Long-Range Diffusion of K Promoter on an Ammonia Synthesis Catalyst Surface—Ionization of Excited Potassium Species in the Sample Edge Fields

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The potassium ions K^+ which diffuse out to the surface from the K promoted ammonia synthesis iron catalyst material do not desorb from there but diffuse rapidly along the surface until they reach the edges of the sample. This is shown by angular distributions of the ion emission at the normal operating temperatures of 900–1100 K. The ionic emission at low field strengths, of the order of 2–50 V cm^{-1}, has a minimum or even a zero signal in the direction of the surface normal. Instead of desorbing from the surface, the ions interact strongly with the surface and give electronically excited states K^* on the surface, which diffuse rapidly along the surface over a distance of several millimeters to the edges of the sample. A detailed model is proposed for this process, based on recent kinetic results. At the edges, ions are formed in the stronger electric field just outside the surface giving lobes along the surface. With the highest field strengths used, these lobes are transformed into strongly peaked distributions at 45–70° from the normal, with a strong minimum in the normal direction. From the open surface, only clusters K_n and neutral atoms K can be emitted. Trajectory calculations show that ions, which are emitted from the edges of the sample with higher then thermal energy, appear in the experimentally observed angular range. Their excess energy may be derived from the work function difference between the catalyst sample and its Ta holder. © 1999 Academic Press

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1. INTRODUCTION

In many heterogeneous catalysts, specific promoter additives are used to improve the catalyst performance. For example, the industrial iron catalyst for ammonia synthesis is promoted very efficiently by K addition (1). The understanding of the K promoter action is still not complete, even if the chemical state of the K promoter in the catalyst has been the subject of a number of investigations (2–4). Pettersson *et al.* (5) have proposed a general model of alkali promotion, in which the promoter function is coupled to the electronically highly excited states (Rydberg atoms) of the promoter atoms at the catalyst surface. In this model, the catalytically active sites might be the sites where the excitation of K to the Rydberg species K^* takes place, or alternatively where the Rydberg species attack the reactant molecules approaching the surface. The present study is concerned with the K promoter in the ammonia synthesis catalyst. The earlier proposed interaction (6) of K^* with the nitrogen molecule at the catalyst surface should result in the formation of intermediates K^*–N–N, which would be adsorbed by and deexcited in contact with the surface. This process could strongly increase the sticking rate of N_2 at the catalyst surface. Since the sticking of N_2 is likely to be the rate limiting step in the ammonia synthesis catalyst, the proposed action of K^* could be very significant.

The problems of emission of different states of alkali from alkali promoted catalysts have been studied for a long period by our group, and the present report is part of the ongoing investigation of one of the most important types, the iron ammonia synthesis catalyst. Recently, we investigated the desorption and emission of excited potassium species from the iron catalyst by field ionization (6) and surface ionization (7, 8) methods. The results show that the angular distributions of excited species are strongly different from those of neutral species, and that nonequilibrium effects thus are involved in the emission from the surface. In this paper, we study the angular resolved desorption of potassium ions K^+. We conclude that the ions are formed at the sample edges with some excess energy along the surface tangent. A detailed comparison is made with an excitation model to Rydberg-like states K^* on the surface, which is based on kinetic investigations. The results show that the promoter only leaves the catalyst surface after ionization in the edge fields, and thus that the Rydberg species which are believed to form complexes of the type K^*–N–N with the reactant gases are mobile but bound to the surface.

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By now all major loss processes of the alkali promoter on iron and iron oxide catalysts have been studied in some detail, and a complete picture can now be constructed. The present results give clues to a few methods useful for reducing the promoter loss and lengthening the life of the catalyst, for example improvement of the shape of catalyst crystallites and pellets so that no edges with strong contact fields exist. Further, the influence of electric fields on the reactions on alkali promoted catalysts, like in electrocatalysis, may be better understood if the Rydberg nature of the desorbing promoter atoms is taken into account.

2. THEORY

The emission of long-lived (see further below) Rydberg species of alkali atoms appears to be a general feature of nonmetallic surfaces and nonmetallic surface layers, due to the covalent character of the bonding of the alkali atoms. A large number of studies show that the lifetimes of excited species of alkali atoms at nonmetallic surfaces are long, and Rydberg states (9, 10) can be emitted thermally from hot nonmetallic surfaces like graphite and carbon (11–15) and metal oxide surfaces (16–21). The excited species, for example K^* and Cs^* seem to be formed from localized bound states on the surface (13, 15) or from covalently bonded compounds on the surface (22). In the case of iron catalysts, Rydberg states could possibly be formed from K covalently bonded to Fe or O sites on the surface, or from compounds like K aluminate (23). Recently, kinetic information has become available for the case of K on graphite, which gives a detailed model of the various states on the surface (15). The alkali promoted catalysts seem to follow the same kind of scheme, and the explicit model which we will use to interpret the data here is shown in Fig. 1.

