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Hydroformylation of mixed octenes over immobilized $Co\text{-}Ph_3PO/PDMS/SiO_2$ catalyst

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The catalyst $Co\text{-}Ph_3PO/PDMS/SiO_2$, $Co\text{-}Ph_3PO$ complex immobilized on polydimethylsiloxane (PDMS) functionalized SiO_2, was prepared by sol-gel method. The characterizations of the catalysts were made by FT-IR, ICP-AES and N_2 adsorption/desorption. The BET surface area, pore diameter and pore volume of the catalyst $Co\text{-}Ph_3PO/PDMS/SiO_2$ were smaller than that of pure $SiO_2 \cdot$ ICP-AES showed that the content of cobalt of $Co\text{-}Ph_3PO/SiO_2$ was almost the same as that of $Co\text{-}Ph_3PO/PDMS/SiO_2$. The conversion of mixed octenes catalyzed by $Co\text{-}Ph_3PO/PDMS/SiO_2$ was 24.6 % (cobalt leaching was only 0.014% after the first run), which was two times about that of $Co\text{-}Ph_3PO/SiO_2$ (the conversion was only 11.6 , 25% cobalt leaching was observed after the first run). The immobilized catalyst $Co\text{-}Ph_3PO/PDMS/SiO_2$ could be reused six times without reducing the activity and selectivity.

KEY WORDS: hydroformylation; mixed octenes; triphenyl phosphine oxide; cobalt; PDMS.

1. Introduction

The practical applications of homogeneous catalysis have been limited by difficulties in achieving industrially viable catalyst product separation [1,2]. Molecular catalysts immobilized on different types of supports have been widely explored for advanced catalyst recycling, such as dendritic [3], polymeric organic, inorganic, or hybrid supports [4].

Immobilization of inorganic materials, such as silica, has advantages due to the physical strength and chemical inertness. The entrapment of homogeneous catalysts inside the porous system of silica matrices prepared by the sol–gel method appears to be a promising strategy for catalyst recovery [5]. Hybrid organic-inorganic co-condensation agents $[(RO)_3Si\text{–}R'\text{–}Si(OR)_3]$ made the classical sol–gel precursors $[Si(OR)_4]$ with three-dimensional networks bearing an organic fragment as an integral component. Several groups have studied such hybrid inorganic-organic matrices [6–8] and polysiloxane-bound transition metal complexes were extensively studied by Lindner *et al.* [9]. Although the entrapment of hydroformylation catalysts, linked or not a hydrolysable ligand, inside the porous system of inorganic matrices has been reported [10,11], there are no studies concerning hydroformylation of mixed octenes with hybrid matrices as support of immobilized catalyst.

Several different groups have paid attention to the hydroformylation of the mixture of isomeric octeness obtained from the dimerization of n-C_4 olefins, to C_9-aldehyde [12,13]. Hydroformylation of mixed isomeric octeness to valuable isononyl-aldehydes (INA) has been attracted for the high performance plasticizer, such as di-iso-nony phthalate (DINP) applied to the development of the plastic industries. Cobalt based catalysts are cheap and widely used in the hydroformylation of olefins. Traditional phosphine ligands are favorable for the synthesis of aldehydes in the hydrformylation of lower olefins but much lower activities for the mixture of long-chain and branched olefins [14]. In addition, it was believed that oxidation of triphenylphosphine ligands to the triphenylphosphine oxide (that are regarded as weak ligands) deactivates the catalyst [15,16]. However, it has been shown that in some cases phosphine oxides do not interfere with the original catalyst, but promote the insertion of carbon monoxide in a metal alkyl complex [17]. Recently, we have studied the hydroformylation of mixed octenes catalyzed by cobalt and triphenyl phosphine oxide system. In this paper we tried to develop $Co\text{-}Ph_3PO$ immobilized catalyst. We report characterization and catalytic efficiency of immobilized $[Co(CH_3COO)_2)] \cdot 4H_2O$ in SiO_2 and SiO_2 functionalized PDMS supports as catalysts for hydroformylation mixed octenes with excellent recyclability. This offers a high level of control and flexibility since, in this approach, it enables the simple reuse of the support ultimately leading to a modular multipurpose system.

