

PRIORITY COMMUNICATION

Boron Nitride: A Novel Support for Ruthenium-Based Ammonia Synthesis Catalysts

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A barium-promoted boron nitride-supported ruthenium catalyst is shown to exhibit unprecedented activity and stability in catalytic ammonia synthesis. The activity is measured at temperatures between 360 and 400°C and at pressures of 50 to 100 bar. The stability of the Ba–Ru/BN catalyst is assessed from a test run conducted at 100 bar and 550°C for 3500 h causing no detectable deactivation.

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INTRODUCTION

Catalytic ammonia synthesis continues to play a central role in sustaining the growing population of the world through provision of nitrogen-containing fertilizers. Alternatives to the classic Haber–Bosch process do not seem to be economically feasible in the near future. It is therefore necessary to continuously improve existing ammonia synthesis technology. Recently, a promoted ruthenium catalyst supported on a graphitized carbon (1, 2) was introduced for industrial operation (3) and was shown to be significantly more active than the conventional multipromoted iron catalyst at moderate pressures. This has aroused new interest in ruthenium-based ammonia synthesis catalysts and in alternative noniron catalysts (4, 5). Previously, promoted ruthenium catalysts supported on oxide supports such as MgO (6–8) and MgAl₂O₄ (9) were found to be active ammonia synthesis catalysts. However, Kowalczyk and co-workers (10, 11) were able to prepare significantly more active ammonia synthesis catalysts using graphitized carbon supports. It is not yet clear why graphite-supported catalysts are more active than oxide-supported catalysts, but several studies have shown that the activity of ruthenium catalysts is highly dependent on the choice of support material (12, 13).

Although graphite-supported catalysts have been shown to be very active synthesis catalysts, it is a significant drawback that they are prone to methanation under industrial ammonia synthesis conditions. Consequently, such catalysts have relatively short lifetimes and cannot be operated at temperatures above 450°C without severe deactivation. It would clearly be desirable to identify a support material that both allows preparation of highly active ammonia synthesis catalysts and has thermodynamic stability under relevant operating conditions. Recently, we suggested that the very different activities observed for promoted ruthenium catalysts on various supports could be explained by the influence of the support on the morphology of the ruthenium crystals (13). This hypothesis inspired the search for support materials with a structure similar to that of graphite. Boron nitride is known to have a layered structure similar to that of graphite except for a different stacking order of the individual layers. As BN can be shown thermodynamically stable under all possible operating conditions of the ammonia synthesis loop, it appears to be an interesting alternative to graphite as a support material (14).

METHODS

Boron nitride is supplied by H. C. Starck GmbH & Company. A boron nitride-supported ruthenium catalyst is prepared by impregnation of a shaped carrier of hexagonal boron nitride (crystal size $D(002) = 7$ nm, surface area 81 m²/g) with an aqueous solution of ruthenium nitroso nitrate to obtain ca. 4.5 wt% Ru/BN. Reduction is conducted in pure dihydrogen at 400°C and atmospheric pressure. After passivation by treatment with 1000 ppm dioxygen in dinitrogen at room temperature for 24 h, the catalyst is promoted with barium by impregnation with an aqueous solution of barium hydroxide to obtain a barium content of ca. 5.6%. The particle density of the Ba–Ru/BN catalyst (4.5 × 4.5-mm cylinders obtained by tableting BN powder) is 1.4 g/cm³. Prior to testing, the shaped particles are

