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Structure sensitivity of supported ruthenium catalysts for ammonia synthesis

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Abstract

The catalytic ammonia synthesis activities of four supported ruthenium catalysts are reported. It is seen that Ru/MgAl₂O₄ is more active than two similar Ru/C catalysts, which are significantly more active than Ru/Si₃N₄. The activity differences cannot be satisfactorily explained solely by the differences in dispersion. Recent results from single crystal studies and DFT calculations have shown that ammonia synthesis over ruthenium catalysts is a very structure sensitive reaction, more so than on iron catalysts. It is suggested that special B₅-type sites are primarily responsible for the catalytic activity of the present supported Ru catalysts. It is shown how the number of such B₅-type sites depends on the Ru crystal size for a given crystal morphology. We have found that the activity of the Ru/MgAl₂O₄ catalyst increases significantly during the initial part of a test run. This activity increase is paralleled by the disappearance of crystals smaller than ca. 1.0 nm due to sintering and a resulting formation of larger crystals. We conclude that there exists a lower limit to the desired crystal size of Ru in supported ammonia synthesis catalysts. This is in agreement with a low number of B₅-type sites expected for such crystal sizes. Furthermore, we suggest that the support plays a decisive role in controlling the morphology of the Ru crystals and the resulting change in abundance of B₅-type sites is the main cause for the significant activity variations observed for Ru catalysts with different supports. Finally, the support may also influence the electronic and catalytic properties of neighboring B₅-type sites. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Ammonia synthesis; Structure sensitivity; B₅ sites

1. Introduction

The catalytic ammonia synthesis technology has played a central role in the development of the chemical industry during the 20th century. This industrial importance has been paralleled by a significant scientific interest in understanding and improving the

ammonia synthesis catalyst. Often new techniques, methods, and theories of catalysis have initially been developed and applied in connection with studies of this system. Similarly, new discoveries in the field of ammonia synthesis have been extended to other areas of catalysis. The combined influence of refined characterization techniques, improved kinetic analyses, and new possibilities in theoretical modeling has led to a detailed insight into the fundamentals of ammonia synthesis catalysts. Several recent reviews give a comprehensive account of the current understanding

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of catalytic ammonia synthesis [1–4]. It is an interesting paradox that despite these efforts the industrial ammonia synthesis catalyst is still very similar to that developed by Mittasch and co-workers.

Ammonia synthesis over iron-based catalysts is the standard textbook example of a structure sensitive [5] heterogeneous catalytic reaction. This was first evident by the variation of the turnover frequency (TOF) with metal particle size, the TOF being higher for large Fe particles than for small ones in an Fe/MgO catalyst [6,7]. Later, measurements of the rate-determining step, the N₂ dissociation [8,9], as well as the ammonia synthesis rate over different Fe surface planes on single crystals [10,11] provided independent support of the structure sensitivity. The Fe(1 1 1) surface is superior to the Fe(1 0 0) and the Fe(1 1 0) surfaces in both reactions. The conclusion from this pioneering surface science study [10,11] and the studies of small iron particles was that the most active site for ammonia synthesis over iron is an ensemble of Fe atoms including a C₇ atom, i.e. a surface atom with seven nearest neighbors. The experimental findings on the Fe(1 1 1) surface have been supported by Density Functional Theory (DFT) calculations [12].

It was first realized by the group of Haber that ruthenium catalysts are potentially interesting ammonia synthesis catalysts [13] and later the work of Ozaki and Aika [3] has led to renewed interest in such catalysts. Recently, promoted Ru/C catalysts have been introduced in commercial operation [14–18]. However, it is still not clear whether the significantly higher cost and shorter life-time is justified by the higher activity compared to traditional iron-based catalysts.

