Catalysis Letters 6 (1990) 85–94

MECHANISM OF POTASSIUM LOSS BY DESORPTION FROM AN IRON OXIDE CATALYST FOR THE STYRENE PROCESS

Jörgen LUNDIN, Klas ENGVALL, Leif HOLMLID

Department of Physical Chemistry GU, University of Göteborg and Chalmers University of Technology, S-412 96 Göteborg, Sweden

and

P. Govind MENON

Department of Engineering Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Received 16 February 1990; accepted 28 June 1990

Styrene catalyst, potassium, promotor, potassium loss, excited states

Several types of experiments have been done with molecular beam and mass spectrometric methods to characterize the desorption processes of potassium from a commercial styrene (potassium promoted iron oxide) catalyst. The loss of potassium as desorption of K is found to be mainly thermal, with an activation energy close to 1.0 eV (97 kJ/mole), which probably is associated with release of K from the initially bound positions in the bulk. The directly measured rate of loss as K appears too small to account for the experimentally observed total rate of loss. A new loss mechanism as electronically excited but not easily field ionizable potassium atoms is detected with an activation barrier of 1.7 eV (164 kJ/mole). Excited states may be important for the total loss both through direct emission of excited K atoms, and since excited states may give rise to cluster formation at the surface and more rapid loss as clusters K_n.

1. Introduction

Even 60 years after the commercialization of the iron-oxide catalyst for the dehydrogenation of ethyl benzene to styrene, the migration of potassium and its loss from the catalyst are still major problems [1–3]. Under the process conditions of 600–630 ° C in steam, the alkali migration occurs in two dimensions: from the top to the bottom of the reactor, containing 100–300 tonnes of catalyst, and from the exterior to the interior of every catalyst pellet [2]. This migration/loss of K results in a serious loss of activity, selectivity, mechanical strength, and hence life of the catalyst.

Recently, Muhler et al. [4,5] have conducted a detailed study of the nature of the active phase in the styrene catalyst under real process conditions. They propose that an equilibrium exists in the solid catalyst,

$$K_2Fe_{22}O_{34} \underset{-K^+}{\overset{+K^+}{\rightleftarrows}} KFeO_2.$$

in which $KFeO_2$ is the catalytically active phase, as was proposed earlier by Hirano [6]. The role of K in the solid-state transformations of the catalyst in its formation, deactivation and spatial disintegration has been brought out clearly in their work [4,5].

The adsorption and desorption processes of K and Cs on metal surfaces like Re, Pt, Ir and graphite have been studied by us previously [7–10], using combinations of kinetics, molecular-beam and mass-spectrometric techniques. These techniques have now been extended to a commercial styrene catalyst to obtain a better insight into the mechanism of alkali loss from the catalyst at typical styrene-process temperatures, which was not studied directly by Muhler et al.

2. Experimental

The experimental apparatus consists of a rotatable quadrupole mass spectrometer in a vacuum chamber with a base pressure of 1×10^{-8} mbar. It has been described previously [11]. In the centre of the chamber, the catalyst sample is mounted in a folded piece of tantalum foil to avoid loss of promotor from the back side of the sample. The construction of the catalyst sample holder and of the ion source is shown in fig. 1. The catalyst is heated by a D.C. current through the tantalum foil, at around 30 A at 600 ° C. The commercial iron oxide catalyst used contained potassium oxide as the major promotor. The catalyst is in the form of 1/8 inch extrudates, which have been cut in half to expose a flat surface to the mass spectrometer.

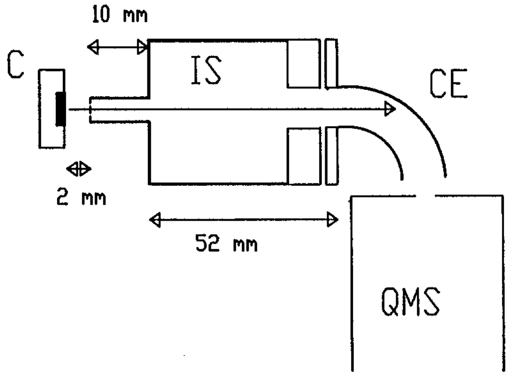

Fig. 1. Schematic view of the apparatus. C is the catalyst part (black) in its holder. IS is the ion source (no internal details shown), CE the cylindrical electrode used as collector for the excited states and QMS the quadrupole mass spectrometer. The arrow shown indicates the transport of the neutral states.

