Effect of additives on properties of vanadia-based catalysts for oxidative dehydrogenation of propane Experimental and quantum chemical studies

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Abstract

Effect of additives (A) comprising main group elements (K, P) and transition metals (Ni, Cr, Mo) to VO_x/SiO_2 catalysts on their catalytic behavior in oxidative dehydrogenation (ODH) of propane are studied. The experimental findings are compared with results of quantum chemical calculations performed for a model $O = V–O–V^*$ cluster in which V^* atom is replaced by an atom of A. The selectivities to propene found in experiments change on introducing the additives, decreasing in the sequence VK(64) > VCr(38) > VMo = VNi(32) > VP(28) ~ V0(27). Quantum chemical calculations indicate the change in the electron density on the atoms of the active $O = V–O$ groups for the clusters with the additives' atoms. The extent of the electron transfer from A towards the active group (the increase in the centre basicity) follows the sequence of the decreasing selectivity to propene, confirming the role of acid–base properties in controlling the selectivity in ODH of propane. Results of calculations show also an exceptional behavior of the potassium (the most effective additive for the increase in the selectivity in experiments); in contrast to all other additivies, K transfers electrons towards both V and O atoms in the active group, and does not form a definite O–K bond, but is rather "adsorbed" on the cluster.
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1. Introduction

One of the main requirements for a selective catalyst in oxidative dehydrogenation, ODH of lower alkanes, a reaction of recent interest as an alternative to classical dehydrogenation for production of cheap olefins [1–3], is to ensure easy desorption of an olefin molecule from a catalyst surface, before it undergoes consecutive total oxidation to carbon oxides. The strength of bonding of an olefin (a base or a nucleophile) should depend on acid–base properties of a catalyst surface, being weaker on the surfaces of low acidity (low acid strength) and high basicity (high base strength). The systems of such properties should facilitate the olefin desorption and hence should be selective catalysts for the ODH of alkanes to olefins. In the case of transition metal oxides, catalysing reaction with one-electron transfer, the notions of Lewis acidity and basicity are frequently used as

equivalent to, respectively electrophilicity and nucleophilicity, and related to the density of electrons over cations (acid or electrophilic centres) and oxide ions (basic, nucleophilic centres). The acid–base properties of an oxide catalyst can be controlled by the introduction of additives [4].

To date studies on the effect of additives to oxide catalysts on their performance in ODH reactions of lower alkanes have been limited mostly to the alkali metal additives. It has been reported in several recent works that introduction of potassium (or generally alkali metal additives), to oxide systems, in particular to titania- or alumina-supported vanadia catalysts, has a beneficial effect on the selectivity to olefins in the ODH of propane or *n*-butane [5–9]. The increase in the selectivity to propene for the alkali-doped VO_x/TiO_2 catalysts has been correlated with the decrease of the catalyst acidity and increase in the basicity [5,6], the acid–base properties being measured by a probe reaction of the isopropanol decomposition. The changes in the rate of isopropanol dehydration and dehydrogenation were ascribed in this case to the modification of strength of respectively acid and basic sites. The lower values of the adsorption heat

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of propene on the same series of alkali-doped catalysts as compared with the undoped vanadia-titania catalysts have been observed [10], confirming the role of the acid–base properties in controlling the strength of the propene bonding to the surface and the selectivity.

The explanation of the effect of additives on a molecular scale has not been, however, reported as yet. It is generally accepted, that an activation of a hydrocarbon molecule on oxide catalysts takes place on a centre involving a M–O acid–base couple, oxide ions (O) playing a role of a hydrogen atom abstraction centre, cationic centres (M) facilitating the electron transfer [11]. Further steps of the reaction are under debate. In view of the above given discussion, to ensure the easy desorption of an olefin in the ODH reactions, a M–O_x active centre should exhibit high electron density. The molecular aspect of the effect of additives would consist in modification of the electron density at the M–O_x centre. One could expect, that cationic additives of lower electronegativity than that of the active cations in a Me–O couple would shift the electrons towards the active centre, rendering it less acidic (less electrophilic) and more basic. The inverse effect can be expected when the additive is more electronegative than the main cationic component of an oxide. In a simple picture, assuming that the electronegativity of a cation is given by a formula: $\lambda_{Me}^{z+} = (1 + 2z)\lambda_{Me}$, where λ_{Me} is an electronegativity of an atom and z its valency, we would expect that addition of ions of higher valency than that of the main cation would increase the electron density over it, whereas that of the lower valency would decrease it. This formula is true for the ions in the solution; the formal charge (and hence the electronegativity) in the solid oxides may be, on the other hand, different.