From recent single crystal studies, DFT calculations, and studies of supported catalysts it was found that ammonia synthesis over ruthenium is an even more structure sensitive reaction than over iron-based catalysts [19–22]. Based on these results, dramatic support and particle size effects can be expected and in order to obtain a more detailed understanding of this structure sensitivity we have conducted an investigation of a series of ruthenium catalysts supported on different materials. From these studies it is apparent that the activities of such catalysts are very dependent on the choice of support. The present high resolution electron microscopy studies suggests that these activity variations can be attributed to a combined in-

fluence of the crystal size distribution and the support induced morphology of the ruthenium crystals.

2. Experimental

2.1. Catalyst preparation

Powdered magnesium aluminum spinel [23] and α -Si₃N₄ (obtained from H.C. Starck) were pressed into pellets using an IR press. Carbon extrudates (Norit RO 0.8) were graphitized at 1900°C according to the procedure of Kowalczyk et al. [24]. The catalyst supports were crushed and sieved to a particle size of 0.1–0.2 mm prior to Ru impregnation using incipient wetness impregnation with ruthenium nitrosyl nitrate (Johnson Matthey). The impregnated support materials were dried at room temperature overnight and reduced at 1 bar in flowing hydrogen at 450°C for 48 h.

2.2. Catalyst testing

After reduction the catalysts were passivated by treatment with 1000 ppm O₂ in nitrogen at room temperature. Subsequently, the sample was weighed and transferred to the testing unit previously described [25]. The catalytic activities were measured after reducing the passivated catalyst at 450°C in synthesis gas. The catalytic activities are reported on basis of the amount of catalyst loaded into the reactor.

2.3. Transmission electron microscopy

TEM images were recorded using a Philips CM200 FEG instrument equipped with an UltraTwin lens (information limit 0.12 nm), EDS and PEELS detectors. The operating voltage was 200 kV. Images were obtained *ex situ* from reduced and passivated samples, and from samples passivated after reactor tests. For each sample, crystal size distributions were obtained from 10 to 20 images recorded at a magnification of 300 000 \times . Image processing, i.e. automatic crystal identification, counting, and measurements were carried out using the ImagePro+ software. To obtain a crystal size distribution the diameter of 500–600 crystals in each sample were measured and the

dispersion was calculated assuming spherical crystal morphology.

2.4. N_2 adsorption/desorption

Surface areas of support materials and reduced catalysts were obtained from dinitrogen adsorption and desorption using a Quantachrome Autosorb analyzer.

2.5. H_2 adsorption

The hydrogen chemisorption was conducted as described by Fastrup [26] for a series of Ru/MgAl₂O₄ catalysts.

3. Results

All catalysts were prepared using ruthenium nitrosyl nitrate as a precursor and the supports were shown by chemical analyses to contain negligible (<15 ppm) amounts of possible poisons such as chlorine or sulfur. Low concentrations of impurities have been shown to be able to significantly alter the reaction kinetics of supported Ru catalysts [27]. It has been shown that oxygen poisoning is negligible in the present testing unit [25]. The compositions of the four catalysts studied are summarized in Table 1 together with the surface areas and pore radii of the support materials.

Table 1
Selected data for supported ruthenium catalysts^a

Catalyst	Ru (wt.%)	Surface area (m ² /g)	Average pore radius (nm)
Ru/MgAl ₂ O ₄	6.8	209	5.8
Ru/carbon(1)	9.9	123	4.4
Ru/carbon(2)	5.4	123	4.4
Ru/Si ₃ N ₄	7.6	12.5	31.7

^a Surface area and pore radius determined from N₂ adsorption/desorption data.

The testing was conducted in 3:1 and 1:1 mixtures of dihydrogen and dinitrogen at temperatures of 320, 360, 400, and 440°C at 50 bar. The space velocity was varied to study the influence of the ammonia exit concentration on the reaction rate. Fig. 1 shows the catalytic activities of the four catalysts tested in a 3:1 mixture of H₂ and N₂ at 400°C.

