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

Published version:

DOI:10.1021/acs.jpcc.9b01399

(Article begins on next page)

Supporting Information

Characterization and modelling of reversible CO_2 capture from wet streams by a MgO/zeolite Y nanocomposite

Matteo Signorile[1], Jenny G. Vitillo[2,], Maddalena D'Amore[1], Valentina Crocellà[1], Gabriele Ricchiardi[1,*] and Silvia Bordiga[1]*

[1]Università di Torino, Dipartimento di Chimica and NIS Interdepartment Centre, Via Giuria 7, 10125 Torino (ITALY) .

[2]Department of Science and High Technology and INSTM, Università degli Studi dell'Insubria, Via Valleggio 9, I-22100 Como, Italy.

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 ν(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 Mg^{2+} 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 ν(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 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}.

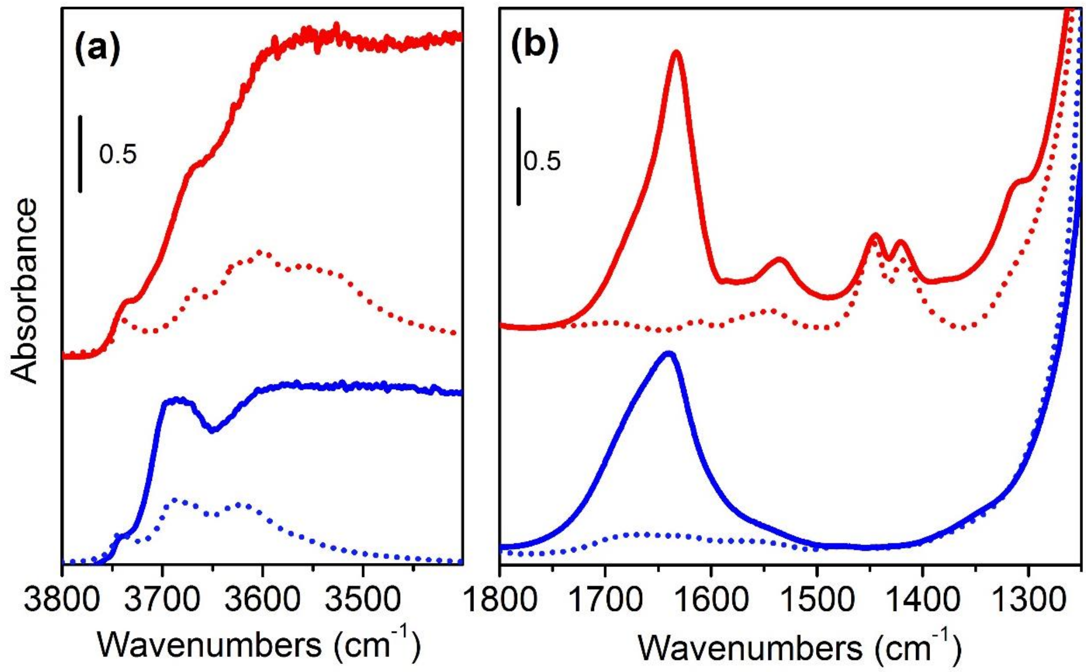

Figure S1. Spectral set (a): activation of the samples. IR spectra of HY (blue) and MgOHY (red) in the spectral regions of OH stretching vibrations (3800-3400 cm^{-1}) after activation at 400°C (dotted curves) and upon contact with H_2O vapor pressure (solid curves). Spectral set (b): IR spectra of HY (blue) and MgOHY (red), in the 1800-1250 cm^{-1} range, after activation at 400°C (dotted curves) and upon contact with H_2O vapor pressure (solid curves).

