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Temperature-Programmed Adsorption and Desorption of Nitrogen on Iron Ammonia Synthesis Catalysts

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Iron catalysts with and without a potassium promoter have been studied in a combined temperature-programmed reaction and flow microreactor system connected to a mass spectrometer. This arrangement has the advantage that sample characterization through temperature-programmed methods can be carried out alternating with measurements of synthesis reaction rates. The desorption studies demonstrate a significant shift of the N_2 desorption peak to lower temperatures with the addition of K to the catalyst. This change suggests a destabilization of dissociated nitrogen. The N_2 adsorption results are generally in good agreement with earlier studies of singly promoted catalysts. Thus the rate was found to be slow and activated. The addition of K has little effect on the temperature-programmed adsorption (TPA) curves, while for multiply promoted catalysts there is a significant shift of the main adsorption dip to lower temperatures. However, the adsorption was still activated even for this type of catalyst.

INTRODUCTION

Iron-based ammonia synthesis catalysts have been studied for most of this century and consequently a great deal is known about the bulk structure, the surface composition, and the nature of the reactions taking place during synthesis (1). However, a few problems still remain to be solved, such as the exact states and effects of the promoters. It is generally accepted that Al is a structural promoter (1), while Ca has some structural effect (2) and K is an electronic promoter (1). The effect of K has been explained by a neutralization of acid sites on the alumina, by a destabilization of hydrogenated nitrogen, or by an increase of the rate of dissociation of N_2 (1), but no final proof of any of these mechanisms has been provided.

Dissociative adsorption of N_2 is the most important surface reaction on this type of catalyst, since it is generally regarded to be the rate-determining step in the ammonia synthesis reaction under industrial conditions. The rate of chemisorption of N_2 was studied by Emmett and Brunauer for doubly and singly promoted samples (3) and by Scholten *et al.* (4) for a singly promoted catalyst. In both studies it was concluded that the process was slow and activated. Unfortunately, many of the reviews of the old literature contain the misleading statement that Emmett found a sticking coefficient of 10^{-6}. This is true, but it is important to bear in mind that Emmett was focusing on results at 450°C and defined the sticking coefficient as the number of molecules adsorbed divided by the number of molecules hitting the surface *with an energy larger than the activation energy*. Particularly the last point is important, since Emmett was using an activation energy of 67 kJ/mol, so only a fraction of ca. 10^{-5} of a thermal distribution has a higher energy. This means that the sticking coefficient is 10^{-11} *without* correction for the activation energy. In contrast to this result, it has been suggested that a nonactivated sticking coefficient on the order of 10^{-6} should provide an adequate description of the chemisorption process (5, 6). The discrepancy between the sticking coefficients was explained by oxygen poisoning of the catalysts (6).

Therefore, it is essential to obtain full control of all possible sources of surface contamination when studying ammonia synthesis catalysts. Oxygen, for instance, will always be present in the promoter phases on the surface of the industrial iron catalyst. Since these oxides may cover half the surface or more (7), it is quite difficult (if not impossible) to verify the absence of O_2 poisoning by spectroscopic analysis of the surface.

For this reason, it is imperative that any surface studies of the (supposedly) active catalyst are carried out in a setup ensuring that the activity of the synthesis reaction itself can be tested in order to evaluate the state of the surface. The synthesis should preferably be performed at high pressure. Accordingly, the present studies were performed in a flow reactor system with these possibilities and with use of a mass spectrometer for gas analysis. Besides the adsorption, the desorption of molecularly and dissociatively adsorbed nitrogen and the effect of preadsorbed hydrogen on the rate of dissociation of N_2 were studied.

The aim of this study was to throw new light on the

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controversy concerning the rate of chemisorption of N_2. Temperature-programmed adsorption (TPA) was found to be a suitable method. The catalyst sample was exposed to a low concentration of N_2 in He (typically 0.5%) and the N_2 signal was monitored while ramping the temperature of the sample. The advantage of this method is that it provides a quick means of monitoring the adsorption/desorption behavior of the catalyst in the relevant temperature range.

METHODS

Catalysts

Samples of singly (Fe, Al), doubly (Fe, Al, K), and multiply promoted (Fe, Al, Ca, Mg, Si, K) fused iron oxide catalysts were studied using a nominal amount of 0.5 g and a sieve fraction of 0.1–0.3 mm, 0.15–0.3 mm, or 0.5–0.85 mm. These model catalysts were all produced by the same method from melts of the constituents. The atomic concentration of the promoters in the reduced catalyst was zero or as follows: Al $\cong$ 4%, Ca $\cong$ 4%, Mg $\cong$ 0.6%, Si $\cong$ 0.7%, K $\cong$ 1.0%. Diffusion limitations of the results can be ruled out, since samples of the sieve size fractions 0.15–0.3 mm and 0.5–0.85 mm demonstrated exactly the same temperature-programmed adsorption (TPA) and desorption (TPD) behavior. These catalysts have been through extensive studies of the activity at 1–90 bar (8), N_2 porosimetry, temperature-programmed reaction of preadsorbed nitrogen (N–*) with H_2 (7), etc., so their properties are well established. Thus the BET areas were rather similar (in the range 10–15 m^2/g) due to the fact that the concentration of the Al promoter and the mode of preparation was the same. No micropores (diameter < 5 nm) were present.

Test Unit

The experimental setup has been described earlier (7). All the gases used were 99.9999% pure. The H_2 and N_2 could be purified further by leading them through a purification unit, which was obligatory during synthesis reaction in order to ensure that the catalyst was not poisoned by oxygen (9).

Possibly some poisoning could have occurred during the TPA/D experiments and the periods of flushing with He. However, since the flow was 50 N ml/min and the impurity level below 1 ppm, the maximum amount of poison received by the samples was less than 0.13 μmol/h. With the duration of an experiment always being less than 10 h and the active surface area corresponding to at least 12 μmol N_2, only the first few percent of the catalyst bed would have been poisoned.

Feed Gases

The gases were analyzed by mass spectrometry. The signals monitored were those of H_2, N_2, and NH_3, as well as of any impurities such as CO, CO_2, CH_4, O_2, and H_2O.

