Effect of Zn/Co initial preparation ratio in the activity of Double Metal Cyanide catalysts for propylene oxide and CO_2 copolymerization

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Abstract

Zn-Co double metal cyanide (DMC) catalysts were prepared by varying the initial amounts of $ZnCl_2$ to analyze the influence of method of preparation on the different copolymerization parameters. Synthesized catalysts were analyzed by different techniques, infrared spectrometry and inductively coupled plasma optical emission spectrometry, scanning electron microscopy, N_2-physisorption and X-ray diffraction to determine whether characteristics affect the catalytic activity. The copolymers were characterized by infrared spectrometry and gel permeation chromatography. Highly active catalyst (2.5 kg polymer/g catalyst) was synthesized, low amounts of cyclic carbonate byproduct were produced (0.4 %) with medium crystallinity catalysts and considerable amounts of K^+ (0.4% to 1.0%wt).

1. Introduction

The world is confronted with a major crisis of climate change due to the increased evolution of greenhouse gases, with CO_2 being the main contributing [1]. Methane is now also a threat, due to permafrost defrosting and subsequent CH_4 liberation related to global warming. In addition, as the current rate of petroleum consumption resources are predicted to be exhausted within the next century, there is a growing effort to develop new chemical processes using renewable resources [2]. In this way, CO_2 have received much more attention to develop processes for its use as a potential carbon resource [3]. Therefore, CO_2 has not only became into an important C1-carbon feedstock because it is

an environmentally benign chemical and a safe alternative, but also because it has received the attention from an economical point of view due to its high purity availability at relatively low cost, and simplicity to handle it on an industrial scale (nontoxic and nonflammable) [4], [5].

As a kind of potential approach, one of the most promising areas for CO_2 is its application as a material for polymer synthesis [6]. Without the intention of competing against natural CO_2 fixation in flora, polycarbonates can be synthesized through the technologically viable process of CO_2 fixation by coupling CO_2 and epoxides with the presence of hetero or homogeneous catalysts [7], [8], [9]. These final polycarbonate products have been proposed as low toxicity and biodegradable alternatives for packaging, engineering polymers and elastomers [8], receiving much more attention because they exhibited good mechanical properties [5]. Appealing economic advantages come from the use of CO_2. It is estimated that producing 1 ton of the final polyol polymer (POL) product will consume approximately 758 kg of propylene oxide (PO) (without including CO_2). Otherwise, when CO_2 is included into the formula, polyol carbonate is produced (PPC) and the PO used is notably reduced. Thus, with a proper catalyst, it can be easily included a 15 wt % of CO_2 into the PPC with savings up to 228 kg of PO in the process. As an example, in the Bayer pilot plant located in Leverkusen, Germany, values above the 30 % CO_2 included into the PPC where obtained and this can lead to high OPEX (operational expenditure) savings. Finally, the impact over carbon footprint is estimated to decrease in 11-19 % [10].

In this sense, the past three decades it has attested a great progress in the fixation of CO_2 into polycarbonates. Since the pioneering work of Inoue in 1969 using $ZnEt_2/H_2O$ as a catalyst [11], many systems have been reported and demonstrated effective utilization

of CO_2 where the importance of a catalyst has never been overestimated [12], [13], [6, 7].

To develop further this promising reaction, various catalyst systems have been developed for the synthesis of polycarbonates [8] and many studies have focused on finding new catalysts with improved activity and selectivity [9]. The target is to synthesize a catalyst fast enough to reduce the reaction time to make the process technically feasible, but at the same time slow enough in PO incorporation to give CO_2 the opportunity to react and incorporate into the polymer chain. Thereafter, a number of catalysts were developed to catalyze the copolymerization of CO_2 and epoxide such as cyclohexene oxide (CHO) and propylene oxide (PO) [5]. Nevertheless, they are generally less effective for the copolymerization of propylene oxide (PO) with CO_2, and undesired byproducts like propylene carbonate (PC) are produced [14]. Propylene carbonate is a byproduct that reduces the atom economy of the reaction, although under certain circumstances it might be of help by reducing the polymer viscosity acting as a solvent and fostering mass transfer.

Several research groups have pursued this path on developing both homogeneous and heterogeneous catalysts for CO_2 fixation [2, 4] and one of the successful examples is double metal cyanide (DMC) catalyst [1, 7]. DMC catalyst generally referred to zinc hexacyanometalate prepared by reaction of zinc halide and hexacyanometalate salt [3] and a complexing agent in some cases [5]. These complexes are considered to be effective not only for propylene oxide ring-opening (ROP) but also for CO_2-epoxides copolymerization [6, 7, 9, 13, 14]. The catalysts are highly active and give polyether polyols that have low unsaturation and narrow molecular weight distribution [6], yielding biodegradable polycarbonates with a wide potential for polyurethane applications [15].

Improvements have made DMC catalysts much more attractive for commercial manufacture of polyoxypropylene polyols [6]. Copolymerization of propylene oxide (PO) and CO_2 using DMC complex based on $Zn_3[Co(CN)_6]_2$ has been successfully carried out by different researchers. Chen et al., 2004 demonstrated that $Zn_3[Co(CN)_6]_2$ enhances the catalytic activity higher than $Zn_3[Fe(CN)_6]_2$. The study showed that lower temperature and lower amount of catalyst was favorable for CO_2 incorporation but propylene carbonate was produced as co-product [3]. Gao et al. (2012) [13] studied the effect of molecular weights of the initial polypropylene glycols (PPG) on polymerization and the reaction conditions. Results showed that the catalytic activity changed with carbonate unit content and molecular weight, it reached 10.0 kg oligomer/g DMC catalyst, also, the carbonate unit content varied between 15.3 % and 62.5 %, and the weight ratio of PC was controlled to less than 8.0 wt %. Li et al. (2011) [14] studied the copolymerization process of CO_2 and PO without initiators. The catalytic activity reached 60.6 kg polymer/g DMC after 10 h. The production of the by-product propylene carbonate (PC) was between 0.4 to 4.4 wt %, but very high molecular weight copolymers were obtain, being the maximum in 130000 g/mol, in this sense they confirmed that a severe oxidative degradation occurred for the low-carbonate-content PPC and that air stability could be significantly improved by adding an antioxidant. Zhang et al. (2011) [9] reported a nanomellar Zn-Co(III) DMCC catalyst with high surface area for copolymerization. Although the molecular weight was so high 31800 g/mol, the resultant copolymer has considerable productivity (6050 g polymer/g Zn), F_{CO2} (72.6%) and low PC (8.5 wt%). Zhou et al. (2011) [16] reported good results on polymerization with high crystallinity catalysts and studied the effect of various reaction conditions such as amount of the catalyst, reaction time and temperature on the copolymerization. The efficiency of catalysts was high, 7488 g polymer/g catalyst and results shown that insertion of CO_2 into chains is significantly

affected by the amount of catalyst and ambient temperature. The PC production was controlled to be less than 5 % while the molar fraction of CO_2 was more than 30 %. On the contrary, Sebastian and Srinivas [17] studied DMC catalysts prepared by different methods and their influence on catalytic activity for CHO-CO_2 copolymerization. They reported that even with moderate crystallinity and without co-complexing agents the catalyst are high active for copolymerization, also, CO_2 adsorption studies revealed that higher the guest-host interaction higher would be the catalytic activity, providing polycarbonates with CO_2 incorporation as high as 86 mol%, average molecular weight of 20900 g/mol and polydispersity index of 1.8.

