JOURNAL OF CATALYSIS **142**, 135–146 (1993)

The Interaction of H_2 and N_2 with Iron Catalysts Used for NH_3 Synthesis: A Temperature-Programmed Desorption and Reaction Study

B. FASTRUP, M. MUHLER,[1] H. NYGÅRD NIELSEN, AND L. PLETH NIELSEN[2]

Haldor Topsøe Research Laboratories, Nymøllevej 55, DK-2800 Lyngby, Denmark

Received June 29, 1992; revised January 18, 1993

Iron catalysts with and without potassium promoter were investigated in a flow reactor system connected to a mass spectrometer. Temperature-programmed surface reaction (TPSR) of preadsorbed dissociated nitrogen with hydrogen has been studied under various experimental conditions. The results suggest that the total amount of ammonia produced gives a good estimate of the active area of the catalyst. The shape of the TPSR spectrum depends on the promoter content, the initial coverage and the partial pressure of H_2 and indicates that the surface is nonuniform. The exact interpretation of the H_2 TPD spectra is influenced by several complications. The evaluation of the results is aided by computer simulations. © 1993 Academic Press, Inc.

INTRODUCTION

Reaction of preadsorbed atomic nitrogen with hydrogen has been studied by several authors both for Fe (*1–7*), Co (*8*), Ru (*9*), and Os (*10*). The results have been applied to estimate the area of the active surface or to evaluate the rates of hydrogenation of atomic nitrogen (N–*) or dissociation of molecular nitrogen.

Most of the earlier experiments were performed under isothermal conditions at a rather high temperature. This resulted in a rate of NH_3 formation which was proportional to the flow of hydrogen, indicating the existence of an equilibrium between NH_3, H_2, and the adsorbed species (*2*).

We have studied the reaction of H_2 with preadsorbed atomic nitrogen on singly or multiply promoted Fe catalysts by heating at a constant rate in a stream of hydrogen (temperature-programmed surface reaction, TPSR). This method results in a flow-independent rate of NH_3 formation, provided that the heating and flow rates are appropriately chosen.

Temperature-programmed desorption of H_2 or other gases can reveal important information about metal surfaces. This has been demonstrated in numerous papers about studies of single crystal faces in UHV systems. The application of the method to real catalysts in reactor systems is not without difficulties, as discussed below.

EXPERIMENTAL

The data for a potassium-promoted sample shown in this paper were obtained for a multiply promoted catalyst (Fe, Al, Ca, Mg, Si, K). Various combinations of promoters were tried in order to identify the causes of any differences between the TPSR results: (Fe, Al), (Fe, Al, Ca), (Fe, Al, Mg), (Fe, Al, Mg, K), and (Fe, Al, Ca, K). Typical BET areas were 20–25 m^2/g. A sieve fraction of 0.1–0.15 mm was used in most of the experiments. This should make certain that pore diffusion does not affect any of the results.

The experimental set-up consisted of three gas lines (He, H_2, N_2), a purification

---

[1] Present address: Fritz-Haber Institut, Berlin, Germany.

[2] Present address: University of Aarhus, Aarhus, Denmark.

0021-9517/93 $5.00

unit, the reactor, and a mass spectrometer or an NH_3 UV detector. All tubes and fittings were stainless steel. The purification unit was necessary in order to ensure that the catalyst was not poisoned by oxygen (*11*).

The sample was placed in a glass-lined U-tube reactor (*12*). The temperature was measured with a calibrated thermocouple inside the catalyst bed. No difference was observed between this thermocouple and one fixed to the outside of the tube. The U-tube was placed inside an aluminum cylinder which ensured negligible temperature differences over the bed. The other leg of the U-tube acted as a gas preheating zone. The Al cylinder could be heated electrically and cooled by pressurized air or liquid N_2. By optimizing the settings of the Eurotherm controller, linear ramps starting at room temperature could be achieved. All ramps starting at −195°C were run with constant output power, which resulted in a slightly decreasing heating rate at higher temperatures. Care was taken to avoid sudden delays during the ramp by isolating the oven and flushing with N_2. If some ice was frozen into the oven, sudden jumps appeared in the TPD spectra at the melting and at the boiling point of H_2O.

H_2, N_2, and NH_3 were monitored at mass 2, 28, and 17 amu, respectively. In order to check for impurities of CO/CO_2 and H_2O, the intensities at 12 and 18 amu were measured simultaneously.

The purity of the gas supply was also verified by continuously measuring the activity when the temperature was ramped down to 300°C according to the procedure described in Ref. (*11*). No deactivation was found even after several hours at 300°C. The reactor was working under plug flow conditions (PFR).

