QUANTUM CHEMICAL STUDIES OF ETHYLENE INTERACTION WITH ZEOLITE OH-GROUPS

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An ab initio quantum chemical study of the mechanism of formation of surface ethoxy groups from ethylene on high silica H-zeolites was carried out using a Gaussian 80 program with the 3-21 G basis set. The obtained results show that the reaction coordinate during ethoxylation of the zeolite surface is rather complicated and that in the transition state the charge distribution and geometry of the ethyl fragment closely resemble those of the classical form of the free ethyl carbenium cation. The mechanism of some acidically catalyzed transformations of olefins over H-zeolites is discussed on the basis of these results.

Keywords: High silica zeolites, alkoxy groups, quantum chemistry, carbenium ions

1. Introduction

At present it is generally accepted that interaction of olefins with strong acid hydroxyls on the surface of oxides or in H-zeolites results in formation of adsorbed carbenium ions and that their further transformations can explain the mechanism of heterogeneous acidic catalytic reactions [1,2]. In our previous publications [3–9] this traditional point of view however was shown as too simplified.

Indeed, the quantum chemical calculations demonstrated that the interaction of olefins with strong liquid acids or with strongly acidic hydroxyl groups in H-zeolites gives rise not to formation of ion pairs, but rather results in the appearance of covalent surface esters (alkoxide structures) [7–9]. In addition to quantum chemical calculations the covalent character of such alkyl intermediates in H–Y zeolites was recently confirmed by the measurements of ^{13}C NMR chemical shifts by the MAS NMR technique [10]. On the other hand, as has been shown by us in [7,8], the adsorbed carbenium ions could be formed from such covalent surface esters via stretching or vibrational excitation of their C–O bonds. Thus, they should be considered as transition states or as energetically excited unstable ion pairs.

The present work deals with further development of this idea. As an example, the formation of the surface alkoxide groups from olefins and their decomposi-

tion is discussed. In addition, the mechanism of some acidically catalyzed transformations of olefins over H-zeolites and other heterogeneous acid type catalysts is considered on the basis of the results obtained.

2. Details of the calculations

All ab initio SCF MO LCAO quantum chemical calculations were carried out using a "Gaussian-80" program [11]. Acidic groups of zeolite were modelled by the simplest clusters $HO(H)Al(OH)_2OH$. The dangling bonds at their edges were saturated by hydrogen atoms. The H–O–Al angles in these terminating OH groups were taken equal to 140° and the O–H bond lengths were accepted as 0.96 Å. The rest of the geometric parameters for the cluster, adsorbed ethylene or alkoxide structures were fully optimized using a gradient technique. The transition state was found by minimizing the gradient norm. All calculations were performed with the 3-21 G basis set [12].

3. Results and discussion

The calculated values of equilibrium geometric parameters for the π-complex of ethylene with the acidic OH-group of a high silica zeolite (*a*), the transition state in the ethoxylation reaction (*b*) and the most stable final state, corresponding to formation of surface ethoxy groups (*c*), are presented in fig. 1. The energy diagram for the ethoxylation of the zeolite surface by ethylene is given in fig. 2.

At first ethylene is adsorbed on OH-groups of a high silica zeolite as π-complex (fig. 1, *a*). The energy of its formation, calculated as a difference between the total energy of the adsorbed complex and the sum of total energies of the

