JOURNAL OF CATALYSIS 41, 312–321 (1976)

The Nature of Active Sites on Catalytic Alumina: Information from Site Poisoning by Sulfur-Containing Molecules

MICHAEL P. ROSYNEK AND FREDLEIN L. STREY

Department of Chemistry, Texas A & M University, College Station, Texas 77843

Received July 17, 1975

The natures of low-temperature (<100°C) catalytic sites on activated alumina have been examined by selective poisoning studies, using various sulfur-containing molecules. Hydrogen sulfide and methyl mercaptan are effective poisons, at 25°C, for sites on alumina that catalyze double-bond migration and *cis/trans* rotation in olefins, but have virtually no effect on sites that promote deuterium exchange reactions of olefins and aromatics. Sulfur dioxide, on the other hand, affects neither type of site at 25°C, but is "lethal" to both types when absorded at 400°C. The results have been correlated with those of previous infrared, EPR, and selective poisoning studies. Olefin isomerization sites on alumina have a surface density of $\approx 5 \times 10^{13}/\text{cm}^2$ and consist of certain exposed Al^{3+} ions at the surface, but may require the presence of adjacent O^{2-} ions. Deuterium exchange sites are much less numerous ($0.3–0.8 \times 10^{13}/\text{cm}^2$) and are associated with a very small fraction of highly energetic surface O^{2-} ions. At 25°C, the two types of sites apparently operate simultaneously but independently of each other.

INTRODUCTION

The nature of active sites on the surface of catalytic (gamma/eta) alumina has been the subject of considerable investigation during the past 15 yr. Particular attention has been focused on selective poisoning studies of surface sites that are active for certain low-temperature (<100°C) test reactions such as double-bond isomerization of olefins and deuterium exchange reactions of hydrocarbons. Both types of reactions are useful surface probes because they proceed at convenient rates on alumina at temperatures as low as 0°C, and, in the case of deuterium exchange reactions, occur without formation of chemically distinct product molecules. These studies have demonstrated that carbon dioxide, for example, selectively poisons surface sites on alumina that catalyze deuterium exchange reactions of hydrogen (*1*), methane (*2*), benzene (*3*, *4*), *n*-butenes (*5*), and various cyclic olefins (*6*), while having virtually no effect on sites that promote double-bond migration and *cis/trans* rotation in olefins (*5*). Quantitative titration techniques, using CO_2, have established an upper limit of $0.3–0.8 \times 10^{13}/\text{cm}^2$ as the average surface concentration of exchange sites (*2*–*4*). In addition, consideration of previous infrared studies of the CO_2/alumina system (*7*, *8*) led to the tentative identification of these sites as exposed Al^{3+} ions on the alumina surface (*9*).

Recently, however, Lunsford *et al.*, using an EPR/selective poisoning technique, have obtained convincing evidence that exposed Al^{3+} species on alumina are associated with olefin isomerization sites rather than with D_2 exchange sites (*10*). These authors studied the hyperfine splitting in the EPR spectrum of nitric oxide adsorbed on alumina that results from the magnetic interaction of unpaired electrons in NO molecules with exposed ^{27}Al species on the alumina surface. They found that such sites do not strongly adsorb CO_2, but can be effectively blocked by preadsorbed hydrogen sulfide, and, moreover, that decreases in both the intensity of the NO EPR spectrum and the catalytic activity of alumina for 1-butene isomerization vary in identical linear fashions with the surface concentration of adsorbed H_2S. Using this technique, an upper limit of approximately $5 \times 10^{13}/cm^2$ was established for the surface density of isomerization sites. Since olefin isomerization sites and D_2 exchange sites on alumina are known to operate simultaneously but independently of each other (*5*), the above results leave in doubt the nature of the exchange sites.

In the present study, we have investigated further the selective poisoning effects of various sulfur-containing molecules on D_2 exchange reactions of benzene and *n*-butenes and on the double-bond isomerization of 1-butene. The objective was to obtain a fuller understanding of the natures of isomerization and exchange sites on alumina and of their relationship to each other. The results have been correlated with those of previous site poisoning and infrared studies in an effort to develop a unified model of catalytic sites on alumina that promote these low-temperature reactions.

EXPERIMENTAL METHODS

Materials. Gamma alumina catalyst was prepared from boehmite (α-alumina monohydrate, Catapal S), kindly supplied by the Continental Oil Co. Thermal dehydration of the boehmite was performed *in situ* by heating in 100 Torr of oxygen at 100°C/hr to 530°C, followed by overnight evacuation at the latter temperature to a residual pressure of $<5 \times 10^{-6}$ Torr. The resulting alumina had a BET–N_2 surface area of 235 m^2/g and a total pore volume of 0.51 cc/g. Because of incomplete regeneration after poisoning by sulfur compounds, a fresh 0.250 g catalyst sample (dehydrated weight) of irregular 30/40 mesh particles was used for each experiment.

