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Dissociative Adsorption of Dinitrogen on a Multipromoted Iron-Based Ammonia Synthesis Catalyst: Linking Properties of Catalysts and Single-Crystal Surfaces

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Isothermal N_2 adsorption experiments were conducted with a multipromoted iron-based ammonia synthesis catalyst. From these measurements a simple model describing the adsorption process over the entire range of N coverages was developed. The model is consistent with both surface science experiments conducted with single-crystal iron surfaces and earlier experiments on promoted iron-based catalysts. The results from these experiments were well described, if it was assumed that N_2 dissociation occurred at only a few active sites, and that the rest of the adsorption sites were filled via diffusion from these sites. The number of active sites amounted to 4 μmol/g, which is approximately 5% of the total number of sites on the catalyst capable of binding nitrogen. The initial sticking coefficient, s_0, of dinitrogen on the active sites was found to be $s_0 = 10^{-5} \exp(-(4\ \mathrm{kJ/mol})/RT)$. © 2001 Academic Press

Key Words: **ammonia synthesis; iron catalyst; dinitrogen adsorption; structure sensitivity; activation energy.**

INTRODUCTION

The promoted iron-based ammonia synthesis catalyst used today in almost all industrial ammonia production plants is basically identical to the original catalyst invented at the beginning of the last century. Since then, the catalyst and the catalytic reaction have been studied intensively with the majority of the techniques available in catalysis research. Nevertheless, controversies and unsolved problems still remain. One such problem is the description of the dissociative adsorption of dinitrogen on the catalyst surface. For many years, this has been known to be the rate-determining step in ammonia synthesis (1, 2) and, therefore, it is conspicuous that this particular reaction is not yet fully understood. Studies of the dissociative adsorption of dinitrogen on different single-crystal surfaces of iron have shown that the reaction is nonactivated on the nonpromoted Fe(111) surface (2, 3) and on the Fe(100) surface plane when promoted by potassium (4). The Fe(111) surface is regarded as the most relevant iron facet since it has been claimed to be the dominant surface plane in the multipromoted iron catalyst (5). In clear contrast to the surface science results, measurements on promoted catalysts suggest that the N_2 dissociation reaction is activated with an activation energy that increases strongly with the nitrogen coverage (6, 7). Due to the high coverage of nitrogen on the catalyst under relevant industrial ammonia synthesis conditions, the corresponding value of the activation energy has been regarded as relevant with respect to the ammonia synthesis reaction (8). There have been various attempts to explain the differences between the results from surface science and from experiments with commercial catalysts. For instance, it was suggested that the earlier catalyst experiments were inconclusive due to problems with oxygen poisoning of the catalyst surface (9). However, recent investigations, where great care was taken to avoid this problem, did not confirm this hypothesis (7). It has also been suggested (10) that the surface science results were not applicable because the gas temperature was not varied in these experiments. Recent surface science experiments (11) also proved this to be an invalid assumption.

Furthermore, it has not been possible to determine whether or not N_2 dissociation is activated during ammonia synthesis by applying microkinetic models (8, 12–14). The reason is that an erroneous description of the N_2 adsorption rate can be compensated by a thermodynamically consistent description of dinitrogen desorption at the temperatures and nitrogen coverages existing during ammonia synthesis (15).

Here, we report isothermal N_2 adsorption experiments performed with the commercial, multipromoted iron catalyst, KM1. We have been able to accurately model these experiments assuming that only a small fraction of the surface sites of the catalyst is active for dinitrogen dissociation and that the rest of the sites are filled by diffusion from these sites. With this model, it is possible to qualitatively understand all the different experimental results mentioned

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above, thereby establishing the desired link between the surface science studies and the catalyst measurements.

