A Fast and Easy Computational Method to Calculate the 13C NMR Chemical Shift of Organic Species Adsorbed on the Zeolite Surface

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Solid-state NMR has became a valuable tool for studying the formation and reactivity of alkoxy species on zeolites.[1,2] Since the framework oxygen atoms of the zeolites can act as nucleophiles, the lifetime[3] of free carbocations are not more than 100 ns, impairing their observation on the NMR time scale. On the other hand, the many different zeolite structures show distinct reactivity toward hydrocarbon transformation. Shape selectivity and acid strength are normally used to explain such behavior, although recent studies[4] indicate that the acid strength of zeolites does not significantly change with structure. Therefore, zeolite activity is ultimately governed by the reactivity of the adsorbed organic species, either alkoxides or transient, short-lived, carbocations, which might be in equilibrium with the alkoxides at high temperatures.

Quite a few theoretical results,[5] to support the experimental NMR findings, are available in the literature. In one hand, treatment of the zeolite structure by quantum mechanical techniques is not trivial. The finite cluster[6] approach has the disadvantage of misrepresenting the zeolite structure, which may provide some confinement and electrostatic effects. To circumvent this problem, advances have been made[7] with the use of the quantum mechanics molecular mechanics approach (QM/MM). The main problem is the high cost in computer time and the inaccessibility of many of the programs used. On the other hand, chemical shifts are computationally intensive calculations and sensitive to the basis set employed. These drawbacks have probably discouraged studies of the chemical shifts of adsorbed species on zeolites.

Recently, Forsyth and Sebag[8] showed that the combination of molecular mechanics geometry miminization, particularly the MM3 force field, and GIAO calculations at B3LYP/3-21G and B3LYP/6-31+G* is an efficient and reliable method to represent the 13C NMR properties of a variety of organic molecules having C, N, and O atoms. The authors used a series of different environments for C to establish a practical method to ascertain the 13C chemical shifts prediction. In this communication we show that the combination of quantum chemical (B3LYP/6-311+G*) and classical molecular mechanics (MM+) calculations is an efficient procedure to reproduce experimental results of solid-state 13C NMR chemical shift of alkoxy species on different zeolite structures.

Calculations were performed on faujasite (Y zeolite) and MFI (ZSM-5) structures. The Y zeolite pore aperture was simulated by a T_{48} cluster with 168 atoms, in which 47 atoms are Si, 1 Al atom, 71 O atoms and 49 H atoms to complete the valence of the external Si atoms. Details about the construction of this cluster were reported elsewhere.[9] For the ZSM-5 zeolite a T_{30} cluster, with 144 atoms, was used, in which 29 are Si, 1 Al, 39 H and 75 O atoms. The coordinates to construct the cluster were taken from published topological data.[10] The alkoxides were added to an oxygen atom
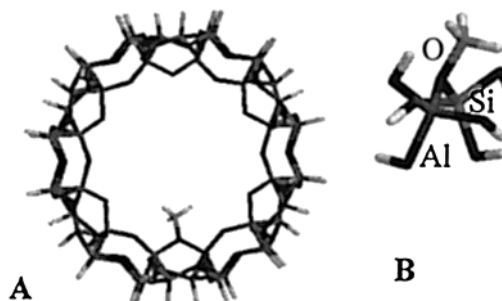

Figure 1. Methoxy-T_{48} (Y zeolite) and T_2 clusters. (a) Structure minimized by MM+. (b) T_2 cluster taken from minimized T_{48} cluster.

next to the aluminum atom to produce a neutral zeolite. The external hydrogen atoms were fixed during MM+ geometry optimization[11] to prevent the collapse of the zeolite structure. All other atoms had angles, bond lengths, and dihedrals relaxed during minimization. After MM+ geometry optimizations of the alkoxy-Y and alkoxy-ZSM-5, a reduction of the cluster's size was performed to calculate the chemical shift. All atoms, except the SiO_3 and AlO_3 around the alkoxides, were removed, leaving a T_2 cluster. The Si−O and Al−O bonds were saturated with hydrogen atoms, keeping constant all original geometric parameters obtained from MM+ optimization of the T_{48} (Y) and T_{30} (ZSM-5) clusters. The constructed OH bonds (to saturate the valences) were set to 0.98 Å length, which was the value obtained for the external OH bonds in the MM+ optimization. The GIAO calculations were performed on the alkoxy-T_2 clusters using B3LYP/6-311+G* level of theory and GAUSSIAN 94 package.[12] A T_3 cluster was also used for comparison. The Si atoms were saturated with hydrogen atoms, and the central Al, with OH. Geometry constrains were imposed only on dihedral angles HSiOAl, SiOAlO, OAlOSi which were kept at 0°, to keep minimum zeolite rigidity. Alkoxy-T_3 geometries and NMR calculations were conducted with B3LYP/6-311+G** level of theory. Calculations were performed for methoxy and ethoxy groups adsorbed on the zeolite surface (Figure 1).

