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— Review —

ACTIVE SITES IN CATALYSIS

An Approach Based on Coordination Chemistry

By

H. NOLLER* and J. M. PARERA**

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Abstract

The question of active sites is discussed, mainly for silica, alumina and mixtures of these oxides regarding the bonds between reactant and catalyst as EPD-EPA interactions. At least two (complementary) interactions between catalyst and reactant are considered to be indispensable to bring about the catalytic effect. Bond weakening caused by these interactions is a decisive phenomenon, which itself depends upon the strength of surface sites. Charge-radius ratios, intermediate electronegativities, XPS values, and ionization energies are considered to be useful for estimating the strength of surface EPA (or cationic) sites. The low catalytic activity of silica is attributed to the low accessibility of its EPA surface sites (cations). The steep increase of activity observed when lower-valent oxides are added to silica is ascribed to the improvement of accessibility of these sites.

Similarly the effect of poisons is expected to increase with the EPD strength of the poisons and/or the EPA strength of cationic surface sites. Indeed silica-alumina is more affected by poisons than alumina and this is analogous to the behaviour of two samples of alumina: The more acidic sample (T 126), which is that of higher EPA strength, is more poisoned.

Thus consistent interpretations of both catalytic activities and poisoning are obtained taking into account the variation of site strength as well as, in case of poisoning effects, the donor strength of poisons without invoking different types of sites.

I. Introduction

The idea of active sites has fascinated everybody concerned with catalysis since it was proposed by H. S. Taylor, and plenty of efforts have been made to localize them. In most cases active sites are considered to be associated with special arrangements of the surface atoms, or special regions of the surface, edges, vertices, steps, kinks, holes, "mountains", etc. or with imperfections of structure or with impurities, which might

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occur accidentally or be brought in willingly, e. g. as dotations. Here the idea shall be put forward to associate active sites with the normal structure, which may, but, of course, need not be an ideal structure. Active sites are expected everywhere on the surface.

Particular attention will be paid to the atom-to-atom bonding between the reactants and the catalyst, as suggested by Heinemann¹⁾, in contrast to most treatments in catalysis. This leads to the question about the type of these bonds. It is a fundamental postulate of our model of catalysis, that, at least in most cases, these bonds can be described as bonds between an electron pair donor (EPD) and an electron pair acceptor (EPA). It is that type, which is called coordinative and usually ascribed to bonds between molecules. Catalysis, of course, should be considered a phenomenon of intermolecular interactions—the catalyst being a giant molecule—and hence a phenomenon of coordination chemistry. The coordination chemical approach to catalysis was outlined by Noller and Kladnig²⁾ and will briefly be summarized.

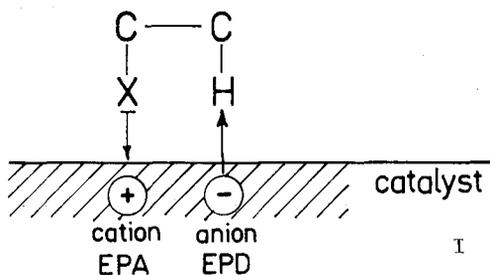
This approach leads us to question the usual concept of Brönsted acid sites because of several incompatibilities and, as a consequence, to propose alternative interpretations of maxima of activity of silica containing catalysts and of the effect of poisons.

II. Coordination Chemical Approach to Catalysis

The fundamental idea is that intermolecular interactions, at least in many instances, can be considered to take place between an EPA and an EPD.

All surface cations and anions are considered to be susceptible to act as EPA or Lewis acid and EPD or Lewis base sites respectively. The terms EPA and EPD (electron pair acceptor and electron pair donor) are usually preferred to (Lewis) acid and base, respectively, because they directly express what they mean. The term Lewis acid is not limited to tricoordinated Al^{3+} , as frequently done in catalysis, but used in the general sense current in coordination chemistry^{3,4)}, *i. e.*, to indicate a site capable of accepting an electron pair. These catalyst sites interact with the "complementary" sites (or functions) at the molecule, *i. e.*, always an EPA with an EPD. At least two EPD-EPA bonds between catalyst and reactant are assumed to be indispensable for catalysis in most cases. Of course, both EPD and EPA functions are considered to be operative in the catalyst as well as the reactant (I).

Such a double interaction was also proposed by Pines and Manassen⁵⁾ for the dehydration of alcohols to form olefins. A minimum condition for a polar solid to be an α (active)



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catalyst is therefore the occurrence of both EPD and EPA sites in its surface.

The EPD-EPA interaction leads to weakening adjacent bonds and this is a fundamental phenomenon in catalysis. This bond weakening was discussed by Noller and Kladnig⁹⁾ based upon the extensive work of Gutmann⁹⁾. There may be further interactions, in addition to those indicated in Structure I, *e. g.* with one more H at C_β. Such an additional interaction (at C_β) could contribute to increase the preferential formation of cis olefin in elimination reactions, as recently discussed by Noller and Thomke.⁹⁾

As the weakening of the bonds in the reactant increases with the strength of the surface EPD and EPA sites, it is of utmost importance to have possibilities to estimate this fundamental property, at least approximately. For cations of groups 1 A, 2 A, and 3 A of the periodic table, e/r (charge, in elementary units, over radius, in Å), denominated polarizing power by Richardson,⁷⁾ is considered a fairly good qualitative indicator of EPA strength.

