

ORIGINAL RESEARCH ARTICLE

Research Progress of Pre - transition Metal Olefin Polymerization Catalyst for Salicylaldehyde Imine

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ABSTRACT

Abstract: Salicylaldehyde imine transition metal catalyst is a kind of olefin polymerization catalyst which is widely used in the coordination of salicylaldehyde imine ligand and pre-transition metal. Salicylaldehyde imine ligands have the characteristics of easily insert different substituents via organic synthesis. Therefore, the regulation of the polymerization activity, polymerization product and product distribution can be achieved by changing the steric hindrance effect, electronic effect and the number of metal active sites which near the catalytic active center. The development status of the transition metal catalyst of salicylaldehyde imine was summarized in this paper. The influence of the ligand structure of salicylaldehyde imine transition metal catalyst on the catalytic performance which involved the high selectivity ethylene trimerization, ethylene / α -olefin, / Polar monomer copolymerization, ethylene polymerization production of ultra-high molecular weight polyethylene and many other areas of olefin polymerization was elaborated and providing references for further study and industrial applications of this catalyst.

KEYWORDS: Salicylic aldehyde ligand; Former transition metal; Ethylene trimerization; Ultra high molecular weight polyethylene

Since the salicylaldehyde imine nickel complex has been found to be used to catalyze the polymerization of ethylene [1], it led to a wave of research on this kind of olefin polymerization catalyst [2]. The main reason is that the synthesis process of salicylaldehyde imine type ligand is simple, and the regulation of its catalytic activity and selectivity can be achieved by adjusting the substituents at each position of the ligand. Among them, the transition metal Ti and Zr are the most in-depth studies of salicylaldehyde imine olefin polymerization catalyst [3]. With the idea of 'ligand structure-oriented catalyst design theory' evolved [4], it break through the concept of catalytic olefin polymerization performance is determine by metal which was widely known previously, now researchers tests on the relationship of its structure and function by continue changing the substituents on salicylaldehyde imine ligand [5]. Finding shows that the steric hindrance effect of the ligand phenol ring and the imine nitrogen had different spatial stereocomplexes (Fig.1), and the catalytic properties were directly affected by the different electronegativity of the substituents. The steric hindrance effect and the electron effect of the ligand substituents on the catalytic activity center play an important role in the regulation of catalytic performance [6]. The present research work has proved that the most significant effect on the catalytic performance of salicylaldehyde imine ligand structure is phenoxy ortho substituents, and its steric hindrance effect directly affects the catalytic activity. The position of N-aryl ortho substituents Resistance and electronegativity directly affect the relative molecular mass of the polymer product. Based on the previous research work, this paper expounds the effect of the new ligand structure on the performance of salicylaldehyde imine catalyst system and the application status in the field of olefin polymerization, such as for the usage in high selectivity of ethylene trimerization, high molecular weight polyethylene, olefin copolymer and etc., which can provide further information of this type of catalyst in the field of olefin polymerization.

