Recent progress in immobilization of late-transition-metal complexes with diimine ligands for olefin polymerization

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Late-transition-metal (LTM) catalysts are a family of very flexible ethylene polymerization catalysts because their catalytic performance can be easily adjusted by modifying the ligand structure. Their less oxyphilicity character, which may promote the production of copolymers from ethylene and polar comonomers, is another aspect that attracts much attention in both academic and industrial fields. The immobilization of LTM catalysts on spherical supports is a crucial step prior to their use in the industrial processes of gas-phase or slurry polymerizations. This paper reviews recent developments in supported LTM catalysts for olefin polymerization, and summarizes loading methods and mechanisms of the immobilization of LTM catalysts on inorganic, organic, and inorganic-organic materials, and the effects of immobilization on catalytic activity, polymerization mechanism, and polymer morphology.

late-transition-metal complexes, diimine, immobilization, olefin polymerization

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Transition-metal catalysis plays a key role in the polyolefin industry. The discovery of Ziegler-Natta catalysts revolutionized the industry. Titanium- and zirconium-based metallocene systems are still the workhorses in the manufacture of commodity polyolefin materials [1–3]. In contrast to complexes of early transition-metals, the late-transition-metal (LTM) complexes reported by Brookhart [4] and Gibson [5] are attracting increasing attention because of the easy preparation and modification of their Schiff base ligands [6–8]. Recently, according to different coordination forms, some LTM-based complexes with novel diimine ligands containing Fe [9–12], Co [13,14], Ni [15–21], Pd [22,23] are applied to olefin polymerization. The products obtained using such catalysts can be changed from polyethylene (PE) to oligomers by tuning the steric and electronic properties of the ligands [24]. Bulky complexes can produce high-molecular-weight branched PE, without the addition of

α -olefin comonomers, in the presence of methylaluminoxane (MAO). Some bulky catalysts with special backbone such as camphyl and acenaphthyl show highly thermal stability and good control ability for olefin polymerization [25]. Late transition-metals are more suitable for the copolymerization of ethylene with commercial polar olefins because of their better tolerance of polar functional groups. Only amorphous polymers can be obtained if the polymerization is catalyzed by homogeneous catalysts, inevitably leading to reactor fouling in industrial units. To meet the requirements of continuous industrial gas-phase or slurry polymerization units, a crucial step for the industrialization of LMT catalysts is the immobilization of such catalysts on spherical supports to obtain morphologically uniform polymer particles.

1 Immobilization methods

There are three major supporting methods applicable for the

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immobilization of LTM catalysts. The first method is direct immobilization of the LTM catalysts on carriers by physical adsorption; this method is very commonly used because it is easy to operate and inexpensive [26]. Catalysts supported by physical adsorption easily leach from the supports during polymerization and cause reactor fouling. The second method is to pretreat the supports with MAO or an alkylaluminum, and then immobilize the LTM catalysts on supports through ionic bonds formed by multicoordinated “crown” aluminoxane complexes and the active sites of the catalysts (Figure 1) [27]. The third method is immobilization of the catalyst ligands using special functional groups on supports pretreated with alkylaluminum through covalent bonds. This method is more effective than previously reported methods for reducing leaching phenomena.

2 Late-transition-metal catalysts immobilized on inorganic carriers

2.1 Late-transition-metal catalysts immobilized on SiO₂ supports

Silica is the most common inorganic support; it provides a high specific surface area, suitable distributions of pore volume and size, good mobility, an appropriate average grain diameter, and good mechanical strength. Ma et al. [28] prepared supported Fe-based diimine catalysts by immobilization of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron chloride (I) on SiO₂ treated with MAO. They used X-ray photoelectron spectroscopy to trace the changes in the binding energies of different elements of the catalysts during the support process. The results confirmed that the immobilization of the Fe-based diimine catalysts on SiO₂ is the result of the bridging effect of MAO. Compared with homogeneous catalysts, the supported catalysts had higher catalytic activities, even at low Al/Fe ratios, and performed more stably. The molecular-weight of the PE obtained was two to three times higher than that obtained under homogeneous conditions. The melting temperature was about 10°C

higher and the particle morphology was better. Xu et al. [27] immobilized the catalysts mentioned above on a novel layered calcosilicate treated with MAO, and explained the bridging effect of MAO. MAO captured hydroxyl groups on the SiO₂ surface to form multicoordinated “crown” aluminoxane complexes, which could immobilize the Fe-based diimine catalysts in the “crown” through ionic bonds, giving supported catalysts.