We further propose the intermediate electronegativity S_{int} according to Sanderson,⁸⁾ which was recently used by Mortier⁹⁾ to discuss the properties of zeolites. For a compound $P_p Q_q R_r$, it is calculated according to:

$$S_{\text{int}} = (S_P^p S_Q^q S_R^r)^{1/(p+q+r)}$$

In the case of oxides, the XPS O 1s binding energy can be used, which increases with the acidity of the oxide¹⁰⁾, which in turn must be related to the EPA strength of the cation involved. Finally, we propose the average \bar{E}_I of the ionization energy of the valency electrons. Example: the values¹¹⁾ (eV) for Al are: I 5.984, II 18.823, III 28.444; average $53.247/3 = 17.7$.

Figures of the above magnitudes are compiled in Table 1 for three oxides, namely MgO, Al₂O₃, and SiO₂, to demonstrate that each one of these magnitudes shows us the increase of EPA strength from MgO to SiO₂.

For quite a lot of reactions of the type of elimination reactions (for literature see ref. (2), p. 168), *i. e.* dehydrochlorinations, dehydrations (to form olefins), cracking reactions, the general activity pattern II has been observed provided compounds with the same anion were compared.

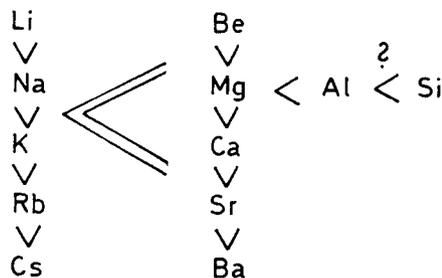
TABLE 1. Estimation of the EPA strength

	MgO	Al ₂ O ₃	SiO ₂
r (Å)	0.66	0.51	0.42
$\frac{e}{r}$	3.0	5.9	9.5
S_{int}	2.85	3.7	4.3
O 1s (eV)*	530	532	533
\bar{E}_I (eV)	11	18	26

* rough, representative values to show the tendency.

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It is easily seen that this, at least in general lines, parallels the magnitudes of $\frac{e}{r}$, S_{int} , and \bar{E}_I used in Table 1 for estimating EPA strength. Si was added, because of its similarity with Al, and since our criteria (Table 1) would lead us to expect a very high EPA strength and hence a very high catalytic activity. There are, however, no results which would allow a direct comparison, since



General activity pattern

II

Si does not form cations, *e. g.* in salts, like the other atoms listed in II.

Hydration enthalpies of the cation, probably solvation enthalpies in general, follow the same pattern as catalytic activity (for literature see ref. (2), p. 182). This suggests a similar interaction with the cation in both cases. There is a variety of further analogies (for literature see ref. (2), p. 182), which were described earlier. It may be reminded that hydration enthalpies are surprisingly high. To only give two examples: Mg^{2+} -437, Al^{3+} -1140 kcal/mol.

Note that for trivalent ions the energy of interaction with one water molecule must be of the order of magnitude of the bond energy of the strongest chemical bonds. We conclude that the interaction of donor molecules with EPA sites of polar surfaces (structure I), *e. g.* oxides, should be remarkably high, possibly of the order of magnitude of solvation enthalpies.

Of course, we do not consider formal charges to be effective charges. We do for example not ascribe the charge +3 to an Al^{3+} in the surface of alumina. But we do ascribe a higher interaction strength to a higher valency cation (other things being equal), just as found in hydration enthalpies. All our criteria are to show a tendency rather than absolute numerical values.

III. Why does Silica have so Poor Activity ?

According to the criteria discussed above, Si^{4+} should be much stronger an EPA than Al^{3+} (see Table 1), and hence the strongest EPA of those indicated in our general activity pattern. Indeed, silica containing catalysts, *e. g.* silica-alumina, have extraordinary catalytic activities. The acidity of zeolites increases with the ratio Si/Al and is ascribed to Brönsted acidity. In all these systems, Brönsted acidity is correlated with electronegativity, which increases with the content of Si.⁹⁾ It is extremely likely that it is Si (or silica respectively), which brings in acidity, and this is to be expected because of its high electronegativity. The compound with highest electronegativity, however, silica itself, has only poor catalytic activity and does not exhibit Brönsted acidity. As far as we can see the usual explanation of the low catalytic activity of silica is its not

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having Brønsted acid sites. In our opinion the question should be asked now: Why does it not have Brønsted acid sites? In other words: Why are the OH groups of silica less acidic than those of silica-alumina and zeolites (except perhaps those with alkali ions), although its electronegativity is higher than that of any mixture with any oxide of lower valence, whatever the structure may be? Until now we have not met a satisfactory answer to this question.

There are further incompatibilities in the usual picture of Brønsted and Lewis sites, to which attention will be drawn.

1) All catalysts with Brønsted sites, in particular silica-alumina and zeolites, also have Lewis sites. In alumina, on the other hand, only Lewis sites have usually been assumed to the present. If now Lewis sites must have activity in alumina, do they not have any importance in catalysts with Brønsted sites?