From kinetic data (15) it is concluded that the ground state of the alkali atom outside the surface does not correlate with any bound state of K on the surface. Instead, the ionization of a K(4s) atom approaching from a distance is rapid, and the state reached on the surface is designated K_s^+ in Fig. 1. This state is then easily transformed after diffusion over a short distance into covalently bound states at such free sites, like O atoms on the surface. In Fig. 1, the two lowest covalent states at one type of site are shown, which correlate with the desorbed electronically excited (very short lived) states K(4p) and K(3d). The desorption from these states crosses the potential curves of highly excited, Rydberg-like states K^*, and a transfer of the desorbing atoms to the long-lived Rydberg-like states is then possible, maybe after collision with the surface. The Rydberg-like states have their potential minima at a relatively long distance from the surface. The depths of these minima are determined by the dispersion interaction between a large part of the surface and the Rydberg atom. The dispersion energy varies strongly with the polarizability, which is
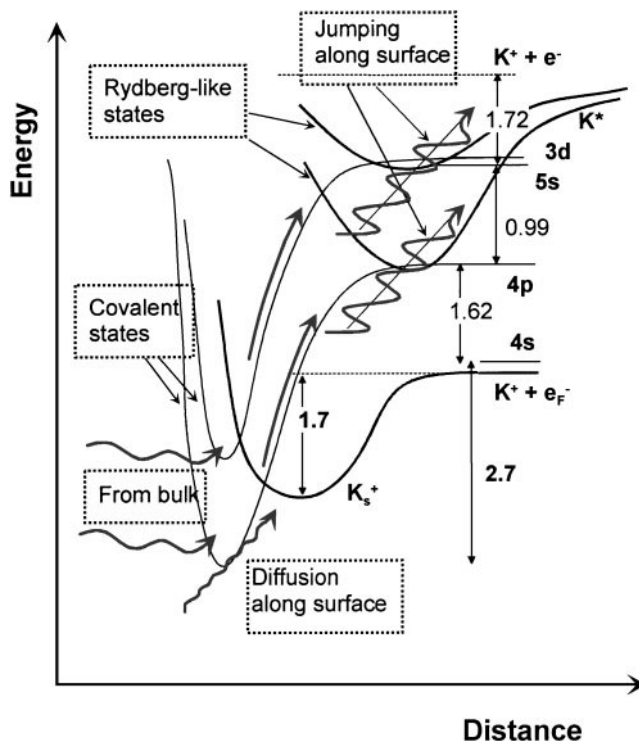

FIG. 1. Potential energy diagram for the interaction of K atoms and ions with the oxidized iron surface in the catalyst sample (ammonia catalyst), modeled after the kinetic results for K on graphite. All energies are given in eV. The slanting lines shows the motion along the surface in perspective.

roughly proportional to the size of the atom. It is known that polarizabilities of Rydberg atoms increase rapidly with the principal quantum number n as n^7 (10). Thus, the dispersion interaction with the surface will be enormous for the Rydberg states. This means that a Rydberg state at a distance larger than a few nanometers outside the surface has a much larger interaction energy with the surface than a ground state or lower excited atom at the same distance and thus that it can diffuse along the surface at some distance from the surface in this distant potential well. The lifetime of the Rydberg-like states will also be rather long. For an ordinary free Rydberg atom in a circular high-l state (l is the angular momentum quantum number), the radiative lifetime varies with the principal quantum number n as n^5, which means a lifetime of approximately 1 ms for $n = 40$ and 100 ms for $n = 100$.

In Ref. (16), the consequences of the long-range force between a Rydberg atom and a surface were discussed, especially the implications for the diffusional motion over the surface, which may take the form of very long jumps over the surface. The long-range interaction also implies that the excited K atoms are efficiently retained in a layer outside the surface, a surface sheath similar to a Knudsen layer. This means that any process which can break the bond or decrease the bond strength to the surface will help in
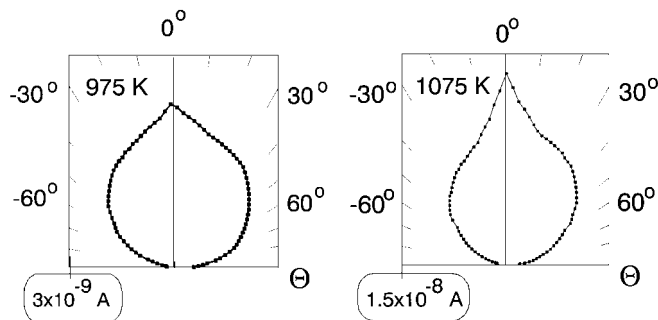
FIG. 2. Angular distributions for neutral particles from the used catalyst at two temperatures, measured by surface ionization detection. Data from Ref. (7).

