

Studies on $\text{VOCl}_3/\text{MgCl}_2/\text{NaY}/\text{Al}_2\text{Et}_3\text{Cl}_3$ Complex Support Catalysts for the Copolymerization of Ethylene and Propylene*

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SYNOPSIS

Using VO^{2+} as a spin probe, a new method to obtain microenvironmental information on supports was developed which can be used in the choice of supports for coordination catalysts. Utilizing the above method, NaY was chosen as second support component. A complex support catalyst $\text{VOCl}_3/\text{MgCl}_2/\text{NaY}/\text{Al}_2\text{Et}_3\text{Cl}_3$ was prepared and used in ethylene-propylene copolymerization. Higher polymerization activity was obtained with this catalytic system. Alternating the ratio of two kinds of supports, the composition and sequence structure of copolymers could be controlled, which showed that NaY participated in the active species, affected the insertion of monomer, and changed the composition and sequence structure of copolymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Recently, there has been renewed interest directed toward the development of third-generation Ziegler-Natta (Z-N) catalysts. The main thrust is to decrease MgCl_2 used in catalyst, to achieve better control of sequence distribution, and to improve processibility and physical-mechanical properties of the products. One approach to accomplishing the above mentioned objective is to develop complex support catalysts. In fact, there were various reports of catalyst systems with complex supports shortly after the discoveries of Ziegler and Natta. It has been known that MgCl_2 is an important type of support for Z-N catalysts. Several inorganic oxides, such as SiO_2 , Al_2O_3 , etc., are also used as supports of Z-N catalysts due to their large surface areas and good morphology. Zeolite, believed to be a compound of SiO_2 and Al_2O_3 , forms a co-support with MgCl_2 ; but the character of polymerization and the effect of this catalyst composition and its structure on copolymers still remain unclear. In this paper, a new method of

obtaining microenvironmental information on supports was developed and a $\text{VOCl}_3/\text{MgCl}_2/\text{NaY}/\text{Al}_2\text{Et}_3\text{Cl}_3$ complex support catalyst was prepared. The copolymerization of ethylene-propylene in the presence of $\text{VOCl}_3/\text{MgCl}_2/\text{NaY}/\text{Al}_2\text{Et}_3\text{Cl}_3$ catalytic system, the electron spin resonance (ESR) spectra of this catalyst, and the composition and sequence structure of copolymer were studied.

EXPERIMENTAL

Materials: Zeolite (made by Wenzhou Catalytic Mill), MgCl_2 (from Fushun Institute of Petroleum Chemical Engineering), $\text{Al}_2\text{Et}_3\text{Cl}_3$, and VOCl_3 (from Beijing Research Institute of Chemical Industry) were used as starting materials to make the catalyst. Polymerization-grade ethylene and propylene (from Zhen-hai Petroleum Chemical Plant) were purified by passing through four 5Å molecular sieve columns and a hexane solution containing 10 wt % triethylaluminum to remove residual traces of moisture and oxygen. The solvent *n*-heptane of analytical reagent grade was commercially obtained and purified before use.

Preparation of catalyst and polymerization: $\text{VOCl}_3/\text{MgCl}_2/\text{NaY}$ catalyst was prepared by the

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ball-milling method.¹ The copolymers of ethylene and propylene were prepared using $\text{VOCl}_3/\text{MgCl}_2/\text{NaY}/\text{Al}_2\text{Et}_3\text{Cl}_3$ as catalyst. Copolymerization was performed at atmosphere pressure in a 200 ml reaction flask provided with a stirrer. In a typical polymerization, 100 ml of anhydrous heptane was introduced into the reactor under nitrogen and thermostated at 20°C. An ethylene-propylene mixture with the appropriate composition was rapidly bubbled through the stirred solvent and the catalyst was introduced. After polymerization was finished, a solution of ethanol containing hydrochloric acid was injected into the reactor, quenching the polymerization. The resultant polymer was washed several times with ethanol and dried in a vacuum oven at 60°C.