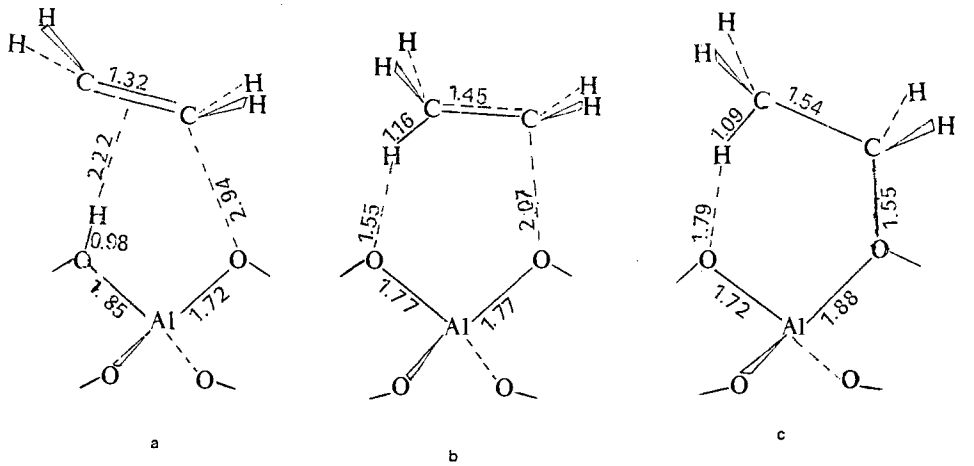


Fig. 1. Calculated structures for adsorbed ethylene (*a*), transition state of ethoxylation reaction (*b*) and final ethoxide (*c*).

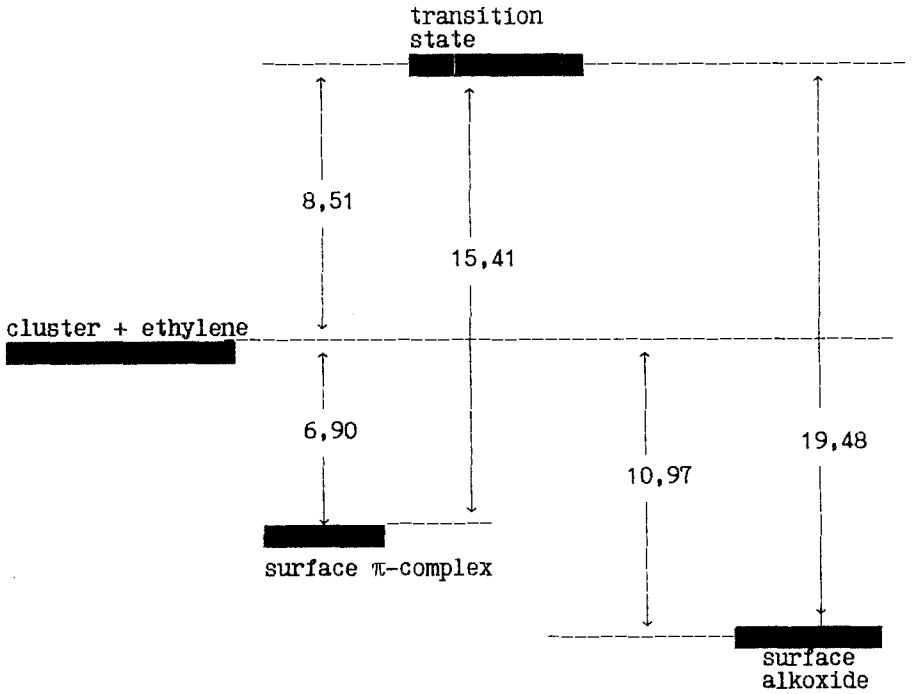


Fig. 2. Energy diagram (kcal/mole) for ethoxy group formation.

isolated cluster and the ethylene molecule, is equal to 6.90 kcal/mole. No considerable change in the C_2H_4 molecule geometry was found after adsorption. The C=C double bond length increases only by 0.006 Å and variations of the C–H bond lengths are even less. The H–C–H angles also show little change only. A slight bending of H-atoms from the ethylene molecule plane is evident. The negative charge on carbon atoms in the adsorbed molecule as well as the positive charge of H-atoms of the OH-group increase only slightly. This results in a small ($+0.021$ e) positive charge on the adsorbed ethylene molecule.

