

PCCP

Low temperature activation and reactivity of CO₂ over a Cr^{II}-based heterogeneous catalyst: a spectroscopic study

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Electronic Supplementary Information

S1. Additional FT-IR spectra.

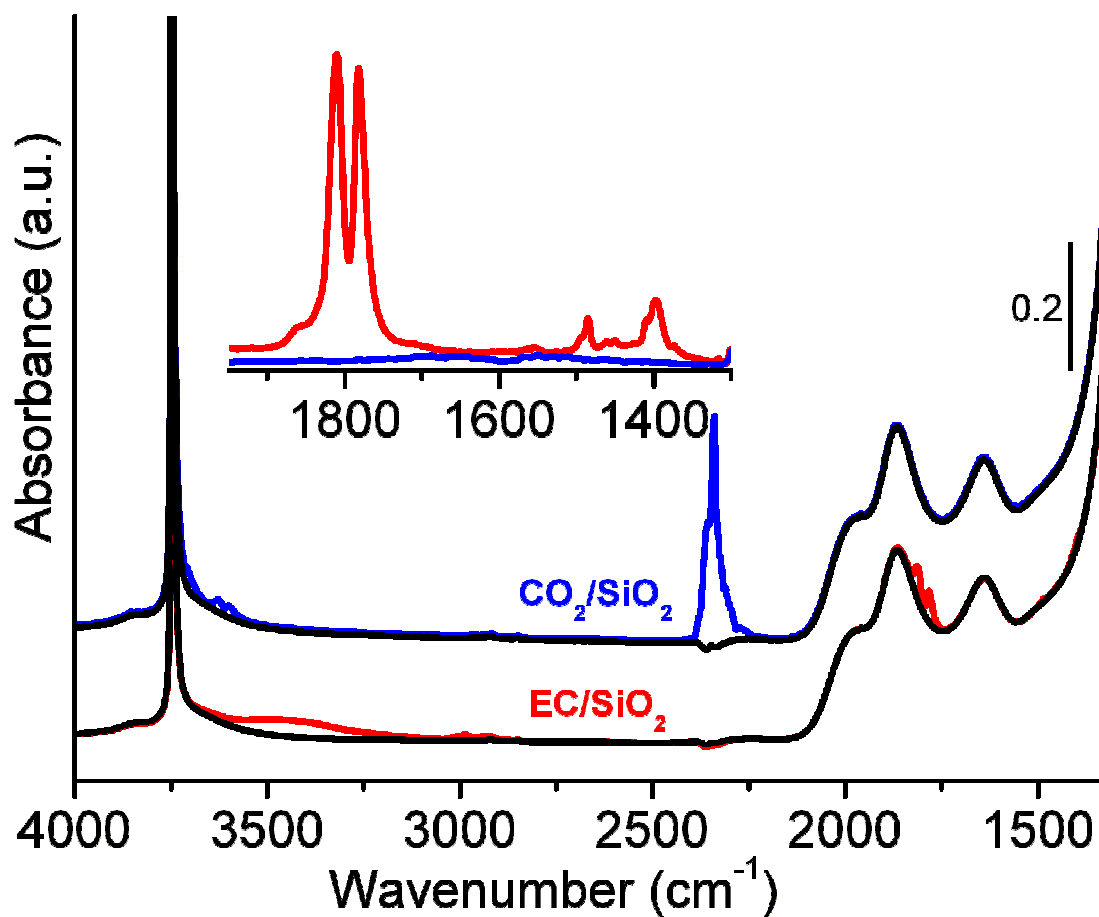


Figure S1. FT-IR spectra of pure silica pre-activated at 923 K before (black spectra) and after interaction with ethylene carbonate (red spectrum) and CO₂ (blue spectrum). The inset shows a magnification of the low frequency region after subtraction of the background.

