Applied Catalysis A: General 419–420 (2012) 13–21

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Preparation of carbon-supported Pt catalysts covered with microporous silica layers using organosilanes: Sintering resistance and superior catalytic performance for cyclohexane dehydrogenation

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ARTICLE INFO

Article history:
Received 9 October 2011
Received in revised form 9 December 2011
Accepted 10 December 2011
Available online 19 December 2011

Keywords:
Carbon-supported Pt catalyst
Silica coating
Microporous silica layer
Sintering resistance
Cyclohexane dehydrogenation

ABSTRACT

Carbon black-supported Pt metal particles (Pt/CB) were covered with microporous silica layers using different organosilanes like methyltriethoxysilane (MTES) (SiO_2(MTES)/Pt/CB) and phenyltriethoxysilane (PhTES) (SiO_2(PhTES)/Pt/CB). Pt metal particles in Pt/CB covered with microporous silica layers were stable at high temperature up to 973 K in a hydrogen atmosphere, because the microporous silica layers that wrapped around the Pt metal particles essentially prevent particle sintering. Methyl or phenyl groups were introduced into the silica layers that covered the Pt metal particles using MTES or PhTES hydrolysis. Micropores were formed in the silica layers effectively after thermal treatment at 973 K. The microporous silica-coated Pt catalysts were used as model catalysts for the dehydrogenation of cyclohexane. The microporous silica-coated Pt catalysts with thermal treatment at 973 K exhibited a higher conversion of cyclohexane compared with Pt/CB. Especially, the SiO_2(PhTES)/Pt/CB catalysts showed relatively higher conversion of cyclohexane compared with the other silica-coated Pt catalysts even when the SiO_2 loading was high. Microporous silica layers with a larger micropore volume promoted the diffusion of cyclohexane during the catalytic reaction.

1. Introduction

Highly dispersed precious metal particles on supports have been shown to be active for various catalytic applications such as automotive catalysts [1], the hydrogenation or dehydrogenation of organic compounds [2,3] and electrocatalysts for fuel cells [4]. The efficiency and lifetime of these supported precious metal catalysts are influenced by the stability of the highly dispersed metal particles. However, it has been reported that supported precious metal catalysts are easily deactivated for reasons like the sintering of metal particles because of high reaction temperatures, the surrounding atmosphere [5,6] and the dissolution of metal particles in the polymer electrolyte fuel cell electrodes under severe conditions [7]. The deactivation of supported metal catalysts has been recognized as a big problem in industrial catalysis. Thus, the development of supported metal catalysts with high resistance toward deactivation is required.

The silica coating technique is a promising method to improve the durability of metal particles toward deactivation. In previous work, we have developed supported metal catalysts covered with silica layers by the hydrolysis and condensation of tetraethoxysilane (TEOS) [8–19]. We have demonstrated that the metal particles in these silica-coated metal catalysts have good resistance to sintering even at high temperatures because the metal nanoparticles were physically covered with silica layers. In addition, the metal particles can react with reactant molecules through the silica layers since the silica layers that are wrapped around the metal particles have a porous structure, therefore, the silica-coated metal catalysts can be applied to catalytic reaction. For example, the coverage of Co, Ni and Pt metal particles with silica layers prevents the sintering of their metal particles during hydrocarbon decomposition, which results in the preferential formation of carbon nanotubes or nanofibers with uniform diameters, while metal catalysts that are not covered with silica layers form carbon nanotubes or nanofibers with various diameters because these metal particles are severely aggregated during hydrocarbon decomposition

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doi:10.1016/j.apcata.2011.12.020

[10–14]. In addition, we prepared the carbon nanotube-supported Pt or Pd nanoparticles covered with silica layers [15–19] and this coverage of Pt or Pd nanoparticles with silica layers prevents the dissolution of Pt or Pd particles from the supports, resulting in the excellent durability for the oxygen reduction reaction under severe cathode conditions in proton-exchange-membrane fuel cells [15,18,19]. Thus, the coverage of metal particles with silica layers is an effective method to enhance the stability of catalysts. Based on our previous studies, we expect that the development of metal catalysts covered with silica layers with larger pores, pore volumes or additional functionality would lead to an increase in their catalytic application. For example, organically functionalized silica structures have advantages for the porosity of silica structures, which allows for the easier adsorption and diffusion of reactants into the silica structure, and ultimately these advantages improve their catalytic activity [20–26]. Recently, only a few studies that focus on the porous silica structure in the preparation of silica-coated metal particles have been reported [24–26] and they showed the high sintering resistance of metal particles and their possible application to catalytic reactions associated with light hydrocarbons at high temperatures [25,26]. We believe that the effective structural design of silica layers in silica-coated metal particles would lead to their wider application as larger reactant molecules may be used. Among the silica-coated metal catalysts, different from the metal catalysts enclosed within spherical silica particles (so-called core-shell structures), the silica-coated structure of the supported metal catalysts would be appropriate for the control of the thickness of silica layers, which are often related to catalytic performance. This silica-coated structure can possibly be applied to various supported metal catalysts.

Consequently, in this study, carbon black (CB)-supported Pt metal nanoparticles (Pt/CB) were covered with microporous silica layers using organosilanes. Methyl and phenyl groups were introduced to the silica layers that wrapped around the Pt metal particles by the successive hydrolysis of 3-aminopropyl-triethoxysilane (APTES) and methyltriethoxysilane (MTES) or phenyltriethoxysilane (PhTES). The Pt/CB that were covered with microporous silica layers were used as catalysts for the dehydrogenation of cyclohexane in a fixed bed flow reactor as it is a potential system for the storage and transport of hydrogen as an organic hydride [27–29]. This was done to demonstrate and compare their catalytic activity with that of Pt/CB prepared by conventional impregnation.

