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Toward Better Understanding of the Catalytic Action of Acidic Zeolites: Investigation in Methane and Ethane Activation and Transformation

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Abstract

Studies of cracking reactions of alkanes with three or more carbon atoms have been central to the development of our understanding of the catalytic action of acidic zeolites, which are important catalysts in petrochemical and chemical industries. However, the mechanisms of the simplest cracking reactions, i.e. the cracking of the C−H and C−C bonds in methane and ethane, have only been studied theoretically, not experimentally. Here we show that ethane is converted over a H-MFI zeolite at 510-550 ^{o}C with formation of such primary products as ethene, hydrogen, methane and propane. To explain these results, we suggest and consider two catalytic cycles of the reaction. The first cycle involves protolytic cracking of the C−H bond with formation of hydrogen and ethoxide group, the latter decomposing into ethene and the zeolite acid site. We propose that the second cycle is initiated by the protolytic cracking of the C−C bond that results in formation of methane and a methoxide group as an intermediate. We theorize that this reacts with ethane molecules regenerating the zeolite acid site and producing (i) methane and ethene via hydrogen transfer and (ii) propane via a C−C bond formation reaction. Both suggested catalytic cycles are fully supported by the kinetic results of this study and are in a good agreement with recent theoretical work. We also demonstrate that the cracking of the C−H bond in methane (that could proceed via methoxide intermediate) does not occur over H-MFI zeolites up to 700 ^{o}C most likely due to high activation energy. The proposed involvement of methoxide groups, as active intermediates, in ethane transformation provides a basis and excellent opportunity for theoretical studies of such interesting reactions as hydrogen transfer and C−C bond formation with participation of these surface species.

1. INTRODUCTION

Zeolites are crystalline aluminosilicates with pore diameters typically in the range between ca 0.3−1 nm. Due to these 'molecular' dimensions of the pores, zeolites are frequently called molecular sieves and display shape-selective properties. Acidic zeolites, which contain Brønsted acid sites (BAS), i.e. hydrogen atoms attached to the oxygen atoms of the zeolite framework, have been widely used for many years in petrochemical and chemical industries as catalysts in such important processes as hydrocarbon cracking, isomerization and alkylation.[1-3] Nowadays, these materials are finding increasing application in the production of fine chemicals.[3,4]

The current understanding of the mechanisms of the zeolite-catalyzed reactions[5-24] has evolved largely on the basis of the concept of carbonium and carbenium ions (species (I) and (II) in Figure 1), which was originally developed for hydrocarbon reactions in superacids (e.g. $FSO_3H−SbF_5$, $HF−SbF_5$, etc).[25,26] In superacids, these ions act as reaction intermediates, while in zeolite catalysis, covalent alkoxide species appear to be the true reaction intermediates and carbocations are likely to represent transition states.[8-24] Protons (H^+_{SA}) are readily available in superacids (Figure 1), while in zeolites, hydrogen atoms (H_Z) required for the acid catalysis are covalently bonded to the framework oxygen atoms. As such, they have a partial positive charge (δ^+) only.[13] This difference in the states of hydrogen atoms results in the much lower acidity of zeolites in comparison with superacids, thus dictating much higher temperatures for reactions occurring on zeolites.[6,13-16]
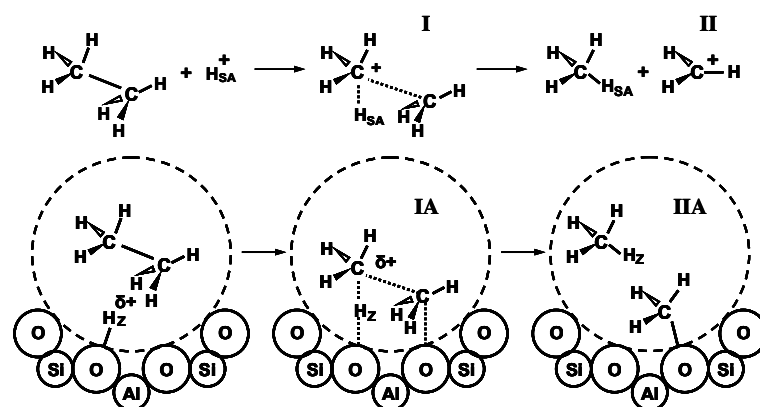