removing the Rydberg atoms from the sheath. One important process is the formation of clusters by condensation of the excited K^* species, which decreases the interaction with the surface since the Rydberg electrons are no longer in contact with the surface but instead form bonds in the cluster. Emission of clusters from catalyst surfaces has been reported in Refs. (6, 16, 22, 24). The condensation of excited atoms is described theoretically by Manykin *et al.* (25, 26), and it has been observed in several experiments (see the summary in Ref. (27)). The formation of alkali clusters from the present kind of catalyst surface was first reported in Ref. (6). Typical results are shown in Fig. 2, where the angular dependence of the emission of all K species from the catalyst is shown at zero electric field strength. The peaks in the normal direction can be described by a model of cluster formation just outside the surface (7), while the broad cosine-like parts of the distributions are due to thermal desorption of all other states of K. In Fig. 3, the detection is made by field ionization, which can detect only electronically excited species (9, 10, 21). The peak in the normal direction is well described by the same model used for the results in Fig. 2. Thus, the results in Fig. 3 are due to electronically excited clusters K_n^*.
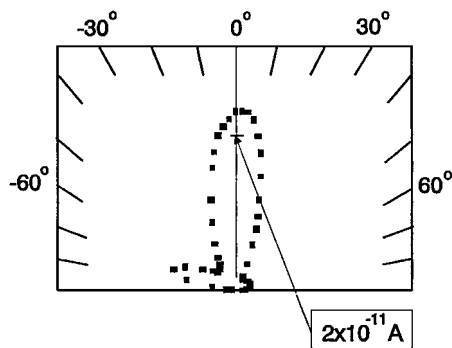

FIG. 3. Angular distribution for excited particles from the prereduced catalyst, measured with the field ionization detector in Fig. 4. Sample temperature was 1070 K. A potential of 20 V was applied to the sample, and the detector slit voltages were +150 and −165 V, respectively, which blocked all charged particles from the sample. Data from Ref. (6).

In the present experiments, the ion emission is understood with reference to the model in Fig. 1. It is unlikely that an ion emission takes place via the K_s^+ state, since this is not populated directly from the bulk. Instead, the main desorption goes via the highly excited species K^* on the surface, which give ions due to field ionization at the sample edges. With no field, there will be no preferential ionization at the edges of the sample, and atoms will instead desorb as long-lived free Rydberg states which will also combine to form a small amount of clusters, as described above.

3. EXPERIMENTAL

The apparatus, which has been described elsewhere (7), has the detectors mounted in a turnable lid. They can be rotated over 360° around the center of the chamber, as shown schematically in Fig. 4. In the present experiments, only the FI detector is used, as described more in detail below. The apparatus has an ultrahigh vacuum (UHV) chamber with a pressure of 10^{-9} mbar during the experiments (16). The catalyst sample was placed in the center of the chamber.

The commercial fused iron catalyst for ammonia synthesis was obtained from Norsk Hydro (type AS4). It is in the form of prereduced and passivated (surface oxidized in a few atomic layers (28)) pieces of sieve fraction 6–10 mm. Without the passivation treatment, the samples would be pyrophoric. The samples are metallic (93% α-Fe) with good electrical conductivity. Also samples of the same catalyst used in the real process for 5 years and passivated after that were studied in the same apparatus. One single piece of the catalyst was mounted in a tantalum foil, which was formed to a tightly fitting tube and then cut to expose a flat surface to the detector. There was no crushing or other
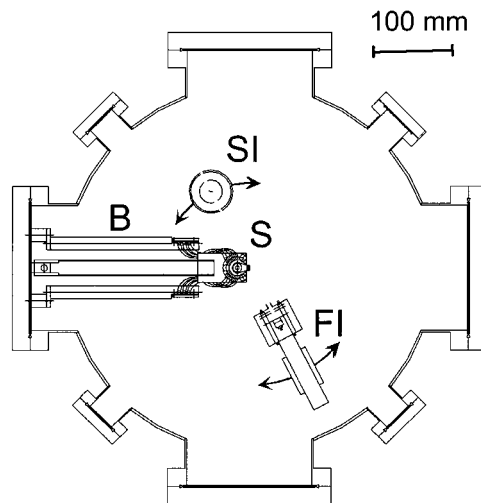

FIG. 4. Schematic drawing of the apparatus, horizontal cut. S, sample in vertical direction; B, sample holder with current conductors; SI, surface ionization detector; FI, field ionization detector.

preparation of the sample, and it showed just one continuous surface. The catalyst sample could be heated up to 1270 K (1000°C) by passing an AC current of 30 A through the tantalum foil. The heating is quite uniform, and there are no hot spots which could give an anomalous behavior, which is confirmed by the straight-line Arrhenius temperature dependence of the ion and electron emissions (8). The sample temperature is measured with NiCr–NiAl (type K) thermocouples. The sample is held at a variable potential which is connected to the heating circuit with a voltage drop of less than 1 V. The total current from the sample is of the order of μA, giving a negligible voltage drop from the Ta holder to the sample. Initially the sample contains 0.5 wt% potassium. The only ion expected to be emitted from the sample is K^+. In Ref. (17), a detailed search was made with negative result for other ions than K^+ in the case of a more complex potassium promoted iron oxide catalyst. Thus, an emission of, e.g., KOH could not be confirmed. In the literature, a large amount of information exists on the chemical composition and physical characteristics (like porosity) of this type of catalyst. The recently published book (4) contains a survey of 724 references of the structure and surface chemistry of ammonia synthesis catalysts.

