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On the role of acidity in catalytic oxidation

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Abstract

The role of the catalyst surface acid–base properties on the heterogeneously-catalyzed oxidation reaction mechanisms is discussed. Acid–base properties depend on the covalent/ionic character of the metal–oxygen bonds and are involved in some steps of the oxidation reactions, such as the activation of the C–H hydrocarbon bonds, the step associated with the evolution of alkoxide species and the desorption/overoxidation of the partial oxidation products. Thus they participate with the cation redox properties in determining the selective/unselective catalyst behavior.

Keywords: Oxidation; Catalytic oxidation; Acidity

1. Introduction

Hydrocarbons arising (directly or indirectly) from petroleum or from natural gas are the feedstocks of petrochemistry [1,2]. Several petrochemical processes involve a partial oxidation of a hydrocarbon molecule that is mostly carried out using oxygen or air as the oxidizing agent and a complex metal oxide as the heterogeneous catalyst. The direct use of alkanes as the feedstocks would be desirable, but is frequently not possible, so that olefins must previously be produced by cracking or dehydrogenation processes. Partial oxidation of organics other than hydrocarbons (like alcohols, aldehydes,....) also play an important role in petrochemistry. In all cases the total oxidation of the reactant organic compound to CO_x is the main side-reaction to be avoided in partial oxidation processes.

All authors agree that partial oxidation of organic compounds almost exclusively involves redox cycles during which lattice oxygen oxidizes the organic molecule leaving a reducing center that is reoxidized by O_2, i.e. the so-called Mars–van Krevelen mechanism [3–6]. On the contrary, authors disagree on the role of 'electrophilic' adsorbed oxygen (O_2, O_2^- or O^-) in total oxidation [3–8], while the details of the activation mode of C–H hydrocarbon bonds are also under debate.

Transition metal oxides also carry surface acid-base properties [9,10] and some authors have attempted to relate these properties with activity or selectivity in oxidation reactions [9]. Attempts to develop quantitative relations and a classification of metal oxides for catalytic oxidation have also been proposed [11,12].

In the past, considerable efforts have been devoted in our laboratory to the characterization of acid–base properties of oxide materials. Moreover, the mechanisms of several heterogeneously-catalyzed oxidation reactions have also been investigated, mainly using IR spec-

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troscopy. In this paper some of these data will be summarized and some ideas on the role of acid–base properties of metal oxide catalysts with respect to their behavior as oxidation catalysts will be proposed.

2. Experimental

Surface characterization studies and mechanistic studies have been performed mostly by FT-IR spectroscopy. The IR spectra were recorded with a Nicolet Magna 750 and with a Nicolet 5ZDX Fourier transform instruments, using pressed disks of the pure catalyst powders, in an heatable cell connected to a conventional gas-handling system. Activation before adsorption experiments was carried out by outgassing at 573–773 K, in different cases. The conditions of the catalytic reactions were simulated in the IR cell. The results have been compared with those obtained in a flow reactor under different temperature and feed composition conditions.

3. Results and discussion

3.1. *The surface acidity–basicity of metal oxides*

3.1.1. *Basic concepts*

In Table 1 the surface acid–base properties of binary metal oxides are summarized and they are tentatively correlated to the charge and size of the corresponding metal cations.

According to basic inorganic chemistry [13,14], the oxides (i.e. the compounds of an element with oxygen) can have a basic, an amphoteric or an acidic character. In this view, metal oxides (i.e. the oxides of the electropositive elements) are generally referred to as 'basic' or 'amphoteric'. The oxides of non-metals (the highly electronegative elements) are instead referred to as acidic oxides or anhydrides. Oxygen is one of the most electronegative elements. Thus, its bond with metals is very ionic, and this gives rise to the basic nature of oxides and hydroxides. On the contrary, the bond of oxygen with non-metals is more or less covalent, and this gives rise to the acidic nature of anhydrides and oxo-acids. On the other hand, in the Sanderson's approach [11–15], the actual electronegativity of an ion increases with its oxidation state. Thus, the oxides of metals in an high oxidation state (e.g. Mn^{VII+}, Cr^{VI+}, Mo^{VI+}, W^{VI+}, V^{V+}, Nb^{V+},...) like those of some semimetals (e.g. silicon as Si^{IV+}) are characterized by covalent M–O bonds and behave as anhydrides too, in contrast to the lower metal oxides that are typically 'basic' oxides.

