Supplementary Material (ESI) for Chemical Communications

SUPPLEMENTARY MATERIAL

Ceria nanoparticles as heterogeneous catalyst for CO_2 fixation by ω−aminoalcohols

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Characterization of surface sites based on FT-IR spectroscopy of adsorbed methanol.

To address the reaction mechanism of the CO_2 fixation, wafers (10 mg) of np-CeO_2, commercial CeO_2 and Au (0.79 wt%)/np-CeO_2 were activated at 160 ^oC 4h in N_2 flow. The FT-IR spectra of the samples prior to activation show the presence of carbonate species. Labile carbonate species are easily removed at the reaction temperature of 160 ºC, while strongly adsorbed CO_2 species still remain on the catalysts surface upon evacuation at this temperature. Free surface sites are further titrated using IR spectroscopy of methanol adsorption. There are precedents in the literature reporting the types of sites of nanoparticulated ceria that are able to interact with adsorbed methanol (A. Badri, C. Binet, J.-C. Lavalley, *Faraday Trans.* 1997, **93**, 1159-1168 and references therein). Based on these reports, free, terminal and bridged CH_3O groups associated to different Ce^{III} and Ce^{IV} sites can be assigned. Figures S1, S2 and S3 present the IR region of the C-O stretching vibration with the assignments of the bands. Overall the results show that after adsorbing CO_2, the ceria samples are still able to interact with methanol. Furthermore, np-CeO_2 has mostly bridged methoxy groups between two Ce^{III} atoms, while in the other two samples methanol becomes mostly adsorbed to Ce^{IV}. These spectroscopic observations are in agreement with nanoparticulated ceria having a large population of Ce^{III} sites that becomes blocked after Au deposition. These Ce^{III} defect sites are much less important as the particle size groups. Interestingly, formation of water was only observed in the case of np-CeO_2 as a result of methanol dehydration catalysed by acid surface hydroxy groups. When methanol was adsorbed on Au (0.79 wt%)/np-CeO_2 appearance of bands characteristic of formate (in spite of the absence of oxygen) was also detected, in agreement to the catalytic oxidation activity of this sample.

Figure S1: ν (C-O) region of the IR spectra recorded for np-CeO_2 after incorporation of methanol in a sample that has been submitted to CO_2 adsorption/desorption.

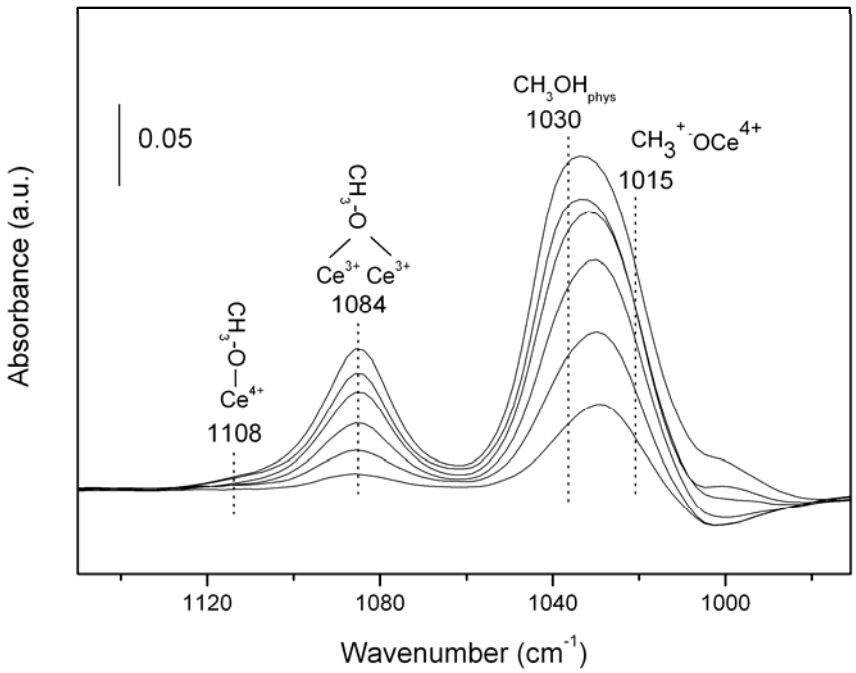

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Figure S2: ν (C-O) region of the IR spectra recorded for commercial CeO_2 after incorporation of methanol in a sample that has been submitted to CO_2 adsorption/desorption.

