Stability and excitation of potassium promoter in iron catalysts – the role of $KFeO_2$ and $KAlO_2$ phases

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Well-characterized catalyst model compounds of $KAlO_2$ and $KFeO_2$ are investigated by thermal desorption of potassium from the material. The desorbing fluxes of ions, atoms and highly excited states (field ionizable Rydberg states) were studied with surface and field ionization detectors in a vacuum apparatus. From the Arrhenius plots the activation energies for desorption of K and K^+ were determined. The chemical state of potassium at the surfaces is concluded to be: ionic on $KAlO_2$ (with the K desorption barrier of 1.76 eV) and covalent on $KFeO_2$ (barrier of 2.73 eV). These results agree with the data obtained earlier for industrial catalysts for ammonia and styrene production. They are interpreted in terms of the Schottky cycle, which is completed for $KAlO_2$ and fails for $KFeO_2$. This failure indicates a non-equilibrium desorption process. K Rydberg states are only found to desorb from $KFeO_2$, in agreement with the suggestion that such states in some way are responsible for the catalytic activity.

Keywords: potassium desorption, stability, excitation, iron catalyst, Rydberg atoms

1. Introduction

Alkali metal compounds play an important role in surface chemistry and particularly in heterogeneous catalysis, where they are widely used as promoters [1]. Potassium is the alkali metal most often added to industrial catalysts. Iron catalysts for ammonia synthesis, Fischer–Tropsch hydrocarbon synthesis or styrene production are well-known examples where the promotion with potassium is one of the critical aspects for reaching a good catalytic performance.

The industrial catalysts in question are highly complex and ill-defined systems [2], especially in the oxidized state, for various reasons. These are mainly the variability of the composition caused by the presence of different iron oxide phases in various proportions, nonstoichiometry of the wustite and magnetite fractions, and the presence of promoters and other minor phases [3]. The minor phases, usually simple chemical compounds, are formed during a reaction between promoters or between a promoter and an iron oxide.

Studies aimed at elucidating the role of potassium in the real catalysts are complex and significant results are usually difficult to achieve. There are two reasons, namely the diversity of the effects caused by the alkali metal and the complexity of the catalyst structure.

Hence, a simplification is obviously needed. In the present contribution we only consider two of the minor phases, namely the potassium aluminate $KAlO_2$ and potassium ferrite $KFeO_2$. The significance of these minor compounds in the catalysts is briefly described below.

The literature gives several hints concerning the existence of potassium aluminate in the iron catalyst for ammonia synthesis. As early as in 1940, Brunauer and Emmet [4] postulated the existence of the $KAlO_2$ phase at the catalyst surface. This concept was essential for the explanation of their classical chemisorption studies and was confirmed by the decreased volatility of K_2O in the presence of alumina. An interaction between Al and K can also explain two observed effects: the enhanced extractability of potassium from Al-containing iron catalysts by water [5], and the increase of the lattice constant of Al-containing magnetite caused by the addition of potassium [6,7]. The results of a microprobe analysis shown by Nielsen [8] are summarized by him in a qualitative way: "There appears to be, in most areas, a correlation between potassium, on the one hand, and aluminum and/or silicon, on the other hand". The existence of $KAlO_2$ was confirmed in a very direct way by the experiments of adsorption of an excess of K onto an Al_2O_3/Fe film, followed by K desorption until a steady state was reached. The amount of K was found to vary linearly with a slope ca. 1.1 relative to the amount of Al. This agrees with the stoichiometric formula of potassium aluminate [9]. Let us also point out that the island model of the iron catalyst surface by Boudart [10] and Bowker's model of an active center of the catalyst [11] directly imply potassium–aluminum interaction. Finally, according to the concept of Andrew [12], $KAlO_2$ due to its

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equilibrated decomposition is a source of potassium promoter. Quite conversely, Somorjai claims that $KAlO_2$ is inactive [9].

