Catalysis Letters 26 (1994) 101–107

Emission of excited potassium species from an industrial iron catalyst for ammonia synthesis

Klas Engvall, Andrzej Kotarba [1] and Leif Holmlid

Reaction Dynamics Group, Department of Physical Chemistry, University of Göteborg and Chalmers University of Technology, S-412 96 Gothenburg, Sweden

Received 12 August 1993; accepted 3 February 1994

The angular dependence of potassium emission–desorption is studied from a fused iron catalyst of the type used for ammonia synthesis. The excited species (K^*, K_n^*, etc.) and positive ions K^+ have strongly different angular distributions. The bilobular distribution measured for ion desorption is concluded to be either due to excited atoms, so-called Rydberg atoms, or excited clusters. Both types of species have to desorb from the edges of the sample and become field ionized and deexcited just outside the sample, as reported in previous studies on an iron oxide catalyst. The peak in the normal direction measured for excited species is due to excited cluster formation outside the catalyst surface. Similarities with previous results for other catalysts are observed. The possibility that the promoter function of potassium in the ammonia synthesis is due to excited species is pointed out.

Keywords: angular dependence; potassium emission–desorption; fused iron catalyst; ammonia synthesis

1. Introduction

In industrial heterogeneous catalysis, alkali is often an important promoter [1]. Promotion with alkali metal influences the catalyst in many ways, e.g. it may increase the activity, or increase the selectivity and/or prolong the useful life of the catalyst.

A major question for all catalysts promoted with alkali is the exact role of the alkali metal. A well-known example is the iron catalyst for the ammonia synthesis. In this case, addition of potassium oxide (about 0.5 wt%) to the iron catalyst increases the catalytic activity by a factor of three [2]. The promoter effect is here commonly believed to be related to the special electronic binding state for alkali on the catalyst surface. There exists, however, no definitive evidence for the chemical state of the alkali metal on magnetite-derived commercial catalysts [3–5].

---

[1] On leave from Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland.

A different approach to the alkali promotion problem is the model proposed by Pettersson et al. [6]. This model discusses the possibility that the promoter function is coupled to electronically highly excited states of alkali atoms (so-called Rydberg atoms) at the catalyst surface. Formation of excited species of alkali has previously been reported for commercial heterogeneous catalysts such as the iron oxide catalyst for the styrene production [7–10] and the vanadium oxide catalyst for the sulfur trioxide process [11]. Besides these oxide catalysts Rydberg atom formation has been observed also at carbon surfaces [12–14]. The excited alkali species are detected by the field ionization technique [15], which is the most widely used for these species.

2. Experimental

A commercial fused iron catalyst for ammonia synthesis was obtained from Norsk Hydro. It is in the form of pre-reduced and passivated grains of sieve fraction 1.5–3.0 mm.

The experimental set-up used consists of a rotatable field ionization detector (FID) in an ultrahigh vacuum (UHV) chamber with a pressure of 10^{-9} mbar during the experiments [9]. The catalyst sample was placed in the center of the chamber. It was mounted in a folded tantalum foil and cut to expose a flat surface to the detector. The catalyst sample could be heated up to 1270 K (1000°C) by passing an ac current of 30 A through the tantalum foil.

In fig. 1a cross section of the field ionization detector (FID) is shown. The FID was used to detect excited states of alkali species. The electrodes U_1 and U_2 were held at +150 and −165 V, respectively, to obtain an electric field between the electrodes, which ionizes the excited alkali species. The field strength is 550 V/cm in the present case. The threshold field strength for the ionization of a Rydberg atom with an effective n quantum number in an electrostatic field is expressed by

$$F_c = 3.2 \times 10^8/n^4 \quad \text{V/cm}. \tag{1}$$

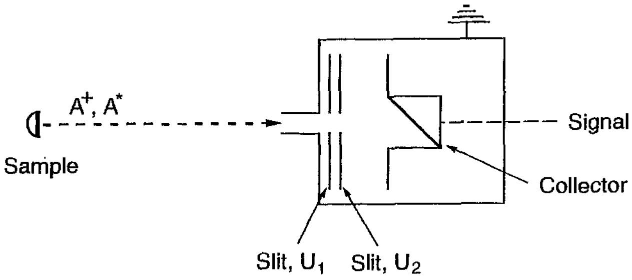

Fig. 1. A cross section of the field ionization detector (FID) with the voltage notation given.