The purity of the feed gas was also verified by continuous measurements of the activity when the sample was rapidly cooled to 590 K according to the procedure described in Ref. (9). No deactivation was found even after several hours at 590 K. Thus, the catalyst is expected to be unaffected by any oxygen-containing impurities from the gas phase.

Activation

The catalysts were reduced in synthesis gas using a temperature program of decreasing heating rate up to 670 K, chosen in order to ensure that the vast majority of the water had disappeared before the temperature reached 670 K. The increase of the heating rate within the range 670 to 770 K did not result in any notable increase in the H_2O level. The catalyst was considered fully reduced when further heat treatment at 770 K did not cause any increase in the activity of the NH_3 synthesis. Finally, the catalyst was held at 670 K for at least 16 h.

The effects of reduction in pure H_2 instead of synthesis gas were also investigated. In these experiments the state of reduction of the samples could not be evaluated by activity measurements. It was tested by monitoring the H_2O signal during a fast increase of the temperature from 770 to 820 K. The procedure was repeated until no H_2O was observed. For the singly promoted sample this procedure resulted in a 12-h reduction period at 820 K, while the doubly promoted sample (Fe, Al, K) received a 43-h treatment at the same temperature. No NH_3 or CH_4 was observed during the reductions in H_2.

TPA and TPD Techniques

The TPA procedure was as follows. First, the ammonia synthesis reaction was run under stable conditions at 670 K for at least 2 h. The nitrogen flow was then shut off and the sample maintained at 670 K in pure H_2 for 1.5–2 h, until N_2 and NH_3 reached their baseline concentrations. Then the reactor was bypassed for 5–10 min in order to make sure that this was a true background (these first parts of the procedure were of course omitted in the TPA experiments carried out directly after reduction in H_2). It was subsequently heated to 770 K, where the background test was repeated.

The reactor was then cooled to 670 K and the gas flow was switched to He. After about 2 h the H_2 had decreased to the baseline level, and the heat treatment 670/770 K was repeated. Usually, no significant increase in desorption was observed during these thermal cycles; i.e., there was significantly less than 1 μmol desorption after each temperature step. An increase of the maximum cycle temperature to 820 K had no effect on the results. Occasionally, the sample was cooled to ca. 600 K and heated again at the end of the heat treatment in order to test for any forced segregation of nitrogen or hydrogen to the surface. None was ever observed.

The sample was cooled to 77 K in He flow and a linear temperature ramp was started. However, a few experiments were performed at constant power supply to the heater. In order to minimize the N_2 condensation and physisorption, the flow was switched to the N_2/He mixture at a temperature around 150 K. The N_2 concentration of the mixture was measured just before the ramp was started and also at the end of the experiment by bypassing the reactor. The flow was always 50 N ml/min during the TPA experiments.

Saturation coverage of adsorbed dissociated nitrogen (N–*) before the TPD experiments was obtained in a similar way by switching off the H_2 flow from synthesis conditions at 670 K and waiting for the NH_3 and H_2 signals to disappear (7). In this case the catalyst was cooled slowly (ca. 5 K/min) to 500 K in order to fill any remaining empty sites.

After each TPA experiment the condition of the catalyst was checked:

(i) by switching the flow to pure H_2 and monitoring the H_2O, NH_3, and N_2 signals, and

(ii) by mixing the H_2 with N_2 to a ratio of 3 : 1 (synthesis gas) and observing the increasing NH_3 signal.

No H_2O was ever observed (i), and the NH_3 production stabilized at its normal value within 10 min (ii). This would not have been the case if the catalyst had been significantly poisoned (9).

TABLE 1

Temperatures of Maximum Desorption and Adsorption and Turnover Frequencies at ca. 40% Conversion for the Four Model Catalysts Included in This Study

Sample	TPD peak (K)	TPA dip (K)	$10^3 \times$ TOF (s^{-1}) 1 bar	$10^3 \times$ TOF (s^{-1}) 50 bar
Multiply promoted	650	460	60	100
Doubly promoted (Fe, Al, K)	650	540	90	70
Singly promoted (Fe, Al)	710	540	40	7
"Doubly promoted" (Fe, Al, Ca)	710	500	30	7

Note. The number of active sites is deduced from Table 2, Peak 1, for 1 bar. The results for 50 bar have been determined from earlier experiments, where CO chemisorption was used (8). Thus the absolute values in the two columns are not directly comparable.

TABLE 2

Observed Amount of N_2 Adsorption and Desorption (μmol)

Sample	Fig.	TPA/(% N_2)	TPD Peak 1[a]	TPD Total[b]
3	5	14/0.38	14	28 [870]
7	6A	12/0.83	10	23 [820]
7	6B	12/0.83		
2	7	16/0.38	13	33 [870]
2	8A	19/0.77	(Desorbing H_2: 1.6)	
2	8B	3/0.77		
2	10	23/0.77	(Desorbing H_2: 33)	

[a] Estimate assuming symmetric peaks.

[b] The total coverage is determined by desorption to the given temperature (indicated between square brackets), switching to H_2 at that temperature, and summing up all the N_2 desorbed as N_2 or NH_3.

High-Pressure Tests

The effects of high-pressure synthesis on the TPD and TPA results were investigated for a doubly promoted sample. The pressure was increased to 30 bar and the sample was held at 670 K for 2 h, at 720 K for 8 h, and again at 670 K for 5 h. A small increase in activity was observed during this procedure (corresponding to a 3–5% increase in the active area). All other experiments were carried out at 1 atm, unless otherwise specified.

