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POTASSIUM PROMOTION OF THE AMMONIA SYNTHESIS REACTION: A COMBINED UHV-HIGH PRESSURE INVESTIGATION

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The ammonia synthesis rate has been measured as a function of the potassium coverage of a polycrystalline iron foil. The results clearly demonstrate a promoting effect of the potassium in agreement with the work of Ertl et al. on the dissociative dinitrogen adsorption at iron single crystal surfaces. However, the results also imply a marked difference between the state of the surface under ammonia synthesis conditions and during the dinitrogen adsorption experiments in ultra-high vacuum. It is suggested that in the former case the potassium atoms are surrounded by several strongly adsorbed atoms effectively blocking the corresponding sites for dinitrogen dissociation.

Keywords: Potassium promotion, iron based catalysts, ammonia synthesis, high pressure - ultra high vacuum (UHV) investigation

1. Introduction

Potassium is known to be a promoter of the activity of iron based catalysts for the ammonia synthesis. The exact nature of the promoting effect is, however, still not completely clear. Studies of potassium promotion of high surface area materials have been reported [1–3] but were not well suited to discuss the detailed role of potassium since no information on the surface composition could be extracted. The Somorjai group has shown that combining the activity measurements with direct surface studies is quite informative [4–7]. In order to obtain more detailed information we have performed a systematic study of the ammonia synthesis rate as a function of the potassium coverage of a well characterized polycrystalline iron foil. The experiments were carried out in a high pressure/ultra-high vacuum setup.

There is a general agreement that the dissociation of dinitrogen is the rate determining step in the ammonia synthesis reaction over iron based catalysts. Ertl et al. [8] have shown that potassium adsorbed at different faces of iron single

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crystals enhances the dinitrogen dissociation rate by one to two orders of magnitude, depending on the face considered. It is therefore tempting to suggest that potassium has the same role in the catalyst. Support for this notion is given by the kinetic modeling studies of Stoltze and Nørskov [9] which show that the difference between the activity of promoted and unpromoted iron based catalysts can at least qualitatively be explained by invoking the difference in the dinitrogen dissociation rate as measured by Ertl et al. [8,10]. The observation of Schlögl et al. [11] that the thermal desorption spectrum of dinitrogen from an industrial catalyst exhibits the same high temperature peak as the spectrum from iron single crystals with adsorbed potassium [12,13] again demonstrates the industrial relevance of experiments carried out on well defined model systems. The high temperature desorption peak mentioned is indicative of stabilized dinitrogen at the surface. Strongin et al. [4] reported an increase in the ammonia synthesis rate over iron single crystals by pre-adsorbing potassium but attributed most of the effect to destabilization of the ammonia molecule.

The message of the present study is twofold. First, the results show that the potassium promotion of the ammonia synthesis reaction varies continuously with the potassium coverage. Secondly, we propose that the immediate proximity of the potassium atoms of a catalytically active iron surface is quite different from that of the model system used by Ertl et al. [8]. The latter experiments were carried out in ultra-high vacuum (UHV) and most probably all the sites surrounding the potassium atoms were initially vacant. However, in our experiments carried out at 3.5 bar and close to steady state we believe that several of the sites near the potassium atoms were blocked by strongly adsorbed oxygen or nitrogen atoms.

2. Experimental and results

The experiments were carried out in a setup which has a catalytic micro-reactor built into an ultra-high vacuum (UHV) chamber enabling rapid change from the ammonia synthesis conditions to the UHV of the surface analysis. The micro reactor is in principle identical to the one of Keck et al. [14] except that the Viton O-ring seal was replaced by a copper gasket/knife edge arrangement in order to increase the pressure and temperature limits. The upper pressure limit is at present 10 bar. The UHV chamber contains facilities for X-ray photoelectron spectroscopy (XPS), static Auger electron spectroscopy, mass spectrometry, noble gas ion sputter cleaning, and potassium vapor deposition. The base pressure is less than 1×10^{-10} mbar. The specimen was a resistively heated polycrystalline iron foil of 0.9999 + purity (Goodfellow) and with the dimensions 18 mm × 7 mm × 0.05 mm. It was cleaned by numerous argon ion sputtering and annealing cycles as well as by simply taking part in the ammonia synthesis. Potassium of 0.9995 purity (Ventron) was deposited from a break-seal glass ampoule.

The concentration of ammonia and other gas components were measured by a mass spectrometer whose inlet was a constricted quartz capillary [15]. The capillary and tubing to the mass spectrometer were kept at temperatures higher than 400 K to prevent the ammonia from adsorbing at the walls before reaching the mass spectrometer.

