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The Kinetics of Ammonia Synthesis over Ruthenium-Based Catalysts: The Role of Barium and Cesium

Dariusz Szmigiel,* Hubert Bielawa,† Melanie Kurtz,† Olaf Hinrichsen,† Martin Muhler,†,[1] Wioletta Raróg,* Sławomir Jodzis,* Zbigniew Kowalczyk,* Leszek Znak,‡ and Jerzy Zieliński‡

**Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland; †Laboratory of Industrial Chemistry, Ruhr University Bochum, 44780 Bochum, Germany; and ‡Institute of Physical Chemistry PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland*

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The effect of barium and cesium on the kinetic behavior of Ru/MgO in ammonia synthesis was studied. The activity measurements were performed in a differential reactor at 400°C under a pressure of 6.3 MPa and supplemented with chemisorption measurements and temperature-programmed surface reaction experiments (TPSR). The latter were performed by titrating preadsorbed atomic nitrogen (N_{ads}) with hydrogen. Both promoted systems proved to be much more active in NH_3 synthesis than the unpromoted one: Ba-Ru/MgO > Cs-Ru/MgO ≫ Ru/MgO. The kinetic behavior of Ba-Ru/MgO was found to be different from that of Cs-Ru/MgO which was much less sensitive to changes in the ammonia content (x_{NH_3}). The dependence of the turnover frequencies (TOF) on x_{NH_3} for Ba-Ru/MgO and Cs-Ru/MgO was found to be analogous to that for Ba-Ru/C and Cs-Ru/C, respectively. For Ba-Ru/MgO and Ba-Ru/C the differences in TOF did not exceed 10 to 30% over the range of x_{NH_3} studied. It is therefore suggested that cesium acts as an electronic promoter, whereas barium plays the role of a structural promoter that controls the concentration of active sites which are most likely B_5-type sites, the effect of the support being negligible. The same onset temperature of ammonia formation during the TPSR experiment observed for Ru/MgO and Ba-Ru/MgO supports this hypothesis. Furthermore, a strong increase in activity was observed for Ru/MgO and Ba-Ru/MgO when heating in synthesis gas up to 520°C. This can be attributed to the sintering of very small Ru particles and to the removal of water traces from both the MgO and the Ba + O adlayer. In contrast, the activity of Cs-Ru/MgO decreased significantly after heating at 520°C. Thus, due to the very high activity, very high thermal stability, and absence of methanation problems, barium-promoted ruthenium catalysts supported on magnesia are considered excellent ammonia synthesis catalysts.

Key Words: **ammonia synthesis; ruthenium catalysts; promotion; magnesia; barium; cesium; chemisorption; temperature-programmed surface reaction; kinetics.**

INTRODUCTION

The supported ruthenium catalysts represent a new group of materials which are very active in ammonia synthesis. Under low-pressure conditions (5–10 MPa) they are much more active than the conventional multipromoted magnetite-based iron catalyst commonly used in industrial plants. Great interest is given to the carbon–based Ru systems promoted with alkali or barium (1–11). A catalyst of that type was commercialized in the mid-1990s by the Kellogg Company (KAAP Kellogg Advanced Ammonia Process) and more recently by Kellogg Brown and Root (KAAP plus KBR Advanced Ammonia Process) (12, 13). There is still doubt, however, whether the high cost of the new Ru/C catalyst and its rather short lifetime compared to iron are compensated by the increase in activity (14).

In contrast to carbon, oxidic supports such as magnesia are stable under ammonia synthesis conditions. The MgO-based Ru catalyst therefore seems to be a promising candidate of industrial importance. It has been shown previously by Aika *et al.* (15–17) that cesium promotes the Ru/MgO system effectively. Recent studies by Muhler and co-workers (18) demonstrated that barium may also be used as an activator of ruthenium, the promotional effect of barium being even stronger than that of cesium. However, neither the role of magnesia as a support nor the role of both the promoters, i.e., barium and cesium, have been fully elucidated so far. Temperature-programmed N_2 adsorption and desorption experiments indicate that the promotion by cesium enhances both the rate constants of dissociative adsorption and associative desorption (19). Fishel *et al.* (20–22) studied ammonia synthesis catalyzed by ruthenium supported on basic zeolites. They concluded that the promotional effect of barium may be due to the creation of highly active sites at the promoter–metal interface (22).

The purpose of this work was to study the effect of Cs and Ba on the kinetic behavior of the Ru/MgO catalyst in NH_3 synthesis under moderate pressure (6.3 MPa). Since the reduction procedure may influence the catalytic activity

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[1] To whom correspondence should be addressed. E-mail: muhler@techem.ruhr-uni-bochum.de.

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(18, 23), the effect of more severe reduction conditions was examined as well. The steady-state kinetic measurements were supplemented with chemisorption experiments and with the temperature-programmed surface reaction (TPSR) of adsorbed atomic nitrogen (N_{ads}) with hydrogen. In consequence, it was possible to compare the rates of NH_3 formation, expressed as turnover frequencies (TOF) to those obtained for the similarly promoted Ru catalysts supported on carbon (9), thus giving a deeper insight into the role of both support and promoters. The TPSR experiment was introduced by Fastrup *et al.* (24) for the *in situ* determination of the number of active sites. Later, the method was developed into a valuable tool for screening unpromoted Ru-based catalysts used in ammonia synthesis (25). Furthermore, this transient experiment provided new insight into the role of the promoters which are crucial for high catalytic activity.