The TPSR procedure was as follows. First the ammonia synthesis reaction was run under stable conditions at 400°C. The hydrogen flow was then shut off and the sample maintained at 400°C in pure N_2 for 1–2 h, until H_2 and NH_3 had reached their baseline concentrations. The reactor was then cooled to room temperature in N_2. This procedure is expected to yield a saturation coverage of atomic nitrogen, N–*. The gas flow was changed to H_2 (25–200 N ml/min), N_2 was flushed out in about 1 h, and then the temperature ramp was started.

The H_2 TPD was run in a similar way. First the N_2 flow was shut off. After 1 h or more, the sample was cooled in H_2 to 78 K. The ramp was then started after 1–2 h of flushing in He. During all H_2 TPD measurements, the purification unit had to be bypassed because it could act as a source of H_2 in the ppm range depending on the prehistory.

Blank runs were performed by testing an alumina sample with a BET area and a pore structure similar to the iron catalyst. This did not give rise to any TPSR or TPD signals except for low-temperature (< -120°C) N_2 desorption.

RESULTS

Temperature-Programmed Surface Reaction (TPSR)

Figures 1–3 show the TPSR peaks for samples with and without K. Figure 1 demonstrates that the peak scales directly with the inverse flow, so the rate of formation of NH_3 is independent of the flow, indicating that readsorption of NH_3 is not important even though the sticking coefficient for NH_3 is high. The reason is probably that H–* immediately blocks most of the free sites. The dependence on the heating rate is shown in Fig. 2. As would be expected, the peak is shifted to higher temperatures when the heating rate is increased.

No desorption of N_2 was observed at temperatures up to 400°C, when the partial pressure of H_2 was 1 atm. This suggests that the integrated amount of NH_3 can be expected to represent the number of active sites on the catalyst. However, the decay of the NH_3 signal at temperatures above 200°C is very slow, so it is not obvious that the surface really is empty, when the signal approaches the resolution of the NH_3 detector. The slow

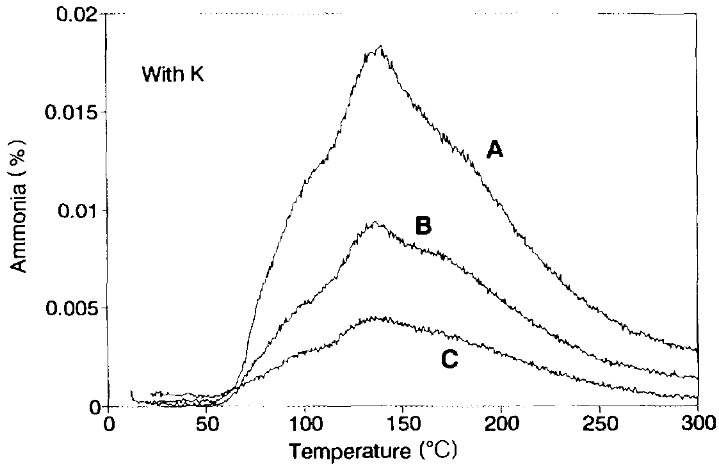

FIG. 1. TPSR of N–* in H_2. K-promoted sample. The effect of variation of the gas flow. (A), (B) and (C): 50, 100, and 200 N ml/min, respectively. Heating rate: 1°C/min.

rate also raises questions about the possible role of nitrogen from the bulk of the catalyst or the walls of the reactor. The solubility of nitrogen in iron at 400°C is only ca 0.3 μmol/g (*13*), so the contribution from the catalyst is negligible. The glass lining of the reactor should rule out any contributions from the walls. In addition, an independent test was made using a glass U-tube.

The difference between K-promoted and K-free samples is striking (Fig. 3). The onset of the production of NH_3 starts out smoothly for the K-promoted samples, while it happens very abruptly for samples without K. This is consistent with the expectation that the surface is approximately totally covered by N–*, leaving almost no sites for H_2 dissociation. Once the desorption of NH_3 has started, the number of sites available for H–* increases, so a self-accelerating effect is observed.

This explanation can be tested by running the TPSR with incomplete initial coverage. The result of an experiment with initial cov-

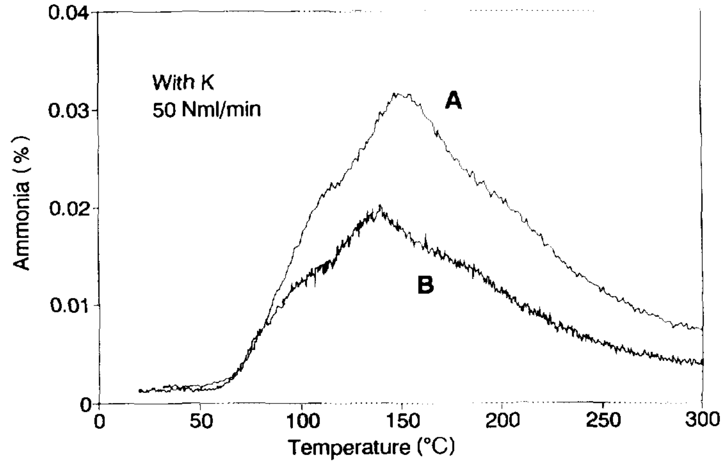

FIG. 2. As Fig. 1. The result of variation of the heating rate. (A) 2°C/min; (B) 1°C/min.

