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A Model for the Surface of a Silica–Alumina Catalyst

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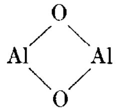
A semiquantitative model is proposed for the surface of a silica–alumina catalyst, based on a previous model for the surface of silica gel. "Acid" sites of various types are assumed to be created by the attachment and subsequent bridging reactions of Al–OH groups on a silica surface resembling a cristobalite 100 face partially covered with randomly distributed paired hydroxyl groups. Three types of "strained" Al–O–Al bridges and three possible types of



bridges are considered. The strong "acid-base" sites (α sites) previously shown to exist on silica–alumina surfaces at about 5×10^{12} sites/cm^2 are identified with one type of strained Al–O–Al link expected at a maximum surface concentration of 6.6×10^{12}/cm^2. Features of the model are discussed and related to experimental observations.

INTRODUCTION

The nature of the catalytically active sites on the surface of silica–alumina cracking catalyst has been the subject of much past research, but evidence on this subject remains inconclusive (*1,2*). The active sites are usually assumed to be either Brønsted (*3–6*) or Lewis (*7–11*) acids, which may possibly be interconverted by addition or removal of traces of H_2O or other hydrogen-containing compounds (*12,13*). Combination of a Lewis acid site with an adjoining Brønsted acid site may, in some cases, be needed for catalytic activity (*9,11*). Evidently, however, not all reactions are catalyzed by the same types of sites, and many different types of acid sites exist on silica–alumina surfaces.

The acidity of silica–alumina catalysts was thought by Hansford (*3*) to originate in surface silanol groups which were rendered more acidic than usual by the presence of a neighboring aluminum ion. Thomas (*4*) attributed this acidity to the protons which were presumably required to preserve stoichiometry when Si^{4+} was replaced by Al^{3+} in tetrahedral sites in the silicate structure. Advocates of Lewis acidity, on the other hand, have considered the strong acidity of dry silica–alumina catalysts to arise from Al ions variously exposed in or on the catalyst surface. Miesserov (*12*) has argued that silica gel acquires catalytic properties exclusively as a result of substitution of aluminum for the hydrogen atoms in certain hydroxyl groups on the silica surface, the maximum acidity of the final silica–alumina being determined by the "hydrolytic acidity" of the original silica.

Only a tenth or less of the acid sites on a typical silica–alumina surface are active in

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catalytic cracking of hydrocarbons (*14*). Silica–alumina appears to hold about $5 \times 10^{12}/\mathrm{cm}^2$ strong Lewis sites which chemisorb trityl derivatives to form carbonium ions (*8,11*). In addition to these sites, a much smaller number of sites (roughly $6 \times 10^{11}/\mathrm{cm}^2$), thought to involve anion vacancies, appear capable of extracting hydride ions from Ph_3CH in the dark (*11*).

Infrared studies (*15,16*) of adsorption of CO_2 and other molecules on silica–alumina have directed attention to the possible catalytic role of certain acid-base sites, called α sites, which are found on both silica–alumina and γ-alumina after strong dehydration. These sites exist at surface concentrations from 3 to 9×10^{12} sites/cm² and may be the sites which chemisorb trityl derivatives. They are formed during dehydration of the surface by condensation of Al–OH groups and contain a reactive oxide ion (or ions) closely adjoining an exposed aluminum ion. Their catalytic role is not clear although they apparently possess at least some catalytic activity (*15, 16*). Weaker Lewis sites, similar in general character to the α sites and similarly produced, also exist on silica-alumina. These "β sites" (*17*) are more numerous and are catalytically more important.

Silica–alumina is normally made by reaction of hydrous alumina or an aluminum salt with silica gel in aqueous suspension. Besides reactions of surface silanol groups in which H is replaced by aluminum, such preparation can entail substitution of aluminum for silicon atoms in silicate tetrahedra, and possible addition of both anions and aluminum cations to the surface through the opening of preexisting siloxane linkages. To minimize some of these complications, silica–alumina can be prepared by initial reaction of gaseous $AlCl_3$ or other volatile Al compounds with the surface hydroxyl groups on dry silica, followed by careful hydrolysis and redrying. The catalytic properties of silica–alumina prepared by such "dry" methods are generally similar to those of silica–aluminas made by "wet" methods. In a typical dry preparation, "virgin" silica gel (*16*) is first heated in air or oxygen and then dried by evacuation at high temperature. The dry surface retains "isolated" hydroxyl groups (i.e., those which do not form H-bonds). These may be single groups or vicinal or geminal pairs (*18*).

A simple model proposed for the surface of certain silica gels (*18*) can through appropriate extension account fairly well for properties of silica–alumina catalysts made from these gels. Silica–aluminas, like silica gels, differ widely in properties, but the extended model, although relating primarily to one type of silica–alumina, may also provide insight into catalytically important features of other silica–aluminas. The stoichiometry of the reactions of $AlCl_3$ with surface hydroxyl groups on silica has been considered in some detail (*12*). Catalytically active sites were postulated to be strained surface oxide links by Cornelius *et al.* (*19*) in explaining the catalytic properties of alumina. The data which the model was primarily developed to explain have been published (*15–17*).

