The temperature-programmed desorption of N_2 from a Ru/MgO catalyst used for ammonia synthesis

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The temperature-programmed desorption (TPD) of N_2 from a Ru/MgO catalyst used for ammonia synthesis was studied in a microreactor flow system operating at atmospheric pressure. Saturation with chemisorbed atomic nitrogen (N–*) was achieved by exposure to N_2 at 573 K for 14 h and subsequent cooling in N_2 to room temperature. With a heating rate of 5 K/min in He, a narrow and fairly symmetric N_2 TPD peak at about 640 K results. From experiments with varying heating rates a preexponential factor $A_{des} = 1.5 \times 10^{10}$ molecules/(site s) and an activation energy $E_{des} = 158$ kJ/mol was derived assuming second-order desorption. This rate constant of desorption is in good agreement with results obtained with a Ru(0001) single crystal surface in ultra-high vacuum (UHV). The rate of dissociative chemisorption was determined by varying the N_2 exposure conditions. Determination of the coverage of N–* was based on the integration of the subsequently recorded N_2 TPD traces yielding $A_{ads} = 2 \times 10^{-6}$ (Pa s)$^{-1}$ and $E_{ads} = 27$ kJ/mol. The corresponding sticking coefficient of about 10^{-14} at 300 K is in agreement with the inertness of Ru(0001) in UHV towards dissociative chemisorption of N_2. However, if the whole catalytic surface were in this state, then the resulting rate of N_2 dissociation would be several orders of magnitude lower than the observed rate of NH_3 formation. Hence only a small fraction of the total Ru metal surface area of Ru/MgO seems to be highly active dominating the rate of ammonia formation.

Keywords: N_2 TPD; N_2 adsorption; Ru; MgO; NH_3 synthesis; microkinetic analysis

1. Introduction

Alkali-promoted Ru-based catalysts are expected to become the second generation NH_3 synthesis catalysts [1]. Main advantages are supposed to be a significantly higher catalytic activity and a higher tolerance towards high NH_3 partial pressures and towards reversible reaction poisons. Efficient Ru catalysts were prepared using carbon [1] and MgO [2] as supports. The rate-determining step of NH_3 synthesis on Ru-based catalysts is generally accepted to be the dissociative chemisorption of N_2. The detailed knowledge of the interaction of N_2 with Ru surfaces thus provides the key to the understanding of NH_3 synthesis kinetics. The dissociation of N_2 is a slow and activated process on unpromoted Ru surfaces [3–5]. Recently, a N_2 sticking coefficient as low as about 10^{-12} was measured on Ru(0001), Ru(10$\bar{1}$0) and Ru(11$\bar{2}$1) surfaces at room temperature which was found to be independent of surface morphology [6].

Both in ultra-high vacuum (UHV) and in high-pressure flow apparatuses it has up to now not yet been possible to achieve a saturated coverage of adsorbed atomic nitrogen (N–*) by dosing molecular nitrogen. Usually, high coverages of N–* have been prepared by the decomposition of nitrogen-containing molecules like NH_3 [3,7,8], N_2H_4 [9] or NH_2CHO [10]. Another method to create N–* is to supply additional energy to activate and break the strong nitrogen–nitrogen bond in the gas phase. For this purpose, a sputter gun [5], a high-frequency plasma discharge in case of a Ru black catalyst [11] and the hot filament of an ionization gauge [6] have been applied. Recently, the dissociation of preadsorbed molecular nitrogen adsorbed on Ru(0001) by 1000 eV He^+ ions has been reported [12]. All methods mentioned have the advantage that the formation of coadsorbates like adsorbed atomic oxygen during high N_2 exposures is avoided.

