

X-ray Photoelectron Spectroscopy and Heterogeneous Catalysis, with Elimination Reactions as an Example

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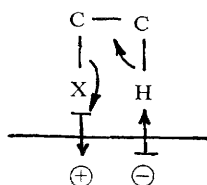
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Assuming that the EPA and EPD strength of catalytically active surface sites is the major factor responsible for catalytic properties, XPS is shown to be a powerful tool for estimating this factor and for predicting (or interpreting) the activity and selectivity of catalysts. This is illustrated with examples taken from elimination reactions. The dehydration activity of MgHPO_4 is higher than that of MgSO_4 , corresponding to the higher Mg $2p$ binding energy and hence higher EPA strength of Mg. The selectivity of oxides for production of terminal olefins from alkan-2-ols, and for dehydrogenation, is related to a high EPD strength of oxygen (low $1s$ binding energy). The tendency of spinels to an E2 mechanism is higher than that of alumina, in accordance with the higher Al $2p$ binding energy and hence higher EPA strength in alumina. In zeolites, the high EPA strength of the exchangeable cations must be considered a decisive factor in the high catalytic activity.

In the transition state of a catalytic process, atoms of the reactant must be bound to atoms in the surface of the solid and this point-to-point, atom-to-atom bonding of surface and reactant should be, according to Heinemann,¹ a most important factor in research. Provided the structure of the transition state is known or reasonable assumptions are possible, the catalytic properties of the solid should depend mainly upon two characteristics of the surface atoms (which may be called active sites or centres) involved in the bonds: the bond forming capacity (and hence the interaction strength) and the accessibility. This paper will be concerned mainly with the bond forming capacity, using elimination reactions as the main example, since a detailed picture has been developed in this field recently.² Within this picture, the bond forming capacity of the catalytically active sites is considered to be fundamental to understanding the catalytic behaviour and it will be shown that X-ray photoelectron spectroscopy (XPS) is a powerful tool for estimating this quantity.

The picture can be summarised as follows. The adsorption structure (I) has been found to account best for the catalytic results:



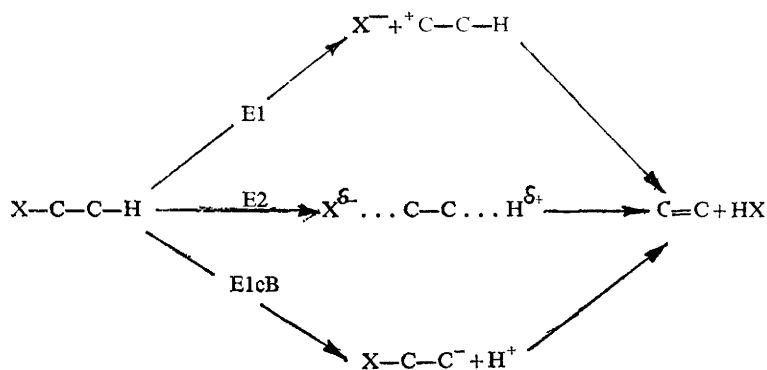
I

The bond rupture is considered to be heterolytic, *i.e.* the leaving groups X and H are abstracted as ions X^- and H^+ (in all cases to be discussed here X is more electronegative than H), and the binding electron pair is taken over by one of the atoms to be separated. Both X^- and H^+ interact with the catalyst surface, both interactions

being coordinative or EPA-EPD interactions (EPA = electron pair acceptor, EPD = electron pair donor). The EPD X has to interact with an EPA site at the surface, which usually is a cation, whereas the EPA H interacts with an EPD site, an anion. So at least two interactions should occur between the reactant and the catalyst and both EPA and EPD sites are required as proposed by Pines,³ Figueras,⁴ Mochida,⁵ Krylov⁶ and other authors. Every cation-anion pair in the surface is capable of being an active centre provided it is accessible. The activity as well as the mechanism, which is closely related to the selectivity, should depend upon the EPA strength and EPD strength of these centres. (EPA and EPD strength is a more precise expression for what was called bond forming capacity and interaction strength above).

Recently Gutmann⁷ presented many examples where the formation of a coordinative bond weakens adjacent bonds. So the C—X bond is weakened by the interaction of X with an EPA site of the catalyst and the C—H bond by interaction with an EPD site. Of course this weakening effect, which in our opinion is the key to understanding catalysis, increases with increasing EPA and EPD strength.

Three possible mechanisms are usually distinguished, which are termed E1, E2 and E1cB and differ in the timing of the bond rupture.