Most of the measurements have employed the ion source and the mass spectrometer in the ordinary way, using electron impact ionization. In some measurements, the signal to the outer cylindrical electrode, CE in fig. 1, is measured. In these cases, the inner cylindrical electrode is kept at +10 V, so that electrons emitted from excited states at the collector surface will be attracted towards this electrode, and thus a positive ion signal can be measured to the outer electrode. Two electrodes in the ion source were held at +150 V and −150 V respectively, to prevent any charged particles as well as easily field ionizable Rydberg states to reach the CE collector. The sample and the front of the ion source were at +20 V, to prevent electrons to drift out from the sample.

3. Results

Several types of experiments have been carried out in this study. Primarily, mass spectrometric measurements of the desorbing flux leaving the catalyst are

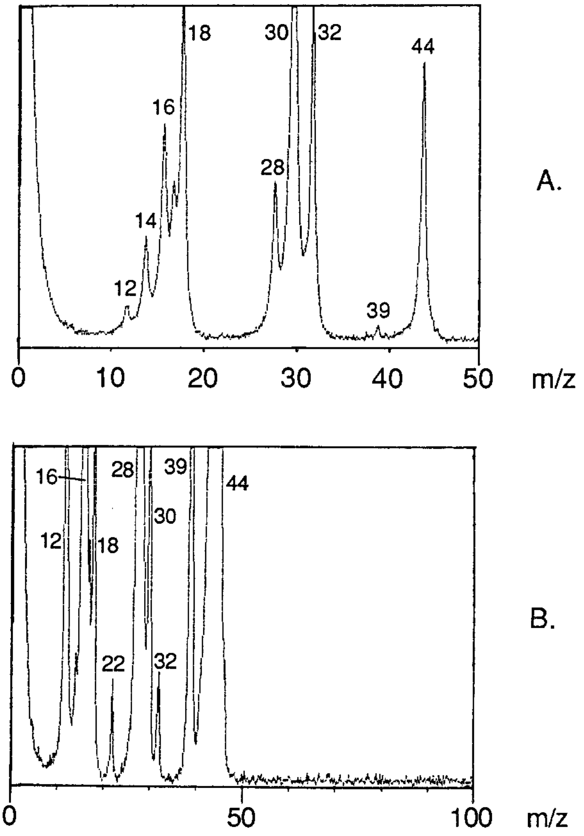

Fig. 2. Mass spectra taken with the mass spectrometer viewing the catalyst front surface. Several reaction product peaks are observed. In (A) the catalyst temperature was 873 K, and in (B) 893 K. Note that no peaks are visible above m/z 50, hence potassium is leaving only as some form of K.

used to identify the molecular state of the alkali flux and to identify the point where the catalyst surface is no longer active for reactions in the UHV environment. Some examples are given in figs. 2 and 3. Secondly, angular distributions were made to identify the thermal or non-thermal behaviour of the desorption, as shown in fig. 4. Thirdly, the temperature variation of the signal at various m/z values was studied. Two typical temperature dependencies are shown in figs. 5 and 6. Experiments designed to measure singly excited states of potassium by field ionization were made, but with no positive identification of such states. Finally, experiments designed to identify doubly excited states or otherwise not field ionizable states of potassium were made. Results from such measurements are shown in fig. 7.

Auger electron spectroscopy experiments have also been done on the fresh and used catalyst samples, which will be fully reported on elsewhere. Of special interest is the studies of the surface of the catalyst which has been in contact with the Ta foil. This surface was found to have the same oxygen content as the fresh catalyst, and no Ta is observed in the spectra. Thus, there appears to be no chemical interaction between the Ta foil and the catalyst sample.

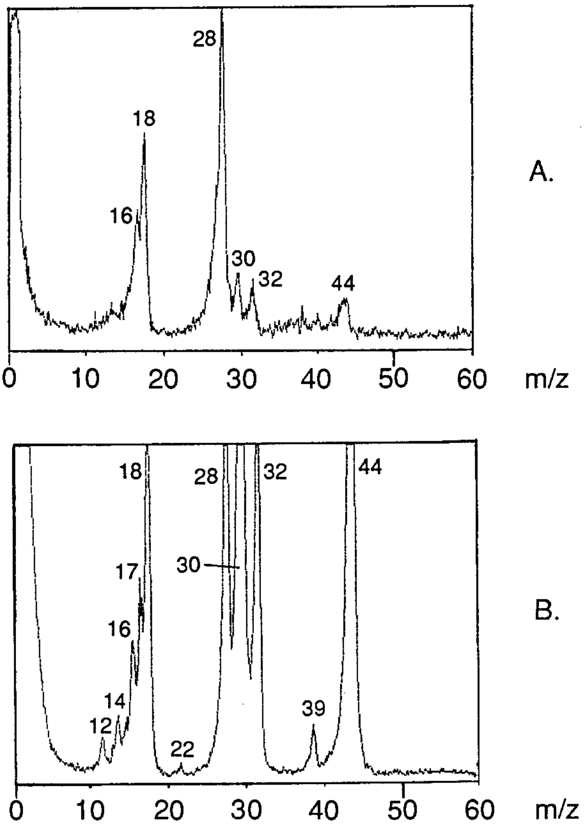

Fig. 3. Mass spectra comparable to fig. 2. In (A), the catalyst was at room temperature, and in (B) at 873 K.