Therefore, as far as the copolymerization of PO and CO_2 is concerned, developing a highly active catalyst system capable of producing high-molecular-weight poly(propylene carbonate) (PPC) and low amount of PC byproduct is fundamental; under the control of the percentage of CO_2 incorporation [14].

In this work, we will address the effect of different Zn/Co initial ratio in the preparation of five DMC catalysts by testing the catalytic activity in the copolymerization process, the cyclic polycarbonate (PC) production and CO_2 coupling. A comprehensive study of all the catalysts, physical and chemical characterization has been performed using a number of different analytical techniques.
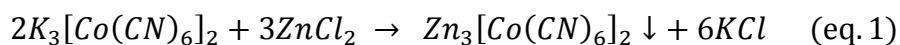
2. Experimental

2.1. Materials

Zinc chloride ($ZnCl_2$), potassium hexacyanocobaltate (III) $K_3[Co(CN)_6]_2$, *tert*-BuOH (t-BuOH) and polyethylene glycol (PEG 1000, Mw=1000 g/mol) were used for catalysts

without further purification and purchased from Sigma-Aldrich. Propylene oxide (PO, $\geq$ 99%, Sigma-Aldrich), polypropylene glycol (PPG 725, Mw= 725 g/mol, Sigma-Aldrich) and CO_2 were used as received.

2.2. Preparation of DMC catalyst

Different amounts of $ZnCl_2$ and $K_3[Co(CN)_6]_2$ were used for the DMC's preparation in order to determine the effect of including one or the other reagent in excess. The different weighted amounts of both reagents can be seen in **Table 1**, 1.77 g of PEG 1000 were added and used as co-complexing agent. Although the stoichiometry of the reaction is 1.5 Zn/Co mol ratio (equation 1), the amounts were changed to determine how can influence the excess of one or another metal on the different catalyst parameters such as, catalytic activity, crystallinity, bounding and copolymerization. The catalyst recovered (g) was the amount of catalyst obtained in each DMC preparation (Table 1).

$$2K_3[Co(CN)_6]_2 + 3ZnCl_2 \;\rightarrow\; Zn_3[Co(CN)_6]_2 \downarrow + 6KCl \quad (\text{eq. 1})$$

Table 1

Amounts of Zn and Co used in the preparation of the different catalysts and experimental Zn/Co mol ratio.

DMC	ZnCl$_2$ (g)	K$_3$[Co(CN)$_6$]$_2$ (g)	Zn/Co mol ratio	Catalyst recovered (g)
A	0.31	6.94	0.1	0.48
B	0.79	5.78	0.3	1.20
C	1.56	3.86	1.0	2.49
D	2.35	1.93	3.0	1.67
E	2.81	0.77	8.9	0.78

The precise K$_3$[Co(CN)$_6$]$_2$ amount for each test was dissolved in 80 ml of mili-Q water and ZnCl$_2$ in 210 ml of miliQ water and 50ml of tBuOH. Both solutions were mixed and vigorously stirred 15 min at 50 °C. After 13 min PEG 1000 was added to the mixed solution, the white suspension was centrifuged 6 min at 5000 rpm. The isolated slurry was resuspended with strong stirring during 20 min in 100 ml of a t-BuOH: H$_2$O (50:50) solution and it was centrifuged as previous. The solid was resuspended in 100 ml of 100% t-BuOH and stirred for 30 minutes, filtered (omnipore PTFE membrane filter, 0.1 µm, Merck Milipore) and dried under vacuum at 50 °C during 30 hours.

2.3. Copolymerization process of CO$_2$ and propylene oxide

Polymerization is a highly exothermic process, and a runaway reaction due to a sudden polyol formation may occur if PO concentration in the liquid phase is high (e.g. due to PO accumulation because of an inefficient agitation). To avoid this situation, completely undesirable that might cause a safety problem indeed and usually leads to overcooked polymers, the PO is often added continuously to the reaction in a batch (semi-batch operation) mode.

Batch copolymerizations of different $Zn_3[Co(CN)_6]_2$ (DMCs) and CO_2 were carried out in a 350 ml reactor. An initial template polymer was used for catalyst activation and for a better control of the final molecular weight. PPG 725 was used for that purpose, assuming that the number of moles of polymer was constant during the reaction and that all the –OH branches grew equally. The amounts of the starter PPG 725 and of the catalyst DMC were fixed at 30 g (0.0413 mol) and 40 mg ($6.38 \cdot 10^{-5}$ mol), respectively and placed in the reactor under continuous stirring and homogenous temperature.

Three successive inertizations using N_2 were carried out at different pressures (5, 15 and 20 barg) to remove all O_2 moieties. The reactor is then heated up to 130ºC under vacuum conditions. Once the temperature was raised, the vacuum continued during 30 min to remove moisture in the starting PPG polymer.

First, under vacuum conditions (-0.80 barg) the activity of the catalysts was tested by two sequential activations at 130ºC inserting a fixed amount of PO. The amount of PO added for the activations was estimated to be around 10% of the total PO required if a 3000 g/mol PPC was pursued.

Once the first amount of PO was pumped into the reactor the following criteria was followed to determine if the catalyst was activated properly. The pressure of the reactor increases due to PO vaporization, up to thermodynamic equilibrium. The catalyst takes typically 10 to 30 min to activate, and after that, the reactor pressure decreases due to PO consumption. If a peak of temperature followed by a decrease on pressure occurred before 1 hour of the first addition, the catalyst passed the activation test. Otherwise, if the pressure did not decrease down to the initial vacuum conditions, the catalyst did not activate properly and the experiment was stopped. The second activation was carried out under the same conditions as the first one. Finally, a third PO addition was performed

with CO_2 at copolymerization pressure (10 barg) only when the catalyst behaved properly in the two previous additions.