EXPERIMENTAL

The Catalysts

Ru/MgO was prepared by the grinding of high-purity MgO (Johnson Matthey, Puratronic, 99.996%) with $Ru_3(CO)_{12}$ (Strem, 99%) to obtain a nominal metal loading of 3.75 wt%. Grinding was performed in an agate mortar for approximately half an hour until a homogeneous lightly orange-colored powder was obtained. The catalyst precursor was pressed into tablets, crushed, sieved into a grain fraction from 250 to 355 μm, and finally thermally decomposed in a quartz ampulla connected to a fat- and oil-free high-vacuum line with a turbomolecular drag pump. High-vacuum thermal decomposition was performed with a detailed heating program consisting of several steps starting at room temperature (2 K min^{-1} up to 40°C, hold for 1 h; in 2 h up to 70°C, hold for 1 h; in 2 h up to 120°C, hold for 1 h; in 5 h up to 450°C, hold for 2 h). Subsequently, the decomposed, dark gray/black-colored precursor was cooled down to room temperature. For Cs-Ru/MgO (3.0 wt% Ru) and Ba-Ru/MgO (2.7 wt% Ru), Ru/MgO was further impregnated with a solution of Cs_2CO_3 in ethanol or $Ba(NO_3)_2$ in a 50/50 water/ethanol mixture to obtain atomic ratios of Cs/Ru = 1/1 and Ba/Ru = 2/1, respectively.

The Temperature-Programmed Surface Reaction of N_{ads} with H_2 ($N_{ads} + H_2$ TPSR)

Catalysts (150 mg) were placed into a glass-lined stainless-steel U-tube reactor between two quartz wool plugs. The reactor was connected to a high-pressure stainless-steel flow setup equipped with a calibrated nondispersive IR-detector (BINOS, Fisher-Rosemount) described in detail in Ref. 26. The reduction was conducted *in situ* in synthesis gas ($H_2/N_2 = 3/1$) using a flow of 40 Nml min^{-1} and a heating rate of 1°C min^{-1} up to 510°C for Ru/MgO and Ba-Ru/MgO or 390°C for Cs-Ru/MgO, respectively. All volumetric flow rates refer to 0°C and 1013.25 mbar (Nml min^{-1}). The $N_{ads} + H_2$ TPSR experiment was performed as follows (21). First, NH_3 synthesis was run under steady-state conditions at a maximum temperature of 510°C with the unpromoted Ru/MgO and Ba-Ru/MgO as well as at 390°C with Cs-Ru/MgO followed by flushing in pure N_2 for 30 min. Then, the catalyst was cooled down in N_2 to 300°C and maintained in flowing N_2 for 14 h. This procedure was chosen in order to achieve saturation coverage by adsorbed atomic nitrogen as known from Ref. 19. Finally, the catalyst was cooled down in N_2 to room temperature for the unpromoted and Ba-promoted Ru/MgO or to −77°C using dry ice for the Cs-promoted catalyst. The gas flow was changed to H_2 (50 Nml min^{-1}), the remaining N_2 was flushed out for 30 min, and then heating was started at a rate of 5°C min^{-1} up to the maximum temperature.

Ammonia Synthesis Studies

The kinetic studies of NH_3 synthesis were performed in a flow differential reactor. The description of the setup has been presented elsewhere (27). Briefly, the gas for synthesis ($H_2/N_2 = 3/1$) was obtained by decomposition of ammonia over a nickel catalyst at 950°C. Subsequently, the mixture was purified from traces of undecomposed ammonia and water vapor over molecular sieves and was pressurized in an oil-free compressor (Sulzer) to constant pressure controlled by the pressure regulator (Brooks). Final purification of the gas was achieved by passing the stream through a large bed of the reduced iron catalyst (KMI, Haldor Topsøe) operating at ambient temperature. The purified H_2/N_2 mixture ($H_2O < 0.5$ ppm) entered the preliminary reactor filled with an iron catalyst (KMI) that synthesized ammonia to the desired level of NH_3 concentration (x_1) controlled by the catalyst temperature. Finally, the $H_2/N_2/NH_3$ stream passed through the main differential reactor filled with a small amount of the catalyst to be tested. Under steady-state conditions of temperature, pressure, flow rate of the gas, and NH_3 concentration (x_1) the increment in NH_3 content ($\Delta x = x_2 - x_1$) was determined, with $\Delta x \ll x_1$. Hence, it was possible to calculate the rate of NH_3 synthesis (r) corresponding to the mean ammonia content in the sample ($x = (x_1 + x_2)/2$) (27).

