

Research Article

Synthesis and Catalytic Performances of a Novel Zn-MOF Catalyst Bearing Nickel Chelating Diimine Carboxylate Ligands for Ethylene Oligomerization

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A novel Zn-MOF[Zn₃(OH)₂L₂] was synthesized from dicarboxylate ligands with diimine groups (1,4-bis(4-CO₂HC₆H₄)-2,3-dimethyl-1,4-diazabutadiene). The physicochemical properties of the material were characterized by a series of technologies including XRD, SEM, and ICP. In order to adapt to the ethylene oligomerization process, a catalyst [Zn₃(OH)₂(L^{Ni})₂] (denoted as Cat.A) possessing active Ni²⁺ centers was prepared by a postsynthetic treatment method using dichloride nickel as a nickel source in this work. For comparison, α-diimine ligands with/without dicarboxylic acid groups reacted with dichloride nickel to obtain homogenous Cat.B and Cat.C, respectively. The effects of reaction parameters, including *n*(Al)/*n*(Ni), temperature, and pressure on the oligomerization activities and oligomers distribution were investigated. The results demonstrated that all of catalysts used with diethylaluminum chloride were active for the ethylene oligomerization. Among them, Cat.A and Cat.B showed higher catalytic activities and higher selectivities to low-carbon α-olefins at atmospheric pressure. The Cat.A exhibited the optimal catalytic activity [6.7 × 10⁵ g/(mol·Ni·h·atm)] for C₄ (91.8%) under the conditions of Al/Ni = 1500, *P* = 1.0 atm, *T* = 20°C. In addition, Cat.A and Cat.B presented large amount of ethylene polymer, while Cat.C had a higher catalytic activity of ethylene oligomerization at high pressure.

1. Introduction

Low-carbon linear α-olefins are extensively used as comonomer of linear low-density polyethylene, plasticizers, and synthetic lubricants [1, 2]. Among technologies of producing low-carbon linear α-olefins, ethylene oligomerization is a major industrial process. Today, the well-known industrial processes of ethylene oligomerization include Shell Higher Olefin Process (SHOP) employing homogeneous nickel catalysts bearing [P,O] ligands and Philips ethylene selective trimerization or tetramerization processes using homogeneous chromium catalysts [3, 4]. Although a lot of research efforts focus on homogenous oligomerization catalysts, the process has a serious drawback of separation of oligomerization products from catalysts and solvent

mixtures. The added separation process will lead to the significant increase of operation costs and environmental pollution. With respect to the green chemistry principles, heterogeneous catalysis is an environmentally friendly alternative to the traditional homogenous process. Heterogeneous catalysts using porous solids (MCM-36, MCM-22, [5] MCM-41 [6]) as supporting materials exhibit good catalysis performances for the ethylene oligomerization. Unfortunately, characteristic results show that anchored active species are not evenly located within pore channels. As a result, a rapid enrichment of polymeric waxes occurs in the part; thus the selectivity to low-carbon linear α-olefins has been seriously affected. This phenomenon is commonly encountered in ethylene oligomerization processes using porous solids as the supports of catalysts. Therefore, the development

of new supporting strategy on porous materials is desirable.

In the past decade, metal-organic frameworks (MOFs) have attracted a great deal of attention [7]. Due to their outstanding features of tunable pore sizes, high specific surface areas, and the possibility to functionalize, they have been widely used in the processes of hydrogen storage [8, 9], gas separation [10], catalysis [11], sensing [12, 13], and drug delivery [14, 15]. In particular, an important feature of MOFs as catalysts is their self-assembled metal active sites, which are uniformly distributed over porous frameworks. Recently, MOFs for ethylene oligomerization have come into notice by several research groups. Kyogoku and coworkers [16] have prepared metal-organic framework (MOF) compounds containing Ni-bipyridyl complex. The material used with diethyl aluminum chloride had high potential as a catalyst for the oligomerization of ethylene with high selectivity for linear butenes. Canivet and coworkers [17] have anchored a molecular nickel complex into a mesoporous metal-organic framework (Ni@(Fe)MIL-101) using the one-pot postfunctionalization method. It is generating a very active and reusable catalyst for the liquid-phase ethylene dimerization to selectively form 1-butene. Mlinar and coworkers [18] have reported two Ni²⁺-containing metal-organic frameworks with high concentrations of coordinatively unsaturated Ni²⁺ sites, which exhibit activity comparable to Ni²⁺-exchanged aluminosilicates but maintain high selectivity for linear oligomers. However, examples of metal-organic framework bearing metal-binding organic ligands as ethylene oligomerization catalysts compared with the before-assembled metalloorganic ligands, particularly in liquid-phase oligomerization reactions, are rare.