Analytical procedures: The composition of copolymers was determined by ^{13}C -NMR on a JEOL FX-90Q spectrometer with hexamethyldisiloxane as internal standard. The solutions were prepared in *o*-dichlorobenzene-*d* up to about 15 wt %. ESR spectra were recorded at room temperature on a JEOL JES-FEIXG spectrometer under nitrogen.

RESULTS AND DISCUSSION

Selection of Zeolite Supports using Spin Probe

According to the literature,² active species-supported catalysts using zeolite as support gave very low polymerization productivity; for example, 8.8×10^{-6} kgPP/gTi.h($\text{TiCl}_3/\text{zeolite}$), which means the active species cannot be directly supported on zeolite. To achieve high polymerization productivity and to decrease MgCl_2 used in the catalyst, the following model support should be available: "active species"- MgCl_2 -zeolite. Thus the dispersing ability of zeolite is very important for obtaining a catalyst with high polymerization activity. In order to choose the zeolite, a VO^{2+} probe method was developed. Briefly, the principle of VO^{2+} probe is as follows.

More than 99% of the natural abundance of V is ^{51}V and its nuclear moment is 7/2. Thus, its expected hyperfine structure may consist of 8 lines, but the anisotropy of the spectrum must be observed on a powder sample. Analysis of the complicated spectrum was successfully accomplished by using the method developed by Hecht and Johnston.³ The spectrum was analyzed using an axial symmetric spin Hamiltonian:⁴⁻⁶

$$H = \beta[(g_{\parallel}H_zS_z + g_{\perp}H_xS_x + g_{\perp}H_yS_y) + A_{\parallel}S_zI_z + A_{\perp}S_xI_x + A_{\perp}S_yI_y]$$

Line width is very important. Although there are various factors affecting the line width of the ESR spectrum, the magnetic dipole-dipole interaction in this case is reasonably assumed to be the major factor. The relationship between ΔH (half-width) and r (the distance to the nearest neighbor) was given by the following equation:

$$\Delta H \propto 1/r^3$$

If the value of ΔH is determined, the distance to the nearest neighbor between VO^{2+} and VO^{2+} on the support and the dispersing ability of the support can be estimated. The line width can be determined via quantum chemistry treatment and by simulation on a computer, choosing the line width as an adjustable parameter.

In a powder system ($S = \frac{1}{2}$), the intensity function is:

$$I(H) = \int_0^{2\pi} \int_0^{\pi} F(H, \theta, \phi) P(\theta, \phi) d \cos \theta d\phi$$

$$I'(H) = \sum_{n=1}^N \int_0^{2\pi} \int_0^{\pi} \frac{\delta/\pi(H - H_R)}{[\delta^2 + (H - H_R)^2]^2} P d \cos \theta d\phi$$

The simulation spectra can be obtained by treating the above equations on a computer. Typical experimental ESR spectra and simulated ESR spectra are shown in Figures 1(a) and 1(b), respectively. The results indicate that the dispersing ability increases in the order of 5A zeolite < 13X zeolite \approx NaY zeolite. This order was also consistent with polymerization activity obtained by complex support catalysts selecting 5A zeolite, 13X zeolite, or NaY zeolite as second component of the support separately.

Copolymerization and ^{13}C -NMR Spectra of Copolymers

Copolymerization of ethylene and propylene were investigated in the presence of the $\text{VOCl}_3/\text{MgCl}_2/\text{NaY}/\text{Al}_2\text{Et}_3\text{Cl}_3$ catalyst. More effective copolymerization for preparation of EPR was obtained as follows: $\text{Al}/\text{V} = 20$, $t = 20^\circ\text{C}$, and $\text{E}/\text{P} = 0.4 \sim 0.8$. $\text{C}_3\%$ (propylene-content %) in copolymers is shown in Figure 2 as a function of MgCl_2/NaY in the catalysts.

