On the interaction of N_2 and H_2 with Ru catalyst surfaces

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A series of ruthenium NH_3 synthesis catalysts with selected promoters added have been studied. It is demonstrated that the rate of N_2 chemisorption can be strongly enhanced by preadsorbed hydrogen. The promoters La and Ba have a weak influence on the rate of N_2 dissociation on the hydrogen free surface, while they cause the rate to increase for a partly hydrogen covered surface. This increase correlates with the effect on the rate of NH_3 synthesis. In contrast, Cs was able to increase the rate of N_2 dissociation by two to three orders of magnitude with almost no change in the activity for NH_3 synthesis.

Keywords: ammonia synthesis, ruthenium, promoters, lanthanum, cesium, barium, H_2 chemisorption, N_2 dissociation rate

1. Introduction

Since the turn of the century, both ruthenium and iron have been known to be very active for NH_3 synthesis. The alkali and earth alkali metals have demonstrated their importance as promoters of the synthesis reaction. Several different suggestions of the mechanism behind the promoting effect of the alkali metals have been forwarded, while the earth alkali metals (mainly Ca in the fused iron catalysts) have received surprisingly little attention. The hypotheses have been that the alkali destabilizes NH–$*$ [1] or NH_3–$*$ [2] on the Fe surface or NH_3 adsorbed on acid sites on the alumina [3], that it increases the rate of chemisorption by lowering the activation energy [4], and the latest suggestion is a destabilization of atomic nitrogen, N–$*$ [5,6]. In the present study, new light is thrown on this issue through an investigation of the effect of Cs and Ba as well as La on Ru catalysts.

Temperature programmed surface reaction (TPSR) methods have demonstrated their utility in catalyst characterization studies. In particular, they can be applied as a quick scanning method in order to localize the appropriate temperature range, where the reaction proceeds with significant velocity. However, the development of new methods should not lead to a displacement of well established conventional methods. An important problem with the TPSR methods is that the temperature and coverage dependencies of the reaction are strongly convoluted. Thus, the application of isothermal studies will frequently be imperative for a profound understanding of the reaction mechanism. An instructive example can be found in the temperature programmed adsorption and desorption studies of iron NH_3 synthesis catalysts [5], the purpose of which was to discriminate between two fundamentally different theories: (1) the old notion that the chemisorption of N_2 on the (Fe, Al) catalysts is slow and strongly activated, and (2) the rather new idea that it should be fast and non-activated [4,7]. The conclusion was in favour of the first suggestion, but the experimental results were too complicated to allow a deconvolution of the coverage and temperature dependencies of the rates of adsorption and desorption. Thus, the original isothermal methods, such as thermogravimetry [8] or volumetric chemisorption were found to be more suitable for quantitative studies [5].

In the present study, the coverage and temperature dependencies of the rate of N_2 adsorption on Ru catalysts are investigated, using conventional volumetric chemisorption, since this was evaluated to be the most accurate method, in particular when the effect of various amounts of preadsorbed H_2 had to be taken into account.

2. Experimental

2.1. Catalysts

All catalysts were prepared from the same batch of prereduced 8.5% Ru on $MgAl_2O_4$. The advantage of this support is that Cs does not cause any sintering, contrary to what is the case for pure MgO [9]. The BET area was 80 m^2/g, and the pore diameter was > 60 Å. The promoters were added by incipient wetness impregnation, using the nitrates of Ba, La or Cs. The concentrations are given as weight%. The reduction was carried out in synthesis gas or H_2 to 500°C for at least 30 h. The NH_3 synthesis activity after reduction in H_2 attained the full value within few min after introduction of the synthesis gas, contrary to what has been observed for Fe catalysts [10,5]. No other significant effects of the reduction gas were observed, and the catalysts in the main series of this study were reduced in synthesis gas. The Ru particle size was estimated by electron microscopy after the experiments.

2.2. Activity measurements

The kinetics was measured in a plug flow setup described previously [11]. The purity of the gas supply was carefully checked by the procedure described in ref. [12]. This test was also carried out in the chemisorption setup, so it was verified that the state of the catalyst was the same in both cases.

After testing, the catalysts were passivated in a stream of N_2 containing 0.1–0.2% O_2.

2.3. Volumetric chemisorption

The catalysts were evacuated at 480°C until the pressure was below 2×10^{-5} Torr, i.e. for at least 1 h. After cooling to the appropriate temperature, the adsorbent was admitted in suitable doses. The isotherms for N_2 at 400 and 450°C were obtained for both adsorption and desorption. As usual, two isotherms were determined for H_2, so both the "weakly" and "strongly" adsorbed H_2 was determined. The evacuation between them was carried out to $< 2 \times 10^{-5}$ Torr (1 h). The equilibration time for the N_2 chemisorption experiments was typically 1 h, after which the rate had declined below the experimental resolution. Between the chemisorption experiments, the catalyst was conditioned in synthesis gas at 500°C for 6–8 h, followed by 1.5–2 h at 400°C. All quoted coverages in μmol refer to the corresponding amount of N_2 or H_2 molecules.

