Estimation of the catalytic centre in double metal cyanide catalysts by XAS

Krystyna Lawniczak-Jablonska*1 and Arkadiusz Chrusciel2
1Institute of Physics, Polish Academy of Sciences, Lotnikow Str 32/46, 02 668 Warsaw, Poland
2MEXEO, 47 225 Kędzierzyn-Kozle, Energetykow Str 9, Poland

*E-mail: jablo@ifpan.edu.pl

Abstract. Double metal cyanide (DMC) catalysts are commonly applied at industrial ring opening polymerization of epoxides. Nevertheless, the knowledge on the molecular nature of their high activity and selectivity is limited. XAS studies were performed to look for the possible catalytic centre in this family of catalysts. DMC catalysts were synthesized from ZnCl2 and potassium hexacyanocobaltate(III) solution, in the presence of the different organic ligands and show significant fraction of the non-crystalline structure. Two ligands were analysed (tert-butanol (tBuOH) or glyme (CH3OCH2CH2OCH3)). EXAFS analysis established that only Zn atoms are the active metallic centers in DMC regardless the used ligand. The coordination around Zn was changed from octahedral in reference non catalytic material to tetrahedral in catalysts, and Cl atoms were detected near some of Zn atoms.

1. Introduction

The double metal cyanide (DMC) type catalysts frequently used in commercial production are the complex compounds of zinc(2+) and hexacyanocobaltate(III)(3-) ions containing appropriate kinds of organic ligands. Owing to the heterogeneous nature of DMCs with complex compositions, it is difficult to obtain detailed knowledge on an exact active center. The explanations of DMC catalysts properties described in the literature are based on the hypothesis that their activity is determined by the properties of Zn metal through the formation of the coordination bond with organic co-ligand oxygen atoms. Such bonding is weaker than strong Zn–NC one [1-5]. Some of the papers indicated also the role of Zn–Cl bond in the catalytic properties [6,7]. Unfortunately, no satisfactory explicit experimental data confirming the existing of Zn–O or Zn–Cl bonds in the DMC catalysts have been communicated. Therefore, in order to build up the experimental basis for the molecular justification of the activity of the DMC catalysts, the X-ray absorption spectroscopy (XAS) was applied, due to its sensitivity on the closest atomic neighbourhood of examined elements regardless an amorphous or crystalline surroundings. Moreover, to exam the influence of the used ligand on the Zn and Co local atomic structure the DMC s with two different organic co-ligands were studied.

2. Experimental

The DMC catalysts and the reference material were synthesized at MEXEO Kędzierzyn-Koźle company according to the method described in [8]. The reference material was the ‘pure’, hydrated trizinc bis-[hexacyanocobaltate(III)] compound (Zn3[Co(CN)6]2·nH2O) of negligibly low catalytic activity, not suitable for practical application. The investigated DMCs were synthesized from ZnCl2 and potassium hexacyanocobaltate(III) solution, in presence of the organic ligands as tert-butanol (tBuOH) and glyme (CH3OCH2CH2OCH3) and discussed here as DMC BuOH and DMC glyme, respectively. These ligands are frequently used in preparation of this family of DMC catalysts. Due to the quantity of the potential coordination centers of these ligands, the tert-butanol is expected to be the mono-dental ligand but glyme (1,2-dimethoxyethane) should be the bi-dental one. Therefore we suspect the essential difference in their performance to coordinate the active catalytic centre (Zn...
atoms). The catalytical activity of investigated catalysts was examined on the base of the standard methyloxirane and polypropylene glycol PPG450 polyaddition reaction, according to the method described in [8] and was estimated to be 1600 gPO/gcat*min and 1700 gPO/gcat*min for DMC-BuOH and DMC-glyme, respectively.

The local atomic structure around Zn and Co atoms was determined by EXAFS. Experiments were performed at the 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 [9].

3. Results and discussion

In the figure 1 the Fourier transformed (FT) data of the Zn K-edge EXAFS measurements for the three studied samples are presented. There is clear difference in FT of data for Zn K-edge. Several models of atomic order around Zn were considered, taking into account the models proposed in the literature discussing the role of O and Cl atoms in DMC catalysts [4,6,10,11].

![Figure 1. K-edges of Zn. The comparison of FT module of the experimental spectra (left); Fit to the EXAFS data of the model for DMC glyme (right).](image)

Similarly as in paper [12] the best fit to the EXAFS data was obtained for the model assuming that considerable fraction of Zn atoms in the catalyst has the local atomic order as should be in the reference anhydrous material with rhombohedral structure (4 cyanide groups) and some of them have Cl in the first coordination sphere (figure 1 (right) and table 1). There is an access of Zn atoms and only 84(3)% and 79(5)% of Zn atoms have 4 NC near neighbour groups for DMC BuOH and DMC glyme, respectively. In the first coordination sphere 0.4 and 0.56 Cl atom per one Zn atom in the distance 2.24 Å, respectively, was identified for investigated catalysts. This Zn–Cl bond length is close to that in ZnCl₂ (2.30 Å), therefore can be considered as characteristic for Zn–Cl bond. Nevertheless, the existence of ZnCl₂ compound was not confirmed, because the atomic order characteristic for ZnCl₂ (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 the 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 since oxygen atoms coordinated to a zinc ion are believed to be a real active center of DMC catalyst [11,13]. From the performed EXAFS studies,
similarly as in ref. [12] in the DMC with the tert-butanol ligand, we cannot confirm the importance of Zn–O bonds in the DMC with the glyme ligand. Instead we do confirm the location of Cl close to Zn atoms as well in this DMC. The role of Cl was also discussed in the literature on the base of XPS experiment [6] and molecular calculation [10]. In the paper by Zhang et al., [6] 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. Results of performed EXAFS studies are fully in line with this statement.