To check the above hypotheses, in the present work oxidative dehydrogenation of propane has been studied on vanadia/silica catalysts containing additives (A) of ions of higher (Mo^{6+}), lower (K^+, Ni^{2+}, Cr^{3+}) and the same (P^{5+}) formal valency as V^{5+}. The additives represented both the main group elements (K, P) and transition metals (Ni, Cr, Mo). The effect of the additives on the electronic (charge distribution) and geometric (bond length) structures in the active centre V–O_x has been approached by quantum chemical calculations based on the density functional approach (DFT), using a simple cluster model. The experimental findings have been compared with the results of the calculations.

2. Experimental

2.1. Preparation and characterization of catalysts

The V_2O_5/SiO_2 catalysts were prepared by impregnation with aqueous solution of ammonium metavanadate of a commercial silica support (Aerosil 200), 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. Before impregnation the support was pre-treated in water at room temperature

and dried at 90 °C for 12 h, its specific surface area after such treatment was 175 m^2/g. The additives (A) were introduced by adding appropriate amounts of their soluble salts or acids (KNO_3, $Ni(NO_3)_2$, $Cr(NO_3)_3$, H_3PO_4, ammonium paramolybdate) to the metavanadate solution. All the reactants used were of ppa grade. The atomic ratio A/V in the calcined catalysts was 0.2 with the exception of K, for which K/V was 0.1. The content of vanadia in the samples corresponded to 1.5 monolayers of V_2O_5 (28.4 wt.%) and was calculated with the assumption that one monolayer contains 10 V atoms per 1 nm^2 of the support surface. The symbols of the samples, adopted further in the text, are VSiA where A is the additive. The specific surface area of the support and the catalysts was determined with the BET method (Quantachrome Autosorb-1), using nitrogen as an adsorbate. The XRD pattern of selected samples (recorded with a Philips PW 1710 diffractometer) exhibited the broad peaks corresponding to V_2O_5 in a poorly crystallized form. In parallel Raman spectroscopy revealed also the presence of monomeric VO_x groups of a vanadyl type. The XPS spectra were recorded with a VG Scientific ESCA-3 spectrometer using Al K$\alpha_{1,2}$ radiation (1486.6 eV) from an X-ray source operating at 12 kV and 20 mA. The working pressure was better than 2×10^{-8} Torr (1 Torr = 133.3 Pa). The binding energies (BEs) were referenced to the C(1s) peak from the carbon surface deposit at 284.8 eV. The surface atomic ratios V/Si and A/V were calculated with the procedure described in [12]. The spectra of the all elements present in the samples were taken for fresh catalysts and for the VSiMo catalyst also after the catalytic reaction at 450 °C. In this latter case the catalyst was cooled down in the reactor from 450 °C to room temperature in a stream of pure helium and transferred immediately to the XPS measuring chamber.