The kinetic experiments were performed according to the following procedure:

- reduction of the samples in synthesis gas at 470°C (Ru/MgO and Ba-Ru/MgO) or 400°C (Cs-Ru/MgO) for 24 h ($p = 0.1$ MPa)
- activity measurement: under constant pressure of 6.3 MPa and at constant temperature of 400°C, the dependence of the reaction rate on the ammonia partial pressure was determined ($r = f(x)$)
- further reduction at 520°C for 16 h ($p = 0.1$ MPa)

TABLE 1

Characteristics of the Chemisorption Measurements

Adsorbate	Experimental conditions	Stoichiometry of chemisorption	Literature
O_2	Pulse (0°C)	$O_{ads}/Ru_s = 1.1$	(38, 39)
CO	Pulse (20°C)	$CO_{ads}/Ru_s = 0.60$	(39)
H_2	Static (0°C)	$H_{ads}/Ru_s = 1$	(37, 38)

- repeated measurement of the reaction rate vs NH_3 content in the gas phase ($T = 400°C$; $p = 6.3$ MPa).

Chemisorption Studies

The experiments were carried out in a glass flow setup (10), equipped with a gradientless reactor operating with high-purity gases (H_2, He, O_2, Ar, and CO). A temperature controller provided linear temperature programming. The concentration of adsorbate in the gas leaving the reactor was monitored by means of a TCD cell, all the experiments being computer controlled.

For better characterization of the catalysts, chemisorption of hydrogen, oxygen, and carbon monoxide was measured. All the chemisorption experiments were performed with the samples being previously reduced in hydrogen in two steps: first at 470°C (Ru/MgO, Ba-Ru/MgO) or 400°C (Cs-Ru/MgO) for 24 h and, thereafter, at 520°C for a further 16 h. Hence, this pretreatment corresponded to the procedure applied in the NH_3 synthesis studies. Typically, a catalyst mass of 250 mg was used for examination. Prior to each chemisorption experiment, the sample was rereduced *in situ* in a hydrogen stream (30 Nml min^{-1}) for 1 h followed by flushing with helium (30 Nml min^{-1}, 0.5 h) to remove hydrogen adsorbed on the surface. Finally, the catalyst was cooled in a stream of helium.

Adsorption of hydrogen was performed at 0°C for 0.5 h under atmospheric pressure. Afterwards, the sample was flushed with argon (30 Nml min^{-1}, 0°C, 0.25 h) to remove weakly adsorbed hydrogen, whereupon the temperature was linearly increased (20°C min^{-1}), and the concentration of hydrogen desorbing into the argon stream was measured (H_2 TPD).

The adsorption of oxygen and carbon monoxide was measured by the pulse method: small portions of 1.61 μmol of O_2 or 4.5 μmol of CO, respectively, were introduced into the helium stream flowing over the sample at 0°C (O_2) or 20°C (CO) until saturation was achieved.

The uptakes of reactant gases were used for determining the dispersion of ruthenium, i.e., the fraction of ruthenium atoms exposed (FE), and for determining the average size of the Ru crystallites (d). The latter parameter was calculated from the equation developed by Borodziński and Bonarowska (28), assuming that the crystallites form cubo-octahedra or icosahedra. The experimental conditions and the stoichiometry of adsorption assumed in the calculations of dispersion are summarized in Table 1.

RESULTS

Chemisorption

All the chemisorption results are collected in Table 2. In general, there is a rather good agreement among the data obtained with different adsorbates. For instance, the values of the fraction exposed (FE) for the unpromoted Ru/MgO sample after its reduction at 470°C were 0.88 (CO), 0.84 (O_2), and 0.58 (H_2) corresponding to average crystallite sizes of 1.1, 1.1, and 1.7 nm, respectively. In the case of the cesium-doped catalyst reduced at 400°C, the differences were even smaller ($FE_{O_2} = 0.66$, $FE_{CO} = 0.73$, $FE_{H_2} = 0.63$). The particle sizes derived from the uptake measurements are in good agreement with those derived from TEM micrographs (18).

The chemisorption studies demonstrate that the average Ru particle diameter increases during the high-temperature stabilization at 520°C, the effect being dependent on the kind of promoter. A rather minor growth in the crystallite size of about 5% was observed for Ru/MgO; a slightly bigger growth of about 10% was found for Ba-Ru/MgO; and the largest one of 20 to 30% for Cs-Ru/MgO, all the effects being referred to the state after the first step of reduction in hydrogen.

A closer inspection of the data reveals that the dispersion of the Ba-promoted sample (FE_{CO}, FE_{O_2}) is lower than the dispersion of the unpromoted Ru/MgO material,

TABLE 2

Results of Chemisorption Studies

Catalyst	Reduction procedure	O_2 uptake (μmol/g)	FE_{O_2}	Crystallite size d_{O_2} (nm)	CO uptake (μmol/g)	FE_{CO}	Crystallite size d_{O_2} (nm)	H_2 uptake (μmol/g)	FE_{H_2}	Crystallite size d_{H_2} (nm)
Ru/MgO	470°C;24 h	172	0.84	1.1	196	0.88	1.05	108	0.58	1.7
Ru/MgO	520°C;16 h	169	0.82	1.15	184	0.83	1.1	104	0.56	1.8
Ba-Ru/MgO	470°C;24 h	53	0.36	3.1	61	0.38	2.9	61.5	0.46	2.3
Ba-Ru/MgO	520°C;16 h	—	—	—	56	0.35	3.2	55	0.41	2.6
Cs-Ru/MgO	400°C;24 h	101	0.66	1.5	122	0.73	1.3	88	0.63	1.6
Cs-Ru/MgO	520°C;16 h	84	0.55	1.9	94	0.56	1.8	64	0.46	2.3

