

Acido-Basic Properties of Selective Oxidation Catalysts – an Overview*

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Various aspects of acido-basic properties of transition metal oxides – catalysts for selective oxidation processes – are reviewed. The acido-basic properties of these catalysts may depend on coordination of the component ions, morphology of oxide crystals and the dispersion of an active oxide phase on a support. The methods for their determination are briefly described and the role of acido-basic properties in controlling the activity and selectivity of selective oxidation reactions is considered.

Key words: oxide catalysts, acidobasic properties

Introduction

Reactions of selective oxidation of organic compounds, in particular of hydrocarbons, on mixed transition metal oxides are used in numerous industrial processes for production of alcohols, aldehydes, organic acids and their anhydrides. The selective oxidation reactions include also oxidative dehydrogenation, ODH of lower alkanes, proposed in recent years as an alternative route to classical dehydrogenation to obtain cheap olefins. The practical importance of these reactions has given in the last 30 years an impetus for numerous fundamental studies, reviewed recently in [1], which aimed at description of the correlations between structure and physico-chemical properties of the catalysts and their performance in the oxidation reactions, and at elucidation of the reaction mechanism. Beside redox properties, the catalysts of selective oxidation processes exhibit also acido-basic properties. It has been shown in numerous cases, that they are capable of adsorbing bases or acids and to catalyse the reactions, which are generally recognized to proceed on acidic centres, such as *e.g.* isomerization of hydrocarbons, dehydration of alcohols and to some extent even cracking of hydrocarbons. These facts encouraged studies and discussions on the role of the acid-base properties of the catalysts in the oxidation reactions reviewed in [2–5].

* Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

The notion of acido-basicity of oxide catalysts comprises the type of the centres (Brønsted or Lewis), their concentration and/or strength and hardness and softness in the sense of Pearson HSBA theory. The approach to the origin of acidity of transition metal oxide systems and the methods to study their acido-basic properties, resemble those of typical acido-basic oxides: the surface cations not fully coordinated and with the excess of charge can adsorb water dissociatively, thus, giving rise to hydroxyl groups, which can be a source of Brønsted acidic or basic centres. Brønsted acid centres have been indeed identified on the surface of some selective oxidation catalysts *e.g.* V_2O_5 [6], V_2O_5/TiO_2 [7] and V–P–O oxide system [8] by registering ammonium or pyridinium ion on sorption of ammonia or pyridine. Transition metal cations exposed on the oxide surface can be considered as Lewis acidic centres, whereas oxide ions O^{2-} as Lewis bases, as proposed by Usanovich [9]. Interactions of a hydrocarbon molecule with such the surface are often compared to typical acid-base reactions. Still, the question arises, whether in the case of transition metal oxides, which catalyse redox reactions involving a one electron transfer, one is entitled to use the notions of the classical Lewis theory, assuming a transfer of an electron pair from or to respective basic or acid centre. When discussing the mechanism of oxidation reactions, the notion of acido-basicity is thus often used as equivalent to electrophilicity-nucleophilicity, acid and base centres being considered as electron (electron density)-acceptor and electron (electron density)-donor centres respectively, without precisising how many electrons are involved in the transfer. The electrophilicity is related to electronegativity of the component cations, whereas nucleophilicity of the oxygen in an oxide to an electron density on oxygen ion, evaluated from the binding energy of 0 1s level in the XPS spectra [10], or from the Auger spectroscopy data [11,12]. Recently, the optical basicity, a parameter which represents the electron donor power of lattice oxygen, has been proposed [13] for description of acido-basic properties of selective oxidation catalysts. It should be observed, however, that intrinsic properties such as *e.g.* electronegativity of component ions or optical basicity, characterize rather the bulk of the catalysts and not the catalyst surface. Such an approach does not preclude the characterization of acido-basic properties selective oxidation catalysts with the methods used for typical acido-basic catalysts, such as *e.g.* adsorption of bases or acids, which involve a transfer of two electrons. These methods have an advantage of characterizing the surface of the catalysts.

Methods of determination of acido-basic properties of selective oxidation catalysts

These methods are essentially the same as those used in studies of typical acido-basic catalysts, based on oxides of main groups elements. The concentration of the acidic centres is usually determined by measuring the amount of adsorbed bases *e.g.* ammonia, pyridine (for acidic centres), of acidic compounds (CO_2 , SO_2) for basic centres, or by measuring the rate of a model, probe reaction. The strength of bonding of model acids or bases to the surface, evaluated from the heat of their adsorption, the desorption temperature in TPD measurements, or the shift of the IR bands of adsorbed

model compounds, is usually taken as a measure of the acid or base strength. The catalysts based on mixed transition oxides possess, however, different characteristics from those based on oxides of main group elements, as summarized in Table 1. These differences may be a source of some limitations set on the methods of determination of their acido-basic properties.

