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Intensities of IR stretching bands as a criterion of the strength of Lewis acid sites in ZSM-5 zeolites with bivalent cations

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The DFT calculations were applied to investigate the impact of the nature of bivalent cations M (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) in cation-exchanged ZSM-5 zeolites on the Lewis acid site (LAS) strength. Intensities and shifts of IR stretching bands of adsorbed methane were calculated. Adsorption leads to a decrease in their frequencies and a marked increase in the intensities of the symmetric stretching band of methane. At the same time the intensities of the asymmetric stretching bands decrease. To characterize the strength of LAS, Fukui functions were computed. A good linear correlation between the intensity of methane vibrations and the LAS strengths (Fukui function f^+) was found.

KEY WORDS: ZSM-5 zeolite; exchange cations; methane adsorption; Lewis acidity; Fukui function.

1. Introduction

Cation-exchanged zeolites are widely used as catalysts of different organic reactions, such as alkylation of side chain of toluene, condensation, aromatization and selective alkylation of oxygen and nitrogen containing aromatics etc [1]. A key role in these reactions catalyzed by zeolites belongs to the Lewis acid sites (LAS). Information on the strength of LAS is of importance for understanding and predicting catalytic and adsorption properties of cation-exchanged zeolites.

Estimation of the LAS strength is fraught with difficulties. A traditional approach to estimating LAS strength of cation-exchanged zeolites is the investigation of interaction between the cationic sites [2–4] and basic molecules such as CO or NH_3. It is widely accepted that the LAS strength is in a good agreement with the blue shift of CO stretching band. Recently [5], an attempt was made to use reaction indices for prediction of LAS strength in zeolites containing alkaline cations. It was indicated that the blue shift of stretching band of adsorbed CO correlates with ratio of Fukui functions f^+/f^-.

Fukui functions are based on electronic populations of atoms as indicated by the following equations [6]:

$$f^+ = \left(\frac{\partial \rho(r)}{\partial N}\right)^+_{v(r)} = q_{N+1} - q_N,$$
$$f^- = \left(\frac{\partial \rho(r)}{\partial N}\right)^-_{v(r)} = q_N - q_{N-1},$$

where ρ is the electronic density on a given atom, N is the number of electrons in the system, q is the electronic population on a given atom. If a f^+ value on a cationic site is available, the LAS strength of cation-exchanged zeolite can be estimated. Physical meaning of f^+ can be interpreted as due to the change in the electronic density on a cation caused by the electron capture.

The development of reliable theoretical and experimental tools to determine the LAS strength in catalysts for transformation of methane or other light alkanes is of importance. Recently a special interest was directed to investigation of C–H bond activation in light alkanes. It appears that methane can be a suitable test molecule for estimating the LAS strength. In particular, Kazansky et al. [7, 8] showed that methane adsorption on M^{2+} cationic sites of zeolites leads to the red shift of IR symmetrical stretching band of methane molecule. Moreover, these authors were the first to indicate that this shift is accompanied by an increase in the intensity of the symmetrical stretching band and by a decrease in the intensities of the asymmetrical stretching bands. To verify the possibility of using the change in the intensities of stretching bands for estimating the LAS strength one can compare the calculated LAS strength (Fukui function f^+) with the intensities of methane stretching bands.

In the present work the account is given on the LAS strength and intensities of the IR stretching bands of methane adsorbed on cation-exchanged MZSM-5 zeolites (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) as indicated by DFT calculations.

2. Computational details

To model the active sites in cation-exchanged MZSM-5 zeolites (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+},

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Ni^{2+}) the cluster approach was used. The cluster includes 18 Si atoms and 2 Al atoms and is based on two ten-membered rings from the straight channel of zeolite. The cluster broken bonds (Si–O and Al–O) were saturated with hydrogens, placed at the 1.6 and 1.5 Å along Al–O and Si–O bonds respectively. All terminal hydrogens were fixed during geometry optimization. The LAS strength depends on the position of cation in zeolite framework. There are different assumptions on the sittings of divalent cations in zeolites [9–11]. In our calculations we used α-cationic position as the site for all bivalent cations in ZSM-5 zeolite as proposed by Wichterlova [12]. This resulted in a cluster having the stoichiometry of $MAl_2Si_{18}O_{26}H_{28}$ with Al–Al distance of 10 Å. The cluster electronic structure was computed at the density functional theory (DFT) level using the Becke's three parameters exchange functional (B3) [13] combined with the Lee-Yang-Parr (LYP) [14] and Vosko-Wilk-Nusair (VWN5) [15] correlation functionals. The SBKJC effective core potential[16] and corresponding basis set augmented with polarization functions were used on all atoms. All the calculations were performed with the PC GAMESS [17, 18] program package. To estimate the LAS strength the Fukui functions f^+ were calculated for the exchanged cation using natural populations (eigenvalues of the first-order reduced density operator) [19].

