Short Communication

Effect of treatment conditions on ruthenium particle size and ammonia synthesis activity of ruthenium catalyst

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ABSTRACT

Ru/Al_2O_3 catalysts with different Ru particle sizes were prepared by changing the metal loading, the treatment temperature in hydrogen or the calcination temperature in air. It is found that the catalysts obtained by different methods cannot directly be used to study the correlation between particle sizes and the catalytic activity. The difference in treatment conditions of Ru/Al_2O_3 catalysts affected the ammonia synthesis activity of Sm-promoted Ru/Al_2O_3 not only by affecting the sizes and the shapes of Ru particles, but also by changing the properties of some active sites available for gas adsorption.

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1. Introduction

Ammonia synthesis has long been a bellwether reaction in heterogeneous catalysis [1]. During the last several decades, considerable efforts have been devoted to the study of supported Ru catalyst, which has been recognized as the next generation catalyst for ammonia synthesis following iron-based catalyst [2–4]. The changes in ruthenium particle sizes, promoters and supports were the most important factors that control the performance of Ru catalysts for ammonia synthesis.

The influence of Ru particle sizes on the ammonia synthesis rates had been studied based on theoretical calculations and experimental results. Dahl et al. [5,6] proposed that the dissociation and desorption of nitrogen exclusively took place at the step sites on the Ru(0001) surface. Their microkinetic analysis [7] further confirmed only part of the surface was active in nitrogen dissociation. Moreover, the microkinetic model for ammonia synthesis described very well the catalytic rates over a $Ru/MgAl_2O_4$ and over a Ru single crystal. It seems that the most active sites for N_2 dissociation and ammonia synthesis are ensembles of five Ru atoms, which expose a three-fold hollow site and a bridge site close together where part of the atoms are edge atoms [5,6,8]. This type of sites has been named as B_5-type sites. Jacobsen et al. [8] found B_5 sites only were present on Ru particles with a size larger than 0.7 nm. The probability of B_5 sites showed maximum for Ru particles of 1.8–2.5 nm, and monotonically decreased for particles larger than 2.5 nm.

However, Kowalczyk et al. [9] found that the TOF values were equal to each other for two different Ba-promoted Ru/C catalysts with Ru particle sizes 7.2 nm and 2.8 nm. Rarog-Pilecka et al. [10] found Ru particle sizes increased monotonically with Ru loading, from about 1 nm for 1 wt.% Ru to about 4 nm for 32 wt.% Ru, but the TOFs all increased versus particle sizes. Liang et al. [11] also showed the TOFs increased from 0.004 to 0.036 s^{-1} with the increase of Ru particle sizes from 1.7 to 10.3 nm. Recently, Karim et al. [12] prepared several $Ru/\gamma\text{-}Al_2O_3$ catalysts with different particle sizes and shapes by controlling the pretreatment conditions. They found the maximum ammonia decomposition activity per gram Ru for the catalysts with 7 nm flat-like particles. Consequently, they proposed that the number of B_5 active sites was dependent on particle shape, and a higher number of B_5 sites were obtained on the flat particles despite the low dispersion. These observations did not agree with the results based on the aforementioned theoretical approach or experiment of Dahl et al.'s group. This controversy points to the need of the further study on the influence of treatment conditions on ruthenium particle sizes and ammonia synthesis activity of Ru/Al_2O_3 catalysts. In this work, we prepared Ru/Al_2O_3 catalysts with different Ru particle sizes by different methods, including change in the metal loading, the treatment temperature in hydrogen or the calcination temperature in air. Our previous study has shown the presence of Sm promoter decreased the amount of adsorbed hydrogen for Ru/Al_2O_3, but did not affect the position of the desorption peak in the temperature range of room temperature to 325 °C [13]. It has also been found that the catalytic activity of Ru catalysts increased up to a certain value and then decreased with the increase of Sm loading [13]. Thus equivalent amount of samarium was introduced to Ru catalysts because the samples without

promoters were completely inactive [14,15]. The non-promoted and Sm-promoted Ru catalysts were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction of hydrogen (H_2-TPR) and temperature-programmed desorption of hydrogen (H_2-TPD) to understand the relation among the preparation methods, the sizes of Ru particles and the catalytic activities of Ru catalysts.

2. Experimental

2.1. Catalyst preparation

γ-Al_2O_3 (WYA-251, 175 m^2/g, Wenzhou Jingjing Alumina Co., Ltd., China.) was calcined in air at 500 °C for 4 h. Ru metal was introduced by the incipient wetness impregnation of alumina with $RuCl_3$ solution. The as-obtained $RuCl_3$/Al_2O_3 catalysts were incipient wetness impregnated with KOH solutions to obtain chlorine-free Ru/Al_2O_3 catalysts [13]. Before the addition of Sm, Ru catalysts were treated under different conditions. Equivalent amount of Sm was introduced to Ru/Al_2O_3 catalysts by the incipient wet impregnation method with an aqueous solution of samarium nitrate, the weight ratio of Sm to alumina was 20 wt.%. Sample codes and the pretreatment conditions of Ru catalysts are given in Table 1. The catalyst was name as SxROyHz, where x was the weight ratio of Ru to alumina, y was the symbol of the calcination temperature ("2" was 250 °C, "3" was 350 °C and "4" was 450 °C), and z was the symbol of the hydrogen reduction temperature ("4" was 450 °C, "7" was 700 °C and "9" was 900 °C).

2.2. Catalyst characterization

TEM analysis was carried out with a FEI (Tecnai G2 F20) microscope. XPS was performed on a Thermo Scientific ESCALAB 250 spectrometer with an Al–Kα X-ray source. H_2-TPR, CO chemisorption and H_2-TPD were measured on an AutoChem 2920 instrument. Details of the characterization methods of the samples were provided previously [16–18].

