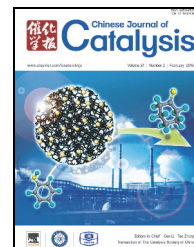


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Article

Effect of lengthening alkyl spacer on hydroformylation performance of tethered-phosphine modified Rh/SiO₂ catalyst

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ABSTRACT

Rh/SiO₂ catalysts with tethered-phosphines with different alkyl spacer lengths have been prepared, tested and characterized. Lengthening the alkyl spacer of the tethered-phosphine improved the flexibility of tethered-phosphine, promoted the formation of active species and enhanced the activity of hydroformylation over other tethered-phosphine modified Rh/SiO₂ catalysts.

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1. Introduction

Aldehydes, the products of olefin hydroformylation, are important intermediates in the production of many organic compounds and have significant value in industry. Homogeneous catalysts are the most commonly used in industrial hydroformylation processes because of their high activity, high selectivity and mild reaction conditions. However, they require complex and costly separation steps to be removed from the reactants and products. In contrast, heterogeneous catalysts can easily be separated from the reaction mixture but their application in hydroformylation industrial processes has been restricted by their low activity and low selectivity [1,2]. For decades, researchers have explored new catalytic systems combining the advantages of heterogeneous and homogeneous

catalysts, and the heterogenization of homogeneous catalysts is one of these hotspots.

A common strategy for heterogenizing homogeneous catalysts is immobilization or heterogenization of a transition-metal complex on a solid support. Immobilization of transition-metal complex on solid supports has achieved some success by chemically bonding the complex to a support, but these catalysts tend to leach the active species into the reaction mixture and thus deactivates the catalyst [3–5].

We have reported a new tethered-phosphine modified Rh/SiO₂ catalyst with excellent stability for use in the hydroformylation of ethylene [6]. Both tethered-phosphines and the supported active metal nanoparticles were anchored to SiO₂, which contributed to the remarkable stability of the catalyst. However, as the phosphines and metal nanoparticles were both

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fixed, their mobility was restricted, and some of the tethered-phosphines could not reach, and coordinate to, the Rh nanoparticles efficiently to form the active species, which resulted in relative low catalytic activity in the olefin hydroformylation.

Ligand flexibility and projection into solution are related to the chain length of the ligand, and Zhou et al. [7,8] have reported a series of S-C_n-PPh₂-Rh catalysts in which Rh complexes were immobilized onto SBA-15 by anchored phosphines with different chain lengths. The catalysts showed excellent activities in 1-octene hydroformylation but the P/Rh molar ratios were variable and significant Rh leaching occurred. In our catalytic system, lengthening the alkyl spacer of the tethered-phosphine may enhance the coordination between the tethered-phosphine and the metal nanoparticles, increase the number of active species, and thus improve the activity of the tethered-phosphine modified Rh/SiO₂ catalyst. In this work, a phosphine with a longer alkyl spacer was prepared, and then used in the production of a Rh/SiO₂ catalyst. The influence of the alkyl spacer length of the phosphine on its catalytic activity was studied and characterized by N₂ adsorption-desorption, in situ Fourier Transform infrared (in situ FT-IR) spectroscopy, and solid-state ³¹P nuclear magnetic resonance (³¹P NMR).

2. Experimental

2.1. Catalysts preparation

Rh/SiO₂ was prepared by impregnating silica gel (≥99%, amorphous silica, Ordos Chemical Co. Ltd., 20–40 mesh, BET surface = 256.3 m²/g, total pore volume = 0.95 ml/g, average pore radius = 7.4 nm) with RhCl₃·xH₂O (37.22 wt% Rh, Johnson Matthey) in ethanol. After drying in air, the RhCl₃/silica was calcined at 573 K for 4 h and then reduced in a H₂ flow at 573 K for 4 h at atmospheric pressure. Then, it was washed to remove Cl⁻, dried at 393 K, reduced again and restored in an Ar atmosphere. The Rh loading was 1.2 wt%.