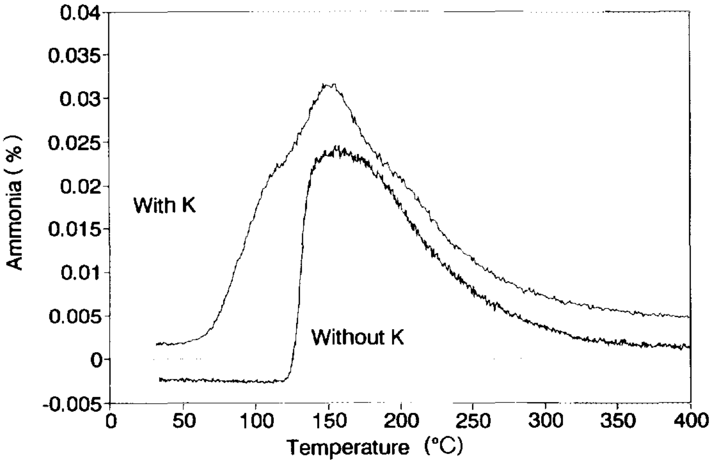

FIG. 3. TPSR of N–* in H_2. Comparison of samples with and without K. The curves have been vertically displaced for clarity.

erage 0.99 of N–* is shown in Fig. 4. The onset is now similar to that observed for the K-promoted samples. The lower coverage was obtained by interrupting a normal TPSR procedure by quench cooling the reactor with liquid N_2 just when the NH_3 signal was observed to increase. The initial coverage was then calculated as the ratio between the integrated peaks for the TPSR following the interruption and a normal TPSR. Addition of the amounts of NH_3 produced before and after the interruption resulted in the same value as found for the normal TPSR.

The earlier and less abrupt onset of the production of NH_3 on K-promoted samples can be understood by looking at the results obtained by Ertl *et al.* for adsorption of H_2 on Fe single crystals. They found that K blocks sites for N_2 (*14*) but not for H_2 adsorption (*15*). This means that there may

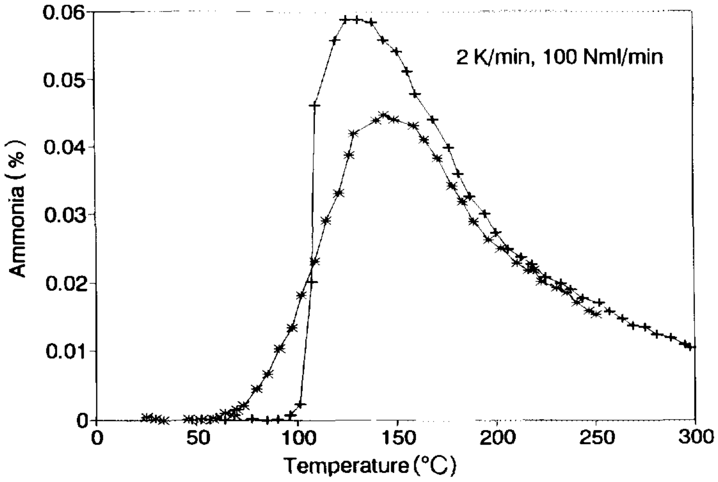

FIG. 4. TPSR of N–* in H_2. Illustration of the effect of decreasing the initial coverage θ of N–* for a sample without K (+) $\theta = 1.0$; (*) $\theta = 0.99$.

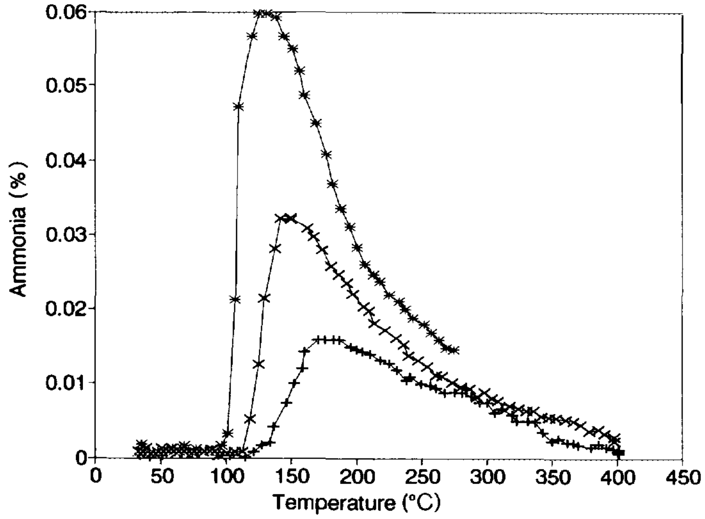

FIG. 5. TPSR of N–* in H_2. Parameter: H_2 pressure in atm. (*) 1 atm; (×) 0.2 atm; (+) 0.05 atm.

always be free sites for H_2 adsorption on samples with active alkali-promoted sites. An alternative explanation could be that the surface is just simply more inhomogeneous.

