

Preparation of Immobilized Co-Ph₃PO/PDMS/SiO₂ Catalyst and Its Catalytic performance in Hydroformylation of Mixed Octenes

Qingrong Peng, Dehua He*

Innovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering (Ministry of Education), Dept. of Chemistry, Tsinghua University, Beijing 100084, China
*hedeh@mails.tsinghua.edu.cn

Introduction

The practical industrial applications of homogeneous catalysis have been often limited by the difficulties of the separation of catalysts and products [1,2]. The entrapment of homogeneous catalysts inside the porous silica matrices prepared by the sol-gel method appears to be a promising strategy for catalyst recovery [3]. Although the entrapment of hydroformylation catalysts inside the porous inorganic matrices has been reported [4], there are no studies concerning the hydroformylation of internal and branched long chain olefins (such as, mixed octenes) with hybrid matrices as support of immobilized catalysts. In addition, the triphenylphosphine oxide (Ph₃PO), which is regarded as a weak ligand, exhibited a positive effect on the hydroformylation of mixed octenes to C₉ aldehydes in a homogeneous reaction catalyzed by Rh catalysts [5]. In this paper, we report catalytic efficiency of immobilized Co-Ph₃PO supported on modified SiO₂ with polydimethylsiloxane (PDMS) as the catalysts for hydroformylation of mixed octenes with a good recycle ability.

Materials and Methods

Co(CH₃COO)₂·4H₂O, polydimethylsiloxane (PDMS), tetraethylorthosilicate (TEOS) and Ph₃PO were used for preparing immobilized Co-Ph₃PO/PDMS/SiO₂ catalyst. Certain amount of Co(CH₃COO)₂·4H₂O and Ph₃PO were dissolved in THF solvent in a Schlenk flask. While stirring the above solution, deionized water, TEOS, methanol and PDMS were added to the solution. The resulted mixture was allowed for gelation. The formed gel was washed with CH₂Cl₂ and dried at 353 K, and the Co-Ph₃PO/PDMS/SiO₂ catalyst was obtained [4]. The hydroformylation of the mixed octenes (containing n-octenes, methyl heptenes, dimethyl hexenes and trimethyl pentanes) was carried out in an autoclave (80ml). The products were analyzed by a gas chromatograph.

Results and Discussion

Figure 1 shows the FT-IR spectra of the immobilized catalysts with PDMS modification and without PDMS (Co-Ph₃PO/PDMS/SiO₂ and Co-Ph₃PO/SiO₂). 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 [6]. The absorption peaks at 2967, 2892, 1264, 1000-1100, 850, 800 cm⁻¹ were from PDMS [7,8]. The peaks at 2967 and 2892 cm⁻¹ were assigned to the symmetric and asymmetric C-H stretching vibration of methyl groups, and strong doublet peak at 1050 to 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 [7,8]. The above IR spectroscopic results suggest that the significant interaction occurred between the OH groups at the surface of SiO₂ and PDMS.

The immobilized catalyst Co-Ph₃PO/PDMS/SiO₂ could be easily separated from the reaction mixtures and reused for several times, and showed an obvious advantage in recycle use over the homogeneous catalyst. The recycling of the catalysts, Co-Ph₃PO/SiO₂ and Co-Ph₃PO/PDMS/SiO₂, was performed through a series of consecutive runs in the hydroformylation of the mixed octenes. The results are presented in Figure 2. The immobilized catalyst without PDMS modification (Co-Ph₃PO/SiO₂), deactivated quickly. However, in the case of the immobilized catalyst with PDMS modification (Co-Ph₃PO/PDMS/SiO₂), 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.

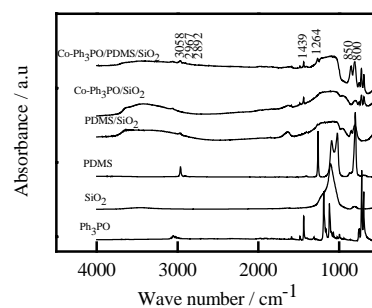


Figure 1 FT-IR spectra for several samples

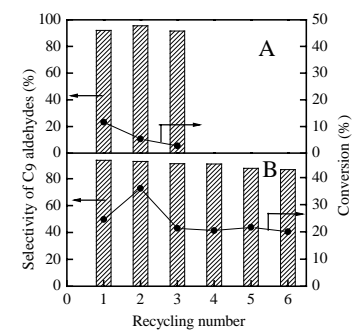


Figure 2 Recycling results of immobilized catalysts in hydroformylation of mixed octenes (A)Co-Ph₃PO/SiO₂, (B)Co-Ph₃PO/PDMS/SiO₂.

Significance

The hydroformylation of mixed octenes is an important process for producing valuable isononyl aldehyde, which is one of the raw materials of di-iso-nony phthalate (a high performance plasticizer). Molecular catalysts immobilized on solid supports have advantages for catalyst recycle. The results obtained in this work implied that the organic-inorganic hybrid support (PDMS-SiO₂) had positive effect on the recycle of the immobilized catalyst in the hydroformylation of mixed octenes.

References

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