RESULTS

Activities

The activities were consistent with several earlier results from conventional reactor systems (7, 8, 10, 11). Typical turnover frequencies (TOF) for the catalysts are given in Table 1. The number of active sites was taken from Table 2 (Peak 1). It has been demonstrated that this number is in good agreement with the results obtained by other methods, such as H_2 and CO chemisorption (7, 11, 12). The results at 50 bar, added for comparison, were taken from earlier experiments (8), where the active area was determined from CO chemisorption after passivation and reactivation of the catalysts, so the numbers in the two columns should not be compared directly. The Peak 1 value can be expected to underestimate the number of active sites, since the peak is probably not symmetric (8). In addition, there was a significant pressure drop across the catalyst bed during the activity measurement. Both these problems will lead to an overestimated TOF at 1 bar. It is interesting to note the difference of an order of

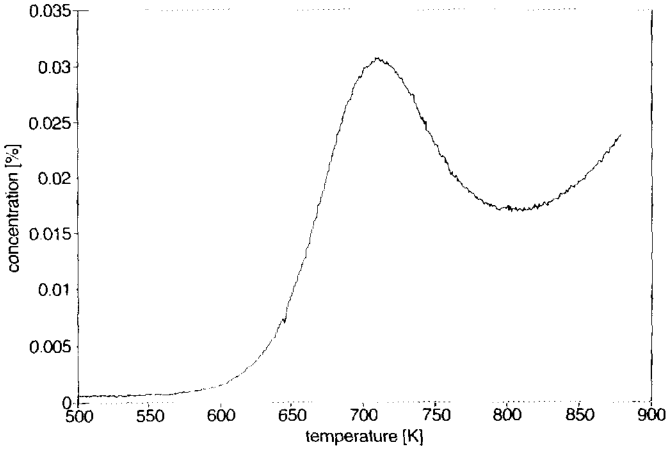

FIG. 1. N_2 TPD in He stream for singly promoted catalysts.

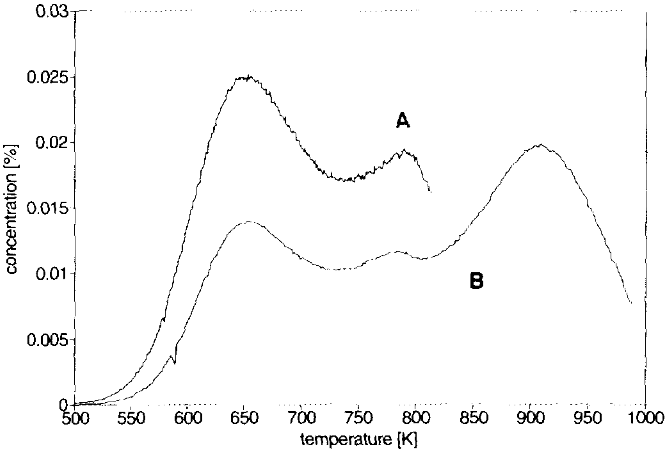

FIG. 3. N_2 TPD in He stream for multiply promoted catalysts: (A) Glass-lined reactor (50 N ml/min) and (B) Quartz reactor (120 N ml/min).

magnitude at high pressure for catalysts with similar TOFs at 1 bar.

Desorption Tests

The most striking result of the desorption studies (TPD) of dissociated nitrogen was that the presence of K in the sample caused a significant shift in the position of the first peak in the spectrum (Figs. 1 and 2). Up to two additional peaks were observed (Fig. 3). TPD traces similar to Fig. 3 have recently been observed for a Topsøe KM1 industrial catalyst (12).

Desorption of molecular nitrogen at low temperature was also studied. The surface was cleaned by the same procedure as for the TPA experiments. The sample was then exposed to 0.004 or 1 atm of N_2 at 150 or 195 K for a few minutes and then rapidly cooled to 77 K. The gas flow was switched to He at about 145 K in order to avoid condensation. The results did not vary strongly with the N_2 exposure, and the same peaks were observed before and after the catalyst (doubly promoted) had been working under high-pressure NH_3 synthesis conditions.

A typical result of a low-temperature TPD experiment on a sample containing K is shown in Fig. 4. After three consecutive low-temperature TPD experiments, the sample was heated in He to 766 K. No desorption of N_2 was observed after the decay of the 200 K peak.

A single experiment on a singly promoted (K-free) sample showed peaks at the same positions. The peak at 200 K was almost a factor of 2 smaller than for the K-promoted sample. However, more experiments are needed before it can be concluded that this difference in peak height is caused by the K and not by other factors, such as the exact procedure for the N_2 exposure.

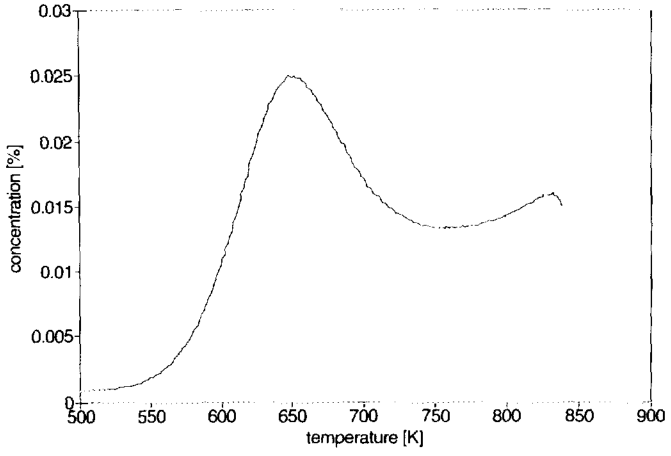

FIG. 2. N_2 TPD in He stream for doubly promoted catalysts.

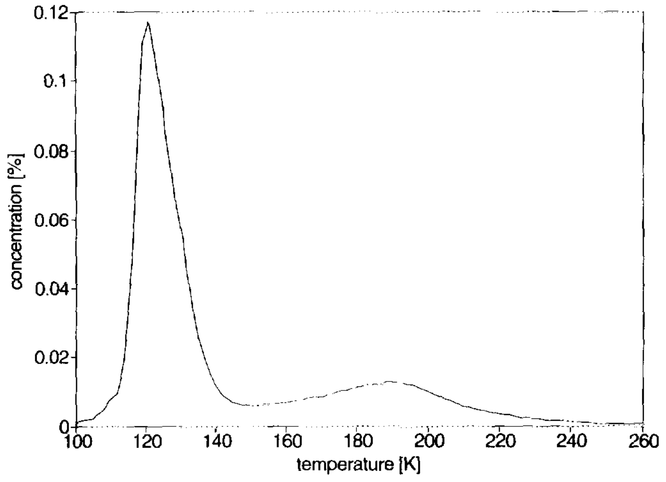

FIG. 4. Low-temperature N_2 TPD in He stream for doubly promoted catalysts.