Taking into account the weakening effect, the mechanism also depends upon the EPA and EPD strengths of the surface sites. Although an absolute prediction of the mechanism is difficult it should be possible to predict variations of the mechanism when the EPA and/or EPD strengths of the catalytic sites are varied, provided this variation can be estimated or even determined. Regarding E1, E2 and E1cB as “limiting cases” of a continuous sequence of possibilities, the mechanistic shifts indicated in table 1 are expected.

TABLE 1.—FACTORS DETERMINING MECHANISM

	E1	E2	E1cB
increasing EPA strength of the cations (increasing charge, decreasing size)	←—————		
increasing EPD strength of the anions		————→	
increasing C—X bond strength		————→	
increasing C—H bond strength	←—————		

In this work the following experimental criteria of mechanism were used:

E1: Since the reaction begins with the complete rupture of the C—X bond a carbonium ion intermediate is formed which has a definite lifetime (minimum in the potential energy surface), during which it can undergo isomerizations, mainly double

bond shifts and *cis-trans* isomerization, but sometimes isomerizations of the carbon skeleton as well. Therefore, both but-1- and but-2-enes are formed from 1-X-butane, with a distribution similar or even equal to that obtained from 2-X-butane.

E2: As this is a one step reaction, without an intermediate, corresponding to a minimum of the potential energy surface, only but-1-ene is obtained from 1-X-butane, whereas but-2-enes (Saytzeff-orientation) are mainly obtained from 2-X-butane, which also forms but-1-enes.

E1cB: Since the reaction begins with the rupture of the C—H bond the most acidic proton is abstracted preferably. Therefore but-1-ene is the preferred product from 2-X-butane (Hofmann-orientation). Furthermore, dehydrogenation is observed as well as dehydration.

More sophisticated criteria can be enforced by use of reactants with two adjacent asymmetric carbon atoms, D-labelled reactants, H—D exchange *etc* [see ref. (2)].

The notation EPA and EPD here is identical with the acid and base notation respectively used by other authors. However, we think that EPA and EPD is more generally applicable and implies the idea of coordinative bonds between the reactant and the surface, which is so important to understanding the catalytic behaviour. Furthermore no special importance is attributed to the difference between Lewis and Brönsted acids. The proton is considered a Lewis acid like other cations [for more details see ref. (2)].

Our fundamental problem is the EPA and EPD strength of the surface sites. It is relatively easy to see that the EPA strength of Mg^{2+} is higher than that of Na^+ and also higher than that of Ba^{2+} and numerous results have been reported previously to illustrate this, yet it is more difficult to compare the EPA strength of Mg^{2+} in MgO , MgSO_4 and in MgX and MgY zeolites, for example, and even more difficult to compare the EPA strength of Al^{3+} in Al_2O_3 and MgAl_2O_4 *etc*. This paper demonstrates that XPS (or ESCA, electron spectroscopy for chemical analysis) is a powerful tool for obtaining information about EPA and EPD strength and enables us to understand most details of the catalytic behaviour of the systems considered.

The XPS technique was described by Siegbahn *et al.*⁸ There are examples of its application to catalysis in the literature.⁹

By far the most important information for catalytic purposes is that deduced from the binding energy E_B of inner orbitals. E_B is determined by measuring the kinetic energy E_K of electrons which are emitted when the sample is irradiated with monochromatic X-rays of energy $h\nu$. The relation is

$$E_B = h\nu - E_K - \Phi$$

where Φ is the work function. Although the E_B values are characteristic of an atom, variations within a few eV are observed when this atom is compared in different compounds. The variations may be regarded as mainly due to two factors: (1) variation of the electron population (electron density, effective charge *etc.*) of the atom itself, (2) variation of the potential of all surrounding ions (atoms) at the site of the atom considered. This effect is known as Madelung potential, to which all surrounding charges to infinity contribute owing to the long range nature of the electrostatic forces.

The first factor refers to the charge of the atom itself, the second to the charges in its environment, *i.e.* to the potential brought about by these charges. Increasing positive charge (decreasing electron population) of the atom should increase the binding energy. Increasing negative charge (increasing electron population) should diminish the binding energy. Increasing positive potential should increase and increasing negative potential should decrease the binding energy.

It must, however, be remembered that such a clean cut separation of the two factors is not possible, as the electron population of an atom (ion) depends on both electronegativity differences and Madelung effects.