Here we are interested in assembling dicarboxylate ligands with diimine groups into MOF framework followed by nickel complexation with α -diimine groups to realize the self-support of nickel active sites. The difference of catalytic performances of these self-supported nickel active sites in the ethylene oligomerization between nickel sites coordinated with corresponding unassembled ligands is of interest. For this purpose, α -diimine ligand with dicarboxylic acid (L₁, Scheme 1) is synthesized according to literature [19]. Such ligand as a linker is connected by Zn^{II} ions nodes to construct MOF framework. The catalyst active Ni²⁺ centers are generated by postsynthetic treatment of MOF with dichloride nickel to form [Zn₃(OH)₂(L₁^{Ni})₂] (Cat.A). For comparison, α -diimine ligands with dicarboxylic acid groups (L₁) and without dicarboxylic acid groups (L₂) react with dichloride nickel to obtain homogenous Cat.B and Cat.C [20]. All the three catalysts are employed in the ethylene oligomerization and their catalytic performance is investigated under various reaction conditions.

2. Experimental

2.1. Material Preparations

2.1.1. Preparation of NiL₁Cl₂ (Cat.B) and NiL₂Cl₂ (Cat.C) Catalysts. NiL₂Cl₂ catalyst was synthesized according to the

method described in the literature [20]. Similarly, the mixture composed of aminobenzoic acid and 2,3-butanedione was stirred at room temperature by Schiff-Alkali condensation reaction to obtain ligand L₁ [19]. The dichloride nickel catalysts Cat.B were obtained by stirring the ligand L₁ (0.84 g, 2.6 mmol), NiCl₂ (DME) (0.57 g, 2.6 mmol) with THF (30 mL) at room temperature for 48 h. Then, the powder was washed by ether for three times and dried to obtain the NiL₁Cl₂ catalyst.