2) Detail of the CO_2 molecular adducts region for the static IR experiments (complement to Figure 2)

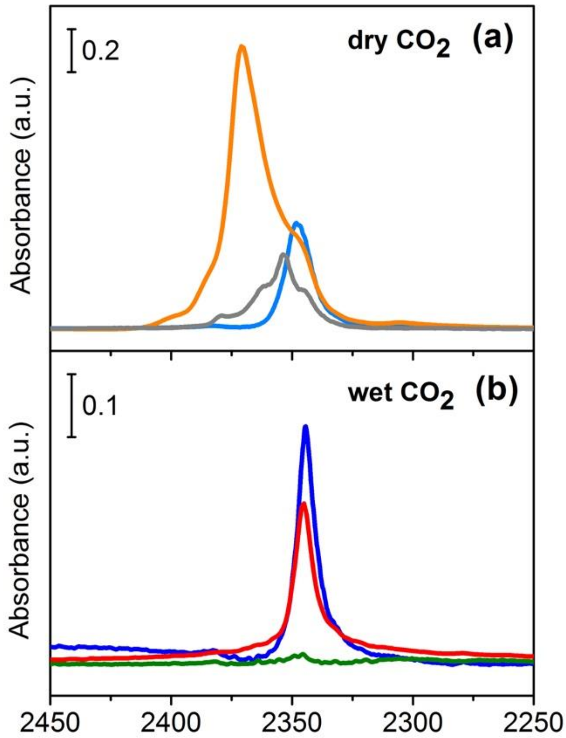

Figure S2. Detail of the IR spectra in the spectral regions relative to Mg^{2+}-CO_2 linear complexes (2450-2250 cm^{-1}) of: (a) samples after contact with 5 mbar of CO_2 at BT: HY (light blue curve), MgO (light grey curve), and MgOHY (orange curve); (b) samples contacted with a mixture of CO_2 (5 mbar) and H_2O (~20 mbar) at BT: HY (blue curve), MgO (dark grey curve), and MgOHY (red curve).

3) Detail of the CO_2 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.

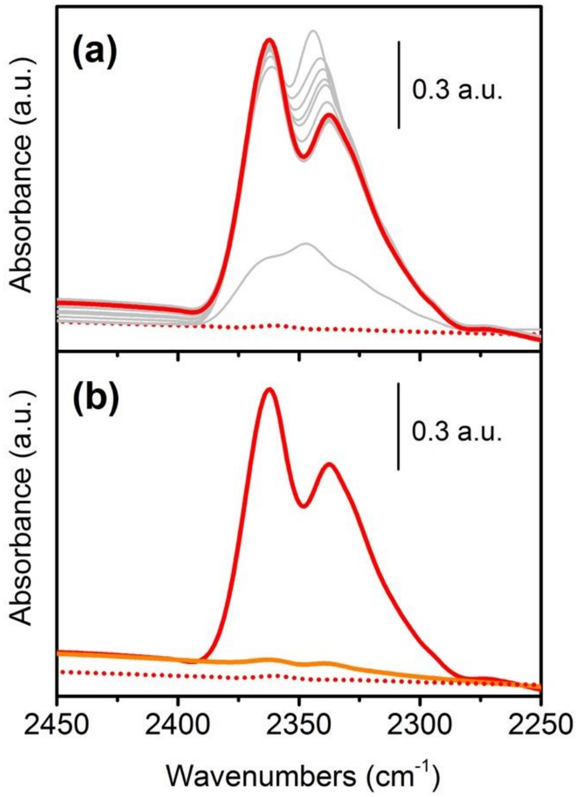

Figure S3. *In situ* IR spectra in the spectral region relative to molecular CO_2 adducts (2250-2450 cm^{-1}) of MgOHY after activation at 400 °C (dotted red cuve) and upon contact of 15 h with a CO_2/H_2O flow at 30 °C (red solid curve). Light grey spectra show the spectra evolution during the contact with the CO_2/H_2O flow. (b): In situ IR spectra in the spectral regions relative to molecular CO_2 (2250-2450 cm^{-1}) of MgOHY after 15 h of contact with a CO_2/H_2O 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 CO_2)

```
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 ì -1.0329000
0 1 1 0.0 1.0
0.193 1.0 1.0
0 3 1 0.0 1.0
0.610 1.0