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ORIGINAL CONTRIBUTION

Su Chen
Li Chen

Fe/Zn double metal cyanide catalyzed ring-opening polymerization of propylene oxide: 2. Characterization of active structure of double metal cyanide catalysts

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S. Chen (✉) · L. Chen
School of Chemistry and Chemical Engineering, Nanjing University of Technology, 210009 Nanjing, China
E-mail: prcscn@yahoo.com.cn

Abstract Double metal cyanide (DMC) complexes based on $Zn_3[Fe(CN)_6]_2$ were synthesized using different molar ratios of $ZnCl_2$ to $K_3[Fe(CN)_6]$ and special complexing agents. IR spectroscopy, electron spectroscopy for chemical analysis, X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, and other analytical techniques were employed to characterize these catalysts. The morphology and structure of these DMC catalysts were attributed to the different complexing agents as well as to the different molar ratios of $ZnCl_2$ to $K_3[Fe(CN)_6]$. In addition, the catalytic activity was strongly correlated with the morphology and noncrystalline content of DMC catalysts. High-activity catalysts could be prepared by controlling the structure of DMC catalysts by incorporating complexing agents. The active species of DMC catalysts for ring-opening polymerization are Zn^{2+}, $[Fe(CN)_6]^{3-}$, Cl^-, and the compound of their ligands.

Keywords Double metal cyanide complex · Catalytic activity · Ring-opening polymerization · Characterization

Introduction

Double metal cyanide (DMC) complexes have interested a broad spectrum of scientists with respect to their outstanding properties for the ring-opening polymerization (ROP) of epoxide(s). DMC catalysts were first discovered to be useful for epoxide polymerization by researchers at General Tire and Rubber Co. in the early 1960s [1]. DMC catalysts were modified starting in 1983, with significant improvement made by others including Shell Co. [2] and Arco Co. [3, 4]. The catalysts can be used to make a wide variety of polymer products, including polyether, polyester, and polyetherester polyols since they give polyether polyols that have a lower level of unsaturation and narrower molecular weight distributions compared with similar polyols made using basic (KOH) catalysis [5]. Also with these catalysts, polyether polyols having high molecular weight and low viscosity can have a wider range of industrial applications. Moreover, these catalysts are active enough to allow their use at low concentrations and this reinforces their advantage.

In the case of the ROP of epoxides, there are a number of catalysts that can be used to catalyze ROP, such as cesium hydroxide [6], potassium hydroxide along with 18-crown-6 ether [7, 8, 9], calcium amide alkoxide [10], porphyrin complexes of aluminum [11], aluminoxane/acetyl acetone [12], and diamidoamines [13]. The drawbacks of many of these catalysts include poor activity, high cost, production of polymers with intense color, and low molecular weight with too excessive crystallinity for polyurethane applications. The preferred commercial catalysts for high-quality polyether polyols are still based on DMC catalysts. In the present study, many patents and articles concerning DMC catalysts are reported [14, 15]. Most of the DMC catalysts documented are zinc hexacyanocobaltate DMC catalysts. We first reported the method of synthesizing zinc hexacyanoferrate DMC catalysts and the sequence structure of polyethers catalyzed by Fe/Zn DMC catalysts [16, 17]. In this paper, we have focused on the characterization of the active structure of Fe/Zn DMC for ROP of propylene oxide.

Experimental

Materials

The reagents were all of analytical grade purity and were purchased from Shanghai Reagent Co.

The synthesis of the Fe/Zn DMC catalysts is illustrated in Scheme 1. Typical DMC-1 and DMC-2 catalysts with a 1:1 molar ratio of $ZnCl_2$ to $K_3[Fe(CN)_6]$ were prepared with and without *t*-butyl alcohol and polyether polyol complexing agents according to the procedures in the literature. The DMC-3 catalyst with a 6:1 molar ratio of $ZnCl_2$ to $K_3[Fe(CN)_6]$ was prepared with *t*-butyl alcohol and polyether polyol complexing agents as detailed in the following. $ZnCl_2$ (20.4 g) was dissolved in a beaker with a mixture of deionized water (30 ml) and *t*-butyl alcohol (14.0 g) (solution 1). Solution 2 was prepared by dissolving $K_3[Fe(CN)_6]$ (8.2 g) in a mixture of deionized water (150 ml) and *t*-butyl alcohol (8.0 g). Solution 1 was added dropwise to solution 2 over 40 min, and was stirred well mechanically. Then, the solution mixture was mixed with a homogenizer for 30 min. After filtration, the yellow slurry was resuspended three times in *t*-butyl alcohol (100 ml) and deionized water (100 g). The final filtered slurry was resuspended in *t*-butyl alcohol (250 ml) and polyether polyol (8.0 g). The resulting catalyst solids were dried under vacuum to a constant weight at 50 °C [17]. The specific gravity and the specific surface area of this DMC catalyst were 0.9464 and 21.2 m^2/g, respectively. A family of Fe/Zn DMC catalysts was also prepared using different molar ratios of $ZnCl_2$ to $K_3[Fe(CN)_6]$. The molar ratios were in the range 1:1–7:1. The procedure for the preparation of Fe/Zn DMC was the same as that just described [16].