A MODEL FOR A SILICA–ALUMINA SURFACE

The silica gels used in previous dry preparations of silica–alumina (*16*) appear to have a surface structure which initially resembles a 100 face of cristobalite largely covered with hydroxyl groups (*18*). Random dehydration of this idealized surface should eventually yield a surface holding only isolated geminal and vicinal pairs of hydroxyl groups at a coverage of roughly 4.5 hydroxyl groups/100 Å² ($4.5 \times 10^{14}/\mathrm{cm}^2$).

Such a surface, shown in Fig. 1, was generated with the aid of a table of random numbers on an edgeless lattice containing 1270 sites. A much smaller lattice was used in generating a similar surface previously (*18*). It is thought to represent a preferred

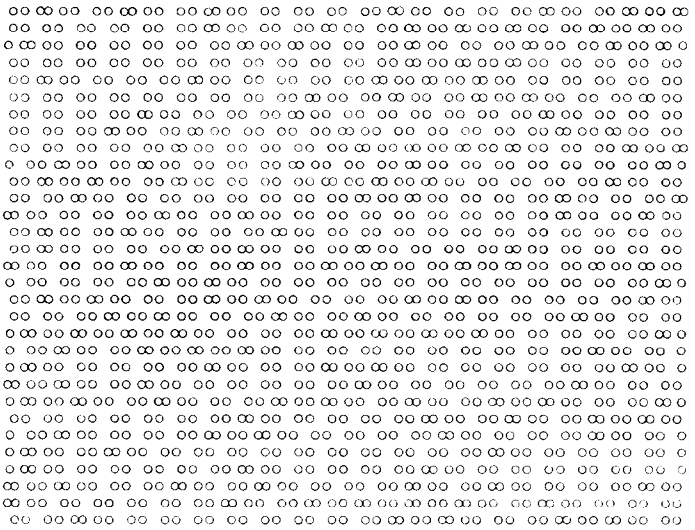
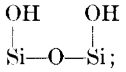
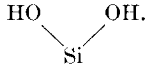


FIG. 1. A surface produced by random dehydration of a cristobalite (100) face:

○ ○, vicinal pair of hydroxyl groups, 

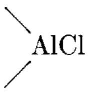
$\overset{OH}{\overset{|}{Si}}-O-\overset{OH}{\overset{|}{Si}}$;

○○, geminal pair of hydroxyl groups, 

$(HO)_2Si$.

configuration for a dry surface, although further dehydration is possible through internal condensation of vicinal hydroxyl group pairs. Ultimately only isolated geminal pair hydrogen groups (and isolated single hydroxyl groups, if originally present on other crystal faces) are thought to remain after drying at very high temperatures.

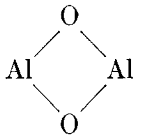
Reaction of $AlCl_3$ with the surface of dry silica can completely remove the residual surface hydroxyl groups. Each $AlCl_3$ molecule typically reacts with two hydroxyl groups (*18*). Such stoichiometry suggests that after reaction with $AlCl_3$ the surface holds mainly



groups. Two types of these groups are possible, however, one formed through reaction with a vicinal pair, and the other through reaction with a geminal pair of hydroxyl groups.

Subsequent hydrolysis is assumed to produce the corresponding two types of AlOH groups as shown in Fig. 2. These groups may exist in equilibrium with Al=O + OH groups as indicated. Hydrolysis may also break Si–O–Al or Si–O–Si links, but, if broken, such links are probably readily reformed on subsequent dehydration of the surface.

During dehydration at high temperatures, the AlOH groups presumably react with one another to form Al–O–Al links wherever possible on the surface. Two Al=O groups might conceivably form an



bridge, but this would not eliminate H_2O. Single oxide bridge structures (Al–O–Al) should thus predominate. Condensation reactions of AlOH groups are assumed to occur wherever surface geometry permits

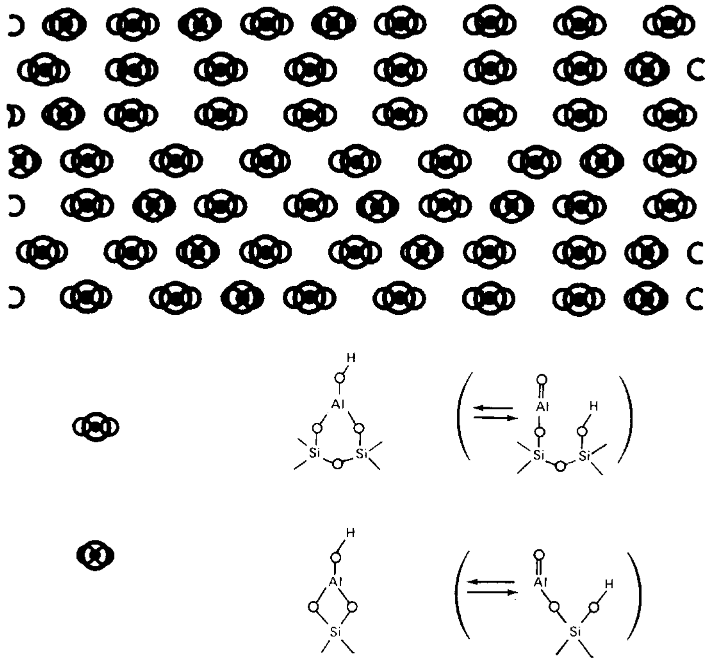
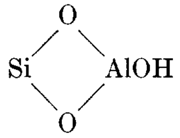


FIG. 2. (Top) Surface left after reaction of silica surface hydroxyl groups with $AlCl_3$ and subsequent hydrolysis. (Bottom) Surface groups.

such oxide bridges to be formed without highly abnormal bond lengths or angles.