These considerations refer to the 'bulk' chemistry of the oxides and 'acidity' refers to the Brønsted acidity of the M–O–H groups of hydroxides and oxo-acids in aqueous solution, that depends on the covalency of the M–O bond and on the number of oxygen atoms where the negative charge of the anion resulting from dissociation can be delocalized. Accordingly, the acidity in water for oxo-acids follows the trend $HMO_4 > HMO_3 > HMO_2 > HMO$ [13,14].

According to our characterization experiments, similar considerations apply also to the surface properties of solid metal oxides. The oxides of low-oxidation state metals are highly ionic, and this gives rise, when the surface is clean, to surface coordinatively unsaturated metal cations (able to act as Lewis acid sites), and oxide anions (able to act as basic and/or nucleophilic sites). The strength of the surface Lewis sites depends, accordingly, on the ionicity of the M–O bond and, also, on the polarizing power of the cation (charge to ionic radius ratio) and, inversely, from its overall coordination (the lower the coordination the higher the Lewis acid strength). When in ionic oxides the cation is very small, highly charged and can have small coordination, Lewis acidity predominates (e.g. transitional aluminas). When the cation has low charge and big size, the basicity predominates (e.g. BaO). Also, the surface of metal oxides can be partly covered by the frag-

Table 1
Tentative summary of the acid–base properties of binary metal oxides

Element	Oxidation state	Cation size (radius [a], Å)	M–O bond nature	Acidity type	Acidity strength	Basicity, nucleophilicity	Examples
Semi-metal	$\geq 3+$	Small ≤ 0.4	Covalent	Brønsted	Medium-weak	None	B_2O_3, SiO_2, P_2O_5
	High $5+-7+$	Small to medium 0.3–0.7	Largely covalent	Brønsted Lewis	Medium to strong	None	WO_3, MoO_3, CrO_3, Ta_2O_5, Nb_2O_5, V_2O_5
Metal	Medium $3+-4+$	Small 0.35–0.5	Ionic	Lewis	Strong	Weak	γ-Al_2O_3, β-Ga_2O_3,
		Medium 0.5–0.6		Lewis	Medium	Medium-weak	TiO_2, Fe_2O_3, Cr_2O_3,
		Large 0.7–1.2		Lewis	Medium-weak	Medium-strong	La_2O_3, SnO_2, ZrO_2, CeO_2, ThO_2 (Bi_2O_3, Sb_2O_3).
	Low $1+-2+$	Large to very large 0.7–1.5		Lewis	Medium to very weak	Strong to very strong	MgO, CaO, SrO, BaO, CoO, NiO, CuO, ZnO, (Cu_2O)

[a] Data from R.D. Shannon and C.T. Prewitt, Acta Crystallogr., B25 (1969) 925.

ments arising from water vapour dissociative adsorption, i.e. the surface hydroxy-groups. However, for ionic oxides such surface hydroxy-groups are just ionically bonded to metal cations, and have, as for metal hydroxides, basic rather than Brønsted acidic behavior.

Conversely, the oxides of semi-metal elements (like silica) are largely covalent, and no coordinative unsaturation is present at their surface in normal conditions (i.e. in the absence of very strong pretreatments) because surface OH groups saturate the coordination of the semimetal atoms at the surface. Thus, they do not show neither Lewis acidity nor basicity, while surface hydroxy-groups are more or less Brønsted acidic.

