

Vinyl Polymerization of Norbornene over Supported Nickel Catalyst

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ABSTRACT: A series of nickel complexes, bis(salicylideneimine)nickel(II), were supported on spherical MgCl_2 and SiO_2 . Scanning electron microscopy, energy-dispersed X-ray spectroscopy, and the BET method for surface areas measurements were utilized to examine the supporting process of the catalysts. The particle morphology of the original support is retained and replicated throughout the

supported catalyst preparation and norbornene polymerization. Spherical polymer particle morphology was achieved, without reactor fouling. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2233–2240, 2006

Key words: nickel catalyst; vinyl polymerization; polynorbornene; morphology; MgCl_2 -supported catalyst

INTRODUCTION

In recent years, nickel-based complexes are becoming one type of important catalysts for vinyl polymerization of norbornene because of their high catalytic activities.^{1–6} We have synthesized various nickel complexes bearing ligands of $[\text{N},\text{O}]^{7–9}$ and $[\text{P},\text{N}]^{10}$ for norbornene polymerization. Those homogeneous catalysts, however, result in serious fouling of the reactor in polymerization process. In general, reactor fouling could be avoided via catalyst supporting on suitable substrates. Significant efforts have been made to immobilize metallocene catalysts on inorganic or polymeric materials.^{11–16} For late transition metal catalysts, silica,^{17–24} silica–alumina derivatives,^{25–27} MgCl_2 ,^{28–32} and polymeric materials^{33–35} were used as support in the preparation of supported catalysts. To the best of our knowledge, there is no report on supporting catalysts for vinyl polymerization of norbornene.

In this work, a series of structurally characterized nickel complexes $\{[\text{N},\text{O}]_2\text{Ni}\}$ 1–5 were studied as precatalysts for the vinyl polymerization of norbornene (Scheme 1).^{8,9} The nickel complexes were supported on spherical MgCl_2 and SiO_2 . The morphologies of supports and supported catalysts as well as the resulting polymeric particles were carefully investigated. The particle morphology of the original support is retained and replicated throughout the supported catalyst preparation and norbornene poly-

merization. Moreover, these polymers produced with the supported catalysts showed higher molecular weights than those of the homogeneous analogues. Herein the preparation of spherical MgCl_2 supported nickel catalysts and the behavior of norbornene polymerization are reported.

EXPERIMENTAL

Materials

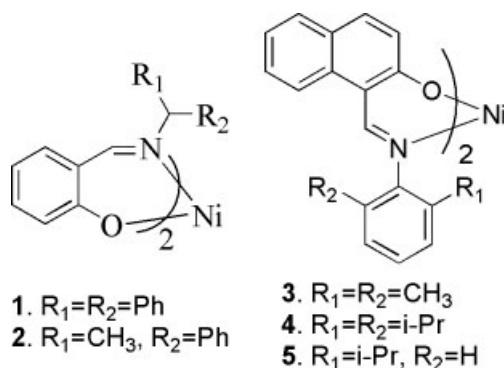
The precatalysts 1–5^{8,9} were obtained by a method previously described. Methylaluminoxane (MAO) was purchased from Albemarle as a 1.4M of toluene solution. Norbornene (from Acros) was purified by distillation over potassium and used as a solution in toluene. Spherical $\text{MgCl}_2 \cdot n\text{EtOH}$ ($n = 2.97$, measured by GC analysis) support was prepared according to the literature.^{28,36} Grace 955 silica was obtained from Daqing Petro-Chemical (China). Toluene and hexane were distilled over sodium benzophenone prior to use.

Typical preparation of MgCl_2 supported nickel catalyst SNC-1

To 40 mL hexane solution containing 4.54 g spherical $\text{MgCl}_2 \cdot 2.97\text{C}_2\text{H}_5\text{OH}$ (19.6 mmol) support in a 500 mL four-necked flask, 29 mL MAO toluene solution (1.4M, 41 mmol) solution was added over a period of 30 min and reacted at -30°C for 4 h. The slurry was filtered under N_2 and the solid was washed twice with *n*-hexane (30 mL each time), dried under N_2 . The resulting powder was placed in the flask containing 30 mL toluene and the slurry was stirred at 25°C , 50 mL toluene containing nickel complex 1 (0.22 mmol) was added to the slurry and stirred for

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Scheme 1 Nickel complexes 1–5.