The ion detector consists of a collector in the form of a Faraday cage with tilted bottom behind two electrodes with circular openings, as shown in Fig. 5. The entire unit is well shielded with all external parts at ground potential, with a small opening for the ion flux from the sample. The sample was at a chosen positive potential during the experiments, and the positive current to the collector was directly measured with an electrometer. Care was taken to avoid stray electric and magnetic fields inside the stainless steel chamber. No external fields are believed to influence the results, which is supported by the quite symmetric form of the distributions.

The various parts of the sample are shown in a horizontal cut in Fig. 6. The work function of the sample was found from Richardson plots varying the sample temperature in
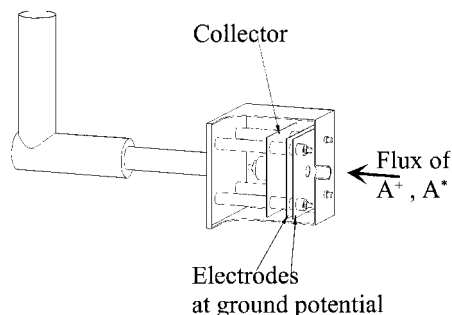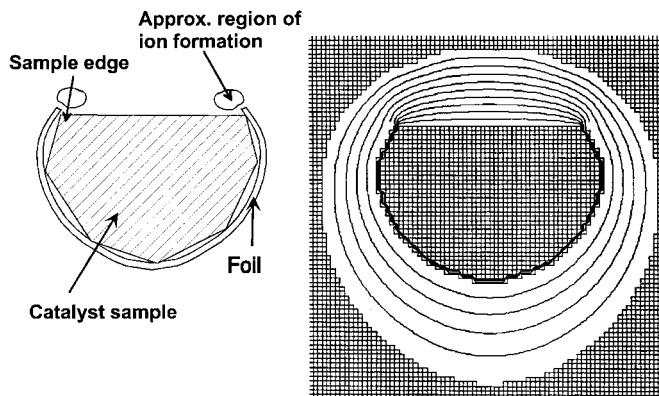

FIG. 6. The sample and its surrounding electric potential, horizontal cut. The resulting potential close to the sample at 21 V is shown to the right. The outer region at a constant potential of 19 V agrees with the equipotential at this position. The foil around the sample is at 20 V. The ion trajectories are not followed outside the region shown. The size of each square is 70 μm.

the range 940–1170 K, with a collector placed in front of the sample and a negative voltage of 300 V applied to the sample (8). No large spatial or temporal variations were found. The work function value is 3.9 eV for the prereduced catalyst, while it is much lower for the used catalyst, around 1.7 eV. This indicates a metallic, slightly alkali covered surface, with more free alkali atoms on the surface for the used catalyst. A clean iron oxide surface would have a work function larger than the pure metal, i.e., at least >4.1 eV. The Richardson method at low temperature gives more weight to the lowest work function patches on an inhomogeneous surface. There is no sign of lower work function patches; on the contrary, the Richardson plots are linear or even steeper at low temperature. Thus, one can conclude that patches with much lower work function than the values given do not exist. The work function of the polycrystalline Ta foil is around 4.1 eV, which means that it contributes little to the electron current. Total ion current obtained was of the order of 10^{-6} A.

The heat treatment during the experiments removes small, measurable quantities of K from the surface, and also oxygen from the topmost layers so that the surface becomes almost metallic, as described above. The heating in the apparatus thus destroys the sample slowly, and it is necessary to determine just how fast this process is. The catalyst is normally used up to 10 years in the plant at 800 K. It may be assumed that the destruction process due to loss of K is completed to 50% after 10 years and that the preexponential for the process is 10^{13} s^{-1} (as for a normal desorption process). This means that a similar 50% change will take place after 4 h at 1000 K, which is the time span of one or a few experimental runs. In reality, the destruction process does not only involve a desorption process with its rapid temperature variation, but also slower, often rate limiting diffusion processes. This means, that the effective temperature

FIG. 5. The construction of the detector (FI detector in Fig. 4) used to measure the emitted ion current. The voltages of the electrodes in the detector are at ground potential when the ion current to the collector is studied.

dependence is much smaller, and the useful life in the apparatus would be considerably longer than the 4 h estimated above. We do not observe any severe changes in the behavior of the catalyst samples during the experiments.

4. FIELD CALCULATIONS

Calculations of the electric fields and ion trajectories have been done with a commercial program (29). Due to the limited resolution available in the layout of the fields, the calculations have been done in several steps to calculate the fields, equipotential lines, and ion trajectories accurately. The detector position has been shown to be of no importance in separate experiments, with cylindrical shields to better define the electrical fields (30), and the detector is not included in the calculations of the fields. The calculations give an electric field strength of 2–50 V cm^{-1} in front of the surface.

