Supplementary Materials

Manuscript: How does CO capture process on microporous NaY zeolite? A FTIR and DFT combined study

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To valid the choice of our small cluster model of 37-39 atoms additional DFT calculations were carried out using an extended cluster of 170 atoms [$Al_{14}Si_{34}$ $Na_{14}O_{84}H_{24}$] representing the entire sodalite cage connecting four hexagonal prisms. The B3LYP/6-31G level of theory was applied for all atoms including fixed terminated hydrogen atoms. During optimization all atoms were allowed to relax except H atoms. The energy convergence criterion of 10^{-7} Ha and a maximum norm of the Cartesian gradient of 10^{-4} Ha/Bohr were rushed for optimized geometries. The calculations using the large cluster predict local minimum energy structures for the three computed configurations considering the interaction of one, two and three CO molecules with $Na_{(SII)}$ cation. This $Na_{(SII)}$ cation is located in the plan of one of the 6-MRs containing 3Al atoms as reported in Figure 1S. Results from the large cluster with those obtained with the small one are compared in Table 1S (the geometric results and energies of both clusters). Let us note that the calculations considering the small cluster are performed at the B3LYP/6-311G** level of theory. The basis set superposition error (BSSE) was not considered for the reported results. The binding energies of the first, second and third CO molecule on [Z] cluster are calculated according to the following reactions:

1^{st} CO: $[Z] + CO \rightarrow [Z{-}CO]$

2^{nd} CO: $[Z{-}CO] + CO \rightarrow [Z{-}2CO]$

3^{rd} CO: $[Z{-}2CO] + CO \rightarrow [Z{-}3CO]$

From table 1S, except for the mono-carbonyl species where a slight polarising effect of the zeolite lattice is found on the binding energy values (the interaction of single CO with 6-MR of the large cluster is greater by about 8 kJ/mol than the one of the small cluster), it is outlined that the capture of the second and third CO molecule occurs with similar binding energies whatever the cluster size under consideration. Using the small cluster, the obtained geometric parameters are underestimated by less then 0.1 Å compared to those obtained with the large

cluster. These results show that similar geometric and energetic properties of adsorbed small molecules can be obtained by using either small or large cluster models.

Figure 1S: DFT/B3LYP/6-31G optimized configurations of *n*CO molecules interacting with $Na^{+}_{(SII)}$ located in the center of the 6MR within the large cluster of 170 atoms [$Al_{14}Si_{34}Na_{14}O_{84}H_{24}$]. a) *n*=1, b) *n*=2 and c) *n*=3. Reported bonding length values are in Angstrom. Read, purple, yellow, grey and green balls were O, Al, Si, C and Na atoms, respectively.

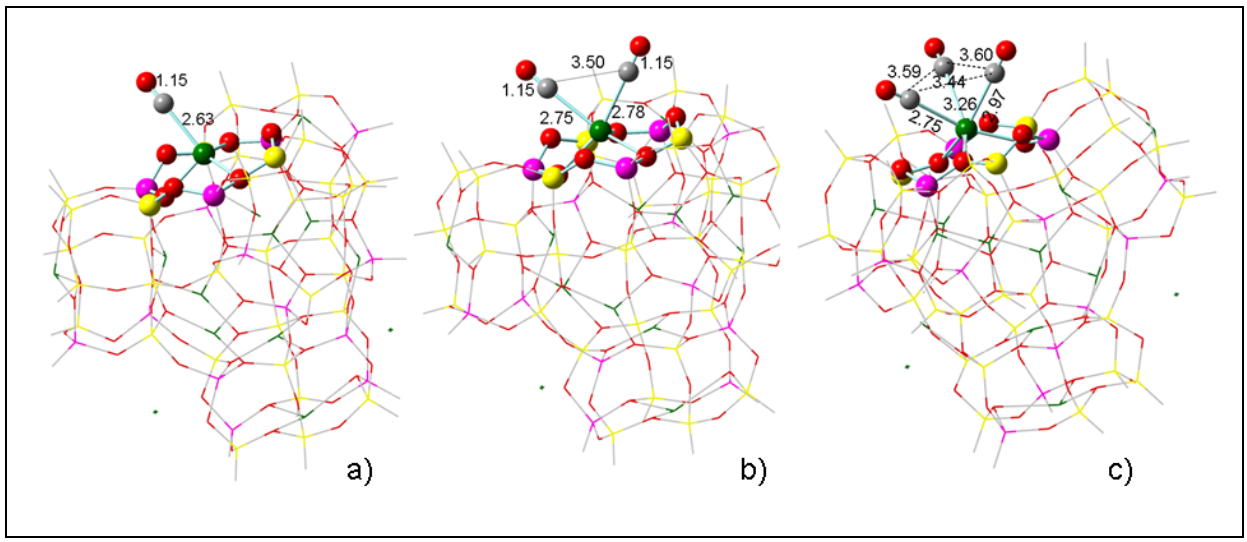

Table 1S: Comparison of the binding energies and $d_{Na\text{-}CO}$ bonding length distances of interacting polycarbonyl species calculated within the small ([$Al_3Si_3Na_3O_{18}H_{12}$]) and large ([$Al_{14}Si_{34}Na_{14}O_{84}H_{24}$]) clusters.

Cluster	CO		2CO		3CO	
	E_{bind} (kJ/mol)	$d_{Na\text{-}CO}$ (Å)	E_{bind} (kJ/mol)	$d_{Na\text{-}CO}$ (Å)	E_{bind} (kJ/mol)	$d_{Na\text{-}CO}$ (Å)
[$Al_{14}Si_{34}Na_{14}O_{84}H_{24}$]*	-36.5	2.63	-14.6	2.75 2.78	-8.8	2.75 2.97 3.26
[$Al_3Si_3Na_3O_{18}H_{12}$]*	-28.2	2.69	-11.2	2.81 2.91	-6.6	2.76 3.07 3.19
Errors**	- 8.3	+ 0.06	- 3.4	+ 0.09	- 2.2	+0.01

* Energy values do not include BSSE corrections
** Calculated relative to the values obtained with the largest cluster