The Effect of Base Exchange on the Oxidizing Properties of Silica-Alumina Catalysts

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A quantitative study has been made of the effect of base exchange on the oxidizing (radical-forming) power of a silica-alumina catalyst. A single base-exchange-dehydration cycle causes a drop in radical-forming activity to about one-third and subsequent base-exchange-dehydration cycles result in a further stepwise reduction in oxidizing power. The sodium uptake and the decrease in surface acidity follow a similar stepwise pattern. These results are interpreted in terms of the Danforth formulation of the acid sites on a silica-alumina surface. They provide support for the view that oxidizing activity is associated with Lewis acid sites produced by elimination of the elements of water from hydroxyl groups surrounding aluminum ions in the surface. The role of silica is to facilitate the formation of these sites and to contribute to their stability. A study of the effect of activation temperature on the oxidizing properties of the unexchanged and exchanged catalysts supports this interpretation.

An explanation of the results based on the blocking of active oxidizing centers by the hydration sheath surrounding metal cations on adjacent sites is also discussed.

INTRODUCTION

Although it is now well established that hydrocarbons may exist in the free radical form on the surface of silica-alumina (*1, 2*) and alumina (*3*) catalysts, the exact nature of the site involved in the electron transfer process remains obscure. It seems probable, however, that acid sites on the surface are in some way involved (*4*). Since these acid sites may be drastically affected by base exchange of the surface protons, the effect of such exchange on the oxidizing properties of the catalyst should provide information about the mechanism of radical formation on the surface.

Early reports stressed the finding that the radical-forming ability of a silica-alumina catalyst was retained after base exchange with sodium ions, whereas cracking activity for cumene and propylene polymerization activity were strongly reduced or eliminated (*2, 4*). Subsequent reports suggested a more complex situation.

Terenin *et al.* (*5*) found that the electron spin resonance (ESR) absorption of anthracene chemisorbed on a 30:70 alumina-silica gel was decreased to one-third when the surface protons were exchanged for sodium cations. Hirschler (*6*), using both Hammett and arylmethanol indicators, concluded that the effect of adding metal ions to a silica-alumina was to bring about a modification of acid strength distribution in which strong acid sites were eliminated and replaced with sites of less acid strength.

According to Danforth (*7*) the sites on a silica-alumina surface which might be expected to show exchange acidity would be those in which the aluminum is connected to the silica lattice by two, three, or four bonds. Exchange with Na+ at such sites and subsequent dehydration (activation) has been formulated by Danforth (*8*) as shown in Fig. 1. Site 1 is a Bronsted and site 2 a Lewis acid; both are eliminated by the base-exchange-dehydration procedure.
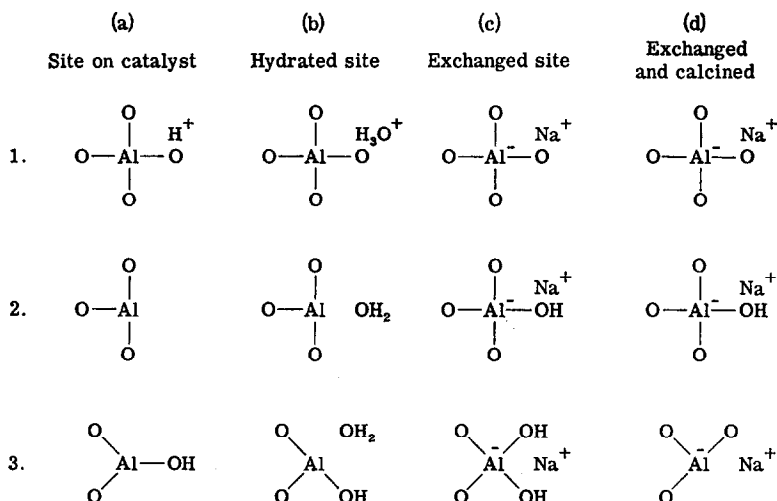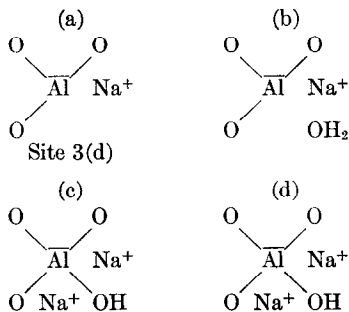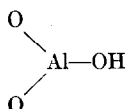
FIG. 1. Base exchange and dehydration at acid sites on a silica-alumina surface (Danforth).

