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Characterization and Modeling of Reversible CO2 Capture from Wet Streams by a MgO/Zeolite Y Nanocomposite

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Supporting Information

Characterization and modelling of reversible CO₂ capture from wet streams by a

MgO/zeolite Y nanocomposite

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1) IR spectra of the activated materials

A prolonged activation in vacuo at 400 °C was preventively adopted to remove any possibly adsorbed species, and in particular water. Once activated, H-Y and MgOHY (dotted lines in Figure S1) are characterized by a complex spectrum in the OH stretching region (part a) due to the presence of a variety of acidic Bronsted sites. The spectrum of H-Y (blue dotted line) shows a broad band centered at 3740 cm⁻¹, due to isolated silanols and a complex envelope of bands (at least 5 different components) in the 3670-3500 cm⁻¹ spectral range associated to the presence of Al. In the case of MgOHY sample (red dotted line), apart from the component due to the isolated SiOH groups at 3740 cm⁻¹ (mostly unaffected), the overall spectrum in the v(OH) spectral region is less intense, simplified (the most reduced component at 3690 cm⁻¹. The persistence of hydroxyls groups in the Mg exchanged sample confirms that the ion exchange with Mg²⁺ takes place only on a fraction

of the available protonic sites, whereas the appearance of the component at 3690 cm⁻¹ has been ascribed to the presence of some hydroxyl species on MgO clusters hosted in the zeolite supercages.^{33,34} In the presence of water, all the components disappear (full line spectra in Figure S1 a), being substituted by a very broad and intense absorption extending in the all v(OH) region.

At lower frequencies (parts b of figure S1) the spectrum of activated H-Y only shows weak bands associated to the overtones of framework modes. Conversely, MgOHY spectrum is characterized by an additional doublet at 1448 and 1417 cm⁻¹, for which we cannot exclude the contribution of some residual NO₃⁻ species, not totally decomposed during the calcination/activation procedure, and probably entrapped in not accessible cavities.³⁵ In both cases, upon dosage of water vapour pressure, the bands due to δ (HOH) modes become predominant. In particular, in the case of H-Y sample (blue line), a very broad and intense band, extending from 1750-1550 (characterized by two main components with apparent maxima at 1690 and 1640 cm⁻¹) rises. In contrast for MgOHY sample (red line), the δ (HOH) bands grow in a narrower interval: 1720-1590 cm⁻¹ and with a clear predominance of the component at lower frequency (with apparent maximum now at 1633 cm⁻¹). No changes are observed for the doublet at 1448 and 1417 cm⁻¹.



Figure S1. Spectral set (a): activation of the samples. IR spectra of HY (blue) and MgOHY (red) in the spectral regions of OH stretching vibrations ($3800-3400 \text{ cm}^{-1}$) after activation at 400° C (dotted curves) and upon contact with H₂O vapor pressure (solid curves). Spectral set (b): IR spectra of HY (blue) and MgOHY (red), in the 1800-1250 cm⁻¹ range, after activation at 400° C (dotted curves) and upon contact with H₂O vapor pressure (solid curves).

2) Detail of the CO₂ molecular adducts region for the static IR experiments (complement to Figure 2)



Figure S2. Detail of the IR spectra in the spectral regions relative to Mg^{2+} -CO₂ linear complexes (2450-2250 cm⁻¹) of: (a) samples after contact with 5 mbar of CO₂ at BT: HY (light blue curve), MgO (light grey curve), and MgOHY (orange curve); (b) samples contacted with a mixture of CO₂ (5 mbar) and H₂O (~20 mbar) at BT: HY (blue curve), MgO (dark grey curve), and MgOHY (red curve).

3) Detail of the CO₂ molecular adducts region for the *in situ* IR experiment (complement to Figure 4)

During the experiment reported in Figure 4 (flow of CO_2 and H_2O) the spectrum in the molecular CO_2 stretching range (2250-2350 cm⁻¹) was also recorded. The spectra show that beside carbonate formation, a significant fraction of CO_2 is molecularly adsorbed.



Figure S3. *In situ* IR spectra in the spectral region relative to molecular CO₂ adducts (2250-2450 cm⁻¹) of MgOHY after activation at 400 °C (dotted red cuve) and upon contact of 15 h with a CO₂/H₂O flow at 30 °C (red solid curve). Light grey spectra show the spectra evolution during the contact with the CO₂/H₂O flow. (b): In situ IR spectra in the spectral regions relative to molecular CO₂ (2250-2450 cm⁻¹) of MgOHY after 15 h of contact with a CO₂/H₂O flow at 30°C (red curve), after desorption in a dry He flow at 200 °C (orange curve) and at 500 °C (red dotted curve).