The result is surprising and, so to our knowledge, no similar work has been reported in the literature. It could be presumed that by reaction between the active species and the complex support, new active

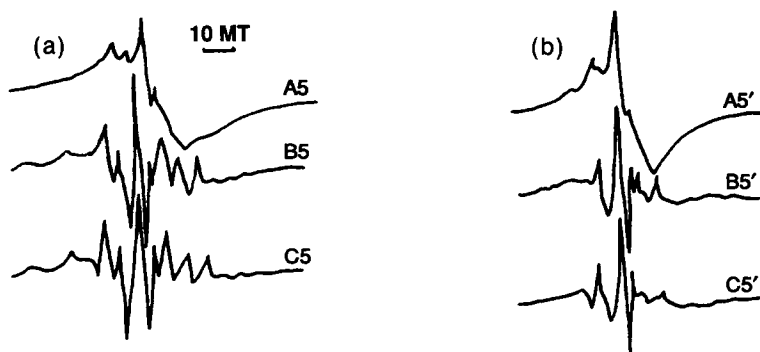


Figure 1 (a) experimental and (b) simulated ESR spectra of samples A5 (5A zeolite), B5 (13X zeolite) and C5 (NaY zeolite).

sites might be formed with a steric effect on the insertion of different monomers. However, the steric effect of a complex support catalyst allowing one kind of monomer to diffuse more easily toward the growing polymer particles and another to do so with more difficulty is far from being understood and still a challenging research goal.

The sequence distribution of ethylene-propylene copolymers directly affects the processibility and physical-mechanical properties of copolymers, and there have been many studies concerning sequence distribution of EPR copolymers by means of ^{13}C -NMR.⁷⁻⁸

By considering inverted propylene units, utilizing all spectrum data, and dividing them into six groups, a new computation method based on the first-order Markov terpolymerization model was developed. The six groups of peaks are: (1) $S_{\alpha\alpha}$, (2) $S_{\alpha\gamma} + S_{\alpha\delta^+}$, (3) $S_{\alpha\beta} + T_{\gamma\delta^+} + T_{\gamma\gamma} + T_{\delta^+\delta^+}$, (4) $T_{\beta\gamma^+} + S_{\gamma\gamma} + S_{\gamma\delta^+} + S_{\delta^+\delta^+}$, (5) $T_{\beta\beta} + S_{\beta\gamma} + S_{\beta\delta^+}$, (6)

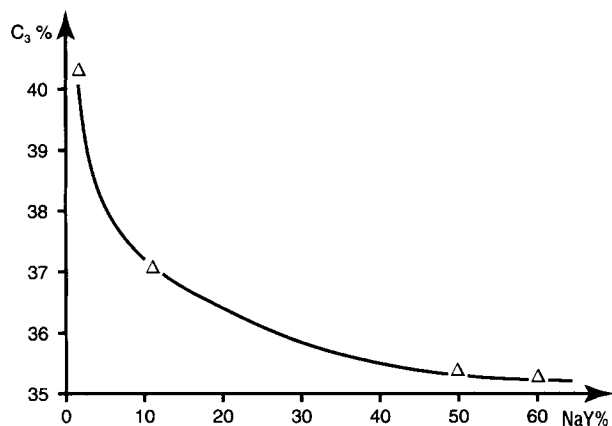


Figure 2 Plot of NaY% (in catalyst) vs. $C_3\%$ (propylene-content % in copolymers) $\text{Al}/\text{V} = 20$, $t = 20^\circ\text{C}$, $\text{E}/\text{P} = 0.4$.