Some structure in the TPSR curve is frequently observed, but only for the K-promoted samples. The shape of the curves in Figs. 1–2 suggests that they might consist of two or even three peaks. Such a structure could not always be resolved, but the trend that the peaks were wider for K-promoted samples (≈ the onset was sharp for K-free samples) was quite general. This suggested inhomogeneity of the surface could be caused by the presence of both promoted and unpromoted sites. The possibility of a shift of the rate-determining step should also be considered in the discussion of the high-temperature shoulder.

Figure 5 shows the TPSR results for partial pressure of H_2 below 1 atm. H_2 was mixed with He and the total flow and pressure was kept constant. It is obvious that not all the N–* has reacted to NH_3 at the end of the ramp at 400°C. The partial pressure was then increased abruptly to 1 atm. This resulted in a second peak of NH_3. The integrated values are shown in Table 1. The numbers suggest that some of the N–* is lost as N_2 when the H_2 pressure is below 1 atm. The mass spectrometer was not available during this series of experiments, so this loss could not be measured directly. As mentioned earlier, we did not observe any desorption of N_2 with the mass spectrometer, when the H_2 pressure was 1 atm.

Temperature-Programmed Desorption (TPD) of Hydrogen

Typical H_2 TPD results are shown in Fig. 6. These curves were obtained after a long waiting time (ca 16 h) in H_2 at 400°C. The results for the K-promoted and the K-free sample are very similar.

A new very pronounced peak showed up around 110°C when the sample without potassium was cooled in synthesis gas (Fig. 7). This peak is also present but much smaller if the waiting time at 400°C in H_2 is cut down from 16 to 1 h before cooling in H_2. It was never observed for the K-promoted samples. An increasing N_2 signal showed up when the ramp was continued above 400°C. Unfortunately, this was only done for the K-promoted sample. The increase stopped and the signal started decaying with a time constant of a few minutes when the ramp was interrupted at 450°C.

TABLE I

Integrated NH_3 Production during TPSR Run

H_2 pressure (atm)	Sample without K			Sample with K		
	Peak 1 (%)	Peak 2 (%)	Sum (%)	Peak 1 (%)	Peak 2 (%)	Sum (%)
0.05	26	41	68			
0.0625				45	55	100
0.2	51	34	84			
1.0	100		100	100		100

Note. Variation with partial pressure, normalized at 1 atm. Peak 1 is the normal TPSR peak; peak 2 is generated when the partial pressure is increased to 1 atm at 400°C after the ramp.

The desorption of N_2 at high temperatures from samples cooled in synthesis gas indicates that the additional H_2 peaks observed after this procedure could arise from decomposition of partly hydrogenated N–*, trapped on the surface during cooling. This would explain why the change is smaller for the K-promoted samples since K is known to destabilize NH_x–*. The possibility that the surface reconstructs when exposed to synthesis gas (N_2 (*16*)) should also be considered as a possible explanation of some of the differences in the H_2 TPD spectra induced by the H_2 exposure/cooling procedure.

Computer Modeling

The series of steps considered in the modeling of the TPSR problem were as follows:

$$N\text{–}* + H\text{–}* \leftrightarrow NH\text{–}* + * \quad (1)$$

$$NH\text{–}* + H\text{–}* \leftrightarrow NH_2\text{–}* + * \quad (2)$$

$$NH_2\text{–}* + H\text{–}* \leftrightarrow NH_3\text{–}* + * \quad (3)$$

$$NH_3\text{–}* \leftrightarrow NH_3(g) + * \quad (4)$$

$$H_2(g) + 2* \leftrightarrow 2H\text{–}*. \quad (5)$$

It was assumed that all surface species occupied the same number of sites. The computer programs were written for a continuous flow stirred tank reactor (CSTR). It was

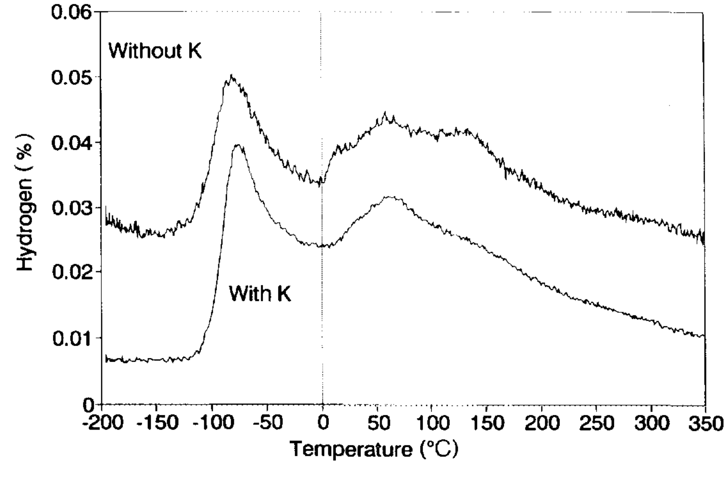

FIG. 6. H_2 TPD for samples with and without K. H_2 exposure: 16 h at 400°C, cooling in H_2.