Table 1. Some properties of transition metal oxides – derived catalysts as compared with typical acido-basic oxide catalysts.

Property	Transition metal oxides	Acido-basic oxides
Specific surface area	Low: – 10 m ² /g	High: – 100 m ² /g
Composition	Cations of IV–VIII subgroups, of variable valency <i>e.g.</i> V, Mo, W, Co, Ni	Main groups elements <i>e.g.</i> Si, Al, Mg
Colour	Coloured	White
Electrical properties	Semiconductors	Insulators
Type of bonds	More covalent bonds, ionicity = 40–60% for 3d transition metal oxides	More ionic bonds
Oxide/O ₂ interactions	Labile lattice oxygen: reducibility at temp. ~400°C (bulk) from ~200°C (surface), capable of exchange of gaseous oxygen with lattice oxygen, Me–O bond strength: 50–60 kcal/mole, capable of oxygen chemisorption	Nonreducible at temperatures of catalysis Me–O bond strength: 100 kcal/mole, no oxygen chemisorption
Catalytic activity in:	Redox reaction (oxidation, dehydrogenation)	Acido-basic reactions (cracking, isomerization, dehydration, alkylation)
Acido-basic properties	Weak and medium acid and basic sites	Weak, medium and strong acid or basic sites

Table 2 gives the methods commonly used in acidity studies on selective oxidation catalysts, examples of their applications and their shortcomings.

Table 2. Methods for determination of acidity of selective oxidation catalysts.

Method	Temp. [°C]	Shortcomings	Catalyst Examples	Reference
Titration with bases (Hammett's indicators)	room	Colour limitations, low sensitivity	MoO ₃ , WO ₃	[14]
Sorption of bases, (NH ₃ , C ₅ H ₅ N) 1) static or pulse technique 2) IR spectra	200–300	Low accuracy, possibility of reduction of catalysts	NiMoO ₄ /SiO ₂ V ₂ O ₅ /TiO ₂	[15] [7]
Acidity probe reactions 1) isomerization: a) butene-1 → butene-2 b) 3.3 di Me Bu-1 → 2.3 di Me Bu-1 + 2.3 di Me Bu-2	100–350 100–350	Sensible to oxygen presence Possibility of oxidation of probe molecule Carbon deposit Mechanism uncertain	Telluromolybdates V ₂ O ₅ /TiO ₂ , MoO ₃ /TiO ₂ CoMoO ₄ /MoO ₃	[16] [17] [18]
2) dehydration of alcohols: isopropanol → C ₃ H ₆	200–300		V ₂ O ₅ /TiO ₂	[17,19]
3) cumene cracking	300		V ₂ O ₅ /TiO ₂ Sn-Sb-O	[20] [21]

The requirements of low specific surface area, posed to the catalysts of selective oxidation (in order to avoid undesirable reactions of consecutive total combustion, which may occur in pores of high-specific area catalysts), put some limit to application of the sorption techniques. The amount of adsorbed species is for the low specific area samples at the limit of detectability of several methods *e.g.* of sorption techniques including registration of IR spectra of adsorbed bases. The titration in the presence of Hammett's indicators may be also in many cases non-applicable, due to the fact that most transition metal oxide systems are coloured. Relatively high mobility of the oxide lattice may lead to easy reduction of the oxides, especially at their surface by the probe molecules. These shortcomings can be partly overcome by applying model reactions, which are recognized to proceed on acidic centres of typical acidic catalysts. The acidity-probe reactions, most often used for characterization of acidity of selective oxidation catalysts include: dehydration of alcohols (isopropanol, ethanol), double bond isomerization of olefins and cumene cracking. They have a higher sensitivity than spectral methods, so are useful for characterization of low-specific surface area samples, and can be studied at temperatures close to those of the oxidation reactions. The disadvantage in using them lies in the fact that in most cases their mechanism is not unanimously described. The distinction between the Brønsted and Lewis sites is then often difficult, and moreover the carbon deposit formed, often in olefin reactions, may obscure the measurements. The latter phenomenon can be reduced when using the pulse technique. Another weak point of the acidity probe reactions is the difficulty in interpretation of their data: it is not clear whether the rate of the reaction reflects the number of acidic centres or their strength. The modification of the latter parameter could change the turnover frequency of a centre without changing the number of centres. In principle, by virtue of the Brønsted-Polanyi relationships, the rate of such reactions can be a measure of the acid strength, provided the number of acidic centres and the mechanism of the reaction are the same. This may be the case for instance in comparative studies on a series of isostructural molybdates, or on systems doped with the same amounts of different promoters *e.g.* alkali metals. One can also estimate the strength of acidic centres from the type of model reactions, assuming by analogy with typical acidic oxides that dehydration of alcohols and double bond isomerization indicate the presence of weak acidic centres, whereas cracking of hydrocarbons and skeletal isomerization require a high acid strength [22]. The measurements with the above given different methods have shown that most of the selective oxidation catalysts possess acidic centres of weak or medium strength.