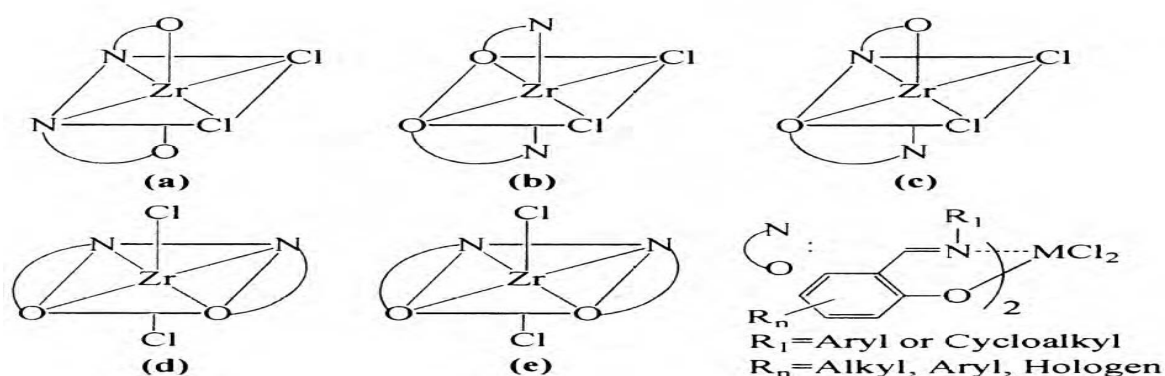


Fig.1

1. To catalyze the oligomerization of ethylene to produce alpha-olefins

Although the transition metal catalyst is widely used in the polymerization of olefins, it has been long used in the field of ethylene oligomerization, such as $\text{Ti}(\text{OR})_4\text{-AlR}_3$, which has been put into industrial production. At present, the 1-butene produced by this catalyst accounts 25% of world total output [7]. However, the catalyst structure is not easy to be adjusted the catalytic performance by inserting substituents. With in-depth study of the post-metallocene catalyst, Suzuki et al. [8] introduced oxygen-containing groups on the basis of the bidentate coordination structure of the salicylaldehyde imine catalyst for ethylene polymerization, and synthesized a series of salicylaldehyde imide tridentate Ti catalysts. Ethylene clustering results as shown in Tab. 1, the ethylene trimerization performance is significantly improved by introducing different oxygen electron donors and phenoxy ortho substituents. This is due to the fact that the introduction of OMe on the catalyst ligand structure changes the catalytic effect of the electron center and stabilizes the ethylene trimerization activity center. The increase in the steric hindrance of the phenoxy ortho substituent protects the catalytic active center from the catalyst decomposition, thereby increasing the activity of ethylene oligomerization. So far, Catalyst 3 is one of the catalyst in ethylene trimerization system with the highest catalytic activity.

A large number of studies have shown that in the ethylene polymerization catalyst system, there is a simultaneous catalytic activity center of ethylene oligomerization and ethylene polymerization, therefore by increasing the stability of specific catalytic activity center can improve the selectivity of the catalyst [9]. As in Catalyst 4 (see Fig.2), under the same conditions, the ethylene oligomerization performance was significantly lower than that of catalyst 3, and the product was predominantly polyethylene, which was due to the activation of the catalyst to produce trivalent Ti as active center which is conducive to ethylene polymerization [10].

Tab.1 Result of ethylene trimerization

General structure	Complex	R	Z	Selectivity of 1-hexene/%	Activity ^a
	1	cumyl	OPh	76.60	4×10^3
	2	cumyl	OMe	86.20	1.2×10^5
	3	adamantyl	OMe	92.30	6.6×10^6

^ag of 1-hexene/(mol Ti h)

Fig.2

With the emergence of new catalysts, the study on its mechanism has never stopped. For example, Catalyst 5, by using the isotope tracing method, had proved that the system catalyzed ethylene oligomerization mechanism is in line with the metal ring mechanism, EPR characterization proved that the byproduct PE formation is a result of the reaction process which generated trivalent Ti [11]. For the catalyst 6, the NMR and EPR results show that the divalent Ti favors the selective formation of the ethylene trimerization product, the trimerization process conforms to the metal ring mechanism, and the trivalent Ti is the active center of ethylene polymerization [12]. In addition, DFT calculations are also popular in the study of catalytic reaction mechanisms. Although it is limited to few catalytic systems [13], it is expected that, in order to further improve the performance of the salicylaldehyde imine Ti catalyst catalyzed ethylene trimerization, these research methods will also be used in the study of polymerization reaction mechanism.

The study of polymerization mechanism provides a valuable reference for designing a catalyst structure with better function. Sattler et al. [14] synthesized catalyst 7 and 8 based on the synthesis of catalyst 5 through the design of an analogous series of zirconocene propane polymerization catalysts. The results show that the catalyst 8 has the highest activity, which the effect toward metallocene catalyst is similar to the corresponding structure.

PNP-type ligand Cr complex is a common ethylene oligomerization catalyst, and there is less reports show that salicylaldehyde imine Cr catalyst used in ethylene oligomerization. Kirillov et al. [15] synthesized a series of salicylaldehyde imine Cr catalyst (Fig. 3) for ethylene polymerization. It was found that only the tridentate catalyst 9 to 11 was catalytically active and the bidentate coordination catalyst 12 has no catalytic activity, the catalysts 10 and 11 are two times more active than the catalyst 9, this is due to the naphthyl group which increases the conjugate area of the active center and stabilizes the catalytic activity center. However, the three catalysts catalyze the product of ethylene polymerization with the number of relative molecular weights ranging from 600 to 1600, which in the range of low molecular weight of polyethylene, thus it is not α -olefins.