4. Discussion

The experiments have not identified any molecular type loss of potassium from the surface via desorption as e.g. K_2 or K_2O, but only loss as K atoms. Figs. 2 and 3 demonstrate that the catalyst surface was active in the experiments and gave mass peaks at m/z 22, 30 and 44, which we connect with both NO and CO_2 formation at the catalyst surface. When this activity deteriorated, the potassium peak at m/z 39 disappeared simultaneously. This shows that no adjacent surfaces, like the sample holder, catalyzed the formation of NO and CO_2.

The detailed studies of potassium desorption in the form of angular variation of desorption indicate close to thermal desorption for the potassium atoms. The distributions of m/z 39 and 30 in fig. 4 are somewhat narrower than the expected thermal cosine distribution, but all distributions measured for different m/z values have this common shape. This somewhat narrower distribution is probably due to the variable region of the sample, which is seen by the ion source in the detector.

The variation of catalyst temperature demonstrated several "volcano" shaped curves, for almost all m/z values except potassium at m/z 39. An example of this shape is given in fig. 5 for m/z 30, which is due to NO. The potassium temperature dependence was almost Arrhenius-like in all cases. Fig. 6 shows data for neutral K desorption (m/z 39). These data may indicate some small contribution to the signal due to excited states, since a variation with the electric field strength used is observed. The low temperature points correspond to the background level in the mass spectrometer. The apparent activation barrier value found for K emission was usually close to 1.0 eV.

Some studies were also made, which aimed at observing high Rydberg states of K in desorption from the catalyst by field ionization [12,13]. The procedure

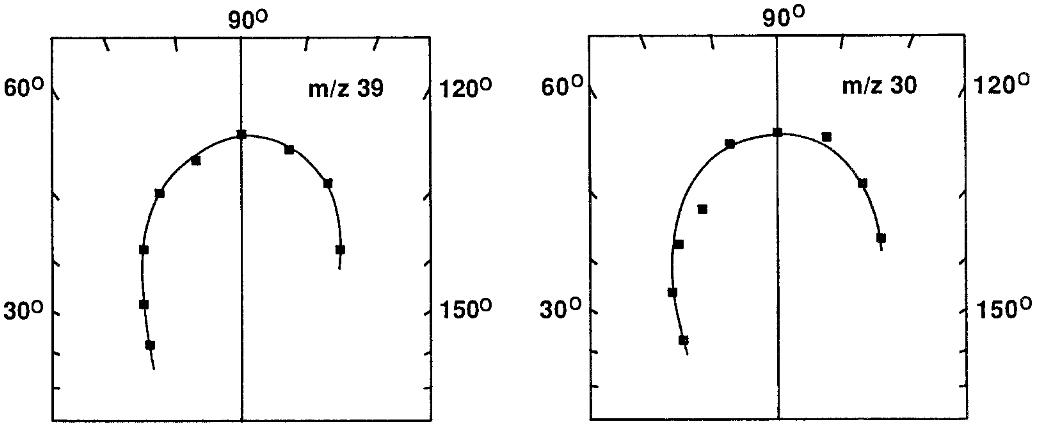

Fig. 4. The angular distribution of K from the catalyst at 743 K, to the left. To the right, angular distribution of mass peak m/z 30, at the same temperature, and with a residual pressure in the chamber of 4×10^{-7} mbar. The detection was made with electron impact mass spectrometry.

