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Effect of potassium on physicochemical properties of CrO_x/Al_2O_3 and CrO_x/TiO_2 catalysts for oxidative dehydrogenation of isobutane: The role of oxygen chemisorption

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The paper is dedicated to the memory of Prof. Jerzy Haber, who initiated some 40 years ago and directed for many years research on selective oxidation at Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences in Krakow.

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ABSTRACT

Potassium addition has different influence on the selectivity to isobutene in oxidative dehydrogenation of isobutane for the two chromium based catalysts: the decrease for CrO_x/Al_2O_3(CrAl) and the increase for CrO_x/TiO_2(CrTi). This contrary effect of potassium was found to be associated with the increase in the rate of oxygen chemisorption (equivalent to the rate of reoxidation) and the increase in coverage with oxygen for CrAl, and with the decrease of these parameters for CrTi catalyst. Acid–base properties, determined by isopropanol decomposition and reducibility, estimated from TPR data, seem to affect less the catalytic properties, since they change on the potassium addition in the same way: acidity and reducibility decrease and basicity increases in the K-doped catalysts. Electron work function was found to decrease for potassium doped CrAl and did not change for CrTi catalyst.

1. Introduction

Addition of alkali metals to oxide catalysts have been found recently to increase selectivity to olefins in oxidative dehydrogenation, ODH of lower alkanes, an advantageous alternative to classical dehydrogenation.

The ammelioration of the selectivity to propene in ODH of propane has been reported for several vanadia and molybdena-based catalysts: V_2O_5/TiO_2 [1–3], V_2O_5/Al_2O_3 [4–6], V_2O_5/SiO_2 [7,8], V_2O_5/ZrO_2 [9], MoO_3/TiO_2 [1] and MoO_3/ZrO_2 [10]. The alkali metal additives improved the selectivity in n-butane ODH on Ni molybdate-based system [11] and potassium – the selectivity to isobutene – in isobutane ODH on vanadia based catalysts [12].

The ameliorating effect was explained by modification of acid–base properties of the catalysts: decrease in the acidity and increase in basicity on alkali metal doping [1,2]. It was suggested, that higher basicity facilitates desorption of olefins (bases) from the catalyst surface, preventing them from consecutive oxidation to non-desirable carbon oxides. The decrease in the electron work function on the K-doping [1,3] could also contribute to the increase in the selectivity, facilitating the catalyst reoxidation to selective O^{2-}.

Only in the case of catalysts based on V_2O_5–MgO system, the K additive was found to decrease the selectivity to olefins in ODH of propane and butane [7,8,13–16]: no explanation was given for this fact.

The negative effect of potassium on selectivity to olefins has been found very recently, also for some of CrO_x/oxide support catalysts [17]. The latter catalysts have been reported in recent years as promising for ODH, of isobutane, IB [18–25]. This reaction could replace classical dehydrogenation, DH, used currently on the indus-

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trial scale to obtain isobutene, IB=, the key reactant for production of methacrylates.

Among the chromia-based catalysts, those containing 1 theoretical monolayer, mnl on Al_2O_3 [20,24], TiO_2 [25], CeO_2 [21,22] and lanthanum carbonate [23] yielded the best results, with the selectivities to IB= of 60–70% at 10% conversion of IB. The selectivities to IB at this chromia loading were higher than that of usupported chromia, which has been ascribed to higher M–O bond and lower acidity of the dispersed CrO_x species (mainly polychromates in the fresh catalysts) as compared with Cr_2O_3 [20].

Compared to other oxide-based systems reported in open literature as active in ODH of IB, such as for instance phosphates of transition metals [26], nickel molybdates [27], VNIiSbO [28], Dawson-type phosphoro-tungstic heteropolycompounds [29], V–Mg–O system [30], the chromia-based catalysts have several advantages: they are active and selective already at relatively low temperatures 280–300 °C as compared to ~500 °C for other, above given systems. Moreover, in contrast to the latter, they do not yield oxygenates, CO_2 being practically the only side product of the ODH reaction.

The potassium additive to CrO_x/oxide support catalysts was found to decrease the selectivity to isobutene for chromia on SiO_2 and Al_2O_3 supports, to increase it for chromia on TiO_2 and showed practically no effect on CrO_x/MgO system, even if the acidity of the catalysts decreased and basicity increased on the K introduction [17].

Other factors beside acid–base properties, which can determine selectivity in oxidation reactions, involve amount and bond strength of the surface oxygen, type of oxygen species and their electronic properties [31,32]. No systematic studies have been reported so far on the effect of potassium on the oxygen properties in oxide catalysts, except a report, that potassium prevents formation of non-selective O^- species on vanadia–titania catalysts [1]. For metal catalysts it has been suggested that potassium facilitates dissociation of an oxygen molecule, by transfer of electrons: K → metal and their back donation to a $1\pi_g$ orbital of an adsorbed oxygen molecule, which causes the weakening and rupture of the O–O bond [33].