Since the above factors should have a similar effect on all orbitals of an atom, all binding energies (regardless of the orbital) are considered to vary in the same way when an atom is compared in different compounds. This is our fundamental postulate in order to use XPS data for interpreting and predicting catalytic phenomena. Provided this postulate is useful, variation in the binding energies of inner orbitals, which can be observed in XPS, are indicative of variations in the binding energy of valence orbitals, and these should be indicative of variations in the EPA and EPD strength, which is most important for the catalytic properties of a solid. Thus a direct relationship between site strength and binding energy should exist. Note there is not necessarily a correlation between binding energy and effective charge (ionic character) or between effective charge and EPA and EPD strength.

It should, however, be possible to establish the following relationship, when an atom is compared in different compounds: decrease of the binding energy of a cation indicates decrease in its EPA strength, increasing binding energy indicates increase in the EPA strength. Decreasing binding energy of an anion indicates higher EPD strength, increasing binding energy indicates lower EPD strength. This information is of particular importance in those cases where the variation in the EPA and EPD strength is not so obvious, for example when the catalytic activity of a given atom or ion in various compounds or even in various preparations of the same compound is to be compared.

With X-rays of ~ 1200 eV (*e.g.* Mg K_{α} radiation, 1253.6 eV), the photoelectrons are emitted from a depth of 5 to 20 Å only. About 70 % of the photoelectrons are emitted from the outer two to five atomic layers, *i.e.* give us information about the actual surface layers and thus yield relevant information.

EXPERIMENTAL

Details of the catalysts and reactants are indicated in table 2.

TABLE 2.—CATALYSTS AND METHOD OF PREPARATION, AND REACTANTS

γ -Al ₂ O ₃	prepared after McIver ¹⁰
MeAl ₂ O ₄	calcination, 24 h at 1100°C, 3 days at 1400°C, of stoichiometric amounts of Al ₂ O ₃ with commercial MeO
(Me = Zn, Ni, Mg)	p.A. Merck (Darmstadt, Germany)
ZnO	reinst Neuber (Vienna, Austria)
NiO	p.A. Merck
MgO	impregnation of γ -Al ₂ O ₃ with Me(NO ₃) ₂ solution after Tauster, ¹¹ 48 h at 500°C
{surface spinels	precipitation of Mg(OH) ₂ from Mg(NO ₃) ₂ with NH ₃ , 24 h at 500°C
{MeO Al ₂ O ₃	p.A. Merck
MgO	reinst, Riedel-De-Haen AG (Hannover, Germany)
MgSO ₄	5 g NaX or NaY (Union Carbide) treated with 500 cm ³ of 10 % MgSO ₄ solution at room temperature; the percentage of exchange was determined by titration with EDTA of the salt solution before and after exchange
MgHPO ₄	puriss. Fluka AG (Buchs, Switzerland)
MgNaX (49 %)	p.A. Merck
MgNaY (51 %)	EGA-Chemie (Steinheim, Germany)
chlorobut 1- and 2-ane	p.A. Merck
1-butyl acetate	
2-butyl acetate	
butan-1-ol and butan-2-ol	

CATALYTIC MEASUREMENTS

The microcatalytic technique was used. Gas chromatograph was a Perkin Elmer F 11, thermal conductivity detector. The carrier gas was 30 cm³ He per min. The column used for separation of butene isomers was propene carbonate, 8 m, $\frac{1}{8}$ inch, at -2°C (detection of isobutene after Kladnig);¹² and for separation of butenes (all isomers together) butanone and butanol was carbowax, 1.5 m, $\frac{1}{8}$ inch, 50°C .

XPS MEASUREMENTS

A McPherson ESCA 36 apparatus was used, with Mg K_{α} radiation (1253.6 eV).

The samples were used as powders. The carbon signal from surface contamination was used to eliminate the charging effect by comparison with that obtained with a conductive gold platelet. The instrument was calibrated according to the method of Ebel.¹³ The C 1s binding energy (from the gold surface contamination) was found to be in accordance with the Bearden's data¹⁴ (C 1s 283.5 eV), thus defining the zero point of the binding energy scale. The error of the values of the binding energy was estimated to be within ± 0.2 eV.

RESULTS AND DISCUSSION

MgO, MgSO₄ AND MgHPO₄

The data in table 3 show that the EPA strength of Mg increases and the EPD strength of oxygen decreases from MgO to MgHPO₄. This is in agreement with the known chemical behaviour of these compounds. MgO is a "solid base", whereas MgSO₄ and MgHPO₄ have the character of solid acids. It seems reasonable that Mg and oxygen undergo the same variations, since the addition of the relatively electronegative element S leads to a stronger binding of all electrons of the compound. Thus, acidic or basic character is associated with the compound as a whole rather than with only one of its sites.