3. Results and discussion

The cluster modeling cation-exchanged zeolite MZSM-5 (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) is shown in figure 1a (cluster I). When introduced in the zeolite matrix the cation takes a cationic position in the vicinity of an Al atom. Accordingly, in the case of Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} cations, Al–O1 and Al–O2 bond lengths increase by 0.05 and 0.1 Å respectively. At the same time Al–O4 bond shortens by 0.05 Å. The Si–O bonds lengthen by 0.04–0.06 Å. By contrast, on introducing Ca^{2+} and Sr^{2+} cations the distance Al–O4 increases by 0.05 Å. Other Al–O and Si–O bonds remain practically unchanged, an insignificant increase (~0.02 Å) can be nevertheless observed. In addition, introduction of cations results in slight changes in Si–O–Al valence angles.

Table 1 contains main parameters that characterize geometry, charge distribution and energetics of cluster I with different exchanged cations. Based on M–O bond lengths, coordination with O1, O2 and O3 oxygens is preferable for Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} cations. At the same time Ca^{2+} and Sr^{2+} cations tend to take position near O1, O2 and O4 oxygens. The M–O bond lengths increase with the cationic radii. Therefore, on introducing Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} cations in the ZSM-5 zeolite, the Al–O bond lengths in the AlO_4 unit adjacent to an exchanged cation notably increase. Alkaline-earth cations with the largest radii (Ca^{2+} and Sr^{2+}) are characterized by the coordination with the oxygens of the nearest AlO_4 unit, whereas for the other cations (Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}), oxygens of six-membered ring are preferable environment.

One of the difficult questions encountered in modeling nanoclusters of transition metals supported on oxide surfaces is the choice of the multiplicity of metal particles. Accordingly, calculations of states with varying spin multiplicity were performed for the neutral, positively (+1) and negatively (−1) charged cluster I containing Mn^{2+}, Co^{2+} and Ni^{2+} exchanged cations.

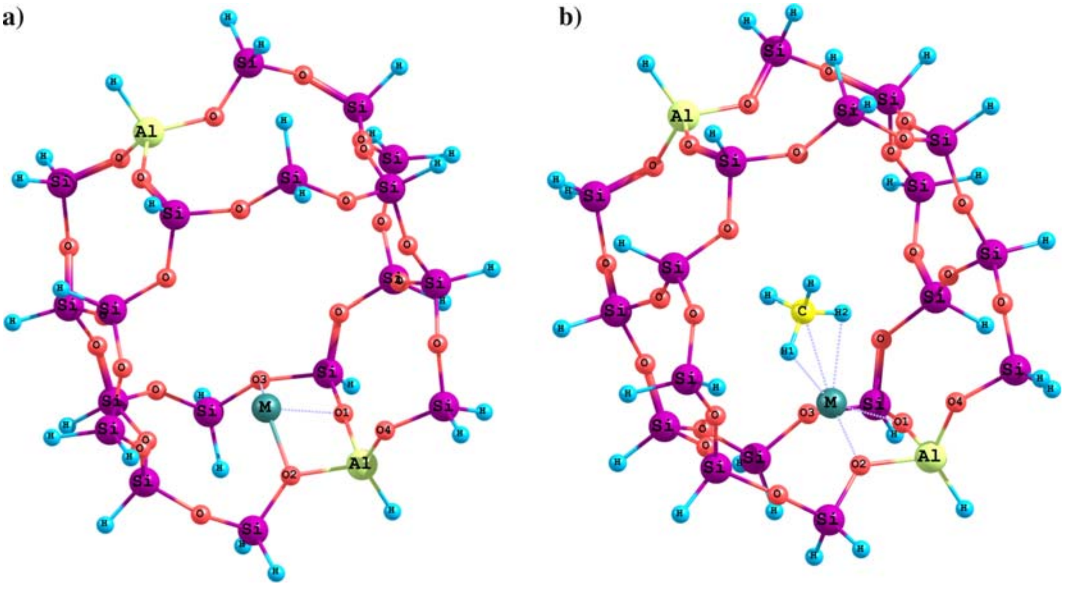

Figure 1. Cluster modeling cation-exchanged zeolite MZSM-5 (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) (a) and its adsorption complex with methane (b).

