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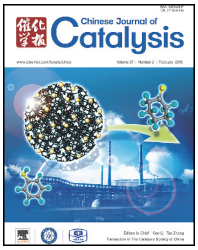

Article

Effect of lengthening alkyl spacer on hydroformylation performance of tethered-phosphine modified Rh/SiO_2 catalyst

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ABSTRACT

Rh/SiO_2 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-phospine, promoted the formation of active species and enhanced the activity of hydroformylation over other tethered-phosphine modified Rh/SiO_2 catalysts.

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/SiO_2 catalyst with excellent stability for use in the hydroformylation of ethylene [6]. Both tethered-phosphines and the supported active metal nanoparticles were anchored to SiO_2, 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-PPh_2-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/SiO_2 catalyst. In this work, a phosphine with a longer alkyl spacer was prepared, and then used in the production of a Rh/SiO_2 catalyst. The influence of the alkyl spacer length of the phosphine on its catalytic activity was studied and characterized by N_2 adsorption-desorption, in situ Fourier Transform infrared (in situ FT-IR) spectroscopy, and solid-state ^{31}P nuclear magnetic resonance (^{31}P NMR).

2. Experimental

2.1. Catalysts preparation

Rh/SiO_2 was prepared by impregnating silica gel (≥99%, amorphous silica, Ordos Chemical Co. Ltd., 20–40 mesh, BET surface = 256.3 m^2/g, total pore volume = 0.95 ml/g, average pore radius = 7.4 nm) with $RhCl_3{\cdot}xH_2O$ (37.22 wt% Rh, Johnson Matthey) in ethanol. After drying in air, the $RhCl_3$/silica was calcined at 573 K for 4 h and then reduced in a H_2 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 [$Ph_2P(CH_2)_2Si(OC_2H_5)_3$, referred as DPPETS] was bought from J&K Scientific and 3-(Diphenylphosphino)propyl-triethoxysilane [$Ph_2P(CH_2)_3Si(OC_2H_5)_3$, referred as DPPPTS] was prepared according to a literature method [9]. The tethered-phosphine modified DPPETS-Rh/SiO_2 and DPPPTS-Rh/SiO_2 catalysts were prepared as described in the Ref. [6]. Rh/SiO_2 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/SiO_2 catalysts was tested in a stainless steel continuous flow fixed-bed reactor with inner diameter of 6 mm. The reaction was conducted under the following conditions: 0.3 g of sample, the pressure of reactant (C_2H_4:CO:H_2 = 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

N_2 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 H_2 was performed on the disc at 323 K and atmospheric pressure. The ^{31}P 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/SiO_2 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/SiO_2 was only 20.9 h^{-1}, while that of DPPPTS-Rh/SiO_2 reached 40.7 h^{-1}. Both catalysts were higher than Rh/SiO_2 (TOF = 0.8 h^{-1}) [10]. Thus, lengthening the alkyl spacer of the tethered-phosphine increased the activity of the tethered-phosphine modified Rh/SiO_2. The ICP-OES results

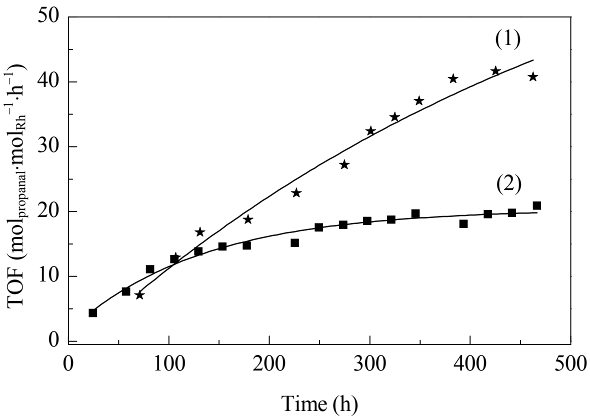

Fig. 1. Catalytic performance of hydroformylation of ethylene over DPPPTS-Rh/SiO_2 (1) and DPPETS-Rh/SiO_2 (2) catalysts at P = 1 MPa, T = 393 K and GHSV = 2000 h^{-1}.