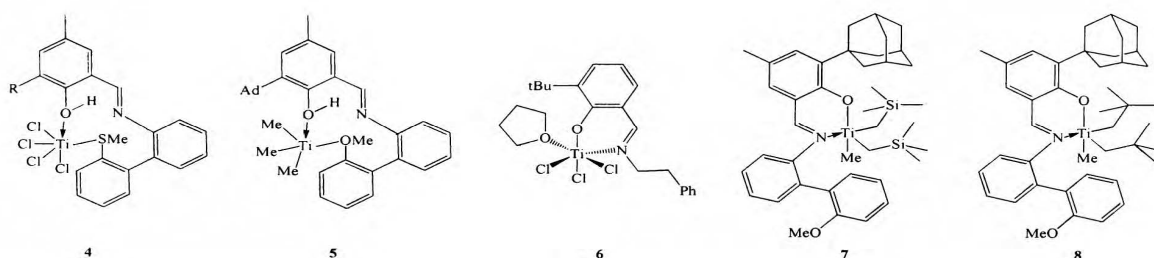


Fig. 3

At present, salicylaldehyde imine transition metal catalyst catalyzed the majority of ethylene oligomerization in the selective formation of trimerization and dimerization products, the research mainly concentrated in the Ti catalyst. The activity of ethylene trimerization is significantly affected by the electronegativity of the O-electron donor and the imine N-substituent structure in the salicylaldehyde imine ligand structure [16], and the insertion of large steric hindered substituents near the catalytic active center or the conjugated group also contribute the stabilization of the catalytic active center. Compared with the ethylene-trimeric PNP ligand Cr-based catalyst, salicylaldehyde imine transition metal catalyst is a single active center catalyst under specific structure, which is beneficial to improve the ethylene oligomerization selectivity. Current study show that by adjusting the salicylaldehyde imine transition metal catalyst structure, will develop a oligomerization catalyst with better selectivity and highest activity.

2. Catalytic Olefin Copolymerization to Prepare Functional Polyethylene

The transition metal catalyst is not only catalyzes ethylene oligomerization, but also catalyzes the copolymerization of ethylene with other monomers to prepare functional polyethylene, and the chemical structure of the catalyst has a great influence on the copolymerization properties. Among them, the phenoxy ortho substituent is one of the substituents closest to the active center, which is located on both sides of the active center plane, and size of its steric hindrance directly affects olefin molecular insertion and the stability of the active center, it have a great impact on the catalytic activity.

As a common comonomer, norbornene has a stronger nucleophilicity, the salicylaldehyde imine ligand structure increases the electrophilic activity of the active center, which is more favorable for catalyzing the copolymerization of ethylene / norbornene. Terao et al. [17] used catalysts 13 to 18 to catalyze the copolymerization of ethylene / norbornene. The catalysts 13 to 15 inhibited the insertion of norbornene due to the large steric hindrance of the phenoxy ortho-substituted R₂, thus they have no copolymerization activity. Whereas the catalyst 16 has good ethylene / norbornene copolymerization activity due to its R₂ substituent has a methyl group with a small steric hindrance.

Catalyst 17 and 18, although the steric hindrance of the R₂ substituent is more than methyl, the catalytic activity is improved by 5 to 10 times, because the phenyl group can be freely rotated about the axis, which is favorable for the insertion of norbornene, at the same time the conjugation effect of the phenyl group with the active site has stabilized the copolymerization activity center and thus increases the copolymerization activity. By comparing the catalysts 17 and 18, although the phenyl and pyrrolyl groups have similar electrophilic properties, the catalyst 18 exhibits a copolymerization activity of twice as much as that of the catalyst 17, indicating that the steric hindrance effect is the key to the copolymerization activity. Compared to phenyl group, pyrrolyl has a smaller steric hindrance, allowing for more comonomer insertion, and thus higher copolymerization activity.

The salicylaldehyde imine transition metal catalyst can also be used for ethylene / α -olefin copolymerization. In 2011, Terao et al [18] used the series of catalyst as shown in Tab. 3 to test on the effects of phenoxy ortho substituents

on the copolymerization of ethylene / α -olefins. When used for ethylene / propylene copolymerization, the phenoxy ortho position substituents R2, the copolymerization performance is quite different, and the catalytic performance is related to the α -C of the R2 substituent is either tertiary carbon or the quaternary carbon. When the α -C of the R2 substituent is tertiary carbon, the propylene insertion rate (25.5% to 26.4%) of the catalysts 13, 19 to 21 is significantly higher than that of the R2 substituents which is quaternary carbon in Catalysts 14, 15 (4.2% to 6.3%). This is due to the fact that the steric hindrance near the active center of the phenoxy ortho substituents is favorable for the insertion of propylene, thereby increasing the propylene insertion rate in the copolymer. When the phenoxy ortho position is used as the catalyst 17, the copolymerization activity of ethylene / norbornene is the same, that is, the copolymerization activity and the monomer insertion rate are greatly improved.

