Support effect and active sites on promoted ruthenium catalysts for ammonia synthesis

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The catalytic activities of three supported, barium-promoted ruthenium catalysts for ammonia synthesis are reported. The three supports are silicon nitride (Si_3N_4), magnesium aluminum spinel ($MgAl_2O_4$), and graphitized carbon (C). The effect of the promoter on the activity is strongly dependent on the choice of support material in accordance with several previous observations. Here, this dependence is ascribed to a difference in the affinity of the promoter for the different supports. It is shown how it is possible to image the barium promoter present on the surface of ruthenium crystals in passivated catalysts by conventional high-resolution transmission electron microscopy (HRTEM). By comparison with *in situ* HRTEM images obtained lately from similar catalysts, and with reference to recent density functional theory (DFT) calculations, we suggest that active B_5-type sites on the surfaces of the ruthenium crystals are promoted by nearby promoter atoms *via* electrostatic interactions.

KEY WORDS: catalytic ammonia synthesis; promoters; TEM; EELS; ruthenium; barium.

1. Introduction

Since 1970, there has been a growing interest in ruthenium-based catalysts for ammonia synthesis. The first reports of such catalysts date back to the pioneering work of Alwin Mittasch in 1913 [1]. However, until Ozaki and Aika [2] initiated their systematic studies, which have been continued by Aika until today, there were only sporadic reports on the use of ruthenium catalysts in ammonia synthesis. From the literature, two topics have attracted continuous interest. They are related to the role of the support and to the role of the promoter. At an early point, it was established that alkali metals exert a dramatic influence on the reaction rate, and the ranking $Cs > K > Na$ of these promoters according to their influence on the activity was soon established [3]. Later, it was reported that barium could be an even more efficient promoter than caesium [4]. Several studies showed that very large variations in activity are observed when different supports are used [5]. These activity variations could not be ascribed solely to different dispersions of the Ru crystals. Generally, the highest catalytic activities are obtained with carbon supports, and particularly with partially graphitized carbons [6–8]. Recently, it was shown that operation of ruthenium catalysts at high pressures (>150 bar) may offer new possibilities in industry [9,10]. Therefore, it is important to find support materials that, unlike carbons, are thermodynamically stable under these industrially relevant conditions. It has often been suggested that the high activity of carbon-supported catalysts is related to the electrical conductivity of carbons [5]. However, equally active catalysts were prepared using a magnesium oxide support [11] and even more active catalysts supported on boron nitride were recently reported [12,13]. Both of these supports are insulators, and this conclusively rules out the possible importance of the conductivity of the support. Recent density-functional-theory (DFT) calculations and single-crystal studies showed that ammonia synthesis over ruthenium is an extremely structure-sensitive reaction [14–17], as is also the case for other transition metals, *e.g.*, Re [18] and Fe [19,20]. For the unpromoted catalysts, it was proposed that the support influences the activity by controlling the morphology of the supported ruthenium crystals and thereby the number of active B_5-type sites [21,22]. Recent studies suggest that B_5-type sites are the active sites of all transition metal catalysts for ammonia synthesis, both in unpromoted [23] and in promoted catalysts [24].

Large differences in the activities of unpromoted ruthenium catalysts for ammonia synthesis supported on Si_3N_4, C, and $MgAl_2O_4$ were reported [22]. Here, the same three catalysts are promoted with barium and it is shown that the effect of adding a promoter to the catalysts is greatly influenced by the choice of support material. The catalytic activity studies combined with high-resolution transmission electron microscopy (HRTEM) studies suggest that these differences are related to the relative affinities of the promoter for the supports. Based on these findings and DFT calculations, we suggest a mechanism for the promotional effect of barium in ruthenium-based ammonia synthesis catalysts.

