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Exposed Aluminum Ions as Active Sites on γ-Alumina

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The EPR spectrum of nitric oxide which is weakly adsorbed on γ-Al_2O_3 exhibits a strong crystal field gradient and a hyperfine structure due to exposed aluminum ions. Hydrogen sulfide is selectively adsorbed on these exposed aluminum ions, whereas H_2O and CO_2 are not. The latter may be removed from the aluminum ions by brief evacuation at 25°C. Quantitative results for the poisoning of the 1-butene isomerization reaction and the decrease in the EPR spectrum of NO strongly suggest that the exposed aluminum ions function as active sites for the isomerization reaction. For one sample of alumina the number of such sites is between $1 \times 10^{12}/cm^2$ as measured from the spin concentration and $5 \times 10^{13}/cm^2$ as measured from H_2S poisoning experiments.

INTRODUCTION

Although the nature of active sites on γ-alumina has been explored for many years, the complexity of the surface in terms of the variety of catalytic and adsorption sites has only recently become apparent. Rosynek and Hightower (1) concluded that 1-butene isomerization and butene–deuterium exchange occur on two different types of sites, which were denoted as I-sites and E-sites, respectively. In addition, two other types of sites held butene so strongly that it is doubtful whether they could be important in catalytic reactions at moderate temperatures. At least part of the more strongly held butene is associated with the α-sites which have been described by Peri (*2*). From CO_2 poisoning experiments an upper limit of $3\text{–}8 \times 10^{12}$ sites/cm^2 has been established for the E-sites, and the estimated number of α-sites falls within this range (*1*, *2*). In the first poisoning experiments utilizing CO_2 Larson and Hall (*3*) showed that the number of sites active for the equilibration of CH_4 and CD_4 over alumina amounted to 4×10^{12} sites/cm^2. The number of sites for isomerization, however, has not been previously determined. Gerberich and Hall (*4*) and Hightower and Hall (*5*) established, mainly from kinetic studies, that the butene isomerization reaction over alumina does not proceed via a carbonium ion. These investigators proposed a mechanism which involved the migration of a proton across an oxide ion at the surface. Other types of active sites may be required for ortho–parahydrogen conversion (*6*), cyclopropane isomerization (*7*) alcohol dehydration and dehydrogenation (*8*), catalytic cracking (*7*), and other reactions which are catalyzed by γ-alumina.

Another approach for determining the nature of possible active sites on γ-alumina involves the use of paramagnetic molecules to probe specific interactions. Magnetic interactions between the unpaired electron and a nucleus with a magnetic moment such as ^{27}Al may appear in the electron paramagnetic resonance (EPR) spectrum as hyperfine structure. The EPR spectrum of nitric oxide adsorbed on γ-alumina indeed confirms that a limited number of exposed aluminum ions are available for adsorption (*9*). The spectrum also indicates that these sites are charac-

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terized by strong crystal field gradients. More recently Lozos and Hoffman (*10*) have used di-*tert*-butyl nitroxide (DTBN) to demonstrate that the Lewis acid strength of the exposed aluminum ions was somewhat less than that of $AlCl_3$ in solution. In the case of DTBN the strong crystal field gradient is not required in order to observe the spectrum; hence, the NO and the DTBN molecules may not be probing the same type of exposed aluminum ions.

In the present work we have used the EPR spectra of adsorbed nitric oxide and poisoning experiments to characterize the active sites for 1-butene isomerization over γ-alumina. It was discovered that H_2S is a reasonably specific poison for the isomerization reaction and that it also bonds strongly with the exposed aluminum ions which give the characteristic hyperfine splitting in the EPR spectrum of adsorbed NO. From the poisoning experiments and the EPR results a reasonable upper and lower limit for the number of active sites has been determined.

EXPERIMENTAL METHODS

Two types of γ-alumina were used in these experiments. One was an American Cyanamid alumina and the other was a Catapal alumina obtained from Continental Oil. The two aluminas had surface areas of 175 and 280 m^2/g, respectively.

