Polish J. Chem., **77**, 923–927 (2003) **COMMUNICATION**

Ammonia Synthesis over the Barium-Promoted Ruthenium Catalyst Supported on Boron Nitride. Effect of the Catalyst Activation

by D. Szmigiel, W. Raróg-Pilecka, E. Maciejewska and Z. Kowalczyk*

Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

(Received February 3rd, 2003)

Ammonia synthesis – one of the most important industrial processes - is performed mainly over fused iron catalysts. Unfortunately, such catalysts require high-pressure conditions for their optimal efficiency, thus, resulting in a high energy consumption. In order to reduce the pressure in an ammonia loop, a completely new catalytic system must be applied. Carbon-based ruthenium, promoted additionally with barium or caesium [1–9], was found to be a prospective catalyst for the low-pressure, low-temperature ammonia synthesis. Although the Ru/C catalysts are known to be rather thermally stable under ammonia synthesis conditions [3,9], there is always a risk of carbon substrate methanation. Therefore, non-carbon materials were also tested as carriers for ruthenium, especially those of a well developed texture [10–22]. According to the recent studies of Jacobsen *et al.* [19–21], large surface area boron nitride (BN) is an excellent support for Ru, even better than the carbon one. The Ba-promoted Ru/BN catalysts exhibit high activities in NH_3 synthesis [19,21] and they are not hydrogenation prone when operating [21].

This paper shows that, in contrast to other supported ruthenium catalysts, *e.g.* Ba-Ru/MgO or Ba-Ru/C, the Ba-Ru/BN catalysts are stabilized very slowly, *i.e.* the NH_3 synthesis rate increases systematically *vs*. time on $H_2 + N_2$ stream, even if the activation is performed at high temperature of 550–600°C. The stabilization of the Ba-Ru/BN system is significantly faster and the NH_3 synthesis rate is enhanced considerably, when activation is performed in an ammonia rich H_2, N_2 mixture under high pressure, thus, indicating the presence of NH_3 in the reducing stream to be essential for the properties of the BN support used.

Boron nitride, a powder of 194 m^2/g BET surface area and of 4.5% B_2O_3 was supplied by H.C. Starck GmbH & Company. The Ru/BN catalyst (9 wt.% Ru) was prepared by the incipient wetness technique, using ruthenium carbonyl ($Ru_3(CO)_{12}$ – the Ru precursor) dissolved in THF. After drying in air, the $Ru_3(CO)_{12}$/BN sample was promoted with barium by impregnation with aqueous solutions of barium nitrate or barium nitrite to achieve the Ba:Ru = 1:1 molar ratio. Finally, the promoted catalysts

---

*Author for correspondence.

were pressed into tablets, crushed and sieved into the proper grain fraction of 0.2–0.63 mm. The measurements of NH_3 synthesis were carried out in a flow reactor fed with a $H_2:N_2 = 3:1$ mixture. The kinetic tests were performed under 63 bar pressure, mainly at 520°C. The detailed description of the setup was presented elsewhere [23]. Typically, small catalyst samples of 300 mg (Ru + BN) were used in the activity studies. The ammonia content in the outlet gas stream was measured at a constant flow rate of 63 dm^3 [STP]/h. Consequently, the integral rate of NH_3 synthesis could be determined. The catalysts activation was performed directly in the NH_3 synthesis reactor. Two different activation procedures (A and B) were applied. The A procedure consisted of several isothermal steps performed at atmospheric pressure with an ammonia free gas mixture ($H_2/N_2 = 3:1$): (step 1) heating of the sample to 520°C, maintaining at 520°C for 24 h; (step 2) further stabilization at 520°C for 168 h; (step 3) heating to 550℃, maintaining for 48 h; (step 4) heating to 600℃, maintaining for 24 h. After each isothermal step, the syngas was compressed and the kinetic measurements were started. The B activation was carried out at constant temperature with an ammonia containing $H_2 + N_2$ stream. More specifically, the sample was heated to 550 ℃ in a flowing 10% NH_3 + $H_2:N_2 = 3:1$ mixture at 90 bar, followed by holding under such conditions for 5 h, whereupon the activation was continued under atmospheric pressure (550℃, 0.4% $NH_3 + H_2:N_2 = 3:1$) for further 16 h. Then, the reaction rate was measured at 63 bar. Subsequently, the sequence: activation - kinetic test was repeated.