$S_{\beta\beta} + P_{\beta\gamma^+} + P_{\beta\beta} + P_{\gamma^+\gamma^+}$. The following equations can be obtained:

$$f_1 = kP_{31}P_{12}(1 - P_{21} - P_{23}) + k(P_{13}P_{23} + P_{13}P_{21} + P_{12}P_{13})(1 - P_{31}) - A_1$$

$$f_2 = 2[kP_{31}P_{12}P_{21} + kP_{31}(1 - P_{12})(P_{13}P_{23} + P_{13}P_{21} + P_{12}P_{23})] - A_2$$

$$f_3 = kP_{31}(P_{21} + P_{23})[(1 - P_{12} - P_{13})P_{12}(P_{23} + P_{21}) + P_{13}P_{31}] + kP_{12}P_{31}P_{23}(P_{31} + 2) + P_{21}P_{12}(P_{21} + P_{23}) + k(P_{13}P_{23} + P_{13}P_{21} + P_{12}P_{22})P_{31}P_{12}(P_{21} + P_{23} + 2)] - A_3$$

$$f_4 = kP_{31}(P_{21} + P_{23})(P_{12} + P_{13} - P_{12}P_{21} - P_{12}P_{23} - P_{13}P_{31} + 2) + kP_{31}P_{12}(-P_{23}^2 - P_{21}^2 - 2P_{21}P_{23} - P_{31}P_{23} - 2P_{21} + P_{23} + P_{21}P_{12}) + k(P_{13}P_{23} + P_{13}P_{21} + P_{12}P_{23})(P_{31}P_{13} + 2P_{12}P_{31} - 2P_{31} - P_{31}^2) - A_4$$

$$f_5 = kP_{31}P_{12}[(1 - P_{21} - P_{23})^2 + 2P_{21}(1 - P_{12})] + (P_{13}P_{23} + P_{13}P_{21} + P_{12}P_{23})[(1 - P_{31})^2 + 2P_{31}(1 - P_{12} - P_{13})] - A_5$$

$$f_6 = P_{31}P_{12}(P_{21}P_{12} + 1) + k(P_{13}P_{23} + P_{13}P_{21} + P_{12}P_{23})(P_{31}P_{13} + 1) - A_6$$

(S, T, and P refer, respectively, to the methylene, methine, and methyl carbons; the Greek subscripts refer to the next nearest methyl substitution; P_{ij} and A refer to conditional probability and spectrum data, respectively.)

Through solving these equations by the Newton-Raphson method, the conditional probability can be obtained from which the reactivity ratio and se-

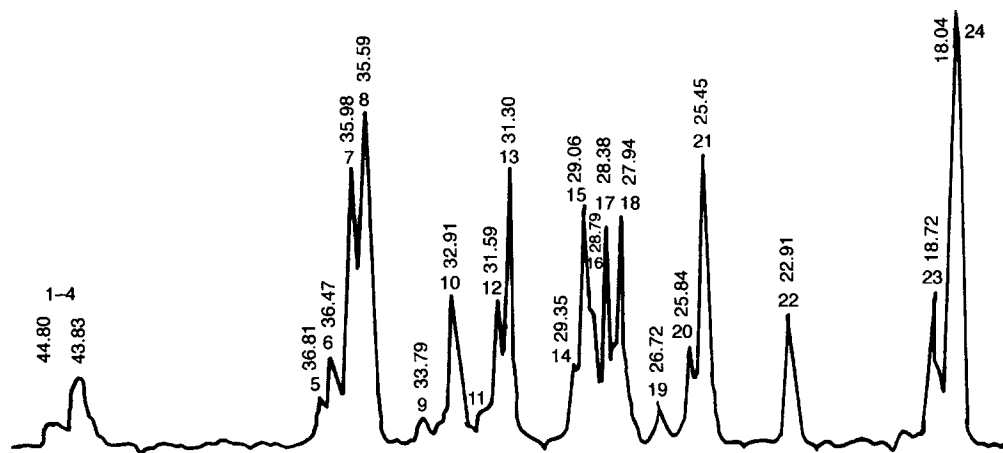


Figure 3 ^{13}C -NMR spectrum of EPR prepared by $\text{VOCl}_3/\text{MgCl}_2(90\%)/\text{NaY}(10\%)/\text{Al}_2\text{Et}_3\text{Cl}_3$.

