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Citation for published version (APA):

Blaszkowski, S. R., Nascimento, M. A. C., & Santen, van, R. A. (1996). Activation of C-H and C-C bonds by an acidic zeolite : a density functional study. *Journal of Physical Chemistry*, 100(9), 3463-3472.
<https://doi.org/10.1021/jp9523231>

DOI:

[10.1021/jp9523231](https://doi.org/10.1021/jp9523231)

Document status and date:

Published: 01/01/1996

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Activation of C–H and C–C Bonds by an Acidic Zeolite: A Density Functional Study

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Received: August 8, 1995; In Final Form: November 17, 1995[⊗]

Density functional theory is used to determine transition states and the corresponding energy barriers of the reactions related to C–H bond activation of hydrogen exchange and dehydrogenation of ethane catalyzed by a protonated zeolite as well as hydride transfer between methanol and a methoxide (CH₃-zeolite) species. Additionally the C–C bond activation involved in the acid catalyzed cracking reaction of ethane was investigated. The computed activation barriers are 118 for hydrogen exchange, 202 for hydride transfer, 292 for cracking and finally 297 for dehydrogenation, all in kilojoules per mole. For the cracking reaction, two different transition states with the same activation barrier have been obtained, dependent on the approach of the ethane molecule to the zeolite cluster. A study of the relation between acidity and the structure of the zeolite shows that the transition state for the hydrogen exchange reaction is rather covalent and its geometry resembles the well-known carbonium ion, while the others are rather ionic carbenium ions. From the calculated activation barriers as well as vibrational, rotational, and translational partition functions, reaction rate constants have been evaluated by means of the transition state reaction rate theory.

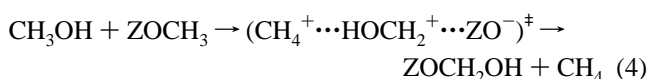
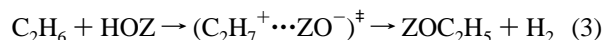
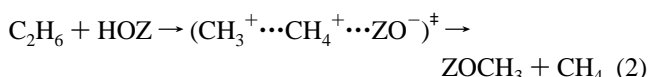
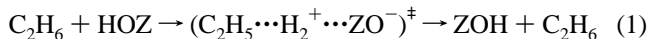
1. Introduction

At the present there is a significant increase in the understanding of the conversion reactions of alkanes catalyzed by zeolites.¹ This is assisted by experimental studies on the conversion of intermediate size molecules at low conversion rates where the primary reactions are prevalent and product distributions easier to analyze.^{2–4a} Together with the increasing computational facilities, those reactions can be studied by means of accurate ab initio quantum chemical calculations, providing a better understanding of the catalytic processes at the molecular level. For the smallest hydrocarbon possible, methane, two different reactions are possible, hydrogen exchange and dehydrogenation. The first reaction has been found^{4–6} to proceed via formation of a structure which resembles a carbonium ion strongly stabilized by the lattice. The second^{5,6} involves a C–H bond breaking, with formation of a transition state carbenium-like structure that becomes attached to the zeolitic framework. Larger molecules involve also the C–C bond cracking as well as hydride transfer reactions. The two major routes for alkane cracking⁷ over acidic zeolites involve bimolecular hydride transfer followed by β -cission or the monomolecular attack of a C–C bond by a H⁺ from the catalyst to form a carbonium ion. This then cracks, giving a paraffin in the gas phase and the remaining fragment staying adsorbed on the catalyst as carbenium ions. The carbenium ion formed can then desorb as an olefin, while restoring the H⁺ of the catalyst. The use of quantum chemical techniques may provide a detailed understanding of such reactions on a molecular level.

The acidic function of a zeolite such as H-ZSM5 is due to protons that are attached to the oxygen atoms of the zeolite framework. The catalytic activity is related to the intrinsic acid strength of those protons. The proton affinity of zeolites is

modified by both chemical and structural variations in the zeolite lattice. A study by Kramer and van Santen⁸ showed that the proton affinity, the theoretical measurement for the zeolite acidity, can be mimicked by constraining the peripheral bonds of the cluster model for the zeolite. In a study on the relation between acid strength and catalytic activity of a zeolite CH₄ deuterium exchange, recently presented by Kramer et al.,⁴ it is shown that the reaction barrier height increases with an increasing proton affinity difference between the two structurally neighboring oxygen atoms. This explains, for this reaction, the difference in activity of two structurally different zeolites.

In the present study, density functional theory (DFT) calculations are used to obtain the transition states involved in the reactions of hydrogen exchange (eq 1), cracking (eq 2), and dehydrogenation (eq 3) of ethane catalyzed by an acid zeolite. Additionally, the transition state for hydride transfer reaction (eq 4) between a methanol molecule and a methoxide (CH₃-zeolite) surface is presented.



A comparison with the analogous reactions for methane⁶ as well as reactions for ethane obtained with a different method⁵ is presented in the text. By means of the transition state reaction rate theory, the elementary rate constants were computed. An analysis of the relation between proton affinity (acidity) and activation barriers will also be presented.

2. Method

2.1. Computational Details. All calculations in this study are based on density functional theory (DFT),⁹ using the DGauss

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⊗ Abstract published in *Advance ACS Abstracts*, February 1, 1996.

program (versions 2.1 and 2.3), part of the UniChem package from Cray Research, Inc.¹⁰ The calculations were carried out applying the local density approximation (LDA) using the exchange-correlation potential in the form parametrized by Vosko et al.¹¹ To the final optimized structures, nonlocal (NL) correlation and exchange corrections due to Perdew¹² and Becke,¹³ respectively, are included to the final total LDA energy. The LDA without any nonlocal correction are shown to be inadequate for the calculation of accurate binding energies for reactions which involve hydrogen transfer.^{6,14}

The basis sets used are of double- ζ quality and include polarization functions for all non-hydrogen atoms (DZPV).¹⁵ A second set of basis functions, the auxiliary basis set,¹⁶ is used to expand the electron density in a set of single-particle Gaussian-type functions.

The total LDA energy gradients are computed analytically.¹⁷ Geometry optimizations are carried out to a minimum in the case of reactants and adsorption complexes and to a saddle point in the case of transition states (TS's). For a TS, the norm of the gradient is minimized and not the energy.¹⁸ The frequencies are obtained by evaluating the matrix of the second derivatives by a finite difference scheme using the analytic first derivatives.¹⁹ Unscaled frequencies have been used and zero-point energy (ZPE) corrections included.

The molecular system used consisted of one ethane molecule and a tritrahedral cluster, $\text{H}_3\text{SiOAlH}_2\text{OHSiH}_3$ (or AlH cluster), that represents the acidic zeolite. In the case of hydride transfer, the system consisted of one methanol molecule and the methoxy species, $\text{H}_3\text{SiOAlH}_2\text{OCH}_3\text{SiH}_3$, where the acidic proton has been replaced by a methyl group. In both, cluster and methoxide surfaces, the aluminum atom was terminated by two hydrogen atoms and the peripheral bonds of the silicon atoms were saturated with hydrogens. All structures were also obtained with a larger cluster, $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$, the AlOH cluster, and the corresponding AlOH-CH₃ methoxide surface. In this case the aluminum atom was terminated by two hydroxyl (OH) groups instead. For the hydroxyl aluminum termination, not all structures were completely optimized, as it will be discussed in the text. No symmetry constraints have been used in any of the calculations.

