



## Preparation and Characterization of Double Metal Cyanide Complex Catalysts

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**Abstract:** A series of double metal cyanide (DMC) complex catalysts were prepared in two different methods by using  $\beta$ -cyclodextrin, PEG-1000 and Tween-60 as an additional complex ligands respectively. It was showed that a mixture of crystalline and amorphous DMC was synthesized by using traditional method in which the additional complex ligand was added after the precipitation of DMC. Amorphous and dispersed DMC with higher activity could be obtained when the additional complex ligand was added in the reactant solution before reaction. The effect of additional complex ligand and preparation method on the crystalline state and catalytic property of DMC were also investigated.

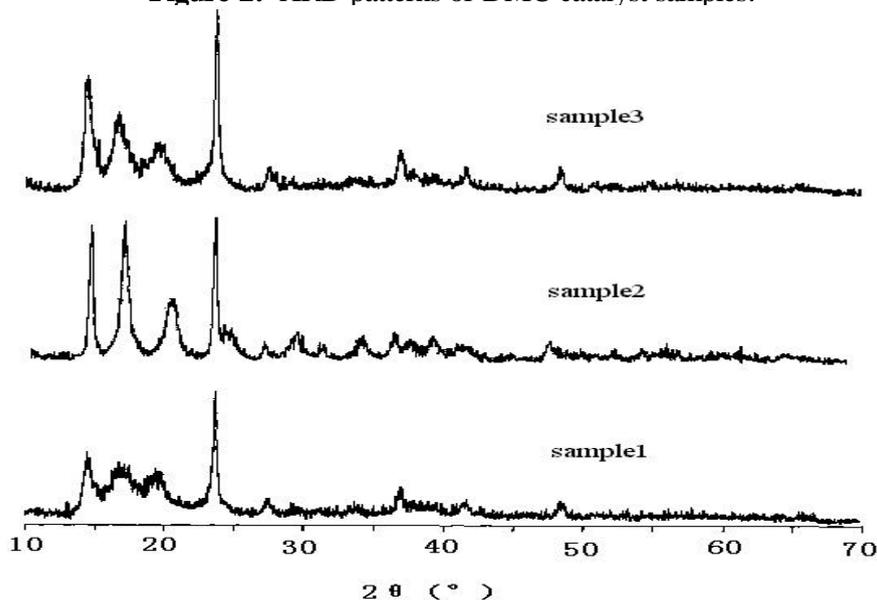
**Keywords:** Double metal cyanide complex; Catalysts; Preparation; Additional complex ligand.

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### Introduction

Double metal cyanide complex catalysts are known to be extremely useful and active catalysts for the ring-opening polymerization of heterocyclic monomers such as epoxides. In particular, the catalysts of this type have been employed to prepare polyether polyols derived from propylene oxide [1]. The catalysts were first prepared in 1960s [2]. Through several decades of research, the DMC catalysts were used in polyether polyols industry in the early stage of 1990s [3]. Double metal cyanide complex catalysts are generally recognized as superior to the caustic catalysts traditionally used to produce polyether polyols for utilization in



**Figure 2.** XRD patterns of DMC catalyst samples.**Table 1.** Datasheet of granularimetric analysis of DMC catalyst samples.

Sample	Mean grainsize (nm)		Mean shape
	FD-0	FD-90	
1	224	228	1.75
2	81	76	1.08
3	224	162	1.28
4	131	98	1.41
5	317	260	1.87

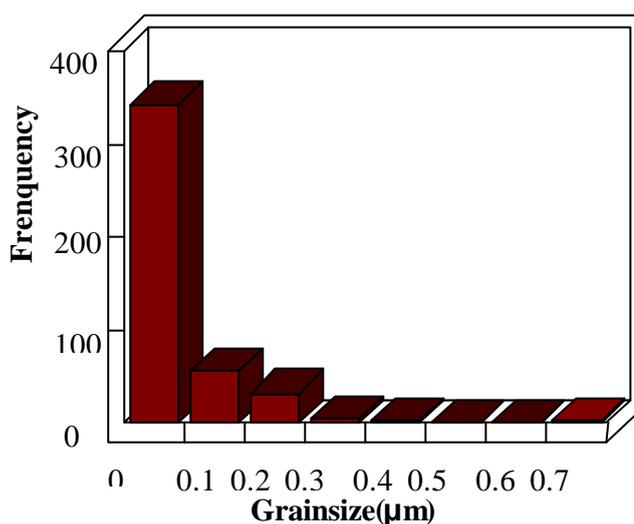
**Table 2.** Elemental analysis results of DMC catalyst samples.

