

Catalytic Function of Hydrogen Bound to the Surfaces of Oxides

W. Keith Hall

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

Received December 27, 1974

The relationships between surface chemistry and catalytic function of several oxides of varying acidity (to basicity) are the subject of the present Account. Attention is drawn to weak forms of chemisorption which may play primary roles in catalysis.

The paper is not intended to be a comprehensive review; for convenience, the author has drawn heavily on work from his own laboratory. Much related work is not mentioned and questions of priority are not considered. The first part is devoted to acid catalysis. Attention is called to the function of surface hydroxyl groups as Brønsted acids; their role in chemisorption (hydrogen bonding) and in carbonium ion formation is discussed. Spectroscopic and chemical data are used to describe the mechanism of proton transfer and to derive a reaction scheme which is shown to hold quantitatively for olefin isomerization. The changes in behavior and mechanisms which occur as the terminal hydroxyl groups become more basic than acidic are next examined. The origin of these changes can be attributed to a corresponding change in the nature of the catalytically active sites which are no longer the hydroxyl groups themselves, but strong polar sites which form as they are removed as H₂O by thermal treatment, i.e., strong Lewis acid-base pair sites. Among other things, some of these tend to dissociate H₂ and catalyze deuterium for hydrogen exchange reactions. At much lower temperatures the same or related sites adsorb H₂ as molecules.

The last half of the paper is concerned with the site-selective chemisorption of molecular hydrogen and with its possible function as an intermediate in the dissociation of H₂ (given sufficient thermal ener-

gy) and in the ortho-para conversion. For many years it has been supposed that the physical (or molecular) conversion requires the presence of centers containing unpaired electrons, e.g., a rare earth ion. Evidence is presented suggesting that the much weaker nuclear paramagnetism may be effective under certain circumstances, e.g., the ²⁷Al ion. These circumstances are defined by the state of the chemisorbed molecular H₂. The conversion is made possible by the convergence of the rotational energy levels of ortho with the para molecule under the influence of a substantial barrier to rotation.

Surface Hydroxyl Groups. The surfaces of oxides are usually terminated by hydroxyl groups which substitute for an extension of the lattice. After evacuation at 500°, a common pretreatment for catalytic studies, the surface densities of these on silica, silica-alumina, and alumina are all similar,¹ i.e., they fall at about 2 to 4 × 10¹⁴/cm². When evacuated at lower temperatures, higher values are obtained, and continued evacuation at still higher temperatures further lowers them. Interestingly, when alumina is evacuated below about 300° a value of about 1.8 × 10¹⁵/cm² is obtained, in fair agreement with the number of oxygens contained in a close-packed two-dimensional sheet.² Such measurements can be made (destructively) by determining the H₂O evolved at about 1000° or (nondestructively) by isotope dilution methods or from the integrated intensities of the proton resonance absorptions.¹ Data from all three methods agree fairly well. When protons are substituted for the Na⁺ base-exchangeable cations of the zeolites, strongly acidic OH groups are formed.³

Surface hydroxyl groups have been extensively studied by infrared spectroscopy. The OH regions from silica gel and silica-alumina are virtually identical;⁴ the single strong band at 3750 cm⁻¹ is characteristic of isolated Si-OH groups. The H-zeolite³ has a sharp band at 3650 cm⁻¹, as well as a broader one at

W. Keith Hall is Distinguished Professor of Chemistry at the University of Wisconsin-Milwaukee. Before joining UWM he was Senior Scientist for the Gulf Research & Development Corporation and, for nearly 20 years, Senior Fellow of the Mellon Institute in charge of Gulf-sponsored research in catalysis. He received his A.B. degree from Emory University, an M.S. from Carnegie Institute of Technology, and the Ph.D. from the University of Pittsburgh. His research interests cover a broad spectrum of problems in adsorption and heterogeneous catalysis: the nature and function of catalytically active sites, tracer studies of mechanisms of catalytic reactions, and the interaction of hydrogen with various metals and oxides. Professor Hall was recipient of the 1974 ACS Award in Colloid or Surface Chemistry sponsored by The Kendall Company. This Account is based on his Award address.

(1) W. K. Hall, H. P. Leftin, F. J. Chesselke, and D. E. O'Reilly, *J. Catal.*, **2**, 506 (1963).

(2) F. H. van Cauwelaert and W. K. Hall, *Trans. Faraday Soc.*, **66**, 454 (1970).

(3) J. B. Uytterhoeven, L. G. Christner, and W. K. Hall, *J. Phys. Chem.*, **69**, 2117 (1965).

(4) M. R. Basila, *J. Phys. Chem.*, **66**, 2223 (1962).

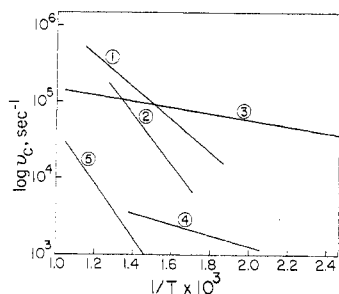


Figure 1. Correlation frequencies for proton mobility on oxide surfaces: (1) HY zeolite, 69% decationated; evacuated at 410°; (2) HX zeolite, 60% decationated; evacuated at 300°; (3) Houdry hard alumina, Grade 200; evacuated at 385°; (4) Houdry S-65 silica-alumina; dried at 100°; (5) Davison silica gel; dried at 100°.