Site 3 dehydrates to a new Lewis acid site 3(d) which is only eliminated after a further base-exchange–dehydration cycle. It is therefore a consequence of the Danforth

formulation that Lewis acid sites on the original unexchanged surface represented by

should only be eliminated by a double base-exchange process. In the same way it can be shown that Lewis acid sites of the type
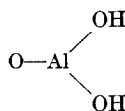
should require a threefold base-exchange–dehydration procedure before being completely eliminated. If, as seems probable,

the oxidizing power of the surface is associated with the Lewis acidity, a further consequence should be a stepwise reduction in the radical-forming ability of the catalyst with repeated base-exchange–dehydration cycles.

The present report describes a quantitative study of the effect of base exchange on the acidity and oxidizing power of a silica-alumina catalyst to test this hypothesis.

EXPERIMENTAL

Materials

Silica-alumina. The catalyst was a commercial sample supplied by Imperial Chemical Industries Limited (Agricultural Division) in pellet form (composition: Al_2O_3, 10%; Fe_2O_3, 0.05–0.10%; Na_2O, 0.05–0.20%; SiO_2, 89.7–89.9%). It had been calcined at 695°C and had a surface area, determined by nitrogen adsorption, of 255 m²/g. After crushing and sieving, particles of 44–60 mesh B.S.S. were heated at 550°C in oxygen for 2 hr, allowed to cool in a vacuum, washed in distilled water, dried at 120°C for 1 hr, and then heated at 550°C in oxygen for 3 hr. Activated catalyst was stored over phosphoric oxide in a desiccator.

Base-exchanged silica-alumina. Activated catalyst samples (1.5 g) were base-ex-

changed with sodium by digesting with aqueous sodium acetate solution (100 ml 0.4 M) at either room temperature or 85°C for periods of 18 hr to 12 days. The exchanged catalyst was washed in distilled water, dried at 120°C, and heated at 550°C in oxygen, as in the pretreatment described above. Samples of base-exchanged catalysts were further exchanged with sodium by the same method. The amount of sodium taken up was estimated by flame photometry using a solution obtained by heating the catalyst sample with AnalaR sulfuric acid in a covered platinum crucible for 30 min at the boiling point of the acid.

A similar procedure was employed to obtain potassium-exchanged catalyst.

Perylene. This was obtained from Rütgerswerke-Aktiengesellschaft. Benzene (AR grade) was used as solvent for the perylene, after being allowed to stand for 24 hr over a large sample of activated silica-alumina and filtered before use. At the end of this period the catalyst was dark brown. When freshly activated catalyst was added to the purified benzene, no brown coloration appeared.

Oxidation of Perylene

The oxidizing power of the unexchanged silica-alumina and of the ion-exchanged silica-aluminas were compared using perylene as the adsorbate. Previous work showed that this hydrocarbon is quantitatively converted into its stable monopositive ion on the surface of unexchanged silica-alumina (9). Present experiments confirmed the quantitative nature of the conversion with perylene on base-exchanged catalyst (see below). The perylenium ion is readily detected by its characteristic ESR spectrum.

Electron resonance measurements were made at room temperature with a reflection-cavity spectrometer operated at 9450 Mc/sec, employing 100 kc/sec magnetic field modulation and phase-sensitive detection. Relative concentrations of perylene radical ions were determined by measuring changes in peak-to-peak height on the first derivative curves. Absolute concentrations were estimated by integrating the derivative

spectrum and determining the area under the integrated curve. This area was compared with that obtained using a standard solution of 1,1-diphenyl-2-picrylhydrazyl.

