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High pressure desorption of K^+ from iron ammonia catalyst – migration of the promoter towards Fe active planes

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The thermal desorption of potassium ions from industrial iron catalysts was studied *in situ* in the wide pressure range of 10^{-8}–10 bar of Ar, N_2 and synthesis gas mixture of N_2:$3H_2$. While high activation energy of 284 ± 1 kJ/mol, for K^+ was determined for the catalyst precursor, in the reaction conditions it drops down to 231 ± 5 kJ/mol, corresponding well to that found for iron single crystals in UHV studies. The results are rationalized in terms of potassium migration from oxide storage phases towards the iron facets developed during the catalyst activation.

KEY WORDS: Potassium desorption; stability; iron catalyst; ammonia synthesis; ion desorption; high pressure kinetics; pressure gap.

1. Introduction

1.1. Potassium promotion in ammonia synthesis

Alkali metal compounds are widely used as electronic promoters in heterogeneous catalysis [1]. A classical example is the fused iron catalyst for ammonia synthesis, where the promotion with potassium is one of the critical aspects for a satisfactory catalytic performance [2]. The industrial synthesis of ammonia over iron catalyst is one of the oldest and most studied catalytic reaction. To explore the chemical origin of the potassium promoting effect a large number of combined catalysis/surface science studies [3] have been carried out on industrial and model catalyst samples. However, in most cases the nature, location, charge transfer and the mode of action of potassium promoter is still not definitely resolved [4]. Usually the beneficial effect has been assigned to the decrease of work function, stabilization of N_2 and destabilization of target NH_3 [3].

The effect of K promotion on the iron catalyst activity depends on the pressure [5]. Thus, one of the principal limitations in a mechanistic understanding of the potassium promotion is undoubtedly the lack of experimental data for the surface state of this promoter under the real high-pressure conditions of NH_3 synthesis. In this paper, potassium surface characterization by thermal desorption was for the first time carried out both in high vacuum and under high pressure of reactants.

1.2. Surface ionization and potassium thermal desorption

All species have a certain probability of becoming ionized during a thermal desorption process, although the probability in most cases is negligible. Surface ionization (SI) technique makes use of the fact that a substantial fraction of an alkali metal flux emitted from a hot surface is often in ionic form. The emission of positive ions is, however, favored when the work function of the surface is comparable to or larger than the ionization potential (IP) of the desorbing atom or molecule. The thermal desorption of alkali ions from hot metal surfaces was first observed by Kingdon and Langmuir [6]. The SI process is well characterized in the literature and quantitatively described by the Saha–Langmuir equation, [7,8,9].

Most species have IPs that are higher than the typical work functions of 400–600 kJ/mol observed for metal and metal oxide surfaces, and neutral desorption is strongly favored. The alkali metals, however, constitute an exception with low IP's for sodium ($IP_{Na} = 496$ kJ/mol), potassium ($IP_K = 419$ kJ/mol) and cesium ($IP_{Cs} = 373$ kJ/mol). For alkali metals thermally desorbing from a surface, the ionic emission may therefore exceed the neutral atom emission by several orders of magnitude. Surface coverage of alkali metal can act to decrease the work function of the metal surface, and thereby influence the ionization efficiency. The fused iron catalysts employed in the present study contain potassium.

The application of thermal desorption of potassium to characterization of the promoter surface state has proved its usefulness in the investigations on various model and commercial catalysts. Since the activation energies for desorption depend on the chemical

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environment of desorbing species their values can serve as indicators of catalyst surface changes. Indeed in the case of iron ammonia catalyst the modification of the catalyst surface during activation, passivation, overheating [10], sulphur poisoning [11], water treatment [12] and industrial usage [13] of the catalyst reveals large changes in potassium desorption parameters. All the experiments, however, were carried out in vacuum conditions. In the present study, we employ the technique of K^+ desorption for *in situ* studies of industrial iron ammonia catalyst at high pressure.

