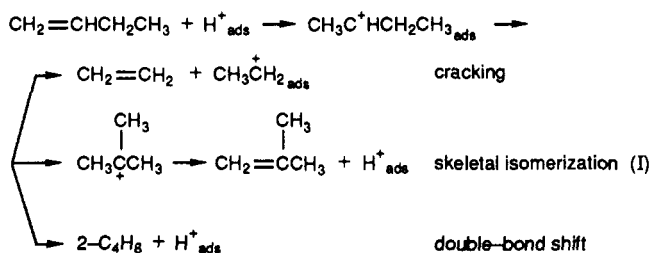# The Nature of Adsorbed Carbenium Ions as Active Intermediates in Catalysis by Solid Acids

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Heterogeneous acid catalysis is of fundamental, broad importance in petroleum refining chemistry, such as cracking, isomerization, and alkylation. Almost 40 years ago, the mechanism of hydrocarbon conversion on solid acidic catalysts was first formulated. It has remained practically unchanged. For instance, the catalytic transformations of 1-butene through adsorbed (ads) intermediates are usually represented as follows:

$$CH_2=CHCH_2CH_3 + H^+_{ads} \longrightarrow CH_3C^+HCH_2CH_{3 ads} \longrightarrow$$

$$\longrightarrow CH_2=CH_2 + CH_3\overset{+}{C}H_{2 ads} \qquad \text{cracking}$$

$$\longrightarrow CH_3\underset{+}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_3 \longrightarrow CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}CH_3 + H^+_{ads} \qquad \text{skeletal isomerization (I)}$$

$$\longrightarrow 2\text{-}C_4H_8 + H^+_{ads} \qquad \text{double-bond shift}$$

Such a mechanism is indistinguishable from that proposed for similar homogeneous reactions, as heterogeneous catalysis is not considered explicitly. Therefore it cannot explain why carbenium ions react differently if adsorbed on various solid catalysts. Thus, in the case of alkenes, the migration of the double bond requires weaker acid sites than cracking or skeletal isomerization. This difference does not follow from I.

In other words, the old mechanism is out of date: it fails to describe the phenomenon of heterogeneous acid catalysis at the molecular level. The aim of this Account is to present more adequate mechanisms of heterogeneous acid catalysis, which include the interaction of active intermediates with the surface of acidic oxide catalysts. Zeolites, now the most widely used of these, are crystalline aluminosilicates that not only have much higher activity and selectivity than the previous amorphous catalysts but also have active-site structures that are much better understood.

Infrared Spectroscopy of Free OH Groups: Their Intrinsic Brønsted Acidity

The most common technique for the direct observation and study of surface Brønsted acid sites is IR spectroscopy. However, in most cases, the OH fundamental stretching frequency is the only spectral feature used for characterization of acid strength.

In our papers,[1–3] diffuse reflectance IR spectroscopy was used to study the acid strength of surface OH

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Table I
Dissociation Energy (D_0) of Surface Hydroxyl Groups with Different Acid–Base Properties[a]

oxide or catalyst	frequency of fundamental vibrations and overtones, cm^{-1}	D_0, kcal mol^{-1}
MgO	3750, 7350, 10760	140
SiO$_2$	3749, 7326, 10735	124
B/SiO$_2$[b]	3705, 7246, 10621	124
AlPO$_4$[c]	3679, 7147, –	126
HY zeolite	3645, 7130, 10460	125
HM mordenite	3611, 7065, 10360	125

[a] Reference 6. [b] Boron-containing porous glass. [c] Partially hydrolyzed amorphous aluminum phosphate.

groups in the near IR region. Besides the fundamental stretching frequency, a number of IR bands originating from overtones or from different combinations of stretching and bending vibrational modes make it possible to construct from near IR spectra the potential energy shape of O–H bonds in surface hydroxyls with different acid strengths. In refs 4–8, this was done by means of the Morse function formalism. This formalism also describes nicely the O–H potential energy shape for surface hydroxyls, since their vibrations are highly characteristic and interact very weakly with those of the oxide crystal lattice. Table I lists the positions of the experimentally observed fundamental transitions and overtones of hydroxyl groups on different oxide surfaces as well as their dissociation energies, D_0, calculated from these data.