All reagents were chemically pure (C.P.) grade or better. Oxygen (99.9%) and deuterium (99.5% minimum isotopic purity) were from Airco and were passed through a trap at −196°C before use. 1-Butene (99.0%), hydrogen sulfide (99.5%), sulfur dioxide (99.98%), methyl mercaptan (99.5%), and carbon dioxide (99.99%) were Matheson C. P. grade and were distilled from −78 to −196°C and outgassed before use. Benzene was Matheson, Coleman, and Bell spectroquality (99+ mole%); it was dried over Linde 5A molecular sieve and outgassed by freeze-pumping.

Apparatus. Experiments were performed using an all-glass, closed-loop recirculation system of the type described previously (*3*, *5*). The system included a circulation pump, a U-shaped reactor containing the catalyst bed which could be thermostatted at desired reaction or pretreatment temperatures to ±0.5°C, a calibrated 3.14 cc doser/bypass system, located just upstream of the reactor, which was used to inject known quantities of gaseous "poisons" into the circulating reactant stream, and provisions for removing gaseous samples by expansion for gas chromatographic and mass spectral analyses. Total system volume was 345 cc, 87% of which was contained in a spherical mixing vessel. The recirculation system was connected to a conventional mercury-free, diffusion-pumped high vacuum gas handling system. Gas pressures were measured with an ionization gauge, calibrated thermocouple gauges, and a Wallace and Tiernan Co. Model 61-050 aneroid gauge.

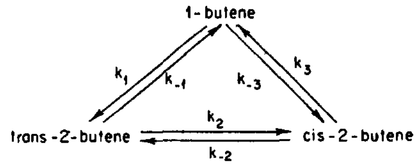
Mass spectral analyses of deuterated benzene and *n*-butenes were made with an Electronic Associates, Inc., Quad 1200 residual gas analyzer, operated at an ionizing voltage of 25 V. Analyses for deuterium content in each species were based on parent-peak heights, after the usual corrections for fragmentation and isotopic carbon-13 contributions. The three n-butene isomers were separated by gas–liquid chromatography using a $\frac{3}{8}$ in. × 30 ft column containing 25 wt% propylene carbonate on Chromosorb W and maintained at 0°C. Quantitative analyses were based on peak area measurements of recorded signals from a Gow–Mac hot-wire thermal conductivity cell. The isomers were collected, when necessary, in individual traps at −196°C for subsequent mass spectral analyses.

Experimental procedure. With the pretreated and evacuated catalyst bypassed, the desired pressure of gaseous benzene or 1-butene was admitted from a storage vessel into the circulation loop and then frozen into an isolated U-shaped trap. The required pressure of D_2 was then admitted, the frozen hydrocarbon revaporized by rapidly warming the trap, and the gas mixture homogenized by circulation for 30 min. At time $t = 0$ the circulating reactant stream was diverted through the catalyst bed by manipulation of appropriate stopcocks. Small samples ($\approx 3\%$) were removed periodically by expansion for mass spectral and/or GLC analysis.

The benzene/D_2 exchange reactions were run using initial reactant pressures of benzene and D_2 of 10 and 100 Torr, respectively. In all cases, the reaction proceeded without detectable saturation of benzene. For the 1-butene/D_2 isomerization/exchange reactions, initial pressures of 1-butene and D_2 were 100 and 400 Torr, respectively. Several experiments were run in which only 1-butene isomerization was studied. In these instances, the initial 1-butene pressure was 100 Torr, and the isomerization rates were not measureably different from those in which gaseous D_2 was present. In every case, D_2 exchange of the n-butenes occurred without saturation to butane, and isomerization proceeded without skeletal rearrangement. All reactions were run at 25°C.

Poison molecules were added to the reacting system by filling the calibrated doser to the required pressure with gaseous poison and then diverting the circulating gas stream through the doser. In some experiments, the catalyst was prepoisoned before admission of reactants. This was accomplished by thermostatting the pretreated catalyst at the desired adsorption temperature, filling the doser to the required pressure with poison, and then exposing the catalyst to the doser volume for 1 hr, followed by evacuation for 1 hr at the same temperature. Accurate pressure measurements of the doser/reactor system after the 1-hr exposure period confirmed that, prior to evacuation, $\geq 95\%$ of the poison was adsorbed in each case. The reactor was then isolated and cooled to reaction temperature, and the reactants admitted as described above.