Procedure. Samples were contained in 6-mm glass tubes which were sealed with a 14-mm ground-glass cap; each tube was provided with a sidearm fitted with a similar cap. A known weight (~0.35 g) of activated catalyst was placed in the tube and heated for 2 hr at 250°C and 10^{-5} mm Hg. The sample was allowed to cool to room temperature and dry nitrogen admitted. A standard solution of perylene in benzene (~7 × 10^{-4} M) was added from an Agla micrometer syringe via the sidearm using a funnel. The tube was then detached from the vacuum line and sealed with a ground-glass cap. After a period of 24 or 48 hr, during which time the contents of the tube were stirred carefully three or four times for several minutes, an aliquot portion of the supernatant solution was withdrawn and its perylene content estimated by the method previously described (9). The amount of perylene adsorbed on the silica-alumina surface was obtained by difference.

Acidity Measurements

Determination of the number of acid sites on the catalyst surface was made by the n-butylamine titration technique developed by Johnson (10). The Hammett indicator used in the present study was benzal-acetophenone (pK_a = —5.61). The acid strength of the catalyst surface was also obtained using triphenylmethanol ($pK_R{}^+$ = —6.63) as indicator. Prior to titration, catalyst samples were heated at 550°C in oxygen for 3 hr and allowed to cool in a vacuum.

RESULTS

Figure 2a shows the effect of exchange with Na$^+$ at room temperature on the radical-forming power of the silica-alumina catalyst. The most active sample of catalyst which had not been ion-exchanged adsorbed 5.21 × 10^{-4} g of perylene per gram of catalyst. This figure is the difference between the amount of perylene added initially and that remaining in solution when adsorption
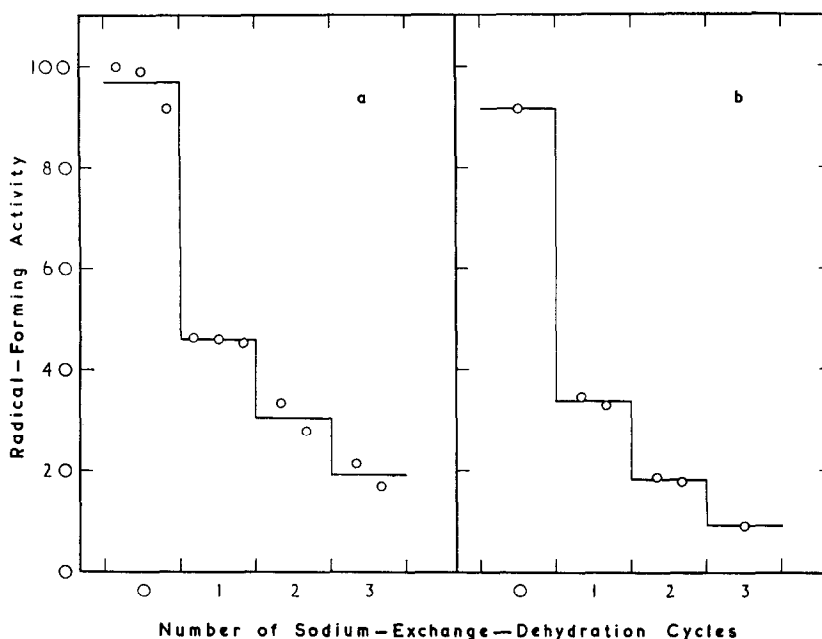
FIG. 2. Radical-forming activity of the silica-alumina catalyst as a function of the number of sodium-exchange–dehydration cycles: (a) exchanged at 20°C; (b) exchanged at 85°C.

is complete. The uptake of perylene and its conversion into the free radical form by this catalyst sample was arbitrarily selected as the standard (100% activity) for the present series of measurements; the oxidizing power of the other catalyst samples are given relative to this standard. As shown in Fig. 2a, repeated ion-exchange–dehydration cycles produced a well-defined stepwise reduction in radical-forming power. Catalyst samples were usually left in contact with the sodium acetate solution for 1–3 days. No further reduction in activity was observed when the contact time was increased to 12 days. Ion exchange at 85°C (Fig. 2b) produced the same stepwise fall in activity although the total reduction in activity was somewhat greater at the higher temperature. A similar stepwise reduction in activity was observed with silica-alumina which had been exchanged with K+ (not plotted), but the poisoning effect of potassium on the radical-forming activity, under comparable conditions, was substantially greater.