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2. Experimental

2.1. Catalyst preparation

Barium promotion of ruthenium catalysts supported on different materials was carried out by incipient-wetness impregnation with barium hydroxide, as previously described in detail [22]. In brief, the catalysts were prepared according to the following steps: α-Si_3N_4 (obtained from H.C. Starck) and powdered magnesium aluminum spinel [25] were pressed into pellets using an IR press. Carbon extrudates (Norit) were graphitized at 1900 °C. The supports were crushed and sieved to a particle size of 0.1–0.2 mm prior to impregnation with Ru. The crushed supports were impregnated with ruthenium nitrosyl nitrate, $Ru(NO)(NO_3)_3$. The metal loading was chosen as 8 w/w%. The impregnated catalysts were dried at room temperature overnight followed by reduction with dihydrogen. The catalysts were promoted using an aqueous solution of barium hydroxide $Ba(OH)_2$. The amount of $Ba(OH)_2$ was chosen to obtain an atomic ratio of Ba : Ru of about 0.6.

2.2. BET, N_2 adsorption/desorption, and H_2 adsorption

Information about surface area, pore volume, and mean pore radius of the support material was obtained by N_2 adsorption/desorption at −196 °C. H_2 adsorption was used to determine the dispersion of ruthenium, the ratio of surface atoms to the total amount of atoms. The samples were treated at 450 °C in a 3 : 1 H_2/N_2 gas-mixture prior to the H_2 adsorption, followed by a vacuum treatment. From the adsorption isotherm, the total amount of adsorbed hydrogen was determined. Pumping out and adsorbing again at room temperature determined the amount of weakly adsorbed hydrogen [22,26]. The difference between the two isotherms determines the amount of strongly adsorbed hydrogen on the ruthenium crystals.

2.3. Catalyst testing

After reduction, the catalysts were passivated by treatment with 1000 ppm O_2 in N_2 at room temperature. Then the samples were weighed and transferred to a testing unit [27]. After reduction of the passivated catalysts at 450 °C in synthesis gas, the activity was measured at 400 °C in a 3 : 1 H_2/N_2 mixture at 50 bar. The catalytic activity data are reported on basis of the amount of catalyst loaded into the reactor.

2.4. Transmission electron microscopy

HRTEM studies were carried out on a Philips CM-200 FEG transmission electron microscope (TEM), equipped with an UltraTwin lens giving an information limit of about 1.2 Å. For spectroscopy, the microscope is equipped with an EDAX EDS detector and a Gatan DigiPEELS 766 electron energy-loss spectrometer (EELS). This system gives an energy resolution of ~1 eV up to energy losses of ~1500 eV. All images were recorded with an MSC 794 multiscan CCD camera and DigitalMicrograph software, both from Gatan Inc. The processing of images was conducted with Image Pro+. For TEM/EELS analysis, the catalyst material was mechanically crushed and dispersed onto Cu grids coated with a holey carbon film.

Particle-size distributions of the Ru crystals were determined from contrast-enhanced TEM micrographs. Particle-size distributions were derived from TEM micrographs treating the crystals as spherical objects. More than 500 crystals were included in the distribution for each catalyst. High-resolution imaging of Ru crystal surfaces was carried out in order to elucidate the location of the Ba promoter, *i.e.*, to study to what extent barium was present on the surfaces of the Ru crystals.

Electron energy-loss spectroscopy was used to determine the composition of such surface coverings. The electron energy-loss edges of the elements of interest here, *i.e.*, the ruthenium $M_{4,5}$-edge, the barium $M_{4,5}$-edge, and the oxygen K-edge, are separated by more than 200 eV, making them clearly distinguishable and suitable for EELS analysis. All electron energy-loss spectra were collected in image mode [28].

3. Results

The surface areas of the support materials were determined by the BET-method and the results are shown in table 1.

After impregnation with Ru, H_2 chemisorption analyses were carried out to obtain estimates of the exposed surface areas of the Ru crystals. The Ru-dispersions determined from the amount of strongly adsorbed H_2 are calculated assuming that one surface Ru atom chemisorbs one H atom and that the exposed facets on the Ru crystals are the close-packed (001) facets. When comparing these numbers with the dispersions obtained by TEM, it should be noted that the TEM values represent the entire surface area of the crystals. The H_2 values only reflect the surface areas that are exposed to the gas phase, *i.e.*, surface atoms covered by the support are not measured. The results

Table 1
BET, N_2 adsorption/desorption, and H_2 adsorption.