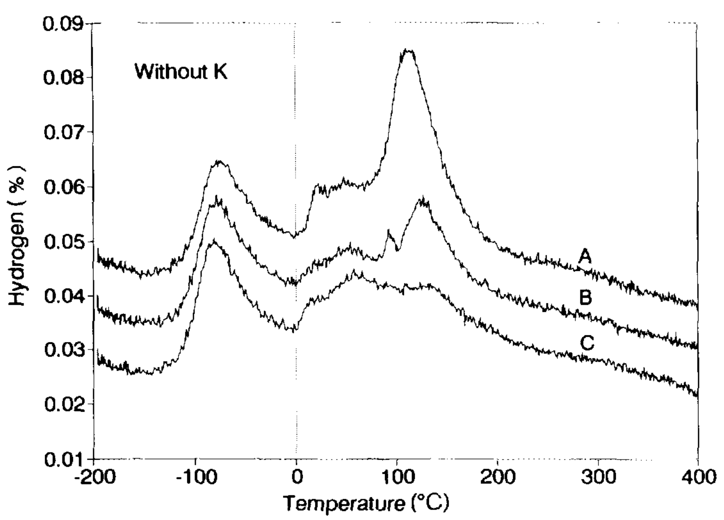

FIG. 7. H_2 TPD, sample without K. (A) cooling in synthesis gas. (B) 1 h waiting time in H_2 at 400°C before cooling in H_2. The tiny peak at 100°C is caused by ice which was accidentally condensed in the oven. (C) 16 h in H_2 at 400°C, cooling in H_2.

possible, however, to simulate PFR conditions by putting a number (*n*) of CSTRs in series. No changes in the results was observed up to $n = 10$. The rate constants (Table 2) were taken from the work by Stoltze (*17*) and Dumesic and Treviño (*18*), estimated from the data of Ertl *et al.* on Fe(111) single crystals [see Refs. (*14*, *16*)].

The effect of the initial coverage of N–* is demonstrated in Fig. 8. No significant reaction will take place below 400°C if the initial coverage is set to be exactly 1, even if the N_2 desorption steps

$$2N{-}* \leftrightarrow N_2{-}* + * \quad (6)$$

$$N_2{-}* \leftrightarrow N_2(g) + * \quad (7)$$

are added. It is interesting to note that the model is able to account for the high-temperature tail so that it is not necessary to invoke the existence of a significant amount of bulk nitrogen which would be in disagreement

TABLE 2

Rate Constant Data for Reactions (1)–(7) Used in TPSR Modeling

Step	Forward rate constant		Reverse rate constant	
	Preexponential factor	Activation energy (kJ/mol)	Preexponential factor	Activation energy (kJ/mol)
1	1.83×10^9 s^{-1}	81.3	1.15×10^7 s^{-1}	23.2
2	1.31×10^{13} s^{-1}	36.4	1.38×10^{12} s^{-1}	0.0
3	3.88×10^{13} s^{-1}	38.7	2.33×10^8 s^{-1}	0.0
4	3.67×10^{12} s^{-1}	39.2	1.81×10^8 atm^{-1} s^{-1}	0.0
5	7.01×10^6 atm^{-1} s^{-1}	0.0	3.24×10^{13} s^{-1}	93.8
6	1.32×10^9 s^{-1}	155	4.29×10^9 s^{-1}	28.5
7	1.87×10^{14} s^{-1}	43.1	2.53×10^6 atm^{-1} s^{-1}	0.0

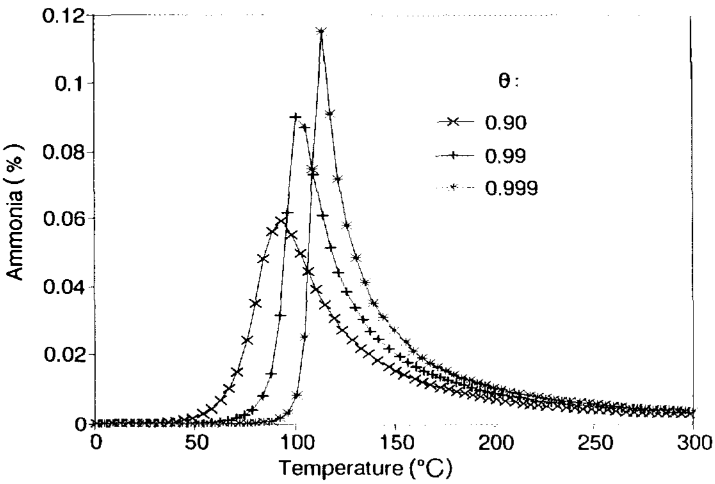

FIG. 8. TPSR of N–* in H_2. Computer simulation. The effect of variation of the initial coverage of N–*.

with Ref. (*13*). The effect of the H_2 partial pressure is shown in Fig. 9. The tail disappears gradually as the H_2 pressure increases past 10 atm. A similar effect can be produced by increasing the heat of adsorption for H_2.