In the coadsorption experiments the H_2 was adsorbed first, with subsequent evacuation, so the amount of H–$*$ left on the surface was identical to the strongly adsorbed part, which could then be varied by changing the temperature. The N_2 was then admitted in one dose (at the same or lower temperature). No observable amount of NH_3 was evolved during this type of treatment.

3. Results

3.1. NH_3 synthesis activities

The activities of the samples and the reaction orders for H_2 and NH_3 are given in tables 1 and 2. Previous studies have verified that the reaction order for N_2 is 1 for a large variety of catalysts [13,14].

Table 1
Catalyst activities at 320°C, 1 atm, $H_2 : N_2 = 3 : 1$, 0.3% NH_3 at the outlet. no P. = no promoter added. N_2 chemisorption rates: rough relative estimates at intermediate coverages

	μmol/(g s)	Relative value	Relative N_2 chemisorption rate	
			no H–$*$	with H–$*$
no P.	0.15	1	1	1
4% Cs	0.17	1.2		
9% Cs	0.8	4.4	300	14
9% Ba	1.5	10	3	2
9% La	2.1	14	4	3.4

Table 2
Reaction orders (Ro) for NH_3 and H_2 in the limit of low conversion (< 10% of equilibrium). Temperature: 320°C

	Ro (NH_3)	Ro (H_2)
no P.	−0.37	−0.33
9% Ba	−0.35	−0.4
9% La	−0.51	−0.2
9% Cs	−0.17	−1.03
(Cs + Ru)/MgO	0	−1.25)

The detailed kinetic experiments will be published later [14]. Here, only an illustrative example of the different behaviour of the catalysts in question is given in figure 1. The most striking feature is the negative pressure variation of the activity of the (strongly) Cs promoted sample.

3.2. Static volumetric chemisorption

The results for the final H_2 and N_2 pressures are given in table 3. The log–log plots of the H_2 isotherms are approximately linear, suggesting a Freundlich type of chemisorption [15]. The variation of the N_2 chemisorption with pressure for both adsorption and desorption is shown in figure 2. The logarithmic increase indicates a Temkin isotherm. The agreement between the adsorption and desorption results was best for the Ba containing sample, while some hysteresis was observed for the other catalysts, Cs being the worst case (figure 2B).

The adsorption of N_2 is plotted versus temperature in figure 3. A minimum in the amount of weakly

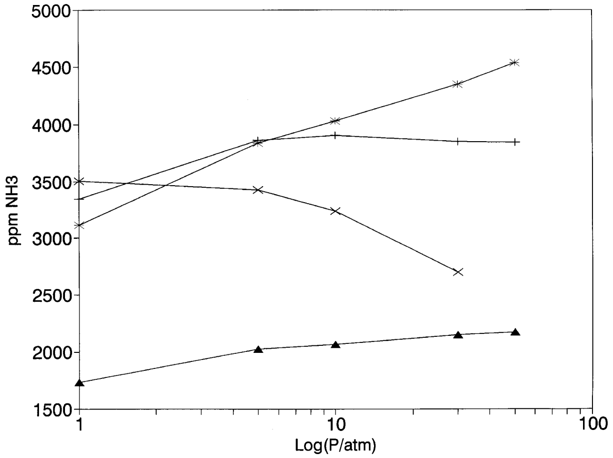

Figure 1. Pressure variation of NH_3 synthesis activity for catalysts with different promoters. Temperature: 320°C. (▲) No promoter (40 Nml/min), ($*$) La (267 Nml/min), (+) Ba (160 Nml/min) and (×) Cs (9%, 80 Nml/min).

Table 3

Chemisorption of N_2 and H_2 (μmol/g). Pressure: H_2: 300 Torr, N_2: 180 Torr. N_2 on Ru + H–∗: chemisorption of N_2 on Ru + strongly adsorbed H–∗ at same temperature. Number in parentheses: with strongly adsorbed H–∗ at 300°C

	T (°C)	N_2			H_2			N_2 on Ru + H–∗
		total	weak	strong	total	weak	strong	
no P.	−78	163	127	37	216	55	161	
	23	63.3	60.3	3.0				
	100	26.1	14.0	12.1	211	87	124	
	200	27.8	3.1	24.7	194	111	83	53
	300	31.9	10.7	21.2	158	130	28	42
	400	27.4	21.1	6.3				
	440	24.5	22.0	2.5				
	480	21.1	18.8	2.3				
Cs 4%	23	43.5	27.0	16.5				
	100	38.2	6.8	31.4				
	200	43.0	5.0	38.0	173	85	88	43
	300	40.9	19.3	21.6	145	96	49	
	400	36.5	29.8	6.7				
Cs 9%	−78	85.8	46.4	39.4				
	23	39.2	22.4	16.8	175	46	129	
	100	33.6	4.5	29.1	171	65	106	
	200	34.2	5.6	28.6	150	80	70	37 (47)
	300	33.6	14.4	19.2	131	95	36	43
	400	30.0	23.9	6.1				
	450	27.5	25.3	2.2				
Ba	23	45.2	40.9	4.3				
	100	25.1	7.3	17.8	202	75	127	
	200	30.9	6.3	24.6	196	111	85	55
	300	30.0	14.2	15.8	156	116	40	42
	400	27.7	24.4	3.3				
	450	25.7	23.6	2.1				
La	23	33.0	33.0	0.0				
	100	16.7	7.0	9.7				
	200	25.5			185	114	71	56
	300	28.1	9.6	18.6	158	127	31	43
	400	24.2	19.4	4.8				
	450	22.9	19.8	3.1				

