Copolymerization of cyclohexene oxide with carbon dioxide over nano-sized multi-metal cyanide catalysts

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Abstract

The copolymerizations of carbon dioxide (CO₂) and cyclohexene oxide (CHO) using nano-sized double and multi-metal cyanide catalysts were investigated. The nano-sized double metal cyanide (NDMC) catalyst was prepared by reacting K₃[Co(CN)₆]₂ and ZnCl₂ in a reverse emulsion condition and nano-sized multi-metal cyanide (NMMC) catalyst by reacting K₃[Co(CN)₆]₂, K₄Fe(CN)₆, YCl₃ and ZnCl₂ at the similar conditions. Neutral surfactant, Igepal CA-520, used in the preparation step played important roles in acting both as an emulsifier and as a complexing reagent. NDMC and NMMC catalysts were demonstrated to be highly effective for copolymerizations of CHO with CO₂. The catalysts showed catalytic activity as high as 41.6 g/mol of Zn per hour at 80°C and the carbonate content in the copolymer was estimated to be 57.8%. Effects of reaction conditions such as reaction time, temperature, CO₂ pressure and catalyst concentration on copolymerizations were investigated.

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1. Introduction

Chemical fixation of CO₂ is a very attractive subject not only from viewpoint of carbon resource utilization, but also from increasing environmental concerns. As a kind of potential approach, one of the most promising areas of CO₂ utilization is its application as a direct material for polymer synthesis. The past three decades witnessed the great progress in fixation of CO₂ into aliphatic polycarbonates since the creative work of Inoue in 1969 [1,2]. To date, many excellent reviews in different period contributed by Kuran [3], Super [4,5] and Darenbourg [6–9] have made good description of this topic, where the importance of catalyst was never overestimated.

Double metal cyanide complexes (DMC) are well-known catalysts for epoxide polymerization. Recent improvements have made DMC catalysts much more attractive for commercial manufacture of polyoxypropylene polyols [10–13]. The catalysts are highly active and give polyether polyols that have low unsaturation and narrow molecular weight distribution compared with similar polyols synthesized using conventional KOH catalysis [14]. While DMC catalysts offer significant advantages for the ring opening polymerization of epoxides, no reports have been published on the copolymerization of epoxide with CO₂ thereby.

In the present paper, the exploitation of new nano-sized double and multi-metal cyanide is investigated for the copolymerizations of CO₂ and cyclohexene oxide (CHO). The influence of copolymerization variables like operating temperature on the yield, the molecular weight, and copolymer structure is discussed. The resultant copolymers are subjected to 1H NMR spectroscopy, infrared spectroscopy, gel permeation chromatography.

2. Experimental

2.1. Material

All materials such as potassium hexacyanocobatate(III) (K₃[Co(CN)₆]₂), zinc chloride (ZnCl₂), potassium ferrocyanide(II) (K₄Fe(CN)₆), Igepal CA-520 and tertiary butyl alcohol (tBuOH) were purchased from Aldrich and...
used without further purification. Yttrium Chloride hexahydrate (YCl₃ 6H₂O) purchased from Aldrich was heated in vacuum at 80 °C for 40 h before use. Cyclohexene oxide (Aldrich) was distilled and stored over Linde type 4A molecular sieves. Carbon dioxide of 99.99% purity was used without further purification.

2.2. Preparation of catalysts

Typical DMC catalyst (DMC) with complexing agent (tBuOH) has been prepared according to the literature procedures [14].

The nano-sized DMC (NMMC) catalyst using Igepal CA-520 as an emulsifier was prepared according to the following procedures. A first beaker contains solution 1: a mixture of cyclohexane (84 g), tBuOH (6 g) and Igepal CA-520 (10 g). ZnCl₂ (1.36 g, 0.01 mol) dissolved in distilled water (2 ml) in a second beaker (solution 2). K₃[Co(CN)₆]₂ (0.66 g, 0.002 mol) dissolved in distilled water (2 ml) in a third beaker (solution 3). Solution 2 was added to solution 1 over 30 mm with mixing using a mechanical stirrer. Solution 3 was then added and the mixture was stirred for 60 min. The resulting catalyst cake separated by centrifugation was washed by boiling tBuOH in a Soxhelet extractor for 24 h. The resulting nano-sized particle was dried at 60 °C under vacuum to a constant weight.

