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Quantum Chemical Study of the Electronic Structure and Geometry of Surface Alkoxy Groups as Probable Active Intermediates of Heterogeneous Acidic Catalysts: What Are the Adsorbed Carbenium Ions?

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Semiempirical (modified neglect of differential overlap) and ab initio (in STO-3G basis set) quantum chemical calculations were carried out on the electronic structure and geometry of alkoxy groups on the surface of zeolites with a high silica content. The net positive charge of the alkyl fragments was found to be low and almost constant when passing from methoxyl to isopropoxyl substituents. It was concluded that carbenium ion properties are a characteristic not of the ground states of surface esters, but of the transition states with elongated C–O bonds, which are formed long before their full dissociation. Such activated complexes also possess some features of adsorbed carbenes or ylides. The mechanisms of some acidic catalytic reactions on zeolites are discussed within this framework. © 1989 Academic Press, Inc.

INTRODUCTION

A modern conception of the mechanism of acidic heterogeneous catalytic conversions of alcohols and hydrocarbons was formulated almost 40 years ago. At that time a number of authors (*1–4*) proposed carbenium (then called carbonium) ion mechanisms of these reactions on the basis of analogies with low-temperature conversions of alcohols and hydrocarbons in the presence of strong acids in the liquid phase. The work of Greensfelder *et al.* (*5*) provided convincing evidence for the ionic nature of the cracking mechanism. The experimental evidence for the acidity of amorphous silica–aluminas and other oxide catalysts (*4–7*) was the next important step in the development and general acceptance of this theory. Despite this, even now the formation of adsorbed aliphatic carbenium ions has never been proved by direct experiments. All arguments supporting their existence and decisive role in the mechanism of acidic heterogeneous catalysis on oxides are of an indirect character and are based on studies of selectivity in product formation, i.e., of the final products of hydrocarbon reactions.

In the case of catalytic conversions of olefins it is usually assumed that at first adsorbed molecules are bound to the surface acidic hydroxyl groups by stable hydrogen bonds (*8*). Then proton transfer takes place resulting in the formation of metastable adsorbed carbenium ions (*9*). It is also believed that such protonated intermediates possess a specific reactivity which accounts for the selectivity of corresponding acidically catalyzed heterogeneous reactions (*4–9*).

As already mentioned (*10, 11*), though such schemes are widely discussed in the literature, they do not take into consideration the absence of solvation effects in high-temperature catalytic conversions of hydrocarbons on heterogeneous oxide catalysts, which are a necessary condition for the formation of carbenium ions in the liquid phase. Therefore, the direct analogy of heterogeneous acidic catalysis with acidic catalytic reactions in the liquid phase

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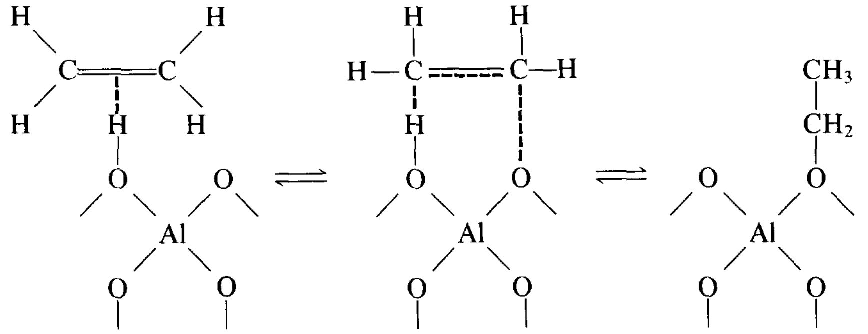
hardly seems possible. In addition, the molecules participating in acid-catalyzed reactions have a broad range of proton affinities. Therefore, if protonated intermediates are formed from adsorbed molecules of ammonia or pyridine, which have a proton affinity of about 9 eV, it does not mean that the proton transfer should occur in the case of paraffins or olefins with affinities of only 5.5–7.5 eV.

In earlier quantum chemical studies of the heteroisotopic H–D exchange of water and ammonia with bridged hydroxyl groups of zeolite (*12–14*), dehydration of ethanol (*15*), and the double-bond shift in olefins (*16*) on zeolites, we have shown that Brønsted acidic sites should always be considered together with neighboring negatively charged oxygen atoms of the oxide surface which play the role of basic sites. The interaction of protonated intermediates with such basic counterpartners facilitates the proton transfer. On the other hand, the conjugate base strongly modifies the electronic structure and reactivity of protonated species.

The bifunctional character of the active sites may also result in concerted mechanisms where one proton is transferred from a Brønsted acidic site to an adsorbed molecule while another is simultaneously abstracted from the protonated substance back to a basic site. This can partially compensate for the energy required for the protonation of substrates with low or moderate proton affinity.

