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Dual roles of trifluoroborate in nickel-catalyzed ethylene polymerization: Electronic perturbation and anchoring for heterogenization

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ABSTRACT

Brookhart-type α-diimine nickel and palladium catalysts have been extensively studied over the past several decades; however, the heterogenization of these metal complexes has received much less attention. In this contribution, we installed a trifluoroborate potassium substituent on an α-diimine framework. The ionic nature of trifluoroborate potassium endowed the α-diimine nickel complex with a strong affinity for the SiO_2 support, while its electron-donating nature enhanced the catalyst stability and polyethylene molecular weight. In the presence of only 100 equiv. of Et_2AlCl cocatalyst, the SiO_2-supported catalyst demonstrated significantly better performance than its homogeneous analog during ethylene polymerization, with extremely high activity ($1.42–6.53 \times 10^7$ g mol^{-1} h^{-1}) and high thermal stability. The heterogeneous system led to the formation of high-molecular-weight polyethylenes (M_n 142,500–732,800 g/mol), narrow polydispersities (2.18–3.00), tunable branching densities (21–64 per 1000 carbon atoms), and great mechanical properties. Moreover, the efficient copolymerization of ethylene with comonomers such as methyl 10-undecenoate, 6-chloro-1-hexene or 5-hexenylacetate was achieved. These superior properties enabled by the trifluoroborate potassium moiety may inspire its applications in other polymerization catalyst systems.

In the 1990s, Brookhart and coworkers reported seminal works on α-diimine nickel and palladium-catalyzed olefin polymerization and copolymerization with acrylates [1,2]. Ever since, this system has attracted continuous interest and has become one of the most extensively studied catalyst systems for olefin polymerization [3–10]. This is attributed to many of their superior properties: (1) the ease of ligand synthesis and modification (Scheme 1a) [11]; (2) the ability to finely control polymer microstructures and topologies through a unique chain-walking mechanism [12]; (3) the ability to copolymerize olefins with polar-functionalized comonomers [13–16]; (4) the high activities of some α-diimine nickel catalysts that are comparable to many early transition metal catalysts [17]. Furthermore, significant industrial efforts have been directed towards this catalyst family [18,19]. Despite the above-mentioned attractive features and more than two decades of extensive studies, there has been no successful commercialization of these catalysts. This is partially due to the lack of investigations into heterogeneous counterparts derived from these homogeneous complexes.

In the polyolefin industry, heterogeneous systems are preferred over homogeneous systems due to their ability to avoid reactor fouling through product morphology control [20–24]. The heterogenization of homogeneous olefin polymerization catalysts on solid supports offers a simple “drop-in” catalyst solution for existing industry slurry or gas-phase polymerization processes [25,26]. Surprisingly, there have been very few heterogenization studies of α-diimine nickel and palladium complexes. In 2002, Brookhart and coworkers prepared hydroxyl- and amino-functionalized α-diimine nickel complexes (Scheme 1b) and supported them on $AlMe_3$ pre-treated silica [27]. The strategy of installing reactive substituents for heterogenization was subsequently investigated by the Bernardo-Gusmão group [28,29]. In 2017, Conley and coworkers reacted (α-diimine)$NiMe_2$ with partially-dehydroxylated sulfated zirconia and obtained a highly-active heterogeneous cata-

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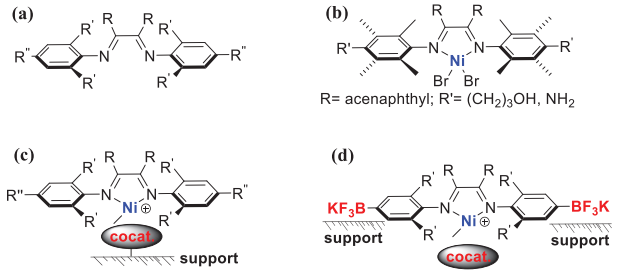


Scheme 1. (a) α-Diimine ligands. (b) Hydroxyl- and amino-functionalized α-diimine nickel complexes. (c) Interaction of α-diimine nickel complexes with a pre-treated solid aluminum support. (d) Interaction of trifluoroborate potassium-functionalized α-diimine nickel complexes with an untreated solid support.

lyst for ethylene polymerization [30]. The reaction of α-diimine nickel complexes with a pre-treated solid aluminum support can also produce potent heterogeneous catalysts (Scheme 1c) [31–33]. It should be noted that aluminum pre-treatment is required for successful heterogenization, and the direct interaction of α-diimine nickel bromide complexes with the solid support is very weak (*vide-infra*).