ROP experiment

ROPs were carried out as described in the literature [16, 17]. Also this ROP of propylene oxide with Fe/Zn DMC catalysts can be carried out at the room temperature. In view of this point, the activity of Fe/Zn DMC catalysts could be measured by the reaction time of the ROP at room temperature. It was found that a higher activity of Fe/Zn DMC catalysts shortens the reaction time.

Characterization

IR spectra of the catalysts were measured using a VECTOR-22 IR. X-ray diffraction (XRD) patterns of the catalysts were obtained with a D/MAX using Cu Kα radiation at 40 kV and 30 mA. The morphology of the surface of the DMC catalysts was observed by scanning electron microscopy (SEM, JSM-5900, Japan Electron Co.). The samples were coated with gold (100 Å) in a Balzere SCD 004 sputter coater. The instrument was operated at 20 kV. X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was performed using a PerkinElmer 7 XPS instrument.

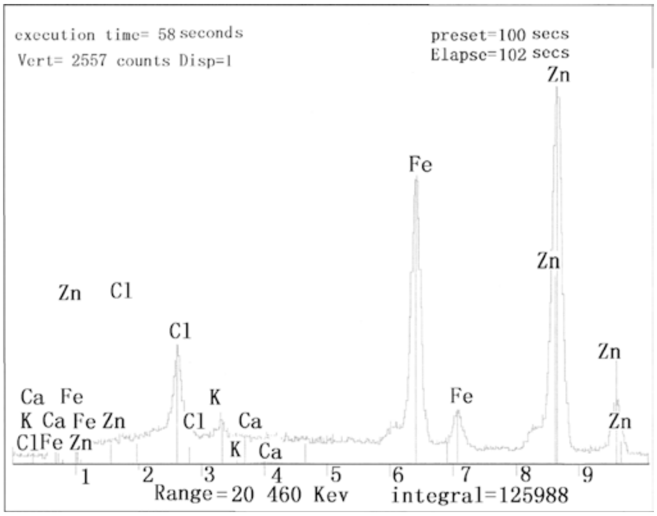


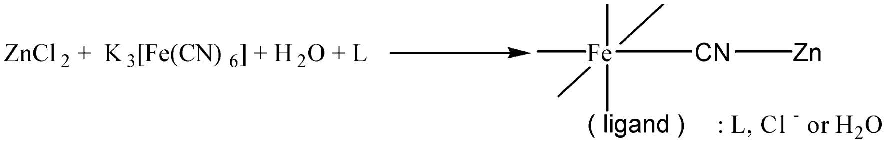
Fig. 1 Electron spectroscopy for chemical analysis spectrum of Fe/Zn double metal cyanide (*DMC*) catalyst with a 6:1 molar ratio of $ZnCl_2$ to $K_3[Fe(CN)_6]$

Results and discussion

Molecular composition of Fe/Zn DMC catalyst

When the molar ratio of $ZnCl_2$ to $K_3[Fe(CN)_6]$ was 6:1, the elemental analysis of the catalyst obtained by electron spectroscopy for chemical analysis (ESCA) (Fig. 1) corresponded with the formula $Zn_3[Fe(CN)_6]_2$ $1.04ZnCl_2$ $3.54H_2O$ xL (L is a ligand, x is a positive number): Zn, 59.0%; Fe, 24.94%; Cl, 14.31%; O, 12.73%; K, 1.73% (calculated values not given); C, 36.%; N, 4.55%; H, 4.55% (where the content of C, N, and H was measured using a microelement analysis instrument). The amount of L and H_2O in the catalyst may vary with the drying conditions. The Fourier transform IR characteristic spectrum of Fe/Zn DMC is shown in Fig. 2. The strong, broad O–H stretch at 3,432 cm^{-1} shows the presence of this catalyst's hydroxyl group. The C–C–O stretch is clearly seen at 1,083 cm^{-1}. The C ≡ N stretch appears at 2,179.2 cm^{-1}. These results show that catalyst has an ether bond and a

