Pergamon

Tetrahedron Letters, Vol. 38, No. 21, pp. 3703-3706, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00717-X

Amphoteric, Water-Soluble Polymer-Bound Hydrogenation Catalysts

David E. Bergbreiter* and Yun-Shan Liu

Department of Chemistry

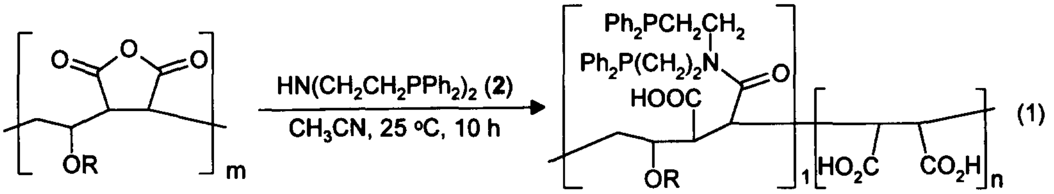
Texas A&M University, College Station, Texas 77843

E-mail: Bergbreiter@chemvx.tamu.edu

Abstract: The synthesis of a water soluble polymer-bound hydrogenation catalyst that is homogeneous and active in basic aqueous media but insoluble and inactive in weakly acidic media is described. This catalyst is also active in organic solvents. In water, the catalyst can be recovered by acidifying the solution to a pH <5. In acetonitrile, the catalyst can be recovered by solvent (ether) precipitation. Activities of the catalyst are comparable to but in every case slightly lower than those of a structurally similar low molecular weight catalyst. Recovery and reuse of the polymeric catalyst is simpler and more efficient.

Polymer-supported catalyst and reagent chemistry has seen a renaissance of interest in the past few years because of the development of combinatorial chemistry and because of the increasing interest in developing new processes that permit recovery and reuse of catalysts.[1,2] There is likewise interest in developing new chemistry to facilitate running organic reactions in non-traditional media as evidenced by the industrial interest in aqueous and fluorous phase chemistry.[3,4] Here we describe our initial work with new sorts of polymer-supported catalysts based on a commercially available copolymer of maleic anhydride and methyl vinyl ether. This poly(maleic anhydride)-*c*-poly(methyl vinyl ether) (Gantrez®) can easily be modified by reaction with a phosphine-containing amine and water to form the equivalent of the terpolymer that could putatively form from methyl vinyl ether, acrylic acid and a phosphine-containing acrylamide. We describe here the hydrogenation activity of rhodium(I) catalysts derived from this phosphine-containing polymer. These catalysts are soluble in water at pH >7.5 and insoluble below that pH. They are recoverable and reusable and have activities that closely resemble those of a low molecular weight analog.

Various sorts of other polymers have been used as supports for ligands for water-soluble catalysts. These include poly(ethylene oxide),[5-8] poly(*N*-alkylacrylamide)s,[9] poly(acrylic acid)s[10] and derivatives of polyamines.[11,12] Such catalysts can be recovered by solvent precipitation, heating, or base treatment. As a result of our other interests in water-soluble polymer supports, we have begun to explore derivatives of another commercially available copolymer – Gantrez®. Gantrez® (**1**) is the tradename for a class of



(1)

1 (Gantrez), R = $-CH_3$
m = 2200
$M_n/M_w = 3.54$

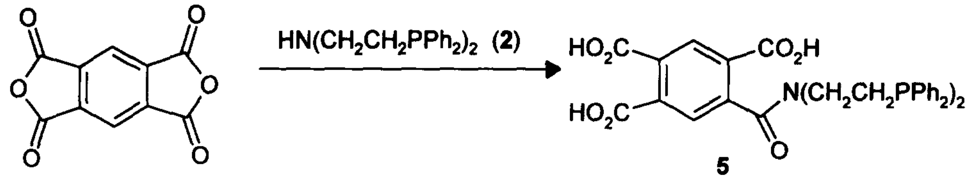
3a: n = 5
3b: n = 10
3c: n = 12
3d: n = 15

alternating copolymers of maleic anhydride with alkyl vinyl ethers and similar vinyl monomers. Due to the presence of the anhydride in **1**, it is a readily modified polymer. We reasoned that it should be possible to modify **1** by addition of a phosphine-containing amine, bis(diphenylphosphinoethyl)amine (**2**), to the anhydride group to form an amic acid-containing polymer (**3**). This expectation has been realized (equation 1), and we have found that we can prepare polymers **3** with varying loadings of phosphine (n = 5, 10, 12, 15). In these polymers, the remaining anhydride groups are hydrolyzed to form amphoteric carboxylic acid groups that serve as a mechanism for recovery and dissolution of the catalysts. Use of the less reactive secondary amine **2** in place of a primary amine (e.g. $H_2NCH_2CH_2CH_2PPh_2$) made it possible to control loading of the phosphine on the polymer **3**. Base-soluble rhodium(I) catalysts **4** were made from these chelating, polymer-bound phosphine ligands. Survey experiments showed that catalysts made with **3c** seemed most active. Ligand **3a** was not used as it did not dissolve in aqueous base.