Upon the K doping, CrO_x/Al_2O_3 and CrO_x/TiO_2 catalysts exhibited a decrease and an increase in the selectivity to IB=, respectively [17]. To understand this difference, in the present paper the effect of potassium on chemisorption of oxygen on these catalysts has been examined. Electron work function, a parameter which may affect the chemisorption and catalyst's reoxidation [34] has been also measured and the bonding of K on the both catalysts was determined with species resolved thermal alkali desorption (SRTAD) method [35].

2. Experimental

2.1. Catalysts

The CrO_x/Al_2O_3 and CrO_x/TiO_2 catalysts, without and with the K additive were the same as those used in [17] in which their preparation and characterization with various physicochemical techniques have been described in detail. Commercial Al_2O_3 (Merck basic, 110 $m^2\,g^{-1}$), and TiO_2 (anatase tioxide 48 $m^2\,g^{-1}$, batch 93/204, calcined additionally at 750 °C to remove the sulphur impurity, 22 $m^2\,g^{-1}$) were used as the supports.

The catalysts were prepared by impregnation with aqueous solution of chromium nitrate (POCH, Poland) of the supports, evaporation of the solute, followed by drying for 12 h at 120 °C and calcination under a flow of air for 5 h at 500 °C. The K additive was introduced by adding appropriate amount of KNO_3 to the chromium nitrate solution to obtain the desired K/Cr ratio equal to 0.1. The content of chromia in the samples corresponded to 1.0 theoretical monolayer, mnl, of Cr_2O_3 on the support surface, and was calculated from the crystallographic data of chromia [36] with the assumption that one mnl contains 10 Cr atoms per 1 nm^2 of the support. The symbols of the samples adopted further in the text are CrS and CrSK, for catalysts without and with potassium respectively, where S is a cation of the support (Al or Ti).

2.2. Catalytic activity measurements

The activity of the catalysts in oxidative dehydrogenation of isobutane was measured in a fixed bed flow apparatus in the temperature range 250–350 °C. The details of the measurement are given in [17]. The reaction mixture contained 9.2 vol.% of isobutane in air. 0.5 ml of a catalyst sample of grain size 0.63–1.0 mm, diluted with quartz beads, was used. The pure supports were not active in the studied temperature range (conversions < 1%).

2.3. Chemisorption of oxygen

Chemisorption of oxygen was studied with a gravimetric method using S 3DV Sartorius microbalance coupled to a conventional vacuum system. Prior to oxygen chemisorption measurements, a sample (0.5 g) was subjected to a vacuum pretreatment at the pressure 10^{-4} kPa at 300–375 °C for 24 h, until a constant mass was obtained. Oxygen (99.99%), purified by vacuum distillation, was then introduced and the mass gain was recorded until the constant mass was attained. The measurements were carried out in the temperature range 300–375 °C and the oxygen pressure range 0.5–0.13 kPa. In view of the large volume of the experimental set-up, the measurements were carried out in isobaric conditions. The accuracy of the measurements was 1 μg. The control chemical analysis of the samples after the vacuum treatment showed a decrease of the total Cr^{6+} content with respect to the fresh samples. The initial value of the amount of Cr^{6+} was restored after the oxygen chemisorption measurements; this suggests that the oxygen uptake consists in the reoxidation of Cr^{3+} ions to Cr^{6+}. It was checked in preliminary experiments, that the oxygen uptake was reversible in successive cycles degassing–reoxidation.

2.4. SR-TAD

The species resolved thermal alkali desorption experiments were carried out in a vacuum apparatus with the background pressure of 10^{-6} Pa, described in detail in [35,36]. The samples were heated from room temperature to 677 °C with a Boralectric heater (Tectra GmbH) in a stepwise mode with the rate of 5 °C/min. The desorbing fluxes of potassium atoms and ions were followed. The flux of potassium atoms was determined by means of a surface ionization detector with the rhenium filament heated to 1227 °C and the positive potential at filament of +150 V. Owing to low ionization potential of potassium only K atoms were surface ionized at such conditions, with the efficiency close to 100%. The flux of potassium K^+ ions was monitored directly as an ionic current of the collector in a field ionization detector. The K^+ ions formed at the surface were accelerated towards the detector by an electric potential of +60 V applied to the sample. In all measurements, the resultant positive current was measured directly with a digital electrometer Keithley 6512.

2.5. Electron work function

The contact potential difference (CPD) measurements were carried out by the dynamic condenser method of Kelvin with a KP-6500 probe (McAllister Technical Services). The reference electrode was a stainless steel plate with the diameter of 10 mm. During the

Table 1
Characteristics of CrO_x/Al_2O_3 (CrAl) and CrO_x/TiO_2 (CrTi) catalysts without and with potassium.

