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# XAFS estimation of the catalytic centre in double metal cyanide catalysts

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Double metal cyanide catalysts (DMC) are widely exploited in industrial ring opening polymerization of the epoxydes [1]. This group of catalysts is successfully applied and continuously improved for few decades, but the knowledge on the molecular nature of their particularly high activity and selectivity is limited to some phenomenological hypotheses. To shine some light on the relation between structural and chemical properties of DMC catalysts and their activity, XAS studies were performed in cooperation with *MEXEO Kędzierzyn-Koźle* Company. The DMC catalysts (MEO-DMC) and the reference material were synthesized by *MEXEO*. The reference material was the hydrated trizinc bis[hexacyanocobaltate(III)] compound ($Zn_3[Co(CN)_6]_2 \cdot nH_2O$) of negligibly low catalytically activity without practical application. Only after introduction to its structure appropriate kinds of organic ligands, catalytic activity increases. The synthesis started from $K_3[Co(CN)_6]_2$ and $ZnCl_2$ raw materials. In the investigated samples, the *tert*-butanol ($^t$BuOH) or 1,2-dimethoxyethane (glyme)) ligands were introduced in catalyst preparation process. These ligands are the most frequently used in commercial application of DMC family of catalysts. The commercial DMC catalyst was used as a comparative DMC catalyst.

All samples were in the form of powder. The introduction of the ligands change the morphology of the DMC material from cubic observed in reference material to kind of irregular sheets with very extended surface. The EXAFS analysis of the Zn and Co K-edges was performed to exam the local atomic order around Zn and Co atom in the reference material, the MEO-DMC catalysts and the commercial catalyst. The XAS measurements were performed at SOLEIL, France (SAMBA station).

In agreement with the XRD results, the model for the reference material was assumed to be a cubic structure (Fm-3m) with water and a lattice constant of 1.0249 nm. This model provides for the EXAFS analysis the starting parameters including the number, kinds and distance of atoms in the subsequence coordination shells in ideal ($Zn_3[Co(CN)_6]_2 \cdot 12H_2O$) reference material. The EXAFS analysis of the Zn and Co K-edge indicated, that in the considered reference material, instead of 24, only few oxygen atoms were detected. Furthermore, the number of other atoms in the coordination spheres was in the agreement with the model. Therefore, the reference material was not fully hydrated.

The EXAFS spectra of investigated materials at Zn K-edge and their FT modules noticeably differed (Fig. 1). In the case of catalysts, the number of atoms in the subsequence coordination spheres was smaller than in the model of reference material. Finally, it was proved, that the atomic order resembles rather a tetrahedral structure with four N atoms around Zn (anhydrous phase) instead of 6 in cubic structure (hydrated phase). Therefore, the stoichiometry and structure change in catalysts after introduction of ligands.

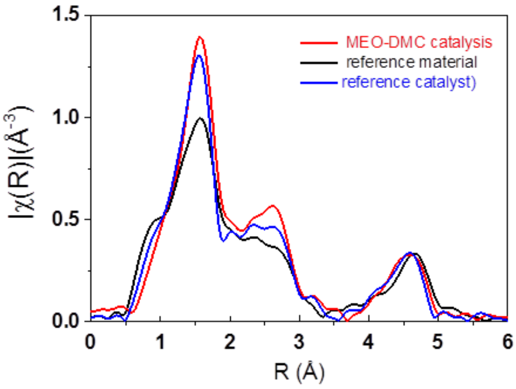

*Figure 1.* The comparison of FT modules of the experimental Zn K-edge spectra for investigated materials.

Several models of atomic order around Zn were considered. The best fit to the EXAFS data was for the model assuming that majority of Zn atoms in MEO-DMC catalyst still have the local atomic order as should be in the reference anhydrous material with tetrahedral structure but about 20% of them have Cl in the first coordination sphere (Fig. 2).

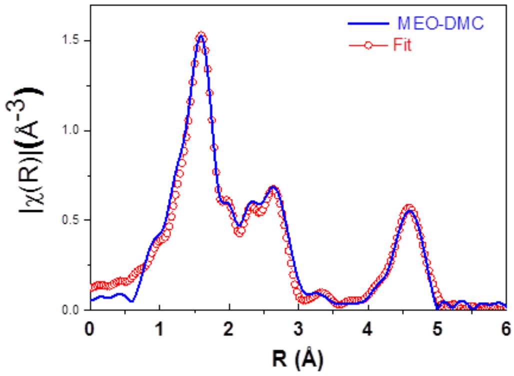

*Figure 2.* Fit of the EXAFS data to the final model of the local atomic structure around Zn atoms for MEO-DMC catalyst.

The local atomic structure around Co atom was practically not changing for all investigated materials (Fig. 3). Moreover, has the atomic order like in the hydrated reference material (octahedral) with 6 C atoms as near-neighbors. This confirmed that Co metallic centre is not active during the catalyst preparation.

On the basis of performed analysis, the following model of investigated DMC catalysts is proposed.

Catalysts form cluster-like complexes with the Co atomic structure not affected as compare to reference hydrated (cubic) material.

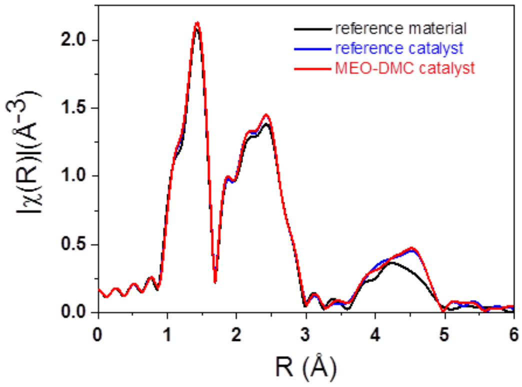

*Figure 3*. The comparison of FT modules of the experimental Co K-edge spectra for investigated materials.

The Zn atoms inside the clusters have atomic order like in anhydrous reference material (4 N atoms). This explains this part of the Zn atoms in EXAFS analysis which have an atomic order similar to that in the reference anhydrous material. At the surface of the clusters, Zn atoms are bounded partially with groups of cyanide and with chlorine atoms from the $ZnCl_2$ or oxygen atoms from the ligand. The amount of Cl detected by EXAFS in all investigated samples was in agreement with that estimated by energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) measurements. This model explains the fact that X-ray diffraction pattern for investigated catalysts cannot be described by any of know phase. The atomic order around majority of Zn atoms resembles anhydrous phase, but that around Co hydrated phase. The performed analysis of EXAFS provided direct experimental evidence for the phenomenological hypotheses postulated by Zhang et al., [2] and for calculation performed by Wojdeł et al., [3].

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