In a typical procedure, 1.87 g of Gantrez® 149 ($M_n = 5 \times 10^4$ Da) was dissolved in 40 mL of CH_3CN and allowed to react with 0.48 g of **2**·HCl and 0.2 mL of Et_3N under N_2. After the aminolysis had proceeded for 10 h, an aliquot of the solution was analyzed by ^{31}P NMR spectroscopy. The absence of a signal at δ -20 indicated that **2** had been completely consumed. At this point, 10 mL of 2 N HCl were added to hydrolyze any remaining anhydride groups of **1**. The white precipitate formed was then collected and dried. This phosphine-containing polymer **3** had a poor quality ^1H NMR spectrum with broad peaks at δ 1.7, 2.5, 3.3 and 7.2. However, the ^{31}P NMR spectrum cleanly shows a broad singlet at δ -20.2 (no peak corresponding to phosphine oxide was present). A rhodium(I) hydrogenation catalyst was then formed from a basic aqueous solution of **3** by allowing 2 equiv of **3** to react with 1 equiv of $[Rh(COD)]^+OTf^-$.

In separate experiments, terephthalic anhydride was allowed to react with **2** to generate the phosphine carboxamide-tri(carboxylic acid) **5**. This carboxylated phosphine was in turn treated with Rh(I) as described above to form a low molecular weigh Rh(I) complex that served as a comparison to **4**.

The cationic Rh(I) catalyst **4** is soluble in basic solutions (pH > 7.5) at catalytically useful concentrations of ca. 1×10^{-3} M. Acidifying such solutions (CF_3SO_3H) produces an easily isolated yellow precipitate that



5

(2)

readily redissolves when it is added to a fresh pH 7.5 solution. At higher pH values (>9), the catalyst **4** is not stable, gradually forming what appears to be a black precipitate of rhodium metal.

Table 1. Activity of Base Soluble, Acid Insoluble Rh(I) Hydrogenation Catalysts in Water and Acetonitrile.[a]

Catalyst and Solvent	Substrate	Turnover Frequency (mol of H_2/mol of Rh-h)	Yield (%)
4, H_2O	Allyl alcohol	8	> 95 [b]
	(second cycle)	7.4	
	(third cycle)	6.9	
	acrylic acid	19	> 95 [b]
	N-isopropyl acrylamide	84	94 [c]
	α-acetamidoacrylic acid	42	90 [c]
	sodium *p*-styrene sulfonate	8	> 90 [b]
5, H_2O	allyl alcohol	17	> 95 [b]
	N-isopropyl acrylamide	97	92 [b]
	α-acetamidoacrylic acid	55	88 [b]
4, CH_3CN	1-octene	14	> 90 [b]
	(second cycle)	12	
$ClRh(Ph_2P(m\text{-}C_6H_4SO_3H))_3$ [d]	maleic acid	53	
	allyl alcohol	115	
$ArCON(CH_2CH_2PPh_2)_2Rh^+Tf^-$ [e]	(*E*)-CH3CH=CHCO2H	13	
$ArCON(CH_2CH_2PPh_2)_2Rh^+Tf^-$ [f]	α-acetamidoacrylic acid	> 275	

[a] Hydrogenation reactions were run at 25 °C using 0.2% catalyst ($[Rh]_{aqueous} = 8 \times 10^{-4}$ M). [b] This yield was estimated based on H_2 uptake. [c] This yield is an isolated yield of product that was characterized by ^1H NMR spectroscopy. The product in this case was obtained by acidifying the solution to precipitate **4**, extracting with ether (**4** is insoluble in ether) and removing the ether. [d] This catalyst and the rate data are from reference 12 and were obtained at 60 °C. [e] This catalyst is described in reference 13 ($ArCON(CH_2CH_2PPh_2)_2$ = 1,2-(HO_2C)-4-$(Ph_2PCH_2CH_2)_2NCO)C_6H_3$). [f] This catalyst is described in reference 14 ($ArCON(CH_2CH_2PPh_2)_2$ = 1-(HO_2C)-2-$(HO_3SCH_2CH_2NHCO)$-4-$(Ph_2PCH_2CH_2)_2NCO)C_6H_3$).

The catalytic activity of **4** is comparable to that of other water-soluble Rh(I) catalysts (Table 1). Modest activity is seen for simple alkenes like allyl alcohol. Higher and more useful hydrogenation rates are achieved using electron deficient alkenes. In every case, the low molecular weight catalyst **5** was more active than **4**. We speculate that this may reflect intramolecular interaction of the cationic rhodium center with nearby carboxylates in the polymer **4**.

Recovery and reuse of these rhodium catalysts is feasible. Recycling small amounts of catalysts did lead to some loss in activity but this appears to be the result of some oxidation of the phosphine ligand. Recycling catalyst from an organic (CH_3CN) solution was also feasible using solvent precipitation (addition into excess ether) to recover the polymer-bound catalyst at the reaction's end. Attempts to recover and reuse catalyst **5** were not successful. While the acidic form of catalyst **5** was less soluble, it did not quantitatively precipitate as a recoverable solid and had partial solubility in ether.

In summary, water-soluble polymer-bound catalysts with amphoteric ligands that can be recovered and reused by small changes in pH can be readily prepared from simple maleic anhydride copolymers. Ongoing studies examining other derivatives of these maleic anhydride polymers as ligands are continuing in our laboratory.

Acknowledgments. Support of this Support of this work by the National Science Foundation (CHE-9222717) and the Robert A. Welch Foundation is gratefully acknowledged.

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(*Received in USA* 17 *March* 1997; *accepted* 10 *April* 1997)