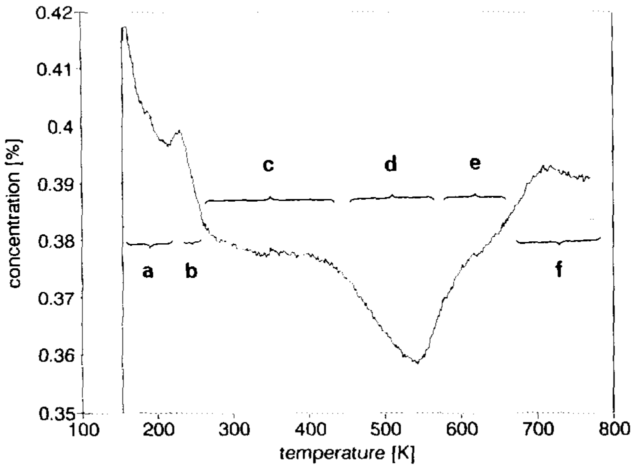

FIG. 5. TPA results for singly promoted catalysts. Ramp: 5 K/min. Switching from He to N_2/He mixture was done at about 144 K, while breakthrough of N_2 was observed at about 151 K. Dashed line: inlet N_2 concentration. (a, b, f) Zones of desorption. (c–e) Zones of adsorption.

The low-temperature TPD experiment was repeated after the sample had been passivated in 1000 ppm of O_2 in N_2 at room temperature. No desorption of N_2 was observed in the range 130–770 K.

Adsorption Tests

Figure 5 shows the results of a typical TPA experiment at a heating rate of 5 K/min and N_2 concentration 0.38%. An abundance of structure is observed. After switching to the He/N_2 mixture, there is a delay of about 1 min in which no N_2 is observed (the data sampling cycle is 16 s). The delay time without catalyst in the reactor is 0.5 min, which implies that all the N_2 is adsorbed during the first 0.5 min, i.e., 2–3 K below the sharp onset of desorption of physisorbed N_2 (labeled "a" in Fig. 5). The peaks labelled "a" and "b" reflect the low-temperature TPD results of Fig. 4. In the range between 255 and 640 K, the adsorption dominates over the desorption. An initial plateau of almost constant net adsorption (c) is followed by an accelerated rate of adsorption (d), starting at around 400 K and with a maximum at about 540 K.

The trend is surprisingly similar for the singly (Fig. 5) and for the doubly promoted samples (Fig. 6B). The only notable difference is that the adsorption in zone (e) is stronger for samples containing K. The partial pressure of N_2 is not the same in Figs. 5 and 6, but the only significant effect of the pressure is an increase in the size of peaks (a, b). After reviewing all the TPA traces, the following weaker trends are noted:

(i) The integrated value of the (a, b) peak is larger for K-free samples.

(ii) The adsorption plateau tends to be more flat for samples without K (perhaps a consequence of (i)).

(iii) The dip is rather sharp for the single promoted samples, while the sides are more rounded for the doubly promoted catalysts. It seems that there are two different structures at the flanks of this dip, the weak structure on the left side and the zone (e) adsorption on the right side.

Figure 6A displays the results of TPA for the doubly promoted sample just after reduction in H_2. The synthesis gas was then switched on with the catalyst at 650 K, and the rise of the activity was monitored for 12 h. At this time the activity was stable, which was verified by thermal cycling between 650 and 770 K for at least 12 h. About 150 min after the first introduction of synthesis gas, the activity had reached 80% of the final activity. When comparing Figs. 6A and 6B, it is clear that the synthesis did not induce any considerable changes of the

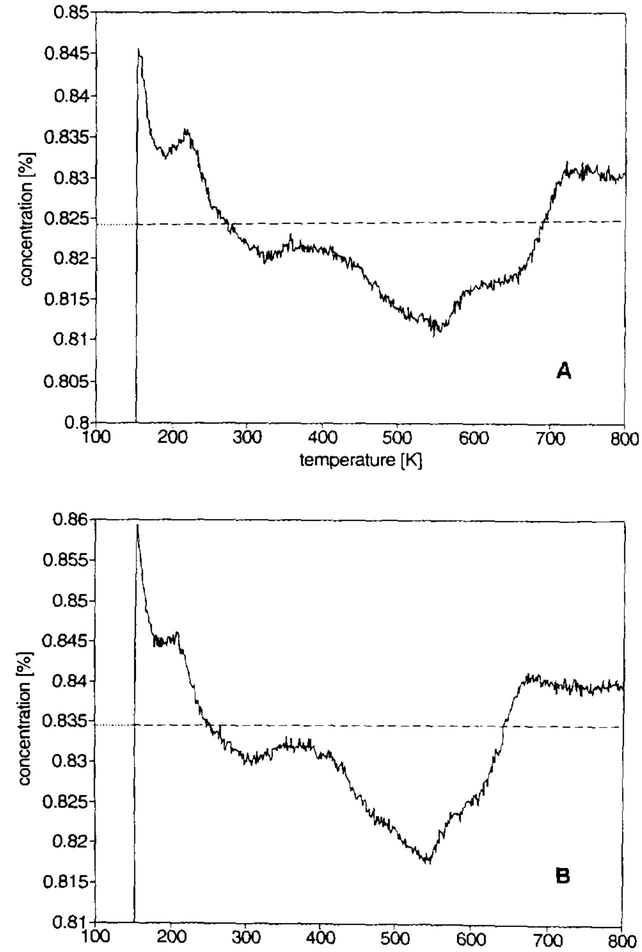

FIG. 6. TPA results for doubly promoted catalysts in a dilute N_2/He mixture (A) after reduction in H_2 (never exposed to N_2) and (B) after NH_3 synthesis. Dashed line: inlet N_2 concentration.

adsorption characteristics. The only significant differences are the decrease in the (e) structure while the magnitude of the main adsorption dip (d) has increased. Similar changes were observed for the singly promoted sample. After exposure to synthesis gas, the only difference found for samples reduced in synthesis gas or in H_2 was that the latter had a lower active surface area, due to the higher final reduction temperature. The shapes of the TPA and TPD were not discernable.