Figure 1. Schematic representation of protolytic cracking of C−C bond in ethane in superacids (top) and in zeolite pores (bottom). In superacids, the reaction intermediates (I) and (II) are stabilized by the interactions with the molecules of superacids.[25,26] In zeolites, the carbonium-like transition state (IA) and the intermediate surface methoxide group (IIA) are stabilized by interactions with the oxygen atoms that form the walls of the zeolite channels.[13]

Qualitative analogies between the two reaction systems, which are illustrated for ethane reaction by Figure 1, are well documented for the protolytic cracking of C−C and C−H bonds in alkanes with three or more carbon atoms (C_{3+}).[5-7,11,12,18,27-35] However, in the case with ethane, only limited experimental information is available.[28,36] It shows that the protolytic cracking of the C−C bond in ethane with formation of methane does indeed take place over acidic zeolites with the MFI structure,[37] but does not contain data regarding the mechanism of this reaction. In particular, it is not clear what happens with the methoxide group (IIA in Figure 1) generated during methane formation (note that the methoxide group is the only one alkoxide group that cannot decompose into proton and alkene).

Interestingly, theoretical studies of ethane transformation[38-40] do not shed light on this question, as the focus is on the cracking of C−C and C−H bonds only and no catalytic cycle is considered in these studies. This lack of understanding is even more striking when considering methane as a reactant. Indeed, the activation of a C−H bond in methane by superacids via formation of the CH_5^+ carbonium ion (eq 1) was discovered in the late 1960s[41,42], yet to date, no analogous reaction has been reported for acidic zeolites in spite of five decades of extensive research in zeolite catalysis. The latter fact is significant in view of the tremendous interest in methane catalytic activation[43-46] and in the mechanisms of alkane cracking reactions over acidic zeolites.[5-7,11-13,15,21,27-35]

$$CH_4 + H^+ \rightarrow CH_5^+ \rightarrow H_2 + CH_3^+ \tag{1}$$

The importance of the cracking of C−H bonds in methane (with formation of a methoxide group and H_2) for in-depth understanding of the mechanisms of the zeolite catalysed reactions was highlighted by theoretical studies of methane activation.[13,47,48] Truly, this is the simplest possible cracking reaction and, therefore, to complete the full picture of alkane protolytic cracking, it is vital to answer the following questions: Does this reaction really take place on acidic zeolites (as indicated by theory[13,47,48])? If not, then what is the reason? If yes, then what is the fate of the methoxide groups (these are the sole alkoxide groups that cannot decompose in alkene and hydrogen)? How do experiments correlate with theory?

In this work, we attempted to address the questions raised above. We will first consider the results of the investigation into ethane cracking, and we will then proceed to the discussion of transformation of methane.

2. EXPERIMENTAL SECTION

Methane and ethane (both 99.9999 %) were obtained from BOC, and the MFI zeolites with Si/Al ratios of 15 and 36 were purchased from Zeolyst. Details of the preparation of the H-forms of the zeolites and their characterization were reported previously.[49,50] Reactions of methane and ethane were studied at atmospheric pressure in a continuous down-flow quartz reactor with methane or ethane as a feed. The reaction mixture was analyzed by on-line GC using Varian CP-3800 Gas Chromatograph,[50,51] which was equipped with a molecular sieve 13X packed column and a thermal conductivity detector (TCD) for analysis of H_2, and a 25 m long PLOT Al_2O_3/KCl capillary column with a flame ionization detector (FID) for analysis of hydrocarbons (argon was used as a carrier gas in both columns). TCD was calibrated using gas mixtures with different H_2 concentrations.[51] Prior to the kinetic experiments, the catalyst samples were heated (1 °C/min) in the reactor under flowing air (30 ml/min) to 700 or 550 °C (for methane and ethane experiments, respectively) and kept at this temperature for 4 h. The temperature was then reduced to the reaction temperature and the catalyst sample was purged with N_2 (50 ml/min) for 1 h before switching to the flowing methane or ethane. Different levels of conversions were obtained at different values of contact time that was varied by changing the reactant flow and/or catalyst loading.