METHODS

All investigations were performed with the KM1R catalyst previously described in detail (16). KM1R has the chemical composition 2.8% CaO, 0.60% K_2O, 2.5% Al_2O_3, and 94% Fe. The experiments were conducted at atmospheric pressure in the setup previously described (17). All gases used were 99.9999% pure and the gas flows were 50.0 or 100 Nml/min (normal ml/min, i.e., ml/min at STP). A catalyst amount of 0.500 g with a particle size of 0.15–0.30 mm was loaded in a glass-lined U-tube reactor of 4 mm diameter, resulting in a bed height of 20 mm. The catalyst was reduced in synthesis gas ($H_2:N_2 = 3:1$) by slowly increasing the temperature to 773 K, and maintaining this for at least 40 h. The activity of the catalyst was tested at 623 K and found to be in agreement with the activity predicted under the given conditions by a recently developed, successful microkinetic model describing the ammonia synthesis over KM1R (13). Between the individual experiments, the catalyst was kept at 773 K in synthesis gas in order to avoid (reversible) deactivation of the catalyst by oxygen adsorption. Before each new experiment, it was checked that the activity at 623 K had not changed in order to ensure that all the experiments were carried out with the same active catalyst.

Adsorption experiments were performed with He gas containing 0.10% N_2 and the adsorption rate was followed as a function of time by measuring the N_2 content in the gas after it had passed the catalyst bed. This was done by using a mass spectrometer with the N_2 signal calibrated just before and after an adsorption experiment. The calibration was performed by measuring the 0.10% N_2 in He with the reactor bypassed. In order to obtain a catalyst surface free of contaminants from the gas phase, the following procedure was adopted prior to an adsorption experiment. In synthesis gas, the temperature was increased to 823 K and H_2 was passed over the catalyst. After a minimum of 30 min, the NH_3 and N_2 levels were identical regardless of whether the reactor was bypassed and the flow was switched to He. Cooling of the catalyst to the adsorption temperature was initiated after minimum 45 min in He flow. At this time, the H_2 level in the gas passing over the catalyst was below 10 ppm. The exact concentration of H_2 was difficult to measure accurately due to a relatively high H_2 background in the mass spectrometer. A considerably longer time was required to achieve a significantly lower H_2 level. Since an even lower concentration of H_2 had only little or no effect on the results at the temperatures (420–560 K) of the adsorption experiments, continuing the He flush after 45 min was regarded as unnecessary. Approximately 1 h elapsed before the desired adsorption temperature had stabilized. The reactor was bypassed when the switch to the adsorption gas was made in order to ensure a stable flow also at the beginning of the adsorption experiment. Passing the gas over the catalyst started the adsorption experiment. The start time was adjusted for the time it took the adsorption gas to replace the He in the reactor, which corresponded to a delay of 8 ± 2 s, with a flow of 100 Nml/min. The delay was measured with a nitrogen-saturated catalyst. After 1 h the experiment was stopped and the amount of adsorbed nitrogen was checked by N_2 temperature-programmed desorption (TPD) conducted with a heating rate of 8 K/min.

RESULTS

The results of all the adsorption experiments are qualitatively similar at all the temperatures studied. Figure 1 shows the results of two adsorption experiments performed at 450 K using two different gas flows and after correction for delay time. It is seen that at first the catalyst adsorbs all the N_2 in the gas, but only for a short period which is approximately inversely proportional to the gas flow. The amount of N_2 passing the catalyst without being adsorbed then increases rapidly and soon reaches a level that only changes slowly with time. The influence of temperature on the adsorption experiments is shown in Fig. 2.

After 1 h, the catalyst was not completely saturated with nitrogen; adsorption was still in progress. The amount of N_2

