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DFT quantum chemical modeling of the interaction of alkenes with Cu^+ sites in zeolites

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Abstract

In this work charge transfer phenomenon between the admolecule and the active site and its consequences for the bond weakening/strengthening in the adsorbed molecule are discussed on the example of unsaturated hydrocarbons (early alkenes) interacting with Cu^+ cation embedded in a model of ZSM-5 zeolitic site. Detailed comparison of ethene interaction with various metallic sites based on this work and comparative analysis of other related studies helps to formulate working rules of charge transfer decomposition and interpretation. All studied alkenes form strongly bonded π complexes and become strongly activated on Cu^+ sites in ZSM-5 by both processes: π donation and π^* back-donation, what clarifies the mechanism by which the activation of the C=C bond in alkenes adsorbed on Cu^+ZSM-5 takes place. Calculated shifts in C=C stretching frequencies qualitatively follow the experiment and are a good measure of the activation.

Keywords: Alkene activation; IR spectra; Copper active sites; CuZSM-5; DFT modeling

1. Introduction

Heterogeneous catalytic systems are extended materials with intricate properties of surfaces and active sites thus the interaction of e.g. a hydrocarbon molecule with the site is complicated and may be ascribed to a wide range of events. Decoupling global effect into individual physical or chemical interactions is hardly possible. In many cases, only minor effects in the intra-electronic structure accompany molecular adsorption and the adsorbing molecule remains almost unchanged in its geometry. In this case usually an overall weak surface interaction reflects weak local adsorbate–substrate binding. This contrasts the systems where the adsorption process leads to a major geometry rearrangement in the adsorbing molecule. This usually denotes strong interaction between the adsorbate and the surface active site. However, this may happen also when the global interaction is weak, such as unsaturated hydrocarbons on metal surfaces [1–3] or on metal sites in zeolites [4,5]. In these systems large intra-molecular electronic structure rearrangements cannot be neglected even for weak adsorption. Therefore it is important to find any relations of molecular properties, charge transfer or spectroscopic parameters to the strength and mode of adsorption and, what follows, to the way the admolecule is affected.

In this work we address charge transfer between alkenes and the active site and its consequences for the bond weakening/strengthening in the adsorbed molecule shown by IR measurements [6,7]. We focus on unsaturated hydrocarbons (early alkenes) and their interaction with Cu^+ cations, where the interaction with the site is fairly weak but its effect on the bond activation is large. Copper sites formed by Cu^+ cations in zeolites, particularly in ZSM-5, are famous from high activation ability, which for NO molecule results in its decomposition. Our former quantum chemical studies on NO–Cu^+ZSM-5 systems showed that π back-donation of *d* electrons of the copper cation to π^* orbitals of NO was crucial for this interaction [8–12]. Clear picture of the source of NO activation emerging from that study suggested that such activation might also occur for other molecules with unoccupied π-antibonding orbitals interacting with the site, e.g. alkenes. Indeed, our experimental and preliminary calculation results, reported already elsewhere [6,7] indicate that Cu^+ in zeolites is also able to activate other π electron systems by π back-donation of *d* electrons of copper to

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π^*-antibonding orbitals. Moreover, in the case of alkenes this mechanism adds to the activation of the C=C bond by π donation, which further enhances the effect compared to NO. In line with this prediction, both experimental and quantum chemical DFT studies of the adsorption of alkenes on copper cationic sites in ZSM-5 showed distinct weakening of the C=C bond (IR red shift reached 78–115 cm^{-1} for CuX, CuY or CuZSM-5). Interestingly, in the case of ethene the stretching of the C=C bond, which was IR inactive in a free molecule became IR active when interacting with Cu^+, indicating the loss of symmetry. On the contrary, the stretching C=C in *trans*-but-2-ene was still IR inactive when *trans*-but-2-ene interacted with Cu^+ site.

