Zeolites

A DFT Study of the Acidity of Ultrastable Y Zeolite: Where Is the Brønsted/Lewis Acid Synergism?**

Claudio J. A. Mota, Daniel L. Bhering, and Nilton Rosenbach, Jr.*

Ultrastable Y zeolites (USY) are the main component of cracking catalysts. They are normally produced from a NH_4Y

[*] Prof. Dr. C. J. A. Mota, Dr. D. L. Bhering, N. Rosenbach, Jr.
Instituto de Química
Universidade Federal do Rio de Janeiro
Cidade Universitária CT, Bloco A
21949-900 Rio de Janeiro (Brazil)
Fax: (+55) 21-2562-7106
E-mail: cmota@iq.ufrj.br

[**] Authors thank PRH-ANP, CNPq and CTPETRO for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  DOI: 10.1002/ange.200353049

derivative, upon treatment with steam at 500–700 °C.[1] Under these conditions, there is a partial loss of aluminium from the zeolite structure, which improves the thermal stability and catalytic properties of the zeolite. Nevertheless, the aluminum atoms released from the framework stay inside the cavities and channels as extra-framework aluminum species (EFAL). The nature of the EFAL species is not completely known, but it is postulated that oxoaluminum cations, such as AlO^+, $Al(OH)_2^+$, $Al(OH)^{2+}$, and some neutral compounds such as AlOOH and hydrated Al_2O_3, could account for some of the EFAL species. [2]

The catalytic activity of USY zeolites is usually higher than the parent HY zeolite.[3] As the framework Si:Al ratio goes up, the acid sites in USY becomes more isolated from each other, increasing the acid strength. However, the presence of EFAL species plays a more important role. Leaching out part of the EFAL of an USY zeolite reduces its catalytic activity.[4] There are also ways to prepare a dealuminated zeolite without EFAL species. The most popular method is treatment with $(NH_4)_2SiF_6$ in aqueous solution. [5] This procedure replaces the framework Al atoms by Si atoms of the SiF_6^{2-} anion, thus leaving no EFAL species, which remain dissolved in the aqueous solution and are subsequently washed away. Notwithstanding, the catalytic activity of the dealuminated Y zeolites prepared by this way is considerably lower[6] than the catalytic activity of an USY zeolite, prepared by steaming. To explain these results, a Brønsted/Lewis synergism has been proposed, aroused upon the interaction of the EFAL species (Lewis acid sites) with the framework hydroxy groups (Brønsted acid sites) as schematized in Figure 1.[7]

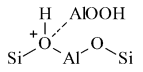

Figure 1. Proposed Brønsted/Lewis synergism in USY zeolites.

Measurements of acid strength of the zeolite are difficult. Methods relied on Hammett bases are criticized, as many bases might be bulk enough to diffuse into the zeolite pores. Recent measurements, based on spectroscopic investigations,[8] ranked the zeolites as strong acids, with acidity comparable to concentrated sulfuric acid solutions. Nevertheless, a study of the acid strength of dealuminated Y zeolites, with and without EFAL species, indicated virtually the same acidity values as those obtained by ammonia microcalorimetry. [9]

On the other hand, theoretical methods have been used[10] to study the acidity and catalytic properties of zeolites. We recently published a DFT study of the structure and coordination of some EFAL species on a zeolite Y cluster.[11] We present herein preliminary results of cluster calculations on the effect of the EFAL species on the zeolite acid strength. Our main objective is to investigate the interactions of the EFAL with the acid site, aiming to observe if the Brønsted/Lewis synergism really occurs on zeolites.

The calculations were performed on a T_6 cluster (T = Si, Al), which represents a real part of the zeolite Y structure. The same cluster was previously used in a study of the structure of EFAL species on zeolites.[11] The border Si atoms were saturated with hydrogen atoms and the framework Al atoms with hydroxy groups, to avoid dangling bonds. The EFAL species studied were AlO^+, $Al(OH)_2^+$, $Al(OH)^{2+}$, $Al(OH)_3$, and AlOOH. To account for system neutrality, we used as many framework Al atoms as necessary. All calculations were performed at the B3LYP6-31G** level of theory by using the GAUSSIAN98 program.[12] The acid strength was theoretically determined as the enthalpy difference for the deprotonation reaction. To better describe this process, single-point energy calculations were performed at B3LYP6–311++G**. The thermodynamic properties were obtained from the frequency calculations, scaled by 0.96. Calculations of the deprotonation energy for T_6 clusters with one and two framework Al atoms were also performed for comparison, as they represent models of Y zeolites without EFAL species.