2) Studying the catalytic activity of oxide mixtures, Vinek *et al.*¹⁰⁾ proposed the rule that site strength (not necessarily the number of sites) of any mixtures must be intermediate between those of the components. This is in agreement with the electronegativity model of Sanderson and the concepts established by Mortier, which should be valid for any mixture. The consequence of these concepts is that mixing can never create acidity or basicity of higher strength than that of the most acidic and most basic component, respectively.

3) XPS studies of Haber and Stoch¹²⁾ showed that the O 1s binding energies of surface OH groups are, within the experimental error, independent of the cations. A value of approximately 531.5 eV was found. There is no indication of an extraordinary acidity in mixtures.

4) The OH frequencies of mixtures of SiO₂ and MgO are close to those of the components, whereas the catalytic activity (for dehydration of butanol) has a very high maximum at low content of MgO.¹³⁾

5) Lercher¹⁴⁾ studying the (downward) shift of the OH frequency, when acetone was adsorbed on the mixtures SiO₂/Al₂O₃, SiO₂/MgO, and Al₂O₃/MgO and the components, found a monotonous variation as a function of (Sanderson) electronegativity^{8,9)} of the solid. The highest shift was found for SiO₂, the lowest for MgO, corresponding to the highest and lowest electronegativity (and hence acidity) respectively.

This, of course, gives rise to questions concerning the interpretation of the catalytic activity of silica-alumina (and also zeolites), which is usually ascribed to a highly acidic proton indicated by the 1540 cm⁻¹ IR band obtained in the adsorption of pyridine. How is such a proton transfer possible with silica-alumina, but not with silica, although silica, according to the electronegativity and other criteria and the OH frequency shift, is more acidic? At present, we are not able to answer this question. We ask it in order to draw attention to incompatibilities.

Let us now propose an alternative explanation of the low activity of silica, which in our opinion has a lesser degree of incompatibilities. Provided both EPD and EPA

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are indispensable for a catalytic effect, the occurrence of both types of sites on the surface is essential. According to Buhl and Preisinger¹⁵⁾ and Preisinger,¹⁶⁾ however, it is likely that only EPD sites (oxygen ions) are present on the surface of silica. This may be considered to be due to stoichiometry, ionic radii and coordination number. A small cation ($r_{\text{Si}^{4+}} = 0.041 \text{ nm}$) is tetrahedrally surrounded by four big anions ($r_{\text{O}^{2-}} = 0.14 \text{ nm}$) the number of which is twice and the size of which is roughly three times that of the cation. Since, furthermore, the bond is very strong, this cation is perfectly shielded by anions and inaccessible for any reactant.

Furthermore, it must be concluded that the OH groups of silica are catalytically less important. Activity is only found for easy reactions, like dehydrochlorination,¹⁷⁾ or at high temperature. Since, however, OH groups of silica are not so active, the question must be asked, how the OH groups of silica-alumina can be so extremely active, although, according to Mortier⁹⁾ silica-alumina is less electronegative and hence less acidic than silica. The only possibility, we can see at present, to overcome these contradictions, is not to ascribe so high an activity to Brönsted sites. The proton of active sites of silica-alumina may be useful for catalytic activity, but it is not the only part of active sites, not even the most important.

IV. A Surprisingly Simple Explanation of Maxima of Catalytic Activity within Mixtures with Silica

One of the most fascinating phenomena of catalysis is the appearance of a maximum of activity in a mixture of two (or more) components at a given composition. Silica and alumina do practically not show cracking activity, whereas silica-alumina does, the maximum being found at roughly 15% alumina. Vinek *et al.*¹⁸⁾ found a mixture of silica with only 3% of MgO to have a dehydration activity many times higher than the components and interpreted this in the following way: When Mg is substituted for Si, a corresponding number of oxygen atoms must (can) be omitted, for stoichiometric reasons. Thus, the coordination sphere of the cations — also that of Si^{4+} , because of the mobility of surface sites — turns out to be incomplete. The cations become accessible now and Si^{4+} displays its enormous EPA strength, to be expected according to all our criteria (Table 1 and general activity pattern II). As to site strength, addition of an oxide of lower valence is unfavorable, as according to the mixing rule of Vinek *et al.*,¹⁰⁾ the EPA strength of Si^{4+} is diminished. However, it is the only possibility to “open the surface”.

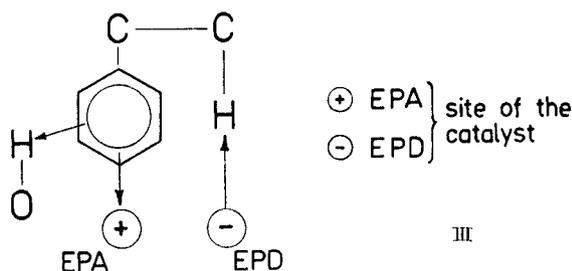
The same explanation holds for the cracking catalysts. Alumina reduces the EPA strength of Si^{4+} to a lesser extent than magnesia, but the surface opening also is lesser, both being due to the higher valency of Al as compared to Mg. Of course, Si^{4+} is considered to be the active site rather than Al^{3+} or Mg^{2+} . However, this question may be of minor importance bearing in mind the principle (of Mortier and Sanderson) of

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equalization of electronegativity,^{8,9} according to which all atoms of a compound become adjusted to the same electronegativity and hence all cations roughly, of course not exactly, to the same EPA strength.