It follows from the above introducing remarks that the charge transfer for the ad-systems between alkenes and the copper active site may have more than two components influencing directly the bond activation that could be not easy to separate. In this paper we present and discuss quantum chemical calculations for a model representing Cu^+ site in ZSM-5, with the focus on molecular properties of an adsorbate that are responsible for a good match between the adsorbate and the site and enhance the ability of an electron accepting molecule to gain charge. The charge is transferred from the framework to the adsorbed molecule via copper center playing a role of a good electron transmitter. Secondly, we underline similarities and differences between copper sites embedded in various environments and illustrate the role of a zeolitic framework acting as a reservoir of electrons [13]. Finally we summarize the mechanism by which the activation of the C=C bond in alkenes adsorbed on Cu^+ZSM-5 takes place.

2. Models and quantum chemical methodology

The calculations have been performed for the interaction of small alkene molecules (n = 2–4) with the model of a cationic copper site in ZSM-5 constructed on a template for MFI structure taken from Accelrys databases (Materials Studio software). Al positions in zeolites with low aluminum content are not known thus the template was used only to model general local structure cut off the framework. On the basis of other previous work [14–16] and our own experience [8–12,17] we selected simple cluster shown schematically in Fig. 1, composed of two fused 5T rings forming simultaneously 6T ring, with two aluminums positioned at the five-ring junctions (M7) as the model for the α copper site in MFI zeolite. OH^- groups saturated cluster boundaries and two protons were positioned on oxygen bridges, which gave neutral cluster model. This cluster served as a host for the exchanged copper monocation, the remaining proton was left on the bridge extending out from the six-ring. Geometry of the cluster was optimized with positions of terminating hydrogens fixed to partly account for the constraints imposed by the surrounding framework. Reference calculations for Cu^+ hosted in the site gave the monovalent copper cation coordinated by two strong and two weaker bonds to framework oxygen atoms with the bond distances equal to 2.04, 2.05, 2.24 and 2.43 Å, respectively (see Fig. 1). This model has already been

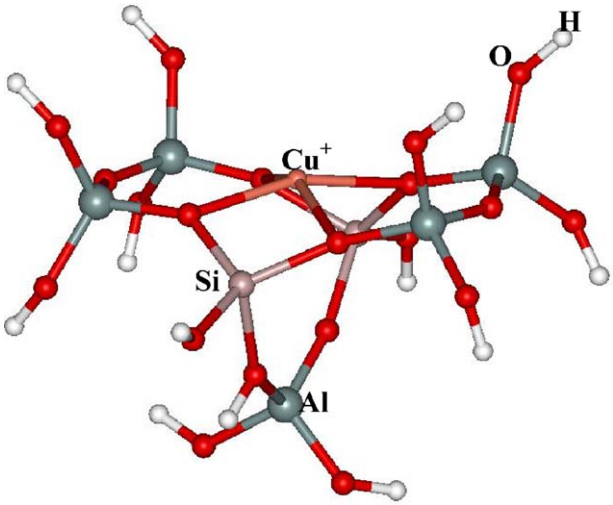

Fig. 1. The model of copper cationic center in zeolite ZSM-5.

successfully used in our previous studies [8–12,17]. Being simple and computationally undemanding, it was found to be useful in qualitative studies on copper sites in ZSM-5 interacting with small diatomic molecules such as CO, N_2 and NO. The molecules studied in this work were ethene, propene, but-1-ene, *cis*-but-2-ene and *trans*-but-2-ene. The calculation protocol consisted in assembling the system composed of the M7-Cu cluster and admolecule. All properties of interest were calculated after geometry optimization for composed system with the use of standard tools. Our aim was to compare alkene series with respect to adsorption properties and activation ability by a copper site in ZSM-5, without precise speciation of the site.

Quantum chemical calculations were performed with DFT method (Dmol software by Accelrys [18]). DFT has already been widely accepted as a standard robust and reliable tool for calculating variety of properties for transition metal systems. Here calculations were restricted to local VWN potential and DNP basis set to allow for reasonable timing and performing relatively large-scale calculations with computer resources at hand. This should be regarded as a reasonable compromise as long as comparative analysis is requested and no accurate energies or absolute values of frequencies are required. It has already been confirmed in our previous studies using pure DFT numerical software for systems including transition metals that such choice leads to rational geometries and frequencies (without scaling factor) and qualitatively acceptable energetical parameters [19,20].