Table 1
Principal parameters characterizing geometry, charge distribution and energetics of MZSM-5 clusters

Parameter	Cation (M)						
	Ca^{2+}	Sr^{2+}	Mg^{2+}	Mn^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}
M–O1, Å	2.28	2.55	2.12	2.20	2.14	2.12	2.09
M–O2, Å	2.32	2.98	1.95	1.98	1.89	1.93	1.92
M–O3, Å	3.15	3.28	2.08	2.15	2.00	2.06	2.07
M–O4, Å	2.25	2.48	3.30	3.38	3.45	3.42	3.43
$q_n(M)$	1.93	1.93	1.88	1.66	1.66	1.41	1.21
f^+	0.9145	0.90445	0.86497	0.78369	0.71694	0.58531	0.38464
IE, eV	7.85	7.98	7.80	9.62	7.74	8.66	7.52
EA, eV	1.41	1.06	2.46	2.73	3.34	4.24	4.50
s^+, 1/eV	0.142	0.131	0.162	0.114	0.163	0.132	0.127

Results of these calculations are collected in table 2. With allowance for the table 2 data, all the calculations of geometric and energetic parameters as well as Fukui functions for clusters containing Mn^{2+}, Co^{2+} and Ni^{2+} cations were conducted for the states having the optimal spin multiplicity ($\Delta E = 0.0$). For the positively charged Ni^{2+} cluster there is degeneracy between spin multiplicities 2 and 4. The calculations carried out for both multiplicities showed no difference between the values of Fukui function.

From the calculations it can be inferred that the lower the difference between neutral and negatively charged clusters in terms of charges on cation (lower f^+), the stronger Lewis acidity of this cationic site. Similar dependence was found for hard acid–hard base interaction [20]. Using Fukui function values (table 1) cation-exchange MZSM-5 zeolites can be arranged in a series of decreasing Lewis acidity: $Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+} > Sr^{2+} > Ca^{2+}$. It is of interest that an increase in the LAS strength is accompanied by an decrease in the natural charge on this site. In other words a cationic site with the highest Lewis acidity carries the lowest positive charge and *vice versa.*

Table 2
Relative stability of MZSM-5 ($M = Mn^{2+}, Co^{2+}, Ni^{2+}$) clusters with different spin multiplicity

Cation (M)	Cluster charge	Spin multiplicity	ΔE, kcal/mol
Mn^{2+}	−1	5	2.3
		7	0.0
	0	4	42.0
		6	0.0
	+1	5	0.0
Co^{2+}	−1	1	46.8
		3	0.0
		5	34.0
	0	2	15.6
		4	0.0
	+1	3	0.0
Ni^{2+}	−1	2	0.0
		4	45.6
	0	1	7.9
		3	0.0
	+1	2	0.0
		4	0.0

In a number of works [21, 22] the local softness value s^+ (table 1) is frequently used for estimating the site electrophylity. It can be calculated using the following formula:

$$s^+ = \frac{f^+}{IE - EA},$$

where f^+ is the Fukui function for a cationic site, *IE* is the ionization energy, *EA* is the electron affinity. The raw of decreasing local softness for cation-exchanged zeolites is as follows: $Zn^{2+} > Mg^{2+} > Ca^{2+} > Co^{2+} > Sr^{2+} > Ni^{2+} > Mn^{2+}$.

