

# MOBILITY OF POTASSIUM IN THE IRON CATALYST

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**Abstract.** A mobility of potassium in the iron catalyst for ammonia synthesis has been studied under various pressure conditions: ultrahigh vacuum, atmospheric pressure and 10 MPa. Under UHV the surface diffusion of potassium from iron catalyst on the iron foil has been studied with AES method. Diffusion of potassium atoms has been observed in the temperature range between 500 °C and 600 °C. A mathematical model for the surface diffusion was proposed and compared with the experimental results. At atmospheric pressure the diffusion of potassium from one layer of catalyst bed to another has not been observed at the temperature of 550 °C. Under the same conditions the intergranular diffusion of potassium has been observed. The intergranular diffusion of potassium has also been observed during the activation of iron catalyst at 10 MPa and 400 – 650 °C.

## 1. INTRODUCTION

Many catalysts are promoted by the addition of a small amount of alkali metal compounds which are known to increase the activity or selectivity of heterogeneous reactions. The most important question for all catalysts promoted with alkali is the exact role of the promoter including formation of intermediate compounds with reactant molecules [1-5].

Potassium is used as a promoter for the iron catalyst of the Fisher-Tropsch [6-8] reaction and ammonia synthesis [9-10]. Since the radius of potassium atoms is relatively big, they do not dissolve in the crystal lattice of iron and remain on the surface of the catalyst. Therefore the surface diffusion of potassium is a very important process. It is especially crucial for catalyst activation. The diffusion of potassium in literature is described scarcely. The main part of experimental data concerning potassium and its influence on the iron surface has been gathered from surface science

studies. Up to now, few results concerning diffusion of potassium on the iron have been presented. The surface diffusion of potassium on the free iron surface or on the iron surface covered with aluminum oxide has been studied using the AES method, by Connell and Dumesic [11]. They showed that potassium oxide can diffuse on the surface of free iron or on the surface of iron covered with aluminum oxide. However diffusion kinetics has not been considered. Several other papers [12-17] described the potassium diffusion studied by various techniques on different substrates.

In this paper the studies of the mobility of potassium on the polycrystalline iron surface under UHV conditions as well as the intergranular mobility of potassium under atmospheric and elevated pressure (10 MPa) is presented.

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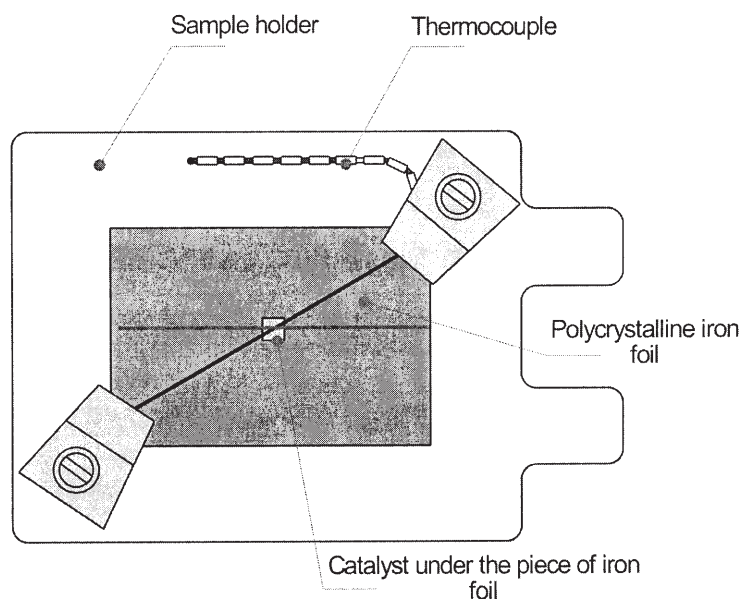


Fig. 1. Polycrystalline iron foil with the iron catalyst as a source of potassium in the middle of the sample.