The calculations provided minimum energy structures after constrained geometry optimization together with the electronic structure of the sites and charge distribution. Charge and bonding distribution were obtained from Hirshfeld population analysis and Mayer bonding analysis, respectively. For the systems with adsorbed alkenes full vibrational analysis was performed providing frequencies to compare with infrared measurements. Since the diagonalisation of the Hessian matrix from constrained minimisation could lead to contamination by constraints, we have checked carefully the nature of normal

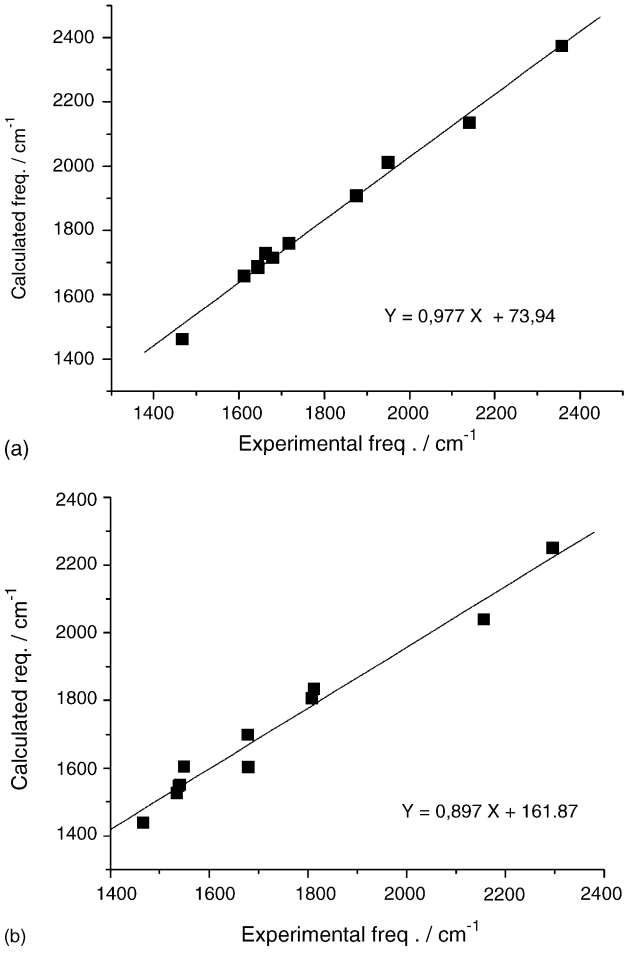

Fig. 2. Plots of calculated vs. measured stretching frequencies: (a) for free molecules (ethene, propene, but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, ethyne, acetone, benzene, CO, NO and N_2) and (b) for molecules adsorbed on Cu^+ZSM-5.

modes ascribed to adsorbed molecule. We have found stretching frequencies corresponding to C=C bonds well resolved from other vibrations and not contaminated by dangling bonds. Also critical analysis of a range of stretching frequencies calculated by us for many systems within the same calculational scheme illustrates predictability limits for our results. Fig. 2a and b present plots of calculated versus measured stretching frequencies for free molecules (ethene, propene, but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, ethyne, acetone, benzene, CO, NO and N_2) and molecules adsorbed on Cu^+ZSM-5, respectively. The plots show that the calculated and measured frequencies correlate well and thus the trends should be well represented in our model calculations.

3. Results and discussion

3.1. Interaction of alkenes with Cu^+ sites represented by cluster models of ZSM-5

Optimized geometries of the isolated alkene molecules and their frequencies were used as a reference to calculate their modification after interaction with the active site and are given in Table 1. Two experimental values are listed in the table, reference values for gas-phase molecules and for alkenes physisorbed in acidic zeolite framework, measured in our group. Each alkene molecule was then put in the range of influence of a metal cation (Na^+ or Cu^+ free cations or Cu^+ in M7 model of the zeolitic site) and the adduct geometry was optimized with property analysis following.