There were no additional changes in the TPA after the doubly promoted catalyst had been working under high pressure NH_3 synthesis conditions.

A pronounced difference in the shape is observed for the multiply promoted sample (Fig. 7). The main adsorption dip is shifted by 80 K toward lower temperatures. The onset of the acceleration of the rate of chemisorption, which was observed at about 400 K for the other samples, is shifted to about 350 K. An intermediate type of behaviour was demonstrated by a (Fe, Al, Ca) catalyst, suggesting a synergetic effect between Ca and K. Such an effect on the synthesis activity has been observed at high pressure (Table 1 and Ref. (8)]. The TPD and the TPA results are summarized in Table 1. However, the position of the main TPA dip is determined by a competition between adsorption and desorption, perhaps even for different types of sites, so the exact number should not be too strongly emphasized.

It is interesting to note that the three types of samples show no strong differences in the rate of adsorption at low temperatures/coverages.

It is difficult to calculate the exact absolute coverage of N–* from these experiments for the following reasons:

(i) the rate of dissociation of N_2 cannot be evaluated directly at temperatures below 255 K because of the simultaneous desorption, and

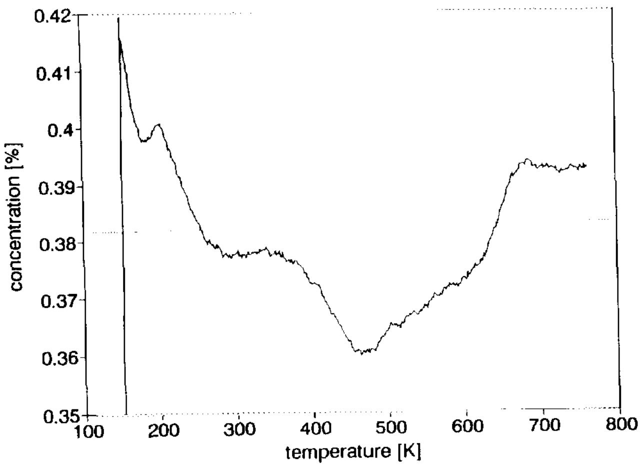

FIG. 7. TPA results for multiply promoted catalysts. Dashed line: inlet N_2 concentration.

(ii) the initial coverage is not exactly zero. There is always a little adsorbed hydrogen (H–*) (≈1.5 μmol H_2), and there may still be *some* N–* left on the surface after the applied cleaning procedure, except after reduction in H_2.

Item (i) is not very serious, since the balance between the adsorption before the breakthrough of N_2, i.e., 150 K, and the integrated amount of N_2 desorbing from the breakthrough to 255 K gives a reasonable estimate of the possible maximum value of dissociated N_2 during this period. It amounts to less than 2 μmol.

The difficulties of evaluating the initial coverage, combined with the fact that the rate of dissociation at *high* N–* coverages is much more relevant for the NH_3 synthesis than at low coverages, inspired the following experiment.

The catalyst was covered by N–*. It was cooled to 500 K and heated again in He until a significant amount (9 μmol) of N_2 had desorbed and at that stage the reactor was quenched. The TPA procedure was then carried out as usual from 77 K. The result is shown in Fig. 8B along with a reference experiment with an attempted initial coverage of zero, as usual (Fig. 8A). It is observed that the adsorption is blocked up to 450 K, so only zone (e) remains.

In order to try to establish a relation between the (c–e) structures and the TPD peaks, we interrupted the TPA procedure at selected temperatures: 376 K (after (c)) and 673 K. In the last case the reactor was quenched with liquid nitrogen to 320 K, and the N_2 was switched off. Only very little N_2 was adsorbed during the cooling procedure (≈0.7 μmol; desorbed during (f) ≈0.8 μmol). The results of the subsequent TPDs are shown in Fig. 9. Comparison of traces A to C demonstrates that the relative height of the two peaks depends on the prehistory of the catalyst.

A few isothermal adsorption rate measurements at temperatures within the range 380–570 K resulted in an average rates consistent with those found during the TPA experiments. The rate was measured directly by monitoring the N_2 concentration in the dilute N_2/He mixture and checked by the subsequent reaction of the dissociated N–* with H_2 (7). It was observed that at 570 K the catalyst was able to absorb all the N_2 in the gas mixture containing 3500 ppm N_2 for a period of about 0.5 min, while there was no significant delay in the breakthrough of N_2 at 510 K.

The effect of H–* on the surface was also investigated. The catalyst was cooled in H_2 to room temperature after the NH_3 and N_2 had disappeared, as in the TPA experiment. It was flushed in He at room temperature for about 0.5 h and then cooled to 200 K. A H_2 TPD ramp was started and quenched at 373 K after some desorption of H_2 (12 μmol). The catalyst was cooled to 77 K and the