3550 cm^{-1} ; these bands are thought to arise from hydroxyls which are part of two tetrahedra, one centered on Si and the other on Al. The higher frequency band stems from OH vibrating freely into the supercages while the lower frequency vibration is sterically hindered. It has been argued³ that the adjacent Al^{3+} draws electrons from the OH bond, lowering its frequency below that of the isolated Si-OH groups. This would, at the same time, greatly enhance the acidity of these groups.

The OH spectra of alumina are quite different. Peri⁵ has reported five bands for isolated OH groups (major bands at 3800, 3744, and 3700 cm^{-1} and minor bands at 3733 and 3780 cm^{-1}) and has suggested that they correspond to OH groups with different nearest-neighbor environments. Our results⁶ from a more typical pure alumina are in general agreement with Peri's assignments, but the bands appear at somewhat different frequencies (3770, 3725, 3675, 3633, and 3580 cm^{-1}). The existence of these OH bands demonstrates that H is covalently bonded to O where it remains localized for times long compared with the reciprocals of infrared frequencies.

The OH groups can also be examined by proton nmr. Early studies^{1,7} revealed indistinguishable spectra for silica and silica-alumina and different spectra for aluminas. For the former two, the spectra were relatively narrow for solids (~ 250 mG), while those for the latter were broadened (to about 5 G) by the $\frac{5}{2}$ th's spin on the adjacent ^{27}Al nuclei. A similarly broadened line (1.44 G) was found with zeolites.⁸ It was concluded, therefore, that the vast majority of OH groups on silica-alumina are not shared by an adjacent Al, as in the zeolites, and probably do not differ materially from those on silica gel. In these early studies, the temperature dependence of the line width was determined to be invariant between about 280° and 20 K, suggesting that the protons remain fixed on particular oxygens. More recent measurements⁸ have shown this to be untrue. The spectra of Dollish and Hall⁸ showed line narrowing at still higher temperatures for H-zeolites, and similar results were obtained for alumina, silica-alumina, and silica gel. These data are shown in Figure 1, plotted in terms of the correlation frequency of Gutowski⁹ (eq

(5) J. B. Peri, *J. Phys. Chem.*, **69**, 211, 220 (1965).

(6) N. W. Cant and W. K. Hall, previously unpublished results.

(7) D. E. O'Reilly, H. P. Leftin, and W. K. Hall, *J. Chem. Phys.*, **29**, 970 (1958).

(8) N. W. Cant and W. K. Hall, *J. Catal.*, **25**, 161 (1972).

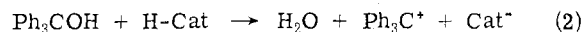
(9) B. Stalinski, C. K. Coogan, and H. S. Gutowski, *J. Chem. Phys.*, **34**, 1191 (1961).

1). ν_c may be viewed as the average hopping frequen-

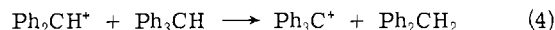
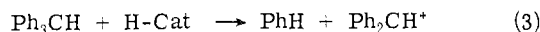
$$\nu_c = \frac{2(2 \ln 2)^{1/2} \Delta\nu}{\tan [\pi(\delta H/\delta H_0)^2/2]} \quad (1)$$

cy, $\Delta\nu$ the line width in frequency units, and $\delta H/\delta H_0$ the fractional width at the temperature of the experiment, referred to the rigid lattice width. These and related¹⁰ data show that the protons of all of these materials are migrating from oxygen to oxygen at all temperatures, but the effect on the spectrum (line narrowing) becomes observable only when the average hopping frequencies become the order of NMR frequencies. Consequently, materials differ in the temperature regions required to effect the line narrowing. It is tempting to suppose that the proton hop occurs by tunneling between the closely adjacent vibrational potential wells situated on these oxygens. This concept will become useful later. Fripiat et al.¹⁰ have obtained closely related data using the spin-echo technique which are in good agreement with ours. Since the hopping frequency increases exponentially with temperature, a picture of an acid site, increasing in activity with temperature, which is most provocative, was derived.¹⁰

The triphenylcarbonium ion is formed spontaneously on aluminosilicates from triphenylcarbinol and with mild heating from triphenylmethane. Its spectroscopic identification is unambiguous.¹¹ With triphenylcarbinol, it seems probable that the reaction is a simple metathesis



and that about 3% of the hydrogen on the silica-alumina surface reacts at room temperature ($5 \times 10^{12}/\text{cm}^2$). The reaction with triphenylmethane is kinetically controlled and only about $5 \times 10^{11}/\text{cm}^2$ ions are formed after heating for some hours at 100°. Moreover, it is not a metathesis, since H_2 gas is not produced.¹² The true chemistry was finally established by Wu and Hall¹³ as follows:



Thus, the net result of these reactions is to replace a proton from the catalyst surface with a stable carbonium ion. About 0.3% of the catalyst hydrogen is active at 100° in spite of estimates many orders of magnitude lower derived from absolute rate theory.^{14,15} Detectable amounts of triphenylcarbonium ion were not formed over alumina.

Pyridinium ion is formed spontaneously on the surfaces of aluminosilicates and can also be identified unambiguously.^{3,16} An estimated 17% of the catalyst hydrogen is involved in this reaction with silica-alumina;⁴ alumina does not protonate pyridine.

(10) M. M. Mestdagh, W. E. Stone, and J. J. Fripiat, *J. Phys. Chem.*, **76**, 1221 (1972); J. J. Fripiat, *Catal. Rev.*, **5**, 269 (1971).

(11) H. P. Leftin, *J. Phys. Chem.*, **64**, 1714 (1960).