2.2. Catalytic test

Catalytic activity of the samples in oxidative dehydrogenation of propane was measured in a fixed bed flow apparatus at 450 °C. The reaction mixture contained 7 vol.% of propane in air, the constant flow of the reactants being maintained by mass flow controllers. The reactor (13 mm in diameter) was made of stainless steel, the thermocouple for the temperature measurements being placed coaxially in the catalyst bed. Analysis of the amount of products and unreacted propane was performed by on-line gas chromatography using Hewlett-Packard chromatograph with catharometric detection. The C_3H_6, CO and CO_2 were found as main reaction products, the amount of oxygenates (acrolein, acrylic acid) was below 1% of the total amounts of products. The samples were kept at a given temperature till a constant value of propane conversion and the yields of products were obtained (usually after 2–3 h). Since the selectivity to propene decreases with the increasing conversion (a typical behaviour for oxidative dehydrogenation reactions on oxide catalysts [1–3,13]), the selectivity data at iso-conversion (10%) obtained for different samples were
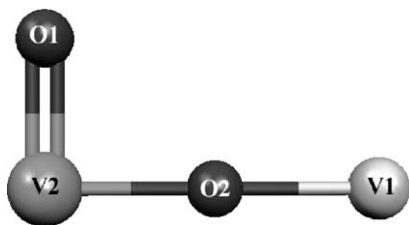
Fig. 1. Schematic view of the model cluster.

compared. The selectivities to different products were calculated from the formula: $S_i = c_i/\Sigma c_i$ where c_i is concentration of ith product. Pure SiO_2 support was found inactive under the adopted conditions of the reaction, the conversion of propane at the reaction temperature being below 1%.

2.3. Computational details

For quantum chemical modelling a simple cluster model, which represents two types of V–O centres, commonly found in vanadia-based catalysts [14,15], was used. Such a model can be regarded as consisting of two components: a vanadyl V=O group (characterized by a short V–O bond) and a V–O–V fragment, with bridging oxygen that links two vanadium atoms, both fragments having one common vanadium atoms (see Fig. 1). Therefore, the model describes two types of oxygen atoms singly and doubly coordinated to vanadium atom(s). Thus, to distinguish between these two types of oxygen atoms the following nomenclature will be used: V1–O2–V2 and V2=O1.

To study the effect of additives on the electronic and geometric properties of the chosen model the V1 atom within the model was sequentially replaced by different additives (A: P, K, Mo, Cr, Ni), which were used in experimental studies, and the electronic/geometric structures obtained for doped cluster results were compared to those obtained for the O1=V2–O2–V1 cluster. Since the location of the additives in the real samples is not resolved, the formation of the V–O–A groups in the studied systems, localized either at the surface or in the bulk, was assumed.

All calculations were carried out at the ab initio DFT level [16] using StoBe quantum chemistry program package [17]. The alternative revision of the Perdew, Burke and, Ernzerhof (RPBE) introduced by Hammer et al. [18] was applied to approximate the exchange correlation interactions. The Kohn-Sham molecular orbitals were expanded as linear combination of atom-centred Gaussian-type orbitals, expressed in terms of a double zeta basis sets including polarization functions. All atoms in cluster were allowed to relax in such a way that the O1=V2 and V2–O2–V1 fragments were moving in perpendicular directions, in order to obtain a minimum of the total energy. The structural optimisations were converged with the accuracy in displacement smaller than 0.1 Bohr and with the accuracy in energy smaller than 10^{-5} Hartree. In starting geometries the entire metal–oxygen bond distances were arbitrary set to 1.8 Å.

Electronic properties of model clusters were analysed in terms of charge distribution using standard Mulliken approach [19–21] and Meyer bond orders [22,23]. Both quantities were used to characterize ionicity and covalency of bonds in the cluster and to discuss the changes in electronic structure (charge transfer, bond distances) introduced by different additives. In addition the structural variations (changes in bond distances) were considered.