Sample	C (%)	N (%)	O (%)	Cl (%)	Ca (%)	Co (%)	Zn (%)
1	43.75	22.42	15.64	1.51	0.54	3.65	12.15
2	25.96	18.67	27.30	1.31	1.39	6.69	18.69
3	30.41	25.00	13.53	1.61	0.15	7.50	21.36

PEG has been used as additional complex ligand before in US patent 6,204,357 [5]. The long chain structure of PEG can reduce the degree of crystallinity of DMC, which lead to higher catalytic activity. It was

shown in Figure 1 and Figure 2 that the catalyst synthesized with PEG-1000 (sample 1) is a mixture of crystalline and amorphous components. The XRD pattern and the elemental composition are consistent with the results of US Patent 5,952,261 [7].  $\beta$ -cyclodextrin was also used as additional complex ligand in US Patent 6,204,357 [6], but the effect on the crystalline state and property of DMC catalyst has not been fully discussed. Tween-60 was not used as additional complex ligand for preparation of DMC before. It can be seen from the results of the SEM and XRD investigations that similar DMC catalysts with crystalline and amorphous components (sample 2 or sample 3) were also obtained by using  $\beta$ -cyclodextrin or Tween-60 as additional complex ligand. In the presence of  $\beta$ -cyclodextrin a nanometer double metal cyanide complex catalyst with a 81nm average size was prepared. It can be seen from Figure 3 that the percentage of the DMC particles smaller than 100 nm is 87%.

**Figure 3.** Granularimetric distribution of sample 2.



## 2. The influence of the preparation method on DMC catalysts

It was reported in US patent 5,712,216 [8] that the preparation method is an important factor which influences the catalytic properties of DMC catalyst. However, the effect of the preparation method on the crystalline state character has not been reported. Figure 4 shows the SEM photographs of sample 4 and sample 5 which were synthesized by method 2 using Tween-60 and PEG-1000 as additional complex ligands, respectively. Figure 5 is the XRD patterns of such samples.

It can be seen from the figures that the DMC catalysts synthesized by method 2 are substantially amorphous components. Tween-60 was added in both of the aqueous reactant solutions before the mix. When the two aqueous were mixed Tween-60 was combined as complex ligand with DMC particles immediately. The further growth, gather and crystallization of DMC particles were halted. Therefore, amorphous and dispersed DMC catalysts were obtained. In a similar way, using PEG-1000 as additional complex ligand also

obtained amorphous and dispersed DMC catalysts. Due to the long chain structure of PEG-1000 which could combine with several particles, big sized particles gathered loosely are existed in sample 5.

Figure 4. SEM photographs of sample 4 and sample 5.

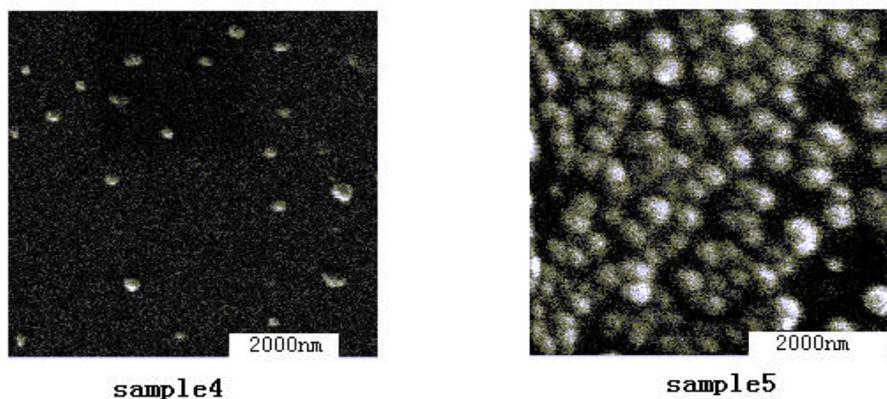
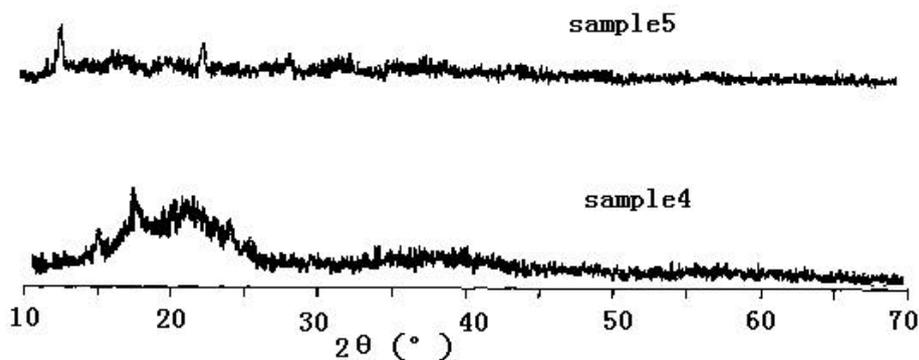


Figure 5. XRD patterns of sample 4 and sample 5.