4 h at 25°C. The final product was washed with toluene, until the liquid layer above became colorless. The solid catalyst (SNC-1) was dried under vacuum until free flowing conditions were reached.

Preparation of $MgCl_2$ supported nickel catalyst SNC-2 to SNC-11

Catalyst SNC-2 was prepared similarly according to the procedure for catalyst SNC-1, but spherical $MgCl_2$ was treated to support MAO at 0°C. The difference between catalyst SNC-1 and SNC-3 is, the amount of nickel complex 1 was 0.22 mmol for SNC-1 while 0.88 mmol for SNC-3. SNC-4 to SNC-7 were prepared according to the procedure of catalyst SNC-1; however, the spherical $MgCl_2$ have different ethanol content in the $MgCl_2$ /ethanol adduct supports. Employing different nickel complexes, SNC-8 to SNC-11 were prepared following the same procedure for catalyst SNC-1 with precatalysts 2–5, respectively.

Preparation of silica supported nickel catalyst SNC-12

Grace 955 silica was calcinated at 400°C for 6 h and dried at 200°C for 2 h in vacuum. Then it was cooled to room temperature and maintained in a pure nitrogen atmosphere. To a three-necked flask, 2.64 g of silica was suspended in 100 mL hexane, 30 mL MAO toluene solution (1.4M, 42 mmol) was added and stirred at 25°C for 4 h. The mixture was filtered, washed several times with *n*-hexane (30 mL each time), dried under N_2 . The MAO-treated silica was then mixed with 60 mL solution of 0.7 mmol of nickel complex 1. The mixture was stirred vigorously for 4 h at 25°C. The solid was filtered, washed several times with toluene, and then dried under vacuum at room temperature.

SNC-13 was prepared using the similar procedure mentioned above except that 15 mL MAO toluene solution used.

With the aim of quantifying the leaching amount of the active complex occurring throughout the polymerization, we suspended 0.13 g of SNC-6 in 25 mL of toluene and then added 7.14 mL of MAO

(Al/Ni = 2000) under vigorous stirring. The suspension was stirred for 2 h at 25°C under an inert atmosphere. The solid was separated, the toluene washings were evaporated under reduced pressure, and the solid residue was dissolved in 10 mL of 1M H_2SO_4 . The Ni content was determined by spectrophotometry analysis. The same procedure was followed for SNC-12. The analysis of the solid residue did not reveal any appreciable amount of nickel precursor. On account of these results, spherical $MgCl_2$ and silica appear to be very promising supporting materials for the immobilization of tailored homogeneous catalysts for obtaining a new class of heterogeneous catalytic systems.

Characterization

The morphologies of the PNB particles and catalysts were examined on a HITACHI S-4300 scanning electron microscope (SEM). Elemental analysis was performed with spectrophotometry (Shimadzu UV-2401PC, Japan) and titration technique. The distribution of Al and Ni on the support was characterized using energy-dispersed X-ray spectrometer (EDX) analysis (SEM Model HITACHI S-4300). Samples for EDX analysis were prepared as follows: the supported catalysts were embedded in an epoxy resin and cured at 60°C for 24 h. Afterwards, the samples were cut with a diamond knife in a LEICA model Ultracut microtome at room temperature using standard methods. The cross-sectioned specimens were coated with gold layer by using an electron impact evaporator (C-IKO model IB-3) to increase the conductivity. Nitrogen adsorption–desorption isotherms were measured at 77 K using an ASAP2010 volumetric adsorption apparatus from Micrometrics. Prior to the BET analysis, the samples were degassed at 200°C for 2 h.

Molecular weights were determined by a Waters Alliance GPCV 2000 system (USA) at 135°C in 1,2,4-trichlorobenzene with polystyrene narrow distribution standards. IR spectra were recorded on a PERKIN ELMER system 2000 FT-IR spectrometer. 1H and ^{13}C -NMR spectra of the poly(norbornene)s were recorded on a Bruker BMX-400 instrument. Chemical shifts were expressed in ppm using TMS as internal standard.