In all cases the activity increased by a factor of 2–3 when the catalysts were tested in a 1:1 mixture of H₂ and N₂. Apparent activation energies for the four catalysts are given in Table 2. These activation energies are reported for constant flow since calculations of the activation energies at constant conversions unfortunately would require extensive extrapolations of our activity data.

Figs. 2–4 illustrate transmission electron micrographs obtained from Ru/carbon(1), Ru/MgAl₂O₄, and Ru/Si₃N₄, respectively. The micrographs shown were obtained prior to the catalysts testing.

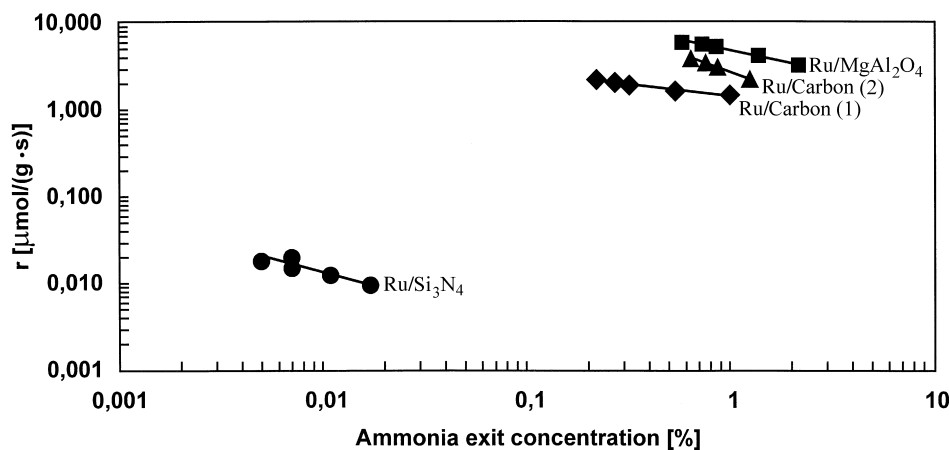


Fig. 1. Catalytic activity of supported ruthenium catalysts measured at 400°C and 50 bar in a 3:1 mixture of H₂/N₂. (◆) Ru/carbon(1); (▲) Ru/carbon(2); (■) Ru/MgAl₂O₄; (●) Ru/Si₃N₄.

Table 2

Activation energies obtained at constant flow for supported ruthenium catalysts^a

Catalyst	$E_{a,CF}$ (kJ/mol)
Ru/MgAl ₂ O ₄	60
Ru/carbon(1)	112
Ru/carbon(2)	110
Ru/Si ₃ N ₄	131

^a It should be noted that due to the very different activities the activation energies are obtained under widely varying ammonia concentrations.

In all cases micrographs were also obtained from the samples after testing. The dispersions determined by TEM and H₂ chemisorption before testing are shown in Table 3. The H₂ dispersions are obtained by considering only the strongly bound hydrogen and by assuming a surface stoichiometry of H/Ru = 1. The TEM dispersions were calculated by assuming spherical Ru crystals without contact to the support.

It was observed that the Ru/MgAl₂O₄ catalyst increased its activity during the initial part of the testing. This behavior is contrary to the other catalysts studied, which exhibited very stable activities throughout the test runs. Therefore, we decided to follow the activity of the Ru/MgAl₂O₄ catalyst in more detail. In Fig. 5 below it is seen how the activity increases during the