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2. Experimental

2.1. General comments

The cobalt precursor $[Co(CH_3COO)_2]] \cdot 4H_2O$ was purchased from Beijing Chemical Reagents Company. Polydimethylsiloxane (PDMS), tetraethylorthosilicate (TEOS) and Ph_3PO was purchased from Acros Organics Company. The quantitative composition of the substrate (mixture octanes, obtained from Hyundai Petrochemical Company) is given in table 1, and the conversion is calculated based on the analysis of converted mixed octanes. The hydroformylation of C_9 aldehydes was qualitative analyzed by GC-MS and quantitative analyzed by GC. The yield was analyzed with a gas chromatography (HP 4890D, capillary column HP-5 30 m × 0.25 mm; 323–553 K; 10 K/min^{-1}; FID detector). Other reagents were purchased from Beijing Chemical Reagent Co.

2.2. Catalyst Preparation

The preparation of immobilized catalysts refers to the procedures described in literature [11]. A typical procedure: 1 mmol $[Co(CH_3COO)_2)] \cdot 4H_2O$ and 2 mmol of the triphenyl phosphine oxide were dissolved in 6 ml of THF in a 50 ml Schlenk flask. After 15 min stirring, 2.0 ml (11.10 mmol) of deionized water, 2.0 ml (13.56 mmol) of TEOS (tetraethylorthosilicate), 1.0 ml (24.69 mmol) of methanol and 1 ml polydimethylsiloxane were added to the blue solution. The resulting solution was stirred for 15 min and then allowed to stand for at least overnight until gelation. The gel was washed with CH_2Cl_2 three times and dried at 353 K. The resulting blue materials were stored under air at room temperature.

2.3. Characterization of Catalysts

FT-IR spectra were recorded between 4000 and 400 cm^{-1} (resolution of 2 cm^{-1}) on Nicolet Magna IR 550 spectrometer. N_2 adsorption/desorption isotherms at liquid nitrogen temperature were obtained on a Micromeritics ASAP 2010C analyzer. Before measurement, the samples were degassed at 355 K for 24 h. The cobalt contents of immobilized catalysts and cobalt leaching content in liquid phase were determined through ICP-AES analyses (Perkin–Elmer Optima 3000 DV).

Table 1
The composition of mixed octenes

Entry	Composition	Percent %
1	4,4-dimethyl-2-para-hexene	3.5
2	3-ethyl-2-hexene	5.9
3	3,4,4-trimentyl-2-pentene	25.8
4	3,4-dimethyl-para-3-hexene	2.0
5	3,4-dimethyl-trans-3-hexene	5.9
6	2-octene	32.6
7	Para-2-octene	
8	3-octene	2.9
9	4-octene	16.6
10	Others	4.6
Total		99.8

2.4. Hydroformylation

The typical olefin hydroformylation was carried out in a stainless steel autoclave of 80 ml with a magnetic stirrer. After the introduction of required amount of the catalyst, solvent and mixed octenes into the autoclave,the autoclave was sealed and pressurized with syngas at 1.0 MPa three times. Then the autoclave was pressurized with syngas at a desirable pressure, and heated to the reaction temperature. CO/H_2 consumption was monitored by the decrease of the pressure during the reaction. Previously we already examined the effect of reaction time on the hydroformylation of mixed octenes [18]. After the reaction, the reactor was cooled with an ice bath to room temperature and decompressed. The oil and the solid catalyst were separated by decantation, and the recovered catalyst was used in a new run. The organic phase was analyzed with a gas chromatography (HP 4890D, capillary column HP-5 30 m × 0.25 mm; 323–553 K; 10 K/min^{-1}; FID detector).

3. Results and discussion

Figure 1 shows the FT-IR spectra for immobilized catalysts with PDMS motification and without PDMS ($Co\text{-}Ph_3PO/PDMS/SiO_2$ and $Co\text{-}Ph_3PO/SiO_2$). The bands observed at 3058, 1439 cm^{-1} were assigned to C-H symmetric stretching of phenyl and C–C asymmetric stretching of the phenyl ring, respectively [19]. The absorption peaks at 2967, 2892, 1264, 1000–1100, 850, 800 cm^{-1} were from PDMS [20,21]. The peaks at 2967 and 2892 cm^{-1} were assigned to the symmetric and

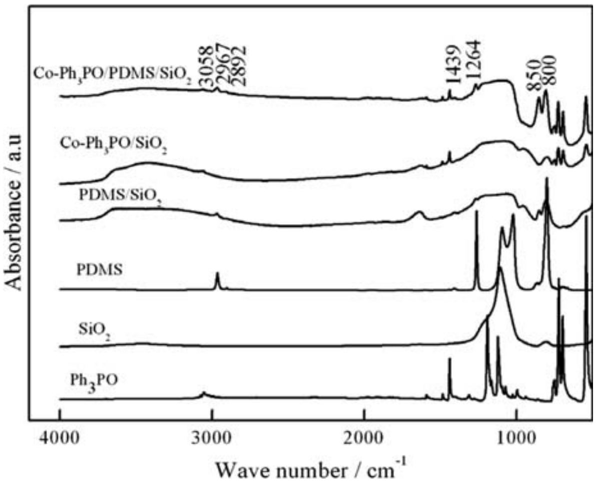

Figure 1. FT-IR spectra for several samples.