Polymerization of norbornene

In a 100 mL Schlenk tube, the supported nickel catalyst (5 μ mol Ni), 14.08 mL of toluene, and 3.78 mL solution of norbornene in toluene (6.61M, 25 mmol of norbornene) were, respectively, introduced. The polymerization was initiated by addition of a 1.4M (10%) solution of MAO (7.14 mL, 10.0 mmol) in toluene via syringe. After 60 min, the polymerization was terminated by pouring into 200 mL acidic methanol (methanol : HCl_{conc} = 95 : 5). The polymer was

TABLE I
Element Analysis and BET Analysis of Supported Catalysts

Catalyst	Precatalyst	Support	T ₁ ^a	Ni/wt %	Mg/wt %	Al/wt %	BET surface area (m ² /g)	Pore volume (mL/g)	Average pore diameter (Å)
SNC-1	1	MgCl ₂ ·2.97EtOH	-30	0.18	10.32	7.65	1.5	0.018	192
SNC-2	1	MgCl ₂ ·2.97EtOH	0	0.28	9.83	7.74	67.2	0.077	46
SNC-3 ^b	1	MgCl ₂ ·2.97EtOH	-30	0.77	10.08	5.75	0.2	0.010	2107
SNC-4 ^c	1	MgCl ₂ ·0.38EtOH	-30	0.26	21.52	3.49	18.7	0.093	198
SNC-5 ^c	1	MgCl ₂ ·1.30EtOH	-30	0.24	16.87	3.60	12.3	0.047	152
SNC-6 ^c	1	MgCl ₂ ·1.72EtOH	-30	0.23	16.22	5.12	5.4	0.022	162
SNC-7 ^c	1	MgCl ₂ ·2.44EtOH	-30	0.21	12.32	6.87	3.9	0.020	154
SNC-8	2	MgCl ₂ ·2.97EtOH	-30	0.50	13.87	7.26	6.3	0.021	134
SNC-9	3	MgCl ₂ ·2.97EtOH	-30	0.28	11.04	7.55	6.2	0.022	142
SNC-10	4	MgCl ₂ ·2.97EtOH	-30	0.04	10.46	5.05	7.1	0.025	214
SNC-11	5	MgCl ₂ ·2.97EtOH	-30	0.22	10.58	5.97	2.9	0.013	185
SNC-12	1	SiO ₂	-30	0.80	0	9.21	218.6	0.83	151
SNC-13	1	SiO ₂	-30	0.82	0	7.10	203.6	0.87	171

^a The temperature during the step of treating spherical MgCl₂ support with MAO.

^b The amount of **1** added in SNC-3 was 0.88 mmol.

^c The catalysts SNC-4, -5, -6, and -7 were prepared using similar method as SNC-1. For the catalyst SNC-4, spherical MgCl₂·2.97C₂H₅OH support was thermally pretreated at 120°C under nitrogen for 2 h, followed by reaction with MAO at -30°C. The catalysts SNC-5, SNC-6, and SNC-7 were prepared similarly except that the support was thermally pretreated at 100, 80, and 60°C, respectively.

isolated by filtration, washed with methanol, and dried in vacuum at 100°C for 100 h. The IR spectra of the poly(norbornene)s obtained with the supported catalysts showed absence of double bond at 1620–1680 cm⁻¹. The conversion was calculated by gravimetric analysis of the polymer.

RESULTS AND DISCUSSIONS

Effects of precatalysts on catalyst activity and polymer properties

As shown in Table I, the content of Ni on the support greatly decreased with the increase of ligand's steric congestion or bulky backbone. The Ni loading increased in the order of SNC-10 < SNC-1 < SNC-11 < SNC-9 < SNC-8. SNC-10 prepared from complex **4** with isopropyl substituents in the 2,6-positions of the aryl ring had

the lowest nickel content. However, the decrease in average pore diameter followed the contrary order of SNC-10 > SNC-1 > SNC-11 > SNC-9 > SNC-8. It may be concluded that the nickel active sites were constructed in the pores and along the pore openings.¹⁵