2.3. Ammonia synthesis measurements

The ammonia synthesis measurements were carried out in a stainless steel reactor. Ru catalysts (0.30 g; particle size, 0.30–0.56 mm) were diluted with quartz powder (the volumetric ratio of catalyst/quartz was 1/30) to prevent temperature gradients. The samples were reduced in gas mixture (H_2/N_2 = 3.0 vol/vol) at different temperatures (200, 300, 400, 450 and 500 °C for 2 h, respectively), and then ammonia synthesis test was performed under the condition of 10 MPa and high space velocity (2.4×10^5 cm^3 h^{-1} g_{cat}^{-1}). After stabilizing under the reaction conditions for more than 3 h, effluent gas analysis was done by absorption in a known amount of diluted H_2SO_4 with Congo red as indicator.

3. Results and discussion

The Ru dispersion and particle sizes calculated based on CO chemisorption varied from 1.9 to 6.2 nm (Table 2). In addition to chemisorption, we used TEM to determine the size of >150 Ru particles. Fig. 1 shows the representative micrographs and the size distribution histograms, the corresponding average particle sizes are listed in Table 2. In Fig. 1, irrespective of their sizes, most visible ruthenium particles were round for the catalysts with the different Ru loadings or the different hydrogen treatment temperatures. Increasing the Ru loadings or hydrogen treatment temperatures slightly increased the sizes of Ru particles. On the other hand, the particle size distribution of the samples with air calcination was bi-modal with particle sizes centered at ca. 3.8 nm and 7.2 nm, respectively. The amount of Ru particles with low sizes decreased significantly with the increasing of calcination temperature in air, whereas the quantity of big Ru particles increased gradually. Consequently, the average values of Ru particle sizes increased with the increase of the temperature, and some rectangular-shaped particles also can be observed, which agrees very well with the study of Karim et al. [12]. They found ruthenium particle shape would change from a round one for smaller particles to an elongated one for larger particles if Ru/Al_2O_3 catalysts were calcined in air. However, the possibility that the rectangular-shaped particles were composed of two particles that either coalesced or were situated in a way that their projections looked like one bigger particle cannot be absolutely excluded, more studies are necessary to fully understand this issue. Ru particle sizes estimated from TEM were similar with the values obtained by CO chemisorption for S2RH4 and S4RH4, which is in good agreement with our previous result [13,16,20]. However, the differences in the Ru particle sizes obtained by different methods were notable. The discrepancy was most marked for the samples with air calcination, which may be as a result of the decrease in active sites available for CO chemisorption.

Fig. 2 displays the representative XPS spectra of Ru 3d region for Ru catalysts. All peaks are curve fitted with a fixed spin-orbit splitting of 4.2 eV [21,22] and an area ratio of 3:2 [22]. The data of Ru $3d_{5/2}$ binding energy for S2RH4, S4RH4 and S8RH4 were ca. 280.6 eV, and the value decreased to 280.4 eV for S12RH4. These results are good in accordance with the study of Larichev et al. [23], who reported that the binding energy (Ru $3d_{5/2}$) value for Ru black was 280.2 eV, and the value would slightly increase for Ru supported on Al_2O_3. The Ru $3d_{5/2}$ binding energy for S4RH4 was higher than those of similar Ru catalysts reported in our previous articles [16,20]. On the other hand, the values of Ru $3d_{5/2}$ binding energy for the catalysts calcined in air all were ca. 280.0 eV. Before XPS analysis, all Sm-promoted Ru catalysts were reduced in hydrogen at 450 °C for 6 h, thus it can be assumed that the different treatment conditions before the addition of Sm led to the changes in the value of Ru $3d_{5/2}$ binding energy. The positions of maximums in the Ru $3d_{5/2}$ spectra shifted to higher binding energy for the samples with higher hydrogen treatment temperature (Fig. 2), above result further confirmed

Table 1
Nomenclature of Ru catalysts pretreated under various conditions.

Sample	Pre-treatment conditions [a]	Ru (wt.%)
S4RH4	H_2 reduction, 450 °C	4
S4RH7	H_2 reduction, 700 °C	4
S4RH9	H_2 reduction, 900 °C	4
S4RO2H4	Air calcination, 250 °C; H_2 reduction, 450 °C	4
S4RO3H4	Air calcination, 350 °C; H_2 reduction, 450 °C	4
S4RO4H4	Air calcination, 450 °C; H_2 reduction, 450 °C	4
S2RH4	H_2 reduction, 450 °C	2
S8RH4	H_2 reduction, 450 °C	8
S12RH4	H_2 reduction, 450 °C	12

[a] The treatment conditions of the correspondence non-promoted Ru/Al_2O_3 catalysts.

Table 2
The dispersion and the particle sizes of Ru catalysts.

Samples	D_{CO} (%)	d_{CO} (nm)	D_{TEM} (%) [a]	d_{TEM} (nm)
S2RH4	53.7	1.9	51.9	2.0
S4RH4	48.3	2.2	49.9	2.1
S4RH7	31.9	3.6	44.8	2.4
S4RH9	26.0	4.7	35.4	3.2
S8RH4	29.6	4.0	40.7	2.7
S12RH4	23.6	5.3	31.5	3.7
S4RO2H4	20.4	6.3	28.4	4.2
S4RO3H4	17.2	7.8	23.5	5.3
S4RO4H4	12.2	11.0	16.6	8.1

[a] The dispersion was calculated from the average particle size based on the equation proposed by Borodzinski and Bonarowska [19].