Support material	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore radius (nm)
Carbon (graphitized)	292.0	0.464	3.2
$MgAl_2O_4$	209.0	0.601	5.8
Si_3N_4	12.5	0.198	31.7

Table 2
H_2 chemisorption data.

Sample	Disp. H_2 (%)	Disp. TEM (%)	Disp. H_2 after Ba prom. (%)	Disp. TEM after Ba prom. (%)
Ru/C	10	30	32	30
Ru/$MgAl_2O_4$	25	68	35	75
Ru/Si_3N_4	8	8	8	9

Table 3
Mean Ru particle diameter as determined by TEM.

Sample	d before promotion (nm)	d after promotion (nm)
Ru/C	1.9	2.7
Ru/$MgAl_2O_4$	1.6	1.3
Ru/Si_3N_4	3.7	4.4

are presented in table 2. Due to the pretreatment of the catalysts prior to H_2 chemisorption, these values are compared to those obtained by TEM after activity testing. We notice a difference between the dispersion calculated from H_2 chemisorption and TEM data for both the Ru/C and the Ru/$MgAl_2O_4$. For Ru/C, this was previously ascribed to partial coverage of Ru by the support material [29]. This coverage of the Ru crystals was suppressed after the addition of Ba in agreement with the present finding. Due to the uncertainty in the interpretation of the dispersions determined by H_2 chemisorption, the dispersions were determined accurately by TEM.

The catalysts were all tested at temperatures between 320 °C and 440 °C. Figure 1 shows the activities determined at 400 °C using different flow rates of the synthesis gas. It is seen that the activity increase by promotion is significant. Specifically, an activity increase by a factor of ~2000 upon promotion with Ba is seen for the Si_3N_4-supported catalyst, whereas only smaller increases in the activities are found for the other two catalysts, *i.e.*, a factor of ~15 for Ru/C and a factor of ~2 for Ru/$MgAl_2O_4$. For a thorough account on the catalytic activity of the unpromoted catalysts, see [22].

From table 2, it is seen that the promotion does not have a significant impact on the dispersions as determined by TEM. For the H_2 chemisorption data, there is a significant change in the dispersion of the Ru/C catalyst, as discussed above. The dispersions calculated for the promoted catalysts using the two methods are in reasonable agreement for the Ru/C and Ru/Si_3N_4 catalysts. The mean metal particle diameter does not change significantly upon promotion for any of the samples (see table 3). For Ru/Si_3N_4, the influence from very large crystals has been excluded from the calculation of the mean particle size since they obscure the result.

From low magnification TEM micrographs, the morphology of the Ru crystals is also found to be unchanged upon promotion. Hence, no dramatic increases in the number of active sites are expected. Therefore, the recent suggestion that barium is a structural promoter does not seem to be supported [29]. Figure 2 shows a typical high-resolution TEM micrograph of Ba-Ru/C. The surface of the Ru crystal is partly covered with a monolayer of another phase (arrowed).

Figure 3 shows the Ba-Ru/$MgAl_2O_4$ catalyst. In this sample no surface features are observed on the Ru crystals. Thus, it seems that the difference between the dispersion obtained by TEM and that obtained by H_2 chemisorption may be due to the support covering—just as is the case for Ru/C. However, in Ru/$MgAl_2O_4$ the barium does not suppress such coverings.

