RESEARCH NOTE

Graphitic Nanofilaments as Novel Support of Ru–Ba Catalysts for Ammonia Synthesis

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A novel graphitic-nanofilament- (GNF-) supported Ru–Ba catalyst is prepared and used in ammonia synthesis reaction. The Ru–Ba/GNFs catalyst shows remarkably high activity and stability for ammonia synthesis, which can be attributed to high purity and graphitization of GNFs with unique structure. TEM micrographs of the Ru–Ba/GNFs catalysts show that Ru metal particles uniformly disperse on the outer wall of GNFs, and the particles become bigger than that before ammonia synthesis reaction after 50 h of operation at 500°C and 7.0 MPa, probably due to the Ru crystals covered by promoter and support materials and/or sintering of Ru crystals.   © 2002 Elsevier Science (USA)

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1. INTRODUCTION

Catalytic synthesis of ammonia is one of the most important industrial processes in which a promoted iron catalyst is widely used at high temperatures and high pressures (1). The process under such reaction conditions is energy-intensive as well as capital-intensive although some advances have been made. Therefore, ammonia synthesis process with low energy consumption has been a longstanding target in chemical industry. One of the keys to reaching this target is to develop catalysts with high activity under milder conditions. The mechanism of the reaction on the promoted iron catalysts has been studied extensively, and a dissociative mechanism where dinitrogen and dihydrogen are broken up into adsorbed nitrogen and hydrogen with successive recombination steps is accepted (2). Ru-based catalysts for ammonia synthesis have also been studied in the early investigation carried out by Mittasch (3), but superior activity was not found. Ru-based catalysts were found to be the most active catalyst for ammonia synthesis by Aika *et al.* (4). Since then, a number of ruthenium catalysts

with various supports and promoters have been studied in both fundamental understanding and industrial application by some groups, including Aika's group (5, 6) in Japan, Tennison's group (7) at British Petroleum, Muhler's group (8, 9) in Germany, Kowalczyk's group (10, 11) in Poland, Forni's group (12) in Italy, groups (13, 14) in Denmark, and others (15–20). Finally, the promoted ruthenium supported on graphite-containing carbon with high-surface-area catalyst was introduced to produce ammonia from dinitrogen and dihydrogen on an industrial scale (21).

A number of studies have shown that carbon-supported catalysts are more active than the oxide-supported catalysts. High-temperature treatment of carbon support leads to graphitization, which was considered to be responsible for the high activity of carbon-supported Ru catalysts (10–12). At the same time, high-temperature treatment can also decrease the methanation reaction even at above 700°C and 100 bar (12), which is more severe than the conventional reaction conditions on Ru-based catalysts. Recently, Chen *et al.* have tested the activity of K–Ru supported on multiwalled nanotubes for ammonia synthesis and found the catalyst is more active than other supports (20). In this paper, graphitic nanofilaments (GNFs) with high surface area are used as support of Ru–Ba catalysts for ammonia synthesis. It is found that the Ru–Ba/GNF catalyst is more active than the activated-carbon- (AC-) supported Ru–Ba catalyst. Furthermore, the Ru–Ba/GNF catalyst does not need high Ba/Ru atomic ratio, which is associated with the AC-supported catalysts.

2. EXPERIMENTAL

GNFs were synthesized by CH_4 decomposition over a nickel-based catalyst, then the catalyst was removed by dissolution typically in aqueous solution of HNO_3. The Ru–Ba/GNF and Ru–Ba/AC catalysts were prepared by using a two-step impregnation method (18). Namely, The Ru precursor salt, $RuCl_3$, was dissolved into acetone and the GNFs

were added to form slurry. The sample was dried overnight at 110°C, reduced at 400°C (until no chlorine ions were detected with the solution of $AgNO_3$), and passivated in 1% O_2 for 2 h at room temperature. The as-prepared sample was impregnated with the solution of $Ba(NO_3)_2$, then dried overnight at 110°C. Ru–Ba/AC catalysts were prepared with the same methods.