The cluster that models the adsorption complex methane–cation-exchanged zeolite MZSM-5 ($M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$) is presented on figure 1b (cluster II) with principal geometric and spectral parameters of complexes summarized in table 3. Methane adsorption on the cationic site of the zeolite affects the cation coordination in a different way. In the case of Ca^{2+} and Sr^{2+} cations, the cation coordination remains unchanged, while the M–O bond lengths vary insignificantly. By contrast, methane adsorption on Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} cations lengthens the M–O3 bond by 0.1 Å, and shortens the M–O4 bond by 0.15 Å, whereas the M–O1 and M–O2 bond lengths show negligible variations. No notable changes in zeolite framework were observed after methane adsorption. Thus, the position of Ca^{2+} and Sr^{2+} cations remains virtually unchanged following the interaction with methane, whereas Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} cations are pulled over the six-membered ring (see figure 1). At the same time the charges on Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+} and Mn^{2+} cationic sites are slightly reduced (by 0.03–0.05), while the charges on Co^{2+} and Ni^{2+} cations increase by 0.05 and 0.14 respectively (see tables 1 and 3). Adsorption brings about changes in the bond lengths of methane molecule by 0.01–0.02 Å. There is nearly no difference between

Table 3
The M–O, M–C, M–H bond lengths and natural charge on cationic site M in adsorption complex methane–cation-exchanged zeolite MZSM-5

Parameter	Cation (M)						
	Ca^{2+}	Sr^{2+}	Mg^{2+}	Mn^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}
M–O1, Å	2.29	2.56	2.13	2.24	2.17	2.08	2.07
M–O2, Å	2.31	3.00	1.98	2.03	1.94	1.95	1.95
M–O3, Å	3.17	3.29	2.16	2.24	2.13	2.13	2.22
M–O4, Å	2.25	2.48	3.22	3.24	3.28	3.24	3.12
M–C, Å	2.56	2.89	2.31	2.43	2.31	2.40	2.34
M–H1, Å	2.55	2.78	2.19	2.13	1.97	1.96	2.03
M–H2, Å	2.45	2.75	2.35	2.32	2.07	2.20	2.01
$q_n(M)$	1.90	1.92	1.83	1.58	1.63	1.46	1.35

M–H1 and M–H2 bond lengths for Ni^{2+} and Sr^{2+} cations, and the difference for Mg^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+} and Co^{2+} cations varies from 0.1 to 0.24 Å.

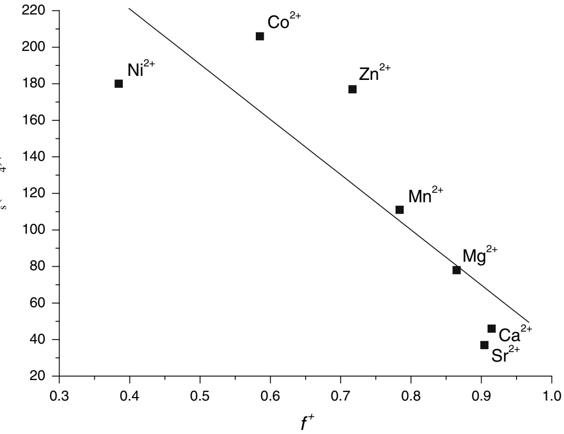

Figure 2. Correlation between red shift of symmetrical stretching band ($\Delta\ \nu_s$) of methane adsorbed on cationic site of MZSM-5 zeolite and Fukui function f^+.

In table 4 the calculated adsorption energies of methane on cationic sites of zeolites along with red shifts of symmetrical stretching band of adsorbed methane molecule relative to free methane molecule are collected. These data are complemented by the intensities of symmetrical stretching band ($I(\nu_s)$) and the ratio of the intensities of the symmetrical band and the asymmetrical stretching bands ($I(\nu_s)/\ I(\nu_{as})$). The adsorption energies of methane on cation-exchanged zeolites decrease in a sequence: $Zn^{2+} > Mg^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Ca^{2+} > Sr^{2+}$. It is known [23] that, B3LYP functional yields underestimated values for weak adsorption interactions. This prompted us to conduct the calculations of adsorption energies at the X3LYP level [24] that gives more reliable energetics. On comparing the data collected in table 4 it is evident that difference in the adsorption energies does not exceed 1–2 kcal/mol. From the data given in tables 1 and 4 it follows that no definite correlation between the adsorption energies for different cations and corresponding Fukui functions can be traced. Likewise no correlation between E_{ads} and $\Delta\ \nu_s(CH_4)$ values emerges. By analyzing figure 2 the conclusion can be made about a weak correlation ($R^2 = 0.72$) between f^+ values (LAS strength) and the red shift of symmetrical stretching band of methane. In particular, the Ni^{2+} cation does not follow the trend. Accordingly, the frequency shift per se cannot serve as a reliable measure for the strength of LAS. The interaction of methane with LAS results not only in the frequency shift but polarizes the C–H bond and modulates the vibration mode. As result the increase in the intensity of the symmetrical stretching band of methane can be observed. The lack of the correlation between the red shift and the Fukui function makes it tempting to search for additional spectral measures of