As illustrated in Fig. 3, condensation reactions are probably limited to those between similar AlOH groups located directly opposite one another in adjacent rows on the surface. Vicinal pair hydroxyl groups never lie directly opposite geminal pairs in an adjoining row (see Fig. 2). Thus,



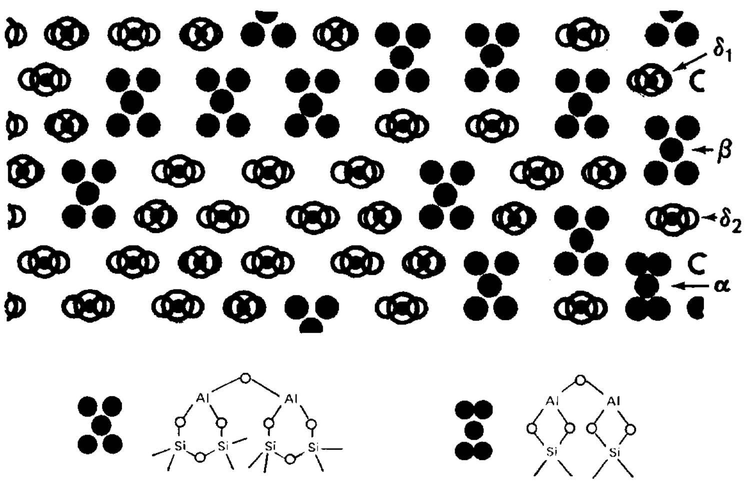


FIG. 3. (Top) Surface after condensation of AlOH groups to form all possible Al–O–Al bridges. (Bottom) Surface groups.

groups will normally react only with similar groups directly opposite in the next row. The AlOH groups attached to two silicon atoms should likewise react only with similarly attached groups.

Two types of Al–O–Al bridges would thus result, as shown in Fig. 4. Although these two types of bridges are similar in general character, the detailed structure of the surface suggests that Al ions in geminal pair bridges would probably be less readily accommodated in "strained" tetrahedral sites than would Al ions in vicinal pair bridges. This results mainly from the extreme difficulty of joining two tetrahedra through a common face, as would be required for tetrahedral coordination of the Al atoms in geminal pair bridges. Tetrahedral coordination of Al in the vicinal pair bridges can be achieved with edge-linking of the oxide tetrahedra, which is less difficult. As illustrated in Fig. 4, geminal pair bridges expose Al ions to a greater extent than do vicinal pair bridges and should therefore represent stronger acid sites. They should, however, be less numerous and more difficult to form than the vicinal pair bridges. They thus seem most likely to represent the α sites (*16*) and will be so designated. The vicinal pair bridges will be referred to as β sites.

Many of the AlOH groups attached on the surface of Fig. 2 are not directly opposite similar AlOH groups and thus presumably cannot condense to form Al–O–Al bridges. The attachment of the AlOH groups through two oxygen atoms to silicon amounts to edge attachment, effectively limiting motion to rotation in one plane and leaving little flexibility for condensation with groups which are not directly opposite, and the bond length needed for an oxide bridge between the Al atoms is substantially greater than that required for reaction with groups which are directly opposite in the next row. These arguments suggest that many AlOH groups should remain on the surface after strong dehydra-

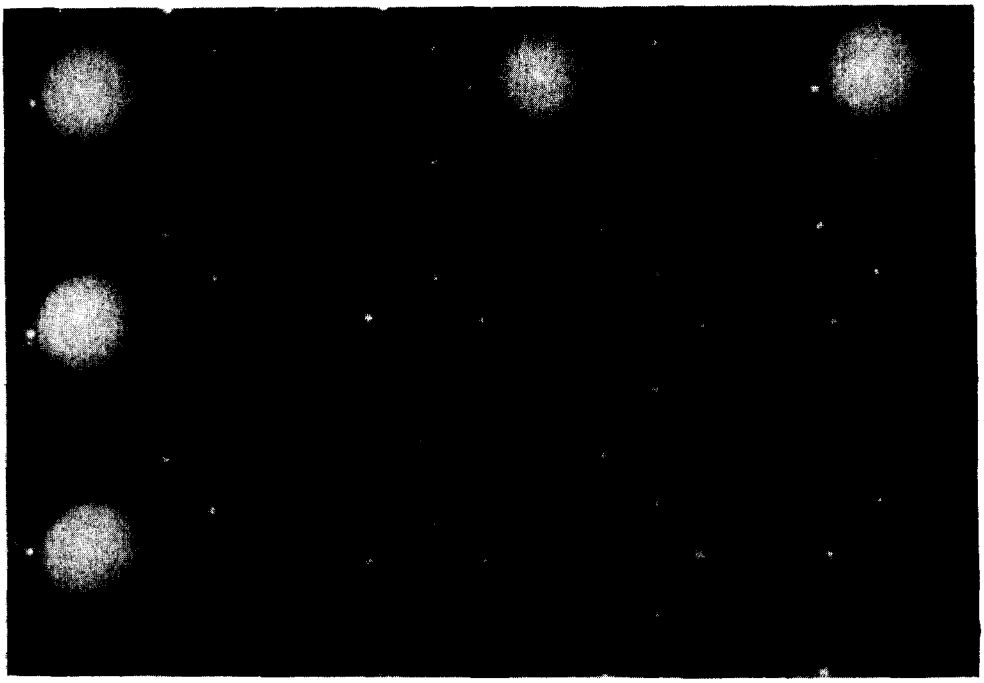
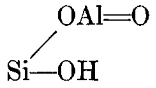