The derivation of this equation is given in ref. [15]. It gives a threshold n value of 28 in the present case, i.e. all Rydberg atoms with a principal quantum number greater than 28 will be field ionized and measured by the detector.

In order to detect positive ions both the electrodes U_1 and U_2 were grounded and the sample was held at +20 V. A positive signal was then measured at the collector.

A computer program SIMION [16] was used to characterize the electrostatic field and to study the ion trajectories inside the detector.

3. Results and discussion

Some examples of the results are presented in figs. 2 and 3. The angular distributions are obtained at a sample temperature of 1070 K (800°C) with a potential of +20 V applied to the sample. The ion signal has a bilobular structure as shown in fig. 2, while the distribution for excited species shows a peak in the normal direction as in fig. 3. The signal due to ions is much larger than that of the excited species, as seen in the figures.

Let us first sum up the evidence that the observed ion signal is not due to surface ionization, e.g. on the edges of the Ta foil holder. In the well-studied case of the iron oxide catalyst for styrene production [9,10], several types of experiments have been done to show this, like determination of the energy of the ions, which is too low to correspond to their formation on the surface and which clearly shows ionization outside the catalyst. In the present case, we have e.g. measured the angular distributions at both high and low voltages on the sample, and those distributions change strongly with the applied voltage. Since the electric field does not change its

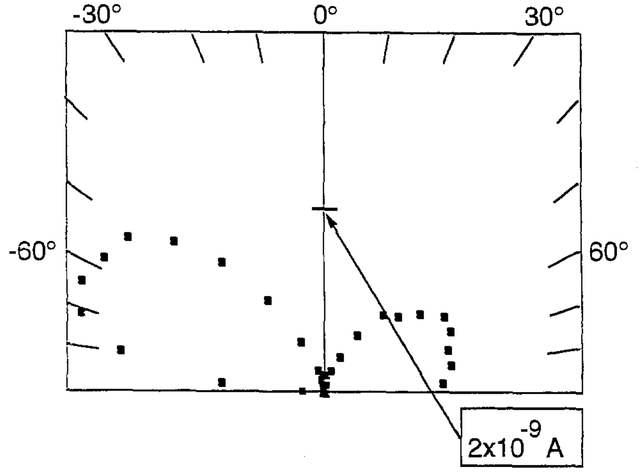

Fig. 2. Angular distribution for emission of positive ions from the catalyst. The electrodes U_1 and U_2 were grounded, and the sample was at 20 V.

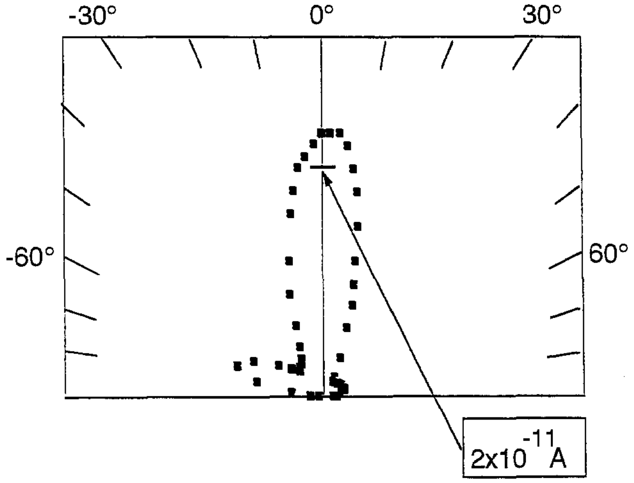

Fig. 3. Angular distribution for emission of excited alkali species from the catalyst, measured with electrodes U_1 and U_2 at +150 and −165 V respectively. The sample was held at 20 V.

shape when the voltage is varied, there would be no such effect if the ions were formed at the same potential, apart from small differences due to the constancy of the thermal initial velocity. Ions starting from rest will move in the same trajectory in an electric field independent of its strength, only the time it takes for the ion to move a certain distance will change.