The supported catalysts performed good activities for norbornene polymerization. It was obvious that in combination with the same support (MgCl₂·2.97C₂H₅OH), the good activities were obtained with the precatalysts **1**, **2**, and **3**, whereas catalysts with nickel complexes **4** and **5** showed lower activities of about 10–30% of that obtained using **1**. The solvent played an important role on the catalytic activity. The lower activity was observed in hexane while higher activity was obtained in toluene. However, higher molecular weights of the resulted poly(norbornene) were obtained when hexane was used as solvent

TABLE II
Polymerization of Norbornene with Supported 1–5^a

Entry	Catalyst	Precatalyst	Solvent	Yield (%)	Activity (Kg PNB/mol Ni·h)	M _w (×10 ⁶ g/mol)	M _w /M _n PDI
1	SNC-1	1	Toluene	59.7	281	1.61	4.91
2	SNC-1	1	Hexane	50.6	238	1.87	3.85
3	SNC-8	2	Toluene	48.7	201	1.31	4.74
4	SNC-8	2	Hexane	39.9	165	1.33	4.10
5	SNC-9	3	Toluene	45.7	198	1.53	5.23
6	SNC-9	3	Hexane	32.5	153	1.64	4.97
7	SNC-10	4	Toluene	5.7	27	1.54	5.02
8	SNC-10	4	Hexane	4.4	21	1.59	4.44
9	SNC-11	5	Toluene	15.7	74	1.52	5.37
10	SNC-11	5	Hexane	14.1	70	1.62	4.05

^a Polymerization conditions: 5 μmol of Ni; 25°C; reaction time, 60 min; total volume, 25 mL; M/Ni = 5000; cocatalyst, MAO.

TABLE III
Polymerization of Norbornene with Supported 1^a

Entry	Catalyst	Yield (%)	Activity (Kg PNB/mol Ni·h)	M_w ($\times 10^6$ g/mol)	M_w/M_n PDI
1	SNC-1	59.7	281	1.61	4.91
11	SNC-2	42.7	201	1.39	5.55
12	SNC-3	42.1	198	2.17	6.42
13	SNC-7	52.5	247	1.28	5.52
14	SNC-6	56.9	268	1.98	5.70
15	SNC-5	53.7	253	1.52	4.97
16	SNC-4	51.6	243	1.50	5.76
17	SNC-13	55.7	262	1.66	6.02
18	SNC-14	55.3	260	1.63	5.94

^a Polymerization conditions: 5 μ mol of Ni; solvent = toluene; 25°C; reaction time, 60 min; total volume, 25 mL; M/Ni = 5000 ; cocatalyst, MAO.

instead of toluene. On the basis of entries 1 and 2, the dispersity index (PDI) of polymer was 4.91 in toluene compared with 3.85 in hexane (Table II).

Effects of supporting condition on catalyst activity and polymer properties

To investigate in detail of the polymerization, the precatalyst 1 was typically investigated under different supporting procedures and reaction conditions. MAO was used to treat the support at different temperatures, then the resultant was used to support the nickel complexes. Table I presents the information of elemental analysis and surface areas. It was assumed that the reaction of MAO and the alcohol in the support fixed MAO on the carrier. The nickel complex reacted with MAO on the support and anchored into the aperture of the support. It is known that the treatment of spherical $MgCl_2 \cdot nEtOH$ adduct produces dealcoholization without structure collapse.³⁶ To evaluate the effect of alcohol on the impregnation

of nickel-based complex, the support was thermally pretreated at different temperature using a fluidized bed reactor, followed by the reaction with MAO. Then nickel-based catalyst solution was mixed with MAO/ $MgCl_2$. The results in Table I indicate that the temperature of pretreatment greatly influenced the Al and Ni loadings. As the result, Al loading on the support greatly decreased with the decreasing of the ethanol content in the $MgCl_2$ /ethanol adducts. The MAO loading increased in the order of SNC-4 < SNC-5 < SNC-6 < SNC-7 < SNC-1. The Ni loading increased in the order of SNC-1 < SNC-7 < SNC-6 < SNC-5 < SNC-4. The BET surface areas and pore volume increased with the decreasing of the ethanol content in the $MgCl_2$ /ethanol adduct.