The oxides of high-oxidation state metals are also characterized by weak or no basicity. However, the cations tend to associate with some oxide ions giving rise to metal–oxygen 'double-bonds' (vanadyl-, wolframyl-, molybdenyl-cations...) whose coordination is very elastic. So, in spite of the covalency of metal–oxygen bonds, strong Lewis acidity can appear. The OH's are covalently-bonded to the metal and the anion charge resulting from dissociation are delocalized on terminal 'doubly-bonded' oxygens. Thus, medium to strong Brønsted acidity appears.

In Table 2 the behavior of transition metal oxides in catalytic oxidation have been tentatively summarized. To have a consistent set of data we used those reported several years ago by Germain and co-workers [16] concerning the oxidation of propene, toluene, benzene and ammonia. Selectivities are related to the production of acrolein, benzaldehyde and benzoic acid, maleic anhydride and molecular nitrogen in the four cases, respectively. Looking at data from other sources too, the summary reported in Table 2 seems quite consistent. Highly ionic metal oxides with highly reducible cations generally behave as total oxidation catalysts, although some of them can have a selective behavior in oxy-dehydrogenation reactions. Metal oxides applicable in selective oxidation catalysis mostly involve transition metals in a high oxidation state, like pentavalent vanadium and hexavalent molybdenum and tungsten. The simple oxides V_2O_5, MoO_3 and WO_3 are, according to the above considerations, acidic oxides or anhydrides. It has been shown that they are Brønsted and Lewis acidic materials, with negligible surface basicity [17–19].

3.1.2. Evolution of the surface acid–base properties with reduction

According to the above considerations, it is obvious that the surface acid–base properties of transition metal oxide are also strongly sensitive to their oxidation state. A typical example is that of chromia and chromites [7,20] which, when oxidized, are covered by chromate species characterized by covalent $Cr^{6+}=O$ bonds (stretching frequencies 1050–800 cm^{-1}) and show Brønsted acidity and negligible basicity. The reduced surfaces of chromia and metal chromites are instead characterized by very ionic Cr^{3+}-O bonds (stretching frequencies below 700 cm^{-1}) without Brønsted acidity but with significant basicity and nucleophilicity. This trend is what is expected by reduction of any metal oxide to lower oxides, that results in lower electronegativity and higher cation size. The modification of the catalyst acid–base properties is also involved when the process variable conditions are converted to less oxidant.

3.1.3. The so-called 'mixed oxides'

Real oxidation catalysts are generally more or less complex materials and are sometimes called 'multicomponent' catalysts. In the simpler cases a main compound is assumed to be the real catalyst (Table 3), the others being activators or promoters. The main compound is frequently assumed to be a 'mixed oxide', i.e. an oxidic material composed by at least two elements, not always two metals.

Strictly speaking 'true' mixed oxides are only those where two metals with a similar oxidation state and electronegativity are involved in the oxy-compound, i.e. the mixture of two 'basic'

Table 2
Catalytic behavior of binary oxides in hydrocarbon and ammonia oxidation

Group	Activity	Selectivity	Oxides	Cation reducibility	M–O character	Acidity type	Acidity strength	Nucleophilicity
A	High to very high	Low to medium	Co_3O_4, Cr_2O_3, Fe_2O_3, MnO_2, NiO, CuO,	Strong	Highly ionic	Lewis	Medium-weak	Strong to medium
B	Medium high	Medium to low	TiO_2, SnO_2, ZnO, ThO_2	Weak	Ionic	Lewis	Medium	Medium
C	Medium to low	High	V_2O_5, MoO_3, WO_3	Medium	Covalent	Brønsted + Lewis	Strong	Weak
D	Very low	Medium	Sb_2O_4, Nb_2O_5, Ta_2O_5	Medium-weak	Partly covalent	Brønsted + Lewis	Strong	Weak
E	Very low	Very low	Bi_2O_3, ZrO_2,	Very weak	Ionic	Lewis	Medium	Medium