Catalyst	S_{sp} [m^2/g]	Cr^{6+} [atoms/nm^2][a]	Surface atomic ratio (XPS)				Isopropanol decomposition[b]		
			Cr/S	K/Cr	Cr^{6+}/Cr^{3+}	O_{II}/O_I[c]	C_3H_6 10^{-2} μmol m^{-2}/pulse	C_3H_6O	C_3H_6O/C_3H_6
CrAl	101.0	2.7	0.3	–	0.31	0.34	0.6	1.4	2.3
CrAlK	93.3	3.5	0.3	0.06	0.25	0.0	0.2	1.4	7.0
CrTi	20.5	1.5	0.4	–	0.18	0.22	0.2	2.6	13
CrTiK	21.3	1.3	0.3	0.10	0.18	0.23	0.06	3.3	55

[a] Total number of Cr ions >Cr^{3+} from chemical analysis, expressed as Cr^{6+} content.
[b] 200 °C, pulse technique.
[c] O_{II}:BE = ~532 eV (OH groups), O_I: BE = ~530 eV (lattice oxygen).

measurements the gradient of the peak-to-peak versus backing potential was set to 0.2, whereas the vibration frequency was equal to 120 Hz. The CPD was calculated from 10 experimental points, each being an average of 50 measurements.

For the both type of experiments (SR-TAD, CPD) the samples were pressed to form wafers of 10 mm in diameter and typical mass of 100 mg.

3. Results and discussion

3.1. Basic characteristics of the catalysts

A detailed characteristic of the studied samples has been described in [17]. The XRD data of the undoped catalysts showed only the patterns of the supports, the Raman spectroscopy revealed the presence of polychromates and Cr_2O_3 [17].

In this section only basic data, necessary for further discussion of the results are summarized from [17] in Tables 1 and 2. The total content of Cr ions of the oxidation state higher than 3+, obtained from chemical analysis, and expressed as the amount of Cr^{6+} ions, is higher for CrAl system in comparison with CrTi. After addition of potassium the amounts of Cr^{6+} ions increases for CrAlK catalysts, whereas it decreases slightly for CrTiK system. The surface atomic ratio Cr^{6+}/Cr^{3+} evaluated from XPS measurements is also higher for CrAl.

The Cr/(Cr + S) ratio, where S is a cation of the support (Al or Ti), is higher for the CrTi catalysts, which indicates better dispersion of the chromium-containing phase on these catalysts. It does not change (CrAl), or slightly decrease (CrTi) on introduction of K. The changes in the coverage of the support surface with Cr are small, the fraction of the surface Cr atoms in total cation content on the surface, calculated from this ratio varying in the studied catalysts from 0.28 (CrTi) to 0.20 (CrAl). The surface Cr/K ratio from XPS studies is equal to the nominal one for CrTi (0.1) and lower for CrAl (0.06).

It can be also observed, that the ratio of oxygen in the surface OH groups (BE = ~532 eV) to the lattice oxygen (BE = ~529 eV) is higher for CrAl: after the potassium doping the OH groups in this catalyst disappear completely, which suggests location of K on these centres.

Decomposition of isopropanol, IsoOH showed that dehydrogenation to acetone is a predominant reaction on the studied samples. The amounts of propene, formed by dehydration on acidic centres, are small, which indicates low acidity (low number of acidic centres) of the samples. For both CrAl and CrTi catalysts the addition of potassium caused a distinct decrease of the amounts of propene and the increase of the acetone/propene ratio (a measure of basicity [37]).

The H_2-TPR data (Table 2) show a single reduction peak at relatively low temperatures LT (reduction onset at temperatures <250 °C i.e. in the region of the onset of the ODH of isobutane) for CrAl and an additional peak (onset temperature > 400 °C) for CrTi. Position of all the peaks in the catalysts with potassium is shifted towards higher temperatures, indicating the decrease in reducibility. Consumption of hydrogen for LT and corresponding to it amount of reduced Cr ions are higher for CrAl and slightly change with the K doping. The amounts of the reduced Cr ions, calculated from the hydrogen consumption, are higher than the total amounts of Cr^{6+}, ions determined from chemical analysis. Since the pure supports are not reduced in these conditions, this fact may suggest, that some Cr^{3+} species are also reduced The total amount of hydrogen consumed up to 300 °C related to the time of the reduction and taken as a rough measure of the reduction rate, v_{red}, is considerably higher for CrTi as compared with CrAl: in both cases it is lower for the K-doped samples.

3.2. Species resolved thermal alkali desorption, SR-TAD

The values of activation energy of desorption of potassium atoms, E_K and ions E_{K+} from the surfaces of the supports and catalysts are given in Table 3. For the supports doped with potassium two values of activation energy for desorption of potassium atoms are observed for Al_2O_3 and TiO_2, whereas for desorption of ions only one value was found for Al_2O_3 and two for TiO_2. This indicates the existence of two different states of potassium on the surface of the support. In turn, for chromia catalysts with potassium addition only single values of energy desorption of potassium atoms and ions, lower than those observed for the pure supports, were obtained. This behavior suggests that when potassium is introduced at the same time as the precursor of the active chromia phase, it is located on single sites, other than those on the pure support, for instance on the chromia phase. The difference in the values of the energies for CrAlK and CrTiK suggests, moreover, that the location of potas-

Table 2
Reducibility of CrO_x/oxide support catalysts, with and without potassium from the H_2-TPR measurements.

