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Poisoning effect of CO on ethylene polymerization with Ni(II)–diimine/MAO

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Abstract

CO was not a comonomer but an inhibitor in ethylene polymerization catalyzed over [1,2-bis(2,6-diisopropylphenylimino)]acenaphthene nickel(II) dibromide (**1**)/MAO. The average number of active sites, $[\bar{C}^*]$, and the average rate constant for chain propagation, $\bar{k}_p$ of the (**1**)/MAO system was determined using CO inhibition method based on the assumption that two molecules of CO coordinate to each active center. At 0 °C, the average number of active centers, $\bar{C}^*$, was increased with the Al/Ni ratio, and $\bar{k}_p$, was not influenced by the Al/Ni ratio. Up to Al/Ni ratio of 3000, the average number of active sites was saturated. Single active site was present at the high ratio of Al/Ni and its reactivity with CO is uniform at 0 °C. The maximum average activity was 5262.07 (kg-PE/mol–Ni/atm/hr) and 65.7% of (**1**) was converted to form active cation complexes at 0 °C and Al/Ni molar ratio of 5000, while 36.5% of (**1**) was activated at the Al/Ni molar ratio of 250. Above 30 °C, the complicated CO poisoning behavior was observed because the reactivity and stoichiometry of active centers with CO were not uniform and their thermal stability was very poor.

Keywords: CO inhibition; Active center; Ni-diimine(II)

1. Introduction

Shortly after the discovery of Ziegler–Natta catalyst [1,2], there have been great efforts to determine active site concentration. A determination of the number of active sites was inevitable for understanding kinetics and mechanism of olefin polymerization. A knowledge of the active site concentration, $[C^*]$, was required to evaluate a rate constant for chain propagation, k_p. Several methods have been used to measure the number of active centers in polymerization with Ziegler–Natta catalyst and metallocene catalyst. Schnecko and Kern used variation of the number average degree of polymerization with time [3]. Method of variation of yield with time was adopted by Haward et al., [4]. Chien used ^{14}C-labelled aluminum alkyl compounds in order to determine values of $[C^*]$ [5]. Simultaneous kinetic and inhibition method was developed by Caunt, Tait and coworkers [6,7]. A small amount of suitable inhibitor was injected into polymerization run and decrease in the overall rate of polymerization were measured simultaneously as well as the amount of inhibitor adsorbed [8–12].

Recently, new generation of olefin polymerization catalysts, based on late transition metals such as Fe, Co, Ni and Pd, has emerged as an alternative to produce the new structure of polyolefins [13–15]. In contrast to early transition metal systems, late transition metal catalysts mostly often dimerize or oligomerize olefins due to competing β-hydride elimination [16]. But, nickel(II)–diimine catalysts were highly active for ethylene and α-olefin polymerization, and produced a polymer with high molar mass. The bulky substituents on the aryl groups of the diimine ligands blocked an associative olefin exchange and β-hydride elimination. Brookhart and others have demonstrated the influence of catalyst structure and cocatalyst type on the catalyst activity [17,18]. However, the average number of active sites for Ni(II)–diimine catalyst has not been studied yet. In this work, we tried to determine the average active site concentration and the propagation constant of Ni(II)–diimine catalyst by the simultaneous kinetic and inhibition method using CO as a catalyst inhibitor at various polymerization conditions.

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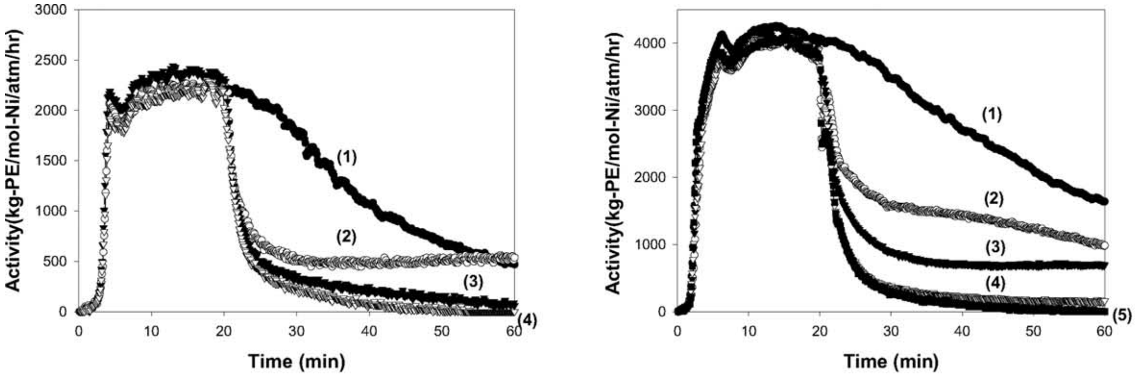
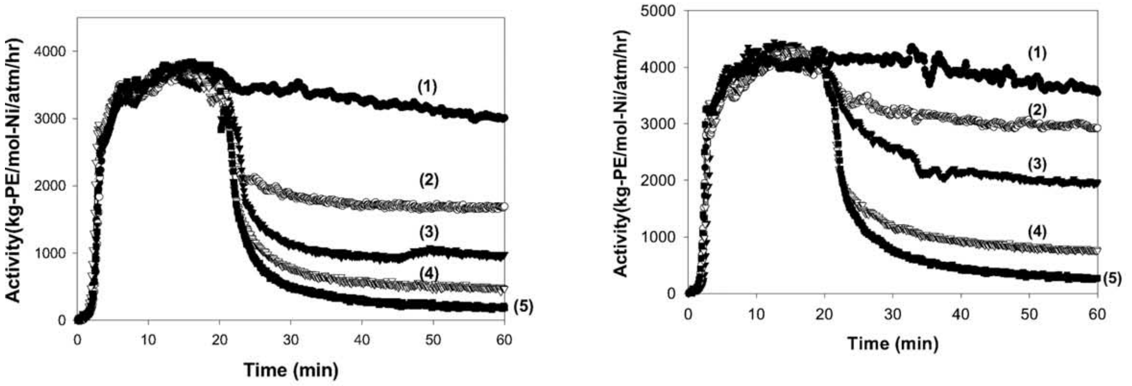