3. Results and discussion

3.1. Main characteristics

Table 1 gives the list of samples and their main characteristics. The introduction of the additives leads to the decrease of the specific surface area with respect to the undoped VSi catalyst; the effect is the strongest for VSiP and VSiMo samples (the decrease by ~40–45% of the value for VSi), and the VSiK (by ~ 20%). The values of binding energies BE obtained in the XPS measurements, indicate that vanadium and the additives are present in the form corresponding to V^{5+}, P^{5+}, Cr^{3+}, and Ni^{2+} ions in oxides. The Mo-doped fresh catalyst contains considerable fraction of Mo^{4+} ions (42%) beside Mo^{6+} ions. After the catalytic reaction, however, the Mo^{6+} ion is dominating (86%). The A/V surface ratios, calculated from the XPS data, show considerable enrichment of the surface with respect to the nominal values in the case of P, Cr and K additives and slight impoverishment in the case of the Ni additive. The additives do not affect markedly the V/Si ratio, i.e. the dispersion of vanadium on the silica surface, with the exception of the Cr additive for which the increase of this ratio is observed. XRD technique showed poorly crystalline vanadia as the main phase. More detailed characteristics of the catalysts performed with XRD, Raman UV-Vis spectroscopies [24] have shown traces of the mixed phases (Vanadates of K, Mo, Cr, Ni) in all the catalysts with the exception of V SiP samples, and octahedral coordination of vanadium (V^V) ions in the samples. No detailed data are available on the location of the additives in the samples. The formation of groups V–O –A on a surface of catalysts is assumed in formulating a cluster modeling the active site (c.f. paragraph on computational details).

3.2. Catalytic data

The last column in Table 1 gives the specific total activity in the ODH of propane of the studied samples. Since the loading with vanadium is the same for all the catalysts and the support is found inactive in the conditions of the catalytic test, the data reflect the activity of the vanadia phase. The activity of the samples with the Mo and P additives is significantly higher than that of the undoped sample, whereas Cr and Ni additives do not exert a marked effect on the activity. The activity of the K-doped doped samples

Table 1
Main characteristics of VO_x/SiO_2 catalysts with additives

| Symbol | S_{sp} (m^2/g) | XPS data | | | | | Total activity (420 °C) conversion/S_{sp} |
| | | BE (eV) | | A/V | | V/Si | |
		V (2p)	A				
VSi	116.6	516.8	–	–		0.07	0.19
VSiMo	76.7	517.1	233.4	0.161 (42% Mo^{4+})		0.06	0.39
			230.4 (3d)				
VSiMo (after reaction)		517.9	232.7	0.211 (14% Mo^{4+})		0.103	–
		516.0	229.7 (3d)				
VSiP	70.2	517.4	133.7 (2p)	0.437		0.08	0.66
VSiCr	109.0	517.1	577.1 (2p)	0.333		0.16	0.22
VSiNi	110.8	516.6	856.5 (2p)	0.133		0.07	0.23
VSiK	92.4	516.9	292.6 (2p)	0.224		0.07	0.1

is considerably lower than that of both undoped and doped with other additives samples. The decrease of the activity for the K-doped samples has been observed previously for most of the vanadia-based catalysts and ascribed, in the first place, to geometrical blocking of active centres on the vanadia surface [4]. The selectivities to propene of different samples at 10% of the propane conversion at 450 °C are presented in Fig. 2. For the VSiK sample, for which conversions higher than 1–3% could not be obtained at this temperature, the data at 500 °C are given.

As seen, the K additive increases considerably the selectivity to propene from about 25% for undoped sample to 65–75%. The distinct increase in the selectivity (though much smaller than for the K-doped sample) is observed also for the samples with the Ni, Cr and Mo additives. Practically no effect is observed for the P additive.