Table 3
Types of mixed oxides used in heterogeneous oxidation catalysis

Type	M–O bond nature	Redox component	Example	Reaction	Redox mechanism [a]
‘True’ mixed oxides	ionic	none	Li_2O-MgO	methane → ethene	NO
		both	$CoCr_2O_4$	combustion	YES
		one	$MgFe_2O_4$	butene → butadiene	YES
	covalent	both	V_2MoO_8	benzene → maleic anhydride	YES
		one	V-silicalite	propane → propene	
Salts	covalent oxo-anion	cation	$(VO)_2P_2O_7$	butane → maleic anhydride	YES
	ionic with cation	oxo-anion	$Mg_3(VO_4)_2$	butane → butadiene	YES
		both	$Fe_3(MoO_4)_2$	methanol → formaldehyde	YES
		none	ZrP_2O_7	ethylbenzene → styrene	NO
Oxide-supported oxides	covalent on ionic	none	B_2O_3-Al_2O_3	ethane → ethene	
		both	V_2O_5-TiO_2	*o*-xylene → phthalic anhydride	YES
		supported	V_2O_5-Al_2O_3	naphthalene → phthalic anhydride	YES
	covalent on covalent	supported	MoO_3-SiO_2	ammonia → nitrogen	YES

[a] YES means that the reaction occurs with a Mars–van Krevelen-type mechanism.

oxides giving rise to an ionic mixed oxide, or of two anhydrides giving rise to a covalent mixed anhydride. The product of the combination of a basic oxide with an anhydride is rather a salt. The crystal structures of mixed oxides and of salts are frequently not directly related to those of the component oxides and their acid–base properties are sometimes dominated by one of the two ‘components’ like we observed in the cases of spinels, perovskites and ilmenites [21–23].

Another type of mixed oxide is that of oxides supported on oxides, where frequently the carrier oxide plays a key role in determining the optimal properties of the catalyst, that cannot be attributed to the supported oxide only. In some cases the amount of the supported oxide is only sufficient to cover the surface with a monomolecular layer of surface complexes, called ‘monolayer’. Often, even in the presence of supported oxide in excess, the ‘monolayer’ is the active catalyst species.

The acid–base properties of the ‘mixed oxides’ obey the same rules for binary oxides and

Table 4
Acid–base properties of ‘mixed oxides’ as determined by experimental data

Types	Structures compunds	Brønsted acidity	Lewis acidity	Basicity	M–O bond type	‘Acidic’ component	‘Basic’ component	Ref.
‘True’ mixed oxides	Rock-salt solid solutions	no	weak	strong				
	Corundum solid solutions	no	medium	medium				
	Spinels AB_2O_4	no	medium-strong	medium	ionic	no	both	[21]
	Ilmenites ABO_3	no	medium-strong	medium	+ ionic			
	Perovskites ABO_3	no	weak	strong				[22,23]
‘Salts’	GeP_2O_7	yes	no	no	covalent	both	no	[24]
	$(VO)_2$ P_2O_7	yes	medium-strong	no	+ covalent	strong	weak	[24]
	Ti P_2O_7	yes	medium-strong	no	covalent	strong	weak	[25]
	Ti-silicalite, TiO_2 in SiO_2	weak	strong	no	+ ionic	medium	weak	[26,27]
	$Mg_3(VO_4)_2$	no	weak	medium		medium	strong	[28]
Supported oxides	V_2O_5-TiO_2, Nb_2O_5-Al_2O_3 ‘monolayers’ or more	yes	medium-strong	no-medium	covalent on ionic	supported	support	[29]

somewhat parallel the behaviour of salts to hydrolysis: i.e. the compounds arising from strong acids and weak bases are acidic, while the compounds arising from strong bases and weak acids are basic. The results of some characterization studies performed by our group on 'mixed oxide' surfaces are summarized in Table 4.