Tsai and Weinberg [8] performed a coverage-dependent analysis of the recombinative desorption of N_2 from Ru(0001) obtaining an essentially constant activation energy of 184 kJ/mol and a likewise constant preexponential factor of 2×10^{12} s^{-1} in good agreement with an activation energy of about 190 kJ/mol reported by Shi et al. [13] for Ru(0001). On the stepped Ru (11(10)) surface, Egawa et al. [14] found two N_2 TPD peaks at 570 and 750 K, respectively. Ogata et al. [4] observed a single broad N_2 TPD peak at 696 K for Ru powder, whereas up to three different adsorbed atomic nitrogen species in the temperature range from 473 to 873 K were detected for Raney Ru using a heating rate of 4 K/min. Kunimori et al. [11] obtained a broad N_2 TPD peak at around 543 K with a Ru black catalyst using a heating rate of 20 K/min.

Due to the difficulties in preparing Ru surfaces saturated with N–*, to our knowledge no detailed reports on the adsorption and desorption kinetics of N_2 from supported Ru catalysts have yet been published. In the present temperature-programmed desorption (TPD) study,

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the kinetic parameters for the desorption of N_2 from Ru/MgO have been extracted from series of TPD experiments with different heating rates. This approach has recently been applied successfully to an iron-based NH_3 synthesis catalyst [15,16]. The kinetic parameters for adsorption assuming Langmuir–Hinshelwood kinetics have been obtained from N_2 adsorption experiments with different exposures to N_2 followed by N_2 TPD experiments yielding the coverages of N–*.

Contrary to Fe, there is no indication for the participation of an adsorbed molecular precursor (N_2–*) for N_2 dissociation on Ru single crystal surfaces. On polycrystalline Ru samples, IR measurements revealed the influence of the alkali promoter on the stretching frequency of N_2–* which was interpreted in the frame of a charge transfer mechanism [17]. The observed shifts of the N_2 IR absorption band to lower wavenumbers were 163 cm^{-1} for Ru/MgO, 117 cm^{-1} for Ru/Al_2O_3 and 111 cm^{-1} Ru/SiO_2 compared with the gas phase stretching frequency. The higher shift for Ru/MgO was assigned to an electron donation by the basic MgO support [17].

2. Experimental

The set-up equipped with a calibrated mass spectrometer has been described in detail in ref. [15]. The gases used had the following purities: He 99.9999%, N_2 99.9999%, H_2 99.9999%, the mixture of 25% N_2 in H_2 used as synthesis feed gas 99.9996%. The feed gas was further purified by means of a self-designed guard reactor [18]. The reactor consisted of a glass lined U-tube similar to the one described in ref. [19] with an inner diameter of 4 mm. No desorption of N_2 or H_2 could be detected from the empty tube within the limits of detection.

The 5 wt% Ru/MgO catalyst was prepared by impregnation in a rotary evaporator at room temperature following the procedures in refs. [20,21,2]. 1.5 g MgO supplied by Johnson Matthey (Puratronic, 99.9955% metals basis) was heated in high vacuum at 773 K for 6 h and then dispersed in a solution of 0.158 g $Ru_3(CO)_{12}$ (Johnson Matthey) in 60 ml THF_{abs} for 4 h at room temperature. After evaporating the solvent, the slightly orange powder was pressed at a pressure of 1.6 MPa into cylindrical pellets of 10 mm diameter which were subsequently crushed and sieved. The 250–800 μm sieve fraction was carefully heated in high vacuum to 723 K to decompose the carbonyl precursor yielding dark gray grains.

The Ru metal area was determined by volumetric H_2 chemisorption in the quartz U-tube of an Autosorb 1-C set-up (Quantachrome) following the procedure described in ref. [22]. Prior to chemisorption, the catalytic activity was measured by passing high-purity synthesis gas ($P_{N_2}/P_{H_2} = 1/3$) from a connected feed system through the U-tube. The U-tube exit gas was analyzed by a non-dispersive infrared detector (BINOS, Fisher-Rosemount). The BET area was measured by static N_2 physisorption in the same set-up.

