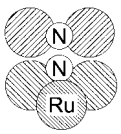
The Ammonia-Synthesis Catalyst of the Next Generation: Barium-Promoted Oxide-Supported Ruthenium

Hubert Bielawa, Olaf Hinrichsen, Alexander Birkner, and Martin Muhler*

Ammonia synthesis is one of the largest energy-consuming processes of the industrialized world requiring approximately 1% of the world's power production. Hence, searching for new and more efficient processes for ammonia synthesis is one of the important targets of chemical technology. Even in the early investigations carried out by Mittasch, which resulted in the industrially used multipromoted iron catalyst, ruthenium was tested as an active component.[1] Ruthenium was found to have the highest catalytic activity after osmium and iron. In the field of ruthenium catalysts the pioneering work was carried out by the Japanese group led by Aika. During the last three decades they prepared a huge number of different ruthenium catalysts containing various promoters and supports which were then investigated by means of a standardized screening procedure.[2]

Work carried out by Tennison and co-workers at British Petroleum (BP) finally led to a ruthenium catalyst of commercial interest. It consists of ruthenium on a specially pretreated carbon support (high surface area graphite, HSAG). The high catalytic activity was achieved by copromoting with cesium and barium.[3] This catalyst is used industrially in the low-energy, low-pressure ammonia synthesis process of Kellogg Brown & Root (KBR Advanced Ammonia Process, KAAP). Since 1998 the two largest plants world-wide for ammonia synthesis are operating in Trinidad with a capacity of 1850 tons of NH_3 per day, each employs the iron catalyst (in the first fixed bed) and the ruthenium catalyst (second to fourth fixed bed) in a multibed reactor.[4] However, the application of carbon-supported ruthenium catalysts is not without problems. The susceptibility of the support to methanization was drastically lowered by a special pretreatment but could not be completely eliminated.[5]

Recently, the question as to what is the active site on ruthenium catalysts was clarified. The Danish group led by Chorkendorff showed that the so-called B_5-type site **1** is responsible for the activity of ruthenium catalysts. The B_5-type site **1** consists of an arrangement of three ruthenium atoms in one layer and two further ruthenium atoms in the layer directly above this at a monoatomic step on an Ru(0001) terrace.[6] For the unpromoted ruthenium catalyst a simple geometric model, established by van Hardeveld and van Montfoort for nickel crystallites,[7] can be used to calculate the optimum size of the ruthenium particles, about 2 nm, to give the maximum number of B_5-type sites.[6] Our studies showed that the B_5-type sites also dominate the activity of promoted ruthenium catalysts (see Table 2).[8]



1·N_2

Herein we first present a solvent-free preparation method of supported ruthenium catalysts. Table 1 compares the results obtained with a catalyst prepared conventionally (by impregnation) with those of a catalyst manufactured in a solvent-free route. It is clearly evident that these two procedures lead to almost identical catalysts. The solvent-free way of preparation is based on the MOCVD technique (chemical vapor deposition of organometallic compounds) which decreases the number of necessary unit operations, avoids solvent effects, and has a significantly higher reproducibility. In Equation (1) a power-law rate expression is given

$$r = k p_{NH_3}^{\alpha} p_{N_2}^{\beta} p_{H_2}^{\gamma} \quad (1)$$

which is often used in chemical reaction engineering for the design of industrial reactors. A kinetic investigation based on this expression gave within the experimental accuracy limits (reaction orders: ± 0.1, activation energies: ± 2 kJ mol^{-1}) identical parameters for the catalysts prepared in both ways (Table 2) thus confirming their similarity.

Table 1. Characterization of two Ru/MgO catalysts prepared either by impregnation or by MOCVD.

	Impregnation	MOCVD
Specific surface area (BET) [$m^2 g^{-1}$]	56	51
Specific Ru surface area[a] [$m^2 g^{-1}$]	12.2	12.2
Ru content (ICP-OES analysis) [wt%]	3.3	3.4
Dispersion[a] [%]	75	73
Ru particle size[b] [nm]	1.3	1.4
Production rate[c] [mmol NH_3 $g^{-1} h^{-1}$]	0.35	0.37

[a] Measured by static H_2 chemisorption. [b] Assuming spherical particles. [c] $T = 588$ K, $p = 0.1$ MPa).

Table 2. Comparison of the reaction orders of the Ru/MgO catalysts and the Ba-Ru/MgO catalyst.