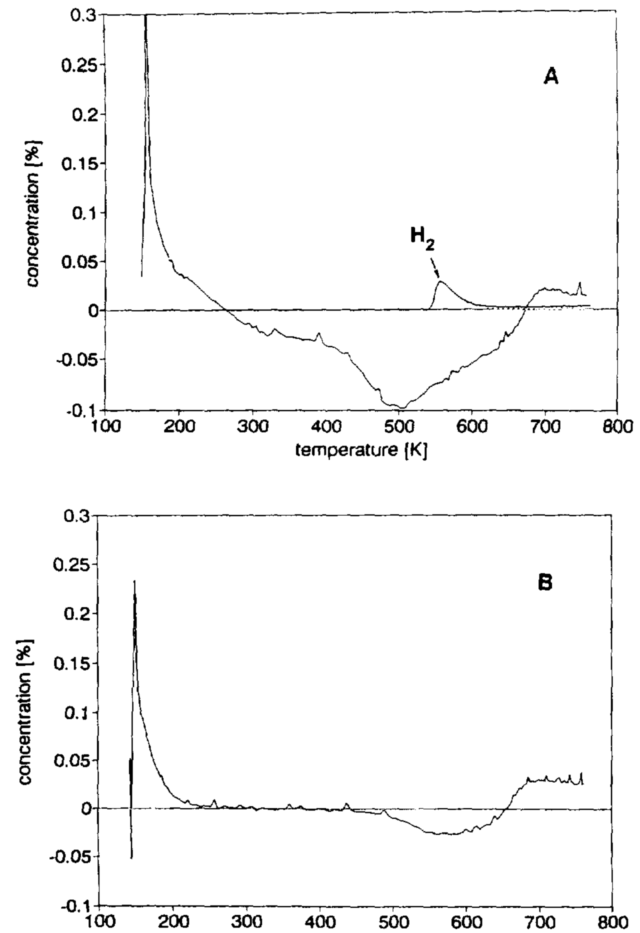

FIG. 8. TPA results for multiply promoted catalysts. N_2 concentration: 0.77% N_2 in He. Ramp: constant power, average heating rate of 20 K/min. (A) initial coverage ≈ 0 and (B) initial coverage of N–*, 0.7. A typical H_2 signal is also included in (A).

TPA was carried out as usual. The results for both N_2 and H_2 are shown in Fig. 10. It can be seen that the adsorption is effectively blocked until the H_2 starts to desorb. The adsorption then accelerates even more than without H–* on the surface (Fig. 8A). From about 570 K, the N_2 signals are identical in Figs. 8A and 10. Small amounts (up to 10 μmol H_2) of H–* accidentally left on the surface during the TPA pretreatment did not affect the TPA results significantly. No NH_3 was ever observed during any of the TPAs.

DISCUSSION

Desorption Studies

The desorption of dissociated nitrogen from Fe single crystals was studied by Boszo *et al.* (13, 14). They found the following peak positions: Fe(111), 860 K; Fe(110), 920 K; and Fe(100), 980 K, using a heating rate of 6–10 K/s. By use of a simple second-order desorption model (8, 15), the corresponding values for a heating rate of 5 K/min can be calculated: 730, 780, and 830 K. The peaks in Figs. 1–3 at 710, 790, and 830 K are not far from these values. However, the peak at 830 K has a peculiar shape: the decline on the right side is rather steep. The last peak in Figs. 1 and 3 is outside the calculated range. Correction for readsorption causes this peak to shift to temperatures within the right range. However, the calculated peaks become much wider, so they are not consistent with the present observations (8).

The possibility that the 900 K peaks arises from bulk nitrogen can be ruled out, since the bulk solubility at 670 K and 1 atm of N_2 is only 0.3 μmol/g of Fe (16). Here, this amounts to a desorption of 0.1 μmol, which is negli-

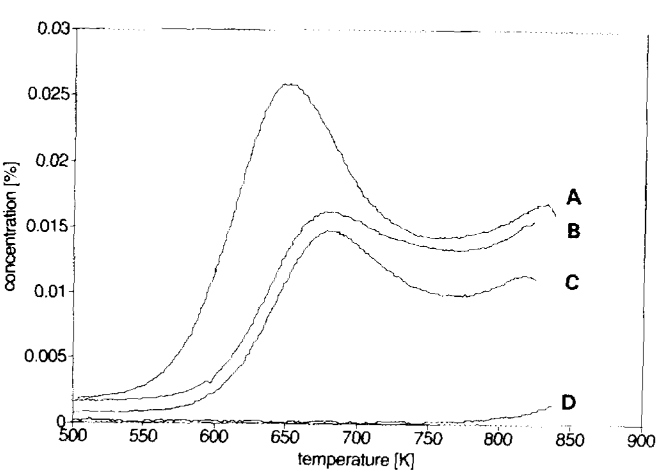

FIG. 9. N_2 TPD after various methods of adsorption: (A) as in Fig. 2, (B) after previous desorption to 643 K, (C) after TPA to 673 K, and (D) after TPA to 376 K.

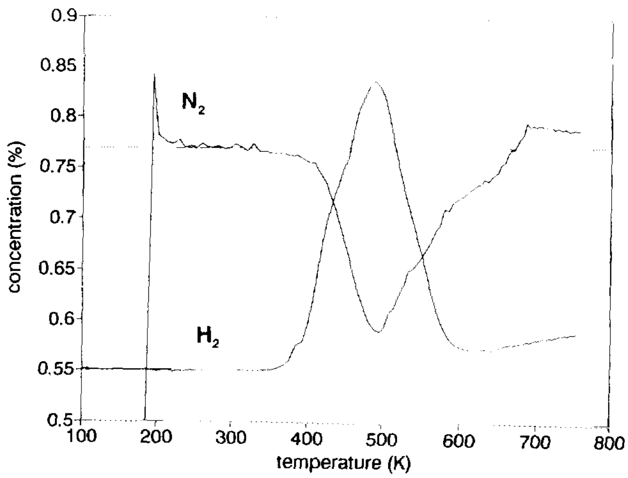

FIG. 10. TPA results for multiply promoted calaysts with a high initial coverage of H–*. Other conditions as in Fig. 8A. Switching to N_2/He was done at 180 K.

gible. Another possibility is that it comes from nitrogen located underneath the promoter oxides (17, 18) or in grain boundaries. It can be added that the N_2 TPD result after synthesis at 30 bar and 670 K was exactly as before the high pressure test (Fig. 2). The TPD procedure was carried out immediately after the pressure reduction as described above, except that the waiting time at 670 K was increased from 1 to 3 h in order to bring the H_2 signal down, while the N_2 decayed to zero very rapidly.