(12) H. P. Leftin and W. K. Hall, *Actes Deuxieme Congr. Int. Catal.*, **2nd**, **2**, 1353 (1960).

(13) C. Y. Wu, R. P. Porter, and W. K. Hall, *J. Catal.*, **8**, 394 (1967); **19**, 277 (1970).

(14) K. H. Bourne, F. R. Cannings, and R. C. Pitkethly, *J. Phys. Chem.*, **74**, 2197 (1970); **75**, 220 (1971).

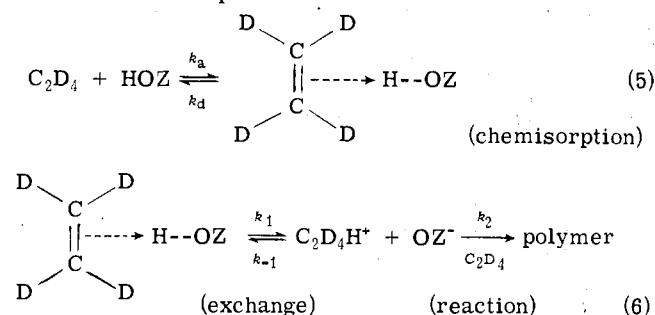
(15) R. W. Maatman, *Catal. Rev.*, **8**, 1 (1973).

(16) E. P. Parry, *J. Catal.*, **2**, 371 (1963); M. R. Basila, T. R. Kantner, and K. H. Rhee, *J. Phys. Chem.*, **68**, 3197 (1964); **71**, 467 (1967).

Hydrogen bonding results when the acid-base interaction is too weak to form a stable conjugate acid. Kiselev et al.¹⁷ showed that the frequency shift of the OH bond of silica gel correlated directly with the heats of adsorption and inversely with the ionization potential of the hydrocarbon when contacted with the series benzene, toluene, xylene, and mesitylene; the shifts fell in the range 120 to 170 cm⁻¹. Much larger shifts were observed¹⁸ when the hydrogen zeolite was contacted with olefins (350–450 cm⁻¹). The interaction with ethylene was studied in detail.⁸ The adsorption appeared to be instantaneously reversible at room temperature and above. The isosteric heat of adsorption (8.4 kcal/mol) was constant with coverage⁸ and the data fit the Langmuir isotherm. Moreover, data obtained spectroscopically (θ vs. P) fell on the same curve with those from volumetric measurements¹⁸ and the limiting adsorption (V_m) from the latter agreed within 25% with the number of decaionated sites. However, a substantial fraction of the OH groups are not directly accessible to the olefin, i.e., those contributing to the 3550-cm⁻¹ band. Thus, if most of the adsorption corresponds to a 1:1 interaction between the OH group and olefin, it is necessary for the latter to trap the hopping proton during its residence time within the supercage. The spectra support this notion, as do tracer results discussed below. The adsorption may therefore be classified as a weak selective chemisorption.

The following picture has emerged. As the temperature is raised, the proton becomes more excited; it hops from site to site at a higher rate. Presumably this means the site becomes more acidic to weak bases. However, because its lifetime on a given site becomes shorter, it becomes more elusive and difficult for the base molecule to trap. The statistics of these interrelated processes affords an interesting avenue for future research.

Catalysis by Aluminosilicates. When perdeuterioethylene was substituted for ethylene in the infrared study of the site-selective chemisorption on zeolites,¹⁸ no exchange occurred at room temperature between the deuterium of the ethylene and the OH groups of the solid. When the temperature was raised above about 150°, however, exchange commenced, as did a slow polymerization; the two processes appeared inseparable.⁸ When propylene was substituted for ethylene, the hydrogen-bonding shift was larger (by 100 cm⁻¹), and these processes both occurred at room temperature; after 72 hr, all of the gas phase was removed by polymerization.¹⁸ These findings are summarized in eq 5 and 6.



(17) G. A. Galkin, A. V. Kiselev, and V. I. Lygin, *Trans. Faraday Soc.*, **60**, 435 (1964).

(18) B. V. Liengme and W. K. Hall, *Trans. Faraday Soc.*, **62**, 3229 (1966).

Table I
Comparison of Theoretical Model with Experiment for *n*-Butene Isomerization

	Silica-Alumina ^a		Na(H) Zeolite ^b	
	Theor	Exptl	Theor	Exptl
1. Product Ratios				
<i>cis</i> -2-Butene/ <i>trans</i> -2-butene	1.00	1.00	1.00	1.29
1-butene/ <i>trans</i> -2-butene	0.75	0.94	3.00	2.90
1-butene/ <i>cis</i> -2-butene	0.75	1.00	3.00	2.46
2. Relative Reactivities				
1-Butene	1.00	1.00	1.00	1.00
<i>cis</i> -2-Butene	0.20	0.15	0.38	0.37
<i>trans</i> -2-Butene	0.04	0.04	0.14	0.18
3. Equilibrium Constants				
1-butene/ <i>cis</i> -2-butene	0.21	0.15	0.61	0.55
1-butene/ <i>trans</i> -2-butene	0.03	0.04	0.18	0.28
<i>Cis</i> -2-Butene/ <i>trans</i> -2-butene	0.14	0.26	0.30	0.51

^a Taken from data of Hightower and Hall.²² ^b Taken from data of Lombardo and Hall.²⁴