3. RESULTS AND DISCUSSION

3.1. Transformation of ethane

Our study was focused on investigation of ethane reaction at very low conversions, as the aim was to figure out the primary products of this reaction and the reaction steps involved in the formation of these products. To achieve this goal, we performed catalytic experiments in a continuous flow reactor at three different temperatures (510, 530 and 550 °C) and different contact times, with an acidic zeolite H-MFI (Si/Al = 36) as a catalyst.

Similar product distributions were observed at three different temperatures, the key difference established was in the conversion levels achieved. Figure 2 shows the strong effect of temperature on the conversion of ethane, which was to be expected on the basis of theoretical calculations of the activation energies of C−C and C−H bond cracking in ethane.[38-40] Figure 3a illustrates the distribution of three dominant products, methane, ethene and hydrogen, at 550 ^{o}C, and similar data obtained at 510 and 530 ^{o}C are presented in Figure S.1 of the Supporting Information. The results demonstrate clearly that these products are formed in the initial reaction steps (the concentrations increase immediately with the increasing conversion). Most likely, these steps involve the protolytic cracking of the C−C and C−H bonds in ethane at the zeolite BAS (HOZ), as shown in equations 2 and 3 (ethene is produced in the desorption step 4). The validity of steps 2 and 3 is strongly supported by theory.[40] Another key point, evident from Figure 3a, is that ethene is formed in excess compared with hydrogen, indicating that it is produced not only in reaction 3. We suggest that the additional step for ethene formation in the initial catalytic cycle is the well known hydrogen transfer reaction[6,13,29-31,35,52] that in our case could occur between ethane and methoxide groups, as illustrated by reaction 5. Thus, reactions 2, 4 and 5 lead to eq 6 that shows the stoichiometry of the catalytic cycle involving the protolytic cracking of the C−C bond in ethane with formation of methane and ethene.
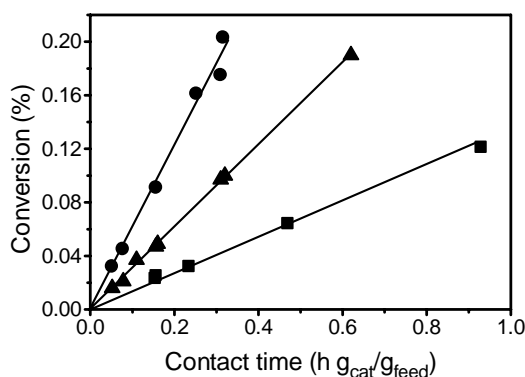
$$CH_3CH_3 + HOZ \rightarrow CH_4 + CH_3OZ \quad\quad (2)$$

$$CH_3CH_3 + HOZ \rightarrow H_2 + CH_3CH_2OZ \quad\quad (3)$$

$$CH_3CH_2OZ \leftrightarrows CH_2CH_2 + HOZ \quad\quad (4)$$

$$CH_3CH_3 + CH_3OZ \rightarrow CH_4 + CH_3CH_2OZ \quad\quad (5)$$

$$2CH_3CH_3 = 2CH_4 + CH_2CH_2 \quad\quad (6)$$

Figure 2. Effects of contact time and temperature on the conversion of ethane. Temperature: (■) 510, (▲) 530 and (●) 550 ^{o}C.

It should be noted that the proposed reaction steps 2 to 5 involve such intermediate species as methoxide and ethoxide groups, which were not observed experimentally in this work (this task was outside the scope of the present study). However, the possibility of formation of these surface species in alkane cracking over acidic zeolites is strongly supported by theoretical studies.[13,15,17-19,39,40] Also, it is essential that the formation of methoxide groups in H-MFI zeolites at elevated temperatures was demonstrated previously by IR spectroscopic experiments.[53-55] The validity of the reaction steps 2 to 5 as well as the stoichiometric equation 6 is further confirmed in our work by the calculation of the ethene concentration that is shown as a dotted line in Figure 3a. This was calculated using concentrations of hydrogen and methane according to the stoichiometry of reactions 3 and 6. Clearly, the

