Loss of alkali promoter by desorption from promoted vanadium oxide catalysts

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Experiments have been done with molecular beam mass spectrometric methods to characterize the desorption and emission processes of alkali promoter from a commercial vanadium oxide catalyst. It is a potassium and cesium promoted catalyst used for SO_3 production, with a K, Cs/V molar ratio of 2.5. An excited state signal is detected, as in our previous studies of other oxide catalysts. Desorption of both K and Cs is also detected. All signals are observed at temperatures above 910 K, which is just above the process temperature range. The values found for atomic desorption are 2.66 ± 0.16 eV for K and 3.89 ± 0.27 eV for Cs, while the excited state emission has a barrier of 0.89 ± 0.08 eV. The difference in desorption energies between Cs and K is larger than expected. This is probably mainly due to different rate limiting steps in the release and diffusion processes. After an approximate compensation for this, Cs still has a larger activation barrier equal to 3.0 ± 0.3 eV towards desorption than K, which indicates a slower loss for Cs from the catalyst.

Keywords: Vanadium oxide catalyst; cesium; potassium; promoter; promoter loss; excited states

1. Introduction

The loss of alkali promoter from commercial, alkali promoted catalysts is a problem with adversely affects both the activity, selectivity, mechanical strength, and thus useful life of the catalyst [1–3]. Commercial iron oxide catalysts have recently been studied by Lundin et al. [4] and Engvall et al. [5] in our research group, using mass spectrometric and molecular beam methods to detect the desorption and emission of different states of K from the catalyst. The detection of the loss of K via emission of excited, not easily field ionizable states designated as K^{2*} is of special interest. The possibility of formation and loss of clusters of K, which may form via condensation on the excited states, was also noted in ref. [4].

It is known that cesium generally has a higher activity as a promoter, compared to potassium which is normally used. However, due to its higher vapour pressure, it could be thought that cesium is lost more rapidly from a catalyst than potassium. The present study is directed towards just this problem. The catalyst used for the present study is commercial and has the advantage that it is promoted both with K and Cs, which gives us the opportunity to compare the losses of these two alkali metals directly. Our results indicate a larger barrier for desorption of Cs than K, i.e. the loss is slower for Cs than for K in this special oxide catalyst which is melted at process temperatures. If these results are transferable also to other systems, the exchange of K for Cs as promoter or addition of Cs to a catalyst promoted with K, would give a slower loss of promoter. It would at the same time retain the activity of the catalyst longer due to the inherent greater reactivity of Cs.

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 was recently described in refs. [4]. The central parts of the apparatus are shown in fig. 1. The catalyst sample is mounted in a folded piece of tantalum foil to avoid loss of promoter from the back side of the sample. The tantalum foil is heated

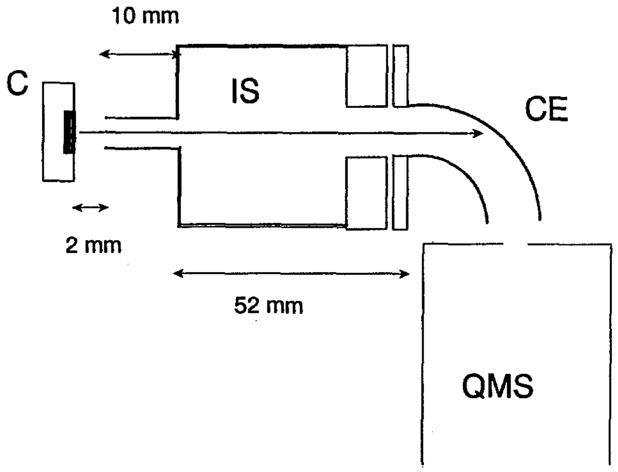

Fig. 1. Schematic view of the apparatus. C is the catalyst (black) in its holder. IS is the ion source (no internal details shown) and CE the cylindrical electrode used as collector for the excited states. The arrow shown indicates the transport of the excited states. The ions formed after electron impact in the ion source are deflected down into the quadrupole mass spectrometer (QMS).

by a D.C. current, at around 30 A at 900 K. The catalyst samples have been cut to expose a flat surface to the mass spectrometer. The sulfur trioxide catalyst is of the type GM-KA 2 08/15 [6]. Initially it contains 4.2 wt% Cs, added in the form of Cs_2SO_4, and 7.8 wt% K, added in the form of K_2SO_4. Its M(K, Cs)/V molar ratio is 2.5. It is ordinarily used at a temperature of 680–900 K (410–630°C) in the process.