4) Basis sets adopted for calculations

The basis sets are reported in the CRYSTAL format.

| HYDROGEN | | OXYGEN (MgO clusters and CO ₂) | | |
|---------------|-----------------|--|---------------|-----------------|
| 14 | | | 8 11 | |
| 0 0 5 1.0 1.0 | | | 0 0 5 2.0 1.0 | |
| 120.0 | 0.000267 | | 15902.6475 | 0.514998037E-03 |
| 40.0 | 0.002249 | | 2384.95378 | 0.398197644E-02 |
| 12.8 | 0.006389 | | 542.719572 | 0.204769719E-01 |
| 4.0 | 0.032906 | | 153.404079 | 0.802623679E-01 |
| 1.2 | 0.095512 | | 49.5457161 | 0.237668399 |
| 0 0 1 0.0 1.0 | | | 0 0 1 2.0 1.0 | |
| 0.5 | 1.0 | | 17.3396499 | 1.0 |
| 0 0 1 0.0 1.0 | | | 0 0 1 0.0 1.0 | |
| 0.13 | 1.0 | | 6.33033553 | 1.0 |
| 0 2 1 0.0 1.0 | | | 0 0 1 0.0 1.0 | |
| 0.3 | 1.0 | | 1.69958822 | 1.0 |
| | | | 0 0 1 0.0 1.0 | |
| CARBON | | | 0.689544913 | 1.0 |
| 6 11 | | | 0 0 1 0.0 1.0 | |
| 0 0 5 2.0 1.0 | | | 0.239360282 | 1.0 |
| 8506.03840 | 0.533736640E-03 | | 0244.01.0 | |
| 1275.73290 | 0.412502320E-02 | | 63.2705240 | 0.607092060E-02 |
| 290.311870 | 0.211713370E-01 | | 14.6233123 | 0.419476887E-01 |
| 82.0562000 | 0.824178600E-01 | | 4.44895180 | 0.161568840 |
| 26.4796410 | 0.240128580 | | 1.52815132 | 0.356827793 |
| 0 0 1 2.0 1.0 | | | 0 2 1 0.0 1.0 | |
| 9.24145850 | 1.0 | | 0.529973159 | 1.0 |
| 0 0 1 0.0 1.0 | | | 0 2 1 0.0 1.0 | |
| 3.36435300 | 1.0 | | 0.175094460 | 1.0 |
| 0 0 1 0.0 1.0 | | | 0310.01.0 | |
| 0.871741640 | 1.0 | | 2.4 1.0 | |
| 0 0 1 0.0 1.0 | | | 0310.01.0 | |
| 0.363523520 | 1.0 | | 0.6 1.0 | |
| 0 0 1 0.0 1.0 | | | | |
| 0.128731350 | 1.0 | | | |
| 0 2 4 2.0 1.0 | | | | |
| 34.7094960 | 0.533009740E-02 | | | |
| 7.95908830 | 0.358658140E-01 | | | |
| 2.37869720 | 0.142002990 | | | |
| 0.815400650 | 0.342031050 | | | |
| 0 2 1 0.0 1.0 | | | | |
| 0.289537850 | 1.0 | | | |
| 0 2 1 0.0 1.0 | | | | |
| 0.100847540 | 1.0 | | | |
| 0310.01.0 | | | | |
| 1.6 1.0 | | | | |
| 0310010 | | | | |