TABLE 3.—BINDING ENERGIES FOR SOME Mg COMPOUNDS

catalyst	Mg 2p/eV	O 1s/eV
MgO	48	530.2
MgSO ₄	49.1	531.1
MgHPO ₄	49.8	531.8

Since the binding energies indicated in table 3 have been determined relative to the gold standard, they "can be compared without any error due to charging", according to Jolly.¹⁵ In this work, for a series of compounds like MgO, MgSO₄ and MgHPO₄ with a common cation only the change in binding energy of the Mg 2p level is used to interpret the EPA strength of Mg. Similarly shifts in the O 1s binding energies indicate changes in the EPD strength of oxygen. A comparison of the Mg 2p shifts with the oxygen 1s shift between two compounds is not important in our interpretation. In such an analysis changes in the Madelung energy as well as the occurrence of other elements (sulphur) have to be taken into account. Butan-2-ol was almost exclusively dehydrogenated over MgO (96 % dehydrogenation at 350°C), whilst, over MgSO₄ and MgHPO₄, only dehydration took place, according to an E2 mechanism, with notable E1 character at higher temperatures (350 – 400°C).

Furthermore, MgHPO₄ was found to be much more active than MgO and MgSO₄, corresponding to its markedly higher Mg 2p binding energy. A temperature difference of $\sim 100^{\circ}\text{C}$ was observed at the beginning of the reaction. If the dehydration activity is considered to be mainly due to the interaction between Mg²⁺ and the OH group of the reactant, which may be called the feature determining interaction,² the higher activity of MgHPO₄ is readily explained by the higher EPA strength of Mg.

CALCULATION OF THE EFFECTIVE CHARGES OF MgO AND MgSO₄

Although there is no straightforward relationship between charge and site strength (or charge and binding energy), the question may be asked, if the charges vary at least in correspondence with the variation of site strength. In other words, if the effective positive charge of Mg in MgSO₄ is higher than in MgO this would fit in well with assigning a higher EPA strength to MgSO₄.

Following Parry,¹⁶ the effective charges were calculated according to the point charge model from the equation:

$$B_{\alpha} = B_{\alpha}^0 + \lambda_{\alpha} q_A + \sum_{C \neq A} M_{AC} q_C + \varepsilon$$

where B_{α} is the binding energy of a core electron in orbital α of atom A, B_{α}^0 is the binding energy of the orbital in the free gaseous A atom, λ_{α} is an intra-atomic coefficient that accounts for the chemical shift $\lambda_{\alpha} q_A$ due to a partial charge q_A on A, the next term is the Madelung energy of all the surrounding ions, and the quantity ε affects all atoms in the system equally. The interatomic coefficients λ were evaluated for Mg, S and oxygen using the expectation values¹⁷ for the 3s, 3p and 2p valence electrons respectively: $\lambda_{\text{Mg}} = 10.87$, $\lambda_{\text{S}} = 17.66$ and $\lambda_{\text{O}} = 30.13$ V. For MgO (space group *Fm3m*, NaCl structure) the following charges are obtained: $q_{\text{Mg}} = -q_{\text{O}} = 0.74$, for MgSO₄ (space group *Cmcm*) $q_{\text{Mg}} = 1.83$, $q_{\text{S}} = 1.18$, $q_{\text{O}_i} = -0.71$ and $q_{\text{O}_{ii}} = -0.79$.

Mg in MgSO₄ is considerably more positive than in MgO, in good agreement with the variation of the chemical behaviour in general and catalytic behaviour in particular. However, according to the point charge model the effective charge of oxygen is about equal in both compounds. The EPD strength is different, as can be seen from XPS data, chemical and especially catalytic behaviour. As far as the calculations can be considered reliable this would be an illustration of the absence of a straightforward relation between effective charge and site strength. The lower EPD strength of MgSO₄ can be accounted for by Madelung effects. As the effective charge of Mg in MgSO₄ is higher than in MgO its positive potential at an oxygen site is also higher and hence the EPD function of oxygen is notably diminished.

A similar calculation for MgHPO₄ is not possible because hydrogen is not accessible to the XPS technique.

DEHYDRATION AND DEHYDROGENATION OF ALCOHOLS

It is known that dehydrating oxides give strikingly different product distributions. Over γ -Al₂O₃ for example mainly but-2-enes are obtained from butan-2-ol,¹⁸ mainly but-1-ene from butan-1-ol, whereas, over ThO₂, > 90 % of the butene obtained from butan-2-ol is but-1-ene.¹⁹ According to the criteria given earlier, the mechanism over γ -Al₂O₃ should be mainly E2, and over ThO₂ mainly E1cB.