Catalyst	T_{onset} [°C]	T_{max} [°C]	H_2 consumption LT peak [μmol H_2 m^{-2}]	Cr^{6+} reduced[a] [at. nm^{-2}] LT peak	$v_{red.}$ [$\times 10^3$ μmol H_2 $s^{-1}m^{-2}$] (up to 300 °C)
CrAl	250	353	9.1	3.7	0.7
CrAlK	280	383	10.0	4.0	0.2
CrTi	220	335	4.7	1.9	2.0
	400	435			
CrTiK	260	360	6.6	2.7	0.4
	420	480			

[a] Total amount of the reduced Cr ions, calculated from the H_2 consumption and expressed as Cr^{6+} content.

Table 3
Activation energies of desorption of K and K^+ from the surface of CrTiK and CrAlK catalysts.

Sample	E_K [eV] (desorption temp. °C)		E_{K+} [eV] (desorption temp. °C)	
AlK	3.2 ± 0.05 (740)	3.39 ± 0.01 (740)	3.48 ± 0.03 (681)	
CrAlK	2.57 ± 0.09 (568)		2.15 ± 0.03 (507)	
TiK	3.13 ± 0.06 (447)	1.55 ± 0.02 (545)	1.39 ± 0.02 (294)	2.26 ± 0.01 (475)
CrTiK	4.40 ± 0.08 (691)		1.20 ± 0.01 (465)	

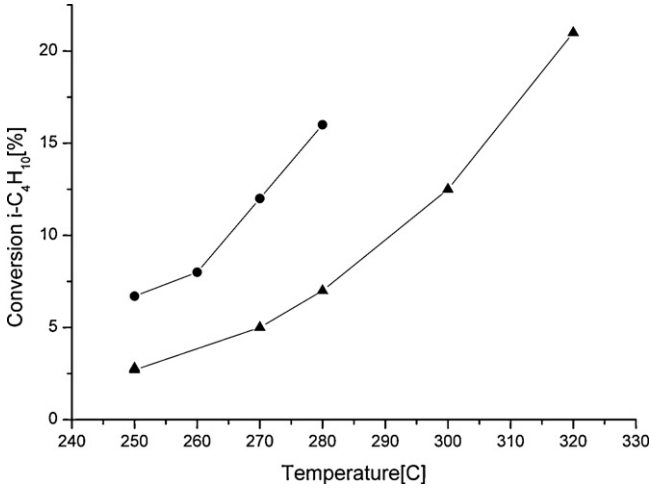

Fig. 1. Changes of isobutane conversion with the reaction temperature for CrAl (●) and CrTi (▲) catalysts.

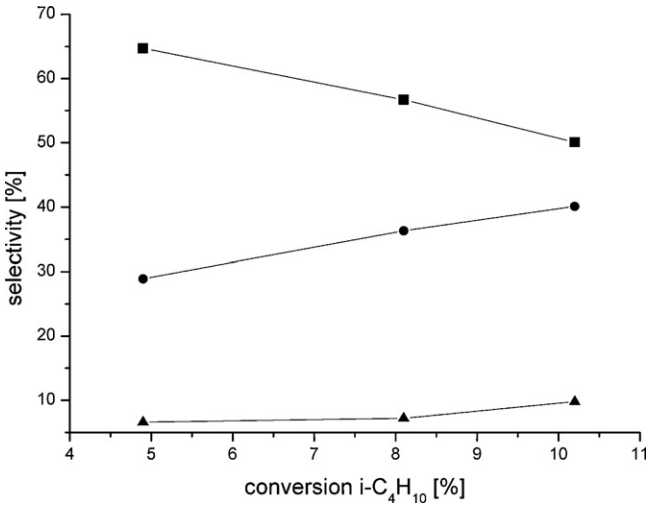

Fig. 2. Selectivities to isobutene (■), CO_2 (●) and CO (▲) as a function of the isobutane conversion at 300 °C for CrAl catalyst.

sium in the both catalysts may be different. The high desorption temperatures of both potassium atoms and ions (>500 °C), much higher than those of the ODH reaction, indicate that there is no loss of potassium during the reaction.

3.3. Catalytic activity

Fig. 1 presents variations of the isobutane conversion with the reaction temperature for CrTi and CrAl catalysts. The increase of the isobutane conversion with the temperature is accompanied by the decrease of the selectivity to isobutene and the increase of the selectivity to CO_2. The amounts of CO are rather small and practically constant in the whole conversion range. Fig. 2 illustrates the changes of the selectivities to different reaction products with the conversion at 300 °C for the CrAl catalyst.