Earlier, Soga et al. [29] prepared a series of metallocene catalysts with special functional groups to immobilize metallocene catalysts on SiO₂ supports through covalent bonds. In recent years, similar methods have been used to prepare supported LTM catalysts. Compared with the ionic-bond supporting method, covalent bonds could give more stable attachment of active centers to the support. Some studies suggested that covalent linking of soluble metal complexes to the support was the most effective way to reduce leaching [30,31], and the negative influence on the active sites was relatively small. Schrekker et al. [32] synthesized α -diimine nickel precatalysts with an amino or hydroxyl functionality at the *p*-aryl position and precatalysts with one or two hydroxyl functionalities in the alkyl backbone (Figure 2).

The surface hydroxyl groups of SiO₂ were treated with trimethylaluminum (TMA), SiCl₄, or BCl₃ to form the linking part, which could react with the amino or hydroxyl functionalities of precatalysts to link the precatalysts with SiO₂ through covalent bonds; treatment with TMA was the most effective. Ethylene-slurry polymerization showed that the supported catalysts had high activities even at low Al/Ni ratios. The productivity increased steadily as the ethylene pressure increased from 1 to 4.5 MPa, and reached 6.0 kg-PE/g-catalyst at 4.5 MPa and 80°C. No reactor fouling as a result of catalyst leaching was observed.

LTM catalysts with different structures (Figure 3) were synthesized by Choi and Soares [33]. **1** was immobilized on the surface of SiO₂ by ionic bonds because of the absence of functionalities that can form covalent bonds with linking groups; **2** and **3** were immobilized on SiO₂ treated with alkylaluminum through covalent bonds.

Among these supported catalysts, **1** was partially extracted

Figure 1 Mechanism of support of Fe-based diimine catalyst on SiO₂.

Figure 2 Homogeneous catalysts and supported catalysts.

Figure 3 Structures of 1–3.

from the SiO_2 surface during the polymerization as a result of the weak ionic interactions between the active sites and the support surface; this led to a poor morphology. The **2**/ SiO_2 and **3**/ SiO_2 catalytic systems, supported by covalent bonds, resulted in higher activities and better morphologies. In some cases, even if covalently attached supported catalysts were used for slurry polymerization, there was still a potential risk of reactor fouling as a result of leaching of weakly attached catalyst species when alkylaluminum activators were used. In addition, to take advantage of existing heterogeneous polymerization plant infrastructure, costly activators should be avoided. Considering the above two points, the researchers added bulky anionic borates such as $\text{B}(\text{C}_6\text{F}_5)_4^-$ as internal activators during preparation of the supported catalysts to replace the extra activators in the polymerization process; higher activities and well-controlled spherical morphologies were obtained.

With the aim of achieving higher loadings of active centers in SiO_2 -supported catalysts reported in previous studies [34,35], Zheng et al. [36] modified the diimine ligands by hydrosilylation of bis(imino)pyridyl containing an allyl

group with dichloromethylsilane to introduce Si-Cl end-groups; these end-groups could react with $-\text{OH}$ groups on the SiO_2 surface. They then prepared a novel series of supported LTM catalysts by coordination reactions of metal compounds with ligands attached to SiO_2 . The metal active center loading of the supported catalyst was 45.9 mg-Fe/g-catalyst, about four times higher than that obtained by Kaul et al. [34] and Kim et al. [35]. Kim and coworkers [37] used three methods to immobilize Ni-based α -diimine catalysts on nonporous SiO_2 covalently, without using any lengthy conventional processes. In the first method, a diimine ligand with an $-\text{OEt}$ end-group reacted with $-\text{OH}$ on the nonporous SiO_2 , eliminating one molecule of EtOH , and then the metal compound was introduced. The second method was more common; the Ni-based α -diimine catalysts were prepared and then immobilized on nonporous SiO_2 . The third method was based on the second one, but with the addition of tetraethyl orthosilicate during the synthesis. The different preparation methods affected the catalytic activity. The supported catalyst prepared by the first method had higher activity and thermostability, even when the Al/Ni ratio was

as low as 100, and the highest activity of 10 g-PE/(mol-Ni Pa h) was obtained. Nonporous SiO_2 was used as a support, without any chemical or thermal treatments, which could save time.