After the PO batch additions, once the system was stationary, the temperature was decreased down to the copolymerization temperature of 105 ºC and PO was pumped in a continuous way (0.35 ml/min). This PO flowrate must consider the maximum heat that the equipment is able to remove by the cooling system, to avoid runaway reactions and hotspots. After this stage, a continuous flow of CO_2 was fed into the system during 2 h to keep the pressure constant. Finally, the pressure was slowly released and the system was kept under a vacuum current of N_2 to eliminate the unreacted monomers of PO during 1 hour. Then, the reactor was cooled down and the final copolymerization product was weighted and prepared for further analyses.

2.4. Characterization of the catalyst

Elemental analyses of Zn (213.857 nm), Co (238.892 nm) and K (766.491 nm) were performed by optical emission ICP (Varian 725-ES), after a previous microwave digestion of samples (ETHOS SEL Milestone). Infrared spectra from 400 to 4000 cm^{-1} were recorded using a Fourier transform infrared spectrometer (FT-IR) from Bruker ALPHA at a resolution of 2 cm^{-1} and data were taken after 64 scans.

An environmental scanning electron microscope (ESEM) was taken by ESEM-FEI-Quanta 200F after coating with 10 nm gold layer. X-ray diffraction (XRD) patterns and crystallinity results were obtained on Bruker D8 Discover A25 diffactometer using Cu ceramic tube at 2.2 kW and LynxEye detector.

Microporous and mesoporous of the catalyst were analyzed by nitrogen-physisorption (Sorptomatic 1900, Carlo Erba Instrument). The sample preparation was as follow, first

an outgassed burette was weighted, and then 0.25 g of DMC A was added to the burette in outgassing conditions during 3h at 150ºC and 0.01 Pa, after that the burette was weighed to determine the moisture of the sample and the specific surface area of the catalyst (m^2/g) were analyzed

2.5. Characterization of copolymer

Spectroscopic analysis of the polymers were performed using FT-IR (Bruker ALPHA) at a resolution of 2 cm^{-1} and the data was taken after 64 scans.

The amount by weight of CO_2 incorporated in the polymer chain was determined by means of 1 H-NRM (Bruker AV III HD 500, 500 MHz, pulse program zg30, waiting time d1:1s, 120 scans). The sample was dissolved in deuterated chloroform. The relevant resonances in the 1 H-NMR spectra (based on TMS = 0 ppm) used for integration were: 1.05–1.25 (methyl group of polyether moieties, area of the resonance corresponds to three H atoms); 1.25– 1.35 (methyl group of carbonate moieties in polyether carbonate, area of the resonance corresponds to three H atoms); 1.50 (methyl group of cyclic carbonate, area of the resonance corresponds to three H atoms). Taking into account the intensities, the relative concentrations as well as the weight fractions were calculated.

Number average molecular weight (Mn) and polydispersity index (PDI) of polymer products were calculated from the obtained curves in a Waters 1515 size exclusion chromatograph (SEC) with 2 Agilent PLGel 5 µm mixed D (300x7.5) columns, the temperature of which was set at 35°C using THF as solvent. Detection was performed with a refractive index detector, solvent flow was 1 mL/min, and calibration was performed with PS standards.

3. Results and Discussion

3.1. Analysis and characterization of the Co-Zn based catalysts

The method of preparation including temperature, purity of feedstock, complexing agent and the mode of reagents addition has significant effects on the catalytic activity of the final DMC [5, 17]. As the DMC catalysts were prepared by mixing $K_3[Co(CN)_6]_2$ and $ZnCl_2$, $KZn[Co(CN)_6]$ or K^+ can be also formed. The presence of potassium ions could result in a drastic decrease of activity of the DMC [5].

The experimental procedure of the DMC synthesis has been already developed by several authors and with different preparation methodologies such as Chen et al., 2004, Zhan et al., 2011, Kim et al., 2004, Zhang et al., 2015 et al., Chruściel et al., 2014 or Li et al., 2011 among them [3, 9, 18-21]. However, just a few publications studied the effect of changing the amount of the initial reactants [1, 17, 22]. In order to examine the effects of how different initial metal concentrations in the DMC can influence its chemical and morphological characteristics and therefore their catalytic activity, five catalysts were prepared by changing the concentration of $ZnCl_2$ and used for polymerization reactions. tert-Butanol (tBuOH) was used as complexing agent (CA) to help the retention of $ZnCl_2$ in the catalyst [5] and the co-complexing agent (co-CA) PEG 1000, according to Guo et al., (2014) was used to decrease crystallinity and increase the catalytic activity [7]. Thus, they play an important role in DMC catalyst and ring opening polymerization (ROP) [13]. The catalyst was prepared following the literature [23]. All samples were analyzed to determine the differences based on the amounts of K, Co and Zn (**Table 2**).

Table 2

Final composition of the different prepared catalysts analyzed by ICP.

| Samples	Zn (% mol/mol)	Co (% mol/mol)	Zn/Co mol ratio	K (mol/g)	Co (mol/g)	Zn (mol/g)
A	60%	40%	1.50	0.0008	0.0022	0.0033
B	58%	42%	1.38	0.0007	0.0022	0.0031
C	59%	41%	1.44	0.0004	0.0028	0.0040
D	60%	40%	1.50	0.0003	0.0028	0.0042
E	61%	39%	1.56	0.0001	0.0026	0.0042

FT-IR spectroscopy was used to identify the coordination and bounding in metal complexes. Differences on the DMCs can be seen on the vibration bands that reveal differences in bonding characteristics. The band that vibes at 2192 cm^{-1} correspond to the –C≡N stretch of the DMC complex $Zn_3[Co(CN)_6]_2 \cdot xH_2O$ ($x = 0 \sim 12$) in the presence of CA and co-CA. According to other researchers [12, 17], the main characteristic vibration bands that appear in all DMC (**Fig 1**) are: at 470 cm^{-1} the Co-C stretching vibration indicates the presence of a coordinated tBuOH in different amounts, 642 cm^{-1} correspond to Co-C bounding, 1199 cm^{-1} to 3º-C-O stretch, 1372 cm^{-1} to -OH bending from tBuOH, 1473 to -CH scissoring, 1615 to –OH bending form water, 1738 correspond to the PEG incorporation into the catalyst, 2981 to –C-H stretch and the –OH stretch in all DMCs vibes from 3661 to 3296 cm^{-1}.

