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Short Communication

Thermoregulated phase-transfer rhodium nanoparticle catalyst for hydroaminomethylation of olefins

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A B S T R A C T

Rh nanoparticles used as catalysts for hydroaminomethylation reaction is reported for the first time. An efficient and recyclable Rh nanoparticle catalyst stabilized by thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ (n = 16) was studied for the hydroaminomethylation of olefins in the aqueous/1-butanol biphasic system through thermoregulated phase-transfer catalysis, which allows not only for a homogeneous catalytic reaction, but also for an easy biphasic separation. Under the optimized conditions, the conversion of 1-octene and the product amine selectivity were as high as 99% and 97%, respectively. After reaction, the Rh nanoparticle catalyst can be separated from products by simple phase separation and recycled directly for the next run.

1. Introduction

Hydroaminomethylation, which was first discovered by Reppe in 1949 [1], has been used as an important tool in the synthesis of amines. Hydroaminomethylation is a tandem reaction involving the olefin hydroformylation to the aldehydes followed by the reaction of resulting aldehydes with a primary or secondary amine to produce the corresponding imines or enamines and finally the hydrogenation of imines or enamines to the desired amines. Among the investigated catalysts, Rh complexes were most often employed for the hydroaminomethylation [2–10].

Over the past decades, soluble transition-metal nanoparticles in catalysis have drawn much attention due to their high efficiency and unique properties. However, very similar to traditional homogeneous catalysts, one of the main disadvantages of soluble nanoparticle catalysts is the problem of separation the catalyst from the products [11,12]. To overcome these drawbacks, several methods have been reported, with most studies focusing on the liquid/liquid biphasic system, for example, the use of aqueous/organic biphasic system [13–17], fluorous/organic biphasic system [18–21], thermoregulated polyethylene glycol (PEG) biphasic system [22,23] and ionic liquid biphasic system [24–28].

Recently, we have reported the Rh nanoparticle catalyzed hydrogenation and hydroformylation of olefins through thermoregulated phase-transfer catalysis (TRPTC) [29,30]. The general principle of TRPTC is illustrated in Scheme 1. At room temperature lower than the cloud point (Cp) of thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ (n = 16), the thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ (n = 16)-stabilized Rh nanoparticle catalyst remains in the lower aqueous phase. On heating to a temperature higher than the Cp, however, the thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ (n = 16)-stabilized Rh nanoparticle catalyst will transfer into the upper 1-butanol phase. Thus, the catalyst and the substrate will be in the same phase and the reaction proceeds homogeneously in the 1-butanol phase. As soon as the reaction is completed and the system is cooled to a temperature lower than the Cp, the catalyst will return to the aqueous phase. Therefore, by simple phase separation the catalyst can be separated from products. Such a novel process provides both the advantages of classic monophase and biphase system, i.e., highly catalytic efficiency and good recyclability. Therefore, TRPTC provides a promising approach for recovery and recycling of soluble transition-metal nanoparticle catalyst, especially for the noble transition-metal nanoparticle catalyst.

Although hydroaminomethylation has been extensively studied with Rh complexes, to the best of our knowledge, using Rh nanoparticles as catalyst for this reaction is not reported so far. Encouraged by our previous successful applications of TRPTC for Rh nanoparticle catalyzed hydrogenation and hydroformylation of olefins, in this paper, thermoregulated phase-transfer Rh nanoparticle catalyst in the aqueous/1-butanol biphasic system was applied for the first time to the hydroaminomethylation of olefins.

2. Experimental

2.1. Materials and analyses

1-Octene was obtained from Acros. 1-Hexene and 1-dodecene were purchased from Fluka. Di-*n*-propylamine was supplied by Sinopharm

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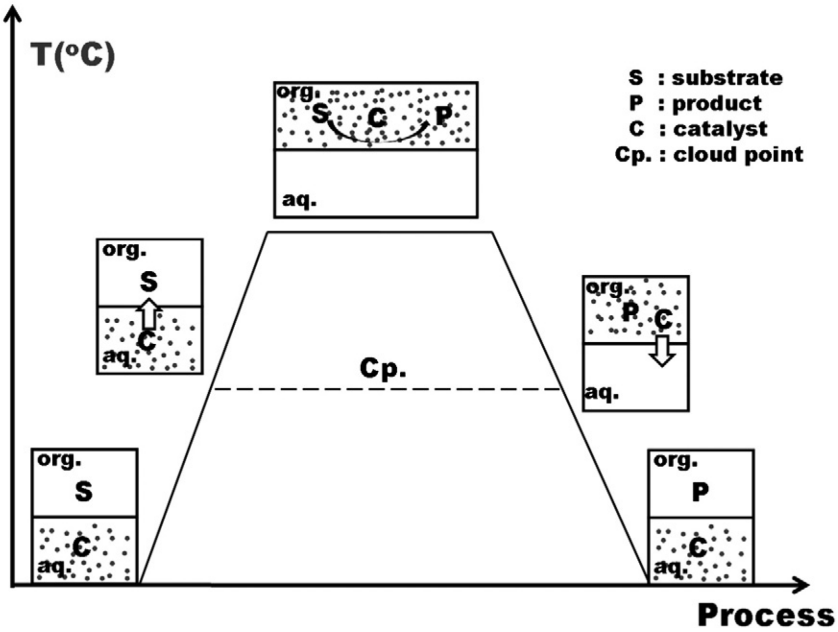