Table 1
Alkenes: bond length $R_{C=C}$ (Å), frequencies calculated $\nu^{calc}_{C=C}$ and experimental $\nu^{exp}_{C=C}$ (cm^{-1})

	Ethene	Propene	But-1-ene	*cis*-But-2-ene	*trans*-But-2-ene
$R_{C=C}$	1.330	1.332	1.331	1.337	1.333
$\nu^{calc}_{C=C}$	1658	1683	1677	1708	1718
$\nu^{exp}_{C=C}$					
Phys.	1613	1646	1640	1663	–
Gas phase	1623	1650	1645	1670	1680

The results show that all molecules are considerably strongly bound by zeolitic copper site. Carbon atoms forming double bond are nearly equally (by about 2 Å) distant from Cu^+ and remain in the first coordination sphere of Cu^+. On the interaction, the cation looses two framework contacts and forms equivalent strong bonds with two framework oxygen atoms. Two oxygen atoms and two carbon atoms have approximately square planar coordination except that for *trans*-but-2-ene, which is midway between square and tetragonal geometry. The angle between the directions determined by two oxygen and two carbon atoms, defined by the CCOO torsion angle, may be regarded as a measure of the out-of-plane distortion in copper coordination. Zero angle corresponds to square coordination while for tetragonal one it should approach 90°. Approximate square (ethene) and half-tetragonal (*trans*-but-2-ene) coordination is shown in Fig. 3a and b, respectively. The adsorption geometry of studied alkenes indicates the formation of a π complex in all cases, thus both π donation and π* back-donation electron transfer mechanisms are expected to influence the electronic structure and the intramolecular bonding.

Results of the calculations showing properties modified by adsorption are collected in Table 2. Both experimental and theoretical frequency shifts are calculated with respect to gas phase molecules. The effect of an alkene interaction with the cationic site is concentrated in the double bond region. In all studied cases the double bond becomes elongated by ca 0.05 Å and its Mayer bond order decreases by about 0.6. This indicates that this bond is substantially weakened and may be classified midway between single and double bond. Calculated frequencies of the double C=C bond in adsorbed alkenes are distinctly lower than these for free molecules. Changes in geometry, bond orders and frequencies show that the bond becomes strongly activated what reflects the experiment. The calculated and measured red shifts of IR stretching C=C bands go in line. Some mismatch observed for ethane and *cis*-but-2-ene should be related to limitations of our small model. Obviously, accurate calculation of absolute stretching frequencies falls out of ability of this study, in addition, the inspection of Tables 3 and 4 shows that similar problems were also found in other studies.