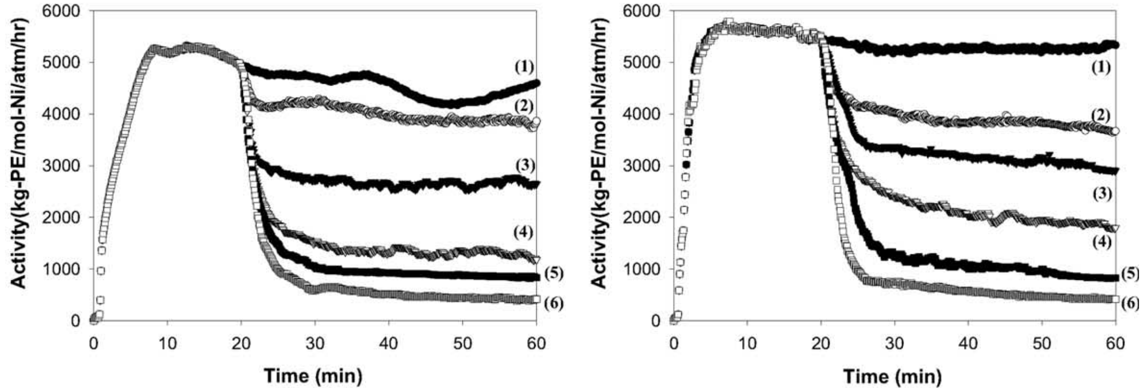
(a) T_p=0℃, Ni=3μmol, Al/Ni=250, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4)0.76

(b) T_p=0℃, Ni=3μmol, Al/Ni=500, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4)0.76 (5)1.02



(c) T_p=0℃, Ni=3μmol, Al/Ni=1000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4)0.76 (5)1.02

(d) T_p=0℃, Ni=3μmol, Al/Ni=2000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4)0.76 (5)1.02



(e) T_p=0℃, Ni=3μmol, Al/Ni=3000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4)0.76 (5)1.02 (6)1.27

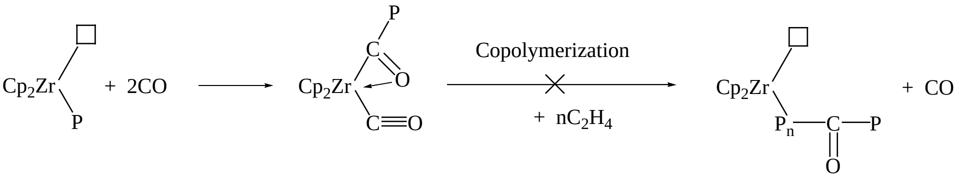
(f) T_p=0℃, Ni=3μmol, Al/Ni=5000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4)0.76 (5)1.02 (6)1.27

Fig. 1. Rate profiles induced by CO injection after 20 min during ethylene polymerization over the (**1**)/MAO system (Effect of Al/Ni ratio).

2. Experimental

2.1. Materials

All manipulations of compounds were carried out by standard Schlenk, vacuum, and glove box techniques. Polymerization-grade ethylene (donated from Daelim Ind. Co., Korea) and nitrogen were further purified by passing through columns of Fisher RIDOX and 5A/13X molecular sieves. Ultra high purity grade of carbon monoxide for the active site measurement was used without further purification. Toluene (from J. T. Baker Chem. Co.) of extra pure grade was purified by refluxing over sodium metal/benzophenone in a nitrogen atmosphere. Methylaluminoxane (MAO) was

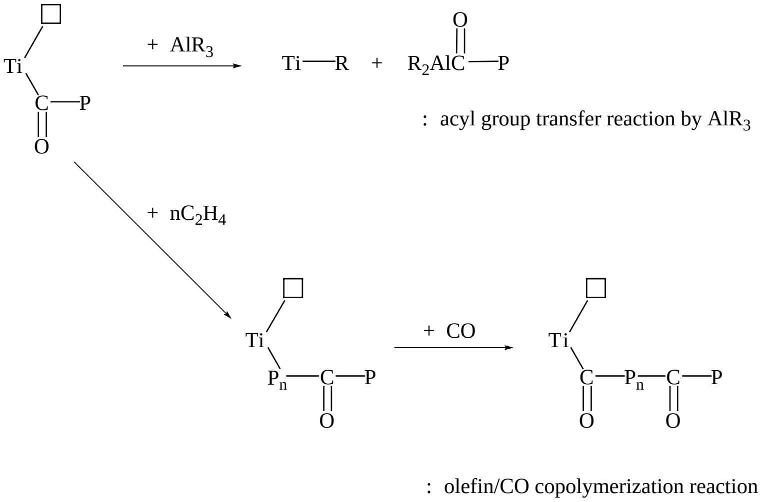


Scheme 1.