The temperature of treating spherical $MgCl_2$ with MAO somehow affected loading of nickel complexes on the carrier. The higher temperature (SNC-2, 0°C) enhanced the Ni adsorption. However, the catalyst SNC-3 with the highest content of Ni performed lower catalytic activity. The maximum molecular weight can

TABLE IV
Norbornene Polymerization using Catalyst SNC-6^a

Entry	Catalyst	Temp (°C)	Time (min)	M/Ni	Yield (%)	Activity (Kg PNB/mol Ni·h)	M_w ($\times 10^5$)	M_w/M_n
19	SNC-6	25	60	2500	32.2	76	9.01	4.19
20	Ni(II) ^b	25	60	2500	58.2	136	3.54	3.17
14	SNC-6	25	60	5000	56.9	268	19.8	5.70
21	Ni(II) ^b	25	60	5000	87.4	412	14.4	4.41
22	SNC-6	25	15	7500	47.2	1333	22.3	6.44
23	SNC-6	25	30	7500	72.5	1024	24.9	7.29
24	SNC-6	25	60	7500	83.3	588	23.1	6.96
25	SNC-6	25	120	7500	95.2	336	22.9	6.45
26	SNC-6	25	240	7500	99.4	175	22.8	6.52
27	SNC-6	25	60	10000	65.9	621	26.4	7.56
28	SNC-6	0	60	5000	58.0	273	27.1	8.08
29	SNC-6	12.5	60	5000	57.1	269	23.4	6.40
30	SNC-6	37.5	60	5000	54.8	258	15.1	5.81
31	SNC-6	50	60	5000	52.9	249	14.7	5.72

^a Polymerization conditions: 5 μ mol of Ni; solvent = toluene; total volume, 25 mL; cocatalyst, MAO.

^b Not supported (homogeneous catalyst).

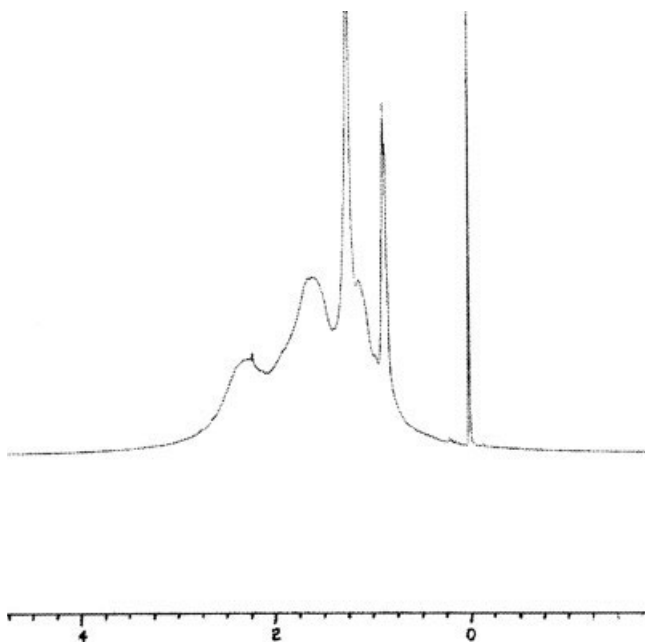


Figure 1 ^1H -NMR spectra of polynorbornene (entry 19) recorded in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at 25°C .

be obtained with polymer by SNC-3, which is densely loaded with nickel. According to Table III, there was no significant change in polymer molecular weight relying on various ratio of EtOH to MgCl_2 . SNC-6 was chosen for study in detail of norbornene polymerization at different conditions for its good morphology. The catalyst activities are in the range of 198–281 Kg PNB/mol Ni h, and the molecular weights were in the range of 1.28×10^6 to 2.17×10^6 g/mol.

For comparison purposes, we used silica as support also. Though the amount of MAO used in preparation of SNC-12 was two times of that in preparation of SNC-13, SNC-12 and SNC-13 exhibited very similar catalytic results. The high surface area of SNC-12 and SNC-13 could not be proved to have a large effect on the norbornene polymerization reaction compared with the lower surface area catalyst SNC-1 to SNC-11.