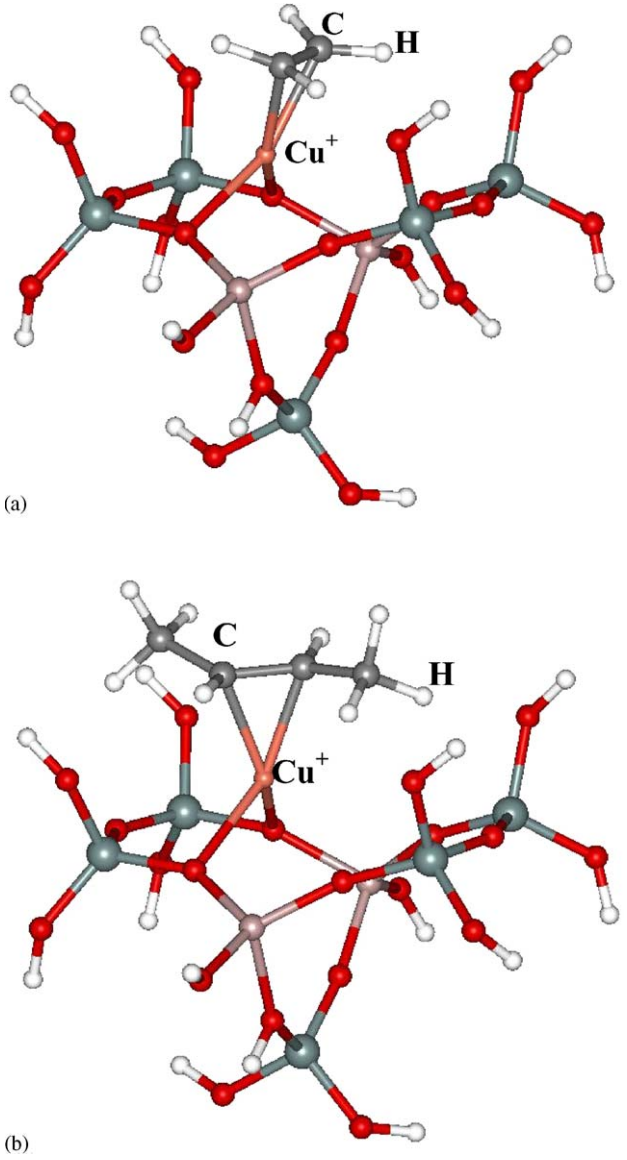

Fig. 3. The model of copper cationic center interacting with ethene (a) and *trans*-but-2-ene (b).

Another interesting phenomenon is the appearance of the symmetry forbidden bands after adsorption of a centro-symmetric molecule. This has usually been attributed to the mode of adsorption, end-on versus side-on and utilized for interpreting the adsorption geometry of small molecules. However, in the case of alkenes the transitions attributed to C=C vibration may become IR allowed even for a symmetrical molecule, e.g. ethene adsorbed side-on due to the distortion of hydrogen atoms in $=CH_2$ fragments from previously planar configuration in a free molecule, which efficiently breaks the symmetry. Indeed, the increase of calculated and measured absorption coefficients correlates well with the out-of-plane distortion of the molecule measured by the (HH midpoint, C, C) angle in ethene (10°) and (HC midpoint, C, C) angle in *trans*-but-2-ene (11°). Perturbation of geometry results in effective mixing of C=C and C–H vibrations in ethene and thus previously forbidden transition becomes allowed even after side-on adsorption [6].

Table 2
Elongation of the C=C bond ΔR (Å), decrease of Mayer bond order $\Delta_{b.o.}$, calculated and observed red shift of C=C stretch $\Delta\nu$ (cm^{-1}), changes of charge on alkene and copper

	Ethene	Propene	But-1-ene	*cis*-But-2-ene	*trans*-But-2-ene
E_{ads}	202	200	181	200	184
ΔR	+0.050	+0.047	+0.046	+0.050	+0.043
$\Delta_{b.o.}$	−0.64	−0.60	−0.54	−0.51	−0.58
$\Delta\nu^{calc}$	−133	−133	−130	−104	−116
$\Delta\nu^{exp}$	−85	−101	−100	−111	−[a]
ΔQ_M	−0.05	−0.06	−0.06	−0.09	−0.06
ΔQ_{Cu}	+0.04	+0.04	+0.04	+0.04	+0.04

[a] Not measurable.

Detailed analysis of charge redistribution gives additional information about the mechanism of C=C bond activation process. As indicated already in Section 1, π* back-donation is expected to be distinct for molecules adsorbed on copper sites in ZSM-5. Indeed, inspection of Table 3 containing analysis of selected properties of ethene adsorbed on various systems shows large red shift of both stretching C=C and CH_2 scissoring vibrations on zeolite compared to other sites. This is an apparent signature of large back-donation on this site. At the same time, high reduction in red shift of the out-of-plane ϖ_{CH_2} band indicates that also π donation is effective here. As discussed already in our previous papers, the calculated reduction of positive charge on the copper cation in ZSM-5 zeolite (from +1.0 for a free cation to +0.32 after embedding) illustrates already strong influence of the zeolitic framework on π donor properties of the cation making it a good donor [8–12]. In addition, the charge gained by each alkene molecule on adsorption exceeds charge lost by the copper cation (see Table 2), which shows the function of a zeolite electron reservoir enhancing the intrinsic ability of Cu^+ to π back-donation. Therefore the global flow of electrons to the adsorbed molecule should be considered as originating from entire catalytic site taken with its zeolitic environment not from the copper center itself [13].