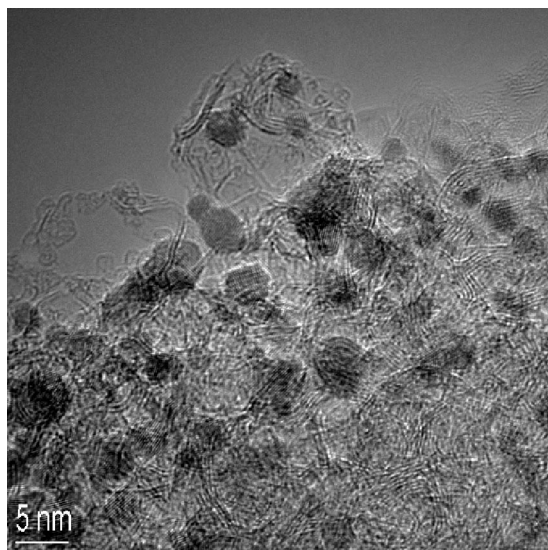
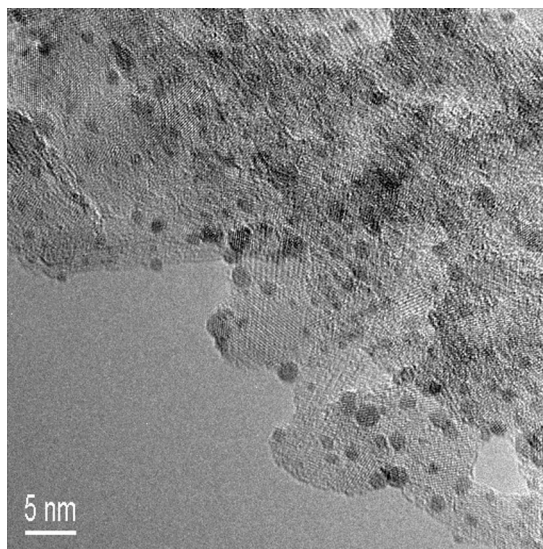


Fig. 2. TEM image of Ru/carbon(1).

Fig. 3. TEM image of Ru/MgAl₂O₄.

test run. The reported activity data for Ru/MgAl₂O₄ (e.g. Fig. 1) were obtained from measurements after the activity reached a stable level. To check that the activity increase is not related to the catalyst not being fully reduced we carried out a temperature programmed reduction (TPR) experiment (up to 600°C) of the catalyst in 1% dihydrogen in argon at 1 atm. It

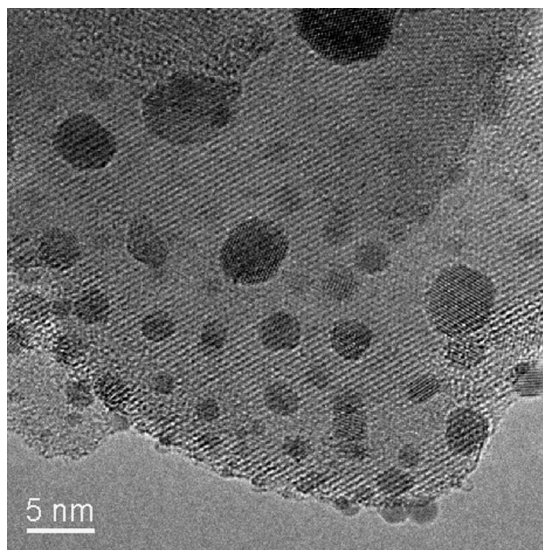
Fig. 4. TEM image of Ru/Si₃N₄.

Table 3
Average ruthenium crystal sizes/dispersions before testing determined by TEM and H₂ chemisorption

Catalyst	Dispersion prior to test (%)	
	H ₂	TEM
Ru/MgAl ₂ O ₄	29	68
Ru/carbon(1)	17	19
Ru/carbon(2)	20	37
Ru/Si ₃ N ₄	20	7

was found that under these conditions the reduction is complete at 450°C and it appears reasonable to assume this is also the case when the partial pressure of dihydrogen is significantly higher. In Fig. 6, we have shown the crystal size distribution of the Ru/MgAl₂O₄ catalyst after reduction (corresponding to situation A in Fig. 6) and after the activity test (corresponding to situation F in Fig. 5).

