

Direct evidence of adsorption induced Cr<sup>II</sup> mobility on the SiO<sub>2</sub> surface upon complexation by CO

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The importance of the Phillips catalyst in the industrial PE production makes Cr/SiO<sub>2</sub> one of the most investigated systems [1] however, the structure of Cr<sup>VI</sup>/SiO<sub>2</sub> and of its relative Cr<sup>II</sup>/SiO<sub>2</sub> is still unresolved. This is mainly due to the amorphous nature of the support that prevents the use of diffraction techniques and is responsible of heterogeneity in the grafted species. Up to now also EXAFS spectroscopy, often used to investigate the local structure of amorphous systems, still didn't fully elucidate the structure of Cr<sup>II</sup> sites due to the low Cr loading (0.5 wt%) and to its high reactivity toward O<sub>2</sub>/H<sub>2</sub>O poisons. Highly diluted systems should be measured in fluorescence mode, a request that increases the acquisition times, making contamination problems more severe [1,2]. Finally, the absence of a structural model and the difficulty in treating open shell systems makes a computational approach not straightforward [3].

In situ, temperature dependent, XAFS experiment allowed us to prove that Cr<sup>II</sup> species grafted on SiO<sub>2</sub> surface are significantly extracted from the surface upon interaction with CO at 100 K, being the Cr-O bond distance elongated of 0.08 Å [4]. This first direct structural evidence quantifies the findings previously obtained via vibrational (IR and Raman) studies. All data allow to conclude that the absorption evolves into two coverage dependent steps: (i) displacement of weak ligands (surface siloxanes), resulting in non classical carbonyls; (ii) relaxation of the Cr-O surface bonds with subsequent optimization of the Cr...CO distance and transformation into classical carbonyls [4].

[1] E. Groppo, C. Lamberti, S. Bordiga, G. Spoto and A. Zecchina, *Chem. Rev.*, **105** (2005) 115.

[2] E. Groppo, et al. *J. Catal.*, **230** (2005) 98; G. Agostini, et al. *J. Phys. Chem. C*, **111** (2007) 16437.

[3] A. Damin, et al. *J. Phys Chem. A*, **113** (2009) 14261.

[4] D. Gianolio, E. Groppo, J. G. Vitillo, A. Damin, S. Bordiga, A. Zecchina, and C. Lamberti, *Chem. Commun.*, **46** (2010) 976.