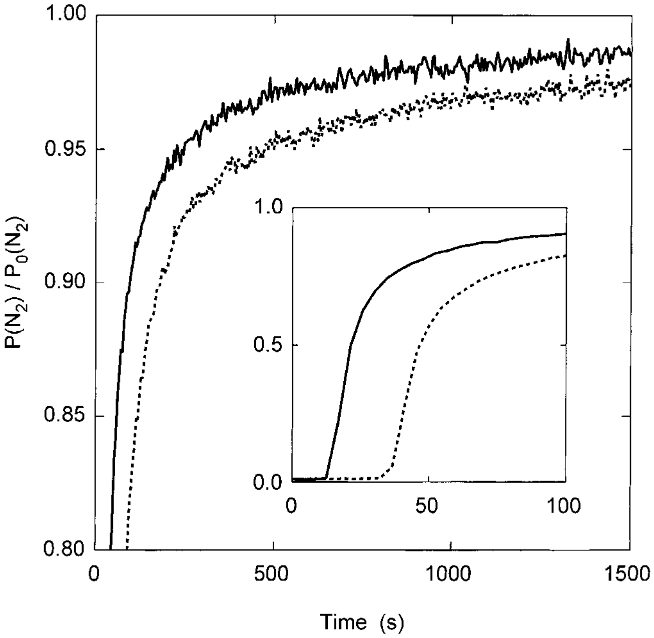

FIG. 1. Two N_2 adsorption experiments on KM1R at 450 K and atmospheric pressure. The flows of 0.10% N_2 in He were 50 Nml/min (dashed line) and 100 Nml/min (full line). The time scale starts at the beginning of the adsorption experiment corrected by the delay time of the setup. $P_0(N_2)$ is 1.0 mbar.

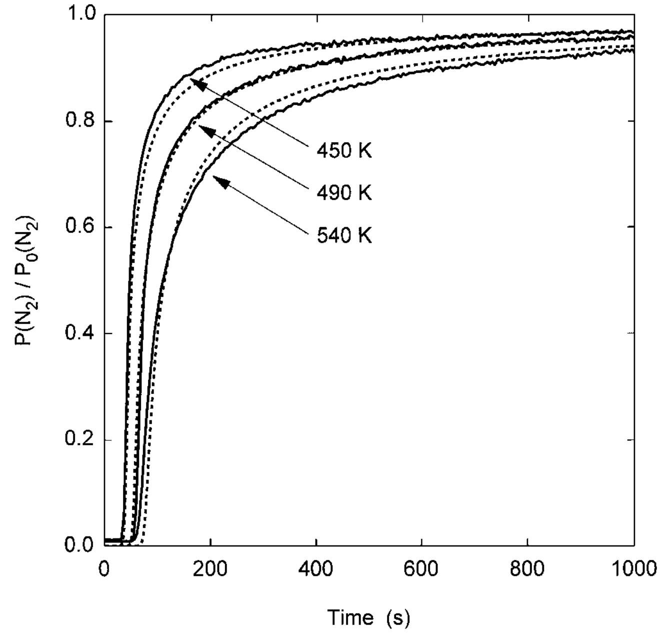

FIG. 2. N_2 adsorption on KM1R at 450 K, 490 K, and 540 K using a gas flow of 50 Nml/min. The experimental results are the full lines while the predictions of the model discussed in the text are shown as dashed lines.

adsorbed was typically 1–2 μmol higher than the amount which could be desorbed by TPD after the experiments, see Fig. 3. This difference is probably due to the slight solubility of dinitrogen in the catalyst at high temperatures (18).

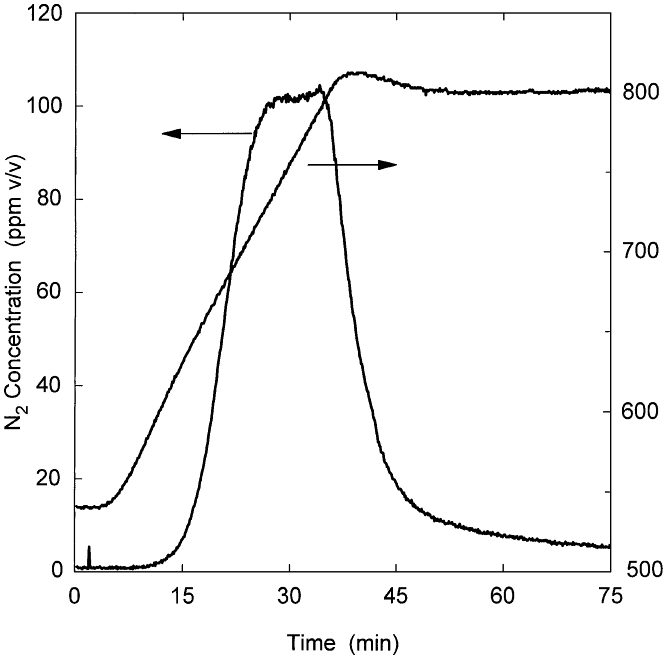

FIG. 3. TPD after N_2 adsorption at 540 K. The heating rate was 8 K/min and the He flow 100 Nml/min. The N_2 desorption peak corresponds to 20 μmol/g while the amount adsorbed was 22 μmol/g.