As can be seen, the dissociation energies D_0 of all of the OH groups are relatively low, definitely indicating a homolytic dissociation. Compare, for instance, the calculated O–H bond strength (about 125 kcal mol^{-1}) with the energy of homolytic dissociation of water (118 kcal mol^{-1}) or of hydrogen chloride (103 kcal mol^{-1}). It is also remarkable that hydroxyls with very different acid–base properties have almost the same homolytic dissociation energies and shapes of the corresponding potential curves. This indicates that their ground states are covalent and very similar.

On the other hand, values of heterolytic dissociation of surface OH groups on solid acids and bases (D_{het}) are quite different. They can be easily estimated from the following cycle: Let us first split the surface O–H bond

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(2) Kazansky, V. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1984**, 33–42.
(3) Kazansky, V. B. In *Structure and Reactivity of Modified Zeolites*; Jacobs, P., et al., Eds.; Elsevier: Amsterdam, 1984; pp 61–75.
(4) Kazansky, V. B.; Gritskov, A. M.; Andreev, V. M. *Dokl. Phys. Chem.* **1977**, *235*, 635–639.
(5) Kazansky, V. B. *Kinet. Catal.* **1977**, *18*, 966–976.
(6) Kazansky, V. B. *Kinet. Catal.* **1980**, *21*, 128–138.
(7) Kazansky, V. B.; Gritskov, A. M.; Andreev, V. M.; Zhidomirov, G. M. *J. Mol. Catal.* **1978**, *3*, 135–144.
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homolytically and then ionize the resulting hydrogen atom and transfer the available electron to the solid, resulting in the heterolytic splitting of the surface hydroxyl with a total energy

$$D_{het} = D_0 + U_H - \phi \qquad (1)$$

The hydrogen atom ionization potential U_H is equal to 13.6 eV, and the work function of oxides ϕ never exceeds 6–7 eV. Therefore, the D_{het} exceeds D_0 by at least 6–7 eV or 150–170 kcal mol^{-1}. Thus, the splitting of protons corresponds to electronically excited heterolytic states, far above the covalent ground states. This difference determines the corresponding difference in acid strength.

Thus, any attempt to determine the acid strength of a given surface OH group from its stretching frequency or any other property of its covalent ground state will fail. The only proper way to proceed is to follow the response of hydroxyl groups to their interaction with adsorbed bases. This is actually the most common approach, using the low-frequency shift of the fundamental stretching OH vibration caused by hydrogen bonding with an adsorbed molecule.

Spectral Study of Proton Transfer to Adsorbed Molecules

In addition to fundamental bathochromic shifts of stretching vibrations, those of overtones can also be determined. With these data, the shape of OH bonds perturbed by hydrogen bonding with adsorbed molecules can be obtained. This was done in the following way, as reported in our papers.[6,9,10]

It is known[11] that the lengths of strong hydrogen bonds in a wide variety of complexes are in the range 2.4–2.6 Å. On the other hand, the equilibrium O–H distance is close to 1.00 Å and similar to that of newly formed bonds in adsorbed molecules after their protonation. For instance, the C–H bond length is 1.09 Å and the N–H bond length is 1.01 Å. This means that in most cases the proton transfer corresponds to the stretching of the initial OH bond for only about 0.5 Å. Therefore, the potential energy profile of the elementary step of protonation can be obtained by the intersection of two potential curves. The first one is that of the initial OH group perturbed by hydrogen bonding, and the second one is that of the newly formed bond in the adsorbed base, with a separation between their minima of about 0.5 Å. This results in an adsorbed protonated molecule which is hydrogen bonded with the basic oxygen of the active site.

The corresponding diagrams for endothermic elementary steps obtained in this way are presented in Figure 1, which demonstrates only a moderate tendency toward proton transfer according to spectral data. Indeed, for the protonation steps with endothermicity higher than about 20 kcal mol^{-1}, there are practically no local minima on the potential curves, or they are so shallow that the resulting intermediates are metastable and should decompose after a few vibrations.