An important point to notice is the amount of N–* left on the surface at the end of the temperature ramp. The calculation gives a number as high as 34% at 400°C for a partial pressure of 1 atm and even higher for the lower H_2 pressures. However, the experi-

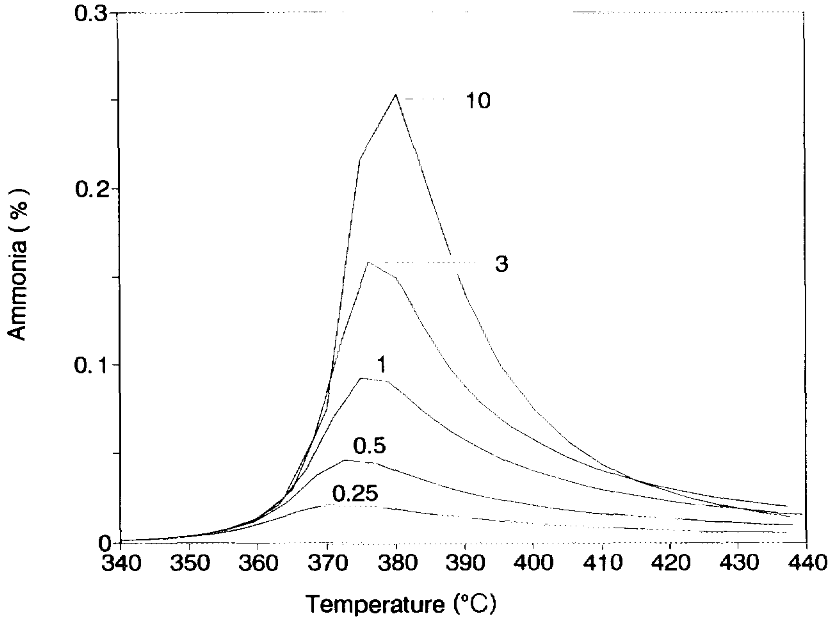

FIG. 9. TPSR of N–* in H_2. Computer simulations for various H_2 partial pressures.

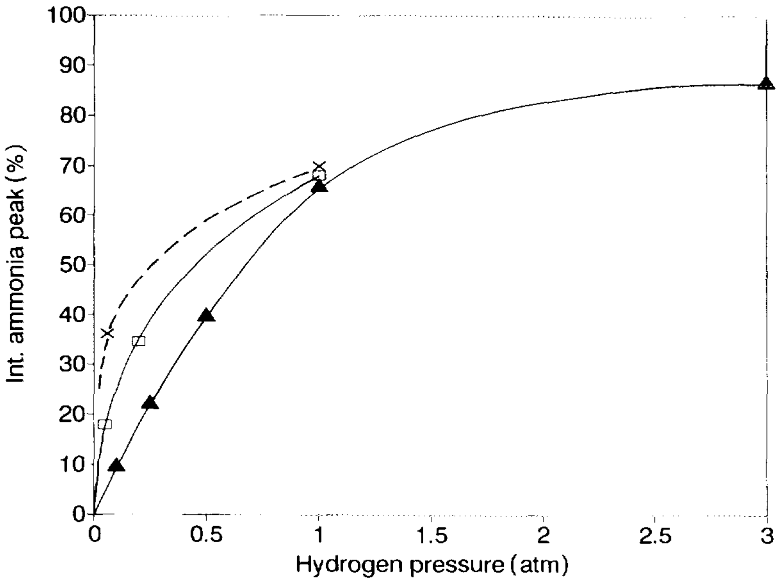

FIG. 10. NH_3 production during TPSR integrated to 400°C vs H_2 pressure. (▲) Model, % of total amount of adsorbed N_2. (×, □) Experiments, scaled in order to facilitate comparison: (×) sample with K; (□) without K.

mentally found H_2 pressure dependence (Fig. 10) suggests that the model overestimates this problem. The same conclusion arises from the results of experiments where the reaction was continued to higher temperatures or at extended times at isothermal conditions at the end of the ramp. The conclusion is that with due respect to this problem we think the evaluation of the amount of N–* on the surface can be made with an accuracy of 10–20%. One way out of the problem could be to use higher H_2 partial pressures, but this solution may be inconvenient.