2.2. Reaction Rate Constants. The reaction rate constants were calculated using transition state reaction rate theory (TST).²⁰ It is based on the application of statistical mechanics to reactants and activated complexes. The reaction rate constant (k_r) expressed in terms of "rate per acidic proton" for ethane activation is given by

$$k_r = \left(\frac{k_B T}{h}\right) (N_A V) \frac{q_{v(\text{TS})}^\ddagger}{q_v q_r q_t q_{(\text{C}_2\text{H}_6)} q_{v(\text{HOZ})}} e^{-(E_{\text{bar}}/k_B T)} \quad (5)$$

where h , N_A and k_B are Planck, Avogadro and Boltzman constants, respectively. V is the volume, and T is the temperature of the system. E_{bar} is the activation barrier which includes already the zero-point energy correction. In the equation, q_v , q_r , and q_t are the vibrational, rotational, and translational partition functions. For the ethane molecule all three must be evaluated. For the transition state and the cluster (HOZ), assuming that the zeolite does not rotate or translate, only the vibrational partition function needs to be calculated. In the case of the hydride transfer, it is considered that a methanol molecule interacts with a methoxide zeolitic surface. In that case q_v , q_r , and q_t must be evaluated for the methanol molecule, and q_v , for the methoxide surface and transition state.

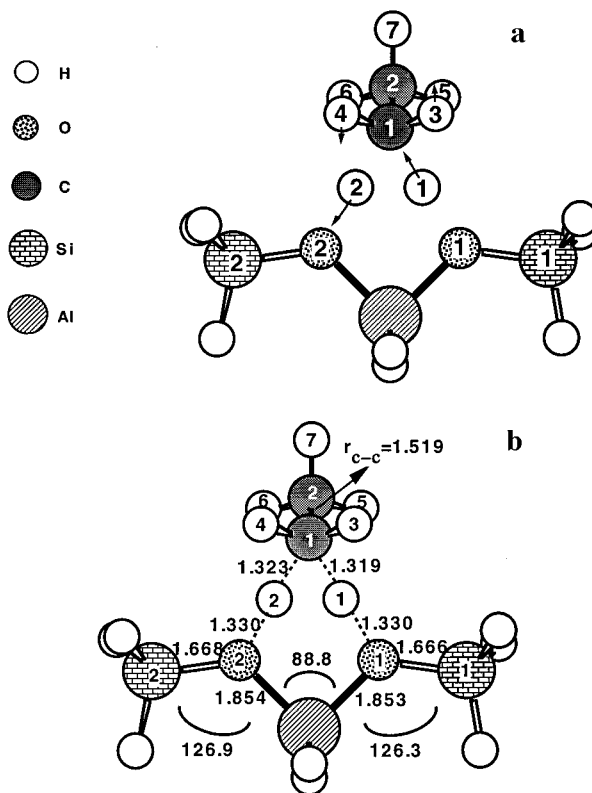


Figure 1. (a) TS for the exchange process between ethane and an acidic zeolite. The arrows indicate the main components for the displacement of the atoms along the reaction coordinate. (b) Geometry of the TS for the acid catalyzed reaction of heteroexchange of ethane. Distances in angstroms and angles in degrees.

The natural logarithm of the reaction rate constant, $\ln k_r$, is a linear function of the reciprocal temperature ($1/T$) according to the equation

$$\ln k_r = -\frac{E_{\text{act}}}{k_B T} + \ln A^{\text{TST}} \quad (6)$$

where E_{act} is the Arrhenius activation energy and A^{TST} is the pre-exponential factor. The latter is related with the change in activation entropy of the system of the reactants and transition state.

Finally, a comparison between the pre-exponent obtained with the transition state theory (A^{TST}) and the hard sphere pre-exponent (A^{HS}), which gives the number of collisions of an ethane molecule approximated as a hard sphere, can be made. The latter sets an upper limit for the former. The hard sphere pre-exponent is given by

$$A^{\text{HS}} = \frac{1}{4} N_A \pi d^2 \left(\frac{8k_B T}{\pi m}\right)^{1/2} \quad (7)$$

where m is the mass of the ethane molecule and d is its kinetic diameter in the gaseous phase (8.1 Å)²¹ obtained from the collision cross section. For the hydride transfer, a methanol molecule is considered instead. Its kinetic diameter was calculated to be 3.6 Å.²² A small ratio $A^{\text{TST}}/A^{\text{HS}}$ means a significant decrease in reaction entropy, due to loss in rotational or translational degrees of freedom.

3. Results

3.1. Hydrogen Exchange. Figure 1a shows the calculated transition state (TS) for the reaction of hydrogen exchange (or hydrogen/deuterium exchange) of ethane catalyzed by an acidic

TABLE 1: Total Energies for the Fragments, and Transition States (TS) (Hartrees), ZPE (kcal/mol), Activation Barriers (E_{bar}) and Arrhenius Activation Energies (E_{act}) (kJ/mol) and Imaginary Frequencies (IF)

	energy	ZPE	E_{bar}	E_{act}	IF
cluster AlH	-977.424 512	51.77			
surface methoxide AlH	-1016.732 150	70.00			
ethane	-79.839 213	45.48			
methanol	-115.749 107	31.35			
TS hydrogen exchange	-1057.214 004	94.34	+118.4	+125.7	-1374
TS cracking(1)	-1057.150 102	95.78	+292.2	+302.5	-543
TS cracking(2)	-1057.151 186	96.48	+292.3	+299.7	-209
TS dehydrogenation	-1057.145 600	94.15	+297.2	+305.2	-836
TS hydride transfer	-1132.400 543	99.03	+202.2	+212.9	-182

zeolite. The arrows in the figure represent the movement of the atoms according to the reaction coordinate (obtained from the imaginary mode). It shows the transfer of the zeolitic proton to ethane and the symmetrical return of the hydrogen atom from ethane to the zeolite. Both oxygens of the lattice are involved in the reaction, one as a proton acceptor (base) and the other as proton donor (acid). Just like for methane,⁶ the hydrogen atoms are nearly half-way between carbon and the zeolitic oxygen atoms. Although no symmetry constraints have been used, the TS obtained for this reaction has nearly the C_s symmetry.

Table 1 shows the energetic and dynamic information obtained for all fragments and TS's for all studied reactions. The activation barrier for hydrogen exchange of ethane with respect to the reactants in the gas phase including ZPE corrections was found to be 118 kJ/mol. The TS obtained using a larger AlOH cluster presented two imaginary modes. The first is the reaction coordinate, and the second, very small, is associated with a bending movement of one of the OH groups bound to aluminum. The activation barrier obtained with this cluster, 117 kJ/mol, is only 1 kJ/mol lower than that for the smaller AlH cluster. The activation barrier calculated for ethane hydrogen exchange is just a few kilojoules lower than for methane using the same cluster and method⁶ (≈ 120 kJ/mol) as well as an estimate from experiment^{4a} (122 kJ/mol). One concludes that the effect of a carbonium ion stabilization due to the attachment of one additional carbon atom is not really important for this reaction. No experimental activation barriers for ethane activation are available in the literature, so a comparison with *n*- and/or isobutane will be made. The experimental apparent activation energy for *n*-butane hydrogen/deuterium exchange in H-ZSM5 zeolite obtained by Lercher et al.² was found to be 85 kJ/mol. The heat of adsorption of *n*-butane in H-ZSM5 zeolite according to different sources^{2,23} is 51–60 kJ/mol. Adding the heat of adsorption to the apparent activation energy, one obtains the true activation barrier, 133–145 kJ/mol. The experimental true activation energy should be compared to the calculated activation barrier with respect to the reactants in the gas phase (118 kJ/mol for hydrogen exchange) plus the adsorption energy of ethane in the zeolite. We have firstly tried to calculate the heat of adsorption of ethane in the zeolite cluster theoretically, but DFT seems not to be suitable to reproduce adsorption energies of systems involving weak van der Waals interactions, even if nonlocal corrections are included self-consistently, giving a slightly endothermic adsorption. Because of that, in order to compare with the experimental data, the experimental heat of adsorption of ethane in H-ZSM5,²³ 29 kJ/mol, is being used. The “theoretical true barrier” for ethane hydrogen exchange is, thus, 147 kJ/mol, which agrees remarkably well with the experimental true activation barrier obtained by Lercher et al.² for *n*-butane.

