Supplementary Material

The interactions of Methyl *tert*-butyl ether on high silica zeolites: a combined experimental and computational study

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Building the mordenite cluster model.

To model the MTBE-MOR adduct a large cluster ($Si_{92}O_{143}$) was extracted from the zeolite periodic structure, featuring a segment of the main channel approximately 14 Å long, with two accessible side-pockets (Figure SM3). The four kinds of tetrahedral sites comprised in the model are shown in Figure SM4.

Then eight tetrahedral atoms (Figure SM3) were removed from 4 T2, 2 T3 and 2 T4 sites, respectively (it is known that T1 sites have the lowest Aluminum concentration in this kind of zeolite), along with eight Oxygen atoms, as shown in Figure SM3: with this choice, the wall between the two adjacent side-pockets was eliminated and a larger, fused cavity was obtained (Figure SM6).

As a consequence, 16 Oxygen atoms were left undercoordinated (Figure SM5) giving rise, ideally, to the same number of silanols: a successive dehydration step led to the removal of 5 water molecules, leaving in the cluster 6 silanol groups, and 5 distorted Si-O-Si moieties (Figure SM5).

To perform actual calculations it was necessary to saturate all the Si valencies with 82 additional Hydrogen atoms, so that the resulting cluster stoichiometry was $Si_{84}O_{124}H_{82}(OH)_6$ (Figure SM8).
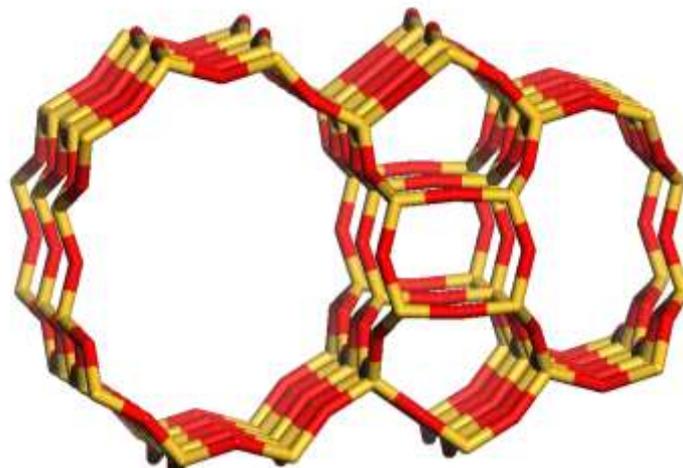
(a)
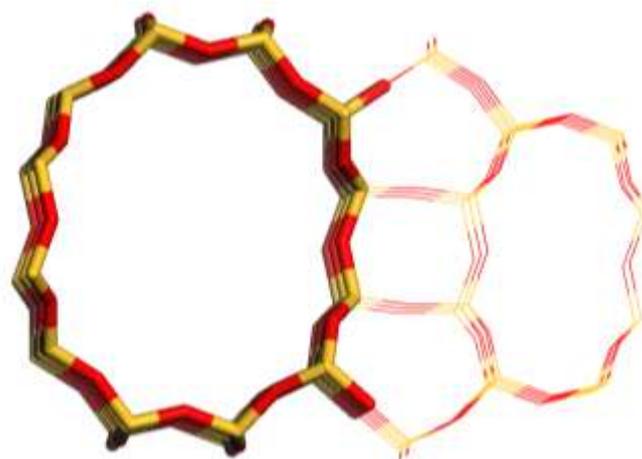
(b)
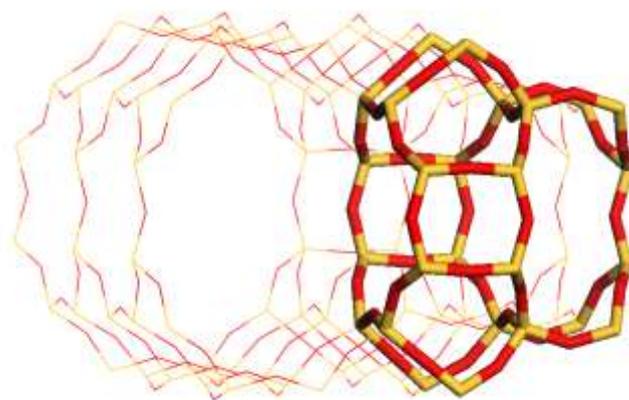
(c)

Figure SM1. Model cluster extracted from MOR periodic structure: (a) $Si_{92}O_{143}$ cluster; (b) highlight of the main channel segment in the model cluster; (c) highlight of one side-pocket in the model cluster.