A simple steady-state treatment based on these equations shows that Langmuir kinetics may be expected for unimolecular reactions such as isomerization. This was found in kinetic and tracer studies^{19,20} with cyclopropane, and analogous equations were developed therefrom. The picture evolved showed the carbonium ion in a metastable potential well near the top of the reaction coordinate. Consequently, the activation step is contained in the transformation characterized by the rate constant, k_1 . (Note, however, that in many other cases carbonium ion formation may not be rate controlling.) Related studies of butene isomerization^{21,22} were consistent with this view, and the product selectivities and relative reactivities of the three butene isomers, as well as a fair approximation of the three equilibrium constants for the isomers, could be derived from a simple model using only the experimental differences in barrier heights between the carbonium ion and isomers (Table I). Thus, the hydrogen-bonded chemisorption of eq 5 suggests itself as the ground state required for carbonium ion formation in eq 6. Stable pyridinium ions form on these same sites.¹⁸

An interesting feature of the isotopic exchange reaction (eq 6) is that both hydroxyl bands (3650 and 3550 cm⁻¹) are removed at the same rate, even though the lower frequency species is inaccessible to the gas (C₂D₄). At the temperature of the exchange, protons are hopping much faster than the molecules are exchanging. Hence, the unavailable protons are made available in the large cavities where they can contact the C₂D₄. This is not surprising since the ac-

(19) J. W. Hightower and W. K. Hall, *J. Amer. Chem. Soc.*, **90**, 851 (1968); J. G. Larson, H. R. Gerberich, and W. K. Hall, *ibid.*, **87**, 1880 (1965).

(20) J. W. Hightower and W. K. Hall, *J. Phys. Chem.*, **72**, 4555 (1968).

(21) J. W. Hightower and W. K. Hall, *J. Amer. Chem. Soc.*, **89**, 778 (1967).

(22) J. W. Hightower and W. K. Hall, *J. Phys. Chem.*, **71**, 1014 (1967); *Chem. Eng. Prog., Symp. Sec.*, **63**, 122 (1967).

tivation energy for hopping is much lower than that for the exchange. It seems reasonable to suppose that these two processes are similar and involve tunneling of the proton between two conjugate bases.

Catalysis by Alumina and Zinc Oxide. When even strong bases such as pyridine are adsorbed on alumina the OH frequencies remain unperturbed.^{16,23} This lack of hydrogen-bonding ability, together with the butene isomerization kinetics,²² suggests that alumina cannot readily furnish protons for acid catalysis. The aluminosilicate results establish a pattern of behavior characteristic of carbonium ion reactions (Table I) which is not followed over alumina.^{22,24} The product selectivities for butene isomerization are not controlled by the energy barriers between a *single* common intermediate and the three isomers, and high initial cis/trans ratios are obtained rather than values near unity. In addition, the catalytic activity for this reaction increases as bound hydrogen is removed from the alumina; the reverse is found for silica-alumina.²⁵ For cyclopropane isomerization,²⁶ on the other hand, the activity increases with hydrogen content with both catalysts, but alumina is much less active, requiring temperatures in excess of 200° to open the ring, whereas silica-alumina will effect the reaction below 100°. The reverse is true for butene isomerization; alumina is the more active, catalyzing this reaction at room temperature. In alcohol dehydration, the elements of H₂O are removed from the methylcyclohexanols and from *threo*- and *erythro*-2-butanol-3-*d* by a concerted anti elimination.²⁷ Syn elimination is the expected reaction for Brønsted acids, at least for weak ones; stereoselectivity would be lost were a carbonium ion intermediate formed. The surface chemistry of alumina is centered around the concept of strong dual acid-base sites, (exposed aluminum ions with adjacent O²⁻ ions) which are capable of cleaving H₂O, ROH, and even NH₃ to form new surface OH⁻ groups by H⁺ addition to the O²⁻ and the related group (OH, OR, and NH₂) filling the vacancy above the exposed aluminum ion. It is likely that during alcohol dehydration OR is converted to the olefin and OH, and that H₂O is produced by condensation of these in a separate step to maintain a steady-state concentration of vacancies.

Chang, Conner, and Kokes²⁸ and Baird and Lunsford²⁹ have studied butene isomerization over ZnO and MgO, respectively. Both found high cis/trans ratios, even higher than those for alumina, and both concluded that the reaction mechanism probably involves an intramolecular transfer of H or D, in agreement with our suggestion.^{21,25} Kokes et al.²⁸ used infrared spectroscopy to identify reaction intermediates, a possibility for which ZnO is uniquely well suited. The spectra showed π complexes and syn- and anti- π -allyl species. The latter were suggested as in-

termediates in the reaction with the transformation between them an essential step in the mechanism. To form the allyl, an H must be removed from the olefin by the catalyst; return of this to the molecule following the transformation completes the isomerization. The chief features of the alumina data appear to be consistent with this mechanism. In particular, it affords a straightforward explanation of the high cis/trans ratios mentioned above as well as the intramolecular transfer of hydrogen during isomerization. It is consistent with the finding that the data cannot be explained by a single common intermediate, but introduces the minimum possible complications by invoking two interconvertible surface complexes which were identified spectroscopically on ZnO. If future work establishes that it is generally operative in those cases exhibiting high cis/trans ratios, isomerization of the *n*-butenes may become an important diagnostic tool for defining catalyst function.

