Preparation of High Activity Catalyst for Ammonia Synthesis by Supporting Well-Defined Ru Nanoparticles on γ-Al_2O_3

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Uniform ruthenium metal nanoparticles with an average diameter of 5 nm have been prepared and supported on γ-Al_2O_3 up to 6.3 wt%. The Ru/Al_2O_3 catalyst prepared by this method had unusually high activity for ammonia synthesis. The rate of ammonia formation was at least 12 times higher than the rate of non-promoted Ru/Al_2O_3 catalysts prepared by conventional impregnation methods.

Ruthenium is known to have one of the highest catalytic activity for ammonia synthesis.[1] The conventional ruthenium catalysts are prepared by impregnation of oxide supports either with aqueous solution of $RuCl_3{\cdot}3H_2O$ or with $Ru_3(CO)_{12}$ dissolved in tetrahydrofuran.[2,3] It is well-known that the catalytic activity of a supported metal is strongly related to the morphology of the particle, i.e., size and shape.[4] However, the conventional preparation way of catalysts, consisting of the impregnation, makes it difficult to control the final size and shape of supported metal particles. An alternative way to obtain supported catalysts with well-defined metal particles is the preparation from metal colloid. Recently, it was reported that the reduction of $RuCl_3$ in ethylene glycol was effective to obtain ruthenium metal colloid with uniform size and shape.[5] We tried to support the ruthenium nanoparticles obtained by this polyol method onto alumina, and tested its catalytic activity for ammonia synthesis.

Two grams of γ-Al_2O_3 (Aerosil Japan Co.) were suspended into 50 mL of ethylene glycol solution of $RuCl_3$, and then the temperature of the suspension was increased up to 453 K in an oil bath. The color of the suspension changed from pale yellow to light brown. After one hour of heating, the suspension was cooled down to the room temperature. Most of the ethylene glycol was removed by washing the alumina with 0.3 M $NaNO_3$ aqueous solution. The solid phase was collected by filtration, and dried at room temperature in vacuum. The concentrations of Ru in the suspension before reduction and in the filtrate were determined by Inductively Compled Plasma spectrometer (ICP, Seiko SPS 400). It was observed that 99.5 % of ruthenium in the solution was supported on γ-Al_2O_3, and the experimental results confirmed the high reproducibility of this method. The Ru/Al_2O_3 obtained was calculated to have 6.3 wt% of ruthenium.

The Ru/Al_2O_3 catalyst was observed by transmission electron microscopy (TEM, Hitachi H8100, 200 kV). The TEM image shows the presence of many black and dispersed particles on the support (Figure 1). The X-ray probe micro-analysis proved that the black spots corresponded to ruthenium particles. It can be seen that the ruthenium particles are uniform in size and shape, and they are dispersed well on the surface of γ-Al_2O_3. The size of ruthenium particles and their dispersion were determined by chemisorption of H_2 and CO. Prior to the chemisorption measurements, the Ru/Al_2O_3 samples were heated in vacuum up to 673 K, treated with H_2 at 200 Torr for 2 h, evacuated, and then cooled down to the room temperature. The size of the supported Ru particles obtained by chemisorption of H_2 and CO were 4.8 and 5.4 nm, respectively. These values agree well with the particle size obtained from TEM observation. An aveage size of 5 nm was obtained by counting around 200 particles in TEM micrographs. The size of the Ru nanoparticles ranges from 3 to 6 nm.

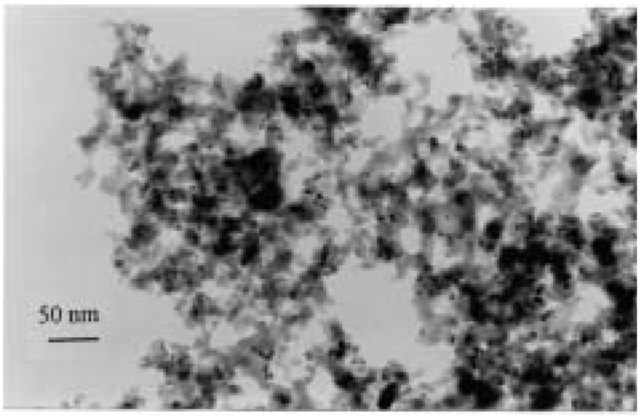

Figure 1. The TEM micrograph of the 6.3 wt% Ru/γ-Al_2O_3 obtained.

The activity of Ru/Al_2O_3 catalyst was measured for ammonia synthesis. The catalytic tests were performed at atmospheric pressure in a stainless steel reactor containing 0.4 g of the Ru/Al_2O_3 (6.3 wt% Ru). Prior to the catalytic tests, the Ru/Al_2O_3 were pelletized, crushed and then sieved. The fraction from 335 to 1000 μm was collected and loaded into the reactor. Before the test, the sample was reduced in H_2 flow at 823 K for 2 h. The catalytic activity tests were carried out at a flow rate of the reaction mixture of 60 cm^3/min STP (45 cm^3/min H_2 and 15 cm^3/min N_2). The rate of ammonia synthesis was measured in the temperature range from 638 to 773 K. The produced ammonia was trapped by a 1×10^{-3} M solution of sulfuric acid, and the rate of ammonia formation was determined from the decrease in the conductivity of the solution.