There is no need to assume another type of sites to interpret the high activity of silica-alumina in comparison with alumina. For both catalysts, activity may be assigned to Lewis sites, *i. e.*, Si^{4+} and/or Al^{3+} , rather than Brönsted sites. The discrepancy of OH groups of silica-alumina having a higher activity but a lower acidity than those of silica is eliminated.

This interpretation does not exclude any participation of OH groups (Brönsted sites), but postulates that OH groups alone are not so active. Their participation in a cracking reaction (dealkylation) can for example be that depicted in Structure III. The proton of the OH group is considered to be an EPA site like other cations.



OH groups alone, however, are not considered to have a high activity in the absence of (other) cations accessible to the reactant, in agreement with the fact that all catalysts, including H-zeolites, with Brönsted sites have also Lewis sites. Differently speaking, the interaction of the ring only with an OH group (Brönsted site), is probably not enough for the cracking reaction to be brought about. If it was enough, silica, which has the most acidic OH groups, should be a cracking catalyst.

Anion vacancies are often claimed in the literature for explaining catalytic activity. It is interesting that this draws attention to the species which must be absent, *i. e.*, the anion. We would like to invert the aspect and draw attention to the species that must be present (and accessible), *i. e.*, the cation. The creation of anion vacancies produces the opening of the surface. These vacancies are the more important, the higher the (stoichiometric) anion-cation ratio and the smaller the cation is. Note that the coordination number is possibly less significant. In MgO (NaCl-lattice, coordination number 6) the surface is probably "open", *i. e.*, both cation and anion are accessible. In silica in spite (or because?) of its low coordination number (of 4 for Si), the surface is not "open".

The observation of Benesi¹⁹ when studying the acidity with Hammett indicators, that addition of magnesia to silica produces more acidic centers, but of lower acidity than the addition of an equivalent amount of alumina is easily interpreted with the

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above concepts. Magnesia "opens" the surface more than alumina, because of its lower valency, *i. e.*, creates more accessible cations, but because of its higher basicity, reduces the acidity more than alumina.

Another frequent observation has an easy explanation. Impurities have often been reported to diminish the acidity of alumina, but to increase that of silica. Provided the impurities contain mono- or divalent ions, which might often be the case, they reduce the acid (EPA) strength in silica as well as alumina. There is, however, an important difference between these two compounds. As alumina has quite a lot of (accessible) Al^{3+} sites in its surface, their number is relatively little changed, when cations of lower valence are added. With silica, on the other hand, which has practically no Si^{4+} sites in its surface, this change can be considerable or even dramatical, as, for example, every divalent ion, when it is located in the very surface, could bring about an accessible Si^{4+} site. Similarly, every two trivalent cations could bring about such a site, whereas every two monovalent cations could create three such sites.

In the last years, several papers have been published by Low and Mark²⁰⁾ about reactive silica, which is obtained when silica is subjected to a methoxylation/pyrolysis procedure. Centers of high adsorption capacity are created this way and this also shows the possibility of strong interaction with silica, which possibly is deficient in oxygen.

V. Poisoning Experiments

It is challenging to apply these concepts to the poisoning studies with alumina and silica-alumina of Parera and coworkers.²¹⁻²⁶⁾ Bases like pyridine and N-methylaniline were found to poison the dehydration at 501 K of methanol to dimethylether reversibly on alumina, but irreversibly on silica-alumina (see Fig. 2 of ref. (22)). This is also shown in Fig. 1, where the effect of pulses of the poison injected into the feed is represented, and in Fig. 2, which shows the effect of continuous addition of poison.

When the methylation of methylaniline was carried out on alumina as catalyst, dehydration of methanol to ether was also observed, whereas only methylation occurred on silica-alumina.

These differences of alumina and silica-alumina were interpreted²²⁾ with the difference between Lewis and Brönsted (acid) sites respectively. However, an explanation is also possible with one type of sites, in our opinion Lewis sites, the strength of which is considerably higher on silica-alumina than on alumina.

It will later on be shown by a model calculation that the percentage of the surface covered with poison is higher on silica-alumina than on alumina and hence the probability of two methanol molecules being in neighbouring positions to form ether much lower, or practically zero. Note that Lewis sites have been reported for both catalysts, but Brönsted sites only for silica-alumina.