The most relevant results of the NH_3 synthesis measurements are presented in Figs. 1 and 2. The data collected in Fig. 1 correspond to the activation procedure A and those in Fig. 2 – to procedure B. As is seen in Fig. 1, the activity of the catalysts,

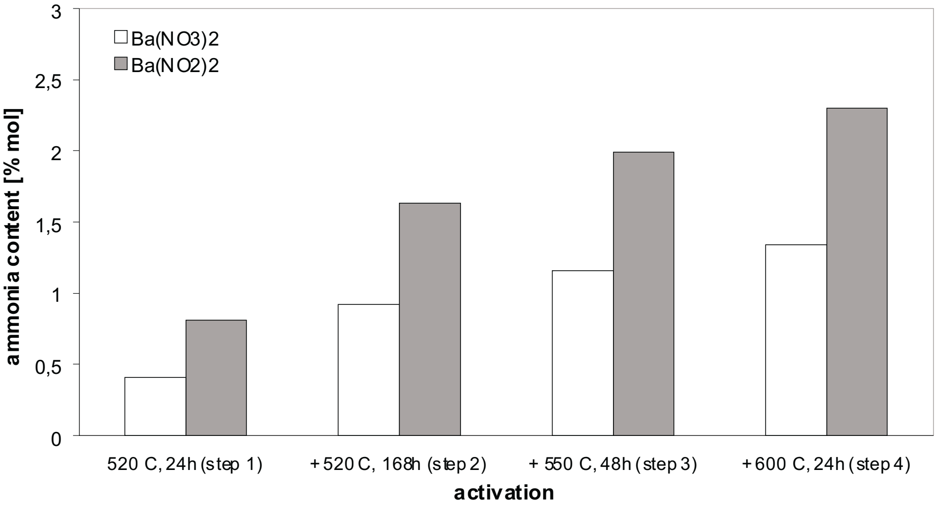

Figure 1. Ammonia concentration in the outlet gas after subsequent activation steps performed in an ammonia free $H_2:N_2 = 3:1$ stream at 1 bar (procedure A). Activity was measured at 520°C and 63 bar.

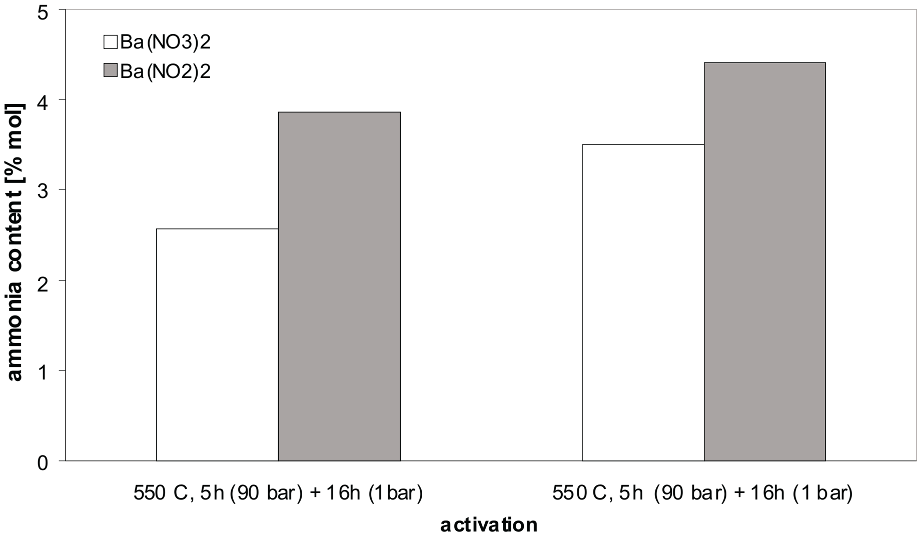

Figure 2. Ammonia concentration in the outlet gas after subsequent activation steps performed in an ammonia rich stream (10% NH_3; H_2:N_2 = 3:1; p = 90 bar – procedure B). Activity was measured at 520°C and 63 bar.