A previous investigation had established that with the unexchanged catalyst all the adsorbed perylene is converted into peryl-

enium ion (9). Experiments confirmed that this is also true of base-exchanged silica-alumina. Thus, for the catalyst which had been twice exchanged with Na+ at 85°C the mass of perylene adsorbed per unit mass of catalyst, calculated from the difference between the initial and final concentrations of the supernatant solution, was found to be 9.25×10^{-5} g. The mass of perylene existing as radical ions on the catalyst surface was obtained from a comparison of the spectrum of the perylene radical–catalyst system with that for a standard solution of perylene. It was found to be 8.69×10^{-5} g/g of catalyst, a difference of ca. 6% or approximately the experimental error of the measurements.

The n-butylamine titers for the unexchanged silica-alumina and the three sodium-exchanged catalysts using both the Hammett indicator (H_o acidity) and the arylmethanol indicator (H_R acidity) are shown in Fig. 3. A stepwise reduction in acidity was observed with both classes of indicator as the sodium content (also plotted) of the catalyst increased. Because this sample of silica-alumina was exchanged
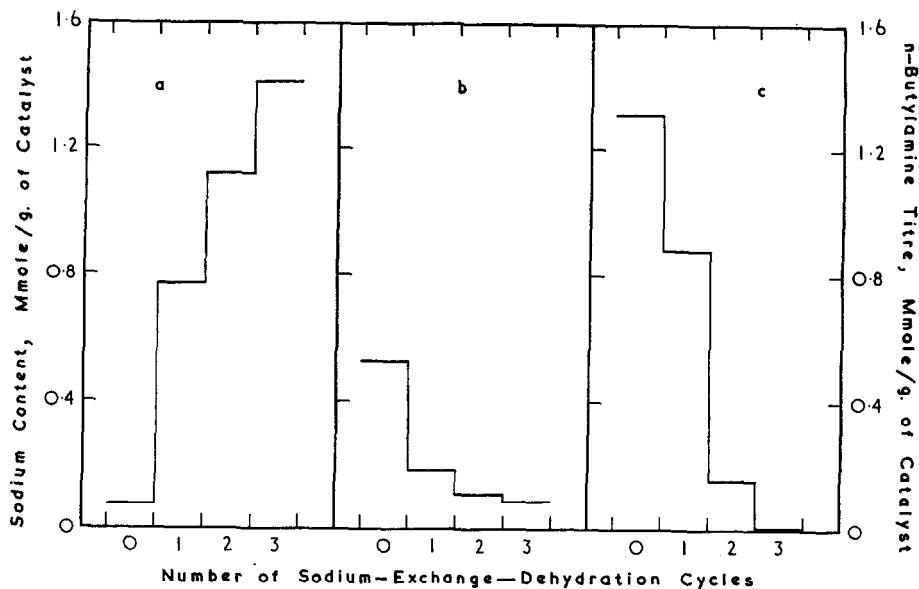
FIG. 3. (a) Sodium content of the silica-alumina catalyst as a function of the number of sodium-exchange–dehydration cycles.

Butylamine titers for the catalyst vs number of sodium-exchange–dehydration cycles: (b) Hammett indicator; (c) arylmethanol indicator.

with Na$^+$ at 85°C, these histograms are to be compared with Fig. 2b.