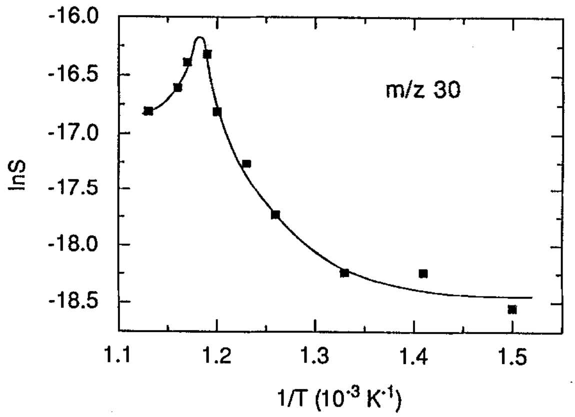

Fig. 5. Temperature variation of the mass spectrometer signal at *m/z* 30, with the typical "volcano" shape.

chosen for the measurements on K* was based on our studies of cesium excited states [9,14]. We could not observe any Rydberg signal by this procedure, and we conclude that just a small fraction of the potassium leaves the surface as atomic Rydberg states of potassium. The experiments done to identify doubly excited states K^{2*} or otherwise not easily field ionizable excited states of K, on the other hand, gave detectable signals and quite good Arrhenius plots with a slope of 1.7 eV. One example is shown in fig. 7. That no K* is observed may be due to the relatively large adsorption energy expected for a Rydberg state with large principal quantum number and thus very large polarizability [13]. K^{2*} may have a lower desorption energy, due to the smaller polarizability.

It could now be possible to identify the main channel by which the loss processes are proceeding by comparison with desorption studies. Studies of this type are in progress in our laboratory [15], but even without detailed kinetic data

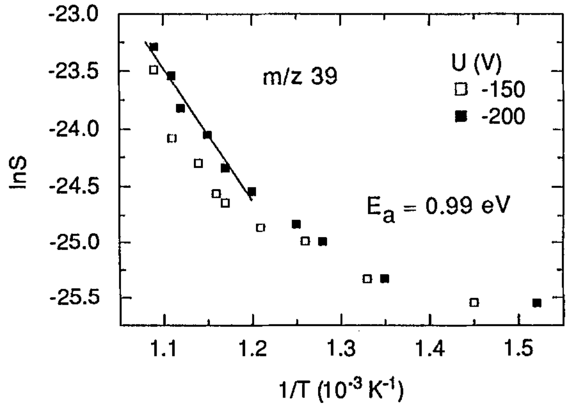

Fig. 6. Temperature variation of the mass spectrometer K signal at *m/z* 39. Observe that the maximum of the curve is at a different temperature than in fig. 5. The indicated voltage is at one of the slits in the ion source.

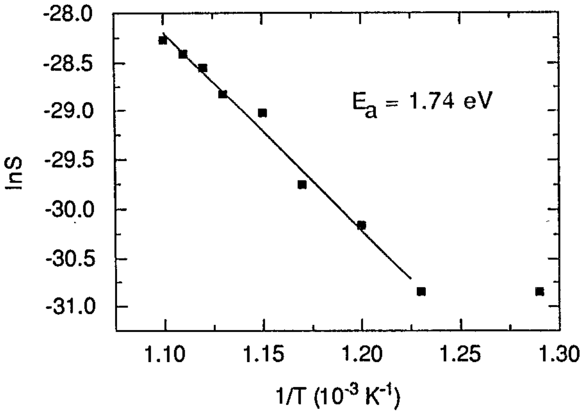

Fig. 7. Temperature variation of the electrostatically filtered signal, due to excited K atoms from the catalyst. The signal was measured at the outer cylindrical electrode in the ion source, see fig. 1.

some general conclusions can be reached. The barriers measured, 1.0 eV for K and 1.7 eV for K^{2*}, are quite low. If they corresponded to ordinary desorption barriers, the time constants for desorption would be 0.7 μs and 27 ms respectively at 773 K, assuming normal pre-exponential factors of 10^{12} s^{-1} in the desorption rate constant [7]. For K desorption, this would mean a total loss time of less than one minute at 500 ° C, assuming a surface coverage of 10%, in contradiction with our experiments where the loss times are of the order of hours at this temperature. This indicates, that the activation barrier value observed for K is not an ordinary desorption barrier but instead a barrier towards diffusion or initial release. Ordinary diffusion barriers should be lower than this, and the likely alternative is a dissociation barrier for the initial potassium containing compound in the catalyst. The temperature variation of the signal will then depend on both the rate of release and of the rate of diffusion to the surface, which may explain the quite bad Arrhenius plots as in fig. 6. The initial form in the catalyst (catalyst precursor) may be K_2O. Estimates of the endothermicity of the reaction $K_2O \rightarrow KO + K$ give values that are too high. The more complex K-Fe oxides proposed by Muhler et al. recently [4,5] may have a lower barrier towards initial release.