The geometry obtained for the AlH transition state for the reaction of hydrogen exchange is shown in Figure 1b. As mentioned before, the hydrogen atoms are nearly half-way

TABLE 2: Mulliken Charges

	hydrogen exchange (Figure 1a)	cracking(1) (Figure 3a)	cracking(2) (Figure 4a)	dehydrogenation (Figure 5a)	hydride transfer (Figure 6a)
C1	-0.657	-0.868	-0.792	-0.511	-0.430
C2	-0.670	-0.662	-0.744	-0.640	-0.810
H1	0.294	0.321	0.339	0.149	0.364
H2	0.294	0.317	0.315	0.050	0.197
H3	0.276	0.288	0.303	0.352	0.293
H4	0.272	0.289	0.304	0.379	0.466
H5	0.246	0.355	0.355	0.269	0.331
H6	0.246	0.346	0.366	0.267	0.350
H7	0.247	0.312	0.313	0.248	0.304
O1	-0.695	-0.683	-0.685	-0.657	-0.678
O2	-0.695	-0.626	-0.637	-0.602	-0.610
O3					-0.309
Al	0.331	0.225	0.213	0.215	0.213
Si1	0.285	0.266	0.270	0.282	0.272
Si2	0.284	0.263	0.253	0.284	0.251

between the carbon atom and the zeolitic oxygens, about 1.32–1.33 Å. These numbers are nearly the same as the ones obtained for methane.⁶ When comparison is made with Hartree–Fock (HF) calculations for methane,^{4,5,24} the difference is larger. In the basis of the computed geometry, one observes that the structure obtained with the HF method seems to be more ionic than that obtained with DFT, where the Hartree–Fock O–H and C–H distances are, respectively, shorter and longer than that for the DFT method. The distance C–C, 1.519 Å, is nearly the same as that calculated for the free ethyl carbonium ion²⁵ using HF/MP2(full)/6-31G** and the gas phase ethane molecule with DFT (both 1.517 Å). The geometry of the calculated TS resembles a free pentacoordinated ethyl carbonium ion.

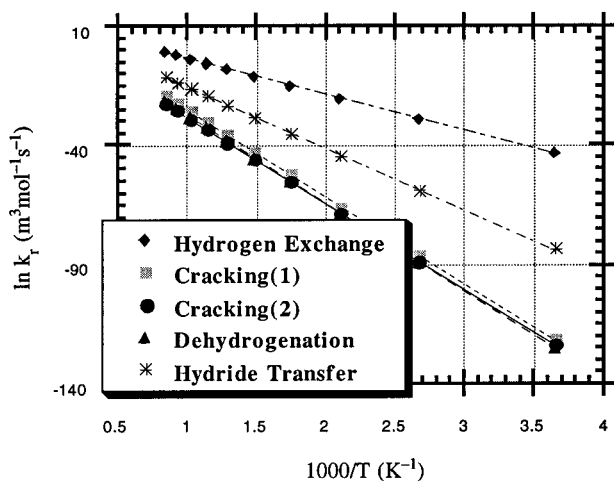
Table 2 gives the Mulliken charges. The charge obtained for aluminum using this small AlH cluster is much too small. Nevertheless, as observed before,^{6,26} properties like infrared spectra, geometry, or energies (activation barriers and adsorption energies) seem to be not too much affected by the kind of terminal group on the aluminum atom. The group $C_2H_7^+$ can be divided in two distinct parts: the C_2H_5 , nearly neutral, and the two hydrogens between the carbon and the zeolitic oxygens, which are positively charged. These results disagree with results obtained in measurements of mass spectroscopy²⁷ and ab initio calculations²⁸ for the free methyl carbonium ion, which is believed to represent a complex of methyl carbenium ion with molecular hydrogen. This difference in charges for the calculated transition state and the free methyl carbonium ion is believed to be a result of the interaction with the lattice oxygens, which are strong proton acceptors (basic).

Table 3 shows the calculated rate constants (k_r) according to different temperatures for all studied reactions. This reaction presents large k_r compared to the other reactions, resulting in a lower activation barrier. The Arrhenius plot is shown in Figure 2. The slope of the curve gives the Arrhenius activation energy, which was obtained from a linear fit of the plot. The activation barrier (E_{bar}) and Arrhenius activation energy (E_{act}), shown in Table 1, differ by a few kilojoules per mole. The pre-exponents ratio $A^{\text{TST}}/A^{\text{HS}}$, shown in Table 4, is in essence rather small (10^{-4}), representing a considerable decrease in the entropy of the system, due to a loss of rotational and translational degrees of freedom. Nevertheless, between all studied reactions for ethane, this is the one which presents the largest $A^{\text{TST}}/A^{\text{HS}}$ ratio. The transition state obtained for the hydrogen exchange reaction is thus the loosest. An explanation for that is the fact the C_2H_5 group is nearly neutral, resulting in a weak interaction with the rest of the system.

3.2. Cracking (Path 1). Two different transition states have been obtained for the cracking reaction of ethane catalyzed by

TABLE 3: Rate Constants (k_r , $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$) for Different Temperatures (T , K)

T	hydrogen exchange	cracking(1)	cracking(2)	dehydrogenation	hydride transfer
273	1.57×10^{-19}	1.36×10^{-53}	1.51×10^{-54}	7.73×10^{-55}	5.85×10^{-37}
473	1.10×10^{-9}	1.66×10^{-29}	1.14×10^{-30}	1.50×10^{-30}	3.79×10^{-20}
673	1.52×10^{-5}	1.53×10^{-19}	8.17×10^{-21}	1.67×10^{-20}	4.03×10^{-13}
873	3.35×10^{-3}	4.85×10^{-14}	2.22×10^{-15}	6.05×10^{-15}	3.36×10^{-9}
1073	1.15×10^{-1}	1.59×10^{-10}	6.58×10^{-12}	2.19×10^{-11}	1.14×10^{-6}

**Figure 2.** Arrhenius plot: temperature (T) dependence of the natural logarithm of the rate constants, $\ln k_r$, obtained for the studied reactions. The symbols represent the calculated $\ln k_r$, and the lines, the linear fit.

a zeolitic proton. The first of them, for easier reference cracking(1), is depicted in Figure 3a. The only imaginary mode obtained has its main components represented in the figure by the arrows. The zeolitic proton has migrated to one of the carbon atoms, and, there, a methane molecule is almost formed. In order to accommodate the proton coming from the zeolite, the hydrogen atom H2 bends a little to the right side. The arrows represent also very clearly the separating motion of the carbon atoms and consequent formation of a methyl group attached to the zeolite. This last group resembles a trigonal planar carbenium ion, with hybridization very close to sp^2 . Additionally, it is also possible to see in this figure the effect of relaxation of the hydrogen atoms. Just like for the previous reaction studied, the oxygens of the lattice play a role of Brønsted acid (donating a proton) and Lewis base (receiving the CH_3 group). The carbenium ion formed is strongly stabilized by the basic oxygen of the lattice.