This behavior indicates a sequential reaction pathway, typical for ODH reactions [38]: isobutene, $IB_=$ formed in the first step is further oxidized to CO_2; in turn CO, whose selectivity is practically independent of the conversion, is formed by the parallel route. The curves of a similar type have been found for other tested catalysts, without and with potassium.

Table 4 summarizes the catalytic data at 300 °C for all the studied catalysts: the selectivities are given for isoconversion (8%). The catalytic activity data are referred to surface area of the samples (column 2). To account for the small changes in Cr content on the surface, and to compare the activity of Cr in chromium oxide phase in the studied catalysts, the activity was also referred to the fraction of Cr atoms in the surface total cations content (column 3). As seen, for both ways of presenting the data, the activities of the CrTi are higher as compared with the CrAl catalysts and practically do not change for the K-doped samples.

The selectivities to $IB_=$ are higher for CrAl catalyst as compared with CrTi for samples without potassium. The effect of the K additive on the selectivity to $IB_=$ is inverse for the two systems: the selectivity increases considerably for CrTi and decreases for CrAl. The increase in the selectivity to $IB_=$ is accompanied by the decrease in the selectivity to CO_2. The selectivities to CO do not differ much for the two systems and are not affected by the presence of potassium. The opposite effect of K on the selectivities is observed at different conversions, as illustrated for CrAl catalyst in Fig. 3. The effect was also observed for CrO_x catalysts with different TiO_2 (anatase tioxide, 48 $m^2\,g^{-1}$, TiO_2 rutile) and different Al_2O_3 (Merck acidic) suppports [17,39]. For CrAl system the decrease in the selectivity to $IB_=$ was seen also at different K content (K/Cr = 0.05 and 0.2) [39].

3.4. Chemisorption of oxygen

For all the catalysts under study the rate of oxygen uptake was determined as a function of oxygen pressure, temperature and degree of coverage of the surface. The results obtained are summarized in Table 5 and Figs. 4–6.

Table 4
Catalytic data in isobutane ODH[a] for CrO_x/Al_2O_3 and CrO_x/TiO_2 without and with the potassium addition.

Catalyst	Activity [μmol IB $s^{-1}m^{-2}$]	Activity [μmol IB/Cr/(Cr + S) $s^{-1}m^{-2}$]	Selectivity at 8% IB conversion [%]		
			$IB_=$	CO_2	CO
CrAl	1.1	5.5	58.2	36.8	5.0
CrAlK	1.1	5.2	48.6	43.3	9.1
CrTi	2.5	8.9	34.8	55.6	9.4
CrTiK	2.0	8.3	55.5	35.8	9.7

[a] 300 °C.

Table 5
Oxygen adsorption data for chromia catalysts.

Catalyst	Δm_∞[a] [μmol O m^{-2}]	% mnl	α [kJ mol^{-1}]	ln k_o	$v_{ox} \times 10^4$[a] [μmol O m^{-2}s^{-1}kPa^{-1}]	$E_{act.ox}$ [kJ mol^{-1}]	v_{ox}/v_{red}
CrAl	1.58	9.5	0.18	38.0	0.81	225.0	0.12
CrAlK	1.55	9.3	0.21	19.4	1.78	133.0	0.89
CrTi	0.98	5.9	0.59	2.9	14,7	44.0	7.4
CrTiK	0.73	4.4	0.61	−2.4	1.08	32.0	0.27

[a] 350 °C.

Fig. 4 shows kinetics of the oxygen chemisorption for a CrAl catalyst at 350 °C and at different oxygen pressures. Similar curves were obtained for other catalysts.

The experimental data can be described by the Langmuir isotherm for the dissociative adsorption:

$$\theta = \frac{\Delta m}{\Delta m_\infty} = \frac{b(p_O)^{1/2}}{1 + b(p_O)^{1/2}} \quad (1)$$

where $(\Delta m)_\infty$ corresponds to maximum coverage of the surface with oxygen at a given temperature, b is an adsorption coefficient and p_O the oxygen pressure.

Values of $(\Delta m)_\infty$ (column 2 in Table 5) are higher for CrAl as compared with CrTi, and do not depend considerably on the presence of potassium. Column 3 in Table 6 gives the oxygen uptake as a percentage of the oxygen monolayer, assumed for most of oxides

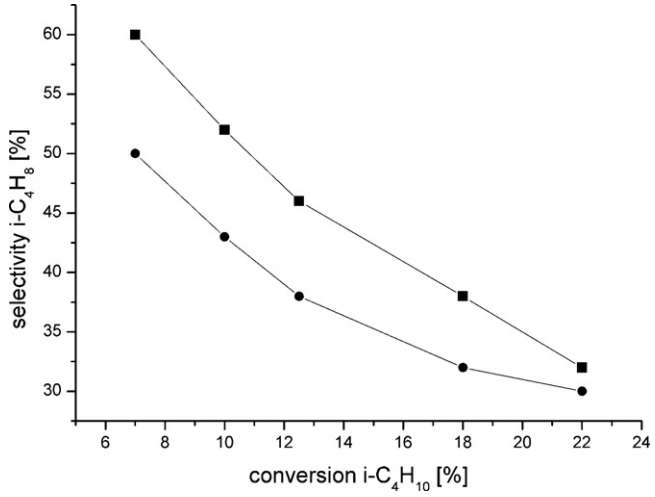

Fig. 3. Changes of selectivity to isobutene with the isobutane conversion for CrAl (■) and CrAlK (●) catalysts.