The standard pretreatment procedure involved degassing a sample under vacuum at temperatures up to 550°C. The temperature was raised in 100°C increments every 30 min. At 550°C the sample was exposed to 150 Torr of O_2 for 2 hr and maintained under vacuum for an additional 1 hr at 550°C. For one set of experiments, involving butene isomerization and H_2S poisoning, the catalyst was evacuated for 16 hr at 530°C, treated with O_2, and evacuated again at the same temperature.

The H_2S and the CO_2 were obtained from a commercial source and were purified by a freeze-pump technique, using liquid nitrogen to freeze the gas. To remove mainly NO_2 the nitric oxide was purified by freezing the impure gas at −196°C and then warming it to −78°C. The nitric oxide sublimed or boiled and was collected in the gas phase.

Nitric oxide was added to the sample tube containing the alumina at 25°C and at pressures ranging from 1 to 20 Torr. The sample tube for the EPR experiments generally had a volume of 17 ml, and a catalyst mass of 0.1 g was typical. In one case a catalytic reactor was used, which had a volume of 6.5 ml. For most of the experiments the amount of nitric oxide corresponded to either 5.5×10^{18} or 5.5×10^{19} molecules/g alumina. After the addition of nitric oxide, the sample was tapped into a side-arm which was 4 mm in diameter. In order to uniformly adsorb the nitric oxide, the side-arm containing the catalyst was cooled at −135°C in pentane slush for 15 min and at −196°C for 15 min, prior to recording the EPR spectrum.

The catalytic reactions were carried out in a recirculation reactor similar to that described by Rosynek *et al.* (*11*). Chemically pure (99.9%) 1-butene was obtained from Air Products Co. and was freeze-pumped before use. The gas at a pressure of 100 Torr was circulated over the catalyst at 25°C. At known times aliquots were removed for analysis by gas chromatography over a 25% propylene carbonate on Chromosorb W column at 0°C.

The gases used as poisons were exposed to the catalyst for times ranging from 5 min to 1 hr. Quantitative additions of these gases involved the use of a calibrated thermocouple gauge for pressures of 3 Torr or less, and a mercury manometer or Wallace and Tiernan Model 61-050 pressure gauge for greater pressures. Gas phase and weakly adsorbed nitric oxide or butene was removed by evacuation prior to the adsorption of the poison. In most cases the dose of the poison was sufficiently small so that all was adsorbed at room temperature, and the amount of poison on the surface was calculated from the number of molecules of gas that were adsorbed.

The EPR spectra were obtained with the sample at −196°C, using a conventional X-band spectrometer. Spin concentrations were determined relative to a phosphorous-doped silicon standard. The estimated error in the absolute spin concentration is ±25%; however, relative errors are much less. Where the shape of the spectra remained unchanged, relative intensities were determined directly from the derivative curves, thus avoiding the errors introduced by integration.

RESULTS

The EPR spectra for nitric oxide adsorbed on Catapal γ-Al_2O_3 at coverages of 2.0×10^{12} and 2.0×10^{13} molecules/cm² are shown in Fig. 1a and c, respectively. Here, the alumina was activated at 550°C. The EPR signal at the lower coverage corresponds to 1.8×10^{12} spins/cm² which, within experimental error, is equal to the coverage of NO on the sample. This agreement, however, is not observed at higher coverages, as shown in Table 1. For the American Cyanamid alumina at the lower coverage the spin concentration was about one-third of the NO concentration, and at higher coverages the spin concentration was considerably less than the NO concentration. The nitric oxide in excess of that detected by EPR either adsorbs as diamagnetic dimers or the adsorption sites are unable to quench the spin–orbit interaction in the NO molecule.

In Fig. 1b a simulated spectrum is given. This spectrum was calculated using a program which was kindly supplied by Drs. George Lozos and Brian Hoffman of Northwestern University. The parameters used to obtain the simulation were $g_{xx} = 1.990$, $g_{yy} = 1.9845$, and $g_{zz} = 1.945$ with $^{Al}a_{xx} = 30$ G, $^{Al}a_{yy} = 5$ G, $^{Al}a_{zz} = 10$ G, $^{N}a_{xx} = 12.5$ G, $^{N}a_{yy} = 10$ G, and $^{N}a_{zz} = 12.5$ G. Half-widths of 10 G for the x and y directions and 20 G for the z direction were adopted.