3.3. Quantum chemical calculations

Table 2 summarizes results of calculations in terms of bond lengths, atomic charges and the charge transfer within the clusters containing different additives. For cluster built of only V and O atoms (no additives) two oxygen atoms exhibit different nucleophilic character; the oxygen bridging two vanadium atoms being more negatively charged than the vanadyl oxygen coordinated to one vanadium atom. Vanadyl oxygen binds to vanadium via a short ($R = 1.6\,\text{Å}$), strong, double bond (BO = 2.28), whereas bridging oxygen links two V atoms by two approximately single bonds, ($R = 1.82, 1.69\,\text{Å}$, BO = 0.85, 1.36). A fact that these two bonds are non-equivalent and two V atoms are differently charged ($q_{V1} = 0.27$, $q_{V2} = 0.66$) is a consequence of the use of rather small model cluster. Substitution of one vanadium
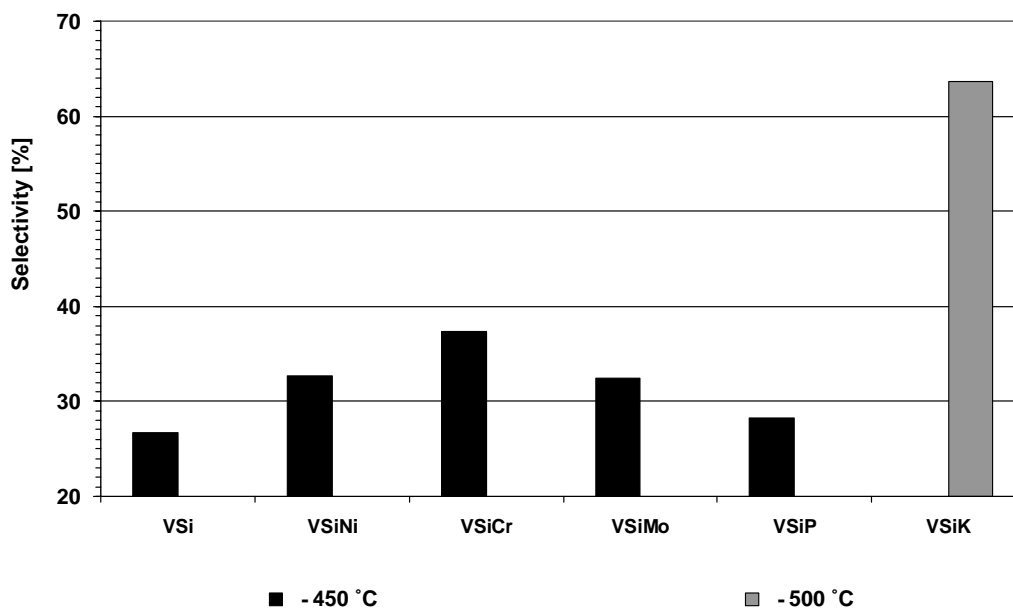

Fig. 2. Selectivity to propene at 10% conversion of propane for VO_x/SiO_2 catalysts with additives.

Table 2

Structural (bond lengths) and electronic (atomic charges, bond orders, charge transfers) properties obtained from DFT calculations for O=V–O–A clusters, where A: V, P, K, Mo, Cr and Ni

Bond lengths (Å)	Bond orders	Atomic charges (a.u.)	Electron transfer (a.u.)
O ‖ 1.60 V —O— V 1.82 1.69	O ‖ 2.28 V —O— V 0.85 1.36	(-0.36) O ‖ (-0.57) V —O— V (0.27) (0.66)	O 0.30 V — O — V 0.27
O ‖ 1.60 V —O— P 1.83 1.60	O ‖ 2.34 V —O— P 0.89 1.24	(-0.34) O ‖ (-0.54) V —O— P (0.16) (0.72)	O 0.38 V — O — P 0.16
O ‖ 1.63 V —O— K 1.68 2.49	O ‖ 2.20 V —O— K 1.75 0.24	(-0.43) O ‖ (-0.65) V —O— K (0.74) (0.33)	O 0.09 V — O — K 0.65
O ‖ 1.62 V —O— Mo 1.85 1.87	O ‖ 2.17 V —O— Mo 0.78 1.21	(-0.44) O ‖ (-0.72) V —O— Mo (0.47) (0.69)	O 0.25 V — O — Mo 0.47
O ‖ 1.62 V —O— Cr 1.87 1.73	O ‖ 2.17 V —O— Cr 0.75 1.16	(-0.45) O ‖ (-0.77) V —O— Cr (0.54) (0.68)	O 0.23 V — O — Cr 0.54
O ‖ 1.63 V —O— Ni 1.76 1.73	O ‖ 2.08 V —O— Ni 1.14 0.77	(-0.47) O ‖ (-0.74) V —O— Ni (0.35) (0.85)	O 0.39 V — O — Ni 0.35

