fig. 2) clearly exhibited that SmRu/CCA3 and SmRu/CCA3–H both had the particle size distribution in the range of 1.0–4.0 nm, the average sizes for SmRu/CCA3 and SmRu/CCA3–H were 2.2 and 2.5 nm, respectively. The discrepancy between the mean metal particle sizes determined from TEM and from CO chemisorption was due to the presence of chlorine would suppress CO chemisorption [21], and then the amount of adsorbed CO decreased. In such a case, the value of particle size based on CO chemisorption was overestimated [16]. From Table 2 and Fig. 2, it also can conclude that residual chlorine and carbon all had a

Table 1
Carbon content and texture properties of Al_2O_3 and CCA samples.

Sample	W_s:W_A[a]	C content (wt.%)	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Micropore surface area (m^2/g)	Micropore volume (cm^3/g)	Pore size (nm)
Al_2O_3	–	–	175	0.53	–	–	11.5
CCA3	0.3:1	7.8	168	0.43	26.2	0.01	9.7
CCA6	0.6:1	14.8	189	0.37	34.9	0.03	7.4

[a] Weight ratio of sucrose to alumina.