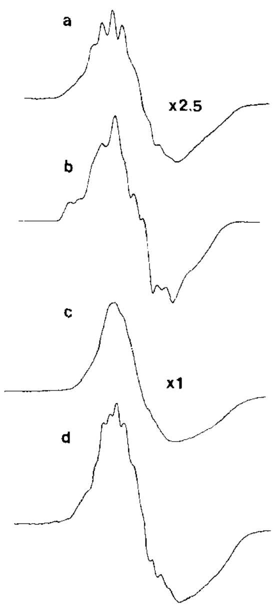

FIG. 1. EPR spectra of NO on γ-alumina: (a) after adsorption of 2.0×10^{12} molecules of NO/cm² on the Catapal sample, (b) computer simulated spectrum using the parameters described in the text, (c) after adsorption of 2.0×10^{13} molecules of NO/cm² on the Catapal sample, (d) after adsorption and partial desorption of CO_2 at 25°C, followed by the adsorption of 3×10^{12} molecules of NO on the American Cyanamid sample. The spectrum of NO on a freshly degassed American Cyanamid sample is identical in shape to spectrum a.

The development of the adsorption sites on which the observed NO is held was followed as a function of the activation temperature for the Catapal alumina. The

TABLE 1

Al_2O_3 Sample	NO concn (molecules/cm² $\times 10^{-12}$)	Spin concn (spins/cm² $\times 10^{-12}$)
Catapal	2.0	1.8
	20	5.0
American Cyanamid	3.1	1.0
	31	4.9

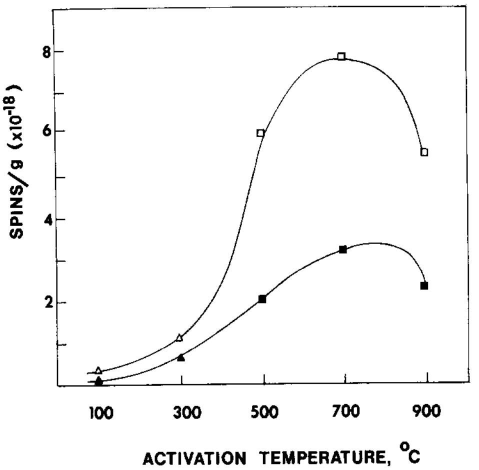

FIG. 2. Variation in spin concentration as a function of activation temperature for the Catapal γ-alumina after the adsorption of 2.0×10^{12} NO molecules/cm^2 (solid symbols) and 2.0×10^{13} NO molecules/cm^2 (open symbols). Different shaped symbols represent modifications in the spectra (see text).

relative intensities of the derivative spectra are depicted in Fig. 2. As indicated by the change in symbols, the spectra change significantly upon increasing the dehydration temperature from 300 to 500°C. At the lower temperatures the spectra reveal mainly a poorly resolved nitrogen hyperfine splitting, similar to that reported for NO on a NaY zeolite (*9*). The aluminum hyperfine structure was barely perceptible following dehydration at 200°C, although it became the dominant feature at low NO coverages for samples which were dehydrated at 500°C and higher temperatures. The intensity of the spectra reached a maximum near 700°C. The decrease at 900°C is probably due to a reordering of the surface from the γ-phase to the θ-phase (*13*).

As shown in Fig. 3, poisoning the surface with CO_2, H_2O, or H_2S resulted in a decrease in the EPR spectrum of NO, which was subsequently adsorbed on the aluminas. Carbon dioxide completely adsorbs on alumina at 25°C up to coverages of approximately 3×10^{13} molecules/cm^2; however, at higher coverages it is less tightly bound to the surface (*6, 14*). The weakly held CO_2 blocked the adsorption sites for the NO, although the shape of the remaining spectrum was unchanged. Upon evacuating the sample tube at 25°C by mechanical pumping for 10 min or by cryo-pumping with liquid nitrogen for 15 min the NO signal regained its original intensity, although as shown in Fig. 2d, certain features of the spectrum are slightly altered. Most of the differences may be explained in terms of a decrease in line width. Adsorption of 1-butene produced the same changes in the spectrum upon removing the weakly adsorbed material.