both reduced at 470°C. Hence, either the Ru surfaces in Ba-Ru/MgO are partly inaccessible to the reactant gases due to the presence of the Ba promoter—in such a case, the average size of Ru crystallites would be overestimated (see Table 2), or barium stimulates the sintering of small Ru particles when operating at a temperature even as low as 470°C. The latter option seems to be unrealistic, since it is known from the studies of the carbon-based catalysts (10) that Ba protects the fine Ru particles from sintering. However, the physisorption measurements performed with the Ru/MgO and Ba-Ru/MgO samples after high-pressure NH_3 synthesis showed the BET surface area of the former to be almost twice as high as that of the latter (42 and 25 m^2/g, respectively). Consequently, the sintering of ruthenium particles during the reduction at 470°C for 24 h might indeed occur, as a result of disadvantageous changes in the texture of the support when doped with barium, which was used most likely in excess (Ba/Ru = 2/1).

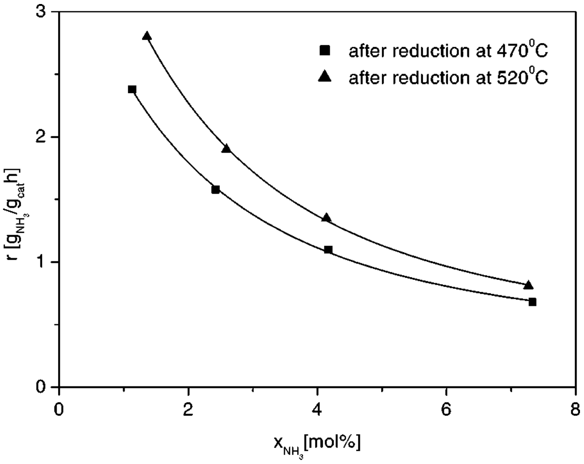

FIG. 2. Dependence of the reaction rate on x_{NH_3} over Ba-Ru/MgO; $p = 6.3$ MPa, $T = 400°C$; ■, after reduction at 470°C (24 h); ▲, after subsequent stabilization at 520°C (16 h).

Activity of the Catalysts in NH_3 Synthesis

The results of the activity measurements are presented in Figs. 1–3. Figure 1 concerns the unpromoted system; the other two figures show the data obtained with the promoted catalysts, i.e., Ba-Ru/MgO (Fig. 2) and Cs-Ru/MgO (Fig. 3). It is evident when comparing the traces shown in the figures that the promotional effect of cesium and especially of barium is very strong. At 5% NH_3, for instance, the ratio of the reaction rates is as follows: Ba-Ru/MgO/Cs-Ru-MgO/Ru/MgO = 40/20/1, when the samples were reduced at 520°C (Ru/MgO, Ba-Ru/MgO) and 400°C (Cs-Ru/MgO). These ratios are in good agreement with the results published previously (18). Attention should be paid, however, to the similarities and to the differences between the systems under consideration. As one may notice, the kinetic behavior of the Ba-doped catalyst is closer to the kinetic behavior of the unpromoted sample rather than to the behavior of Cs-Ru/MgO. Both Ru/MgO and Ba-Ru/MgO show a similar sensitivity to the changes in ammonia concentration in the gas phase. An increase in the NH_3 content from 0.15 to 7% leads to a roughly sixfold drop in the reaction rate over Ru/MgO (see Fig. 1), thus indicating the mean ammonia reaction order to be about −0.5. A similar effect of the activity reduction vs the ammonia content in the whole range of NH_3 concentration is observed for the catalyst promoted with barium as shown by the trend in Fig. 2. It is noteworthy that Bielawa *et al.* (18) found the apparent orders in ammonia to be −0.6 for both Ru/MgO and Ba-Ru/MgO, respectively, the values being obtained at 2 MPa for samples prepared in the same way as those in the present study.

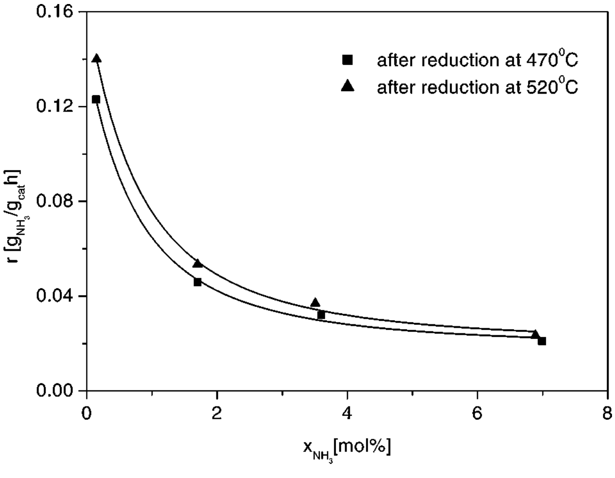

FIG. 1. Dependence of the reaction rate on x_{NH_3} over the unpromoted Ru/MgO catalyst; $p = 6.3$ MPa, $T = 400°C$; ■, after reduction at 470°C (24 h); ▲, after subsequent stabilization at 520°C (16 h).