The nano-sized multi-metal cyanide catalysts using Igepal CA-520 has been prepared by the same procedure except using K₃[Co(CN)₆]₂ (0.33 g, 0.001 mol) and K₃Fe(CN)₆ (0.42 g, 0.001 mol) mixture for solution 3 (NMMC-1), and using YCl₃ 6H₂O (0.15 g, 0.0005 mol) and ZnCl₂ (1.36 g, 0.01 mol) mixture for solution 2 (NMMC-2), respectively.

2.3. Copolymerization

Copolymerization of CHO and CO₂ was carried out by using 30 ml glass reactor at various temperatures. The reactor was charged with 5 ml of CHO monomer and catalyst (10 mg) under inert atmosphere, and then purged with CO₂. The mixture was transferred to the bath controlled to a desired temperature. Then the reactor was pressurized by CO₂ to 100 psi (6.8 atm) and kept constant at this pressure. The reaction was stopped after 4 h and white polymer powder was separated by precipitation using excess methanol containing HCl (5 vol.%) followed by filtration. The polymerization yield was determined by gravimetric analysis.

2.4. Characterization

X-ray diffraction (XRD) patterns of the catalysts were obtained with a RINT2000 wide angle goniometer 185 using Cu Kα radiation at 40 kV and 30 mA. X-ray photo-electron spectroscopy (XPS) analysis of the catalysts was performed on an ESCALAB 250 induced electron emission spectrometer with Al Kα (1486.6 eV, 12 mA, 20 kV) X-ray sources. Transmission electron microscopy (TEM) pictures were taken using CM-10 Phillips electron microscope, using a voltage of 100 kV. Samples were suspended in methanol and spread on copper grids coated with Fromvar foil. IR spectra of the catalysts were obtained in transmission mode using a React IR. ¹H NMR spectra of the polymers were performed on a Varian Gemini 2000 and HP5P CDCl₃ as a solvent. Molecular weight distributions (MWD) were measured using a Waters 150-C instrument, operated at 35 °C, with a set at 103, 104 and 500 Å columns (dimethylformamide as a solvent).

3. Results and discussion

3.1. Catalyst characterization

The DMC catalyst prepared by ZnCl₂ and K₃[Co(CN)₆]₂ in the presence of tBuOH as a complexing agent (CA) is expected to have a general formula:

\[ \text{Zn}_3[\text{Co(CN)}_6]_2 \cdot x\text{ZnCl}_2 \cdot y\text{H}_2\text{O} \cdot z\text{CA} \]

The nano-sized double metal cyanide catalyst prepared by using ZnCl₂ and K₃[Co(CN)₆]₂ in the presence of Igepal CA-520 should have a similar formula; however, the Igepal CA-520 used in this study plays roles in acting both as an emulsifier and as complexing reagent together with tBuOH. The similar general formula is expected for the NMMC-1 catalyst, using K₃Fe(CN)₆ together with K₃[Co(CN)₆]₂, and NMMC-2 catalyst, using and YCl₃ together with ZnCl₂.

