Applied Catalysis A: General 352 (2009) 214–222

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Synergistic effect of Pt or Pd and perovskite oxide for water gas shift reaction

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ARTICLE INFO

Article history:
Received 15 August 2008
Received in revised form 6 October 2008
Accepted 6 October 2008
Available online 15 October 2008

Keywords:
Water gas shift
Pt catalyst
Pd catalyst
Perovskite oxide
Synergistic effect
Lattice oxygen

ABSTRACT

The water gas shift (WGS) reaction over Pt and Pd catalysts supported on various perovskite oxides has been investigated at 573 K without catalyst pretreatment. The Pt and Pd catalysts on $LaCoO_3$ support showed high catalytic activity. Interaction between Pt or Pd and the support is considered to promote the WGS reaction: Pt/$LaCoO_3$ had high initial activity but deactivated immediately; Pd/$LaCoO_3$ was less active than Pt/$LaCoO_3$, but had superior stability. Catalysts were characterized using XRD, STEM, XPS, and H_2-temperature programmed reduction (TPR). Results of this study showed that reduction of the support decreased the CO conversion on Pt/$LaCoO_3$. On the other hand, Pd/$LaCoO_3$ showed stable activity for the WGS reaction. Therefore, Pd was added to Pt/$LaCoO_3$ for stabilizing the catalyst activity, and 0.5 wt.% Pd/1 wt.% Pt/$LaCoO_3$ catalyst showed higher activity and stability.

1. Introduction

Hydrogen for fuel cells is produced via steam reforming or autothermal reforming of hydrocarbons. The reformed gas contains not only hydrogen but also considerable amounts of carbon monoxide. The CO concentration must be reduced to less than 10 ppm for application in proton exchange membrane fuel cells (PEMFC) to prevent irreversible adsorption of CO onto the Pt anode electrode. The CO reduction process consists of the water gas shift (WGS) reaction and subsequent preferential oxidation (PrOx). The WGS reaction,

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H = -41.2\,\mathrm{kJ/mol},$$

is an exothermic reaction. This reaction offers thermodynamic advantages at lower temperature, but it is kinetically disadvantageous. WGS is commercially achieved in a two-step process: a high temperature shift (HTS; 623–723 K) using a Fe–Cr catalyst and a low temperature shift (LTS; lower than 573 K) using a Cu–Zn catalyst [1]. One-step WGS at low temperature is expected to miniaturize the on-site hydrogen production process for use in fuel cells. The existing Cu–Zn catalyst has lower potential for WGS because of its low activity. It is deactivated by daily start-up and shut down (DSS) operations under oxidizing atmospheres. Therefore, a WGS catalyst is required which not only has high activity and stability at low temperature but also has robustness under an oxidizing atmosphere.

Two approaches for the solution of these issues exist: one is modification of the Cu–Zn catalyst; another is exploration of noble metal catalysts. Several examples can be given of investigations of Cu–Zn catalysts. Shishido et al. prepared ternary Cu/ZnO/Al_2O_3 catalysts by homogeneous precipitation (HP), which showed higher activity for WGS than the catalyst prepared by co-precipitation [2,3]. Tanaka et al. found that the Cu–Mn spinel oxide showed high WGS reaction activity comparable to that of conventional Cu/ZnO/Al_2O_3, despite its low surface area. They postulated that Cu–Mn spinel oxide was reduced by H_2 in the reformed gas and worked as Cu/MnO [4,5]. Noble metal catalysts are anticipated for their properties of thermal stability, obviation of pretreatment, and sulfur tolerance.