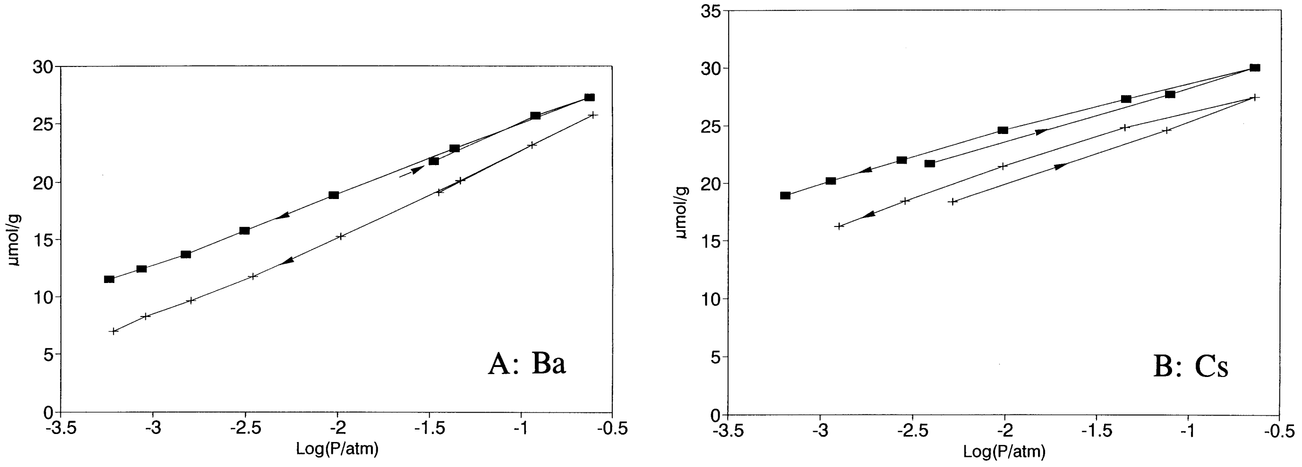

Figure 2. Isotherms for N_2 for adsorption and subsequent desorption (arrows). (■) 400°C and (+) 450°C. (A) With Ba and (B) with 9% Cs.

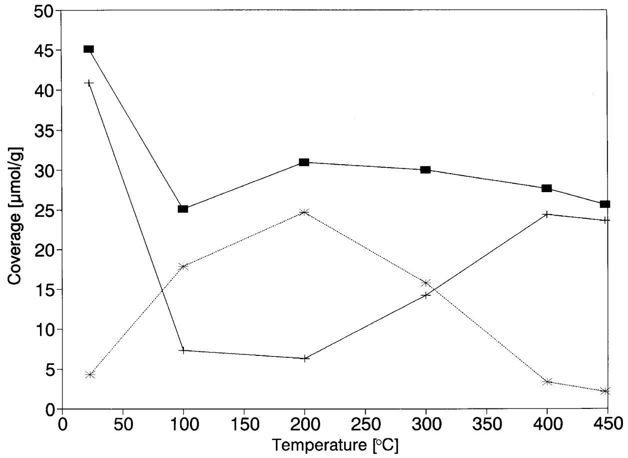

Figure 3. Temperature variation of chemisorption of N_2 for Ba promoted sample. N_2 pressure: 18 cm Hg. (■) Total amount, (+) weakly adsorbed and (∗) strongly adsorbed.

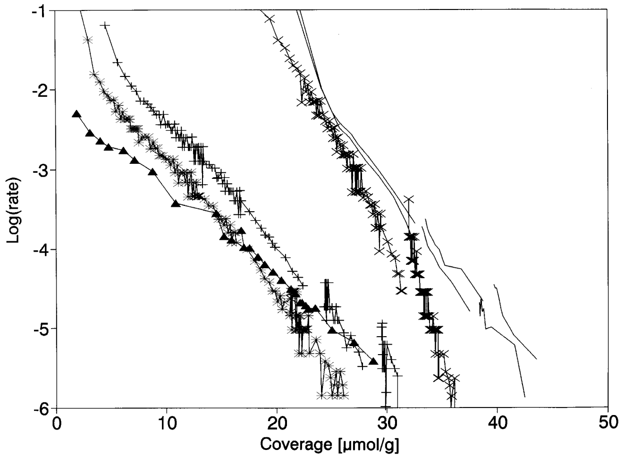

Figure 5. Rate of chemisorption of N_2 vs. coverage for different samples (0.01 μmol/(min Torr)). (▲) No promoter, (∗) La, (+) Ba, (×) Cs (9%) and (–) repeated experiments for Cs (4%). (∗) and (×) two doses, others: three doses. Temperature: 200°C.

adsorbed N_2 is observed. Figure 4 compares the total N_2 adsorption for the different samples. An interesting point is that the temperature variation is similar for samples with Ba and Cs, and distinctly different for catalysts with La or no promoter.