Data treatment. Interconversion of the three n-butenes is governed by the triangular equilibrium



(1)

and a rigorous treatment involving all six rate constants is complex. At low conversions ($<50\%$) of 1-butene reactant, however, the two 2-butenes can be considered as a single product (*5*), and the extent of 1-butene isomerization is effectively described by the first-order equation

$$\ln[X_e/(X_e - X_t)] = Skt, \qquad (2)$$

where X_t and X_e are the total fractional conversions of 1-butene to 2-butene products at time t and at equilibrium, respectively (at 25°C, $X_e = 0.969$); S is the total catalyst surface area (in square meters); and k is the first-order rate constant. Plots of the left-hand side of Eq. (2) vs time are linear with slopes equal to Sk, and poisoning effects of added molecules are indicated by abrupt slope changes that occur immediately after poison additions. The ratio of slopes after and before poison addition is thus the fraction of isomerization activity remaining after poisoning.

The benzene/D_2 exchange reactions were treated by the linear Kemball equations (*11*). An extent of reaction variable, ϕ, is defined by

$$\phi = \sum_{i=1}^{n} id_i, \quad (3)$$

where d_i is the fraction of total hydrocarbon species that contains i D-atoms, and n is the number of exchangeable H-atoms in each hydrocarbon molecule (for benzene, $n = 6$). The value of ϕ at any time t thus represents the average number of D-atoms per hydrocarbon molecule. Progress of the exchange reaction is then described by the pseudo-first-order equation

$$-\ln (\phi_\infty - \phi) = \frac{k_\phi t}{\phi_\infty} - \ln (\phi_\infty - \phi_0), \quad (4)$$

where k_ϕ is the first-order rate constant and represents the average number of D-atoms entering each hydrocarbon molecule per unit time at the beginning of the reaction; ϕ_∞ is the statistical equilibrium value of ϕ calculated from the initial pressures of benzene (P_{bz}) and deuterium (P_D) reactants

$$\phi_\infty = \frac{2P_D}{2P_D + 6P_{bz}} \cdot 6, \quad (5)$$

and ϕ_0 is the value of ϕ at time $t = 0$ and was identically zero for all experiments in the present work. Plots of the left-hand side of Eq. (4) vs time are linear with slopes of k_ϕ/ϕ_∞ and intercepts of $-\ln \phi_\infty$. Poisoning effects, if any, of added molecules are again made evident by slope changes in these plots.

In the case of the n-butenes, D_2 exchange in all three isomers occurs simultaneously with the double-bond isomerization process, and Eq. (4) cannot be directly applied to describe the course of the exchange reaction. For these experiments, plots of ϕ vs time were employed. Such plots are not linear, but poisoning effects are still apparent by abrupt changes in curvature (vide infra).

RESULTS

Sulfur Dioxide

Sulfur dioxide, when adsorbed at 25°C, poisons neither D_2 exchange sites nor olefin isomerization sites on alumina (*5*). Its poisoning effect for both types of sites increases, however, with increasing temperature of exposure to the catalyst. This was demonstrated for the benzene/D_2 exchange reaction in separate experiments by preadsorbing, at various temperatures, a "lethal dose" of SO_2, i.e., that amount (1.0×10^{13} molecules/cm^2) which, if it were carbon dioxide added at 25°C, would just poison all the exchange sites (*5*). As seen in Fig. 1, the exchange reaction rate con-

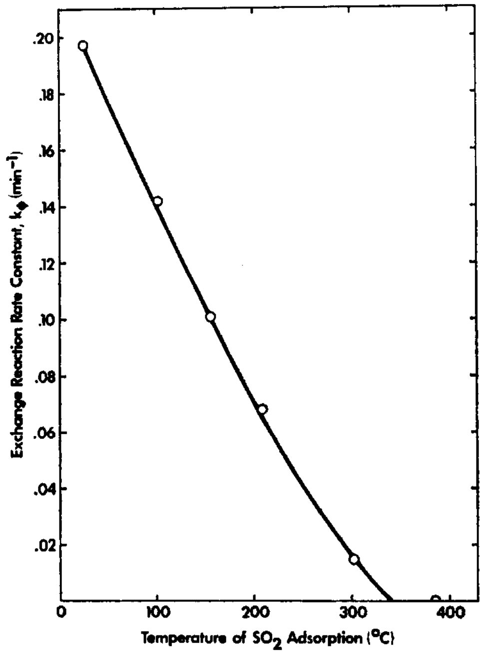


FIG. 1. Poisoning of benzene/D_2 exchange reaction by SO_2 (1.0×10^{13} molecules/cm^2) preadsorbed at various temperatures for 1 hr followed by evacuation for 1 hr.

stants [Eq. (4)] decrease uniformly with increasing temperature of SO_2 adsorption, and complete poisoning occurs only at exposure temperatures of > ≈ 350°C.

Active sites for both exchange and isomerization were titrated in individual experiments by preadsorbing various amounts of SO_2 at 400°C prior to running benzene/D_2 exchange and 1-butene isomerization reactions. The results (Figs. 2 and 3) gave average site densities ($0.9 \times 10^{13}/cm^2$ for exchange sites and $5.3 \times 10^{13}/cm^2$ for isomerization sites) in good agreement with those obtained previously on alumina by CO_2 and H_2S poisoning, respectively (3, 10).