Potassium ferrite is the key catalytically active phase during the ethylbenzene dehydrogenation, which was reported in the series of papers by Hirano [13,14] and Muhler et al. [15,16]. Desorption of potassium from the iron oxide catalysts for styrene production was thoroughly studied by Holmlid et al. [17–19]. These papers will be discussed below together with the recent data. Little is known about the importance of $KFeO_2$ for the iron ammonia synthesis catalyst. The presence of $K_2Fe_2O_4$ inside a glassy slag-like phase of the unreduced fused catalyst was concluded by Egubayev from microscopy data [20]. According to Spinzi [21], the reaction of hematite with potassium oxide yields $K_2Fe_2O_4$ during the formation of the sintered catalyst.

It should also be mentioned that a high surface concentration of atomic potassium is a typical feature of the real iron catalysts. However, the source of potassium remained unclear until the paper by Caceres and Behbehani [22]. They found potassium ferrite $K_2O{\cdot}4FeO{\cdot}15Fe_2O_3$ uniformly distributed at the centers of magnetite dendrites of a fused iron Fischer–Tropsch catalyst. In the present study, we relate the activity of the catalyst to the formation of K Rydberg states, and thus to the covalently bonded K atoms on the surface.

The origin of alkali promotion is often thought to be related to the electron transfer, which induces an electric field gradient at the surface: alkali metals are sometimes called electronic promoters. This facile electron transfer and the resulting strong electrostatic interaction with reacting molecules may account for their use for bond activation.

In the recent decade ultrahigh vacuum molecular beam techniques have been employed by the group in Göteborg to study the characteristics of desorption of atoms, ions and excited states of alkali from various catalysts and model surfaces.

A new concept of the alkali action at a catalytic surface was proposed by Pettersson et al. [23]. The model includes the reaction between a Rydberg state of an alkali atom A^* and a reactant molecule at the surface. This reaction was proposed to explain the increase in sticking probability of the reacting molecules upon alkali doping. Emission of highly excited potassium species (K^*) from an industrial iron catalyst for ammonia [24] and styrene [17] production were experimentally proved by the field [24] and surface [25] ionization methods. Moreover, the flux of K^* was shown to correlate with the catalyst activity [26]. The emission of Rydberg atoms was high for active catalysts and low for the spent one, even though the total flux of potassium in the latter case increased due to surface segregation [26]. Finally, the transfer of excitation energy from K^* Rydberg species to reacting molecules has been proved experimentally [27].

To bridge the material gap between the industrial catalysts and the model phases, which may exist at their surfaces, we have done the following:

- synthesized the model compounds $KAlO_2$ and $KFeO_2$,
- ascertained their structure,
- determined the relative intensities of potassium desorption modes and their activation energies by the molecular beam technique.

Since the activation energy corresponds to the strength of some surface chemical bond, which breaks during the desorption process, the activation energies for potassium desorption have the characteristic values of the phases it desorbed from. Thus, the correspondence between the energies for industrial catalysts and model compounds can provide a kind of fingerprint that the model compound in question may be a component of the real catalyst. The results obtained will be compared with our data concerning the industrial and model iron catalysts.

2. Experimental

2.1. The samples

The samples were prepared according to the procedure given in [28,29]. Potassium ferrite $KFeO_2$ and potassium aluminate $KAlO_2$ were synthesized by reaction of stoichiometric amounts of K_2CO_3 with α-Fe_2O_3 or $Al_2O_3{\cdot}H_2O$, respectively. All reactants used in the synthesis were of analytical grade. In both cases the mixtures of solids powders were heated in air at the temperatures 800 °C for $KFeO_2$ and 950 °C for $KAlO_2$. After the synthesis X-ray diffraction measurements were performed without exposition of the samples to humid air.

Additionally, the analogous syntheses were carried out *in situ* in the high-temperature camera (HTK Anton Paar) of a PW 3020 Philips powder diffractometer. The temperature of the sample was continuously measured using a Pt/RhPt thermocouple. The mixture (0.1–0.2 g) of substrates was placed on the platinum ribbon and heated up from room temperature to 950 °C in steps of 100 °C. The XRD measurements were performed at the end of each step. For both types of compound the evolution in time was observed. The measurements were performed in Bragg–Brentano geometry with Co K_α radiation for $KFeO_2$ and Cu K_α for $KAlO_2$. The structures were refined using the Rietveld method by DBWS program [30].