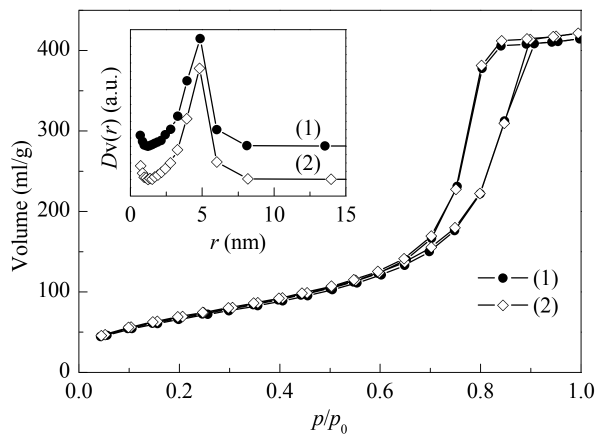

Fig. 2. N_2 adsorption-desorption isotherms and corresponding pore size distributions (insert) for DPPPTS-Rh/SiO_2 (1) and DPPETS-Rh/SiO_2 (2) catalysts.

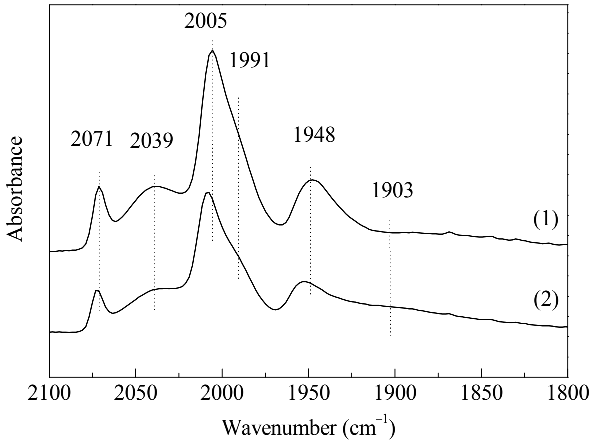

Fig. 3. *In situ* FT-IR spectra of CO and H_2 co-adsorbed on DPPPTS-Rh/SiO_2 (1) and DPPETS-Rh/SiO_2 (2) catalysts at atmospheric pressure and 323 K for 0.5 h.

showed that very little Rh leaching had occurred, even after long reaction times: 11040 ppm Rh for the fresh DPPETS-Rh/SiO_2, compared with 10060 ppm Rh for the used one, and 10450 ppm Rh for the fresh DPPPTS-Rh/SiO_2 and 10580 ppm Rh for the used catalyst.

The preparation of pure phosphines with longer alkyl spacers was hindered by the formation of cyclic compounds that did not contain the PPh_2 group. This paper therefore focuses on the available chain lengths, and other, longer chains will be presented later.

3.2. N_2 adsorption-desorption results

N_2 adsorption-desorption isotherms and corresponding pore size distributions of DPPETS-Rh/SiO_2 and DPPPTS-Rh/SiO_2 are shown in Fig. 2, and the detailed values are listed in Table 1. It can be seen that the catalysts had only small differences in pore structure, pore size distribution, BET surface (S_{BET}), total pore volume (V_p) and average pore radius (R_p). In other words, lengthening the alkyl spacers of the tethered-phosphine did not change the textural properties of the catalysts and mass transfer during the reaction. Hence, the difference in activity of catalysts was not the result of their textural properties.