The starting point of our explanation is that in an interaction between a molecule

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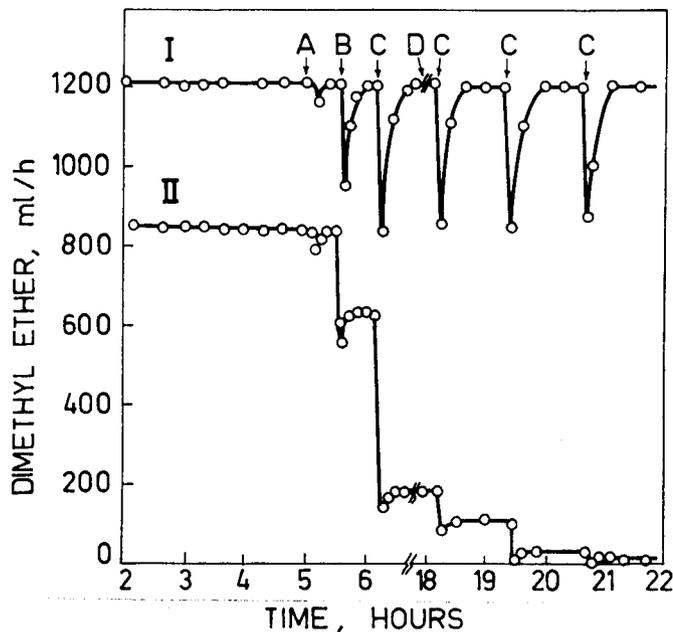


Fig. 1. Dimethylether produced versus time during the poisoning with a solution of 0.5 N pyridine in benzene. Mass of catalyst, 8 g; feed 8 ml methanol/h; temperature 501 K; I, etha alumina; II silica-alumina 13% Al₂O₃; A, injection of 1 ml benzene; B, injection of 0.5 ml pyridine solution; C, injection of 1 ml pyridine solution; D, 11 hours in nitrogen stream at 501 K.

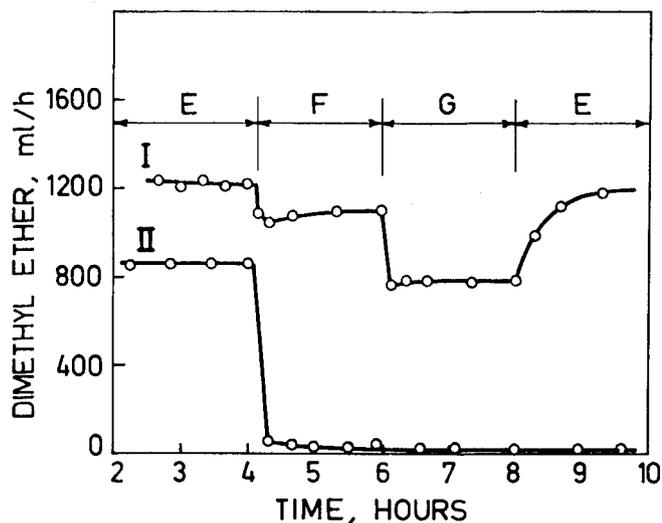


Fig. 2. Dimethylether produced versus time. Conditions and symbols, idem Fig. 1. E, methanol as feed; F, 4% wt dimethylaniline in methanol; G, 10% wt dimethylaniline in methanol.

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and a surface, both donor and acceptor functions are invoked on both sides. Since, on the part of the catalysts studied here, the acceptor functions are more pronounced, on the part of the molecules the donor functions, only these interactions shall be discussed.

TABLE 2. pK_a values, donor number (DN), and intermediate electronegativity of reactants and poisons

Molecule	pK_a	DN	S_{int}
Methanol	-2.2	19	3.83
Pyrrole	0.4		3.73
Pyridine	5.3	33	3.74
N-Methylaniline	4.8		3.70
NN-Dimethylaniline	5.1	55	3.69
N-Butylamine	10.6		3.66
Diethylamine	11.0	57	3.66

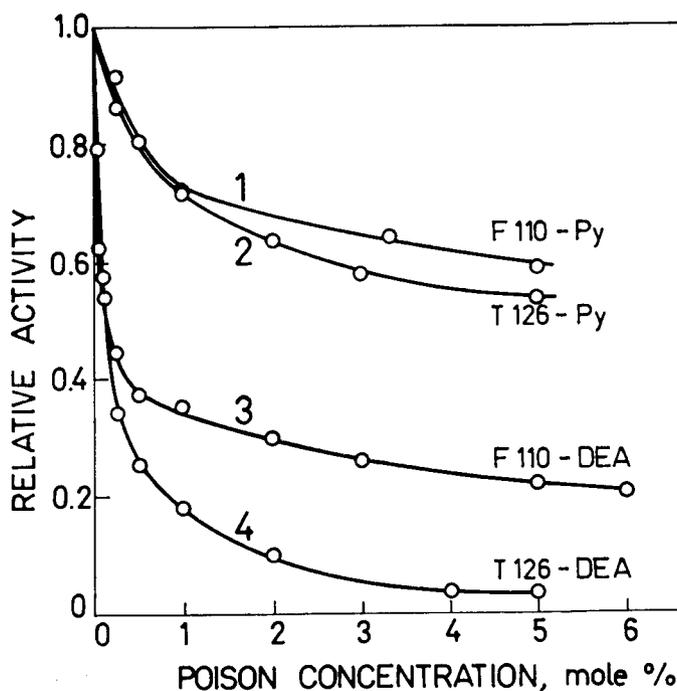


Fig. 3. Relative activity of aluminas T 126 and F 110 as a function of poison concentration in the methanol feed. Poisons, pyridine and dimethylamine. Temperature 501 K.

