Barium Hexaaluminate as a Novel Promising Support for Ruthenium-based Ammonia Synthesis Catalysts

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High-surface area (49 m^2/g) barium hexaaluminate (BHA) has been successfully synthesized by reverse microemulsion method. The BHA supported Ru catalyst showed significantly higher activity and structural stability than Ba-promoted Ru catalyst supported on MgO under ammonia synthesis conditions.

Alkali- or alkaline earth-promoted Ru catalysts have been extensively studied as second generation catalysts for ammonia synthesis because of the higher activity than that of the multi-promoted iron catalysts.[1–7] The activity of the Ru catalysts is strongly related to the support properties as well as to the nature of promoters.[3,6] According to the accumulated knowledge, the ideal support materials for Ru-based catalysts should meet the following three requirements: low acidity (to enhance the electronic effects of the promoter), high surface area (to optimise Ru dispersion), and morphological stability under the reaction condition. The most investigated support materials for Ru-based catalysts are carbon,[1] MgO,[4,5] Al_2O_3,[1,2,8] zeolite,[9] CeO_2,[10] $MgAl_2O_4$,[11] and BN.[7] The problems with respect to the support encountered in the practical use are methanation for carbon,[12,13] sintering for MgO,[14] high acidity for Al_2O_3 and zeolites. Therefore, the development of better support materials is still of great practical interest. The present work shows for the first time that BHA is an ideal stable support material for ruthenium with remarkably high promoting effect.

High surface area BHA was prepared with the combined microemulsion and hydrothermal techniques.[15] A stable (transparent) microemulsion was prepared by mixing 70 mL of distilled water, 30 mL of polyethylene glycol 200, 190 mL of isooctane, and 360 mL of n-propanol. Appropriate amounts of barium and aluminium isopropoxides ($Ba/Al = 1/12$ molar ratio) were dissolved in 20 mL of ethyl acetoacetate and 20 mL of isooctane at 353 K. The dissolved aluminium and barium precursors were added to the microemulsion to allow their hydrolysis in ambient conditions, under stirring, for around 20 h. Subsequently, the hydrolyzed mixture was hydrothermally treated in an autoclave at 423 K for 20 h. The resulting nanocomposite was recovered via solvent removal, by using a rotary evaporator. The surfactant decomposition was carried out at 773 K for 2 h. Finally the resultant material was calcined at 1373 K for 24 h to obtain the high-surface area (49 m^2/g) BHA support.

The 8 wt % Ru catalyst was prepared by impregnating the BHA support with the THF (tetrahydrofuran) solution of $Ru_3(CO)_{12}$. After THF removal by evaporation, the material was treated under vacuum ($\approx 10^{-4}$ Pa) at 673 K for 3 h to decompose the $Ru_3(CO)_{12}$ precursor. The obtained catalysts will be denominated as Ru/BHA (fresh). The Ba to Ru molar ratio in the Ru/BHA catalyst was 1.6. The ammonia synthesis activity of Ru/BHA was compared with that of other impregnated supports having the same Ru loading (8 wt %). Thus, Ru was supported on commercial γ-Al_2O_3 (Aerosil Japan) and MgO (Soekawa Chemicals) by using the same impregnation and calcination procedures. These catalysts will be called as Ru/γ-Al_2O_3 and Ru/MgO, respectively. Portions of Ru/γ-Al_2O_3 and Ru/MgO catalysts were further impregnated with $Ba(NO_3)_2$ and then dried at 383 K. The Ba to Ru molar ratio for these catalysts was also 1.6. The aim was to observe the Ba-promoting effect on their catalytic activity.

Prior to the activity tests, all the catalysts were pre-treated in H_2 at 473 K for 1 h and then at 773 K for 3 h. The ammonia synthesis rates at 588, 623, and 653 K under 0.1 and 1.1 MPa were measured by using a fixed-bed plug-flow tubular reactor loaded with 0.20 g of catalyst as a stable activity was obtained after 30 min on stream for all the examined catalysts. The total flow rate of the reactant mixture ($H_2/N_2 = 3/1$) was 60 mL (STP)/min.

The acidic property of the studied supports was characterized by NH_3-TPD as shown in Figure 1. Compared to the γ-Al_2O_3 support that chemisorbed NH_3 at a level of 2.64 μmol/m^2, the BHA support chemisorbed only 0.11 μmol-NH_3/m^2, which was quarter of the value for MgO (0.54 μmol-NH_3/m^2). These results reveal that the BHA support has quite small number of acidic sites.

The activity data presented in Table 1 clearly show that Ru/BHA is the most active catalyst both under 0.1 and 1.1 MPa. At

Table 1. Ammonia synthesis rate over Ru/BHA, Ru/γ-Al_2O_3, BaO–Ru/γ-Al_2O_3, Ru/MgO, and BaO–Ru/MgO catalysts. In addition, the BET specific surface areas of the aforementioned catalyst are listed in the same table

Catalyst	[a]SBET, m^2/g	NH_3 synthesis rate at 0.1 MPa, μmol/g_{cat}/h			NH_3 synthesis rate at 1.1 MPa, μmol/g_{cat}/h		
		588 K	623 K	653 K	588 K	623 K	653 K
Ru/BHA	47 (45)	827	2267	3497	1202	3141	5426
Ru/γ-Al_2O_3	80 (–)	<100	<100	<100	<100	<100	<100
BaO–Ru/γ-Al_2O_3	64 (–)	446	1097	1897	328	895	1700
Ru/MgO	46 (24)	429	1109	2017	340	928	1920
BaO–Ru/MgO	57 (15)	293	735	1197	483	1326	2567

a) BET surface area for the fresh and spent (in parenthesis) catalysts.