This explanation is consistent with the observation of a long desorption tail observed when keeping the temperature at 527 K after the TPD. In the TPD experiments following the adsorption experiments performed at the lowest temperatures, small amounts of H_2 were also observed to desorb from the catalyst.

DISCUSSION

The dissociation of N_2 on Fe surfaces proceeds via one or more molecular precursors (19, 20). At the temperatures and partial pressure of N_2 used in our experiments, the molecular precursor is in equilibrium with gas-phase N_2 and the coverage of this species is very low. This means that the adsorption process is equally well described by a single dissociative adsorption step (8),

$$N_2(g) + 2* \rightarrow 2N\text{–}*, \qquad [1]$$

where $*$ denotes an adsorption site. This approach will be used in the following discussion. Due to the existence of the molecular precursor, a negative apparent activation energy for the above reaction is possible.

A simple Langmuirian model was unable to satisfactorily describe the results of the adsorption experiments. The assumption that all sites had the same coverage-independent activity for N_2 dissociation made it impossible to describe both the fast N_2 adsorption in the beginning of the experiment and the long tail of slow adsorption at the end.

A more successful approach was to keep the Langmuirian model and to assume that only a fraction of the sites on the catalyst surface was able to dissociate dinitrogen, and that the remaining sites were filled with nitrogen atoms via diffusion from these active sites. This simple model was inspired by the present experimental results and by the recent findings for N_2 dissociation on a ruthenium surface. Here, both surface science experiments and density functional theory (DFT) calculations agree that only surface sites exposing five atoms in an optimal geometry can dissociate N_2 with a significant rate at the relevant temperatures (21–23). Most recently, DFT calculations of the N_2 dissociation barrier at different surface sites on different metals strongly suggest that this is general and also holds for N_2 dissociation over iron (24). The N_2 dissociation rate at two sites with different geometry can thus be different by many orders of magnitude even though nitrogen binds equally strongly at the two sites. The well-known structure sensitivity observed for nitrogen dissociation (2) and ammonia synthesis (25) on iron single-crystal surfaces, and for ammonia synthesis on supported iron catalysts (26), can also be explained by this.

Due to the fast diffusion of nitrogen atoms on iron at the relevant temperatures (27), it is assumed in the model that an equilibrium exists between the nitrogen coverage, θ_a, on the active sites and the coverage, θ_i, on the inactive sites. Using the Langmuirian approach, the relationship between the two is given by

$$\theta_{\mathrm{i}} = \frac{K\theta_{\mathrm{a}}}{1 + \theta_{\mathrm{a}}(K - 1)}, \qquad [2]$$

where K is the equilibrium constant for the reaction

$$\mathrm{N}{-}* + \text{¤} \rightleftharpoons * + \mathrm{N}{-}\text{¤}, \qquad [3]$$

where $*$ and ¤ denote an active site and an inactive site, respectively. The nitrogen adsorption rate is

$$\frac{d\theta}{2dt} = ckp_{\mathrm{N}_2}(1 - \theta_{\mathrm{a}})^2, \qquad [4]$$

where c is the fraction of active sites, $\theta = c\theta_{\mathrm{a}} + (1 - c)\theta_{\mathrm{i}}$ is the total coverage of nitrogen on the catalyst surface, and k is the rate constant for adsorption on the active sites. In the following this rate constant will be given as the initial sticking coefficient, s_0. The following relationship holds between k and s_0,

$$k = \frac{as_0}{\sqrt{2\pi mk_{\mathrm{B}}T}}, \qquad [5]$$

where a is the geometric area of an active site (we use 10^{-19} m^2), m is the mass of the dinitrogen molecule, k_{B} is the Boltzmann constant, and T is the temperature.

Applying earlier results on KM1R (18), the total number of sites on the catalyst surface was fixed at 80 μmol/g. If 4 μmol/g of these sites are assumed to be active, and if

$$K = 8\exp\left(\frac{-26\ \mathrm{kJ/mol}}{RT}\right), \qquad [6]$$

good agreement between the experimental results and the model at all temperatures was obtained only by fitting s_0. Equation [6] says that nitrogen is bonded more strongly to the active sites than to the inactive sites.