quence distribution can be calculated. The calculated values are very consistent with the observed values, which shows that this method (a) is applicable to polymer both having and not having inverted propylene in the chain, and (b) not only can be utilized for calculating the area of peaks and kinetic parameters r_1 , r_2 but also can avoid the difficulties of separating peaks and the errors caused by such difficulty. A typical ^{13}C -NMR spectrum is shown in Figure 3. The typical calculated results for copolymer are listed in Tables I, II, and III. For comparison, the typical calculated results of copolymer prepared by the $\text{VOCl}_3/\text{MgCl}_2/\text{Al}_2\text{Et}_3\text{Cl}_3$ catalytic system are also included.

From the above results it can be seen that the reactivity ratio of ethylene for bisupported catalyst is greater than for monosupported catalyst; the amount of long sequence distribution (length 5 and 6+) and the amount of EE + PE diads rises while the amount of short sequence distribution (length 1 and 2) and PP + PQ diads declines for bisupported catalyst. All these show that the addition of a second support component to the catalytic support can cause the sequence distribution of copolymers to

change, which may result from the active species states of the bisupported and monosupported catalysts being different.

ESR Spectra of Vanadium

For catalysts based on V, the active species are usually trivalent, but V^{3+} shows no ESR signal at room temperature. Fortunately, V^{2+} and V^{4+} are ESR active. Thus ESR could be a logical research tool to aid in elucidating the structure of the active sites and to obtain some information about active species V^{3+} through the variations in V^{2+} and V^{4+} ESR signals.

There was a signal with $A = 106\text{G}$ in the spectrum of VOCl_3 which was similar to that of V^{4+} . The V^{4+} probably resulted from reduced V^{5+} subsequently being preserved for a long time [see Fig. 4(a)]. Eight lines with hyperfine structure $A = 60\text{G}$ immediately appeared when $\text{Al}_2\text{Et}_3\text{Cl}_3$ was introduced into VOCl_3 ($\text{Al}/\text{V} = 5$), which was similar to the spec-

Table I The Reactivity Ratios of Ethylene (r_1) and Propylene (r_2)

r	Catalyst	
	$\text{VOCl}_3/\text{MgCl}_2/\text{Al}_2\text{Et}_3\text{Cl}_3$	$\text{VOCl}_3/\text{MgCl}_2(90\%)/\text{NaY}(10\%)/\text{Al}_2\text{Et}_3\text{Cl}_3$
r_1	5.02	5.24
r_2	0.15	0.15
$r_1 \times r_2$	0.75	0.79

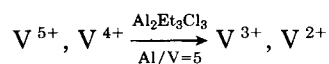
Table II The Percentage of Methylene Distribution in the Copolymer Chain

Length	Catalyst	
	$\text{VOCl}_3/\text{MgCl}_2/\text{Al}_2\text{Et}_3\text{Cl}_3$	$\text{VOCl}_3/\text{MgCl}_2(90\%)/\text{NaY}(10\%)/\text{Al}_2\text{Et}_3\text{Cl}_3$
1	26.86	24.56
2	20.24	19.90
3	21.68	23.33
4	8.48	7.75
5	9.32	10.27
6+	13.42	14.28

Table III The Percentage of Diad Distribution in the Copolymer Chain

Diad	Catalyst	
	VOCl ₃ /MgCl ₂ / Al ₂ Et ₃ Cl ₃	VOCl ₃ MgCl ₂ (90%)/ NaY (10%)/Al ₂ Et ₃ Cl ₃
EE	23.84	23.98
PE	23.10	23.28
EP	35.02	35.85
PP	12.08	11.45
Pq	5.90	5.45

trum of V²⁺ reported by Natta⁹ [Fig. 4(b)]. Thus, Al₂Et₃Cl₃ mainly causes the following transformation:



With the ratio of Al/V increasing, the intensity of ESR signals decreased [Fig. 4(c)], which suggests that ESR-active V continues to transform to ESR-inactive V. The result indicates homogeneous va-

nadium catalysts are sensitive to this reducing agent, which may be the reason why homogeneous vanadium catalysts are initially very active, followed by rapid decay.