Hydrogen Sulfide

Hydrogen sulfide is an effective poison, at 25°C, for olefin isomerization sites on alumina (*10*), but its effect on D_2 exchange sites has not been previously reported. Using the benzene/D_2 reaction, a series of experiments was performed in which varying amounts of H_2S, up to twice the "lethal dose," were added during the reaction at 25°C, and rate constants before and after H_2S addition were obtained from appropriate plots of Eq. (4). The results (Table 1) demonstrate that H_2S has virtually no poisoning effect on the exchange reaction. Even at coverages as high as 2.1×10^{13} molecules/cm^2 (three to five times the exchange site concentration), 93% of exchange activity remained after H_2S addition.

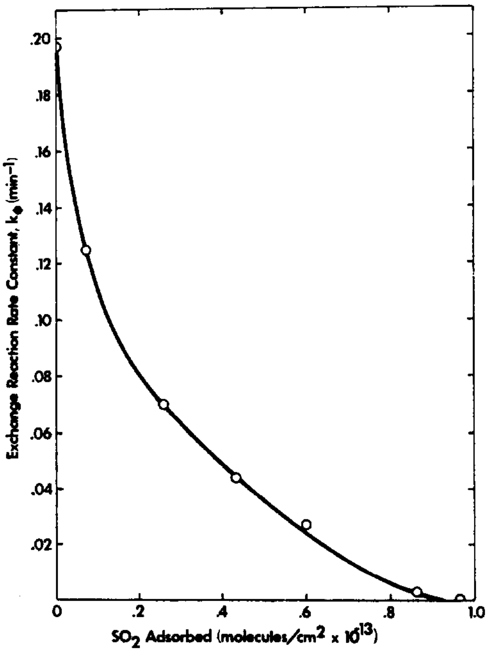


FIG. 2. Poisoning of benzene/D_2 exchange reaction by various doses of SO_2 preadsorbed at 400°C for 1 hr followed by evacuation for 1 hr.

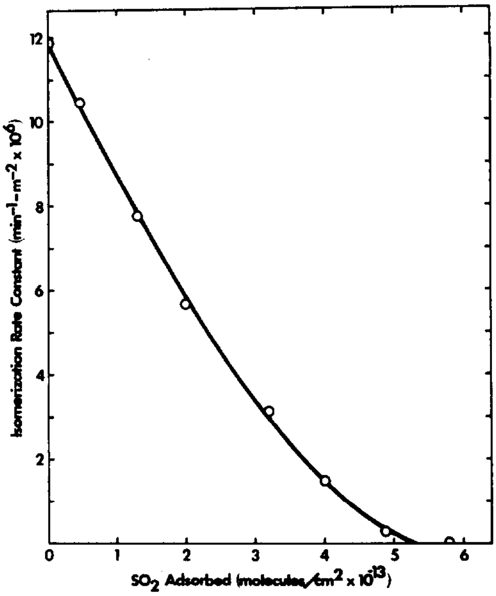


FIG. 3. Poisoning of 1-butene isomerization reaction by various doses of SO_2 preadsorbed at 400°C for 1 hr followed by evacuation for 1 hr.

The simultaneous effect of H_2S on both exchange and isomerization sites was explored using the 1-butene/D_2 reaction at 25°C. Beginning at 90 min of reaction time, doses of H_2S (0.95×10^{13} molecules/cm^2) were added every 90 min, and samples were removed at 30 min intervals for mass spectral/gas chromatographic analysis. Isomerization rate constants after each H_2S addition were obtained from plots of Eq. (2). The effect of H_2S on the isomerization reaction is summarized for a typical experiment in Table 2. The isomerization site density derived from a linear plot of these data ($5.3 \times 10^{13}/\text{cm}^2$) is virtually identical to that obtained from the high-temperature SO_2 poisoning (Fig. 3) and to that reported previously for H_2S poisoning of a different commercial alumina sample (*10*).

The results for the butene/D_2 exchange process in the same experiment are shown in Fig. 4, where ϕ-values of each *n*-butene isomer are plotted as a function of reaction time. It is apparent that, as for the benzene/D_2 reaction, no appreciable poisoning of D_2 exchange occurred, even after a cumulative amount of H_2S equivalent to 5.7×10^{13} molecule/cm² had been added. Beyond 540 min of reaction time, isomerization was completely poisoned and further interconversion of the three *n*-butene isomers did not occur, but the D_2 exchange reaction of each isomer proceeded apparently unabated. At 630 min of reaction time, a "lethal dose" (1.0×10^{13} molecules/cm²) of carbon dioxide was added, and the exchange reaction of all three isomers was completely poisoned (Fig. 4). The added CO_2 had no further effect on the already completely poisoned isomerization reaction, which had attained ≈30% total conversion of 1-butene before complete stoppage occurred.