asymmetric C-H stretching vibration of methyl groups, and strong doublet peak at 1050–1100 cm^{-1} and 800 cm^{-1} were due to Si-O-Si bonds. A strong absorption peak at 1264 cm^{-1} was the characteristic of methyl groups bonded to silicon and attributed the symmetric deformation of C-H [20,21]. The above IR spectroscopic results suggest that the significant interaction occurred between the OH groups at the surface of SiO_2 and PDMS.

The specific surface areas (S_{BET}), average pore diameters and cumulative volumes are given in table 2. The surface area of pure SiO_2 was higher than that of SiO_2 immobilized with $Co(Ac)_2 \cdot 4H_2O$ (Co/SiO_2) or Ph_3PO (Ph_3PO/SiO_2). When Co-Ph_3PO or Co-PDMS immobilized on SiO_2, the specific surface areas of the catalysts (Co-Ph_3PO/SiO_2, Co-PDMS/SiO_2), were much smaller than that of pure SiO_2. Also, the catalyst Co-Ph_3PO/PDMS/SiO_2 showed a considerable decrease in surface area compared with pure SiO_2. Cumulative pore volume, and BJH pore diameter, exhibited the same trend as the surface area. Such decreases in BET surface area, cumulative pore volume, and BJH pore diameter for Co-Ph_3PO/PDMS/SiO_2 compared to that of pure SiO_2 and the results of element analysis of Co and phosphine (table 3) imply that the considerable amounts of PDMS and Co species were located on the internal surfaces of SiO_2 [22–24]. On the other hand, the literatures demonstrated that there was no recognizable phase separation in this system [25,26]. In this work, it was also found no phase separation on PDMS/SiO_2 sample.

A comparison of the result of the hydroformylation of mixed octenes over a series of catalysts is listed in table 3. The cobalt leaching of the immobilized catalysts after reactions was obtained from ICP-AES analyses. The results of ICP-AES showed that the amount of cobalt of Co-Ph_3PO/SiO_2 (2.9 wt% Co) was just larger than that on Co-Ph_3PO/PDMS/SiO_2 (2.4 wt% Co). When Co-Ph_3PO was directly immobilized on SiO_2, the conversion of mixed octenes in the hydroformylation was low (table 3 No.4) and 25% cobalt leaching was observed after the first run. On the contrary, the catalyst that Co-Ph_3PO was immobilized on the PDMS-functionalized SiO_2 afforded 24.6% conversion (table 3 No.5) and TON value was similar to that of the homogeneous Co-Ph_3PO catalyst (table 3 No. 2), whereas cobalt leaching was only 0.014% after the first run. On the other hand, the Co/PDMS using SiO_2 as a carrier without Ph_3PO showed a reasonable mixed octenes conversion, but gave a lower selectivity of C_9 aldehydes as compared with the Co-Ph_3PO/PDMS/SiO_2 under identical conditions. These results imply that perhaps there was an interaction between PDMS and the active cobalt species.

Table 2
Physical properties of immobilized catalysts with and without PDMS modification

No.	Catalyst	Surface area $_{(BET)}/m^2 \cdot g^{-1}$	Average Pore Diameter/nm	Cumulative Pore volume/$ml \cdot g^{-1}$
1	SiO_2	364	9.3	0.79
2	Co-Ph_3PO/SiO_2	230	6.9	0.48
3	Co-Ph_3PO/PDMS/SiO_2	161	3.1	0.25
4	Co/PDMS/SiO_2	227	2.0	0.23
5	Ph_3PO/SiO_2	269	2.4	0.21
6	Co/SiO_2	270	2.0	0.47

Table 3
The performance of immobilized catalyses in hydroformylation of mixed octenes[a]

No.	Catalyst	Co wt %	Olefin/Co (mol/mol)	P wt %	P/Co (mol/mol)	Conv. (%)	Sele. of C_9 alde. (%)	TON	% Co leaching[e]
1	Co-Ph_3PO[b]	–	0.031	–	2.0	56.8	92.5	18.2	
2	Co-Ph_3PO[c]	–	0.0077	–	2.0	21.5	81.8	33.4	
3	SiO_2	–		–	–	0	–	–	
4	Co-Ph_3PO/ SiO_2[d]	2.9	0.0019	2.6	1.6	11.6	92.1	15.1	25
5	Co-Ph_3PO/ PDMS/SiO_2[d]	2.4	0.0015	2.2	1.7	24.6	93.7	38.7	0.014
6	Co/PDMS/ SiO_2[d]	3.9	0.0025	0	0	22.6	88.6	21.9	0.019
7	Co/SiO_2[d)]	3.9	0.0025	0	0	10.9	79.7	10.6	

[a] Reaction condition: mixed octeness = 5 ml (3.6 g), Methanol (solvent) = 15 ml, reaction temperature = 433 K, reaction pressure = 5.0 MPa, reaction time = 150 min.