Table 1. The local atomic order around Zn atoms in the reference material, and both catalysts. Number of atoms (No) in the given coordination sphere, distance (R) from Zn atom in Å, and Debye–Waller factors. In the parentheses the confidence interval indicated by IFEFFIT code is given. R_f factor indicate the quality of the fitting.

| Shell | Elem. | Reference material 100% No | R (Å) | Sigma^2 | DMC BuOH 84(3)% No | R (Å) | Sigma^2 | DMC glyme 79 (5)% No | R (Å) | Sigma^2 |
|-------|-------|-----------------------------|-------|---------|---------------------|-------|---------|----------------------|-------|---------|
| 1     | N     | 6                           | 2.09(4)| 0.013(1)| N                   | 1.974(3)| 0.003(1)| N                    | 1.98(1)| 0.005(1)|
| 2     | C     | 6                           | 3.23(1)| 0.006(2)| C                   | 2.98(2) | 0.013(4)| C                    | 3.00(1)| 0.009(3)|
| 3     | O     | 24                          | 4.50(6)| 0.008(6)| Co                  | 5.006(4)| 0.004(1)| Co                  | 5.00(1)| 0.007(1)|
| 4     | Co    | 6                           | 5.15(8)| 0.018(8)| Co                  | 5.038(4)| 0.004(1)| Co                  | 5.04(1)| 0.007(1)|

Zn–Cl

| Shell | Elem. | Reference material 100% No | R (Å) | Sigma^2 | DMC BuOH 84(3)% No | R (Å) | Sigma^2 | DMC glyme 79 (5)% No | R (Å) | Sigma^2 |
|-------|-------|-----------------------------|-------|---------|---------------------|-------|---------|----------------------|-------|---------|
| 1     | Cl    | 0                           | 0.40(2)| 2.24(1)| 0.003(1)           | 0.56(5)| 2.24(1)| 0.005(1)           |
| R_f   |       | 0.013                       | 0.003 | 0.018    | 0.018               | 2.24(1)| 0.005(1)|

Figure 2. K-edges of Co. The comparison of FT module of the experimental spectra (left); Fit to the EXAFS data of the model for DMC glyme (right).

Finally the local atomic structure around Co atom was investigated for DMC glyme and compared with DMC BuHO and reference material. As can be seen in figure 2 (left) practically this structure is not changing for all investigated materials up to about 3 Å. After the fitting of the EXAFS of the reference material to it’s model of crystal structure, the atomic order around Co was found like
follows: in first shell 6.0(2) carbon atoms at the distance 1.89(1) Å, next 6.0(2) nitrogen at 3.09 Å and 10(4) and 9(3) oxygen atoms in distances of 3.12(1) Å and 4.6(1) Å, respectively, and 6.0(2) Zn atoms at distance of 5.13(3) Å. In best fits of EXAFS data to investigated catalysts the difference in respect to reference material was noticed only in the number of oxygen atoms. All distances of shells and coordination numbers of other than oxygen shells was not changed. In the DMC glyme oxygen shells 12.6(4) and 15.5(3) atoms were found but in DMC BuHO 10(4) and 11(3), respectively. These oxygen atoms can originate from water molecule or ligand. The error indicated by IFEFFT code for the number of these atoms is quite large indicating that oxygen can be distributed no 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 $\text{Zn}_3[\text{Co(CN)}_6]^2\cdot n\text{H}_2\text{O}$ with cubic ($Fm\overline{3}m$) structure. Therefore, in catalyst both metals have different atomic order. Zn atoms like in anhydrous structure (tetrahedral ($R-3c$)) bonded with four NC groups and Co atoms like in hydrated structure bonded with six CN groups.

4. Conclusions
The results of the EXAFS analysis performed for DMC with glyme ligand, in line with the results reported in [12] for DMC BuHO ligand, support the model proposed by Zhang et al., [6] and the model resulting from molecular calculation performed by Wojdel et al., in [10]. 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 [1-5,11,13] is not confirmed. We do not detected Zn atoms in the distance 4.38 Å as resulted from calculation performed in the ref. 11 but in distance 5.13 Å. Therefore, we postulate that catalysts form cluster-like complexes with the Co atomic structure not affected, as compared to reference cubic hydrated material. The Zn atoms inside the clusters have changed atomic order which becomes like in anhydrous structure (tetrahedral coordination). This explains that part of Zn atoms having an atomic order similar to that in the reference anhydrous material. Remaining Zn atoms can be bound 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 confirmed the existence around Zn atoms the atomic order like in ZnCl$_2$ compounds. Instead the nanoclusters are formed in catalyst with different atomic order around Co and Zn with new, until now not resolved structure, which incorporates Cl atoms.

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