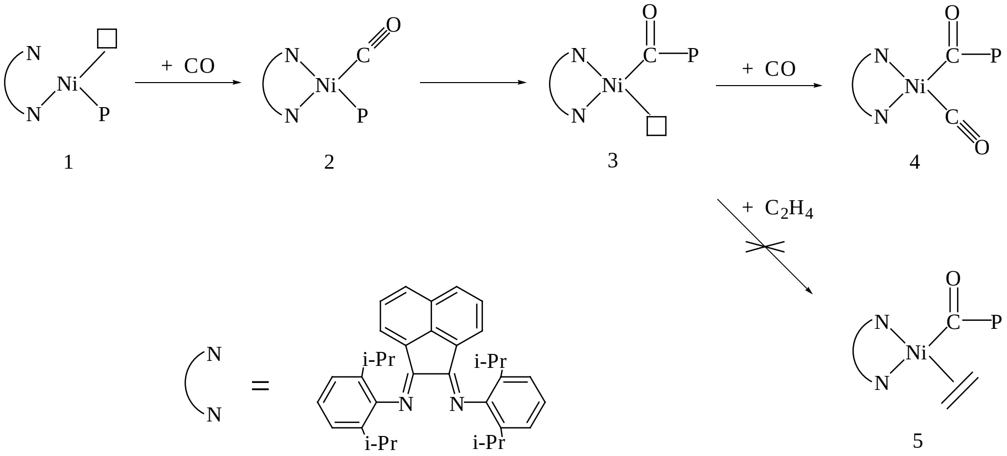
purchased from Akzo Co. as a toluene solution and was used without further purification. The catalyst, [1,2-bis(2,6-diisopropylphenylimino)]acenaphthene nickel(II) dibromide (**1**) was synthesized according to the literature [19].

2.2. Polymerization

The slurry polymerization was carried out at the ethylene pressure of 1.2 atm in a 1 L mechanically stirred glass reactor (Büchi AG, Ulster/Switzerland). Toluene (200 ml) was introduced into the reactor, the temperature was controlled to the polymerization temperature, and then a prescribed amount of MAO dissolved in toluene was injected into the reactor by tuberculin syringe. After ethylene was saturated in toluene, 3 μmol of catalyst dissolved in toluene was injected into the reactor by syringe and then the polymerization was started. The maximum consumption rate of ethylene was controlled at about 200 cm^3/min and mechanical stirring speed was 300 rpm. The polymerization rate was acquired at 6 s intervals from the rate of ethylene consumption measured by a hot wire flow sensor (model 5860 from Brooks Instrument) connected to a personal



Scheme 2.

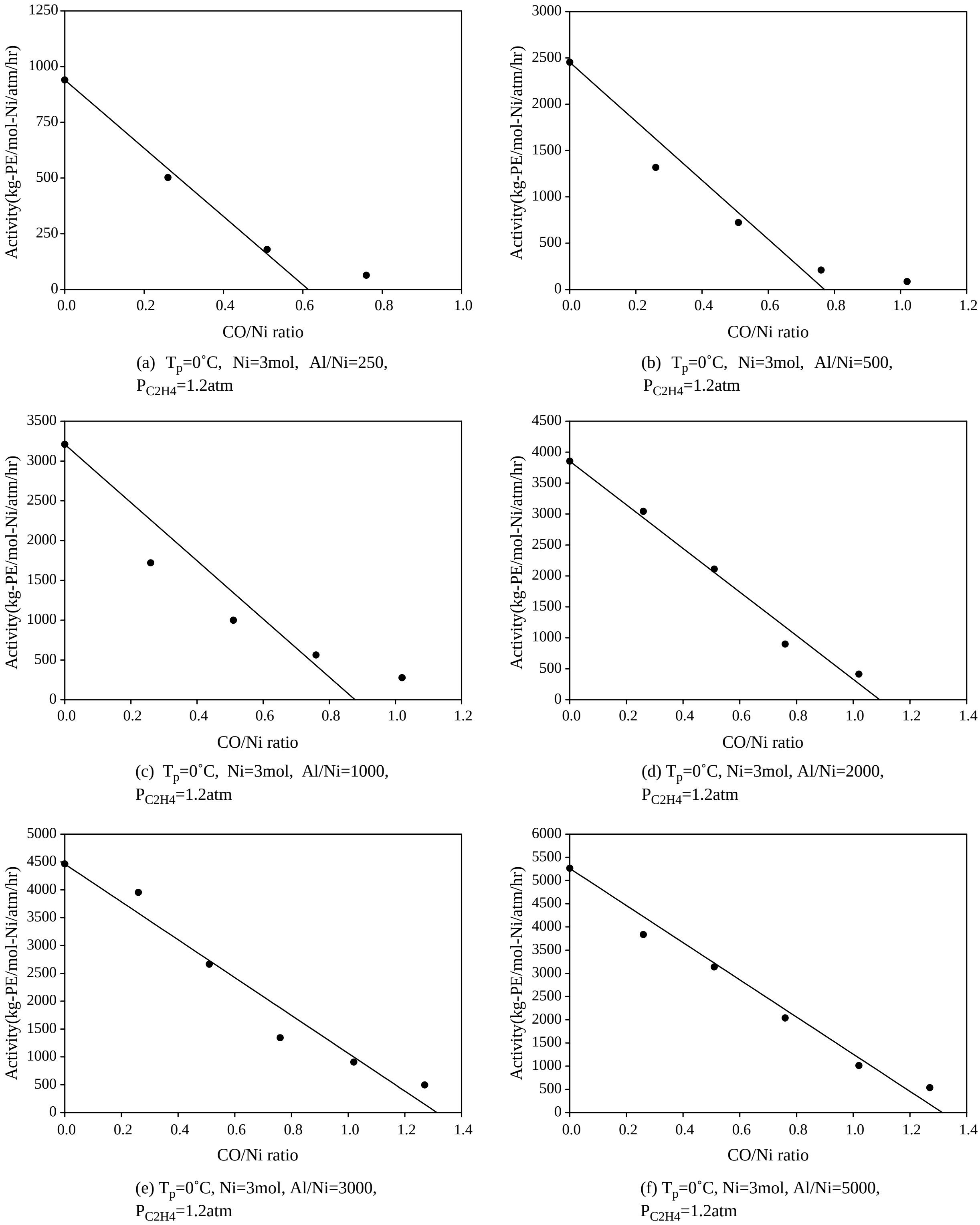


Scheme 3.