The calculated transition state for cracking is slightly different than that obtained previously by Kazansky et al.²⁹ with the HF/3-21G method using the small $\text{HOAl}(\text{H}_2)\text{OH}_2$ cluster. In that work, the right side CH_3 group is rotated by approximately 90° with respect to the zeolitic proton compared to the present study. As will be discussed later, it is closer to the transition state of path 2 for cracking. In a recent study Collings and O'Malley³⁰ performed AM1 calculations for the cracking reaction of butane and hexane, using as a model for the zeolitic system the $\text{H}_3\text{-SiOHAlH}_3$ cluster. There the acidic proton attacks directly the C–C bond, and a smaller alkene and alkane are formed from the resulting carbonium ion. They predict that the protolysis reaction is then not driven by an acid–base pair type reaction. Their model for the zeolite, however, does not include the basic oxygen, hence not allowing for the possibility of a Brønsted acid/Lewis base catalyzed reaction.

An activation barrier of 292 kJ/mol with respect to the reactants in the gas phase was found for the cracking(1) reaction. A slightly lower activation barrier was found for the larger cluster AlOH (287 kJ/mol). However, in this case the transition state was not fully optimized, since four imaginary modes were

present. Except the one related to the reaction coordinate, all others are related to the hydrogen's and hydroxyl's terminations of silicon and aluminum, respectively. The experimental apparent activation barriers obtained by Stefanadis et al.³¹ for isobutane cracking and dehydrogenation catalyzed by H-ZSM5 are, in both cases, 57 kcal/mol (238 kJ/mol). Including the adsorption energy (51–60 kJ/mol^{2,23} for *n*-butane, which is only 1 kJ/mol higher than that for isobutane on HX zeolite⁶), the true activation energy becomes about 289–298 kJ/mol. Corma et al.^{3b} have obtained in experiments of isobutane cracking in highly dealuminated USY-2 zeolite an apparent activation barrier of 37.5 ± 4.5 kcal/mol ($\approx 157 \pm 20$ kJ/mol), what is considerably lower than that obtained by Stefanadis et al.³¹ despite the different kinds of zeolites that were used. Adding the adsorption energy (for *n*-butane in H-ZSM5^{2,23}), the true activation energy becomes $(208\text{--}217) \pm 20$ kJ/mol. Lercher et al.² found an apparent activation barrier for *n*-butane of 140 kJ/mol. Adding the adsorption energy^{2,23} the true barrier is 190–200 kJ/mol. These results differ considerably from each other, specially the last two^{2,3b} as compared to the experiment performed by Stefanadis et al.³¹ If one realizes that, in the work of Stefanadis et al.³¹ for isobutane, a secondary carbenium ion is formed, which is more stable than the primary carbenium ion formed for *n*-butane in the work by Lercher et al.,² such a large difference is really surprising. It is possibly due to the experimental conditions applied. In the work of Stefanadis et al.³¹ also propane appeared to be the primary product, possibly formed due to hydride transfer reaction, which could be responsible for the difference in the experimentally measured overall activation barrier. In a previous study on methane⁶ it has been shown that in the gas phase the carbenium ion CH_3^+ is nearly 200 kJ/mol less stable than a primary carbenium ion and 300 kJ/mol less stable than a secondary carbenium. Comparing the “theoretical true barrier” (ethane cracking E_{bar} , 292 kJ/mol, plus the adsorption energy of ethane,²³ 29 kJ/mol) obtained in the present study (321 kJ/mol) with the experimental true activation energies for the experimental studies just mentioned, one can conclude that the results are consistent when taking into account the difference in energy between the intermediates formed. The difference with the experiment of Stefanadis et al.³¹ seems to be very small, only 23–32 kJ/mol, especially considering that in their experiment a secondary carbenium ion is formed. This has to be considered accidental. In comparison with the other two studies (Lercher et al.² and Corma et al.^{3b}), the difference seems to be, initially, very large (over 100 kJ/mol). Nevertheless, it is much smaller than the difference in energy between the respective intermediates in the gas phase, indicating strong stabilization by the frame. The activation barrier obtained in the calculation performed by Kazansky et al.,²⁹ 390 kJ/mol, is nearly 100 kJ/mol higher than the one obtained in the present work. This is certainly due to a much too small cluster model for the zeolite as well as the basis set used. The semiempirical method used by Collings and O'Malley³⁰ is not suitable for calculating total energies or activation barriers, as discussed in their own paper and shown before.⁶ Their activation barrier was calculated to be 370 kJ/mol, which is 80 kJ/mol higher than the one obtained in the present work.

TABLE 4: Preexponent Ratio ($A^{\text{TST}}/A^{\text{HS}}$) for Different Temperatures (T, K)

T	hydrogen exchange	cracking(1)	cracking(2)	dehydrogenation	hydride transfer
273	8.61×10^{-4}	5.33×10^{-4}	1.53×10^{-5}	1.08×10^{-4}	7.27×10^{-4}
473	6.54×10^{-4}	4.05×10^{-4}	1.16×10^{-5}	8.22×10^{-5}	5.52×10^{-4}
673	5.48×10^{-4}	3.39×10^{-4}	9.72×10^{-6}	6.89×10^{-5}	4.63×10^{-4}
873	4.81×10^{-4}	2.98×10^{-4}	8.53×10^{-6}	6.05×10^{-5}	4.07×10^{-4}
1073	4.34×10^{-4}	2.69×10^{-4}	7.70×10^{-6}	5.46×10^{-5}	3.67×10^{-4}

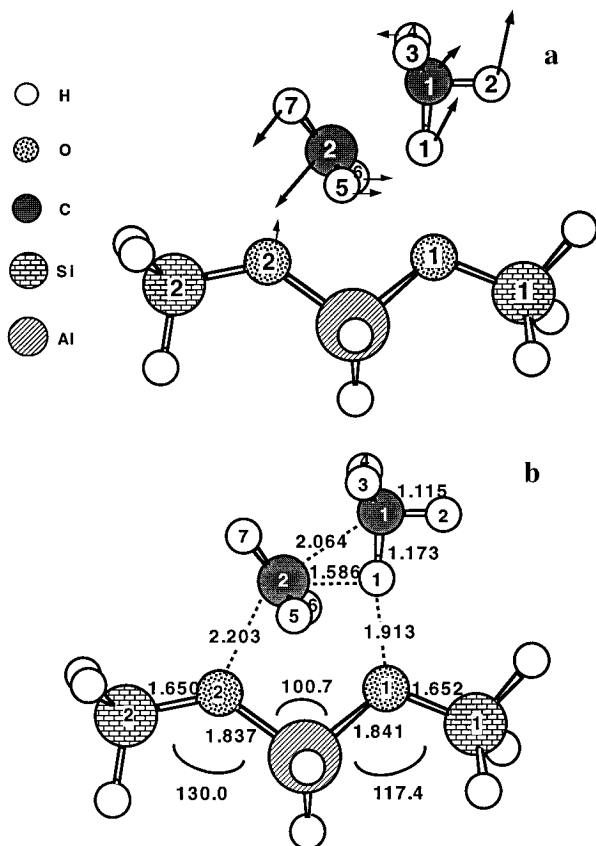


Figure 3. (a) Reaction coordinate and (b) geometry of the TS for the reaction of acid catalyzed cracking(1) of ethane. Distances in angstroms and angles in degrees.

Figure 3b shows the TS geometry for the acid catalyzed cracking(1) reaction. The zeolitic proton is at a distance of only 1.17 Å from the CH₃ (right-side) group, in such a way that the methane molecule is almost formed. In the opposite direction, the distance H1–O1 is very long, 1.91 Å. Parallel to the zeolitic proton is C2, at a distance of 1.59 Å. It is possible to imagine that a small interaction between H1 and C2 exists. All other C–H distances are in turn of 1.10 Å, except the bond C1–H2, which is slightly longer, 1.12 Å. The distance C–C, 2.064 Å, is much longer than in the free ethane molecule (≈ 1.54 Å). The geometry of the CH₃ group (left side) is trigonal planar, with the H–C–H angles in the order of $120 \pm 3^\circ$, like in classical carbenium ions. Its distance from the basic oxygen (O2) is 2.20 Å. The angles Si–O–Al are quite different from each other, (117 and 130°), according to the approach of the CH₃ group to the basic oxygens, especially if compared with the cluster's angles in the case of hydrogen exchange, which is a symmetrical structure.