Scheme 1 Synthesis of Fe/Zn double metal cyanide catalysts



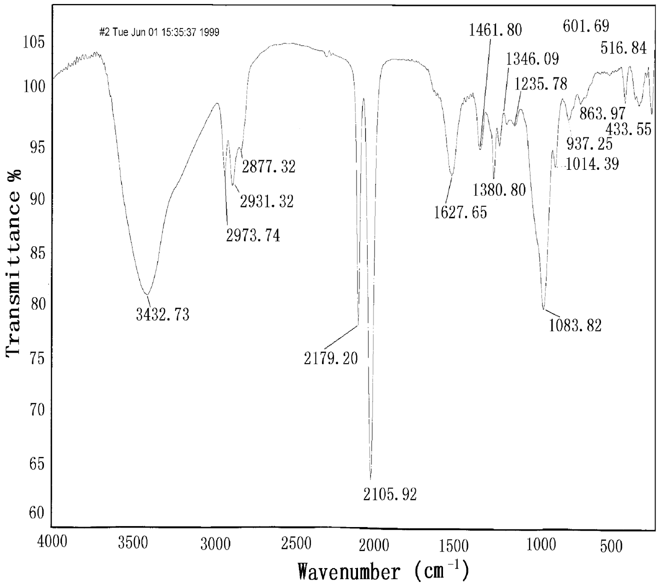


Fig. 2 Fourier transform IR spectra of Fe/Zn DMC catalyst with a 6:1 molar ratio of $ZnCl_2$ to $K_3[Fe(CN)_6]$

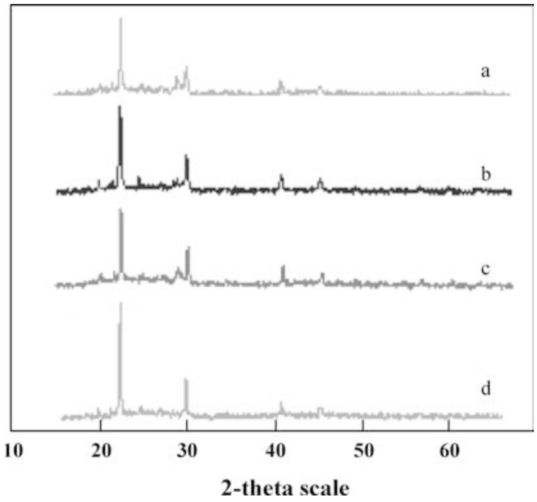


Fig. 3 X-ray diffraction (XRD) spectra of DMC catalysts with different molar ratios of $ZnCl_2$ to $K_3[Fe(CN)_6]$: *a* 6:1; *b* 4:1; *c* 3:1; *d* 1:1

–CN group. In order to understand more about the crystallinity of DMC catalysts, XRD was employed. The XRD patterns of $ZnCl_2$, $K_3[Fe(CN)_6]$, and DMC catalysts are shown in Fig. 3. The characteristic sharp crystalline peaks at *d* spacings of 0.428, 3.76, and 0.228 nm are ascribed to the cubic lattice structure of $Zn_3[Fe(CN)_6]_2$ and there were no peaks corresponding to $ZnCl_2$, which is caused by the incorporation of butyl alcohol and polyether polyol in the catalyst.

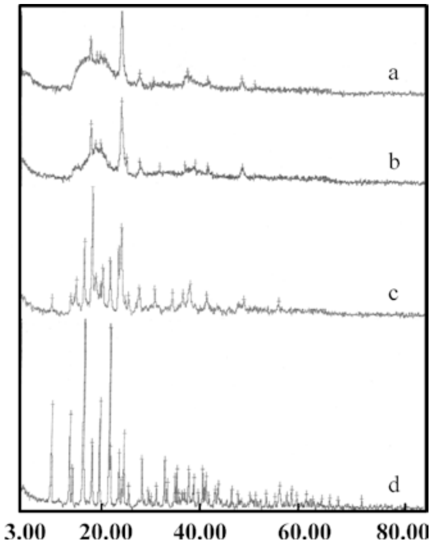


Fig. 4 XRD spectra of DMC catalysts prepared with different complexing agents: *a* with *t*-butyl alcohol and polyether; *b* with *t*-butyl alcohol; *c* with ethylene glycol dimethyl ether; *d* without complexing agent