The sample will in general have a larger alkali content and also surface coverage of K atoms than the Ta foil sample holder. This means that in general the initial work function of the sample surface is lower than that of the Ta foil in the holder. Some work function data were given in the previous section, which also show that the work function of the Ta holder will be larger than that of the sample surface. This work function difference means that electrons are transferred to bring the Fermi levels to approach each other (31). The resulting electric field has the direction to accelerate electrons from the Ta foil to the sample. This is the same as to say that the sample is at a higher potential than the surrounding Ta foil sample holder. To simulate this effect in the calculations, the sample is always kept at a voltage which is 1 V higher than that of the Ta foil. The work function difference is a fundamental quantity and will not be changed by the external electric field used to accelerate the ions from the sample. This means that there exists a stronger edge field between the sample and the Ta foil in the holder, of the order of a few hundred V cm^{-1}. The shape of the electric field around the sample found with such a calculation is shown in Fig. 6. The lower field strength at the back of the sample is due to existence of an arm which holds the sample in the vertical direction, which is not seen in the plot. However, the field at the back side of the sample does not influence any of the results calculated.

Besides the small initial energy of 0.1 eV used for the ions, the calculations are scaleable, such that a calculation with 1 V edge difference and 21 V sample voltage gives the same result as the case with 4.8 V edge difference and 101 V sample voltage. It is thus possible to get a reasonably correct view of the angular distributions also for values other than 1 V for the edge difference, i.e., the voltage between the sample and its foil holder.

Due to the shape of the sample and its foil holder, the field strength at the edges is higher than that on the plane
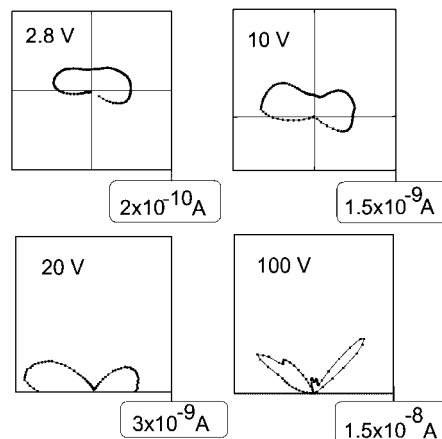
FIG. 7. Angular distributions for ions from the prereduced catalyst, at a sample temperature of 980 K. The sample voltage is given in the panels. Observe the increase in signal with voltage.

surface. Field ionization of K Rydberg species at the sample edges can take place even without the work function difference accounted for above. However, angular distributions of the ion trajectories with only thermal energies are not in agreement with the experiments, as described further below.

5. RESULTS

The signal obtained with the electrodes in the detector at ground potential is due to ions from the sample or from ionization outside the sample of particles emitted from the sample. Examples of results of this kind are given in Fig. 7 for the prereduced catalyst and in Fig. 8 for the used one. An ion signal is observed only with a voltage applied to the sample, since otherwise no field ionization of the K Rydberg species takes place. Even if ions desorbed directly from the surface, space charge limiting would allow only very small currents to leave the sample. However, even if the voltage of the sample is just a few volts, as at 2.8 V in Fig. 7, a signal is observed, i.e., at a field strength at the surface of the order of 2 V cm^{-1}. With higher voltages in Fig. 7, various forms
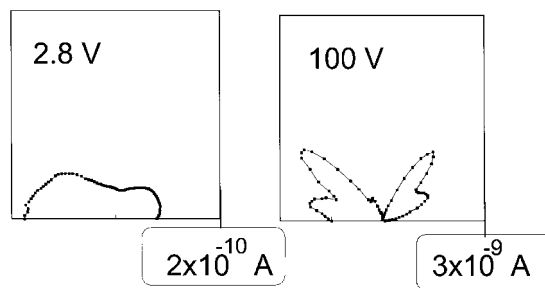
FIG. 8. Angular distributions for ions from the used catalyst, at a sample temperature of 980 K. The sample voltage is given in the panels.

of the angular distributions are obtained. The minimum in the normal direction becomes more pronounced with increasing voltage. Since the shape of the field is the same independent of the voltage, i.e., the form of the equipotentials does not change but only the specific voltage values related to them, it is clear that direct field effects exist. In the studies of the neutral emission from the catalyst (7), the angular distribution has an almost cosine shape as in Fig. 2; i.e., the observed flux is due to emission under equilibrium conditions at the front surface of the sample. The distributions found for ion emission instead show a localized emission from the edges of the sample and no emission from the front surface. This shows that different processes are responsible for the neutral emission and for the ionic emission, as for the potential energy model in Fig. 1, where the ion emission is due to ionization at the sample edges, while the atom emission at zero field strength is due to desorption of Rydberg species K^* from the front surface.

At very low voltages, the signal is not a maximum in the direction of the sample normal, and at higher voltages the signal is very small in the normal direction. Instead, the highest signal at low voltage is found at 90° toward the normal of the sample, i.e., parallel to the sample surface. This shows that the emission is along the surface. The asymmetry of the angular distributions relative to the surface normal is obvious in some cases in the figures. This is mainly due to slow variation of processes in the material, which leads to drifts in the measured currents.

