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Activation of light alkanes over Cd^{2+} ions in ZSM-5 zeolite: a theoretical study

Evgeny A. Pidko*[†] and Rutger A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands. Fax: +31 40 245 5054; e-mail: e.a.pidko@tue.nl

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A DFT study of ethane activation over cadmium exchanged ZSM-5 zeolite shows that the interaction of C_2H_6 with the Cd^{2+} sites results in a strongly perturbed molecular adsorption leading to heterolytic cleavage of the C–H bond with a moderate activation barrier.

High silica zeolites modified with transition metal ions possess unique chemical properties. For instance, zinc and gallium exchanged ZSM-5 zeolites catalyze the dehydrogenation and aromatization of light alkanes.[1] It was suggested that the high activity of Zn^{2+} ions in high silica zeolites is due to their unique location resulting in very strong polarization of the adsorbed light alkanes, which facilitates heterolytic C–H bond cleavage.[2] Another related and very interesting material is CdZSM-5, which is the most active of the cationic zeolites for hydration of acetylene.[3] It also exhibits a four times higher activity than GaZSM-5 in C_2H_6 dehydrogenation.[4] The low temperature DRIFTS study of H_2 adsorption on CdZSM-5 revealed that different cationic species are being formed within the zeolite depending on the method of preparation.[5] It was also found that H_2 molecules heterolytically dissociate on this catalyst. The proposed active sites are isolated Cd^{2+} cations stabilized at distant anionic sites in ZSM-5. Note that Cd^{2+} and Zn^{2+} ions have very similar electronegativity, while the ionic radius of cadmium is 0.2 Å larger than that of bivalent zinc.[6] A larger cation is less shielded by the surrounding lattice oxygens. Recently, we have shown that this results in a stronger electrostatic field of the exchanged cation and, hence, leads to the stronger polarization of adsorbed molecules.[7,8] Thus, one can expect that Cd^{2+} ions exchanged to ZSM-5 zeolite will exhibit even more pronounced unusual adsorption and enhanced catalytic properties as compared to the ZnZSM-5.

Here we present a DFT study of C_2H_6 activation over isolated Cd^{2+} ions stabilized in ZSM-5 zeolite. Two adjacent five-rings from the wall of the straight channel of ZSM-5 have been suggested as a possible cationic site for the cadmium ion. A $CdAl_2Si_6O_9H_{14}$ cluster was chosen for subsequent DFT modeling.[‡] Aluminum atoms were placed in T12 and T8 lattice positions[15] to model a charge-alternating Z_d cation site with distant anionic sites [Figure 1(*a*)], whereas the next nearest T12 and T6 lattice positions were occupied with aluminum atoms to model the conventional ion-exchange site Z_s [Figure 1(*b*)].

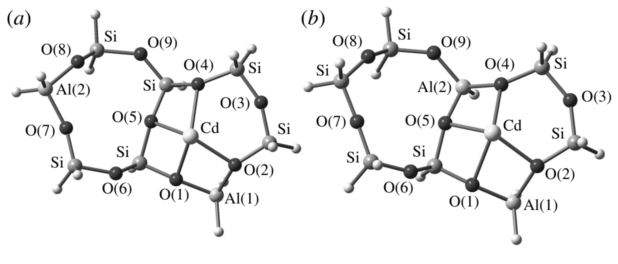


Figure 1 Optimized structures of (*a*) Cd Z_d and (*b*) Cd Z_s cluster models.

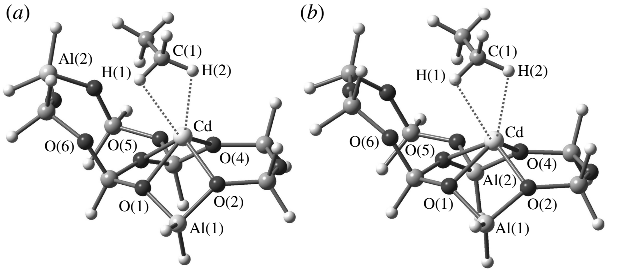


Figure 2 Optimized structures of (*a*) C_2H_6/Cd Z_d and (*b*) C_2H_6/Cd Z_s adsorption complexes.