3.2. The reaction pathways upon selective and total oxidation

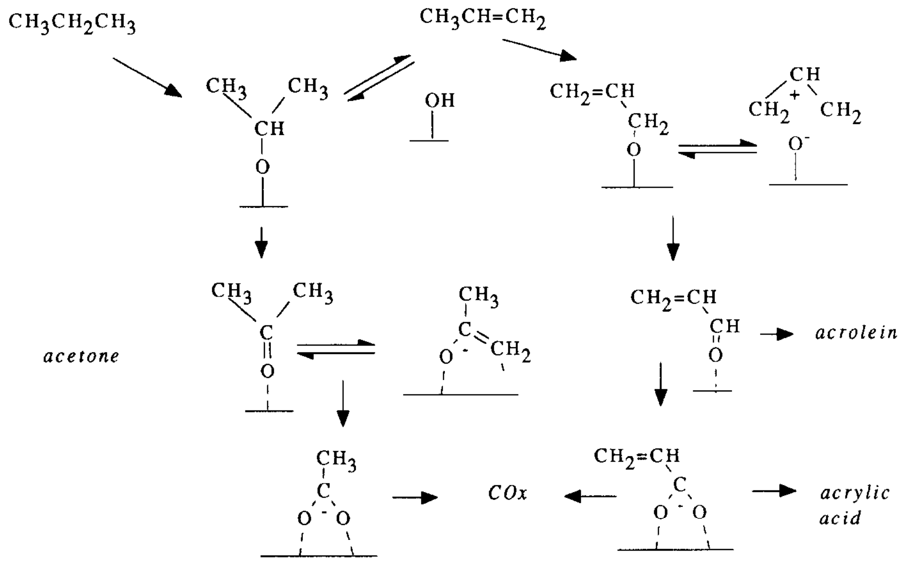
We previously investigated the reaction pathways of C_1, C_3 and C_4 organic compounds (hydrocarbons and oxygenates) at the surface of both partial and total oxidation catalysts [7,8,30,31] and we concluded that partial oxidation occurs also at the surface of combustion catalysts, although in this case overoxidation of the partially oxidized products also occurs. Another conclusion from our studies is that the same oxygen species (i.e. nucleophilic or lattice oxygen) could be involved in both partial and total oxidation. It seems reasonable to propose that some steps in the pathway, i.e. among perhaps others, the desorption of the products, the evolution of intermediate alkoxides and the activation of the reactant, are largely influenced by the acid–base properties of the catalyst surface. In the case of C_3 hydrocarbon oxidation we proposed the general pathway reported in Scheme 1.

3.3. The surface acidity–basicity and the desorption of partial oxidation products

A key factor for performing selective oxidation catalysis is to allow the desired product to desorb without further transformation and overoxidation. So, the catalyst should not react too strong with these compounds.

3.3.1. Production of carbonyl compounds and nitriles

Carbonyl compounds and nitriles carry electrophilic carbon atoms that are susceptible of nucleophilic attacks (those bonded to oxygen or nitrogen) [32]. Moreover, they can carry hydrogens at their α position so that they can undergo base- or acid-catalyzed enolization at the surface with the production of strongly bound



Scheme 1. Surface reaction pathway for propane and propene oxidation over metal oxides.

enolate anions. As a matter of fact, carbonyl compounds and nitriles actually obtained with relevant yields by selective oxidation and ammoxidation are those that cannot undergo enolization and that have weakly electrophilic carbon atoms, mainly due to charge delocalization. They are formaldehyde, acrolein, methacrolein, benzaldehyde, acrylo- and benzo-nitriles [4,5]. On the contrary, carbonyl compounds that can undergo enolization and have not α,β-unsaturations (like acetaldehyde, acetone, acetonitrile) cannot be produced with high yields by heterogeneously catalyzed (amm)oxidation.