FIG. 4. The structures of α (left) and β (right) sites. Dark balls represent bridging oxide ions. Small metal balls represent Al ions; other oxide ions are grey and hydroxyl groups white.

tion, but below temperatures where mobility of surface atoms and loss of surface area become important. This conclusion is, however, contrary to experimental findings, which indicate that SiOH groups predominate on dry silica–alumina.

Two explanations can be offered for the persistence of SiOH rather than AlOH groups on dry silica–alumina. First

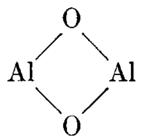


and

$$\begin{array}{l}\mathrm{Si{-}OAl{=}O}\\ \mathrm{Si{-}OH}\end{array}$$

configurations may be more stable than the corresponding AlOH configurations. Alternatively, the formation of bridges in which two oxide ions are held between the Al atoms may be possible. Neither alternative involves removal of OH from the surface; both leave the residual OH groups attached to silicon atoms.

Examination of the model surface suggests that the formation of



bridges between oxide ions in two nonopposite geminal pairs in adjoining rows is highly improbable owing both to the distance to be bridged and to the difficulty in providing more than tricoordination of the Al ions with oxide ions.

On the other hand, such bridging might well occur between an oxide ion in a geminal pair and the nearest oxide in a vicinal pair in the next row. Such bridges, shown in Fig. 5, will be referred to as γ_1 sites. Double oxide bridges between oxide ions in nonopposite vicinal pairs seem less probable. Such bridges, also seen in Fig. 5, will be called γ_2 sites. A third conceivable, but still

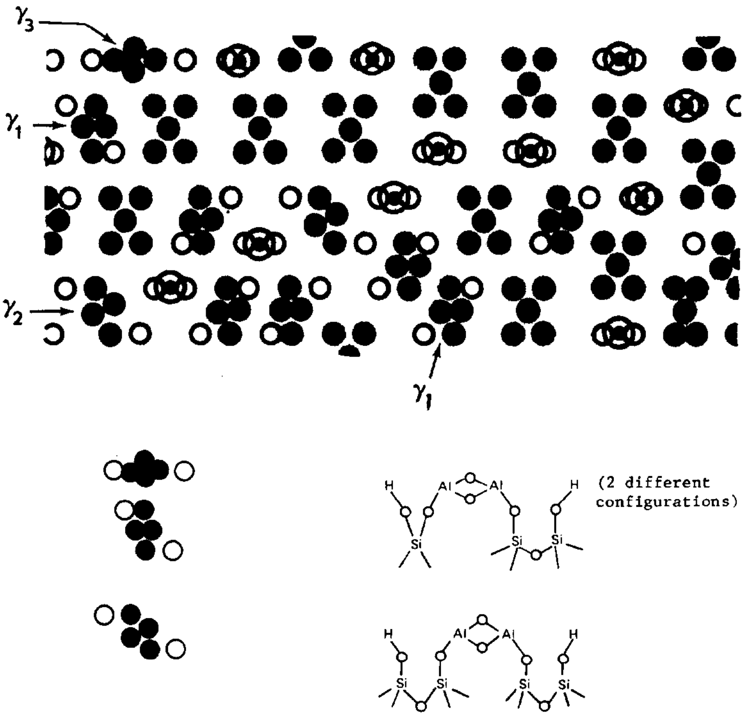


FIG. 5. Surface after formation of various double oxide bridge structures.