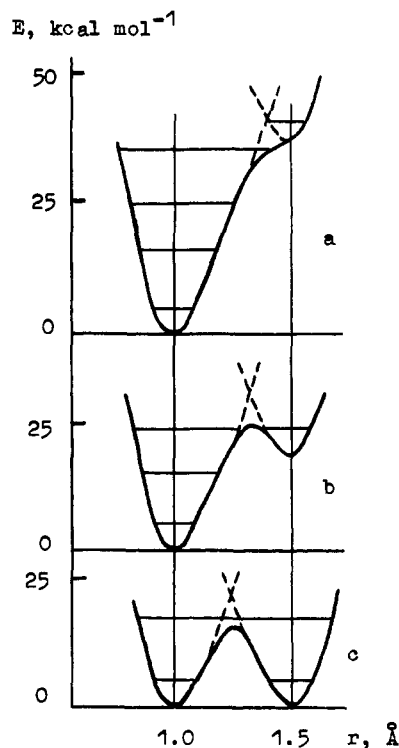The reason for such a weak tendency toward proton transfer is that when constructing energy profiles, we

Figure 1. The potential energy profiles for the elementary proton transfer steps reconstructed from the spectral data: (a) process endothermicity, 35 kcal mol^{-1}; (b) process endothermicity, 20 kcal mol^{-1}; (c) thermal neutral process.

did not take into account the relaxation of geometry in the resulting species. Indeed, when exciting the OH bond by light absorption to the higher vibrational levels, we certainly push the proton to the adsorbed base, but do not follow its response for protonation. In other words, the stretching of the OH bond is by no means consistent with the optimum reaction coordinate of this elementary step.

In reality, relaxation effects yield intermediates that are much more covalent than usually believed. For example, in the chemical reaction of ethylene with concentrated sulfuric acid, the covalent ethyl ester of sulfuric acid is formed instead of an ion pair. This follows in particular from the comparatively small low-field chemical shift in the ^{13}C NMR spectrum of the α-carbon atom in the alkyl substituent.[12] It is practically the same as in ethyl alcohol, which certainly is a covalent compound.

Recently, similar ^{13}C MAS NMR shifts of about 60–70 ppm were also reported for adsorbed alkyl groups resulting from the reaction of surface OH groups of an HY zeolite with *tert*-butyl alcohol[13] or propylene.[14] Thus, the nature of corresponding surface esters is also covalent.

It follows from this discussion that the energy profile of proton transfer cannot be inferred directly from spectral data, since the latter do not properly take into account the relaxation of protonated intermediates or their interaction with the surface of the catalyst. To do this correctly, quantum chemical calculations with

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(10) Kazansky, V. B. *React. Kinet. Catal. Lett.* **1987**, *35*, 237–246.

(11) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; J. Wiley and Sons, Inc.: New York, 1988.

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Table II
Results of MNDO Calculations of the Geometric and
Electronic Structures of Various Alkyl Substituents in the
$(HO)_3SiORAl(OH)_3$ Cluster[a]

parameter	substituent		
	CH_3	C_2H_5	i-C_3H_7
R_{C*-O*}, Å	1.461	1.474	1.487
q_{C*}, eu	+0.183	+0.126	+0.071
q_{O*}, eu	−0.417	−0.413	−0.408
$\sum q_R$, eu	+0.322	+0.326	+0.326
D_{het}, eV	7.25	6.05	4.93

[a] Reference 17.

complete optimization of molecular geometry are required.

The Nature of Adsorbed Carbenium Ions

Our very first quantum chemical calculations performed with the optimization of the geometry of protonated species predicted the covalent character of alkyl groups in surface esters. For example, a comparative analysis of the electronic structure of the ethyl fragment in ethyl sulfuric acid and on the surface of a high silica zeolite was carried out.[15] The results of both nonempirical and semiempirical calculations showed that the carbon–oxygen bond is covalent and that the electronic structure of ethyl fragments in both cases has little in common with that of free carbenium ions.

Similar comparative semiempirical calculations were carried out[16,17] for methyl, ethyl, and isopropyl surface alkoxy groups in a bigger cluster $(HO)_3Si(O*-R*)Al(OH)_3$. The net positive charge of alkyl fragments was also found to be rather low and practically constant, when passing from the methoxyl to the isopropoxyl substituent. The slight increase of C*–O* distance in this series and the geometry of alkyl groups confirmed their covalent nature. On the contrary, the values of heterolytic C*–O* bond-dissociation energies, D_{het}, were strongly decreasing in this sequence (Table II). This is similar to the relationship between the homolytic ground states of the surface OH groups and their heterolytic dissociation, as already discussed above. Therefore, it was suggested by analogy that the carbenium ion properties of the surface alkoxyls are exhibited not by their covalent ground states, but by the excited transition states with stretched C–O bonds. The importance of the more ionic character of elongated chemical bonds was also discussed earlier[18] and further stressed recently:[19] nonempirical quantum chemical calculations were performed for interaction of ethylene with acidic OH groups of a high silica zeolite and for the reverse reaction of the decomposition of surface ethoxy groups. The geometry of adsorbed ethylene or of resulting alkoxide was fully optimized with the help of the gradient procedure of a "Gaussian 80" program. Acidic groups of the high silica zeolite were modeled by the simplest $HO(H)Al(OH)_3$ cluster (Figure 2). At first ethylene is adsorbed as a π-complex (Figure 2a). The energy of its formation is equal to 6.90 kcal mol^{-1}. No