The ESR spectra of VOCl₃/MgCl₂/Al₂Et₃Cl₃ and VOCl₃/MgCl₂/NaY/Al₂Et₃Cl₃ are shown in Figure 5, from which it can be seen that supported catalysts are insensitive to reducing agent. A possible structure for the active species of bisupported catalyst may be represented by Figure 6. As drawn in Figure 6, the support can stabilize the active species, and supported catalyst can provide a higher catalytic efficiency than the homogeneous catalyst. The difference between the ESR spectra of mono- and bisupported catalyst can be attributed to participation of NaY in the active species.

From this plausible structural model of the bisupported catalyst, the effect on the insertion of a different monomer and the sequence distribution in the polymer chain can be explained as follows: Owing to the steric effect of NaY participating in the active species, the insertion of propylene with its larger branching group becomes difficult, so that the sequence distribution is altered. In addition, by comparing with the liquid phase ESR spectra of bi- and monosupported catalyst [Fig. 5, (a)8 and (b)8], it

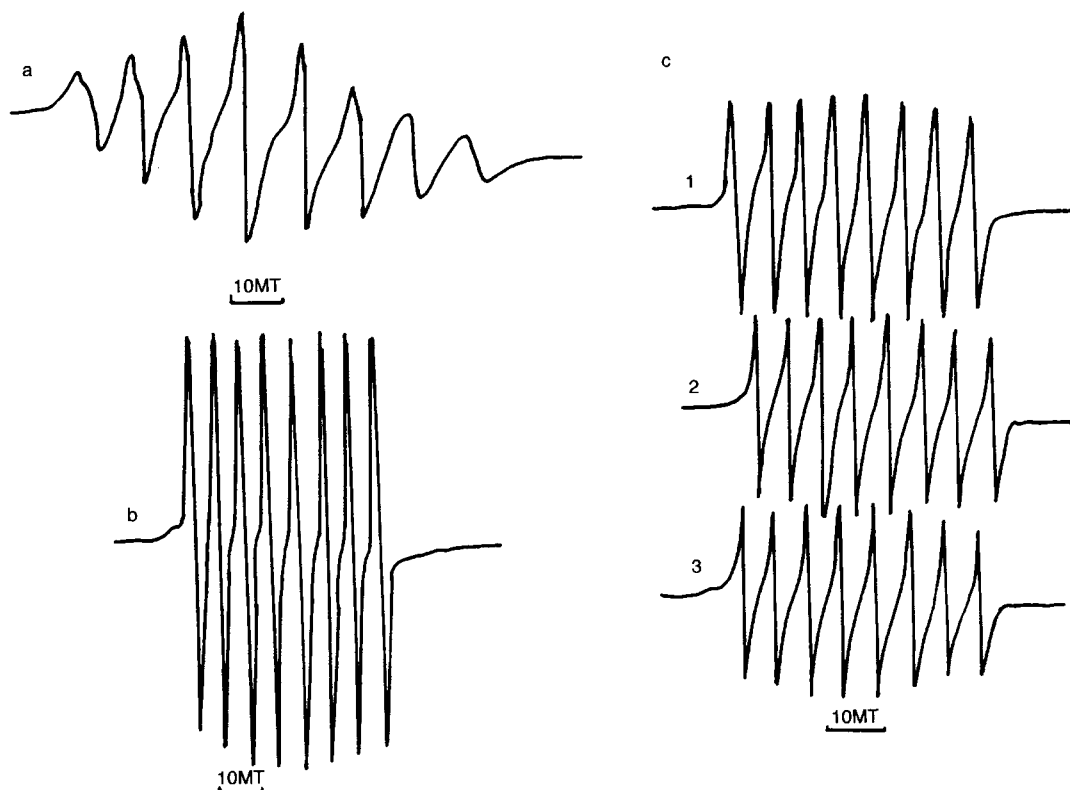


Figure 4 ESR spectra of (a) VOCl₃; (b) VOCl₃/Al₂Et₃Cl₃ (Al/V = 5); (c) VOCl₃/Al₂Et₃Cl₃, (1) Al/V = 10, (2) Al/V = 20, (3) Al/V = 30.

can be found that there was a signal evident for monosupported catalyst and no signal for bisupported catalyst, which indicates that the supporting ability of the bisupport is stronger than that of the monosupport. This is another advantage of bisupported catalysts.