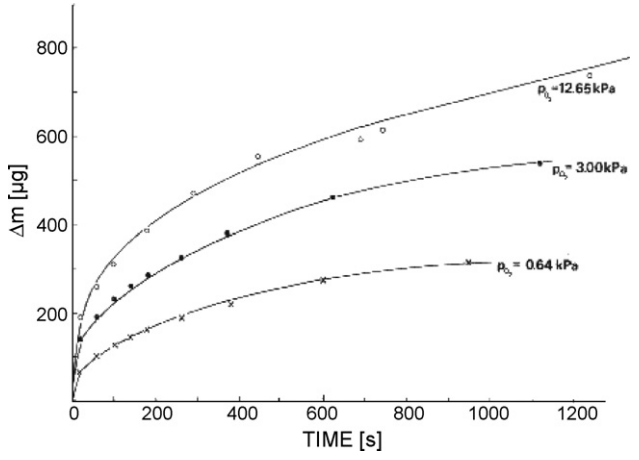

Fig. 4. Kinetics of oxygen chemisorption at 350 °C at different oxygen pressure for CrAl catalyst.

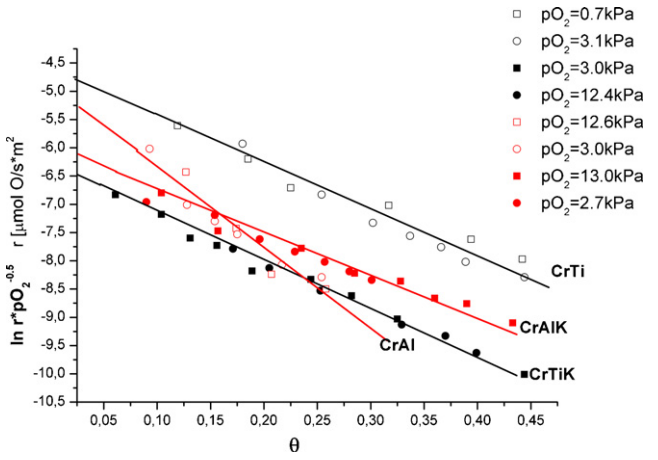

Fig. 5. Rate of oxygen chemisorption at 350 °C as a function of coverage for CrTi and CrAl catalysts without and with the potassium additive.

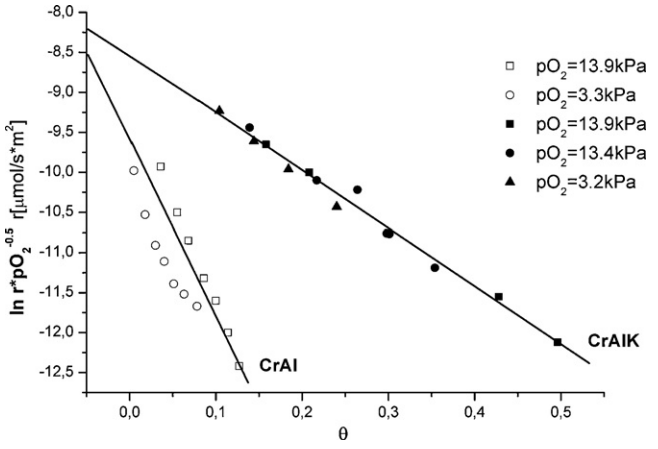

Fig. 6. Rate of oxygen chemisorption at 300 °C as a function of coverage for CrAl and CrAlK catalysts

as equivalent to 16 μmol O m^{-2}. Since the oxygen uptake consists of reoxidation of the Cr^{3+} ions to Cr^{6+}, we can conclude that only 5–10% of the surface oxygen take part in the desorption–adsorption cycles involved in the chemisorption.

Kinetics of the oxygen uptake can be described by the Elovich equation:

$$R = \frac{d\theta}{dt} = k_a(p_O)^{0.5}(1-\theta)e^{-\beta\theta} \quad (2)$$

Table 6
Values of work function $W_{Kel.}$ for CrTi and CrAl catalysts, with and without potassium.