## 2. EXPERIMENTAL

### 2.1. Diffusion of potassium from iron catalyst onto polycrystalline iron sample studied under UHV

The diffusion of potassium from iron catalyst to the iron surface of a foil under UHV conditions was studied using AES method. The experiments were performed in a standard ultra-high vacuum system (a base pressure in a range of  $10^{-8}$  Pa) SIA 100 system of CAMECA (France) with facilities for AES and XPS. A focused electron beam with a primary energy of 2.5 keV and current density  $10 \mu\text{A}/\text{cm}^2$  was applied and the spectra were acquired by means of a CMA analyser.

A grain of a prerduced industrial iron catalyst for ammonia synthesis was used as a source of potassium in this experiment. A chemical composition of catalyst precursor was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The catalyst contained 0.9 wt.% of  $\text{K}_2\text{O}$ , 2.9 wt.% of  $\text{CaO}$  and 3.0 wt.% of  $\text{Al}_2\text{O}_3$  in addition to iron. The iron foil used in this experiment was first cleaned under UHV. To remove sulphur from the polycrystalline iron sample, the sample was heated at 820K and concurrently sputtered with  $\text{Ar}^+$  ions at  $E_f=3$  keV. After this procedure the signal of sulfur was negligible and the carbon signal was below the detection level. Then, in the air, at room temperature a grain of iron

catalyst was placed in the middle of a polycrystalline iron sample (see Fig. 1). The grain of iron catalyst was screened by a piece of iron foil to avoid its damage by argon ions during sputtering. Such prepared sample was put back into UHV chamber where the iron surface was cleaned again by sputtering with  $\text{Ar}^+$  ions.

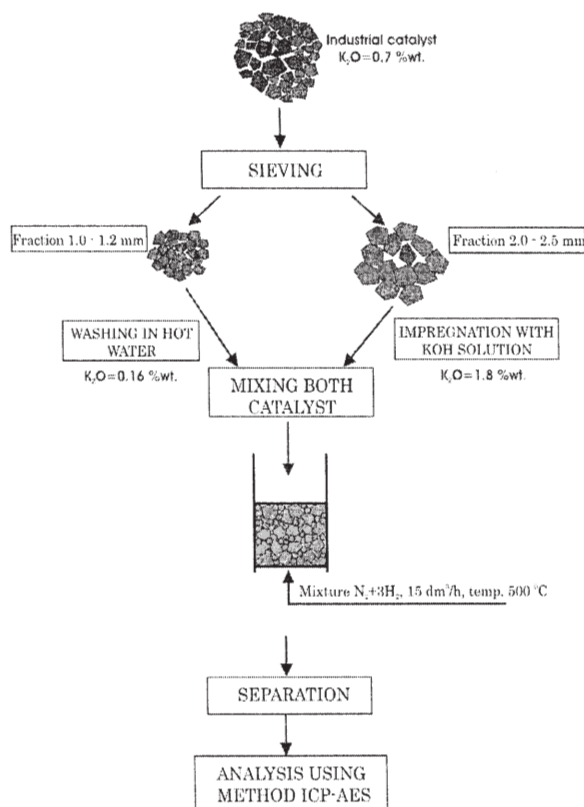
The sample was annealed at 500 °C, 550 °C, and 600 °C. During each heating cycle the composition of the spot located 2mm in respect to the center of the grain was studied by AES. After completion of each heating cycle the composition of the surface in several points on the both sides of the iron catalyst was also examined. Before the start of the next annealing the surface of the sample was cleaned by sputtering.

### 2.2. Diffusion of potassium in iron catalyst at atmospheric pressure

Under atmospheric pressure the experiments were carried out in an integral glass flow reactor under the flow of hydrogen – nitrogen mixture. Two experiments have been carried out.

**2.2.1.** The aim of the first experiment was to investigate the potassium diffusion with a gas stream. Seven layers of the iron catalyst were placed in a glass reactor. Each layer was separated by a fine grid made of steel.