200 mg of the 250–800 μm sieve fraction were used for the transient kinetic experiments resulting in a bed height of 15 mm which prevented limitations by heat or mass transport. The reduction was carried out in synthesis gas using 80 Nml/min with a heating ramp of 60 K/h up to 773 K. Prior to carrying out a N_2 desorption experiment, NH_3 synthesis was run at steady state at 773 K. Then the gas composition was changed from the stoichiometric synthesis gas mixture to 50 Nml/min He at the same temperature. After flushing with He for 120 min the temperature was lowered to the N_2 dosing temperature. For the N_2 exposure a flow of 50 Nml/min N_2 was used. Subsequently, the catalyst was cooled to room temperature and the flow was switched to 50 Nml/min He before the temperature ramp was started.

3. Results and discussion

The results of the sorption measurements obtained with the 5 wt% Ru/MgO catalyst after NH_3 synthesis are summarized in table 1. The Ru metal particles were assumed to be spherical for the calculation of the particle diameter.

The particle size of 1.9 nm is in good agreement with results obtained by transmission electron microscopy (TEM) displaying a rather uniform particle size distribution with an average of about 2.0–2.5 nm [23]. Aika et al. [2] report a value of 272 μmol/g Ru surface atoms for a similarly prepared 5 wt% Ru/MgO catalyst corresponding to a particle size of 2.5 nm.

The catalytic activity was determined at atmospheric pressure (fig. 1) using 0.138 g catalyst. After a minor initial decrease, the catalytic activity was found to be stable for a time on stream of about two months at temperatures up to 773 K. The calculated partial pressure of NH_3 in thermodynamic equilibrium is displayed as dotted traces to illustrate thermodynamic limitations at higher temperatures. The observed NH_3 partial pressure is compared with the results obtained with the same initial weight of a multiply promoted iron-based catalyst. Upon changing the P_{N_2}/P_{H_2} ratio from 1/3 to 3/1, the NH_3 partial pressure increased significantly for

Table 1
Results of the BET and H_2 chemisorption measurements obtained with the Ru/MgO catalyst after NH_3 synthesis. The Ru metal particles were assumed to be spherical for the calculation of the particle diameter

BET area	25 m^2/g
H_2 monolayer capacity	130 μmol/g
Ru surface atoms	260 μmol/g
specific Ru metal area	12.9 m^2/g
dispersion	53%
particle diameter	1.9 nm

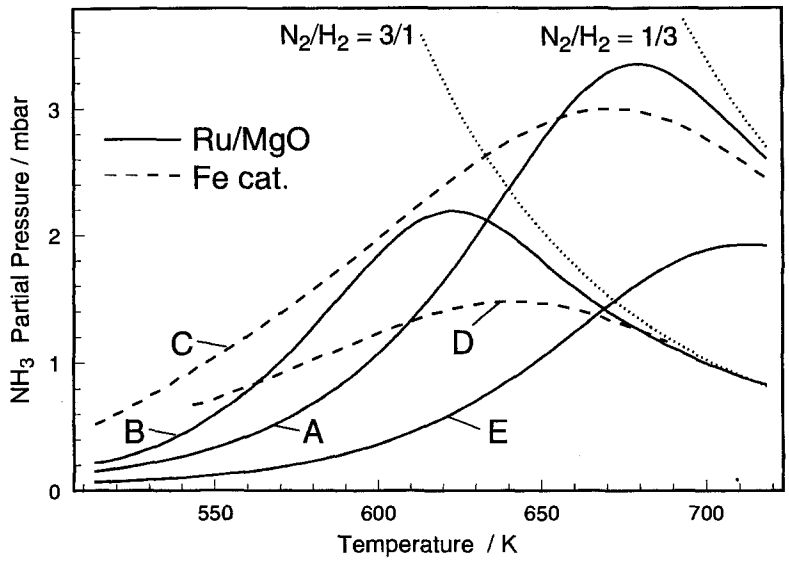

Fig. 1. NH_3 partial pressure in the reactor exit gas observed for 138 mg of the Ru/MgO catalyst (traces A and B, solid lines) and a multiply promoted iron-based KM1 catalyst (traces D and C, dashed lines) using a total flow of 40 Nml/min. Traces A and C were obtained with $P_{N_2}/P_{H_2} = 1/3$, traces B and D with $P_{N_2}/P_{H_2} = 3/1$. The corresponding NH_3 equilibrium partial pressures are displayed as dotted lines. Trace E was obtained with Ru/MgO using 160 Nml/min with $P_{N_2}/P_{H_2} = 1/3$.