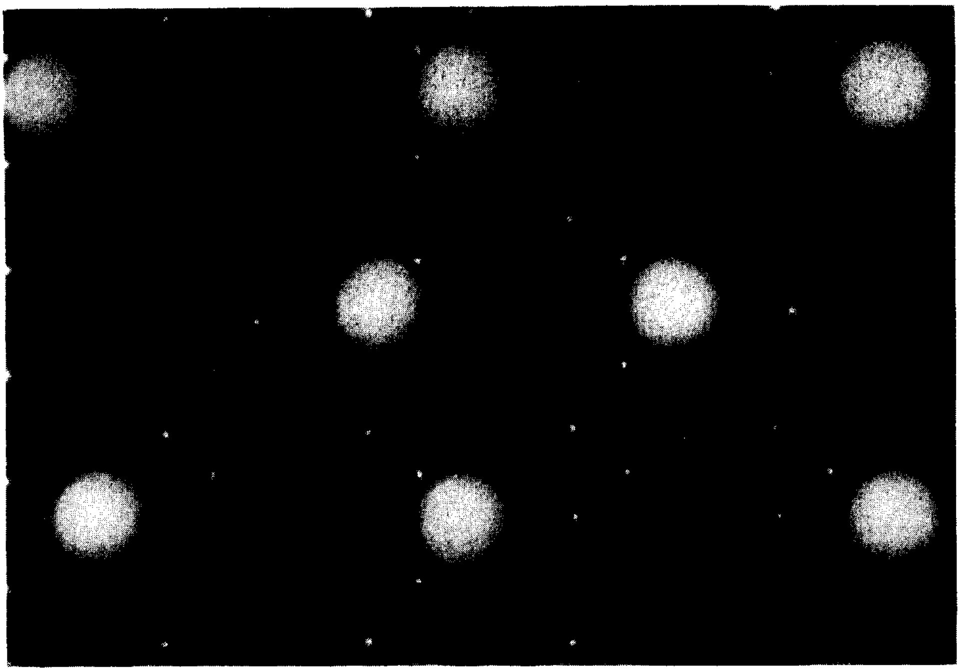


FIG. 6. The structures of γ_1 (upper right), γ_2 (upper left), and γ_3 (lower right) sites.

less likely, bridge of this kind, denoted γ_3 sites, might be made between an oxide ion in a geminal pair and one in an adjoining vicinal pair in the same row.

Figure 6 reveals that the γ_1 and γ_2 sites both provide quasi-tetrahedral coordination for the Al atoms without requiring face-linking of the oxide tetrahedra. Formation of a γ_3 site would, however, require tricoordination of at least one, and probably both, of the Al atoms. The γ_3 sites could, therefore, be created only where no alternative bridging was possible. They would be highly acidic.

All nonbridged Al-containing sites will be referred to as δ sites, which can be of at least two types: δ_1, formed from geminal pairs, and δ_2, formed from vicinal pairs. Both are also shown in Fig. 3.

If the original silica gel is predried sufficiently (e.g., at 800°C) to remove all vicinal pair hydroxyl groups before reaction with $AlCl_3$, no subsequent formation of β, γ, or δ_2 sites should be possible; but α and δ_1 sites can still be formed.

Table 1 summarizes the various types of sites discussed above. The ϵ-sites will be discussed below.

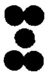
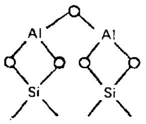
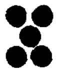
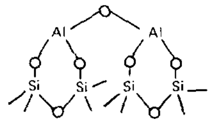
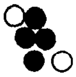
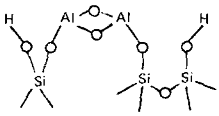
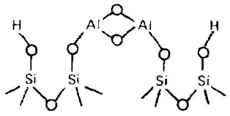
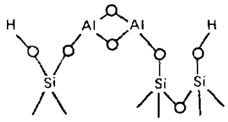
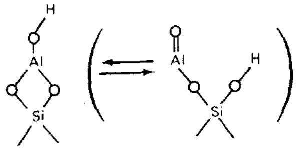
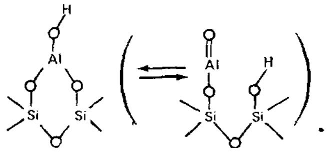
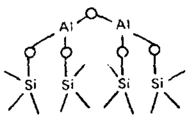
Surface Concentrations of α and β Sites

Hydroxyl groups can presumably be removed from the hydroxylated silica–alumina surface only through formation of either α or β sites. The possible numbers of α and β sites should depend on the numbers of geminal and vicinal hydroxyl pairs originally present on the silica surface before reaction with $AlCl_3$ vapor, and on the probability that such pairs lie opposite similar pairs in adjacent rows.

Maximum numbers of isolated geminal pairs and vicinal pairs occur on a cristobalite surface after drying to the extent shown in Fig. 1. It was reported previously (*18*) that 15.4% of the possible geminal pair sites remained filled after all possible removal of hydroxyl groups through random condensation between adjacent geminal pairs. However, on the larger surface shown in Fig. 1, only 13.5% of the geminal pairs remained

TABLE I

POSSIBLE TYPES OF SITES ON SILICA-ALUMINA

α			SINGLE OXIDE BRIDGE BETWEEN Al ATOMS ATTACHED TO 2 GEMINAL PAIRS IN ADJOINING ROWS.
β			SINGLE OXIDE BRIDGE BETWEEN Al ATOMS ATTACHED TO 2 VICINAL PAIRS IN ADJOINING ROWS.
γ_1			DOUBLE OXIDE BRIDGE BETWEEN VICINAL PAIR IN ONE ROW AND GEMINAL PAIR IN ADJACENT ROW.
γ_2			DOUBLE OXIDE BRIDGE BETWEEN VICINAL PAIRS IN ADJACENT ROWS.
γ_3			DOUBLE OXIDE BRIDGE BETWEEN GEMINAL AND VICINAL PAIRS IN SAME ROW.
δ_1			Al-OH ATTACHED TO GEMINAL PAIR (UNBRIDGED)
δ_2			Al-OH ATTACHED TO VICINAL PAIR (UNBRIDGED)
ε			SINGLE OXIDE BRIDGE BETWEEN Al ATOMS EACH ATTACHED TO 2 NON-LINKED ADJACENT SILICON ATOMS IN ADJACENT ROWS.

at a total surface OH coverage equal to 56.7% of the original. Weighted averaging of these and previous results (15.4 and 58%, respectively) gives an isolated geminal pair coverage or 13.8% and a total OH coverage of 57% at this stage of OH removal. (On the surface shown in Fig. 1, 171 geminal pairs and 549 vicinal pairs remain.)