computer through an A/D converter. Prescribed amounts of carbon monoxide dissolved in toluene were injected during polymerization for the simultaneous measurement of a decrease in the overall rate of polymerization. The carbon monoxide concentration in toluene is 7.64×10^{-6} mol/ml at 25 °C and 1 atm [20].

2.3. Characterization

After ethylene polymerization, gas phase in polymerization reactor was analyzed with a gas chromatograph (HP5890, TCD) equipped with a molecular sieve 5A column. ^{13}C NMR (75 MHz) spectra of polymers were recorded at 120 °C using a



(a) T_p=0°C, Ni=3mol, Al/Ni=250, P_{C2H4}=1.2atm

(b) T_p=0°C, Ni=3mol, Al/Ni=500, P_{C2H4}=1.2atm

(c) T_p=0°C, Ni=3mol, Al/Ni=1000, P_{C2H4}=1.2atm

(d) T_p=0°C, Ni=3mol, Al/Ni=2000, P_{C2H4}=1.2atm

(e) T_p=0°C, Ni=3mol, Al/Ni=3000, P_{C2H4}=1.2atm

(f) T_p=0°C, Ni=3mol, Al/Ni=5000, P_{C2H4}=1.2atm

Fig. 2. Decrease in polymerization rates with the amounts of CO injected. Polymerization conditions are the same as those in Fig. 1.

Bruker AMX-300 FT NMR spectrometer. Obtained polymers were dissolved in 1,2,4-trichlorobenzene/benzene-d_6 (4/1 vol) up to a concentration of 15 wt% at 120 °C in NMR tubes (5 mm od).

3. Results and discussion

3.1. Characterization of CO inhibition

Fig. 1 shows ethylene polymerization rate profiles by (**1**)/MAO system at 0 °C with the various Al/Ni molar ratios. After carbon monoxide was saturated in toluene at 25 °C and 1 atm, toluene saturated with CO was injected in polymerization reactor by syringe at adequate time (20 or 30 min after start of polymerization). Polymerization rates were sharply decreased to a level that can be determined for catalyst (**1**) after the injection of CO dissolved in toluene. The polymerization rate decreased with the increase in the amounts of CO added. This decreased polymerization rate was not recovered during polymerization. This phenomenon was also observed in the early transition metal olefin catalyst system [9]. Our group reported that CO affected steep decrease of ethylene polymerization rates on Cp_2ZrCl_2/MAO system and ethylene/propylene copolymerization rates on *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO system [9]. Ethylene polymerization and ethylene/propylene copolymerization rate sharply decreased after CO injection and was not recovered. $(C_5R_5)_2Zr(CH_3)Me^+$ species leaded to the formation of unusual d^0 carbonyl complexes $(C_5R_5)_2Zr(\text{–}COCH_3)(CO)^+$ (R = Me, H) [21]. The eternal decay of polymerization rates implied that two CO molecules coordinated to one Zr site producing a carbonyl compound [21], which is not active (Scheme 1).

However, our group reported that the catalytic activity gradually recovered after a steep decrease in the polymerization rate for the heterogeneous Zigler–Natta catalyst system [10]. The gradual recovery after sudden decrease of polymerization rate has been interpreted in terms of the slow transfer reaction by AlR_3 for a titanium–acyl bond or copolymerization of CO with olefin, as shown in Scheme 2 [22,23].

As mentioned earlier, the ethylene polymerization kinetic profiles of (**1**)/MAO system were similar to those of metallocene catalysts system. In the case of the (**1**)/MAO system, coordination of CO to the active site of the (**1**)/MAO system was not reported yet. Morokuma and co-workers only reported theoretical expectation for Ni(II)–diimine complexes catalyzed alternating copolymerization of carbon monoxide with ethylene using the hybrid density functional B3LYP method [24]. They reported that the copolymerization of CO and ethylene was predicted to be significantly faster using the Ni(II)–diimine based catalyst compared to the Pd(II)–diimine based catalyst. But, these theoretical predictions were different from our experimental results. In the (**1**)/MAO system case, it is reliable that CO did act as an inhibitor, not comonomer by following two evidences. Firstly, if the copolymerization of CO and ethylene were progressed, the rate profiles of ethylene consumption should be gradually recovered. However, the ethylene polymerization rates were sharply decreased and not recovered during polymerization. Secondly, the ^{13}C NMR spectra of the obtained polymer by the (**1**)/MAO system showed no carbon peak of ketone group. The special peaks of ^{13}C NMR spectra of polyketone was obtained around 217.1 $(CH_3CH_2C(O)(CH_2CH_2C(O))_nCH_2CH_2C(O)CH_3)$, 212.9 $(CH_3CH_2C(O)(CH_2CH_2\mathit{C}(O))_nCH_2CH_2C(O)CH_3)$, 176.4 $(CH_3CH_2C(O)(CH_2CH_2C(O))_nCH_2CH_2\mathit{C}(O)CH_3)$ ppm [25]. Brookhart group reported that the living polymerization of ethylene with Ni/Pd(II) diimine complexes coupled with use of a functionalized initiator such as OEt_2, Me_2S and NCMe [26]. Functionalized initiator and ethylene reacted with Ni/Pd(II) diimine precursor competitively. Because the electrophilicity of CO is higher than that of OEt_2, Me_2S and NCMe resulting in the strong poisoning of CO in the ethylene polymerization, copolymerization of CO and ethylene should not be accomplished.