Catalyst	p [MPa]	T [K]	$\alpha(NH_3)$	$\beta(N_2)$	$\gamma(H_2)$	E_a [kJ mol^{-1}]
Ru/MgO (impreg)	0.1	543–623	−0.5	0.9	−0.4	74
Ru/MgO (MOCVD)	0.1	543–643	−0.6	0.8	−0.5	76
Ru/MgO (MOCVD)	2	588–673	−0.6	0.8	−0.7	79
Ba-Ru/MgO	2	513–588	−0.6	0.8	−0.6	77

Catalytic measurements with various samples showed that both preparation methods lead to catalysts with activities between the maximum described by trace d (Figure 1) and the minimum described by curve e in Figure 1. These unpromoted, oxide-supported ruthenium catalysts are less active than the industrially used multipromoted iron catalyst (trace c). In contrast, cesium-promoted ruthenium catalysts display an activity many times higher than that of the industrial iron catalyst (trace b). The activity at 588 K is three to four times higher than that of the iron catalyst.[9] Promoting oxide-supported ruthenium catalysts with barium resulted in

[*] Prof. Dr. M. Muhler, Dr. H. Bielawa, Dr. O. Hinrichsen
Laboratory of Industrial Chemistry
Ruhr University Bochum
44780 Bochum (Germany)
Fax: (+49) 234-32-14115
E-mail: muhler@techem.ruhr-uni-bochum.de
Dr. A. Birkner
Physical Chemistry I
Ruhr University Bochum

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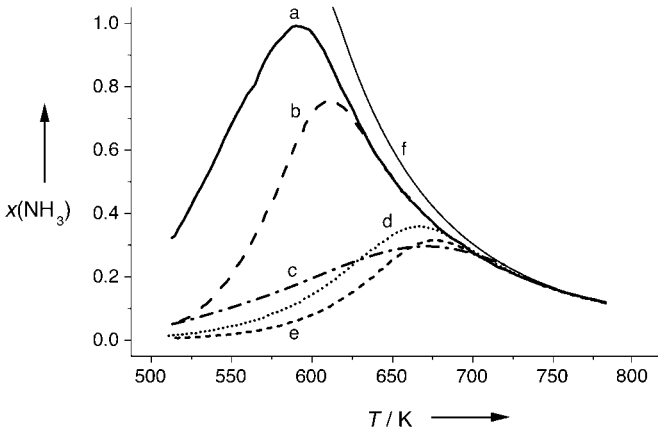

Figure 1. Catalytic activity of a) the barium-promoted catalyst (Ba-Ru/MgO), b) the cesium-promoted catalyst (Cs-Ru/MgO), c) the industrial iron catalyst, d, e) unpromoted Ru/MgO catalysts (Ru/MgO), and f) values of ammonia mole fractions at equilibrium are shown. Measurements were performed using a mixture of $p_{N_2}:p_{H_2}=1:3$ ($Q=40\ mL\,min^{-1}$ (STP), $p=0.1$ MPa) at quasi-stationary conditions while decreasing the catalyst-bed temperature ($2\ K\,min^{-1}$). All measurements were conducted in our microreactor set-up using the same conditions. $x(NH_3)$ is given in %.

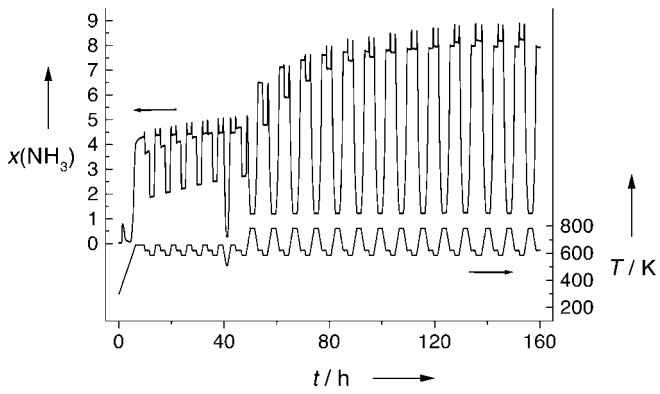

Figure 2. Activation of the barium-promoted catalyst as a function of temperature and time. Conditions: $p_{N_2}:p_{H_2}=1:3$, $Q=40\ mL\,min^{-1}$ (STP), $p=0.1$ MPa. $x(NH_3)$ as a function of time (top curve) is given in 10^3 ppm; the bottom curve shows the temperature change with time.