On the other hand, looking at the tables above it seems quite evident that most partial oxidation catalysts are predominantly characterized by quite covalent M–O bonds, with consequently low surface nucleophilicity and /or basicity. We found experimentally that acrolein (the desired product of propene partial oxidation) is adsorbed almost intact over the rather selective catalysts MoO_3-TiO_2 and V_2O_5-TiO_2 [33,34], while acetone and acetaldehyde immediately enolize over them [34]. On less selective catalysts, like Co_3O_4 [8] and $MgCr_2O_4$ [7] also acrolein immediately undergoes nucleophilic attack and oxidation to strongly bonded acrylate species and is finally overoxidized. Similarly, we found that acetonitrile easily gives rise to enolate anions on some oxide surfaces where acrylonitrile is adsorbed intact [35].

3.3.2. Production of carboxylic acids and their anhydrides

It seems quite obvious that the catalysts employed to produce acids or anhydrides cannot be strongly basic. In fact, these compounds are adsorbed strongly in the form of carboxylate ions over basic catalysts. Accordingly, the catalysts for the oxidation of acrolein to acrylic acid are mixed anhydrides (V-Mo mixed oxides) while those employed for the oxy-dehydrogenation of isobutyric acid to give metacrylic acid are the salts of heteropolyacids, that are very strong acids. The catalysts for the production of maleic anhydride (VPO catalysts from butane, V–Mo–O from benzene) are also definitely acidic. Less pronounced (although still dominant) is the acidity of the V_2O_5-TiO_2 catalysts (above a complete 'monolayer' of V_2O_5) employed for the synthesis of phthalic anhydride from *o*-xylene (see Table 4), according to the very high product stability.

3.3.3. Production of olefins through oxy-dehydrogenation

As it is well-known from basic organic chemistry, olefins are very reactive towards electrophiles and in particular Brønsted acids. We previously emphasized the role of weak Brønsted acidity in favouring combustion of olefins through 'oxyhydration' (hydroxylation followed by oxidative dehydrogenation) to ketones and successive by enolization [31]. So, necessarily, Brønsted acid catalysts cannot be used to produce olefins with high selectivity.

Accordingly, the catalysts for butene oxy-dehydrogenation are, in fact, ionic mixed oxides (like ferrites) while those proposed for light alkanes dehydrogenations have the acidity of their main component (V_2O_5) neutralized by other components, like for Mg-vanadates, K-doped vanadia-titania and V-SnO_2 solid solutions [36].

3.4. The surface acidity–basicity and the evolution of the intermediate alkoxide species

According to our data, both on very active and poorly selective catalysts like Co_3O_4 and $MgCr_2O_4$ [8] and on poorly active and highly selective catalysts like heteropolyacid salts [37] the activation of the hydrocarbon C–H bonds gives rise first to surface alkoxide species. On $MgCr_2O_4$ the active site is constituted by chromate ions at the surface of the oxidized catalyst. This behavior parallels that of chromic acid in water solution as an oxidant of C–H bonds of alkanes, giving rise to alcohols [1]. Secondary alkoxides can evolve in two different ways, either by oxy-dehydrogenation giving rise to ketones (that, if they have hydrogens in α position enolize and finally burn) or by elimination giving rise to olefins and surface hydroxy-groups. Thus, the alkoxide evolution plays role of a 'selectivity determining step' [36] among total oxidation and selective oxy-dehydrogenation. Tertiary alkoxides can either by oxidized by C–C bond breaking or eliminate to the branched olefin. Allyloxy- and benzyloxy-species, arising from propene and toluene oxidation, respectively, cannot eliminate. Thus, they give rise easily to the unsaturated aldehydes like acrolein and benzaldehyde. This is another reason why these compounds can be produced with relevant yields by heterogeneously-catalyzed partial oxidation. Surface alkoxides have a carbocationic character that increases with the catalyst Brønsted acidity. Allyloxy- species arising from propene oxidation on molybdates have the character of symmetric allyl cations.