 $\begin{array}{ccc} 0 \ 3 \ 1 \ 0.0 \ 1.0 \\ 0.4 \ 1.0 \end{array}$

| OXYGEN (ze | eolite fi | ramew | ork) |
|---------------|-----------|-------|---------|
| 8 5 | | | ŕ |
| 0 0 8 2.0 1.0 | | | |
| 8020.0 | 0.0010 | 08 | |
| 1338.0 | 0.00804 | | |
| 255.4 | 0.0532 | 24 | |
| 69.22 | 0.168 | 1 | |
| 23.90 | 0.3581 | | |
| 9.264 | 0.3855 | | |
| 3.85 | 0.1468 | 8 | |
| 1.212 | 0.0728 | | |
| 0 1 4 6.0 1.0 | | | |
| 49.43 | -0.00883 | | 0.00958 |
| 10.47 | -0.0915 | | 0.0696 |
| 3.235 | -0.0402 | | 0.2065 |
| 1.217 | 0.379 | | 0.347 |
| 0 1 1 0.0 1.0 | | | |
| 0.4520495 | 1.0 | 1.0 | |
| 0 1 1 0.0 1.0 | | | |
| 0.1678880 | 1.0 | 1.0 | |
| 0310.01.0 | | | |
| 0.4509895 | 1.0 | | |
| ALUMINUM | [| | |
| 13 5 | | | |
| 0 0 8 2.0 1.0 | | | |
| 70510.0 | 0.000226 | | |
| 10080.0 | 0.0019 | | |
| 2131.0 | 0.0110 | | |
| 547.5 | 0.0509 | | |
| 163.1 | 0.1697 | | |
| 54.48 | 0.3688 | | |
| 19.05 | 0.3546 | | |
| 5.402 | 0.0443 | | |
| 0 1 5 8.0 1.0 | | | |
| 139.6 | -0.011 | 20 | 0.0089 |
| 32.53 | -0.1136 | | 0.0606 |
| 10.23 | -0.0711 | | 0.1974 |
| 3.810 | 0.5269 | | 0.3186 |
| 1.517 | 0.7675 | | 0.2995 |
| 0 1 1 3.0 1.0 | | | |
| 0.59 | 1.0 | | 1.0 |
| 0 1 1 0.0 1.0 | | | |
| 0.35 | 1.0 | | 1.0 |
| 0310.01.0 | | | |
| | | | |

MAGNESIUM

| / | |
|---------------|-----------------|
| 0 0 7 2.0 1.0 | |
| 31438.3496 | 0.609123113E-03 |
| 4715.51534 | 0.470661965E-02 |
| 1073.16292 | 0.241358207E-01 |
| 303.572388 | 0.936289598E-01 |
| 98.6262510 | 0.266467421 |
| 34.9438084 | 0.478909299 |
| 12.8597852 | 0.336984903 |
| 0 0 3 2.0 1.0 | |
| 64.8769130 | 0.191808893E-01 |
| 19.7255208 | 0.909137044E-01 |
| 2.89518043 | -0.395637561 |
| 0 0 2 0.0 1.0 | |
| 1.19604547 | 1.68276034 |
| 0.543294512 | 0.521410920 |
| 0 0 1 0.0 1.0 | |
| 0.100991041 | 1.0 |
| 0 2 5 6.0 1.0 | |
| 179.871896 | 0.537995490E-02 |
| 42.1200694 | 0.393180141E-01 |
| 13.1205030 | 0.157401295 |
| 4.62575036 | 0.359190941 |
| 1.66952110 | 0.455333793 |
| 0 2 1 2.0 1.0 | |
| 0.585510121 | 1.0 |
| 0 2 1 0.0 1.0 | |
| 0.189 1.0 | |

SILICON

| 14 5 | | |
|---------------|-----------|------------|
| 0 0 8 2.0 1.0 | | |
| 149866.0 | 0.0001215 | |
| 22080.6 | 0.0009770 | |
| 4817.5 | 0.0055181 | |
| 1273.5 | 0.0252000 | |
| 385.11 | 0.0926563 | |
| 128.429 | 0.2608729 | |
| 45.4475 | 0.4637538 | |
| 16.2589 | 0.2952000 | |
| 0 1 8 8.0 1.0 | | |
| 881.111 | -0.0003 | 0.0006809 |
| 205.84 | -0.0050 | 0.0059446 |
| 64.8552 | -0.0368 | 0.0312000 |
| 23.9 | -0.1079 | 0.1084000 |
| 10.001 | 0.0134 | 0.2378000 |
| 4.4722 | 0.3675 | 0.3560066 |
| 2.034 | 0.5685 | 0.3410000 |
| 0.9079 | 0.2065 | 0.1326000 |
| 0 1 3 4.0 1.0 | | |
| 2.6668 | -0.0491 | 0.0465000 |
| 1.0780 | -0.1167 | -0.1005000 |
| 0.3682 | 0.2300 ì | -1.0329000 |
| 0 1 1 0.0 1.0 | | |
| 0.193 | 1.0 | 1.0 |
| 0310.01.0 | | |
| 0.610 1.0 | | |
| | | |