In addition, as early as 2008, Terao et al. [19] also found that the Group IVB transition metal catalyst can be used for the copolymerization of ethylene with oxygen-containing polar groups, which catalyzes the copolymerization of ethylene / 1-hexenoate, catalytic activity achieved 337kg Polymer / (mol Ti h), polar monomer insertion rate of 0.81%. At present, a large number of studies have found that salicylaldehyde imine structure before the transition metal catalyst (Fig.4) can be used for ethylene / polar monomer copolymerization, such as ethylene / acrylonitrile, 10-undecen-1-ol copolymerization showed good polar monomer insertion capacity and polymerization activity [20].

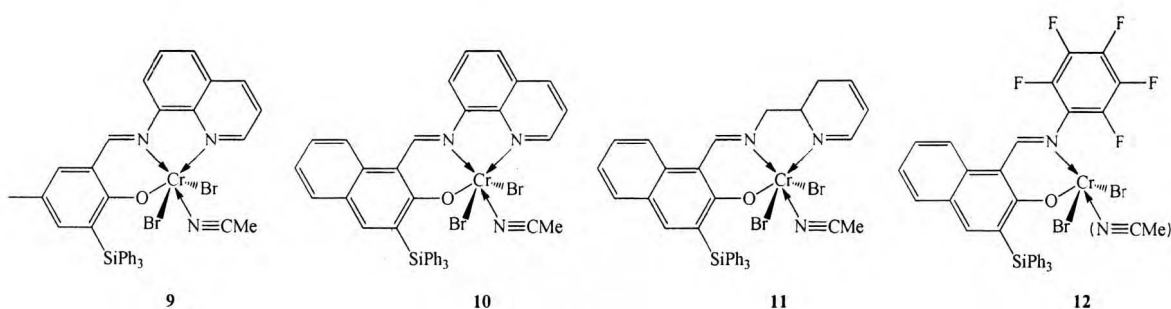


Fig.4

By analyzing the structure of the transition metal catalyst and the metallocene catalyst of salicylaldehyde imide, it is found that the zeolite of the bis-salicylaldehyde imide Ti has an octahedral structure, similar to the tetrahedral structure of the zirconocene and zirconocene catalyst and the catalyst with these structures has good polymerization properties. Huang et al. [21] synthesized a series of monocarbamate Schiff base mixed ligand Zr complex (catalyst 29 ~ 31). The effects of substituents on cyclopentadiene on the copolymerization of ethylene / 1-hexene were investigated. The results showed that when the insertion of substituents on cyclopentadiene, 1-hexene insertion rate is only 0.89% to 1.39%. This is due to the fact that the steric hindrance of the substituent inhibits the insertion of 1-hexene and the insertion rate decreases with the increase of the steric hindrance effect of the substituent. However, the catalytic activity is improved by the effect of the steric hindrance. Where the steric hindrance of the catalyst 31 was the largest, but the catalyst activity was the highest, achieving 1.2×10^6 g Copolymer / (mol Zr h). In 2014, Liu et al. [22] synthesized two novel monocarbophore Schiff base mixed ligand Zr complexes 32 and 33, and the phenoxy groups were *t* Bu substituents to catalyze the ethylene / 1-hexene copolymerization. The relative molecular mass of the activity and the polymerization product is higher than that of the unsubstituted catalyst, which is due to the electron effect of the *t* Bu substituent, where it stabilizes the cationic active center of the catalyst and increases the catalytic activity.

In addition, the adjustment of the catalyst ligand can also change the number of metal active centers, through the coordination of metal between the active center to further improve the performance of the catalyst. Han et al. [23] designed and synthesized a dinuclear salicylaldehyde imine Ti catalyst 34 which catalyzes the ethylene / α -olefin copolymerization activity and the α -olefin insertion rate is 2 times higher than that of the corresponding mononuclear catalyst 35. This is because the insertion of olefin monomer will produce hydrogen bond with the other active center and thus stabilize the polymerization activity center, and compared to single-core catalyst, dual-core catalyst active center of the local concentration increased, is conducive to increase the polymerization activity and the relative molecular mass of the polymerization product.