Molecular C_2H_6 adsorbed on the exchanged cadmium cation is a precursor to subsequent chemical activation. The ethane molecule coordinates to the Cd Z_s and Cd Z_d clusters with two hydrogen atoms from one methyl group (η^2-coordination), as shown in Figure 2. The calculated adsorption energies are 27 and 49 kJ mol^{-1}, respectively, for Cd Z_s and Cd Z_d. The four-fold coordination of Cd by the lattice oxygen atoms remains unchanged after ethane adsorption. However, all of the Cd–O bonds become somewhat longer, and the Cd^{2+} partially leaves the cation site towards the adsorbed molecule (Table 1). More important changes are observed in the geometry of the C_2H_6 species. The C–H bonds directly interacting with the exchanged cation are elongated in comparison with the corresponding bonds of gas-phase ethane. In addition, the respective H(1)–C(1)–H(2) bond angles increase remarkably upon adsorption (Table 1).

[†] A former student of the Higher Chemical College of the RAS (1999–2004).

[‡] The starting geometry of the clusters corresponded to the real lattice of the ZSM-5 zeolite according to X-ray diffraction data.[9] For convenience, we choose the outer H-atoms as a rigid container for the model. DFT, with the B3LYP[10] hybride functional was used to perform all of the calculations. Geometry optimizations and saddle point searches were all performed using the Gaussian 03 program.[11] The DGDZVP[12] basis set was used for the Cd atom, whereas the C_2H_6 and the zeolitic oxygen atoms were described by the 6-311G(d,p) basis set. Al and Si atoms as well as the boundary H atoms were treated by the D95-Dunning/Huzinaga basis set.[13] Special restrictions were imposed on the procedure of optimization of the positions of the boundary H-atoms as described in ref. 14. All of the energies obtained from the DFT calculations used for estimating the reaction heats and the activation barriers were corrected for the zero-point energy.

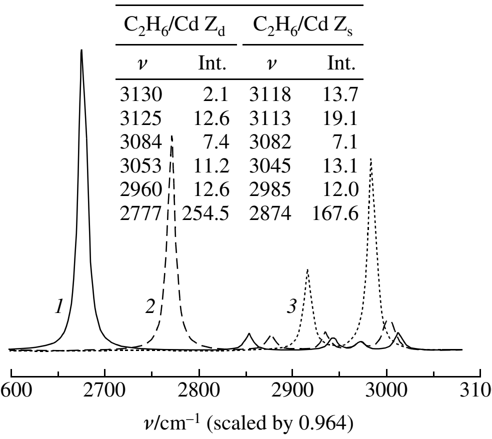
Table 1 Selected geometry parameters [interatomic distances/Å and H(1)–C(1)–H(2) bond angle/°] for the C_2H_6[a] adsorption complexes and the respective free adsorption sites.

	Cd–O(1)	Cd–O(2)	Cd–O(4)	Cd–O(5)	C–H(1)	C–H(2)	Cd–H(1)	Cd–H(2)	∠H(1)–C(1)–H(2)
Cd Z_d	2.229	2.194	2.314	2.316	—	—	—	—	—
C_2H_6/Cd Z_d	2.251	2.211	2.373	2.364	1.103	1.119	2.385	2.216	114.0°
Cd Z_s	2.283	2.194	2.208	2.272	—	—	—	—	—
C_2H_6/Cd Z_s	2.302	2.207	2.231	2.299	1.101	1.110	2.461	2.332	112.7°

[a] The calculated C–H bond length in the gas phase of C_2H_6 is equal to 1.094 Å; the H–C–H bond angle is equal to 107.5°.