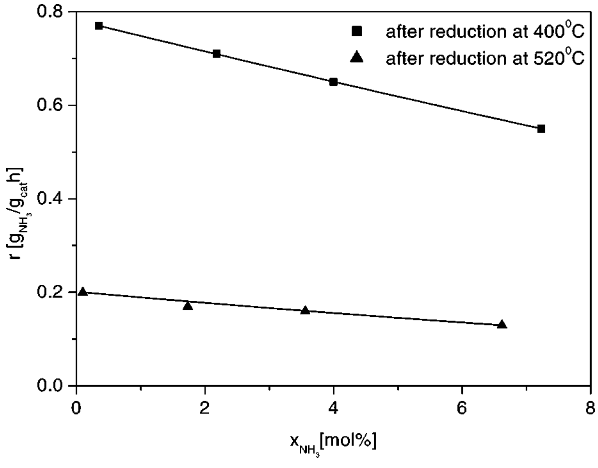

FIG. 3. Dependence of the reaction rate on x_{NH_3} over Cs-Ru/MgO; $p = 6.3$ MPa, $T = 400°C$; ■, after reduction at 400°C; ▲, after subsequent stabilization at 520°C.

The similarity between the unpromoted and Ba-promoted catalysts is not only restricted to the shapes of the kinetic curves. In both cases, the subsequent reduction at 520°C led to a noticeable enhancement in the reaction rates: about 10 to 15% for Ru/MgO and about 20% for Ba-Ru/MgO (see Figs. 1 and 2), although the dispersion of ruthenium in the materials decreased slightly (Table 2). Consequently, the turnover frequencies (TOFs) of ammonia synthesis, which are more suitable to characterize the catalytic properties, increased by about 15 to 20 and 30%, respectively. Analogous correlations were observed recently by Jacobsen *et al.* (23), who studied an unpromoted ruthenium catalyst supported on a magnesia–alumina spinel. The increase in activity during the initial period of ammonia synthesis in their experiments was accompanied by the disappearance of extremely small Ru crystallites (<1.0 nm) due to sintering and a resulting formation of larger crystallites, as evidenced by a detailed TEM study (23). According to Jacobsen *et al.* (23), slightly larger particles exhibit more of the so-called B_5-type sites which are assumed to be primarily responsible for the catalytic activity of the supported Ru catalysts. Hence, the effect of the activity increase was attributed by Jacobsen *et al.* (23) to the shift in the average diameter of the Ru particles toward the optimal value of about 2 nm with the highest concentration of B_5-type sites.

The previously cited interpretation might be fully accepted in the present study both for Ru/MgO and Ba-Ru/MgO. There is one doubt, however. Oxide supports, including magnesia, are capable to keep water (OH groups) on their surfaces even when heated up to high temperatures. Water, in turn, is known to be a very strong poison of all ammonia synthesis catalysts. To clarify the problem, additional experiments were performed in which the H_2O concentration in the outlet gas was monitored during the two-step reduction (470 and 520°C) of Ru/MgO and Ba-Ru/MgO in high-purity H_2 (see Fig. 4). After the sudden onset of H_2O formation in the beginning of the run, the concentration of H_2O decreased quickly (this part of the experiment is not presented in Fig. 4) reaching, for both the samples, the same value of about 1 ppm after 20 h at 470°C (Fig. 4). This means that the catalysts were highly reduced when starting the NH_3 synthesis measurements after the reduction at 470°C for 24 h. However, a broad H_2O peak appeared for each sample when the temperature was increased up to 520°C (see Fig. 4). The total amounts of H_2O released into the gas phase during the pretreatment in H_2 at 520°C for 4 h were equal to 3.5 and 10 μmol/g for Ru/MgO and Ba-Ru/MgO, respectively. It cannot be excluded, therefore, that OH groups bound strongly to magnesia and possibly to barium could influence the ruthenium surfaces during the activity test which followed the first step of reduction at 470°C. Simply speaking the Ba + OH or Mg + OH species might be less efficient as promoters than the Ba + O adlayer or Mg + O, or they might be even inefficient. It is impossible, at present, to give a decisive answer to the question which of the phenomena—the sintering of Ru particles or the removal of water from the catalysts—is essential for the observed increase in activity.

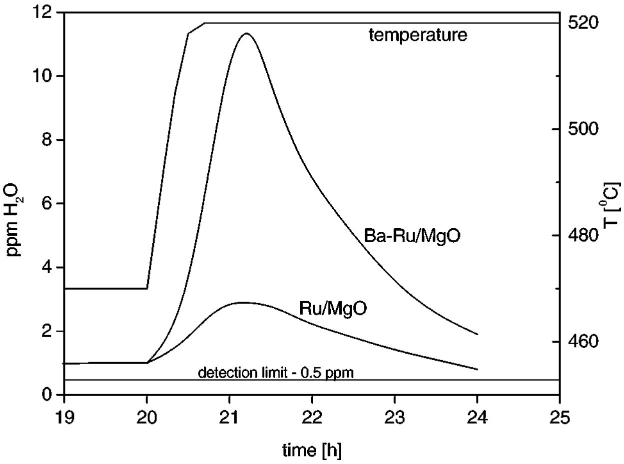

FIG. 4. Water vapor concentration in the outlet gas during the reduction of Ru/MgO (250 mg) and Ba-Ru/MgO (250 mg) in H_2 (40 N ml/min).