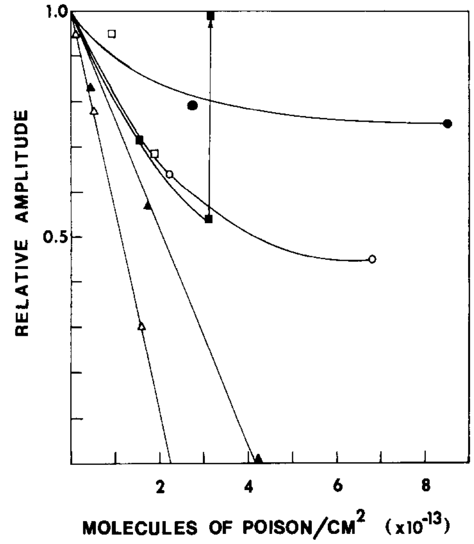

FIG. 3. Effects of various poisons on the relative amplitude of the NO spectrum: (▲) H_2S on American Cyanamid; (△) H_2S on Catapal; (●) H_2O on American Cyanamid; (○) H_2O on Catapal; (■) CO_2 on American Cyanamid; (□) CO_2 on Catapal. The vertical arrow represents the effect of degassing the sample at 25°C after the addition of CO_2. All spectra were recorded after the addition of 5.5×10^{18} molecules of NO/g alumina.

The addition of water resulted in both a decrease in intensity of the NO signal and a change in its shape. The spectra reveal a decrease in the intensity of the aluminum hyperfine structure and a shift in g_{zz} to larger values. Desorption of the water for 1 hr at 300°C only partially restored the surface to its original state. It appears from the shape of the poisoning curve of Fig. 3 and the EPR spectrum that part of the water is adsorbed on exposed aluminum ions, but that these modified sites are still able to adsorb NO, yielding an EPR signal.

Hydrogen sulfide is a very effective poison for covering the exposed aluminum ions which give rise to the hyperfine structure. The linear relationship of Fig. 3 by no means proves that H_2S is adsorbed only at these sites, but it does confirm that a constant fraction of the poison is tightly held on the aluminum cations. Only 50% of the original nitric oxide spectrum was restored after a poisoned sample was degassed for 1 hr at 300°C. Unlike water, the H_2S did not result in any new or modified sites. At higher coverages of NO on Catapal the poisoning with H_2S was not nearly as effective, which indicates that at these coverages the nitric oxide may also be adsorbed on sites which are not poisoned by H_2S.

In order to determine whether the exposed aluminum ions, as detected by the NO spectrum, may be related to the active sites for 1-butene isomerization, hydrogen sulfide poisoning experiments were performed using two samples of the American Cyanamid alumina which were pretreated in the same manner. The same dosing system and reactor was used, except that a 4 mm diameter side tube was attached to the reactor for the EPR experiments. For the EPR experiments the amount of NO corresponded to 3.1×10^{12} molecules/cm^2. The activity of the catalyst for 1-butene isomerization was determined from the usual first-order relationship (*1*), and an initial rate constant of 1.50×10^{-3} min^{-1} was observed. The plot of k/k_0 or i/i_0 versus the amount of H_2S added is linear (Fig. 4) with an intercept at 5.2 (±0.1) $\times 10^{13}$ molecules/cm^2. It is apparent that the EPR spectra of NO and the catalytic activity for the isomerization reaction show an identical response to H_2S poisoning.