The effective transfer of electron density from ethane to the Cd^{2+} cation equals 0.124 and 0.173 electrons,[§] respectively, for the C_2H_6/Cd Z_s and C_2H_6/Cd Z_d complexes. The smaller charge transfer and the weaker C_2H_6 adsorption reflect a lower Lewis acidity of the cadmium cations stabilized in the conventional ion-exchange sites (Z_s). Therefore, one expects a lower chemical activity of these species. This supports the assumption that the heterolytic dissociation of H_2 occurs over cadmium ions, which compensate the negative charges of distant aluminum-occupied oxygen tetrahedra.[5]

In addition to the geometry changes, the interaction of ethane with the positively charged Cd^{2+} ion results in a strong polarization of the adsorbed C_2H_6. These perturbations affect the vibrational properties of the C_2H_6 species in the adsorption complexes. The calculated IR spectra of C–H vibrations of the C_2H_6/Cd Z_s and C_2H_6/Cd Z_d are shown in Figure 3. Note that, although the method and the model used have some deficiencies for modeling of the hydrocarbon–zeolite system, it was shown[8] that thus simulated IR spectra of the adsorbed light alkanes well agree with the experimental ones and reproduce all their qualitative features. One can see that both spectra contain five slightly perturbed bands with frequencies close to those observed in the gas phase (2960–3130 cm^{-1}), whereas for each of the complexes one band (at 2874 or 2777 cm^{-1}, respectively, for the Z_s or Z_d site) is very strongly red-shifted and exhibits a very high relative intensity compared with those of the other C–H stretching bands. This band corresponds mainly to the displacements of the H(1) and H(2) from the C–H bonds directly interacting with the Cd^{2+} ion. Due to the excessive positive charge of the cadmium ion in the Z_d site, the polarization of the adsorbed C_2H_6 in this case is much stronger than for the Cd Z_s model. This, along with the stronger Lewis acidity of the Cd Z_d site, results in about 100 cm^{-1} stronger red shift, as well as remarkably higher intensity of this band, as compared to the Cd Z_s case. Recently, using the C_2H_6 adsorption on ZnZSM-5 zeolite as an example, it was shown that such a strong perturbation of adsorbed molecules leads to their chemical activation at higher temperatures.[2] The calculated red shift and the intensity of the low frequency C–H stretching vibration in the C_2H_6/Cd Z_d complex are significantly higher than those for the similar complex with the Zn^{2+} cation.[16] Thus, one can expect that cadmium cations stabilized in the charge-alternating cation sites of high silica zeolites will be at least as active but most probably even more active than the respective sites in ZnZSM-5 for light alkanes activation.



C_2H_6/Cd Z_d		C_2H_6/Cd Z_s	
ν	Int.	ν	Int.
3130	2.1	3118	13.7
3125	12.6	3113	19.1
3084	7.4	3082	7.1
3053	11.2	3045	13.1
2960	12.6	2985	12.0
2777	254.5	2874	167.6

Figure 3 Calculated IR frequencies (ν/cm^{-1}) of C–H stretching vibrations with their intensities (Int./km mol^{-1}); simulated IR spectrum for (*1*) C_2H_6/Cd Z_d, (*2*) C_2H_6/Cd Z_s structures and (*3*) free C_2H_6 based on the DFT computed vibrational frequencies scaled by a factor of 0.964.

The appearance of the low-frequency C–H vibration is evidence of a significant weakening of the corresponding chemical bonds. Therefore, one expects facilitation of the dissociation of the adsorbed molecules. Chemical activation of the adsorbed ethane proceeds *via* heterolytic C–H bond cleavage resulting in the formation of a Brønsted acid proton and cadmium-alkyl group. In case of the Cd Z_s model, two different pathways are possible, which differ in the mechanism of H abstraction from C_2H_6 by either O(4) or O(6) zeolite oxygen (Figure 4). When Cd^{2+} is stabilized in the Z_d cation site, the pathway resulting in formation of Brønsted acid site attached to the O(4) atom is strongly unfavoured due to the repulsion of the two adjacent positively charged species (H^+ and $[Cd–Et]^+$). The geometry optimization of the corresponding product leads to an improbable structure.