The coverages of the various surface species were measured by taking the adsorbate to substrate XPS peak area ratios and correcting for the different photoelectron cross sections as well as for the spectrometer function [16]. Under the assumption that the peak area ratios scale with the adsorbate concentrations the relative errors should be small. The absolute errors are probably not significant either since the measured work function changes for a few different potassium coverages (with no other adsorbates present) agrees well with those reported in [17]. The change in the work function was taken as the difference in the low energy onsets of the XPS spectra (produced by the "true secondary electrons") with the sample biased at -35 V relative to ground.

Note that all the coverages given here are relative to the surface atom density of the substrate and not to the saturation density of the various adsorbed species. The value of 1.6×10^{15} cm^{-2} was chosen as the substrate surface atom density which is obtained from the density and atomic weight of iron and assuming spherical atoms.

During the ammonia synthesis experiments the sample was exposed to a mixture of 75% dihydrogen and 25% dinitrogen at 3.50 bar. The problem of potassium stability at the iron surface during ammonia synthesis [4] was given considerable attention and many experiments were carried out. Here will only be discussed the results obtained at the quite low reaction temperature of 643 K which represent a compromise between potassium stability and ammonia detectability. A large amount of potassium was deposited on the surface (close to saturation) followed by a series of relative short synthesis experiments with analysis of the surface in between. The sample was "untouched" between the short experiments, i.e. the decrease in the potassium coverage only occurred during points (iii) and (iv) below.

The course of a typical measuring cycle was according to the following: (i) studying the sample surface by XPS, (ii) introducing flowing synthesis gas (110 Nml/min) at 3.50 bar through the reactor, (iii) heating the sample to 643 K and keeping it at this temperature for 30 minutes, (iv) recording the partial pressure buildup of ammonia for 30 minutes after closing the inlet and outlet valves of the reactor (fig. 1), and (v) cooling the sample, evacuating the reactor, and studying the surface by XPS. The reason for closing off the reactor was that the concentration of ammonia produced by the small surface area of the specimen was below the detection limit of the mass spectrometer. Even reducing the flow to 10 Nml/min gave unsatisfactory small signals above the background and at even lower flows one would have to worry about back diffusion from the ambient. The waiting time of 30 minutes before closing off the reactor was necessary to get a

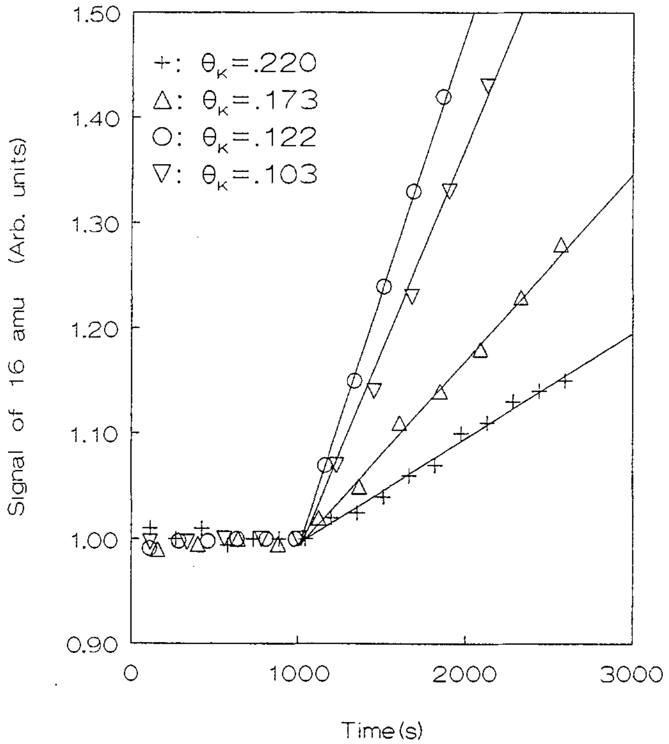

Fig. 1. Ammonia partial pressure (16 amu) versus time for a few different potassium coverages. At about 1000 seconds the inlet and outlet valves of the reactor were closed. Only the stable part of the signals before closing the valves is shown, i.e. the heating of the sample started at about −800 s. The coverages given are the average values of the ones measured before and after each cycle.

stable ammonia signal after its sharp drop caused by turning on the sample heating. Since the orifice of the quartz capillary was located at about 2 mm from the sample the gas flowing through it was also heated when the sample heating was turned on. This changed the density and viscosity of the gas decreasing the flow through the constriction and thereby lowering the partial pressures in the mass spectrometer one half to one order of magnitude.