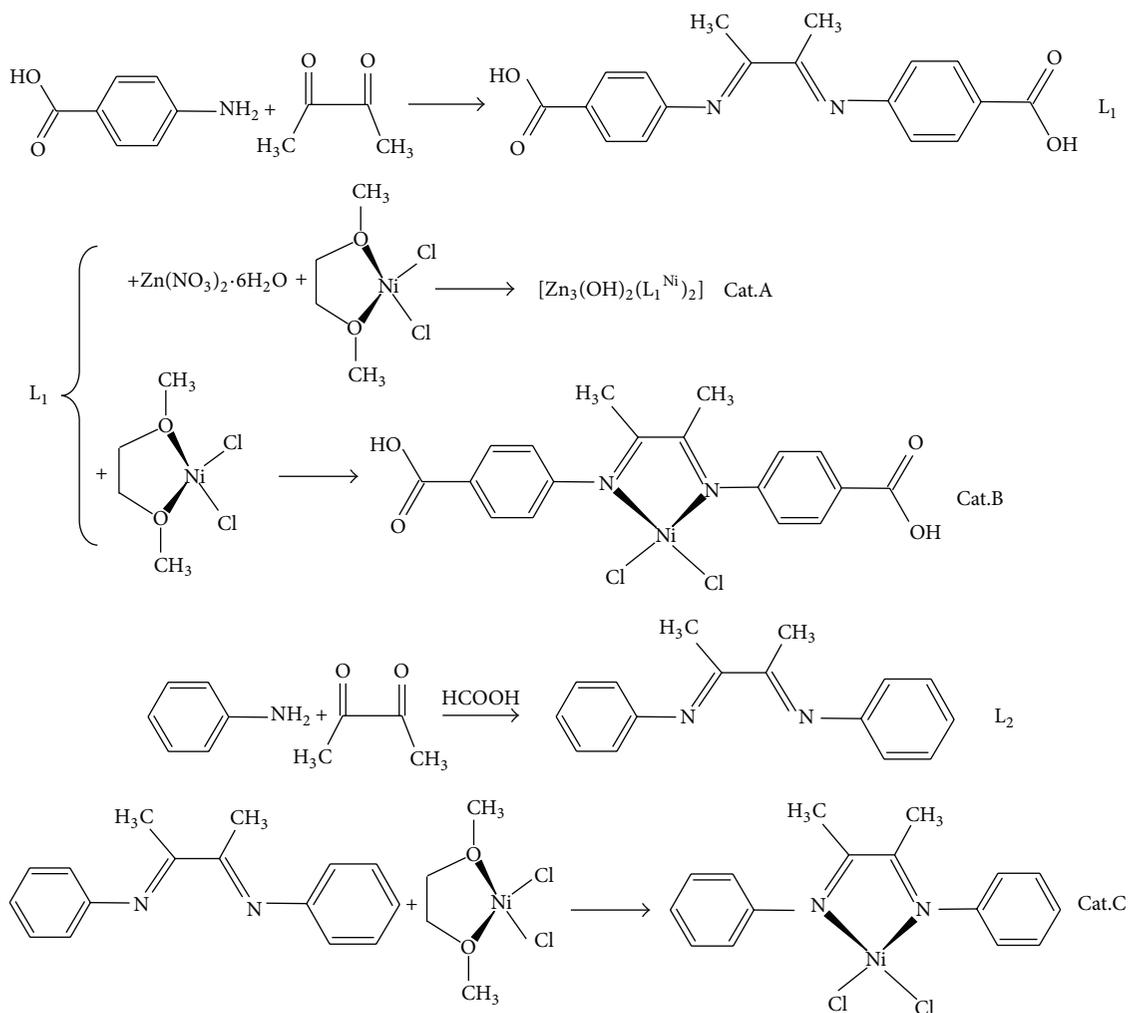
2.1.2. Preparation of [Zn₃(OH)₂(L₁^{Ni})₂] (Cat.A) Catalyst. [Zn₃(OH)₂(L₁^{Ni})₂] catalyst was synthesized according to the method described in the literature and divided into two processes [21]. First, ligand L₁ (0.97 g, 0.3 mol) was added to ethanol solution and stirred at room temperature for 4 hours, then Zn(NO₃)₂·6H₂O was added to the mixture, dripping 1.5 mL triethylamine and stirred for 8 h, and the power (Zn-MOF) was collected by repeated centrifugation and thorough washing with distilled water and dried in vacuum at 60°C for 5 h. Then, the mixture composed of Zn-MOF (0.84 g, 2.6 mmol), NiCl₂(DME) (0.54 g, 2.5 mmol), and THF (30 mL) was stirred for 48 h to obtain powder. The powder was washed by ether for three times and dried. The obtained product is [Zn₃(OH)₂(L₁^{Ni})₂] catalyst.

2.2. Characterization. The crystallinity and phase purity of the product were measured by means of XRD patterns, which were recorded in a Shimadzu X-6000 diffractometer in the 2 theta range of 1.3–30° at a scan speed of 4°/min using Cu KR radiation to determine the crystallinity. The photographs of samples were taken by scanning electron microscopy (SEM) analyses, which were performed using FEI-QUANTA 200F equipment. The chemical compositions of the samples were measured by inductively coupled plasma (ICP) technique on a Perkin-Elmer Optima 3300DV spectrometer.

2.3. Ethylene Oligomerization

2.3.1. Procedure for Atmospheric Pressure Ethylene Oligomerization and Polymerization. The as-prepared nickel catalyst was added to a fully dried Schlenk flask under nitrogen. The flask was backfilled three times with N₂ and twice with 1 atm ethylene, and then charged with toluene and AlEt₂Cl solution in turn. Under prescribed temperature, the reaction solution was vigorously stirred under 1 atm ethylene for the desired period. The polymerization reaction was quenched by addition of 10% HCl/EtOH solution. About 1.0 mL of organic solution was taken for GC analysis. The remained mixture was poured into 100 mL of ethanol to precipitate the polymer. The polymer was isolated via a filtration and dried at 60°C to constant weight in a vacuum oven. The activity of oligomer (Ao) or polymer (Ap) was calculated according to the following equation:

$$Ao (Ap) = \frac{\text{Yield (g)} / \text{catalyst (mol)}}{\text{Time (h)} \times \text{Pressure (atm)}}, \quad (1)$$