The same mechanism as in the case of ethene (see next paragraphs), will prompt both π donation and π* back-donation to contribute to charge transfer for higher alkenes. Negative charge on a molecule shows that π* back-donation prevails over π donation for all alkenes adsorbed on the Cu^+ site. The electron flow between the site and an interacting molecule may be moderated not only by the ability of the framework to switch on additional electron flow but also by electron affinity of the molecule that reveals its ability to be an acceptor of π* back-donation. In order to qualitatively assess the latter factor we have calculated approximate electron affinities for a series of studied molecules as the differences between total energy of an anion and neutral molecule. Estimated electron affinities for alkenes fall in the range of 1.45–1.7 eV, which shows that alkenes are weaker electron acceptors than NO (E_a = 0.5 eV) but stronger than CO or N_2 (E_a = 1.9 and 2.1 eV, respectively). Therefore, in addition to π donation that is activation-effective for any adsorbate forming a π complex, alkenes are generally more prone to the π*

Table 3
Ethene interacting with Me cations: CC, MeC and Me/(CC midpoint) distances (Å), out-of-plane CH_2 angle (ΔT_{CH_2}, deg) and shifts in frequencies: stretching $\Delta\nu_{CC}$, symmetric scissoring $\Delta\delta^{s}_{CH_2}$ and out-of-plane $\Delta\boldsymbol{\varpi}_{CH}$ (cm^{-1}); Me to ethene charge transfer ΔQ

	Cu^+-zeolite		Cu^+		Na^+		Ag^+, Ref. [24]
	This work	Ref. [4]	This work	Other	This work	Ref. [24]	
R_{CC}	1.38	1.38	1.38	1.36 [23]	1.34		
R_{MC}	1.99	2.03	2.00		2.62		
$R_{M\perp}$	1.87	1.88	2.03	2.012 [22], 2.25 [23]	2.53	2.67	2.28
ΔT_{CH_2}	10	22	11	7 [22]	14		
$\Delta\nu_{CC}$	−133	−131	−131		+17		
$\Delta\delta^{s}_{CH_2}$	−76	−66	−57		+5		
$\Delta\varpi_{CH_2}$	−1		+74		+48	+83	+101
ΔQ	−0.05		+0.34	+0.22 [22]	+0.23	+0.10	+0.27

back-donation than CO or N_2 molecules. On the other hand, NO molecule which does not form a π complex leading to effective π donation, is the best electron acceptor and its bond becomes distinctly weakened by π* back-donation alone. The extent of the double bond activation in alkene molecules after electron redistribution should be further enhanced due to strongly antibonding and bonding character of LUMO and HOMO orbitals, respectively. The two effects are additive here and therefore much higher shift in C=C frequency should be expected for alkenes than that for CO or N_2; for NO, where π donation would oppose the activation, the activation should be less pronounced than that for alkenes.

Table 4
Selected results for ethene: CC and MeC bond distances (Å), out-of-plane CH_2 bend (ΔT_{CH_2}, deg) and shifts in frequencies (cm^{-1}): stretching $\Delta\nu_{CC}$, symmetric scissoring $\Delta\delta^{s}_{CH_2}$ and out-of-plane $\Delta\varpi_{CH_2}$ (exp. values in parentheses wherever available); Me to ethene charge transfer and its decomposition into π* and π components

	Cu^+-zeolite	$Cu_m{}^{ST}$ [3]	$Pd_m{}^{ST}$ [3]	$Ag_m{}^{LT}$ [3]
R_{CC}				
This work	1.38			
Other	1.38 [4]	1.377	1.396	1.353
R_{MeC}				
This work	1.99			
Other	2.03 [4]	2.363	2.319	2.864
$\Delta T^{*}_{CH_2}$				
This work	10			
Other	22 [4]	5.678	9.508	1.377
$\Delta\nu_{CC}{}^{*}$				
This work	−133 (−78)			
Other	−131 (−80)	−115 (−91)	−140 (−98)	−45
$\Delta\delta^{s}_{CH_2}{}^{*}$				
This work	−76			
Other	−70 (−66)	−73 (−67)	−109 (−107)	−18
$\Delta\varpi^{*}_{CH_2}$				
This work	−1			
Other	(−19)	−76 (−40)	−64 (−49)	+15 (+6)
ΔQ				
This work	−0.05			
[3]		−0.16		+0.07
π (et → Me) [3]		0.12		0.10
π*(Me → et) [3]		0.28		0.03