As has also been reported previously [4] oxygen was always seen at the surface after an ammonia synthesis rate measurement in the reactor.

3. Discussion

The variation of the ammonia synthesis rate with the potassium coverage of a polycrystalline foil is displayed in fig. 2. The ordinates are obtained from the slopes (examples of which are shown in fig. 1) divided by the slope for the pure iron surface. The variation is seen to be qualitatively similar to the one of the dinitrogen dissociation probability with the potassium coverage of iron single

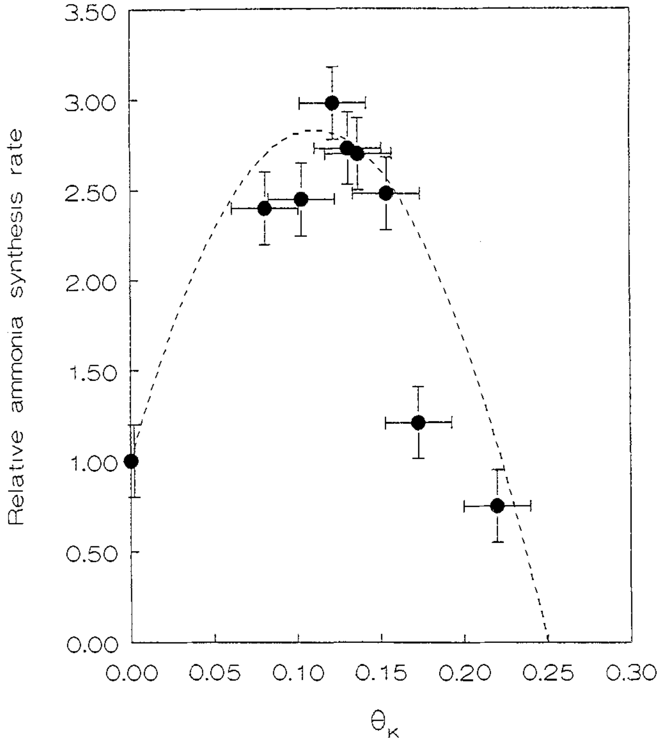

Fig. 2. The ammonia synthesis rate relative to the value at zero potassium coverage versus potassium coverage. The ordinates are slopes of which a few are shown in fig. 1 divided by the slope for $\Theta_K = 0$. The broken curve is a fit using the data by Ertl et al. [8]. See the text for details.

crystal surfaces reported by Ertl et al. [8]. Given that the dinitrogen dissociation is the rate determining step in the ammonia synthesis, this is not so surprising. However, the systematic study of the synthesis rate as a function of potassium coverage reveals important differences between the dinitrogen dissociation probability and the ammonia synthesis rate. First of all, the maximum increase in the rate is only a factor of three, whereas the maximum increase in the dissociation probability is a factor of between 5 and 100 depending on the crystal face considered. Secondly, the dissociation probabilities decrease very slowly after having reached the maximum, while the synthesis rate decreases sharply after the maximum and approaches zero as the potassium coverage approaches one quarter.

The difference in the dissociation probability data of Ertl et al. [8] and ours leads us to suggest that there is an important difference between the clean surface used in the dinitrogen dissociation studies and the state of the iron surface during ammonia synthesis. The simplest way of reconciling the two measurements is by assuming that under synthesis conditions the potassium on the surface is surrounded by on the average four strongly bound atoms, presumably either oxygen or nitrogen. X-ray absorption spectroscopy studies by Clausen et al. [18,19] of a rubidium promoted model catalyst recorded during synthesis indicate in fact that a phase with short rubidium-oxygen or rubidium-nitrogen distance is formed. It is important to note that the adsorption experiments by Ertl et al. [8] were carried out in ultra-high vacuum (UHV) whereas our specimen had seen 3.5 bar of synthesis gas at 643 K for 30 minutes before the rate was measured. Even though the conversion was quite small (of the order 10^{-4}) at these conditions there was nevertheless a distribution of reactants and reaction intermediates at the surface when the activity was measured. With the assumption that there are four strongly adsorbed atoms around the potassium atoms the synthesis rate r should vary with the potassium coverage Θ_K as

$$r(\Theta_K) = s(\Theta_K)(1 - 4\Theta_K), \tag{1}$$

where $s(\Theta_K)$ is the measured variation of the dissociation rate with coverage. The $(1 - 4\Theta_K)$ factor reflects that each potassium atom induce a blocking of four sites.