A plausible mechanism for the CO inhibition in (**1**)/MAO system is shown in Scheme 3. Therefore, we assumed that two molecules of CO coordinate to one active nickel site for determination of the number of active sites.

3.2. Effect of Al/Ni ratio on the formation of active sites

Fig. 2 shows the decrease in polymerization rates with the amounts of the CO injected at various CO/Ni ratios. In order to check complete consumption of CO, gas phase in reactor was analyzed with a gas chromatograph after polymerization.

Table 1
Effect of Al/Ni ratio on the number of active sites in ethylene polymerization over the (**1**)/MAO system

Run no.	Amount of Ni (μmol)	Al/Ni	T_p (°C)	$[M]^a$ (mol/L)	CO injection time (min)	$\bar{R}_p{}^b$ (kg-PE/mol–Ni/atm/hr)	Mol % of $[\bar{C}^*]^c$/mol of Ni	$\bar{k}_p$ $(M\ s)^{-1}$
1	3	250	0	0.145	20	939.63	30.7	208.37
2	3	500	0	0.145	20	2451.98	38.5	433.57
3	3	1000	0	0.145	20	3208.72	43.9	497.60
4	3	2000	0	0.145	20	3852.83	54.7	479.52
5	3	3000	0	0.145	20	4462.87	65.7	462.45
6	3	5000	0	0.145	20	5262.07	65.7	545.27

Polymerization conditions: ethylene pressure = 1.2 atm, solvent = toluene (200 ml), polymerization time = 1 h.

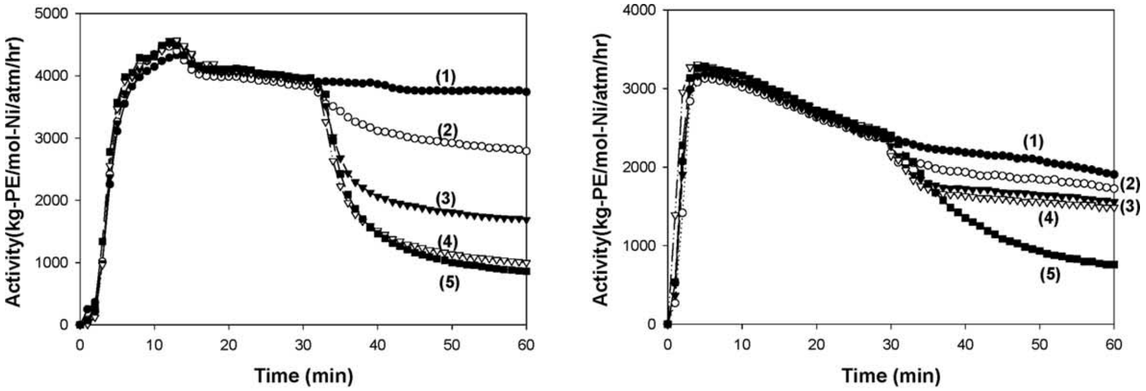
[a] Calculated from Chao-Seader's program for phase equilibrium.

[b] Average polymerization activity from 30 min to end of polymerization.

[c] Extrapolation for 100% drop of rates versus the two-fold amount of CO injection shown in Fig. 2.

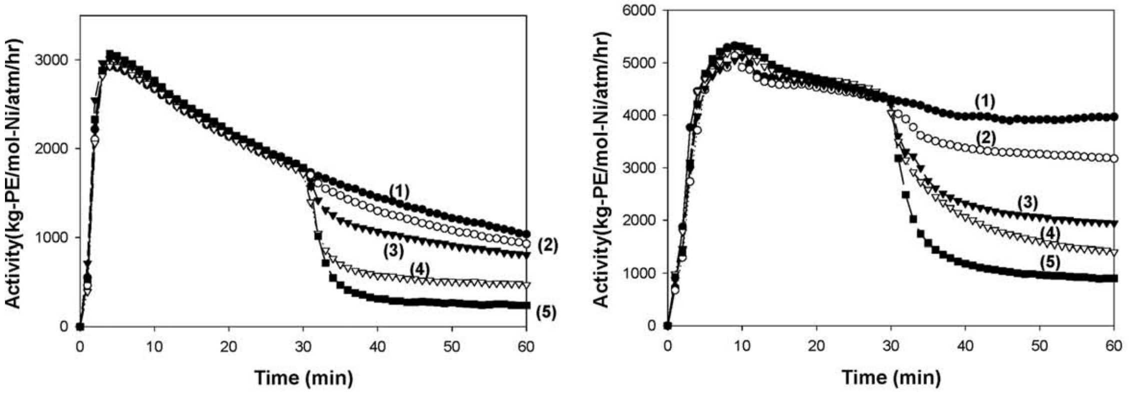
The average ethylene polymerization activity was measured from 10 min after CO injection to end of polymerization because the rate profile of ethylene consumption was stabilized after 10 min of CO injection. Based on the assumption that two molecules of CO coordinate to each active center, the average number of active centers was evaluated by the amount of CO added necessary to poison all nickel active centers.