The main difference on the FT-IR analysis correspond to the synthesized catalysts with higher amounts of $K_3[Co(CN)_6]_2$. Catalysts A and B showed one more vibration band at 2129 cm^{-1} (**Fig. 1**). This band may be caused by the –CN group from the excess of $K_3[Co(CN)_6]_2$ added to the catalyst (AIST spectra database).
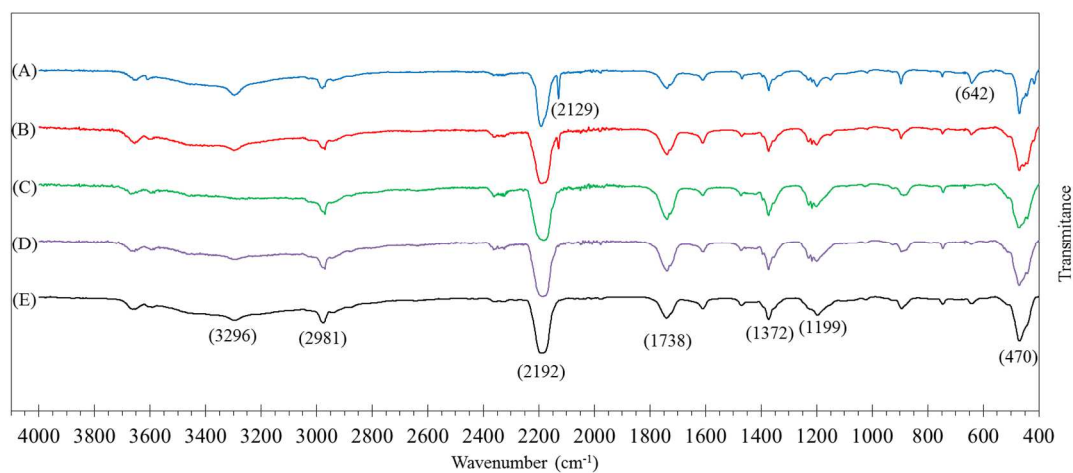
**Fig. 1.** FT-IR spectra of the Co-Zn catalysts.

Selected ESEM images showed that the amount of reagents affects particle size and morphology (**Fig. 2**) of the catalyst. The DMCs prepared showed lamellar, spherical and cubical distributions. Lamellar structures thickness changed from approximately 125nm for A sample to lowers sizes while $ZnCl_2$ was increased in the synthesis. E sample exhibited lamellar structures with thickness of approximately 33 nm together with more spherical agglomerates. It is interesting to note that more agglomerates and spherical structures were formed when Zn^{2+} was increased in the catalyst recipe; although the final Zn/Co ratio was almost the same (see **Table 2**). In agreement to Lee et al. (2009) [12] this fact could lead to an aggregation of DMC particles as well as co-CA acts as protecting agent. As can be seen in **Fig. 2**, catalyst A and B present mostly lamellar and cubical structures while in C catalyst more agglomerates are formed and cubical structures change to spherical, finally in D and E catalyst, the excess of Zn^{2+} could lead to thin lamellar structures surrounded by spherical agglomerates which could mean that the aggregation process is completed in these cases (**Fig. 2**).
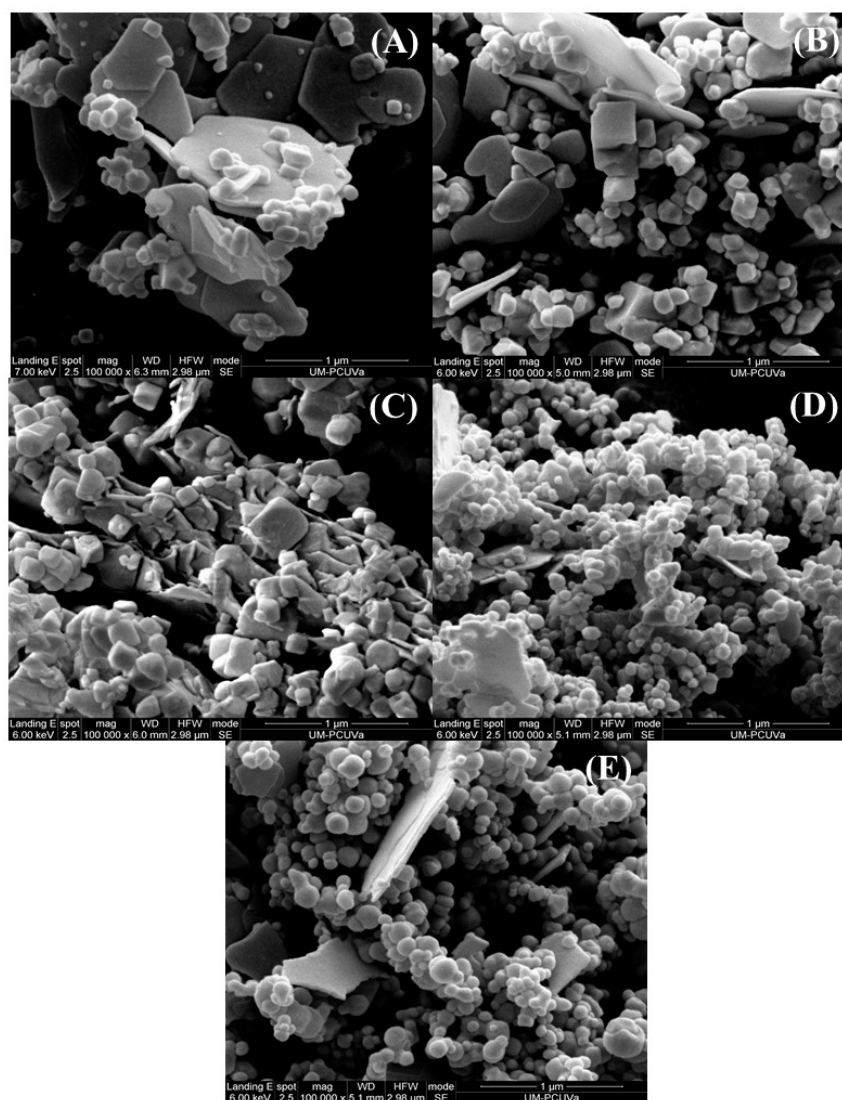
Fig. 2. SEM images of DMC catalysts prepared with different initial concentrations of Zn and Co.