Recently, Chen and coworkers reported an ionic anchoring strategy (IAS) to support OM (M: Li, Na, K) tagged homogeneous transition metal complexes on solid support to prepare heterogeneous olefin polymerization catalysts [34]. In this contribution, we extend this IAS strategy by changing the OM tags to BF_3K-based tag (Scheme 1d), thereby demonstrating the generality of this strategy in various systems. The installation of ionic trifluoroborate potassium tag on α-diimine nickel complexes significantly increased their affinity for solid supports, leading to the formation of a heterogeneous catalyst *via* simple mixing. An added benefit of this strategy is that the trifluoroborate substituent is strongly electron-donating, which can increase the catalyst stability and polyethylene molecular weight in α-diimine systems [35–37].

The reaction of bromo-substituted aniline with 2,3-butanedione formed a bromo-substituted α-diimine ligand. The subsequent reaction with bis(pinacolato)diboron converted the bromo substituent into a pinacolato group that was subsequently transformed into a trifluoroborate potassium group with a high yield (Scheme 2a). Unfortunately, the direct reaction of the trifluoroborate potassium-substituted α-diimine ligand with (DME)$NiBr_2$ (DME = ethylene glycol dimethyl ether) led to the formation of KBr and nickel black. To address this issue, 18-crown-6 ether was added to afford the desired ligands (**L1** and **L2**) in quantitative yield, which are more soluble in common organic solvents and easier to handle than their trifluoroborate potassium counterparts. The reactions of the ligands with the nickel precursor led to the formation of the corresponding nickel complexes (**Ni1** and **Ni2**) with a high yield and purity. The methyl and isopropyl-substituted nickel analogs (**Ni1-A** and **Ni2-A**) without a trifluoroborate potassium moiety were prepared for comparison. The supported catalysts (**Ni1@SiO_2** and **Ni2@SiO_2**) were prepared by stirring in a CH_2Cl_2 solution containing nickel complexes with SiO_2 support, followed by washing the solid precipitate with CH_2Cl_2. The maximum supporting capacity was *ca.* 10 μmol **Ni1/Ni2** per 100 mg of SiO_2, corresponding to Ni loadings of *ca.* 0.5 wt%. The ICP-AES analysis of the supported catalysts confirmed the loading content of the nickel (see Supporting information). A similar supporting procedure using **Ni1-A** or **Ni2-A** failed to load any significant amount of nickel complexes on the SiO_2 support, possibly due to the weak interaction between the Ni-Br moiety and the silica surface.

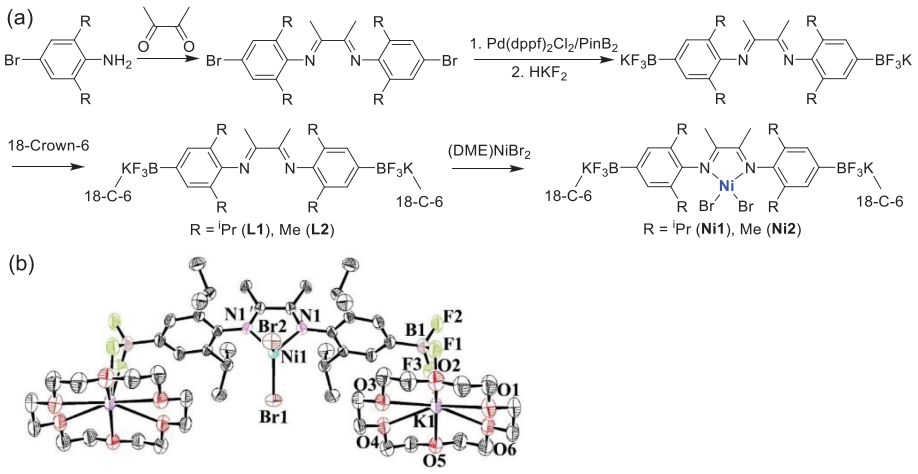
The molecular structure of **Ni-1** was determined by X-ray diffraction (Scheme 2b). The geometry at the nickel center is a distorted tetrahedron with the two bromine atoms lying above and below the Ni-N-N plane. The presence of trifluoroborate potassium and 18-crown-6 ether slightly perturb the coordination environment of the ligand toward the nickel center, and the bond lengths and angles are similar to previously reported α-diimine nickel complexes.