catalysts (trace a) with the highest activity of all the catalysts reported so far including the commercial ruthenium/carbon catalyst.[3, 8] The activity of the barium-promoted catalyst in the kinetically controlled regime up to approximately 600 K is an order of magnitude higher than that of the iron catalyst. This sequence of activity remains unchanged even at high pressures. Barium-promoted catalysts lead to more than double the yield of NH_3 compared with a cesium-promoted catalyst under roughly the same high-pressure conditions (Table 3). To reach such a high yield with the industrial iron catalyst, a pressure of 10.7 MPa instead of 5 MPa (for the Ba-Ru/MgO system) and higher temperatures would be necessary. The generation of such high pressures is a key part of the energy demand in the conventional ammonia synthesis process.

Table 3. Comparison of high-pressure activity of Ru/MgO, Cs-Ru/MgO, Ba-Ru/MgO, and the industrial multiply promoted iron catalyst. Results are expressed as NH_3 mole fraction in the effluent using a GHSV (gas hourly space velocity) of about $16000\ h^{-1}$.

	T [K]	p [MPa]	GHSV [h^{-1}]	Q [$mL\,min^{-1}$ (STP)]	$x(NH_3)$
Ru/MgO	783	5	13900	40	5.04
Cs-Ru/MgO	665	5	13900	40	5.90
Ba-Ru/MgO	684	5	16100	40	12.8
Iron[a]	723	10.7	16000	305	13.2

[a] Data taken from ref. [10].

Figure 2 indicates the lengthy activation procedure and the dependence of the catalytic activity on the reduction temperature for the barium-promoted catalyst. During the activity measurement the reduction of the catalyst took place by increasing the catalyst-bed temperature in a flow of synthesis gas. The maximum temperature during an activity measurement thus corresponds to the maximum reduction temperature. After approximately 45 h steady state was still not achieved (upper part of Figure 2). By increasing the maximum temperature from 663 to 783 K after about 50 h (lower part of Figure 2) the catalytic activity almost doubled at the measurement temperature of 588 K and continued to rise during the measurement. Finally, after more than 120 h a constant catalytic activity was achieved. This example clearly demonstrates the limits of conventional fast-screening methods used, for example, by Aika et al; they would have found only a moderate activity of the Ba-Ru/MgO-catalyst.[11] In spite of a large number of experiments in the field of supported Ru catalysts during the last 30 years, Aika et al. did not discover the most active catalyst because of the fast and not sufficiently thorough testing method. The same risk is inherent to highly developed throughput methods in which the time on stream can be less than one minute per sample.[12] However, if the catalyst screening is accelerated by using several reactors connected in parallel, then the risk of wrong assessment of catalysts requiring long activation periods is minimized.

Aika and co-workers also investigated the influence of the reduction temperature and of the Ba:Ru ratio of the MgO-supported ruthenium catalyst. They observed a decrease in catalytic activity for reduction temperatures above 573 K in disagreement with our results.[11] Our investigations showed an increasing rate of ammonia production and an increase in metal surface area at reduction temperatures up to 783 K. Further investigations of the influence of the reduction temperature beyond 783 K revealed a decrease in metal surface area although the catalytic activity still increased.[8] This indicates particle growth up to an optimum particle size which, in turn, is determined by the maximum number of B_5-type sites.[6–8] The identical reaction orders within the experimental accuracy limits (Table 2) of the barium-promoted Ru catalyst and of the unpromoted Ru/MgO catalyst indicate the same active sites for both catalysts.[6, 8] Clearly, the Ba+O coadsorbate is able to induce a reconstruction of the Ru surfaces, whereby the number of the B_5-type sites is increased. Figure 3 shows a transmission electron microscopy (TEM) micrograph of the Ba-Ru/MgO catalyst after reduction at 783 K revealing the presence of very small Ru particles, approximately 2 nm in size. This value is in good agreement with the average particle size of 1.3 nm derived from static chemisorption measurements. The high dispersion (76 %), the

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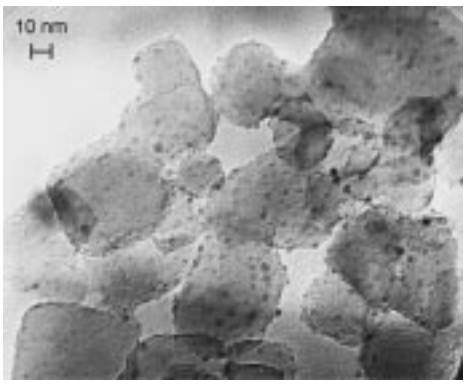

Figure 3. TEM image of the Ba-Ru/MgO catalyst after reduction at 783 K.

evenly distributed Ru particles on the cubic MgO particles, and the narrow particle-size distribution demonstrate the high quality of the MOCVD preparation.