SCHEME 1: Prepared processes of the three catalysts.

wherein the yield of oligomers was calculated by referencing with the mass of the solvent on the basis of the prerequisite that the mass of each fraction is approximately proportional to its integrated areas in the GC trace, and the yield of polymer was directly obtained by weighing polymer product with an electronic balance.

2.3.2. Procedure for High-Pressure Ethylene Oligomerization and Polymerization. High-pressure ethylene polymerization was performed in a stainless steel autoclave (500 mL capacity) equipped through a solenoid valve for continuous feeding of ethylene at constant pressure. 100 mL toluene containing the catalyst precursor was transferred to the fully dried reactor under ethylene atmosphere. Then the required amount of cocatalyst (AlEt_2Cl) was injected into the reactor using a syringe. As the temperature was reached 20°C , the reactor was pressurized to prescribed pressure. After stirring for one hour, the reaction was quenched and worked up using the similar method described above for ordinary pressure reaction.

3. Results and Discussion

The NMR, element analysis, and IR characterization results of catalyst NiL_2Cl_2 and NiL_1Cl_2 are in well agreement with the literature [19], confirming the successful synthesis of homogenous diimine Cat.B and Cat.C. In the following part, the new material $[\text{Zn}_3(\text{OH})_2(\text{L}_1)_2]$ (Zn-MOF) will be characterized in detail.

3.1. Characterization of the $[\text{Zn}_3(\text{OH})_2(\text{L}_1)_2]$

3.1.1. XRD. XRD pattern of a synthesized Zn-MOF is displayed in Figure 1. The result showed that the XRD pattern of the synthesized sample was similar to that of a simulated pattern obtained from the single-crystal structure in the literature [21]. The crystallographic planes (110) and (220) of the sample have been denoted on the XRD patterns. However, there was a slight shift to lower angle region in the peak positions and the weakening of the peak intensities at higher angle region compared with those of the simulated one. The difference can possibly be caused by the unique

TABLE 1: Effects of $n(\text{Al})/n(\text{Ni})$ on the activity and distribution of oligomer^a.

Entry	Cat.	$n(\text{Al})/n(\text{Ni})$	Oligomer distribution ^b				α -Olefin ^b /%	Ao ^c	Ap ^c
			C4/ Σ C	C6/ Σ C	C8/ Σ C	\geq C10/ Σ C			
1	A	200	29.8	15.4	24.3	30.5	30.7	0.9	trace
2	A	500	42.5	30.9	20.2	6.4	37.0	1.6	0.018
3	A	1000	87.4	2.9	5.2	4.5	85.8	8.9	trace
4	A	1500	91.8	2.9	3.3	2.0	92.2	6.7	trace
5	B	200	34.4	27.5	28.4	9.7	69.1	2.5	trace
6	B	500	49.2	19.4	18.2	13.2	50.2	7.1	trace
7	B	1000	58.9	14.4	10.5	16.2	20.9	12.0	trace
8	B	1500	72.4	14.1	4.5	9.0	15.0	8.2	trace
9	C	200	29.9	16.6	15.2	38.3	24.9	4.7	—
10	C	500	35.9	22.1	18.9	23.1	19.8	5.7	—
11	C	1000	37.7	18.5	22.5	21.3	23.7	6.9	—
12	C	1500	49.6	25.6	22.8	2.0	24.4	3.2	—

Note: ^areaction conditions: $\theta = 1$ h, $c = 1 \times 10^{-4}$ mol/L, $p = 1.0$ atm, $T = 20^\circ\text{C}$; ^b α -olefin content determined by GC; ^cAo represents the activity for oligomers, Ap is the activity for polymer, both activities have the same unit of $\times 10^5$ g/(mol·Ni·h·atm).