3.3. Chemisorption rates

The rate of H_2 chemisorption was too fast to be measured except at very high coverages ($>$ 80% of saturation). It has been claimed that alkali may cause the H_2 chemisorption to be activated. However, no difference between the rates for the samples without promoter and with 9% Cs could be resolved, even at −78°C.

Figure 5 displays the rates of chemisorption of N_2 at 200°C for differently promoted samples. The rates approximately follow an Elovich relation [15]. Cs increases the rate by two to three orders of magnitude, while the most significant effect of the other promoters is an increase of the slope.

The effect of preadsorbed H–∗ is demonstrated in figure 6. The trend was comparable for all samples except Cs, for which the effect of H_2 was much less pronounced, probably at least partly due to the high intrinsic rate. However, the total N_2 chemisorption on the H–∗ precovered surface is significantly smaller than for the other samples. The difference is too large to be explained by the sintering caused by the Cs, calling for an alternative explanation.

The quantitative effects of the promoters on the rates of N_2 chemisorption with or without preadsorbed H–∗ are summarized in table 1.

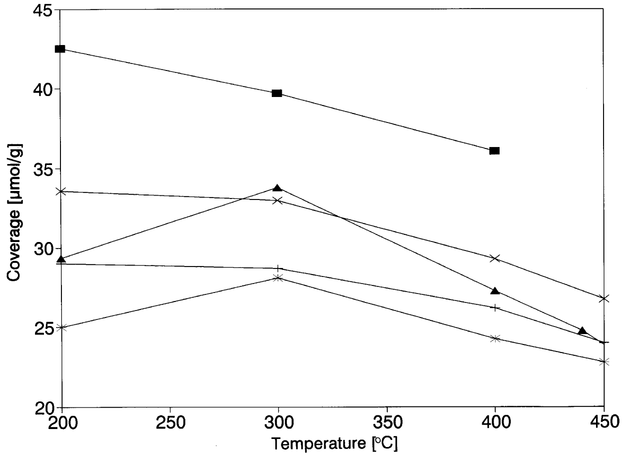

Figure 4. Temperature variation of chemisorption of N_2 for samples with different promoters. (▲) No promoter, (∗) La, (+) Ba, (■) Cs (4%) and (×) Cs (9%).

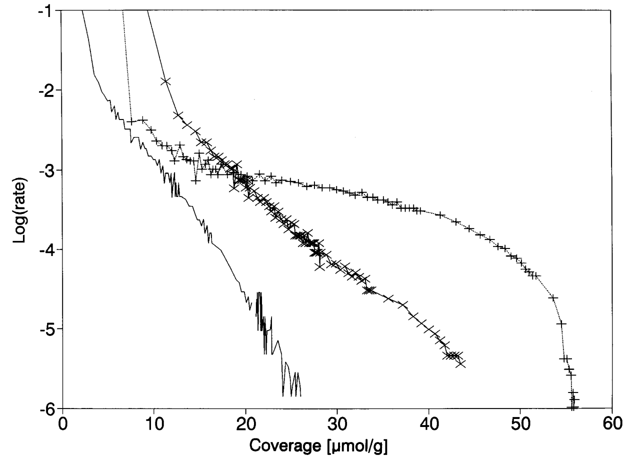

Figure 6. Rate of chemisorption of N_2 vs. coverage for different coverages of H–∗ (100 μmol/(min Torr)). Sample: La. (–) No H–∗, (×) 37 and (+) 72 μmol/g of preadsorbed H_2. Temperature: 200°C.

4. Discussion

4.1. Chemisorption

The nature of the weakly adsorbed H_2 is still under discussion. However, it was not the aim of this study to address this question, rather to investigate the changes introduced by the addition of the promoters. The focus was on relatively high temperatures in order to get an estimate of the changes in the equilibrium constant for the H_2 chemisorption. A normalization of the coverage by the total number of active sites would be desirable. The most frequently applied estimate is the strongly adsorbed H_2 at room temperature [16]. However, this choice is not obviously the most relevant one here, since strongly and weakly adsorbed H_2 varies rather smoothly with the temperature (table 3). In addition, no obvious value can be deduced from the data for the ratio between the saturation chemisorption values for N_2 and H_2. Fortunately, the variation between the samples in both the N_2 and H_2 chemisorption values is less than a factor of 0.75 (table 3), which is not important for any of the discussion, so a normalization is not urgently necessary.