As a first approximation the plug flow reactor was modeled as a continuous-flow stirred tank reactor (CSTR). However, this approximation was too crude to describe the shape of the steepest part of the curves in Fig. 2. This problem was overcome by modeling the reactor as 12 CSTRs in series. Using even more CSTRs had very little effect on the shape of the curves.

Due to the small amount of dihydrogen in the adsorption gas, some of the active sites were covered by hydrogen during the adsorption experiments. The hydrogen coverage was determined by assuming equilibrium with 3 ppm H_2 in the adsorption gas and applying the equilibrium constant for hydrogen adsorption used by Sehested *et al.* (13). However, this had only little effect on the results and only at the low temperatures where desorption of hydrogen could be observed after the adsorption experiments. Examples of the very good agreement between the simple model and the experimental results are given in Fig. 2.

The factor of 8 in Eq. [6] can be interpreted as an entropy difference between N adsorbed at the active sites and at the inactive sites. However, it more likely reflects that the diffusion of nitrogen to some adsorption sites is slow because of a "rugged" path, e.g., a patch of Al_2O_3 along the way. The existence of subsurface sites or sites in the grain boundaries of the catalyst (18) might result in the same phenomenon. The model does not directly take into account the existence of sites that are hard to access by diffusion. This means that the 26 kJ/mol in Eq. [6] is probably not the correct difference between the nitrogen adsorption energies at the active sites and the inactive sites readily accessible by diffusion. A better estimate for this energy difference is obtained by using a pre-exponential factor of 1 in Eq. [6], resulting in a value of approximately 18 kJ/mol. It is also possible that surface reconstructions induced by the adsorbed nitrogen (3, 11) can affect the adsorption energy of nitrogen and the number of active sites during the experiments.

The initial sticking coefficients obtained from the modeling are plotted in Arrhenius form in Fig. 4. It is only possible to obtain these initial sticking coefficients from the experimental results by modeling. The direct experimental evidence of the "high" initial sticking coefficient is the short period of time when the catalyst adsorbs all N_2 in the adsorption gas. It is therefore important to estimate the uncertainties of the initial sticking coefficients obtained by applying the model. In order to do this, we have tried to use other values for the equilibrium constant, the number of active sites, and the initial sticking coefficient. From these tests, we find that the uncertainties on the initial sticking coefficients in Fig. 4 are approximately a factor of 3.

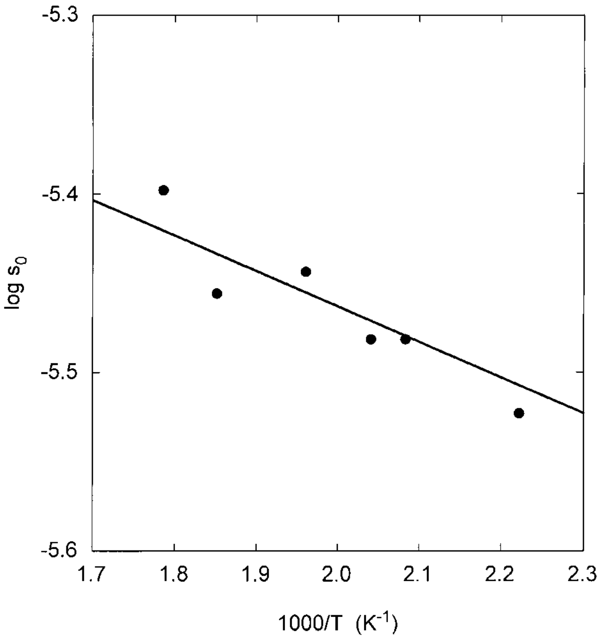

FIG. 4. Initial sticking coefficients of dinitrogen on the active sites obtained by fitting the model presented in the text to the experimental results. The solid line, $s_0 = 10^{-5}\exp(-(4\ \mathrm{kJ/mol})/RT)$, is the best fit to the data.

