Applied Catalysis A: General 353 (2009) 266–270

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

A new concept of tethered ligand-modified Rh/SiO_2 catalyst for hydroformylation with high stability

Xianming Li [a,c], Yunjie Ding [a,b,*], Guiping Jiao [a,c], Jingwei Li [a,c], Ronghe Lin [a,c], Leifeng Gong [a,c], Li Yan [a], Hejun Zhu [a]

[a] Laboratory of Applied Catalysis, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, China
[b] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, China
[c] Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 27 June 2008
Received in revised form 30 October 2008
Accepted 30 October 2008
Available online 8 November 2008

Keywords:
Tethered ligand
Rh/SiO_2 catalyst
Hydroformylation

ABSTRACT

A tethered ligand-modified Rh/SiO_2 catalyst was developed for hydroformylation with high stability. The catalyst was prepared by fastening both organic ligand and metal directly on the surface of support to avoid leaching, while at the same time the active species were formed in situ by coordination of the flexible ligand to the metal on the surface of SiO_2. The immobilization of ligand on SiO_2 and the interaction between ligand and metal were investigated by means of TG, solid-state NMR and FTIR. Hydroformylation of ethylene was selected as a probe reaction to evaluate the immobilization and coordination of ligand to the nano-metal particles. High activity and excellent stability were observed during a 1000-h run.

1. Introduction

While homogeneous catalysis is often well defined and can be operated under mild conditions with high efficiency, the practical applications of homogeneous catalysts have been limited by complicated and expensive catalyst separation from the products and starting materials [1]. Heterogeneous catalysts are more frequently used in large-scale commercial operations due to the ease of separating the solid catalysts from fluid media, but relatively low activity and selectivity are often observed [2–5]. Over the past few decades, major research efforts have been devoted to develop a new generation of heterogenized metal complex catalysts. This type of catalyst can combine the advantages of easy catalyst separation and recovery of heterogeneous catalyst with the high efficiency of soluble complexes. The most common method is to tether organometallic fragments to inorganic oxide [6–9] or organic polymers [10,11], which allows the catayst to be separated by filtration or by using a fixed catalyst bed in carried out continuous operation. Nevertheless, such methodology often leads to some drop in catalyst activity; metal leaching slowly takes place over prolonged operation [12,13] due to the fracture of the weak coordination bonds between metal and organic fragments. Researchers need to find new methods and strategies in order to overcome these limitations.

Bilhou et al. [14] has reported that supported Rh^0 could be converted to Rh^+ by the coordination of carbon monoxide under carbon monoxide atmosphere. Inspired by Bilhou's work, a triphenylphosphine (PPh_3) modified Rh/SiO_2 catalyst has been developed for hydroformylation of olefins in our earlier studies [15–17]. Over PPh_3-Rh/SiO_2 catalyst, the homogeneous active species could be formed in situ by coordinating PPh_3 to Rh species under syngas atmosphere and high activity was observed [15]. Though no Rh leaching was observed due to the direct fastening of Rh to SiO_2, the catalyst activity dropped a lot after a period of operation, caused by PPh_3 leaching. Therefore, we proposed to modify Rh/SiO_2 catalyst with a tethered ligand to avoid ligand leaching. TG, solid-state NMR and FTIR were used to investigate the immobilization of the ligand on SiO_2 and the interactions between ligand and Rh. Hydroformylation of ethylene was carried on as a probe reaction to evaluate the immobilization and coordination of ligand to Rh.

2. Experimental

2.1. Preparation of catalyst

Rh/SiO_2 was prepared according to a procedure reported earlier [17]. The Rh metal loading of Rh/SiO_2 was 1 wt%.

* Corresponding author at: Laboratory of Applied Catalysis, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, China. Tel.: +86 411 84379143; fax: +86 411 84379143.
E-mail address: dyj@dicp.ac.cn (Y. Ding).

0926-860X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2008.10.052

Tethered-ligand modified Rh/SiO_2 catalyst was prepared by mixing 0.22 g 2-(diphenylphosphino) ethyltriethoxysilane (DPPTS) with 0.3 g Rh/SiO_2 in 3.0 ml toluene. This mixture was stirred at room temperature for 15 h and subsequently heated to reflux for 6 h. After cooling to room temperature, the mixture was recovered by filtration and washed copiously with toluene until no DPPTS could be detected by liquid chromatography in the filtrate. Finally, the solid was dried in vacuum at room temperature and the resulting black DPPTS-Rh/SiO_2 was stored under argon atmosphere. All manipulations were carried out under an argon atmosphere, and all reagents were dehydrated with CaH_2 and degassed with argon.

DPPTS/SiO_2 was prepared similarly to DPPTS-Rh/SiO_2, but SiO_2 was used instead of Rh/SiO_2. DPPTS/SiO_2 (unwashed) was prepared similarly to DPPTS/SiO_2, but the solvent was directly removed under vacuum after stirring without filtration and washing. Diphenyl ethyl phosphine (DPEP)-modified Rh/SiO_2 was prepared similarly to DPPTS/SiO_2 (unwashed), but DPEP and Rh/SiO_2 were used instead of DPPTS and SiO_2.

2.2. Testing of catalyst

The hydroformylation of ethylene was conducted in a continuous flow fixed bed reactor. The effluent was passed through a condenser filled with 100 ml of cold de-ionized water. Propanal in the products of hydroformylation was captured completely by dissolution into the water in the condenser. An HP-6890N GC with a FFAP column, using an FID detector and ethanol as an internal standard, analyzed the aqueous solution containing propanal. The tail gas was analyzed on-line using an HP-6890N GC with a Porapak-QS column and a TCD detector. The turnover frequency (TOF) of the catalyst was calculated based on the Rh content of the catalyst.