As table 4 demonstrates, the addition of Cs causes significant sintering of the Ru particles. However, the decrease in the H_2 and N_2 equilibrium chemisorption was only 20–25%, both for the strongly, weakly and total values. This suggests that the smallest particles may be inactivated by the support oxides. The sintering may then cause them to be reactivated, partly balancing the decrease in surface area of the larger particles. Alternative explanations could be that the sintering results in a wider particle size distribution, or in changes in the ratio between adsorption states with different saturation coverages [17]. The change in the total H_2 and N_2 chemisorption by the addition of La or Ba is slightly smaller than expected from the weight increase.

It is obvious from figures 3 and 5 that the dissociative N_2 chemisorption does not reach equilibrium for temperatures below 200°C. The increased adsorption below 100°C must be due to a contribution from molecular N_2.

Even at 300°C the equilibrium is not reached, except perhaps for the most strongly (9%) Cs promoted sample. At 400°C or above, the rate curves drop almost vertically, and, in addition, the adsorption and desorption isotherms are in reasonable agreement (figure 2), indicating that the equilibrium state is attained.

Table 4
Ru particle diameters (in Å)

no P.	< 30
La	< 30
Cs 4%	20–70
Cs 9%	25–90

The differences in the temperature variation demonstrated in figure 4 are due to the equilibration problems, which are strongly reduced by addition of Cs, since the rate of chemisorption is increased by two to three orders of magnitude. The fact that Ba shows the same type of temperature variation can be explained by the low value of the activation energy for this promoter (see below and table 5). The only samples which were able to dissociate N_2 at room temperature were those with Cs or Ba promoters.

In figure 5 the curvature of the trace for the first dose for the sample with 9% Cs suggests that the adsorption is starting to approach an equilibrium value, so the rate of desorption is non-negligible for coverages above 25 μmol/g. This also explains the jump in the curve, when the second dose is applied.

The activation energy E_a for the (dissociative) N_2 chemisorption process can be estimated from the shift with temperature of the log rate curves such as figure 5. Table 5 gives the results. The following complications were encountered: (1) the rate of desorption was non-negligible for the higher coverages and temperatures, (2) molecular adsorption was significant below 100°C, (3) the rate for the Cs promoted samples was too high to be estimated for coverages below 20 μmol/g. The optimal temperature range for the determination of the activation energy was around 200°C, but unfortunately, the useful temperature interval for the Cs promoted sample was too narrow to allow a reasonably accurate estimate. For these reasons two different approaches were applied:

(1) It was assumed that the zero coverage slope of the log rate vs. coverage should vary with temperature as α/RT, where α is a constant [15]. After obtaining the best fit to the 100–400°C results, the initial activation energy could then be calculated from the shift of the intercept with the second axis.

(2) The curves were shifted to coincide at ca. 10 μmol/g, which was the coverage range where the largest overlap could be obtained. This method has the advantage that it is model independent, and that the value at non-zero coverages are of more practical relevance.

The result for a (Fe, Al) catalyst [5] is added to table 5 for comparison. The agreement with previously published values is excellent, since Scholten et al. found a constant value of 96 kJ/mol for coverages above 0.25 [8]. No hydrogen induced enhancement of the N_2 chemisorption was observed for this sample, in spite of previous suggestions that such effects could exist [18–20].

Another interesting point to notice when comparing the results for the Ru/$MgAl_2O_4$ and the fused iron oxide catalysts is that Ba decreases the activation energy for N_2 chemisorption on Ru, just as it was observed for Ca on Fe [5].

The extended extrapolation involved in the estimation of the intrinsic E_a for the Cs promoted sample is inhibiting for a definitive conclusion concerning the pos-

Table 5
E_a for N_2 chemisorption (kJ/mol). (a) Extrapolated to zero coverage, assuming a slope $= \alpha/RT$, (b) estimated at low coverages (~ 10 μmol/g). "with H_2" means with the amount strongly adsorbed at 300°C. In this case the estimate is made for coverages around 20–25 μmol/g. The preexponential factor in the last column arises from the extrapolations under (a)

	No H_2		With H_2	Preexponential factor (relative)
	(a)	(b)		
no P.	32	39	60	1
Ba	10	22	46	0.06
La	30	44	69–80	4
Cs, 4%	−5–0[a]			0.8
Cs, 9%	−17[a]	0	73	0.9
(Fe,Al)		95	– for more than 14 μmol/g	

[a] Based on extrapolations (see text)!

sible effect of Cs on E_a for Ru. Anyway, it does not appear to be completely analogous to the effect of K on (Fe, Al), since no increase in the rate of N_2 dissociation with alkali content was observed for the latter case [5].

4.2. Coadsorption of N_2 and H_2

The activation energy was also estimated for samples with preadsorbed H_2, here the amount strongly adsorbed at 300°C. In this case the estimate is made for a nitrogen coverage of around 20–25 μmol/g, since for this range the log rate curve for the La and Ba promoted samples had an approximately linear part with the same slope for both 200 and 300°C, resulting in a N–$*$ coverage independent E_a, at least for this range. As before, or perhaps even more so, this result is probably more relevant for the NH_3 synthesis conditions than the zero coverage value.