Many noble metal catalysts have been proposed in recent years, such as Pt/CeO_2 [6–17] and Pd/CeO_2 [10]. As a general trend, Au, Rh, Pt, and Pd are known as active metals for WGS; as supports, CeO_2, TiO_2, and Fe_2O_3 are frequently used. However, these noble metal catalysts present issues of tolerance in an oxidative atmosphere. Consequently, we attempted to use oxide catalysts as LTS catalysts, which are expected not to be deactivated under DSS conditions. We specifically examined perovskite oxides, which are known for their oxygen ion conductivity and oxygen effusion property [18]. This redox property of perovskite oxides might accelerate CO oxidation and H_2O reduction. A DSS-tolerant catalyst would be preferred if the LTS reaction occurred on the oxidative active site of the catalyst. For this study, we used Pt or Pd/perovskite oxides for

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doi:10.1016/j.apcata.2008.10.008

the WGS reaction. Then high-activity catalysts were characterized using several methods: XRD, XPS, STEM, and H_2-temperature programmed reduction (TPR).

2. Experimental

2.1. Catalyst preparation

Perovskite oxides $LaBO_3$ (B = Cr, Mn, Fe, Co and Ni) were prepared using the Pechini method. Nitrates were used as precursors for perovskite oxides. Ethylene glycol and citric acid were used as polymerization/complexion agents for the process. The precursors, ethylene glycol and citric acid, were dissolved in water; the solution was heated to 353 K in a water bath. The obtained sol was dried on a hot stirrer (573 K) before calcination at 673 K for 2 h. The resulting solid was further heat-treated at 1123 K for 10 h. Furthermore, $SrTiO_3$ was prepared using the same Pechini method, except that titanium isopropoxide was used as the titanium precursor. Titanium isopropoxide required dissolution in water in advance because of its low solubility to water. The Pt catalysts were prepared by impregnation of perovskite oxides powder with an aqueous solution of the metal precursor salt $Pt(NH_3)_4(NO_3)_2$. The resulting slurry was dried on a hot plate under continuous stirring with subsequent calcination at 773 K for 1 h. The Pd catalysts were prepared using the same impregnation method with an acetone solution of $Pd(CH_3COO)_2$.

2.2. Activity test

The WGS reaction was carried out using a fixed bed flow reactor at atmospheric pressure. A pyrex glass tube with 8 mm inner diameter was used as a reactor. The catalyst, which was pelletized and sieved to 250–500 μm diameter, was weighed and 250 mg was charged in the reactor. Water was supplied to the reactor with a bubbler. The feed gas was simulated reforming gas ($CO/H_2O/H_2/N_2/Ar$ = 6/30/42/9/13). The total flow rate was 168 cm^3/min (NTP) and *W*/*F* (CO) = 9.32 g-cat h/mol. The reaction was carried out at 573 K without pretreatment. The reaction conditions are not close to an equilibrium condition but are in a kinetic region. Therefore, we can evaluate the real activities of these catalysts. The exit gas was passed to a cold trap at 273 K; the dry gas was analyzed using GC-TCD and GC-FID. Table 1 presents the defined sample names of the catalysts after various reactions and post-treatments. *In situ* post-treatment of the used catalyst with air or steam was carried out after WGS reaction. Post-treatment by air was carried out using 100 cm^3/min (NTP) at 573 K for 1 h. Post-treatment by steam was carried out in a flow of steam (H_2O/N_2 = 30/70). The total flow rate was 168 cm^3/min (NTP) at 573 K for 1 h.

Table 1
Sample names and various reactions/post-treatments.

Abbreviations	Step 1 WGS reaction	Step 2 post-treatment	Step 3 WGS reaction
1 wt.% Pt/$LaCoO_3$			
Pt–fresh	–	–	–
Pt–5 min	5 min	–	–
Pt–3 h	3 h	–	–
Pt–3 h–Air	3 h	Air, 1 h	–
Pt–3 h–Air–5 min	3 h	Air, 1 h	5 min
Pt–3 h–Air–1 h	3 h	Air, 1 h	1 h
Pt–3 h–H_2O	3 h	H_2O, 1 h	–
Pt–3 h–H_2O–5 min	3 h	H_2O, 1 h	5 min
Pt–3 h–H_2O–1 h	3 h	H_2O, 1 h	1 h
1 wt.% Pd/$LaCoO_3$			
Pd–fresh	–	–	–
Pd–5 min	5 min	–	–
Pd–3 h	3 h	–	–
Pd–3 h–Air	3 h	Air, 1 h	–
Pd–3 h–Air–5 min	3 h	Air, 1 h	5 min
Pd–3 h–Air–1 h	3 h	Air, 1 h	1 h
Pd–3 h–H_2O	3 h	H_2O, 1 h	–
Pd–3 h–H_2O–5 min	3 h	H_2O, 1 h	5 min
Pd–3 h–H_2O–1 h	3 h	H_2O, 1 h	1 h