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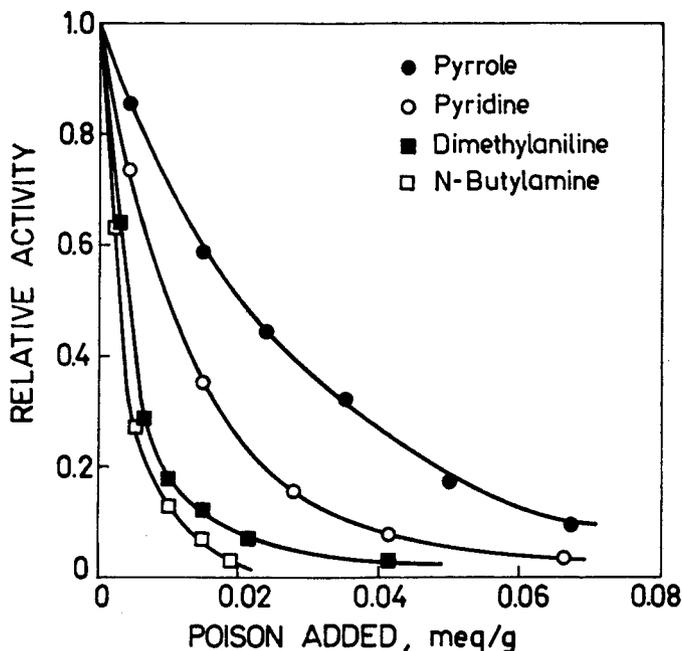


Fig. 4. Relative activity of silica-alumina Kao Spheres as a function of the amount of poison injected to the methanol feed. Temperature 503 K.

All the poisons used here are bases and have a higher basicity than the reactant, as can be seen in Table 2, where the pK_a values²⁷⁾ are indicated as well as Gutmann's²⁸⁾ donor numbers (DN), which are the negative (in order to obtain positive figures) enthalpies (in kcal/mol) of the formation of an adduct between the (donor) molecule and $SbCl_5$. Thus the poison is superior in the competition for the acceptor sites of the surface and displaces the reactant to a high extent.

It is obvious that, of two poisons, the stronger base should have a higher poisoning effect. This is shown in Fig. 3 for two samples of alumina of different acidity. Diethylamine (curves 3 and 4) is a stronger base than pyridine (curves 1 and 2) and, consequently, has a higher effect on both types of alumina. This, of course, should be so for any catalyst. It is demonstrated for silica-alumina in Fig. 4. The poisoning effect increases with base strength, dimethylaniline has a higher effect than expected from its pK_a value, which is roughly equal to that of pyridine. Gutmann's donor numbers better parallel the poisoning behaviour of the bases. But the donor number of dimethylaniline is estimated (not measured). On the other hand, the intermediate electronegativity, S_{int} , calculated according to Sanderson²⁹⁾ and also indicated in Table 2, parallels the poisoning effect of the bases except for pyrrole.

The basicity of a compound may be assumed to increase with decreasing inter-

mediate electronegativity, but the comparison should only be applied to homologous series. It must always be borne in mind that each one of these magnitudes, pKa, donor number, and electronegativity, may be useful for orientation. However, the order of the bases must not be the same for each one of these magnitudes, as the conditions for determining the values are different.

Moreover, attention must be drawn to further factors which can influence poisoning phenomena, *e.g.*, the volatility of the poison and the possibility of decomposing and polymerizing.²⁰⁾

Whereas it is obvious that the poisoning effect of the stronger base (*i.e.*, that of higher EPD strength) must be higher, it is not so clear that the poisoning effect of a given base must be higher on the catalyst of higher EPA strength. A model calculation with fictitious numbers may demonstrate, that the superiority of the poison, which is a stronger EPD than the reactant, is more pronounced on the catalyst of higher EPA strength, in other words, the degree of displacement of the reactant from the EPA sites of the catalyst is higher for the catalyst of higher EPA strength.

The energy of the donor-acceptor bond between the molecule (reactant, poison) and the catalyst, or the interaction strength, IS, should be proportional to the product of the donor strength of the reactant or poison, DN_{mol} , and the acceptor strength of the catalyst, AN_{cat} :

$$IS \propto DN_{mol} AN_{cat}$$

Unfortunately, we do not have figures of the acceptor strength of the catalyst surface sites. But as Si^{4+} has a higher e/r value than Al^{3+} , 9.8 instead of 6, the acceptor strength of silica-alumina must be higher than that of alumina. The other criteria of Table 1 indicate the same tendency. This is also in agreement with Sanderson's and Mortier's concepts of electronegativity. For a certain difference between the donor numbers of reactant and poison, the difference of IS for the catalyst with higher AN, *i.e.*, silica-alumina, should be higher. For instance, with methanol as reactant (R) and pyridine as poison (P), the donor strength of which may be expressed by Gutmann's²¹⁾ donor numbers, and with fictitious acceptor numbers of $AN_A=1$ and $AN_{SA}=1.4$ for alumina (A) and silica-alumina (SA) respectively, the interaction strengths and the differences ΔIS should be proportional to the following values:

	Methanol (R)	Pyridine (P)	$\Delta IS = IS_P - IS_R$
Alumina	19	33	14
Silica-alumina	27	46	19

In order to see the importance of these figures for the displacement of the reactant by the poison, we have to take into account that, in the interaction constant (adsorption constant) K , a figure proportional to the interaction strength appears in the exponent

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of the exponential function. Assuming the pre-exponential factors (of reactant and poison) to be equal, the ratio of the constants obtained with the above figures is:

$$\text{Alumina} \quad K_P/K_R = e^{14\alpha}$$

$$\text{Silica-alumina} \quad K_P/K_R = e^{19\alpha}$$

where α is a constant which, of course, includes $1/RT$.