1.3. *From high vacuum to high pressure – bridging the pressure gap*

Hagström *et al.* [14] used SI technique to study the kinetics of potassium and cesium ion desorption from polycrystalline platinum surfaces in ambient air. Desorption rate constants in the range 10^{-2}–10^{3} s^{-1} were measured at surface temperatures of 820–1290 K. The results were in excellent agreement with literature data obtained under ultra high vacuum conditions, which confirmed that SI methods can be successfully applied under pressurized conditions. In a subsequent study, alkali interactions with polycrystalline rhodium, an important component in several catalysts were also studied at atmospheric pressure [15]. Phase transitions on the surfaces were observed as changes in the desorption kinetics for Na, K, and Cs ions, and a higher alkali stability was in general found on oxidized surfaces compared to metallic ones.

In the present study, SI technique is used to investigate the desorption of potassium ions from fused iron catalyst used for industrial synthesis of ammonia. The studies are performed in the pressure range from 10^{-8} up to 10 bar on oxidized and reduced (activated) iron catalyst samples in Ar, N_2 and $3H_2$:N_2 synthesis gas mixtures. The binding energy of potassium on the different catalyst surfaces is determined, and the results are compared to results from earlier studies on single crystal surfaces in ultra high vacuum. To our knowledge, this is the first application of the SI technique to investigation of a catalyst surface at high pressure, and the study demonstrate that the technique is complementary to other methods developed to determine the state of an active catalyst surface under realistic conditions.

2. Experimental method

A schematic view of the combined high vacuum–high pressure apparatus used in the present experiments is shown in figure 1. The stainless steel chamber (200 × 200 mm) with six-flanges (3 × CF35, 3 × CF63) could be pumped down to 1×10^{-8} bar and pressurized up to 10 bar. The main parts are a sample holder (30 × 5 mm) and a stainless steel ion collector (30 × 10 mm) situated at a distance of 3 mm from the sample surface. The distance was adjusted to prevent the collector from extensive heating and assure the transport of ions by diffusion to the collector and thus the collection efficiency. The commercial iron catalyst (AS-4, Norsk Hydro AS) was triply promoted with 2.5% CaO, 3.0% Al_2O_3 and 0.5% K_2O. The unreduced fused catalyst was in the form of grains of sieve fraction 6–10 mm. More detailed information concerning the catalyst samples can be found elsewhere [16,17]. The samples were cut to expose a flat surface of 4 × 9 mm and mounted in a platinum foil (thickness 0.1 mm) to enable resistive heating up to 1000 K by passing an AC current of up to 30 A through the foil. The samples were heated from room temperature to 650 °C in the

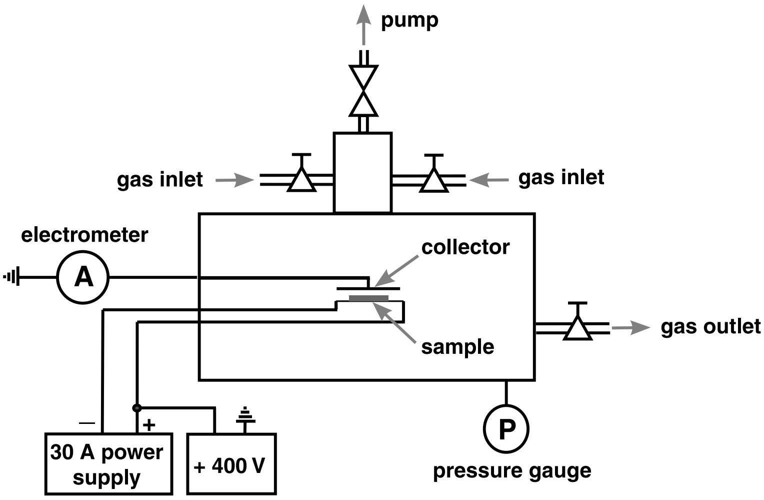

Figure 1. A schematic view of the combined high vacuum–high pressure apparatus used in the experiments. The catalyst sample holder and the ion collector were placed 3 mm from each other in the center of the chamber. The gases used in the experiments were introduced through two inlet valves.