Methylaluminoxane (MAO) is probably the most commonly used aluminum cocatalyst in polyolefin research, but it is expensive and pyrophoric. In this work, we explored cheap and easy-to-handle aluminum cocatalysts as alternatives. All four aluminum cocatalysts ($AlEt_2Cl$, $AliBu_3$, $AlEtCl_2$, $Al_2Et_3Cl_2$) afforded highly-active systems during ethylene polymerization (Table S1 in Supporting information, entries 1-4). $AlEt_2Cl$ was the best choice in terms of activity (1.61×10^7 g mol^{-1} h^{-1}) and polyethylene molecular weight ($M_n = 732800$ g/mol). Lowering the amount of $AlEt_2Cl$ led to a slightly decreased activity and polyethylene branching density, along with an increased molecular weight (Table S1, entries 5 and 6). Remarkably, 100 equiv. of $AlEt_2Cl$ produced a highly active catalytic system (1.49×10^7 g mol^{-1} h^{-1}) that could generate high-molecular-weight polyethylene ($M_n = 783300$ g/mol). This represents a significant advantage since most homogeneous α-diimine nickel bromide complexes require the addition of hundreds of equivalents of aluminum cocatalyst to reach such a high activity. By lowing the **Ni1** loading on the SiO_2 support, the catalytic activities remained unchanged, while the polyethylene molecular weight was significantly increased to well above one million (Table S1, entries 7 and 8). Most importantly, narrow polydispersities were observed in all these polymerization studies, indicating that the single-site characteristics of these catalysts were unaffected by immobilization on the SiO_2 support.

Based on these results, 100 equiv. of Et_2AlCl cocatalyst was chosen for subsequent studies. Interestingly, the trifluoroborate potassium-substituted nickel complexes (**Ni1** and **Ni2**) showed better performances (higher activity and higher polyethylene molecular weight) than their unsubstituted analogs (**Ni1-A** and **Ni2-A**; Table 1, entries 1 and 2 *versus* 3 and 4). This is likely due to the electron-donating nature of the trifluoroborate potassium group. The heterogenization of nickel complexes led to a significantly enhanced activity and polyethylene molecular weight (Table 1, entries 5 and 8 *versus* 1 and 2). Meanwhile, the polyethylene branching density was dramatically decreased, and the melting temperature increased. These results can be explained by the increased steric environment around the nickel center and the decreased chain transfer rate induced by heterogenization. The electron-donating ability of trifluoroborate substituent may also contribute to this effect. More importantly, the homogeneous catalyst generated continuous materials that stuck to the polymerization vessel (Fig. S1 in Supporting information). In contrast, the heterogeneous nickel complex generated free-flowing materials with good morphology control (Fig. S1), which makes the system suitable for industrially preferred continuous processes.

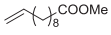
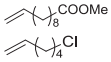
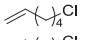
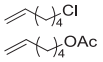
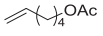
When the polymerization temperature was increased from 30 °C to 80 °C, the catalytic activity only slightly decreased (12% for **Ni1@SiO_2** and 24% for **Ni2@SiO_2**; Table 1, entries 5-10). Meanwhile, the polyethylene molecular weights slightly decreased. By tuning the catalyst structure and polymerization temperature, the polymer branching density could be tuned over a very wide range (21–64/1000 C). Furthermore, time-dependent studies at 80 °C showed that the homogeneous catalysts (**Ni1**, **Ni2**, **Ni1-A** and **Ni2-A**) completely lost activity within 30 min, while the heterogeneous catalysts (**Ni1@SiO_2** and **Ni2@SiO_2**) remained highly active for 60 min (Figs. 1a and b).