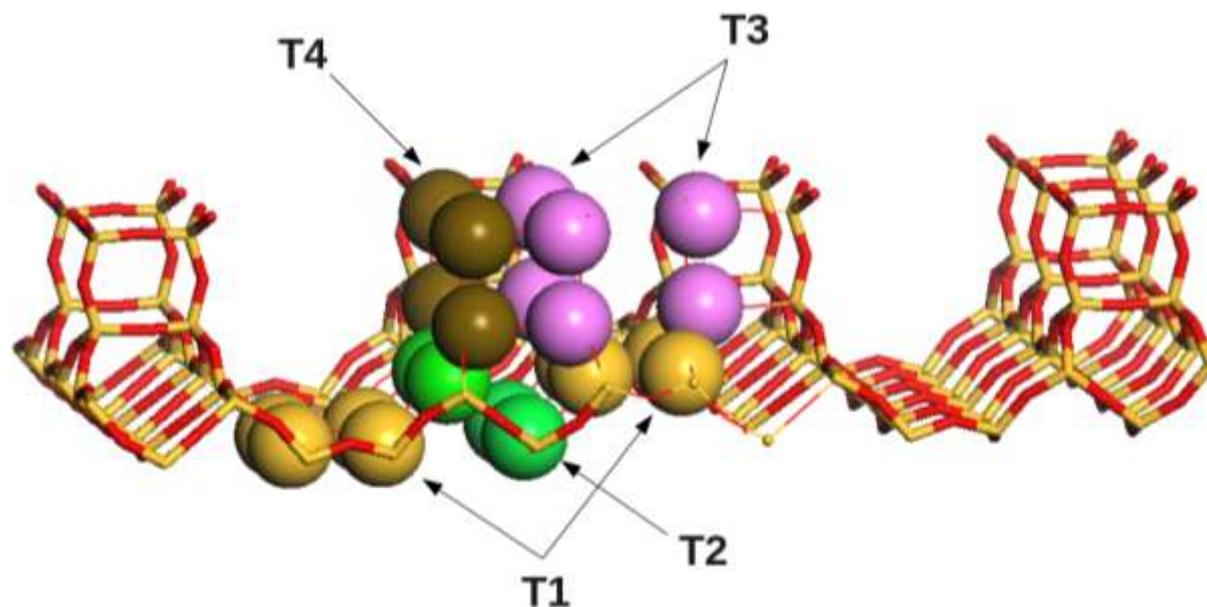
Figure SM2. Tetrahedral sites in the MOR structure.
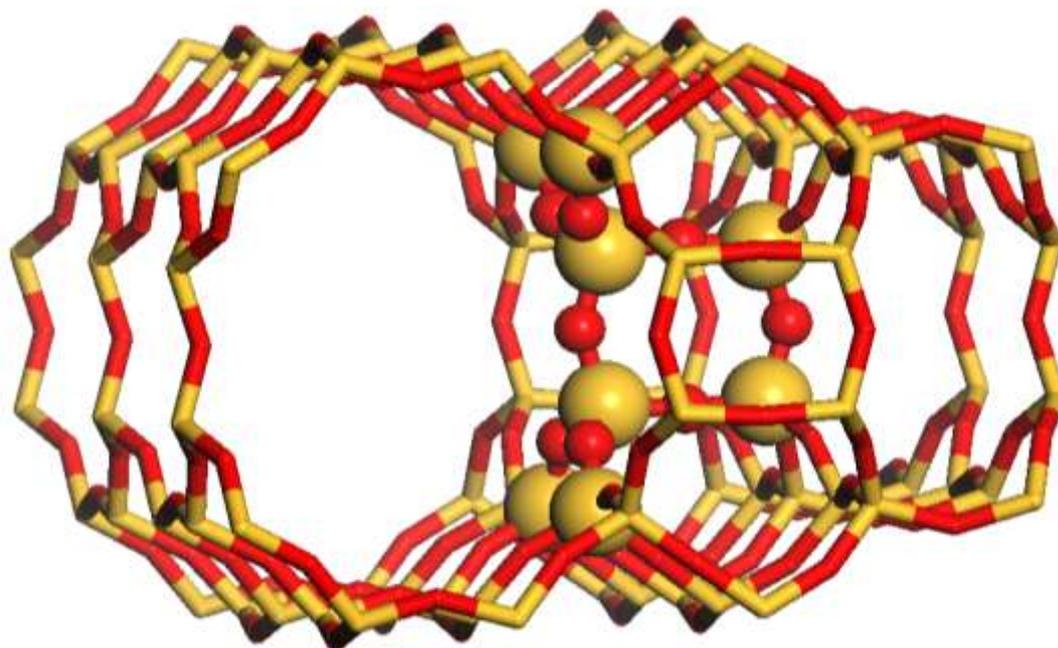
Figure SM3. The eight Silicon and Oxygen atoms removed to simulate the formation of defects due to the dealumination process.