CONCLUSIONS

By using VO^{2+} as a spin probe, a new method of obtaining microenvironmental information on supports was built. Through utilizing this method it was found that the dispersing ability of different zeolites increases in the order of $5A < 13X = NaY$, which corresponds to the catalytic efficiency of the catalysts when employing them as co-supports.

A new model for calculating sequence distribution and reactivity ratio from ^{13}C -NMR spectrum data

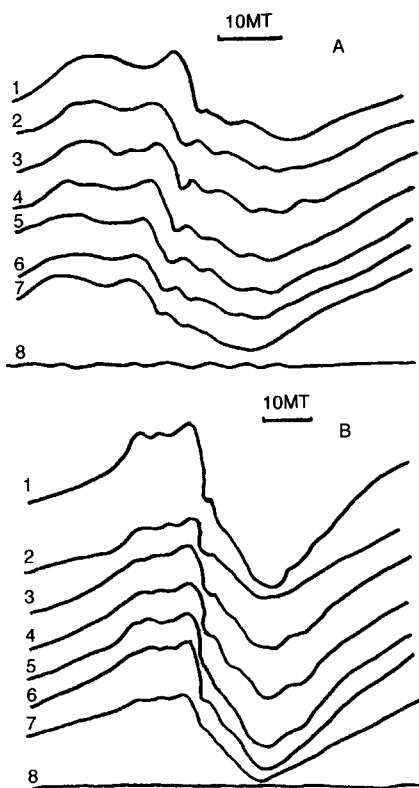


Figure 5 (a) ESR spectra of $VOCl_3/MgCl_2/Al_2Et_3Cl_3$. Al/V: (1) 0; (2) 5; (3) 10; (4) 20; (5) 30; (6) 40; (7) solid phase; (8) liquid phase; (b) ESR spectra of $VOCl_3/MgCl_2/NaY/Al_2Et_3Cl_3$. Al/V: (1) 0; (2) 5; (3) 10; (4) 30; (5) 40; (6) 50; (7) solid phase; (8) liquid phase.

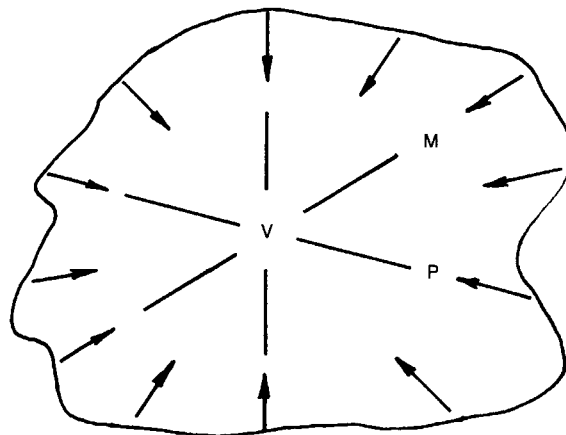


Figure 6 A plausible structure model of bisupported catalyst. M: monomer; P: polymer.

was developed. The results showed that the reactivity ratio of ethylene and the amount of EE + PE diads for bisupported catalysts were greater than for monosupported catalysts, and the sequence distribution of copolymers could be altered by addition of NaY to monosupported catalysts.

The bisupported catalysts could stabilize the active species and had stronger supporting ability. A plausible active species model for bisupported catalysts was proposed, which can be used in a rough explanation of the steric effect of bisupported catalysts.

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