In contrast to Ru/MgO and Ba-Ru/MgO, the cesium-promoted catalyst demonstrates a quite different behavior in the ammonia synthesis reaction. First of all, the Cs-doped catalyst is much less sensitive to the variations in the NH_3 concentration (see Fig. 3): in the 0–7% NH_3 range, the activity changes only by about 30% indicating that the ammonia reaction order for Cs-Ru/MgO is close to zero. Furthermore, overheating of the sample at 520°C results in a dramatic, about fourfold drop in the reaction rate. Such a strong thermal deactivation cannot be explained by the decrease in the Ru dispersion (about 20–25%, see Table 2) but should rather be attributed to the loss of the promoter at high temperatures. A loss of the alkali promoter at elevated temperatures seems to be a serious disadvantage that limits the practical potential of all the cesium-promoted Ru catalysts including those supported on carbon. Such catalysts ought to be operated at relatively low temperatures (<400°C) which are characteristic for the final bed of an industrial multibed reactor.

The $N_{ads} + H_2$ Temperature-Programmed Surface Reaction

Finally, TPSR experiments were performed to gain deeper insight into the role of the promoters. The temperature of NH_3 formation, T_{onset}, turned out to be an important parameter in the evaluation of different Ru-based catalysts (25): for unpromoted Ru/MgO catalysts with different Ru loading, T_{onset} was found to vary between 82 and 167°C, but the scatter of the experimental data did not allow a direct correlation of T_{onset} with the

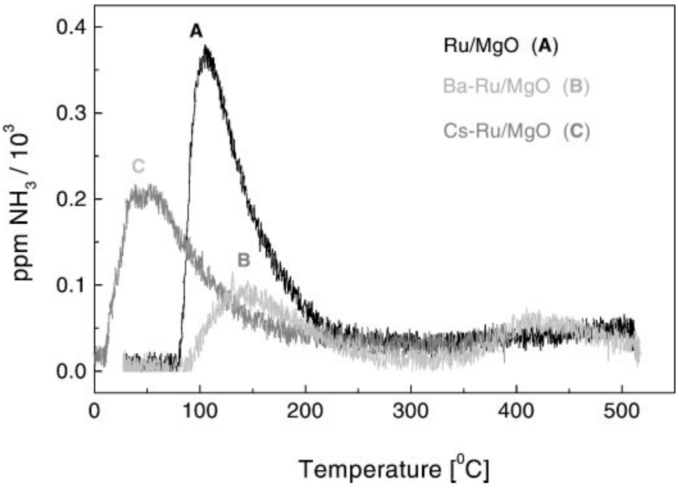

FIG. 5. $N_{ads} + H_2$ TPSR data obtained with Ru/MgO (trace A), Ba-Ru/MgO (trace B), and Cs-Ru/MgO (trace C) after dosing N_2 at atmospheric pressure for 14 h at 300°C followed by cooling in flowing N_2. A flow of 50 Nml min^{-1} H_2, a heating rate of 5°C min^{-1}, and a catalyst weight of 150 mg were used.

catalytic activity of the catalyst. However, for those catalysts, which exhibited the highest catalytic activity, an onset temperature of about 82°C was observed. Figure 5 compares the TPSR experiments performed with unpromoted Ru/MgO, Ba-Ru/MgO, and Cs-Ru/MgO. In all TPSR experiments a sudden onset of NH_3 formation is observed indicating that saturation with N_{ads} was achieved during the exposure to N_2. The quantitative results are summarized in Table 3. Assuming a surface stoichiometry at saturation of $N_{ads}/Ru_s = 1/3$ (29), the amount of Ru surface atoms is in good agreement with the results obtained by chemisorbing O_2, CO, and H_2 (Table 2), when considering the slightly different pretreatments. The steep increase in the rate of NH_3 formation might be due to the autocatalytic titration mechanism (24). Whereas for Cs-Ru/MgO a shift of the onset of NH_3 formation to lower temperature is found, unpromoted Ru/MgO and the barium-promoted catalyst exhibited similar behavior in the TPSR experiment. Thus, the similarity of Ru/MgO and Ba-Ru/MgO found in the steady-state kinetic experiments is also observed in the transient TPSR experiment, again indicating different modes of action of the alkaline and Earth–alkaline promoters. It is noteworthy that only for Ba-Ru/MgO a second TPSR peak is observed centered at about 400°C. This may indicate, taking into account that Ba is known to form stable nitrides, that more strongly bound N_{ads} is present originating from the stabilizing interaction with adsorbed Ba.

TABLE 3

Quantitative Results of the $N_{ads} + H_2$ TPSR Experiments

	Onset temperature (°C)	Amount of NH_3 formed (μmol/g)
Ru/MgO	80	106
Ba-Ru/MgO	89	55
Cs-Ru/MgO	20	46

DISCUSSION

From the results presented previously, an obvious question arises as to the role of individual promoters. To discuss the problem, reference should be given to the data obtained by Raróg *et al.* (9), who measured the rates of ammonia synthesis over the carbon-based Ru samples promoted with cesium or barium, the experiments being performed under the same conditions of temperature and pressure (400°C, 6.3 MPa). Figures 6 and 7 show the results of the comparison between the magnesia-supported catalysts and the catalysts derived from the graphitized carbon using the TOFs of the ammonia synthesis reaction based on the extent of hydrogen chemisorption.