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calculated concentration is marginally higher than the experimentally observed ethene concentration. This can be explained by secondary reactions of ethene. However, another alternative reason for the observed discrepancy could be the existence of other reaction steps that complete the catalytic cycle involving the cracking of the ethane C−C bond with formation of methane molecules and methoxide groups (reaction 2). If the latter assumption is correct than formation of other primary products in addition to methane, ethene and hydrogen can be expected.
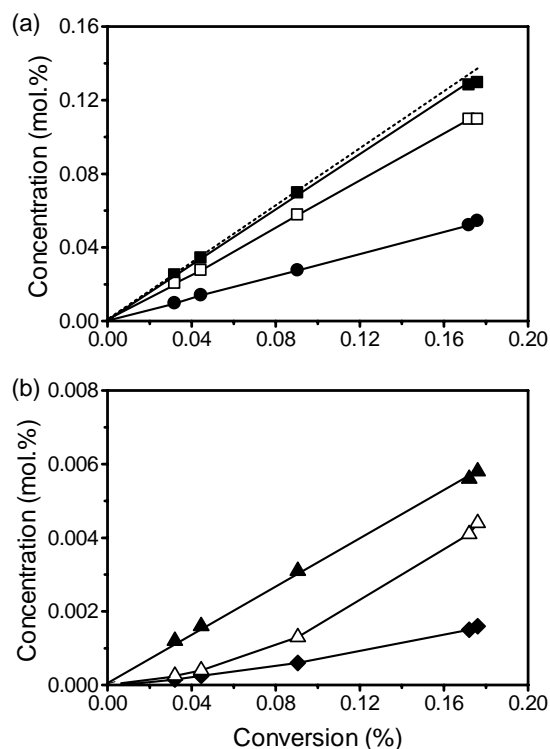

Figure 3. Product concentrations as functions of ethane conversion at 550 $^{\circ}$C: (a) methane (●), ethene (■) and hydrogen (□), and (b) propane (▲), propene (△) and C_4 hydrocarbons (◆). The dotted line corresponds to the calculated concentration of ethene if one mole of ethene were formed for each mole of hydrogen (eqs 3 and 4) and every two moles of methane (eq 6).

A range of other products were formed in our experiments, however those that were consistently observed in measurable amounts were propane, propene and C_4 hydrocarbons (mixture of butanes and butenes), as shown in Figure 3b for 550 $^{\circ}$C and Figure S.1 of the Supporting Information for 510 and 530 $^{\circ}$C. The first key point to note is the apparent linearity of propane formation with concentrations tending to zero as ethane conversion goes to zero, thus indicating the propane formation in the primary catalytic cycle. In contrast, the concentrations of both the propene and C_4 hydrocarbons appear to go to zero before ethane conversion drops to zero. Such behavior is characteristic for formation of secondary reaction products[35,56], and we can therefore conclude that propene and C_4 hydrocarbons are secondary products of ethane reaction over acidic H-MFI zeolite. A number of reaction steps could be responsible for their formation, and the most likely steps include the oligomerization and cracking of alkenes,[6,29,35,56,57] initiated by ethene dimerization in our case, and the hydrogen transfer reactions[6,29,31,35,52] between propyl and butyl alkoxide groups and ethane.

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The apparent formation of propane as a primary product of ethane reaction over an acidic zeolite appears to be quite surprising at the first glance. However, if one recalls the chemistry of ethane transformation in superacids,[41,42] then such an event can be explained by the formation of the C−C bond in the reaction between ethane and a methoxyde group as shown in eq 7. Further consideration reveals that this chemistry, although unexpected for the zeolite catalysis, could in fact be predicted, since reaction 7 is simply the reverse step to the protolytic cracking of propane, which is well documented reaction in catalysis by acidic zeolites.[13,28,30-35,56] Thus, assuming that reaction 7 is indeed taking place, we can now depict the stoichiometry of the catalytic cycle that involves the protolytic cracking of the C−C bond in ethane with formation of methane and propane. This stoichiometry is shown in eq 8 that is based on reactions 2 and 7 considered together.