The shift of the first high temperature N_2 TPD peak with the addition of K is interesting. It suggests an increase in the preexponential factor or a decrease in either the heat of chemisorption or the activation energy for adsorption (and desorption). No strong effect of K is seen in the TPA, which is in agreement with earlier studies of chemisorption of N_2 on singly and doubly promoted catalysts (3), and this seems to rule out the last suggestion. The choice between the two other possibilities is not easy. Probably a combination would be most appropriate. Results of various studies of the heat of chemisorption range from 67 to 210 kJ/mol (19). Obviously, more work on guaranteed nonpoisoned catalysts with various promoters is needed, and in particular, direct calorimetry studies would be useful.

Both the decrease of the heat of chemisorption and the increase of the preexponential for desorption lead to a decrease of the equilibrium coverage of N–* at high temperatures. This particular result is interesting, since it is generally assumed that the promoting effect of K on the NH_3 synthesis reaction arises from a decrease of the activation energy of dissociative sticking (5) or from a destabilization of hydrogenated N–* (20). The present results suggest that it is the N–* itself which is destabilized.

Low-temperature TPD results similar to Fig. 4 have been reported by Waugh *et al.* (21), who interpreted the peak at about 200 K as α–N_2 from K-promoted Fe(100). A striking similarity between the low temperature N_2 TPD spectra for industrial NH_3 synthesis catalysts and for Fe(111) + K was observed by Schlögl *et al.* (22). However, no K-free reference sample was included in their study. This is unfortunate, in the light of the present result that peaks are observed at the same temperatures for catalysts with and *without* K, both during the TPA experiments and the during low-temperature TPD.

Adsorption Studies

The type of adsorption experiments presented in this paper have several advantages:

(i) The state of the catalyst can be checked by running the synthesis reaction immediately before and after each experiment to make sure that the activity is reasonable and that it is not affected by poisons.

(ii) The adsorption is monitored directly, contrary to the experiments where N_2 is adsorbed for a well-defined period, whereupon the adsorbed amount is determined either by desorption or by reaction with H_2. These methods also measure any N_2 adsorbed during the cleaning and cooling procedure.

(iii) The TPA is a convenient scanning experiment, when there is doubt about the onset temperature of the adsorption process.

The main disadvantage is that the rate variation with temperature and coverage is convoluted.

A deconvolution of the TPA data will call for many more experiments using different N_2 concentrations, heating rates and initial coverages. It is questionable whether the necessary accuracy of the results can be attained for all the parameter variations needed, in order to study the coverage range from, say, 0.1 to 0.9.

The deconvolution problem was evaded by using the opposite approach. Scholten *et al.* (4) went through the elaborate procedure of measuring the rate at various N_2 pressures, temperatures, and coverages for a catalyst without K (singly promoted with Al). The results were presented as an activation energy and a preexponential factor, which were both strongly coverage-dependent. This made it rather easy to use the data to calculate the expected outcome of the TPA experiment by means of a TPD type of program (15) after splitting up the relevant coverage range into suitable intervals. The number of active sites were taken from Table 2 (TPD, Total). The result is given in Fig. 11. The presence of molecular N_2 on the surface below 255 K has not been taken into account in the computer analysis. The shape of the adsorption curve is reproduced quite well, except that the calculated temperature of the main adsorption dip is too low. However, this disagreement is not considered very seri-

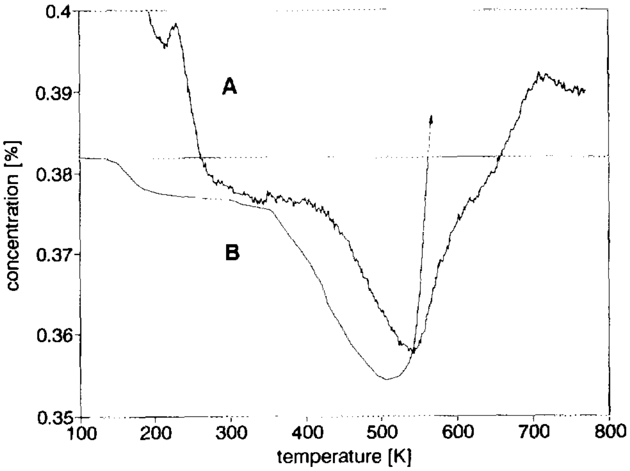

FIG. 11. Comparison between TPA curves: (A) experimental, taken from Fig. 5, and (B) calculated.

ous, taking into account the uncertainties both in the experiments and in the splitting of the adsorption rate into an activation energy and a preexponential factor. It should also be borne in mind that the catalyst studied in Ref. (4) had a much lower Al content than the catalysts in the present study (ca. ⅓). Since the rate of N_2 chemisorption at low temperatures seems to be higher rather than lower than in the present study, there is no reason to believe that the results obtained by Scholten *et al.* were affected by poisoning to any significant degree.

The calculation indicates that dissociation may occur at a non-negligible rate even below 200 K, but only up to a very low coverage of N–*. A comparison of the experiments carried out with very low and very high H–* coverages (Table 2) suggests that a few μmol (2–3 μmol) may be dissociated during the low-temperature, net desorption period, which is in full agreement with the calculation.

A more serious deviation is found above 550 K. The desorption starts very abruptly at 573 K, contrary to what is found experimentally, where it begins much more gradually at about 640 K. The coverage where the calculated rate of desorption exceeds the rate of adsorption is ca. 0.58, corresponding to a heat of chemisorption of 61 kJ/mol (4), a value much lower than found in most other studies. A plausible explanation might be found in the apparent presence of different sites on the surface. The instantaneous coverages in the adsorption and desorption experiments will only be identical if the N–* species on the various sites adsorb and desorb in reverse order. If this is not the case, then the calculation of Scholten *et al.* of the energy of chemisorption as the difference between the desorption and adsorption activation energies is questionable. If we compare the size of the peaks in Fig. 9, we note that the second peak is relatively larger for curve C than for curve A. This suggests that the second peak may result from sites for which the adsorption starts earlier than the sites of the first peak. The TPA structures can then be related to the TPD peaks as follows:

$$(c) \approx \text{peak } 3, \quad (d) \approx \text{peak } 2, \quad (e) \approx \text{peak } 1.$$

However, the difference in the relative sizes of the peaks in Fig. 9 trace C is not larger than could be explained by the desorption at the end of the TPA and the adsorption during the cooling period afterward, so we cannot exclude the possibility that the identification should be

$$(c) \approx \text{peak } 3, \quad (d) \approx \text{peak } 1, \quad (e) \approx \text{peak } 2.$$

It should be noted that the mobility of N–* may be high, so trace D in Fig. 9 does not prove the relation (c) ≈ peak 3. The possibility that the adsorption in zone (c) is molecular should perhaps not be ruled out completely. The studies of single crystal surfaces are not in favor of this suggestion. However, desorption of molecular N_2 at 350 K from evaporated iron films has been reported (23).