The fraction 1.0–1.2 mm of catalyst grains was taken. The first layer of catalyst from gas inlet



**Fig. 2.** The idea of experiment under atmospheric pressure.

contained some excess of potassium (2.0 wt.% of  $K_2O$ , 2.9 wt.% of  $CaO$  and 3.0 wt.% of  $Al_2O_3$ ). The catalyst in the next six layers contained 0.16 wt.% of  $K_2O$ . The reactor was heated at 500 °C under a flow of  $H_2:N_2$  (3:1) gas mixture (15 dm<sup>3</sup>/h) during 160 hours. After the process the reactor was cooled and the catalyst was passivated using nitrogen with traces of oxygen. The concentration of potassium in each of catalyst's layers was determined using ICP – AES method.

**2.2.2.** The aim of the second experiment was to investigate the possibility of the intergranular diffusion of potassium between the catalyst grains of different potassium concentration. The scheme of a sample preparation is presented in Fig. 2.

The industrial prerduced catalyst was crushed and sieved to obtain two grain fractions: (1.0–1.2 mm) and (2.0–2.5 mm). The fraction (1.0–1.2 mm) was washed in hot water to remove potassium. In this way the catalyst with low concentration of potassium (0.16 wt.% of  $K_2O$ ) was obtained. The second fraction (2.0–2.5 mm) was impregnated with KOH solution to obtain

the concentration of 1.81 wt.% of  $K_2O$ . Both catalysts were mixed together in proportion 1:1 and placed in a steel reactor. The reactor was heated at 500 °C under a flow of  $H_2:N_2$  (3:1) gas mixture (15 dm<sup>3</sup>/h) during 160 hours. After the process the reactor was cooled and the catalyst was passivated, separated and the concentration of  $K_2O$  in each fraction of iron catalyst was determined by ICP-AES.

### 2.3. Intergranular diffusion of potassium under the conditions of ammonia synthesis

The intergranular diffusion of potassium in the prerduced (0.9 wt.% of  $K_2O$ , 2.9 wt.% of  $CaO$  and 3.0 wt.% of  $Al_2O_3$ ) catalyst has been studied during the ammonia synthesis under the pressure of 10 MPa at the temperature from 400 to 500 °C. To obtain a catalyst's sample without potassium, the iron catalyst was washed in hot water. After the reduction of the catalyst with  $H_2:N_2$  (3:1) gas mixture, the potassium compounds were washed out again. In this way the catalyst with low concentration of potassium (0.05 wt.% of  $K_2O$ ) was prepared (sample 1, Table 1). A part of this catalyst was impregnated with KOH solution to obtain 0.74 wt.% of  $K_2O$  in a grain (sample 2). The samples 3 and 4 were obtained by grounding and mixing sample 1 and sample 2 in proportion 1:1 and 1:2. Mixed powder was tabletted, crushed and sieved to obtain the grain fraction of 1.0-1.2 mm.

The studies of the catalytic activity were carried out in a six-channel integral steel reactor at 10MPa. Four channels were filled with 2g of the iron catalyst of different potassium concentration (see Table 1). The fifth channel was filled with a reference catalyst

**Table 1.** Composition of iron catalysts

Catalyst sample	wt.% of $K_2O$
1	0.055
2	0.74
3	sample 1 and 2 mixed in mass proportion (s1:s2=1:1)
4	sample 1 and 2 mixed in mass proportion (s1:s2=1:2)
5	industrial catalyst
6	industrial catalyst ground and tabletted

and the sixth channel – with the same catalyst ground and then tabletted. The catalysts were reduced polythermally in the temperature range from 350 to 500 °C by means of a purified nitrogen–hydrogen mixture, the space velocity of reducing gas was about 20.000 h<sup>-1</sup>, pressure 0.1 MPa. The process was carried out until steady reaction rate was reached. The rate constant was calculated from the Temkin–Pyzhew equation, as given by Kuzniecowa [18].

$$r = k(0.75)^{1.5} P^{-0.5} \frac{(1-Z)^{2.5}}{Z} \cdot \left[ \frac{Z_r^2}{(1-Z_r)^4} - \frac{Z^2}{(1-Z)^4} \right] \quad (1)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Mobility of potassium under UHV

The diffusion of potassium from iron catalyst onto the iron foil has been studied at 500 °C, 550 °C, and 600 °C. Initially the iron surface was covered by iron oxide. The oxygen concentration was stable under these conditions. At the final state the surface was covered with oxygen and potassium atoms.

