Temperature dependent adsorpion of CO on CrII/SiO2 system inducing Cr mobility on the surface

Temperature dependent adsorption of CO on Cr^{II}/SiO_2 system inducing Cr mobility on the surface

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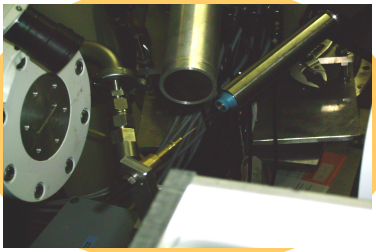
1 Introduction

The Phillips catalyst is nowadays widely used in the industrial polyethylene (PE) production.[1] Its possibility to produce different kinds of PEs without the intervention of any activators, made Cr/SiO_2 one of the most investigated systems.[2] Nevertheless its structure is still unresolved because of:

- amorphous nature of support,
- low Cr loading (0.5 wt%),
- high reactivity toward air,
- difficulty in treating computationally open shell systems.[3]

We present here a detailed in situ, temperature depending, XAFS investigation on the Cr^{II}/SiO_2 structure and its reactivity towards simple reagents (CO).[4]

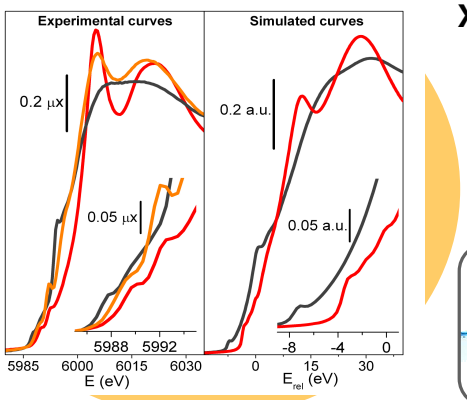
2 Methods



XAFS measurements were performed at BM26A beamline at ESRF.

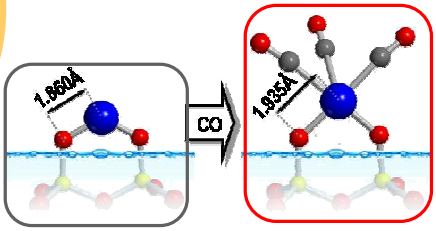
Cr^{II}/SiO_2 system was prepared inside capillaries sealed in absence or in presence of CO.
Data were acquired in fluorescence mode using a 0.3 mm-vertically focused beam.
The temperature was changed from RT to 77 K by means of a liquid nitrogen cryostream coaxial to capillaries.

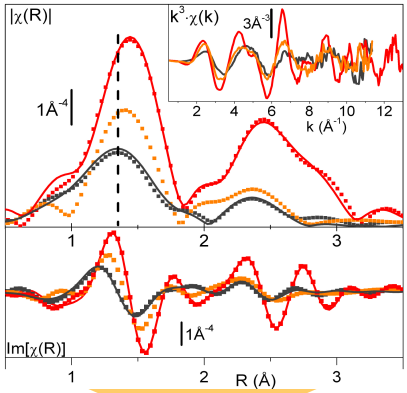
3 Results



XANES and EXAFS

- Cr/SiO_2 (dark grey)
- Cr/SiO_2 +CO @300K (orange)
- Cr/SiO_2 +CO @100K (red)





XANES calculation were performed by using FDMNES code, on clusters able to correctly predict the Cr(II) carbonyl vibrational features.[3]

The spectrum of Cr/SiO_2 sample presents:

- **two weak pre-edge features due to $Cr_{1s} \rightarrow Cr_{3d} + O_{2p}$ dipole-forbidden transitions**
- **a strong pre-edge band due to $Cr_{1s} \rightarrow Cr_{4p}$ transition.**

Upon progressive CO adsorption:

- **the weak pre-edge features blue shift and increase in intensity**
- **the strong pre-edge band approaches the edge, becoming less visible**
- **after edge two components arises due to Cr1s $\rightarrow \pi_{CO}$ transitions.**

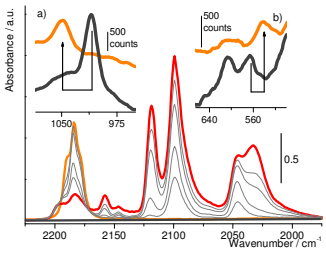
Cr^{II}/SiO_2 (S_0^2=0.9, ΔE=-1 R_{fact}=0.024)		Cr^{II}/SiO_2 + CO (S_0^2=0.9, ΔE=0, R_{fact}=0.007)	
N_{Cr-O1}	2	N_{Cr-O1}	2
d_{Cr-O1} (Å)	1.86 ± 0.03	d_{Cr-O1} (Å)	1.935 ± 0.007
σ^2_{Cr-O1} (Å²)	0.015 ± 0.005	σ^2_{Cr-O1} (Å²)	0.007 ± 0.001
N_{Cr-Si}	2	N_{Cr-Si}	2
d_{Cr-Si} (Å)	2.70 ± 0.02	d_{Cr-Si} (Å)	2.76 ± 0.02
σ^2_{Cr-Si} (Å²)	0.012 ± 0.001	σ^2_{Cr-Si} (Å²)	0.014 ± 0.002
N_{Cr-O2}	2.8 ± 0.4	N_{Cr-CO}	2.3 ± 0.3
d_{Cr-O2} (Å)	2.64 ± 0.03	d_{Cr-CO} (Å)	1.995 ± 0.008
σ^2_{Cr-O2} (Å²)	0.015	σ^2_{Cr-CO} (Å²)	0.009 ± 0.001

- elongation of the Cr-O1 distance +0.08 Å (consequently of Cr-Si)
- appearence of MS Cr-CO contributions (around 2.5–3 Å)

4 Conclusion

Both XANES and EXAFS data confirm and quantify findings previously obtained by vibrational studies (IR and Raman)[2] and allow to conclude that the absorption evolves into two coverage dependent steps:

- displacement of weak ligands (surface siloxanes Si-O-Si), resulting in non classical carbonyls;
- relaxation of the Cr-O surface bonds with consequent optimization of the Cr···CO distance and transformation into classical carbonyls.



5 References

[1] B. M. Weckhuysen and R. A. Schoonheydt, *Catal. Today,* 1999, **51**, 215.
[2] E. Groppo, C. Lamberti, S. Bordiga, G. Spoto and A. Zecchina, *Chem. Rev.,* 2005, **105**, 115.
[3] A. Damin, J. G. Vitillo, G. Ricchiardi, S. Bordiga, C. Lamberti, E. Groppo and A. Zecchina, *J.Phys. Chem. A,* 2009, **113**, 14261.
[4] D. Gianolio, E. Groppo, J. G. Vitillo, A. Damin, S. Bordiga, A. Zecchina and C. Lamberti, *Chem. Commun.,* 2010, **46**, 976-978

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