Some researchers thought that noncovalent immobilization of LTM catalysts on SiO_2 treated with alkylaluminum was the result of physisorption. A new series of Ni-based diimine catalysts with terphenyl structure were prepared by Wegner et al. [38] and immobilized on SiO_2 treated with MAO; the author considered the loading method to be physisorption, and ascribed the leaching [39] of some catalysts from the support during polymerization to the low oxophilicity of LTMs. Gas-phase ethylene polymerization experiments showed that higher activities of up to 1 g-PE/(g-Ni Pa h) could be obtained. Scanning electron microscopy (SEM) analysis showed that the polymers replicated the morphology of the catalyst particles.

2.2 Late-transition-metal catalysts immobilized on MgCl_2 supports

MgCl_2 is another inorganic support commonly used in industry. Xu and coworkers [40] successfully immobilized Ni-based α -diimine complexes on spherical MgCl_2 supports obtained by thermal dealcoholization of $\text{MgCl}_2 \cdot 2.56\text{C}_2\text{H}_5\text{OH}$. The activity of the supported catalyst and the properties of the resultant polymers strongly depended on the dealcoholization temperature. By using catalysts on supports treated at 170°C , activities even higher than those of homogeneous catalysts were obtained. In high-pressure ethylene polymerization, the activity reached 13 g-PE/(mol-Ni Pa h). The morphology of the resultant PE particles was spherical, which was similar to that of the MgCl_2 support.

An effective method for the immobilization of Ni-based catalysts using spherical supports of composition $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ was reported by Severn and Chadwick [41]. MgCl_2 -supported catalysts for ethylene polymerization can have an activity of around 71.58 g-PE/(mol-Ni Pa h). Through a study of the resultant products and the polymerization mechanism, the authors considered that the support had an effect on chain-walking [42], resulting in higher degrees of branching in PE prepared by heterogeneous systems than had been reported for PE prepared using homogeneous systems. The branching degree of the PE increased with increasing size of the substituent groups at axial sites.

Huang et al. [43] successfully immobilized 2,6-bis(imino)pyridyl Fe, Cr, and V precatalysts on $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ supports. They studied the effects of different transition-metals on catalytic activity, molecular-weight, and molecular-weight distribution of the resultant PE, and found that the activities of heterogeneous systems were higher than those of homogeneous systems. The Fe-based catalyst gave an activity as high as 367.2 g-PE/(mol-Fe Pa h); the molecular-weight distribution of PE ranged from 3 to 12 with changes in the substituents at the 2,6-positions of the

aryl groups in the ligand. Because of the nature of Cr-based catalysts, some of the catalyst was easily leached from the support to form multi-active centers during polymerization. Although higher molecular-weights than those of PE prepared using Fe-based supported catalysts could be obtained, leaching resulted in poor morphology. An unusual result was observed when the V-based catalysts were reacted with excess MAO. In this case, alkylation of the pyridine ring took place [44], so the PE prepared using V-based catalysts had narrow molecular-weight distributions. These characteristics were maintained after immobilization.

Using supported 2,6-bis(imino)pyridyl Fe catalysts for ethylene polymerization could avoid reactor fouling and improve the morphology of the resultant PE, but the low catalytic activity is still an unsolved problem, and is the result of limitations caused by slow monomer diffusion. Chadwick et al. [45] found that the diffusion limitation can be alleviated by introducing a comonomer; moreover, incorporating a Ni-based catalyst into an MgCl_2 -immobilized Fe-based system can lead to a significant decrease in the monomer diffusion limitation, thereby further increasing the activities of the Fe-based catalysts. Activity increases equivalent to around 30–40 g-PE/(mol-Fe Pa h) were obtained. The synergistic effect was obtained with relatively small quantities of the Ni-based catalysts, so the resultant products retained the characteristics of those prepared using Fe-based catalysts, and were essentially linear and high density.