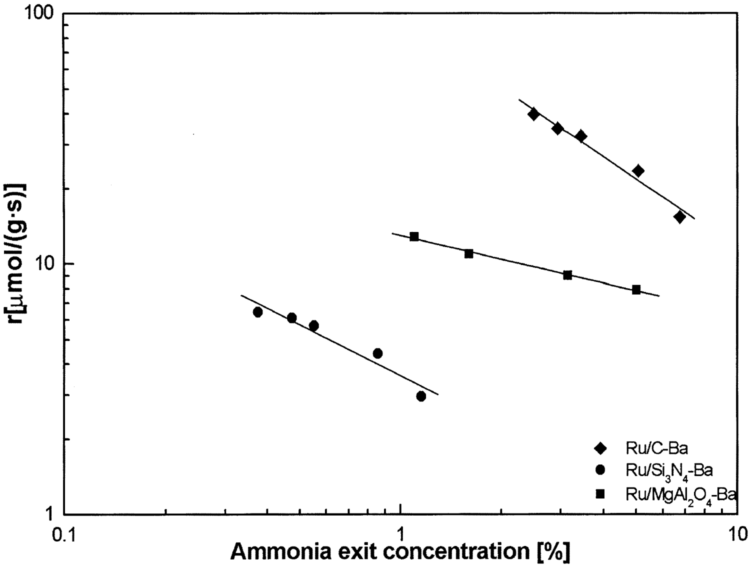

Figure 1. Catalytic activity of supported ruthenium catalysts promoted with barium, measured at 400 °C and 50 bar in a 3 : 1 mixture of H_2/N_2.

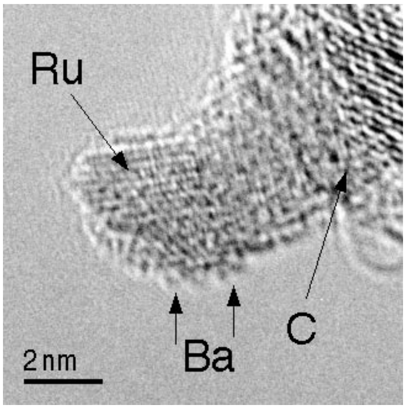

Figure 2. HRTEM micrograph of Ba-Ru/C.

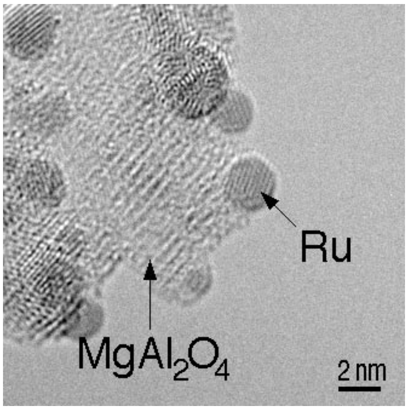

Figure 3. HRTEM micrograph of Ba-Ru/$MgAl_2O_4$.

Figure 4 shows the Ba-Ru/Si_3N_4 catalyst. Here, surface features are clearly evident on multiple facets of the Ru crystal. The periodic spacing between these features closely match the (011) lattice spacing of BaO (3.9 Å).

Figure 5 shows the energy-loss spectrum from Ru/Si_3N_4. The peak at 532 eV is the K-edge of O, the peaks at 781 eV and 796 eV are the Ba $M_{5,4}$-edges. No oxygen peak is observed in spectra of the unpromoted catalyst, indicating that the oxygen observed must be part of a BaO_x phase.

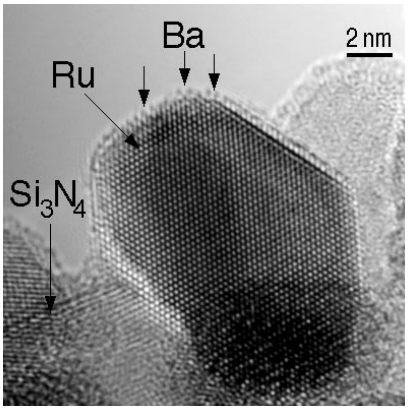

Figure 4. HRTEM micrograph of Ba-Ru/Si_3N_4.