TABLE 1

Effect of H_2S on Benzene/D_2 Exchange Reaction

H_2S added (molecules/ cm² $\times 10^{-13}$)	Exchange reaction rate constant, k_ϕ (min⁻¹)		Fraction of exchange activity remaining after poisoning
	Before H_2S	After H_2S	
0.2	0.20	0.20	0.99
0.4	0.20	0.20	1.02
0.7	0.20	0.20	0.99
1.0	0.21	0.20	0.96
1.2	0.19	0.19	1.01
1.6	0.20	0.19	0.98
1.8	0.20	0.19	0.96
2.1	0.21	0.19	0.93

TABLE 2

Effect of H_2S on 1-Butene Isomerization Reaction

Cumulative total of H_2S added (molecules/cm² $\times 10^{-13}$)	Isomerization rate constant, k ($\text{min}^{-1}\ \text{m}^{-2} \times 10^6$)	Fraction of unpoisoned isomerization activity remaining
0.0	11.0	1.00
1.0	8.9	0.81
1.9	7.0	0.64
2.9	4.7	0.42
3.8	3.0	0.28
4.8	1.0	0.09
5.7	0.0	0.00

In a separate experiment, 5.5×10^{13} molecules/cm² of H_2S was preadsorbed at 25°C before admission of 1-butene and D_2 reactants. When the reaction was subsequently run at 25°C, no double-bond isomerization of 1-butene occurred, but its exchange with D_2 proceeded in a manner almost identical to that depicted in Fig. 4. Addition of a "lethal dose" of CO_2 again halted completely the 1-butene/D_2 ex-

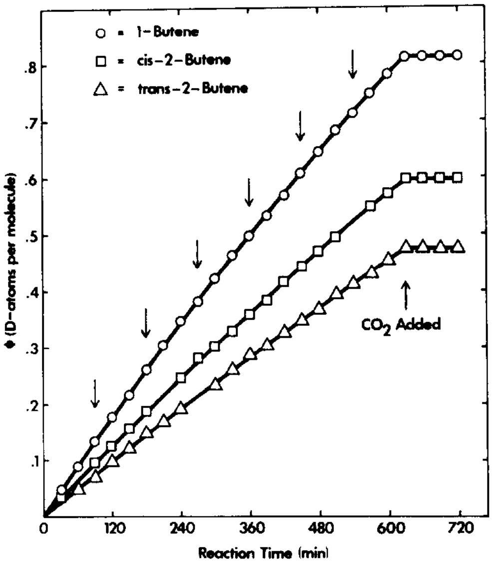


FIG. 4. Effect of H_2S on *n*-butene/D_2 exchange reactions. Arrows indicate times of H_2S additions (0.95×10^{13} molecules/cm²). At 630 min of reaction time, 1.0×10^{13} molecules/cm² of CO_2 was added.

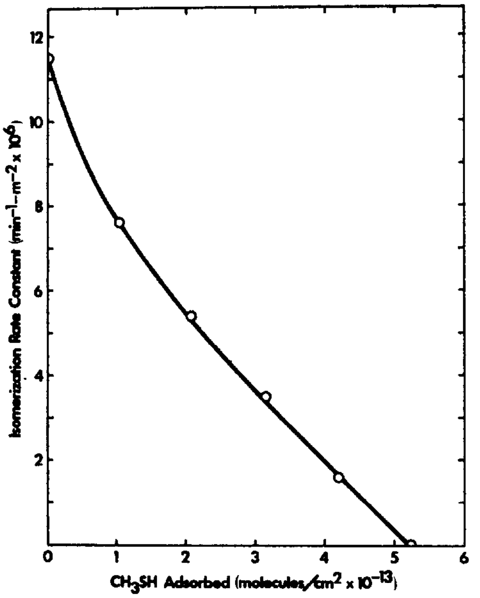


FIG. 5. Poisoning of 1-butene isomerization reaction by various doses of CH_3SH added at 25°C.

change process. Preadsorption of both CO_2 (1.0×10^{13} molecules/cm^2) and H_2S (5.4×10^{13} molecules/cm^2) resulted in complete poisoning of the catalyst for both isomerization and D_2 exchange of 1-butene.

Methyl Mercaptan

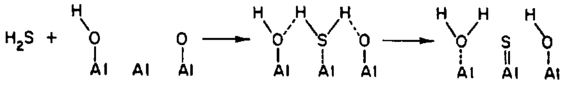
The site poisoning effects of methyl mercaptan on alumina closely paralleled those of H_2S. No apparent poisoning of D_2 exchange reactions of benzene or the *n*-butenes occurred when experiments analogous to those described above for H_2S were performed. Titrative poisoning of 1-butene isomerization by CH_3SH (Fig. 5) gave almost the same isomerization site density (5.0×10^{13}/cm^2) as did H_2S.