Ru/MgO whereas it decreased for the iron-based catalyst. The different response to the change in feed gas composition reflects the inhibition of the rate of NH_3 formation by P_{H_2} in the case of Ru/MgO. It is remarkable that with the $P_{N_2}/P_{H_2} = 3/1$ feed gas composition, the catalytic activity per weight of the Ru/MgO catalyst corresponds roughly to the one measured with the iron-based catalyst with $P_{N_2}/P_{H_2} = 1/3$ at higher temperatures. The Fe metal area was determined to be 8 m^2/g compared with 12.9 m^2/g for the present Ru/MgO catalyst consequently yielding higher turnover frequencies for the multiply promoted iron catalyst [15]. It is noteworthy that the catalytic activity of particularly the iron-based catalyst extends even below the lowest investigated temperature of 513 K (trace C in fig. 1) indicating the absence of poisoning by oxygen-containing compounds [18]. Aika et al. [2] report a turnover frequency of 1.9×10^{-4} s^{-1} for a 5 wt% Ru/MgO catalyst at 588 K measured in a closed circulation set-up at 80 kPa ($P_{N_2}/P_{H_2} = 1/3$). For the 5 wt% Ru/MgO catalyst used in the present study, a turnover frequency of 6.7×10^{-4} s^{-1} at 588 K was derived using a total flow of 40 Nml/min at atmospheric pressure (trace A in fig. 1).

In order to achieve a saturated coverage of N–*, the catalyst was exposed to a flow of 50 Nml/min N_2 at 573 K for 14 h followed by cooling in flowing N_2 to room temperature. The resulting N_2 TPD data are displayed in fig. 2. The heating rates (β) used were 1 K/min (trace A), 5 K/min (trace B) and 15 K/min (trace C) resulting in TPD peaks at 608 K, 636 K and 662 K, respectively. As expected from second-order desorption $2N{-}* \rightarrow N_2 + 2*$, the peak shape is quite symmetric. Plotting $\ln(T_{max}^2/\beta)$ versus $1/T_{max}$ yields $k_{des} = 1.5 \times 10^{10}$ molecules/(site s) $\exp[-(158\ kJ/mol)/RT]$ by applying linear regression. Modelling a TPD experiment with these desorption parameters under UHV conditions using a heating rate of 10 K/s yields a N_2 TPD peak at 750 K in good agreement with the results obtained on Ru(0001) [8,13]. The Ru metal particles on the MgO support seem to provide similar threefold hollow adsorption sites for atomic nitrogen as the hexagonal close-packed Ru(0001) surface. These adsorption sites were identified for N–* by recent STM studies [24].

The inset in fig. 2 shows a comparison of trace C and a calculated TPD peak normalized to the same peak height using the value of k_{des} obtained by the variation of the heating rate and $\beta = 15$ K/min. The full widths at half maximum (FWHM) differ only by 22 K indicating the absence of readsorption of desorbed N_2 molecules within the catalyst bed. Readsorption would give rise to asymmetric TPD peak broadening to higher temperatures due to the delayed elution of the desorbed N_2 molecules. The good agreement of the FWHMs furthermore demonstrates that the desorption parameters are essentially independent of coverage.