4. Discussion

Table 1 shows some selected data for the catalysts studied. It is seen that the surface areas of MgAl₂O₄ and the carbon are significantly higher than that of α -Si₃N₄. For all catalysts the pore sizes are large enough that the activity data are not influenced by mass transfer limitations at the relatively low conversions reported (this has been shown to be the case for

much more active catalyst under the same conditions [25]).

From Fig. 1 it is seen that the activity varies by more than two orders of magnitude for the different catalysts. The one supported on MgAl₂O₄ is more active than the carbon supported catalysts which is much more active than the Si₃N₄ supported catalyst. Si₃N₄ has not attracted much interest as a catalyst support although it has several interesting properties and can be prepared with a high surface area. Recently, a palladium/Si₃N₄ was reported to be active in methane oxidation [28]. For ammonia synthesis Si₃N₄ could be interesting [29] since it is stable to hydrogenation contrary to carbon supports [30]. From Table 2, it is seen that the apparent activation energies vary significantly for the different catalysts. Aika et al. [31–33] and Rosowski et al. [34] have previously reported that both the activity and activation energy seem to depend strongly on the choice of support material and promoter. Aika et al. attempted to correlate the activity with the electronegativity of the support [3,32,33]. In their data both promoted and unpromoted catalysts are included and a fair correlation can be achieved. However, recent DFT calculations show that the promoter can only exert a significant influence on the activity if it is situated in the immediate neighborhood of the sites for dinitrogen dissociation [35,36].

In Table 3, the dispersions calculated from TEM and H₂ chemisorption are given. It is seen that no satisfactory agreement between the numbers can be found.

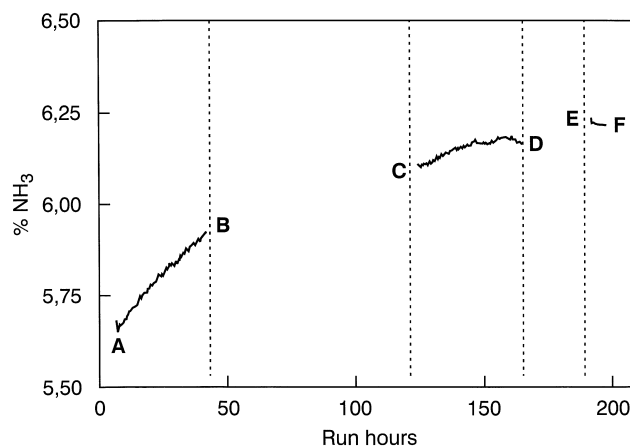


Fig. 5. Catalytic activity at 475°C and 50 bar in 3:1 H₂/N₂ of Ru/MgAl₂O₄ as a function of time on stream and pretreatment conditions. (A) Reduction at 450°C; (B, C) 500°C in synthesis gas; (D, E) 550°C in synthesis gas; (F) end of run.

