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Ethylene Polymerization Activity of $(R_3P)Ni(codH)^+$ (cod = 1,5-cylcooctadiene) Sites Supported on Sulfated Zirconium Oxide

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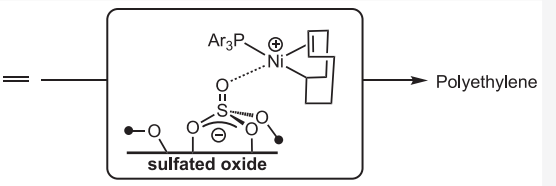
ABSTRACT: PAr_3 containing *o*-OMe, *o*-Me, or *o*-Et substituents reacts with Brønsted sites on sulfated zirconium oxide (**SZO**) to form $[HPAr_3][\mathbf{SZO}]$. The phosphonium sites on this material react with bis(cyclooctadiene)nickel $[Ni(cod)_2]$ to form $[Ni(PAr_3)(codH)][\mathbf{SZO}]$ that are active in ethylene polymerization reactions. Selective poisoning studies with pyridine show that ~90% of the $Ni(PAr_3)(codH)^+$ sites in this material are active in polymerization reactions.



INTRODUCTION

Organometallic complexes of nickel and palladium containing the *o*-phosphinoarenesulfonate ligand ({PO}) catalyze polymerization of olefins. In contrast to (α-diimine)Pd-R^+ catalysts,[1] {PO}Pd-R complexes polymerize ethylene to form linear polymers[2] and show broad functional group tolerance in copolymerization reactions with polar comonomers.[3] The formation of linear polymers with {PO}Pd-R complexes is related to the cis arrangement of a strong-trans-influence phosphine and a weak-trans-influence sulfonate that results in electronic asymmetry in the palladium complex,[4] which inhibits β-H elimination and reinsertion steps that result in branches in the polymer chain.[5] This general design strategy continues to find application in new cationic palladium and nickel catalysts that incorporate electronically dissymmetric ligands and have very high polymerization activities and good functional group tolerance.[6]

Industrial olefin polymerization catalysts are almost always heterogeneous.[7] Silica pretreated with alkylaluminum or methaluminoxane (MAO) is a very common support for polymerization catalysts but is not generally compatible with late-transition-metal polymerization precatalysts. For example, (α-diimine)Ni catalysts supported on MAO/SiO_2 have low polymerization activities, but modified (α-diimine)$NiBr_2$ complexes containing hydroxyl groups react with SiO_2/MAO and polymerize ethylene in the presence of an $Et_3Al_2Cl_3$ activator to give polymers with broad molecular weight distributions.[8]

Formation of well-defined organometallics on oxide surfaces is a potentially attractive synthetic strategy to access active sites for polymerization reactions.[9] In this reaction, a partially dehydroxylated oxide containing −OH groups on the surface reacts with an organometallic to form covalent M−O_x (O_x = surface oxygen) or an electrophilic M---O_x ion pair. Supports containing −OH groups with weak Brønsted acidity (e.g., SiO_2) form M−O_x and are inactive in polymerization reactions in the absence of exogenous activators.[10] However, M---O_x ion pairs form on supports containing −OH sites more Brønsted acidic than silica, such as sulfated oxides[11] or Lewis-acid-activated silica.[12] The reaction of (α-diimine)$NiMe_2$ or (α-diimine)$PdMe_2$ with sulfated zirconium oxide partially dehydroxylated at 300 °C ($\mathbf{SZO}_{300}$) forms the active sites shown in Figure 1a that have activities close to those of their solution analogues and show single-site behavior.[13]

The application of this strategy to surface analogues of {PO}M-R (M = Ni, Pd) is not as straightforward.[14] {PO}PdR(L) are expected to react with −OH sites on oxides to form $[\{PO\}ML][\mathbf{SZO}_{300}]$ ion pairs that lack the organometallic unit that is critical to propagate polymer growth (Figure 1b). Early reports of polymerization reactions with {PO}Pd complexes were generated from the reactions of Pd_2dba_3 or $Pd(OAc)_2$ and {PO}H, which presumably forms {PO}Pd-H under the reaction conditions (Figure 2).[15] The Brønsted sites on $\mathbf{SZO}_{300}$ react with sufficiently basic R_3P to form $[R_3PH][\mathbf{SZO}_{300}]$,[16] which may serve as heterogeneous {PO}H-type surface sites. This paper describes the reaction of $[R_3PH][\mathbf{SZO}_{300}]$ with bis(cyclooctadiene)nickel $[Ni(cod)_2]$ to produce active sites for the polymerization of ethylene.