Table 1 lists some geometric parameters found for the alkoxides on T_3 (MM+ and B3LYP/6-311+G** methods) cluster and on the T_2 cluster derived from minimization of the Y (T_{48}) and ZSM-5 (T_{30}) zeolites. Comparing both clusters at MM+ level of calculation, one can see that bond lengths are almost the same, but the angles show significant differences. The SiOAl angle in the MeT$_3$ was 109.1° at MM+, while the same angle is 122.5° and 113.8° for minimization of the Y and ZSM-5 clusters, respectively. The most strinking difference however, is in the AlOSiC dihedral angle. While the T_3 cluster showed values near 60°, the computed value for the Y and ZSM-5 clusters were significantly different for the methoxy and ethoxy groups. Calculations at B3LYP/6-311+G** level on the T_3 cluster gave the lowest values, being 0° for the methoxy

Table 1. Geometric Parameters for Different Levels of Theories and Clusters

geometrry optimization	cluster	alkoxide	bond length (Å)			bond angle (deg)	
			C–O	SiO	AlO	SiOAl	AlOSiC
MM+	T_3	methoxide	1.441	1.776	1.848	109.1	60.6
		ethoxide	1.447	1.778	1.850	107.9	60.8
MM+	T_2 from Y	methoxide	1.443	1.781	1.851	122.5	47.1
		ethoxide	1.448	1.781	1.850	122.8	39.4
MM+	T_2 from ZSM-5	methoxide	1.412	1.645	1.851	113.8	41.6
		ethoxide	1.426	1.651	1.854	112.7	39.8
B3LYP/6-311+G**	T_3	methoxide	1.459	1.732	1.944	119.7	0
		ethoxide	1.477	1.728	1.940	119.8	18.2

Table 2. ^{13}C Chemical Shifts for the Methoxy and Ethoxy Groups[a]

species		σ absolute (ppm)	σ calculated (ppm)
Y-methoxide	C	138.80	58.6 (58.9[14])
Y-ethoxide	C1	122.96	69.1 (71.6[14])
	C2	169.16	22.7 (15.7[14])
ZSM-5 methoxide	C	141.53	50.3 (49.2[16])
ZSM-5 ethoxide	C1	131.87	60.0
	C2	176.01	15.8
T_3 methoxide	C	120.55	63.4
T_3 ethoxide	C1	106.07	77.9
	C2	166.47	17.1

[a] The calculated σ values are relative to tetramethylsilane computed at GIAO/B3LYP/6-311+G**//B3LYP/6-311+G**. Brackets account for the experimental shifts reported in the references.

and 18.2° for the ethoxy. The difference in bond and dihedral angles between the T_3, Y, and ZSM-5 clusters is probably associated with repulsive interactions between the alkyl chain and the zeolite framework. Hence, the system responded to minimize these interactions, which are significantly less important in the T_3 cluster.

Table 2 shows the NMR chemical shifts calculated at GIAO/B3LYP/6-311+G**//B3LYP/6-311+G** (T_3 cluster) and GIAO/B3LYP/6-311+G**//MM+ levels, as well as reported experimental values. As can be seen, on one hand results from the T_3 cluster are not good enough to reproduce experiments. This is probably due to the calculated geometry of the alkoxides in the T_3 cluster. On the other hand, results from GIAO/B3LYP/6-311+G**//MM+ level of theory on a T2 cluster obtained from the optimized geometry of realistic Y and ZSM-5 clusters are more precise and can support the experimental findings. The correct assignment of the chemical shifts observed in methanol reactions over zeolites is not trivial. Many species such as physisorbed methanol, methoxonium ion, dimethyl ether, and the methoxy group, among others, have been proposed[13] and assigned different chemical shifts. The NMR data for the methoxy and ethoxy groups on faujasite were taken from a study[14] of alkyliodide adsorption on NaY and CsX. We also observed the methoxy at 58 ppm and the ethoxy at 71 (methylene) and 16 (methyl) ppm from the adsorption of the respective alkyliodides on AgY zeolite.[15] The calculated methyl shift for the ethoxide on Y zeolite is not well predicted (22.7 ppm calculated vs 15.7 ppm observed) probably due to the T_2 fragment, which may not be large enough to include necessary interactions. Yet, the experimental shift may represent an average value, since rotation around the C–C bond may lead to different conformations.

For the MFI we found a good correlation of the calculated chemical shift for the methoxy group with a study[16] of methanol protonation on HZSM-11, a zeolite whose structure is very similar

to that of ZSM-5. Hence, the difference in the reported chemical shift for the methoxy group on Y and MFI zeolites is unequivocally shown by calculations to be real and related to the different structure of the alkoxy groups on the two zeolites, supporting both experimental results. This has other implications, as the difference in chemical shift may be related with differences in reactivity of the alkoxides, and by consequence, differences in activity and selectivity of the zeolites.

These results show how important is the adequate treatment of the zeolite environment to have realistic NMR shielding values. When computing molecular properties in systems with a high degree of complexity, the use of a high computational level of theory is not enough to achieve experimental agreement. However, as shown in this communication, one must use an appropriate description of the zeolite environment.

Supporting Information Available: Seven tables with the *z*-matrix and total energies of the calculated structures and one figure with the optimized structure of the ZSM-5-ethoxide at MM+ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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