intermittent mode with the heating rate of 5 K /min. After each step the heating was stopped until the signal was stabilized for the new temperature. Since iron catalysts are efficient electron emitters a positive potential of 80–400 V was applied to the samples during the experiments to block the emission of electrons and accelerate desorbing potassium ions towards the nearby collector. In all the measurements the positive ionic current (10^{-14}–10^{-8} A) was measured directly with an electrometer. The measurements were performed in up to 10 bar of argon, nitrogen, or a $H_2 : 3N_2$ mixture. The gases supplied by AGA Gas AB were of 99.999% purity and contained less than 2 ppm of oxygen. Additional experiments were also carried out in high vacuum at 1×10^{-8} bar for comparison with the high pressure data. To simulate industrial conditions and to obtain an active state of the catalyst, it was reduced in a steady flow of the H_2:$3N_2$ gas mixture at a pressure close to 1 bar, while the temperature was increased from 573 to 823 K with a heating rate of 10 K/h.

3. Results and discussion

3.1. K^+ desorption in vacuum and inert gases

We first performed a separate study in order to prove that the only ions leaving the catalyst were indeed potassium ions. A quadrupole mass spectrometer was adapted to the experimental system, and the ions emitted from the sample were accelerated into the mass spectrometer. The sample was biased with a positive potential of +80 V, which was a convenient voltage to transport the ions into the ion optic of the spectrometer. The electron impact ionization of the mass spectrometer was turned off during these experiments. Figure 2 shows a typical mass spectrum obtained at a catalyst temperature of 870 K. The only ion mass observed was $m/z = 39$, which shows that K^+ are the only detectable ions emitted from the catalyst.

Several measurements have been performed with the oxidized and the reduced catalyst surfaces in different gas environments. The temperature dependence of the ion current to the collector is shown in figure 3. Straight lines are observed in the Arrhenius-like plots (with the correlation coefficient higher than 0.999) of the measured ion currents, and the activation energies for potassium ions emission are reliably determined (all values given below are with the error of 95% confidence limit) for the temperature range 650–920 K. For the unreduced sample an activation energy barrier of 284 ± 1 kJ/mol is obtained under vacuum conditions, and an activation energy of 288 ± 2 KJ/mol in nitrogen gas at 10 bar. A similar activation energy barrier of 286 ± 2 kJ/mol was also found in 10 bar of argon. However, as seen in figure 3 the signal level is strongly influenced by the total pressure, P. The effect of P on the measured K^+ ion current from the oxidized iron ammonia catalyst is shown in figure 4 for a nitrogen atmosphere. Since the mean free path of an ion in gas is reversely proportional to pressure, it can be expected

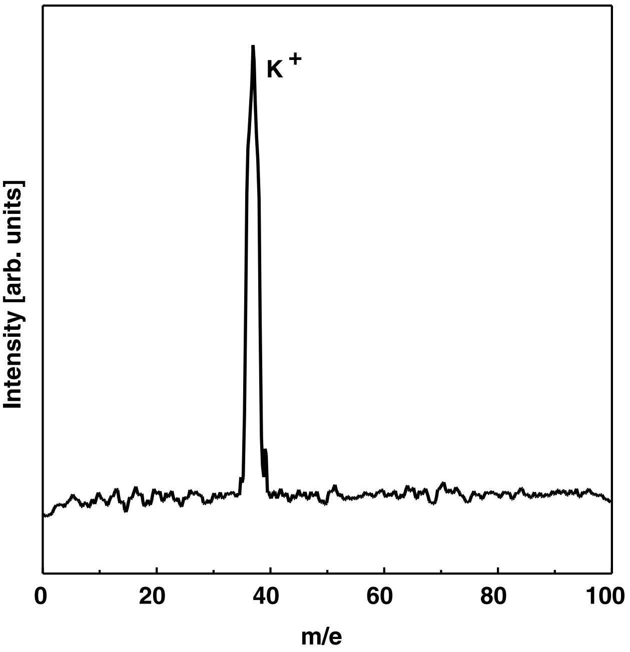

Figure 2. Mass spectrum for positive ions desorbing from an iron catalyst surface at 870 K. The electron impact ionization of the quadrupole mass spectrometer was turned off during the experiments. The chamber pressure was 1×10^{-8} mbar, and a potential of +80 V was applied to the sample.