In the case of K^{2*}, the activation barrier observed indicates a total loss time of hundreds of hours, using the same assumptions as in the calculation for loss as K. However, such a calculation assumes that the surface density is constant, independent of temperature. Since the surface density of K should vary with the rate of release from the bulk compound, as discussed above, the temperature variation of the release process has to be subtracted. This would indicate a lower desorption barrier for loss as K^{2+}, approximately 0.7 eV. This barrier is low enough to explain the loss from the catalyst, if the loss process is characterized by an ordinary pre-exponential factor for the desorption. However, the rate-determining step still seems to be the release of K from the bulk compound. This is in broad agreement with the conclusions from the comprehensive study on a commercial styrene catalyst by Muhler et al. [4,5], using several different methods to study the catalyst bulk and surface compositions.

It is likely that the barrier found in excited K emission is not a desorption barrier, but a diffusion barrier in the material, as found in other cases [7,8]. If this is so, a normal desorption preexponential is not applicable, but the emission may be much more rapid than ordinary desorption. The signal observed for excited K emission is many orders of magnitude smaller than would be required to account for the loss of K from the catalyst sample. However, we are not convinced that such a measurement can detect the entire flux of K^{2*}, so there may exist a relatively large flux of excited states which is not observed in the measurements. Further, in other experiments with desorption of excited states of alkali metals we observe cluster formation [16], due to the large interaction potentials which such states have with other atoms and molecules. Thus, we are well aware of the possibilities of cluster formation in desorption of alkali from the catalyst.

5. Conclusions

Several types of experiments have been done with molecular beam and mass spectrometric methods to characterize the desorption processes of various states of potassium from a commercial iron oxide catalyst. The catalytic activity for several surface processes under vacuum conditions is observed to exist only when a desorption of potassium is observed, i.e. as long as there is some surface density of potassium on the catalyst. The loss of potassium as desorption of K is found to be mainly thermal. The rate determining step up to 600 ° C seems to be the release of K from the bulk compound. The rate of loss as K appears too small to account for the total rate of loss. On the other hand, a new loss mechanism as excited but not easily field ionizable K^{2*} is detected, which may account for an appreciable loss. The emission of excited K may also be associated with cluster formation [16]. SO far too little is known about this mode of loss to give support for any strict conclusions about its influence on the total loss from the catalyst. The excited state emission may be quite independent of the surrounding gas pressure, as discussed in ref. [17] in connection with a discussion of the possible relation between excited states of alkali and the promotor action of alkali. Experiments like the ones described here may thus give results of direct importance for real catalysts.

The detection of the desorption channel to excited states of K presents a step forward in understanding the fundamental processes at alkalipromoted catalyst surfaces. Since excited state emission may initiate cluster emission [16], experiments which can detect cluster formation are needed to reach final conclusions about the loss of alkali promotors from catalysts. Such experiments are in progress [15].

Acknowledgements

We thank Chemetall GmbH, Frankfurt, for generous financial support of this research.

References

[1] E.H. Lee, Catal. Rev. 8 (1973) 285.
[2] W.-D. Mross, Catal. Rev.-Sci. Eng. 25 (1983) 637.
[3] G. Connell and J.A. Dumesic, J. Catal. 92 (1985) 17.
[4] M. Muhler, R. Schlögl, A. Reller and G. Ertl, Catal. Lett. 2 (1989) 201.
[5] M. Muhler, J. Schütze, M. Wesemann, T. Rayment, A. Dent, R. Schlögl and G. Ertl, J. Catal. (in press);
G. Ertl, personal communication.
[6] T. Hirano, Appl. Catal. 26 (1986) 65; ibid. 28 (1986) 119.
[7] K. Möller and L. Holmlid, Surface Sci. 179 (1987) 267.
[8] K. Möller and L. Holmlid, Surface Sci. 204 (1988) 98.
[9] J.B.C. Pettersson and L. Holmlid, Surface Sci. 211 (1989) 263.
[10] S. Wriedt and L. Holmlid, Appl. Surface Sci. 31 (1987) 197–210.
[11] J.B.C. Pettersson, A. Sigurdsson, G. Nyman and L. Holmlid, Surface Sci., in proof.
[12] R.F. Stebbings and F.B. Dunning, *Rydberg States of Atoms and Molecules* (Cambridge University Press, Cambridge, 1983).
[13] P.P. Herrmann, J. Hoffnagle, N. Schlumpf, V.L. Telegdi and A. Weis, J. Phys. B.: At. Mol. Phys. 19 (1986) 535.
[14] T. Hansson, C. Åman, J.B.C. Pettersson and L. Holmlid, J. Phys. B., in proof.
[15] C. Åman and L. Holmlid, to be published.
[16] C. Åman, J.B.C. Pettersson and L. Holmlid, Chem. Phys., accepted.
[17] J.B.C. Pettersson, L. Holmlid and K. Möller, Appl. Surface Sci. 40 (1989) 151.