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crushed and sieved to a size of 0.3–0.5 mm. The unpromoted and barium-promoted Ru/BN catalysts are tested in an integral plug-flow reactor operated isothermally. Approximately 2 g of catalyst is loaded in the setup previously described (15). The inlet gas contains 4.5% ammonia in a 3:1 dihydrogen:dinitrogen and the flow rate is varied to obtain an exit concentration of ammonia of 12.0%. The activity is recorded at temperatures from 360 to 400°C and pressures from 50 to 100 bar and calculated from the amount of catalyst loaded. The catalyst is activated by heating to 550°C in synthesis gas with an ammonia inlet concentration of 4.5%. The stability of the catalyst is evaluated by increasing the temperature to 550°C for 3500 h. During this treatment, the ammonia exit concentration decreases to the equilibrium value. After 1000 and 2000 h, the temperature is lowered to 400°C to measure the activity and then increased to 550°C again. After 3500 h, the catalyst is passivated by treatment with 1000 ppm dioxygen in dinitrogen at room temperature for 24 h. The catalyst then is exposed to air for 24 h, reloaded into the reactor, and activated as described above.

A spent Ba–Ru/BN catalyst (1000 h) is characterized by *ex situ* transmission electron microscopy using a Philips CM200 FEG instrument with an operating voltage of 200 kV. Chemical analysis of the spent catalyst gives 4.1 wt% Ru, 5.5 wt% Ba.

RESULTS AND DISCUSSION

In Fig. 1 is shown the ammonia synthesis activity of the Ba–Ru/BN catalyst at various temperatures. The activity of this catalyst is significantly higher than those reported recently for promoted Ru catalysts supported on graphitic carbon. This increased activity is even more pronounced when the lower ruthenium concentration on the boron

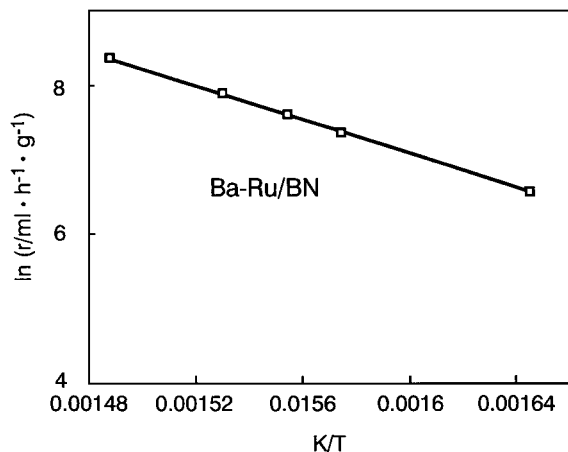


FIG. 1. Activity of Ba–Ru/BN catalyst in 3:1 mixture of H₂:N₂ at temperatures from 360 to 400°C and 100 bar, with ammonia inlet and outlet concentrations of 4.5 and 12.0%, respectively.

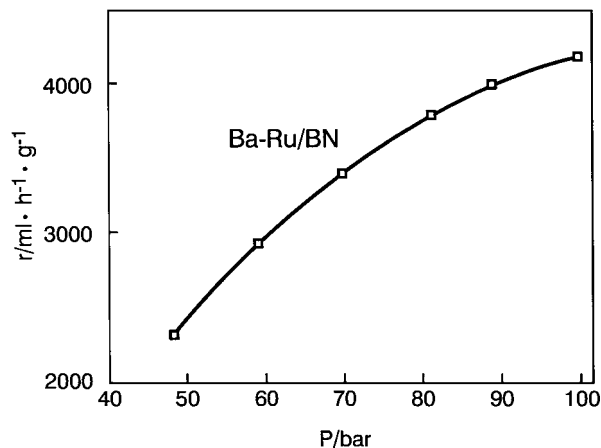


FIG. 2. Pressure dependence for ammonia synthesis over Ba–Ru/BN at 400°C in 3:1 mixture of H₂:N₂, with ammonia inlet and outlet concentrations of 4.5 and 12.0%, respectively.

