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Communications

Zn(II)-Co(III)-Fe(III) Multi-metal Cyanide Complexes as Highly Active Catalysts for Ring-Opening Polymerization of Propylene Oxide

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Introduction

The nanoporous Prussian blue analogues $M_3[M'(CN)_6]_2$, where M is a divalent metal and M' is a trivalent metal,^{1,2} are constructed from octahedral $M^{3+}(CN)_6^{3-}$ complexes which

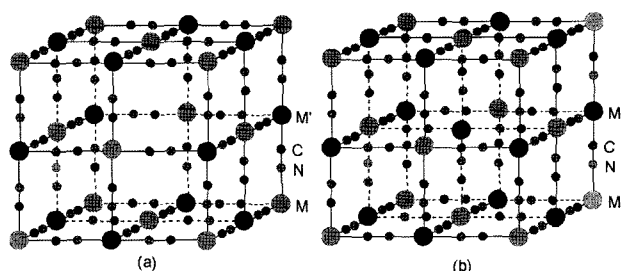


Figure 1. Structure of Prussian blue analogues showing two pore environments: the large pores created in 1/3 of the unit cells because of $M'(CN)_6$ vacancies (a) and the smaller pores present in the remaining defect-free unit cells (b).³

are bridged into a simple cubic lattice by M^{2+} ions. This creates a crystal consisting of alternating M^{2+} and M^{3+} ions connected through cyanide linkers resulting in “defect-free” pores without any unsaturated metal centers (Figure 1).³ The charge imbalance between the $[M^{3+}(CN)_6]^{3-}$ complex and the M^{2+} ions causes disordered $[M^{3+}(CN)_6]^{3-}$ vacancies to occur at 1/3 of the M^{3+} sites to maintain charge neutrality in the crystal. The unsaturated metal centers present in these materials have been hypothesized as high-binding energy sites for hydrogen, resulting in plausible hydrogen storage materials.¹

A type of Prussian blue analogues base upon $Zn_3[Co(CN)_6]_2$ framework, so called multi-metal cyanide (MMC) complexes, are also well-known catalyst for the ring-opening polymerization of propylene oxide (PO) to produce poly(propylene oxide) polyol (PPG), one of the main raw materials in a wide range of polyurethane applications.⁴ Recent improvements have made MMC catalysts much more attractive for commercial manufacture of polyether polyols since they give high-quality PPG products that have low unsaturation level (UL), narrow molecular weight distribution (MWD) and low viscosity, especially compared to conventional base catalysts.⁴ While MMC catalysts offer attractive advantages over most widely used base catalysts, they must be activated for a long time before the polymerization starts.^{4,5} This long induction period (IP), e.g. several hour, undercuts the economic advantage of MMC catalysts. In addition, heating the catalyst for a prolonged period at high polymerization temperature above 100 °C may deactivate it completely.⁵

In this communication, we show our preliminary results how to tune the activity and IP of MMC-catalyzed PO polymerizations by changing catalyst formulations of the MMC catalysts.

Results and Discussion

Highly crystalline $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ prepared according to the reported procedures¹ showed no activity in PO polymerizations. In order to activate this catalyst, some organic complexing agent (CA) should be coordinated to the catalyst matrix. In $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ complex,

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charge balance with the Zn^{2+} ions leads to vacancies at one-third of the $[Co(CN)_6]^{3-}$ sites in the framework.² The water molecules fill the resulting cavities as Zn^{2+} -bound and solvate.¹ Treating with organic CAs, they also be able to interact with the open coordination sites on the Zn^{2+} ions arising upon substituting the bound water molecules, resulting in forming active catalyst.

As a means of preparing highly active MMC catalysts, aqueous $ZnCl_2$ was reacted with aqueous $K_3Co(CN)_6$ in the presence of *tert*-butyl alcohol (*t*BuOH) as a complexing agent.^{5a} Elemental analysis confirmed the MMC compound has a molecular formula, $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0} \cdot 2.0$ *t*BuOH \cdot 1.0 H_2O (**MMC1**). The complexation of *t*BuOH may result in framework (Figure 1) collapse.⁵ Detailed catalyst characterizations including IR, x-ray photoelectron spectroscopy, and x-ray powder diffraction were reported elsewhere.⁵

The performance of the MMC catalyst for PO polymerization was tested by semi-batch runs carried out at 115 °C by using difunctional PPG (MW=700) as a starter. As illustrated in Figure 2, the MMC catalysts show high activity once it is activated. Taking a look at the rate profile, it is evident that it needs a long IP before polymerization starts.