For a similar reason, when adsorbed olefins are protonated by acidic surface hydroxyl groups, a new covalent bond with the surface basic oxygen may be formed simultaneously with the proton transfer. In such cases, the protonated hydrocarbon intermediates should be considered surface alkoxy groups rather than real carbenium ions or ionic pairs:



(1)

Similar suggestions have recently been advanced by McVicker *et al.* (*17*). This suggestion has found support (*18*) in the comparative quantum chemical analysis of the electronic structure of ethyl fragments in ethyl sulfuric acid and in the corresponding ethyl ester on the surface of zeolites with a high silica content. The results of both semiempirical and nonempirical calculations showed that the carbon–oxygen bond in both cases is covalent and that the electronic structure of the ethyl fragments themselves has little in common with the free $C_2H_5^+$ carbenium ions. Therefore, if the homogeneously catalyzed hydration of ethylene in the presence of sulfuric acid follows a carbenium ion mechanism, the heterolytic dissociation of the ester by the solvation with water molecules may account for the reaction rather than the high polarity of the oxygen–carbon bond. Furthermore, in the absence of solvation effects, the active intermediates of acidic heterogeneous catalytic transformations of hydrocarbons may not be as ionic as is usually supposed, but may rather represent the covalent surface esters of alkoxides. Alternatively, the reaction may pass through an ionic transition state, where the activation energy for the reaction is the excitation energy into ionic structures. Substantial tracer data (*9, 19*) support this view for simple reactions over silica–alumina catalysts.

According to carbenium ion chemistry the ionic properties of surface alkoxides should increase with the number of carbon atoms and with the extent of branching. This is explored in the present paper which deals with a comparative quantum chemical study of the electronic structure and geometry of different surface alkoxy groups on zeolites with a high silica content and with their possible role in the mechanism of acidic heterogeneous catalytic reactions.

MODEL AND METHODS OF CALCULATIONS

As in earlier calculations (*12, 13, 18, 20*), the zeolitic structures were modeled by clusters consisting of one, two, or three silicon or alumina–oxygen tetrahedra. Dangling bonds were saturated by hydrogen atoms. The geometry of clusters was similar to that adopted earlier (*12–16*). It was assumed that SiO_4 and AlO_4 fragments have a regular tetrahedral structure and that the HOAl, HOSi, and SiOAl angles were equal to 140°. Lengths of Si–O and Al–O bonds were taken to be equal to 1.63 Å and those of OH bonds 0.96 Å. The length of the OH bond in the bridged hydroxyl group was optimized. Various alkoxide structures were formed by substitution of H atoms by different alkyl fragments. The bond length and the valence angles in the surface alkoxides were optimized by the gradient technique.

Most of the quantum chemical calculations were carried out by the SCF MO LCAO semiempirical MNDO method (modified neglect of the differential overlap) (*21*). The MNDO method was chosen for analysis of the electronic and geometric structures of surface alkoxides because it has been used satisfactorily in studies of the potential energy surfaces of many organic reactions (*22–24*) and has led to good agreement with the experimental data on energetics (heats of formation, dissociation energies of chemical bonds, etc.) and on structural characteristics of free molecules (*24*).

For comparison, the electronic structures of different clusters were also calculated by other semiempirical [CNDO/2 (*25*), INDO (*26*), MINDO/3 (*27*)] and nonempirical SCF MO LCAO methods (STO-3G) according to the "Gaussian-80" program (*28, 29*). The latter was also used for the calculations of the electronic structure and geometry of the surface methoxy and ethoxy groups in their ground and vibrationally excited states. In these nonempirical calculations the zeolite fragment was modeled by the simples $HOHAl(OH)_3$ cluster (cluster I), and optimization of the geometry of the alkyl fragments by the gradient technique was performed.

RESULTS AND DISCUSSION

(*1*) *On the Nature of Adsorbed Protonated Intermediates in the Acid Catalyzed Heterogeneous Transformations of Olefins*

Table 1 represents the results on the electronic structure of clusters of various sizes calculated by different methods. It is evident that even the simplest of them properly describes the charge of the acidic proton q_H, that of the bridged oxygen atoms q_O^{OH}, and those of the Si and Al cations, since these values do not change significantly for the clusters of larger size. The difference in the charge distribution for various methods of calculation is greater. For instance, the nonempirical method with the minimal STO-3G basis set gives somewhat more ionic structures than MNDO calculations. In any case, independent of the method of calculation and the cluster size, the negative charge of the oxygen atom bound to the aluminum is always noticeable

TABLE 1

Chemically Calculated Quantum Charges of Cations and Anions in Various Clusters in Parts of an Electron Charge[a]