Effect of ratios of $ZnCl_2$ to $K_3[Fe(CN)_6]$ on catalytic activity

As shown in Fig. 3, DMC catalysts synthesized with different ratios of $ZnCl_2$ to $K_3[Fe(CN)_6]$ indicated differences in the crystalline content and catalytic activity. When the ratio of $ZnCl_2$ to $K_3[Fe(CN)_6]$ is 6:1, the DMC catalyst has the lowest crystalline phase compared with other ratios, such as the ratios of $ZnCl_2$ to $K_3[Fe(CN)_6]$ of 4:1, 3:1, and 1:1. The catalytic activity of Fe/Zn DMC catalysts is in the order of the preparation ratios a > b > c > d.

Effect of complexing agents on catalytic activity

The XRD patterns of DMC catalysts prepared with and without different complexing agents are shown in Fig. 4 and the corresponding values are tabulated in Table 1. As in our previous work [16, 17], a lower content of the noncrystalline phase of the DMC catalyst indicated a higher activity of the DMC catalyst. Also it was proven that the crystalline peaks of the XRD patterns are too sharp in the absence of any complexing agents. However, the sharp peaks in the XRD patterns decreased greatly after the complexing agents had been incorporated into the DMC catalysts. The polyether and *t*-butyl alcohol complexing agents made the DMC catalysts more noncrystalline and amorphous. It was noted that the noncrystalline content increased as the complexing agents were incorporated into the DMC catalysts. Also the activity of DMC catalysts is related to the noncrystalline content. Usually DMC catalysts with higher

Table 1 X-ray diffraction (*XRD*) results of different double metal cyanide (*DMC*) catalysts. *X* shows that there is an XRD peak. *Absent* shows that there is no XRD peak. DMC catalysts prepared with different complexing agents: *DMC-A* *t*-butyl alcohol and polyether; *DMC-B* t-butyl alcohol; *DMC-C* ethylene glycol dimethyl ether; *DMC-D* without any complexing agents

	Location of diffraction peak					
	5.07	4.82	3.76	3.59	2.54	2.28
DMC-A	Absent	X	X	Absent	Absent	X
DMC-B	X	X	X	Absent	Absent	X
DMC-C	X	X	X	X	X	X
DMC-D	Absent	Absent	X	X	X	X

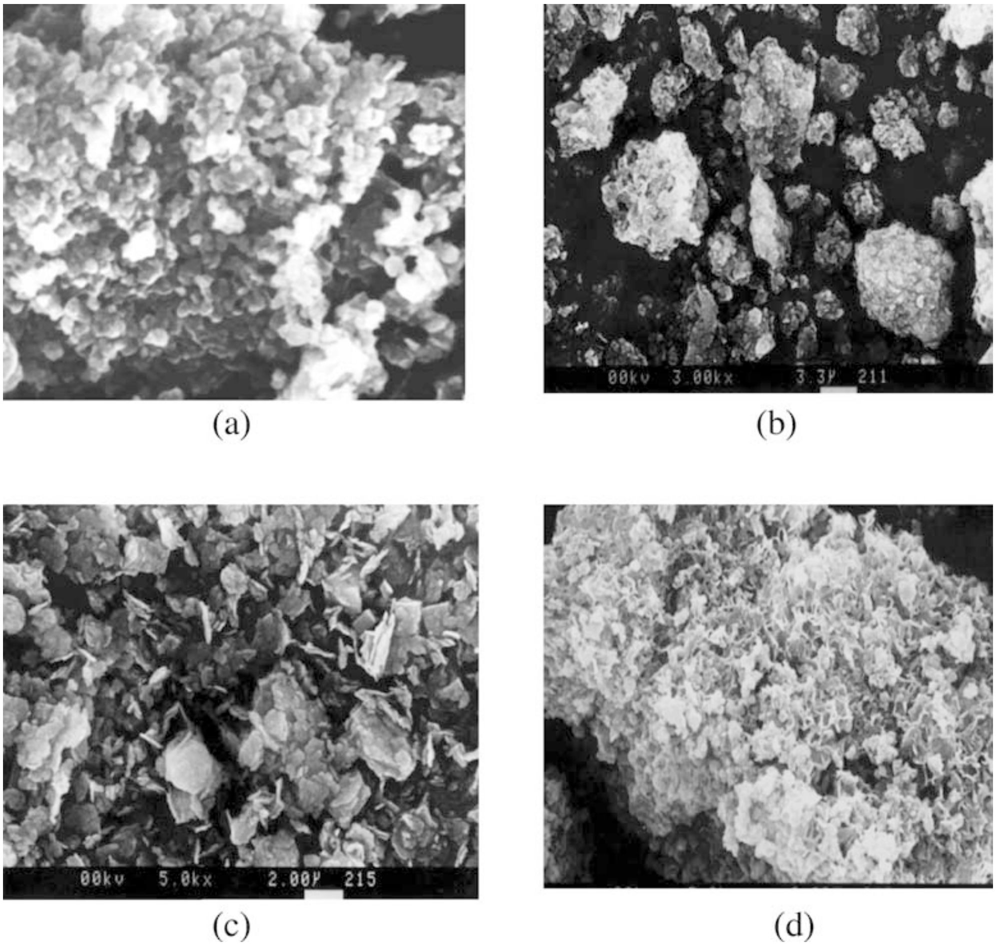
activity have a lower level of crystalline content and a higher level of noncrystalline content. Similar conclusions were drawn from SEM pictures of DMC catalysts (Fig. 5). Fig. 5 shows that the introduction of organic complexing agents decreases the crystalline content of DMC catalysts and the crystal particle size. The introduction of the organic complexing agents also resulted in well-dispersed and fine particles.