One of the most attractive features of α-diimine nickel systems is their ability to copolymerize ethylene with polar functionalized comonomers; however, although numerous studies have used homogeneous catalysts [38–41], there have been very few studies concerning the copolymerization capabilities of heterogeneous



Scheme 2. (a) Synthesis of trifluoroborate potassium-functionalized α-diimine ligands and the corresponding nickel complexes. (b) Molecular structure of complex **Ni-1** in the solid state; Hydrogen atoms have been omitted for clarity. Atoms are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Br1−Ni1 2.332(3), Br2−Ni1 2.316(3), Ni1−N1 1.990(7), Ni1−N1′ 1.990(7), N1−Ni1− N1′ 82.2(4), N1−Ni1−Br1 116.7(2), N1′−Ni1−Br1 116.7(2), N1−Ni1−Br2 110.3(2), N1′−Ni1−Br2 110.3(2), Br1−Ni1−Br2 115.94(11).

Table 1
Comparison of the homogeneous and heterogeneous systems in ethylene polymerization and copolymerization.

Entry	Cat.	Como.	T (°C)	Yield (g)	Act. [c]	Incorp. (mol%)[d]	M_n[e] (10^4)	M_w/M_n[e]	B[f]	T_m (°C)[g]
1 [a]	Ni1	-	30	0.42	1.01	-	27.15	2.16	78	93.5
2 [a]	**Ni2**	-	30	1.58	3.79	-	15.50	2.31	39	116.8
3 [a]	**Ni1-A**	-	30	0.36	0.86	-	21.90	2.52	81	-
4 [a]	**Ni2-A**	-	30	0.78	1.87	-	10.90	2.96	43	110.8
5 [a]	**Ni1@SiO$_2$**	-	30	0.67	1.61	-	73.28	2.18	34	115.3
6 [a]	**Ni1@SiO$_2$**	-	50	0.73	1.75	-	59.03	2.46	43	114.8
7 [a]	**Ni1@SiO$_2$**	-	80	0.59	1.42	-	39.36	2.55	64	110.2
8 [a]	**Ni2@SiO$_2$**	-	30	2.53	6.07	-	22.32	2.95	21	124.4
9 [a]	**Ni2@SiO$_2$**	-	50	2.72	6.53	-	19.50	3.00	24	123.5
10 [a]	**Ni2@SiO$_2$**	-	80	1.93	4.63	-	14.25	2.28	28	121.7
11[b]	**Ni1@SiO$_2$**		30	0.13	1.3	0.17	3.67	2.15	22	118.6
12[b]	**Ni2@SiO$_2$**		30	0.17	1.7	0.22	2.07	2.14	10	121.7
13[b]	**Ni1@SiO$_2$**		30	0.09	0.9	0.30	11.80	2.00	30	115.5
14[b]	**Ni2@SiO$_2$**		30	0.21	2.1	0.48	3.62	2.21	16	124.2
15[b]	**Ni1@SiO$_2$**		30	0.10	1.0	0.36	2.34	2.08	27	114.4
16[b]	**Ni2@SiO$_2$**		30	0.15	1.5	0.39	1.53	3.11	11	120.4

[a] Polymerization conditions: precatalyst (0.5 μmol), $AlEt_2Cl$ (100 equiv.), hexane (20 mL), 8 atm ethylene pressure, 5 min.
[b] Polymerization conditions: precatalyst (1.0 μmol), $AlEt_2Cl$ (100 equiv.), hexane (20 mL), 8 atm ethylene pressure, 60 min, [Como.] = 0.5 mol/L.
[c] Activity is in units of 10^7 g mol^{-1} h^{-1}.
[d] Determined by ^{1}H NMR spectroscopy.
[e] Determined by gel permeation chromatography (GPC) in trichlorobenzene at 150 °C with polystyrene standards.
[f] Number of branches per 1000 carbon atoms, as determined from ^{1}H NMR spectroscopy.
[g] Determined by differential scanning calorimetry (DSC, second heating).