The measurements just reported refer to catalyst activated at about 550°C. Varia-

tion in the temperature of activation discloses another marked difference in behavior between unexchanged and base-exchanged silica-alumina. Figure 4 shows for
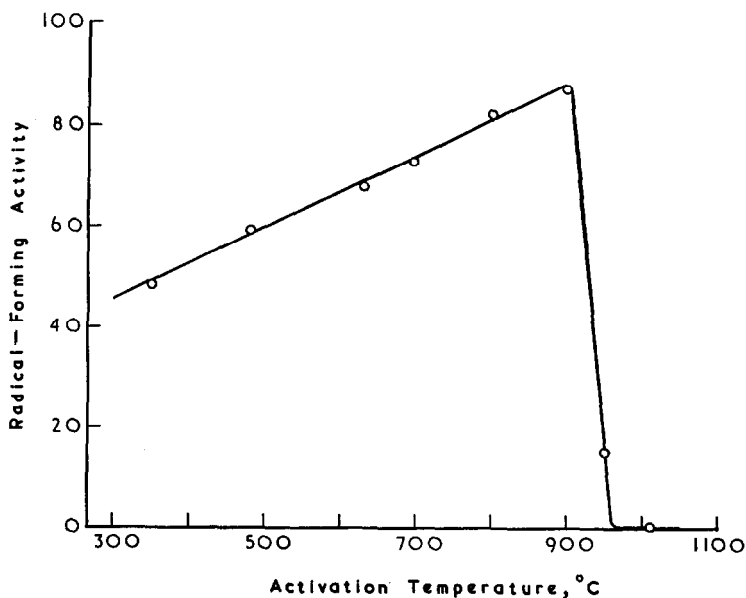

FIG. 4. Radical-forming activity of the unexchanged silica-alumina as a function of activation temperature.

the unexchanged catalyst a plot of signal amplitude (peak-to-peak height on the first derivative curve), obtained when a constant amount of perylene in benzene in excess of that required for saturation of the catalyst sample was added to a fixed weight of the catalyst, plotted against activation temperature. The ability of this catalyst to oxidize perylene to the monopositive ion is approximately doubled between 300° and 900°C. Above 900°C the oxidizing power falls sharply, the catalyst becoming inactive for perylenium ion formation between 950° and 1000°C.

The effect of variation in activation temperature on the radical-forming activity of the three sodium-exchanged silica-aluminas is similar and differs markedly from that of the unexchanged catalyst. The base-exchanged catalysts show only a moderate increase in oxidizing power as the activation temperature is raised from 300° to 600°C. This moderate increase is followed, however, by a dramatic increase between 600° and 900°C (Table 1). Above 900°C the radical-forming ability falls sharply. The marked difference in behavior between

TABLE 1

RADICAL-FORMING ACTIVITY OF
SODIUM-EXCHANGED SILICA-ALUMINAS

Activation temperature (°C)	Number of sodium-exchange-dehydration cycles		
	1	2	3
300	1.2	0.4	0.2
500	3.7	2.1	1.5
700	11.8	7.7	5.2
900	31.4	20.3	800°C/10.5

the unexchanged and the ion-exchanged silica-alumina in the 600–900°C temperature range is emphasized in Fig. 5. This figure presents plots of signal amplitude versus activation temperature for the four catalyst samples, the amplitudes being expressed relative to the signal for the corresponding catalyst sample heated at 800°C. The sharp increase in oxidizing power shown by the ion-exchanged catalysts above 600°C contrasts with the continuing linear increase in radical-forming activity exhibited by the unexchanged silica-alumina as it is heated through this temperature range. Another significant feature of Fig. 5
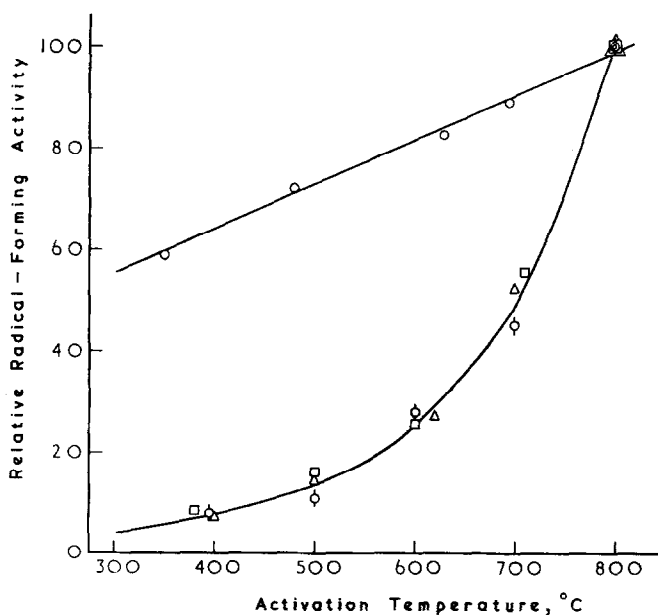