Table 2 Relative surface components (compared to Zn atom content) of different DMC catalysts measured by X-ray photoelectron spectroscopy (*XPS*)

Element	Relative content		
	DMC-1	DMC-2	DMC-3
Zn	1	1	1
Fe	1.0612	1.0219	0.8076
N	4.3739	4.2547	3.7911
O	7.9697	2.4505	5.4549
Cl	0.0936	0.04976	0.3457

XPS characterization of DMC catalysts

To gain insight into the activity of DMC catalysis, XPS was employed to characterize DMC-1, DMC-2, and DMC-3 catalysts. Table 2 shows that the relative contents of oxygen and chlorine of DMC-1 prepared with complexing agents are greater than those of DMC-2 prepared without complexing agents. This may be because the introduction of complexing agents into the DMC catalysts makes oxygen atoms in the



(a) (b)

(c) (d)

Fig. 5 Scanning electron microscopy spectra of DMC catalysts prepared with different complexing agents: **a** without complexing agents; **b** with *t*-butyl alcohol and polyether; **c** with ethylene glycol dimethyl ether; **d** with polyether complexing agent coordinate with zinc atoms of the DMC catalyst, and chlorine atoms in DMC catalysts are not easy to remove during the preparation of DMC catalysts; in addition, the noncrystalline content is increased with addition of complexing agents. On the other hand, when zinc chloride is in excess, the chlorine content in the DMC catalyst increases with the decrease of the relative content of Fe. This may be because Zn^{2+} is rich in the surface of the DMC catalyst; the partial charge of Zn^{2+} is attracted and neutralized by Cl^{-}. Fe $2p$ XPS results and the spectra of DMC-1, DMC-2, and DMC-3 are given in Table 3 and Figs. 6, 7, and 8, respectively. There are two remarkable ($2p_{1/2}$ and $2p_{3/2}$) peaks in these spectra. It is noted that the Fe $2p$ binding energy of DMC-1 and DMC-3 prepared with complexing agents is lower than that of DMC-2 prepared without any complexing agents. This may presumably be due to the introduction of complexing agents into the DMC catalysts which facilitates the interaction between Zn^{2+} and $[Fe(CN)_6]^{3-}$, along with the electrons of CN^{-} transferring onto Fe^{3+} and then it reinforced the coordination between the complexing agents and Zn^{2+}. Also this is the reason why the binding energy of Fe $2p_{3/2}$ and $2p_{1/2}$ decreased on introducing complexing agents into the DMC catalysts. Moreover, Table 3 shows that the ratios of the peak area of the high binding energy to the low binding energy of DMC-1 and DMC-3 at Fe and Zn peak positions are greater than those of DMC-2. This may be caused by oxygen atoms of the complexing agents coordinating with Zn^{2+}. It can be concluded that the active center of the DMC catalyst is Zn^{2+}, $[Fe(CN)_6]^{3-}$, Cl^{-}, and the compound of their ligands.