Comparison between model and experiment is shown in Fig. 11. Obviously the model does not reproduce the experimental results perfectly. This is not surprising, since some of the applied rate constants should only be considered as estimates which were made in order to evaluate the possible influence on the rate of the steady state NH_3 synthesis of reaction steps other than (6), in particular (1). Considering these limitations, the agreement at the onset of the peak is striking. A perfect fit might be possible to obtain, but it would involve too many unknown parameters, since, in addition to the rate and equilibrium constants, the exact value of the initial N–* coverage is critical, as demonstrated in Fig. 8. In addition, the structure suggesting the existence of up to three types of sites should discourage any attempts to fit an oversimplified model with only one type of sites.

Preliminary results of additional computer experiments suggest that there may be a shift in the rate determining step during the reaction procedure, probably between step (2) and (3).

DISCUSSION

The general trends of the TPSR results are reproduced reasonably well by the computer model. The method is useful for the evaluation of available iron surface sites on the catalyst, since it can be applied to the catalyst in the reactor directly after running an activity test.

The integrated values of the TPSR and

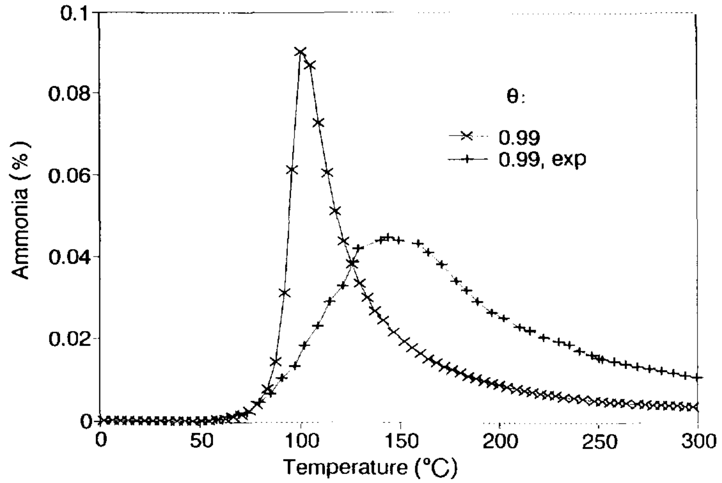

FIG. 11. TPSR of N–* in H_2. Comparison between model (×) and experiment (+).

TPD peaks are shown in Table 3. The ratio between full coverages of chemisorbed N_2 and H_2, respectively, has been subject to much discussion [see, e.g., Refs. (*19*) and (*20*)]. The reason for some of the discrepancies lies in the fact that the chemisorption values depend on the exact procedure, and that the surface stoichiometry is not necessarily the same on all crystal planes. Thus, we would not be surprised if a simple relation between the numbers in Table 3 was missing. However, we find that H_2 TPD results in an amount of H_2 twice as large as that of N_2 (= half of the TPSR result). In addition, an independent experiment resulted in a ratio of 2 between TPSR and CO chemisorption (strongly absorbed at −78°C). These observations are in fair agreement with Ref. (*20*). A Fe : CO stoichiometry of 2 : 1 is usually assumed. Under this assumption, our results indicate the following ratios after cooling in 1 atm of the respective gases: H : Fe = 2 and N : Fe = 1.

TABLE 3

Integrated Peaks from the TPSR and TPD Experiments

	TPSR	H_2 TPD
With K (multiply promoted)	115	109/105
Without K	124	109/118

Note. The two values for H_2 TPD were found for cooling in H_2/synthesis gas. The results are averages of typical experiments. Unit: μmol of NH_3 or H_2 per g of catalyst.

The shape of the H_2 spectrum is not well understood, as discussed previously (*20*, *23*, *24*). It is possible that the H_2 in the peak at −75°C comes from loosely bound states which are not observed when H_2 is adsorbed at low pressure as in UHV experiments or at room temperature or higher as in the conventional chemisorption experiments. Support of this opinion can be found in Ref. (*21*), where the H_2 TPD spectrum for a Fe(111) surface is shown. For increasing exposures at −120°C (up to 2000 L), a peak labelled β_1 is observed to grow and to shift down in temperature in the range between −75 and −125°C. It cannot be ruled out that this would result in a pronounced peak at −75°C if the exposure was made at −195°C and 1 atm of H_2 for an extended period of time. It should also be noticed that an H/metal ratio larger than 1 is frequently found for high index surfaces, even in UHV experiments (*22*). However, more work is needed in order to settle the question of the origin of the low temperature peak.

It is tempting to try to assign the other observed peaks to some of the low index crystal planes by comparing to the peak positions observed in UHV experiments. In order to do so, we will have to consider the following problems, in addition to what has already been mentioned:

1. The heating rate is some °C/s in the UHV experiments, °C/min here. This difference results in a shift of the peaks to ca. 85% of the UHV peak temperature (second-order desorption modeling).
2. Readsorption may cause a shift to higher temperatures and a broadening of the peak.