Effects of polymerization conditions on catalyst activity and polymer properties

Increase of monomer concentration (reaction volume and catalyst amount were kept constant), which serves as the increase of the M/Ni ratio (M refers to monomer of norbornene), causes rapid increase of catalytic activities combined with a drastic increase of molecular weight. The explanation is similar to that of the regular olefin polymerization, in that case, higher concentration of monomer gives rise to higher catalytic activity and higher molecular weight. The morphology of the polynorbornene particles changed gigantically with monomer concentration. At an M/

Ni ratio of 10,000 : 1, polymer particle started to agglomerate along with reactor fouling, and therefore morphological control was gradually lost.

Compared with the homogeneous catalyst counterparts under the same reaction conditions, the supported catalyst showed relative lower catalytic activity. The activity of the heterogeneous catalyst is about 50–70% of its homogeneous catalyst under the same conditions (entry No 19, 20, 14, 21) in Table IV, and this is a well-known phenomenon^{27,37–40} in olefin polymerization using supported catalyst and believed to be due to steric effects exerted by support on catalyst active centers, thus limiting the monomer incorporation ability. However, comparing entries 19 and 20, we observed that the molar mass of the polynorbornene obtained with SNC-6 was around two times higher than that obtained with the homogeneous catalyst **1**. The broadening of the molecular weight distributions was evident with the supported catalyst systems. Often the PDI values in the literature are higher for supported catalysts compared with homogeneous system.^{32,37,41} A PDI of 5.70 was observed in entry 14 indicating multisite behavior of the immobilized catalyst.

The longer the reaction time was used, the higher the yield of polymer was obtained. The results of norbornene polymerization with different time are presented in Table IV (entry No 22–26). The conversion of norbornene into PNB was almost complete at 240 min. These results are in agreement with previous results by our group in norbornene polymerization with a soluble system.⁸

The norbornene polymerization proceeded at different temperatures. Both the catalytic activity and molecular weight of PNB decrease with an increase in temperature. It can be explained that the active species show low thermal stability in toluene. Increase of temperature from 0°C to 50°C results in the decrease of catalytic activity from 273 to 249 Kg PNB/(mol Ni h) and molecular weight M_w from 2.71×10^6 to 1.47×10^6 g/mol.

The temperature dependence reported herein is similar to that observed for equivalent unsupported

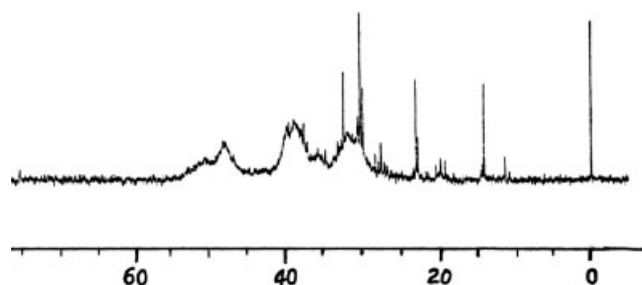


Figure 2 ^{13}C -NMR spectra of polynorbornene (entry 19) recorded in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at 25°C .