The Mulliken charges, shown in Table 2, depict a situation where a carbenium ion in the left side (+0.351) approaches the basic O4 and an almost neutral CH₃ group in the right side (+0.03) receives a proton (+0.347). This picture is different than the one obtained by Kazansky et al.,²⁹ where the right-side CH₃ group is negatively charged (–0.30) and the carbenium ion more positively charged (+0.57). This could be due to the small distance and consequent interaction between C2 with the

zeolitic proton H1. In essence, it is difficult to compare the charges obtained with the two different methods, especially because Mulliken charge analysis is a rather arbitrary method. The charge on Al is much too small, for the same reason as discussed in the previous section.

The reaction rate constants for the cracking(1) reaction are much smaller than for hydrogen exchange, as can be seen in Table 3. This is due to a higher activation barrier. The Arrhenius activation energy obtained from a linear fit of the Arrhenius plot (Figure 2), 302 kJ/mol, is higher than the directly calculated activation barrier, 292 kJ/mol (Table 1). The ratio $A^{\text{TST}}/A^{\text{HS}}$ shown in Table 4 is rather small representing a considerable decrease in the entropy of the system due to a loss of rotational and translational degrees of freedom. It is almost two times smaller than the ratio obtained for the hydrogen exchange reaction. It is possible to say that the TS for cracking(1) is, thus, a little more tight than for hydrogen exchange.

3.3. Cracking (Path 2). The second transition state obtained for the reaction of cracking, for easier reference called cracking(2), is depicted in Figure 4a. In the picture, according to the arrows, one sees the attachment of the CH₃ group to the basic oxygen, O2, as well as the simultaneous transfer of the proton, H1, from the zeolite to the carbon atom C1, with formation of a methane molecule. Following the reaction path for cracking(2), which is depicted in Figure 4b, it is possible to see that in this path an additional step was required, involving the rotation of the CH₃ group. Structure I in Figure 4b is the calculated adsorbed complex of the ethane molecule in the zeolitic cluster, which corresponds to a local minimum in the potential energy surface, lying 19 kJ/mol higher in energy than ethane + the AlH cluster in the gas phase. The repulsive interaction obtained indicates that ethane interacts very weakly with the cluster. In order to obtain a better description of the system, it would be necessary to include nonlocal corrections self-consistently²⁶ as well as a larger basis set would be necessary, which makes the calculation a lot more expensive. Structure II in Figure 4b presents only one imaginary mode, being thus a transition state which is related to the rotation of the CH₃ group around the C–C bond. Structure II (where ethane is the *eclipsed* isomeric form) is 9 kJ/mol less stable than structure I (where ethane is the *staggered* isomeric form). The experimental activation barrier for such rotation of the ethane in gas phase³² is 3 kcal/mol (12.5 kJ/mol), just a little higher than that calculated here. Transition state II in Figure 4b is a very interesting structure because the carbon atoms are indistinguishable, being free to also rotate along an axis perpendicular to the C–C bond. Starting from the transition state for the cracking(2) reaction, structure III in Figure 4b, suppose the carbon atom C1 donates its proton to the zeolite and binds to C2, generating the structure II. There the ethane molecule is free to rotate perpendicularly to the C–C bond, where C1 takes the place of C2 and vice versa. From this rotation, no changes in the system will be observed since the carbon atoms are indistinguishable. Suppose now the reaction does not proceed, but it cracks back to structure III. It is now C2 that will get the proton back from the zeolite and not C1. Such is an indirect path for the reaction of hydride transfer. It is important to note that if structure II is a transition state, and it is, this means that in both sides of the reaction

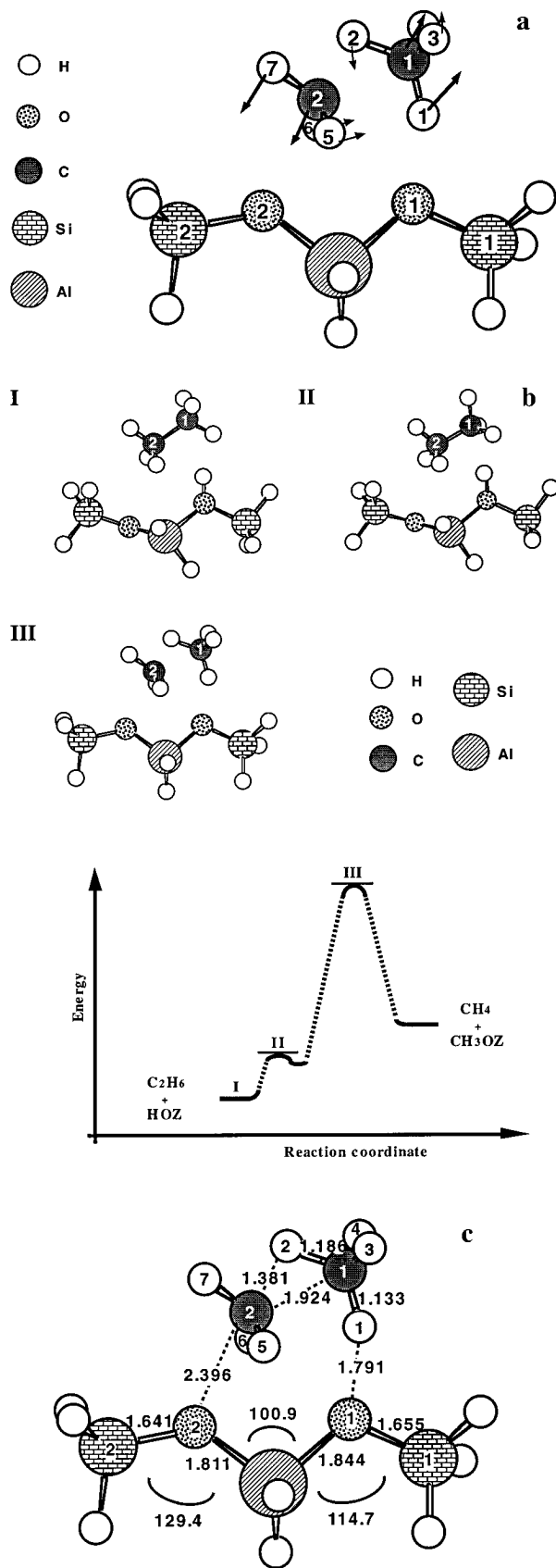


Figure 4. (a) Reaction coordinate (represented by the arrows), (b) simplified reaction path, and (c) geometry of the TS for the acid-catalyzed cracking(2) reaction of ethane. Distances in angstroms and angles in degrees.

coordinate there exists a minimum point. Structure I is one of the minima, while, between transition states II and III, another minimum should be found. Despite a big effort, such a

minimum could not be found. It is certainly a very flat minimum. It is also interesting to call attention to the fact that for cracking(1) the reaction path is simpler, involving only the adsorption complex depicted in Figure 4b (structure I) and the transition state itself depicted in Figure 3a.

The activation barrier with respect to reactants, 292 kJ/mol (see Table 1), is exactly the same as that obtained for the other transition state for cracking(1). For the AlOH cluster, where two imaginary modes are present, the barrier is 287 kJ/mol. All comparison with experiments^{2,3b,31} and other calculations,^{29,30} already made for cracking(1), are also valid here.