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(18) Kazansky, V. B. In *Proceedings of the International Congress on Catalysis, 6th, Imperial College, London*, 1976; Royal Society of Chemistry: Letchworth, Herts, 1977.
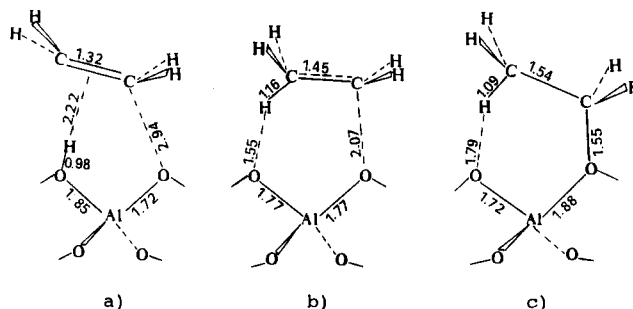(19) Kazansky, V. B.; Senchenya, I. N. *Catal. Lett.*, in press.

Figure 2. The structures of the quantum chemically calculated intermediates in ethoxylation of the zeolite surface: (a) π-complex of ethylene; (b) the transition state of the ethoxylation reaction; (c) the final ethoxide structure.
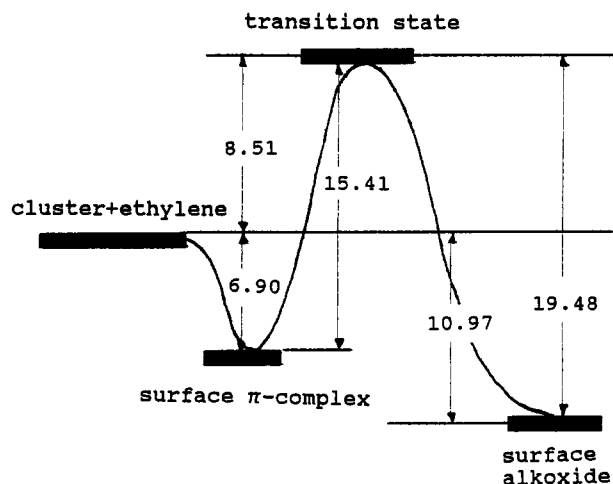

Figure 3. The energy diagram (kcal mol^{-1}) of surface ethoxy group formation.

considerable change in the C_2H_4 molecule geometry was found after adsorption. It results only in a very small (+0.021e) positive charge. In accordance with the above results, the most stable structure resulting from the proton transfer is not an ion pair, but a covalent ethoxy group (Figures 2c and 3). This follows from the relatively low positive charge of the ethyl fragment (+0.384e) and from its geometry, which is typical of covalent organic compounds. Indeed, the equilibrium C–O bond length is close to the mean length of these bonds in alcohols or esters. The obtained C–C distance of 1.536 Å and the nearly tetrahedral O–C–H and O–C–C angles in the alkyl fragment also confirm covalent character. Finally, the calculated heat of zeolite surface ethoxylation (11 kcal mol^{-1}) is consistent with the thermochemical data on the heat of decomposition of a covalent sulfuric acid ester.[20]

The transformation of adsorbed ethylene to surface ethoxide proceeds via the transition state shown in Figure 2b, with an activation energy barrier of 15.4 kcal mol^{-1} (Figure 3). The geometry and the electronic structure of the C_2H_5 fragment in such an activated complex are very similar to those of the classical form of the ethyl cation. This follows from the marked enhancement of positive charging of the C_2H_5 group from +0.384e up to +0.565e and from the new length of the C–C bond between those of a double and a single bond.