The surface properties, crystal structure and crystallinity values of the synthesized catalysts were examined by X-ray diffraction. All of them were identified as Prussian blue analogues (characteristic reflections of $Zn_3[Co(CN)_6]_2 * 12 H_2O$ are marked with lines in **Fig. 3**) [12]. Sample A was characterized by cubic (14.9, 17.3, 24.5, 34.8, 39.2º) and monoclinic structures (14.5, 20.7, 23.5, 24.9º) [17, 24]. This sample presented an amorphous structure, as it had a pronounced intensity reflection at 23.7º [7]. Sample B

presented a mixture of cubic and in a lesser extent monocyclic structures, the monoclinic phase characteristic peaks at 20.7 and 23.5º [24] had low intensity. Particularly, sample C showed a cubic lattice structure with no monocyclic phase together with the highest crystallinity (50.3%). On the other hand, samples D and E presented also a mixture of cubic and monoclinic structures, being the monoclinic structure more intense in sample E. The extent of the monoclinic structures was more intense at Zn/Co ratios away from the stoichiometric value.
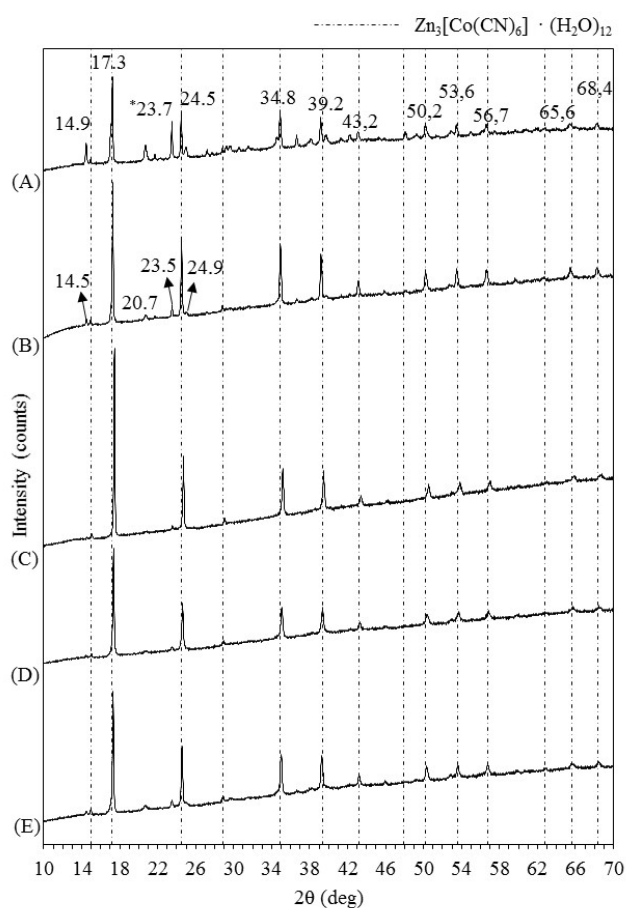

Fig 3. X-ray diffraction of the different Co-Zn catalysts. *characteristic peak of an amorphous state.

3.2 Catalytic test

From our results we can conclude that a proper activation of the catalysts only occurred when $ZnCl_2$ was in excess on the DMC preparation. This fact leads to changes on the catalyst structure, thus is according with other researches [1, 7, 13, 24, 25, Gao, 2012 #8].

In our case, samples D and E activated properly. Differences on the activation are exclusively due to the method of preparation. Catalyst D with a molar starting mixture of Zn:Co:tBuOH:PEG formulae 1.0:0.3:30.6:0.1, finished its first activation after 40 min with 7.2 gr of PO added and its second activation was carried out with 2.2 gr of PO and finished after 80 min. A quicker activation was carried out by catalyst E with a molar starting mixture of 1.0:0.1:25.6:0.1 that activated much faster, the first activation finished after 28 min with 7.4 gr of PO and its second activation finished after 52 min with 2.3 gr of PO added (**Fig. 4**). The catalyst yield is 1.4 kg polymer/g catalyst for D sample and 2.5 kg polymer/g catalyst for E. Compared to other studies, this value is high for 10 barg (working pressure), other studies have similar catalytic activities working at higher pressures [17, 18], as an example Chen et al. (2004) [3] obtained catalytic activities from 1.5 to 2.1 working at pressures of 20 to 45 bar. Recently Gao et al. (2012) [13] obtained a yield of 3.8 (kg/g) working at 40 bar.
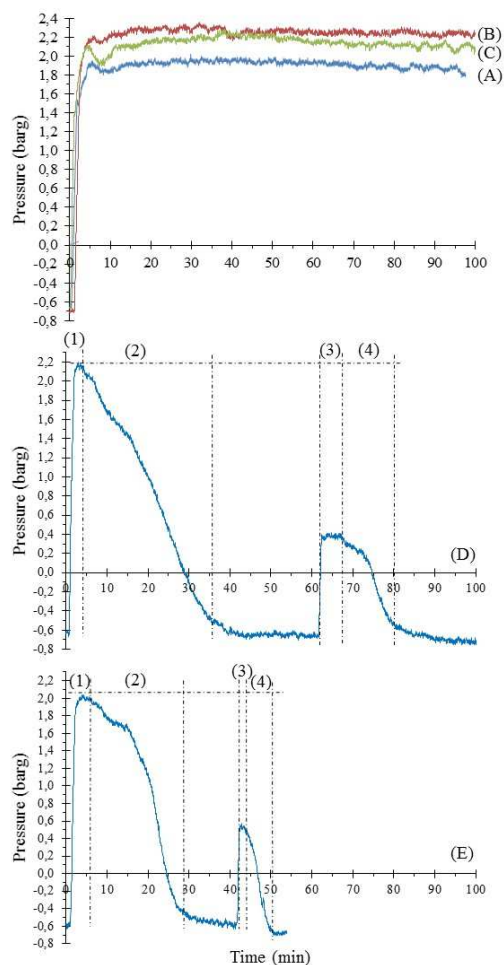
Fig. 4. Catalyst activation. A, B and C no active catalyst, D and E active catalysts. (1) first catalyst activation, (2) PO consuming stage, (3) second catalyst activation, (4) second PO consuming stage.

Therefore, we suggest that the proper catalyst for DMC polymerization should be one with the characteristics of the catalyst D/E. GPC figures (**Fig. 5**) showed that E sample has consumed half of the starter peak while D sample has consumed almost all that peak. This means that D catalyst is more reactive than E, but lacks of activity to decrease the PDI on the final product. In this sense, specific surface area analysis was performed in both active catalyst to evaluate the pore volume and relate it to the catalytic activity and polymerization process. As can be seen in **Table 3**, the specific surface area of both

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catalysts is high (846 m^2/g D sample, 743 m^2/g E sample for microporous analysis and 533 m^2/g D sample, 515 m^2/g E sample for mesoporous analysis). Sample D had less amount of water than E and the highest value of mesoporous volume (0.51 cm^3/g).

Both catalysts D and E are characterized as porous, however the values of specific surface area and eliminated water % are different (**Table 3**). Authors suggest that once the reagent molecule gets inside the pore, some of them are not able to release that molecule. This fact also avoids the release of water content in the pore, obtaining long polymer chains which mean high PDI values. This phenomena occurs for catalyst D (**Table 4**). Nevertheless, when the pore allows the incorporation of the reagent molecule as well as the subsequent release of water and polymer molecules, it results in shorter polymer chains. In this case, PDI value decreases as it can be seeing in catalyst E (**Table 4**).