For NMMC − 1 : Zn₃[Co(CN)₆]₂ \cdot Zn₄[Fe(CN)₆] \cdot x\text{ZnCl}_2 \cdot y\text{H}_2\text{O} \cdot z\text{CA}

For NMMC − 2 : Zn₃[Co(CN)₆]₂ \cdot Y₃[Co(CN)₆]₂ \cdot x\text{ZnCl}_2 \cdot y\text{H}_2\text{O} \cdot z\text{CA}

Even if the insolubility of this complex makes the analysis difficult, the surface formulation of the catalyst could be investigated by XPS. Atomic identification in an insoluble solid is possible using XPS to measure the energy required to create a role in a core electronic structure. The results of XPS analysis of the catalysts are summarized in Table 1. The binding energy (1023.7 eV) of zinc atom of ZnCl₂ shifted towards higher value by 2.2 for NDMC catalyst and lower value by 2.7 for NMMC-1 and 3.7 eV for DMC catalyst after complexation. These chemical shifts results from the coordination of oxygen atoms in complexing agents to Zn by reacting ZnCl₂ with K₃[Co(CN)₆]₂ and K₃Fe(CN)₆ in the presence of tBuOH and Igepal CA-520 as CAs. It is interesting to note that the O/Zn value indicating a presence of CA increased from 0.37 (DMC) to 1.01.
(NDMC) and to 1.03 (NMMC-1), demonstrating that Igepal CA-520 still remains coordinated in the catalyst matrix even after extraction by tBuOH. The type and the amount of oxygen coordinated to Zn play an important role in the ring opening polymerization of epoxide since oxygen atoms coordinated to zinc ion are real active centers [14]. Co 2P 3 of K 3[Co(CN) 6] shifts from 781 to 778 eV for DMC, to 784 eV for NDMC and to 779 eV for NMMC-1, respectively, by forming complexes with oxygen coordinated zinc. Fe 2P 3 of K 4Fe(CN) 6 shifted from 707.2 eV for NMMC-1.

The particle size of the catalyst using an emulsifier was in the range of 50–100 nm as shown in Fig. 1. The emulsifier was not completely removed by extraction due to the coordination to zinc atom through oxygen atom in it. Fig. 1 shows that several catalyst particles are embedded in emulsifier matrix. The Zn–O bonds are important in that they can be dormant active sites. Form these results, it can be expected that Igepal CA-520 acts as an emulsifier to control the size of the catalyst particle and as a complexing agent to generate active sites. The amount of emulsifier contained in catalyst matrix can be controlled by choosing suitable extraction solvents and by changing extraction conditions. The effect of the type and the amount of emulsifier on the catalyst performance is under study.

Infrared spectra of K 3[Co(CN) 6] and catalysts (Fig. 2) show a shift of the ν(CN) band from 2133.4 cm⁻¹ for K 3[Co(CN) 6] to 2195.9 for DMC catalyst to 2192.5 for NDMC, NMMC-1 and NMMC-2 catalysts. The ν(CN) band of free CN⁻ is 2080 cm⁻¹ [15]. The ν(CN) shift to higher frequencies demonstrates that the CN⁻ ion acts as not only a σ-donor by donating electrons to the cobalt but also an electron

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**Table 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Zn 2p3 B.E.</th>
<th>Co 2p3 B.E.</th>
<th>Fe 2p3 B.E.</th>
<th>O 1s B.E.</th>
<th>N 1s B.E.</th>
<th>C 1s B.E.</th>
<th>Cl 2p B.E.</th>
<th>O/Zn [AT]</th>
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<tr>
<td></td>
<td>(eV) [AT]</td>
<td>(eV) [AT]</td>
<td>(eV) [AT]</td>
<td>(eV) [AT]</td>
<td>(eV) [AT]</td>
<td>(eV) [AT]</td>
<td>(eV) [AT]</td>
<td>(eV) [AT]</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>1023.7 –</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>K₃[Co(CN)₆]</td>
<td>–</td>
<td>781 –</td>
<td>–</td>
<td>530 7.0</td>
<td>397 20.5</td>
<td>284 42.0</td>
<td>197 2.4</td>
<td>0.37</td>
</tr>
<tr>
<td>K₄Fe(CN)₆</td>
<td>–</td>
<td>–</td>
<td>707.2</td>
<td>533 8.7</td>
<td>398 21.6</td>
<td>284 50.0</td>
<td>197 5.3</td>
<td>1.01</td>
</tr>
<tr>
<td>DMC</td>
<td>1020.0 19.2</td>
<td>778 8.8</td>
<td>–</td>
<td>530 7.0</td>
<td>397 20.5</td>
<td>284 42.0</td>
<td>197 2.4</td>
<td>0.37</td>
</tr>
<tr>
<td>NDMC</td>
<td>1025.9 8.7</td>
<td>784 3.7</td>
<td>–</td>
<td>533 8.7</td>
<td>398 21.6</td>
<td>284 50.0</td>
<td>197 5.3</td>
<td>1.01</td>
</tr>
<tr>
<td>NMMC-1</td>
<td>1021.0 4.7</td>
<td>779 0.8</td>
<td>706.7 0.7</td>
<td>530 4.9</td>
<td>396 10.0</td>
<td>284 73.1</td>
<td>197 5.9</td>
<td>1.03</td>
</tr>
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</table>