Since the dissociative chemisorption of N_2 is known to be an activated process, the dosing temperature was chosen as high as possible. The dosing temperature of 573 K is at the onset of N_2 desorption which may lead to a loss of N–* in case of flushing with He at this temperature. Hence the sample was cooled with about 2 K/min in N_2 to room temperature prior to switching to He. Since longer exposure times up to 30 h did not result in any further increase in Θ_N, the value of 28.2 μmol N_2/g obtained after dosing for 14 h is assumed to represent the saturation coverage of N–*. Comparing 56.4 μmol N–*/g to a total amount of 260 μmol/g Ru surface atoms determined by H_2 chemisorption results in an

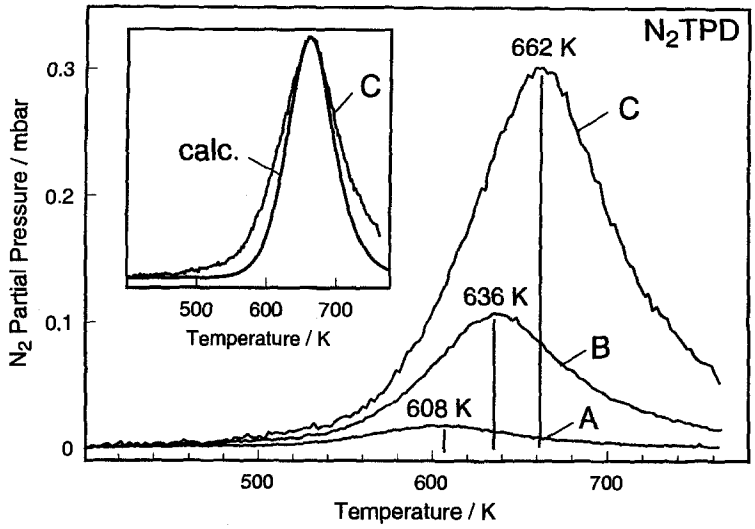

Fig. 2. N_2 TPD data with different heating rates. The TPD data were obtained by dosing N_2 at 573 K for 14 h and subsequent cooling in N_2 to 298 K. The heating rates used were 1 K/min (trace A), 5 K/min (trace B) and 15 K/min (trace C). The inset displays the comparison between trace C obtained with 15 K/min and a calculated TPD trace based on second-order desorption without readsorption using $k_{des} = 1.5 \times 10^{10}\ s^{-1} \exp[-(158\ kJ/mol)/RT)$.

absolute coverage of $\Theta_N = 0.22$. The values reported in the literature for Θ_N^{max} are somewhat contradictory and depend on the N-containing molecule dosed and the dosing conditions. The values reported recently range from 0.25 to 0.33 based on c(2 × 2) and $\sqrt{3}$ LEED patterns, respectively. The value of 0.5 reported previously, see e.g. refs. [8,13], has turned out to be erroneous [6,25]. H_2 chemisorption is known to overestimate the amount of Ru surface atoms due to a possibly higher H/Ru stoichiometry than 1/1 usually found for metal particles smaller than 2 nm [26]. Also spillover of H–* from the Ru particles to the MgO support may occur [27]. Hence the actual amount of H–* corresponding to H/Ru = 1/1 is presumably somewhat lower leading to an absolute coverage of N–* within the range of values reported for Ru(0001).

The N_2 TPD data obtained after different exposure conditions to 50 Nml/min N_2 at atmospheric pressure are reproduced in fig. 3. After dosing N_2 at 298 K for 1 h, the subsequent desorption of N_2 (trace A) was hardly detectable. Increasing the temperature of N_2 exposure to 373 K yielded a rather symmetric N_2 TPD peak at 660 K (trace B). Upon increasing the dosing time, the N_2 TPD peak increased in intensity and shifted to lower temperatures as expected for second-order desorption kinetics (trace C). Increasing the N_2 dosing time from 1 to 3 h resulted in a higher amount of desorbing N_2 at 373 K (traces B and C), 423 K (traces D and E) and 473 K