(20) *Thermochemistry of Organic and Organometallic Compounds*; Cox, J. D., Pilcher, G. L., Eds.; Academic Press: New York, 1979; p 390.
(21) Jacobs, P. A. *Carbogenic Activity of Zeolites*; Elsevier: Amsterdam, 1977.

In addition, an essential flattening of the CH_2 fragment occurs with O–C–H angles now close to 90°. Moreover, the deprotonation tendency is clearly revealed in the formation of the hydrogen bond between one of the protons of the CH_3 group with the neighboring basic oxygen.

The reaction coordinate of ethoxylation of the zeolite surface is very complicated. It includes a stretching of the O–H bond in the acidic hydroxyl group and of the C–C bond in the adsorbed molecule as well as some change of the angles in methyl and methylene fragments and a shift of the adsorbed ethylene toward the neighboring basic center. The activation barrier of this elementary step is low enough only if all of these parameters are changing simultaneously. Thus, the possibility of proton transfer over a low potential barrier can be explained by the concerted mechanism, which enables maximum energy compensation of the bonds to be broken by those to be formed.

The decomposition of the surface alkoxy structures follows the opposite pathway. The reaction coordinate mainly includes here the stretching of the C–O bond in the surface ester and the deprotonation of the resulting transition state resembling a carbenium ion. Although the homolytic abstraction of an ethyl group is considerably more favorable than its heterolytic dissociation, the initial stages of C–O bond stretching result in an increase of its polarity. This effect is maximal in the transition state, which resembles a carbenium ion as just said above. Furthermore, heterolytic dissociation is extremely unfavorable energetically. Therefore, instead of abstraction of a carbenium ion or alkyl radical, the deprotonation of the transition state occurs. This requires that an activation energy barrier of only about 20 kcal mol^{-1} (Figure 3) be overcome as compared to a homolytic dissociation energy of about 90 kcal mol^{-1} or a heterolytic dissociation energy of about 150 kcal mol^{-1} (Table II).

According to these ideas, the acid-catalyzed double-bond shift in olefins proceeds via a concerted mechanism. It includes the subsequent formation and decomposition of the surface alkoxy groups. This is consistent with experimental activation energies of double-bond isomerization on zeolites of 15–20 kcal mol^{-1},[20] which is close to the height of the activation barrier estimated by us. On the other hand, since the transition state has an ionic character, the double-bond shift obeys all the rules of the carbenium ion formalism.

A similar approach applies to other acid-catalyzed transformations of olefins. For instance, their oligomerization is also believed to proceed via adsorbed carbenium ions. They are easily formed from branched olefins but not from ethylene. In our opinion, this should be understood in the sense that the formation of carbenium ion like transition states becomes easier with increasing branching of the corresponding covalent alkoxide intermediates.

The reaction coordinate probably includes here mainly a concerted C–O bond stretching and approaching of the second ethylene molecule to the surface carbenium ion like excited complex. Again, a low activation barrier is possible only if in addition to these main parameters some others also contributing to the reaction coordinate are changing simultaneously. Other examples of such concerted mechanisms of acid-cata-

lyzed heterogeneous reactions are discussed in more detail elsewhere.[17,22]

Bifunctional Nature and Nonuniformity of Brønsted Acid Active Sites

In accordance with the above discussion, the close connection between Brønsted acid sites and neighboring basic oxygen should always be kept in mind.[6,9,10,22] Therefore an important feature of heterogeneous acid catalysis is the bifunctional nature of its active sites. Their acid moiety acts as a proton donor, while the basic moiety either stabilizes intermediate protonated species or favors the proton abstraction from the transition state. The result is a broad variety of concerted reaction mechanisms.

This idea suggests the need for a proper description of the acid strength of dual acid–base active centers. Indeed, any approach that does not take into account the interaction of protonated species with the surface of the catalyst is obviously not sufficient, e.g., using only the proton abstraction energies.

In this connection, let us compare the most commonly used methods of surface acidity measurement: determination of adsorption heat, temperature programmed desorption, and OH stretching vibration shifts caused by adsorption of bases. It is clear from Figure 3 that each of them deals with different features of the interaction of adsorbed molecules with the acid active sites.