Diffusion of potassium atoms was described assuming that a small catalyst grain was an infinite source of potassium, and that concentration profiles can be expressed by the well-known Fick's diffusion laws:

$$C(x, t) = \frac{M}{2\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (2)$$

where  $D$  [cm<sup>2</sup>/s] is the diffusion coefficient of potassium,  $C(x, t)$  [atoms/cm<sup>2</sup>] is the concentration distribution,  $t$  (s) is the diffusion time,  $x$  [cm] length of plane sheet,  $M$  [atoms/cm] is the amount of substance diffusing in a plane sheet. The potassium concentration along the line crossing potassium spot is shown in Fig. 3. All model concentration profiles show good fit with experimental data.

The profiles of potassium were interpolated by a bell-shaped curve assuming the model expressed by the above Eq. [2]. The apparent diffusion coefficient was determined from the Arrhenius plot in Fig. 4 according to equation:

$$\ln D = \ln D_0 - \frac{E_a}{RT}. \quad (3)$$

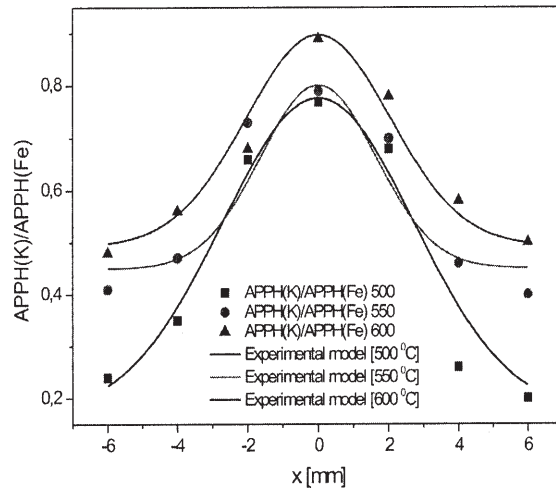


Fig. 3. Potassium concentration profiles.

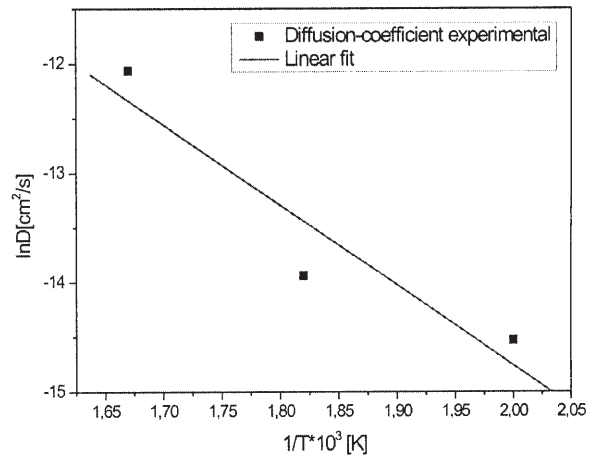


Fig. 4. Temperature dependencies of potassium diffusion coefficient.

The prefactor value was  $D_0 = 2.3 \cdot 10^{-7}$  cm<sup>2</sup>/s and the activation energy was  $E_a = 63$  kJ/mol.

Below 500 °C the diffusion of potassium from iron catalyst to the iron foil has not been observed. However, in our former paper on potassium mobility from pure KOH spot, the diffusion was observed at lower temperature (300 °C).

#### 3.2. Studies at atmospheric pressure

The concentration of potassium in six layers of the catalyst bed has not changed after the experiment. Therefore it is concluded that the diffusion of potassium from iron catalyst with a gas stream does not occur at temperatures below 500 °C.