The geometry for the cracking(2) transition state is presented in Figure 4c. The H2-C1 bond, 1.186 Å, is longer than a regular C-H bond. The distance H2-C2 is relatively short (1.381 Å), indicating that the interaction of H2 with the carbenium ion is strong. Comparing this transition state with the one obtained for cracking(1), shown in Figure 3b, it is possible to see that for cracking(2) the carbenium ion is further from the zeolitic cluster, while the methane molecule is closer to it. Also the carbenium ion itself does not present a sp^2 hybridization as it is for cracking(1), due to the presence of the H2 atom close by. Comparing such TS with the one obtained by Kazansky et al.²⁹ for cracking with the HF/3-21G method, the basic differences are that in the present work the distance C1-C2 is 0.21 Å shorter and the angle H2-C1-C2 (45°) obtained in the present work is 30° smaller than the one obtained by Kazansky et al.²⁹ The Si1-O2-Al angle obtained here is rather small, 115° . The Mulliken charges are presented on Table 2. In a general point of view, they do not differ too much from that obtained for cracking(1). The charge of the carbenium ion (left side) is smaller than for cracking(1), while the methane molecule (right side) is more positively charged than that in cracking(1). Discussion over the aluminum atom has been already presented in section 3.1.

Although the activation barrier of cracking(2) is exactly the same as that for cracking(1), the rate constants presented in Table 3, are slightly smaller as a consequence of a different geometry and, so, different vibrational frequencies. The plot of the natural logarithm of k_r in Figure 2 shows a different slope of the curve comparing cracking(1) and -(2). Thus, the Arrhenius activation energy (Table 1) obtained for cracking(1), 303 kJ/mol, is also different than that for cracking(2), 300 kJ/mol. The ratio A^{TST}/A^{HS} for cracking(2), presented in Table 4, is the smallest compared to all reactions (10^{-5} - 10^{-6}). This implies that the transition state formed is the most rigid of all studied reactions. The fact that the CH_3 group is very close to the hydrogen H2, from the just formed methane molecule, which provides an additional stabilization to the system, could be an explanation for the fact that this transition state is more rigidly attached to the zeolitic cluster than in the other cases. The loss in rotational and translational degrees of freedom is, so, the largest.

3.4. Dehydrogenation. Figure 5a shows the calculated transition state and the corresponding reaction coordinate for the reaction of dehydrogenation of ethane catalyzed by an acidic zeolite. The reaction coordinate shows the simultaneous movement of the proton (H1) together with a hydrogen of ethane (H2) into the direction of formation of a H_2 molecule. From the figure it is possible to see that the H_2 molecule is almost formed. The carbon atom (C1) moves toward the basic oxygen atom (O2) of the zeolite cluster, resulting in the formation of a methoxide (CH_3 -zeolite) surface. The carbon (C1) resembles a primary trigonal planar carbenium ion. The movement of the other hydrogens is just of relaxation around the basic site. Just

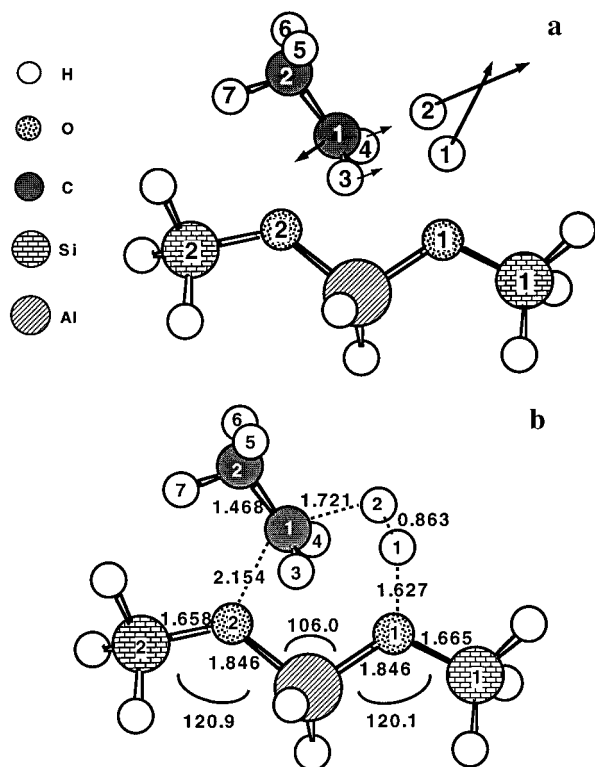


Figure 5. (a) Reaction coordinate and (b) geometry of the TS for the acid catalyzed dehydrogenation of ethane.

as for the previous reactions, this is a Brønsted acid–Lewis base catalyzed reaction.

Table 1 shows the corresponding energies for this system. The computed activation barrier (with respect to the gas phase) for this reaction is 297 kJ/mol. The AlOH cluster successfully optimized to only one imaginary mode presents an E_{bar} only 3 kJ/mol lower than AlH, 294 kJ/mol. The corresponding computed activation barrier obtained for methane,⁶ 343 kJ/mol, is nearly 50 kJ/mol higher than for ethane. This shows that the carbenium ion formed is strongly stabilized on going from CH_3^+ to the primary, CH_3CH_2^+ carbenium ion. Considering that for the reaction of dehydrogenation a primary carbenium is formed, while for cracking a CH_3^+ carbenium ion is involved, the small difference obtained, 5 kJ/mol, between those two reactions seems initially somewhat surprising. Nevertheless, if one keeps in mind that it is more difficult to break a C–H bond than a C–C bond, it is possible to conclude that there is a compensation between the stability of the intermediate formed and bond strength. The experimental apparent activation energy obtained by Stefanadis et al.³¹ for isobutane dehydrogenation was reported to be 238 kJ/mol, the same as that measured for the cracking reaction. Corma et al.^{3b} have found an apparent activation barrier for the dehydrogenation of isobutane in USY zeolite of 39.6 ± 5.3 kcal/mol ($\approx 165 \pm 20$ kJ/mol), just a few kilojoules per mole higher than that measured for cracking. This is consistent with the calculated difference in the present study, where the dehydrogenation E_{bar} is 5 kJ/mol higher than cracking. Lercher et al.² found an apparent activation barrier for dehydrogenation of *n*-butane of 105 kJ/mol, which, contrary to that obtained by Corma et al.^{3b} and in the present study, is 35 kJ/mol lower than the barrier obtained for cracking. Comparing the experimental results for *n*- and isobutane with those calculated for ethane, one sees that similar conclusions as already made for cracking can be also made for dehydrogenation. The true activation energies obtained by Lercher et al.,² 156–165 kJ/mol, Corma et al.,^{3b} 216–225 kJ/mol, and Stefanadis et al.,³¹ 289–298 kJ/mol, should be compared to the theoretical true

barrier, 326 kJ/mol, for ethane dehydrogenation. The difference is over 100 kJ/mol compared to the work of Lercher, nearly 100 kJ/mol compared to the work of Corma and only 30 kJ/mol compared to the work of Stefanadis. The additional information here is the comparison with the previous calculation for methane that gives the effect of stabilization of the intermediate formed in contact with the zeolite frame rather than in the gas phase, found to be only 50 kJ/mol. Taking only this last element into account, it is possible to say that the present results agree well with the measurements of Stefanadis et al.,³¹ but if one thinks that also a hydrogen transfer reaction has occurred in their reaction, this similarity must be accidental. Also the difference between the activation barriers obtained by Lercher et al.² and Corma et al.^{3b} with respect to the kind of intermediate formed is not clear. A more conclusive comparison is, at present, not possible. Kazansky et al.⁵ have performed calculations for the transition state of dehydrogenation of ethane, and their activation barrier was calculated to be 397 kJ/mol, the same as that for the cracking reaction, and so 100 kJ/mol higher than for the present study.