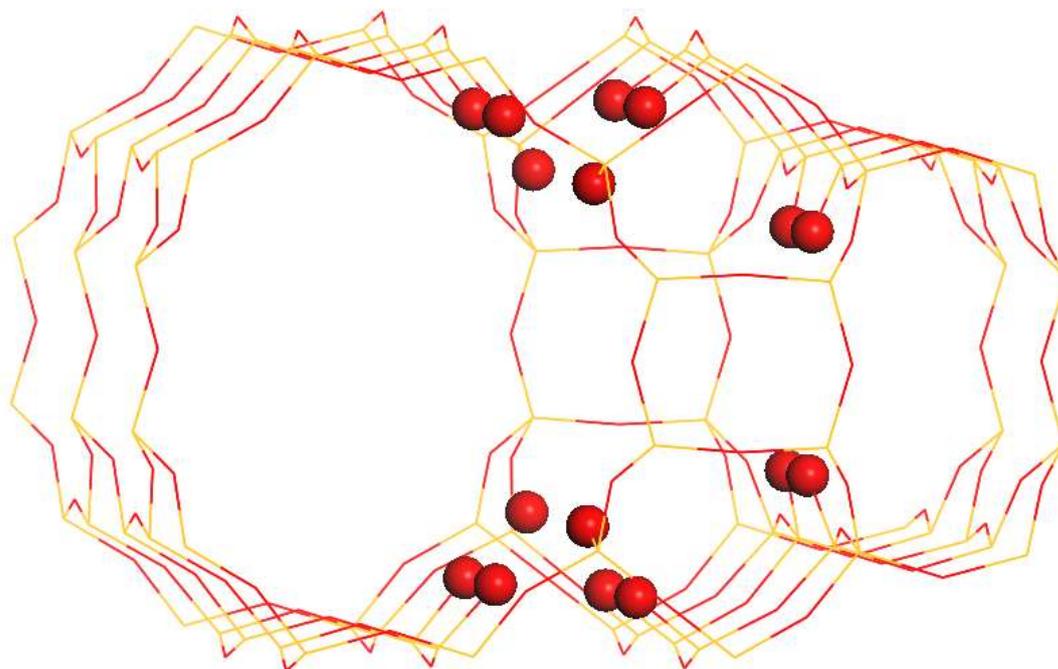
Figure SM4. Undercoordinated Oxygen atoms after removal of the eight tetrahedral sites. Five atoms were removed to simulate dehydration process, then five distorted Si-O-Si bridges are formed and six silanol groups are left.