The lowest activation energy is found for ethane dissociation on the Cd Z_d site (**TS1**, ΔE^{TS} 113 kJ mol^{-1}). Taking into account the strong molecular adsorption of ethane (49 kJ mol^{-1}), the overall activation energy for the formation of species **1** is equal to 64 kJ mol^{-1}. These barriers are much lower than those calculated within the same model for ethane activation over GaZSM-5 (210 kJ mol^{-1}).[14] This suggests a significantly higher activity of CdZSM-5 zeolite, which is in agreement with experimental data.[4] The true activation energies for both pathways of the heterolytic dissociation of ethane over Cd Z_s model are slightly higher. In addition, the molecular adsorption to Cd Z_s is weaker (27 kJ mol^{-1}) and the dissociation is facilitated to a lesser extent. In contrast to the Cd Z_d, the basicity of the O(4) atom in the Cd Z_s site is high; therefore, the H-abstraction by this atom leads to formation of a rather strong O–H bond. The resulting energy gain dominates the energy loss due to repulsive interaction between the positively charged H^+ and $[Cd–Et]^+$ ions. Therefore, corresponding product **2** of C_2H_6 dissociation is rather stable. On the other hand, abstraction of the proton to another zeolite ring, which is favoured for the Cd Z_d, exhibits a remarkably higher activation energy and results in the formation of unstable structure **3** (Figure 4). Thus, the activation of C_2H_6 over Cd^{2+} ions stabilized in conventional ion-exchanged sites of ZSM-5 is both kinetically and thermodynamically less favourable compared to the case of stabilization at the distant anionic sites.

Summarizing the above results, based on the DFT cluster modeling, we predict a CdZSM-5 zeolite to be highly active for alkane activation. Molecular adsorption of ethane to the exchanged cations results in formation of rather stable σ-CH complexes. The subsequent heterolytic dissociation of C_2H_6 is a favourable process, and we predict it to occur at moderate

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[§] Mulliken atomic charges calculated for the optimized adsorption complexes were used for estimation of the effective electron transfer.