If the isolated hydroxyl pairs left on the original silica are randomly distributed, either as in Fig. 1 or after further dehydration of the surface of Fig. 1, the probable number of α sites on a silica–alumina surface made from this silica can be predicted fairly well.

The approximate number of α sites can be shown to be given by

$$N_\alpha \cong N\theta_g^2(1 - 0.9\theta_g + 0.4\theta_g^2). \qquad (1)$$

Similarly, the expected number of β sites is approximated by

$$N_\beta \cong N\theta_v^2(1 - 0.9\theta_v + 0.4\theta_v^2), \qquad (2)$$

where $\theta_g = N_g/2N$ and $\theta_v = N_v/2N$, N_g and N_v being the numbers of geminal and vicinal OH groups and N the total number of possible sites for the groups. (N is the same for vicinal and geminal OH groups though the two sets of sites are different.)

The maximum numbers of both isolated geminal and isolated vicinal hydroxyl pairs on silica exist when the surface hydroxyl coverage has been reduced by drying to about 57% of its theoretical maximum value. At this point, $\theta_g = 0.138$ and $\theta_v = 0.432$. When N is taken as 3.95 $\times 10^{14}/\text{cm}^2$, the maximum number of α sites is $6.62 \times 10^{12}/\text{cm}^2$ and of β sites $5.1 \times 10^{13}/\text{cm}^2$.

As the silica is predried further, the number of geminal pair hydroxyls remains relatively constant, while the number of vicinal pair hydroxyls decreases continuously. The maximum possible number of α sites on silica alumina should thus be independent of the predrying of the original silica above 400°C. The maximum number of β sites should decrease continuously with progressive dehydration of the original silica surface below 57% hydroxyl coverage, reaching zero at 13.8% coverage. The maximum numbers of α or β sites on a given silica–alumina should, however, only be formed after the catalyst has been very strongly predried (e.g., at 800°C).

Surface Concentration of Hydroxyl Groups on Dry Silica–Alumina

The concentration of hydroxyl groups left on the model silica–alumina surface after formation of all possible α and β sites can be predicted, provided that the concentration of hydroxyl groups on the surface of the original silica is known and the silica had been predried sufficiently so that only isolated geminal and vicinal hydroxyl pairs remained. If, during preparation of silica–alumina, each $AlCl_3$ molecule reacts with two hydroxyl groups, and hydrolysis then gives one Al–OH group, we would expect that, at most, 50% of the hydroxyl groups originally present would remain. Formation of Al–O–Al bridges should further reduce the number of hydroxyl groups, each bridge replacing two hydroxyl groups.

The maximum concentration of hydroxyl groups as isolated hydroxyl pairs on silica, 57% of the theoretical maximum hydroxyl concentration, corresponds to 4.5×10^{14} OH groups/cm^2. The maximum numbers of α and β sites on silica–alumina made from such a silica surface are 6.6×10^{12} and 5.1×10^{13} sites/cm^2, respectively. The expected hydroxyl concentration on the final (800°C-dry) silica–alumina is thus $0.5\ (4.5 \times 10^{14}) - 2\ (5.76 \times 10^{13}) = 1.10 \times 10^{14}/\text{cm}^2$, roughly equal to the concentration of hydroxyl groups expected on pure silica dried to the same extent. In the case of silica, however, only isolated geminal pairs (1.09×10^{14} OH groups/cm^2) should remain after drying at 800°C. If the original silica is predried at 800°C, with removal of all but isolated geminal pair hydroxyl groups before being converted to silica–alumina, the expected level of residual OH is only $0.5\ (1.09 \times 10^{14}) - 2\ (0.066 \times 10^{14}) = 4.1 \times 10^{13}$ OH/cm^2. The simple model thus predicts that on 800°-dry silica-alumina the number of residual OH groups

TABLE 2

Adsorption Sites and OH Groups[a]

	$NH_3/cm^2 \times 10^{-13}$		α Sites/ $cm^2 \times 10^{-12}$		$OH/cm^2 \times 10^{-13}$	
	Observed	Predicted[b]	Observed[c]	Predicted[b]	Observed	Predicted[b]
SAV-1	12.5	13.4	8.1	6.6	~8	9.7
SAV-2	7.4	5.4	7.3	6.6	8.3	4.1

[a] Samples predried at 800°C.

[b] Predictions from model, given the number of OH groups on original silica.

[c] By "titration" with butene to displace CO_2.

should be less than half the number expected on the original silica similarly dried at 800°C.

Agreement with Data

As shown in Table 2, the available experimental evidence (*15–17*) seems consistent with the predictions of the model as to the maximum number of α sites. The concentrations of α sites on two 800°-dried silica–aluminas (SAV-1 and SAV-2) made from silica aerogel predried at 600° and 800°C were found, by titration with butene, to be 8.1×10^{12} and 7.3×10^{12} sites/cm², respectively. Allowing for titration errors, these values are in good agreement with the predicted concentration of 6.6×10^{12} sites/cm².