RESULTS AND DISCUSSION

This study focuses on Ar_3P containing two aryl fragments with ortho subsituents that are common in typical {PO}M-R catalysts. The reaction of triarylphosphines with the Brønsted sites on $\mathbf{SZO}_{300}$ is expected to form $[Ar_3PH][\mathbf{SZO}_{300}]$, provided that the pK_a value of $[Ar_3PH]$ is greater than ~6 in acetonitrile (MeCN).[16] For example, $P(o\text{-}OMeC_6H_4)_2Ph$

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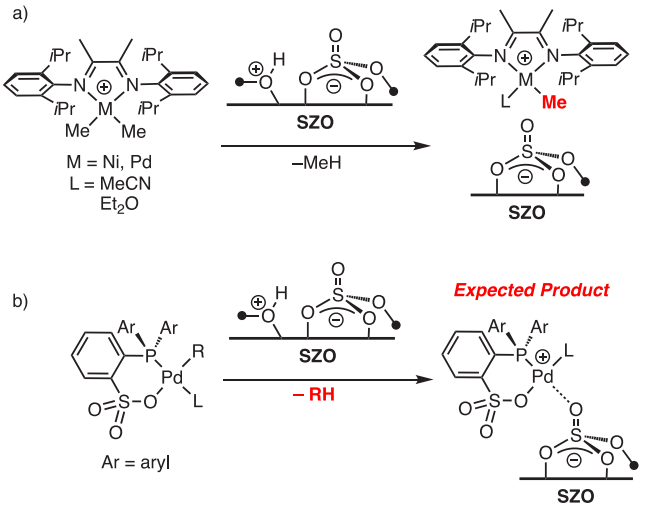

Figure 1. Heterogeneous (α-diimine)Ni or -Pd catalysts supported on **SZO$_{300}$** for the polymerization of olefins (a). Related reaction of a {PO}Pd–R catalyst with **SZO$_{300}$** to form [{PO}Pd][**SZO$_{300}$**], which are unreactive toward olefins (b).

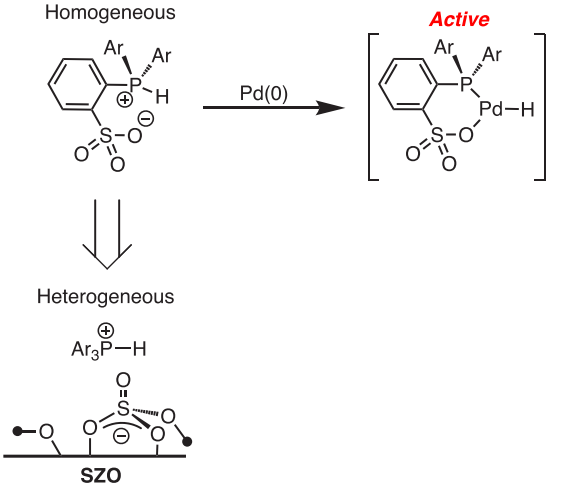

Figure 2. Reaction of {PO}H with Pd(0) to form Pd-H that is active in olefin polymerization in solution and design of [HPAr$_3$][**SZO$_{300}$**] to form heterogeneous {PO}M-R active sites.

reacts with **SZO$_{300}$** to form [HP(*o*-OMeC$_6$H$_4$)$_2$Ph][**SZO$_{300}$**] (**1**; Figure 3a). The ^{31}P magic-angle-spinning (MAS) NMR spectrum of **1** contains a signal at 10 ppm (Figure 3b, top spectrum). The Fourier transform infrared (FTIR) spectrum of **1** is shown in Figure 3c (top) and contains a characteristic ν_{PH} stretch at 2456 cm^{-1}, consistent with formation of the phosphonium in [**1H**][**SZO$_{300}$**]. Similar results were obtained for reactions of P(*o*-MeC$_6$H$_4$)$_2$Ph or P(*o*-EtC$_6$H$_4$)$_2$Ph with **SZO$_{300}$** to form [HP(*o*-MeC$_6$H$_4$)$_2$Ph][SZO$_{300}$] ([**2H**]-[**SZO$_{300}$**]) or [HP(*o*-EtC$_6$H$_4$)$_2$Ph][SZO$_{300}$] ([**3H**][**SZO$_{300}$**]), respectively.

