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BRIDGING THE "MATERIAL GAP" BETWEEN SINGLE CRYSTAL STUDIES AND REAL CATALYSIS

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Recent theoretical models for the kinetics of ammonia synthesis,–based on the mechanism derived from UHV-studies with single crystals and using data on the adsorptive properties of nitrogen on potasium covered Fe(111) surfaces as essential input parameters–,were found to successfully describe the rate with industrial catalysts. Using thermal desorption spectroscopy, it is demonstrated that the K-Fe(111) model systems and industrial ammonia synthesis catalysts exhibit indeed very similar properties with respect to nitrogen adsorption which result is considered as direct confirmation for the assumptions underlying the theoretical treatment.

In a paper entitled *"Bridging the pressure gap between ultra high vacuum surface physics and high pressure catalysis"*, Stoltze and Nørskov [1] demonstrated that it is possible to calculate the rate of ammonia formation under industrial conditions with a model which is solely based on kinetic parameters derived from studies with well-defined single crystal surfaces under UHV conditions [2]. A somewhat different approach (however, based on the same philosophy) by Bowker et al. yielded large discrepancies in its first version [3]; but after recent improvement it also provides data which are close to the experimental findings with industrial systems [4]. The good agreement over a broad range of conditions without adjusting any parameters is at a first glance rather surprising for different reasons:

(i) There is a difference by roughly ten orders of magnitude in the pressures applied in the UHV studies versus those of industrial catalysis. However, if the essential kinetic and thermodynamic parameters of a reaction are known, it is a straightforward matter to overcome this pressure gap. We want to remind in this connection, that measurements by Somorjai et al. [5] on the rate of ammonia formation at well-defined Fe single crystal surfaces at 20 atm pressure are in full accordance with UHV studies of the adsorptive properties of these surfaces [2].

(ii) Traditionally, the kinetics of ammonia synthesis is successfully described by applying the Temkin model [6] which is based on the assumption of a

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heterogeneous surface with a continuous distribution of nitrogen adsorption states. The Stoltze-Nørskov model, on the other hand, assumes the surface to be energetically homogeneous and neglects adsorbate-adsorbate interactions. In a recent analysis, however, Boudart [7] showed that the rate expression following from the Temkin formalism resembles closely the Langmuir-type relation for an ideal surface with parameters pertaining to low coverage which justifies the made approach.

(iii) Dissociative nitrogen chemisorption is the rate-limiting step of ammonia synthesis for which step the Fe(111) surface shows the highest activity which can be further enhanced by K coadsorption [2]. Hence the quoted models are essentially based on data on the adsorptive properties of nitrogen on a potassium promoted Fe(111) surface. Although the surface properties of the industrial ammonia catalyst have been studied in detail [8] and although the decisive role of the so-called C7-sites as present on the Fe(111) surface has been recognized early [9], there exists so far still another gap: It remains still to be demonstrated that the nitrogen adsorption states on an industrial ammonia catalyst are closely related to those of the K-Fe(111) model system. This was the purpose of the present work, in which essentially thermal desorption spectroscopy (TDS) served as a sensitive probe for the adsorptive properties.

Experiments were performed with samples of industrial ammonia catalysts from two manufacturers. About 1 mg of powdered catalyst (0.1–0.3 mm particle size) was supported on a 6×9 mm^2 gold foil mounted on the sample holder of a UHV system which allowed temperature variation between 80 and 1000 K. A transfer rod enabled transport of the sample from a high pressure cell into the spectrometer chamber which was equipped with XPS and other facilities. Thermal desorption spectra were recorded with variable heating rates between 1 and 10 K/s by means of a quadrupole mass spectrometer. The data for $m/e = 28$ and $m/e = 14$ were identical in shape which results ascertains that there existed no interference by CO.

Catalyst activation was performed in a 3:1 H_2:N_2 mixture of 600 Torr pressure for 120 h with a temperature program following the manufacturers' instructions, whereby the total gas volume was replaced several times. In order to remove adsorbed gases such as CO or H_2O, the sample was subsequently flashed several times in alternating O_2 and H_2 atmospheres up to 810 K. Surface characterization by XPS demonstrated the presence of appreciable amounts of metallic iron and of a substantial K concentration (with 2p binding energy of 293.7 eV) as characteristic for the active catalyst [8]. After cooling the sample down to 80 K, N_2 was admitted through a variable leak valve with pressures typically in the 10^{-6} to 10^{-5} Torr range.

Curve a in fig. 1 is a reproduction of the N_2 thermal desorption spectrum reported by Whitman et al. [10] for a Fe(111) surface precovered with about

1.2×10^{14} K-atoms/cm^2 and then exposed to 10×10^{-6} Torr · s N_2 at 74 K. The low-temperature γ-state is due to desorption of a terminally bonded N_2 species [10], while the α_1 and α_2 states have to be associated with nitrogen molecules exhibiting considerable π-interaction with the surface and representing the immediate precursor for dissociation [11]. A potassium-free Fe(111) surface exhibits only the α_1-state, while the presence of K atoms on the surface stabilizes the Π-bonded N_2 molecules in their immediate vicinity which then show up as α_2 state in TDS. The growth of the population of the α_2-state with increasing K coverage parallels the continuous increase of the net sticking coefficient for dissociative nitrogen adsorption up to a maximum, beyond which it decreases due to overcompensation by site-blocking [12]. Thus the TDS data of the molecularly adsorbed N_2 species are a sensitive probe for the activity of the surface. The K concentration of the Fe(111) surface leading to the discussed thermal desorption spectrum is in the range of highest sticking coefficient for dissociative nitrogen adsorption ($\sim 4 \times 10^{-5}$ at 430 K) which quantity was also used as input parameter in the Stoltze-Nørskov model.