4. Discussion

Table 1 illustrates the different porosities of the support materials used. For all catalysts, the pore sizes are sufficiently large so that mass-transfer effects do not influence the activity data. The surface areas given in table 1 show that the surface area of $MgAl_2O_4$ is larger than that of carbon and much larger than that of Si_3N_4. Table 2 shows that dispersions of the unpromoted catalysts obtained from TEM are larger than those obtained by chemisorption for two of the samples. Kowalczyk *et al.* [29] show a similar effect for a carbon-supported catalyst and ascribe the effect to covering of the metal particles by support material. It is also found that the promotion suppresses this effect for Ru/$MgAl_2O_4$. Kowalczyk *et al.* [29] argue that the promoter prevents the support material from covering the metal particles. This argumentation is substantiated by the dispersion data presented here. For Ba-Ru/C and Ba-Ru/Si_3N_4, no significant differences in dispersion are observed. From the activity data (figure 1), it is evident that the promotion has the most marked effect on the activity of the Si_3N_4-supported catalyst. Whereas the activities of the other catalysts are also increased upon promotion, the effect is not as pronounced. Since the increase in activity could not be explained solely from the dispersion data in accordance with previous reports, we decided to make use of high-resolution transmission electron microscopy to elucidate the position of the promoter. Recently, *in situ* HRTEM showed that the Ba promoter of a supported Ru catalyst is present as a monolayer on the surface of the Ru crystals during reaction conditions. However, such *in situ* TEM studies are currently not widely available and are also very time-consuming. Therefore, we decided to study the promoted Ru catalysts after passivation by conventional TEM. As seen from table 3, the Ba promotion does not significantly alter the mean particle size. At least the observed changes are much too small to be the cause of the observed changes in activity. This strongly suggests that the changes result from electronic promotion by the surface compound. HRTEM imaging of the surfaces of the ruthenium crystals were carried out. On the Si_3N_4-supported catalyst, surface coverings were detected on most Ru crystals (see figure 4). The spacings found between the dark features on the surface of the ruthenium crystal can be identified with lattice spacings in the BaO structure. In the HRTEM micrographs of the $MgAl_2O_4$ and C supported catalysts, these overlayers on the Ru crystal surfaces are not as evident. On Ba-Ru/C, overlayers were detected only on a small number of the crystals, and on Ba-Ru/$MgAl_2O_4$, no overlayers were found at all. EELS analysis was carried out on the surface layer of the Ru/Si_3N_4 sample. The spectra show the presence of both oxygen and barium. Based on these findings, the surface layer is tentatively ascribed to a BaO_x phase. This agrees well with the catalytic data

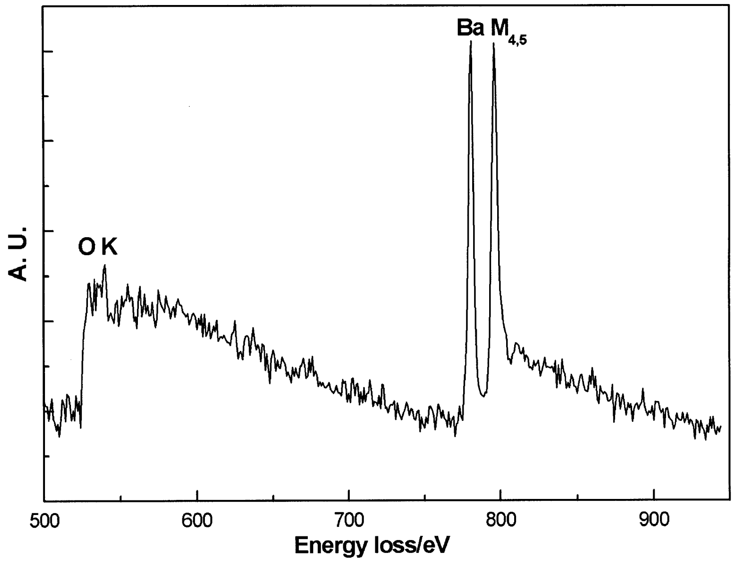

Figure 5. EELS spectrum of Ba-Ru/Si_3N_4.

where a large increase is found for the Si_3N_4, more than two orders of magnitude, and only small increases for the others. It also complies with DFT calculations, showing that an electronic promoter will only have a significant influence on the activity if it is situated in the vicinity of the active sites [30,31].

