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Highly Active Supported Nickel Diimine Catalysts for Polymerization of Ethylene

Peter Preishuber-Pflugl and Maurice Brookhart*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

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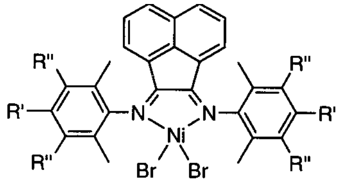
Recently, new late transition metal catalysts for the polymerization of olefins have attracted attention in academics and industry. These catalysts have many unique and practical features such as the potential to produce branched polyethylene from ethylene alone.[1,2] And, because of their low oxophilicity, late transition metal complexes can copolymerize ethylene with certain polar comonomers,[3] and polymerizations in polar media like water have been reported.[4] In particular, aryl-substituted α-diimine nickel(II) complexes in combination with different cocatalysts show remarkably high activities in polymerization of ethylene.[5] With these catalysts, the microstructure of the polymers can be varied by changing the bulk of ortho substituents on the aryl rings and by changing pressure or temperature.[1,5] This combination of high activities and unique polymer structures make the nickel(II) catalysts desirable for applications in commercial polymerization processes.[1]

Supporting of soluble single-site catalysts on preferably inorganic substrates is essential to provide “drop-in” catalysts for use in existing technologies for slurry or gas-phase polymerization processes. One technique previously used to support Ni(II) diimine catalysts is based on methylaluminoxane (MAO) tethered to inorganic material.[6] Silica was treated with a solution of MAO, followed by reaction with Ni(II) diimine precursors. Alternatively, MAO and Ni(II) diimine complexes were combined in a solvent, followed by addition to silica.[6a] Though this technique is common for early transition metal catalysts such as metallocenes,[7] the activities reported for Ni(II) diimine catalysts supported in this manner were low, in particular at higher temperatures. It is probable that limiting the cocatalyst to MAO leads to the low activities. For late transition metal complexes aluminum alkyl cocatalysts are not only responsible for activation but also implicated in deactivating the active catalyst by reduction of the Ni(II).[8] The use of reoxidants to improve catalyst performance was described in the literature.[9] A careful choice of the cocatalyst is of great importance.

Covalently attaching Ni(II) diimine complexes to supports is a method that allows ready use of a range of activators other than MAO. Polymer-supported nickel diimine complexes have been previously synthesized by first attaching ligands to the support material; the Ni(II) diimine catalyst complexes were then constructed by addition of the labile (1,2-dimethoxyethane)NiBr$_2$.[10] We were interested in the synthesis of nickel diimine complexes whose ligands contained a functionality for reaction with a second functional group on the surface of the support. A rather similar method for supporting SHOP-type oligomerization catalysts has been reported earlier.[11] Recently, covalently attached bis(imino)pyridyl Fe(II) catalysts were used successfully for ethylene polymerization.[12] We report here (1) preparation of supported catalysts through use of aryl α-diimine Ni(II) complexes substituted with hydroxy or amino functionalities as reactive complexes and silica pretreated with trimethylaluminum as activated support material and (2) use of these supported catalysts for slurry polymerization of ethylene in the presence of various activators.

Scheme 1. Nickel(II) Diimine Complexes



	R'	R''
1	H	H
2	$(CH_2)_3OH$	H
3	$CH_2(3,5\text{-}Me_2\text{-}Ph)NH_2$	H
4	NH_2	Me

The hydroxy- and amine-functionalized ligands shown in Scheme 1 were synthesized using standard procedures as described in the Supporting Information. Nickel diimine complexes **1**−**4** (Scheme 1) were prepared following modified methods previously reported.[1] No protecting groups for hydroxy or amino functionalities of the ligand were necessary during formation of the nickel diimine complexes. To support compounds **2**−**4**, methylene chloride solutions of the complexes were combined with the pretreated silica (Scheme 2). Using this procedure, only methane is generated as a byproduct eliminating any salt formation. No color change occurred during the supporting process, so we assume that no significant amount of the complex was activated by the aluminum species on the silica surface. As soon as cocatalyst activator was added to the supported catalysts, the brownish powder changed to purple, the color of the active catalyst in solution. For comparison purposes, catalyst **1** was supported by reaction of the metal complex with silica pretreated with MAO as described in the literature.[6]

The supported catalysts were tested in slurry polymerization runs at 150 psig ethylene in pentane at temperatures between 30 and 80 °C. A polymerization time of 2 h was chosen to simulate a common residence time in commercial polymerization processes. The results are summarized in Table 1. The Ni(II) diimine complexes covalently attached to silica through hydroxy-functionalized ligands showed very high activities in ethylene polymerization when activated with alkylaluminum halides. With Ni loadings of 0.6 wt %, activities up to 750 kg of PE/g of Ni were obtained with ethylaluminum sesquichloride (EASC) as cocatalyst (entry 2). When increasing the load of Ni to 2.0 wt %, activities of 10 kg of PE/g of heterogeneous catalyst were achieved (entry 11).