Scheme 1. General principle of TRPTC involving Rh nanoparticles.

Chemical Reagent Co. Ltd. N-Methylaniline was obtained from Alfa Aesar. 1-Butanol was of analytical grade and supplied from Fluka. *n*-Decane was purchased from Kermel. $RhCl_3 \cdot 3H_2O$ was received from Beijing Research Institute of Chemical Industry and used without further purification. Thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ (n = 16) was prepared according to the method reported in the literature [31]. Gas chromatography analyses were performed on a Tianmei 7890 GC equipped with a 50 m OV-101 column (inner diameter 0.25 mm) and an FID detector (N_2 as a carrier gas). GC–MS measurement was performed on a HP 6890 GC/5973 MSD instrument (with a 30 m HP-5MS column, inner diameter 0.25 mm; He as a carrier gas). ICP-AES analyses of Rh were carried out on Optima 2000 DV (Perkin Elmer, USA).

2.2. Preparation of the Rh nanoparticle catalyst

In a typical experiment, a mixture of $RhCl_3 \cdot 3H_2O$ (2 mg, 0.0076 mmol), thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ (n = 16) (13.9 mg, 0.015 mmol), 1-butanol (4 mL) and water (4 mL) was added in a 75 mL standard stainless-steel autoclave and stirred under hydrogen (4 MPa) at 70 °C for 2 h. Then, the reactor was cooled to room temperature and depressurized. The color of the aqueous phase turned from light yellow to brownish black, indicating the formation of Rh nanoparticle catalyst.

2.3. TEM of the Rh nanoparticle catalyst

The size of Rh nanoparticle catalyst was characterized by transmission electron microscopy (TEM). The solution containing the Rh nanoparticle catalyst was diluted with ethanol. Then, a drop of the solution was placed onto a carbon-coated copper grid, which was dried at ambient temperature. The TEM images were taken with a Philips Tecnai G^2 20 TEM at an accelerating voltage of 200 kV.

2.4. Hydroaminomethylation of olefins

Hydroaminomethylation of olefins was carried out in a 75 mL standard stainless-steel autoclave immersed in a thermostatic oil bath. The stirring rate was the same for all experiments performed. The autoclave was charged with Rh nanoparticle catalyst, 1-butanol,

Table 1
Hydroaminomethylation of 1-octene with di-*n*-propylamine catalyzed by thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ (n = 16)-stabilized Rh nanoparticles.[a]

Entry	*P* (MPa)	*T* (°C)	*t* (h)	1-Octene/Rh (molar ratio)	Conv.[b] (%)	Selectivity (%)			*n*/b
						Isomeric octenes	Aldehydes	Amines	
1	6	90	4	1000	97	29	14	57	93:7
2	6	100	4	1000	97	16	5	79	91:9
3	6	110	4	1000	98	5	5	90	89:11
4	6	120	4	1000	99	3	0	97	79:21
5	2	120	4	1000	97	38	5	57	95:5
6	3	120	4	1000	98	23	3	74	89:11
7	4	120	4	1000	98	10	2	88	84:16
8	5	120	4	1000	98	5	0	95	80:20
9	6	120	2	1000	99	13	8	79	96:4
10	6	120	3	1000	99	8	3	89	88:12
11	6	120	4	1500	98	25	4	71	87:13
12	6	120	4	2000	98	28	14	58	93:7
13[c]	6	120	4	1000	99	3	78	19	89:11

[a] Reaction conditions: 4 mL 1-butanol, 4 mL water containing 7.6×10^{-3} mmol Rh ($Ph_2P(CH_2CH_2O)_nCH_3$ (n = 16)/Rh = 2 (molar ratio)), di-*n*-propylamine/1-octene = 1.5 (molar ratio), 200 mg of *n*-decane as internal standard, and *n*/b: the ratio of normal to branched amine.
[b] Conversion of 1-octene.
[c] The mercury poisoning experiment.