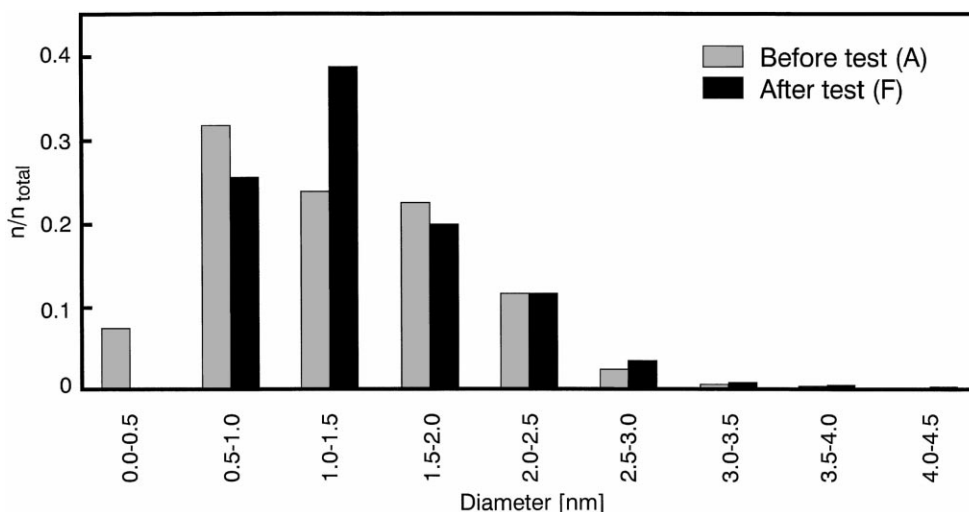


Fig. 6. Crystal size distribution determined by TEM of Ru/MgAl₂O₄ before (A) and after (F) test conditions shown in Fig. 5.

It has recently been shown by Kowalczyk et al. [37] that the dispersions obtained from H₂ chemisorption on Ru/carbon catalysts are not reliable. Therefore, a careful study of the transmission electron micrographs was conducted to obtain accurate estimates of the particle sizes and these numbers will also be used in the following discussion. It is seen that the activity difference between the carbon supported and magnesium aluminum spinel supported catalysts can be explained by the difference in the number of active sites calculated from the metal concentrations and the TEM dispersions but not from the hydrogen chemisorption data. Also, the two catalyst systems show quite different activation energies. The activity of the Si₃N₄ supported catalyst is much lower than expected based on either the TEM or H₂ dispersions. The present results show, in agreement with previous work [3], that there is no direct correlation between the activity of Ru supported on different supports and the dispersion. In our recent microkinetic analysis we have shown that an excellent fit to the activity data can be obtained by taking the structure sensitivity of a Ru/MgAl₂O₄ catalyst into account [21].

Single crystal studies and DFT calculations [19,20] have indicated that the most active sites for N₂ dissociation and ammonia synthesis are ensembles of five Ru atoms fulfilling two requirements: (1) they have to expose a three-fold hollow site and a bridge site close together and (2) part of the atoms have to be

low-coordinated surface atoms such as edge atoms on small crystals. By fulfilling these requirements it is secured that the two nitrogen atoms of a dinitrogen molecule are not simultaneously bonded to the same Ru surface atom during dissociation. In the terminology of Van Hardeveld and Van Montfoort [38] these active sites are B₅ sites involving edge atoms. In their analysis of marble models of Ni fcc crystals with a basic cubo-octahedral morphology, they found that B₅ sites were only present on crystals with a size larger than ca. 1.5 nm. The maximum probability for B₅ sites was found for particles of 1.8–2.5 nm and for particles larger than that, the probability for B₅ sites monotonically decreased. In Fig. 7, we have similarly counted the relative number of B₅-type sites, which are part of edges on small Ru crystals with only hcp (001) and (100) surfaces exposed.

Our results show the same trend as calculated by Van Hardeveld and Van Montfoort [38]. The reason for the lack of B₅-type sites on very small crystals is identical in the two calculations; the crystals simply have to be of a certain size before the ensembles are formed. However, in our case the decreasing fraction of B₅-type sites with increasing crystal size is not due to a general decrease in the number of these sites but to the fast decrease in the fraction of edge atoms as also shown in Fig. 7. These arguments are general for any crystal morphology, hence a maximum in the number of the most active sites at some intermediate crystal

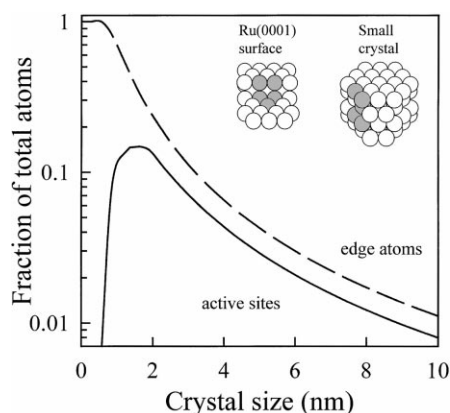


Fig. 7. Fraction of edge atoms and active sites on small Ru crystals relative to the total number of atoms as a function of crystal size. The numbers are obtained from crystal models (see insert) exposing only (001) and (100) hcp surface planes. The active sites are present at the (100) surface. They consist of five Ru atoms exposing a three-fold hollow hcp site and a bridge site close together (a B₅-type site) where part of the atoms are edge atoms. This criterium is based on the structure of the active step site on the Ru(0001) surface also shown.