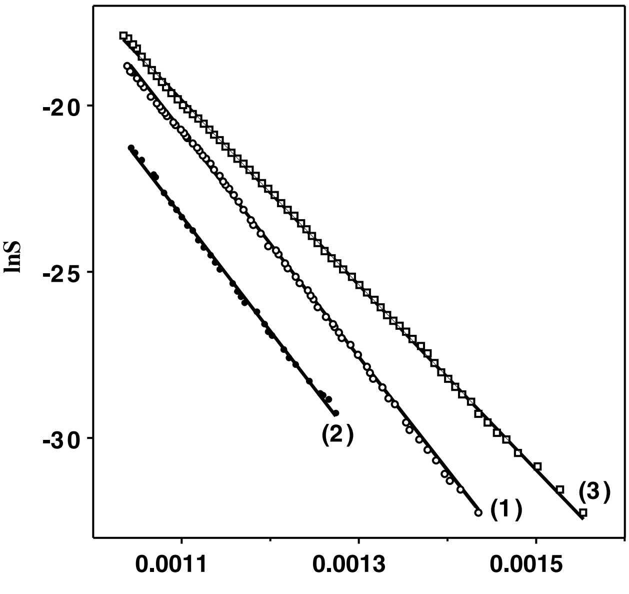

Figure 3. Temperature dependence of the potassium ion emission signal (S) from different iron catalyst surfaces. Unreduced catalyst in vacuum (1×10^{-8} bar) (1), unreduced catalyst in 10 bar of nitrogen (2), and activated (reduced) catalyst in 10 bar of a $H_2 : N_2$ (3 : 1) mixture (3).

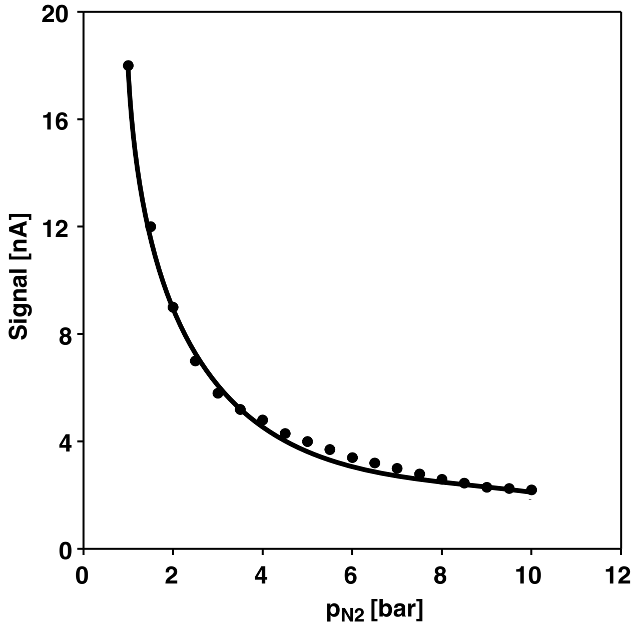

Figure. 4. Potassium ion current to the collector placed in front of the iron catalyst surface as a function of nitrogen pressure. The catalyst temperature was 773 K.

that the probability for K^+ to reach the collector (and thus the measured collector current) decreases as ~1/*P*.

3.2. K^+ desorption in synthesis gas mixture

The reduction of the catalyst and the use of the $N_2 : 3H_2$ gas mixture in the chamber changed substantially the desorption characteristics. The lower activation energy barrier of 231 ± 1 kJ/mol is obtained in 10 bar of the $N_2 : 3H_2$ mixture, as illustrated in figure 3. The ion current is also about a factor of 40 higher compared to that observed for the unreduced samples at the same pressure of nitrogen. Potassium thus has a lower stability on the reduced surface compared to the oxidized one. Co-adsorption of oxygen on iron surface increases the maximum of potassium desorption temperature from 550 to 750 K [18]. This is comparable to the effects of surface oxides seen for rhodium surfaces [15].

3.3. Elucidation of the results

The values of activation energies for K^+ desorption obtained for the vacuum and inert gas atmosphere of Ar and N_2 are the same within experimental error and has been observed in previous vacuum studies for passivated iron catalyst surfaces[19], as well as the $KFeO_2$ ferrite [20]. The results indicate that the activation energy for K^+ desorption from the oxidized catalyst is independent of the inert gas atmosphere outside the catalyst surface, and only depends on the chemical state of potassium on the surface. Earlier studies[3,21,22] have shown that potassium is directly bonded to oxygen surface species remaining after reduction in the form of ternary oxides of other promoters, mainly Al, Si and Ca. This is consistent with typical temperatures for NH_3 synthesis being above the desorption temperature for K from iron surface.