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* Binding energy.
** At.%.

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**Fig. 1.** TEM photographs of the catalyst particles: (a) NDMC and (b) NMMC-1 catalysts.
donor by coordination to zinc metal. A slight \( \nu(CN) \) shift to lower frequencies from DMC catalyst to NDMC, NMMC-1 and NMMC-2 catalysts seems to be the effect of electronegativity. Since the electronegativity of Zn is became smaller as the coordinated amount of bulky Igepal CA-520 and/or BuOH complexing agents increased, electron donation from cyanide ligands to Zn decreased, and the \( \nu(CN) \) is expected to be lower. Thus, the coordination strength between Zn and complexing agents in the catalyst is expected to be DMC>NDMC, NMMC-1 and NMMC-2. Evidently, the coordination strength is expected to influence CHO copolymerization behavior (vide infra).

Alteration of the crystal structure can be shown by X-ray diffraction (XRD) patterns to be dependent on the different surfaces. Fig. 3 shows typical powder X-ray diffraction curves of the catalysts highly crystalline \( \text{Zn}_3[\text{Co(CN)}_6]_2 \) prepared in the absence of an organic complexing agent, which does not actively polymerize propylene oxide, shows a characteristic XRD fingerprint of sharp lines at \( d \)-spacings of about 5.07, 3.59, 2.54, and 2.28 Å \[10,14,16\]. When a DMC and MMC catalysts are made in the presence of an organic complexing agent, the XRD patterns show lines for the highly crystalline material in addition to broader signals from relatively amorphous material, suggesting that the catalysts prepared in this study are actually mixtures of highly crystalline compound and an amorphous component. Typically, NMMC-1 catalyst (Fig. 3(c)), which is prepared by using multi-metal in the presence of an organic complexing agent employing emulsion technique, is substantially amorphous according to the substantial absence of sharp lines in the XRD patterns. No one has previously recognized the desirability of preparing substantially amorphous catalysts, and the potential value of reducing the content of highly crystalline DMC compounds in these catalysts. It appears, based on our previous results \[14\] and a negligible activity of highly crystalline \( \text{Zn}_3[\text{Co(CN)}_6]_2 \) compound, that the highly crystalline compound acts as either a diluent or as a poison for the more active amorphous form of the catalyst. In this way, the size and the crystallinity of the heterogeneous catalyst may strongly influence the catalytic activity.

### 3.2. Copolymerization of cyclohexene oxide and carbon dioxide

Semi-bath copolymerizations of CHO and \( \text{CO}_2 \) using DMC, NDMC, NMMC-1 and NMMC-2 catalysts have been carried out at temperature range between 40 and 100 °C by keeping the pressure of the reactor constant at 100 psi (6.8 atm). As far as we know, this is a first report on this copolymerization by using double metal cyanide catalysts. Alternating copolymerization of CHO and \( \text{CO}_2 \) leads to the following general structure:

\[
\begin{align*}
\text{CHO} + \text{CO}_2 & \rightarrow \text{CHO}_{\text{alt}}
\end{align*}
\]