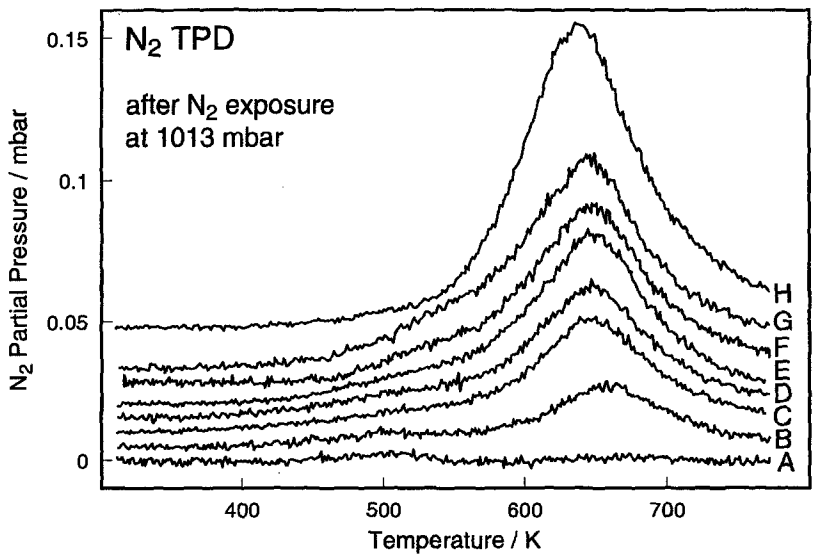

Fig. 3. N_2 TPD data obtained by (from bottom to top) dosing N_2 at atmospheric pressure at 298 K for 1 h (trace A), at 373 K (traces B and C), 423 K (traces D and E) and 473 K (traces F and G) for 1 and 3 h, respectively, and at 573 K for 14 h (trace H). The baselines of the displayed traces were shifted for the sake of clarity.

Table 2
Quantitative results of the N_2 chemisorption measurements with the Ru/MgO catalyst at atmospheric pressure for 1 and 3 h at different temperatures. The amount of chemisorbed atomic nitrogen was obtained by integrating the subsequently obtained N_2 TPD peaks. The experimental accuracy was about ±0.5 μmol N_2/g. The coverage of N–* was calculated relative to the saturated amount of 28.2 μmol N_2/g equal to 56.4 μmol N–*/g

Temperature (K)	Dosing time (h)	Amount of N_2 (μmol/g)	Θ_{N-*}	k_{ads} ((Pa s)$^{-1}$)	Trace in fig. 3
300	1	0.8	0.03	4.2×10^{-11}	A
373	1	6.7	0.24	4.3×10^{-10}	B
373	3	12.4	0.44	3.6×10^{-10}	C
423	1	14.0	0.50	1.4×10^{-9}	D
423	3	17.4	0.62	0.8×10^{-9}	E
473	1	16.0	0.57	1.8×10^{-9}	F
473	3	24.2	0.86	2.8×10^{-9}	G
573	14	28.2	1	–	H

(traces F and G). The maximum amount of 28.2 μmol N_2/g was obtained by dosing N_2 at 573 K for 14 h followed by cooling in N_2 to room temperature (trace H). The quantitative results are summarized in table 2 in which Θ_N was evaluated relative to the saturation amount of 28.2 μmol N_2/g. The accuracy of the determination of the amount of adsorbed N–* was about ±1.0 μmol N–*/g. The rate constant of adsorption (k_{ads}) was calculated in the dosing temperature range from 300 to 473 K assuming Langmuir–Hinshelwood kinetics by integrating the following equation for dissociative chemisorption:

$$r_{ads} = \frac{d\Theta_N}{2dt} = k_{ads} P_{N_2} (1 - \Theta_N)^2 . \quad (1)$$

In addition, there is a small TPD peak at about 500–550 K which seems to saturate independently from the main TPD peak at 636 K as will be discussed further below. The additional TPD peak does not appear in trace H obviously due to the high dosing temperature of 573 K.