Cluster	Method of calculation	q_{Si}	q_{Al}	$-q_O^{Si}$	$-q_O^{Al}$	$-q_O^{OH}$	q_H^{OH}
$HOHAl(OH)_3$ (I)	MNDO	—	0.996	—	0.647	0.185	0.258
$HOHAl(OH)_3$ (I)	CNDO/2	—	1.334	—	0.599	0.276	0.230
$HOHAl(OH)_3$ (I)	MINDO/3	—	1.023	—	0.694	0.319	0.306
$HOHAl(OH)_3$ (I)	STO-3G	—	1.326	—	0.654	0.406	0.296
$(HO)_3SiOHAl(OH)_3$ (II)	MNDO	1.567	0.981	0.623	0.646	0.389	0.280
$(HO)_3SiOHAl(OH)_3$ (II)	CNDO/2	1.661	1.349	0.552	0.597	0.487	0.183
$(HO)_3SiOHAl(OH)_3$ (II)	STO-3 G	1.542	1.328	0.582	0.653	0.536	0.287
$(HO)_3SiOHAl(OH)_3$ (II)	INDO	1.808	1.336	0.623	0.640	0.530	0.206
$(HO)_3SiOHAl(OH)_2OSi(OH)_3$ (III)	MNDO	1.586	0.969	0.669	0.744	0.346	0.282
$(OH)_3AlOHSi(OH)_2OHAl(OH)_3$(IV)	MNDO	1.521	1.015	—	0.753	0.377	0.265

[a] The column headings q_O^{Si}, q_O^{OH}, etc., indicate the charge of oxygen connected with Si or in the corresponding OH group.

higher than that linked to the silicon. This evidences a higher basicity of oxygen in the vicinity of an aluminum atom than in the neighborhood of silicon.

Table 2 represents characteristics of the electronic structure and geometry of different clusters with various alkyl substituents obtained by MNDO: $HORAl\ (OH)_3$ (I), $(OH)_3SiORAl(OH)_3$ (II), and $(HO)_3SiORAl\ (OH)_2OSi(OH)_3$ (III). The calculations for clusters I and II were carried out with complete optimization of all geometric parameters of alkoxide structures.

It was found from these calculations for

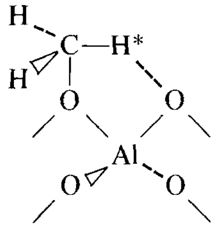
TABLE 2

Results of MNDO Calculations of the Geometry and Electronic Structure of Different Clusters with Various Alkyl Substituents[a]

Substituent:	Methoxyl			Ethoxyl			Isopropoxyl	
Cluster:	I	II	III	I	II	III	I	II
R_{C-O}	1.449	1.461	1.465	1.457	1.474	1.476	1.466	1.487
R_{C-H^*}	1.110	1.112	1.108	1.124	1.118	1.118	1.121	1.130
$R_{H^*\cdots O}$	2.337	2.080	2.085	2.440	1.984	1.997	2.287	1.899
∠COAL	120.8	112.5	112.5	120.2	111.2	111.4	109.4	109.7
∠H*CO	112.8	115.1	115.1	111.8	112.0	112.2	109.0	110.1
q_{Si}	—	1.569	1.587	—	1.566	1.583	—	1.564
$-q_O$	0.209	0.417	0.380	0.207	0.413	0.374	0.201	0.408
q_{Al}	1.000	0.983	0.971	0.998	0.982	0.971	0.998	0.981
$-q_O^{Si}$	—	0.624	0.670	—	0.624	0.669	—	0.622
$-q_O^{Al}$	0.648	0.654	0.747	0.647	0.644	0.745	0.647	0.641
q_C	0.168	0.183	0.186	0.130	0.126	0.126	0.067	0.071
q_{H^*}	0.092	0.091	0.101	0.087	0.105	0.110	0.109	0.114
Σ^q_{alk}	0.281	0.322	0.332	0.283	0.326	0.335	0.281	0.326

[a] Here and in the following tables bond lengths are in angstroms, bond angles in degrees, and charges in parts of an electron charge. Σ^q_{alk} indicates the total charge of the alkyl group.

methyl and isopropyl substituents, that one of their hydrogen atoms, marked here by an asterisk, is hydrogen-bonded with the neighboring basic oxygen:



Therefore the fragment H*COAlO is practically flat. A similar flat structure was also postulated for alkoxy fragments in the more complicated cluster III where only the bond lengths and bond angles in the substituents were optimized.

The results of both nonempirical and semiempirical quantum chemical calculations showed that the protonation of adsorbed olefins results in the formation of covalent surface esters instead of carbenium ions. This is evident from the almost tetrahedral angles in hydrocarbon fragments and the calculated C–O distances, which are close to the lengths of C–O covalent bonds in esters (see Table 2).