Most of the measurements have employed the ion source and the mass spectrometer with electron impact ionization to detect K and Cs desorption. In the excited state 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, to collect electrons emitted from the excited states. The signal observed is due to doubly excited and also to excited, otherwise not easily field ionizable, alkali atoms M^{2*} and M^*, which either field ionize at field strengths of 1000 V/cm between two electrodes in the source or deexcite via Auger like processes [7] at the outer cylindrical electrode outside the ion source. During the excited state measurements two electrodes in the ion source, between the catalyst sample and the CE collector, were held at +150 V and −150 V respectively, to prevent any charged particles from the catalyst, like electrons, 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 into the gas phase.

The chemistry of the vanadium oxide catalyst has been studied in detail in several recent publications [8–12]. The catalyst phase is molten at operating process temperatures, and consists mainly of V_2O_5-$M_2S_2O_7$, where M is the alkali metal. Both Cs and K containing compositions have been used in these studies. Several publications are concerned with the loss of activity at temperatures below 450°C, which is concluded to be related to precipitation of solid compounds from the melt. Of special interest in the present context is the melting point of the catalyst material, which is decreased when Cs is added. The catalyst material would certainly be melted under actual working conditions. We can not conclude from the literature data that the catalyst material (initially containing alkali sulfates) is melted under the conditions of the experiments. However, the mass spectra indicate a conversion of the catalyst after initial heating to 920 K, giving mass peaks which could be due to pyrosulfate decomposition (see below).

3. Results and discussion

The experiments done with the catalyst are of the same types as reported for the iron oxide catalysts in refs. [4,5]. Mass spectrometric measurements of the desorbing flux leaving the catalyst is the method used to detect desorption for all possible ground state species. In addition to this, excited state emission is

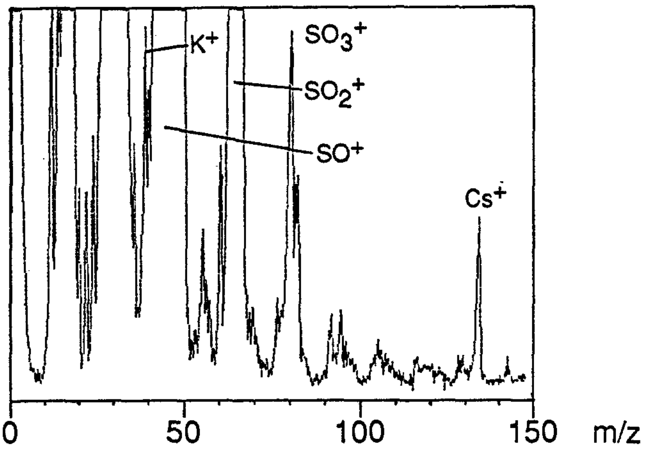

Fig. 2. Mass spectrum using electron impact ionization with the sulfur trioxide catalyst as the sample. Sample temperature was 920 K.

monitored by the electrostatic methods used previously and described for this set-up in ref. [4]. The temperatures used in the present study are 800–1200 K, which is somewhat higher than the process temperatures of 680–900 K, but no detectable emission of alkali took place below 800 K.

A comparison of the emission channels for the two alkali metals Cs and K is possible with the present catalyst. In the desorption, both Cs and K desorption can be observed, as in the mass spectrum in fig. 2. The direct comparison in fig. 3 indicates that the Cs activation barrier towards desorption, 3.89 eV, is considerably larger than that for K, which is 2.66 eV. (It is interesting to note

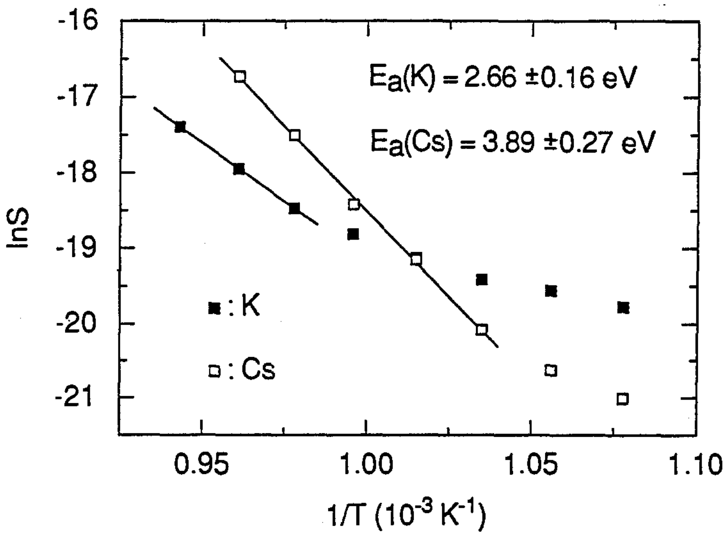

Fig. 3. Temperature variation of the mass spectrometer K and Cs signals from the sulfur trioxide catalyst.