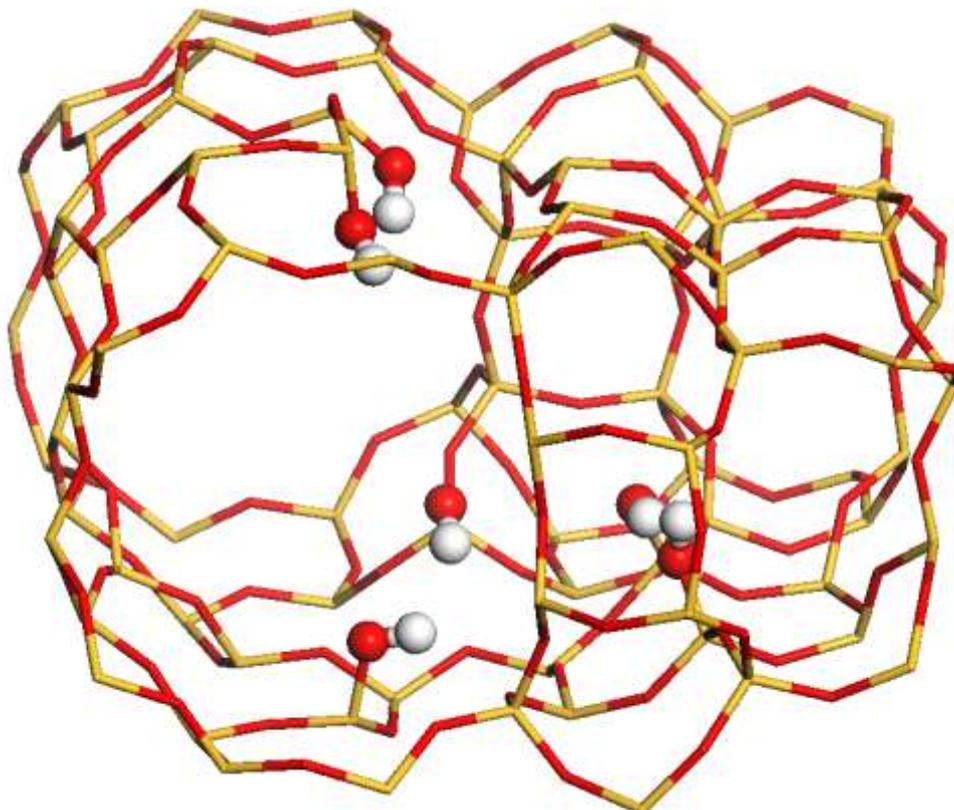
Figure SM5. The six silanol groups left in the model cluster after the simulated dealumination/dehydration.
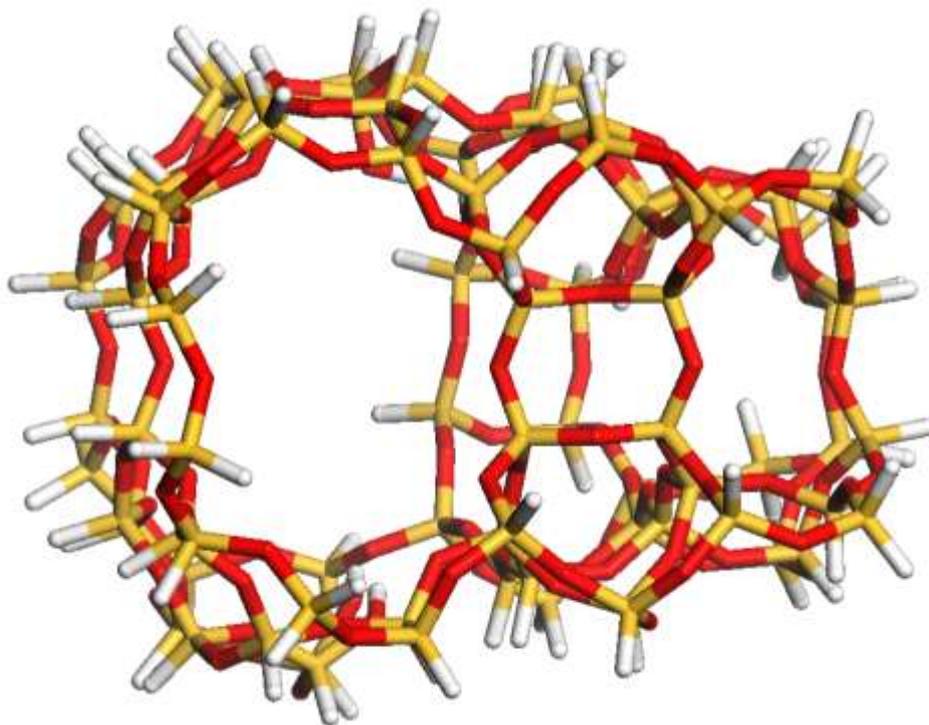
Figure SM6. $Si_{84}O_{124}H_{82}(OH)_6$ cluster used in actual calculations: all the "external" Silicon valencies are saturated with H.