Figure 5b shows the geometry for the calculated transition state of dehydrogenation. The hydrogens H1 and H2 are at 0.86 Å away from each other, showing an almost formed H_2 molecule. The C–C bond, 1.47 Å, is shorter than in the free ethane molecule, calculated to be 1.517 Å, probably as a consequence of the stretching of the bond C1–H2. The geometry obtained is nearly the same as that obtained by Kazansky et al.⁵ except for the O1–H1 bond distance, which is 0.14 Å longer and, as a consequence, H2–C1 is 0.05 Å shorter. The O–Al–O angle is also different, but since different cluster models for the zeolite have been used, no adequate comparison is possible. The Mulliken charges are shown in Table 2. The tricoordinated carbenium ion has a total charge equal to +0.364. The almost formed H_2 molecule has a charge of +0.199, where H1 is almost neutral, +0.050, and H2 is +0.149. Kazansky et al.⁵ found a negative charge for H1, –0.207, resulting in an almost neutrally charged H_2 molecule. The charge of Al has been discussed in section 3.1.

At last, a discussion of the rate constants can be presented. Due to nearly the same activation barrier, the rate constants obtained for dehydrogenation are of the same order as those obtained for cracking(1) and cracking(2). The Arrhenius activation energy, 306 kJ/mol, as expected, is a little higher than the activation barrier, 297 kJ/mol. The ratio $A^{\text{TST}}/A^{\text{HS}}$ is almost 10 times smaller than for the reaction of hydrogen exchange. This indicates that, in this transition state, the ethyl group is more rigidly attached to the zeolite than for the previous reactions. Looking back to geometry and Mulliken charges for all discussed reactions, for hydrogen exchange, the system is nearly covalent and the C_2H_5 group neutral, indicating no strong interaction. For cracking, the carbenium ion formed is stabilized not just by the lattice oxygen but also by the almost formed methane molecule. In the case of the dehydrogenation, it is the lattice that is actually involved in the stabilization process of the carbenium ion formed, since the H_2 molecule contributes very few for that. This makes such a carbenium ion become rigidly bound to the zeolite, with a larger loss in rotation and translation movements.

3.5. Hydride Transfer. It was not possible to find a transition state for hydride transfer between methane and adsorbed methoxy, but only between methanol and the methoxide surface. Figure 6a shows the calculated transition state for the reaction of the hydride transfer of methanol when in contact with a methoxide species (ZOCH_3). The basic idea is

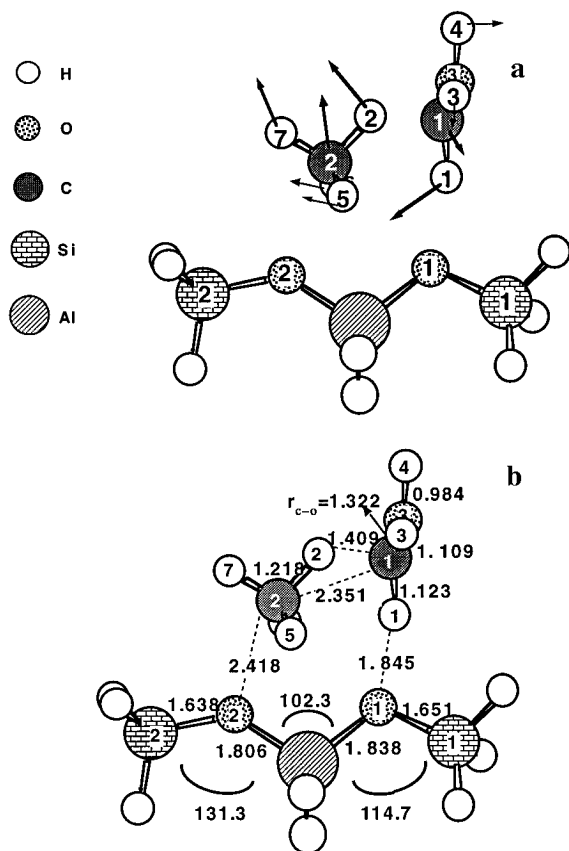


Figure 6. (a) Reaction coordinate and (b) geometry of the TS for the reaction of hydride transfer between methanol and a methoxy surface. Distances in angstroms and angles in degrees.

that methanol donates one of its hydrogens to the methyl group of the zeolite and becomes itself adsorbed in the zeolite. The arrows which represent the displacement of the atoms according to the imaginary mode show the left side almost formed methane molecule moving away from the zeolite surface. The right-side HOCH₂ group moves in the opposite direction toward the zeolitic oxygen, O1. The movement of methane formation is very clear. On the other hand, the movement of the HOCH₂ group toward the zeolitic oxygen involves the rotation of the C–H bond. Considering that C1, H1, and O1 are nearly in the same line, H1 needs to bend to the left side in order to give the chance to C1 to bind with O1. Due to the size limitation of the cluster used, where the silicon atoms are terminated by simple hydrogen atoms, at the end of the path search one of the hydrogens of the silicon atom was donated to C1. Such would not happen in a real zeolite. It is also interesting to note that the transition state obtained is very similar to the transition state for cracking(2). The basic difference is that, in this case, H2 is much closer to the methyl group than in the cracking(2) reaction.

On calculating the activation barriers, the system to be taken into account is now a methanol molecule and the zeolitic cluster which had its proton replaced by a methyl group (methoxide surface). The corresponding difference in energies can be found in Table 1. The activation barrier for this reaction is 202 kJ/mol. For the AlOH cluster it is 203 kJ/mol. Both AlH and AlOH transition states have been successfully optimized to only one imaginary mode. It has been shown earlier²⁶ that for the cases where a strong nonbonding hydrogen interaction exists, specially for adsorbed structures, it is necessary to include nonlocal corrections self-consistently. Nevertheless, no large difference in energy was observed²⁶ for the transition structures. So, in order to decrease the costs of the calculations, the

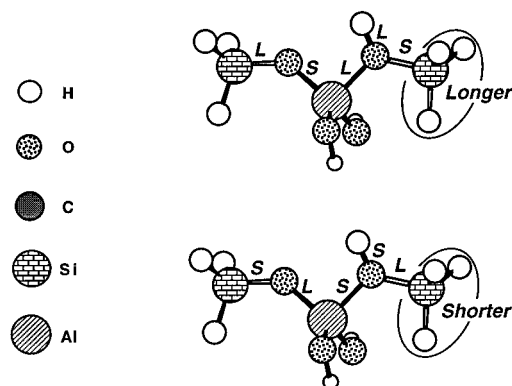


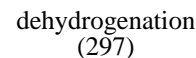
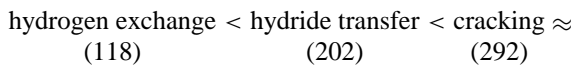
Figure 7. Change in the bond distances of the cluster according to changes in the Si–H bonds: S = shorter; L = longer.

structures have been obtained only with the NL correction, which has been included to the final LDA optimized geometry. This reaction is more difficult than that for dehydrogenation of methanol, 140 kJ/mol, with respect to the reactants.²⁶

The geometry of the transition state for hydride transfer is presented in Figure 6b. As discussed before, it resembles closely the transition state for cracking(2) (Figure 4a), except that now the C–C bond is longer by 0.4 Å and H2 has been almost totally transferred to the methyl group, with a C2–H2 distance of 1.218 Å. The hydrogens of the carbenium ion needed to bend a little in order to accommodate the hydrogen which came from methanol, not showing anymore the trigonal planar geometry. Mulliken charges show a little different picture for this transition state than for cracking(2). If the methanol molecule is considered, its total charge is +0.587, a lot positive, while the carbenium ion is less positive, +0.175. If one considers the methane molecule (+0.372) and the HOCH₂ group (+0.384), the charge seems to be more equally distributed. The oxygen and carbon atoms of methanol do not have large negative charge, –0.309 and –0.430, respectively. Actually it is somewhat surprising that the oxygen is less negative than C1.