The activity after CO injection linearly decreased with the amount of CO added above Al/Ni molar ratio of 2000 (Fig. 2(d)–(f)). However, as Al/Ni ratio decreased from 2000 to 250, the degree of activity decrease was lessened with



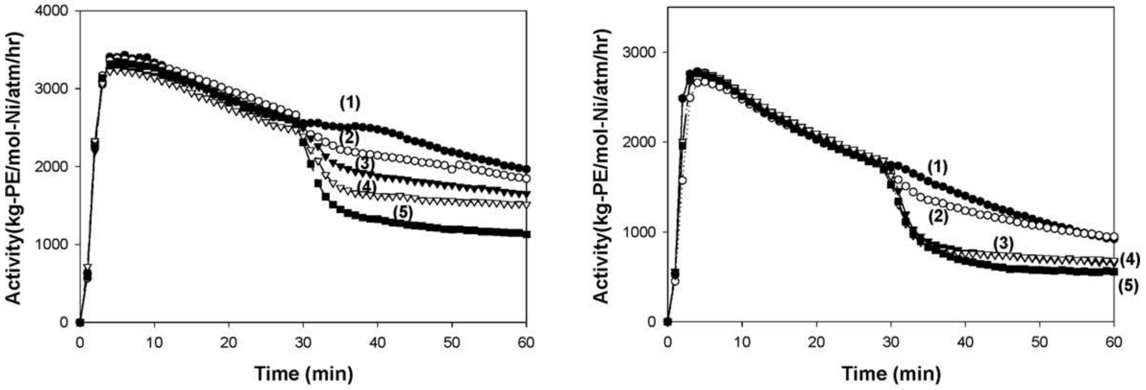
(a) Polymerization conditions : T_p=0℃, Ni=3μmol, Al/Ni=1000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4) 0.76 (5) 1.02

(b) T_p=30℃, Ni=3μmol, Al/Ni=1000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4) 0.76 (5) 1.02



(c) T_p=50℃, Ni=3μmol, Al/Ni=1000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4) 0.76 (5) 1.02

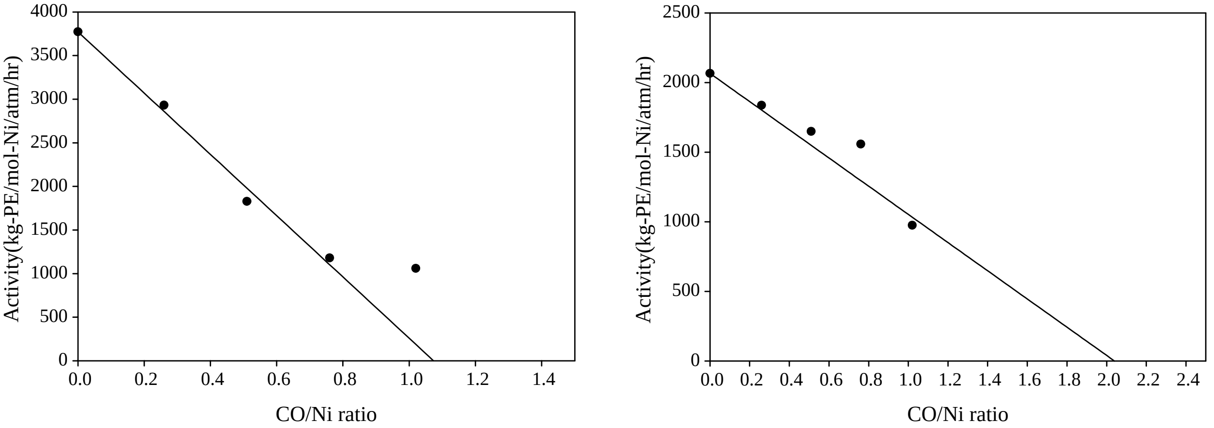
(d) T_p=0℃, Ni=3μmol, Al/Ni=2000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4) 0.76 (5) 1.02



(e) T_p=30℃, Ni=3μmol, Al/Ni=2000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4) 0.76 (5) 1.02

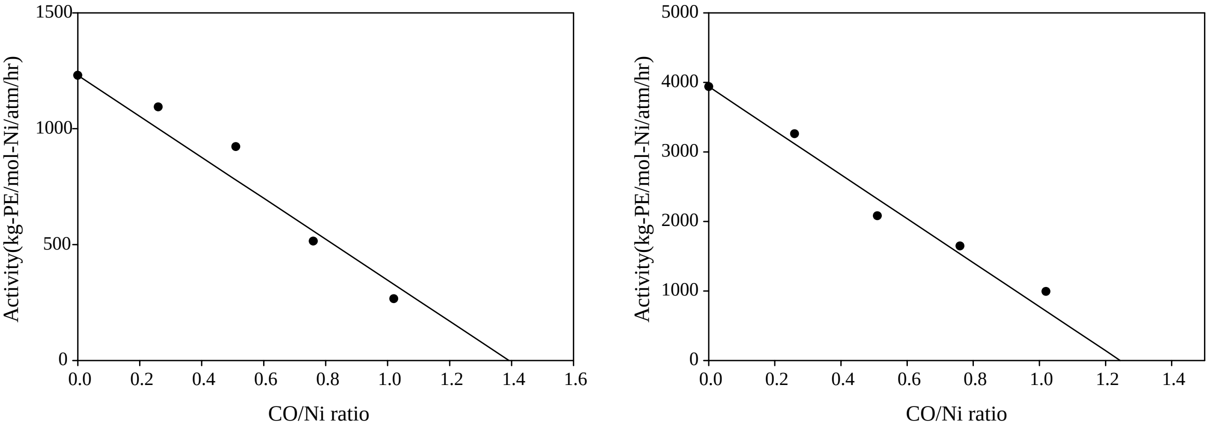
(f) T_p=50℃, Ni=3μmol, Al/Ni=2000, P_{C2H4}=1.2atm, CO/Ni in; (1) 0 (2) 0.26 (3) 0.51 (4) 0.76 (5) 1.02

Fig. 3. Rate profiles induced by CO injection after 30 min during ethylene polymerization over the (**1**)/MAO system (effect of the polymerization temperature).