Salicylaldehyde imine pre-transition metal catalyst can be used to regulate the copolymerization activity and the α -olefin insertion rate by adjusting the steric hindrance of the substituents and controlling the stereostructure of the catalyst. The insertion of the comonomer can be directly controlled by the regulation of the steric hindrance of the phenoxy ortho substituents, and thereby stabilize the catalytic activity center. In addition, it is possible to effectively increase the copolymerization activity and the α -olefin insertion rate by introducing a substituent group which can conjugate with the active center or by increasing the local concentration of the metal active center by changing the ligand structure. The introduction of the cyclopentadienyl group in the ligand structure not only enables the catalyst to have a positive octahedral structure favoring the polymerization performance, but also has the advantage of high

activity and controllable insertion rate of the comonomer, and insertion of [N, O] Schiff base ligands also improves the thermal stability of the cyclopentadienyl ligand catalyst, thus effectively prolonging the catalyst life and improving the catalytic activity. Therefore, the salicylaldehyde imine transition metal catalyst has a great potential in the field of olefin copolymerization. Through the adjustment of ligand substituents, it is possible to effectively control the α -olefin insertion rate and maintain high activity. It is envisioned that salicylaldehyde imine transition metal catalysts will be used more extensively in the field of olefin copolymerization.

3. Preparation of ultra - high molecular weight polyethylene by catalytic polymerization of ethylene

Salicylaldehyde imide transition metal catalyst can form a single active center catalyst by adjusting the ligand substituents, catalyzed ethylene polymerization can obtain ultra-high molecular weight polyethylene with narrow molecular weight distribution, which overcomes the metallocene catalyst which need low temperature reaction conditions in the current industrial application, but now has a broad application prospects [24].

The relative molecular mass of the polymer products was significantly affected by steric hindrance. For example, Makio et al. [25] synthesized the catalyst 36 to 41, the relative molecular mass of the ethylene polymer product increases with the increase of the steric hindrance of the R1 substituent. This is because when the steric hindrance is large, the transition state of 6-membered ring structure is favors for the transfer of β -H to the monomer chain of ethylene, and promote the chain growth. When the steric hindrance is small, the transition state of 4-membered ring structure is not conducive to the growth of the polymer product chain [26]. The performance of the catalysts 38, 40, 41 was verified to increase the polymerization activity of the catalytic system by increasing the steric hindrance of the phenoxy ortho substituents.

Chain transfer is rarely occurs in active polymerization reaction, yet can catalyze the polymerization of ethylene to produce ultra-high molecular weight polyethylene. Weiser et al. [27] synthesized the catalysts 42 to 44, and the N-aryl ortho has an electron-attracting F substituent, which can react with the β -H on the polymer chain to give the catalytic system a characteristic of active polymerization. This indicating that the ethylene polymer products are ultra-high molecular weight polyethylene, among the catalysts, catalyst 43 has the highest polymerization activity and the polymer with highest relative molecular mass. This is due to the electron-attracting halogen-substituted groups accelerate the insertion of the ethylene molecules, and the catalyst structure with the appropriate electron effect contributes to the separation of the cationic pairs of active centers.

In addition, the imine N para position on the polymerization reaction also have a certain impact. Such as catalysts 45 and 46, which catalyze the polymerization of ethylene products are ultra-high molecular weight polyethylene. Under the same conditions, the catalyst 45 polymerization activity and polymerization products relative molecular weight is low. This is because the styryl substituents can coordinate with the active center, occupy a part of the active center, hinder the insertion of ethylene, so that the activity decreased, the relative molecular mass of polymer products also decreased [28].

Ultra-high molecular weight copolymers are less studied. Liu et al. [29] synthesized the catalyst 47 which can catalyze the copolymerization of ethylene / 1-octene to produce an ultrahigh molecular weight copolymer with a 1-octene insertion amount of up to 32.7%. Guo et al.[30] synthesized the catalyst 48 used to catalyze the copolymerization of ethylene / 1-hexene. The number average molecular weight of the copolymer was as high as 1.4×10^6 , which are the ultra-high molecular weight copolymer, and the amount of 1-hexene was 25 %. The results of the above studies show that the catalyst can effectively control the relative molecular mass of the polymerization products because of the characteristics of active polymerization of salicylaldehyde imine catalyst. Therefore, these catalysts also show good prospects in the preparation of ultra-high molecular weight polyolefin materials in the field of application.

4. Conclusion

With the development of the post-metallocene catalyst, the catalyst design theory is based on the ligand structure in control the performance of the olefin polymerization catalyst. The emergence of salicylaldehyde imine catalyst proves the importance of ligand structure in the field of olefin polymerization catalyst. It can be predicted that more high-performance olefin polymerization catalyst can be synthesized according to the influence of the ligands structure on the catalytic performance, by insertion of different substituents which has different steric hindrance and electronic effects.

The high-performance catalyst can be used in the field of polymerization where the molecular structure of polymer products is controllable, and the design of the ligand structure design will also be the dominant direction for catalyst design.

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