2-(Diphenylphosphino)ethyltriethoxysilane [Ph₂P(CH₂)₂Si(OC₂H₅)₃, referred as DPPETS] was bought from J&K Scientific and 3-(Diphenylphosphino)propyl-triethoxysilane [Ph₂P(CH₂)₃Si(OC₂H₅)₃, referred as DPPPTS] was prepared according to a literature method [9]. The tethered-phosphine modified DPPETS-Rh/SiO₂ and DPPPTS-Rh/SiO₂ catalysts were prepared as described in the Ref. [6]. Rh/SiO₂ was added to a solution of DPPETS (or DPPPTS) in toluene and the P/Rh molar ratio was 2.24. The mixture was stirred for 16 h at room temperature and then for a further 6 h at reflux. After cooling to room temperature, the toluene was removed under vacuum. All manipulations referring to the use of phosphine were carried out under an Ar atmosphere.

2.2. Catalytic activity

The catalytic performance of ethylene hydroformylation over the tethered-phosphine modified Rh/SiO₂ catalysts was tested in a stainless steel continuous flow fixed-bed reactor with inner diameter of 6 mm. The reaction was conducted un-

der the following conditions: 0.3 g of sample, the pressure of reactant (C₂H₄:CO:H₂ = 1:1:1) 1.0 MPa, temperature 393 K, and the GHSV of reactant 2000 h⁻¹. No gaseous products could be detected in the tail gas, and the main product in the aqueous sample was propanal. The effluent was passed through a condenser filled with 70 ml of de-ionized water giving an aqueous solution of propanal, which remained completely dissolved for the duration of the experiment. The activity of the catalyst was measured by the turn-over-frequency (TOF) of propanal on the basis of the Rh loaded, counting all Rh atoms as active sites.

2.3. Catalyst characterization

N₂ adsorption-desorption isotherms of the samples were measured using a Quantachrome Autosorb-1 instrument to obtain the textural properties of catalysts. The in situ FT-IR spectra were recorded on a Thermo Scientific iS50 instrument equipped with a high temperature high pressure cell (Specas). A sample of 15 mg was pressed into a self-supporting disc. The adsorption of CO and H₂ was performed on the disc at 323 K and atmospheric pressure. The ³¹P NMR spectra were acquired using a VARIAN infinity plus spectrometer. The Rh concentrations of catalysts were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).

3. Results and discussion

3.1. Catalytic studies

Fig. 1 shows the catalytic performance of the modified Rh/SiO₂ catalysts with different alkyl spacer lengths of the tethered-phosphine. The TOFs of the catalysts in Fig. 1 increased with the time on stream, implying a gradual formation of the active species on the catalysts during the ethylene hydroformylation reaction. The TOF reached a steady state after 400 h. The TOF of DPPETS-Rh/SiO₂ was only 20.9 h⁻¹, while that of DPPPTS-Rh/SiO₂ reached 40.7 h⁻¹. Both catalysts were higher than Rh/SiO₂ (TOF = 0.8 h⁻¹) [10]. Thus, lengthening the alkyl spacer of the tethered-phosphine increased the activity of the tethered-phosphine modified Rh/SiO₂. The ICP-OES results

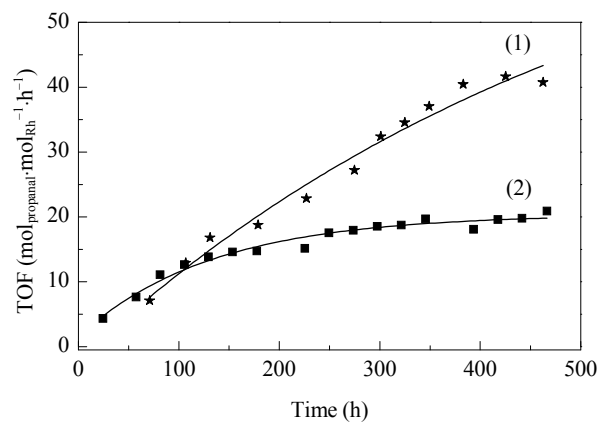


Fig. 1. Catalytic performance of hydroformylation of ethylene over DPPPTS-Rh/SiO₂ (1) and DPPETS-Rh/SiO₂ (2) catalysts at $P = 1$ MPa, $T = 393$ K and GHSV = 2000 h⁻¹.

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