No equivalent methods now exist to measure the concentration of β or other sites. Titrations with *n*-butylamine showed that two classes of strong acid sites ($pK_a = -5.6$ and -3.0) existed on SAV-1 while only the stronger of these was present on SAV-2. This would be predicted by the model. As measured by butylamine titration, however, there are many more acid sites than the α and β sites predicted by the model. Adsorption of NH_3 also occurs on many sites other than the α or β sites. Under some conditions selective chemisorption of HCl might provide a measure of the total number of $\alpha + \beta$ sites, but any free alumina would also chemisorb HCl readily, rendering this method questionable for general use.

On SAV-2 there should be few, if any, β sites, but 4.1×10^{13} δ_1 sites plus 6.6×10^{12} α sites should remain, even when all vicinal pairs are removed from the original silica gel before reaction with $AlCl_3$. Assuming that one NH_3 molecule is strongly held by each exposed Al atom, the limiting strong adsorption of NH_3 should never fall below $5.4 \times 10^{13}/cm^2$ ($7.4 \times 10^{13}/cm^2$ was actually observed on SAV-2). On SAV-1, we should expect roughly $8 \times 10^{13}/cm^2$ more NH_3 adsorption sites than this minimum, or 13.4×10^{13} sites/cm², including about 1.5×10^{13} β sites/cm² plus α, γ, and δ sites. The number actually found was 12.5×10^{13}. Butylamine titration gave 5.8×10^{13} total sites/cm² for SAV-1 and 2.5×10^{13} for SAV-2, less than half the values obtained from NH_3 adsorption; but steric effects probably prevent the adsorption of one butylamine molecule for each exposed Al atom.

Absorbance measurements on OH spectra (*16*) indicated that after drying at 600°C, silica–alumina (SAV-2) prepared from 600°C-predried silica held 1.25×10^{14} OH/cm² and that this number decreased to $8.3 \times 10^{13}/cm^2$ after drying at 800°C. Silica–alumina (SAV-1) prepared from silica predried at 800°C also appeared to retain about 8×10^{13} OH/cm² after drying at 800°, rather than 4.1×10^{13} as predicted by the model. Both silica–aluminas were, however, prepared from silica samples which held some nonpaired hydroxyl groups.

The model assumes that the original silica surface holds only paired hydroxyl groups. Experimental data showed that only 64% of the surface hydroxyl groups behaved as if paired during preparation of SAV-2 and only 86% appeared paired in preparation of SAV-1. The reaction of $AlCl_3$ with isolated single-surface hydroxyl groups on a dry silica surface could in principle lead to formation of types of acid sites not considered by the model. In the simplest case, if no oxide bridging involving singly attached Al atoms were possible, each singly attached Al atom might ultimately give only one "δ_3 site" (Si—O—$Al^{\delta+}$=$O^{\delta-}$). Bridging could greatly increase the number of possibilities, but it seems unprofitable to consider these at present.

Effect of Arrangement of Hydroxyl Groups on Dry Silica on Properties of Silica–Aluminas Made Therefrom

The numbers of α and β sites should depend on the arrangement of hydroxyl groups on the dry silica surface from which the silica–alumina is made. The calculations above assume that the silica surface resembles a partially dehydrated cristobalite 100 face holding randomly distributed paired hydroxyl groups. Calcination at high temperatures with subsequent rehydration can, however, cause changes in the surface which are not fully reversible. Surfaces may result on which the hydroxyl groups are single, rather than paired, or on which paired hydroxyl groups are distributed regularly, rather than randomly. Such changes in the distribution of hydroxyl groups should affect the numbers and types of acid sites generated by subsequent treatment in making silica–alumina. Redistribution of paired hydroxyl groups could, for example, permit the formation of many more α sites by yielding a surface on which isolated geminal pairs are always directly opposite one another in adjoining rows. More probably, however, rearrangement would instead minimize both the number of isolated geminal pairs and the frequency with which hydroxyl pairs, either geminal or vicinal, occur directly opposite one another in adjacent rows rather than in alternate rows. This would yield fewer α and β sites rather than more. In the limit, no such sites could be made.

Formation of Acid Sites by Reaction of Al Salts With "Wet" Silica Surfaces

Although the model was designed to describe silica–aluminas prepared by reaction of $AlCl_3$ vapor with a "dry" silica surface, it may be worthwhile to consider the changes that might result when preparation involves reaction with more fully hydrated silica surfaces or even in normal aqueous preparation. In such circumstances additional possibilities exist for surface groups, but the extent to which they are realized cannot presently be determined. On a fully hydroxylated cristobalite 100 face, aluminum atoms would probably react preferentially with hydroxyl groups on two adjoining silicon atoms rather than with two groups on the same silicon atom. In principle, such reaction of all surface OH groups (two per attached Al) could produce a silica–alumina holding 20.7 wt% Al_2O_3 from silica having a surface area of 800 m^2/g; but, as shown in Fig. 7, the bridge sites left after dehydration (ϵ sites) would be different from those made from drier silica. In ϵ sites the aluminum ions would only be tricoordinated, rather than essentially four-coordinated as in the α or β sites. They should thus behave as stronger acids, but, because of the lower coordination of the aluminum, they should also prove unstable toward transformation into α, β, or other sites on heating in the presence of H_2O vapor (which facilitates rearrangement of the surface). Sites of this type may explain the stronger acid sites ($pK_a < -8.2$) typically observed on fresh silica–alumina catalysts prepared by normal aqueous methods. Loss of these sites is known to occur readily on steaming fresh catalyst. Steaming apparently transforms them, at least partially, into sites of lower acid strength. Typical acidity ($\sim$0.45 m equiv/g on 550 m^2/g silica–alumina), corresponding to roughly 5×10^{13} sites/cm^2, observed for catalysts which show only the strongest acid sites, is well below the maximum the-