Structure of selective oxidation catalysts and their acido-basic properties

Selective oxidation catalysts are usually complex, mixed oxide systems, in which the oxide components may be arranged in different ways forming monophasic systems (definite compounds *e.g.* molybdates, vanadates or solid solutions of one oxide in another, *e.g.* MoO_3 in V_2O_5) or multiphasic systems (oxides on supports in form of bidimensional monolayers, or tridimensional grains of the dispersed oxide

phase). Moreover, relatively high reducibility of transition metal oxides as compared with oxides of the main group elements, gives rise to the presence of several oxidation states in one system, even in the oxidizing conditions. Cations of lower valency *i.e.* of lower electronegativity should exhibit lower Lewis acidity.

In V_2O_5 – TiO_2 system, for example, we may deal with: a) a solid solution of V^{4+} ions in rutile modification of TiO_2 and V_2O_4 at high temperature of preparation, b) a monolayer of vanadia (V^{5+} ions) phase on anatase TiO_2 (at low concentration of V_2O_5 and low temperature of preparation), or c) TiO_2 and V_2O_5 in contact (at higher V_2O_5 content), the morphology of the latter oxide being modified by epitaxy [23]. The acidity in each of the three situations is different.

The possibility of different modes of arrangement of the same oxide components limits the application for mixed transition metal oxides of the Tanabe's theory of generation of acidity in binary oxides [24], since the basic assumptions of the theory *i.e.*: a) preservation of original coordination of positive elements in mixed oxide and b) coordination of oxygen of major oxide, are fulfilled for transition metal oxide systems only in very few cases *e.g.* solid substitutional solutions.

Similarly, the concept of relating acidity to electronegativity of component ions may be of limited use when comparing various systems, since versatility of structures, different coordination of ions and different ways of joining the unit $Me-O$ polyhedra may influence markedly the electronegativity of ions. Attempts at generalization of acidity data in terms of properties of component ions and explanation of the acidity changes in mixed transition metal oxides systems are then met with severe obstacles. Some general observations on the dependence of the acido-basic properties on structure of mixed oxide catalysts can be, however, made.

For the mono-phasic transition oxide systems the acidity may depend on: a) the coordination of the cations, b) morphology of crystals, c) valency of the constituent cations. Usually, those of lower coordination number exhibit a higher acidity. An example is provided by cobalt molybdate, the low-temperature polymorphic modification α (green) of this compound, in which Mo is octahedrally coordinated, has a lower acidity than high-temperature, (violet) β modification, containing tetrahedrally coordinated Mo [4].

Crystallographic structures of transition metal oxides, usually of low symmetry, and often of layer arrangement give rise to different morphologies of crystals: the different arrangement and bond saturation of atoms on various crystallographic planes may lead to the dependence of acido-basic properties on the crystal morphology. Examples of such dependence are provided by V_2O_5 [25] and MoO_3 [4], for which the crystal faces, exhibiting practically fully saturated (coordinatively and electrically) V^{5+} or Mo^{6+} ions (001 and 010 faces respectively for vanadia and molybdena), exhibit a lower acidity and higher basicity as compared with faces perpendicular to them.

In multiphasic systems, *e.g.* transition metal oxides dispersed on oxide supports, the acido-basic properties depend in the first place on loading with the active phase. The considerable decrease in the acidity as compared with that of the unsupported

phase, was observed for vanadia or molybdena dispersed on titania [4, 26], or chromia on alumina [27] at low loading of these oxides, corresponding to monolayer coverage. The advantageous effect of formation of the monolayer species on the activity and selectivity in oxidation reactions of several supported oxide systems has been reported [28]. The monolayer VO_x species, strongly attached to the support, showed no activity in isopropanol dehydration (no acidity) and exhibited only the dehydrogenating properties [23], whereas for catalysts containing bulk vanadia, the dehydration was the main reaction. It should be noted that in the above cases the pure supports were in the conditions of the probe reaction ~ 10 times less active than the catalysts containing active oxides, thus, the observed effects were due only to the changes in the active phase structure. The considerable decrease in the acidity at low loading for some oxides on the supports can be used as an easy method for identification of the monolayer species formation without recurrence to costly and time-consuming spectral methods of structural characterization of the deposited phase. This method is particularly useful for low specific surface catalysts, for which the spectral methods have low sensitivity.