The samples proved to be very sensitive to humidity. This is why, during the *in situ* syntheses and measurements, dried gas was always flowing over the sample. For $KAlO_2$ dried air, N_2, O_2 or CO_2 were used, while dried air, N_2 and additionally vacuum (10^{-3} mbar) were employed for $KFeO_2$. The investigated compounds were stabile until the water partial pressure exceeded about 0.01 atm. When the samples were exposed to atmospheric air they became wet and amorphous after 24 h.

The surface purity of the samples was verified by the XPS spectra. The measurements were performed on a VSW ESCA 100 spectrometer with Mg K_α radiation (1253.6 eV, 120 W). The samples were prepared by deposition from hexane suspension. For both samples only the constituent elements were found within the surface layer.

For the thermal desorption experiments all samples were pressed to form wafers of 10 mm in diameter and a typical mass of 100 mg.

2.2. The apparatus

The experiments were carried out in a vacuum apparatus with a background pressure of 10^{-7} mbar. The samples were heated from room temperature to 700 °C at a rate of 2 °C/min. The desorbing fluxes of potassium atoms and ions were measured. The atomic fluxes of K and K^* were determined by means of surface [26] and field [24] ionization detectors, respectively. In the surface ionization detector the rhenium filament was heated to 1200 °C. Due to low ionization potential, under such conditions, only potassium atoms were surface ionized. The field strength between electrodes in the field ionization detector was 550 V/cm. This implies that only Rydberg states excited to a principal quantum number greater than 28 were detected [31]. Potassium ions were measured by the collector in the field ionization detector with both electrodes grounded. K^+ ions formed at the sample surface were accelerated towards the detector since the sample was held at a positive potential of 100 V. In all measurements, the positive current was measured directly with a digital electrometer Keithley 6512.

3. Results and discussion

The X-ray diffractograms obtained for $KFeO_2$ and $KAlO_2$ (figure 1) show that the samples were monophasic. The Rietveld analysis of the diffraction pattern revealed that the $KAlO_2$ crystallizes in the same space group (Pbca) as described in the literature for $KFeO_2$ [28]. The shift in the plane separation towards the lower d values of corresponding peaks in $KAlO_2$ is due to a smaller size of Al^{3+} in comparison with Fe^{3+} in $KFeO_2$.

Arrhenius plots for K^+ and K desorption from $KAlO_2$ and $KFeO_2$ are presented in figures 2 and 3. For both samples the activation energies for desorption of potassium ions and atoms can be reliably determined from the linear parts of the plots. The values of activation energy obtained are listed in table 1. In the case of $KAlO_2$ one value of activation energy for K was determined, while for K^+ two values were found. The change in slope for the ionic flux and the nonlinear character for the atomic flux can be attributed to the phase transition revealed by XRD at about 500 °C [32].

All the observed activation energies represent typical values of bond breaking (for instance the dissociation energy for K_2O to K and KO is 3.0 eV). For $KFeO_2$ both activation energies are higher than for $KAlO_2$. This is consistent with the signal intensities (please note the difference in the scale of $\ln S$ in figures 2 and 3). Hence, the activation energies show that the potassium is more strongly bonded in the ferrite. For both samples, the barriers for ion desorption are larger than for neutrals; however, the relative intensities of the ionic and neutral fluxes are reversed. For $KAlO_2$, the ionic flux dominates, while for $KFeO_2$ the atomic one (including excited states) does. This difference in preexponential factors indicates that the de-

