Supporting Information for

Direct evidence of adsorption induced Cr^{II} mobility on the SiO_2 surface upon complexation by CO

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1. Sample preparation

Cr^{II}/SiO_2 samples, at 0.5 wt% Cr loading, were prepared following the standard recipe well known in literature. Silica aerosil (surface area = 400 m^2g^{-1}) was impregnated with a solution of chromic acid, outgassed at 650°C in high vacuum conditions, oxidized at 650°C for 1 h and finally CO reduced at 350°C for 1 h.[1] The correctness of all the steps has been checked by looking at the color of the samples (light orange in the oxidized state, light blue in the reduced state). All the activation procedure was conducted by using a vacuum/gas dosage line connected to a cell hosting the sample and three empty capillaries. Once the desired treatment has been performed, capillaries have been filled under controlled atmosphere (CO or vacuum) and then sealed. Sealed capillaries were mounted on BM26A beamline as shown in Figure 2 of the main text.

2. X-ray absorption set up and related data analysis

X-ray absorption experiments at the Cr K-edge (5989 eV) were performed at the BM26A beamline (DUBBLE) of the ESRF facility (Grenoble, F). The white beam was monochromatized using a Si(111) double crystal; harmonic rejection has been performed by using a meridionally focusing mirror with an angle of incidence of 2.8 mrad and a silicon coating. Due to Cr dilution, EXAFS spectra were collected in fluorescence mode, by means of a 9 elements germanium monolithic detector. The intensity of the incident beam was monitored by an ionization chamber filled with 1 bar of 20% N_2 − 80% He. The beam transmitted through the sample passed further through a second ionization chamber, a Cr foil and a third ionization chamber to ensure the correct energy calibration for any acquisition.[2]

Due to the high air sensitivity, the samples have been measured inside sealed capillaries (1.5 mm in diameter), following the well established procedure adopted for XRPD experiments,[3] both in absence and in presence of CO. For this reason, the beam was vertically focused in order to reach a dimension on the sample of 0.3 mm. For each sample, the horizontal slits were optimized to fit with the interval of uniform filling of the capillary. An Oxford Instruments N_2 cryostream was mounted in front of the capillary to allow a control of the sample temperature in the 80-300 K interval.

The XANES part of the spectra was acquired with an energy step of 0.4 eV and an integration time of 2s/point. The EXAFS part of the spectra was collected up to 12 $Å^{-1}$ with a variable sampling step in energy, resulting in $\Delta k = 0.05$ $Å^{-1}$, and an integration time that linearly increases as a function of k from 5 to 20 s/point to account for the low signal-to-noise ratio at high k values. For each sample, three equivalent EXAFS spectra were acquired and averaged before the data analysis.[4]

EXAFS data analysis has been performed using the Arthemis software.[5] Phase and amplitudes have been calculated by FEFF6.0 code[6] using as input the simple Cr-O, Cr-Si and Cr-CO fragments, the latter assumed to be linear. The validity of the FEFF6.0 code to compute correctly phases and amplitudes for Cr^{II}-(light scatterers) has been successfully verified with Cp_2Cr in toluene solution model compound.[7,8] For each sample, the averaged $k^3\chi(k)$ function was Fourier transformed (FT) in the $\Delta k = 2.0\text{-}10.0$ Å^{-1} interval so that a direct comparison among the different fits can be done. In the case of the Cr^{II}/SiO_2 system in presence of CO, the experimental signal was stronger, due to the high intensity of the Cr^{II}–CO multiple scattering paths; consequently also a FT in the $\Delta k = 2.0\text{-}13.0$ Å^{-1} was performed. The fits were performed in different R-spaces as detailed for each specific case, by respecting the Nyquist theorem: number of independent points $< 2\Delta k\Delta R/\pi$ in its more strict form.[9,10]

Table S1. Summary of the optimized parameters and of the refinement strategies adopted to analyze the EXAFS data of the Cr^{II}/SiO_2 system after CO adsorption at 100 K. Non optimized parameters can be distinguished by the absence of the corresponding error bar.