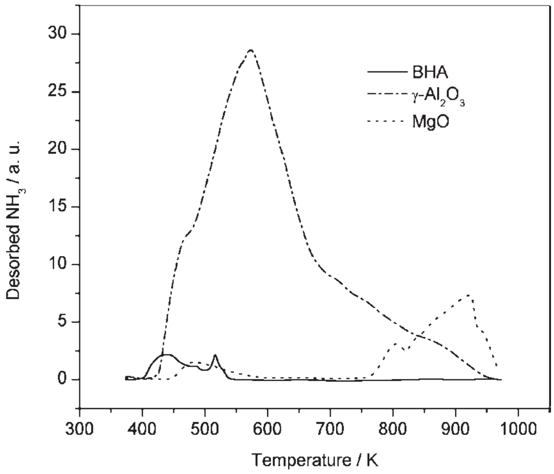

Figure 1. NH_3-TPD profiles of BHA, γ-Al_2O_3 and MgO support.

each investigated reaction temperature, the NH_3 synthesis rate at 0.1 MPa over Ru/BHA catalyst is almost twice as compared to BaO–Ru/γ-Al_2O_3 or Ru/MgO catalysts. So far, MgO has been known as the best oxide support for Ru-based catalysts for ammonia synthesis.[16] The ammonia synthesis rates over Ru/MgO catalyst (Table 1) are comparable with those reported for 5 wt % Ru/MgO.[14] The superiority of Ru/BHA catalyst is even more remarkable at higher reaction pressures (see Table 1). The Ru/BHA is almost three times more active under 1.1 MPa than the best of the other investigated catalytic systems. Typically, the ammonia synthesis rate over the metal oxide-supported Ru catalysts has a decreasing trend with increasing total reaction pressure. The stronger adsorption of H_2 compared to N_2 on the catalytic active sites is the possible reason of the decrease in ammonia formation rate. As can be observed in Table 1, this was the case with all the investigated catalysts except Ru/BHA and BaO–Ru/MgO. The Ru/BHA catalyst especially showed remarkably high activity under high-pressure conditions (Table 1). In spite of its relatively high surface area ($80\,m^2/g$), the Ru/γ-Al_2O_3 catalyst exhibited very low activity (<100 $\mu mol/g_{cat}/h$) regardless the reaction conditions (temperature and pressure). This can be explained by the detrimental effect of the support acidity (Figure 1) on Ru activity.[8] The Ba addition to Ru/γ-Al_2O_3 catalyst, although having significant beneficial effects, was not able to enhance the catalytic activity to a level comparable to Ru/BHA.

The morphological stability of the catalyst in reaction conditions should be also taken into consideration to explain the high catalytic activity and stability of the Ru/BHA catalyst. It is established that the anisotropic growth of the BHA increases the stability against sintering. The surface area of the Ru/BHA catalyst underwent only to a slight shrinking (from 47 to $45\,m^2/g$) during the activity test as compared to MgO-supported catalysts (from 46 to $24\,m^2/g$ for Ru/MgO and from 57 to 15 for BaO–Ru/MgO). The XRD results confirmed also that the spent Ru/BHA catalyst preserved not only the surface area but its crystalline structure too.

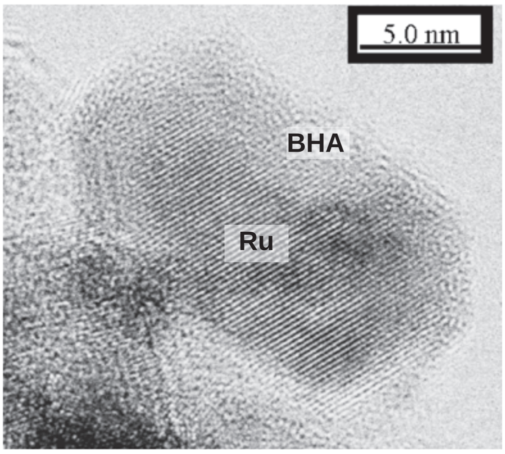

Figure 2. TEM evidence for coverage of Ru by BHA support.

The high-resolution TEM images (Figure 2) showed that the BHA-supported Ru nanoparticles are covered to some extent by barium promoter (probably in the form of BaO). This leads to the idea that the strong metal–promoter interaction has a key role in exhibiting high activity. From TEM and H_2 chemisorption results it comes out that around 34% of the exposed Ru metal surface was covered with barium precursor. The catalytic activities of Ru metal, metal–promoter boundary area and barium-covered Ru should be different. It can be imagined that the strongest promotion effect (probably via electron donation from the promoter to ruthenium) is in the Ru–barium oxide boundary area. This effect should be smaller on the exposed surface of Ru metal. On the other hand, the catalytic activity of the half-way covered (sinking) Ru particles will be high. The pronounced activity of the Ru/BHA may be temporarily explained like this. Further investigations are in progress to understand the complex interaction between alkaline earth element precursor(s) and supported Ru particles.

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