The rate constants for hydride transfer are between hydrogen exchange and the other reactions, according to the increasing activation barrier. The ratio $A^{\text{TST}}/A^{\text{HS}}$, just like for hydrogen exchange and cracking(1), is in the order of 10^{-4} . It is thus a looser transition state than for cracking(2) and dehydrogenation. The Arrhenius activation energy (Table 1) difference with the activation barrier is large, 10 kJ/mol.

The reactivity sequence found for C–H and C–C activation of ethane (hydrogen exchange, dehydrogenation, and cracking reactions) and methanol (hydride transfer reaction) is (activation barrier in kilojoules per mole):



3.6. Acidity Effects. Kramer and van Santen⁴ have shown how the proton affinity (the theoretical measurement of the zeolite acidity) can be modified by chemical and structural variations in the zeolitic lattice. The proton affinity can be mimicked by constraining the peripheral bonds of the zeolite cluster. They^{4,7} show that by assigning different bond lengths to the terminal Si–H bonds of the cluster and optimizing all other parameters, the proton affinity varies over a range of 1–2 eV, which is the same magnitude as the expected variation in real zeolites. Figure 7 shows the general effect of changing the peripheral Si–H's distances for the zeolite cluster. On making Si–H's longer, the bond Si–O becomes shorter, and

TABLE 5: Effect of the Si–H's Distances (Proton Affinity) of the Zeolite over the Activation Barriers (kJ/mol)

Si–H's distance	hydrogen exchange	cracking(1)	cracking(2)	dehydrogenation	hydride transfer
equilibrium	118	292	292	297	202
left, shorter	132	297	301	303	213
left, longer	115	297	295	303	186
right, shorter	132	313	312	314	203
right, longer	115	279	283	291	199
left/right, shorter	125	310	310	311	216
left/right, longer	122	279	280	291	185

as a consequence, O–H longer. In another words, the bond O–H becomes weaker, and the zeolite, more acidic. In the opposite way, to make Si–H bonds shorter represents making the zeolite cluster less acidic. If the Si–H bonds in the left side of the cluster are changed instead, the effect is nearly the same, but now it is of “long distance”, and so, weaker. To change the Si–H bonds in the transition structures will provoke a different response according their nature, more covalent or ionic. The alternation in the bond distances due to the change in Si–H bond length are in agreement with the bond order conservation (BOC) arguments.³³ A few distances presented an anomalous behavior according changes in the peripheral Si–H bonds. An example is the case where the Si–H's are made shorter in the AlH cluster, which results in the O–H bond becoming longer. This effect is probably because the compression of the Si–H bond changes mainly the repulsive interaction potential between the hydrogen and silicon atoms. This can cause a significant rehybridization of the valence electrons around Si, so that the bond order conservation principle no longer applies.

Table 5 shows the effect of changes in the proton affinity of the zeolite on the activation barriers for the studied reactions. Making the Si–H distances for the cluster and hydrogen exchange's TS (Figure 1a) in one side shorter, which means making the zeolitic site less acidic by decreasing the bond strength of the zeolite–proton, the activation barrier is found to increase to 132 kJ/mol. To make the O–H bond longer, resulting in the weakening of the O–H bond, results in the decrease of the activation barrier to 115 kJ/mol. Changes in the Si–H bond lengths on the right-hand site have a similar effect as changes in the left-hand site, due to the symmetrical characteristic of the transition state. When the Si–H's in both sides are made longer or shorter simultaneously, there is compensating change in the relative energies, as it can be seen in the small increase in the activation barrier for both cases (longer and shorter). This was found before,⁴ and it is due to the covalent nature of the transition state. The energy barrier depends on the difference in the proton affinity of O1 and O2.

The effect of changing the distances of the terminal Si–H bonds for the reactions of cracking(1) and -(2) and dehydrogenation (Figures 3a, 4a, and 5a) is nearly the same, but very different than it was for hydrogen exchange. This difference in behavior between these transition states is due to the difference in the ionic contributions to the interaction energy. When the interaction is purely ionic, it only depends on the oxygen charges and is thus not significantly affected by changes in Si–H bonds. In agreement with this, the dominating parameter that controls the activation barrier is the bond energy of the proton in its ground state. Changes in the left-side Si–H bonds almost do not affect the activation barrier, but only in the right side. The increasing acidity (longer zeolite–proton distance or, in another words, lower proton bond energy) reduces the activation barrier for dehydrogenation reaction less than for cracking, implying that the transition state for cracking is more ionic.

The general effects of the zeolitic structure on the hydride transfer activation barrier are the same as for cracking and

dehydrogenation, except that now it is the left-side Si–H bond distances which actually affect the barrier. This is because the barrier is now controlled by the strength of the O–C bond of the methyl group, adsorbed on the left side of the cluster. To increase the acidity of the zeolite, making the Si–H's longer in the left side represents the largest reduction of the barrier, compared to all other transition structures. So, the hydride transfer reaction can be considered as having the most ionic transition structure comparing to all studied reactions.

4. Conclusions

The reactions of hydrogen exchange, cracking, and dehydrogenation of ethane catalyzed by an acidic zeolite cluster model and additionally, the reaction of hydride transfer between methanol with a methoxide surface have been studied using the DFT method. The consequences of the changes in oxygen proton affinity on the activation barriers were investigated. Reaction rate constants were obtained by means of the transition state reaction rate theory.

The activation barrier for the acid catalyzed hydrogen exchange of ethane, 118 kJ/mol, is nearly the same as that previously estimated⁴ and calculated⁶ for methane. The effect of an additional carbon atom in this structure is small. The transition state obtained is rather covalent, and its geometry resembles a carbonium ion. Its Mulliken charges represent, nevertheless, a neutral C₂H₅ group covalently bonded to H₂⁺···OZ⁻. Between all studied reactions for ethane, the hydrogen exchange transition state is the loosest. To increase the zeolite acidity by making the Si–H's bonds in one side of the hydrogen exchange TS and cluster longer makes the barrier decrease and vice versa. If both sides are changed, the activation barrier almost does not change, showing the covalent character of this transition state.

Two different transition states were obtained for the cracking reaction. For the first, the direct cracking takes place. For the other, the reaction path involves one more step corresponding the rotation of the ethane molecule from the conformational isomer *staggered* to *eclipsed*. This last is close to the one obtained in a previous HF calculation.²⁹ Both transition states obtained present the same activation barrier, 292 kJ/mol, which is nearly 2.5 times larger than that for hydrogen exchange. They are of ionic nature and have the characteristics of a carbenium ion.

The activation barrier for the dehydrogenation reaction, 297 kJ/mol, is slightly larger than that for cracking. Again the transition state has to be characterized as ionic, generating a carbenium-type fragment. The activation barrier for dehydrogenation is less sensitive to the initial proton–oxygen interaction energy than it is for the cracking reaction, which is more strongly affected by an increase in acidity.

Hydride transfer of methanol has a calculated activation barrier of 202 kJ/mol. The transition state obtained is again to be characterized as loose, implying a weak interaction with the zeolitic cluster. An increase in the acidity decreases the barrier for the hydride transfer reaction more strongly than for all other reactions, showing this to be the most ionic transition structure between all other presented in this study.

Acknowledgment. S.R.B. thanks the National Council of Scientific and Technologic Development (CNPq, Brazil) for a scholarship. M.A.C.N. thanks CNPq and Finep for financial support. Computational resources were supplied by the national computing facilities foundation (NCF, The Netherlands) under Project SC-183.

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JP9523231