Specific surface area follows the previous assumption (**Table 3**). In terms of pore volume, smaller pore values (catalyst E) allow the polymer molecule remain less hold inside the pore. This enables a higher number of short polymer chains, a decrease on PDI value and higher water % elimination. By optimizing the agitation system, this effect is less pronounced due to the improvement in mass transfer and internal and external diffusion processes.
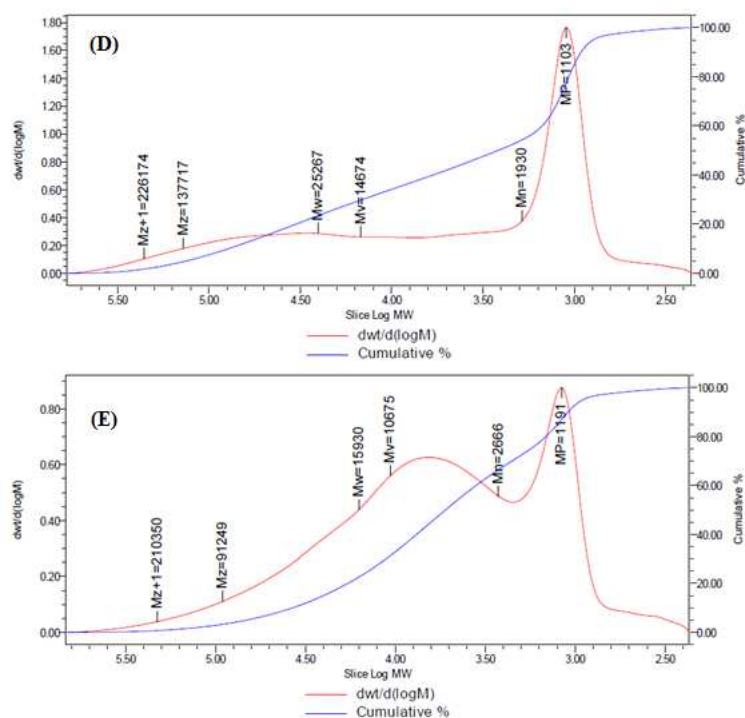
Fig. 5. GPC analysis of active catalyst samples D and E

Table 3.

Microporous, mesoporous and surface area of the active catalysts D and E analyzed by

N$_2$-physisorption

Sample	% water	Specific surface area m^2/g	Pore volumen cm^3/g
D_microporous	18.15	846.80	0.30
D_mesoporous	12.86	533.12	0.51
E_microporous	21.43	743.07	0.26
E_mesoporous	21.80	515.24	0.35

Moreover, we state that thorough washing to eliminate all K$^+$ of the catalyst is not

strictly necessary for a proper working of the catalyst due to with 4000 ppm for E

(0.4%wt) or even 10000 ppm for D (1.0%wt) of K^+ in the DMC the activation and polymerization reactions exhibit good results (vide infra).

Although it was reported in other studies that DMC with lower crystallinity are more active for copolymerization and the DMC exhibited high catalytic activity only when crystallinity degree was $\leq 30\%$ our results as the ones reported by Zhou et al. (2011) [16] or Sebastian et al. (2014) [17] showed significant differences provided D and E are active catalysts with medium crystallinity ($> 40\%$). Rather, is consistent with the theory reported by Peeters et al. (2013) [24] that the influence on the catalytic activity is based on the structure properties of the Zn^{2+} ion. At the surface of cavity generated by a block vacancy, Zn atoms with an incomplete coordination sphere are found [26] so higher activity can be achieved by more vacancies around Zn [7]. Also, coordinated CA and disperse Cl- in the structure activates Zn^{2+} ions that are critical for high activity of catalysts [17].

3.3 PPC copolymer characterization

For the copolymerization reaction, the total amounts required of catalyst, PO and PPG were estimated depending on the desired molecular weight for the final copolymer, in this case approximately 3000 g/mol. Considering this value, the amounts of PO and PPG to be used in the reaction were calculated.

FT-IR spectrum of the obtained copolymers is shown in **Fig. 6**. A sharp C=O asymmetric vibration absorption at 1744 cm^{-1} and a C-O stretching vibration at 1260 cm^{-1} was found, providing the evidence of the incorporation of CO_2 into the polymer chain [3, 7]. At the same time, it can be seen low intensity peaks at 1790 and 790 cm^{-1} which are characteristics of cyclic carbonate (PC).

The copolymerization reaction resulted in the main product, polypropylene carbonate (PPC) and the byproduct, cyclic polycarbonate (PC). Before the reaction is carried out it is recommendable to estimate the $\%CO_2$ that could be incorporated as well as the amount that is going to be formed of PC, in order to predict the PO amount needed for the PPC synthesis reaction. The more incorporation of CO_2, the less PO will be necessary for the reaction, for a similar final molecular weight. On the contrary, when a higher the amount of PC be generated by reaction, the higher the amount needed of PO.

Comparing the calculated data to the experimental analyzed by NMR (**Table 4**), data showed that the incorporated CO_2 values are similar that the estimated values, 5.6 %wt for D and 6.7 %wt for E. Comparing to other studies that have carried out the experiments at similar conditions and similar pressures (10 bar), the CO_2 incorporation is higher than in the case of Langanke and Wolf (2015). This authors obtained 4.1 %wt of CO_2 working at a higher pressure 22 bar [27]. Calculating the CO_2 incorporation on %CU (mol) units, values correspond to 7.7 and 9.4 %CU (values obtained by NMR). These results are close to the ones obtained in other studies that work at higher pressures. Chen et al., (2004) obtained values of 15% working at 20 bar [3] and Li et al., (2011) obtained 13 %CU but in this case working at 40 barg [21].

The benefit of these DMCs was that the cyclic carbonate produced in the reaction was very low, 0.4% for D and 0.3% for E (**Fig. 6**). Thus, these DMCs were more selective catalysts regarding to the main product PPC, also the production of high amount of the byproduct PC leads to a lesser production of PPC. In this way, we have achieved a high selective DMC that can be used at high temperatures (105ºC) on the contrast to the study of Darensbourg et al. (2003) [28] where the tendency to produce large quantities of PC increased with elevated temperatures.

Table 4

Data of copolymerization of CO_2 and PO for the active catalysts[a]

Catalyst	PPG/DMC (g/mg)	t (h)	Yield[b]	TON[c]	TOF[c]	W_{PC}[d] (%wt)	CTR[d] (%wt)	PPC product Mw	Mn	PDI
D	30/42	6.5	1.4	34	7	0.3	5.6	25267	1930	13.09
E	30/41	6.0	2.5	99	14	0.4	6.7	15930	2660	5.97

(a) All copolymerization were carried out at 105ºC, 10 barg with 30 gr of PPG (725 g/mol) and 90 gr of PO.

