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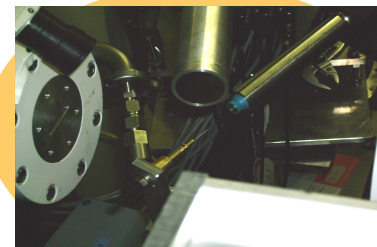
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(Article begins on next page)

Temperature dependent adsorption of CO on Cr^{II}/SiO₂ 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/SiO₂ 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}/SiO₂ structure and its reactivity towards simple reagents (CO).^[4]

2 Methods

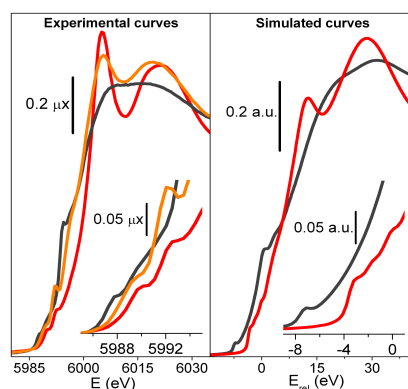
XAFS measurements were performed at BM26A beamline at ESRF.

Cr^{II}/SiO₂ 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.

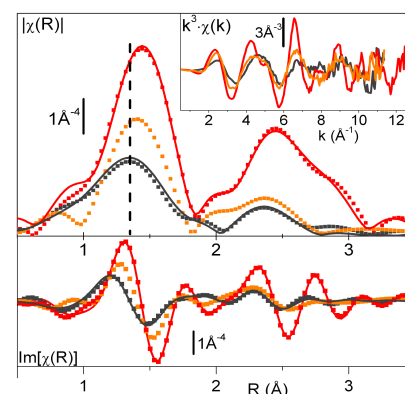
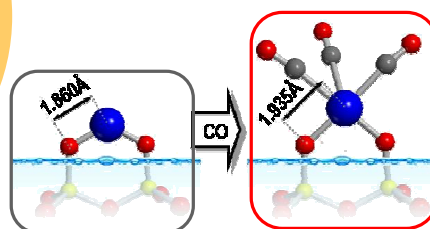
The temperature was changed from RT to 77 K by means of a liquid nitrogen cryostream coaxial to capillaries.

3 Results



XANES and EXAFS

- Cr/SiO₂ (dark grey)
- Cr/SiO₂+CO @300K (orange)
- Cr/SiO₂+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/SiO₂ sample presents:

- two weak pre-edge features due to Cr_{1s} → Cr_{3d} + O_{2p} dipole-forbidden transitions
- a strong pre-edge band due to Cr_{1s} → 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 → π_{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} (Å ²)	0.015 ± 0.005	σ ² _{Cr-O1} (Å ²) 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} (Å ²)	0.012 ± 0.001	σ ² _{Cr-Si} (Å ²) 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} (Å ²)	0.015	σ ² _{Cr-CO} (Å ²) 0.009 ± 0.001

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

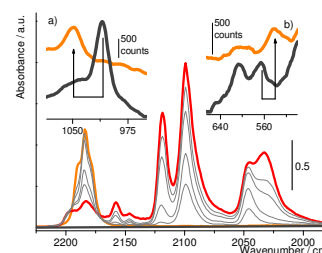
4 Conclusion

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

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