DISCUSSION

The surface of activated (gamma/eta) alumina is complex, and several types of catalytic and absorption sites have been identified. At low temperatures (<100°C), however, two kinds of sites are of primary importance, viz, those catalyzing deuterium exchange reactions of hydrogen and hydrocarbons and those promoting double-bond migration and *cis*/*trans* rotation in olefins. Considerable information about these sites on alumina has been accumulated, and results obtained from infrared, EPR, and selective poisoning studies of this and previous investigations allow the development of a reasonably complete description of their natures and behaviors. Although the susceptibilities of the two types of sites to some "poison" molecules are parallel, they apparently operate quite independently of each other at low temperatures, and it is useful to consider their characteristics separately.

Olefin Isomerization Sites

At 25°C, olefin isomerization sites on alumina are impervious to poisoning by ammonia (*12*), sulfur dioxide (*5*), and carbon dioxide (*5*), but are poisoned by NH_3(12) and SO_2 (Fig. 3) when either is preadsorbed at 400°C. On the other hand, the isomerization activity of alumina is inversely related to its surface hydroxyl content (*14*), and is readily poisoned, at 25°C, by hydrogen sulfide (Table 2) and methyl mercaptan (Fig. 5). The poisoning effect of H_2S (and probably that of CH_3SH) has been shown to be due to blockage of exposed Al^{3+} ions on the alumina surface by either molecular H_2S or by one of its dissociation products (*10*). Infrared studies have demonstrated that H_2S does, in fact, dissociatively adsorb on Al^{3+} sites at 25°C to form sulfide-type surface species (*15*):

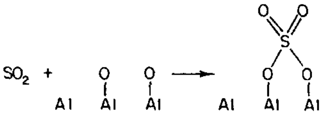


(6)

It is likely that a necessary feature of olefin adsorption on the active sites involves interaction, probably via vinylic carbon atoms, with vacant *p*-orbitals of single, electron-deficient Al^{3+} ions at the surface, and subsequent isomerization may occur by a concerted 1,3-sigmatropic transformation (*10*). Hightower and Hall, however, in studying the isomerizations of various cyclic olefins on alumina, found that double-bond migration occurred only when the olefin contained "a chain of at least three carbon atoms, including the double-bond, which could appear concave when viewed from outside the molecule" (*6*). Such a geometric restriction may be due either to highly restricted disrotatory twisting of methylene groups in cyclic olefins, or to an inherent structural feature of the active sites, such as adjacent O^{2-} ions, whereby olefin molecules must be "draped" over the sites and isomerization occurs by proton migration across the oxide ions (Fig. 6). Such sites are analogous to the "acid-base" sites described by Peri (16), to which he attributed isomerization activity.

Titrative poisoning by H_2S [Table 2 and Ref. (*10*)] and CH_3SH (Fig. 5) at 25°C and by SO_2 at 400°C (Fig. 3) have established an upper limit for the surface concentration of isomerization sites of $\approx 5 \times 10^{13}/cm^2$. This value is less by an order of magnitude than the total number of exposed Al^{3+} ions expected for a 90% dehydroxylated alumina surface (*17*), and suggests that additional criteria are also required for isomerization activity. These may include more energetic locations at corner or edge positions of microcrystallites, or a particularly favorable surrounding environment of surface hydroxyls, oxide ions, or next-nearest neighbor Al^{3+} ions.

The isomerization sites are sensitive to H_2O because its adsorption hydroxylates O^{2-} ions and reforms surface hydroxyl groups over previously exposed, underlying Al^{3+} ions. The sites are unaffected by CO_2, NH_3, and SO_2 at 25°C because all of these are likely either physically adsorbed or only weakly and associatively chemisorbed on exposed Al^{3+} sites at this temperature and are easily displaced by olefin molecules (*5*). At elevated temperatures (400°C), however, NH_3 that has not desorbed forms amide (NH_2^-) linkages with Al^{3+} ions (*12*) and, hence, effectively blocks a necessary interaction at the isomerization sites. Sulfur dioxide, at 400°C, forms very stable SO_4^{2-} species (*18*) which may sterically hinder olefin interaction with Al^{3+} species or prevent a necessary "draping" effect over O^{2-} ions:



(7)

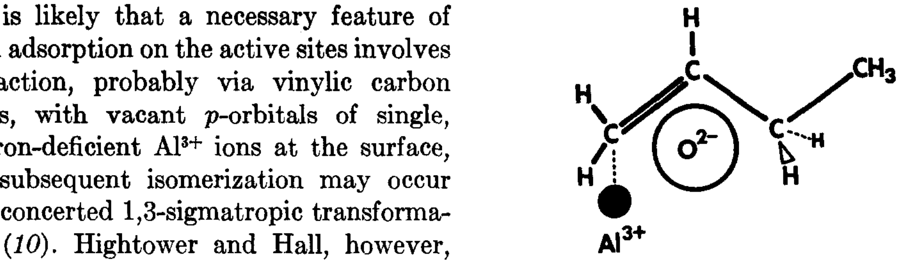
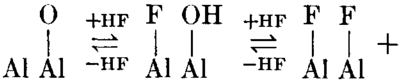


FIG. 6. Interaction of 1-butene molecule with olefin isomerization site on alumina.