If the alternating copolymerization is perfect, only carbonate groups (-OC(O)O-) should be generated. However, kinetically controlled homopolymerization of CHO results in ether linkage (-COC-). The polymers were characterized by FT-IR and \(^1\)H NMR spectroscopies utilizing the previously established methodology for similar copolymers produced from other zinc catalyst systems \[6–8\]. The intense

![Fig. 2. Infrared spectra of (a) \( K_2\text{Fe(CN)}_6 \), (b) \( K_3[\text{Co(CN)}_6]_2 \), (c) DMC, (d) NDMC, (e) NMMC-1 and (f) NMMC-2 catalysts.](image)

![Fig. 3. XRD patterns of catalysts: (a) DMC, (b) NDMC, (c) NMMC-1 and (d) NMMC-2.](image)
asymmetric ν(C=O) stretching vibration of the polycarbon-ate linkages was observed at 1750 cm⁻¹. Relative amount of carbonate linkage could be estimated by ¹H NMR spectroscopy. Fig. 4 shows a ¹H NMR spectrum of the copolymer obtained by using NDMC catalyst at 80 °C and 100 psi (6.8 atm) CO₂. Percentage of carbonate linkage in the purified polymer was calculated from the relative intensities of the ¹H NMR signals the methine protons next to the carbonate linkages (δ = 4.6 ppm) and ether linkages (δ = 3.5 ppm).

Table 2 shows the results of copolymerization. The polymer yield using NDMC catalyst is presented as g of polymer/g of Zn/h, showing values ranging from 2.5 at 40 °C to 48.2 at 100 °C. Comparing to the results obtained by using a homogeneous diethylzinc-based catalyst by Kuran [3] and Darensburg [7,8], all catalysts used in this study showed comparable or higher activities. In general, DMC catalyst showed higher activity than NDMC, NMMC-1 and NMMC-2; however, DMC catalyst showed much lower carbonate content (f = 0.22) than NDMC (f = 1.37), NMMC-1 (f = 1.44) and NDMC-2 (f = 1.20 at 80 °C) catalysts possibly due to starvation of active sites for CO₂. These results demonstrate that NDMC, NMMC-1 and NMMC-2 catalysts using reverse emulsion method give a favorable condition to generate active sites for CO₂. Also, the incorporation of iron complex into the NDMC catalyst also gives a favorable condition to generate active sites for CO₂. CO₂ reactivity decreased sharply at high polymerization temperature (say 100 °C). NMMC-2 catalyst showed lower activity than NDMC and NMMC-1. A low yield resulting from the presence of yttrium might be due to the fact that active sites generated by Y–O bonds are less reactive than those by Zn–O bonds caused by a much more positive charge of yttrium. However, NMMC-2 catalyst showed higher carbonate content (f = 1.20 at 80 °C). All catalysts produce copolymers showing very narrow MWD and medium molecular weight. Further work is underway to identify a factor leading such a low polydispersity and to identify the exact active site of this double and multi-metal cyanide catalyst system.

4. Conclusions
An alternating polycarbonate was synthesized from the copolymerization of carbon dioxide and CHO in the presence of double and multi-metal cyanide catalyst systems which were prepared, by using reverse emulsion method employing neutral emulsifier (Igepal CA-520). The particle size of the resulting catalyst was in the range between 50 and 100 nm. In these catalyst systems, the
emulsifier acted as a complexing agent generating active sites. These catalyst systems have been originally developed for the ring opening polymerization of propylene oxide to produce high performance polyols. The NDMC and NMMC-1 catalysts were very efficient for the copolymerizations of carbon dioxide and cyclohexene oxide, which showed catalytic activity as high as 41.6 and 25.6 g/mol of Zn per hour at 80 °C, respectively. The carbonate unit content in the copolymer was estimated to be 57.8%. The use of carbon dioxide as a monomer to produce aliphatic polycarbonate as investigated in this study provides a means to consume. Since the catalyst systems of this study are effective, further attention should be paid to apply this kind of catalyst systems to the other copolymerization reactions.

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References