Catalytic reactions of ammonia synthesis were carried out in a fixed-bed stainless-steel microreactor with a stoichiometric H_2 and N_2 mixture ($H_2/N_2 = 3$) flow at 3.0 MPa. The purity of H_2 or N_2 gases is over 99.99%, and the mixture gases were further purified before the reaction by self-designed guard containers packed with palladium catalyst and molecular sieves. The catalyst in the reactor was activated in the stream of $N_2 + 3H_2$ according to the following temperature program: heating to 450°C in 100 min, standing at 450°C for 240 min, and then cooling to the reaction temperature in 30 min. The amount of ammonia in the effluent was determined by a chemical titration method. A well-dispersion 4.0 wt% Ru/AC catalyst was used as the reference catalyst.

Transmission electron microscopy (TEM) studies were carried out using a JEOL JEM-2000EX electron microscope with 100 kV.

3. RESULTS AND DISCUSSION

TEM micrographs of the GNF material are shown in Fig. 1. It can be seen that the GNF sample does not contain the residues such as Ni catalyst and its support, and few carbonaceous impurities agglomerate. The outer diameters of the GNFs were in the range of 20–60 nm, and inner diame-

ters were in the range of 5–10 nm. The BET surface area of the GNFs, determined by nitrogen adsorption at 77 K, was about 140 m^2/g.

Figure 2 shows the ammonia synthesis activity of the aforementioned catalysts changing with Ba/Ru atomic ratio. The improved activity of ammonia synthesis on Ru–Ba/GNF relative to that on Ru–Ba/AC is evident. The ammonia synthesis activity of the Ru–Ba/GNF catalyst increases when the Ba/Ru atomic ratio is below 0.25, but decreases with further increasing of the amount of promoter, while that of the Ru–Ba/AC catalyst increases gradually in the range of the Ba/Ru atomic ratio studied. This behavior may be attributed to various reasons, including (a) decreased impurity in GNF support, (b) increased electronic conductance of GNFs when compared to the activated carbon, and (c) the attainment of the sites with high activity because of specific interaction between Ru and GNFs.

It is suggested that the surface impurities from carbon materials such as S, N, O, and Cl can suppress the catalytic activity and consume part of promoter (18, 22). Element analysis shows that AC contains some impurities such as S (0.15%), N (0.04%), O (7.75%), and Cl (0.10%), while GNFs only contain traces of oxygen (1.22%) and hydrogen (0.02%) besides carbon (98.76%). The highest rate of ammonia synthesis is reached when the Ba/Ru atomic ratio is about 0.25, which is much lower than the optimum Ba/Ru on graphite support. This indicates that the nature of GNFs, such as structural and electronic properties, plays an important role on the catalytic activity for ammonia synthesis.

For the ammonia synthesis on the Ru catalysts, it has been shown that the B_5-type sites dominate the activity of the catalyst (13, 14). In the case of the Ru–Ba/GNF catalyst, the
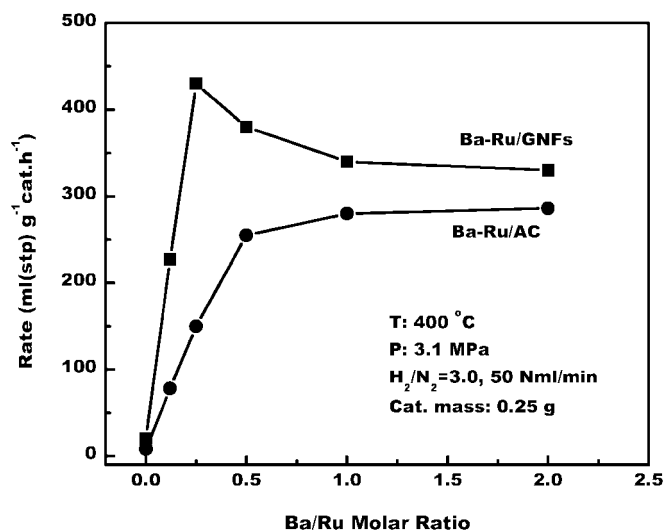

FIG. 1. TEM micrographs of the GNF samples.