Earlier studies were carried out to determine the active sites on an Ru single crystal [15,16,17]. These studies showed that the dissociation of N_2 was totally dominated by steps on the surface. The sites found at the steps are of B_5-type, characterized by having five contact points for a chemisorbing molecule [20]. These sites are $>10^9$ times more active than sites on the terraces of the Ru (001) surface. Adding the electronic promoter to the catalyst, the BaO_x phase located near B_5-type sites will electrostatically modify the potential around these sites, making them even more active for N_2 dissociation [23]. Figure 6 shows a model of a surface containing two distinct B_5-type sites. Figure 7 shows a model of how the barium is thought to electrostatically promote the ruthenium in the catalytic synthesis of ammonia.

Based on the above results, we propose the following explanation of the Ba-promotion of Ru catalysts for ammonia synthesis. The promotional effect of barium on supported ruthenium-based catalysts depends to a large extent on the choice of support material. The promoter must be located at positions near active B_5-type sites to significantly enhance the activity for catalytic ammonia synthesis. The amount of promoter in the right location is determined by the relative affinities of the promoter for the support and for the metal surface. For support materials with high acidity or a large number of non-basic $-OH$ groups, the promoter material is likely to be located on the support rather than on the ruthenium surface. Consequently, suitable

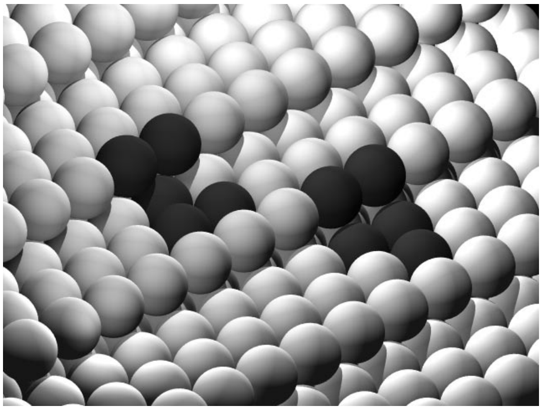

Figure 6. B_5-type sites. N_2 adsorbs on the surface with one atom in the bridge site and one atom in the three-fold hollow site. Two distinct sites are shown black. The facet shown is the (105) of Ru.

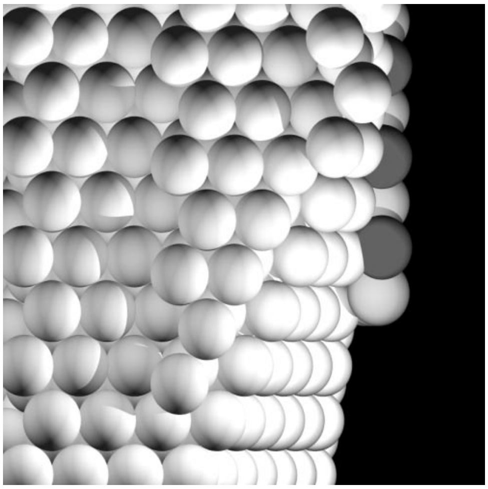

Figure 7. A ruthenium crystal with a layer of BaO on the surface (Ba: light gray; O: dark gray; Ru: white). This surface layer is suggested to promote N_2 dissociation through electrostatic interactions with N_2 during the dissociation process.

support materials for promoted ammonia synthesis catalysts have either basic or non-reactive surfaces. This explains why graphite, boron nitride and magnesium oxide have been found to be useful support materials. The promotion of ruthenium by barium is suggested to be of an electronic nature since no structural modifications of the Ru crystals are observed and since the activity increase is correlated with the amount of surface coverings by barium. This means that the primary effect of barium is to lower the activation energy for N_2 dissociation as has similarly been suggested for Ba-Co/C catalysts [33]. Furthermore, the changes found in surface areas and dispersions of the ruthenium catalysts are not sufficiently large to account for the increase in catalytic activity. As expected from the dispersion data, the catalytic activity of Ba-Ru/$MgAl_2O_4$ is almost unchanged upon promotion. The small Ba surface covering found on Ba-Ru/C, together with the modest increase in activity, substantiate the conclusion that the promotional effect is of an electronic nature. Similar results were found for Ru supported on BN [13].

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