In order to overcome these shortcomings we modified the MMC formulation by reacting aqueous $ZnCl_2$ with combined ratios of aqueous $K_3Co(CN)_6$ and $K_3Fe(CN)_6$ in the presence of *t*BuOH as a complexing agent.^{5a} After fixing $Zn^{II}/(Co^{III}+Fe^{III})$ molar ratio to 5.0, six more MMC catalysts were prepared by changing Co^{III}/Fe^{III} molar ratio to 9/1, 7/3,

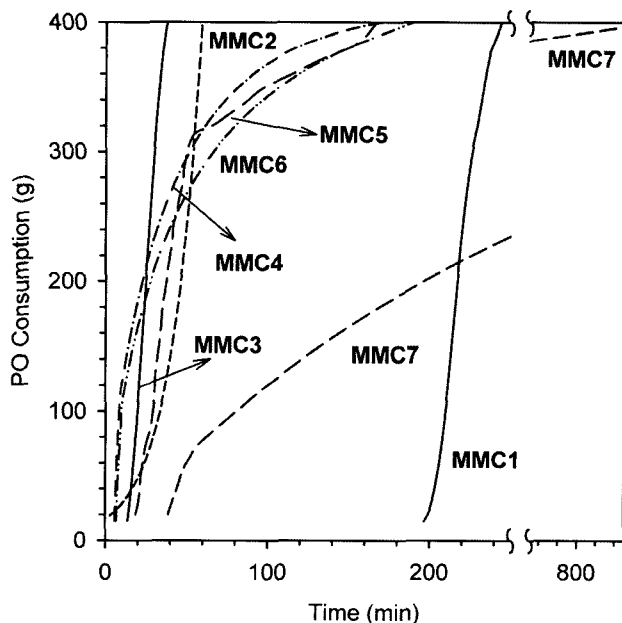


Figure 2. Monomer consumption versus time profiles obtained by various MMC catalysts at 115 °C. Conditions: PPG starter=70 g, catalyst=0.1 g. Polymerization stopped when total PO consumption reached 400 g for a facile agitation.

5/5, 3/7, 1/9, and 0/10. Element analysis of Zn, Co, Fe, and Cl was obtained by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), on a Agilent 7500 ICP-MS and element analysis for C, H and N was performed by combustion analysis, on a Perkin Elmer CHN Analyzer (Model 2400). The results showed that the six catalysts have molecular formulas of $Zn_{2.3}Cl_{0.9}[(0.92Co(CN)_6) \cdot (0.08Fe(CN)_6)]_{1.0} \cdot 2.1$ *t*BuOH \cdot 0.9 H_2O (**MMC2**), $Zn_{2.2}Cl_{1.0} [(0.77Co(CN)_6) \cdot (0.23Fe(CN)_6)]_{1.0} \cdot 2.3$ *t*BuOH \cdot 1.0 H_2O (**MMC3**), $Zn_{2.1}Cl_{0.9} [(0.62Co(CN)_6) \cdot (0.48Fe(CN)_6)]_{1.0} \cdot 2.5$ *t*BuOH \cdot 0.8 H_2O (**MMC4**), $Zn_{2.3}Cl_{1.1} [(0.38Co(CN)_6) \cdot (0.62Fe(CN)_6)]_{1.0} \cdot 2.5$ *t*BuOH \cdot 0.9 H_2O (**MMC5**), $Zn_{2.5}Cl_{1.2} [(0.17Co(CN)_6) \cdot (0.83Fe(CN)_6)]_{1.0} \cdot 2.3$ *t*BuOH \cdot 0.7 H_2O (**MMC6**), and $Zn_{2.6}Cl_{1.2} [Fe(CN)_6]_{1.0} \cdot 1.8$ *t*BuOH \cdot 1.2 H_2O (**MMC7**), respectively. As expected, the introduction of two metal cyanide salts together with organic CA into the unit cell shown in Figure 1 makes the structure more complicated, resulting in a collapse of unit cell structure.

XRD analysis of the MMC catalysts showed that all MMC catalysts have much smaller crystallite size and/or lower crystalline order than $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound. The formation of catalyst through cyano bridges between Zn and other metals (Co^{III} and/or Fe^{III}) was also confirmed by x-ray photoelectron and infrared spectroscopies. For example, the cyano bridged complexes could be easily identified since they exhibit sharp $\nu(CN)$ at 2200–2000 cm^{-1} . The $\nu(CN)$ of free CN^- is 2080 cm^{-1} (aqueous solution). Upon coordination to a metal the $\nu(CN)$ shifts to higher frequencies.