The absolute values and activation energy for the initial sticking coefficient are very close to the values given in the literature for the clean Fe(111) surface (3, 11) and likewise the values obtained for promoted iron surfaces (2, 4). However, this does not mean that the earlier measurements on catalysts are in any way incorrect. If for instance the outcome of the model was analyzed assuming that all sites are equally active, then a strong increase of the "apparent" activation energy for adsorption could be found in the low-coverage regime with increasing coverage. This is due to the fact that the active sites are filled first (nitrogen is bonded strongest here) and it is "an activated process" to "push" the adsorbed nitrogen from the active to the inactive sites on the surface in order to be able to adsorb more nitrogen. The behavior of the apparent activation energy is shown in Fig. 5 and, qualitatively, it is in very good agreement with the results presented by Scholten *et al.* (6).

By using the above model, it is also possible to understand the N_2 temperature-programmed adsorption (TPA) traces, which Fastrup (7) obtained on different iron catalysts, but only if it is assumed that there is a small amount of hydrogen in the adsorption gas, which blocks N_2 adsorption at the low temperatures. This is a reasonable assumption since some hydrogen desorption was observed at high temperatures in some of these experiments (7). The model TPA is compared to the experiment in Fig. 6. The parameters describing the N_2 desorption were taken from Muhler *et al.* (18) but an increased pre-exponential factor was used to take into account the lower number of active sites in the present model. As seen in the figure, the agreement between the experiment and the model is not perfect but importantly the model captures both the low- and the high-temperature adsorption peaks. Using the same approach to model the TPD trace shown in Fig. 3 results in a narrow peak at the low-temperature side of the observed desorption peak. This is a general observation in our experiments where the nitrogen coverage is below saturation. The explanation for this might be that the surface does not end up in the most stable configurations during the adsorption experiments. The most stable configurations probably involve subsurface nitrogen and surface reconstructions. The heating during the TPD experiments might therefore induce changes that stabilize the nitrogen, explaining the broad desorption peaks at higher temperature than expected from the modeling of the adsorption experiments. It has been observed that high temperature is needed to reconstruct the nitrogen-covered Fe(111) surface (11). N_2 desorption is therefore quite complex and needs a more thorough study to be discussed in detail.

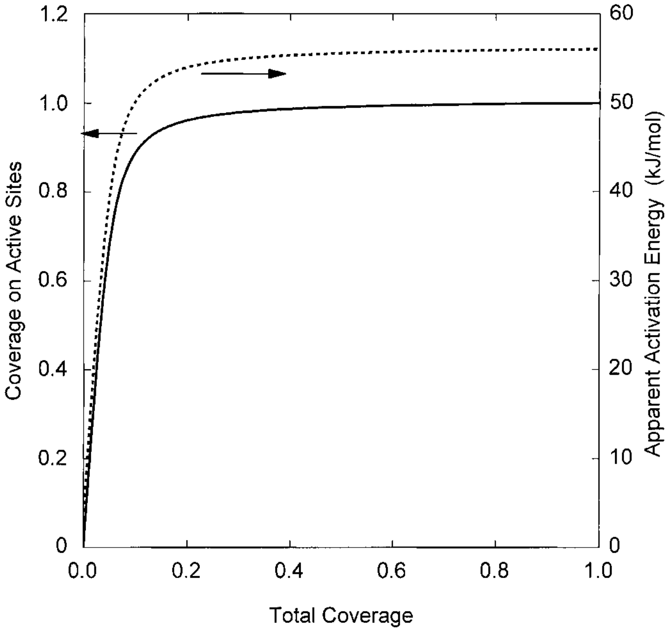

FIG. 5. The coverage on active sites and the apparent activation energy for nitrogen adsorption determined as a function of the total coverage of nitrogen as predicted by the model described in the text. There is a linear relationship between the coverage at the active sites and the apparent activation energy.