The thermal emission of potassium atoms from the rough catalyst surface is expected to follow a cosine distribution, since the sample surface area is small compared to the distance between the sample and the detector. However, neither of the two distributions has that form.

The observed angular distribution in fig. 2 for ions agrees with that found by Åman et al. [9,10] for the styrene catalyst. They studied the variation of the peaks systematically, varying several parameters. The explanation for the symmetrical bilobular structure is probably field ionization of excited species (atoms or clusters) at the edges of the sample. At the edges, the field strength is larger, due to both the physical form of the sample and due to the difference in work function between the catalyst sample and the Ta foil in the holder. Since Rydberg atoms can desorb from a surface [7–14], they can also easily diffuse over the surface, the diffusion process being a part of the desorption process (the unsuccessful desorption attempts). The strong potential for the interaction between the surface and a Rydberg atom is due to the extremely large polarizability of the Rydberg atom, which is described and discussed in ref. [9], and the potential is thus also very long-range. Due to this long-range interaction with the surface [9,10], the Rydberg atoms can diffuse rapidly over macroscopic distances, and the flux of such species will leave the sample preferentially from the sample edges. The Rydberg species are then ionized in the electric field outside the edges of the sample [9]. Whether these excited desorbing species are atoms or clusters is, however, more difficult to conclude.

Excited clusters can be formed rather easily due to the strong long-range interaction between the Rydberg atoms, which is caused by the very large polarizabilities of Rydberg atoms (they increase rapidly with the principal quantum number n as n^7 [17]).

The sharp peak in the normal direction seen in fig. 3 is a very distinctive feature. Since the catalyst surface is very rough, but macroscopically plane, a peak in the normal direction indicates a formation process which only depends on the *gross* features of the surface, i.e. the macroscopically plane surface. First, the nature of the particles observed should be clarified. The SIMION calculations show that the positive and negative charged species formed outside the FID are prevented from reaching the collector by the potentials applied to the electrodes. Excited species, however, pass through the first electrode in a low field strength but may be ionized in the much stronger field between the electrodes. If the ionization takes place close enough to the positive U_1 electrode, the ions formed are accelerated towards the collector. Thus, only field ionizable excited species are observed by the detector. Then, the nature of these species should be discussed. Above, it was concluded that the effects of the rough surface are averaged out, such that the peak in the normal direction can be found. This can only be true if many atoms combine to form a cluster outside the surface. As mentioned above, the probability of condensation for the excited alkali atoms to excited clusters is very large due to the large interaction potentials between the excited species [18]. In the case of excited alkali clusters, field induced fragmentation to ions between the electrodes is a possible mechanism for ionization.

It is interesting that in spite of the different chemical composition, the angular distributions of potassium emission from the ammonia synthesis catalyst are so similar to that from the catalyst for styrene production [9,10]. Emission of excited species has also been observed from the vanadium oxide catalyst for the sulfur trioxide process [11]. Excited alkali species formed by emission from the industrial catalyst surfaces seem to be a general feature of alkali-promoted catalysts. This behavior points at the promoter function model, proposed by Pettersson et al. [6], which involves excited alkali species on the surfaces of catalysts. In the case of the iron catalyst, the highly reactive excited potassium species might react with the nitrogen molecule and form an intermediate N–N–K or N–N–K*. This will result in an increase in the sticking probability. It is a well known fact that the sticking coefficient for N_2 on iron increases greatly with potassium coverage [19]. Since the dissociative adsorption of nitrogen is the rate determining step in the ammonia synthesis, the interaction between the excited alkali species and the nitrogen molecule may be coupled to the enhancement in the catalytic activity through an increased rate of dissociation.