The heats of formation of surface esters from complexes with different olefins lie within 10–15 kcal/mole depending on the method of calculation and the nature of the olefin. Thus the surface esters are definitely stable intermediates in heterogeneous acidically catalyzed transformation of olefins. In addition, it follows also from Table 2 that the total charges of the different hydrocarbon fragments calculated by the MNDO method are practically constant, whereas the positive charges of carbon atoms linked to the surface oxygen in methyl, ethyl, and isopropyl radicals are even decreasing (for cluster II they are equal to +0.183, +0.126, and +0.071, respectively). These values are close to the charges calculated by the same method for the corresponding carbon atoms in methyl (0.186), ethyl (0.146), and isopropyl (0.093) alcohols, which certainly are of a covalent nature.

The similar electronic structure of alkyl fragments in liquid alcohols and esters has also been demonstrated earlier by ^{13}C NMR chemical shifts which are often used as an indication of the formation of carbenium ions (*30*). For instance, for CH_3OH, $(CH_3)_3PO_4$, and $(CH_3)_2SO_4$ they are 50.5, 54.2, and 59.1 ppm, respectively (*31*). These values are far from the ^{13}C shift for stable $(CH_3)_3^{13}C^+$, i.e., 335.7 ppm which therefore has a quite different electronic structure and charge on the central carbon atom.

The MNDO calculations presented in Table 2 also show that the transition from the methyl to ethyl and isopropyl substituents results in the noticeable elongation of C–O bonds and in the slight decrease in the negative charges of their oxygen atoms. This indicates not the increase but rather the decrease in the C–O bond polarity in this order, in agreement with the slight drop of the experimentally measured dipole moment when passing from methanol to ethanol to isopropanol (1.69, 1.70, and 1.58 D, respectively) (*32*).

These results are quite natural, since methyl groups are donors of the electronic density. Therefore, an increase in their number in the alkyl group will result in a lower positive charge on the carbon atom linked to the surface oxygen. Therefore, the (calculated) positive charge on these carbon atoms in free carbenium ions is much higher and the range of variation is much broader (from +0.655 eV in the methyl to +0.432 eV in the isopropyl cation). Thus, despite the generally accepted opinion, even the electronic structure of the surface isopropyl group in its ground state has very little in common with the free carbenium ion; it resembles more the alkyl fragment in the corresponding alcohol.

On the other hand there is no doubt that an increase in the tendency of the *R*O fragment to dissociate heterolytically occurs with the number of methyl substituents. For instance, according to the MNDO calculations for cluster II, the energies of heterolytic abstraction of methyl, ethyl, and isopropyl carbenium ions are equal to 7.25, 6.05, and 4.93 eV, respectively. This is much less than the energies of proton abstraction from this cluster (12.2 eV) or those of heterolytic splitting of the corresponding alcohols according to the reactions

$$\begin{aligned} CH_3OH &\rightleftharpoons CH_3^+ + OH^- + 12\ \text{eV} \\ C_2H_5OH &\rightleftharpoons C_2H_5^+ + OH^- + 10.6\ \text{eV} \\ i\text{-}C_3H_7OH &\rightleftharpoons i\text{-}C_3H_7^+ + OH^- + 9.7\ \text{eV} \end{aligned} \quad (2)$$

(These dissociation energies were calculated from thermochemically obtained energies of the homolytic C–O bond dissociation, the ionization potentials of the corresponding alkyl fragments, and the previously published (*32*) affinities of OH radicals.)

The much easier (in comparison with alcohols) heterolytic C–O bond splitting in surface esters may be accounted for by the higher electron affinity of the surface oxygen "holes" O^- than that of free OH radicals. For instance, if one supposes that O^- affinity is close to the zeolite band gap, e.g., about 6 eV, then the thermodynamically calculated energies of heterolytic dissociation of the surface methyl, ethyl, and isopropyl esters would be, respectively, equal to 7.8, 7.4, and 5.5 eV. These figures are very close to those calculated by the MNDO method.

The general findings concerning the covalent character of the surface methyl and ethyl esters were also confirmed by the results of the nonempirical STO-3G calculations presented in Table 3 (see the data for the ground state, e.g., for $\Delta r = 0$). Thus the quantum chemical calculations indicate that the surface protonated intermediates which are formed via proton transfer from acidic hydroxyl groups to adsorbed olefins are not of an ionic, but of a covalent nature similar to esters of strong acids in general. Therefore, in contrast to what is commonly thought, the positive charge on the alkyl fragment is a rather inadequate index of carbenium ion characteristics of surface intermediates, which are covalent in their ground state. Instead, one might better use for this purpose the energies of heterolytic splitting of surface covalent esters which more properly reflect the carbenium ionic character of these species.