Ertl et al. showed that the sticking coefficient at potassium promoted sites is roughly independent of the face [8]. By using this and assuming that 30% of the foil's surface exposes Fe(111) faces, eq. (1) gives the broken curve in fig. 2. The rate is normalized to the value at $\Theta_K = 0$. $s(\Theta_K)$ is taken as a linear combination of the sticking coefficients for unpromoted Fe(111) sites and promoted sites (at any face) using the results of Ertl et al. [8]. These results are converted to our temperature of 643 K by using the measured activation energy for Fe(111) [8]. The sticking coefficient for unpromoted sites at other faces than Fe(111) is so small [8,20] that it is neglected here. Qualitatively, the general shape of the curve is convincing even though the model obviously represents a very simplified description. The uncertainty of the surface structure of the specimen means that a more detailed account of the blocking is not possible. However, the conjecture that about 30% of the surface area of the polycrystalline foil is Fe(111) is compatible with measurements of the potassium induced work function changes at Fe(100), Fe(110), Fe(111), and polycrystalline Fe [17].

Boudart and Löffler [21] compared the single crystal data of Spencer et al. [7] and the industrial catalyst data of Topsøe et al. [22] and concluded that during ammonia synthesis the industrial catalyst exhibits predominantly Fe(111) faces. This may be true but it is difficult to arrive at a definitive conclusion solely on that basis. The ambiguity is related to the fact that potassium promotion of other sites than those at the Fe(111) faces essentially brings their activity up to approximately the same level as promoted Fe(111) sites. Also, the difference in the activity between promoted and unpromoted Fe(111) is not very large (about a factor of 1.2 at 643 K and 3.5 bar [4,23]). Thus by simply analyzing the activity it is difficult to distinguish between the presence of different promoted Fe faces or unpromoted Fe(111) faces.

The kinetic modeling by Stoltze and Nørskov [9] on the effect of potassium also showed that the difference between the activity of a promoted and an unpromoted catalyst could be qualitatively accounted for by assuming that only the Fe(111) faces contribute to the synthesis at the unpromoted catalyst and that all promoted sites have the same activity at the promoted catalyst. In their study the active area was measured independently by chemisorption of CO on the reduced catalysts. Any strongly adsorbed species close to the potassium at the promoted surfaces was thus implicitly taken into account by the obtained value for the active area since it would include the $(1-4\Theta_K)$ factor.

The present results show that there exist a marked decrease in the ammonia synthesis rate at high potassium coverages. This effect is much more pronounced than the corresponding decrease in the nitrogen dissociation probability. As shown above, the difference may simply be accounted for by introducing the factor $(1-4\Theta_K)$. Thus, for the same potassium coverage more sites are being blocked during ammonia synthesis than during dinitrogen dissociation at UHV conditions. This suggests that during ammonia synthesis there are atoms surrounding the potassium atoms which are absent on potassium covered surfaces in UHV. These atoms are most likely nitrogen or oxygen. It is known that potassium induces changes in the electrostatic potential at neighboring sites [24] and it is thus likely that atoms, such as oxygen and nitrogen, will be more stable in the immediate vicinity of the potassium atoms. In fact the above results suggest that the atoms are stabilized to the extent that they will remain there during ammonia synthesis and block the sites. The presence of these oxygen or nitrogen atoms is expected to modify the electrostatic potential around the potassium atoms and this would also have an influence on the ammonia synthesis rate. Clearly, a complete model describing our results should also take this effect into account and the blockage may therefore not necessarily be of exactly four neighboring sites to potassium. However, such a detailed analysis will clearly have to await further investigations preferably involving ammonia synthesis on potassium covered single crystal surfaces.

4. Conclusion

To our knowledge we have presented the first systematic investigation of the promotion of the ammonia synthesis reaction over a polycrystalline iron foil as a function of the potassium coverage. The study has demonstrated a clear promoting effect with an optimum potassium coverage of around one quarter of a monolayer. It also showed a coverage dependence which was different from the one measured for the dinitrogen dissociation rate on iron single crystals at UHV conditions. We suggest that one possible explanation for this discrepancy is that at the working surface of the ammonia synthesis the potassium atoms are surrounded by several strongly adsorbed oxygen or nitrogen atoms which block the sites on the surface.

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