The ion signal increases strongly when the voltage of the sample is increased, as seen in Figs. 7 and 8. One factor which could give a variation with the applied voltage is space charge limiting. The typical dependence on the applied voltage is $V^{3/2}$ in the case of space charge limiting, thus stronger than linear. The results here in general show a slower variation, close to linear, as often found in the case with emission of Rydberg species (32).

The results in Fig. 9 exemplify the temperature effects observed, showing as expected that the total signal increases strongly with temperature. The angular distributions of ions are strongly peaked with several peaks at low temperature, but with increasing temperature the peaks are broadened into two lobes. The broadening of the peaks is due to increased thermal motion of the emitted atoms or ions from the sample. The directions of the main peaks do not change appreciably when temperature is raised from 890 to 1080 K. Complementary results on the temperature variation of the neutral signal are given in Ref. (8). Small peaks or lobes in the normal direction are also observed with increasing temperature in Fig. 9. Such peaks could be due to ions formed by field ionization at the sample or due to clusters formed in the increased density of K atoms at the surface (7, 24).

We have performed detailed calculations to be able to specify the location and nature of the ionization of the excited species which form the ions observed. The starting point was the previously supported view that the ions are formed over the whole sample surface, with a kinetic energy of a few eV along the surface tangent. It must be stated clearly that we do not aim at quantitative agreement between the experiments and the calculations, since it is obvious that many factors, like the surface structure, the structure of the sample edges, and the edge shape of the metal foil, are not included in any detail. Experiments have, on the other hand, proved that these factors do not influence the results strongly. Thus, we here attempt to understand the main factors creating the ion peaks at large angles towards the normal. The broad lobes observed at low voltages, for example in Fig. 7, are due to a weaker projecting (accelerating) external field, which gives a larger influence of the initial thermal motion of the ions.

Figure 10 shows the angular results of ion trajectory calculations at three different sample voltages, assuming that ions are formed only at the edges of the sample with thermal energy in the normal direction of the sample. At low voltage, the flux is broad and mainly sideways, which agrees at least qualitatively with the result at low voltage in Fig. 7. At 20 V on the sample, the lobes are still broad but with a larger angle toward the sample normal, also in agreement with Fig. 7. At high voltage, 101 V in the calculation, the lobe is much sharper, having its center in a direction of 30° toward the sample normal. This is somewhat closer to the normal than found experimentally in, e.g., Fig. 7. In Fig. 11 the results are shown with a thermal spread in initial energies along the surface tangent for two different points of ionization at a sample voltage of 101 V. The calculation agrees in this case better with the observed direction of ion emission.
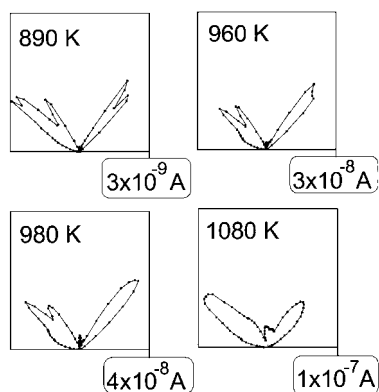
6. DISCUSSION

K atoms diffusing from the bulk of the catalyst to the surface area covered by the Ta foil will not be able to leave the sample directly. They have to diffuse to the slit between
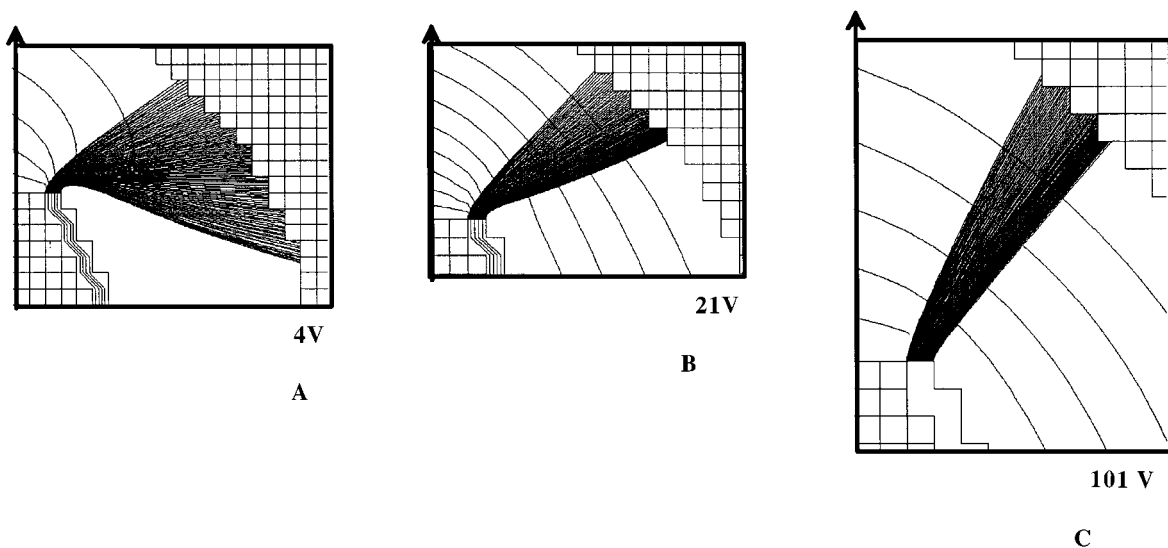

FIG. 9. Angular distributions for ions from the prereduced catalyst, at a sample voltage of 200 V. The sample temperature is given in the panels.