The observation that it is possible to chemisorb approximately twice as much N_2 at 200°C on a Ru surface partly covered by hydrogen than on the empty surface could be explained by several different mechanisms, for instance the following:

(1) molecular N_2 precursor states may exist on top of the hydrided surface,

(2) surface reconstruction effects caused by the chemisorption of H_2,

(3) a hydrogen assisted mechanism for the N_2 dissociation step,

(4) formation of NH_x–$*$ species on separate sites [21], or

(5) removal of poisoning (e.g., oxide).

The last suggestion was ruled out through various careful tests [5,12]. Number (1) is not likely, since the low temperature molecular adsorption of N_2 was observed to decrease approximately proportionally to the amount of chemisorbed H_2 (or N_2). (4) The variation of the amount of extra N_2 with the amount of preadsorbed H_2 was approximately 1 : 2, suggesting the formation of NH_2–$*$, except for the Cs promoted sample, for which the relation was closer to 1 : 1. These species will not be kinetically interesting if they are strongly bound on separate sites, since their formation will then just be a "blind alley", so the evaluation of this possibility is not an easy task. It is also quite difficult to distinguish between the remaining two suggestions. At present, No. (3) has been chosen as working hypothesis, but much of the discussion in the following will probably apply equally well to suggestion No. (2).

An interesting point to notice is that the amount of N_2 adsorbed after H_2 at 300°C is larger than the value without H_2, even for the Cs (9%) promoted catalyst, for which the N_2 chemisorption does seem to reach equilibrium at this temperature. This is even more surprising, since alkali is expected to destabilize NH_x–$*$, while these observations point in the opposite direction, i.e. NH_x–$*$ seems to be more strongly bound than N–$*$.

4.3. Relation between activity and rate of N_2 chemisorption

The fact that the rate of N_2 chemisorption declines exponentially with coverage makes it relatively easy to find a coverage for which the chemisorption rate is identical to the rate of NH_3 synthesis. This is not quite so for the rate of chemisorption with preadsorbed H–$*$, since the curve is rather flat over a wide coverage range. Table 6 gives the value of coverages for which there is (exact) agreement between the rates at 300°C of NH_3 synthesis and the chemisorption of N_2 on a surface with or without preadsorbed H_2. However, the effect of H–$*$ on the surface during synthesis is more complicated than accounted for by this treatise, since the site blocking effect of H–$*$ will most likely be important for the high H–$*$ coverages, which may be present on the Ru surface during synthesis conditions. The resulting delicate balance between the hydrogen induced enhancement and the site blocking effect cannot be expected to be easily modelled, in particular since strong coverage dependencies are at work.

Tables 1 and 6 suggest that a correlation may exist between the NH_3 synthesis activity and the rate of N_2 chemisorption except for the Cs containing catalysts.

Table 6
Nitrogen coverage (μmol/g-N_2) for which the rate of N_2 chemisorption for 0.25 atm N_2 is the same as the rate of NH_3 synthesis in 1 atm of 3 : 1 synthesis gas (both at 300°C). (a) No hydrogen, (b) strongly adsorbed hydrogen

	(a)	(b)
no P.	19	32
Ba	15	26.5
La	13	26.5
Cs (9%)	26.5	35
Cs (4%)	35	35

The deviation is less pronounced for the H–∗ precovered surfaces.

4.4. Kinetics

The suggested reaction paths are illustrated in figure 7. In the left route (A) it is assumed that the hydrogen enhanced reaction proceeds through the formation of a dehydrodiimide as suggested by Carrà and Ugo [22]. However, the possibility exists that the intermediate could be $N_2H_2{-}*$, as suggested by Ozaki, Taylor and Boudart [23].

The forward rate of NH_3 synthesis for reaction schemes A and B can be written as

$$R_B(NH_3) = k_A P(N_2)(\theta_{-*})^{2n} ,$$

$$R_A(NH_3) = k_B P(N_2) P(H_2)^r (\theta_{-*})^{2n} ,$$

where $P(x)$ is the partial pressure of gas x, $\theta{-}*$ the fraction of free sites and n is the ratio between the saturation chemisorption of H_2 and N_2 ($n \geqslant 1$). In a Langmuir model r would be expected to be 0.5 or 1, depending on the number of hydrogen atoms taking part in the hydrogen assisted mechanism, i.e. 1 or 2. A more realistic prediction is $r \leqslant 0.5$ or $r \leqslant 1$.