The co-immobilization of metallocene catalysts which give high-molecular-weight PE, and Fe-based α -diimine catalysts which give low-molecular-weight PE on $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ supports was investigated by Kukalyekar and coworkers [46]. Gel-permeation chromatography (GPC) analysis showed that the resultant polymer was bimodal PE, indicating that in this catalytic system there was no synergistic effect of co-immobilization on catalyst productivity, unlike the combination of metallocene catalysts and Ni-based catalysts. The ratio of high- and low-molecular-weight fractions depended on the amounts of the two catalysts. This approach resulted in an intimate bimodal blend of high- and low-molecular-weight PEs; the high-molecular-weight component suppressed the nucleation barrier to form “shish-kebab” polymer morphology. This new synthetic route makes an improvement on the base of traditional methods of preparing bimodal PE.

Choi and Soares [47] treated MgCl_2 /methanol with TMA to form the linking group $-\text{AlMe}_2$, and then prepared MgCl_2 -supported Ni-based catalysts by the reaction of one or two $-\text{NH}_2$ groups in the aryl groups of Ni-based diimine catalysts with $-\text{AlMe}_2$ in the support (Figure 4).

Researchers used a homogeneous system, an MgCl_2 -supported catalyst, and a SiO_2 -supported catalyst, respectively, to catalyze ethylene polymerization under the same conditions. The results showed that the activity of the MgCl_2 -supported catalyst was higher than that of the SiO_2 -sup-

Figure 4 Preparation of MgCl_2 -supported catalyst.

ported catalyst, and was nearly 90% of that obtained under homogeneous conditions. The polymers made using the MgCl_2 -supported catalyst were free-flowing particles that did not cause reactor fouling, although they were weaker and more porous than those prepared using the corresponding SiO_2 -supported catalyst.

Jiang et al. [48] prepared a SiO_2 - MgCl_2 bi-support by removing HCl generated from the reaction of MgCl_2 with pretreated SiO_2 (Scheme 1), and then immobilized a Ni-based α -diimine catalyst on the bi-support. The bi-supported catalyst could be used to polymerize ethylene, with high activity, using diethylaluminum chloride as an inexpensive cocatalyst, resulting in branched PE (100.9/1000C). SEM analysis showed that the polymers replicated the support morphology, indicating that the bi-supported catalyst had a uniform distribution of active sites and high porosity.

Scheme 1 Formation mechanism of SiO_2 - MgCl_2 bi-support.

2.3 Late-transition-metal catalysts immobilized on other inorganic supports

Besides SiO_2 and MgCl_2 , some other inorganic materials with special structures, such as mica, molecular sieves, and palygorskite, can be used to immobilize catalysts. Different loading methods were used for various supports.

Kurokawa et al. [49] chose fluorotetrasilicic mica with an interlayer space structure as a support for Fe-based diimine catalysts. X-ray diffraction (XRD) and thermogravimetric-differential thermal analysis of the supported catalysts confirmed the loading mechanism. Fe^{3+} was immobilized in the interlayer spaces of the mica through Na^+ -mica ion-exchange reactions, and then bis(imino)pyridyl ligands intercalated into the LTM ion-exchanged clay mineral interlayers. The catalytic activities of mica-supported catalysts decreased with increasing steric bulk of the substituent groups since sterically bulky ligands have difficulty inter-

calating into the mica interlayers.