The catalyst prepared by supporting Ru colloid on γ-Al_2O_3 showed a remarkable high activity for ammonia synthesis. The reaction rates (μmol $g^{-1}h^{-1}$), expressed as a function of temperature, are shown in Figure 2. It can be seen that the rate of ammonia synthesis over 6.3 wt% Ru/Al_2O_3 increased progressively with increasing temperature, reaching a maximum at 723 K. Above this temperature, the rate of the reverse reaction (ammonia decomposition) increased more than the rate of ammonia formation, and therefore the overall rate decreased. The highest reaction rate of 923 μmol $g^{-1}h^{-1}$ was observed at 723 K. The reproducibility at each reaction temperature was within the range of experimental errors (± 25 μmol $g^{-1}h^{-1}$).

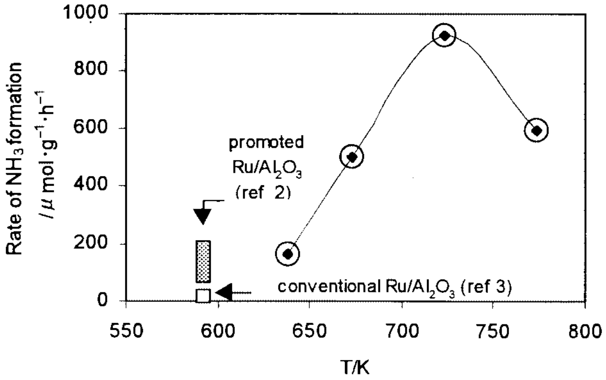

Figure 2. Temperature dependence of the rate of ammonia syntehsis over 6.3 wt% Ru/γ-Al_2O_3.

In the results presented above, there are two points that are worthy of remark. One is the temperature of highest activity for ammonia synthesis. The highest activity of the conventional Ru/Al_2O_3 catalysts was observed at 588 K,[3] whereas the catalyst prepared from Ru colloid had the maximum activity at higher temperature, 723 K. This may be caused by the size of Ru particles. The Ru particles on the Ru/Al_2O_3 catalyst prepared from Ru colloid are significantly larger than the conventional one. The large Ru particles can have low activity.

The other point is that the Ru/Al_2O_3 catalyst prepared from Ru colloid showed unusually high activity although it was not promoted. The highest catalytic activities of promoted and non-promoted Ru/Al_2O_3 catalysts prepared by the conventional methods, using $RuCl_3$ or $Ru_3(CO)_{12}$ as precursors, are shown in Figure 2, together with the activity of the catalyst prepared from the Ru colloid. The reported activity of the non-promoted conventional Ru/Al_2O_3 catalysts is very low, ranging from 10 to 65 μmol $g^{-1}h^{-1}$.

The acidity of alumina has been considered to be the main reason for the low activity of the conventional Ru/Al_2O_3 catalysts for ammonia synthesis. The addition of alkaline (Cs, Rb, K) or rare earth (La, Ce, Sm) elements to the Ru/Al_2O_3 leads significant increase in the catalytic activity.[2,6] Typically, the activity of the promoted Ru/Al_2O_3 catalysts ranges from 130 to 250 μmol $g^{-1}h^{-1}$ (Figure 2). The Ru/Al_2O_3 catalyst prepared from Ru colloid showed significantly higher activity as compared with the promoted catalysts. The activity of the conventionally prepared Ru catalysts is strongly dependent on the conditions of preparation. Slight changes of the preparation variables give significant changes in the catalytic activity.

The differences observed between Ru/Al_2O_3 catalysts prepared by conventional impregnation method and the catalyst obtained via colloid deposition bring up the problem about the role played by the supports in the formation of catalytically active phases. We have reported that the support plays an essential role in the formation of the active phase(s) when the catalysts were prepared by impregnation method.[6,7] The variation of the activities of Ru/Al_2O_3 catalysts prepared by conventional method has been attributed to various factors such as, size distribution of the supported metal particles, support influence on the morphology of the ruthenium crystals, calcination and reduction processes. However, it is possible that the low and unstable activity of Ru/Al_2O_3 catalysts prepared by conventional impregnation method is caused not only by the acidity of the support but also by the contamination of Ru metal by aluminum.

The novel preparation method of supported ruthenium catalysts presented in this letter has the following advantages: (i) it is relatively easy to control the size and shape of metal particles, and (ii) the interaction between the metal particles and the support is minimized, and therefore the metal active sites are not contaminated by support.

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References

1 K. Aika, *Petrotech*, **17**, 127 (1994).
2 S. Murata and K. Aika, *J. Catal.*, **136**, 118 (1992).
3 S. Murata and K. Aika, *J. Catal.*, **136**, 110 (1992).
4 T. S. Armadi, Z. L. Wang, T. C. Green, A. Henglein, and M. A. El-Sayed, *Science*, **272**, (1996).
5 A. Miyazaki, K. Takeshita, K. Aika, and Y. Nakano, *Chem. Lett.*, **361** (1998)
6 I. Balint, A. Miyazaki, and K. Aika, *Chem. Mater.*, **11**, 378 (1999).
7 I. Balint, A. Miyazaki, and K. Aika, *Chem. Mater.*, **13**, 932 (2001).