(2) *What Are the Adsorbed Carbenium Ions?*

It follows from the above that the classical carbenium ion properties usually associated with acid catalysis are not displayed by the protonated surface intermediates in their ground states; instead, they must be properties of the transition states. Experimental verification of this is available in the literature (*9*, *33–35*) from analysis of the kinetics of these reactions. The present quantum chemical calculations provide a description of the electronic properties and the geometry of such activated complexes in some detail and thus a proper analysis of the mechanism of heterogeneous acid catalysis.

As we have pointed out earlier (*36*, *37*), the ionicity of chemical bonds generally increases considerably as they are stretched or vibrationally excited. This effect is of a rather common character and follows both from an analysis of the vibrational spectra (extinction coefficients) (*38*) and from quantum chemical calculations. Therefore, the surface alkoxides with elongated C–O bonds formed prior to their full dissociation would be more ionic than the corresponding covalent ground states. In our opinion, such vibrationally excited fragments might be really very similar to free carbenium ions and could play the role of the transition states in heterogeneous acid catalysis.

A precise quantum chemical analysis of these effects requires nonempirical calculations taking into account configurational interaction of the ground and the electronically excited states of perturbed C–O bonds. Unfortunately, for such compli-

TABLE 3

Results of STO-3G Calculations of Geometry and Electronic Structure of Cluster II with Methyl or Ethyl Substituents in the Ground States ($\Delta r = 0$) and with Elongated C–O Bonds

Substituents:	Methoxyl					Ethoxyl				
Δr:	0.00	0.05	0.10	0.15	0.20	0.00	0.05	0.10	0.15	0.20
$R_{H^* \ldots O}$	1.928	1.931	1.931	1.914	1.884	1.920	1.924	1.923	1.909	1.885
R_{C-H^*}	1.102	1.102	1.103	1.105	1.108	1.103	1.103	1.103	1.106	1.108
∠COAl	113.1	112.8	112.4	111.6	110.6	113.4	113.1	112.7	112.0	111.1
∠H*CO	104.3	103.2	102.1	100.8	99.4	102.7	101.7	100.6	99.3	97.9
∠HCO	109.6	108.8	108.0	107.3	106.6	107.6	106.7	105.8	105.1	104.2
$-q_O$	0.373	0.374	0.376	0.381	0.387	0.378	0.381	0.384	0.390	0.397
q_{Al}	1.334	1.332	1.331	1.330	1.329	1.333	1.332	1.330	1.329	1.328
$-q_O^{Al}$	0.635	0.636	0.636	0.636	0.635	0.635	0.635	0.635	0.635	0.635
$-q_C$	0.079	0.078	0.076	0.073	0.071	0.003	0.001	0.001	−0.004	−0.007
q_{H^*}	0.156	0.158	0.161	0.165	0.169	0.146	0.148	0.150	0.154	0.158
Σ_{alk}^{q}	0.259	0.268	0.279	0.291	0.303	0.274	0.286	0.297	0.312	0.327
ΔE[a] (kcal/mol)	0.00	1.21	4.53	9.51	15.75	0.00	1.17	4.33	9.06	14.98

[a] ΔE, the excitation energy required for the corresponding elongation of the C–O bond in the alkyl fragment.

cated systems as surface esters they are so far impossible. Therefore, in the present paper we shall discuss the mechanism of such vibrational polarization of the surface alkoxy groups at the level of nonempirical SCF calculations with the minimal STO-3G basis set or within the framework of semiempirical MNDO calculations. In both cases the full optimization of the geometry of the alkoxides was carried out. Only the small elongations of C–O bonds in the surface esters (up to 15% of their equilibrium length) were considered. The results obtained should therefore be regarded as similar to the indexes of reactivity or to those of the chemical bonds activation, which are widely used in quantum chemistry.

The results of the nonempirical calculations for methoxy and ethoxy groups are presented in the Table 3. The equilibrium lengths of C–O bonds in their ground states were obtained by the optimization of all the parameters of alkoxy fragments. Then C–O distance was increased and fixed in steps of 0.05 Å and the optimization of geometry was again carried out for each of the steps. It is evident that even a small stretching of the C–O bond is accompanied by rearrangement of the electronic density, resulting in an increase in the net positive charge on the surface alkoxides. In addition, a noticeable flattening of their alkyl groups (decrease of the HCO angles) also occurs. Thus, when the C–O bond is stretched the alkyl groups actually become structurally more like carbenium ions. In other words, the thermal vibrational excitation of the C–O bond is favorable for the nucleophilic attack at the carbon atom. This gives carbenium ion character to the surface alkyl fragments, which are covalent in their ground state. *The important feature of this mechanism is the relatively low activation energy required for such excitation.* This follows from the data presented in Tables 3 and 4, which show that the "vibrational polarization" of C–O bonds occurs long before its full dissociation. For instance, the vibrational exitation of the C–O bond for only 10–15 kcal/mol results in considerable change in the geometry and in the charges of alkyl fragments (see the last two rows of Tables 3 and 4). Of course, this effect would be even more pronounced in the