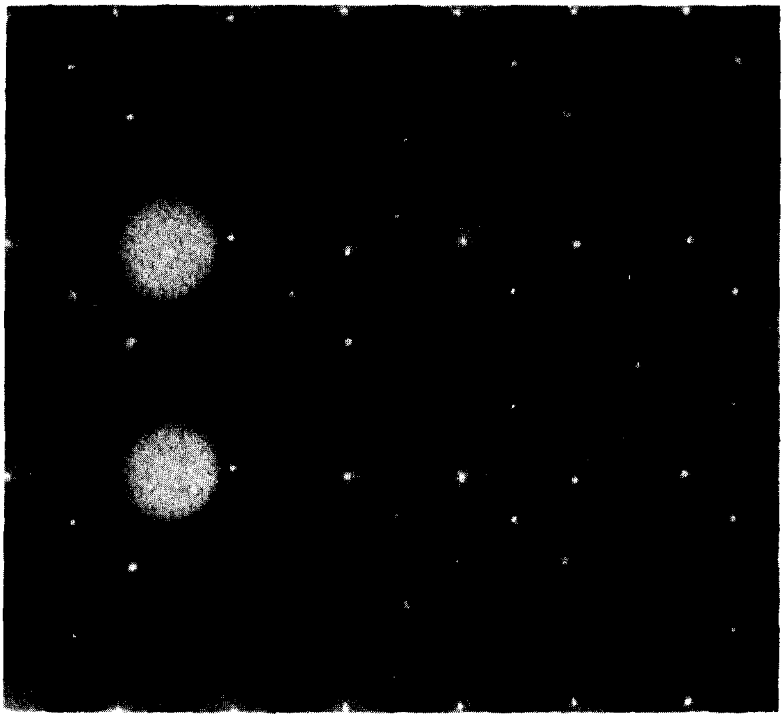
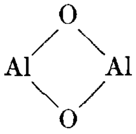


FIG. 7. The structure of ϵ sites.

oretically possible through ϵ site formation (2×10^{14} sites/cm^2). If, however, both the hydroxyl groups on a surface silicon atom cannot simultaneously react with Al (i.e., a surface Si atom cannot be joined through oxygen to two Al atoms), and if adjacent rows of hydroxyl groups behave independently, the expected maximum concentration of ϵ sites should be the same as that calculated for the β sites (5.06×10^{13} sites/cm^2).

It might also be possible to attach each Al atom to only one surface hydroxyl group and thus to attach two Al atoms (through oxygen) to each surface silicon atom. Each such Al would eventually hold two OH groups which on subsequent heating would presumably condense with similar groups on adjoining Al atoms to form

Al—O—Al or



bridges. The Al atoms in such bridges would apparently be tricoordinated, giving very strong acid sites which would be readily converted to weaker, but more stable, α and β sites. Such sites could provide an alternative explanation for the strongest acid sites seen on fresh normally prepared silica–aluminas.

The Adsorptive and Catalytic Properties of α and β Sites

The ionic character of the α sites could be important in facilitating reactions of hydrocarbons through formation of ionic intermediates. On the other hand, HCl is chemisorbed on the same sites, producing H-bonded OH groups which act as catalytically active protonic acids. Presumably, other H donors could act similarly. Both aspects of these sites are probably catalytically important, and for certain reactions their combined effect may be essential. The β sites are presumably similar to the α sites in their properties except that their ionic character is less marked. Adsorption of HCl on β sites also forms H-bonded OH groups. Although the catalytic properties of these OH groups or their behavior as protonic acids has not yet been investigated, it seems likely that they should also be highly acidic. Because the β sites are formed with less "strain" they can probably participate more readily than can the α sites in reaction steps which require reversible opening and closing of the oxide link: for example, reversible abstraction of a proton or hydride from an organic molecule, with transient donation of the hydrogen to either the oxide or an aluminum atom. Further study of the catalytic properties of silica–aluminas which hold well-defined types of sites is needed, however, before firm conclusions can be drawn regarding the relative importance of the various types of sites.

CONCLUSION

The proposed model can explain the nature and numbers of some of the "acid" sites on certain silica–alumina catalysts reasonably well. Present analytical methods and data do not, however, adequately distinguish between all the types of sites postulated by the model, and evaluation of some predictions is therefore not currently possible.

Although the silica–aluminas which the model was designed to explain represent a special class of catalysts whose preparation differs in important particulars from that of other silica–aluminas, there is reason to think that the postulated types of acid sites may be common to most well-aged silica–aluminas. The α sites, differing slightly in properties, appear to exist on a wide variety of silica–aluminas as well as on pure alumina.

The α sites probably include a range of generally similar structures, but it seems remarkable that the concentration of these sites is relatively constant on various silica–aluminas and on γ-alumina. This constancy may reflect statistically-similar processes occurring during dehydration of the surfaces.

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