Fluoridation of alumina, on the other hand, greatly increases its activity for olefin isomerization (*19*), even though the primary mode of fluoride incorporation involves formation of Al–F bonds at the surface (*20*):



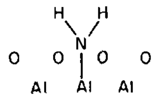
$$\begin{array}{cc} & \mathrm{O} \\ & | \\ \mathrm{Al} & \mathrm{Al} \end{array} \underset{-\mathrm{HF}}{\overset{+\mathrm{HF}}{\rightleftharpoons}} \begin{array}{cc} \mathrm{F} & \mathrm{OH} \\ | & | \\ \mathrm{Al} & \mathrm{Al} \end{array} \underset{-\mathrm{HF}}{\overset{+\mathrm{HF}}{\rightleftharpoons}} \begin{array}{cc} \mathrm{F} & \mathrm{F} \\ | & | \\ \mathrm{Al} & \mathrm{Al} \end{array} + H_2O. \quad (8)$$

Activity enhancement occurs because highly electronegative fluorine atoms increase the acidity of neighboring hydroxyl groups, even at 25°C, and provide an alternative, carbonium-ion-type, pathway for the isomerization process. The surface acidity and catalytic properties of fluorided alumina are very similar, in fact, to those of silica–alumina (*19*).

Deuterium Exchange Sites

Deuterium exchange sites on alumina can be completely poisoned at 25°C by sufficient CO_2(3, 4), are only partially susceptible to poisoning by H_2O(3), and are completely unaffected by H_2S (Table 1 and Fig. 4) and CH_3SH, even at surface concentrations as high as five times the active site density. NH_3 and SO_2 have no effect at 25°C, but are "lethal" when adsorbed at 400°C (*13*, Figs. 1 and 2). Infrared studies have shown that at 25°C adsorbed CO_2 exists on alumina in at least three forms, each giving rise to characteristic absorption bands (*7*, *8*, *21*, *22*). These forms include a weakly held Al^{3+}–CO_2 species and a monomeric bicarbonate (HCO_3^-) entity, formed by interaction with surface hydroxyl groups. Neither of these, however, appears to be "lethal" to the exchange sites. The adsorbed form of CO_2 that correlates with its poisoning effect for D_2 exchange sites gives an infrared band at 1480 cm^{-1} (*9*), and has been assigned to a relatively free carbonate (CO_3^{2-}) species formed by interaction of molecular CO_2 with O^{2-} ions on the alumina surface (*23*). Entropy calculations have shown that, at >150°C, this species has a high surface mobility, even at low coverages, and probably experiences only transitory localization at any particular O^{2-} ion (*23*). This finding is puzzling, considering the highly specific poisoning effect of CO_2 for the exchange sites at these temperatures (*3*, *4*).

Deuterium exchange sites on alumina are thus apparently associated with a very small fraction of surface oxide ions, since the upper limit site density of 0.3–$0.8 \times 10^{13}/cm^2$ determined by CO_2 poisoning represents only 1–2% of the total O^{2-} ions in an ideal surface layer (*17*). Energetic differences associated with varying surface locations are undoubtedly important, as for the isomerization sites, and a particular surrounding environment of cation and/or anion vacancies, hydroxyl groups, etc., may be necessary as well. The O^{2-} ions of the exchange sites are evidently structurally and/or energetically distinct from those that may be associated with isomerization sites (Fig. 6), since the latter are unaffected by CO_2, even in excess, at 25°C. Sulfide species resulting from H_2S adsorption at 25°C apparently have no effect on neighboring O^{2-} ions acting as exchange sites. The high-temperature (400°C) poisoning effect of SO_2 on the exchange sites (Figs. 1 and 2) is probably due to simple obstruction of O^{2-} ions by the resulting SO_4^{2-} species [Eq. (7)]. Deactivation by NH_3 at 400°C, on the other hand, may be due to a simple steric site blockage by NH_2^- species:



(9)

or, more likely, to hydroxylation of neighboring "active" O^{2-} ions by released protons.