On the other hand, the formation of the π-complex results in some changes in the geometry of the cluster itself. As was noted by us earlier [14], the bond between bridged OH-group and the aluminum atom of the zeolite matrix should be considered as a donor-acceptor one, since according to calculations with the 3-21 G basis set for the cluster under consideration it is by 0.112 Å longer than other chemical bonds of the AlO_4 unit. After ethylene adsorption (fig. 1 *a*), the difference in the bond lengths is diminished. Thus the π-complex with the adsorbed ethylene molecule tends to be in some extent already prepared for catalytic action.

Fig. 2 shows, that in accordance with our previous conclusions [7–9], the most stable structure, which is formed when ethylene interacts with the bridged hydroxyl group of a high silica zeolite, is not an ion pair $C_2H_5^+$–Z^- (Z is a zeolite fragment, containing Al and O atoms), but a covalent ethoxy group. This follows

Table 1
Results of 3-21 G calculations of the geometry and electronic structure of the classical form of the carbenium ion, the ethyl fragment in the surface ethoxy structure and in the transition state (TS) of the ethoxylation reaction (bond lengths are given in Å, angles–in degrees and charges–in electron units)

	R(C–C)	$R_{C-H}^{CH_2}$	$R_{C-H}^{CH_3}$	< HCH	< HCC	$-Q_C^{CH_2}$	$-Q_C^{CH_3}$	$Q_H^{CH_2}$	$Q_H^{CH_3}$	ΣQ^{CH_2}	$\Sigma Q^{C_2H_5}$
$C_2H_5^+$	1.436	1.078	1.082	117.4	102.8	0.054	0.793	0.380	0.377	0.706	1.0
			(1.115) *		(114.3) *				(0.355) *		
TS	1.548	1.077	1.082	120.0	107.1	0.123	0.849	0.302	0.474	0.481	0.565
			(1.156) *		(111.2) *				(0.231) *		
ethoxide	1.536	1.076	1.082	114.5	111.1	0.175	0.755	0.247	0.382	0.379	0.384
			(1.088) *		(110.0) *				(0.219) *		

* The values in brackets correspond to the atoms which are out of plane of the ethyl fragment.

from a relatively low positive charge of the ethyl fragment (0.384 *e*) and from its geometry, which is typical of covalent organic compounds. Indeed, the equilibrium C–O bond length (1.549 Å) is close to the mean lengths of these bonds in alcohols (1.445 Å) or esters (~ 1.5 Å), which were calculated using the same basis set. Furthermore, the obtained C–C bond length (1.536 Å) and nearly tetrahedral O–C–H and O–C–C angles in the CH_2 group of alkyl fragment are the characteristics of covalent organic compounds. Thus they also can be taken as an evidence in favor of a covalent structure of the adsorbed ethyl group.

The calculated heat of zeolite surface ethoxylation of 11 kcal/mole is consistent with the thermochemical data on the heat of decomposition of sulfuric acid esters [13]. Thus, our conclusion on the formation of covalent surface esters instead of ion pairs upon interaction of ethylene with bridged zeolite hydroxyl groups seems to be sufficiently supported.

Transformation of adsorbed ethylene to surface ethoxide proceeds via a transition state, which is presented in fig. 1 *b*. When overcoming the activation energy barrier of 15.4 kcal/mole the adsorbed molecule is tilted towards the neighboring basic oxygen of the zeolite framework. One of its carbon atoms then approaches this oxygen and simultaneously the proton of the acidic OH-group is transferred to another carbon atom.

The geometry and the electronic structure of the C_2H_5 fragment in such transition state are very similar to those of the classic form of ethyl cation. This follows from the marked enhancement of positive charging of the C_2H_5 fragment from $+0.384$ up to $+0.565e$, from the elongation of the C–C bond, which becomes intermediate between a double and a single one, as well as from an essential flattening of the CH_2-fragment (O–C–H angles are now close to 90°). On the other hand, in such a transition state the deprotonation tendency is clearly revealed, as a H-bond formation between one of the CH_3-group protons with the neighboring basic oxygen atom becomes more evident.