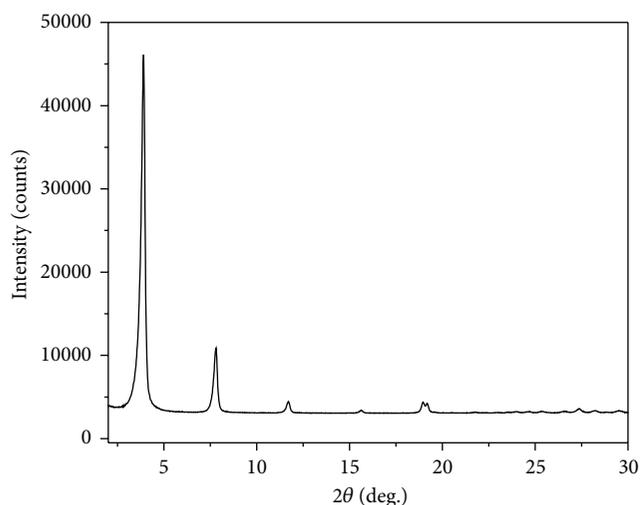


FIGURE 1: XRD pattern of Zn-MOF.

diimine ligands. As a result, it can also be concluded that the synthesized sample and the simulated one possess the similar porous structure.

3.1.2. SEM. As shown in Figure 2, the SEM images of $[\text{Zn}_3(\text{OH})_2(\text{L}_1)_2]$ present a regular flat stick crystal with average size of about $20 \mu\text{m}$ in the length direction and $3 \mu\text{m}$ in the width direction. Moreover, a small amount of irregular particles appears (Figure 2(a)), which could be unreacted ligands.

3.1.3. ICP. The elemental contents of samples were analyzed by the inductively coupled plasma (ICP) method. The analysis results showed that the content of elements C, H, and N over the Zn-MOF was 31.41, 3.08, and 4.12%. Furthermore, the total Ni content of porous coordination polymer $[\text{Zn}_3(\text{OH})_2(\text{L}^{\text{Ni}})_2]_n$ was 11.39%. Obviously, the content is

apparently higher than those of traditional heterogeneous catalysts reported by some researchers before [22]. The results also suggested that the catalyst $[\text{Zn}_3(\text{OH})_2(\text{L}^{\text{Ni}})_2]_n$ (Cat.A) had much more metal active sites for oligomerization catalysis compared to the other heterogeneous oligomerization catalysts. Much more metal active sites are helpful to improve the catalytic performance of ethylene oligomerization catalysts.

3.2. Ethylene Oligomerization and Polymerization with Et_2AlCl as Cocatalyst

3.2.1. Effects of $n(\text{Al})/n(\text{Ni})$ Values. In the present work, the catalytic activities of three catalysts (Cat.A, Cat.B, and Cat.C) were investigated. The catalytic test results were listed in Table 1.

As can be seen in Table 1, the optimal catalytic activities of all three catalysts were obtained when the $n(\text{Al})/n(\text{Ni})$ value was 1000 : 1, respectively. As suggested in the literature [23], the surface of active species being overlaid with an excess amount of Et_2AlCl can lead to the deactivation of active catalytic sites. It indicated that the proper $n(\text{Al})/n(\text{Ni})$ value was the key factor for the catalytic performance of the catalyst. However, for the product distributions, it was surprising to observe that the content of C4 oligomers increases significantly with the increase of the $n(\text{Al})/n(\text{Ni})$ values. In particular, for Cat.A, the content of C4 oligomers was obviously increased from 29.8% to 91.8%. One reason for these results is that the chain transfer rate increased with the increase of $n(\text{Al})/n(\text{Ni})$ values. Meanwhile, it also led to the decrease in the molecular weight of polyethylenes. In addition, the contents of C4 oligomers obtained over different catalysts were different; they followed the order: Cat.C (49.6%) < Cat.B (72.4%) < Cat.A (91.8%). This is because nickel active sites locate in different electronic and special environments in three catalysts. The electron withdrawing inductive effect of carboxyl substituent groups attaching to the diimine ligands in Cat.A and Cat.B has positive effects