The deviation between the calculated and experimental results in Fig. 11 could also be explained by the following hypothesis. At intermediate coverages the adsorption occurs on a nonrestructured surface, while at higher coverages N_2 is desorbing from a restructured surface. However, the results shown in Fig. 8 do not support this hypothesis, since they display consistent rates even though the immediate prehistory of the surface had a low and a high nitrogen coverage, respectively.

As mentioned earlier, the present experiments cannot distinguish between coverage and temperature dependences. Thus, the structure of the TPA profile could be caused by

(i) pure temperature effects (activated chemisorption, increased mobility on heterogeneous surface, etc.) or

(ii) pure coverage effects (adsorbate–adsorbate interactions, intrinsic surface heterogeneity or restructuring, etc.).

Apparently, Scholten *et al.* succeeded in separating the temperature and coverage effects, since the calculations for the different coverage intervals, temperatures and N_2 pressures result in smooth curves for the activation energy and the preexponential factor vs coverage. However, the variation in N_2 pressure and the overlap between the range of coverages attained at each temperature was small.

It has been suggested (24) that the presence of H–* on the surface enhances the rate of dissociation of N_2. The fact that the adsorption dip in Fig. 10 is almost twice as deep as that in Fig. 8A points in the same direction. However, it should be noted that the adsorption is blocked by the H–* up to almost 400 K. The integrated amount of dissociated N_2 is only slightly larger for Fig. 10 than for Fig. 8A (Table 2), so the most likely explanation is that the increased rate just makes up for the adsorption taking place at low temperatures on the clean surface, i.e., free from H–* and N–*. The sharpness of the H_2 desorption peak in Fig. 10 is striking, compared to the TPD peaks reported earlier for an iron-based NH_3 synthesis catalyst (7, 25, 26). Apparently, chemisorption of N_2 accelerates the desorption of H_2 from the surface.

Surface Recontruction, Heterogeneity, and Coverage Dependence

It was suggested long ago that the surface of an industrial NH_3 synthesis catalyst is heterogeneous (19). The opposite has been claimed by others, based on the experimental findings that all N–* atoms on the surface undergo hydrogenation with equal probability (27). However, these experiments were performed under conditions where surface mobility and readsorption of NH_3 could conceal any intrinsic differences between the properties of the N–* atoms. New results, based on temperature-programmed reaction methods, indicate the existence of significant variations over the surface of the rate of hydrogenation (7).

The idea that surface reconstruction can take place during chemisorption of N_2 at Fe single crystal surfaces is well established (see, e.g., (13, 14, 28). Bozso *et al.* (13) actually show two different sets of TPD spectra for a Fe(111) surface, reconstructed and nonreconstructed for adsorption at high (640 K) and low (313 K) temperatures, respectively. The reconstruction of the surface of Fe/MgO catalysts has also been demonstrated (29). This inspired the following further investigation of the origin of the slow activity increase after reduction in H_2. A sample was flushed with N_2 at 650 K for 16 h after reduction to 820 K in H_2. Again, the same type of slow increase in activity after switching to synthesis gas was observed. This suggests that the synthesis reaction plays a role in the process. The chemisorption of N–* alone is not enough.

It should be noted that the N_2 adsorption rates (Fig. 5) are several orders of magnitude lower than extrapolated from low coverage sticking coefficient measurements on Fe(111) single crystal surfaces (5, 6). The deviation amounts to 4–6 orders of magnitude at room temperature.

The reason for this deviation is not clear. One possibility could be that the dissociation is strongly coverage dependent. Some degree of coverage dependence was, in fact, observed for the Fe(100) surface (13), but not enough to explain the large variation reported in Ref. (4). Almost no coverage dependence was observed for the Fe(111) surface at low coverages, but the time variation of the N : Fe Auger peak height ratio suggested a much stronger effect at higher coverages. An alternative explanation could be found in the presence of the promoter oxides on the surface (30). Based on H_2, CO, and CO_2 chemisorption studies it was concluded in Ref. (17) that practically all the Fe atoms on the surface have a promoter atom neighbor. The possible consequences of such a fine "dispersion" of the Fe sites over the surface have not been evaluated.

CONCLUSIONS

The N_2 adsorption for nonpoisoned iron NH_3 synthesis catalysts has been studied by temperature-programmed adsorption. All samples demonstrate activated N_2 chemisorption, and the results for the singly promoted sample are in reasonable agreement with earlier results (4) obtained for a similar catalyst. However, the rate is orders of magnitude lower than extrapolated (5, 6) from low coverage studies on single crystals of iron.

The TPA results for singly and doubly promoted catalysts were very similar. This is in agreement with earlier measurements of the N_2 chemisorption rate (3). Ca has a more striking effect in combination with other promoters in particular. Obviously, more work is needed in order to elucidate the role of Ca in the industrial NH_3 synthesis catalyst.

The high-temperature N_2 TPD results demonstrate a significant effect of K, which can be interpreted as resulting from a destabilization of N–* rather than from a decrease of the height of the energy barrier resulting from a stabilization of adsorbed N_2 (N_2–*). It remains an open question if this is a result of a direct (electronic) interaction or rather an indirect effect, caused by restructuring of the surface. A detailed interpretation of the TPD and TPA results and the consequences for the calculations of the rates of NH_3 synthesis, will be published later (8).

High-pressure synthesis reaction had no effect on either the TPA or the molecular or the associative TPD.

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