Direct comparison with the UHV results (*15*, *21*) does not allow us to make any such assignment, and attempts to correct for the abovementioned problems do not appear to be successful.

In a recent paper (*23*), Vandervell and Waugh use H_2 TPD results similar to ours to conclude that the surface of an industrial NH_3 catalyst is not dominated by the Fe(111) crystal plane. As we have pointed out earlier (*24*), we think that more work is needed in order to justify such conclusions.

CONCLUSION

The active area of an iron catalyst can be evaluated by H_2 TPD or by reaction of preadsorbed atomic nitrogen with hydrogen. The last method is the easiest since it can be done simply by absorbing the NH_3 in an acid solution, which can then be titrated. When performed as a TPSR, it may provide interesting information about the Fe surface. However, a detailed interpretation of both the TPSR and TPD spectra will require further studies. The modeling done so far has been reasonably successful since it reproduces the main features of the TPSR, such as the high-temperature tail. This type of modelling may prove useful as an independent test for evaluation of various sets of kinetic parameters for the NH_3 synthesis reaction derived from different approaches.

The question as to which Fe crystal planes are dominating the surface of the active industrial catalyst cannot be settled by simple comparison between the TPD results published so far for single crystals and catalysts.

ACKNOWLEDGMENTS

We have benefited from discussions with J. A. Dumesic, E. Törnqvist, B. S. Clausen, H. Topsøe, J. K. Nørskov, and S. Andersen. We are grateful to P. E. Højlund-Nielsen for suggesting the TPSR experiment and to J. A. Dumesic, L. Aparicio, and A. Treviño for making available their kinetic analysis computer programs. This work has been supported by the Danish Research Councils through the Center for Surface Reactivity.

REFERENCES

1. Nakata, T., and Matsushita, S., *J. Chem. Phys.* **76,** 6335 (1982).

2. Rambeau, G., and Amariglio, H., *J. Chim. Phys. Phys Chim. Biol.* **75,** 333 (1978).

3. Tamaru, K., *in* "Proceedings 3rd International Conference on Catalysis, Amsterdam, 1964" (W. M. H. Sachtler, G. C. A. Schuit, and P. Zwietering, Eds.), Vol. 1, p. 664. North-Holland, Amsterdam, 1965.

4. Boreskova, E. G., Kuchaev, V. L., and Temkin, M. I., *Kinet. Katal.* **25,** 112 (1984).

5. Takezawa, N., *J. Catal.* **24,** 417 (1972).

6. Ertl, G., Huber, M., Lee, S. B., Paál, Z., and Weiss, M., *Appl. Surf. Sci.* **8,** 373 (1981).

7. Artyukh, Yu. N., Batychko, S. V., and Roev, L. M., *Katal. Katal.* **9,** 72 (1972).

8. Rambeau, G., Jorti, A., and Amariglio, H., *J. Catal.* **94,** 155 (1985).

9. Rambeau, G., and Amariglio, H., *J. Catal.* **72,** 1 (1981).

10. Rambeau, G., Jorti, A., and Amariglio, H., *J. Catal.* **74,** 110 (1982).

11. Fastrup, B., and Nygård Nielsen, H., *Catal. Lett.* **14,** 233 (1992).

12. Srnak, T. Z., Dumesic, J. A., Clausen, B. S., Törnqvist, E., and Topsøe, N.-Y., *J. Catal.* **135,** 246 (1992).

13. Grabke, H. J., *Z. Phys. Chem. Neue Folge* **100,** 185 (1976).

14. Ertl, G., Lee, S. B., and Weiss, M., *Surf. Sci.* **114,** 527 (1982).

15. Ertl, G., Lee, S. B., and Weiss, M., *Surf. Sci.* **111,** L711 (1981).

16. Bozso, F., Ertl, G., Grunze, M., and Weiss, M., *J. Catal.* **49,** 18 (1977).

17. Stoltze, P., *Phys. Scr.* **36,** 824 (1987).
18. Dumesic, J. A., and Treviño, A. A., *J. Catal.* **116,** 119 (1989).
19. Topsøe, H., Topsøe, N.-Y., Bohlbro, H., and Dumesic, J. A., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" p. 247. Kodansha/Elsevier, Tokyo/Amsterdam, 1981.
20. Amenomiya, Y., and Pleizier, G., *J. Catal.* **28** (1973) 442.
21. Bozso, F., Ertl, G., Grunze, M., and Weiss, M., *Appl. Surf. Sci.* **1,** 103 (1977).
22. See, for instance, Christmann, K., *in* "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), Dekker, New York, 1988.
23. Vandervell, H. D., and Waugh, K. C., *Chem. Phys. Lett.* **171,** 462 (1990).
24. Muhler, M., Pleth Nielsen, L., and Fastrup, B., *Chem. Phys. Lett.* **181,** 380 (1991).