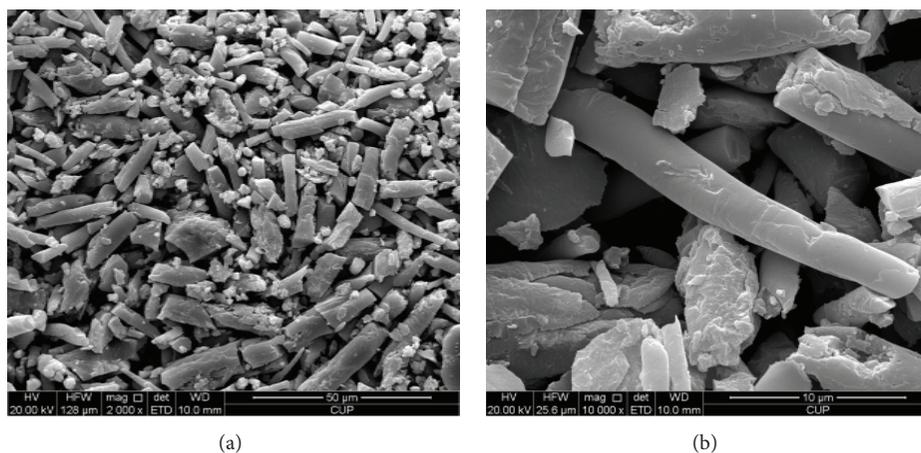


FIGURE 2: SEM images of Zn-MOF.

TABLE 2: Effects of temperature on the distribution of oligomer.

Entry	Cat.	$T/^\circ\text{C}$	Oligomer distribution				α -Olefin/%	Ao	Ap
			C4/ Σ C	C6/ Σ C	C8/ Σ C	\geq C10/ Σ C			
1	A	0	29.8	30.9	34.8	4.5	37.0	0.9	trace
2	A	20	87.4	2.9	5.2	4.5	85.8	8.9	trace
3	A	40	39.9	26.1	26.8	7.2	55.3	1.1	0.02
4	A	60	20.1	37.0	39.1	3.8	30.3	0.76	trace
5	B	0	21.8	23.9	27.1	27.2	27.2	1.6	trace
6	B	20	58.9	14.4	10.5	16.2	50.2	12.0	trace
7	B	40	50.9	26.3	22.4	0.4	30.5	5.7	trace
8	B	60	38.9	26.7	28.9	5.5	27.7	1.2	—
9	C	0	59.4	6.1	9.5	25	28.1	10.9	—
10	C	20	37.7	18.5	22.5	21.3	23.7	4.7	—
11	C	40	35.9	14.3	11.6	38.2	43.9	2.9	—
12	C	60	26.9	21.1	17.1	34.9	15.1	1.6	—

Reaction conditions: $\theta = 1$ h, $c = 1 \times 10^{-4}$ mol/L, $n(\text{Al})/n(\text{Ni}) = 1000$, $p = 1.0$ atm.

for C4 formation. Apparently, Cat.A with self-supported nickel active sites possessed the best catalytic activity for C4 oligomer.

3.2.2. Effects of Reaction Temperature. As shown in Table 2, the result phenomena for the oligomerization activities of the catalysts with temperatures changing from 0 to 60°C were the same as those for the influences of $n(\text{Al})/n(\text{Ni})$ values on the catalytic activities. The optimal activity of the catalyst was obtained at 20, 20, and 0°C for Cat.A, Cat.B, and Cat.C, respectively. And the reaction temperature was continued to increase and it resulted in the decreasing of catalytic activity. The reason might be caused by deactivation of some active centers and the lower concentration of ethylene in the reaction solution [24].

In addition, with the increasing of the reaction temperature, both catalytic reaction rate and the reversible β -H elimination rate increase, which also led to the lower selectivity for C4 [25]. In our experiments, the major products are C4

and the minor products are C6 and C8 by using Cat.A and Cat.B, while the Cat.C also produced a large amount of C10. This phenomenon might be attributed to the carboxyl group, which led to stereo-hindrance effects.