3.5. The surface acidity–basicity and the activation of C–H hydrocarbon bonds

According to our proposal [7] the activation of C–H hydrocarbon bonds (that is generally believed to be rate-determining for the overall process) could occur through the interaction of the σ or the σ* C–H orbitals with d-type orbitals of a transition metal cation at catalyst surface. This interaction should give rise to a direct flow of a couple of electrons from the reductant (the hydrocarbon) to the oxidant (the cation), leaving a proton and a carbocation, that give rise to an hydroxy- and an alkoxy-group, respectively, by interacting with lattice oxygens.

As a matter of fact, the C–H bond which is actually broken first in every hydrocarbon is the weakest one (i.e. that associated to the weaker dissociation energy), as shown in Table 5. In any case, the interaction between C–H groups and the cations previous to the bond rupture could have a role in the kinetics of the process. For this reason, attempts have been made to correlate the treshold oxidation temperature we obtained with molecular properties calculated with accurate ab initio methods. In particular, atomic point charges in hydrocarbons have been computed with different methods.

Table 5
C–H bond dissociation energies, atomic charges on hydrogens and threshold oxidation temperature of hydrocarbons on $MgCr_2O_{4+x}$

Hydrocarbon	E_{diss} (kcal/mol) [a]	Atomic charge CHELPG	Threshold oxidation (K)
C_6H_5–H	110		623
CH_3–H	104	+0.087	773
CH_3–CH_2–H	98	+0.002	473
$(CH_3)_2$CH–H	95	−0.051	423
C_2H_5–(CH_3)CH–H	< 95 [b]		423
$(CH_3)_3$C–H	92	−0.088	423
CH_2 = CH–CH_2–H	88	+0.021 av	373
C_6H_5–CH_2–H	85	+0.066 av	423
CH_2 = CH–(CH_3)CH–H	< 88 [b]		300

[a] From [32].

[b] Our estimates; av = average values.

Atomic point charges have been calculated at the Hartree–Fock + MP2 level with a 6-31G** basis set according to three different methods: Mulliken population analysis, NBO population analysis and from the fit of the molecular electrostatic potential (CHELPG).

Poor correlation is found between our data and the charges on the H atoms derived from the two population analysis methods. Instead, the correlation with the electrostatic potential derived charges can be interesting. These charges are obtained by fitting the electrostatic potential generated by the calculated electron density and can be regarded as the best indicators of how the molecule is 'seen' from outside and how it interacts with external polarizing fields produced at the catalyst surface. The calculated charges at hydrogens are positive for methane, nearly neutral for ethane, and convert to negative for the methylene group of propane and for the methine group of isobutane. Interestingly, catalysts used for methane oxidative coupling and ethane dehydrogenation are essentially basic while activation of higher hydrocarbons occurring at methylenes and methines (oxidation, oxy-dehydrogenation or isomerization) are acidic in nature. In the former reactions the catalyst should abstract positive hydrogens, while in the latter they should abstract negative hydrogens. However, for unsaturated compounds like propene and toluene the calculated charges at methyl groups are positive too.

Additional calculations have been performed for hydrocarbons upon polarization by a closed shell cation. To model this interaction of hydrocarbons with cationic centers the ion Na^+ has been chosen. Such calculations indicate that, upon this interaction, the charge at the hydrogen is always converted to negative and increased in absolute value.

In any case, it can be remarked that the activity trend in C–H bond breaking is also quite well correlated to the stability of the carbocations that can be formed by an heterolytic dissociation, that follows the trend: benzyl ≈ allyl > *tert*-butyl > isopropyl > ethyl > methyl. These data support (or at least do not disagree with) our proposal that the C–H bond breaking consists of a direct oxidation of the hydrocarbon C–H bond by the transition metal cation. It seems reasonable to correlate for related catalysts the activity in catalytic oxidation (assuming the C–H bond breaking step to be rate determining) with the Lewis acidity of the active cation, like we proposed by comparing acidities and activities of vanadia-based catalysts in butane oxidation [31].

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