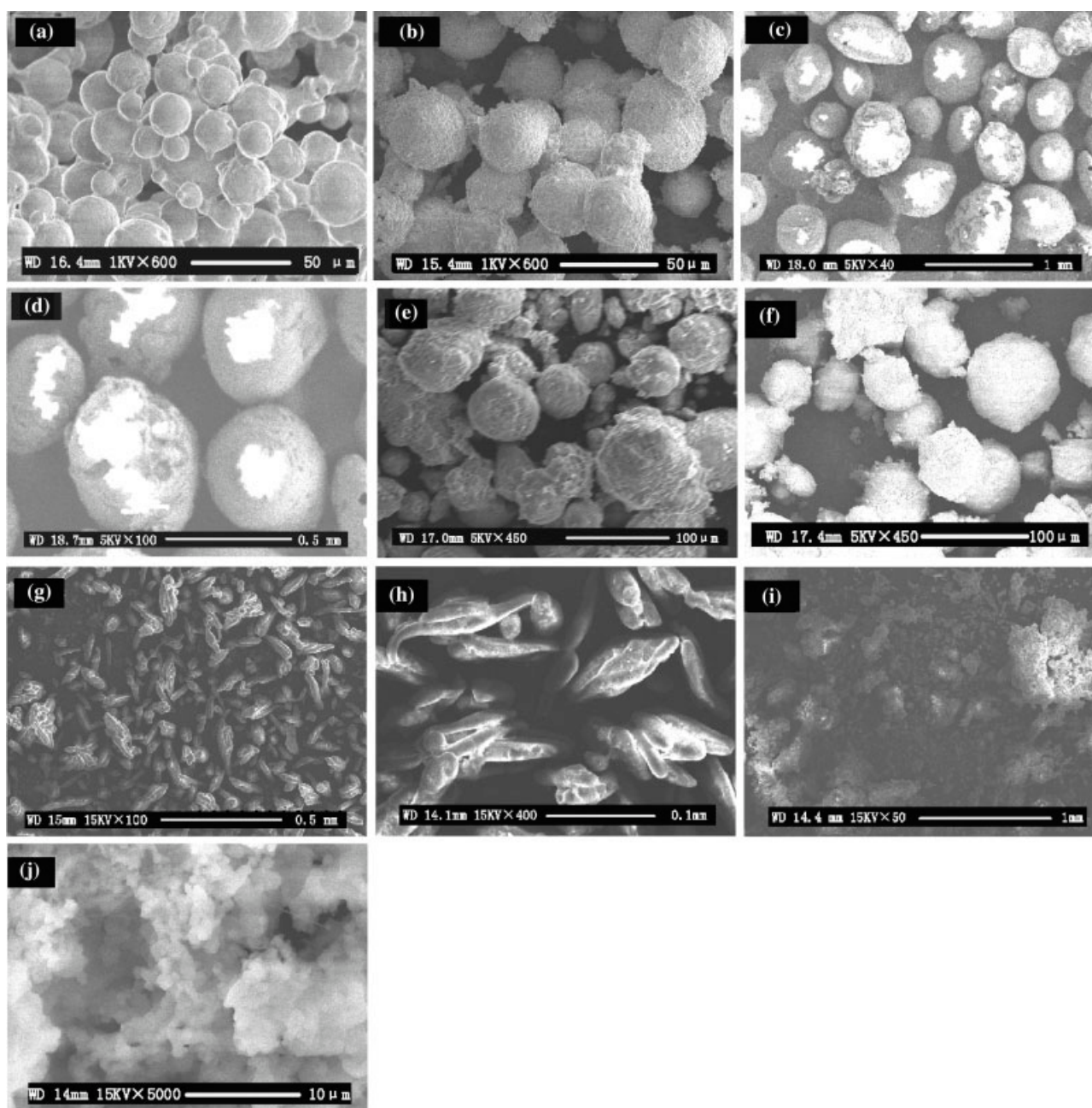


Figure 3 SEM micrographs of the support, supported catalyst, and PNB particles. (a) Spherical $\text{MgCl}_2 \cdot 2.97\text{EtOH}$ (600 \times), (b) SNC-6 (600 \times), (c) PNB particles (entry 14, 40 \times), (d) PNB particles (entry 14, 100 \times), (e) SiO_2 (450 \times), (f) SNC-12 (450 \times), (g) PNB particles (entry 17, 100 \times), (h) PNB particles (entry 17, 400 \times), (i) PNB particles (entry 21, 50 \times), (j) PNB particles (entry 21, 5000 \times).

systems.⁸ The morphology of the polymer particles changed markedly with polymerization temperature. From 12.5 to 37.5 $^\circ\text{C}$, a free-flowing white powder was obtained. Polymerizations performed at 0 and 50 $^\circ\text{C}$ have no particle morphological control.