α-diimine nickel catalysts. In this system, moderate activities and comonomer incorporation were observed for ethylene copolymerization with methyl 10-undecenoate, 6-chloro-1-hexene and 5-hexenylacetate. Semicrystalline copolymers with high molecular weights and low branching densities were obtained (Table 1, entries 11-16). The low comonomer incorporation ratio is likely due to steric effect from heterogenization.

Different polyethylene microstructures (molecular weight, branching, *etc.*) will translate into different mechanical properties (Figs. 1c and d). The polyethylene products generated by **Ni1** and **Ni2** both showed enhanced tensile strength at break and elongation at break than the products generated by **Ni1-A** and **Ni2-A**. The polyethylene products generated by the heterogeneous systems (**Ni1@SiO$_2$** and **Ni2@SiO$_2$**) showed typical thermoplastic behavior with tensile moduli comparable to those of commercially-available polymers. For both systems, a higher polymerization temperature led to reduced tensile strength and slightly increased elongation at break. This was probably due to the lower molecular weight and higher branching density at higher polymerization temperatures.

In summary, two trifluoroborate potassium-functionalized α-diimine nickel complexes (**Ni1** and **Ni2**) were prepared and characterized. Their analogs (**Ni1-A** and **Ni2-A**) without the trifluoroborate potassium moiety were prepared for comparison. **Ni1-A** and **Ni2-A** showed very low affinity towards the **SiO$_2$** solid support. In contrast, heterogeneous catalysts (**Ni1@SiO$_2$** and **Ni2@SiO$_2$**) with a high nickel content (0.5 wt%) could be easily prepared by simply mixing the nickel complexes with SiO_2. The heterogeneous catalysts demonstrated greatly enhanced properties (high activity, high thermal stability, and high polymer molecular weight) during ethylene polymerization compared with their homogeneous counterparts. The narrow polydispersities of the resulting polyethylenes indicate the single-site characteristics of these heterogeneous catalysts. Furthermore, these heterogeneous catalysts could be used to copolymerize ethylene with methyl 10-undecenoate/6-chloro-1-

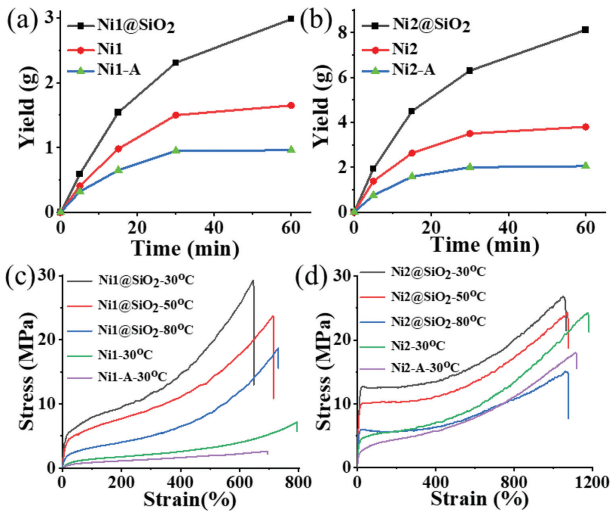


Fig. 1. (a, b) Time-dependent studies (polymer yields versus polymerization time) for different nickel catalysts at 80 °C. (c, d) Stress-strain curves for the polyethylene products.

hexene and 5-hexenylacetate, leading to the formation of polar semicrystalline polyolefins. The trifluoroborate potassium moiety played two key roles: (1) Its electron-donating ability led to high catalyst stability and high polymer molecular weights; (2) Its ionic nature gave it a strong affinity for the solid support. It is expected that this trifluoroborate potassium-based heterogenization strategy will find applications in other olefin polymerization systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.107918.

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