$$CH_3CH_3 + CH_3OZ \rightarrow CH_3CH_2CH_3 + HOZ \qquad (7)$$

$$2CH_3CH_3 = CH_4 + CH_3CH_2CH_3 \qquad (8)$$

To verify quantitatively the suggested reaction steps 2 to 5 and 7, we determined the rates of formation of ethene, hydrogen, methane and propane using the experimental data shown in Figure S.2 of the Supporting Information. These rates are presented in Table 1 that also includes the calculated rate of ethene formation (bottom row) based on the experimental rates of formation of hydrogen, methane and propane and following the stoichiometry of eqs 3, 6 and 8. Clearly, the calculated rate of ethene formation is in excellent agreement with the experimental one, thus providing strong support for the reaction scheme proposed above and highlighting the similarity of the alkane reactions occurring over acidic zeolites and in superacids.[41,42] It should also be noted that the suggested propane formation (reaction 7) agrees very well with the recent work of Gounder and Iglesia that demonstrates the formation of the C−H and C−C bonds in reactions of alkenes with hydrogen[58] and methane.[59]

Table 1. Rates of formation of the primary products of ethane reaction at different temperatures[a]

Temperature (°C)	510	530	550
Ethene	33.3	76.9	152
Hydrogen	27.4	63.9	125
Methane	13.6	31.2	59.5
Propane	1.60	3.53	6.68
Ethene (calculated)[b]	33.4	77.7	151.4

[a] Rate units are μmol/(h g$_{cat}$). [b] Rate of ethene formation in the bottom row was calculated according to the following stoichiometry: $R_{C2H4} = R_{H2} + 0.5(R_{CH4} − R_{C3H8})$.

Let us now consider the experimental data on the rates of formation of methane, ethene and hydrogen at different temperatures. This data is shown in Figure 4, and it is clear that the rates are following the Arrhenius dependence. We use the rates of formation of hydrogen and methane to estimate the activation energies of the protolytic cracking of the C−H and C−C bonds, respectively, and obtain the following estimates for these two reactions: 196 and 194 kJ/mol. Our value of 194 kJ/mol for the C−C bond cracking (reaction 2) is only slightly lower than the theoretical value of 208 kJ/mol for this reaction. The latter was calculated using a large H-MFI zeolite cluster with 58 tetrahedral (Si, Al) atoms at the MP2(FC)/6-311+G(3df,2p)//MP2(FC)/6-31G9d) level of theory,[40] and represents the difference between the "true" activation energy of the C−C bond cracking in the adsorbed ethane molecule (226 kJ/mol) and the adsorption energy of ethane (18 kJ/mol). Taking into account that the adsorption energy of ethane in the MFI zeolites[40,60] is likely to be higher than 18

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kJ/mol, we can conclude that our experimental estimate of the activation energy agrees well with the theoretical value obtained with the 58T cluster model. It is also worth to note that the apparent activation energies of the protolytic cracking of the C−H and C−C bonds, obtained in this work, are very similar. This finding is in a good agreement with the earlier theoretical study of these two reactions that yielded the values of 297 and 292 kJ/mol for the cracking of the C−H and C−C bonds, respectively[39] (the absolute values of the activation energies are significantly overestimated in this study, as noted by the authors, due to very small zeolite cluster (3T) model used).
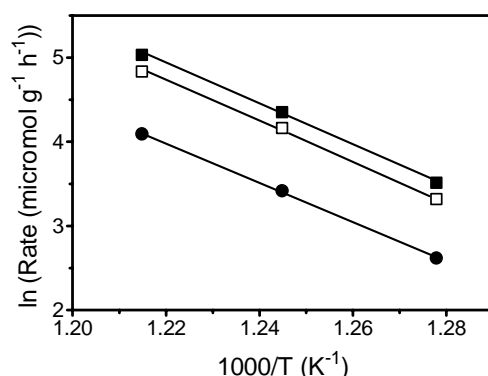

Figure 4. Arrhenius plots for the rates of formation of (■) ethene, (□) hydrogen and (●) methane. Based on the rates of hydrogen and methane formation, the activation energies were calculated to be 196 and 194 kJ/mol for cracking of the C−H and C−C bonds, respectively.