Our knowledge-based approach, leading to the Ba-Ru/MgO catalyst relies on a combination of kinetic and spectroscopic techniques including results from single-crystal surfaces, contrasts with the "trial and error" method. The latter method was used by Mittasch who tested more than 3000 catalyst compositions in over 20000 experiments at the beginning of the last century,[1] and it is also used today in combinatorial chemistry.[12] Our barium-promoted Ru/MgO catalyst also displays a high long-term stability. Correspondingly, the high catalytic activity remained constant after more than 1000 hours on stream at a pressure of 5 MPa and temperatures up to 1023 K.[8] Because of this high stability and the very high catalytic activity the Ba-Ru/MgO catalyst can be considered as an alternative, not only to the iron catalyst, but also to the industrially used multipromoted Ru/C catalyst, the long-term stability of which is limited by the inevitable methanization of the carbon support. Furthermore, the Ba-Ru/MgO catalyst offers the advantage that the components are completely recyclable. The components can be separated and reclaimed with high purity (promoter $>97\,\%$, ruthenium $>94\,\%$, support) by a simple three-stage process.[13]

The yield of ammonia can be further increased by a knowledge-based optimization of the Ba-Ru/MgO catalyst with respect to the ruthenium loading, the properties of the support, and the synthesis process conditions (ratio of N_2 to H_2 etc.). In this way, an additional increase of the ammonia production rate can be achieved far exceeding that of the Ru/C catalyst that is considered an alternative to the industrially used iron catalyst. Consequently, the barium-promoted ruthenium catalyst supported on oxides represents the ammonia-synthesis catalyst of the next generation.

Experimental Section

Typically, an unpromoted Ru/MgO catalyst with 5 wt% ruthenium was prepared from MgO (2 g, Johnson Matthey) and $[Ru_3(CO)_{12}]$ (0.222 g, Strem) by mixing in an agate mortar for 0.5 h. The completely homogeneous precursor mixture was pressed into tablets then crushed and sieved to obtain a particle size fraction of 250–355 μm. Afterwards the precursor was thermally decomposed in a quartz ampoule on a vacuum line equipped with a turbomolecular pump under high vacuum conditions by executing a multistage temperature program (2 K min^{-1} up to 313 K, hold for 1 h; in 2 h up to 343 K, hold for 1 h; in 2 h up to 393 K, hold for 1 h; in 5 h up to 723 K, hold for 2 h; cooling down to ambient temperature). The decomposed precursor was reduced in situ in the microreactor flow set-up at 1 bar in a stream of synthesis gas while the temperature was increased to 723 K at 1 K min^{-1}. The preparation by impregnation is described in a previous publication.[9]

To obtain the precursor of the barium-promoted ruthenium catalyst in the molar ratio of Ba:Ru = 1:1 the thermally decomposed, unreduced precursor (1 g) was stirred in a solution of $Ba(NO_3)_2$ (0.129 g) and solvent (H_2O:EtOH = 50:50; 60 mL) for 4 h. Subsequently, the solvent was removed on a rotary evaporator at 363 K and 10 kPa. The promoted precursor was dried at 363 K in vacuum by using a diaphragm pump (final pressure: 1 kPa) and reduced in the flow set-up. The temperature program used for the activation of the promoted ruthenium catalyst was very important (see Figure 2).

The catalytic activity of the catalysts was determined in a high-pressure microreactor flow set-up which was equipped with two fixed-bed reactors, two independent gas supplies, and two NH_3 detector channels (NH_3 infrared detector BINOS, Fisher Rosemount). This set-up allows parallel catalyst screening to be performed. Accordingly, while the activity of one catalyst was measured another catalyst was activated. This arrangement was necessary because of the lengthy activation procedure of the catalysts (see Figure 2).

The H_2 chemisorption measurements were used to derive the specific surface area, the dispersion, and the particle size of ruthenium. For this purpose the catalyst samples were reduced in an Autosorb 1C unit supplied by Quantachrome. The TEM micrograph of the Ba-Ru/MgO after synthesis was obtained with a Hitachi H 8100 microscope.

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