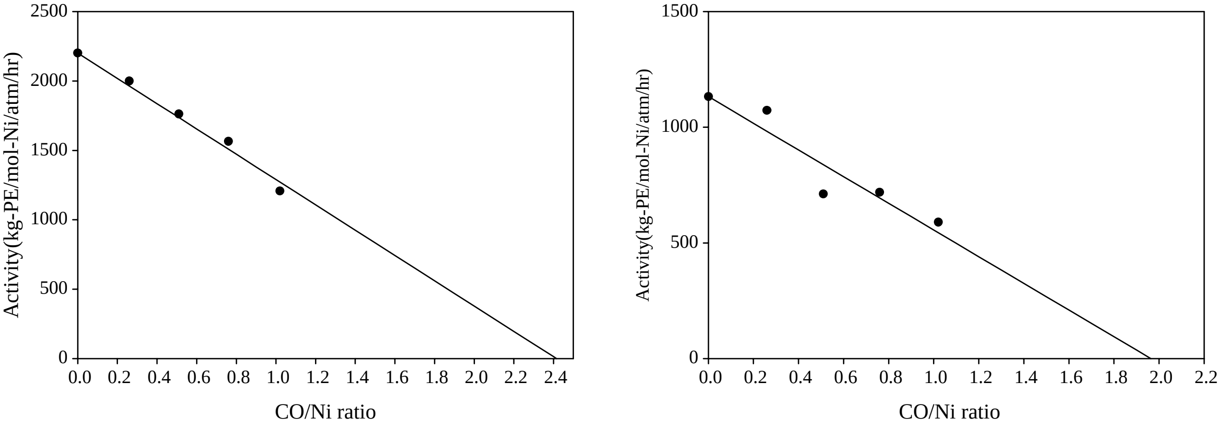
(a) Polymerization conditions : T_p=0˚C, Ni=3μmol, Al/Ni=1000, P_{C2H4}=1.2atm

(b) T_p=30˚C, Ni=3mol, Al/Ni=1000, P_{C2H4}=1.2atm



(c) T_p=50˚C, Ni=3mol, Al/Ni=1000, P_{C2H4}=1.2atm

(d) T_p=0˚C, Ni=3mol, Al/Ni=2000, P_{C2H4}=1.2atm



(e) T_p=30˚C, Ni=3mol, Al/Ni=2000, P_{C2H4}=1.2atm

(f) T_p=50˚C, Ni=3mol, Al/Ni=2000, P_{C2H4}=1.2atm

Fig. 4. Decrease in polymerization rate with the amounts of CO injected. Polymerization conditions are the same as those in Fig. 3.

the increase in the amount of CO injection as shown in Fig. 2(a)–(c). These results can be explained by equilibrium between a dormant state and real active species, C^*. At low Al/Ni ratio, the equilibrium goes toward a dormant state or inactive species which can be reconverted to active species reversibly. One of the strong σ-coordinating sites is vacant in $[L_2NiR]^+$ which is widely known as an active sites. Thus, CO coordinates much faster to that cationic species than to other inactive species. If the amount of CO injected was small, most of the CO molecules might preferentially coordinate to the

Table 2
Effect of polymerization temperature on the number of active sites in ethylene polymerization over the (**1**)/MAO system

Run no.	Amount of Ni (μmol)	Al/Ni	T_p (°C)	$[M]$[a] (mol/l)	CO injection time (min)	$\bar{R}_p$[b] (kg-PE/mol–Ni/atm/hr)	Mol % of $[\bar{C}^*]$[c]/mol of Ni	$\bar{k}_p$ $(\mathrm{M\ s})^{-1}$
7	3	1000	0	0.145	30	3772.00	53.7	478.22
8	3	1000	30	0.090	30	2066.00	102.0	222.17
9	3	1000	50	0.066	30	1230.43	69.6	264.42
10	3	2000	0	0.145	30	3938.57	62.2	431.10
11	3	2000	30	0.090	30	2200.73	120.8	199.82
12	3	2000	50	0.066	30	1132.43	98.2	172.48

Polymerization conditions: ethylene pressure = 1.2 atm, solvent = toluene (200 ml), polymerization time = 1 h.

[a] Calculated from Chao-Seader's program for phase equilibrium.

[b] Average polymerization activity from 40 min to end of polymerization.

[c] Extrapolation for 100% drop of rates versus the two-fold amount of CO injection shown in Fig. 4.

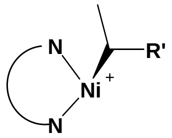
active site. In contrast, for the case of a large amount of CO added, some of the CO molecules coordinate also to dormant and inactive sites, resulting in a slow decrease in polymerization rate. The increase in Al/Ni ratio makes the equilibrium proceed toward a formation of active sites. Therefore, the activities linearly decrease at even large amounts of CO added at high concentrations of MAO as shown in Fig. 2(d)–(f). The similar result was reported in the case of metallocene system [9].