3.2. Transformation of methane

In this section, we will focus on the consideration of activation and transformation of methane on acidic zeolites. This reaction has not yet been reported, but theory indicates that it could take place at high temperatures.[13,47,48] Based on the theoretical studies, one can suggest that methane activation at the zeolite BAS, if it indeed takes place, should proceed via protolytic cracking of the C−H bond with formation of molecular hydrogen and methoxide groups (eq 9). The subsequent reactions of these groups were not considered previously in the literature. Hence, using the analogy with reactions in superacids,[41,42] we suggest that the most likely reaction of the methoxide groups (that complete the catalytic cycle) is their interaction with methane molecules as shown in eq 10.

$$CH_4 + HOZ \rightarrow H_2 + CH_3OZ \qquad (9)$$

$$CH_4 + CH_3OZ \rightarrow CH_3CH_3 + HOZ \qquad (10)$$

At first glance, the idea of the C−C bond formation from the methoxide group and methane may look unrealistic. However, this reaction represents the reverse reaction of the C−C bond cracking in ethane at BAS (Figure 1 and reaction 2) and, as such, should proceed with lower activation energy than the forward (cracking) reaction.[38-40] Thus, it is likely that methane, if activated, can produce ethane as a major product (together with H_2). This hypothesis, if confirmed, would lead us to the second example of the formation of a C−C bond from alkanes at the acid sites of zeolites (the first example being the formation of propane from ethane as discussed earlier in this paper).

To test our hypothesis, we conducted catalytic experiments with pure methane (99.9999 %) and the same H-MFI catalyst as was used for ethane reaction. We did not observe any products in measurable amounts up to 600 $^{\circ}$C. At higher temperatures, formation of ethane and hydrogen was observed, as shown in Figure 5 for 700 $^{\circ}$C.
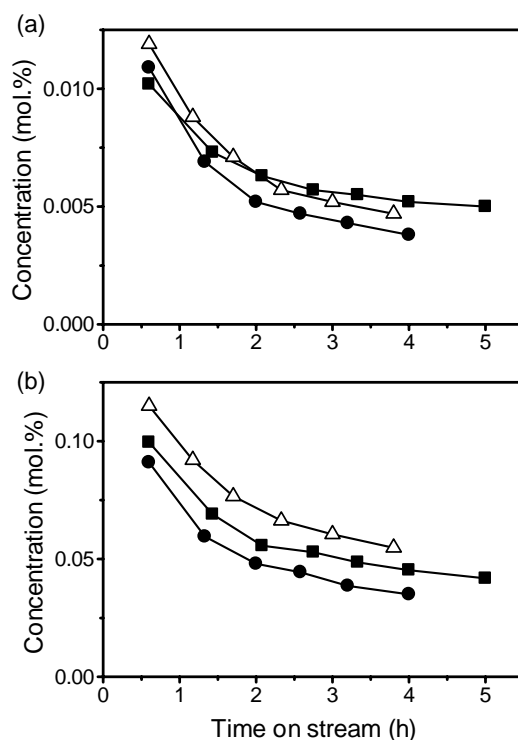

Figure 5. Effect of time on stream on the products of methane transformation at 700 $^{\circ}$C. (a) Concentration of ethane. (b) Concentration of hydrogen. Reaction was carried out over (■) H-MFI (Si/Al = 15) and (△) H-MFI (Si/Al = 36) catalysts, and (●) without a catalyst. The same flow of methane (15 ml/min) was used in all three experiments, and the catalyst loading was 500 mg in the experiments with the catalysts.

Figure 5 reveals that hydrogen was formed in very large excess (~10 times) in comparison with ethane, indicating formation of the carbon-rich deposits in the reaction system. The product concentrations were changing with time on stream in contrast to the transformation of ethane, which was stable between 1 and 5 hours on stream. Similar amounts of the products were observed in the methane experiments with more acidic H-MFI zeolite (Si/Al = 15) and, what is even more significant, in the experiments without a zeolite catalyst (Figure 5). Clearly, methane was not activated over acidic H-MFI zeolites under the reaction conditions used in this work, but was probably undergoing non-catalytic transformation (methane pyrolysis). In our opinion, the likely reason for the observed "inertness" of methane with regard to its transformation on BAS of H-MFI zeolites is the high activation energy of reaction 9. The latter, according to theory,[39,48] may be about 50 kJ/mol higher than in the case of the analogous reaction of ethane (eq 3). This estimate, however, requires re-evaluation, as it was obtained using very small zeolite cluster model.[39,48]