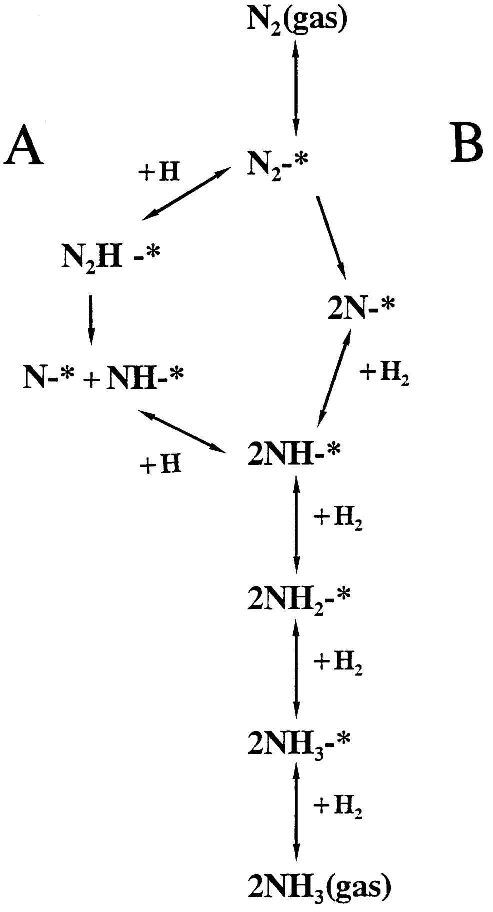

Figure 7. Possible reaction paths. (A) Involving hydrogen in the N_2 dissociation step, (B) conventional N_2 chemisorption.

For high conversions, the density of free sites can be expected to be given by

$$(\theta_{-*})^2 = (1 + K_1 P(NH_3)/P(H_2)^w)^{-2\alpha}$$

when the most abundant reaction intermediate (MARI) is $N{-}*$ ($w = 1.5$) or $NH{-}*$ ($w = 1$). Similarly, the low conversion limit (MARI = H–∗) yields

$$(\theta_{-*})^2 = (1 + K_2 P(H_2)^{0.5})^{-2\alpha'} .$$

For reaction path B, the reaction order for H_2 is $-\alpha n$ in the limit of zero conversion. For the industrial iron NH_3 synthesis catalyst the value of α has been determined to be 0.64–0.75 ($w = 1.5$) [24]. If we tentatively use the same values here, we find for $n = 2$ (Ru : H–∗ = 1 and Ru : N–∗ = 2 [25])

$$-1.5 \leqslant \mathrm{Ro}(H_2) \leqslant -1.28 ,$$

in fair agreement with the most extreme case in table 2 (Ru + Cs/MgO). It can be noted that if the surface stoichiometry of H–∗ and N–∗ is the same ($n = 1$), then the reaction order for H_2 should not be lower than −1, but stoichiometries like Ru : H–∗ = 1 and Ru : N–∗ = 2 (or larger) can obviously lead to a more negative reaction order for H_2. It is interesting to notice that the value −1.25 will lead to the following dependence on the total pressure P:

$$P(N_2)/P(H_2)^{1.25} = P^{-0.25} ,$$

i.e. the activity decreases with the total pressure P for a fixed $H_2 : N_2$ ratio, as demonstrated in figure 1 for the strongly Cs promoted sample.

The rate of chemisorption of N_2 described by reaction path B is very fast for the strongly Cs promoted catalysts, so we can expect mechanism B to be dominant for these samples. For the other catalysts, the hydrogen assisted mechanism (reaction A) may be more important, consistent with the observation that the reaction order for H_2 is 0.6–0.8 higher (table 2), resulting also in a positive pressure dependence (figure 1).

The concept of two parallel mechanisms for the N_2-dissociation on the catalyst surface at NH_3 synthesis conditions can (e.g.) be used to explain the earlier reported S-shape of the plots of the activity versus alkali content, which is in contrast to the more linear variation for the other promoters [26]. The idea is that the hydrogen-mediated dissociation mechanism B dominates strongly for the alkali-free catalysts, so strongly, actually, that the addition of alkali may result in a two to three orders of magnitude increase in the ("hydrogen free") rate of chemisorption of N_2, even though it hardly influences the NH_3 synthesis activity, as shown in figure 5 and table 1 (4% Cs)! The promoting effect of Cs only comes into action when the number of free sites has increased significantly, due to the destabilization of the adsorbed species N–∗ and H–∗ (figures 8 and 9). The destabilization of N–∗ is not as strong for Cs as for the other promoters, as demonstrated in figure 8.

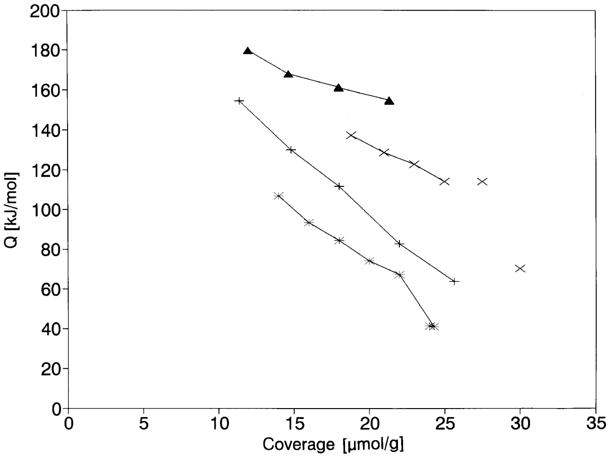

Figure 8. Heat of chemisorption of N_2. Symbols as figure 4.