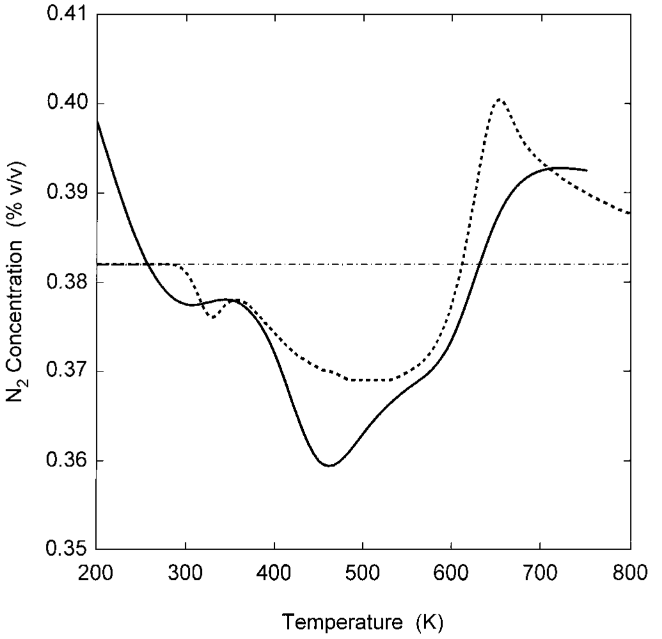

FIG. 6. Experimental N_2 TPA (full line) from Fastrup (7). This experiment was conducted at atmospheric pressure with a multipromoted Fe-based catalyst using a flow of 50 Nml/min of 0.38% N_2 in He and a heating rate of 5 K/min. The dashed line represents the simulation of the TPA experiment using the model described in the text.

The idea of a small number of sites being responsible for N_2 adsorption on an iron-based catalyst is by no means new. In 1959 Scholten *et al.* (6) wrote, "Another possibility is, however, that the rate of chemisorption is governed by the activity of a very small number of sites on the surface from which the chemisorbed species diffuse very rapidly along the surface." Knowing both the surface science and catalyst results, one can speculate why this model has not reappeared before now. One reason might be the observation that the less active Fe surfaces become equally active for dissociating N_2 as the Fe(111) surface when they are promoted by potassium (4). However, this might be a somewhat misleading observation since potassium is oxidized in the reduced catalyst (5). The oxidation has been observed to decrease the effect of K on the N_2 dissociation rate (28). The relatively small effect of potassium promotion on N_2 adsorption is supported by the very small differences in the TPA traces obtained over Fe catalysts with and without potassium promotion (7).

With respect to microkinetic analysis of the ammonia synthesis reaction, it is very easy to incorporate the present model. If nitrogen dissociation is considered to be the rate-determining step, the inactive sites will have no influence on the steady-state synthesis rate since the coverage of different surface species on different surface sites will be in equilibrium with H_2 and NH_3 in the gas phase. Hence, the reaction rate is only determined by the properties of the active sites and the gas pressures (29). Taking this into account makes it understandable why microkinetic models based on Langmuir–Hinshelwood kinetics work very well for describing ammonia synthesis over iron. It is found that the present results are in best agreement with the microkinetic model by Sehested *et al.* (13), which was developed by fitting the model to measured reactivity data while still keeping consistency with most surface science data. In this model the initial sticking coefficient is approximately $s_0 = 5.4 \times 10^{-7} \exp((-8.6\ \text{kJ/mol})/RT)$, which is in excellent agreement with the result shown in Fig. 4 if correction is made for the fact that the number of sites used in the microkinetic model is 60 μmol/g and not 4 μmol/g, implying that the pre-exponential factor above should be increased by a factor of 15 before the comparison.

CONCLUSION

Isothermal experiments of dissociative N_2 adsorption on a multipromoted iron-based catalyst were conducted. A simple model capable of describing the outcome of these experiments was obtained. In the model it is assumed that N_2 only dissociates on 4 μmol/g of the approximately 80 μmol/g sites that are able to adsorb nitrogen. Due to fast diffusion, the nitrogen coverage on the inactive sites is assumed to be in equilibrium with the coverage on the active sites. The initial sticking coefficient of N_2 on the active sites is found to be $s_0 = 10^{-5} \exp((-4\ \text{kJ/mol})/RT)$ which is very close to what was found on the Fe(111) single-crystal surface. The model is also consistent with earlier measurements on catalysts. Hence, the model links for the first time the surface science and catalyst-dissociative N_2 adsorption results, and thereby resolves the long-standing controversies regarding this reaction on iron-based catalysts.

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