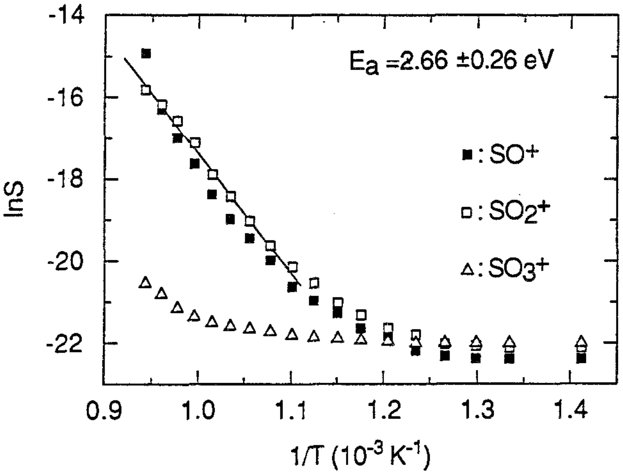

Fig. 4. Temperature variation of the mass spectrometer signals from the catalyst, at *m/z* 48 (SO^+), 64 (SO_2^+) and 80 (SO_3^+).

that the observed barrier for Cs agrees with the ionization potential of Cs, which may indicate that the emission process directly gives excited states close to the ionization limit.) The signals at low temperatures in fig. 3 are probably due to electron impact ionization of excited states emitted from the catalyst surface with an activation barrier less than or equal to the diffusion barrier. (See further below.) This signal also prevents the measurement of the temperature dependence of the K desorption at lower temperatures. The simultaneous desorption of sulfur oxides observed at *m/z* 48 (SO^+) and 64 (SO_2^+) in fig. 4 gives the same barrier as for K, 2.66 eV, which supports the determination of the value of the activation energy for K desorption. This indicates further that the barrier observed for K and sulfur oxide emission corresponds to the initial release from the potassium sulfate (or pyrosulfate) in the bulk. In the range *m/z* 80–83 peaks from SO_3^+ and $H_nSO_3^+$ with $n = 1$–3 are observed. These peaks increase relative to *m/z* 48 and 64 with time after initial heating, and may be due to pyrosulfates formed in the catalyst. No ions corresponding to vanadium or its compounds have been observed.

The emission of excited states has an activation barrier of 0.9 eV, as shown in fig. 5. It is not possible to conclude if the observed signal is due to K^{2*} or Cs^{2*}, but it is likely that both species contribute to the signal. This barrier is similar in size to the K^{2*} emission barrier found for the most active iron oxide catalyst (named type B) in ref. [4]. It is concluded in that case, that the barrier corresponds to a diffusion type barrier, which is the barrier over which the emission of the excited states takes place. This barrier could be similar to the barrier connected with site changes, from one M–O–S– (M = Cs, K) position to another. It is also close to the dissociation energy < 0.8 eV for the process

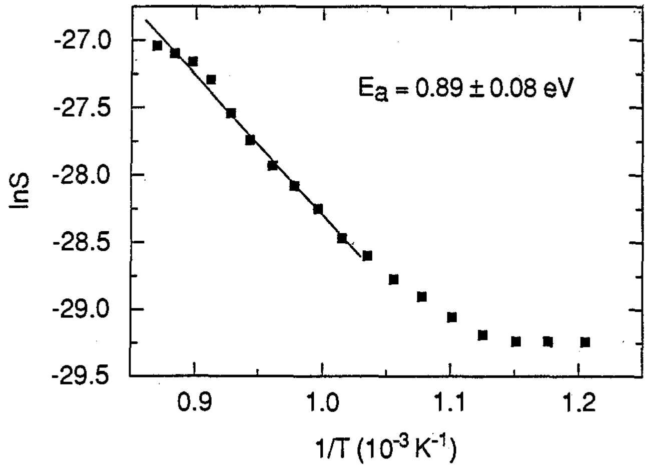

Fig. 5. Temperature variation of the signal due to excited K and Cs atoms from the sulfur trioxide catalyst. The signal was measured at the outer cylindrical electrode in the ion source, see fig. 1.