3. Results and discussions

3.1. Thermogravimetric analysis (TG)

TG and DTG profiles of DPPTS-modified Rh/SiO_2 catalyst are shown in Fig. 1. There were two peaks in curve A [DPPTS/SiO_2 (unwashed)]: a large peak at 532 K was assigned to the physically adsorbed DPPTS and a relatively small peak at 720 K was assigned to the chemically adsorbed DPPTS which was tethered on SiO_2 by Si–O–Si bonds. Because no weight losses occurred at about 532 K in curve B (DPPTS/SiO_2) or C (DPPTS-Rh/SiO_2), we could conclude that only tethered DPPTS remained over these two catalysts. It was worth mentioning that a new weight loss at 848 K was observed over DPPTS-Rh/SiO_2. This new peak might be attributed to the coordination between the flexible tethered DPPTS and the highly dispersed Rh species on the surface of SiO_2, and the coordination of DPPTS to Rh species might stabilize the immobilization of DPPTS on SiO_2.

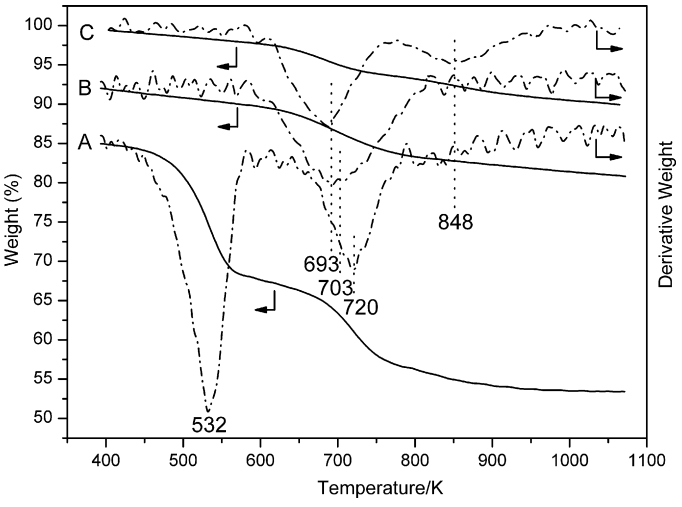

Fig. 1. TG and TG derivative profiles: (A) DPPTS/SiO_2 (unwashed); (B) DPPTS/SiO_2 and (C) DPPTS-Rh/SiO_2.

3.2. FTIR analysis

The FTIR spectra are often used to give evidence of the immobilization of organic ligand on the support. As shown in Fig. 2, besides those peaks observed in Rh/SiO_2, DPPTS-Rh/SiO_2 displayed a number of new peaks including one peak at 696 cm^{-1} corresponding to the wagging vibration of benzene ring, one peak at 741 cm^{-1} characterizing the –H rocking vibration of the mono-substituted benzene ring and one peak around 1435 cm^{-1} resulting from the vibration of $P–CH_2$. These new peaks demonstrated that no substantial changes occurred in phosphine's structure and that DPPTS was successfully tethered on SiO_2. The absorption peak at 1080–1164 cm^{-1} corresponding to the P-phenyl vibration could not be clearly distinguished due to the overlap by the intense bonds at 1095 cm^{-1} resulting from the Si–O vibration.

3.3. ^{29}Si MAS NMR analysis

The immobilization of DPPTS on SiO_2 could be further confirmed by solid ^{29}Si NMR spectra, as shown in Fig. 3. Comparing with Rh/SiO_2, besides a large peak at −113 ppm corresponding to the silica support, two new peaks corresponding to T^2 ($\delta = -55$ ppm) and T^3 ($\delta = -64$ ppm) were observed over DPPTS/SiO_2 and DPPTS-Rh/SiO_2, where $T^n = RSi(OSi)_n(OH)_{3-n}$, $n = 1–3$. The presence of T^n peaks indicated the immobilization of organic silane moieties on silica support [7]. Moreover, T^2 and T^3 peaks could also be observed over DPPTS-Rh/SiO_2 after 1000 h reaction, which indicated that no DPPTS leaching had occurred.

3.4. ^{31}P MAS NMR analysis

The solid-state ^{31}P NMR was carried out to confirm the interaction between DPPTS and Rh. As shown in Fig. 4, only a sharp

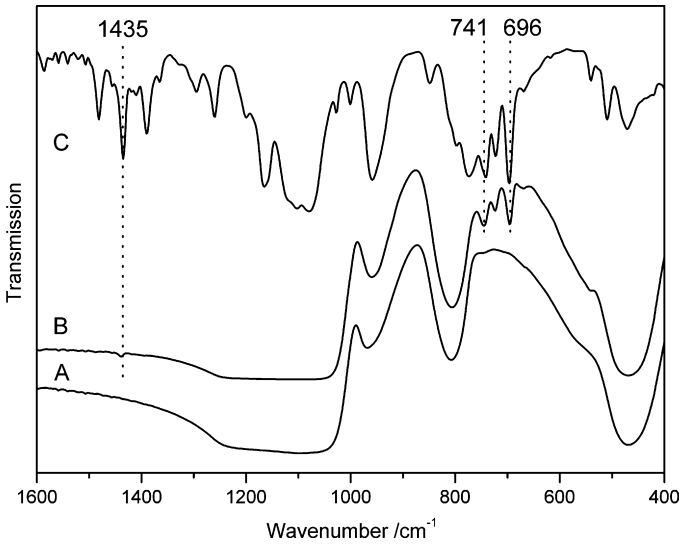

Fig. 2. FTIR spectra of DPPTS-modified Rh/SiO_2: (A) Rh/SiO_2; (B) DPPTS-Rh/SiO_2 and (C) DPPTS.