3.3. In situ FT-IR

In situ FT-IR is a powerful technique in identifying the active adsorbed species on heterogeneous catalysts. Fig. 3 shows the *in situ* FT-IR spectra of H_2 and CO co-adsorbed on the surfaces of the DPPPTS-Rh/SiO_2 and DPPETS-Rh/SiO_2 catalysts. Five bands at 2071, 2039, 2005, 1991 and 1948 cm^{-1} appeared in the DPPPTS-Rh/SiO_2. The bands at 2071 and 1991 cm^{-1} have been assigned to *ee*-HRh(CO)$_2$(DPPPTS)$_2$/SiO_2 (i.e., tethered *ee*-HRh(CO)$_2$ (DPPPTS)$_2$ on SiO_2), while the bands at 2005 and 1948 cm^{-1} have been assigned to *ea*-HRh(CO)$_2$(DPPPTS)$_2$/SiO_2 [10–12].The band at 2039 cm^{-1} has been assigned to linear adsorbed CO, as Rh-CO [13–14]. This band has been significantly red-shifted compared with the heterogeneous Rh/SiO_2 catalyst [15–17], because of the weaker C–O bond resulting from π* back-donation from the Rh to the CO in the presence of the tethered-phosphine. There were five analogous bands in the spectrum of DPPETS-Rh/SiO_2, which were similarly assigned to *ee*-HRh(CO)$_2$(DPPETS)$_2$/SiO_2, *ea*-HRh(CO)$_2$(DPPTES)$_2$/SiO_2 and the linear CO adsorbed on the Rh nanoparticles, respectively. Compared with the bands of DPPPTS-Rh/SiO_2, the spectrum of DPPETS-Rh/SiO_2 was slightly blue-shifted, a result of the different tether length on the Rh/SiO_2 catalysts.

Table 1
Textural properties of the catalysts.

Catalyst	S_{BET} (m^2/g)	V_p (ml/g)	R_p (nm)
DPPPTS-Rh/SiO_2	244.4	0.6	5.3
DPPETS-Rh/SiO_2	256.5	0.7	5.1

Because HRh(CO)$_2$(DPPPTS)$_2$/SiO_2 and HRh(CO)$_2$ (DPPETS)$_2$/SiO_2 are the analogous active species for the homogeneous Wilkinson-type hydroformylation [18], they were assumed to be the active species that catalyzed the olefin hydroformylation on the tethered-phosphine modified Rh/SiO_2 catalysts. Furthermore, linear CO has been shown to promote hydroformylation in heterogeneous catalysts [19]. The FT-IR spectrum of DPPPTS-Rh/SiO_2 was more intense than DPPETS-Rh/SiO_2. Rasband et al. [20] have reported the concentration of adsorbed CO is proportional to the corresponding FT-IR band intensity. The increased band intensity implies higher concentration of CO was adsorbed on the catalysts. Therefore, higher concentration of CO has been adsorbed on the DPPPTS-Rh/SiO_2 catalyst than on the DPPPET-Rh/SiO_2 catalyst, which explains the increased activity of DPPPTS-Rh/SiO_2. In addition, a band at 1903 cm^{-1} appeared in the DPPETS-Rh/SiO_2 catalyst, but was not seen in the DPPPTS-Rh/SiO_2 spectrum. This band has been assigned to bridging CO on the Rh nanoparticles [21], suggesting that some Rh atoms on DPPETS-Rh/SiO_2 were not modified by the tethered-phosphine and remained as Rh nanoparticles. This would also contribute to relative low catalytic activity of DPPETS-Rh/SiO_2.

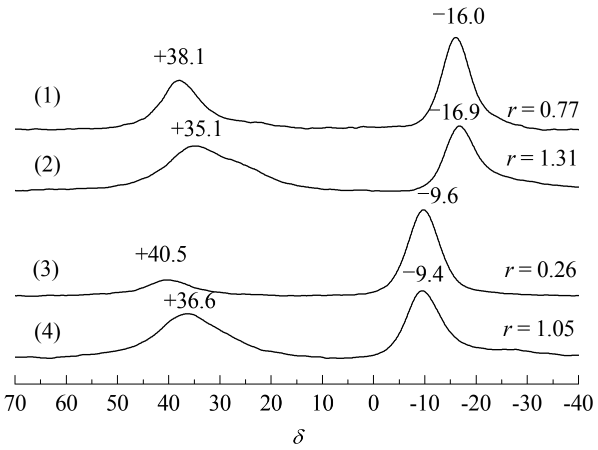

Fig. 4. ^{31}P NMR spectra of the fresh DPPPTS-Rh/SiO$_2$ (1), used DPPPTS-Rh/SiO$_2$ (2), fresh DPPETS-Rh/SiO$_2$ (3), and used DPPETS-Rh/SiO$_2$ (4) catalysts.