It is clearly seen from Fig. 6 that Ba-containing samples of both types, i.e., Ru/MgO and Ru/C exhibit a very similar dependence of the TOF on x_{NH_3}: the shape of the traces is similar and, what is striking, the absolute level of the activity is similar, too, as the differences in TOF do not exceed 10 to 30% depending on x_{NH_3}. The unpromoted Ru/MgO system is orders of magnitude less active (TOF) than the promoted ones (Fig. 6). This implies that the catalytic properties of the Ru surfaces in both Ba-Ru/MgO and Ba-Ru/C are dominated by the presence of the promoter, the effect of the support being rather negligible. Should barium indeed act as a structural promoter, as suggested

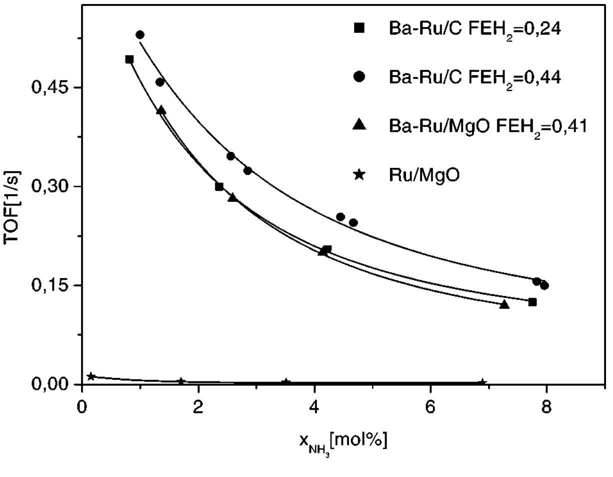

FIG. 6. TOF of NH_3 synthesis vs x_{NH_3} for the barium-promoted catalysts supported on magnesia or graphitized carbon and for Ru/MgO: p = 6.3 MPa, T = 400°C. TOF values are referred to the H_2 chemisorption data; the shown activities of Ba-Ru/MgO and Ru/MgO were determined after the stabilization at 520°C for 16 h, and the data for Ba-Ru/C were taken from Ref. 9.

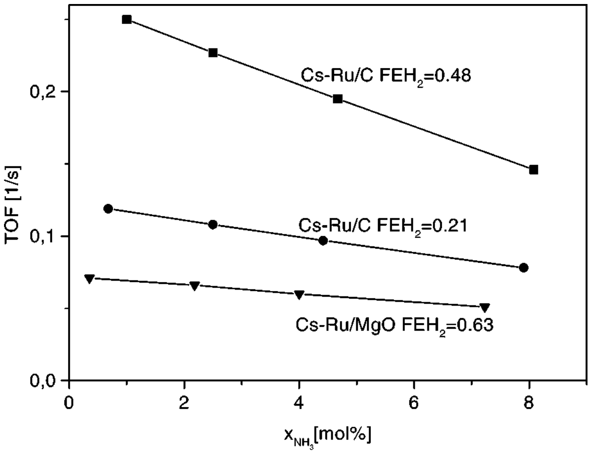

FIG. 7. TOF of NH_3 synthesis vs x_{NH_3} for the cesium-promoted catalysts supported on magnesia or graphitized carbon: $p = 6.3$ MPa; $T = 400°C$. TOF values are referred to the H_2 chemisorption data, Cs-Ru/MgO was reduced at 400°C, and the data for Cs-Ru/C were taken from Ref. 9.

previously (9, 18), the number of active sites, most likely B_5-type sites, would be controlled by the Ba promoter, even if the support plays a decisive role in controlling the morphology of the Ru crystallites as postulated by Jacobsen *et al.* (23).

Contrary to what is observed for barium, the support seems to play a significant role in the case of the cesium-promoted catalysts (see Fig. 7). The TOF values for Cs-Ru/C are considerably higher than those for Cs-Ru/MgO, the advantage of the former being dependent on the Ru dispersion. On the other hand, however, the analogous trends in the activities (TOF) vs x_{NH_3} indicate the promotional mechanism of cesium to be the same both for Cs-Ru/MgO and Cs-Ru/C. The differences in the activity levels (TOF) for the systems compared might be explained as follows: the alkali promotion is commonly assumed to proceed *via* electron transfer from the alkali to ruthenium leading to a direct electrostatic attraction between the adsorbed alkali atoms and the dissociating N_2 molecule (30). Such a concept requires the alkali to be in a highly reduced state when operating. Since the alkali promoters are added as ionic salts to the catalysts, the resulting adsorbed alkali species are present together with coadsorbed atomic oxygen (K_xO_y/Fe, Cs_xO_y/Ru). Oxygen neutralizes partly but not totally the promotional effect, and it acts as a stabilizing agent for the alkali under ammonia synthesis conditions (31, 32). Such a model seems to be characteristic for the cesium-promoted Ru/MgO with Cs_xO_y groups covering the Ru surfaces. Graphitic carbon, however, is known to form intercalates with alkali metals (graphite intercalated compounds), and cesium is therefore expected to be essentially in its zero valent state on the support. Consequently, promotion may originate both from the mobile Cs_xO_y groups which cover uniformly the ruthenium surfaces and from highly reduced cesium which is adsorbed on carbon but in an intimate contact with the Ru particles—the so-called "hot ring promotion" (5). The contribution of Cs^0 ("hot ring") to the overall effect depends, for obvious geometrical reason, on the Ru dispersion and is higher for smaller crystallites (the Ru surface area is proportional to $d_{Ru}{}^{-1}$, whereas the length of the hot ring is proportional to $d_{Ru}{}^{-2}$). This hypothesis rationalizes not only the differences between Cs-Ru/MgO and Cs-Ru/C but also the effect of the Ru dispersion in the latter case on its areal activity (TOF) (9). Further studies with catalysts of various dispersions are necessary to confirm this hypothesis.