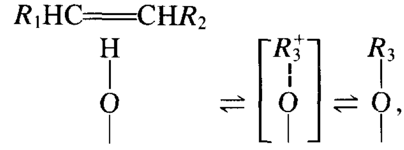
TABLE 4

Results of MNDO Calculations of Cluster II with Different Substituents and Various Degrees of C–O Bond Elongation, Δr

Substituent:	Methoxyl				Ethoxyl				Isoproxyl			
Δr:	0.05	0.10	0.15	0.20	0.05	0.10	0.15	0.20	0.05	0.10	0.15	0.20
$R_{H^*...O}$	2.093	2.103	2.114	2.127	1.993	2.008	2.018	2.026	1.192	1.920	1.927	1.933
R_{C-H^*}	1.107	1.103	1.101	1.099	1.114	1.110	1.107	1.104	1.126	1.122	1.118	1.115
$\angle$COAl	112.5	112.4	112.3	112.1	110.9	110.9	110.8	110.7	109.4	109.3	109.1	108.9
$\angle$H*CO	114.0	112.8	111.6	110.6	111.2	110.1	108.9	107.5	109.4	108.3	107.1	105.9
q_C	0.206	0.231	0.255	0.281	0.151	0.176	0.202	0.228	0.096	0.122	0.148	0.175
q_{H^*}	0.090	0.089	0.090	0.090	0.104	0.103	0.103	0.103	0.122	0.111	0.111	0.112
Σ^q_{alk}	0.350	0.379	0.409	0.439	0.354	0.383	0.414	0.446	0.354	0.384	0.415	0.447
q_{Si}	1.568	1.566	1.564	1.563	1.565	1.564	1.562	1.560	1.564	1.562	1.561	1.559
$-q_O$	0.436	0.456	0.475	0.494	0.432	0.452	0.472	0.493	0.428	0.448	0.469	0.490
$-q_O^{Si}$	0.625	0.627	0.629	0.630	0.625	0.627	0.628	0.630	0.623	0.624	0.626	0.627
$-q_O^{Al}$	0.646	0.647	0.648	0.649	0.645	0.645	0.646	0.647	0.642	0.643	0.644	0.645
Δ^E_{alk} (kcal/mole)	0.92	3.69	7.38	11.76	0.92	3.23	6.69	10.61	0.91	3.00	6.00	9.46

presence of the nucleophilic substrates, which would create an additional polarization of the surface alkoxy groups.

Since the similar quasicarbenium ion transition states could be also formed from π-complexes of OH groups with olefins (*8*), the following equilibria should exist during catalytic transformations of olefins:



$$\begin{array}{c} R_1HC{=\!=}CHR_2 \\ \mathrm{H} \\ | \\ \mathrm{O} \\ | \end{array} \rightleftharpoons \left[\begin{array}{c} R_3^{+} \\ | \\ \mathrm{O} \\ | \end{array}\right] \rightleftharpoons \begin{array}{c} R_3 \\ | \\ \mathrm{O}, \\ | \end{array} \qquad (3)$$

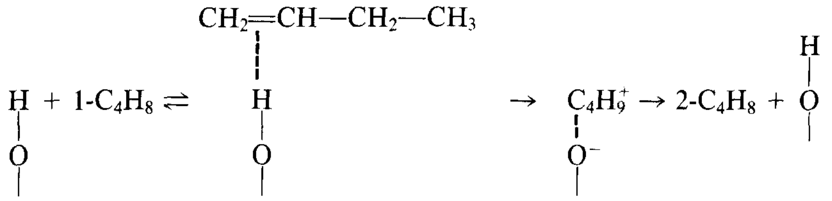
where $R_3 = R_1CH_2CHR_2$. The carbenium-ion-like transition state corresponds here to the maximum of the potential energy.

The π-complexes are less stable than the covalent alkoxyls. Therefore, the activation energy for proton transfer to olefins is lower than that of the carbenium ion formation from alkoxides. On the other hand for the same reason the π-complexes would decompose at elevated temperatures more rapidly than the surface esters. Therefore, at high temperatures the role of π-complexes as the source of carbenium ions decreases while that of alkoxides increases. In other words, the role of quasicarbenium ion transition states could be similar to related phenomena found in the majority of the heterogeneous catalytic reactions, i.e., the possibility of two different rate-limiting steps: the chemisorption of olefins, which is more important at low temperatures, and the decomposition of surface alkoxides, which becomes the main route of the reaction at high temperature.