Catalyst	$W_{Kel.}$ [eV]
CrAl	4.754 ± 0.015
CrAlK	4.378 ± 0.009
CrTi	4.745 ± 0.015
CrTiK	4.745 ± 0.011

where k_a and β are constants. According to Elovich, Roginski and Zeldovich, the exponential term in the equation indicates the energetic inhomogeneity of the catalyst surface [40]. The activation energy of chemisorption increases linearly with the increase in θ: $E = E_0(1 + \alpha\theta)$. The constant α, which characterizes the degree of the energetic inhomogeneity of the surface, is related to the kinetic parameter β by a simple relation: $\alpha = R_g T\beta/E_0$, where R_g is a gas constant and E_0 is the lowest value of activation energy (at $\theta = 0$). Considerably higher values of α for CrTi catalysts than for CrAl (column 4 of Table 5), indicate higher degree of inhomogeneity of the oxygen chemisorption centres. The presence of potassium does not affect the values of α.

In Fig. 5 the linearized form of (Eq. (2)) is plotted for oxygen chemisorption at 350 °C on all the studied catalysts. Fig. 6 gives the plot of the same type for CrAl catalysts at 300 °C. As seen from the plots Eq. (2) is well obeyed for all the catalysts and that the rates decrease with the increase in the oxygen coverage.

Table 5 gives also the values of initial rate of chemisorption at 300 °C, ν_{ox} and the activation energies calculated from the Arrhenius plot for the initial rate.

It can be observed that the initial rate of chemisorption for undoped catalysts is much higher for CrTi catalysts as compared with CrAl. The effect of the potassium addition on the chemisorption rate is, however, inverse for the two catalysts: in the case of CrTi system the dramatic decrease of the rate of chemisorption is observed, whereas for CrAl system the rate increases at 300 °C i.e. at the temperature of the catalytic reaction for all the oxygen coverages and at 350 °C for the higher coverage.

For both catalytic systems: CrAl and CrTi the decrease of the activation energy on introduction of potassium is observed. This effect is particularly distinct for CrAl catalysts. It can also be noticed, that the activation energy for CrAl catalysts is remarkably higher than for CrTi samples.

The high value of activation energy indicates high barrier for dissociation of the oxygen molecule, the latter step being r.d.s. of the oxygen chemisorption process. The considerably different reoxidation rates and $E_{act.ox.}$ observed for CrAl and CrTi catalysts may arise from higher reduction rate for CrTi catalyst, which would lead to higher number of Cr^{3+} ions – centres for the oxygen chemisorption – during the catalytic reaction. This fact, together with the relatively low value of $E_{act.ox.}$, could account for the much higher ν_{ox} and higher oxygen coverage for undoped CrTi catalyst as compared with CrAl.

We may speculate, that higher fraction of surface Cr^{3+} ions (indicated by XPS) and higher reduction rate for CrTi, ions, may lead to different mode of adsorption of an oxygen molecule (parallel to the surface, involving two chemisorption centres) on this catalyst, as compared to CrAl catalyst. For the latter catalysts lower concentration of Cr^{3+} ions would lead to a vertical adsorption of an oxygen molecule on isolated centres, more difficult to activate, hence to much higher activation energy. It can be recalled that quantum chemical calculations of oxygen chemisorption on vanadia and molybdena surface have shown, that parallel mode of the chemisorption on two vicinal chemisorption centres (oxygen vacancies) is more favourable energetically [41].

It can also be observed, that the values of $\ln k_o$ are much higher for the CrAl as compared with CrTi system. The potassium additive decreases considerably the value of $\ln k_o$ for the both systems.

Column 8 of Table 5 gives the ratio of the oxygen chemisorption initial rate (300 °C) to the rate of total reduction up to 300 °C, ν_{red}, given in Table 2. In selective oxidation reactions, occurring in most cases by the redox, Mars and van Krevelen or steady state adsorption model mechanisms, the value of this ratio can be taken as a rough measure of the degree of the oxygen coverage in the stationary state of the reaction in the oxygen/reducer mixture [32]. For catalysts without potassium the value of this ratio is higher for CrTi system as compared with CrAl. After introduction of potassium the ν_{ox}/ν_{red} ratio decreases for CrTi system whereas for CrAl increases.

The inverse effect of potassium on the rate of the oxygen chemisorption and the oxygen coverage for the two systems is difficult to explain. Formally potassium decreases activation energy of chemisorption and the rate of reduction for both CrAl and CrTi. We may, however, observe, that the extent of the changes is considerably different for the two catalysts. Activation energy is reduced much more for CrAl and this decrease could account for the increase of the chemisorption rate. The data of the next paragraph show, moreover, that for this catalyst the electron transfer to an adsorbed oxygen molecule is enhanced, which contributes to the high rate of reoxidation.

On the other hand the reduction rate for CrTi is more affected by the K introduction: a marked decrease of the amount of the Cr^{3+} ions, which act as the oxygen chemisorption centres is observed. This effect may prevail over the smaller decrease in the activation energy and lead to the decrease in the rate of reoxidation and in the oxygen coverage for CrTi.