The last question concerns the role of magnesia as a support. Unfortunately, no direct comparison between Ru/MgO and Ru/C was feasible—it was simply impossible to measure the reaction rates over the latter material due to its very low activity. MgO was shown, however, to act as a very poor promoter of the Ru/C system being much less effective than strontium or especially barium (33). It seems reasonable to assume, therefore, that MgO plays a double role in Ru/MgO, i.e., as a support and as a poor promoter. The promotional role of MgO was rationalized previously as being due to the contact points between the support and the ruthenium crystallites according to the hot ring model (34). It cannot be excluded that Mg + O also covers partly the ruthenium surfaces. For instance, such a decoration was postulated by Zieliński (35) and confirmed by Lamber and Schulz-Ekloff (36) for a nickel catalyst deposited on alumina. In this case the Mg + O adlayer might act as a structural promoter that modifies the ruthenium surfaces in the same way as Ba + O.

Some comments should be made in the end on the practical aspects of the Ru catalysts supported on MgO. Both the promoted systems, i.e., Ba-Ru/MgO and Cs-Ru/MgO

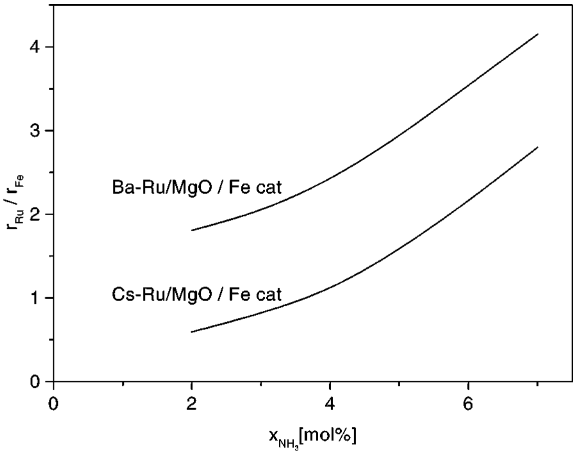

FIG. 8. The comparison between the activities of the promoted ruthenium catalysts supported on magnesia and the fused iron catalyst (taken from Ref. 9) at $p = 6.3$ MPa; $T = 400°C$ by showing the ratio of the reaction rates over the Ru/MgO catalysts and magnetite catalyst vs x_{NH_3}.

proved to be much more active than the conventional iron catalyst as shown in Fig. 8 especially at high conversions. Due to its high stability, the Ba-promoted catalyst seems to be the better alternative for iron than the catalyst promoted with cesium—but its optimization is necessary with respect to the loading of both ruthenium and barium.

CONCLUSIONS

Both cesium and barium proved to be very effective promoters of ruthenium supported on magnesia. The dependence of the reaction rate on the ammonia content (kinetic characteristics) at 400°C, 6.3 MPa for Ba-Ru/MgO was shown to be totally different from that for Cs-Ru/MgO, the latter catalyst being much less sensitive to the changes of x_{NH_3}.

The Ba-promoted catalyst is very stable under ammonia synthesis conditions. The heat treatment at 520°C for 16 h results even in an increase in the ammonia synthesis rate, the effect being attributed to the sintering of extrafine Ru particles as postulated in the literature (23) and to the removal of water traces from the support and from the Ba precursor. In contrast, the Cs-Ru/MgO catalyst exhibits a low thermal stability. The drop in the reaction rate observed during the high-temperature treatment at 520°C should rather be ascribed to the decrease in the Cs content in the catalyst than to the sintering of Ru particles.

The kinetic characteristics of Ba-Ru/MgO (TOF_{H_2} vs x_{NH_3}) resembles closely that of Ba-Ru/C and the characteristics of Cs-Ru/MgO is akin to that of Cs-Ru/C. Consequently, the promoting mechanisms of Ba and Cs are expected to be analogous in the systems Ru/MgO and Ru/C. It is suggested that Ba controls the concentration of the very active sites which are most likely B_5-type sites, whereas Cs acts as an electronic promoter, the effect of which depends upon its valence state.

Due to the very high activity, very high thermal stability, and absence of methanation problems, barium-promoted ruthenium catalysts supported on magnesia are considered excellent ammonia synthesis catalysts.

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