**Table 2.** The change of potassium concentration in iron catalyst grains.

Fraction of iron grain [mm]	wt.% of K <sub>2</sub> O	
	Before process	After process
1.0 – 1.2	0.16	0.265
2.0 – 2.5	1.78	1.685

After the experiment described in 2.2.2, the concentration of potassium changed, as shown in Table 2. This suggests that, the integranular diffusion of potassium occurs under these conditions.

### 3.3. Intergranular diffusion of potassium under the conditions of ammonia synthesis

The potassium diffusion process for catalysts mixed in proportion 1:1 and 1:2 was similar and it was led in temperature program as follows: 400 °C for 16h, 425 °C for 13h, 450 °C for 16h, 465 °C for 6h, 475 °C for 7h, and 500 °C for 6h. The results of activity

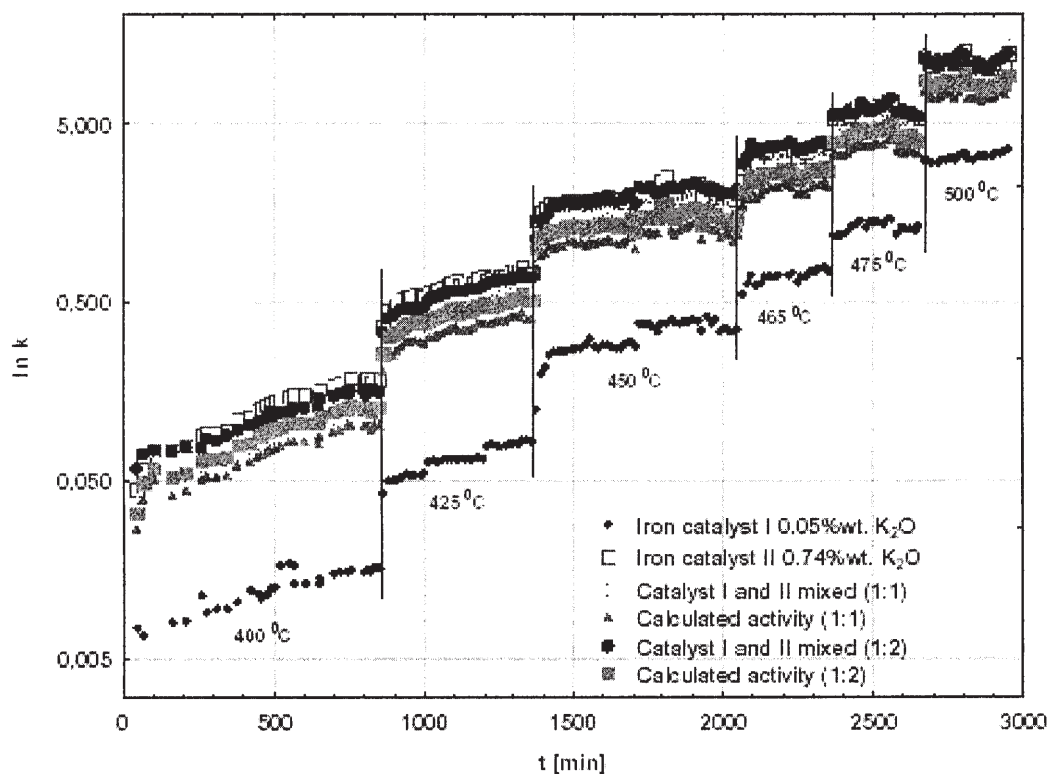
measurements expressed as reaction constant rate *k* are presented in Fig. 5. On the basis of the reaction constant rates of initial catalysts (see Table 1), the calculated reaction constant rates for mixed catalyst were determined as:

$$k_{(1:1)} = 0.5k_1 + 0.5k_2, \tag{4}$$

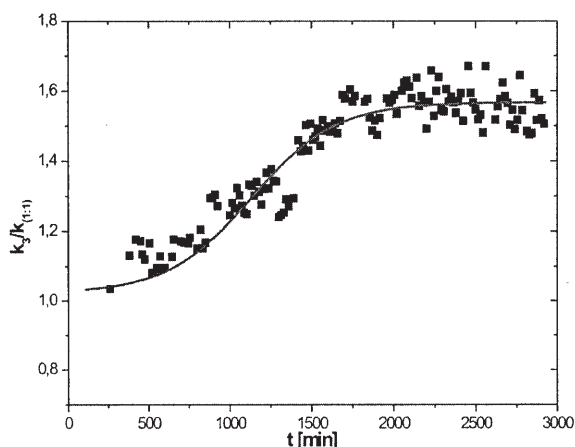
$$k_{(1:2)} = 0.33k_1 + 0.67k_2. \tag{5}$$

The activity calculated according to the above equations corresponds to the case when there is no diffusion of potassium between the two catalysts. The measured activity of mixed catalyst (Fig. 5) is higher in comparison to that calculated according to Eqs. (4) and (5). Then, it can be stated that integranular diffusion of potassium occurs under the conditions of ammonia synthesis. Fig. 6 and Fig. 7 show a ratio of the measured to the calculated activity during the process of the catalyst activation. For the mixture (1:1) – see Fig. 6 – as well as for the mixture (1:2) (Fig.7) the activity ratio  $k_3/k_{1,1}$  or  $k_4/k_{1,2}$  increases during the process from 1 to about 1.5 and then stabilizes.

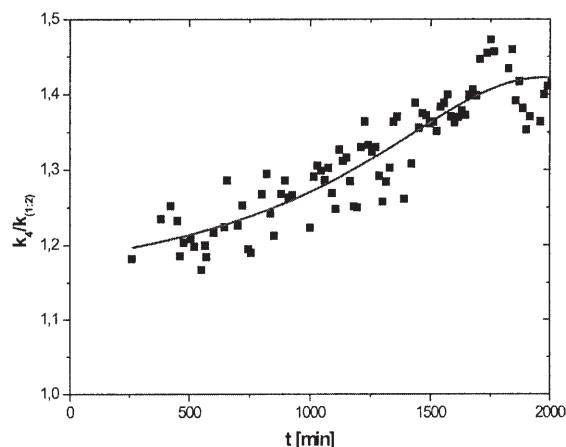
It was already reported that the activity of iron catalyst is dependent on the concentration of potassium [19]. The experiments carried out in our group [20] points out that the optimal (maximum)



**Fig. 5.** The changes of the activity during heating of the catalyst mixed (1:1),(1:2).



**Fig. 6.** Ratio of the measured to the calculated activity for catalyst mixed in proportion (1:1).



**Fig. 7.** Ratio of the measured to the calculated activity for catalyst mixed in proportion (1:2).

activity of iron catalyst promoted with  $K_2O$  by impregnation occurs at about 0.5 wt.% of  $K_2O$ . Both higher and lower concentrations of  $K_2O$  lead to the lower activity. In this light we can suppose that in case of the mixture (1:1), in which average  $K_2O$  concentration is about 0.45 wt.%, diffusion of potassium atoms leads to the homogenization of potassium concentration on the level no higher than 0.45 wt.% of  $K_2O$  in each catalyst's grain. Therefore at final state mixed catalysts reaches maximum activity and then stay unchanged.

#### 4. CONCLUSIONS

The mobility of potassium contained in industrial iron catalyst under the conditions of ammonia synthesis has been proved by UHV, atmospheric and high pressure studies. The apparent diffusion coefficient of potassium on the iron foil covered with oxygen is  $D_0 = 2.3 \cdot 10^{-7} \text{ cm}^2/\text{s}$ . The results obtained during the experiment under ammonia synthesis conditions suggest that intergranular diffusion of potassium takes place. This process influences the reaction rate of ammonia synthesis. The diffusion of potassium in the catalyst bed is only intra and intergranular, a diffusion of potassium with gas stream does not occur in the temperature range of 400–500 °C.

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