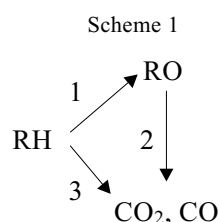
Correlations of catalytic performance in selective oxidation reactions with acido-basic properties

a) Activity. The acid-base couple $\text{Me}^{\text{n}+}-\text{O}^{2-}$ is often considered as an active centre for the activation of a C–H bond in a hydrocarbon molecule, which is a rate determining step (r.d.s.) of the oxidation reactions. Two possibilities can, however, be envisaged assuming heterolytic splitting on such a couple: a) abstraction of a proton on an oxide, basic ion and formation of a carboanion which by donation of electrons to a cation (a Lewis site) is transferred into a carbocation, b) abstraction of a hydride ion H^- on an acidic cationic site with the formation of a $\text{Me}^{\text{n}+}-\text{H}$ bond, and of a carbocation.

In the case of oxidation of olefins the activity was found to increase with the increase in the nucleophilicity (basicity) of the oxide oxygen, determined from electron spectroscopy (XPS or Auger data) [11,12], which supports the first hypothesis. For the alkane oxidation the problem is under discussion. For n-butane oxidation to maleic anhydride on VPO catalysts the dependence of the activity on the nucleophilicity of oxygen was reported [10]. On the other hand, some authors [29,30] bring attention to the strong Lewis acidity, observed for the VPO system, and ascribed to the special environment of V^{4+} ions in this system, claiming path b as determining the activity in the alkane oxidation. No experimental correlation between the strength of the acidic centres and the activity has been, however, reported. The correlation between the catalytic activity in the propane ODH and the number of acid sites, observed *e.g.* for the MgMoO catalysts of different Mo/Mg ratio, was assumed to indicate the involvement of the acid centres in the reaction [31]. The correlations of this type cannot, however, constitute a proof for the direct participation of acid centres in the activation of a hydrocarbon. They reflect only the fact, that it is the transition metal cation (Mo), which is involved in an active site for both the oxidation and the sorption of bases.

The quantum chemical calculations show that the activation of the C–H bond occurs by a concerted mechanism [32,33]. The flow of electrons (electron density) from a hydrocarbon molecule to empty d orbitals of the metal cation modifies the strength of the bond and the charge on the molecule atoms, thus, making possible the abstraction of a hydrogen atom by oxide ions of a catalyst. Simultaneously the alkyl group formed is attached to a neighbouring oxide ion forming an alkoxy species. No formation of a Me–H bond has been found in these calculations, which excludes path b. It seems then more appropriate to consider the electron density around the ions constituting the oxide catalyst as a parameter inherent for a solid. Depending on the type of species reacting with the solid the changes in the electron density may vary from very small to the transfer of two electrons, required in typical acid-base reactions. It is difficult to conceive the transfer of a pair of electrons in the case of oxidation reactions, since hydrocarbons possess rather weak acid-base properties. Such a transfer may, however, occur when molecules of stronger acid-base character (ammonia, CO₂) interact with the surface.

b) Selectivity. Oxidation reactions of hydrocarbons, RH follow a general parallel-consecutive scheme shown below, in which RO denotes a selective oxidation product (an olefin, alcohol, aldehyde, organic acid, which can be also formed consecutively).



Scheme 1 suggests that the selectivity to partial oxidation products depends on the relative rates of consecutive (2) and parallel (3) routes of formation of undesirable carbon oxides CO_x to the rate of step (1), in which the selective product is formed. In oxidation of hydrocarbons to aldehydes and organic acids or anhydrides step 2 is usually slow, due to much smaller reactivity of the reaction products with oxygen as compared with that of the initial hydrocarbons. The small amounts of CO_x are due then to step (3). On the other hand in oxidative dehydrogenation reactions of alkanes to olefins, these latter are oxidized much faster to carbon oxides than the substrates, and the main source of carbon oxides is consecutive oxidation of olefins (step 2). In terms of a rake mechanism [34] the formation of a given product in a succession of reactions: saturated hydrocarbon – olefin – alcohol – aldehyde – organic acid or anhydride – CO_x, the selectivity to a given product depends on the relative rates of its desorption to its further surface reaction.