The assertion that the excited species formed and observed in the present type of experiment could have an influence also in real industrial catalysis should also be discussed. There are two problems: the influence of the surrounding gas in the process on the *formation* of the excited species, and also on the *lifetime and concentra-*

tion of the excited species. Firstly, the formation of excited potassium species is due to diffusion of potassium out of the bulk. Thus, their existence is largely independent of the gas pressure outside the catalyst surface, and such species are likely to be formed also under industrial conditions. Secondly, the lifetime and concentration of the excited species will be influenced rather strongly by the surrounding gas. However, one of the main effects will be that the rate of condensation to clusters decreases strongly, since instead the excited atoms will collide and possibly react directly with the gas phase molecules. Thus, this does not mean that the importance of the excited species decreases with increasing pressure, but instead there will be more free reactive species than in the vacuum case studied here. However, more experimental works on different catalyst samples are needed to verify how the alkali promoter functions in heterogeneous catalysis.

Finally, the similarity of the catalyst studied in the vacuum apparatus with the catalyst used in the process will be discussed. Of course, the samples we study are in quite different surroundings than those used in the process. The prereduced and stabilized catalyst samples are likely to loose most of the oxygen bound in the surface layer during the experiments. Despite this, the behavior of the catalyst relating to excited species formation is very similar to the iron oxide catalyst used for styrene production, as remarked above. This indicates only a weak sensitivity to the oxidation state of the surface. Also used catalysts behave in a similar fashion (details to be published separately), which gives further support to this conclusion. The temperature of the sample in our study is above that used in the industrial process. However, the process of diffusion in the material, which is the process of greatest importance for the formation of the excited species does not change strongly with temperature. That we have to raise the temperature to observe the excited species is probably mainly due to our quite low sensitivity (electrometer measurements). Another possibility is that we have to desorb an adsorbed layer of water or similar, which in the process would be replaced by reactant and product molecules. Thus, we believe that the important features of the catalyst sample in our experiments are similar to those of the catalyst in the process.

Acknowledgement

We thank P. Govind Menon and P. Skaugset for helpful discussions and for reading and commenting on the manuscript. We are grateful to Norsk Hydro AS for providing the catalyst samples, and for supporting this study.

References

[1] W.-D. Mross, Catal. Rev.-Sci. Eng. 25 (1983) 591.
[2] A. Ozaki, *Catalysis, Science and Technology*, Vol. 1 (Springer, Berlin, 1981) ch. 3.
[3] M. Bowker, Catal. Today 12 (1992) 153.
[4] M.S. Spencer, Catal. Lett. 13 (1992) 45.

[5] S.P.S. Andrew, Appl. Catal. A 90 (1992) N13.
[6] J.B.C. Pettersson, K. Möller and L. Holmlid, Appl. Surf. Sci. 40 (1989) 151.
[7] J. Lundin, K. Engvall, L. Holmlid and P.G. Menon, Catal. Lett. 6 (1990) 85.
[8] K. Engvall, L. Holmlid and P.G. Menon, Appl. Catal. 77 (1991) 235.
[9] C. Åman and L. Holmlid, Appl. Surf. Sci. 62 (1992) 201.
[10] C. Åman and L. Holmlid, Appl. Surf. Sci. 64 (1993) 71.
[11] K. Engvall, L. Holmlid, H. Prinz and H. Hofmann, Catal. Lett. 11 (1991) 41.
[12] J.B.C. Pettersson and L. Holmlid, Surf. Sci. 211 (1989) 263.
[13] T. Hansson, C. Åman, J.B.C. Pettersson and L. Holmlid, At. Mol. Opt. Phys. 23 (1990) 2163.
[14] C. Åman and L. Holmlid, J. Phys. D 24 (1991) 1049.
[15] R.F. Stebbings and F.B. Dunning, *Rydberg States of Atoms and Molecules* (Cambridge Univ. Press, Cambridge, 1983) p. 91.
[16] D.A. Dahl, SIMION PC/PS 2 version 4.02, Idaho National Engineering Laboratory, EG&G Inc. (1989).
[17] P.P. Herrmann, J. Hoffnagle, N. Schlumpf, V.L. Telegdi and A. Weis, J. Phys. B 19 (1986) 535.
[18] C. Åman, J.B.C. Pettersson and L. Holmlid, Chem. Phys. 147 (1990) 189.
[19] G. Ertl, in: *Catalytic Ammonia Synthesis*, ed. J.R. Jennings (Plenum Press, New York, 1991) ch. 3.