It is conceivable that the well known beneficial effect of basic supports on the NH_3 synthesis activity is caused by the promotion by the basic oxides of the hydrogen enhanced route to N_2 dissociation. In the light of these ideas, we can also easily understand the fact that Ru on carbon has an extremely low activity, which can be increased (in an approximately linear way) by several orders of magnitude by the addition of alkali (or other promoters). However, preliminary results for a Ru/SiO_2 catalyst demonstrates the same type of effect of H_2 on the rate of N_2 chemisorption as observed here for $Ru/MgAl_2O_4$. At any rate, we would not expect the promoting affect of alkali on these catalysts to be caused by neutralization of acid sites, since the support is basic from the beginning.

4.5. Heats of chemisorption

In ref. [5], it was demonstrated that K may have a destabilizing effect on N–∗, for unknown reasons. Here, the heat of chemisorption can be estimated from the isotherms by use of the Clausius–Clapeyron relation. The results for N_2 (figure 8) suggest that the effect is increasing for the promoters in the following order: Cs, Ba, La, and it is very pronounced for the last. The ranking is the same as for the NH_3 synthesis activity (tables 1 and 7).

The calculated heat of chemisorption of H_2 is displayed in figure 9. As for N_2, a decrease of the heat with the addition of a promoter is observed. However, it is an unfortunate fact that the experimentally accessible coverage range is partly dominated by the weakly chemisorbed H_2.

It is a new observation that H–∗, as well as N–∗, may be destabilized by all of the promoters included in this study, most strongly by Cs and La. However, a similar effect was recently reported for La on Co by Vada et al. [28]. This suggestion should be verified by more direct methods, and the possible implications for other reactions should be evaluated.

The observed effects of the promoters are summarized in table 7. Only the destabilization of N–∗ has the same ranking as the synthesis activity. However, the fact that the NH_3 inhibition is the reverse as expected from the N–∗ destabilization (tables 2 and 7) is then a puzzle. The lack of NH_3 inhibition observed for the Cs promoted samples is even more strange, when the results by Nwalor and Goodwin [27] are taken into account, since they also reported a low NH_3 inhibition for K promoted Ru/SiO_2, even for high N–∗ coverages. More work on the simultaneous interaction of H_2 and N_2 with Ru surfaces is obviously needed.

Table 7
Ranking of the promoters with respect to their effect on catalyst properties, which are relevant for NH_3 synthesis activity

	Activity	Rate of N_2 chemisorption		Destabilization of	
		no H–∗	with H–∗	N–∗	H–∗
La	3	1[a]	2[a]	3	2
Ba	2	1[a]	1[a]	2	1
Cs	1	3	3	1	2

[a] Depending on temperature. La dominates at high temperatures.

5. Conclusions

A series of ruthenium NH_3 synthesis catalysts with selected promoters added have been studied. It is demonstrated that the rate of N_2 chemisorption can be strongly enhanced by preadsorbed hydrogen. The promoters La and Ba have a weak influence on the rate of N_2 dissociation on the hydrogen free surface at 200°C, while they cause the rate to increase for a partly hydrogen covered surface. This increase correlates with the effect on the rate of NH_3 synthesis. In contrast, Cs was able to increase the rate of N_2 dissociation by two to three orders of magnitude with almost no change in the activity for NH_3 synthesis.

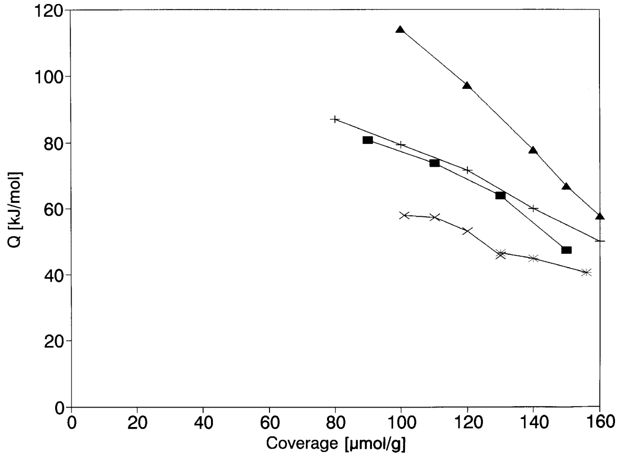

Figure 9. Heat of chemisorption of H_2. Symbols as figure 4.

These observations suggest that there may be two competing mechanisms for the N_2 dissociation, a direct path, promoted by alkali, and a hydrogen assisted process, which is promoted by Ba and La. This mechanism dominates strongly for the alkali free catalysts, so a minimum amount of Cs has to be added in order for the direct dissociation process to exceed the hydrogen assisted mechanism. This explains the frequently observed S-shaped curve of NH_3 synthesis activity versus alkali concentration.

The activation energies for the N_2 chemisorption have been estimated. The value was lowered by the addition of Ba or Cs. The heats of chemisorption of H_2 and N_2 were calculated using the Clausius–Clapeyron relation. All of the promoters appear to have a destabilizing effect on adsorbed hydrogen or nitrogen. A correlation has been established between NH_3 synthesis activity and heat of N_2 chemisorption at non-zero coverage.

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