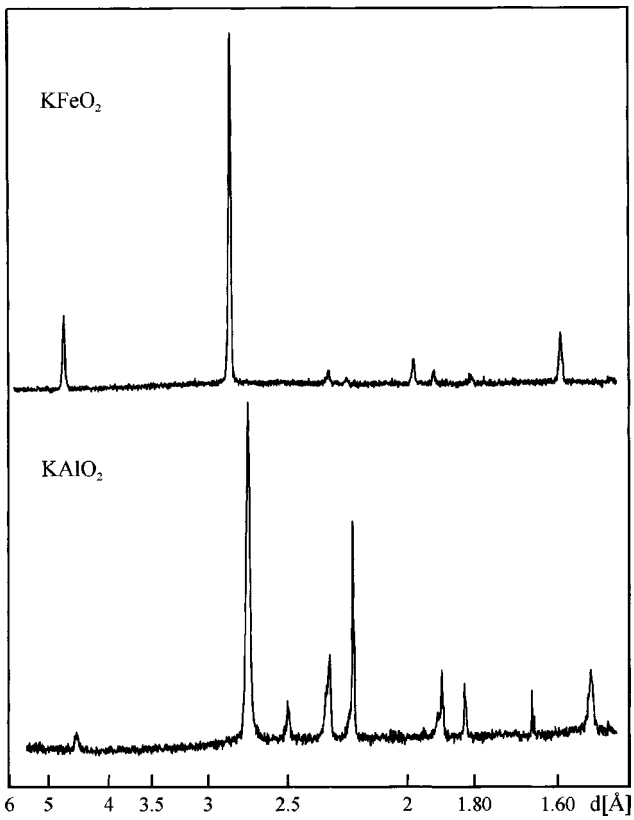

Figure 1. The X-ray diffraction patterns of $KAlO_2$ and $KFeO_2$ obtained at room temperature.

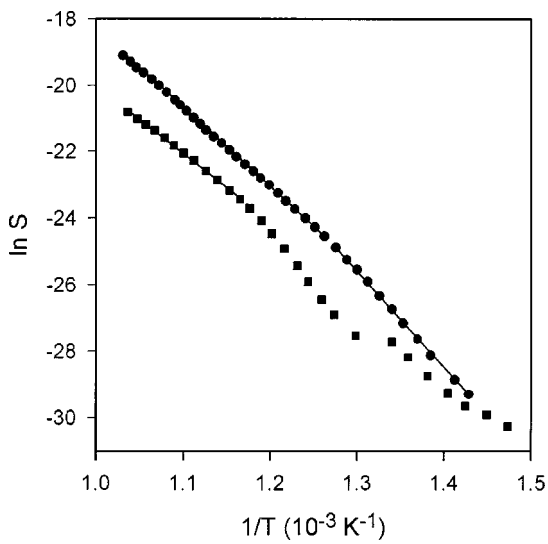

Figure 2. Arrhenius plots for potassium atoms (■) and ions (●) desorbing from the surface of $KAlO_2$.

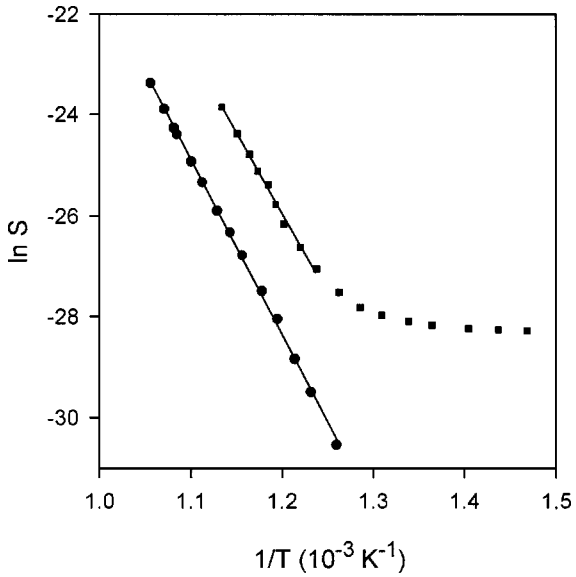

Figure 3. Arrhenius plots for potassium atoms (■) and ions (•) desorbing from the surface of $KFeO_2$.

Table 1
The activation energies E_a (eV) for K and K^+ desorption from $KAlO_2$ and $KFeO_2$.

Phase	E_a(K) (eV)	$E_a(K^+)$ (eV)
$KAlO_2$	1.76 ± 0.01	2.02 ± 0.01, 2.50 ± 0.01
$KFeO_2$	2.84 ± 0.06	2.95 ± 0.01

sorption mechanisms for the ionic and atomic channels are different for both compounds.