expressed as the NH_3 content in the exit gas, increases after each of the isothermal steps performed, thus, showing the stabilization of the systems to be very slow, when the activation is performed in a pure H_2, N_2 mixture at 1 bar. The Ru/BN sample doped with barium nitrite is about twice as active (twice higher conversions) as that doped with barium nitrate (see Fig. 1), throughout the whole activation procedure. The activation in an ammonia rich stream (Fig. 2) leads, first of all, to the significantly higher level of conversions (higher NH_3 concentrations in the outlet gas) and the difference between the promoter precursors ($Ba(NO_3)_2$, $Ba(NO_2)_2$) becomes less pronounced than in the case of procedure A. Furthermore, the effect of the prolonged activation is not so strong. Table 1 gives a comparison of the integral reaction rates obtained for the Ba-Ru/BN catalysts (520°C, 63 bar), after their final treatments in the two reducing streams, *i.e.* in the ammonia free and ammonia rich mixtures, respectively. The difference between the most and the least active samples reaches a factor of 3, that would certainly be higher if the reaction rates were determined for the same average values of NH_3 contents in the catalytic beds compared (ammonia is known to suppress the reaction rate over Ru catalysts, the effect being the stronger, the higher the NH_3 concentration in the gas phase is [8,24]). A very slow stabilization of the supported ruthenium catalysts in hydrogen containing streams as well as an advantageous effect of ammonia observed for Ba-Ru/BN in this study have not been reported so far for other Ru catalytic systems. The studies of unpromoted and Ba-promoted Ru catalysts, deposited on magnesia [24] or graphitized carbon [8,9], demonstrate that the samples reach their steady-state level of activity after a short time (< 24 h) of activation at 470–520°C and at 1 bar. The prolonged treatment in $H_2 + N_2$ at 520°C may even lead to deactivation, due to the sintering of Ru particles [24]. Hence, an increase in the reaction rate over Ba-Ru/BN *vs*. time on stream at 550°C and especially at 600°C (see Fig. 1) can be justified neither by a slow reduction of the Ru surface, nor by a slow decomposition of the Ba precursors to their oxide species. The only reasonable explanation of the phenomenon observed is based on the slow, systematic changes in the BN support during the activation process. We suppose that B_2O_3 present in the support acts as a deactivating agent for ruthenium. Most likely, B_2O_3 migrates onto the Ru surface and blocks the sites that are active for N_2 adsorption (N_2 adsorption is believed to be the rate-limiting step of NH_3 synthesis). Small amounts of ammonia formed in the $N_2 + H_2$ mixture during activation at 1 bar might slowly convert B_2O_3 into BN, thus, resulting in the systematic activity enhancement. The $B_2O_3 \rightarrow BN$ transformation is expected to proceed significantly faster when activation is performed in a 10% NH_3 stream at 90 bar. Under such conditions, the ammonia partial pressure in the gas mixture is several orders of magnitude higher than that at atmospheric pressure. In consequence, a higher activity of the catalysts is observed (see Table 1).

Table 1. Integral reaction rates over the Ru/BN catalysts promoted with $Ba(NO_3)_2$ and $Ba(NO_2)_2$ after the final steps of activation in ammonia free gas stream (procedure A) and in ammonia rich stream (procedure B).

promoter precursor	activation procedure	average NH_3 content [mol. %]	integral reaction rate $r[g_{NH_3}/(g_{cat} \cdot h)]$
$Ba(NO_3)_2$	A	0.67	2.17
	B	1.75	5.05
$Ba(NO_2)_2$	A	1.15	3.57
	B	2.21	6.05

The concept of Ru poisoning by B_2O_3 explains not only the slow stabilization of the Ru/BN system, but it explains also the supremacy of the barium nitrite precursor *vs*. its nitrate. The nitrogen oxides, evolved during decomposition of both precursors, might oxidize partly the BN surface. Since barium nitrate releases more NO_x than barium nitrite, the effect of BN oxidation is stronger for the former. The BN oxidation by evolving nitrogen oxides was probably less pronounced, when the catalysts were activated in an ammonia rich stream (procedure B), as evidenced by the small difference between the reaction rates over the Ba-Ru/BN specimens derived from barium nitrate and barium nitrite, respectively.