4. CONCLUSION

This work demonstrates that ethane is converted over a H-MFI zeolite at 510-550 ^{o}C with formation of such primary products as ethene, hydrogen, methane and propane. Formation of propane as a primary product was quite unexpected, so was the noticeable excess of ethene in comparison with hydrogen. To explain these results, we suggested and then considered two catalytic cycles of the reaction that are shown in the upper part of Figure 6.
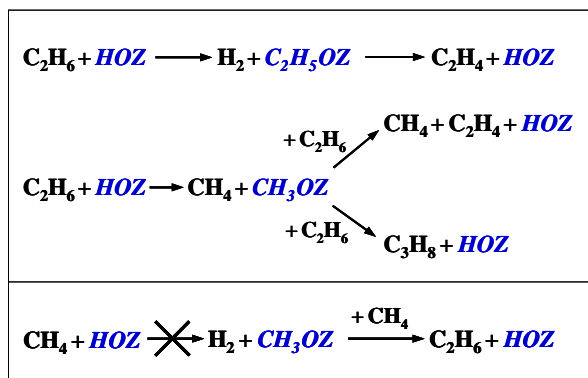

Figure 6. Proposed catalytic cycles of ethane (top) and methane (bottom) transformations over BAS in zeolites. Ethane reaction was observed. Methane reaction was considered but was not observed.

According to the kinetic data, the first cycle involves the protolytic cracking of the ethane C−H bond with formation of hydrogen and ethoxide group, the latter decomposing into ethene and the zeolite BAS. We propose that the second cycle is initiated by the protolytic cracking of the ethane C−C bond that results in formation of methane and a methoxide group as an intermediate. We theorize that this reacts with ethane molecules regenerating the zeolite BAS and producing (i) methane and ethene via hydrogen transfer and (ii) propane via a C−C bond formation reaction. Both suggested catalytic cycles are in a good agreement with theory[13,15,17-19,39,40] and are fully supported by the kinetic results of this study. We also demonstrate that the protolytic cracking of the C−H bond in methane (that could, in principle, proceed via a methoxide intermediate, as shown in Figure 6) does not occur over H-MFI zeolites up to 700 ^{o}C most likely due to high activation energy.

In our opinion, the proposed involvement of methoxide groups, as active intermediates, in ethane transformation provides a basis and excellent opportunity for theoretical studies of such interesting reactions as hydrogen transfer and C−C bond formation with participation of these surface species. Another important and challenging task is to confirm experimentally (with spectroscopic techniques) the formation of methoxide groups during ethane cracking reaction.