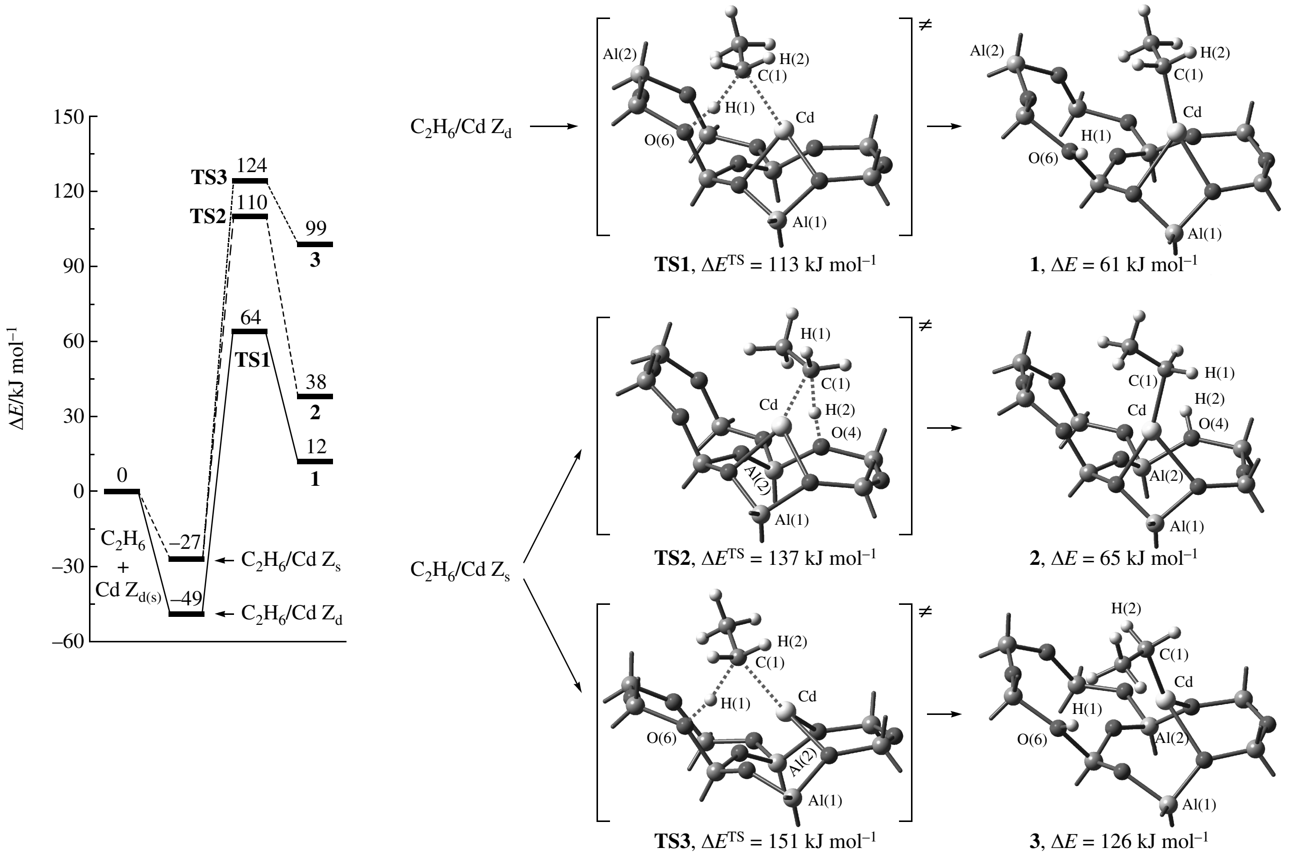

Figure 4 Activation of ethane over Cd^{2+} in ZSM-5 zeolite.

temperatures. Depending on the local environment of Cd^{2+} in the zeolite, these complexes exhibit different vibrational and chemical properties. Thus, we believe that using IR spectroscopy of light alkanes adsorption as a molecular probe one can distinguish different location of Cd^{2+} in ZSM-5.

References

1 A. Hagen and F. Roessner, *Catal. Rev.*, 2000, **42**, 403.
2 V. B. Kazansky and E. A. Pidko, *J. Phys. Chem. B*, 2005, **109**, 2103.
3 D. Kallo and G. Onyestyak, in *Stud. Surf. Sci. Catal.*, eds. B. Delman and G. F. Fróment, Elsevier, Amsterdam, 1987, vol. 34, p. 605.
4 J. Bandiera and Y. Ben Taarit, *Appl. Catal. A: General*, 1997, **152**, 43.
5 A. I. Serykh, *Microporous and Mesoporous Materials*, 2005, **80**, 321.
6 *CRC Handbook of Chemistry and Physics*, 80th edn., ed. D. R. Lide, CRC Press, New York, 1999.
7 E. A. Pidko and R. A. van Santen, *ChemPhysChem*, 2006, **7**, 1657.
8 E. A. Pidko, J. Xu, B. L. Mojet, L. Lefferts, I. R. Subbotina, V. B. Kazansky and R. A. van Santen, *J. Phys. Chem. B*, 2006, **110**, 22618.
9 D. H. Olson, G. T. Kokotailo, S. L. Lawton and W. M. Meier, *J. Chem. Phys.*, 1981, **85**, 2238.
10 (*a*) A. D. Becke, *Phys. Rev.*, 1988, **A38**, 3098; (*b*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; (*c*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03 (Revision B.05)*, Gaussian, Inc., Pittsburgh PA, 2003.
12 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.
13 T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, ed. H.F. Schaefer III, Plenum Press, New York, 1976, vol. 3, pp. 1–28.
14 E. A. Pidko, V. B. Kazansky, E. J. M. Hensen and R. A. van Santen, *J. Catal.*, 2006, **240**, 73.
15 H. Lermer, M. Draeger, J. Steffen and K. K. Unger, *Zeolites*, 1985, **5**, 131.
16 G. M. Zhidomirov, A. A. Shubin, V. B. Kazansky and R. A. van Santen, *Theor. Chem. Acc.*, 2005, **114**, 90.

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