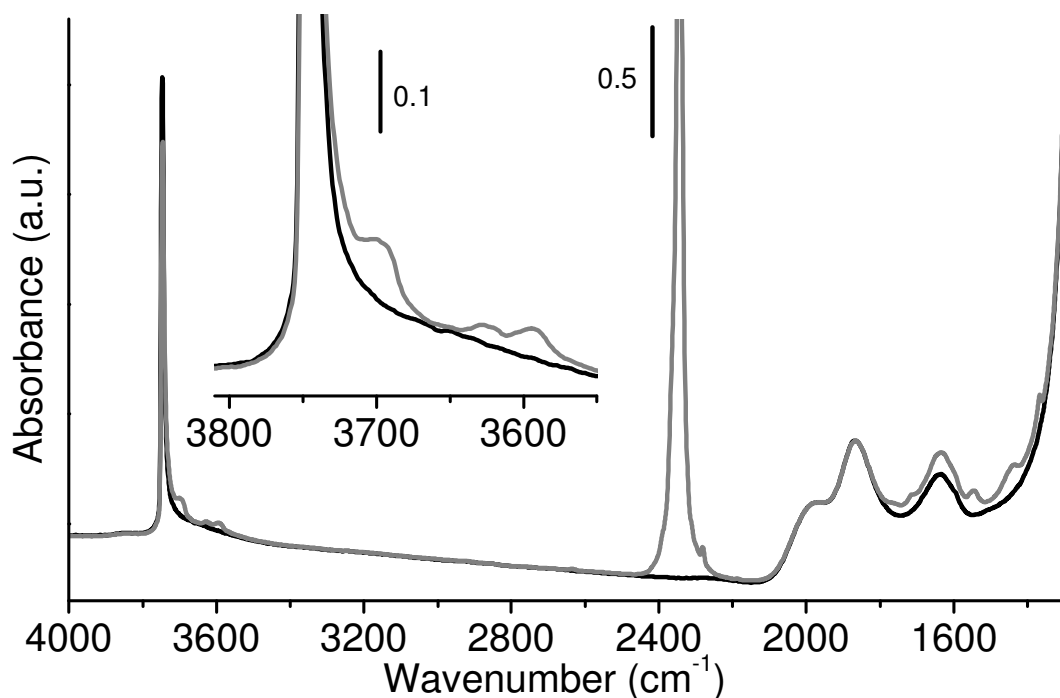


Figure S2. FT-IR spectra of Cr^{II}/SiO₂ catalyst before (bold black) and after (bold dark grey) dosage of CO₂ (equilibrium pressure 100 mbar). Inset: Magnification of the spectra in the v(OH) region.

S2. Theoretical calculations.

All the calculations have been performed with the *Gaussian 09* software package¹ at the B3LYP level of calculation.^{2, 3} The polyethylene oxide (PEO) has been simulated by CH₃CH₂OCH₂CH₃ whereas for the polyethylenecarbonate (PEC) CH₃CH₂OCOCH₂CH₃ has been used. The C, H, Na and O elements have been modeled by means of the fully optimized triple- ζ valence basis sets proposed by Ahlrichs *et al.* with polarization (TZVp).⁴ The effect of the presence of a cation on the IR spectra of ethylene carbonate and poly(ethylene-carbonate) has been simulated by using a Na⁺ ion instead of a Cr²⁺ ion order to avoid faked due to the inability of DFT methods to correctly describe open shell ions mediated interactions.⁵ Geometry optimization has been carried out by means of the Berny optimization algorithm with analytical gradient. The thresholds were set to 0.000450 and 0.000300 a.u. for the maximum and the rms forces respectively; and to 0.001800 and 0.001200 a.u. for the maximum and rms atomic displacements, respectively. A (99,590) pruned grid was used (i.e. 99 radial points and 590 angular points per radial point). No symmetry constraints have been imposed.

Harmonic frequencies have been obtained by analytically determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming them to mass-weighted coordinates.