The identification of terminal olefin production (Hofmann-orientation) with the E1cB mechanism was discussed by Canesson and Blanchard.²⁰ Substantial experimental evidence was recently afforded by Thomke,²¹ who could show a ready H-D exchange to take place in all β -positions, in both the product and the reactant, but not in the α -position. D at C _{α} was strictly retained. The reactant is likely to be bound to the surface over its OH group in the carbanion intermediate stage and this bond does not break, unless the reactant is desorbed or undergoes conversion to the products. After Bunnett,²² this exchange is a reliable criterion of a reversible E1cB mechanism.

Lundeen and Hoozer¹⁹ reported, besides ThO₂, a variety of oxides with a high selectivity for terminal olefins, namely oxides of the actinides, rare earths and other elements of the third group (table 4). They proposed a special cyclic adsorption structure for interpreting these results. All oxides with this characteristic also exhibit a variable percentage dehydrogenation.

TABLE 4.—O 1s BINDING ENERGIES OF SOME OXIDES²⁴ AND DEHYDRATION OF 4-METHYL-PENTAN-2-OL¹⁹

oxide	temp/°C	alk-1-ene	olefin products/% alk-2-ene	O 1s/eV
Y ₂ O ₃	412	96	4	529.5
La ₂ O ₃	414	96	4	529.0
CeO ₂	350	86	14	529.4
Sm ₂ O ₃	415	94	6	529.2
Dy ₂ O ₃	404	97	3	529.4
Al ₂ O ₃	—	—	—	531.8
SiO ₂	—	—	—	533.1
GeO ₂	—	—	—	532.4
P ₂ O ₅	—	—	—	532.4
Fe ₂ O ₃	—	—	—	530.3

A cyclic transition state was also proposed by Davies and Brey Jr.²³ to explain the high selectivity for oct-1-ene of octan-2-ol over ThO₂, and different active sites were assumed for dehydration and dehydrogenation, which was also found.

A more satisfactory explanation can be given, by taking into account the results of the XPS studies (table 4). A comparison of the O 1s binding energy shows that oxides with an alumina-like behaviour, for example SiO₂, GeO₂ and P₂O₅, which give an E2 or also E1 mechanism, have values between ~ 531 and 533.5 eV, whilst for the ThO₂-like oxides considerably lower values are reported, between ~ 529 and 530.5 eV. Obviously, the EPD strength of oxygen is much higher in the second group. They are rather basic oxides, whereas the first group has more acidic character. In the alumina-like group, the interaction between the OH group and the EPA in the surface (the cation) is feature determining, whereas in the thoria-like group the interaction between H and the EPD in the surface (the oxygen) is feature determining.

Some dehydration was observed on MgO (4 % at 350°C). The terminal olefin was greatly favoured, as on ThO₂. The low O 1s binding energy (table 3), which indicates a high EPD strength of oxygen, indicates such a behaviour. Note that the EPA strength of Mg in MgO is much lower than in MgSO₄ and MgHPO₄. So the feature determining interaction on MgO is that between H of the reactant and O of the catalyst rather than that between OH and Mg. This interaction is strongest with the most acidic proton (strongest EPA), *i.e.* that of the terminal CH₃ group.

All catalysts with a selectivity for terminal olefins (Hofmann-orientation) give dehydrogenation as well as dehydration. So the O 1s binding energy indicates the occurrence of dehydrogenation. This striking coincidence of E1cB dehydration and dehydrogenation can be understood better taking into account one of our recent results.²⁵ It is likely that the initial stage for both reactions is the same, *i.e.* abstraction of a β-H⁺. In a subsequent dehydrogenation step, the α-H must be abstracted as H⁺, and the enol formed rearranges to the ketone. Such a mechanism would explain the importance of another factor, the Me—O distance as suggested by several authors.⁶ Small distances are generally assumed to favour dehydrogenation, because the distance between α- and β-H is notably smaller than that between

the O of OH and β -H. Therefore oxides with small cations should have a higher selectivity for dehydrogenation. Compare, *e.g.*, MgO and ThO₂, the percentage dehydrogenation is much higher on MgO than on ThO₂.

The method of preparation could be another example where the Mg—O distance in the surface influences catalytic selectivity. Winfield²⁶ reported modification in the selectivity of MgO towards dehydration by increasing the Mg—O distance. A similar observation was made for Cr₂O₃.

Another illustration is the difference between γ -Al₂O₃ and γ -Fe₂O₃. Although both oxides have the same crystal structure a high percentage of dehydrogenation is found over γ -Fe₂O₃, whereas γ -Al₂O₃ only gives dehydration. This is again in agreement with the difference in O 1s binding energy (table 4). The EPD strength of γ -Fe₂O₃ is much higher. Note that in our discussion, we did not need several types of active centre.