nitride support is taken into account. Kowalczyk *et al.* (10, 11) used a Ru concentration of ca. 9 wt% and Forni *et al.* (16) used ca. 14 wt% Ru. The activation energy (at constant conversion) of the Ba–Ru/BN catalyst is 95 kJ/mol, which is identical to what was reported for Ba–Ru/C by Kowalczyk *et al.* (11). It has been shown that carbon-supported ruthenium catalysts are prone to methanation at high pressures of dihydrogen (10, 16). The stability of the carbon support is improved by promotion of Ru/C catalysts with barium. However, methane formation cannot be completely avoided and is found to be rapid at temperatures above 450°C. Consequently, ruthenium-based ammonia synthesis catalysts supported on carbon have significantly shorter lifetimes than the conventional magnetite catalyst. This is a fact even if the Ru catalysts are operated at lower temperature and pressure than the magnetite catalysts. We have studied the stability of our Ba–Ru/BN catalyst by continuous operation at 550°C and 100 bar pressure in a 3:1 mixture of dihydrogen and dinitrogen. Under these conditions, the catalysts equilibrate the synthesis gas. The activity is measured at 400°C after 1000, 2000, and 3500 h of operation and there is no sign of deactivation. Under similar conditions, carbon- or spinel-supported Ru catalysts show severe deactivation (7). The stable activity of the Ba–Ru/BN catalysts is undoubtedly related to the thermodynamic stability of BN under the test conditions.

The pressure dependence of the ammonia synthesis activity of the Ba–Ru/BN catalysts is shown in Fig. 2. Generally, the reaction kinetics of the Ba–Ru/BN catalysts are similar to those reported for Ba-promoted ruthenium catalysts supported on graphite (11). The structure of the boron nitride support is closely related to that of graphite. The behavior of Ba–Ru/BN and Ba–Ru/C catalysts, which is similar both in terms of kinetics and in terms of optimal Ba/Ru ratio, provides support for the proposition (13) that

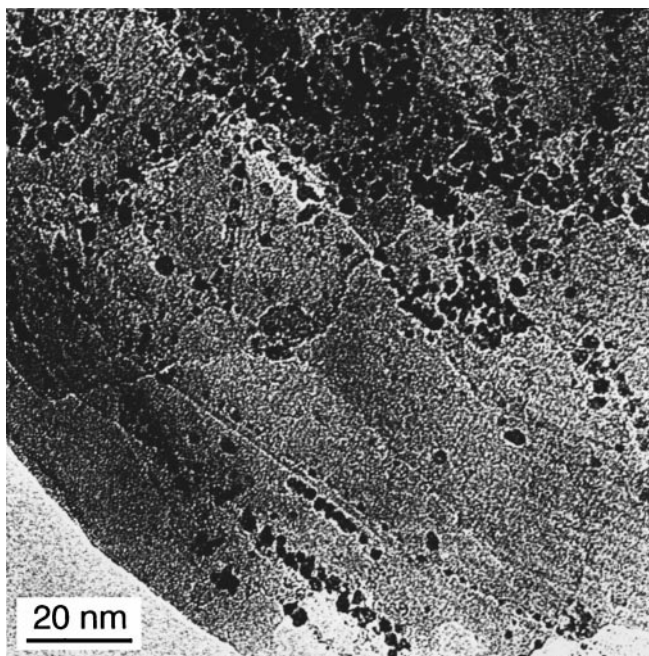


FIG. 3. Transmission electron micrograph of spent Ru/BN ammonia synthesis catalyst.

ammonia synthesis kinetics is determined by the ruthenium morphology, which is largely controlled by the choice of support material.

Figure 3 is a representative *ex situ* transmission electron micrograph of a Ba-Ru/BN catalyst after 1000 h of operation at 550°C. It is seen that the Ru crystals are about 2.0–2.5 nm and are localized primarily along steps in the basal planes of the boron nitride support. Similar structures have been observed for ruthenium crystals supported on graphite (18).

After 3500 h of testing, the catalyst was passivated as described under Methods. After reactivation in the test set up, the catalysts regained their original activity. This shows that boron nitride is a significantly improved support

relative to carbon and other supports used for promoted ruthenium catalysts in ammonia synthesis. Boron nitride can be prepared with surface areas even higher than those used here and could also be an interesting support for other catalytic materials.

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