FIG. 5. Radical-forming activity expressed relative to that of the same sample activated at 800°C vs activation temperature: unexchanged silica-alumina (○); catalyst once (□), twice (△), and thrice (◇) exchanged with sodium ion.

is that a single curve fits all the relative signal amplitude–activation temperature data for the sodium-exchanged catalysts.

Plots of catalyst radical-forming activity as a function of the number of base-exchange–dehydration cycles were prepared from the experimental results presented in Fig. 4 and Table 1 for different activation temperatures. (The signal amplitudes reported in Fig. 4 and Table 1 are for the same spectrometer gain setting.) These plots (not shown) all exhibited a stepwise fall in activity similar to that shown in Fig. 2. However the activity possessed by the four catalyst samples at the various activation temperatures was appreciably less than that expected from Fig. 2 when the samples were heated at 550°C. This partial deactivation was due to absorption of moisture. The results shown in Fig. 4 and Table 1 were obtained with catalyst samples cooled in a desiccator over phosphoric oxide at atmospheric pressure. Data for Fig. 2 were obtained with samples cooled *in vacuo* and brought up to atmospheric pressure with dry nitrogen. Experiments showed that samples of the same catalyst could differ in radical-forming ability by an order of magnitude depending on which cooling procedure was followed.

DISCUSSION

The present results show that although the oxidizing power of a silica-alumina catalyst is not eliminated by a single base-exchange procedure, repeated base-exchange–dehydration cycles modify drastically its radical-forming ability (Fig. 2). At the same time the sodium ion uptake of the silica-alumina increases in a stepwise fashion with increase in the number of base-exchange–dehydration cycles (Fig. 3a), as required by the Danforth formulation. To this extent the results now described may be taken as strong support for the view that radical formation on silica-alumina surfaces occurs at Lewis acid sites of the type postulated by Danforth and, by implication, that the formulation of the base-exchange–dehydration process set out in the introduction is well founded. From the data in Fig.

2b the proportions of oxidizing centers eliminated by one, two, and three base-exchange–dehydration cycles are 63%, 80%, and 90%, respectively. The drop in activity to about one-third produced by a single base-exchange–dehydration cycle is in excellent agreement with the findings of Terenin *et al.* (*5*).

Although caution is needed in interpreting the results, the measurements of H_o and H_R acidity (Fig. 3b and 3c) lend some weight to these conclusions. There is still uncertainty as to whether the Hammett surface acidity is a measure of the number of Lewis acid sites or Bronsted acid sites, or both (*11*). Bronsted centers should however be totally eliminated on contact with alkali acetate solution. Evidence is available to support this view. Thus, a silica-alumina catalyst once exchanged with sodium ion is completely ineffective for olefin polymerization (*12*). The stepwise reduction in acidity following the first base-exchange–dehydration cycle is probably therefore a stepwise fall in Lewis acidity.

According to Hirschler (*6*) only acid sites of the Bronsted type are measured when a solid catalyst is titrated with *n*-butylamine using an arylmethanol indicator. It seems likely however that some Lewis acidity is also titrated. If arylmethanols react with strong protonic acids according to the equation

$$ROH + H^+ = R^+ + H_2O$$
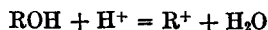
the water produced in this reaction may interact with Lewis sites to form Bronsted centers. Thus, even if stringent precautions are taken to exclude moisture initially, some Lewis acidity may still be measured. As strict precautions were not taken in the present experiments to exclude traces of water vapor, the figures reported in Fig. 3c may be those for total surface acidity. Comparison of these measurements with the sodium content of the catalyst (Fig. 3a) gives at least qualitative support to this contention.