The active structure of the catalyst is the metallic iron surface that is formed during the reduction of the catalyst. By using temperature programmed desorption, Lee *et al.* [23] determined potassium desorption activation energy barriers of 238 ± 8, 225 ± 8, and 217 ± 8 kJ/mol for Fe(1 1 0), Fe(1 0 0), and Fe(1 1 1), respectively. These values correspond to the activation energy observed in the present study for industrial iron catalyst under reducing condition (10 bar of $3H_2 : N_2$).

An anhydrous KOH, the most stable form of potassium on active catalyst surface [22,24] or K_2O were not identified in our experiments but it does not mean that they may not be present at the catalyst surface. The dissociation energy of KOH to K and OH is 362 kJ/mol, whereas for K_2O to K and KO is 294 kJ/mol. Although on the surface these values can be lowered the obtained barrier for potassium loss from the surface of 231 kJ/mol suggests that these compounds are probably not directly involved in the potassium desorption process. Since potassium, especially in the presence of hydrogen, can easily migrate on the catalyst surface, in the thermal desorption experiments the lowest barrier is determined.

Other possible interpretation of the drop in the desorption barrier caused by the reduction process consists in the interaction of potassium with alumina in the presence of water vapor produced in the reduction of iron oxides. The segregation of Al to the surface during the activation process has been well documented by the number of techniques including XPS, AES, SEM, XRD and chemisorption measurements [3]. The interaction of potassium and alumina leading to formation of surface potassium aluminate has been also postulated [18,25,26]. For potassium ions thermal desorption from monophasic $KAlO_2$ the activation barrier of 242 kJ/mol was determined [20]. This value was also found for the ammonia catalysts deactivated by water or by use in the industrial installation for several years [12]. Undoubtedly, the GHSV of the synthesis gas in our experiments was much smaller than in industrial installation. The formation of $KAlO_2$ cannot be excluded; however, the time of the experiments seems to be too short.

Combining the literature information with the present results, we propose that potassium to a moderate extent is released from the stable storage compounds and diffuse on the iron crystallites developed during the reduction. In a subsequent step, desorption can take place from the iron crystallites. Since the iron catalyst surface is very sensitive to oxidation [27], this only occurs under strongly reducing conditions prevailing in ammonia synthesis. In vacuum experiments, we have observed a change of the potassium ion desorption behavior already at a oxygen partial pressure of 5×10^{-7} mbar.

4. Conclusions

By monitoring the potassium ion desorption, we have investigated the states of the potassium promoter at surfaces of the iron catalyst for ammonia synthesis under vacuum and elevated pressure conditions. Catalyst samples in oxidized and reduced forms were studied. The measured activation energy barriers for potassium desorption from the oxidized catalyst were found to be independent of the inert gas environments used. In the case of the reduced catalyst, an activation energy barrier for the desorption of potassium of 231 ± 1 kJ/mol was obtained at 10 bar of a $3H_2 : N_2$ mixture. This barrier is concluded to correspond to the desorption of potassium from different iron crystal faces that are developed during the reduction process. Under real process conditions potassium is stored as ternary oxides at the surface. However, a small fraction is released and moves relatively freely on the iron crystallites.

The importance of the present study arises from the discussion concerning the relevance of surface science investigations of single crystals under vacuum conditions for real industrial catalyst systems, the so-called "material and pressure gap". We observed the same activation energy for the potassium desorption from an industrial catalyst at 10 bar of $3H_2 : N_2$ as previously reported by Lee *et al.* [23] for K desorption from well-defined iron single crystal surfaces. The stability of K on single crystals of Fe in UHV is quantitatively obtained also with industrial catalysts under close to operating conditions. This result promotes the view that the pressure gap between high vacuum and high pressure investigation can be successfully balanced. The alkali desorption experiments can serve in characterization of the states of the promoters on complex surfaces under high temperature and pressure of reactants, thus close to industrial conditions.

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