### 3. Catalytic properties

The catalytic properties of DMC prepared by different methods using different additional complex ligand were investigated by examining their catalysis of epoxide polymerization. The results are shown in Table 3. It can be seen that the catalysts prepared by using PEG-1000,  $\beta$ -cyclodextrin and Tween-60 as additional complex ligands were all of higher catalytic activity for epoxide polymerization. Among the catalysts prepared by method 1, sample 2, using  $\beta$ -cyclodextrin as additional complex ligand, is of highest catalytic activity due to the small particle size. The catalysts prepared by method 2 have higher activities and faster reaction rates than those obtained from method 1 because of the substantially amorphous components of sample 4 and sample 5.

**Table 3.** Results of catalytic property experiments.

Sample	Additional complex ligand	Preparation method	Catalyst concentration mg(Cat)/kg(PO)	Reaction time ( h )	Yield kg/g
1	PEG-1000	method 1	100	5.5	11.2
2	$\beta$ -cyclodextrin	method 1	100	5.0	12.6
3	Tween-60	method 1	100	5.0	10.8
4	PEG-1000	method 2	50	3.5	15.2
5	Tween-60	method 2	50	4.0	14.6

## Conclusions

In this paper, a series of double metal cyanide (DMC) complex catalysts were prepared by two different methods using  $\beta$ -cyclodextrin, PEG-1000 and Tween-60 as additional complex ligands, respectively. It was shown that a mixture of crystalline and amorphous DMC was synthesized by using the traditional method in which the additional complex ligand was added after the precipitation of DMC compound. Amorphous and dispersed DMC with higher activity could be obtained when the additional complex ligand was added in the reactant solution before reaction.

## Experimental

### General

Potassium hexacyanocobaltate, zinc chloride and *tert*-butanol were analytical grade and were used without further purification. PEG-1000,  $\beta$ -cyclodextrin and Tween-60 were chemical grade. Water used in the reaction was deionized by means of a Mili-Q Water purification system (Millipore Corp., Bedford, MA).

### Preparation

*Method 1:* Potassium hexacyanocobaltate (2.960g), calcium chloride (32.360g) and calcium oxide (0.120g) were dissolved in deionized water (80mL) in a beaker. Zinc chloride (1.854g), calcium chloride (32.740g) were dissolved in the solution of deionized water (210mL) and *tert*-butanol (50mL) in another beaker. The aqueous solutions were slowly combined and stirred for fifteen minutes under 50°C. Then additional complex ligand (1.000g) was added to the mixture. The catalyst was isolated from the slurry by vacuum filtration and washed twice with 75% *tert*-butanol in water and pure *tert*-butanol respectively. The DMC catalyst was obtained in final form by drying the filtered wet solids for 35 hours in a 50°C vacuum oven.

*Method 2:* A correct quantity of additional complex ligand was added into aqueous solution of potassium hexacyanocobaltate and aqueous solution of zinc chloride respectively. Then the DMC catalyst was obtained by mix, filtration, washing and desiccation as described in Method 1.

### *Characterization*

Powder XRD data were collected on a D/MAZ- IIIA X-ray diffractometer with CuK $\alpha$  a radiation source at 40 kV (Japan). Scan electron microscopy (SEM) measurement was carried out with a S-2500 microscope (Japan).

### *Catalytic properties*

The catalytic properties were investigated by catalyzing an epoxide polymerization. A one-liter stirred reactor is charged with polyoxypropylene triol (400 mol. wt.) initiator and DMC catalyst (50 to 100 mg). The mixture was stirred and heated to 100°C. The reactor is pressurized to about 1 psi with nitrogen. Propylene oxide (5g) was added to the reactor in one portion. When catalyst activation is verified, the remaining propylene oxide (280 g) is added gradually over about 2-3 h. After propylene oxide addition is complete, the mixture is held at 110°C. Residual unreacted monomer is then stripped under vacuum from the polyol product, and the polyol is cooled and recovered

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