Whatever the constant may be, the superiority of the poison in the competition for the acceptor sites (expressed as K_P/K_R) is higher on silica-alumina than on alumina. This means that the chance of the reactant to occupy an acceptor site is much lower on silica-alumina than on alumina and so is the probability of two methanol molecules being in neighbouring positions. So the poisoning effect on silica-alumina is always higher. The stronger interaction of poisons with silica-alumina leads to an irreversible adsorption and irreversible poisoning, as shown in Fig. 1 and 2.

In the same way, the different behaviour of two different samples of alumina can be interpreted. Table 3 shows that T-126 is the more acidic sample, *i.e.*, that of higher EPA strength, and this is the sample on which the poisoning effect is stronger with both poisons, pyridine and dimethyl amine (Fig. 3). Note that an explanation with different types of sites would be difficult here. Note further the interesting detail that the difference of the poisoning effect for the two samples of alumina is more pronounced for dimethylamine, which is a stronger base and hence a stronger poison than pyridine, in agreement with our approach.

TABLE 3. Acid strength distribution

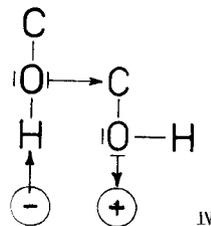
Catalyst	H_0 acidity, meq/g					
	pK _a	-8.2	-5.7	-3.0	+1.5	+3.3
Gamma Alumina T-126 (Girdler Catalyst)		0.12	0.18	0.21	0.21	0.24
Gamma Alumina F-110 (Alcoa)		0	0.13	0.21	0.21	0.21

This may be summarized once more in the following statement. The poisoning effect, for a given catalyst, increases with the base strength (donor number) of the base (Fig. 3 for alumina, Fig. 4 for silica-alumina). For a given poison, the poisoning effect is higher with the catalyst of higher acceptor strength (higher acidity) (Fig. 1 and 2 for alumina and silica-alumina, Fig. 3 for two samples of alumina of different acidity). There is no need of invoking two different types of sites (Lewis and Brönsted sites) in order to come to a consistent interpretation.

VI. Mechanisms

The mechanism of the formation of ether on alumina is assumed to be that proposed by Jain and Pillai²⁸⁾ and accepted also by others (Structure IV):

The same mechanism probably occurs on silica-alumina. One methanol molecule is adsorbed on a surface EPD-site, an oxygen ion, another one on an adjacent surface EPA-site, an Al^{3+} or Si^{4+} ion. In the first methanol molecule, the EPD function must be activated. It interacts as an EPD with the second one (arrow), the EPA function of which is activated by its donor interaction with a surface EPA site. In other words, the (oxygen of the) first molecule nucleophilically substitutes the OH group of the second one.



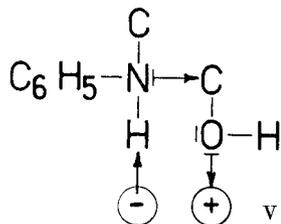
Interestingly, it seems to be somewhat more favorable to have a catalyst of balanced EPA and EPD strength, as alumina. A catalyst with very high EPA and correspondingly low EPD strength like silica-alumina is somewhat or notably less favorable,²⁹⁾ probably because it is most efficient to activate both molecules to the same extent approximately.

For the dehydration of isopropanol, however, silica-alumina is much more active than alumina. Here breaking of the C-O bond probably is the most difficult step. As soon as this bond is broken and the carbonium ion formed, the reaction is accomplished.

A similar mechanism may be assumed for the methylation of methylaniline, the nucleophilic agent being the nitrogen of methylaniline (Structure V). As methylaniline is a stronger donor than methanol, it will more strongly interact with acceptor sites (Al^{3+} or Si^{4+}). However, a methylaniline molecule adsorbed in this way is probably not able to react, because it is so strongly and irreversibly adsorbed and its donor strength toward methanol is greatly reduced. The reacting molecule should come from the gas phase or be adsorbed on another kind of sites. It nucleophilically attacks the positively charged CH_3 and needs a surface EPD site (oxygen) to leave its proton.

This agrees with the kinetic equation found applying all the possible Hougen and Watson models to the data.²⁹⁾

The kinetic equations are empirical rate equations and it is not correct to assign a physical meaning to their coefficients. Nevertheless, as they are deduced according to certain reaction models, they are useful guides to verify a model, which possibility was suggested by other methods. The kinetic expression which best fits the data in methylaniline methylation is²⁹⁾:



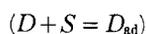
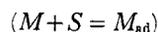
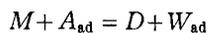
$$r = \frac{LkK_A(p_M p_A - p_D p_W / K)}{1 + K_M p_M + K_A p_A + K_D p_D + K_W p_W}$$

Where L is the concentration of active sites, k is the rate constant, K_A is the adsorp-

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tion equilibrium constant of reactant *A* etc, p_A is the partial pressure of gas *A* etc, and K is the equilibrium constant of the reaction in the gas phase.