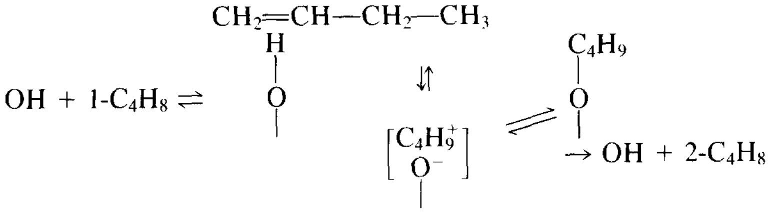
There are some spectroscopic data supporting this conclusion. For instance, earlier IR studies (*39, 40*) indicated that the interaction of the strongly acidic OH groups of ZSM-5 zeolite with ethylene at room temperature resulted in rapid formation of linear oligomers, which filled the channels of the zeolite framework. This was evident from the decrease in IR bands of both free and hydrogen-bonded OH groups and from the appearance of C–H stretching bands of the linear oligomers instead. Similar findings have been reported on the basis of MAS NMR data (*41, 42*).

The desorption of the products, on the other hand, occurs only above 200–250°C, mainly in the form of C_3–C_6 hydrocarbons. In terms of the equilibria expressed by Eq. (3), this means that at elevated temperatures aliphatic oligomers could generate carbenium ion transition states, which then become involved in secondary chemistry, e.g., cracking and hydrogen transfer.

Another simple example is the isomerization of the *n*-butenes which has been thoroughly discussed by Hall and Hightower (*9, 33–35*). They considered the π-complexes of olefins with OH groups as the only *stable* intermediates of this reaction and the adsorbed carbenium ions as the excited transition states. The mechanism formulated may be illustrated by the example


(4)

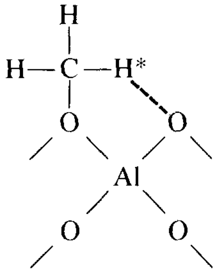
According to our results, this scheme should be supplemented by introducing the alkoxy structures, which are certainly more stable then the π-complexes. The mechanism of the double-bond shift would then be


(5)

The adsorbed carbenium ions are formed in this scheme by two pathways: protonation of π-bonded olefins and the vibrational excitation of the covalent surface esters. The contribution of the latter is important, since otherwise the surface esters would block the acidic active sites and inhibit the catalytic reaction.

(*3*) *On the Ylide-like Character of Vibrationally Excited Methoxy Groups and on the Probable Mechanism of Synthesis of Hydrocarbons from Methanol on Zeolites with High Silica Content*

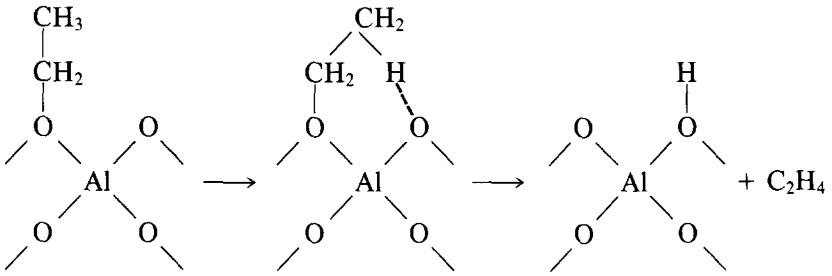
Analysis of the geometry of the surface esters shows also that one of their α-hydrogen atoms, marked in Tables 2–4 by an asterisk, may be hydrogen-bonded to a neighboring basic oxygen, i.e.,


(6)

This is evident in the results of both nonempirical and semiempirical quantum chemical calculations carried out with full optimization of the geometry of surface esters (Tables 3 and 4). They show that in the ground state the corresponding C–H* bond is slightly elongated and the alkyl group itself is noticeably inclined toward neighboring oxygen due to the decrease in C–O–Al and H*–C–O angles. This accounts for both the decrease in the H*---O distance and the somewhat higher positive charge on the H*.

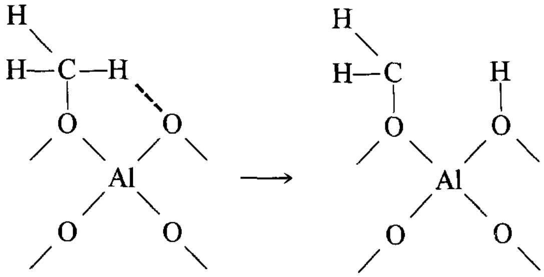
When the C—O bond becomes vibrationally excited, the tendency for hydrogen bonding is increased. This also follows from Tables 3 and 4 which show that when the C—O bond is stretched, the length of the weaker H*---O bond remains unchanged or is even slightly decreased. Thus when the oxygen–carbon bond is elongated the likelihood of deprotonation of the surface alkyls increases.