According to the above discussion both very pure, oxygen-free boron nitride of high surface area and an appropriate activation procedure, *i.e.* high pressure activation in the ammonia rich mixture, should be applied to obtain a very active Ba-Ru/BN catalyst. Further studies are necessary, however, to support such a suggestion.

Acknowledgments

This work has been carried out within the Research Project 4T09B 118 23, sponsored by the Polish State Committee for Scientific Research. W. Raróg-Pilecka is grateful to the Foundation for Polish Science for financial support.

REFERENCES

1. Zhong Z. and Aika K., *J. Catal*., **173**, 535 (1998).
2. Zeng H.S., Inazu K. and Aika K., *J. Catal*., **211**, 33 (2002).
3. Forni L., Molinari D., Rossetti I. and Pernicone N., *Appl. Catal. A: General*, **185**, 269 (1999).
4. Kowalczyk Z., Sentek J., Jodzis S., Mizera E., Góralski J., Paryjczak T. and Diduszko R., *Catal. Lett.*, **45**, 65 (1997).
5. Rossetti I., Pernicone N. and Forni L., *Appl. Catal. A: General*, **208**, 271 (2001).
6. Liang Ch., Wei Z., Xin Q. and Li C., *Appl. Catal. A: General*, **208**, 193 (2001).
7. Zheng X.L., Zhang S.J., Xu J.X. and Wei K.M., *Carbon*, **40**, 2597 (2002).
8. Raróg W., Kowalczyk Z., Sentek J., Składanowski D. and Zieliński J., *Catal. Lett*., **68**, 163 (2000).
9. Kowalczyk Z., Jodzis S., Raróg W., Zieliński J. and Pielaszek J., *Appl. Catal. A: General*, **173**, 153 (1998).
10. Bielawa H., Hinrichsen O., Birkner A. and Muhler M., *Angew. Chemie Int. Ed*., **40/6**, 1061 (2001).
11. Hinrichsen O., Rosowski F., Hornung A., Muhler M. and Ertl G., *J. Catal*., **165**, 33 (1997).
12. Rosowski F., Hornung A., Hinrichsen O., Herein D., Muhler M. and Ertl G., *Appl. Catal. A: General*, **151**, 443 (1997).
13. McClaine B.C. and Davis R.J., *J. Catal*., **210**, 387 (2002).
14. McClaine B.C. and Davis R.J., *J. Catal*., **211**, 379 (2002).
15. McClaine B.C., Siporin S.E. and Davis R.J., *J. Phys. Chem., B* , **105**, 7525 (2001).
16. Siporin S.E., McClaine B.C., Anderson S.L. and Davis R.J., *Catal. Lett.*, **81**, 265 (2002).
17. Fastrup B., *Catal. Lett*., **48**, 111 (1997).
18. Jacobsen C.J.H., Dahl S., Hansen P.L., Tornqvist E., Jansen L., Topsoe H., Prip D.V., Moenshaug P.B. and Chorkendorff I., *J. Mol. Catal. A: Chemical*, **163**, 19 (2000).
19. Jacobsen C.J.H., *J. Catal*., **200**, 1 (2001).
20. Hansen T.W., Wagner J.B., Hansen P.L., Dahl S., Topsoe H. and Jacobsen C.J.H., *Science*, **294**, 1508 (2001).
21. *Nitrogen & Methanol*, **257**, 34 (2002).
22. Hansen T.W., Hansen P.L., Dahl S. and Jacobsen J.H., *Catal. Lett*., **84**, 7 (2002).
23. Kowalczyk Z., *Catal. Lett.*, **37**, 173 (1996).
24. Szmigiel D., Bielawa H., Kurtz M., Hinrichsen O., Muhler M., Raróg W., Jodzis S., Kowalczyk Z., Znak L. and Zieliński J., *J. Catal.*, **205**, 205 (2002).