Table 4
The adsorption energies of methane and principal spectral parameters characterizing adsorption complex methane – cation-exchanged zeolite MZSM-5

Parameter	Cation (M)						
	Ca^{2+}	Sr^{2+}	Mg^{2+}	Mn^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}
E_{ads}(B3LYP), kcal/mol	12.6	11.2	20.0	18.3	21.0	15.8	13.0
E_{ads}(X3LYP), kcal/mol	13.7	12.3	21.2	19.7	22.4	17.9	15.0
$\nu_s(CH_4)$, cm^{-1}	2918	2927	2886	2853	2787	2757	2784
$\Delta\nu_s(CH_4)$, cm^{-1}	46	37	78	111	177	206	180
$I(\nu_s)$	1.03	1.24	1.35	2.37	2.93	3.09	3.95
$I(\nu_s)/I(\nu_{as})$	0.77	0.95	0.71	1.23	3.62	4.12	5.72

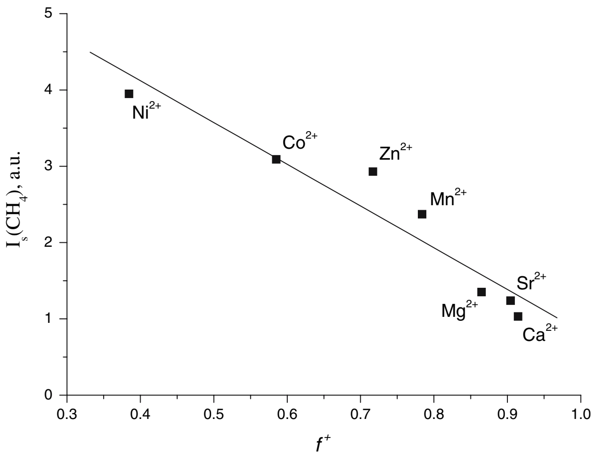

Figure 3. Correlation between intensities of symmetrical stretching band of methane adsorbed on cationic site of MZSM-5 zeolite and Fukui function f^+.

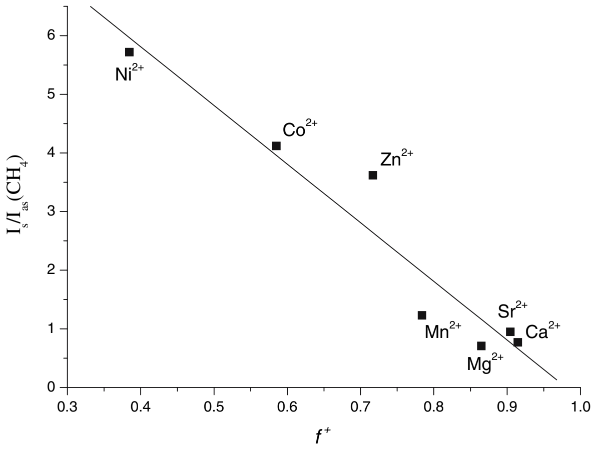

Figure 4. Correlation between the ratio of intensities of symmetrical stretching band and asymmetrical stretching bands of methane adsorbed on cationic site of MZSM-5 zeolite and Fukui function f^+.