For instance, the adsorption heat characterizes most directly adsorption or desorption enthalpy, but not the corresponding activation energy. The latter is more closely related with thermodesorption data that are controlled by the desorption activation barrier, or with bathochromic OH stretching vibrational shifts that can be correlated with the adsorption activation barrier. As follows from Figure 3, both of these characteristics are also connected with the activation energies of adsorbed carbenium ion formation from the side of the less stable complexes or of the more strongly adsorbed alkoxides. Therefore it is not surprising if acid strength measurements obtained with the help of these very different methods fail to agree with each other. Finally, the bifunctional nature of the active sites brings forth one more new important concept: the relative geometry of Brønsted acid and neighboring basic sites.

The influence of the O–Al–O angle on the height of the activation-energy barrier is qualitatively clear from Figure 3. The role of Si–O–Al angles is not so obvious, but could be illustrated by comparing structures I and II that represent the π-complexes for dual sites with different Si–O–Al angles. Structure II seems to be

I   II
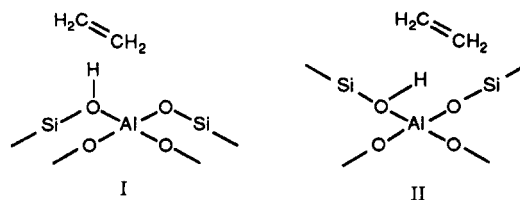
more prepared for proton transfer as it requires less relaxation of the resulting alkyl fragment. In addition, the basic properties of the neighboring oxygen could be also strongly influenced by the values of the Si–O–Al

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angles. This should also result in the dependence of the reaction rate on the geometry of the active sites.

Such structural nonuniformity of active sites is most important for high silica zeolites, where the local distortions of the crystal lattices are most pronounced. For instance, there are 12 crystallographically different tetrahedral sites in ZSM-5 zeolite[23] with the O-Si-O (or O-Al-O) angles varying between 96° and 129°, and Si-O-Si angles between 140° and 175°. The similar broad distribution of these angles is also typical of mordenite, ZSM-11, and other high silica zeolites prepared either by direct synthesis or by dealumination. Thus, depending on the local distortions of $[AlO_4]^-$ tetrahedra, such dual active sites could be different even for the same zeolite structure.

The important point in this connection is that these effects should be specific to the geometry of the reagents. Therefore they may play a decisive role in catalysis, but at the same time have only little influence on the adsorption of different probe molecules. This could result in apparent uniformity of acid strength, but different activity and selectivity of corresponding sites in catalytic reactions.

Such structural nonuniformity may well explain very recent results[24,25] where it was shown by the ammonia poisoning technique that only about 10% of the total aluminum content in high silica zeolites is responsible for their catalytic activity in cracking of paraffins. A similar conclusion was reached on the basis of poisoning the acidity of dealuminated Y-type zeolite by sodium.[26] It was found that only one-fifth of the framework aluminum atoms are associated with catalytic activity. It is also notable that these effects are not connected with different distributions of aluminum in the crystal framework, since in both cases high silica zeolites were studied with presumably isolated aluminum atoms. Further discussion of this problem requires additional experiments and quantum chemical calculations, which are now in progress.

Conclusion

This Account shows that the ground states of surface OH groups are essentially covalent, while the difference in their acid strength depends on the position of electronically excited heterolytic states. In a similar way the interaction of adsorbed carbenium ions with the surface results in active intermediates that are much less ionic than usually believed. Therefore these heterolytic fragments should be considered as transition states of the heterogeneous catalytic reactions rather than as real surface active intermediates. The interaction of molecules with the surface of heterogeneous catalysts also suggests the bifunctional nature of active sites in heterogeneous acid catalysis. Their Brønsted acid moiety protonates the adsorbed molecule, while interaction with the neighboring basic oxygen converts the initial transition state into more stable covalent intermediates. This dual nature of the active sites may also result in their nonuniformity, related to a varying geometry between Brønsted surface acid sites and neighboring basic sites.

Another important feature of heterogeneous acid catalysts is the concept of concerted mechanisms with very complicated reaction coordinates. This results in reaction trajectories with low activation energies due to almost complete compensation of the energy required for the rupture of the reacting chemical bonds in the initial compounds by the energy released by the formation of new bonds in the final products. All of these ideas should not be regarded as a criticism of the original carbenium ion concept but rather as an attempt at its further development in the light of new data.

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(25) Lombardo, E. A.; Sill, A. A.; Hall, W. K. *J. Catal.* **1989**, *119*, 426-440.

(26) Fritz, P. O.; Lunsford, J. H. *J. Catal.* **1989**, *118*, 85-98.