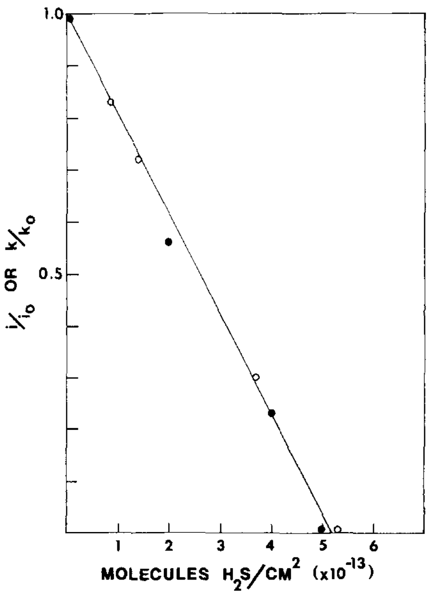

FIG. 4. Variation in the relative rate constant for 1-butene isomerization k/k_0 (open symbols) and relative NO spin concentration i/i_0 (solid symbols) as a function of the amount of H_2S which was added to an American Cyanamid alumina.

DISCUSSION

Interpretation of the EPR spectra. Nitric oxide is a 15-electron molecule which is paramagnetic in the gas phase except at low temperatures, where the spin and orbital magnetic moments cancel one another. For the free molecule the unpaired electron is in degenerate $2p\pi^*$ orbitals, and the EPR spectrum reflects strong orbital, spin and rotational interactions. If the molecule is adsorbed at specific sites on a surface where it comes under the influence of a large crystal field gradient, the degeneracy of the $2p\pi^*$ orbitals is removed and the spectrum is characterized by $g_{xx} \simeq g_{yy} \simeq g_e$ with $g_{zz} < g_e$, in agreement with the spectra of Fig. 1. The splitting Δ of the $2p\pi^*$ orbitals of NO by the crystal field at the adsorption site is given by $\Delta = 2\,\lambda/(g_e - g_{zz})$. Here, λ is the spin-orbit coupling constant, g_e is the free electron g-value, and z is the N–O direction. Miller and Haneman (*15*) have developed the theory which relates the value of δ to the difference in the crystal field gradient, $(\partial^2V/\partial x^2 - \partial^2V/\partial y^2)$. A $\Delta = 0.55$ eV for NO on γ-alumina corresponds to a value of 0.4 V/Å^2 for $(\partial^2V/\partial x^2 - \partial^2V/\partial y^2)$.

The spectrum of Fig. la also reflects hyperfine splitting both by ^{14}N ($I = 1$) and ^{27}Al ($I = 5/2$) nuclei. The computed spectrum of Fig. 1b adds additional support for the presence of the aluminum hyperfine structure. A value of $a_{xx} = 12.5$ G for the aluminum hyperfine splitting is believed to be more accurate than the value of 14 G which was reported earlier (6). Although the ^{27}Al and ^{14}N hyperfine splitting along the y and z principal directions is not evident in the experimental spectrum, the values of $^{\mathrm{Al}}a_{yy}$ and $^{\mathrm{N}}a_{yy}$ are reasonably accurate since the simulated spectrum was quite sensitive to changes in these parameters. The values of the hyperfine splitting in the z direction are subject to considerable error. It should be noted, however, that the superoxide ion, O_2^-, in a decationated zeolite exhibited a similar, but not identical, aluminum hyperfine splitting along the three principal directions (*16*). A similar interaction between the adsorbed NO molecule and the aluminum ion would be expected.

The precise number of exposed aluminum ions having the appropriate crystal field gradient is difficult to establish because (a) there is no assurance that all of the sites are covered and (b) there is evidence from poisoning experiments that nitric oxide adsorbed at other sites contributes to the EPR spectrum, particularly when a larger amount of NO is adsorbed. From the spin concentration measurements a reasonable lower limit of 1×10^{12} sites/cm^2 may be estimated for the surface concentration of these unique aluminum ions on both types of γ-alumina. For reasons which will become evident later in the discussion these sites will be denoted as I-sites.