Hydrogen-exchange reactions with hydrocarbons over alumina are facile, usually occurring below 50°. With olefins^{30,31} the vinyl hydrogens are exchanged preferentially and independently of the isomerization reaction; the two reactions occur on different sites.³² The vinyl hydrogens of cyclopentene exchange without isomerizing the molecule;³¹ hence, nearly pure 1,2-dideuteriocyclopentene can be prepared. This behavior suggests that the vinyl hydrogen is removed and then replaced with deuterium; were the deuterium added and *then* hydrogen removed, it is difficult to see why isomerization would not result. Cyclopropane can be completely deuterated without much isomerization.³³ Remarkably, CH₄ exchanges at room temperature with D₂ or with CD₄.³⁴ The exchange is stepwise and shows an important isotope effect ($k_H/k_D = 1.85$) for the cleavage of the C-H *vs.* the C-D bond. Selective poisoning experiments with CO₂ showed that this reaction occurs on less than 1% of the available surface sites ($\sim 3 \times 10^{12}/\text{cm}^2$). H₂O is not a selective poison, but the H₂O formed by reaction of H₂ with O₂ on these same sites is selective, and these results agreed very nicely with the CO₂ data. Uppal and Hightower³⁵ have related these sites to those which produce an infrared band at 1480 cm⁻¹ on adsorption of CO₂. This is said to be a bicarbonate site.

The H₂-D₂ exchange and the allotropic conversion reactions proceed at even lower temperatures over alumina and are also poisoned by CO₂.² The former reaction follows the Arrhenius law and becomes immeasurably slow below about 125 K. Around room temperature both the exchange and conversion have similar activation energies (1.9 kcal/mol), with the latter being faster by a factor of about two. As the temperature is lowered, however, the Arrhenius plot for the ortho-para conversion changes slope to 430 cal/mol and thus remains easily measur-

(23) H. Jeziorowski, H. Knözinger, W. Meye, and H. D. Müller, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1744 (1973).

(24) E. A. Lombardo and W. K. Hall, *Catal., Proc. Int. Congr.*, **5th**, 1972, **2**, 1365 (1973).

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

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

(27) C. L. Kibby, S. S. Lande, and W. K. Hall, *J. Am. Chem. Soc.*, **94**, 214 (1972).

(28) C. C. Chang, W. C. Conner, and R. J. Kokes, *J. Phys. Chem.*, **77**, 1957 (1973).

(29) M. J. Baird and J. H. Lunsford, *J. Catal.*, **26**, 440 (1973).

(30) J. W. Hightower and W. K. Hall, *J. Catal.*, **13**, 161 (1969).

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

(32) M. P. Rosynek and J. W. Hightower, *Catal., Proc. Int. Congr.*, **5th**, 1972, **2**, 851 (1973).

(33) J. G. Larson, J. W. Hightower, and W. K. Hall, *J. Org. Chem.*, **31**, 1225 (1966).

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

(35) S. S. Uppal and J. W. Hightower, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **18** (2), 262 (1973).

able at the temperature of liquid nitrogen. This behavior has been observed many times with other catalysts and usually has been interpreted as a change from the dissociative mechanism required for the exchange reaction to a physical mechanism corresponding to interaction of molecular H_2 with paramagnetic sites on the surface of the catalyst. In fact, using the experimental rate constant found for alumina² at 78 K to estimate the number of paramagnetic centers based on the Sandler-Eley model,³⁶ a value of 2×10^{12} sites/cm² was obtained, using the parameters given by Eley and Zammitt.³⁷ The amount of CO_2 required to poison the reaction was only a little larger, i.e., about 8×10^{12} CO_2 /cm² at 0° to 2×10^{13} /cm² at 78 K. The difficulty with this seemingly fair agreement arises when one considers that the density of unpaired electrons required, i.e., 8×10^{12} /cm² or 2×10^{19} /g, is a value that appears impossibly high for alumina. The alumina used in this work was very pure; it had a total cation impurity of less than 50 ppm or at least two orders of magnitude lower than the number of sites, were it all on the surface. Moreover, no paramagnetism was detected by EPR when an exhaustive search was made² at both room and liquid nitrogen temperatures. Thus, the number of unpaired electrons must be much lower than the impurity level and probably lies below $\sim 10^{14}$ /g ($\sim 10^8$ /cm²). Consequently, another explanation seemed necessary.

Certain salient features stood out.^{2,38} The low-temperature conversion reaction appeared to proceed by a molecular adsorption of H_2 on sites, an important fraction of which dissociate this molecule at higher temperatures. These sites may be poisoned (made unavailable) by the selective chemisorption of CO_2 , giving rise to a species which generates a band in the infrared spectrum at 1480 cm^{-1} .³⁵ Moreover, the sites develop as the alumina surface is dehydroxylated, the rate constant for the conversion reflecting the extent of dehydroxylation. Thus, the sites which are poisoned by CO_2 are uncovered by dehydroxylation. Finally, it was found³⁸ that the chromatographic separation of the isotopes and allotropes of H_2 could be substantially altered (although not completely destroyed) by the chemisorption of CO_2 , indicating that the sites which effect dissociation of H_2 above 125 K adsorb H_2 molecularly at the temperature of liquid nitrogen. The sum of this evidence suggested that aluminum ions which become exposed on dehydroxylation are somehow involved. The ²⁷Al nucleus is a paramagnetic center; could it be responsible for the facile conversion reaction over alumina? It has always been supposed that the answer to this question is no, based on the following reasoning. In 1933, Wigner³⁹ derived an equation for the transition probability for the ortho-para conversion by collision of H_2 with paramagnetic gas molecules. This expression led to fair agreement between theory and experiment for the homogeneous conversion effected by paramag-

netic molecules such as NO. According to the Wigner theory the transition probability is proportional to μ_a^2 , the magnetic moment of the paramagnetic molecule. Thus, if a nuclear magnetic moment is used rather than an electronic moment, the resulting transition probability is lowered by nearly six orders of magnitude. Eley and coworkers^{36,37} have found that specific rates calculated on the basis of the Sandler-Eley model are usually too low by a factor of about 10^2 when electronic moments are used. Hence, it would appear completely unreasonable to expect nuclear moments to function with the required efficiency. Before dismissing this possibility, however, it will be worthwhile to examine the Wigner theory and its use by Eley and coworkers in some detail.

