Polyethylene-entrapped Nickel(0) Diene Cyclo-oligomerization Catalysts

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The use of precipitates of polyethylene as a matrix quantitatively to entrap and recover selective homogeneous Ni(0) diene cyclo-oligomerization catalysts complexed by ligands composed of ethylene oligomers containing dialkylphosphito and diarylphosphito groups is described.

The use of polymers to immobilize homogeneous catalysts has developed into a subject of continuing interest because of the desire to combine the most desirable features of heterogeneous and homogeneous catalysts.[1] Insoluble polymers such as divinylbenzene cross-linked polystyrene have most commonly been used as organic polymeric supports in such studies although many other polymers have been sporadically examined.[2] Soluble polymers have received less attention although examples of their use exist.[3,4] Here we describe new procedures which employ polyethylene entrapment techniques to recover and reuse the active form of a transition metal catalyst.

The choice of polyethylene as a matrix for recovery of transition metal catalysts is based on the low reactivity of this polyalkene and our observations that high density polyethylenes or ethylene oligomers readily form solutions in hot organic solvents which on cooling selectively entrap functionalized ethylene oligomers.[5] Using functionalized ethylene oligomers as ligands, we can thus prepare a catalyst which is homogeneous at 110 °C and which can be recovered and separated from the reaction products by entrapment in polyethylene at 25 °C.

In a typical experiment, ethylene oligomer [0.5 g, *ca.* 0.2 mmol of $Me–(CH_2)_n–P(OAr)_2$] was placed in a pressure reactor along with polyethylene (2 g). After several evacuations and purges with Ar, anhydrous $Ni(acac)_2$ (acac = MeCOCHCOMe) (0.05 g, 0.2 mmol) was added to this reaction vessel in a dry box. Addition of toluene (40 ml) produced a suspension of $Ni(acac)_2$ and polymer which on heating to 120 °C formed a light green solution. Cooling this solution produced a suspension of polyethylene-entrapped catalyst precursor. Addition of a 25% $AlEt_3$ hexane solution (0.8 g, 1.7 mmol) and butadiene (8 g, 150 mmol) followed by heating to 110—120 °C produced a light yellow solution which was stirred for 3—4 h. After cooling this reaction solution, the polyethylene containing the phosphite ligand and catalyst precipitated from solution and was separated from the reaction mixture by centrifugation. Analysis of the reaction mixture showed a high, selective conversion of butadiene into cyclo-octa-1,5-diene (Table 1). Addition of fresh toluene and butadiene to the recovered polyethylene precipitate containing the active catalyst followed by heating to 110 °C reformed a homogeneous solution of active catalyst without addition of more organoaluminium reagent. The activity of this polymer-entrapable catalyst is comparable to that of a low molecular weight alkyldiarylphosphite-ligated Ni(0) catalyst. Changes in the structure of the oligomeric phosphite ligand produced changes in catalyst activity and selectivity analogous to those reported previously for homogeneous Ni(0) catalysts (Table 1) showing that ligand–metal interactions are readily controlled using these oligomeric catalyst ligands.[6]

Preparation of oligomeric phosphite ligands was accomplished most readily by reaction of a triarylphosphite or dialkyl- or diaryl-chlorophosphite with the lithium salt of a hydroxylated ethylene oligomer. The hydroxylated ethylene oligomers were prepared by quenching an anionic oligomerization of ethylene with ethylene oxide.[7] Each of the oligomeric phosphite ligands was characterizable by i.r., ^1H and ^{31}P n.m.r. spectroscopy, and molecular weight measurements.

Analysis of the solutions by ICP (inductively coupled plasma atomic emission spectrophotometry) after the catalyst–polyethylene precipitation had occurred indicated that very little nickel remained in solution after the first few cycles. Less than 10 p.p.b. Ni was present in the third cycle's filtrate. This corresponds to loss of <0.1% of the active catalyst to solution and shows that the catalyst recovery is essentially quantitative.

Table 1. Catalytic activity of polyethylene-entrapped catalysts for butadiene cyclodimerization.[a]

Catalyst	Cycle	Conversion/% [b]	Products (%) [b]
$[Pe–O–P\{O(o\text{-}C_6H_5)C_6H_4\}_2]Ni$	1	80	COD (92); VCH (5); CDT (2); others (1)
	2	60	COD (87); VCH (6); CDT (6); others (1)
	3	56	COD (80); VCH (16); CDT (4)
	4	45[c]	COD (10); VCH (83); CDT (7)
$[Me(CH_2)_{16}CH_2OP\{O(o\text{-}C_6H_5)C_6H_4\}_2]Ni$	1	86	COD (90); VCH (4); CDT (6)
$[P\{O(o\text{-}C_6H_5)C_6H_4\}_3]Ni$	1[d]	96	COD (95); VCH (3); CDT (2)
	2[e]	2	COD (87); VCH (5); CDT (8)
$[PE–O–P(OC_6H_5)_2]Ni$	1	70	COD (60); VCH (14); CDT (26)
	2	50	COD (70); VCH (20); CDT (10)
	3	47	COD (35); VCH (45); CDT (20)
$[Me(CH_2)_{16}CH_2OP(OC_6H_5)_2]Ni$	1	75	COD (75); VCH (15); CDT (15)
$[P(OC_6H_5)_3]Ni$	1	82	COD (77); VCH (6); CDT (15)

[a] All reactions were carried out at 110°C in toluene and were visually homogeneous; PE = ethylene oligomer. [b] The products were characterized by g.c.–mass spectroscopy. Yields of cyclo-octa-1,5-diene (COD), 4-vinylcyclohexene (VCH), and *trans,trans,trans*-cyclododeca-1,5,9-triene (CDT) were determined by g.c. [c] In this case, additional $AlEt_3$ was added. The altered product distribution is possibly due to acid catalysed formation of dialkylaryl- or trialkyl-phosphite along with loss of some of the hindered aryl groups from the oligomer. [d] Literature values for the product selectivity of this ligand and nickel catalyst are 96% COD, 3.1% VCH, 0.2% CDT and 0.2% others (Table III-3 of ref. 6). [e] This was a control experiment in which polyethylene had been added to this low molecular weight catalyst in its first cycle. Recovery of the polyethylene and re-use of the polyethylene as a catalyst in this second cycle resulted in low activity indicating that the catalyst was only entrapped in polyethylene precipitates if oligomeric phosphite ligands were used.

These entrapment procedures are a viable alternative to existing procedures for recovery and separation of homogeneous catalysts. The homogeneity of the catalysts permits easier control of ligand/metal ratios, heat transfer, study of catalyst species, and modification of catalyst selectivity through ligand modification. Recovery and limited reuse of reactive catalysts without reactivation in subsequent cycles is also possible. The selectivity and quantitative nature of the precipitation process make catalyst recovery feasible. Catalyst concentrations during the reactions are comparable to those used with known homogeneous catalysts and are high enough to produce useful reaction rates.

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