Nanocomposites synthesized from silicates such as montmorillonoids and clays have been studied extensively. The extension strengths and heat resistances of the nanocomposites were higher than those of the original polymers or other materials mixed with silicates [50,51]. Rong et al. [52,53] were the first to use palygorskite clay as the support for Ziegler-Natta catalysts to produce PE/clay nanocomposites. The palygorskite provided a new environment as a result of clustering of palygorskite nanofibers, which provided a large surface area and strong adsorptive capacity. Yan et al. [54] immobilized Ni-based diimine catalysts on palygorskite and on palygorskite pretreated with MAO. Transmission electron microscopy showed that after MAO treatment, the densely packed nanofibers evolved into numerous nanofiber clusters consisting of single fibers. An inductively coupled plasma-atomic emission spectroscopy examination of the supported catalysts indicated that the MAO pretreatment improved the catalyst loading and resulted in high catalytic activity. Although the activity was lower than that of homogeneous systems, it was higher than that of SiO_2 -supported catalysts. The polymerization of ethylene was initiated on the active sites at the fiber surface and then PE encapsulated palygorskite fibers to form capsules. Finally, the PE/palygorskite nanocomposite was obtained.

Ni-based diimine catalysts with $-\text{NH}_2$ in the aryl groups of the ligands were prepared by Choi et al. [55], and they immobilized the catalysts on montmorillonite (MMT) with organic modifiers. The activities of MMT-supported catalysts were higher than those of homogeneous systems. The catalytic activities of the supported catalysts were almost the same, whether or not there were cocatalysts present. When the polymerization time was prolonged to 9 h, the activity of the system in the absence of cocatalysts increased 1.5-fold. XRD revealed that particle intercalation and exfoliation were initiated by the insertion of Ni-based diimine complexes into MMT galleries. SEM and TEM micrographs confirmed the formation of a nanophase of

MMT layers distributed in the polymer matrix, and showed polymer fibrils that seemed to grow from the surfaces of the clay platelets.

In recent years, molecular sieves have been used as supports for olefin polymerization catalysts. Guo et al. [56] immobilized LTM complexes capable of oligomerizing ethylene to α -olefins, and metallocene catalysts that could catalyze copolymerization of ethylene and α -olefins, on mesoporous molecular sieves (MCM-41 and SBA-15). The activities obtained using the molecular-sieve-supported Fe-based diimine catalysts in the absence of MAO were higher than those obtained using homogeneous systems, up to 43.5 g-PE/(mol-Fe Pa h). The selectivity for lower α -olefins (C_4 – C_{10}) increased significantly as a result of restriction of the molecular sieve pore size. The two-catalyst system can use ethylene as the only raw material in the preparation of linear low-density PE (LLDPE) possessing a suitable degree of branching, high molecular-weight, and broad molecular-weight distribution. The MCM-41-supported catalyst system produced LLDPE with the best physical and mechanical properties, partly because of the distribution of molecular sieves in the LLDPE structure during polymerization; this resulted in the formation of a uniform and stable structure, and PE that had excellent shear-thinning behavior and a high storage modulus. Molecular-sieve-supported hybrid catalysts were prepared by Li et al. [57] through immobilizing a Ni-based diimine catalyst and a Cp_2TiCl_2 catalyst on MCM-41 molecular sieves. The catalytic properties of the catalyst with two types of active site were investigated at low ($0^\circ C$) and high ($50^\circ C$) temperatures. MCM-41 provided a constrained nanoscale chemical environment that limited the distribution of the ethylene monomer, resulting in lower catalytic activity than that of homogeneous systems. The Ni-based diimine catalyst and Cp_2TiCl_2 catalyst produced linear PE and branched PE, respectively, and the supported hybrid catalyst improved the miscibilities of the polymer blends. The SEM results showed that the miscibility of the polymers obtained at $50^\circ C$ was the best; no phase separation was observed.

Currently, most reports are of direct immobilization of LTM complexes on molecular sieves, which does not completely avoid leaching. Supporting LTM catalysts on molecular sieves via covalent bonds can not only effectively avoid leaching, but can also provide polymer-grafted molecular sieves with improved mechanical properties. Xu et al. [58] tried many LTM catalysts, and finally succeeded

in immobilizing a Brookhart Pd-diimine catalyst on molecular sieves (SBA-15 and MSU-F) with acryloyl through covalent bonds (Scheme 2). This is the first report of the preparation of PE-grafted molecular sieves using a supported LTM catalyst. The active sites are distributed in the pore canals of the molecular sieves, and this prevents highly branched PE from blocking the pore canals. Thermogravimetric and N_2 adsorption-desorption analyses of the resultant polymers showed fast formation of long polymer grafts close to the pore openings as a result of the high activity of the Pd-catalyzed ethylene polymerization; these grafts blocked the pore openings and restricted further monomer diffusion. This phenomenon was more apparent for the SBA-15-supported catalyst. The amount of grafted PE in the composite increased with increasing polymerization time.