Table 3 XPS analytical results of different DMC catalysts. *B*/*A* is the ratio of the peak area of high binding energy to that of low binding energy

Sample	Binding energy (eV)				B/A	
	Fe $2p_{1/2}$ (high)	Fe $2p_{3/2}$ (low)	Zn $2p_{1/2}$ (high)	Zn $2p_{3/2}$ (low)	Fe	Zn
DMC-1	720.90	708.20	1044.70	1021.60	1.93	1.92
DMC-2	721.30	708.30	1044.60	1021.60	1.45	1.86
DMC-3	720.90	707.90	1044.850	1021.50	1.75	1.93

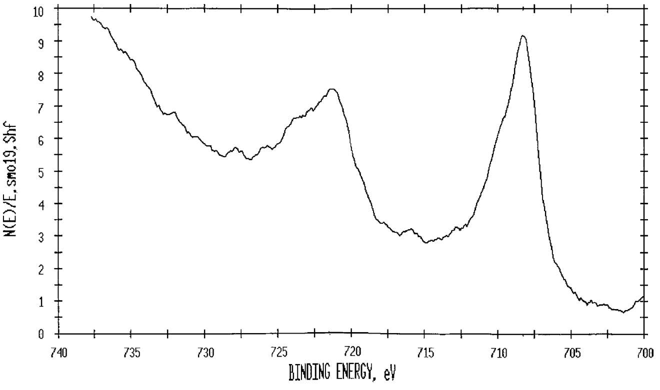


Fig. 6 Fe $2p$ X-ray photoelectron spectroscopy (*XPS*) spectra of DMC-1

Conclusions

A new family of DMC catalysts based on *t*-butyl alcohol and co-complexing agent polyether has been

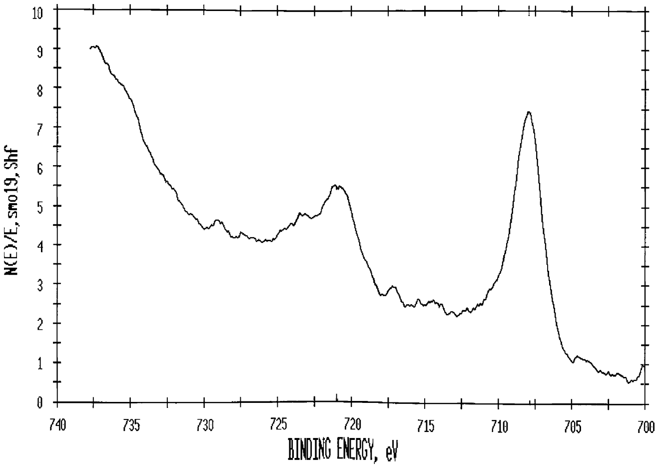


Fig. 7 Fe $2p$ XPS spectra of DMC-2

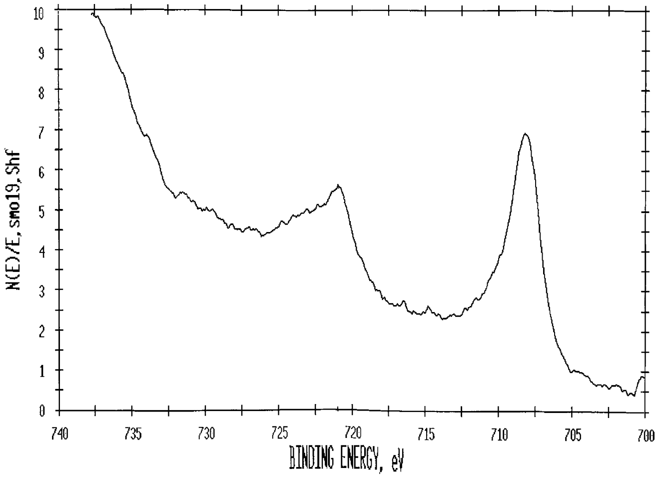


Fig. 8 Fe $2p$ XPS spectra of DMC-3

discovered. To gain better understanding about the active species of DMC catalysts, ESCA, IR, XRD, SEM, and XPS analytical techniques were used to characterize the DMC catalysts. It was found that the activity of these catalysts is strongly dependent not only on the crystalline structure or special effective complexing agents, but also on some combination of the two. The active center of the DMC catalysts for ROP is Zn^{2+}, $[Fe(CN)_6]^{3-}$, Cl^-, and the compound of their complexing agents.

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