Table 1 presents the average number of active sites of the (**1**)/MAO system together with the rate constant for chain propagation, $\bar{k}_p$, calculated from the relation that the average polymerization rate, $\bar{R}_p$, was given by the equation, $\bar{R}_p = \bar{k}_p[\bar{C}^*][M]$ ($[M]$, concentration of ethylene). The average number of active centers, $[\bar{C}^*]$, was increased with the Al/Ni ratio and saturated above Al/Ni of 3000 at 0 °C. $\bar{k}_p$ was not influenced by the Al/Ni ratio up to 500. It can be concluded that single active site was present at the high ratio of Al/Ni and its reactivity with CO is uniform at 0 °C. The increase in activity with the increase in Al/Ni ratio is due to the increase in the average concentration of the active center rather than increase in $\bar{k}_p$. The maximum activity was 5262.07 (kg-PE/mol–Ni/atm/hr) and 65.7% of (**1**) was converted to form active cation complexes at 0 °C and Al/Ni molar ratio of 5000, while 30.5% of (**1**) was activated at the Al/Ni molar ratio of 250.

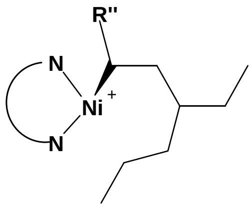
3.3. Effect of the polymerization temperature on the formation of active sites

The influence of the polymerization temperature on the average active site concentration and $\bar{k}_p$ was investigated at various temperatures and at Al/Ni = 1000 or 2000. Figs. 3 and 4 show rate profiles induced by CO injection after 30 min from start of polymerization and decrease in polymerization rate with the amounts of CO injected, respectively. Table 2 presents the effect of polymerization temperature on the number of active site at Al/Ni molar ratio of 1000 and 2000.

At Al/Ni of 2000, the fraction of active sites increased from 62.2% at 0 °C to 120.8% at 30 °C. Rate measurements are accurate within ±5%. 120.8% is not the physically obtainable value. This suggested that the stoichiometry of CO reacted with active Ni complex should not be two at high polymerization temperatures. The fraction of active site decreased to 98.2% at 50 °C, indicating that polymerization centers were not stable and converted to inactive species at 50 °C. $\bar{k}_p$ decreased from 431.10 $(\mathrm{M\ s})^{-1}$ at 0 °C to 199.82 $(\mathrm{M\ s})^{-1}$ at 30 °C and 172.48 $(\mathrm{M\ s})^{-1}$ at 50 °C. This can be explained by the formation of long-chain branched polymerization center at high temperature as depicted in the following [13]. Methyl branched polymerization center is the dominant species at 0 °C, which should have a higher $\bar{k}_p$ value because of less steric hindrance than long-chain branched polymerization center. However, $\bar{k}_p$ increased from 222.17 $(\mathrm{M\ s})^{-1}$ at 30 C to 264.42 $(\mathrm{M\ s})^{-1}$ at 50 °C and Al/Ni of 1000.



methyl branched
polymerization center



long chain branched
polymerization center

The complicated nature of these results could arise from several reasons, the low thermal stability of Ni(II)–diimine cation polymerization center, the formation of long chain branch polymerization center caused by the higher β-hydride elimination reaction rate and chain walking reaction rate of Ni(II)–diimine cation polymerization center in ethylene polymerization at high polymerization temperature and 'simple' unligated species [13,14]. Janiak group reported the finding of 'simple' unligated species upon activation in cycloolefion polymerization [27]. Brookhart group reported that some kinds of the Ni-diimine complexes easily decomposed to different Ni-complexes at high temperature [28]. Accordingly, the structures of polymerization active center were not single and obtained results showed a complicated behavior at high polymerization temperature because the reactivity and stoichiometry of active centers with CO were not uniform. Therefore, simultaneous CO inhibition method will be suitable method for the determination of $[\bar{C}^*]$ and $\bar{k}_p$ in ethylene polymerization catalyzed by the (**1**)/MAO system at low polymerization temperature. At high polymerization temperature, the method of variation of the number average degree of polymerization with time or variation of yield with time will give more reliable $[\bar{C}^*]$ and $\bar{k}_p$ because theses methods will not be influenced by reactivity of various polymerization centers of the Ni(II)–diimine complexes with carbon monoxide. It can be suggested that even single site catalyst can form multiple polymerization centers reflecting the unusual kinetic behavior.

4. Conclusion

When [1,2-bis(2,6-diisopropylphenylimino)] acenaphthene nickel(II) dibromide/MAO was used, it was found that CO was inhibitor in ethylene polymerization. The average number of active sites and the average rate constant of chain propagation of the (**1**)/MAO system were determined by means of simultaneous CO inhibition method. At 0 °C, the average number of active centers, $[\bar{C}^*]$, was increased with the Al/Ni ratio, and $\bar{k}_p$, was not influenced by the Al/Ni ratio up to 500. Single active site was present at the high ratio of Al/Ni and its reactivity with CO is uniform at 0 °C. The maximum activity was 5262.07 (kg-PE/mol–Ni/atm/hr) and 65.7% of (**1**) was converted to form active cation complexes at 0 °C and Al/Ni molar ratio of 5000, while 30.7% of (**1**) was activated at the Al/Ni molar ratio of 250. Above 30 °C, the complicated polymerization behavior was caused by the higher β-hydride elimination reaction rate, chain walking reaction rate of Ni(II)–diimine cation polymerization center and poor thermal stability. The simple stoichiometry of CO with active center was not present indicating that CO inhibition method to determine the active sites is inadequate.

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