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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 $\nu(\text{OH})$ spectral region is less intense, simplified (the most reduced components are those at lower frequencies) and is characterized by the presence of a new 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 $\nu(\text{OH})$ 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 NO_3^- 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 $\delta(\text{HOH})$ 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 $\delta(\text{HOH})$ 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} .

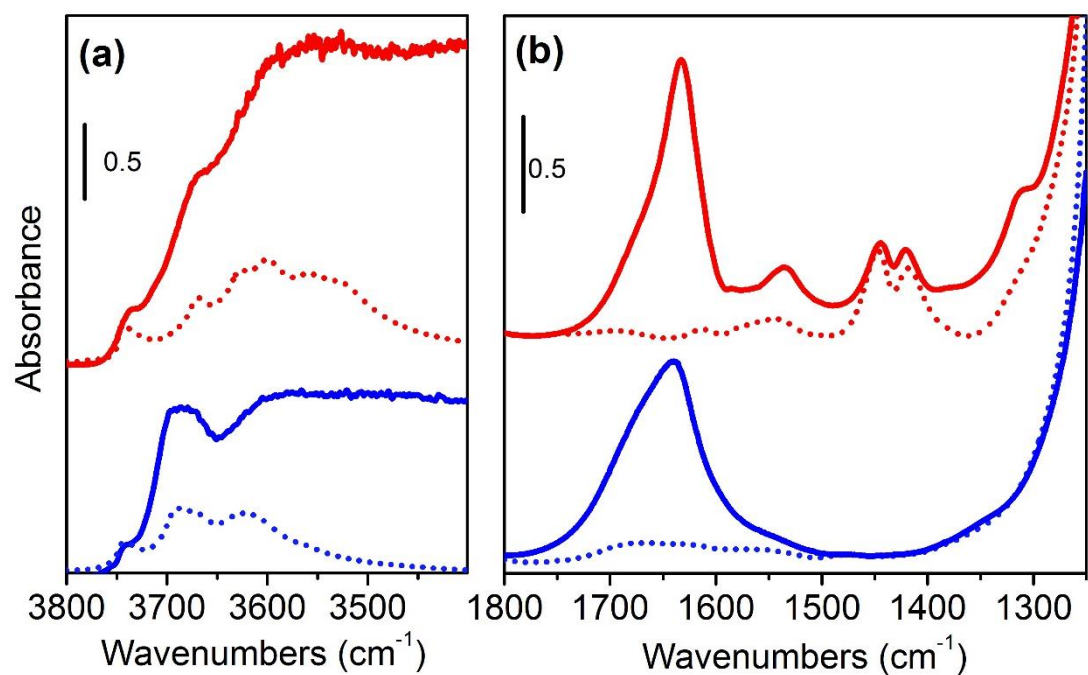


Figure S1. Spectral set (a): activation of the samples. IR spectra of HY (blue) and MgOHY (red) in the spectral regions of OH stretching vibrations (3800-3400 cm⁻¹) after activation at 400°C (dotted curves) and upon contact with H₂O vapor pressure (solid curves). Spectral set (b): IR spectra of HY (blue)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

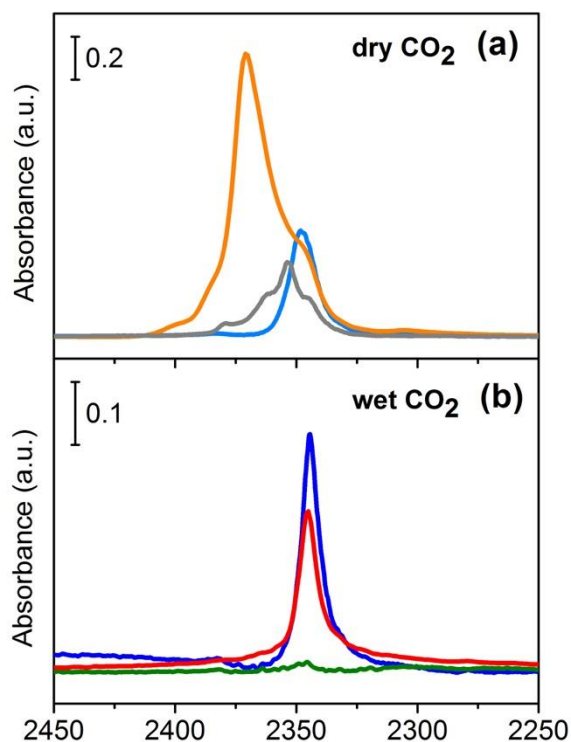


Figure S2. Detail of the IR spectra in the spectral regions relative to Mg²⁺-CO₂ linear complexes (2450-2250 cm⁻¹) of: (a) samples after contact with 5 mbar of CO₂ at BT: HY (light blue curve), MgO (light grey curve), and MgOHY (orange curve); (b) samples contacted with a mixture of CO₂ (5 mbar) and 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 CO₂ and H₂O) the spectrum in the molecular CO₂ stretching range (2250-2350 cm⁻¹) was also recorded. The spectra show that beside carbonate formation, a significant fraction of CO₂ is molecularly adsorbed.