3 Late-transition-metal catalysts immobilized on organic carriers

Since the catalyst can remain in the polymer product when inorganic carriers are used, the residues may affect the optical and mechanical properties of the final products [59,60]. To avoid such drawbacks, replacing inorganic supports with organic materials with special structures has been investigated in industry and by academics.

Li et al. [61] modified α -diimine ligands containing allyl groups with chlorodimethylsilane to introduce reactive Si–Cl end-groups, enabling their immobilization via a direct reaction of the Si–Cl groups with –OH groups on an ethanolamine-modified Merrifield resin. After coordination of the immobilized ligand with $NiBr_2$, resin-supported Ni-based diimine catalysts were obtained. The corresponding SiO_2 -supported catalysts were prepared for comparison. It was found that the Ni loadings of the modified Merrifield resin were much higher than those of SiO_2 . The catalysis behaviors of the Merrifield-resin-supported catalysts in the presence of MAO were similar to those of the silica-supported catalysts, but with lower activities. Both catalytic systems avoided reactor fouling well.

Xia et al. [62] first synthesized hyperbranched PEs bearing different numbers of pendant acryloyl groups by nonliving chain-walking copolymerization of ethylene with 1,4-butanediol diacrylate. Hyperbranched polymers with specific acryloyl anchoring sites could be used as supports for covalent immobilization of Pd-based diimine catalysts to

Scheme 2 Formation of supported Pd-diimine catalyst.

generate hyperbranched PEs encapsulating multinuclear covalently tethered Pd-based diimine catalysts. These catalysts were used to catalyze ethylene multifunctional “living” polymerization at 2.75 MPa and 5°C, and led to simultaneous multidirectional arm growth from the hyperbranched core to form star polymers with very high molecular-weights. Alkaline hydrolysis experiments were carried out to cleave the arms from the hyperbranched PE core. GPC analysis of the polymer arms indicated a narrow polydispersity index (about 1.0). The molecular-weights of the polymer stars increased linearly with increasing polymerization time. The intrinsic viscosities of these star polymers were found to depend on the arm length rather than on the average arm number.

Although organic supports such as gel-type polystyrene and arborization polymers are effective for ethylene polymerization, and yield PE beads, their synthesis generally requires sophisticated pathways, which may limit their potential for industrial applications. Bouilhac and coworkers [63] investigated a new type of organic support based on a self-assembled copolymer of polystyrene and poly(4-vinylbenzoic acid), and immobilized Fe-based diimine catalysts on the novel support. Ethylene polymerization was carried out at an ethylene pressure of 1×10^5 Pa at 30°C. The highest activity obtained was 29.8 g-PE/(mol-Fe Pa h), when the Al/Fe ratio was 325. SEM images of the PE showed the formation of spherical particles of average diameters between 400 nm and 2 μ m. The formation of a small amount of low molar-mass particles was attributed to some homogeneous polymerization that occurred as a side reaction. Heurtefeu et al. [64] performed the anionic polymerization of isoprene in cyclohexane, initiated by *s*-BuLi, and quenched the reaction by adding benzophenone to obtain diphenylhydroxy-terminated polyisoprene (PI- ϕ_2 OH). The effects of MAO and TMA addition on PI- ϕ_2 OH were investigated by dynamic light scattering. The addition of TMA led to an increase in the particle size, with no formation of larger aggregates, whereas the addition of MAO increased the particle size through the formation of larger aggregates. PI- ϕ_2 OH with a micellar structure was used to support the tridentate bis(imino)pyridyl Fe catalyst

and a Ni-based diimine catalyst. The effect of the support on the production of PE using a PI- ϕ_2 OH-supported Fe-based catalyst was investigated; with MAO, the activity of the PI- ϕ_2 OH/Fe catalytic system reached 29.87 g-PE/(mol-Fe Pa h), which was higher than that of the PI- ϕ_2 OH/Ni system and a homogeneous system. The resultant PE particle size was strongly affected by the PE microstructure (linear or branched). Amorphous branched PE yielded large PE particles as a result of the effect of chain-walking at high temperature. A low temperature restricted chain-walking, leading to small PE particles.