FIG. 2. Effects of Ba/Ru atomic ratio on ammonia synthesis activity of the Ru–Ba/AC and Ru–Ba/GNF catalysts.
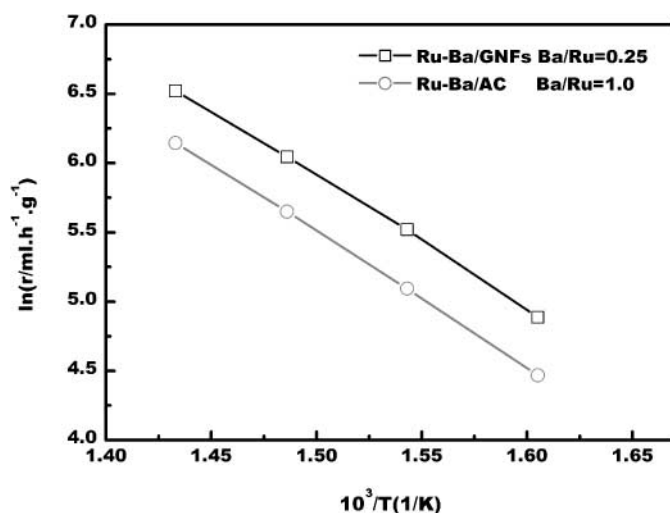

FIG. 3. Activity of Ru–Ba/GNF catalyst with the Ba/Ru = 0.25 and Ru–Ba/AC catalyst with Ba/Ru = 1.0 at temperatures from 350 to 420°C. The inlet gas does not contain ammonia and the flow rate is varied to obtain an exit concentration of ammonia of 2.0%.

B_5-type sites are formed more easily than in the Ru–Ba/AC catalyst as a result of the specific interaction between metal and support. However, the nature of this interaction is unclear. In the case of cinnamaldehyde hydrogenation on the Ru supported on carbon nanotubes catalyst, a specific interaction between metal and support was suggested to explain the high selectivity and high conversion (23). Recently, the GNF-supported platinum catalysts showed improved oxidation activity for methanol when compared to Vulcan carbon. The improvement is believed to be due to metal particles adopting specific crystallographic orientations when dispersed on GNFs (24). Therefore, it is believable that the support, where the crystallographic orientations of Ru are determined, may play an important role in the catalytic activity of ammonia synthesis.

Figure 3 compares the ammonia synthesis activities of the Ru–Ba/GNF catalyst with Ba/Ru = 0.25 and the Ru–Ba/AC catalyst with Ba/Ru = 1.0 at temperatures from 350 to 420°C. The activity of the Ru–Ba/GNF catalyst is remarkably higher than that of the Ru–Ba/AC catalysts under the same conditions. The activation energy of ammonia synthesis on the Ru–Ba/GNF catalyst at constant flow is about 84 kJ/mol, which is close to that reported in the literature (4–6, 8, 9). The pressure dependence of the ammonia synthesis activity of Ru–Ba/GNF catalysts is shown in Fig. 4. The reaction kinetics of the Ru–Ba/GNF catalysts are similar to those reported for Ba-promoted ruthenium catalysts supported on other carbon materials and BN (11, 18, 25). The stability of the Ru–Ba/GNF catalyst is also studied under continuous reaction for 50 h at 500°C and 7.0 MPa with a mixture of $3H_2 + N_2$. During this process, the ammonia concentration in the exit reaches the equilibration value. No obvious deactivation is observed un-

der those conditions, while the Ru–Ba/AC catalyst shows severe deactivation under similar conditions. It is evident that the degree of GNF graphitization is responsible for the catalyst stability. The graphitization of GNFs is higher than the activated carbon from XRD. The d(002) diffraction peak of graphite was observed in the GNF sample, while no obvious diffraction peak of graphite (002) was observed for the AC samples. At the same time, GNFs with high electrical conductivity (26) also offer possibility for electron transfer from promoters to Ru metal since most promoter and Ru particles are not in contact with each other.
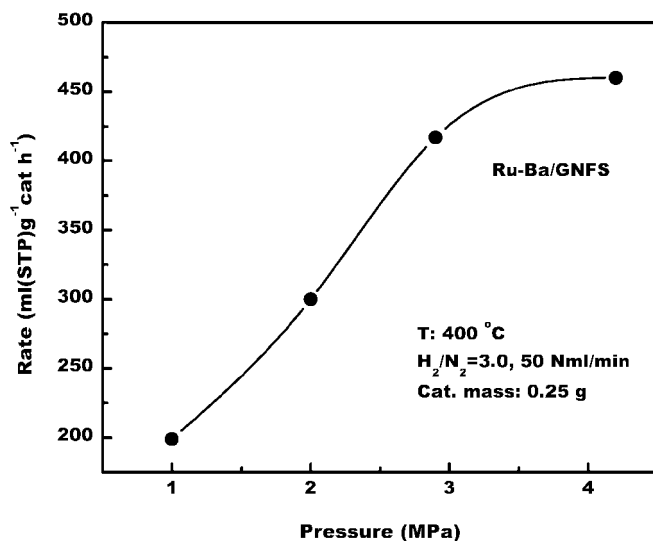