Frequently, XPS binding energies are correlated directly with effective charges. In fig. 1 the XPS binding energies of some oxides as determined by Sergushin *et al.*²⁴ are plotted against the effective charges calculated according to Pauling.⁸ The linear correlation between these quantities demonstrates that at least in some cases the XPS-shifts can be interpreted without considering Madelung effects.

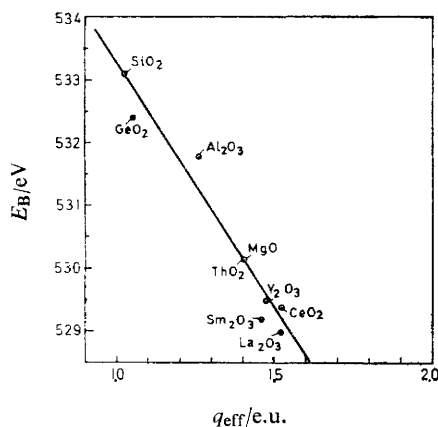


FIG. 1.—Correlation between XPS binding energy E_B and effective charge per oxygen calculated according to Pauling.

SPINEL COMPOUNDS AND γ -Al₂O₃

Since spinel compounds and γ -Al₂O₃ have the same crystal structure and nearly the same lattice parameter, (the only difference being the divalent cation) they are well suited to this study.

Ni, Zn and Mg were used as divalent cations. Besides bulk spinels, MeAl₂O₄ and aluminas impregnated with MeO were studied. As shown by XPS measurements of MeO and MeAl₂O₄, surface spinels had been formed by impregnation. Similar results were reported for CoO/ γ -Al₂O₃²⁷ and CuO/ γ -Al₂O₃.²⁸ Three samples with a different Me content, designated MeO Al₂O₃-1,-2,-3 were prepared with each divalent metal. The XPS data for Zn-spinels are given in table 5 as a representative example (the results with other divalent metals were similar).

The oxygen in the components γ -Al₂O₃ and ZnO is seen to give a relatively weak and strong EPD respectively. Correspondingly, dehydration is found over γ -Al₂O₃, whereas dehydrogenation is predominant over ZnO. In ZnAl₂O₄ and in the surface

spinel the EPD strength of oxygen was found to be between those of the components. Dehydration occurred on the spinels.²⁹

However, an interesting mechanistic difference was observed between γ - Al_2O_3 and the spinels, again in agreement with the variation of the EPA strength and in particular that of Al as indicated by the variation of the binding energy. The Al 2p binding energy in the spinel is lower, the Zn 3p binding energy higher than in the components. Since Madelung effects are practically equal in these compounds, binding energies should be directly related to charges. Al, the higher valent species, has increased its electron population at the expense of the divalent metal and hence decreased its EPA strength. Provided Al is the catalytically active EPA site a change in the mechanism toward E2 or even E1cB (depending upon the reactant) is expected going from γ - Al_2O_3 to spinel and this was found with all reactants studied.

TABLE 5.—BINDING ENERGIES (eV) FOR $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ COMPOUNDS

	Zn/100 Al	Zn 2p	Zn 3p	Al 2p	O 1s
γ - Al_2O_3	—	—	—	75.3	531.8
ZnO	—	1020.8	89.8	—	530.4
ZnAl_2O_4	50	1021.4	90.6	74.6	530.8
$\text{ZnO} \cdot \text{Al}_2\text{O}_3$ 1	3.6	1021.4	90.9	74.6	530.9
$\text{ZnO} \cdot \text{Al}_2\text{O}_3$ 2	28	1021.3	90.9	74.3	530.8
$\text{ZnO} \cdot \text{Al}_2\text{O}_3$ 3	52	1021.5	90.7	74.6	530.9

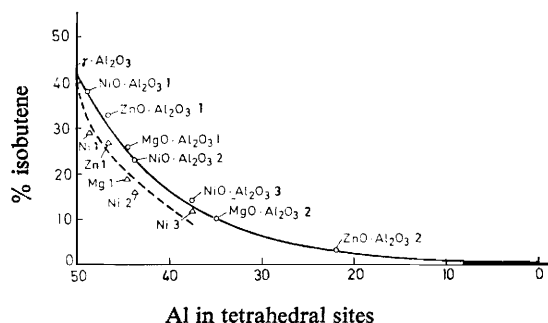


FIG. 2.—Yield of isobutene as a function of the (relative) number of Al in tetrahedral sites, — reactant: 1-chlorobutane, --- reactant: 2-chlorobutane [from ref. (31)].