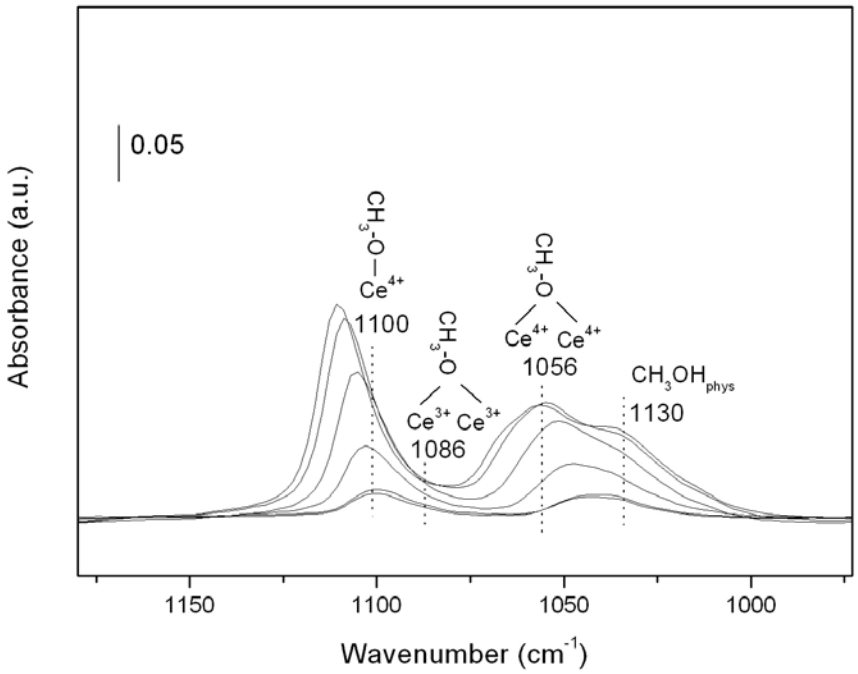
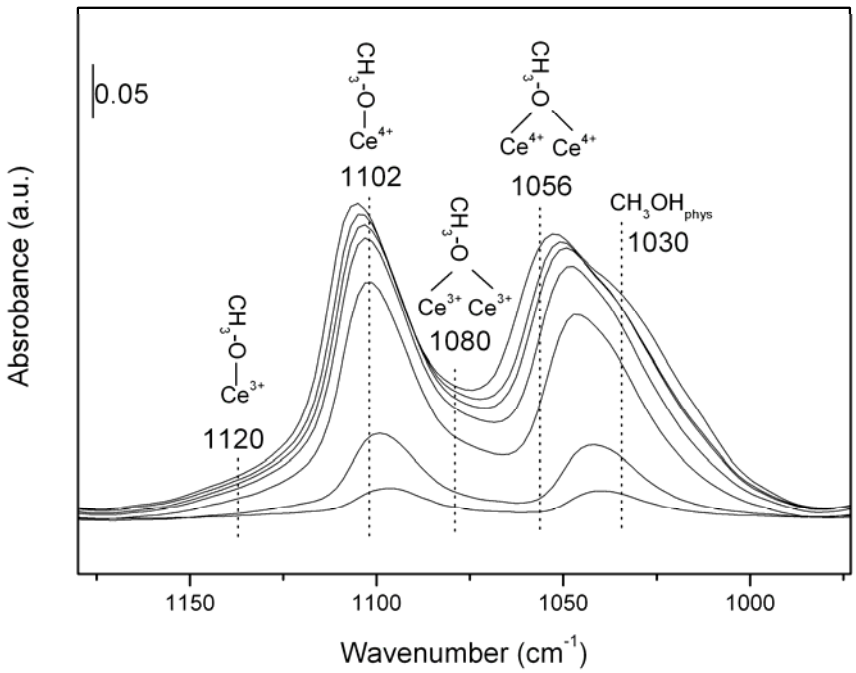


Figure S3: ν (C-O) region of the IR spectra recorded for Au (0.79 wt%)/np-CeO_2 after incorporation of methanol in a sample that has been submitted to CO_2 adsorption/desorption.



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