3.2. Comparative study of ethene interaction with metallic sites

The interaction of alkenes with free metal cations was studied additionally to compare with the literature [21–24] and to compare alkali metal (Na^+) with transition metal (Cu^+), free or embedded in a zeolite framework. This analysis makes clearer the scheme of decoupling the two mechanisms of charge transfer, described in previous paragraphs. To this end, ethene is used as the case study to compare geometric and spectroscopic properties of one molecule interacting with the metal cationic site, free or embedded in a zeolite matrix (Table 3). Because majority of relevant extended systems studied by other authors were transition metal surfaces (see [3] for review), Table 4 contains additional selection of results concerning ethene molecule interacting with various transition metal systems: metallic (Cu, Pd and Ag) and zeolitic (Cu, this work and results from Ref. [4]). Transition metal surfaces were studied by Itoh et al. [3] for cluster models of Cu (1 1 0), Pd (1 1 0) and Ag (1 1 0) surfaces. We have selected the largest model describing a top adsorption parallel to the <1,−1,0> direction for Cu or Pd and parallel to the <1 0 0> direction for Ag.

The binding of ethene to free monovalent cations is distinctly different from that to the monovalent copper sites in zeolites. Kim et al [24] and Itoh et al. [3] have found that the blue shift in the highly active out-of-plane CH_2 bending mode ($\Delta\varpi_{CH_2}$) of the π systems observed in the complexes as well with metal cations as with metal surfaces, may be taken as the representative of the strength of the metal-π interaction. However, the correlation between the value of the overall hydrocarbon-to-metal charge transfer and this shift or with the calculated change in binding energy was not clear in the case of free metal cations. This could be due to the fact that the authors classified this adsorption as the pure π bonded state and ascribed this charge transfer to the π donation alone, which is not necessarily true. Indeed, our rough estimate of ethene binding energy to Cu^+ZSM-5 (about 200 kJ/mol) is larger than binding energies of ethene to free monovalent cations (from about 50 kJ/mol for Na^+ to 180 kJ/mol for Cu^+) [21–24] while the net electron transfer is small in the former case and large in the latter one. Unfortunately, clear decomposition of the charge transfer to π donation and π* back-donation is possible only for model, highly symmetrical systems. Therefore qualitative rules

based on analyzing other related properties may be very helpful here.

For the zeolitic site, where strong interaction partially breaks double π bond in the adsorbed molecule, the discussion of the nature of the bonding and decomposition of charge transfer is difficult. The frequency (ϖ_{CH_2}), regarded as the index of the strength of the metal-π interaction, is shifted up by 74 and 48 cm^{-1} for copper and sodium cations, respectively, but it becomes shifted slightly downwards (red shift by -1 cm^{-1}) for the Cu^+ zeolitic site, where the interaction is the strongest. Small value of the total CT found here seems even more unexpected when it is considered together with the activation of the C=C bond, evidenced as well by the calculated bond elongation as by both calculated or experimental IR stretching frequencies that are very large (see Table 2). This apparent discrepancy may be explained by invoking the case of NO, where metal-to-NO π* back-donation (the flow of electrons opposite to π donation), is the major contribution to the bond weakening. In the case of alkenes both processes operate simultaneously thus the interaction energy and the bond activation are large even if the net charge transfer is small and ϖ_{CH_2} frequency shift is moderate.