Another important feature of such a transition state is that, when it is formed, the lengths of the Al–O bonds in the aluminum-oxygen tetrahedron of the zeolite framework, lying in the plane of fig. 1, become equal to each other. Furthermore, in the final alkoxide structure (fig. 1, *c*) the donor-acceptor bond is already completely transformed into a chemical one, while the chemical bond becomes a donor-acceptor one. In other words, during zeolite ethoxylation by ethylene a "switching" of the chemical bonds occurs: a donor-acceptor bond transforms to a chemical one, while a chemical bond converts to a donor-acceptor one. Thus, during chemical reaction on the zeolite surface an alteration of the bond strength in the aluminum-oxygen zeolite framework occurs.

Such relaxation of the geometry affects the bond lengths only inside the six-membered cycle of the transition state, since as was shown in [14], other bond lengths in the Si–O–Al zeolite framework are practically not altered. Thus, the obtained data confirm our earlier conclusion, that enhancement of the donor-acceptor Al...O bond and weakening of the chemical Al–O bond during

catalytic reaction is one of the important factors favoring proton transfer in the adsorbed molecule.

In accordance with these ideas [4–9,14,15], Broensted acidic centers should be always considered in close connection with the neighboring basic sites. Their role plays the negatively charged oxygen atoms of the zeolite lattice, bonded to the aluminum atom. The interaction of the adsorbed molecule with the basic oxygen favors the proton transfer to the adsorbed molecule. 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, as in the case of ammonium ions [16], or favors proton abstraction from the transition states if a concerted reaction mechanism is valid.

These results show that the reaction coordinate during ethoxylation of zeolite surface is rather complicated. Actually, it includes a stretching of the O–H and C–C bonds in the acidic hydroxyl group and in the adsorbed molecule as well as some change of the angles in methyl and methylene fragments and a shift of the adsorbed ethylene molecule to the surface basic center. It is of essential importance to note that the activation barrier of the ethoxylation can be low enough only if all of these parameters are changing simultaneously. In other words, the corresponding variations must be in phase. Naturally, such a complicated elementary step has a low probability, and therefore one may expect low values for preexponential factors of the corresponding rate constants. However, this is more than compensated by the low activation energy. Thus, the possibility of proton transfer over low potential barrier can be explained by a complex reaction pathway which enables maximum energy compensation of the bonds to be broken by those to be formed.

The results obtained can be used for the discussion of reaction mechanisms of some acidically catalyzed transformations of olefins. For instance, the decomposition of the surface alkoxy structures follows the opposite pathway than the alkylation of the zeolite surface.

In this case the main contributions to such a very complicated reaction coordinate is offered by the stretching of the C–O bond in the surface ester and by the deprotonation of the resulting carbenium ion like transition state. The marked tendency of deprotonation is already evident for the starting most stable covalent alkoxy structure. This follows from the rather short distance of 1.792 Å of one of the CH_3 protons from the neighboring basic oxygen of the zeolite lattice which is typical of intramolecular hydrogen bonds (fig. 1 *c*). This tendency to deprotonation is even more increased in the transition state, since this distance becomes shorter (1.55 Å) and the corresponding C–H bond is markedly elongated from 1.09 to 1.16 Å (fig. 1 *b*).

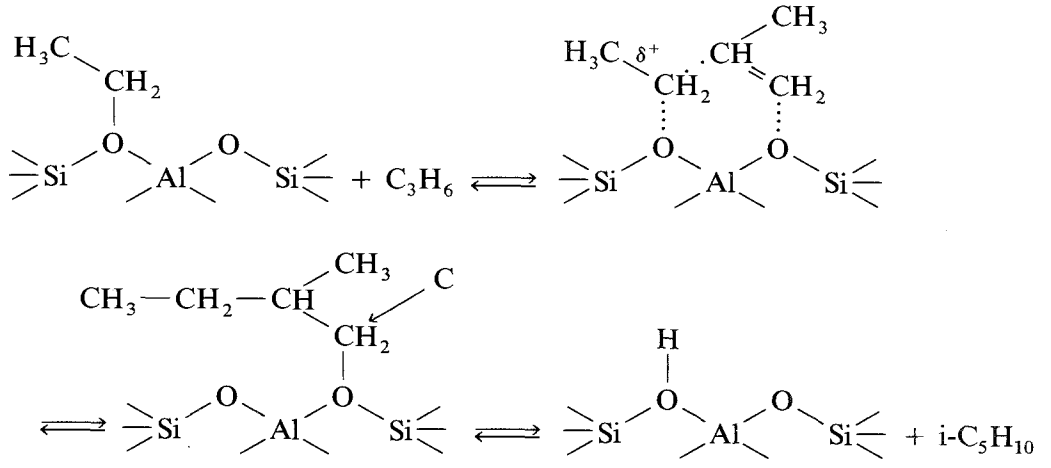
Thus, the decomposition of the surface alkoxy groups could be described in the following way:

Although the homolytic dissociation of the C–O bond in surface esters is considerably more favorable then the heterolytic dissociation, the initial stages of

the C–O bond stretching result in an increase of its polarity. This effect is maximal in the transition state, which therefore is of a carbenium ion like character. The further heterolytic dissociation is extremely energetically unfavorable. Therefore the following stretching of the C–O bond results instead of abstraction of carbenium ions or alkyl free radicals in the deprotonation of the transition state. This requires to overcome the activation energy barrier only of about 20 kcal/mole instead of the heterolytic dissociation energy of about 300 kcal/mole or the homolytic dissociation energy of about 90 kcal/mole.

According to these ideas the acidically catalyzed double bond shift in olefins also occurs via subsequent formation and decomposition of the surface alkoxy groups. At high temperature, where π-complexes are unstable this probably occurs by interaction of gaseous ethylene directly with the free surface OH-groups. The reaction limiting step is the decomposition of the resulting alkoxyls. This is consistent with experimental activation energies of the double bond isomerisation on zeolites of about 15–20 kcal/mole [2] which is close to the height of the barrier estimated by us. On the other hand, since the transition state of the limiting elementary step is of a carbenium ion like character, the double bond isomerisation obeys the regularities of the carbenium in formalism.

A similar approach could be used for the discussion of some other catalytic transformations of olefins. For instance, their oligomerisation is also believed to proceed via adsorbed carbenium ions, which 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 surface alkoxide intermediates. This is supported by the results of our quantum chemical calculations published in [7,8]. They show, that the trend towards heterolytic dissociation is increasing when going from an ethyl to an isopropyl surface alkyl fragment. Therefore, it is very likely that the oligomerisation of olefins also proceeds via a synchronous mechanism, similar to that proposed in [17] (scheme 1).



Scheme 1.

The reaction coordinate includes here a simultaneous C–O bond stretching, approaching of the second ethylene molecule to the surface exited complex, and the change of the bond lengths and valence angles in a carbenium ion like transition state. Again, a low activation barrier is possible only if all of these parameters are changing simultaneously. However, an analysis of the oligomerisation reaction in more detail is out of the scope of this work and will be the subject of one of our future publications.

The present paper is certainly only a very first step in a precise quantum chemical analysis of the mechanism of heterogeneous acidically catalyzed transformations of olefins. Its obvious disadvantages are the very small dimensions of the clusters modelling the Broensted acid sites and the roughness of the nonempirical method used for the calculations. However, our aim was not the quantitative, but rather a qualitative interpretation of the main features of these reactions. In particularly we tried to illustrate more clearly the idea, that the adsorbed carbenium ions are not the really existing intermediates, but rather the transition states of acidically catalyzed heterogeneous reactions.

However, even these preliminary results do reproduce the main experimental features of the acidically catalyzed transformations of olefins. For instance, as already has been discussed, they properly describe the covalent character of the protonated intermediates, give the correct value of the heat of their formation from olefins and acidic hydroxyl groups, and reasonably reproduce the activation energy for the double bond isomerization. To make these conclusions more convincing and more quantitative further more precise calculations for larger clusters employing higher level basis sets and taking into account the electron correlation effects are required.

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