	Cr^{II}/SiO_2 + CO	
k-range (Å^{-1})	2.0-10.0	2.0-13.0
N_{var} / N_{ind}	8 / 16.3	8 / 22.4
S_0^2	0.9	0.9
ΔE_0 (eV)	0 ± 1	0 ± 1
N_{Cr-O1}	2	2
d_{Cr-O1} (Å)	1.935 ± 0.007	1.92 ± 0.01
σ^2_{Cr-O1} (Å^2)	0.007 ± 0.001	0.006 ± 0.001
N_{Cr-Si}	2	2
d_{Cr-Si} (Å)	2.76 ± 0.02	2.74 ± 0.03
σ^2_{Cr-Si} (Å^2)	0.014 ± 0.002	0.017 ± 0.004
N_{Cr-CO}	2.3 ± 0.3	1.9 ± 0.4
d_{Cr-CO} (Å)	1.995 ± 0.008	2.00 ± 0.01
σ^2_{Cr-CO} (Å^2)	0.009 ± 0.001	0.007 ± 0.002
R_{factor}	0.007	0.038

In the Cr^{II}/SiO_2 system in vacuo at 300K, in the high-K region of the spectra, we have a border limit value of the signal/noise ratio: this is due to the fact that we collected the data in fluorescence mode on very diluted samples. In order to avoid to carry on this noise in the successive steps of the data analysis, we decided to perform the FT in a safe, but short K-range stopping at K = 10.0 Å^{-1}. We chose the same value for all the spectra to allow a direct comparison, even if for the data collected on the Cr^{II}/SiO_2 system in presence of CO at 100 K we could extend the K-range until K < 13.0 Å^{-1} for the best quality of the data (see Figure 1a of the main text). The enhancement of the signal to noise ratio in this data set does not depend only on the thermal factor (lower temperature contributes in decreasing the noise) but predominantly on the addition of carbonyls groups that produce an important contribution and increase the EXAFS signal. Moroever, the extraction of the Cr(II) species from the SiO_2 surface "solvation effect" significantly reduce the heterogeneity among Cr(II) hosted on the amorphous surface. Looking the results of the two fit performed on this system with different k-ranges (reported in Table S1), it is clear that all the values obtained for the optimized parameters are comparable within the errors, as expected.

3. Experimental details on IR and Raman spectroscopies

Raman spectra of the Cr^{II}/SiO_2 system in vacuo have been recorded using a Renishaw micro-Raman System 1000 spectrometer and a He-Cd laser emitting at 442 nm (22625 cm^{-1}). Measurements on the CO contacted sample have been performed employing the 442 nm and 325 nm (30769 cm^{-1}, He-Cd laser) laser lines. As the reduced sample is extremely sensitive to oxygen contaminations, suitable cells, allowing an accurate control of the atmosphere surrounding the sample, have been used.

The change of laser line is dictated by the fact that interaction with CO modifies the Cr^{II} electronic configuration (as clearly testified by our XANES study, see Figure 3b in the main text) and thus its optical absorption spectrum. In fact, due to the high Cr dilution of the samples and to the fact that we are looking to surface vibrations, which density of states is much lower than bulk vibrations, the only way to get Raman spectra of vibrations involving Cr centers was to operate under resonant or pre-resonant conditions.[11] Such conditions are obtained when the laser line is able to excite a specific charge transfer transition involving the metal center of interest.[12,13]

For IR experiments the sample has been pressed into a self supporting pellet, successively transferred into an IR cell designed to allow thermal treatments of the sample in the 1000-77 K range, either under vacuum or in presence of a desired equilibrium pressure of gases.[14] The FTIR spectra have been collected on a Bruker IFS-66 spectrophotometer equipped with and HgCdTe cryo-detector, at 2 cm^{-1} resolution.

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