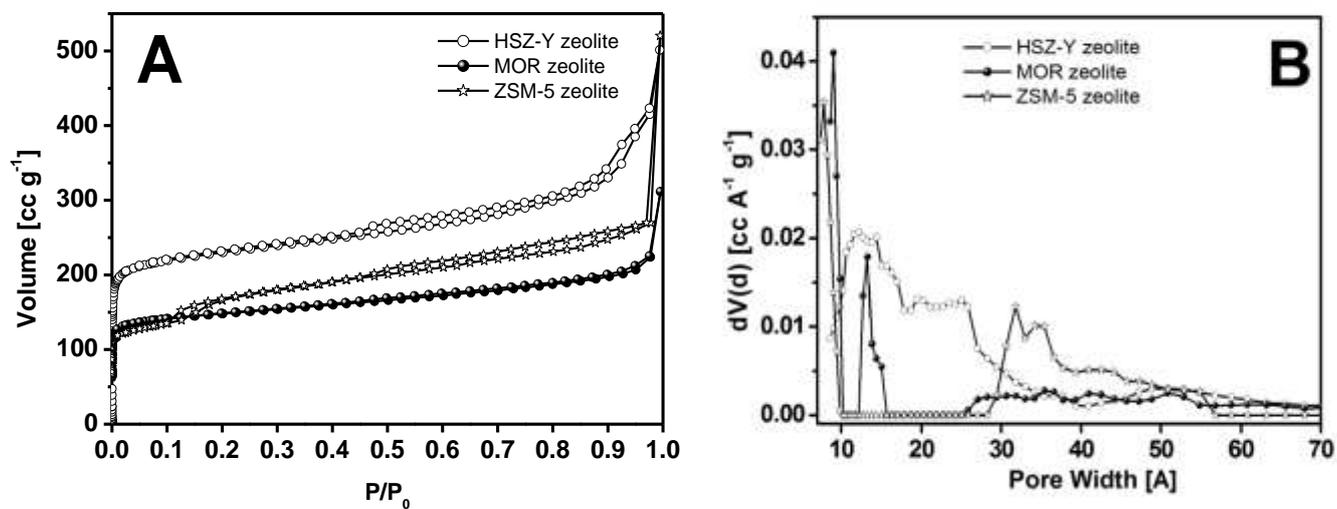
Figure SM7. N$_2$ adsorption/desorption isotherms at -196 °C (A) and pore size distribution (B) of HSZ-Y, MOR and ZSM5 samples.
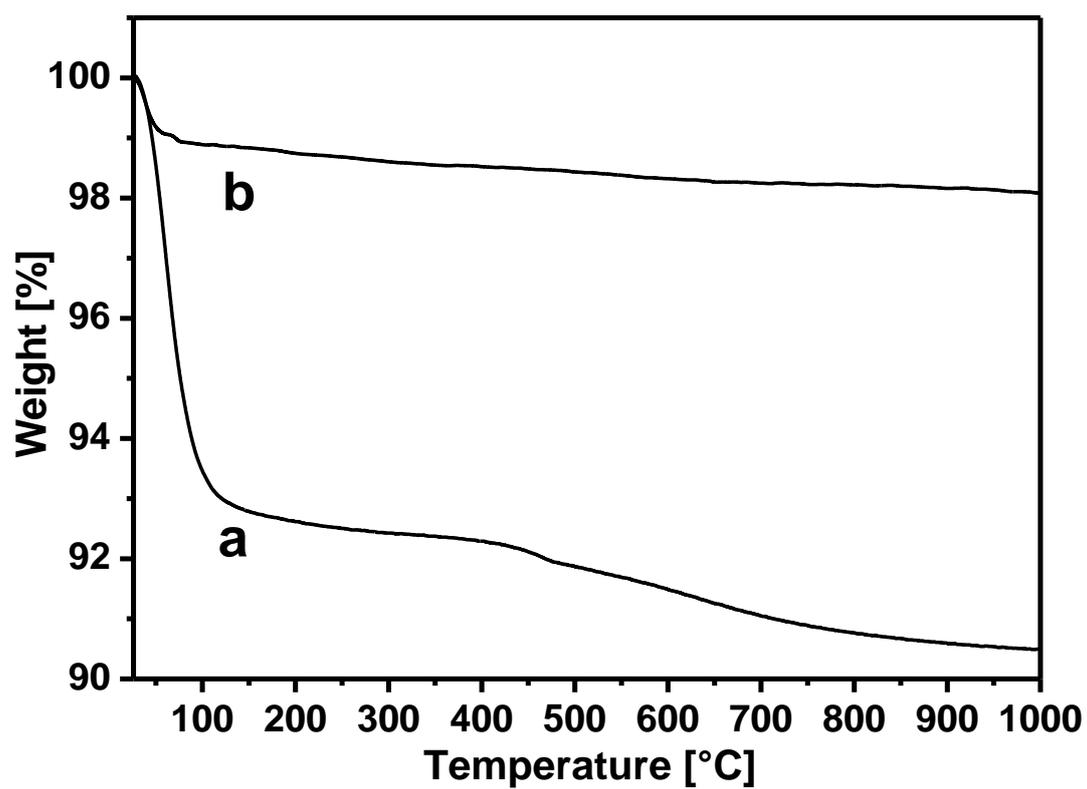
Figure SM8. TGA analyses of high silica MOR (a) and Y (b) zeolites recorded under O_2 flow (100 mL/min).
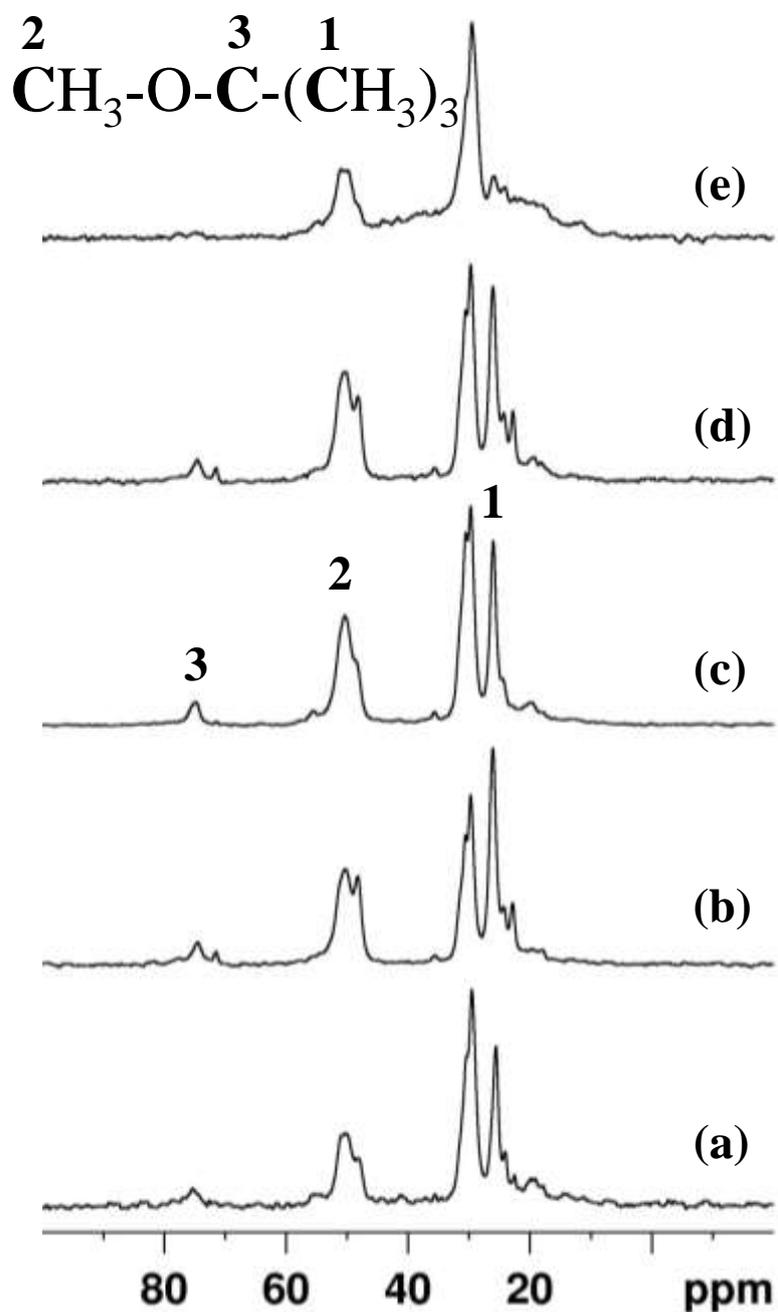
Figure SM9. ^{13}C CPMAS NMR spectra of zeolite MOR after MTBE adsorption at 0.5 mbar (a), 5 mbar (b), 10 mbar (c) and 20 mbar (d). ^{13}C CPMAS NMR spectrum recorded (previously adsorbed at 20mbar on MOR) after overnight evacuation of MTBE at RT (e). A MAS rate of 10 kHz and a CP contact time of 5 ms was used in all the experiments.