3.5. Electron work function, W

The electron work function is an energy barrier for electrons to pass from a catalyst to an oxygen molecule during the chemisorption process. The $Cr^{3+} \rightarrow Cr^{6+}$ reaction, occurring during the chemisorption, involves an electron transfer $O_2 + 4e^- \rightarrow 2O^{2-}$, which may proceed in a sequence of reactions: $O_2 + e^- \rightarrow O_2^- + e^- \rightarrow 2O^- + 2e^- \rightarrow 2O^{2-}$ [31,32].

The rate of such processes, involving an electron transfer, will be proportional to the fraction of the catalyst's electrons, capable to cross over the energy barrier (work function, W). This fraction is given by the formula: $[e^-]\ \exp[-W/kT]$, where $[e^-]$ is total number of electrons in a catalyst. The values of average electron work function for the surfaces of undoped and K-doped catalysts from CrAl and CrTi systems are given in Table 6.

As seen, the addition of potassium causes the decrease of electron work function by about 0.4 eV for CrAl catalyst, whereas for CrTi this value does not change. The lowering of W will lead to the increase in the fraction of electrons transferred to oxygen molecule and hence to the increase in the rate of chemisorption (reoxidation) for CrAl.

In view of the fact, that work function depends not only on the position of the Fermi level in a solid, but also on dipole moments of the species in the uppermost layer of the solid (i.e. on its structure), the different effect of K on the values of W for the two catalysts (a decrease for CrAl and no change for CrTi) suggests, that location of K on the two catalysts and the structure of the surface may be different.

The decrease of the electron work function on addition of alkali metals was previously observed for several vanadia and molybdena dispersed on TiO_2 [1,3,42] and was considered to contribute to the increase in the selectivity to propene in ODH of propane.

3.6. Correlations between physicochemical properties and selectivity in isobutane ODH; conclusions

The data described above show that, for both CrAl and CrTi catalysts the potassium additive leads to: (a) a decrease in the acidity (number of acidic centres) as can be inferred from the decrease in the amount of propene formed in the isopropanol dehydration and (b) increase in the acetone/propene ratio (a rough measure of

the basicity). The reducibility of the studied systems-a measure of the M–O bond energy – is affected by potassium also in a similar way. T_{max} of low temperature reduction peak, situated in the temperature region in which the isobutane ODH was measured, is shifted towards higher temperatures and the reduction rate is lower for both CrAl and CrTi catalysts. This suggests that for both Cr and CrAl catalysts, M–O bond energy is higher for the K-doped samples.

Thus, neither the data on acid–base properties nor on reducibility can explain the inverse effect of potassium on the selectivity to $IB_{=}$ observed for CrTi and CrAl; this additive exerts the same effects i.e. decrease in acidity, increase in basicity and decrease in reducibility in the both cases, but it increases the selectivity for CrTi and decreases it for CrAl.

As shown by the oxygen chemisorption data, the K additive influences, however, in a different way the rate of the oxygen chemisorption (equivalent to reoxidation of reduced catalyst) and the oxygen coverage in the stationary state of the reaction: it increases these parameters for CrAl and decreases them for CrTi. This opposite effect can be partly due to lowering of the electron work function on doping with K for CrAl catalyst.

The opposite effect of potassium on the selectivity to $IB_{=}$ for CrTi (increase) and CrAl (decrease) can be then related to its different effect on the rate of reoxidation and the oxygen coverage. One can expect that in the case of higher oxygen coverage (CrAlK catalyst) a reacting isobutane molecule is surrounded by higher number of oxygen species, which may attack different C–H and/or C–C bonds simultaneously, leading to its disruption and formation of CO_2, and thus to the lower selectivity to $IB_{=}$.

It can also be observed, that for the studied catalysts, the sequence of the decreasing selectivity to $IB_{=}$ (values in brackets for isoconversion of isobutane):

$$CrAl(60) \sim CrTiK(60) > CrAlK(50) > CrTi(35)$$

follows the sequence of the increasing oxygen coverage,

$$CrAl(0.12) < CrTiK(0.27) < CrAlK(0.89) < CrTi(7.4)$$

and the order of the increasing rate of the oxygen chemisorption:

$$CrAl(0.8) \sim CrTiK(1.1) < CrAlK(1.8) < CrTi(14.7),$$

which suggests a correlation between these properties.

The reason for different properties of CrTi and CrAl catalysts on the potassium doping in interaction with oxygen remains to be solved. One may only speculate, that different concentration and distribution of Cr^{3+} ions-active centres for chemisorption could affect a mode of the oxygen molecule adsorption [vertical to the surface for isolated ions (CrAl) and parallel when they are in the vicinity (CrTi)]. The location of K in the CrTi and CrAl catalysts may also be different, as suggested by different energy of the K desorption from the both systems, by different behavior of the OH surface groups in CrTi and CrAl on the K doping, and by different K effect on the values of work function. The different location of K may affect the local structure of $Cr^{3+}O_x$, leading to their different properties in interaction with oxygen.

Further studies on molecular structure of the centres are required to solve these problems.

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