The concentration of oxidizing centers in the unexchanged catalyst, calculated from the data in Fig. 2, is about 1.2×10^{18}/g. Comparison with the Hammett surface

acidity shows that about one in 250 of the sites with acid strength greater than 70% sulfuric acid is capable of oxidizing perylene to the ion radical. On the other hand, about one in 630 of the sites responding to the triarylmethanol indicator (>50% sulfuric acid) is active for this oxidation. Thus only a very small fraction of the total acid sites measured by either indicator is capable of converting perylene into the free radical form. Even when adequate allowance is made for Bronsted acidity, this low value for the number of active oxidizing centers suggests that there is a range of Lewis sites of widely differing acid strength on the catalyst surface. However, according to Benesi 90% of the acid centers on silica-alumina are stronger than 90% sulfuric acid (13). This would suggest that only surface sites with acidity approaching that of 100% sulfuric acid are effective for perylene radical-ion formation. Alternatively, a particular grouping of Lewis acid sites may be necessary for electron transfer to occur. Steric considerations may also be important in that only a small proportion of Lewis sites with the necessary electron-abstracting power may be accessible to the large planar hydrocarbon molecule.

Aalbersberg, Hoijtink, Mackor, and Weijland (14) have shown that in sulfuric acid solution polynuclear hydrocarbons may exist either as the radical cation or as a covalent complex. The present experiments provided no evidence for the existence of a similar covalent complex on the surface of silica-alumina. Within the ±6% experimental error all the perylene chemisorbed was converted into the radical-ion form.

Various workers have speculated about the way in which the acid sites of Fig. 1 may arise. According to Peri (15) Lewis acid centers are formed by elimination of the elements of water from hydroxyl groups surrounding aluminum ions in the outermost layer of the crystal lattice. Since it is now well established that the elements of water are still being removed from hydrated aluminas at 1000°C (16), this would suggest that the radical-forming activity of a silica-alumina catalyst should increase as the temperature of activation is raised to this level. Figure 4 shows that for the unexchanged silica-alumina there is in fact a linear increase of oxidizing power as the activation temperature is raised from 300° to 900°C. Trambouze, de Mourgues, and Perrin (17), using a thermometric titration method, also found that the number of Lewis acid sites on a silica-alumina catalyst increased with activation temperature between 300° and 750°C, the maximum temperature reached in their investigation. This behavior of silica-alumina is closely paralleled by that of alumina itself, which shows a maximum in oxidizing power after activation at about 900°C (3) and is in sharp contrast with the effect of activation temperature on the activity of silica-aluminas for propylene polymerization and for cumene cracking. Thus the propylene polymerization activity of a silica-alumina catalyst containing 10% alumina reaches a maximum at 550°C and then declines sharply, reaching a value of approximately one-half the maximum value when the catalyst is activated at 900°C (18). Again the cumene-cracking activity of a silica-alumina catalyst containing 10% alumina falls to one-half as the activation temperature is increased from 400° to 900°C (19). Because a Bronsted site is probably involved in both the propylene-polymerization (18) and the cumene-cracking (20) reactions, this contrast provides additional evidence for the view that oxidizing power on the one hand and polymerization and cracking activity on the other are associated with different sites on the silica-alumina surface.

Above 900°C there is a dramatic decrease in radical-forming activity. Catalysts activated at 950°C are virtually inactive and remain so when heated subsequently at a lower temperature. On the other hand, a silica-alumina catalyst originally activated at 550°C and subsequently deactivated by a succession of base-exchange–dehydration cycles generates new active oxidizing centers as the temperature of activation is raised to 900°C. As with the unexchanged catalyst a further increase in the activation temperature results in complete loss of oxidizing power. On heating to ca. 1100°C
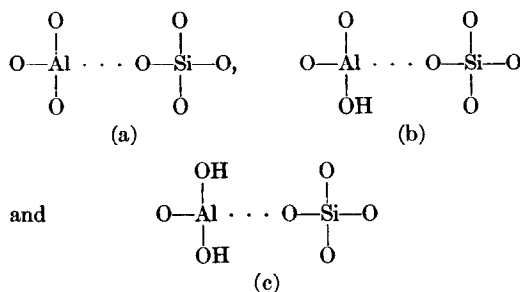
the alumina lattice is converted into the inactive ordered corundum form (21). With silica-alumina the corresponding phase change apparently occurs at a lower temperature.