EASC was found to be a suitable cocatalyst for polymerization runs at 60 °C (entries 2−5).[13] Remarkably, activities remained high at Al:Ni ratios as low 80 (720 kg of PE/g of Ni, entry 3). When raising the temperature to 80 °C, methylaluminum dichloride (MADC) was found to provide higher activities than EASC (entry 10 vs entry 7). We attribute this fact to a

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Scheme 2. Synthesis of Supported Complex 2

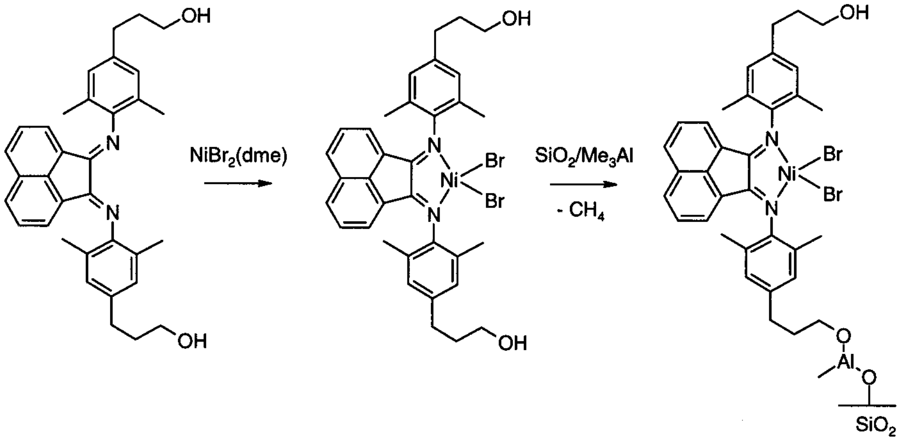

Table 1. Slurry Polymerization Results[a]

entry	cat.	wt % Ni	temp [°C]	cocat I	cocat II	Al:Ni ratio	kg of PE/ g of het cat	kg of PE/ g of metal	mp[b] [°C]	Mw[c] ($\times 10^3$) [g/mol]	PDI[c]	branches/ 1000C[d]
1	**1**	0.46	60			60	0.21	44				
2	**2**	0.60	60	$Et_3Al_2Cl_3$		700	4.5	750	126.1	131	3.3	13
3	**2**	0.60	60	$Et_3Al_2Cl_3$		80	4.3	720				
4	**2**	0.60	60	$Et_3Al_2Cl_3$	$AlCl_3$	700 + 900	4.9	820				
5	**2**	0.60	60	$Et_3Al_2Cl_3$	$AlCl_3$	700 + 30	4.3	720				
6	**2**	0.60	30	$Et_3Al_2Cl_3$		1000	2.4	400				
7	**2**	0.60	80	$Et_3Al_2Cl_3$		800	1.2	200	122.3	74	3.5	
8	**2**	0.60	30	$Me_2Al_2Cl_4$		1000	2.2	370				
9	**2**	0.60	60	$Me_2Al_2Cl_4$		800	3.9	650	127.0	131	3.4	
10	**2**	0.60	80	$Me_2Al_2Cl_4$		800	1.7	280	121.4	73	3.7	
11	**2**	2.0	60	$Et_3Al_2Cl_3$		500	10.8	530	125.3	136	3.4	14
12	**3**	0.56	60	$Et_3Al_2Cl_3$		500	3.3	580	127.7	153	3.6	
13	**4**	0.23	60	$Et_3Al_2Cl_3$		500	0.9	390	134.2	218	3.8	<5

[a] 300 mL reactor, 100 mL of pentane, 2 h runs. [b] Melting point was determined by DSC. [c] Molecular weight and polydispersity were determined by SEC. [d] Total branching was determined by ^{1}H NMR.

slower deactivation of the active species. Activities at 30 °C (entries 6 and 8) were again lower than those at 60 °C with both cocatalysts.

Amino-functionalized complex **3** showed activities up to 580 kg of PE/g of Ni (entry 12). The maximum load of Ni was lower (0.6 wt %) in these complexes due most likely to the steric bulk next to the amino group. Complex **4** supported through an amine directly para-substituted on its aryl ring showed activities of 390 kg/g of Ni (entry 13). The change in activity might be caused by changes of the electronic properties of the ligand.

Compared to the activity of catalyst **1** supported by reaction with MAO/silica (entry 1), the described method improved the activities by more than 10-fold by supporting the catalysts covalently through their ligands.

In all polymerization runs no reactor fouling was found with the covalently attached catalysts. The polymers obtained showed molecular weights in the range of 10^5 and polydispersities around 3.5. The melting points of the polymer drop with increasing polymerization temperature. The same behavior had been observed with the unsupported catalysts.[5]

In summary, we report here a new technique to synthesize highly active supported Ni(II) diimine complexes. Hydroxy- and amino-functionalized Ni diimine complexes were synthesized without the need for protecting groups. By reaction of these functionalities with activated silica, the catalysts were covalently bound to the support. These tethered complexes could be used to polymerize ethylene with high activity using alkylaluminum halides as inexpensive cocatalysts at low Al:Ni ratios. The supported Ni(II) diimine complexes showed 10-fold higher activities than MAO-supported systems described in the literature.[6] High activities (up to 10 kg of PE/g of heterogeneous catalyst), the ease of synthesis of these tethered Ni diimine catalysts, and effective activation with low loads of inexpensive cocatalysts suggest possible utility in commercial processes. The support of other late transition metal catalysts using the same method is under investigation.

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Supporting Information Available: Synthesis of compounds **2**−**4**, supporting procedures, and polymerization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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