Since the energies of potassium desorption from different industrial catalysts [17,19,26,31,36] agree well, it seems that the energetics of potassium desorption is rather independent of the particular catalyst, and it appears to be a general property of the surroundings of the promoter atoms at the surface. Oxygen is commonly considered as an alkali promoter anchor at the catalyst surface [33]. The general model of K desorption energetics from graphite [34] and iron catalyst [35] surface is here assumed to be applicable. The experimentally found desorption barriers of 2.84 eV for K from $KFeO_2$ and 2.95 eV for K^+ are on this basis assigned to desorption from the lowest covalent state, which is at 3.0 eV below the K(4s) level as given by the model. The model data for this process imply the value $2.05 + 0.95 = 3.0$ (eV) [35].

In the case of $KAlO_2$, the barrier for K desorption of 1.7 eV is definitely from the ionic state on the surface [35]. On the other hand, the values of 2.0 and 2.5 eV for K^+ desorption are somewhat unexpected. One might expect 2.1 and 2.7 eV for the ion desorption from the two covalent states, but these states may be slightly shifted upwards in the case of Al instead of Fe. This would presumably be due to the weaker bonding of K to Al relative to K–Fe since there is no partially filled d shell in Al. Alternatively, the value 2.0 eV corresponds to K^+ desorption from

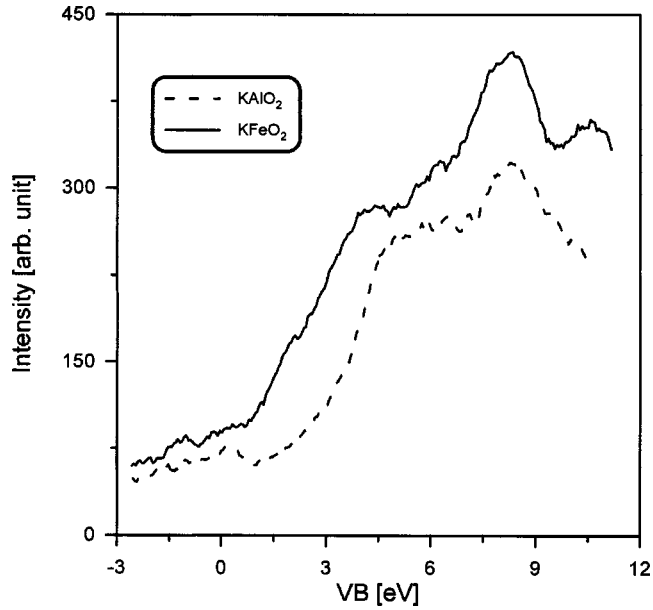

Figure 4. Variation of the signal of excited potassium species for $KAlO_2$ and $KFeO_2$ with sample voltage. The sample temperature was 650 °C.

the ionic state, while 2.5 eV is from the lowest covalent state.

Some of these values were previously observed for industrial catalysts. The energy of 1.7 eV was observed for the iron catalysts for ammonia synthesis: deactivated by water treatment or stored in moist atmosphere [36] and used in the industrial reactor for five years [26]. This value was also found in the case of the styrene catalyst [17,18].

The emission of highly excited atoms from both samples was examined by means of the field ionization detector. The interesting results are shown in figure 4. A large emission of excited states is observed for $KFeO_2$, while for $KAlO_2$ the signal is low, only about 10^{-13} A, which represents the background in our experiments. A variation of the field ionization signal with positive sample voltage is observed. This kind of behavior was previously noted for other oxidic surfaces [37]. Since the K Rydberg atoms are positive core ions with electrons at large distances, the applied electrostatic field will influence the deexcitation and desorption processes of such states. The ionic desorption is very sensitive to the sample voltage especially when excited atoms are surface ionized according to the mechanism described in [35].

The emission of Rydberg atoms is in agreement with the desorption energies observed for $KFeO_2$. The emission from the lowest covalent state goes to the K(4p) state when the electric field is weak or zero, and crosses over to Rydberg states, as is shown in [34], where the model for K desorption from graphite is proposed. In the case of $KAlO_2$, the barrier for K desorption of 1.7 eV is for the ionic state and thus Rydberg states are not formed here.

