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CO diffusion as re-orientation mechanism in NaY zeolite

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Part S1. NaY models with NaIII

Comparing our models with the earlier data obtained by Nour *et.al.* in NaY, one should emphasize two differences, *i.e.*, Si/Al = 2.5 and cut-off for kinetic energy of 600 eV¹ *versus* 3.0 and 500 eV herein. Hence we obviously do not obtain the same results as with the periodic models presented in ref. 1. As comparison, for NaII-CO-NaIII, the periodic 48T models of NaY named PBE1 or PBE2 give $\Delta\omega_{\text{LF}} = -7$ or -20 cm⁻¹, (see Table 2 in ref. 1) while our $\Delta\omega_{\text{LF}}$ value is -22.7 cm⁻¹ for NaII-OC at the PBE level. The results of the calculations using 42T-cluster models of NaY at the B3LYP/6-311++G(d, p) (Na-CO-Na)/6-31G (d)(Al, Si, O_z, Na') level¹ coincide nicely to the experimental ones for both $\Delta\omega_{\text{HF}}$ (30 cm⁻¹ for NaIII-CO-NaII) (Figure 2a) and $\Delta\omega_{\text{LF}}$ (-19 cm⁻¹ for NaII-CO-NaIII). Our OC-NaIII-CO model with one NaIII per supercage (Table S2) leads to a similar ω_{HF} splitting into 40.6 cm⁻¹ and 20.8 cm⁻¹ relative to the main peak of NaIII-CO ($\Delta\omega_{\text{HF}} = 30.9$ cm⁻¹ or $\omega_{\text{HF}} = 2166.4$ in Table S2). The values 9.7 (9.7 = 40.6 – 30.9 cm⁻¹) and -10.1 cm⁻¹ ($-10.1 = 20.8 – 30.9$ cm⁻¹) are close to the experimental positions for the red and blue shifted branches as 12 and -15 cm⁻¹ (see Part 3.3).² Let us note that no proper NaII-CO-NaIII model could be obtained herein for the blue shifted ω_{LF} band (relative to the gas phase frequency). All three theory levels result in the ($\Delta\omega_{\text{HF}}$, $\Delta\omega_{\text{LF}}$) pairs of (30.9, 0.4 cm⁻¹), (26.3, -2.7 cm⁻¹), (30.7, 9.9 cm⁻¹) using PBE, PBEsol, and optB86d, respectively. The NaII-CO-NaIII models considered at the PBE and optB86d theory levels possess higher interaction energy (in absolute value), *i.e.*, 6.0 (for CO)/5.3 (for OC) kcal/mol and 9.9 (for CO)/9.9 (for OC) kcal/mol (Table S2), respectively, compared to CO-NaII, *i.e.*, 5.4 (for CO)/3.3 (for OC) kcal/mol and 8.1(CO)/7.0(OC) kcal/mol (Table 2). If the NaIII sites are present initially in the system, they should be the first occupied with ($\Delta\omega_{\text{HF}}$, $\Delta\omega_{\text{LF}}$) pairs of (30.9, 0.4 cm⁻¹) and (30.7, 9.9 cm⁻¹). Such intensive peaks around gas frequency values are not visible in IR for NaY;² the idea of the NaIII presence can hence be further discussed only at the PBEsol level. The $\Delta\omega_{\text{HF}}$ peak is assigned to the favored NaII-CO site (-39.1 cm⁻¹) and the $\Delta\omega_{\text{LF}}$ peak to NaII-OC (-29.7 cm⁻¹).

However, at this level we did not obtain a reasonable $\Delta\omega_{\text{HF}}$ splitting, *i.e.*, the analogue of the branch at 2183 cm^{-1} red-shifted relative to the main peak at 2171 cm^{-1} ,² while the OC-NaII-CO site ($\Delta\omega_{\text{HF}} = 31.6$ and 21.9 cm^{-1}) led to analogues of the experimental blue-shifted branch (peak 2156 cm^{-1}).² We thus have not yet reached a correct assignment at the PBEsol level for the model with NaIII cation, this one being present at small CO coverage.¹ But more importantly, let us remark that the comparison of the calculated HF and LF bands in the NaY model with NaIII at the cluster level can be not complete as the authors in ref. 1 did not consider any relative destabilization of the system due to proposed mechanism of NaIII formation at definite CO coverage³⁻⁶ (see Discussion).

Table S1. Total energy (eV) of CO and molecular length ρ (Å) and frequency (cm⁻¹) in the gas phase calculated at the different DFT levels.