1–**3** react with a clear yellow solution of Ni(cod)$_2$ in diethyl ether (Et$_2$O) to form orange [Ni(PAr$_3$)(codH)][**SZO$_{300}$**] (**1Ni**–**3Ni**; Figure 3a). This reaction also evolves 1,5-cyclooctadiene (0.10 mmol g^{-1}), which is consistent with the loss of one cod per Ni in **1Ni**–**3Ni**. Figure 3b (bottom) shows the FTIR spectrum of **1Ni**, which lacks a ν_{PH} stretch. In addition, the ^{31}P MAS NMR spectrum of **1Ni** contains a new signal at 47 ppm, 37 ppm downfield from that of **1**. These

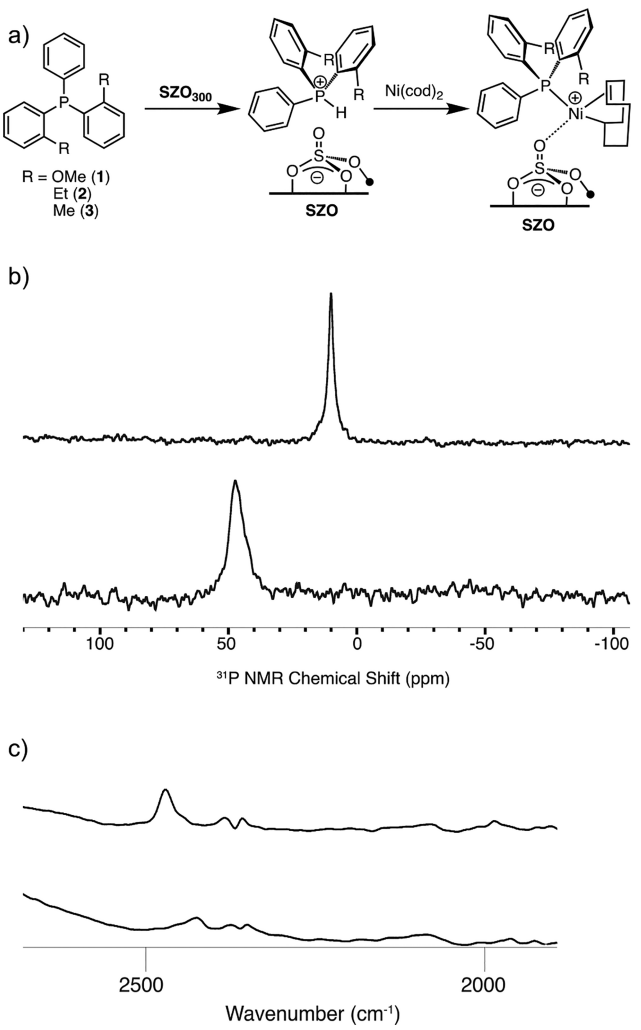

Figure 3. Formation of [Ni(PAr$_3$)(codH)][SZO] (a). ^{31}P{^{1}H} MAS NMR spectrum of **1** (top) and [Ni(P(o-OMeC$_6$H$_4$)$_2$Ph)(codH)]-[SZO$_{300}$] (bottom, b). FTIR of **1** (top) and [Ni(P(o-OMeC$_6$H$_4$)$_2$Ph)(codH)][SZO$_{300}$] (bottom, c).

results indicate that the phosphonium in **1** reacts with Ni(cod)$_2$ to form **1Ni**. The cross-polarization ^{13}C MAS NMR spectra of **1Ni**–**3Ni** contain signals assigned to the (codH)$^+$ fragment in Ni(PAr$_3$)(codH)$^+$.[17] The key NMR and FTIR features of **1** and **1Ni** are summarized in Table 1.

1Ni reacts with 150 psi of ethylene on demand at 50 °C, which results in the formation of polyethylene containing 35 branches/1000C (Table 2, entry 1). ^{13}C NMR analysis of the polymer shows that methyl, ethyl, and butyl branches are present in this polymer. Contacting **1Ni** with a slight excess of

Table 1. Key Spectral Data for [HPAr$_3$][SZO$_{300}$] and [Ni(PAr$_3$)(codH)][SZO$_{300}$]

		[HPAr$_3$][**SZO$_{300}$**]		[Ni(PAr$_3$)(codH)]
PAr$_3$	δ^{31}P (ppm)[a]	δ^{31}P (ppm)[b]	ν_{PH} (cm^{-1})	δ^{31}P (ppm)[b]
1	−26.4	10	2456	47
2	−22.4	13	2447	45
3	−20.8	11	2454	45

[a]C$_6$D$_6$ solution, referenced to 85% H$_3$PO$_4$. [b]10 kHz MAS spinning speed, referenced to 85% H$_3$PO$_4$.