Table 1 shows the results for the calculated systems. One can see that the cluster with one framework Al atom presented a lower deprotonation enthalpy than the cluster with two Al atoms. This is consistent with other calculations that show that the acid strength decreases as the sites become closer to each other. There is a drastic change in geometry upon deprotonation. The Al–O bond length shrinks from 1.95 Å in the acid form, to 1.77 Å in the deprotonated structure. The Si-O(H)-Al bond angle varies from 128.4° in the acid form to 147° in the anion. These results account for the HT_6 (1 Al), with one framework Al atom, but the trend is the same for the other calculated structures.

All the EFAL·HT_6 clusters studied, excepted the $Al(OH)_2^+$, presented a higher deprotonation enthalpy, compared with the respective HT_6 clusters. Contrary to what is proposed in the literature, the EFAL reduced the acid strength of the framework hydroxy groups and no Brønsted/Lewis synergism was found. The optimization of the $Al(OH)_3$·HT_6(1Al), AlOOH·HT_6(1 Al) and AlO^+·HT_6(2 Al) led to an intramolecular proton transfer and all ended with the proton being bound to one of the oxygen atoms of the EFAL (Figure 2). Hence, deprotonation of these species

Table 1: Calculated deprotonation energies at 298.15 K.[a]

Reaction[a]	B3LYP6-31G**			B3LYP6-311++G**//B3LYP6-31G**		
	ΔH [kcal mol^{-1}]	ΔS [cal mol^{-1} K^{-1}]	ΔG [kcal mol^{-1}]	ΔH [kcal mol^{-1}]	ΔS [cal mol^{-1} K^{-1}]	ΔG [kcal mol^{-1}]
HT_6(1 Al)⇌T_6^-(1 Al) + H^+	297.9	20.4	291.8	295.5	20.4	289.4
H_2T_6(2 Al)⇌HT_6^-(2 Al) + H^+	303.9	3.7	302.8	298.1	3.7	297.0
$Al(OH)_3$·HT_6(1 Al)⇌$Al(OH)_3$·T_6^-(1 Al) + H^+	309.6	13.1	305.7	303.4	13.1	299.5
Al(OOH)·HT_6(1 Al)⇌Al(OOH)·T_6^-(1 Al) + H^+	367.5	14.5	363.2	360.8	14.5	356.4
AlO^+·HT_6 (2 Al)⇌AlO^+·T_6^- (2 Al) + H^+	347.7	27.3	339.6	342.6	27.3	334.5
$Al(OH)_2^+$·HT_6 (2 Al)⇌$Al(OH)_2^+$·T_6^- (2 Al) + H^+	298.6	21.0	292.3	294.2	21.0	287.9
$Al(OH)^{+2}$·HT_6(3 Al)⇌$Al(OH)^{+2}$·T_6^-(3 Al) + H^+	311.2	31.1	301.9	305.8	31.1	296.6

[a] All frequency calculations were done at the B3LYP6–31G** level.

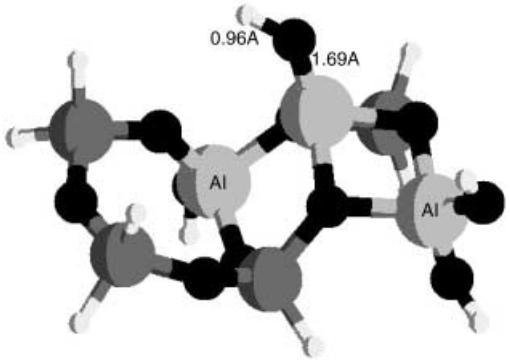

Figure 2. Optimized structure of the $AlO^+{\cdot}HT_6(2\,Al)$, showing the formation of an EFAL hydroxy group (framework Al assigned).

involves considerably higher energy, compared to deprotonation of the isolated acid site. For the AlOOH and AlO^+ species, the intramolecular proton transfer forms a stable structure, as indicated by the highest deprotonation enthalpy among the calculated structures. This may imply that Al=O bonds are not favored, but are protonated to form EFAL hydroxy groups.