[b] $Co(Ac)_2 \cdot 4H_2O$ as precursor, $[Co] = 1 \times 10^{-3}$ mol, $Co(Ac)_2 \cdot 4H_2O = 0.2419$ g.

[c] $Co(Ac)_2 \cdot 4H_2O$ as precursor, $[Co] = 0.21 \times 10^{-3}$ mol, $Co(Ac)_2 \cdot 4H_2O = 0.05$ g.

[d] 500 mg immobilized catalyst.

[e] Co-leaching (%) after first run: ppm of Co-leached × 100/ppm of Co-content (evaluated from Co-content wt/wt%).

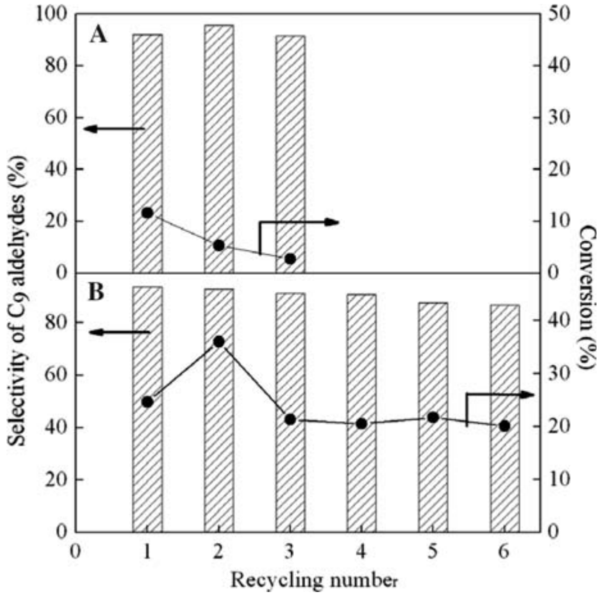

Figure 2. The recycling results in mixed octenes hydroformylation over (A) Co-Ph_3PO/SiO_2 (B) Co-$Ph_3PO/PDMS/SiO_2$. Reaction condition: immobilized catalyst = 500 mg, mixed octeness = 5 ml, Methanol (solvent) = 15 ml, reaction temperature = 433 K, reaction pressure = 5.0 MPa, reaction time = 150 min.

The conversions of mixed octenes in the hydroformyation over the immobilized catalysts were near same to that over the homogeneous Co-Ph_3PO catalyst with same cobalt amount. Moreover, the immobilized catalyst Co-$Ph_3PO/PDMS/SiO_2$ could be easily separated from the reaction mixtures by decantation and reused for several times, and showed an obvious advantage in recycle use over the homogeneous catalyst. The recycling of the catalysts, Co-Ph_3PO/SiO_2 and Co-$Ph_3PO/PDMS$ /SiO_2, was performed through a series of consecutive runs in the hydroformylation of mixed octenes. The results are presented in figure 2. The immobilized catalyst without PDMS modification (Co-Ph_3PO/SiO_2) deactivated quickly, which may be relative to cobalt leaching. However, in the case of the immobilized catalyst with PDMS modification, Co-$Ph_3PO/PDMS/SiO_2$, the results showed clearly that the catalyst could be recycled at least six times with only a slight loss in activity, with the exception of the catalytic activity increasing in the first recycle (second run).

4. Conclusions

The immobilized catalyst with PDMS functionalized Co-$Ph_3PO/PDMS/SiO_2$ showed higher activity and stability than that without PDMS modification (Co-Ph_3PO/SiO_2) in the hydroformylation of mixed octenes. The catalyst Co-$Ph_3PO/PDMS/SiO_2$ could be reused six times without reducing the activity and selectivity. In addition, the selectivity of C_9 aldehydes of Co-$Ph_3PO/PDMS/SiO_2$ was higher than that of Co/$PDMS/SiO_2$. The results implied that there existed considerable effect of organic-inorganic support with PDMS functionalized in the mixed octenes hydroformylation.

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