3.2.3. Effects of Ethylene Pressure. The effects of pressure on the activities and distributions of oligomer and polymer are listed in Table 3. It can be seen that when the reaction pressure changed from 10 to 20 atm, for Cat.B and Cat.C, the catalytic activity of oligomerization increased. It attributed to the higher monomer concentration around active nickel centers at a proper higher pressure. However, further increasing reaction pressure resulted in lower catalytic activities. The reason was considered the saturation of ethylene and obstruction contacted with active species by polymer. Interestingly, the oligomerization activity of the Cat.A only varied between 9.15 and 11×10^5 g/(mol·Ni·h·atm). Its activity was less affected by pressures compared with those of other catalysts. The reason can be concluded that the heterogeneous catalyst Cat.A was

TABLE 3: Effects of pressure on the distribution of oligomer.

Entry	Cat.	p/atm	Oligomer distribution				α -Olefin/%	Ao	Ap
			C4/ Σ C	C6/ Σ C	C8/ Σ C	\geq C10/ Σ C			
1	A	10	71.9	2.3	3.6	22.2	50.6	11.0	0.023
2	A	15	86.3	0.8	3.6	9.3	61.4	9.15	9.4
3	A	20	86.4	5.6	5.3	2.7	71.7	10.8	0.24
4	A	25	87.6	6.0	4.6	1.8	72.3	9.25	0.025
5	B	10	58.9	2.2	1.9	37.0	50.2	13.0	0.65
6	B	15	66.5	23.5	4.6	5.4	48.8	19.5	22.5
7	B	20	93.0	3.2	2.4	1.4	60.4	24.0	34.0
8	B	25	94.9	1.1	2.4	1.6	93.4	10.0	5.0
9	C	10	39.7	25.9	24.1	10.3	31.7	16.0	0.19
10	C	15	44.0	18.4	13.1	24.5	36.3	69.0	0.24
11	C	20	49.0	20.2	11.2	19.6	51.4	108	0.38
12	C	25	48.2	12.6	10.2	29.0	71.4	16.3	0.225

Reaction conditions: $\theta = 1$ h, $n(\text{Al})/n(\text{Ni}) = 1000$, $T = 20^\circ\text{C}$, $c = 1 \times 10^{-4}$ mol/L.

insoluble in the toluene. Moreover, Ni active sites were able to be effectively immobilized and to be evenly distributed on the metal-organic framework of the catalyst.

Comparing the catalytic activities over Cat.B and Cat.C, it is able to be found that the Cat.B with carboxyl groups in diimine ligands was inferior to the Cat.C without carboxyl groups in diimine ligands. However, the content of C4 compounds for the Cat.B had a distinct advantage over that for the Cat.C. The phenomena were due to the fact that the electron withdrawing effects of the carboxyl groups in Cat.B decreased the electron cloud density of nickel centers and thus increased its infinity with ethylene molecules. Compared with the results at 1 atm, the higher pressure showed that the activity of polymer remarkably increased, especially for Cat.A and Cat.B. It can be explained that the propagation rate was faster than hydrogen elimination rate at higher pressure [26].

4. Conclusions

An original Zn-MOF[$\text{Zn}_3(\text{OH})_2\text{L}_2$] was synthesized by the self-assembly of diimine ligands (1,4-bis(4- $\text{CO}_2\text{HC}_6\text{H}_4$)-2,3-dimethyl-1,4-diazabutadiene). In addition, the novel ethylene oligomerization catalyst [$\text{Zn}_3(\text{OH})_2(\text{L}_1^{\text{Ni}})_2$] was successfully prepared by a postsynthetic treatment method. The ICP characterization results demonstrated that this material possessed a higher Ni content than traditional heterogeneous catalysts. All catalysts showed the catalytic performance of ethylene oligomerization under various reaction conditions. Among the catalysts, the heterogeneous Cat.A exhibited the optimal selectivity for the low-carbon olefin C4. It was attributed to carboxyl electronic effects and space-confined channel effects. It is noteworthy that the Cat.B with dicarboxylic acid groups had the best activity obtained at 20°C . The activity was higher than that of the Cat.C without dicarboxylic acid groups (obtained at 0°C). Obviously, the system temperature had a distinct influence on the catalytic performances. Compared with Cat.C, the dicarboxylic acid groups of Cat.A and Cat.B played important roles in promoting ethylene polymers at high pressure. Furthermore, the system pressure

also presented a significant effect on the activities of the catalysts.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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