With chlorobutane a pure E1 mechanism was observed over γ - Al_2O_3 and a shift toward E2 on the spinels (the result was obscured by the HCl produced in the reaction). The same tendency could be derived from the formation of isobutene which is usually assumed to proceed via a carbonium ion, see fig. 2.

Isobutene formation is lower when the EPA strength of Al^{3+} is lower.³¹ As Al^{3+} occupies both tetrahedral and octahedral sites in these compounds, the question may be asked, if its EPA strength is different or in which one of these sites its catalytic activity is higher. A comparison of Ni-spinels with other spinels is helpful here. The deactivating effect of Ni was found to be less than that of other divalent cations. Since Ni occupies both tetrahedral and octahedral sites, in contrast to the other cations (Mg, Zn), which occupy only tetrahedral sites,³⁰ the number of Al^{3+} ions in tetrahedral sites is higher in the Ni compounds. Therefore the activity is attributed to tetrahedral Al^{3+} . If the electron population around the oxygen is assumed to be equal throughout the whole crystal it is reasonable to conclude that the electron population around a given cation increases, and hence the EPA strength decreases

with the coordination number. Taking into account Madelung effects only, we would arrive at the same conclusion; increase in negative charges around a cation shifts the potential to more negative values and hence decreases the EPA strength. So that an Al^{3+} should be a stronger EPA in a tetrahedral environment or tricoordinated in the surface, than in an octahedral environment, or with five oxygens around it in the surface.

The plot of the isobutene yield against the (relative) amount of tetrahedral Al present in the surface is not linear, but similar to poisoning curves. It is suggested that not only the number of Al^{3+} ions present in the surface, but also their EPA strength is decreased by substitution for the divalent metal. The divalent metal acts as a poison, providing electrons which decrease the EPA strength (acidity) of the catalytically important sites. This is exactly what a poison does; it is usually a base, *i.e.* an EPD, which not only blocks the active (acidic) sites and so diminishes their number, but also, since it is an EPD, diminishes the EPA strength of neighbouring EPA sites and so the catalytic activity. In our opinion, it is for this reason that most poisoning curves have been found to be non-linear.

With butylacetate as a reactant with a stronger C—X bond than chlorobutane, an E2 mechanism was observed on $\gamma\text{-Al}_2\text{O}_3$ which shifted toward E1 with increasing temperature. On the impregnated samples, however, the E2 mechanism was more pronounced and even displaced to Elcb on ZnAl_2O_4 .³¹

A useful rule for estimating the effect of additions upon the site strengths may be derived from the comparison of Al_2O_3 and spinels. In this case substitution for lower-valent cations increases the electron population on both the higher-valent cation and the anion, and substitution for higher-valent cations decreases the electron population and hence decreases the EPA strength of this cation and increases the EPD strength of the anion. Substitution for higher-valent cations decreases the electron population and so increases the EPA strength of the (original) lower-valent cation and decreases the EPD strength of the anion. This is probably an important rule for understanding and predicting the effect of small additions upon the activity and selectivity of catalysts provided the crystal structure is not changed, so that the Madelung effects are practically equal. Of course an increase in the electron population is an increase in basicity and a decrease in acidity and vice versa.

ZEOLITES

The high catalytic activity of zeolites has often been attributed to Brönsted sites (OH-groups) but cations are also regarded as active sites. From XPS measurements, it may be concluded that cations should play an important role in the catalytic process. XPS data for AgNaA and AgCaNaA were reported by Finster and Lorenz.³² Whereas the Ag binding energy in AgNaA is similar to that in Ag(I) compounds, it is shifted to that of more ionic compounds like AgBF_4 by the addition of Ca. The Ca 2p binding energy is similar to that of CaF_2 , indicating a high ionic character in the zeolites and hence a high EPA strength.

A similar result was obtained in our studies of MgNaX and MgNaY (table 6). Mg in the zeolite is obviously a much stronger EPA than in MgO. The EPA strength is comparable to that in salts or even stronger. The O 1s binding energy is smaller than that of $\text{SiO}_2\text{-Al}_2\text{O}_3$, indicating that oxygen in the zeolites is a stronger EPD, (more basic) than in the oxides. Al and Si in the zeolites have a lower EPA strength probably because of a higher electron population than in $\text{SiO}_2\text{-Al}_2\text{O}_3$, the electrons being provided by the mono- and divalent cations.