From the calculations at the B3LYP6-311++G** level, the highest acidity was found for the $Al(OH)_2^+{\cdot}HT_6(2\,Al)$. If we take the ΔG (G is the Gibbs free energy) between the $Al(OH)_2^+{\cdot}HT_6(2\,Al)$ and the two EFAL free clusters, $HT_6(2\,Al)$ and $HT_6(1\,Al)$, to estimate the increase in acidity, we find that the EFAL has an effect on the pK_a value by about -15.5 for $HT_6(2\,Al)$ and -2.5 for $HT_6(1\,Al)$ at 298.15 K. Nevertheless, this increase in acid strength is not due to a Brønsted/Lewis synergism, but to hydrogen bonding between the EFAL hydroxyls and the oxygen atoms of the formed AlO_4^- tetrahedral (Figure 3). Hence, anion stabilization through hydrogen bonding, instead of Brønsted/Lewis synergism in the acid form, should account for the enhanced activity of USY zeolites. Therefore, structural defects in USY, formed upon the release of framework aluminum atoms, might also contribute to the increased activity of these zeolites, compared with those dealuminated by $(NH_4)_2SiF_6$.

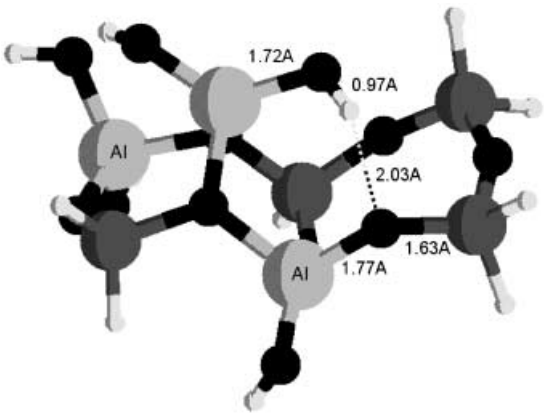

Figure 3. Structure of the conjugated base of $Al(OH)_2{\cdot}HT6(2\,Al)$, showing the hydrogen bonding between the EFAL hydroxy group and the framework oxygen atom (framework Al assigned).

The defects generate SiOH nests, which could also contribute to anion stabilization through hydrogen bonding.

We also ran calculations with ammonia as base, as suggested by one of the referees. We have identified that there are many possibilities for the NH_3 molecule to interact with the EFAL, which constitutes a separate work. However, we found the same behavior of reducing the acid strength with respect to an isolated acid site. For the $Al(OH)_2^+{\cdot}HT_6$ interacting with ammonia, we found, at least two possible reaction pathways: one leading to $NH_4^+{\cdot}Al(OH)_2^+{\cdot}T_6$, in which the proton is transferred to ammonia; the other leading to the formation of a complex between NH_3 and $Al(OH)_2^+{\cdot}HT_6$. This second structure was found to be more stable by 4.6 kcal mol^{-1} at B3LYP6-31G** level, and involves an internal proton transfer to the EFAL OH group, which is hydrogen bonded with the NH_3 and the zeolite conjugated base. This may explain the better stabilization of this structure. Nevertheless, we stress that these are initial results and a careful investigation of the adsorption of NH_3 on $EFAL{\cdot}HT_6$ is under way.

It was recently proposed[13] that the presence of cationic species near the acid site stabilizes the conjugated base and increase zeolite acidity. Our calculations show that hydrogen bonding of the hydroxylated EFAl species with the conjugated base also contribute to an increase in acid strength. These concepts may change the direction of developing new structural modifications in zeolites to improve catalytic activity.

Supporting Information: Structure of the optimized minima.