Kinetics and energetics of the sorption – desorption of the reaction products can be controlled by Lewis acid-base properties as suggested by Ai [2]. In general terms olefins and dienes (considered as basic molecules) should be adsorbed strongly on acidic sites, and only weakly on basic sites, whereas organic acids and anhydrides

only weakly on acidic and strongly on basic centres. A catalyst selective for formation of olefins or dienes in the ODH reactions should then possess a low acidity (low concentration and strength of acidic centres) and a high basicity to facilitate desorption of the products before they undergo further consecutive reactions. On the other hand, a catalyst selective to acidic products should be characterized by low basicity and high acidity. Mixed oxide systems containing vanadium provide an example of applicability of this approach: VPO catalysts of high acidity and low basicity are selective in the formation of maleic anhydride, while basic VMgO catalysts in the olefin formation in the ODH reactions. Several studies on the effect of the alkalis additives, in particular of potassium, to the supported vanadia catalysts indicate, that indeed the decrease in the acidity observed for the alkalis-doped systems is accompanied by the increase in the selectivity to propene in the ODH of propane, or n-butane [35–37]. The decrease in the heat of adsorption of propene, observed for the alkali-doped vanadia catalysts [38], confirmed, that the increase in the selectivity is due to weaker adsorption of the olefin on the less acidic surface. It should be, however, observed that for the same catalysts the potassium additive has no effect on the selectivity to ethene in the ODH of ethane [37]: the absence of such effect has been ascribed to the lower basicity (nucleophilicity) of ethene, as compared with that of propene or n-butene. The latter facts confirm that the selectivity-acidity correlations can then depend on the type of the oxidized hydrocarbon molecule and of the products obtained.

Table 3 presents, after [4], the acidity determined from the rate of isopropanol dehydration (a probe of weak acidic centres) and of cumene cracking (strong centres) of two groups of oxide catalysts: a) catalysts yielding selectively the products of the first steps in oxidation of different hydrocarbons *i.e.* aldehyde, or dienes (bismuth molybdate, cobalt telluromolybdate, tin-antimony mixed oxide and b) catalysts which yield the acidic products (cobalt molybdate, vanadia – based catalysts). As seen, the catalysts producing mainly acidic products exhibit a much higher concentration of weak acidic centres, and generally possess more of strong acidic centres, as compared with group a), in agreement with the general hypothesis

Table 3. Type of products of hydrocarbon oxidation reactions for catalysts of different acidities.

Catalyst	Isopropanol dehydration 10^7	Cumene cracking 10^8	Products of oxidation of:		
	[mole/m ² s]		C ₃ H ₆	C ₄ H ₈	o-xylene
Bi ₂ (MoO ₄) ₃	1.4	1	Ald	BD	Ald
CoTeMoO ₆	0.6	tr	Ald	BD	Ald
Sn-Sb-O	0.5–1.0	1–2	Ald	BD	Ald (PA)
Co-Mo-O	5–11	0.1–0.5	Acid (Ald)	BD (MA)	PA (Ald)
V ₂ O ₅	20–30	5–8	CO ₂	CO ₂ (MA)	PA
V ₂ O ₅ - 20% TiO ₂	10	1.4	CO ₂	MA	PA
Ald – aldehyde	MA – maleic anhydride		() – minor product		
BD – butadiene	PA – phthalic anhydride				

mentioned above. No information about basic centres in these two series of the catalysts is available to allow for the more advanced discussion of the problem on the molecular scale. Still the data on the correlation of the selectivity on the catalyst acidity can be useful for selection of the type of catalyst for a given reaction, or for improvement of the existing catalysts by introduction of the additives.

Besides controlling the desorption processes in the consecutive steps of the oxidation, the acid centres may affect also the parallel route of formation of carbon oxides (step 3). At low conversions of hydrocarbons, at which the contribution of the parallel route is more evident, the increase of the selectivity to partial oxidation products with the decrease in the acidity was observed for several cases, even if the products were of acidic character (*e.g.* oxidation of *o*-xylene to phthalic anhydride on vanadia-titania catalysts doped with alkalis [20,39]). To explain this fact one may propose that the parallel route involves hydrocarbon molecules strongly bound on the acidic sites, which react directly to carbon oxides. On the other hand, the addition of protons derived from the Brönsted centres to a hydrocarbon molecule may lead to typical acidic reactions *e.g.* cracking *via* the carbocation route, the broken fragments of the initial molecules being easily oxidized in the oxygen presence to carbon oxides.

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