size should always be found. A maximum in ammonia synthesis activity would also be found if the number of active sites was taken relative to the number of surface atoms since the number of edge atoms is decreasing more rapidly than the number of surface atoms.

In the transmission electron micrographs of the four catalysts studied (see Figs. 2–4) it is found that a significant fraction of the Ru crystals exhibit a hexagonal morphology. The crystal size distributions are generally broad and no specific orientation of the Ru crystals relative to the support seems favored in the Ru/C and Ru/MgAl₂O₄ catalysts.

However, in the micrographs of Ru/Si₃N₄ it is seen that the Ru crystals appear to be faceted by the support material (Fig. 4 is typical for Ru/Si₃N₄), i.e. the edges of the Ru crystals are parallel to the lattice planes of the Si₃N₄ support. Such an effect is not observed for the Ru/C but cannot be excluded for the Ru/MgAl₂O₄ catalyst.

In Fig. 5, it is shown how the activity of Ru/MgAl₂O₄ progressively increases during the initial part of the test run. It might be argued that the reduction has not been completed at the start of the run. However, this is not in agreement with our TPR results. To understand this activity increase, the crys-

tal size distribution was determined before and after the test run as shown in Fig. 6. It is seen, that the smallest crystals have disappeared and larger crystals have formed. Therefore, we conclude that there exists a lower limit to the optimal ruthenium crystal size as also suggested in Fig. 7. Previously, similar slow activation phenomena have been observed by Aika et al. [33] and by Bossi et al. [39] for promoted and unpromoted Ru/MgO catalysts, and by Jacobsen and Fastrup [40] for promoted Ru/MgAl₂O₄ catalysts, but the cause(s) for the activation was not determined.

In order to understand the activity pattern for the four Ru catalysts it appears necessary to take into account both the dispersion and the different interactions with the supports. It is suggested that both the size and the morphology of the Ru crystals is determined by the interaction with the support. This has a dramatic influence on the activity because of the extreme structure sensitivity. In addition to these structural and morphological effects we cannot exclude that electronic effects due to the support partially covering the Ru crystals may also be of importance. The difference in activation energies could be indicative of such a promotion/poisoning by the support and this might also explain why there is not a general agreement between the H₂ and TEM dispersions. When the activity is determined by very few sites it is necessary to be very careful relating activity differences to one specific effect.

The slow activation of unpromoted Ru catalysts also appears to be valid for promoted catalysts [3,39,40] and further studies are in progress to obtain more information about the behavior of promoted Ru catalysts on various support materials.

5. Conclusion

The catalytic ammonia synthesis over supported Ru catalysts is a very structure sensitive reaction. The activity depends on the crystal size as shown in Fig. 7 for a given morphology. Generally, the exact position of the maximum depends on the morphology of the ruthenium crystals and it appears that the morphology is influenced by the support material. This must be taken into account when rationalizing the activities of different supported Ru catalysts. From the inspection of crystal models combined with experimental obser-

vations it is concluded that there exists a lower limit to the optimal crystal size in supported ruthenium catalyst for ammonia synthesis. Optimal catalysts exhibit the highest possible concentration of B₅-type sites. The results indicate that partial coverage of the Ru crystals by the support may also take place and this may influence the electronic and catalytic properties. Due to the extreme structure sensitivity small changes in structural, morphological and electronic properties may have dramatic catalytic consequences and in view of the dominating role of a very low number of sites it may in real Ru catalyst systems be quite difficult to determine the relative role of the different effects.

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