Critical inspection of the interaction of ethene molecule with transition metal surfaces further supports the above analysis. Table 4 shows adsorption geometry, IR frequencies and charge transfer for zeolites compared to metal surfaces. It may be easily seen that in all cases distinct activation of the C=C bond goes in line with the red shift in symmetric scissoring CH_2 frequency ($\Delta\delta^s_{CH_2}$) and the out-of-plane distortion of the CH_2 group (ΔT_{CH_2}). On the other hand only in the case of Cu^+-zeolite and copper or palladium surfaces it is accompanied by a net metal-to-hydrocarbon charge flow and red shift in ϖ_{CH_2}, whereas for silver just the opposite effect occurs. The analysis of the decomposition into the π donation and π* back-donation when possible, brings valuable insight into the charge transfer processes. Both π donation and π* back-donation make appreciable contributions to the ethene-surface interaction on Cu (1 1 0) or on Pd (1 1 0), whereas for the ethene on-Ag (1 1 0) the π* back-donation is negligible. Thus only for ethene on Ag (1 1 0) the frequency increase of the CH_2 out-of-plane wagging vibration is a good measure of the contribution of the π donation to the ethylene-surface interaction. However, when both mechanisms of charge transfer operate, such clear dependence is not seen. The π donation is large for both copper or silver cation and Ag metal but while for silver it dominates the bonding, it is overcome by π* back-donation in the case of metallic copper. Both contributions are apparently balanced for Cu^+-zeolite. The π donation involves a transfer of electrons from a π orbital of the adsorbate to unoccupied metal orbitals, whereas the π* back-donation populates a π* orbital of the adsorbate with electrons from the occupied metal orbitals. Both processes lead to a loss of bond order and thus to an increased C=C bond distance accompanied by partial rehybridization toward the sp^3 configuration. The rehybridization causes a frequency lowering of both stretching C=C and CH_2 symmetric scissoring ($\delta^s_{CH_2}$) modes of the adsorbed ethene and therefore these IR characteristics correlate with the covalent component of the bonding and the extent of the C=C bond activation. On the other hand, the opposite trend in frequency shifts of the ϖ_{CH_2} band of ethylene adsorbed on Cu (1 1 0) and Ag (1 1 0) may be explained by the difference in the contribution of π donation and π* back-donation. On copper surface the larger the frequency lowering of the (ϖ_{CH_2}) band, the stronger the ethylene-surface interaction. On the contrary, the larger the frequency increase on Ag (1 1 0), the stronger the ethylene-surface interaction. Therefore the shift in the (ϖ_{CH_2}) band may be taken as a measure of the importance of both components, with blue shift indicating large π donation and red shift indicating large π* back-donation.

In summary we may conclude that for copper sites in ZSM-5 π* back-donation is distinct (large red shift of both stretching C=C and CH_2 scissoring frequencies) but also π donation occurs (high reduction in red shift of the ϖ_{CH_2} band). In the case of a free Cu^+ cation π donation from ethene molecule is large (large positive shift of the ϖ_{CH_2} band) but also partial interaction via π* back-donation mechanism is switched on (red shift of the scissoring band). This may explain why the activation of the C=C bond is comparable for a copper cation free and embedded in a zeolite, even if total charge transfer is opposite. These conclusions may help to formulate by analogy similar rules for other members of homologous series where no reference data are available. In the paragraph 3.1 we have already assumed transferability of such rules to higher alkenes in zeolites, where neither well resolved calculations nor clear-cut measurements are available for frequencies other than the C=C stretch.

4. Conclusions

Discussion of the results of our calculations for alkene molecules interacting with model copper site in MFI has been enriched by extensive comparison with ethane interaction with variety of other metallic systems taken from the literature. This allowed drawing the following conclusions of general nature, concerning the charge transfer processes accompanying alkene adsorption. The copper is very good candidate to make an efficient active site both in metallic and cationic form due to its electronic structure containing full 3d shell, with good spatial accessibility and easily tunable Fermi level. Thus it may be regarded as an electron transmitter that moderates and tunes the contact between an electron reservoir (a zeolite) and the molecule (an alkene), making a good match between the donor and the acceptor.

Alkenes have the electronic structure that makes them prone to activation by both π donation and π* back-donation charge transfers; both processes will weaken the C=C bond as the HOMO has strongly bonding and the LUMO has strongly antibonding character. The difference in the effects of the interaction between alkene molecules with the free or embedded cation consists in much more significant π back-donation from the cation to the molecules when surrounding of a zeolite framework is present. Therefore on copper sites in zeolites where alkenes form strongly bonded π complexes, they become strongly activated by both mechanisms: π donation and

π^* back-donation. The interaction shows up in calculated C=C stretching frequencies that are good measures of adsorbate activation and agree well with the experiment.

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