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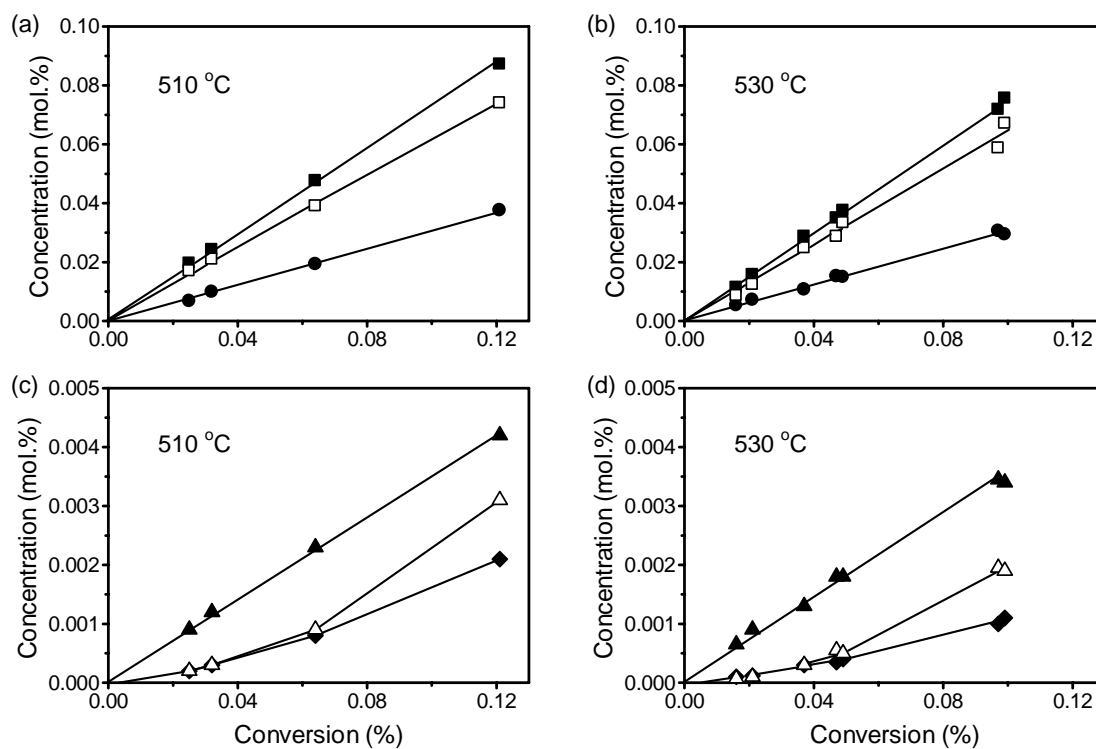
Figure S.1. Product concentrations as functions of ethane conversion at 510 and 530 ^{o}C. (a) and (b) Concentrations of methane (●), ethene (■) and hydrogen (□). (c) and (d) Concentrations of propane (▲), propene (△) and C_4 hydrocarbons (◆).
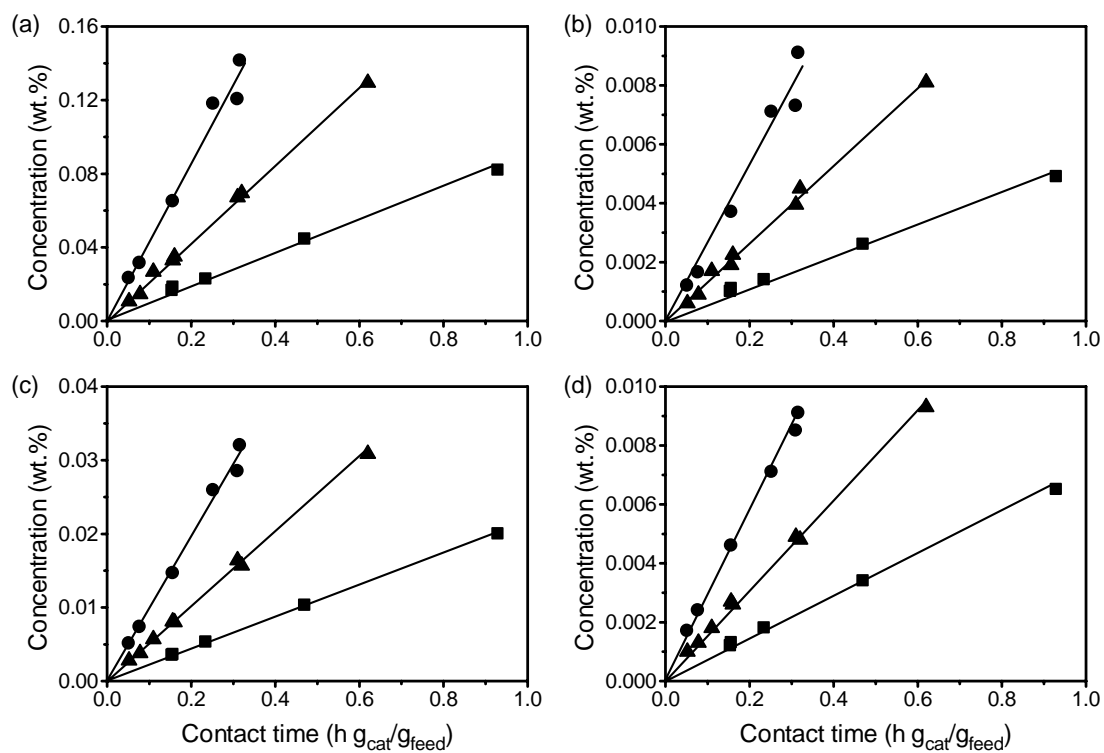
Figure S.2. Effect of contact time and temperature on the product concentrations: (a) ethane; (b) hydrogen; (c) methane; (d) propane. Temperatures: (■) 510, (▲) 530 and (●) 550 °C.