The Wigner expression for the probability of transition, W_{01} , between the zeroth and first rotational levels of the hydrogen molecule is given by

$$W_{01} = \frac{24\mu_a^2\mu_p^2I\pi^2t^2}{h^2mr^8} \quad (7)$$

where μ_a is the magnetic moment of the paramagnetic molecule (or center); μ_p , the magnetic moment of the proton; I , the moment of inertia of the H_2 molecule; h , Planck's constant; m , the mass of the hydrogen molecule; and r , the distance between its center of mass and the paramagnetic center during the collision time, t . Wigner assumed that the hydrogen molecule approached the paramagnetic center with infinite velocity, remained at the collision distance, r , for time $t = r/3v$, where v is the true relative velocity before the collision, and then separated with infinite velocity. Moreover, he assumed $v = (3kT/m)^{1/2}$. Making these substitutions, the form of the equation used by Harrison and McDowell⁴⁰ and by Eley et al.³⁶ is obtained, i.e.

$$W_{01} = \frac{8\mu_a^2\mu_p^2I\pi^2}{9h^6r^6kT} \quad (8)$$

Several points may be made here: (a) these equations are invalid for a collision time longer than $\sim 10^{-13}$ to 10^{-14} sec;^{39,40} (b) the substitution made in arriving at eq 8 defines t in this range, whether this is true or not; (c) the same substitution changes the r^{-8} dependence of eq 7 to r^{-6} in eq 8; since r is the order of 10^{-8} cm, this can have a considerable effect on the value calculated (vide infra); (d) there is the question of whether a vibration of frequency 10^{11} to 10^{13} sec⁻¹ is equivalent to a high energy collision; (e) the expected inverse quadratic dependence on the transition energy does not appear in eq 7 and 8. van Cauwelaert and Hall² pointed out that the general equation for a transition probability obtained from modern quantum theory is

$$W_{01} = \frac{\langle \psi_1 | H_m | \psi_0 \rangle^2}{(E_1 - E_0)^2} \quad (9)$$

where E_0 and E_1 are the energies of the $J = 0$ and $J = 1$ rotational states of para- and orthohydrogen, respectively. If the H_2 molecule is held in a strong electric field, the energy difference ($E_1 - E_0$) may be greatly reduced and W_{01} increased. This factor had not been taken into account in previous calculations.

Conner and Kokes⁴¹ noted recently that in Wig-

(36) D. R. Ashmead, D. D. Eley, and R. Rudham, *Trans. Faraday Soc.*, **59**, 207 (1963).

(37) D. D. Eley and M. A. Zammitt, *J. Catal.*, **21**, 366 (1971); D. D. Eley and D. Shooter, *ibid.*, **2**, 259 (1963).

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

(39) E. Wigner, *Z. Phys. Chem., Abt. B.*, **23**, 28 (1933).

(40) L. G. Harrison and C. A. McDowell, *Proc. R. Soc.*, **220**, 77 (1953).

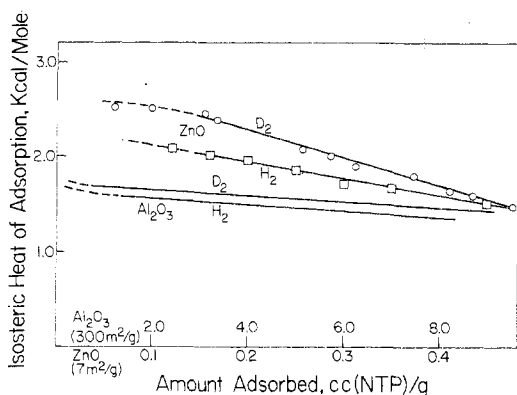


Figure 2. Comparison of heats of adsorption of H_2 on ZnO and Al_2O_3 .

ner's relation, before a final approximation was made, the denominator did contain this term, i.e.

$$W_{01} = \frac{36\mu_a^2\mu_p^2d^2}{\hbar^2r^8\omega^2} \sin^2 \left[\frac{\omega t}{2} \right] \langle \cos \theta \rangle^2 \quad (10)$$

where d is the hydrogen internuclear distance, $\omega = (E_1 - E_0)/\hbar$, and θ is the angle between \mathbf{r} and \mathbf{d} . Wigner estimated that for gas molecules the time of interaction on collision ($\sim 10^{-14}$ sec) was sufficiently short so that $\omega t/2$ was close to zero. Thus, by substituting its argument for the sin term, the difference in energy was canceled. The form of eq 10, which contains the periodic function $\sin^2(\omega t/2)$, seems more suitable for calculation of W_{01} for a model involving vibration of H_2 against a surface site than eq 8. Before proceeding, however, it is necessary to consider the values of the parameters to be used.