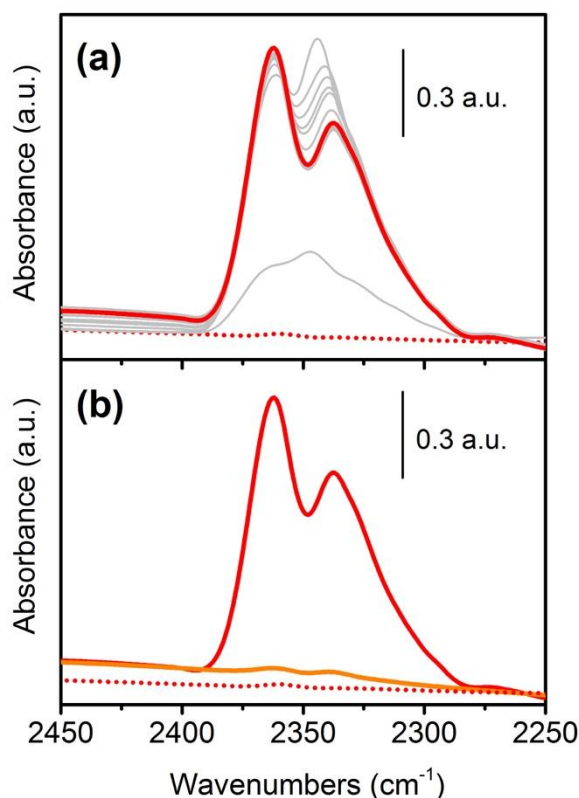


Figure S3. *In situ* IR spectra in the spectral region relative to molecular CO₂ adducts (2250-2450 cm⁻¹) of MgOHY after activation at 400 °C (dotted red curve) and upon contact of 15 h with a CO₂/H₂O flow at 30 °C (red solid curve). Light grey spectra show the spectra evolution during the contact with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

1 4
0 0 5 1.0 1.0
120.0 0.000267
40.0 0.002249
12.8 0.006389
4.0 0.032906
1.2 0.095512
0 0 1 0.0 1.0
0.5 1.0
0 0 1 0.0 1.0
0.13 1.0
0 2 1 0.0 1.0
0.3 1.0

CARBON

6 11
0 0 5 2.0 1.0
8506.03840 0.533736640E-03
1275.73290 0.412502320E-02
290.311870 0.211713370E-01
82.0562000 0.824178600E-01
26.4796410 0.240128580
0 0 1 2.0 1.0
9.24145850 1.0
0 0 1 0.0 1.0
3.36435300 1.0
0 0 1 0.0 1.0
0.871741640 1.0
0 0 1 0.0 1.0
0.363523520 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
0 3 1 0.0 1.0
1.6 1.0
0 3 1 0.0 1.0
0.4 1.0

OXYGEN (MgO clusters and CO₂)

8 11
0 0 5 2.0 1.0
15902.6475 0.514998037E-03
2384.95378 0.398197644E-02
542.719572 0.204769719E-01
153.404079 0.802623679E-01
49.5457161 0.237668399
0 0 1 2.0 1.0
17.3396499 1.0
0 0 1 0.0 1.0
6.33033553 1.0
0 0 1 0.0 1.0
1.69958822 1.0
0 0 1 0.0 1.0
0.689544913 1.0
0 0 1 0.0 1.0
0.239360282 1.0
0 2 4 4.0 1.0
63.2705240 0.607092060E-02
14.6233123 0.419476887E-01
4.44895180 0.161568840
1.52815132 0.356827793
0 2 1 0.0 1.0
0.529973159 1.0
0 2 1 0.0 1.0
0.175094460 1.0
0 3 1 0.0 1.0
2.4 1.0
0 3 1 0.0 1.0
0.6 1.0

OXYGEN (zeolite framework)

8 5

0 0 8 2.0 1.0

8020.0 0.00108

1338.0 0.00804

255.4 0.05324

69.22 0.1681

23.90 0.3581

9.264 0.3855

3.85 0.1468

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

0 3 1 0.0 1.0

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 -0.01120 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

0 3 1 0.0 1.0

0.51 1.0

MAGNESIUM

12 7

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 i	-1.0329000

0 1 1 0.0 1.0

0.193	1.0	1.0
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0 3 1 0.0 1.0

0.610	1.0
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