A convenient one-pot method for covalently tethering an amino-functionalized Ni-based diimine catalyst to a spherical periodic mesoporous organosilica (SPMO) was reported by Bahuleyan et al. [65]. Since this one-pot method reduced the number of lengthy and sensitive preparation steps, it has good industrial potential. The SPMO-supported catalyst catalyzed ethylene polymerization with high activity [>10 g-PE)/(mol-Ni Pa h)]. TEM and SEM analyses of the PE showed that the resultant products had excellent morphologies as a result of replicating the catalyst morphology.

Hoštálek et al. [66] prepared polybutadiene (PBD) with aliphatic carboxylic acid end-groups (PBD-MA and PBD-TRIMA) by reactions of PBD-OH groups with maleic anhydride (MA) and trimesoyl chloride (TRIMA) (Scheme 3).

The high polarity of MAO had a positive effect on the self-assembly of PBD-MA, which increased the polarity of the system, leading to more stable particles. Different catalytic systems were used to catalyze ethylene polymerization under the same conditions; the activity order was PBD-MA > PBM-TRIMA > homogeneous system. Low Al/Ni ratios resulted in poor morphologies. SEM analysis of the polymers revealed that in the case of homogeneous polymerization, the particles were connected by fibers and formed clusters, which increased the viscosity, producing a negative influence on agitation. When supports were used, the micellar structures of the supports restricted the formation of branched PE, leading to the formation of a crystalline phase; this was confirmed by the higher melting temperatures and higher heats of fusion of the polymers.

Scheme 3 Synthesis of PBD-MA and PBD-TRIMA.

Figure 5 POSS-supported Pd-based diimine catalyst.

4 Late-transition-metal catalysts immobilized on inorganic-organic composites

The novel inorganic-organic composites not only possess the advantages of organic materials, such as excellent processability, toughness, and low cost, but they also retain the heat and oxidation resistances of inorganic materials. In addition, the constituents of inorganic-organic composites can be easily controlled, which is convenient for the design and clipping of materials. As a result of their many advantages, novel inorganic-organic composites have the potential for applications in many fields.

Polyhedral oligomeric silsesquioxane (POSS) has recently received much attention as a nanoscale building block, and various polymers containing covalently tethered POSS nanoparticles have been synthesized [67]. Zhang and Ye [68] reported a novel POSS-supported Pd-based diimine catalyst (Figure 5). For loading of the Pd-based diimine catalyst, a POSS bearing acrylate functionalities was chosen. The ethylene polymerization results showed that the molecular-weights of the polymers increased linearly with polymerization time, and the polydispersity index values were low (1.11–1.19). ^1H NMR spectra showed that the polymers were highly branched (88/1000C). Differential scanning calorimetry and XRD analyses indicated that POSS was present in the resultant polymers and showed the effects of POSS on the polymers.

5 Summary

Supported LTM catalysts offer new opportunities in the development of the polyolefin industry. The immobilization of LTM catalysts can not only prolong the catalyst age (some increase the activity) and stabilize the polymerization reaction, but can also void the difficulties of slow heat dissipation and reactor fouling during polymerization. The particle morphologies and processabilities of polymers prepared using supported catalysts were significantly better than those of polymers prepared using homogeneous systems. By co-immobilizing LTM catalysts with other cata-

lysts on the same support, and combining their respective catalytic properties, we can produce bimodal polyethylene or produce LLDPE using ethylene as the sole feedstock. The choice of supports that could retain (or even increase) the activities of LTM catalysts will continue to be a hot research topic. More research should focus on better applications to industrial slurry and gas-phase polymerizations, which are important in accelerating the use of LTM catalysts in industrial processes.

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