3.4. ^{31}P NMR results

Fig. 4 displays the ^{31}P NMR spectra of fresh and used DPPPTS-Rh/SiO$_2$ and DPPETS-Rh/SiO$_2$ catalysts. The spectrum of the fresh DPPPTS-Rh/SiO$_2$ shows bands at −16.0 and +38.1 ppm, assigned to free DPPPTS tethered to the SiO$_2$ carrier, and tethered-DPPPTS coordinated to Rh nanoparticles, respectively [6,10,22]. Two bands at −16.9 and +35.1 ppm can be observed in the spectrum of used DPPPTS-Rh/SiO$_2$, which have shifted up-field compared with the fresh one. This shift is because of a change in the chemical environment of the phosphorous in the used sample. Similarly, the fresh and used DPPETS-Rh/SiO$_2$ catalysts also show two bands assigned to free DPPETS-SiO$_2$ and coordinated tethered-DPPETS, respectively.

The down-field band (α) and up-field band (β) were integrated and the ratios of the areas of band α to band β (*r*) are shown in Fig. 4. For both catalysts, the *r* value of the used catalyst was higher than that of the fresh one, which means more phosphine was coordinated to the Rh nanoparticles after the hydroformylation reaction. The gradual formation of the active tethered Rh-phosphine complex as the reaction proceeded confirms the previous results where the TOF increased with time on stream. The *r* value of the used DPPPTS-Rh/SiO$_2$ (1.31) was significantly higher than that of the used DPPETS-Rh/SiO$_2$ (1.05). This observation suggests that the proportion of the tethered-phosphine coordinated to the Rh nanoparticles in DPPPTS-Rh/SiO$_2$ was higher than in DPPETS-Rh/SiO$_2$, corroborating the assumption that tethered-phosphines with longer alkyl spacers can more easily coordinate to Rh nanoparticles to form a more active Rh-phosphine complex than those with shorter alkyl spacers.

4. Conclusions

This study shows that the catalytic activity of tethered-phosphine modified Rh/SiO$_2$ catalyst for olefin hydroformylation could be improved by lengthening the alkyl spacer of the tethered-phosphine. *In situ* FT-IR results confirmed that the active species were a HRh(CO)$_2$(DPPPTS)$_2$/SiO$_2$ or HRh(CO)$_2$(DPPETS)$_2$/SiO$_2$ complex. The intensity of the IR bands showed higher concentration of active species were formed on the catalyst modified by the tethered-phosphine with the longer alkyl spacer. ^{31}P NMR results suggest that it is easier for the tethered-phosphine with longer alkyl spacer to coordinate to Rh nanoparticles and produce the active Rh-phosphine complex. In conclusion, lengthening the alkyl spacer of the tethered-phosphine was beneficial in forming more active species and enhancing the performance of tethered-phosphine modified Rh/SiO$_2$ catalysts for olefin hydroformylation.

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Graphical Abstract

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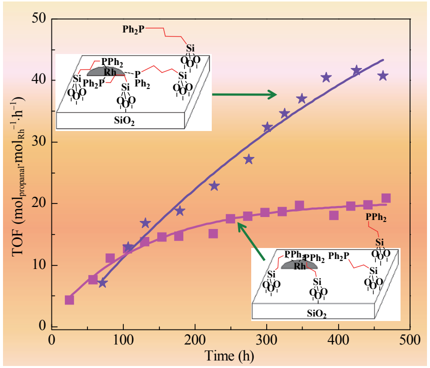

Lengthening the alkyl spacer of the tethered-phosphine was beneficial in forming more active species and enhancing the catalytic performance of a tethered-phosphine modified Rh/SiO$_2$ catalyst for ethylene hydroformylation.

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