FIG. 4. Pressure dependence of the ammonia synthesis activity of Ru–Ba/GNF catalysts at 400°C.
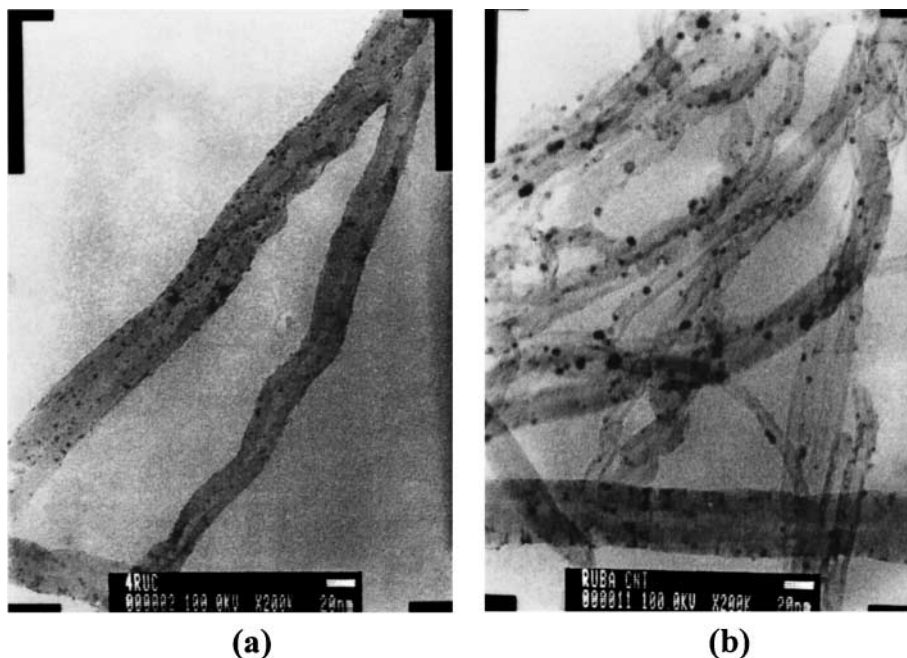
FIG. 5. Representative transmission electron micrographs of (a) the Ru/GNF sample and (b) the spent Ru–Ba/GNF ammonia synthesis catalyst.

Representative transmission electron micrographs of the Ru/GNF sample and the Ru–Ba/GNF catalyst after ammonia synthesis reaction are shown in Fig. 5. In the case of Ru/GNFs, high dispersion of Ru metal particles with a narrow size distribution of 2–4 nm were seen as shown in Fig. 5a, and Ru particles mainly deposited in the outer surface of the GNFs; the result is similar to that of Pt/GNFs (24, 27). The Ru crystals dispersed on the GNFs were relatively thin, with a highly crystalline faceted structure, while Ru particles supported on the activated carbon adopted a globular morphology. This difference may be due to the interaction between Ru and support. It is the interaction that mainly results to high activity for ammonia synthesis on the Ru–Ba/GNF catalyst. Fig. 5b is a representative *ex situ* transmission electron micrograph of a Ru–Ba/GNF catalyst after 50 h of operation at 500°C and 7.0 MPa. It can be seen that Ru crystals and Ba compounds are about 4–7 nm and localized primarily in the outer surface of the GNFs. It should be noted that the particles become bigger after reaction, probably because the Ru crystals are completely covered by promoter or support materials, as shown by Hansen *et al.* (28), and/or sintered.

4. CONCLUSION

The Ru–Ba/GNF catalyst shows remarkably high activities for ammonia synthesis, which are higher than that on the Ru–Ba/AC catalyst. The high purity, high graphitization, and unique structure of GNFs are likely to be responsible for the high activity for ammonia synthesis on the Ru–

Ba/GNF catalyst. The catalyst particles become bigger after reaction, probably because the Ru crystals are completely covered by promoter or support materials and/or sintered. Therefore, rational design of catalysts and experiments can lead to a high active catalyst based on GNFs as support for ammonia synthesis.

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