Application of the above ideas about site strength enables us to interpret the results obtained with zeolites. Again Madelung effects are considered to be roughly

constant in the following discussion. In the framework Si is expected to increase its electron population at the expense of the (lower-valent) aluminium. The same variation in electron population should occur in silica-alumina in comparison with the components. The presence of mono- and/or divalent cations increases the electron population of both Si and Al beyond that in silica-alumina. A comparison of the values in table 6 shows that the increase is considerable, particularly for Si. Of course, these electrons must be taken from the lower-valent (exchangeable) ions. Note the enormous difference between Mg in MgO and MgNaX. Therefore the EPA strength of the exchangeable cations is higher than in any other compound. This explains the extraordinary catalytic effect of these cations in zeolites, which can also be explained by the fact that in the (catalytically active) S_{II} and S_{III} sites of the zeolite the cation is coordinated to three oxygens only and is therefore easily accessible. It is likely that the comparably high EPD strength of oxygen also contributes to the extraordinary activity of the zeolites.

TABLE 6.—BINDING ENERGIES OF ZEOLITES, $Al_2O_3-SiO_2$ and Na_2SO_4

	O 1s	Na 2p	Mg 2p	Al 2p	Si 2p
$Al_2O_3-SiO_2$ (COK 84)	532.1	—	—	73.6	102.4
Na_2SO_4	530.6	29.2	—	—	—
MgNaX (49.5 %)	530.6	29.4	50.2	72.9	100.7
MgNaY (50.7 %)	530.9	29.5	49.4	72.6	100.7

The EPA-leaving group X interaction is expected to be feature determining in the mechanism, because of the high EPA strength of the exchangeable cation, rather than the interaction between β -H and oxygen of the zeolite. Indeed, the mechanism has been found to be E2 or E1.

In the above discussion, cations are assumed to be active sites rather than OH groups (Brönsted sites), although a similar reasoning should be possible for OH groups as well. In that case the effect of the exchangeable cation would be transmitted to the reactant over the OH groups. We think, however, that the direct effect of the cations upon the reactant should be at least as strong as that transmitted over the OH groups. A further argument is that the influence of the cations upon the frequency of OH groups, particularly the band near 3650 cm^{-1} , has never been particularly noted.² In H zeolites, protons must be the catalytically active EPAs.

Using, as a guide-line, the EPA and EPD strengths of the species present in the surface, many phenomena could be explained. We consider the surprisingly good agreement between conclusions drawn from XPS data, chemical behaviour in general and catalytic behaviour in particular to be a strong argument in favour of both the usefulness of our approach to catalysis² and the interpretation of XPS data as indicative of site strength. This concept will also be useful for interpreting the effect of small additions and of supports. Furthermore it will also be useful for all those designated acid-base or ionic reactions⁶ (e.g. additions to the double bond, substitution and isomerization).

There is at least one further factor determining the catalytic properties, the accessibility of sites. Consider SiO_2 , which is a poor catalyst, although Si^{4+} should have a high EPA strength. We think this is due to the "unfavourable" cation-anion ratio of 1 : 2, the "unfavourable" small size of Si^{4+} and the "unfavourable" spacial arrangement of the atoms. Every Si, even in the surface, is surrounded by four (rather large) O^{2-} ions and is therefore not accessible to reactants. The relatively

small catalytic effect which has been observed is possibly due to surface OH groups, (*i.e.* OH groups, Brönsted sites, cannot have as high an activity as is usually believed).

On MgO, however, with the "favourable" cation-anion ratio of 1 : 1, the cations are easily accessible. The EPA strength of Mg, however, is relatively low, the EPD strength of oxygen rather high. Thus MgO is a catalyst for dehydrogenation rather than dehydration. Al_2O_3 , a good elimination catalyst, is possibly a good compromise between valency (EPA strength) and cation-anion ratio (accessibility). In order to increase the activity of Al_2O_3 further, cations of higher valency have to be put into Al positions. This may be what occurs in silica-alumina, the cracking catalyst. Furthermore, addition of Si^{4+} should increase the EPA strength of Al^{3+} . In order to increase the activity of SiO_2 we must put Si^{4+} into accessible positions. This is achieved by adding lower-valent cations, even though it reduces the EPA strength of Si^{4+} . The effect is to make it accessible, because some oxygen can now be omitted from the surface, provided the lower-valent ion is incorporated into the SiO_2 structure. With Al, we return to the cracking catalyst, but here also addition of some Mg increases the activity of SiO_2 enormously.

As far as we can see, (EPA and EPD) strength and accessibility of the surface atoms are the major factors determining the activity and selectivity of catalysts. In X and Y zeolites, both the site strengths and the accessibility (apart from the fact that the reactants have to enter a cage system) are exceptionally favourable.

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