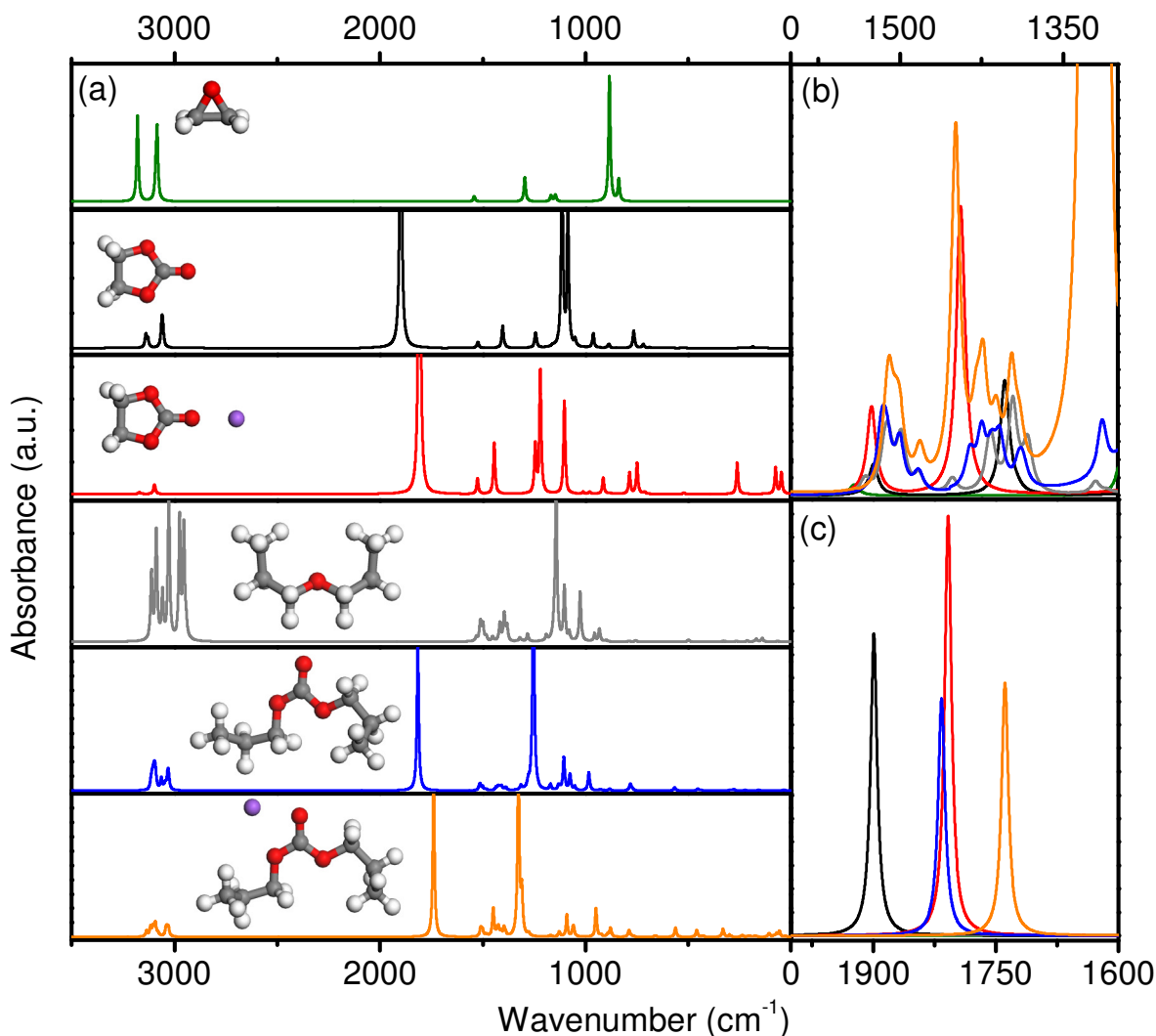


Figure S3. Part a) Calculated infrared spectra at the B3LYP/TZVp level for (from top to bottom) ethylene oxide (EO), ethylene carbonate (EC), EC...Na⁺ complex, polyethylene oxide (PEO), polyethylenecarbonate (PEC) and the PEC...Na⁺ complex. Part b). Inset of the plots reported in part a) in the 1600-1300 cm⁻¹. Part c). Inset of the plots reported in part a) in the 2000-1600 cm⁻¹.

The calculations have evidenced as the C=O stretching frequency of both EC and PEC are strongly perturbed after the interaction with a charged ion (Na⁺). For what concerns EC a shift of -92 cm⁻¹ is obtained (from 1900 to 1808 cm⁻¹) whereas for PEC the frequency moves of -78 cm⁻¹ (from 1816 to 1738 cm⁻¹).

References

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