2.3. Characterization

X-ray diffraction (XRD) analyses of the catalysts were performed using an X-ray diffractometer (operating at 40 kV and 20 mA, Cu Kα radiation filtered by nickel, RINT-2000; Rigaku Corp.). Particle sizes of the catalysts and loading states of active metals were observed using scanning transmission electron microscopy (STEM, operating at 200 kV, HF-2210; Hitachi Ltd.). Samples were crushed and subsequently suspended in acetone using ultrasonic vibration. A drop of this suspension was loaded onto a copper micro-grid (Okenshoji Co., Ltd.). X-ray photoelectron spectroscopy (XPS, ESCA1800; Ulvac-Phi Inc.) was performed using non-monochromatic Mg Kα radiation. The pass energy of the analyzer was set at 23.5 eV. Charging effects were minimal (<0.2 eV). The C 1s peak at 284.5 eV was used as a reference to correct for charging of the samples. Spectrum of each element was normalized according to the intensity. The reduction of each catalyst was monitored using TPR with 10% hydrogen in nitrogen. The gas flow rate was 50 ml/min. The heating rate was 5 K/min from ambient temperature to 1073 K. The weight loss of each catalyst was determined using a thermogravimetry (TG) analyzer (TG8120; Rigaku Corp.).

3. Results and discussion

3.1. Synergistic effects of Pt, Pd and perovskite oxides

First, we examined WGS reactions with various perovskite oxides without active metal, but they showed no activity for the WGS reaction. For that reason, we impregnated Pt or Pd on these oxides as an active site for WGS.

Next, we examined various platinum-supported catalysts on various perovskite oxides. Fig. 1 shows catalytic activities and properties of Pt catalysts supported on various perovskite oxides: $LaCoO_3$, $LaFeO_3$, $LaCrO_3$, $LaNiO_3$, $LaMnO_3$, and $SrTiO_3$. The Pt metal content was fixed to 1 wt.%. Actually, Pt supported on SiO_2 showed little activity; the CO conversion was only 0.3% (not shown).

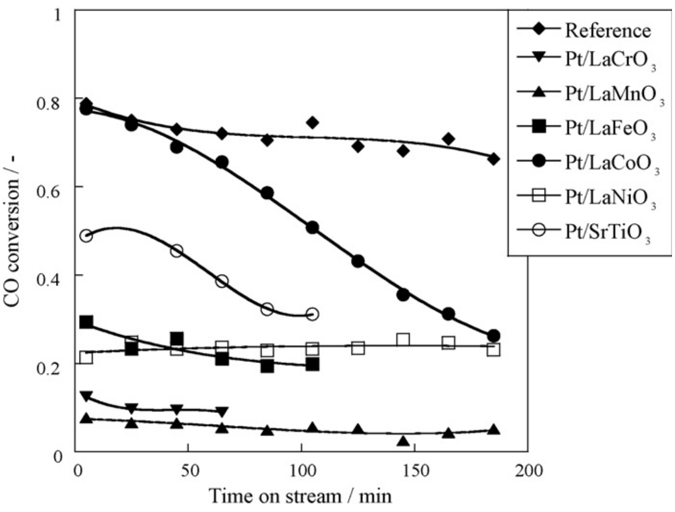

Fig. 1. Activities of Pt (1 wt.%) catalysts supported on various perovskites.