(b) Calculated by kg polymer/g catalyst

(c) TON calculated as mol PPC/mol catalyst, TOF calculated as TON/h

(d) Carbonate content unit (CTR) and ratio of PC in the product (W_{PC}) was determined by NMR
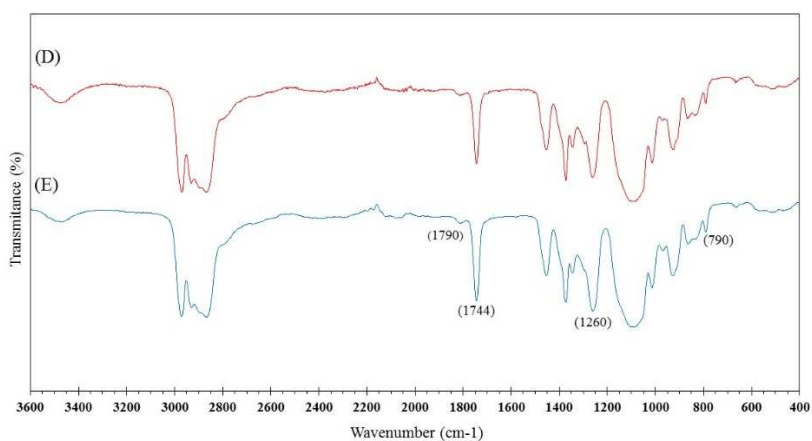
Fig. 6. FT-IR spectra of the copolymer obtained with catalysts D and E

The copolymers obtained were of high and low molecular weights that implied a high polydispersity (PDI), this fact was due to a lesser agitation on the reactor during

copolymerization process. The increased viscosity of the polymer caused mass transfer limitations due to the agitation, as the magnetic stirring was insufficient and therefore ineffective. PO dripping always in the same area and such inefficiency of the agitation led to formed molecules with a long carbon chain in that area, and other molecules with shorter chain, in more remote PO feeding areas. This resulted in an unexpectedly high polydispersity value, as can be seen in **Table 4**. The increase on the viscosity may be due to low formation of the cyclic polycarbonate, however, this is a characteristic result and one of the objectives to achieve, because it avoids the need of further purification processes to remove the cyclic polycarbonate. A low PDI is essential for optimum properties of the polyol in its subsequent use for the synthesis of polyurethanes. This could be improved by including a vigorous agitation system or a mechanical stirring, during the copolymerization reaction that will lead to decrease notably the PDI and so the molecular weight. Thus, two more reactions were carried out in a Parr reactor (Parr Instrument Company, Inc. Moline, Illinois, U.S.A), with a volume of 382 cm^3 with a mechanical stirrer (Parr Instrument Company, Moline, Illinois, U.S.A. A1120HC II55 with a motor from Bodine Electric Company, Chicago, USA) to prove this fact. Variables such as temperature, and amount of catalysts used where the same as in the other experiments. The PO amount was changed in order to prove the agitation effect on the PDI of the final polymer. As the final molecular weight is not an influence variable on the PDI value the reaction was performed to 1000 g/mol instead of 3000 g/mol. Results showed a considerable decreased on the PDI. Obtained values for PDI were 1.11 and 1.10 for D and E catalysts, respectively being Mw and Mn 1066 and 960 for catalyst D and 1139 and 1034 for catalyst E. Therefore, both catalysts are appropriate for copolymerization processes because both can decrease the final PDI, producing low amounts of PC.

Finally, the incorporated CO_2 in the chain will be increased while the working pressure also increases. As Guo et al. (2014) [29] reports, higher pressure, lower temperature and longer reaction time increase the speed of ring opening.

It is worth to mention that using these DMC catalysts, low amounts of PC are produced and once this active catalyst is obtained, they can be used for increasing the CO_2 incorporation by varying the temperature and increasing the pressure.

4. Conclusions

In this study, Zn/Co double metal cyanide catalysts were synthetized by varying the amounts of $ZnCl_2$ on the preparation method. The main goal was to synthesize active DMC catalysts which lead to produce very low quantities of the byproduct (cyclic carbonate) and a greater production of the main product, polypropylene carbonate. Different DMC catalysts were tested for that purpose.

Only when Zn was in excess the catalyst was active but a thorough washing to eliminate K^+ until is not detected, it was appreciated that it is not necessary in order to obtained high active catalysts. With amounts between 0.40% and 1.00 %wt ppm K^+ the catalyst exhibited good catalytic activity and only 2 washings were necessary. This fact might help in the reduction of time and solvent costs in the preparation of DMCs.

Active catalysts showed medium crystallinity, which implies that the amorphous state was not override. Thus, it leads to the fact that the catalytic activity was influenced based on the structural properties of the Zn^{2+} ions where Zn-OH group in DMC catalyst is the active center for polymerization.

The study reveals that the preparation method based on initial amounts of Zn^{2+} can affect the copolymerization process. Although the PDI was between 5.97 and 13.09 due to the high viscosity of the polymerization in the bulk fluid (as low amounts of PC were obtained), it could be improved by enhance the stirring system. To prove it, two more reactions were carried out using a mechanical stirrer, the effect was clear producing a decrease in the PDI value.

The N_2-physisorption and GPC analysis of these catalysts showed that with higher amount of water and similar specific surface area, catalyst E is less reactive but the catalytic activity is higher than for catalyst D. The specific surface area and pore volume are crucial to characterize the catalytic activity in order to obtain short polymer chains which implies a good value of PDI on the final product.

Highest catalytic activity (2.5 kg polymer/g catalyst), more CO_2 incorporation (6.7%) and less production of PC (0.3%) even at high temperatures (105ºC) were performed by the DMC E, prepared with the highest amount of $ZnCl_2$, although the stoichiometric reaction was similar in all cases.

References

[1] M.M. Dharman, J.Y. Ahn, M.K. Lee, H.L. Shim, K.H. Kim, I. Kim, D.W. Park, Moderate route for the utilization of CO_2-microwave induced copolymerization with cyclohexene oxide using highly efficient double metal cyanide complex catalysts based on $Zn_3[Co(CN)_6]$, Green Chem. 10 (2008) 678-684.

[2] G.W. Coates, D.R. Moore, Discrete metal-based catalysts for the copolymerization of CO2 and epoxides: discovery, reactivity, optimization, and mechanism, Angew Chem. 43 (2004) 6618-39.

[3] S. Chen, Z. Hua, Z. Fang, G. Qi, Copolymerization of carbon dioxide and propylene oxide with highly effective zinc hexacyanocobaltate(III)-based coordination catalyst, Polymer 45 (2004) 6519-6524.

[4] L. Gharnati, N.E. Musko, A.D. Jensen, G.M. Kontogeorgis, J.D. Grunwaldt, Fluid phase equilibria during propylene carbonate synthesis from propylene oxide in carbon dioxide medium, J Supercrit Fluids 82 (2013) 106-115.