The origin of this effect is the higher proton affinity of the basic surface oxygen (about 12 eV as mentioned above) than the energy required for proton abstraction from the quasicarbenium ion species; the latter are formed prior to the complete C—O bond dissociation. (For free alkyl carbenium ions the deprotonation energies fall in the range 7 to 9 eV.) Therefore, in the case of ethyl and isopropyl substituents, instead of C—O bond rupture the proton abstraction from such quasi-ionic intermediates may occur. This results in desorption from the surface of the olefins (the reverse of the protonation step, Eq. (3)), and in regeneration of acidic surface hydroxyls:



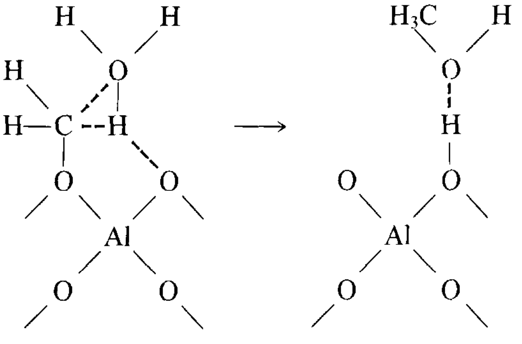
(7)

For methoxy groups such as elementary step is obviously impossible. Instead α-proton elimination would lead to the formation of adsorbed carbene or ylide-like surface intermediates:



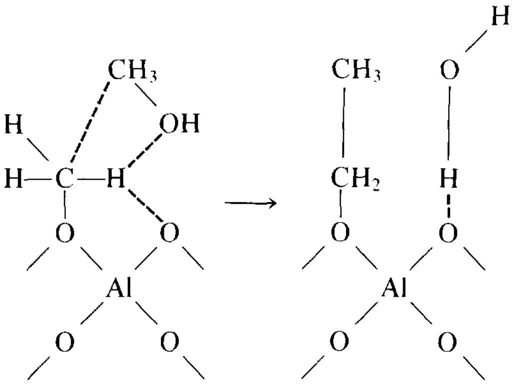
(8)

Although estimations made by the ab initio method with the STO-3G basis set showed that such reactions are energetically unfavorable by about 1.5 eV, they still might be significantly facilitated by interaction with a second molecule of substrate; e.g., in a way similar to that of homogeneous systems (*40, 43, 44*) the proton transfer may be promoted by a second polar molecule of water. The corresponding transition state is then converted into adsorbed methyl alcohol resulting in hydrolysis of the surface ester:



(9)

In a similar way a mechanism of the initial C—C bond formation in the conversion of methanol into hydrocarbons on ZSM zeolites of high silica content may be presented by the scheme (*43*)



(10)

Following desorption of H_2O, the ethoxyl fragment can be alkylated by the next methanol molecule into surface isopropoxyl or can decompose with the ethylene desorption. The driving force of these concerted mechanisms is a compensation of the broken bonds by those that are newly formed. In this way, high activation barriers are avoided.

The mechanism of the synthesis of hydrocarbons from methanol on zeolites of high silica content is presently controversial. The elementary steps which have been considered involve, among other possibilities, ylides or adsorbed carbenes (*45–49*). Our mechanism (*10*), which is based on the dual acid–base nature of Brønsted active sites, should be therefore regarded as a more detailed interpretation of one possibility which is supported by quantum chemical calculations.

There are also some experimental results confirming the carbene-like nature of the surface methoxy groups. For instance, it was shown in (*50*) that the interaction of the premethoxylated hydrogen form of the ZSM-5 zeolite of high silica content with benzene results in desorption from the surface toluene and the interaction with ethane results in the formation of propane.

CONCLUSIONS

The aim of this paper is not to criticize the carbenium-ion conception of heterogeneous acid catalysis, but rather to provide its further development. It is our belief that in its present form, this theory is oversimplified. Owing to the absence of solvation effects, the surface intermediates of high-temperature catalytic conversions of hydrocarbons are simply not as ionic as is usually supposed. Instead, the carbenium ionic properties are the characteristics of the transition states.

Another feature of heterogeneous acid catalysis that is usually not taken into account is the bifunctional nature of the Brønsted active sites. In the course of catalytic reactions, the adsorbed molecules are protonated, but interaction of the protonated transition states with the surface basic oxygen either stabilizes them in the form of covalent intermediates or enables the reverse proton abstraction. For substrates with low proton affinity this results in the concerted mechanisms. Such deprotonation explains also the carbene-like or quasi-ylide-like properties of methoxy groups on the surface of zeolites with high silica contents.

For a more detailed analysis of these and other mechanisms of heterogeneous acid-catalyzed transformations of hydrocarbons, further quantum chemical calculations will be required. We hope to contribute some of these in future publications.

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