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Catalytic centre of double metal cyanide catalysts as resulted from XAS studies

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Double metal cyanide (DMC) catalysts are commonly applied at industrial ring opening polymerization of the epoxides. Nevertheless, the knowledge on the molecular nature of their high activity and selectivity is limited. XAS studies were performed to look for possible catalytic centre in this family of catalysts.

The DMC catalysts and the reference material were synthesized at MEXEO Kędzierzyn-Koźle according to the method described in [1]. The reference material was hydrated trizinc bis-[hexacyanocobaltate(III)] compound ($Zn_3[Co(CN)_6]_2 \cdot nH_2O$) of negligibly low catalytic activity, not suitable for practical application. The investigated DMC materials were synthesized from $ZnCl_2$ and potassium hexacyanocobaltate(III) solution, in presence of two organic ligands: *tert*-butanol (*t*BuOH) and glyme ($CH_3OCH_2CH_2OCH_3$). These ligands are frequently used in commercial application of this family of DMC catalysts. These catalysts were denote here as DMC BuOH and DMC glyme, respectively.

The local atomic structure around Zn and Co atoms was determined by EXAFS. Experiments were performed at beamline SAMBA of the Soleil synchrotron at room temperature in atmospheric pressure and in transmission mode. Appropriate amounts of the samples were mixed with cellulose and pressed into a pellet. The analysis was performed using IFEFFIT package [2].

The catalysts are heterogeneous materials. Moreover, they did not form the mix of several phases. As was discussed in ref. [3] the diffraction pattern of the part of catalysts with crystalline phase till now was not resolved and probably is not responsible for good catalytic properties of these materials. Catalysts have a considerable fraction of amorphous material. Therefore we have applied in analysis the least squares linear combination (LC) method, the most popular for analyzing the content of different chemical compounds of given element in heterogeneous material. Several models of atomic order around Zn were considered. The models proposed in the literature discussing the role of O and Cl atoms in DMC catalysts were taken into account [4, 5, and 6].

Similar as in paper [3] the best fit to the EXAFS data was obtained for the model assuming two different local atomic order around Zn atoms. Local atomic order of the considerable fraction of Zn atoms was as should be in the reference anhydrous material with rhombohedral structure. Zn was bonded directly to four cyanide groups.

The rest of Zn had Cl in the first coordination sphere (Fig. 1). According to synthesis procedure, there is an excess of Zn atoms in catalyst. And indeed we found that only 84(3) % and 79(5) % of Zn atoms have 4 NC near neighbour groups for DMC BuOH and DMC glyme, respectively. For the rest of Zn atoms Cl was identified in the first coordination sphere in the distance 2.24 Å. This Zn-Cl bond length is close to that in $ZnCl_2$ (2.30 Å), therefore can be considered as characteristic for Zn-Cl bond. Nevertheless, the existence of $ZnCl_2$ compound was not confirmed, because the model with the atomic order characteristic for $ZnCl_2$ (in first coordination shell 2 Cl in distance 2.3 Å and 2 Cl in distance 3.2 Å and next 4 Zn atoms at distance 3.75 Å and 2 Cl in distance 3.8 Å) could not be fitted. Substituting some of Cl atoms with oxygen leads to an increase of the errors of estimated parameters and to an increase of the R_f parameter which estimate the quality of the fit. Nevertheless, one cannot exclude that oxygen atoms can be bonded to Zn but in very limited amount. In many reports it is emphasized that the type (coming from water or ligands) and amount of oxygen atoms coordinated to Zn should play an important role in the ring opening polymerization of propylene oxide since oxygen atoms coordinated to a zinc ion are believed to be a real active center of DMC catalyst [6]. From the performed EXAFS studies we cannot confirm this role. Instead we do confirm the location of Cl close to Zn atoms. The role of Cl is also discussed in the literature on the base of experiment [4] and molecular calculation [5]. In the paper by Zhang et al., [4] based on overall chemical premises the role of Cl atoms in the catalytic properties of DMC was postulated and reported that the ligand influences on catalytic activity only by helping to form the amorphous structure.

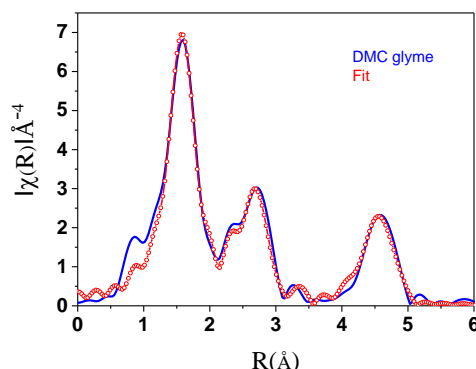


Figure 1. Fit to the EXAFS data of the model for DMC glyme.

The local atomic order around Co atom was practically not changing for all investigated materials (Fig. 2). In fits to given catalyst the differences in number of oxygen atoms in distance 3.10 Å and 4.62 Å were only noticed.

These oxygen atoms can originate from water molecule or ligand. The error indicated by IFEFFIT code for the number of these atoms is quite large demonstrating that oxygen can be distributed non homogeneously. This confirms that Co metallic center is not active during the catalyst preparation. Interestingly, the atomic order around Co remains like in hydrated

form of $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ with cubic ($Fm-3m$) structure. Therefore, in catalyst both metals have different atomic order. Zn atoms like in anhydrous structure (rhombohedral ($R-3c$)) bonded with four NC groups and Co atoms like in hydrated structure bonded with six CN groups.

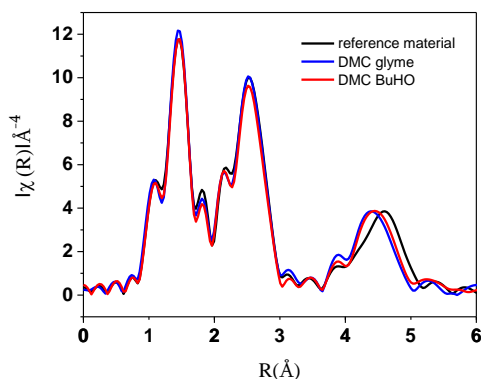


Figure 2. K-edges of Co. The comparison of FT module of the experimental spectra of the investigated catalysts and hydrous reference material.

Summarizing the performed studies, one can state that results of the EXAFS analysis support the model proposed by Zhang et al., [4] and the model resulting from molecular calculation performed by Wojdeł et al., in [5]. These models postulate the important role of Zn-Cl bonds in the activity of examined catalysts. The role of Zn-O bond postulated in other papers [e.g. [6] and references therein] is not confirmed. We do not detect Zn atoms in the distance 4.38 Å as resulted from calculation

performed in the ref. [6]. Therefore, our earlier postulate that catalysts with BuOH ligand form cluster-like complexes [3] was confirmed now also for catalysts with glyme ligands. The Zn atoms inside the clusters have changed atomic order which becomes like in anhydrous structure (tetrahedral coordination). Whereas, the Co atomic structure remains not affected, as compared to reference cubic hydrated material. Remaining Zn atoms can be bonded partially with groups of cyanide and with chlorine atoms. These atoms can be located at the surface of the clusters and be catalyst active centres. EXAFS analysis does not confirm the existence around Zn atoms the atomic order like in ZnCl_2 compounds. Therefore, the performed XAS studies give direct evidence that formula $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot x\text{ZnCl}_2 \cdot y\text{L}$ used to describe DMC catalyst is not valid. Instead the nanoclusters are formed in catalyst with different atomic order around Co and Zn with new structure, which incorporates Cl atoms.

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