Poisoning of surface sites. In an attempt to relate the role of the I-sites to previous infrared and catalytic experiments (*1–4*) a detailed study was made on the effects of adsorbing various gases on γ-alumina. Carbon dioxide was of interest because of its ability to selectively poison deuterium exchange with olefins and aromatics (*1*, *14*), as well as the ortho–parahydrogen conversion (*6*). It is evident from the work of Van Cauwelaert and Hall (*6*) that up to 1×10^{13} molecules of CO_2/cm^2 are strongly held on the surface of a γ-alumina which was pretreated at 530°C. A weaker form of adsorbed CO_2 is held at the α-sites described by Peri (*2*) and this may be displaced by the adsorption of other gases including 1-butene. This form of CO_2 was not readily removed by a brief evacuation at room temperature.

The minor variation in the spectrum of Fig. 1d which was caused by strongly adsorbed CO_2 or 1-butene is attributed to a second order effect such as an alteration in the mean lifetime of the NO molecule on the I-site.In the present experiments we observed that adsorption at levels up to 10 times the dose required to poison all of the exchange sites or to fill all of the α-sites resulted in only a modest decrease in the number of available I-sites. Furthermore, the CO_2 held on these sites could be removed by evacuating the sample for 10 min at room temperature, as shown in Fig. 3. We conclude, therefore, that the I-sites are neither responsible for the exchange reaction, the ortho–para conversion reaction, nor are they the α-sites.

As may be deduced from Fig. 3, water is very nonselectively adsorbed on the I-sites. It is more strongly held than CO_2, yet it required large amounts to reduce the available I-sites by 40–60%. Previous work (*9*) revealed that approximately 4×10^{13} water molecules/cm^2 of alumina added back at 300°C was effective in decreasing the spin concentration by a factor of 10, and the residual EPR spectrum showed no aluminum hyperfine interaction. The same type of spectrum was observed following the activation at 100°C in the present experiment. It is likely that hydroxyl groups are initially located on the exposed aluminum ions, but these may be removed by activation at elevated temperatures. Degassing the alumina at temperatures at low as 200°C resulted in a small number of exposed aluminum ions; however, most of the I-sites became available only after activation at 400–500°C. The adsorption of water at room temperature is only partially effective in reforming these hydroxyl groups, but at 300°C the poisoning is more efficient. Gerberich and Hall (*4*) studied the relationship between surface hydroxyl groups and the catalytic activity for 1-butene isomerization over γ-alumina. They concluded that the activity of alumina was inversely proportional to the number of hydroxyl groups present. A hydroxyl concentration of approximately 2×10^{13} ions/cm^2 was effective in poisoning most of the isomerization activity.

Hydrogen sulfide was the most selective poison of the three used in this experiment. A previous adsorption study by De Rosset *et al.* (*17*) showed that H_2S was held on a limited number of sites on dehydrated γ-Al_2O_3 with a heat of adsorption up to −38 kcal/mole. Exposed aluminum cations were proposed as the adsorption sites. The ability of H_2S to block the sites which yield the characteristic ^{27}Al hyperfine structure in the nitric oxide spectrum confirms that the H_2S, or possibly a dissociation product of H_2S, is adsorbed on the exposed aluminum ions. Furthermore, the remarkable agreement demonstrated in Fig. 4 between the poisoning of the I-sites as detected by the EPR spectrum and the activity for 1-butene isomerization indicates that a common site is involved. The hyperfine structure and the poisoning experiments suggest that this site has only one aluminum ion with adjacent oxide ions.

An upper limit of 5×10^{13} sites/cm^2 for the number of I-sites on the American Cyanamid alumina was determined from the poisoning experiments (Fig. 4). The amount of H_2S required to completely poison these sites is termed a "lethal dose." Poisoning of the nitric oxide–aluminum sites on the Catapal sample yielded a value of 2×10^{13} I-sites/cm^2. The large difference in the minimum value of I-sites obtained from the spin concentration and these values is attributed mainly to the weak, nonselective adsorption of NO on the alumina. When the larger amount of NO was adsorbed, a lethal dose of H_2S blocked only 40% of the adsorption sites. At these larger nitric oxide coverages the ^{27}Al hyperfine structure is not observed and we assume that much of the nitric oxide is adsorbing at sites on the surface which are not strongly poisoned by H_2S. There is also evidence from the adsorption studies of De Rosset *et al.* (*17*) that the sites for H_2S adsorption are not homogenous. Because of these complications it is only possible to establish that the number of I-sites is within these rather broad limits.