LAS strength. As evidenced by the data in tables 1 and 4, the conventional method of determining LAS strength can be added by the analysis of the intensities of the stretching bands of adsorbed molecules. In this context it is of interest to compare $I(\nu_s)$ and $I(\nu_s)/I(\nu_{as})$ values with f^+ (LAS strength) for exchanged cations. Values of $I(\nu_s)$ and $I(\nu_s)/I(\nu_{as})$ as a function of f^+ (LAS strength) are shown in figures 3 and 4, respectively. A good correlation ($R^2 > 0.92$) between intensities and LAS strengths can be readily recognized. Correspondingly, the intensities of the symmetrical stretching band of methane as well as the ratio of the symmetrical stretching band and the asymmetrical stretching bands of methane can serve as an additional criterion for the LAS strength of cation-exchanged zeolites. Correlations described above suggest that higher values of $I(\nu_s)$ and/or $I(\nu_s)/I(\nu_{as})$ are directly related to higher LAS strength. In contrast to $I(\nu_s)$ values that can be hardly obtained by IR experiments, the $I(\nu_s)/I(\nu_{as})$ values can be used for experimental estimation of LAS strength of cation-exchanged zeolites.

4. Conclusions

The investigation of the interaction between methane molecule and cation-exchanged zeolites shows that the use of the shift of the stretching band of adsorbed molecule can not be always used for adequate description of the LAS strength in framework alumina-silicates. The analysis of calculated IR-spectra of adsorbed CH_4 indicates a clear correlation between the intensities of stretching band of adsorbed methane and the LAS strength. Since experimental measurements of intensities are difficult, the ratio of the intensities of the symmetrical stretching band and the asymmetrical stretching bands of adsorbed methane can be suggested as an additional criterion for measuring the LAS strength. It is shown that the LAS strength increase with the increase of this ratio. It appears that this approach when combined with the shift measurements can be applied for more adequate estimation of the LAS strength in the high-silica zeolites.

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References

[1] D. Barthomeuf, Catal. Rev. 38 (1996) 521.

[2] H. Knozinger and S. Huber, J. Chem. Soc., Faraday Trans. 94 (1998) 2047.

[3] A.M. Ferrari, K.M. Neyman and N. Rösch, J. Phys. Chem. B 101 (1997) 9292.

[4] A.M. Ferrari, P. Ugliengo and E. Garrone, J. Chem. Phys. 105 (1996) 4129.

[5] R.C. Deka, R.K. Roy and K. Hirao, Chem. Phys. Lett. 389 (2004) 186.

[6] W. Yang and W.J. Mortier, J. Am. Chem. Soc. 108 (1986) 5708.

[7] A.Y. Khodakov, L.M. Kustov, V.B. Kazansky and C. Williams, J. Chem. Soc., Faraday Trans. 89 (1993) 1393.

[8] V.B. Kazansky, A.I. Serykh and E.A. Pidko, J. Catal. 225 (2004) 369.

[9] J. Hafner, L. Benco and T. Bučko, Topics Catal. 37 (2006) 41.

[10] S.A. McMillan, L.J. Broadbelt and R.Q. Snurr, J. Phys. Chem. B 106 (2002) 10864.

[11] V.B. Kazansky, A.I. Serykh and A.T. Bell, Catal. Lett. 83 (2002) 191.

[12] J. Dedecek and B. Wichterlova, J. Phys. Chem. B 103 (1999) 1462.

[13] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[14] C. Lee, W. Yang and R.G. Parr, Phys. Rev. B 37 (1988) 785.

[15] S.H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58 (1980) 1200.

[16] W.J. Stevens, M. Krauss, H. Basch and P.G. Jasien, Can. J. Chem. 70 (1992) 612.

[17] A.A. Granovsky, *PC GAMESS version 7.0*, http://classic.chem.msu.su/gran/gamess/index.html.

[18] M.W. Schmidt, K.K. Baldridge and J.A. Boatz, , J. Comput. Chem. 14 (1993) 1347.

[19] NBO 4.M. E.D. Glendening, J.K. Badenhoop, A.E. Reed, J.E. Carpenter, F. Weinhold, *Theoretical Chemistry Institute* (University of Wisconsin, Madison, WI, 1999).

[20] Y. Li and J.N.S. Evans, J. Am. Chem. Soc. 117 (1995) 7756.

[21] K.R.S. Chandrakumar and S. Pal, J. Phys. Chem. A 107 (2003) 5755.

[22] R.C. Deka, D. Ajitha and K. Hirao, J. Phys. Chem. B 107 (2003) 8574.

[23] W. Kohn, A.D. Becke and R.G. Parr, J. Phys. Chem. 100 (1996) 12974.

[24] X. Xu, Q. Zhang, R.P. Muller and W.A. Goddard III, J. Chem. Phys. 122 (2005) 014105.