Assuming that the Schottky cycle [38] is applicable, the work function of the model compounds was calculated from the formula $\Phi = E_a - E_i + V$, where E_a and E_i are activation barriers for atoms and ions, respectively, and V is

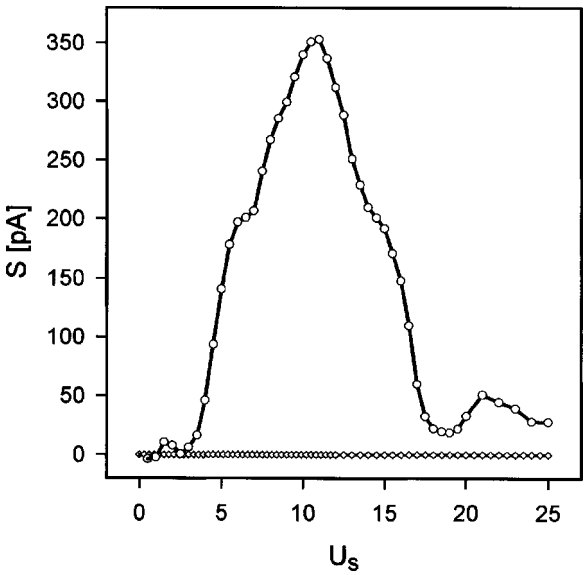

Figure 5. The XPS spectra in the valence band region for $KAlO_2$ and $KFeO_2$.

the first ionization potential for potassium (4.3 eV). The obtained values are 3.5 or 4.0 eV for the higher temperature range, for $KAlO_2$ and 4.2 eV for $KFeO_2$. The work function calculations were verified by XPS studies in the VB region. The spectrum is shown in figure 5. Since both samples are non-conducting, the Fermi edge is not sharp enough to determine the work function value quantitatively. Nevertheless, one can estimate that for $KAlO_2$ the "edge" correlates well with the data obtained from the Schottky cycle, while for $KFeO_2$ the discrepancy is large. In the latter case the work function seems to be much lower, at least by 1 eV, than the value obtained from the cycle. This can be attributed to the non-equilibrium desorption and invalidity of the Saha–Langmuir equation for the surface ionization phenomenon. The existence of Rydberg atoms at the surface leads to a dramatic decrease of the work function value, due to their very low ionization potential. Since the highly excited atoms have large dimensions and give strong interatomic forces they even form clusters in the adsorbate boundary layer [25,39]. For the condensed phase of excited states, so-called Rydberg matter, a very small value of $\Phi = 1.0$ eV has been measured [40].

The ferrite $KFeO_2$, which is considered to be the catalytically active phase [13–16], stabilizes potassium by stronger bonding, which is revealed by the larger desorption energies. This phase is also an efficient source for potassium Rydberg atoms, which are proposed to be closely related to the promoter function of alkali.

In the case of $KAlO_2$, the barriers for K and K^+ desorption are distinctly smaller and the preexponential factors higher, thus, this phase, if formed at the catalyst surface, may be responsible for enhanced potassium loss. The value 1.7 eV indicates that the ionic state of potassium is primarily occupied, which means that Rydberg atoms cannot be formed at its surface. $KAlO_2$ is catalytically inactive.

The correlation between the activity and excited state formation at the catalyst surface already suggested, using industrial catalysts [24], is now considerably strengthened by the investigations of the well-defined model compounds. This implies that it might be possible to identify the active phase by excited state detection also for many other catalysts.

4. Conclusions

The data obtained by thermal desorption of potassium atoms, ions and excited states from model compounds of $KAlO_2$ and $KFeO_2$ are presented. The method proves to be useful in the characterization of potassium surface states by the activation energies of desorption. Comparing the desorption energies for $KAlO_2$ and $KFeO_2$, it may be concluded that potassium is stronger bonded in the form of ferrite. Also the kind of bonding is distinctly different: for $KAlO_2$ desorption of K from an ionic state on the surface is involved, while for $KFeO_2$ the desorption takes place from a covalent state. The activation energies for potassium atom desorption of 1.76 eV for $KAlO_2$ and 2.84 eV for $KFeO_2$ agree well with the literature data for industrial ammonia and styrene catalysts. This indicates that these phases are formed at the catalyst surfaces. For $KFeO_2$ non-equilibrium desorption of potassium and the electronic excitation of the K promoter atoms to Rydberg states are observed.

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