This equation was deduced for the mechanism :



The rate controlling step is the surface reaction between a monomethylaniline molecule, M , in the gas phase and an adsorbed methanol molecule, A_{ad} , to produce dimethylaniline, D , in the gas phase and adsorbed water, W_{ad} .

Methylaniline and dimethylaniline are adsorbed (but do not react) on the same active sites, S , as methanol and water. The rate controlling step involves only one active site (provided the proton of methylaniline is given to the surface after that step).

VII. Strength of EPA Sites for Dehydration of Methanol and Methylation of N-Methylaniline

Figure 5 shows that dehydration of methanol parallels strong acidity ($pK_a < -8.3$), whereas methylation of methylaniline parallels weak acidity ($pK_a < 3.3$). It must be concluded that on silica-alumina poisoned with NaOH, weak acid sites are able to catalyze the reaction of methanol with methylaniline, whereas strong acid sites are

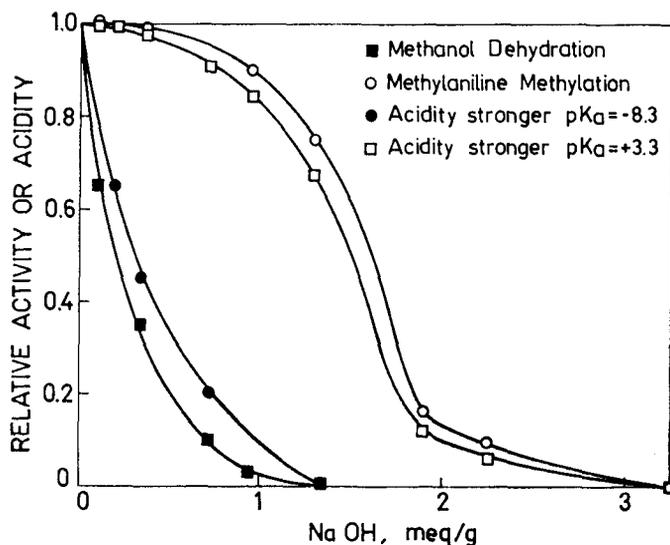


Fig. 5. Relative acidity and relative activity of silica-alumina 13% Al_2O_3 poisoned with NaOH as a function of poison concentration on the catalyst. Temperature 503 K.

necessary for the reaction of methanol with another methanol molecule.

This may be interpreted in the following way: methanol dehydration needs strong acidity in order that the positive charge in the CH_3 (EPA function) is high enough to interact with the EPD function of another methanol molecule (nucleophilic attack of the oxygen of the other methanol molecule). However, as the nitrogen of methylaniline is a stronger donor than the methanol oxygen, a smaller positive charge on CH_3 may be enough for the attack, which means that a weaker surface acidity is sufficient. This is why ether formation is much more sensitive to (basic) poisons than methylation of methylaniline.

In other words, a minimum strength of the acceptor-donor interaction is necessary to have the reactant molecule in an activated form. A rather strong base, with high donor number as methylaniline demands only weak acid strength (small acceptor number) of the catalyst; whereas a molecule with a smaller donor number, as methanol, demands a higher acceptor number or stronger acid sites on the side of the catalyst.

VIII. Concluding remarks

The high electronegativity, but low acidity and low catalytic activity of silica is one of the discrepancies seen in the usual picture of active sites, in which distinction is made between Lewis and Brönsted sites. Therefore, alternative explanations are proposed based upon the idea that Lewis sites are indispensable for the catalytic effect (all accessible cations being considered to be Lewis acid sites).

Applying the EPD-EPA (or coordination chemical) approach, the catalytic behaviour of the systems discussed in this article is mainly related to the EPA strength of the cation and criteria are proposed for estimating the EPA strength. These criteria correspond to a frequently found activity pattern.

The activity of Si^{4+} should be extraordinary high according to all these criteria. This is found for Si containing catalysts, but not for silica itself. The low activity of silica is not ascribed to the lack of Brönsted acid sites on silica, but to a complete shielding of the strong EPA Si^{4+} by oxygen. Activity maxima of silica with alumina and magnesia are not attributed to the appearance of Brönsted acid sites in these mixture, but to much higher EPA strength (in comparison with alumina or magnesia) due to the presence of Si.

Similarly, the different behaviour of alumina and silica-alumina in poisoning experiments is related to the higher EPA strength of silica-alumina rather than a different type of site (Lewis on alumina, Brönsted on silica-alumina).

This model enables us to interpret several further details, which are more difficult to explain with the (usual) idea of different types of sites, for example the difference in poisoning effects between two samples of alumina of different acidity or the high difference between alumina and silica-alumina (which is more active) in the dehydration

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of isopropanol (to propene) in comparison with the low difference in the dehydration of methanol (to ether).

It must be reminded that in all the reactions discussed above anions (EPD sites) must also be involved. However, their effect is less noted, as the interaction between the EPD site of the reactant and the EPA site of the catalyst appears to be the strongest one and hence feature determining.²⁾

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