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Table 2. Ethylene Polymerization Activity of [Ni(PAr$_3$)(codH)][SZO$_{300}$][a]

entry	PAr$_3$	P (psi)[b]	T (°C)	yield (mg)	activity[c]	B/1000C[d]
1	**1**	150	50	71	3000(150)	35
2	**2**	150	50	82	3400(100)	20
3	**3**	100	50	12	510(10)	n.d.
4	**3**	150	50	83	3500(100)	24
5	**3**	200	50	91	3500(500)	n.d.
6	**3**	250	65	80	3400(300)	n.d.

[a]Catalyst loading (12 μmol) in toluene (see the Supporting Information for details). [b]Pressure of ethylene on demand. [c]g_{PE} mol_{Ni}^{-1} h^{-1} calculated from triplicate polymerization runs assuming that all Ni in [Ni(PAr$_3$)(codH)][**SZO$_{300}$**] is active in polymerization. The values in parentheses are the associated standard errors based on the polymer yield. [d]Measured by ^{1}H NMR spectroscopy in CD_2Cl_4 at 120 °C.

pyridine (Ni:pyridine = 1:1.2) results in complete suppression of the polymerization activity, indicating that pyridine poisons Ni sites in the polymerization reaction. The addition of substiochiometric pyridine to **1Ni** followed by reaction with 150 psi of ethylene on demand results in the formation of polyethylene, although with a lower activity than that of reactions conducted in the absence of pyridine. Plots of the activity versus the molar ratio of pyridine to Ni are linear and indicate that ∼90% of the Ni sites in **1Ni** are capable of initiating ethylene polymerization (Figure S8).

The polymerization activity data for **1Ni**−**3Ni** are given in Table 2. The activity of **1Ni** under these conditions is 3000(150) g_{PE} mol_{Ni}^{-1} h^{-1}. This activity is modest compared to that of {PO}M−R species but similar to that of catalysts prepared from {PO}H with similar steric profiles and Pd(0) sources in situ.[18] **2Ni** (Table 2, entry 2) and **3Ni** (Table 2, entry 4) show similar activities and similar branching of the polyethylene produced with these catalysts. Running polymerization reactions at lower pressures with **3Ni** results in lower polymerization activity (Table 2, entry 3), but higher pressures do not result in significant activity gains (Table 2, entries 5 and 6). The formation of branched polymer products using **1Ni**−**3Ni** is in contrast to polymers obtained with homogeneous {PO}Pd−R or {PO}Ni−R catalysts in solution. The origin of this difference is unclear but may be related to the formation of a weakly coordinating ion pair between Ni(PAr$_3$)(codH)$^+$ and the sulfate sites on **SZO$_{300}$**,[11] which may facilitate chain walking.

1Ni−**3Ni** are not compatible with allyl chloride or methyl undecenoate, suggesting that further optimization of the Ni sites in these catalysts is needed to accommodate functionalized olefins. Attempts to analyze the polymers by gel permeation chromatography to obtain molecular weight information were unsuccessful because of the low solubility of the polymer in 1,2,4-trichlorobenzene at 140 °C and complications in removing **SZO** from these solutions.[19]

CONCLUSIONS

Triarylphosphines react with **SZO$_{300}$** to form [HPAr$_3$]-[**SZO$_{300}$**]. Subsequent reactions of the phosphonium sites with Ni(cod)$_2$ to form [Ni(PAr$_3$)(cod)H][**SZO$_{300}$**] are active in the polymerization of ethylene to give polymers with moderate branching in the polymer chain. The activity of [Ni(PAr$_3$)(cod)H][**SZO$_{300}$**] in polymerization is modest but similar to that of first-generation {PO}Pd catalysts. This suggests that modification of the coordination environment of the Ni(codH)$^+$ site by tuning the sterics and electronics of the phosphine may result in more active catalysts or catalysts tolerant of olefins containing functional groups.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00454.

Experimental details, solid-state NMR spectra, SEM images, and FTIR data (PDF)

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Notes

The authors declare no competing financial interest.

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