In previous studies, (*1*, *11*), it was concluded that the isomerization of *n*-butenes and the exchange of olefinic and aromatic hydrogen atoms with gaseous D_2 can occur simultaneously but independently on two different kinds of sites on γ-alumina. In addition, it was suggested that the E-sites may correspond to exposed aluminum ions on the alumina surface (*1*). The results of the present study have shown, however, that the surface concentration of the I-sites is at least five times greater than that of the E-sites (5×10^{13}/cm^2 vs 1×10^{13}/cm^2), under similar conditions of measurement. Thus, although the E-sites may consist of exposed Al^{3+} ions in very specific and infrequently occurring environments of surrounding oxide ions and/or hydroxyl groups, it is possible that olefin isomerization may occur on both kinds of sites, while D_2 exchange reactions occur only on the E-sites. The rate of 1-butene isomerization was, in fact, reduced approximately 20% (*11*) by adsorption of an amount of CO_2 that completely poisoned its D_2 exchange reaction.

Speculation on the reaction mechanism. To explain the high *cis/trans* ratios observed in 1-butene isomerization over γ-Al_2O_3 Gerberich and Hall (*4*) proposed a four-membered cyclic species lying over a surface oxide ion, with each end of the butene molecule partially bonded to different aluminum ions. In view of the results presented here, it seems that a butene molecule may strongly interact with only *one* exposed aluminum atom at an I-site. We have explored the possibility of using orbital symmetry rules to explain how a vacant *p*-orbital on such an aluminum atom could result in a concerted catalytic reaction.

Mango (*18*) has reviewed the role of transition metal catalysts in concerted reactions, which are either allowed or forbidden due to molecular orbital symmetry conservation. His work is an extension of the Woodward–Hoffman rules which are based on orbital symmetry considerations (*19*). In the context of these rules the 1-butene isomerization reaction is a 1, 3-sigmatropic rearrangement in which a hydrogen atom migrates from C_1 to C_3 while the molecule retains the same orbital symmetry as it moves along the reaction coordinate. The symmetry of the highest occupied molecular orbital of the radical left by the migrating hydrogen atom dictates the path of rearrangement. For the uncatalyzed reaction, the highest occupied molecular orbital is a nonbonding ψ_2 level as shown in Fig. 5. In order to preserve symmetry the hydrogen migration must proceed with conrotatory twisting of the methylenes as described in Fig. 6a. Although this pathway is symmetry allowed, it yields a highly strained transition state; therefore, the uncatalyzed reaction is slow. The alternate transition state of Fig. 6b is symmetry forbidden.

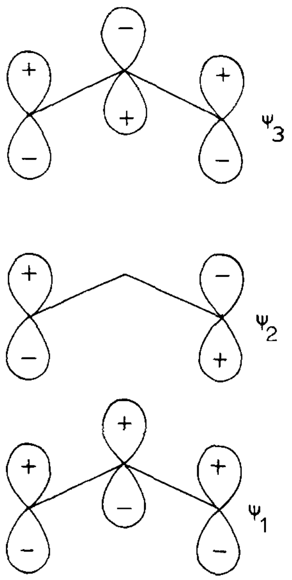

FIG. 5. Molecular orbitals of the π-allyl system.

According to the mechanism described by Mango (*18*), the reaction may be catalyzed by donation of electrons from *d*-orbitals of transition metals to the olefin, thus yielding electronic occupation of the next highest molecular orbital (ψ_3). The transition state described in Fig. 6c is therefore allowed and the hydrogen atom easily moves across the face of the plane described by the olefin.

For 1-butene isomerization over γ-alumina we propose that a limited number of empty *p*-orbitals from exposed aluminum ions are available *in the plane of the surface.* These orbitals have the same symmetry as ψ_2 (Fig. 6d) and it is postulated that as a result of electron flow out of this level, the ψ_1 orbital becomes the highest filled orbital in the transition state. Migration of the hydrogen atom, as described in Fig. 6e, is thus allowed. Some rotation around the C–C bonds is required, but this is not a difficult geometric rearrangement in simple olefins (*18*). Stereochemistry must still be invoked to explain the predominant formation of *cis*-2-butene.