2. Experimental

2.1. Preparation of CB-supported Pt nanoparticles covered with microporous silica layers

Commercially available CB (Vulcan XC-72 supplied by the Cabot Co.) was used as a support for the Pt particles. The coverage of Pt/CB with silica was performed by the successive hydrolysis of APTES and other organosilane [16,17]. CB (1.00 g) was immersed in 220 ml of an aqueous solution containing H_2PtCl_6 (0.55 mmol). The pH of the solution was adjusted to ca. 11.8 by the addition of aqueous NH_3 and the Pt metal precursors were then deposited onto the CB surfaces. After this solution was filtered, the sample was dispersed in 220 ml of an aqueous solution including aqueous NH_3 (pH 11.8). The successive hydrolysis of APTES and the other organosilane (TEOS, MTES or PhTES) was performed to enable the formation of the organosilica layers onto CB. APTES (0.975 g) was added to the solution and the solution was stirred at 333 K for 0.5 h. An appropriate amount of TEOS, MTES or PhTES that is corresponded to each organosilane concentration listed in Table 1 was then added to the solution and stirred at the same temperature for 1 h. After centrifuging and drying the samples at 333 K, they were exposed to an atmosphere of H_2 at 623 K for 3 h. Hereafter, the obtained samples are designated SiO_2(TEOS)/Pt/CB, SiO_2(MTES)/Pt/CB and SiO_2(PhTES)/Pt/CB, respectively. The silica-coated Pt catalysts were further treated at 973 K for 3 h in an atmosphere of H_2 to determine the durability of the sintering of Pt metal particles in the catalysts. The treatment temperature for these Pt catalysts in H_2 is shown in parenthesis after the catalyst's name, for example, SiO_2(PhTES)/Pt/CB treated at 973 K is denoted as SiO_2(PhTES)/Pt/CB (973 K).

Table 1

SiO_2, Pt and carbon content in Pt/CB, SiO_2(TEOS)/Pt/CB, SiO_2(MTES)/Pt/CB and SiO_2(PhTES)/Pt/CB upon reduction and thermal treatment under different conditions.

Catalyst	Organosilane concentration (mol l^{-1})	Temp.[a] (K)	Content (wt%)		
			SiO_2	Pt	C
Pt/CB	–	623	–	1.3	98.7
		973	–	1.7	98.3
SiO_2(TEOS)/Pt/CB	0.022	623	17.4	2.9	78.2
		973	17.4	2.7	78.6
	0.038	623	28.1	1.9	68.0
		973	30.7	2.8	64.5
	0.060	623	43.2	1.5	51.8
		973	47.7	1.5	49.6
SiO_2(MTES)/Pt/CB	0.025	623	11.0	1.4	85.7
		973	11.6	2.1	84.9
	0.050	623	17.0	1.4	79.5
		973	18.6	2.1	77.5
	0.100	623	41.1	0.8	54.2
		973	50.5	1.2	46.7
SiO_2(PhTES)/Pt/CB	0.017	623	10.8	1.6	85.2
		973	11.2	2.0	85.5
	0.025	623	17.3	1.5	79.1
		973	22.9	1.7	73.9
	0.100	623	25.8	1.1	70.0
		973	37.8	1.8	58.8

[a] Temperature of the reduction or thermal treatment with hydrogen.

For comparison, Pt/CB without silica layer was prepared by a conventional impregnation method. CB (2.00 g) was dispersed in 100 ml of acetone containing H_2PtCl_6 (0.21 mmol). The suspension was stirred and dried at 333 K. The sample thus obtained was reduced under a H_2 atmosphere at 623 K for 3 h.

2.2. Characterization of the samples

The content of Pt, SiO_2 and carbon in the Pt/CB that were covered with silica layers was evaluated by X-ray fluorescence spectroscopy and elemental analysis. Transmission electron microscope (TEM) images of the samples were recorded with a Hitachi H-800 instrument (Hitachi High-Technologies Co.) and a JEM-2100F instrument (JEOL Ltd.). Specific surface areas were calculated from the adsorption isotherm obtained with a conventional BET nitrogen adsorption apparatus (BELSORP-18SP, Bell Japan Inc.). The exposed surface areas of the Pt metal particles in the silica-coated Pt catalysts were evaluated by the CO chemisorption method (BEL-CAT, BEL Japan Inc.) at 323 K assuming an adsorption stoichiometry of 1:1 for CO/Pt. Before the measurement of CO chemisorption, the samples were treated with hydrogen at 393 K. Thermogravimetric analysis (TG) was carried out with a TG/DTA 6300 apparatus (SII Nanotechnology Inc.) with a heating rate of 10 °C min^{-1} under flowing N_2. Fourier transform infrared spectroscopy (FTIR) spectra were recorded in the 400–4000 cm^{-1} range using an FTIR-8200PC spectrometer (Shimadzu Co.).

Measurements of X-ray absorption near-edge structure (XANES) and extended X-ray adsorption fine structure (EXAFS) were performed at the Photon Factory in the Institute of Materials Structure Science for High Energy Accelerator Research Organization, Tsukuba, Japan (proposal nos. 2006G343 and 2009G087).