$K_2SO_4^+ \rightarrow K^+ + KSO_4$ [13]. This type of diffusion barrier will be quite similar for both Cs and K.

Since this barrier is smaller than the barriers measured for loss of alkali atoms in the present case, the two different forms of alkali loss must come from different states in the material. The state of alkali from which the emission of excited states takes place can not be the diffusing state of M, since the density of this must vary much more rapidly with temperature. Instead, some other compound must be formed at the surface of the catalyst, which emits the excited states. The composition of this compound is not known at present. One possibility is of course molten pyrosulphate, but several other crystalline species have been observed in experiments with vanadium oxide-alkali pyrosulfate melts [10].

We now interpret these results, using the same type of energy diagram as in refs. [4,5]. The result in fig. 6 is somewhat tentative, and other possibilities do exist. However, this description is the simplest possible consistent with the available information and agrees with the model used in [4,5]. The difference in the activation energies observed for K and Cs emission is 1.23 eV, which is considerably larger than expected. For example, the bond energy of Cs in CsO is 3.04 ± 0.26 eV [14] and of K in KO is 2.71 ± 0.04 eV [15], giving a difference of 0.33 ± 0.26 eV. We thus conclude that the large experimental difference is not due simply to different binding states in the bulk. Instead, it is probably also due to different rate determining steps in the release and desorption. If equilibrium is attained in the bulk between bound and free K, the observed barrier equals the energy difference between these two states, as indicated in fig. 6. In the case of Cs, the much larger barrier indicates that the transport processes are more rapid than recombination to the initial form of the Cs compound, and thus no

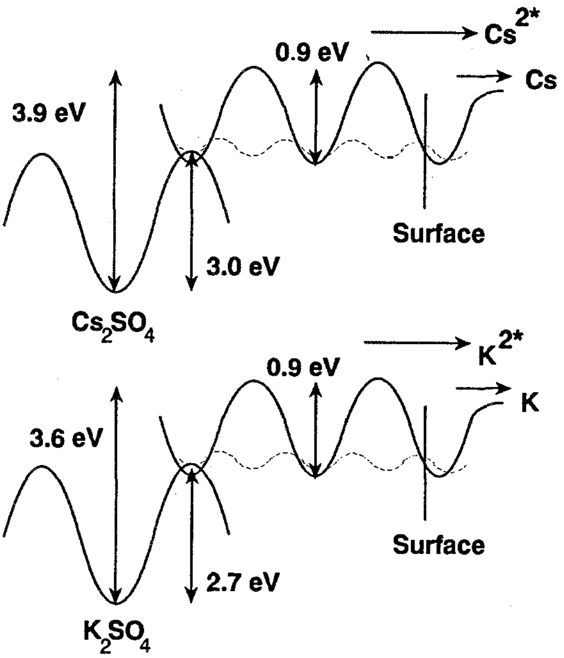

Fig. 6. Tentative energy diagram for emission of Cs and K from the sulfur trioxide catalyst.

equilibrium is found. This gives a large barrier for the observed emission, equal to the sum of the barrier towards initial release and the diffusion barrier, as indicated in fig. 6. It is interesting to note that the activation barrier of 3.89 eV observed for Cs is equal to the ionization potential of Cs. This indicates as in fig. 6 that the loss of Cs from the catalyst does not pass the adsorbed surface state, but instead involves emission of Cs as highly excited states with energies close to the ionization limit. That this process is not an equilibrium process, as also concluded above for the Cs emission, is obvious. After taking into account the different rate determining steps, one finds the difference in the bond energy of Cs and K in the bulk to be 0.34 + 0.32 eV, using the experimental uncertainties. A difference of this size agrees with the difference cited for the alkali-oxygen bonds above.

4. Conclusions

The initial release and loss of alkali is studied at temperatures of 700–1200 K, which is slightly above typical process temperatures. The direct comparison between loss of Cs and K in this catalyst shows that the activation barrier for Cs loss is larger than for K, being 3.89 ± 0.27 eV for Cs and 2.66 ± 0.16 eV for K. The observed emission barrier for the excited states of Cs and/or K is 0.89 ± 0.08

eV, which is attributed to the diffusion barrier for the alkali species in the oxide material. An analysis of the results takes into account, that the details in the loss mechanisms probably differ. However, the energy barrier towards loss from the catalyst is still larger for Cs than for K after this compensation, being 3.0 ± 0.3 eV for Cs. These results indicate a slower loss of Cs than for K from the catalyst, contrary to what could be expected from the vapour pressures of the metals.

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