Received: October 9, 2003
Revised: February 17, 2004 [Z53049]

Keywords: ab initio calculations · acidity · aluminum · Lewis acids · zeolites

[1] a) Q. L. Wang, G. Giannetto, M. Torrealba, G. Perot, C. Kappenstein, G. Guisnet, *J. Catal.* **1991**, *130*, 459; b) M. Guisnet, Q. L. Wang, G. Giannetto, *Catal. Lett.* **1990**, *4*, 299.
[2] a) R. D. Shannon, K. H. Gardner, R. H. Staley, G. Bergeret, P. Gallezot, A. Arnoux, *J. Phys. Chem.* **1985**, *89*, 4778; b) M. J. Remy, D. Stanica, G. Poncelet, E. J. P. Feijen, P. Grobet, *J. Phys. Chem.* **1996**, *100*, 12440.
[3] J. R. Sohn, S. J. DeCanio, P. O. Fritz, J. H. Lunsford, *J. Phys. Chem.* **1986**, *90*, 4847.
[4] Q. L. Wang, G. Giannetto, G. Guisnet, *J. Catal.* **1991**, *130*, 471.
[5] G. Garralon, V. Fornés, A. Corma, *Zeolites* **1988**, *8*, 268.
[6] a) R. A. Beyerlein, G. B. McVicker, L. N. Yacullo, J. Ziemiak, *J. Phys. Chem.* **1988**, *92*, 1967; b) R. Carvajal, P. J. Chu, J. H. Lunsford, *J. Catal.* **1990**, *125*, 121; c) C. J. A. Mota, R. L. Martins, L. Nogueira, W. B. Kover, *J. Chem. Soc. Faraday Trans.* **1994**, 2297.
[7] a) P. O. Fritz, J. H. Lunsford, *J. Catal.* **1989**, *118*, 85; b) S. Beran, *J. Phys. Chem.* **1990**, *94*, 335; c) A. Corma, V. Fornés, F. Rey, *Appl. Catal.* **1990**, 59, 267; d) Q. L. Wang, G. Giannetto, M. Guisnet, *J. Catal.* **1991**, *130*, 471; e) F. Lónyi, J. H. Lunsford, *J. Catal.* **1992**, *136*, 566.
[8] a) B. S. Umansky, W. K. Hall, *J. Catal.* **1990**, *124*, 97; b) B. S. Umansky, J. Engelhadt, W. K. Hall, *J. Catal.* **1990**, *127*, 128; c) T. Xu, E. Munson, J. Haw, *J. Am. Chem. Soc.* **1994**, *116*, 1962.

[9] a) A. I. Biaglow, D. J. Parrillo, G. T. Kokotailo, R. J. Gorte, *J. Catal.* **1994**, *148*, 213; b) R. A. Beyerlein, . C. Choi-Feng, J. B. Hall, B. J. Huggins, G. J. Ray, *Top. Catal.* **1997**, *4*, 27.
[10] a) G. J. Kramer, R. A. van Santen, *Chem. Rev.* **1996**, *96*, 637; b) J. Sauer, P. Ugliengo, E. Garrone, V. R. Saunders, *Chem. Rev.* **1994**, *94*, 2095; c) J. B. Nicholas, A. C. Hess, *J. Am. Chem. Soc.* **1994**, *116*, 5428; d) M. Brändle, J. Sauer, *J. Am. Chem. Soc.* **1998**, *120*, 1556; e) J. R. Hill, C. M. Freeman, B. Delley, *J. Phys. Chem. A* **1999**, *103*, 3772; f) M. Sierka, U. Eichler, J. Datka, J. Sauer, *J. Phys. Chem. B* **1998**, *102*, 6397; g) N. O. Gonzales, A. T. Bell, A. K. Chakraborty, *J. Phys. Chem. B* **1997**, *101*, 10058.
[11] D. L. Bhering, A. Ramirez-Solís, C. J. A. Mota, *J. Phys. Chem. B* **2003**, *107*, 4342.
[12] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
[13] G. N. Vayssilov, N. Rusch, *J. Phys. Chem. B* **2001**, *105*, 4277.