In fig. 4, the Arrhenius plot of the values for k_{ads} specified in table 2 is shown together with the result of linear regression yielding $A_{ads} = 2 \times 10^{-6}$ (Pa s)$^{-1}$ and $E_{ads} = 27$ kJ/mol. The correlation coefficient of 0.988 suggests that k_{ads} is essentially independent of coverage as observed for k_{des} (fig. 2). The activation energy of adsorption of 27 kJ/mol is in good agreement with 33 kJ/mol estimated by Matsushima [5] based on the analysis of the angular distribution of the recombinative N_2 desorption from Ru(0001). However, the preexponential factor of 2×10^{-6} (Pa s)$^{-1}$ is many orders of magnitude lower than the usual value for dissociative chemisorption with mobile transition state of 10^3 (Pa s)$^{-1}$ [28]. Based on the determined values for A_{ads} and E_{ads}, an initial sticking coefficient of about 10^{-14} is obtained for dissociative nitrogen chemisorption at room temperature in reasonable agreement with the value of 2×10^{-12} observed by Dietrich et al. [6] in the coverage range of $\Theta_N = 0.002$ to the highest obtained coverage of $\Theta_N = 0.08$. The data reported by Dietrich et

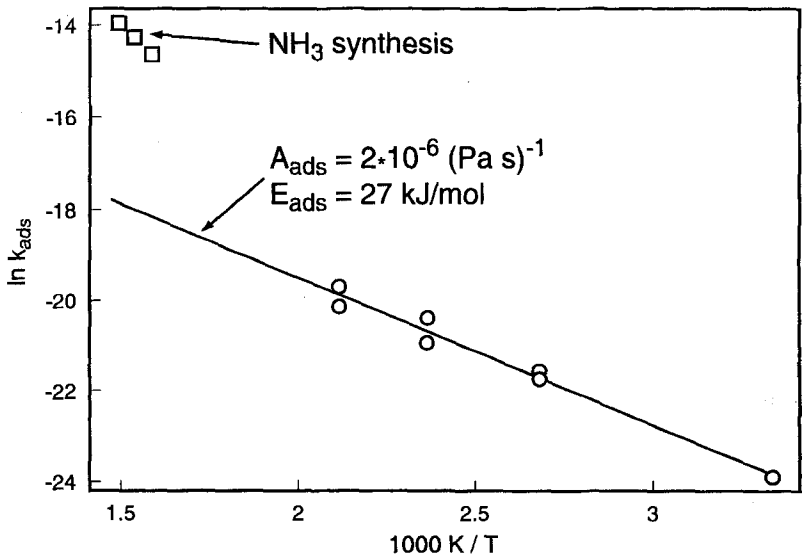

Fig. 4. Arrhenius plot of the rate constants of adsorption (table 3) shown as circles assuming $r_{ads} = d\theta_N/dt = 2k_{ads}p_{N_2}(1 - \theta_N)^2$. The straight line results from linear regression. The three rate constants shown as squares are pseudo-first-order rate constants $r_{syn} = k_{syn}P_{N_2}$ calculated from the rate of NH_3 synthesis (trace E in fig. 1).

al. [6] provide some evidence that the sticking coefficient may decrease even further with increasing Θ_N since 4×10^{-13} was obtained for $\Theta_N = 0.08$.

The present kinetic study shows that nitrogen dissociation is indeed a slow and activated process leaving no doubt that it is the rate determing step for the formation of NH_3. The question arises whether the rate of dissociative nitrogen adsorption (r_{ads}) is high enough to account for the rate of NH_3 formation (r_{syn}) observed with the same catalyst in the same set-up. Fig. 4 additionally displays values for k_{syn} at 630, 650 and 670 K obtained by assuming pseudo first-order NH_3 synthesis kinetics: $r_{syn} = k_{syn} P_{N_2}$, which are significantly larger and exhibit a higher apparent activation energy than the data for k_{ads} extrapolated in this temperature range. A comparison of the values for r_{syn} (see trace E in fig. 1) reported as turnover frequencies and r_{ads}^{max} is given in table 3 and underlines an increasing difference with rising temperature. Both rates are based on 56.4 μmol/g active sites determined by N_2 chemisorption (table 2), i.e., the number of active sites is there assumed to be equal to the number of adsorption sites for N–*. The values for the rate of dissociative adsorption shown in table 3 were calculated according to eq. (1) assuming $1 - \Theta_N = 1$ and therefore represent the maximum values for r_{ads}. Under NH_3 synthesis conditions, a significant coverage of mainly adsorbed atomic hydrogen seems to exist as indicated by the partial pressure dependence shown in fig. 1 which decreases r_{ads} even further.