The question of orbital overlap such as that described in Fig. 6d has been dis-

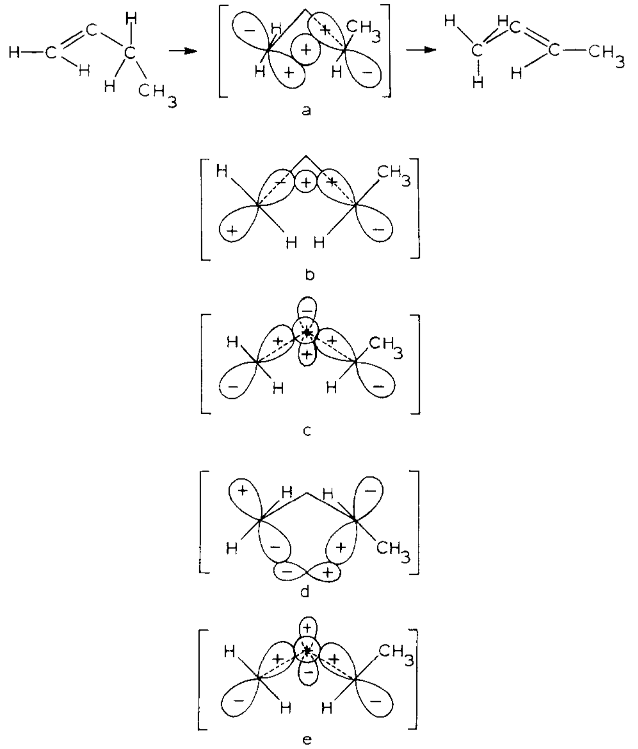

FIG. 6. Transition states during the 1,3-sigmatropic rearrangement: (a) uncatalyzed reaction showing conrotatory motion of orbitals, (b) symmetry-forbidden transition, (c) symmetry-allowed transition involving the ψ_3 orbital, (d) interaction between filled ψ_2 orbital and empty *p*-orbital of aluminum, (e) symmetry-allowed transition involving the ψ_1 orbital.

cussed by Berson (*20*), except that in his experiments the *p*-orbital was associated with a carbon atom. There is clear evidence that such overlap can occur. From the aluminum hyperfine structure in the EPR spectrum of the superoxide ion (O_2^-) on AlSb and decationated zeolites (*15, 16*), one may also conclude that empty *p*-type orbitals of aluminum are available on the surface.

Hightower and Hall (*21*) studied the double-bond migration in small cyclic olefins such as methylenecyclobutane and cyclopentene. They observed that a double bond external to the ring could move into the ring, but that further double-bond migration around the ring did not occur. For example, methylenecyclobutane isomerized to 1-methylcyclobutene, but the reaction did not proceed on to 3-methylcyclobutene. Furthermore, cyclopenetene did not isomerize but cyclohexene did. The authors concluded that "stringent geometric molecular requirements for isomerization must reflect geometric properties of the surface sites which catalyze this reaction." If the isomerization reaction is indeed a concerted reaction, it appears that the limiting factor in the small cyclic olefins may be their rigidity; that is, the required disrotatory twisting of two methylenes in the ring may be highly restricted. Greater flexibility is expected in cyclohexene. Indeed, Mango (*18*) has suggested that the intramolecular hydrogen shift in cyclohexene, as proposed by Smith and Swoop (*23*), may be interpreted in terms of a metal-catalyzed suprafacial 1,3-sigmatropic transformation.

The primary purpose of this discussion has not been to prove that 1-butene ismerization over γ-alumina is a concerted process, but rather to emphasize the possible role of the exposed aluminum atom.

It is widely recognized that alumina possesses Lewis acidity (*22*) and by using this simple molecular orbital approach it is now possible to visualize how such acid sites may effect a catalytic transformation.

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