The transition energy, $(E_1 - E_0) = \hbar\omega$, will be dependent on the electric field at the adsorption site.^{2,41,42} An estimate of this field, and better still, values of $(E_1 - E_0)$, can be derived from chromatographic separation factors for the hydrogen allotropes. The theory for these is fairly well understood and has been reviewed in the present context elsewhere.³⁸ Sandler⁴³ was first to note that orthohydrogen ($J = 1$) is more strongly adsorbed than parahydrogen ($J = 0$); to explain this fact he found it necessary to assume the rotation of the adsorbed molecule is hindered. White and Lassette⁴⁴ derived the splitting of the energy levels as a function of the height of the barrier to rotation, and Katorski and White,⁴⁵ in an extension involving coupled rotation-vibration, were able to show that the separation factors for all the isotopes and allotropes of H_2 could be calculated, given the single parameter—the barrier to rotation. The calculations include the results of quantum mechanical derivation of the rotational energy levels of the allotropes and isotopes as a function of the height of the barrier to rotation. Thus, by measuring a separation factor, the barrier is determined and from this $(E_1 - E_0)$ can be derived. Plots of the energy levels vs. barrier to rotation have been published by several authors;^{42,44,46} those of Chang et al.⁴⁶ are used here

because they appear most suitable.

van Cauwelaert and Hall³⁸ obtained values between 900 and 1200 cal/mol for the barrier for the same alumina previously used in the conversion experiments, depending upon the extent of dehydroxylation. For ZnO,⁴⁶ a constant pressure ratio, $P_{H_2}/P_{D_2} = 1.57$, was required to maintain the same coverage of the two gases. This fact, together with heats of adsorption and rotational energy levels, indicated, "a sizeable barrier to rotation" for these molecules. In fact the data suggest a value near 1 kcal/mol, in substantial agreement with that obtained from chromatographic separation factors for alumina. Their data⁴⁶ on heats of adsorption on zinc oxide are compared with those for alumina⁴⁷ in Figure 2. The value⁴⁶ of $(E_1 - E_0)$ for a barrier of 1 kcal/mol is about 29 cal/mol as compared with about 175 cal/mol for the free rotor. This leads to a value for $\omega = 1.905 \times 10^{12} \text{ sec}^{-1}$.

The allotropic separation could be used for the determination of the barrier to rotation³⁸ at low extents of dehydroxylation where the half-time for conversion was much greater than the retention time; at high extents of dehydroxylation the rapid conversion prevented separation of the allotropes, but the separation of the isotopes having equilibrated allotropes was possible and a bit more informative. The vibrational frequency, ν_0 , of the molecule vibrating against the surface site could be derived from the zero-point energy required to satisfy these data. This value, $7.7 \times 10^{12} \text{ sec}^{-1}$, can be used as a measure of t in eq 10, i.e., $t = 1/\nu_0$. We are now in a position to make some calculations.

Following Conner and Kokes,⁴¹ eq 10 may be written

$$W_{01} = C/\omega^2 \sin^2(\omega t/2) \langle \cos \theta \rangle^2 \quad (11)$$

For reasons given later $\langle \cos \theta \rangle^2$ is taken as unity.

Some results are collected in Table II. In line 1, Eley's parameters³⁶ have been used, including $\nu_0 = 4.5 \times 10^{11} \text{ sec}^{-1}$. It can be seen that $\omega t/2$ is too large for Wigner's approximation (eq 7) to be valid; matters would be much worse if ω were larger (in the absence of a high barrier to rotation). In line 2 the calculation is repeated, but using our value for ν_0 ; now the approximation is valid, but W_{01} is lowered by a factor of about 42. In line 3, 1 Bohr magneton was used for the paramagnetic center instead of 3.68 (for Nd^{3+}) and 2.79 nuclear magnetons (the NMR value) instead of $1/1840$ Bohr magnetons; the value of r was also reduced to 1.25 Å (from 2.0). This value corresponds to the distance between the Al^{3+} nucleus and the center of the H-H bond when the molecule is centered between an exposed Al^{3+} and O^{2-} on a site above an adjacent Al^{3+} 2.85 Å away; r could conceivably be further reduced to 0.85 Å. Lines 4 and 5 use the same model, but now the nuclear moment for ^{27}Al was substituted for the paramagnetic center for our and for Eley's value of ν_0 , respectively. Line 6 contains the value used by Eley and Zammitt³⁷ (eq 8) for the alumina surface for comparison. If nothing more, these calculations illustrate the degree of uncertainty involved in the question of whether or not nuclear

(41) W. C. Conner and R. J. Kokes, *J. Catal.*, **36**, 199 (1975).
 (42) J. King and S. Benson, *J. Chem. Phys.*, **44**, 1007 (1966).
 (43) Y. L. Sandler, *J. Phys. Chem.*, **58**, 58 (1954).
 (44) D. White and E. N. Lassette, *J. Chem. Phys.*, **32**, 72 (1960).
 (45) A. Katorski and D. White, *J. Chem. Phys.*, **40**, 3183 (1964).
 (46) C. C. Chang, L. T. Dixon, and R. J. Kokes, *J. Phys. Chem.*, **77**, 2643 (1973).

(47) F. H. van Cauwelaert and W. K. Hall, previously unpublished results.