FIG. 10. Ion emission from the edge region of the sample. Initial ion energy 0.1 eV, starting in the normal direction (the arrow). The sample voltage is the parameter given in A, B, and C. The equipotentials visible are at (A) 3.8, 3.6, 3.4, 3.2, and 3.0 V counted from the sample at 4 V; (B) 20.8, 20.6, 20.4, 20.2, 20.0, 19.8, 19.6, 19.4, and 19.2 V at 21 V on sample; and (c) 100, 99, 98, 97, and 96 V at 101 V on sample.

the foil and the sample, from where they may leave as ions or atoms. A process of this kind could give an appreciable flux of atoms and ions in some distribution, probably in two peaks directed sideways. If such a flux existed it should have been observed with the surface ionization detection used, e.g., in Fig. 2, but no such peaks were observed. They should not change strongly with the applied voltage and should thus also have been observed in Fig. 7. No such effect of the enclosing Ta foil seems to exist.

The main problem which was to be solved by the calculations was the origin of the ions in the sharp peaks, which are observed outside ±45° with sample voltages of 100 V or larger, giving no ion flux in the normal direction. It is

FIG. 11. Ion emission from the edge region of the sample. The arrow indicates the normal of the sample. Initial ion energy varying from 0.05 to 0.15 eV, starting in the direction parallel to the surface, moving out from the sample. The sample voltage is 101 V. The ions start at the surface in (A) and outside the surface in (B). For voltages of the equipotentials, see Fig. 10.

apparent that a large flux in the normal direction will be obtained in the case of a more or less uniform emission of ions over the sample surface. As discussed previously (6, 19), the sample edges are very important for the formation of the peaks. However, direct tests varying the sample holder opening angle (19) did not reveal any direct influence on the peaks. The field between the foil holder and the sample, which may exist due to the difference in work functions, can have an important role in the ion emission. In fact, this voltage difference may in reality be smaller than that used in the calculations, since the sample has a work function of 3.9 eV and the Ta foil a work function close to 4.1 eV. However, if the potential difference between the sample and its holder is smaller than 0.2 eV, this work function difference is not sufficient to account for the ion emission as concluded from the calculations. In the case of the used catalyst with a substantially lower work function of 1.7 eV (8), similar peak directions are found, as seen in Fig. 8. (In the right-hand panel of this figure, some extra flux is observed close to the surface. We have shown that this flux for the used catalyst is due to Rydberg states which can be removed by field ionization in the detector. Thus, it does not indicate a change in the ion emission pattern.) It may be expected that the boundary layer containing K^* outside the catalyst surface modifies the potential difference due to the work function difference during the experiments.

A final test has also been done of the previously supported view (19) that the peak structure observed is due to ions from the whole sample surface, which are emitted with a few electron volts of kinetic energy along the surface tangent. The decisive results are shown in Fig. 12. While the broad distribution at low sample voltage does
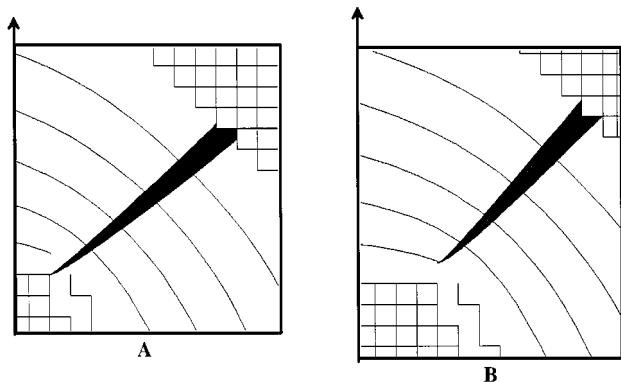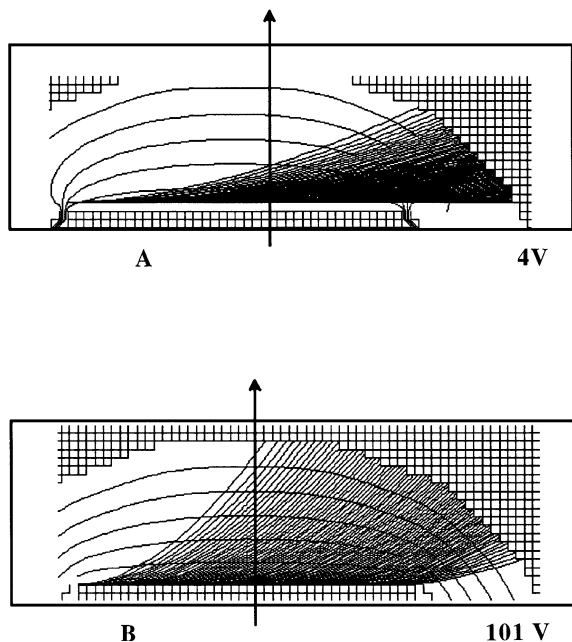
FIG. 12. Ion emission from the surface of the sample. The arrow indicates the normal of the sample. Initial ion energy was 4 eV, starting in the direction parallel to the surface. The sample voltage is the parameter given in A and B. For voltages of the equipotentials, see Fig. 10.

not depart strongly from that of the experimental results, the even broader distribution at 100 V, with the maximum signal still close to ± 80–90°, is clearly at variance with experiments. This indicates that it is not sufficient that the ions are formed with an excess energy along the sample surface, as suggested previously (19).