Figure 2 shows rate profiles of PO polymerizations obtained by a series of MMC catalysts. MMC1 catalyst (Zn^{II} - Co^{III}) shows very high activity once it is activated, while MMC7 catalyst (Zn^{II} - Fe^{III}) showed relatively low activity: i.e. it takes about 15 hours for PO consumption to reach 400 g. However, the former catalyst is featured by long IP (~200 min) and the latter by short IP (~40 min). It is very interesting to note that the activity and IP of MMC catalysts are tunable by simply combining Co^{III} and Fe^{III} together with Zn^{II} . As shown in Figure 2, when Co^{III} is a major component over Fe^{III} (**MMC2** and **MMC3**), the IP becomes almost negligible, keeping the activity almost similar to **MMC1** catalyst. However, the activity decreases, especially at the later part of polymerization, as the amount of Fe^{III} increases (**MMC4**-**MMC6**), reflecting the low activity of **MMC7** catalyst. Note that the IPs are still negligible in these cases. Zn^{II} - Co^{III} - Fe^{III} MMC catalysts have another advantage over Zn^{II} - Co^{III} catalyst, since the former (e.g. **MMC4** in Table I) catalyst can be activated at much lower temperature than **MMC1** catalyst.

The combination of Co^{III} and Fe^{III} cyanide salts also influences polymer properties (Table I) such as MW, viscosity and UL. The UL value of polymer is the one of the most important features characterizing MMC catalysts differentiating from conventional base catalysts. Typically KOH cat-

Table I. Properties of Polymers Produced by Various MMC Catalysts at the Polymerization Conditions Given in Figure 2

Cat.	Polym. Temp. (°C)	Unsat. ^a (mequiv/g)	Viscosity ^b (cP)	M _n ^c (g/mol)	MWD
MMC1	115	0.015	1,790	3,700	1.43
	95	0.010	1,260	3,920	1.07
	75	0.008	975	4,410	1.14
MMC2	115	0.005	950	4,390	1.07
MMC3	115	0.008	2,460	4,530	1.21
MMC4	130	0.015	1,675	4,120	1.60
	115	0.012	2,850	5,220	1.63
	95	0.008	9,250	5,520	2.69
	75	0.007	120,000	7,080	5.53
	60	0.005	910,000	6,240	7.16
	50	0.005	540,000	4,800	4.19
	40	0.004	298,000	4,060	4.21
MMC5	115	0.014	6,250	3,640	4.06
MMC6	115	0.017	15,425	3,550	4.44
MMC7	115	0.021	95,000	3,360	5.69

^aTotal degree of unsaturation measured by titration method according to ASTM D2847. ^bMeasured by Brookfield DV-II+ Programmable Viscometer at 25 °C. ^cMeasured by GPC at 25 °C in THF with polystyrene standards.

alyzed polyols are characterized by high UL (0.03 to 0.10 meq/g), so that they have limited applications as high performance polyurethane products.⁴ As shown in Table I, the UL values of polyols produced by MMC catalysts are much lower than that of polyol produced by base catalysts. The polymer UL produced by **MMC1** (0.015 meq/g) is lower than **MMC7** (0.021 meq/g). It is noted that the UL value is tunable to by combining metal cyanide salts, so that the polymer UL obtained by **MMC2** at 115 °C records ultra low value, 0.005 meq/g. In general, the UL increases as the amount Fe^{III} cyanide salt increases and as the temperature increases (see **MMC1** and **MMC4** in Table I).

The metal cyanide salt influences the polymer MW and especially MWD as well. The MWs of polymers obtained at 115 °C by **MMC2** through **MMC6** catalysts are higher than

those of polymers by **MMC1** or **MMC7** at the same conditions. The MWDs of polymers become broader considerably as the amount Fe^{III} cyanide salt increases and they are dependent on polymerization temperature. The viscosity of polymer is also an important property during handling and reacting with isocyanate compounds. It is expected that the viscosity is dependent on many parameters such as MW, MWD and unsaturation level of polymer (Table I). It is quite surprising that the viscosity changes by almost 1,000 folds from 975 to 910,000 cP. In fact the polymer obtained by **MMC4** at 60 °C was a gel, while the polymer obtained by **MMC2** at 115 °C a clear viscous liquid. It is hard to conclude the effect of individual parameter on viscosity, the MWD values influence polymer viscosity most deeply.

In summary, we showed that MMC-catalyzed PO polymerization behavior is tunable by combining Co^{III} and Fe^{III} cyanide salts together with Zn^{II}. Thus, by combining small amount of Fe^{III} cyanide salt together with Co^{III} cyanide salt, IP and activation temperature of polymerization, and UL, MW, MWD and viscosity of resulting polyols could be tuned.

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