This discussion demonstrates that, if the whole catalytic surface had the same low sticking coefficient, then the resulting rate of N_2 dissociation would be several orders of magnitude lower than the actually observed rate of NH_3 formation. Hence a certain fraction of the total Ru metal surface area of Ru/MgO seems to have a significantly higher activity dominating the rate of ammonia formation. Evidence for the existence of such sites with a higher rate of adsorption can be found by a closer inspection of fig. 3. Whereas the main amount of N_2 was found to desorb in the temperature range from 550 to 750 K, there is a small additional TPD peak at about 500–550 K which seems to saturate faster at lower dosing temperatures compared with the main TPD peak at 640 K. Since the N_2 TPD peak of alkali-promoted Ru catalysts was found to be shifted to lower temperatures [29], it appears plausible to assume that the additional TPD peak is due to desorption from Ru sites promoted by a strong interaction with MgO at the interface. Aika et al. [2] showed that also the alkaline earth metals act as promoters for supported Ru catalysts. Further studies using the isotopic exchange reaction $^{28}N_2 + {}^{30}N_2 \rightleftharpoons 2\,{}^{29}N_2$ and the temperature-programmed adsorption of N_2 are in progress to provide evidence for the postulated non-uniformity of Ru/MgO with respect to the dissociative adsorption of nitrogen.

Table 3.
Comparison of r_{syn} with r_{ads}^{max}. The values for the rate of NH_3 synthesis (r_{syn}) observed at 588, 623 and 673 K using a flow of 160 Nml/min (trace E in fig. 1) are reported as turnover frequencies. The values for the rate of dissociative nitrogen adsorption (r_{ads}^{max}) were obtained based on $A_{ads} = 2 \times 10^{-6}$ (Pa s)$^{-1}$ and $E_{ads} = 27$ kJ/mol assuming $(1 - \Theta_N) = 1$ and thus represent the maximum rate r_{ads}^{max}. Both rates are based on 56.4 μmol/g active sites

Temperature (K)	r_{syn} (1/s)	r_{ads}^{max} (1/s)
588	4.2×10^{-3}	4.7×10^{-4}
623	9.2×10^{-3}	6.4×10^{-4}
673	2.3×10^{-2}	9.4×10^{-4}

4. Conclusions

The preparation of a 5 wt% Ru/MgO sample from $Ru_3(CO)_{12}$ and MgO was shown to result in a long-term and high-temperature stable NH_3 synthesis catalyst. Its catalytic activity per weight was found to be comparable to that of a multiply promoted iron-based catalyst, if the feed gas composition is varied from $P_{N_2}/P_{H_2} = 1/3$ to $P_{N_2}/P_{H_2} = 3/1$ in order to suppress hydrogen inhibition.

It was possible to achieve saturation with chemisorbed atomic nitrogen by dosing N_2. A detailed microkinetic analysis of the adsorption and desorption kinetics of nitrogen on Ru/MgO was performed yielding rate constants in agreement with results obtained with a Ru(0001) single crystal surface. The dissociative adsorption of nitrogen was found to be a slow and activated process with a sticking coefficient below 10^{-12} at 300 K.

However, if the whole catalytic surface had such a low rate constant of adsorption, then the resulting maximum rate of N_2 dissociation would be several orders of magnitude lower than the rate of NH_3 formation observed for the same catalyst in the same set-up. Hence only a small fraction of the total Ru metal surface area of Ru/MgO seems to be highly active dominating the rate of ammonia formation. Such promoted sites might originate from the interaction with the MgO support.

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