Method	-U	ρ	ω
PBE	14.777	1.1431	2135.5
PBEsol ^{a)}	14.549	1.1415	2153.3
optB86d	12.676	1.1424	2129.5
Exp.	-	1.128 ⁷	2143, 2169.8 ⁷

^{a)} same values for PBEsol-D2 and PBEsol-D3(BJ).

Table S2. Total energy U (eV), its change ΔU (kcal/mol) corresponds: a) to the increase (destabilization) of the cell energy due to the shift of NaII to the NaIII site, if no CO is adsorbed, b) to the adsorption energy per one CO molecule relative to the non-interacting zeolite and gas phase CO (the data in Table S1), if CO is adsorbed, molecular |C-O| bond length and other distances (Å), CO frequencies (ω , cm^{-1}), and its shift $\Delta\omega$ versus gas phase CO calculated at different theory levels at the presence of one NaIII cation per supercage. The orientation is given in column 2 where the first atom of CO or OC is directed towards Na. The number $N = 1, 2$, of the occupied Na sites is shown in the parentheses (column 2). Cases CO and OC correspond to NaII-CO-NaIII and NaII-OC-NaIII, respectively.

DFT	Case (N)	-U	$-\Delta U$	C-O	C/O-Na ^{a)}	Na-O _z	$\omega_{\text{HF}}, \omega_{\text{LF}}$	$\Delta\omega_{\text{HF}}, \Delta\omega_{\text{LF}}$
PBE	-	1160.88	7.6	-	-	2.311, 2.316, 2.356 2.441, 2.464, 2.519, 2.776	-	-
	CO ^{b)}	1175.92	6.0	1.1400	2.606 (NaIII), 3.042*(NaII)	2.500, 2.501, 2.478, 2.715	2166.4	30.9
	OC	1175.88	5.3	1.1435	2.545*(NaIII), 2.933 (NaII)	2.469, 2.496, 2.495, 2.764	2135.9	0.4
	CO, CO (NaII/ NaIII)	1190.89	5.3	1.1390, 1.1382	2.611, 2.592	2.326, 2.359, 2.332, 2.466, 2.470, 2.511, 2.740	2183.7, 2178.1	48.2, 42.6
	2CO/ NaII	1190.82	4.5	1.1396, 1.1437	2.747, 2.849	2.382, 2.374, 2.454	2168.2, 2133.9	32.7, -1.6
	2CO/ NaIII	1190.90	5.4	1.1384, 1.1417	2.647, 2.698	2.507, 2.513, 2.587, 2.806	2176.1, 2156.3	40.6, 20.8
PBEs ol	-	1129.05	6.1	-	-	2.249, 2.290, 2.330, 2.408, 2.478, 2.428, 2.742	-	-
	CO	1143.89	5.0	1.1371	2.608 (NaIII), 3.026* (NaII)	2.445, 2.471, 2.471, 2.688	2179.8	26.3
	OC	1143.84	3.8	1.1419	2.592*(NaIII), 2.845 (NaII)	2.330, 2.330, 2.330, 2.349, 2.436, 2.456, 2.734	2150.8	-2.7
optB8 6d	-	1056.70	5.8	-	-	2.302, 2.306, 2.337, 2.439, 2.440, 2.462, 2.715	-	-
	CO	1069.81	9.9	1.1404	2.640(NaIII), 2.872*(NaII)	2.317, 2.317, 2.352, 2.442, 2.465, 2.488, 2.679	2160.2	30.7
	OC	1069.81	9.9	1.1425	2.788(NaII), 2.590*(NaIII)	2.322, 2.322, 2.374, 2.455, 2.458, 2.467, 2.728	2139.4	9.9

a) the distance between O-atom and nearest Na cation (its type is given in brackets) is shown by star; b) see Figure 2a.

Table S3. Distances between the C and O atoms of CO molecule and the O_z atoms (Å) of the NaY, calculated at the different DFT levels.

Type	Case	C/O-Na ^{a)}	O _{CO} -O _z	C-O _z
PBE	CO, OC (1)	2.802	3.384, 3.373	3.406, 3.914
PBEsol	CO, OC (1)	2.705	3.290, 3.664	3.156, 3.742
optB86d	CO, OC (1)	2.951	3.403, 3.357	3.380, 3.419
	CO, OC (1)	2.628	3.548, 3.587	3.709, 3.773
	2CO (1)	2.984	3.530, 3.373	3.538, 3.312

^{a)} The data corresponds to those in 6th column of Table 2.

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