The ordinary description of diffusion on a surface (33) easily gives estimates of the distances of diffusion over the surface. An ion K_s^+ with a typical desorption energy of 1.7 eV, as given in Fig. 1, which jumps 0.2 nm (to the next site) in each diffusion step, will be able to diffuse only 2 μm before desorbing from the surface, i.e., too short to move to the sample edge. Similar values will also apply to ground state atoms of K on the surface, if such states exist. Thus, K ions or ground state atoms on the surface cannot give rise to the prohibited desorption and consequent long-range diffusion of K. A covalently bound K atom in the lowest state shown in Fig. 1 will have a desorption energy of 4.3 eV. Assuming also in this case a jump length of 0.2 nm and no diffusion barrier gives a diffusion length of 13 m. Due to the covalent bonding, the barrier to diffusion will be considerable. Assuming the relatively large value of 2 eV, the diffusion length is small, approximately 0.1 mm. For the high Rydberg-like states of which two examples are shown in Fig. 1, the desorption energy is 1.7–2.7 eV, while the diffusion jump length may be 1 μm and the diffusion barrier is probably very low. This means diffusion lengths of 2 cm–7 m, which is more than enough to allow the K atoms to diffuse to the sample edges.

It is possible to propose a simple consistent model which agrees with these mechanistic conclusions. The Rydberg atoms bound to the surface move along the catalyst surface within the boundary layer. They move with thermal energy mainly parallel to the surface. When they reach the edge of the catalyst, where the metal foil of the sample holder covers the sample, they cannot move further as Rydberg species coupled to the metal surface. Instead, it is possible for them to transfer their excited electron to the metal surface, either by an Auger-like process or by field ionization. Since they on the average move along the surface at a distance which is large compared to the ordinary binding distance for alkali ions, the ion–surface adsorption forces are already weak at this distance, and the ions may thus proceed in the direction they moved before the ionization, i.e., in the direction of the sample tangent. The excess energy of the ions after leaving the surface field is close to thermal by this mechanism. However, the ions may be further accelerated due to the work function difference between the metal foil holder and the sample.

7. CONCLUSIONS

Results are presented for the potassium ion emission from samples of an iron catalyst used for ammonia production. No ions desorb from the front surface of the sample, but only from the sample edges. This is supported by ion trajectory calculations over a large range of field strengths. Diffusion of K Rydberg-like species several millimeters along the surface to the sample edges, with subsequent ionization and slightly exoergic emission in the direction of the diffusional motion is the likely process which agrees with all the results. Thus, the Rydberg species of the alkali promoter, which are thought to form reactive complexes with reactant gas molecules, are mobile over the catalyst surface but still bound to it. By now, all the important loss processes of the alkali promoter have been studied in detail, which means that the promoter loss is understood. Solutions of this problem may then be found; for example the loss may be diminished by controlling the geometrical form of the catalyst crystallites and the catalyst pellets. The promoter function and loss may also be influenced by an external electric field through the Rydberg states of the promoter.

APPENDIX: DETECTOR FUNCTION

The detector is used as an ion collector in the present experiments, i.e., with the two defining electrodes and the collector at ground potential. The most obvious particle type which can be measured in this detector mode is K^+ ions which could be formed at the sample surface or at some distance outside the sample. K Rydberg atoms may give emission of electrons by Auger processes at the collector. Such atoms will move in straight line trajectories from the sample and hit the collector inside the cylindrical trap. This

will prevent most secondary electrons from leaving the trap. Thus, only a strongly suppressed signal will be observed for such excited species. The excited species are known to have an angular distribution which is different from that found for the ion signal in the present case. Due to this difference in shape, one can conclude that excited species do not give the signal observed with the electrodes in the detector at ground potential.

Another possible cause of the signal is neutral clusters which are formed at the sample surface, as previously demonstrated in studies of this catalyst (6). Such clusters could be large enough to give electron emission on impact in the detector due to the large energy released when all the atoms in the cluster become bound to the surface. In Refs. (6, 7) it is shown that the clusters from the surface leave the sample in the direction of the macroscopic surface normal, and just a small cluster signal of this kind is observed in some of the present experiments. If neutral clusters would also constitute the peaks from the sample edges, the narrowing of the lobes outside $\pm 45°$ when the applied voltage increases is not easy to understand. Thus, we conclude that neutral clusters are not involved in the formation of the sideways lobes and peaks.

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