Unlike the situation for olefin isomerization sites, surface fluoridation of alumina greatly reduces its activity for D_2 exchange reactions (*13*). This probably occurs because of hydroxyl group formation involving previously available O^{2-} ions [Eq. (8)], or because of a strong induction effect of surface fluorine atoms which reduce the basicity of neighboring O^{2-} sites.

Other Sites on Alumina

At low temperatures (<100°C), the surface hydroxyls of alumina are not acidic, in contrast to those of, for example, silica–alumina, and play no direct role in olefin isomerization (*24*) or D_2 exchange reactions (*13*). The surface acidity of alumina at these low temperatures is primarily of the Lewis type and is commonly associated with electron-deficient Al^{3+} sites (*25*). With increasing temperature, however, the surface protons become more labile, and proton acidity is displayed (*26*). Hence, at temperatures higher than ≈ 200°C, surface hydroxyls on alumina can function as active centers for typical acid-catalyzed, carbonium-ion-type reactions, such as alcohol dehydration (*24*, *27*) and hydrocarbon cracking (*28*).

In addition to catalytically active sites, temperature-programmed desorption studies have shown that at least two additional kinds of sites exist on an activated alumina surface which adsorb olefins and aromatics at 25°C (*4*, *29*, *30*). Adsorption at these locations is not blocked by CO_2, and interaction with these sites is sufficiently strong ($\Delta H_{ads} = 20$–40 kcal/mole) to preclude participation of the adsorbed species in low-temperature reactions (*4*). It is likely that immediate saturation of these sites occurs upon initial exposure of a fresh alumina surface to unsaturates, after which they are inert until the adsorbed species are thermally removed.

ACKNOWLEDGMENT

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES

1. van Cauwelaert, F. H., and Hall, W. K., *J. Colloid Interface Sci.* **38**, 138 (1972).

2. Larson, J. G., and Hall, W. K., *J. Phys. Chem.* **69**, 3080 (1965).

3. Saunders, P. C., and Hightower, J. W., *J. Phys. Chem.* **74**, 4323 (1970).

4. Rosynek, M. P., and Hightower, J. W., *in* "Proceedings of the Fifth International Congress on Catalysis, p. 851, 1973.

5. Rosynek, M. P., Smith, W. D., and Hightower, J. W., *J. Catal.* **23**, 204 (1971).

6. Hightower, J. W., and Hall, W. K., *Trans. Faraday Soc.* **66**, 477 (1970).

7. Parkyns, N. D., *J. Chem. Soc., A*, 410 (1969).

8. Parkyns, N. D., *J. Phys. Chem.* **75**, 526 (1971).

9. Hightower, J. W., Preprint, *Div. Petr. Chem., Amer. Chem. Soc.* **18**, 262 (1973).

10. Lunsford, J. H., Zingery, L. W., and Rosynek, M. P., *J. Catal.* **38**, 179 (1975).

11. Kemball, C., *Advan. Catal.* **11**, 223 (1958).

12. Peri, J. B., *J. Phys. Chem.* **69**, 231 (1965).

13. Rosynek, M. P., Doctoral Dissertation, Rice University 1972.

14. Gerberich, H. R., and Hall, W. K., *J. Catal.* **5**, 99 (1966).

15. Slager, T. L., and Amberg, C. H., *Can. J. Chem.* **50**, 3416 (1972).

16. Peri, J. B., *J. Phys. Chem.* **69**, 211 (1965).

17. Peri, J. B., *J. Phys. Chem.* **69**, 220 (1965).

18. Deo, A. V., Dalla Lana, I. G., and Habgood, H. W., *J. Catal.* **21**, 270 (1971).

19. Hightower, J. W., Gerberich, H. R., and Hall, W. K., *J. Catal.* **7**, 57 (1967).

20. Peri, J. B., *J. Phys. Chem.* **72**, 2917 (1968).

21. Peri, J. B., *J. Phys. Chem.* **70**, 3168 (1966).

22. Grigor'ev, Ya. M., Pozdnyakov, D. V., and Filimonov, V. N., *Russ. J. Phys. Chem.* **46**, 186 (1972).

23. Rosynek, M. P., *J. Phys. Chem.* **79**, 1280 (1975).

24. Hightower, J. W., and Hall, W. K., *J. Phys. Chem.* **71**, 1014 (1967).

25. Parry, E. P., *J. Catal.* **2**, 371 (1963).

26. Knozinger, H., and Kaerlein, C., *J. Catal.* **25**, 436 (1972).

27. Pines, H., and Haag, W. O., *J. Amer. Chem. Soc.* **82**, 2471 (1960).

28. Hall, W. K., Lutinski, F. E., and Gerberich, H. R., *J. Catal.* **3**, 512 (1964).

29. Cvetanovic, R. J., and Amenomiya, Y., *Advan. Catal.* **17**, 103 (1967).

30. Cvetanovic, R. J., and Amenomiya, Y., *Catal. Rev.* **6**, 21 (1972).