Curve b of fig. 1 shows the N_2 thermal desorption spectrum from an industrial catalyst which had been subject to 50×10^{-6} Torr · s N_2 exposure at 81 K. The similarity with the data of curve a is striking: Not only the peak temperatures, but also their relative populations are almost identical (within the limits of accuracy). Both commercial catalysts exhibited nearly identical properties.

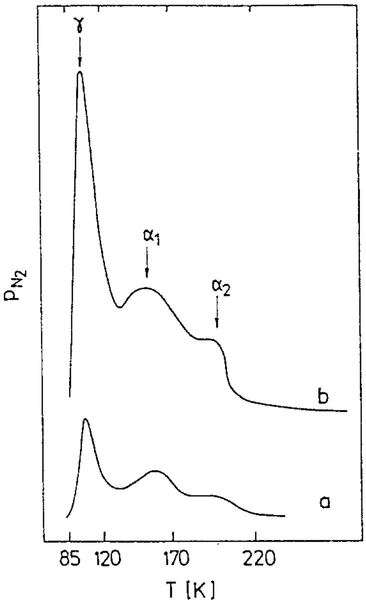

Fig. 1. Thermal desorption spectra for molecularly adsorbed nitrogen species. a) Data for K-Fe(111) after Whitman et al. [10]. b) Data for an industrial ammonia catalyst. Heating rate 5 K/s in both cases.

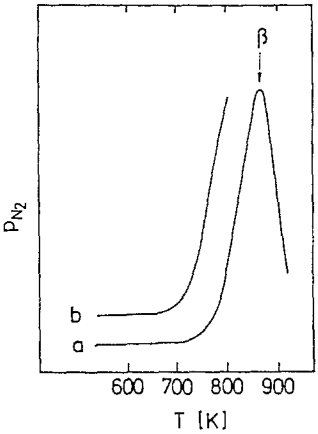

Fig. 2. Thermal desorption of N_2 following surface recombination of atomic nitrogen (β-state) a) Data for Fe(111) after ref. [13] and reproduced by the kinetic parameters used by Stoltze and Nørskov in their theoretical model. b) Onset of desorption from the industrial catalyst.

The atomic nitrogen species formed by dissociation of the α-species is very strongly held at the surface and desorbs after recombination as a β-state above 700 K. Figure 2, curve a, shows TDS data for this state recorded with a Fe(111) surface [13]. The peak temperature is between 800 and 900 K, depending on initial coverage. Stoltze and Nørskov [1] adjusted their input parameter for the N chemisorption energy (which is crucial for the coverage under steady-state reaction conditions and therefore, besides the sticking coefficient for dissociative nitrogen adsorption, this quantity affects the results of the calculations most sensitively) by correctly reproducing these thermal desorption spectra, so that it is of importance to check if the industrial catalyst behaves similarly also in this respect.

Heating up the catalyst beyond 800 K caused irreversible changes of its properties and hence recording of the full β-desorption trace was not feasible. As can be seen from curve b of fig. 2 the onset of desorption occurs in the same temperature region as with the Fe(111) sample, so that also the transferability of these data is obviously justified.

This conclusion does not necessarily imply that the actual catalyst surface consists indeed predominantly of K-covered Fe(111) planes: in fact it contains also substantial amounts of chemisorbed oxygen atoms which are thermally stabilizing the adsorbed K atoms and are not reduced under reaction conditions [8,14]. Secondly, at least for Fe(100) the addition of K causes an increase of the nitrogen sticking coefficient to exactly the same optimum value as with Fe(111). The α_2-state on Fe(100) was found to exhibit the same adsorption energy as with Fe(111), and there is therefore strong indication that the TDS data for molecular nitrogen adsorbed on other potassium-promoted Fe single crystal surfaces are qualitatively similar, although detailed experiments have not yet been performed:

The essentially electrostatic action of the promoter [15] levels off the activity differences between the various clean Fe planes [2].

In conclusion, the data presented here demonstrate that the adsorptive properties towards nitrogen of industrial ammonia synthesis catalysts as probed by thermal desorption spectroscopy are very similar to those determined for K-covered Fe(111) single crystal surfaces. It is therefore justified to use kinetic data derived for the latter systems for successfully modelling the behavior of industrial catalysts which closes the 'material gap' between single crystal surface physics and 'real' catalysis. We consider ammonia synthesis now as a good example of a catalytic reaction for which knowledge about the elementary steps derived from UHV studies with well-defined single crystals not only provides conceptual insight into the mechanism and progress of an important industrial process, but for which even successful quantitative description of the kinetics gets its sound physical basis along this approach.

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