A significant feature of the relative signal amplitude–activation temperature data for the sodium-exchanged silica-aluminas (Fig. 5) is that all the values fall along the same curve. Following Benesi's suggestion (22), this result might be taken as evidence for regions of closely packed exchange positions on the catalyst surface. All such exchange positions cannot therefore be occupied because of steric hindrance (or electrostatic repulsion) between the solvated cations. Upon heating, the solvation shell surrounding each cation is removed, thereby exposing some unexchanged acid sites. Because the number of sites thus freed will depend on the number of bound sodium ions, an approximately constant fraction of the potentially active oxidizing centers on the surface may be exposed after each base-exchange–dehydration cycle.

Clearly the above picture provides a possible explanation of the data presented in Fig. 5, and at the same time offers an alternative explanation of the stepwise reduction in radical-forming ability of the catalyst with repeated base-exchange–dehydration cycles. One objection to this interpretation of the results may be raised. For the unexchanged silica-alumina the concentration of oxidizing centers is ~1.2 $\times 10^{18}$/g, corresponding to ~5 $\times 10^{11}$ per cm^2 of catalyst surface. On the assumption that these sites are uniformly distributed over the surface the distance between adjacent sites would be about 140 Å. There is some uncertainty about the area on the surface, which is likely to be blocked by the hydration sheath of a sodium cation. The number of water molecules closely associated with the cation in solution is known with reasonable certainty to be about four, but the "secondary" solvation shell may contain as many as 70 water molecules, although there are considerable discrepancies among the experimental data (23). Even on this basis, however, the diameter of the hydrated ion on the surface

is unlikely to exceed 15 Å. Blocking of an oxidizing center by the hydration shell of a cation on an adjacent *oxidizing* site seems therefore improbable unless there is very pronounced clustering of the oxidizing centers. Worth noting, however, is the fact that the exchange acidity of this silica-alumina catalyst is much higher than its perylene-oxidizing ability. When the hydration sheath surrounding sodium ions on sites other than oxidizing centers is also considered, an explanation of the present results based simply on the blocking of active centers offers an attractive alternate to that based on the Danforth hypothesis.

The experiments now described provide support for the view that radical-ion formation on silica-alumina surfaces occurs at Lewis acid sites located around aluminum ions in the surface. The role of silica however cannot be ignored. It may function primarily by facilitating the formation of the electron-deficient structures of Fig. 1 which are active as oxidizing centers and, at the same time, contribute to their stability. If this view is correct, the active sites on a silica-alumina surface should be formulated as

$$
\begin{array}{cc}
\begin{matrix} O \\ | \\ O-Al \cdots O-Si-O, \\ | \quad\quad\; | \\ O \quad\quad\; O \\ \text{(a)} \end{matrix}
&
\begin{matrix} O \\ | \\ O-Al \cdots O-Si-O \\ | \quad\quad\; | \\ OH \quad\quad O \\ \text{(b)} \end{matrix}
\end{array}
$$

and

$$
\begin{matrix} OH \quad\quad O \\ | \quad\quad\; | \\ O-Al \cdots O-Si-O \\ | \quad\quad\; | \\ OH \quad\quad O \\ \text{(c)} \end{matrix}
$$

The data of Fig. 2 suggest that for catalyst activated at 550°C the main contribution to the oxidizing power is from site (a).

Because sites capable of converting perylene into perylenium ion are produced on an alumina surface at high temperatures (600°–900°C) (3), it seems safe to assume that some active oxidizing centers, not involving silica, also occur on silica-alumina surfaces activated at these temperatures. With alumina molecular oxygen is necessary for radical formation. Therefore it seems possible that in the active oxidizing center

of the alumina type oxygen may occupy a role similar to that played by silica in a silica-alumina catalyst. The nature of the sites on an alumina surface and the role of oxygen in both silica-alumina and alumina catalysts will be discussed elsewhere.

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