The polynorbornenes thus obtained by entry 19 are examined by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (Fig 1). $^1\text{H-NMR}$ spectra confirms the polymerization of norbornene with these MgCl_2 -supported nickel catalyst systems in the model of vinyl addition polymerization.⁴²

As shown in Figure 2, the $^{13}\text{C-NMR}$ spectra is similar to those reported by Greiner's and Arndt's.^{43,44}

Microscopy studies of catalysts and polymers

Figure 3(a) showed that spherical $\text{MgCl}_2 \cdot 2.97\text{EtOH}$ had a smooth and less porous surface. Although the supported catalyst still remained spherical in morphology, there appeared a rough and porous area on the surface of the supported catalyst. This indicates

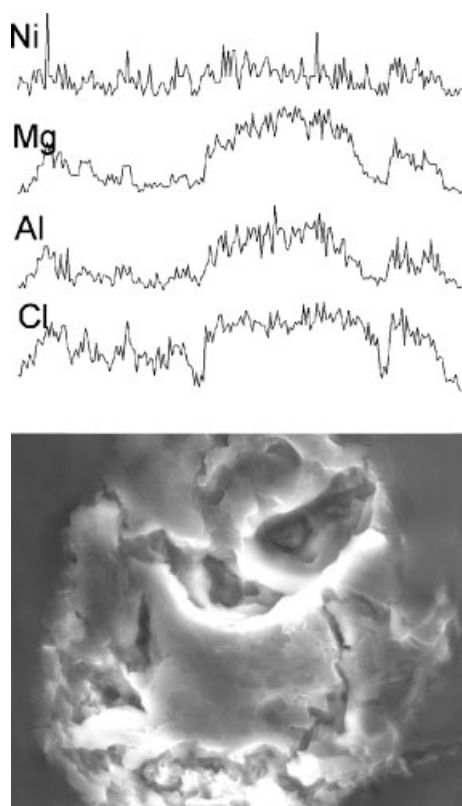


Figure 4 EDX line scan analysis of a nickel-based late transition/MAO-supported spherical MgCl_2 (SNC-6) regarding the nickel, aluminum, and magnesium distribution in the volume (5 kV accelerating voltage, $\times 3000$).

that some MAO had been adsorbed on the surface through the reaction of hydroxyl group in spherical MgCl_2 with MAO. In addition, MAO penetrated into the cavities with which nickel catalyst reacted and supported the nickel catalyst without breaking up support. That means, complex **1** was supported through the "bridge" of MAO. The evidence is given in the EDX line scan (Fig. 4). The distribution of the catalytic components on the support is determined by X-ray analysis. EDX line scan analysis of cross section in a supported catalyst particle depicted in Figure 4 showed a homogeneous distribution of the cocatalyst MAO. Although the nickel weight percentage in the catalyst is in a low level of about 0.1–0.3%, it has good distribution on the carrier. Under this condition, it can be sure that the active sites are formed not only on the outer surface but also inside of the particle and it is desirable that the final product replicates the support morphology.

In addition to its effect on polymer molecular composition, a particular important feature of any immobilized catalyst for olefin polymerization is the ability to give controlled particle size and morphology. From Figures 3(c and d), PNB particles are spherical, similar to the original support and the supported catalyst. It is generally well accepted that

particle size and morphology of catalysts directly impact the size and shape of the resulting polymer particle, and this is called catalyst replication. The resulting PNB particles were similar in morphology to catalyst SNC-6, except that the diameter of the polymer (typical $450\ \mu\text{m}$) is around 15–20 times larger than that of the catalyst SNC-6 (typical $30\ \mu\text{m}$). The granulated morphology of the polymer is important for industrial purposes because it facilitates processing. However, as shown in Figures 3(g) and 3(h), the polymer obtained with **1** immobilized on the SiO_2/MAO exhibited rodlike morphology. The SEM photographs of polymers prepared with **1**/MAO homogeneous catalytic system were shown in Figures 3(i) and 3(j). The polymer particles agglomerated together.

CONCLUSIONS

The bis(salicylideneiminato)nickel(II) precursor was supported on spherical MgCl_2 and silica. Norbornene polymerization was carried out using supported catalysts. The catalytic activities and polymer properties were relied on various polymerization conditions. Compared with catalyst prepared with thermally untreated support, the catalyst prepared with thermally pretreated support had fine morphology and similar activity. Replication of supported catalyst morphology was found in the polymers produced under some suitable conditions. In general, the polynorbornenes produced with supported catalyst have higher molecular weight and slightly broader molecular weight distribution than that produced with the homogeneous catalyst.

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