[5] S. Chen, G.R. Qi, Z.J. Hua, H.Q. Yan, Double metal cyanide complex based on $Zn_3[Co(CN)_6]_2$ as highly active catalyst for copolymerization of carbon dioxide and cyclohexene oxide, J Polym Sci A Polym Chem. 42 (2004) 5284-5291.

[6] I. Kim, M.J. Yi, K.J. Lee, D.W. Park, B.U. Kim, C.S. Ha, Aliphatic polycarbonate synthesis by copolymerization of carbon dioxide with epoxides over double metal cyanide catalysts prepared by using ZnX_2 (X=F, Cl, Br, I), Catal Today 111(3-4) (2006) 292-296.

[7] Z. Guo, Q. Lin, Coupling reaction of CO_2 and propylene oxide catalyzed by DMC with co-complexing agents incorporated via ball milling, J Mol Catal A: Chem. 390 (2014) 63-68.

[8] X. Fu, H. Jing, Quaternary onium modified SalenCoXY catalysts for alternating copolymerization of CO_2 and propylene oxide: A kinetic study, J Catal. 329 (2015) 317-324.

[9] X.H. Zhang, R.J. Wei, X.K. Sun, J.F. Zhang, B.Y. Du, Z.Q. Fan, G.-R. Qi, Selective copolymerization of carbon dioxide with propylene oxide catalyzed by a nanolamellar double metal cyanide complex catalyst at low polymerization temperatures, Polymer 52 (2011) 5494-5502.

[10] N. von der Assen, A. Bardow, Life cycle assessment of polyols for polyurethane production using CO_2 as feedstock: insights from an industrial case study, Green Chem. 16 (2014) 3272.

[11] S. Inoue, H. Koinuma, T. Tsuruta, Copolymerization of carbon dioxide and epoxide, J Polym Sci B Polym Lett. 7 (1969) 287-292.

[12] I.K. Lee, J.Y. Ha, C. Cao, D.W. Park, C.S. Ha, I. Kim, Effect of complexing agents of double metal cyanide catalyst on the copolymerizations of cyclohexene oxide and carbon dioxide, Catal Today 148 (2009) 389-397.

[13] Y. Gao, Y. Qin, X. Zhao, F. Wang, X. Wang, Selective synthesis of oligo(carbonate-ether) diols from copolymerization of CO_2 and propylene oxide under zinc-cobalt double metal cyanide complex, J Polym Res. (2012) 19:9878. doi:10.1007/s10965-012-9878-5

[14] Z. Li, Y. Qin, X. Zhao, F. Wang, S. Zhang, X. Wang, Synthesis and stabilization of high-molecular-weight poly(propylene carbonate) from ZnACo-based double metal cyanide catalyst, Eur Polym J. 47 (2011) 2152-2157.

[15] R. Srivastava, D. Srinivas, P. Ratnasamy, Fe–Zn double-metal cyanide complexes as novel, solid transesterification catalysts, J Catal. 241 (2006) 34-44.

[16] T. Zhou, Z. Zou, J. Gan, L. Chen, M. Zhang, Copolymerization of epoxides and carbon dioxide by using double metal cyanide complex DMC with high crystallinity, J Polym Res. 18 (2011) 2071-2076.

[17] J. Sebastian, D. Srinivas, Effects of method of preparation on catalytic activity of Co–Zn double-metal cyanide catalysts for copolymerization of CO_2 and epoxide, Appl Catal A 482 (2014) 300-308.

[18] I. Kim, J.T. Ahn, S.H. Lee, C.S. Ha, D.W. Park, Preparation of multi-metal cyanide catalysts and ring-opening polymerization of propylene oxide, Catal Today 93-95 (2004) 511-516.

[19] M. Zhang, Y. Yang, L. Chen, Preparation of crown ether complexing highly active double metal cyanide catalysts and copolymerization of CO_2 and propylene oxide, Chin J Catal. 36 (2015) 1304-1311.

[20] A. Chruściel, W. Hreczuch, J. Janik, K. Czaja, K. Dziubek, Z. Flisak, A. Swinarew, characterization of a double metal cyanide (DMC)-type catalyst in the polyoxypropylation process: Effects of catalyst concentration, Ind Eng Chem Res. 53 (2014) 6636-6646.

[21] Z. Li, Y. Qin, X. Zhao, F. Wang, S. Zhang, X. Wang, Synthesis and stabilization of high-molecular-weight poly(propylene carbonate) from ZnCo-based double metal cyanide catalyst, Eur Polym J. 47 (2011) 2152-2157.

[22] Y.J. Huang, G.R. Qi, L.S. Chenb, Effects of morphology and composition on catalytic performance of double metal cyanide complex catalyst, Appl Catal A 240 (2003) 263-271.

[23] H. Liu, X. Wang, Y. Gu, W. Guo, Preparation and Characterization of Double Metal Cyanide Complex Catalyst, Molecules 8 (2003) 67-73.

[24] A. Peeters, P. Valvekens, R. Ameloot, G. Sankar, C.E.A. Kirschhock, D.E. De Vos, Zn–Co double metal cyanides as heterogeneous catalysts for hydroamination: A structure–activity relationship, ACS Catal. 3 (2013) 597-607.

[25] X.H. Zhang, Z.J. Hua, S. Chen, F. Liu, X.K. Sun, G.R. Qi, Role of zinc chloride and complexing agents in highly active double metal cyanide catalysts for ring-opening polymerization of propylene oxide, Appl Catal A 325 (2007) 91-98.

[26] C.P. Krap, B. Zamora, L. Reguera, E. Reguera, Stabilization of cubic and rhombohedral phases of zinc hexacyanocobaltate (III), Microporous Mesoporous Materi 120 (2009) 414-420.

[27] J. Langanke, A. Wolf, Intensified co-oligomerization of propylene oxide and carbon dioxide in a continuous heat exchanger loop Rreactor at elevated pressures, Org Process Res Devt 19 (2015) 735-739.

[28] D.J. Darensbourg, J.C. Yarbrough, C. Ortiz, C.C. Fang, Comparative kinetic studies of the copolymerization of cyclohexene oxide and propylene oxide with carbon dioxide in the presence of Crhomium salen derivates. In situ FTIR measurements of copolymer vs cyclic carbonate production, Department of Chemistry, Texas A&M UniVersity, College Station, Texas 77843 125 (2003).

[29] Z. Guo, Q. Lin, X. Wang, C. Yu, J. Zhao, Y. Shao, T. Peng, Rapid synthesis of nanoscale double metal cyanide catalysts by ball milling for the cycloaddition of CO_2 and propylene oxide, Mater Lett 124 (2014) 184-187.