Table II
Calculation of Transition Probability per Collision According to Equation 10^a

Calc no.	$\mu_a \times 10^{24}$, ergs/G	$\mu_p \times 10^{24}$, ergs/G	$r \times 10^8$, cm	$C \times 10^{-12}$, sec ⁻¹	$l = 1/\nu_0 \times$ 10^{12} , sec	$\frac{\omega l}{2}$	W_{01}
1	34,100	5.05	2.0	1,830	2.2	2.12	3.5×10^{-10}
2	34,100	5.05	2.0	1,830	0.13	0.12	8.3×10^{-12}
3	9,273	14.10	1.25	52,520	0.13	0.12	2.1×10^{-10}
4	18.35	14.10	1.25	0.2	0.13	0.12	7.9×10^{-16}
5	18.35	14.10	1.25	0.2	2.2	2.12	3.8×10^{-14}
6 ^b							7×10^{-13}
7 ^c							8×10^{-14}

^a Conner and Kokes formulation;⁴¹ corresponds to eq 10. ^b Value used by Eley and Zammit;³⁷ corresponds to eq 8. ^c Value required to fit data of ref 2, using eq 14; see text.

paramagnetism can be effective for the ortho-para conversion.

Kokes and coworkers⁴⁶ found the Raman stretching bands of the hydrogen isotopes became infrared active, although shifted to lower frequency when these gases were adsorbed on ZnO or alumina. The normalized frequency shifts, $\Delta\omega/\omega$, for ZnO were constant $(3.39 \pm 0.05) \times 10^{-2}$. It was concluded, therefore, that the bands correspond to the pure vibrations of the adsorbed molecular species. These forbidden bands appear because interaction with the surface induces a dipole moment in the molecule which is dependent on the internuclear displacement, as would be expected were the molecules held in a strong electric field between electropositive and electronegative centers. The fact that the infrared frequency becomes active for adsorbed H₂ and D₂ indicates an attractive interaction of considerable importance; this is reflected in heats of adsorption over ten times more than the heat of liquefaction. Thus, to desorb, the molecule must escape from the potential well in which it is held. The characteristic frequency of desorption may be estimated as

$$\nu = \nu_0 e^{-q/RT} \quad (12)$$

where q is the heat of adsorption. From Figure 2, two values of q , 1330 and 1570 cal/mol, may be selected for alumina, the former corresponding to the total adsorption at 100 Torr and the latter to the "site monolayer", both at 78 K. Using our value of ν_0 given above, the corresponding values of the lifetime, $\tau = 1/\nu$, can be estimated; these values are 6.5×10^{-10} and 3×10^{-9} sec, respectively. Thus, the residence time of H₂ on a given site is long compared with the time for one vibration. Following Eley et al.,³⁶ the ratio ν_0/ν can be taken as the number of vibrations before desorption. The rate of desorption may be written

$$\beta = N_s \theta \nu_0 e^{-q/RT} \quad (13)$$

so that the specific rate of the conversion is

$$k_m = N_s \theta \nu_0 W_{01} G(T) = \beta (\nu_0/\nu) W_{01} G(T) \quad (14)$$

where N_s is the number of active sites per unit area, θ is the fraction of these covered, and $G(T)$ is a partition function ratio which allows for the ortho-para equilibrium at each temperature and the endothermicity of the para to ortho transitions.³⁶ It is of interest to estimate the numerical value of W_{01} required to fit the data. From our measurements on alumina we

have at 78 K $k_m = 2.5 \times 10^{12}$ molecules/cm² sec, $N_s = 2 \times 10^{13}$ /cm², $\theta \approx 1$, and $\nu_0 = 7.7 \times 10^{12}$ sec⁻¹; $G(T)$ as calculated by Eley et al.³⁶ is 0.210 at this temperature. Thus, $W_{01} = 7.9 \times 10^{-14}$. With reference to Table II, we see that it is not possible to exclude nuclear paramagnetism as the source of the conversion.

The requirement of a substantial barrier to rotation to explain the behavior of adsorbed hydrogen on these surfaces seems firmly established. King and Benson⁴² considered the origin of this barrier and logically related it to the interaction of the electric field with the asymmetric polarizability tensor for the H₂ molecule. The most stable configuration was found to be that with the H-H bond parallel to the field. Thus, we have taken $(\cos \theta)^2 \approx 1$. The magnitude of the field may be estimated³⁸ by assuming this is the sole factor contributing to the barrier, but it must be remembered that the neglect of other possible factors which could contribute could lead to calculation of an electric field higher than it really is. The electric fields calculated from the barriers determined from our chromatographic experiments³⁸ were in the range 2.3 to 2.7 V/Å. These values, which may be regarded as upper limits, may be compared with those estimated by Cochrane et al.⁴⁸ for alumina and by Kokes and coworkers⁴⁶ for ZnO, which may be considered lower limits. Both the latter sets of data yielded 0.6 V/Å. It can be readily appreciated that electric fields ~ 1 V/Å are sufficient to provide a substantial barrier to rotation and would severely distort if not ionize the H₂ molecule. Given enough thermal energy, the molecule should dissociate as it does above 125 K. If the field is developed between two ions of opposite sign, the molecule should become sufficiently polarized to become infrared active and should librate around the line of centers as envisioned by Kokes.⁴⁶ This picture is far removed from that considered by Wigner,³⁹ and theoretical work is needed to establish the validity or shortcomings of the application of his theory to the present problem. However, the physical situation has now been clarified to the point that progress may be expected in the important problem of understanding the requirements for the activation of H₂ by oxides.

The author wishes to express his gratitude to the late Professor R. J. Kokes for many stimulating discussions and for his friendship over many years.

(48) H. Cochrane, B. A. Henderson, D. R. Pierce, and R. Rudham, *Sci Monogr.*, 25, 370 (1967).