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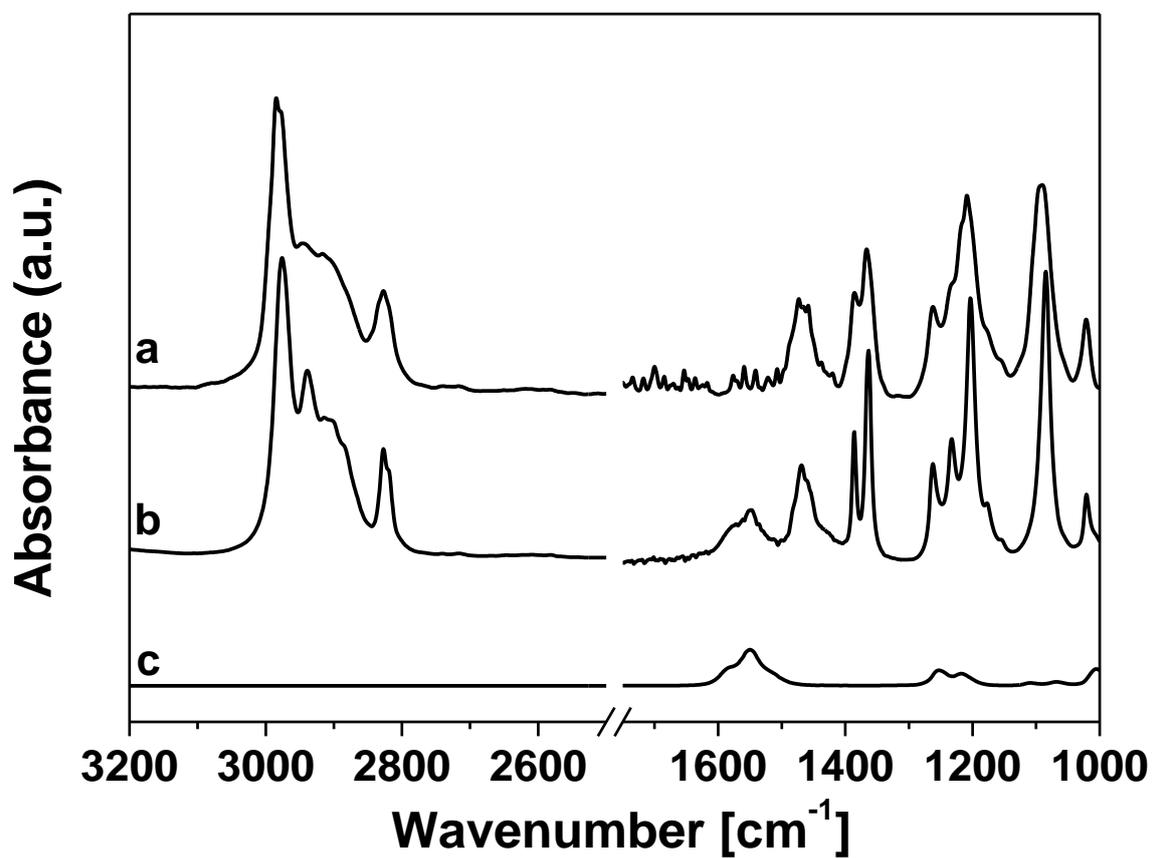
Figure SM10. Experimental infrared spectra of MTBE in gas phase (a) and in carbon tetrachloride solution (b). FTIR spectra of carbon tetrachloride (c).