atom (V1) in the cluster by additives, such as Mo, Cr and Ni leads to the formation of the respective A–O2 bond with the typical bond distance (R in a range of 1.7–1.8 Å) and bond order indicating the single bond (BO = 1.21, 1.16 and 0.77, respectively). Analysis of bond lengths indicates also the specific characteristic of bond formed between potassium and oxygen, the K–O bond equal to 2.5 Å being the longest one. All other A–O bonds are of the order of 1.7–1.8 Å; the shortest one (1.6 Å) characterizes the P–O bond. One should stress that the different bond distances are associated with the different strengths of the O–A bond. The short bonds are usually very strong (see vanadyl bond, which is a of a double type), the typical M–O bond is of the order of 1.7–1.8 Å and is characterized by the bond order about 1, whereas very long bonds ($R > 2$ Å) forms weak chemical binding. The interaction between potassium and oxygen, which results in the K–O2 bond of the distance 2.5 Å and BO = 0.24 only, should be associated with the electrostatic interaction rather than with the typical chemical bond.

Substitution of one vanadium atom (V1) in the cluster by additives, such as K, Mo, Cr, and Ni results in increase of the negative charge of about 0.1–0.2e on both bridging and vanadyl oxygen atoms, which is equivalent to increase in oxygen basicity. For the P-substituted cluster the situation is different, the charges on oxygen atoms are practically the same as in the undoped cluster. Therefore, increase in the selectivity to propene for all the additives except P, which is observed in experiments, can be associated with increase in the oxygen basicity, obtained from quantum chemical calculations.

Looking at the acidity of vanadium atoms one can see that the positive charge on V2 atom changes in the presence of dopant; it is considerably lower for cluster substituted with K (positive charge decreases from $q = 0.66$ to 0.33) and distinctly higher for cluster containing Ni (positive charge increases to $q = 0.85$). No evident correlation is found between the selectivity to propene and acidity of vanadium centre.

3.4. Comparison between theory and experimental data

The considerable increase in the activity over P and Mo containing catalysts, observed in experiments (c.f. Table 1) is not reflected in any marked differences of the bond length (i.e. bond energy) or of the charge on oxygen atoms (the presumed centres of the C–H activation) with respect to clusters with other foreign atoms or to the original cluster.

From the experimental data the selectivities to propene can be written in the following sequence:

$$VK(64) > VCr(38) > VMo$$
$$= VNi(32) > VP(28) \sim V0(27) \tag{1}$$

where values in brackets correspond to selectivities (in percent). This sequence, which illustrates decrease in selectivity caused by the introduction of additives, corresponds quite well to sequence (2) illustrating the decrease of charge transfer towards the O=V–O centre (equivalent to the decrease of electron density or, in other words, the decrease in basicity), obtained from the results of quantum chemical calculations:

$$K(0.74e) > Cr(0.54e) > Mo(0.47e) > Ni(0.35e)$$
$$> V(0.27e) > P(0.16e) \tag{2}$$

where numbers in brackets correspond to the number of transferred electrons.

Both experimental and theoretical data underline a specific effect of potassium as additive; experiment indicates its most pronounced selectivity to propene whereas theory points out the fact that out of all the additives K is capable to transfer its electrons not only to the nearest oxygen (O2), but also to vanadyl group ($q_{V=O} \sim -0.1$) leading to the reduction of vanadium. In addition K–O bond seems to result from electrostatic interaction rather than from chemical attraction. Results of other calculations indicate that potassium tends to interact with many oxygen atoms [24].

The results of the calculations confirm then and explain on a molecular scale the hypothesis about the role of acid–base properties in controlling the selectivity in ODH reactions on some vanadia-based catalysts [4]. Again exceptional effect exerted by potassium, observed in both experiment and quantum-chemical calculations should be underlined.

It cannot be excluded that in real catalysts potassium atom may also decrease the Brönsted acidity of the system by replacing hydrogen atom in surface acidic OH groups. The presence of such groups have been observed on vanadia-based catalysts [25,26]. Removal of Brönsted acid centres, which can form sites of non-selective total oxidation [11] would also contribute to the increase in the selectivity to propene. Further experimental studies on the effect of the additives on both Brönsted and Lewis acid sites in the system, now in course [27], as well as deeper theoretical analysis [24] will help to decide between the role of both types of the centres.

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