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ScienceDirect

Applied Catalysis B: Environmental 77 (2007) 206–214

APPLIED CATALYSIS B: ENVIRONMENTAL

www.elsevier.com/locate/apcatb

Catalysts for the hydrolysis of aqueous borohydride solutions to produce hydrogen for PEM fuel cells

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Received 15 October 2006; received in revised form 20 June 2007; accepted 23 July 2007

Abstract

The objective of the present study was to understand the superior catalytic performance of PtRu-$LiCoO_2$ catalyst for hydrogen (H_2) generation from aqueous sodium borohydride ($NaBH_4$) solutions by comparing the catalytic activity of various PtRu-supported catalysts. Three of the support materials namely cobalt oxide (Co_3O_4), lithium nickel oxide ($LiNiO_2$) and lithium manganese oxide ($LiMnO_2$) were synthesized and characterized using XRD. The PtRu-supported catalysts with eight different support materials were prepared and characterized using XRD and BET surface area measurements. The results revealed excellent hydrogen generation activity of Co_3O_4 and $LiCoO_2$ for the hydrolysis of $NaBH_4$. Actually, the catalytic activity of Co_3O_4 and $LiCoO_2$ is due to the formation of cobalt boride (CoB) by the reduction of these oxides by $NaBH_4$. A model is proposed to explain the hydrogen generation profile of the above catalysts. The CoB formation is confirmed by XPS studies. Further, the performance of Co_3O_4 and $LiCoO_2$ was compared with various noble metal catalysts. The performance of Co_3O_4 is at par with the noble metal based catalysts at low concentration of $NaBH_4$ and far superior to noble metal based catalysts at higher concentration.

Keywords: Borohydride hydrolysis; Hydrogen; PEM fuel cells; Cobalt oxide (Co_3O_4); Lithium cobalt oxide ($LiCoO_2$); PtRu-supported catalysts

1. Introduction

Research activities on alternative clean energy technologies are increasing exponentially due to the dwindling fossil-fuel reserves and a global concern for environmental pollution. The fuel cells offer great promise as pollution free power sources for various applications ranging from mobile phones to automobile traction [1]. The polymer electrolyte membrane (PEM) fuel cell technology is in an advanced stage of commercialization and fuel cell systems for various applications are being introduced on experimental basis [2]. At present, it is being argued that the widespread application of PEM fuel cells mainly depends on the successful establishment of hydrogen (H_2) infrastructure [3,4]. The complexities involved in setting up the reformer along with the carbon monoxide clean up unit have made the on-board fuel processing a very difficult option for the automobile applications. Since volumetric energy density of gaseous H_2 is very low, it is stored in pressurized cylinders around 200 atm. Apart from safety concerns, heavy weight, space occupancy etc., are the disadvantages of high-pressure H_2 storage. Moreover, adequate technologies for the high-pressure storage materials are yet to be advanced. The metal hydrides, such as $LaNi_5H_6$ that incorporate H_2 in their crystal structure, are also being investigated as H_2 storage materials. But their gravimetric storage capacity is too low (1–2 wt.%), they are expensive and require relatively high temperature for the release of H_2. Considering the above difficulties in establishing the H_2 supply infrastructure, the chemical hydrides may offer a feasible solution. The chemical hydrides have good gravimetric storage capacity and their alkaline solutions are absolutely safe for transportation. Among the chemical hydrides, sodium borohydride ($NaBH_4$) is desirable due to its high H_2 content of 10.57 wt.% and the excellent stability of its alkaline solutions [5]. The aqueous solutions of $NaBH_4$ undergo hydrolysis in

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doi:10.1016/j.apcatb.2007.07.024

presence of suitable catalysts to produce H_2 free from any impurities. The H_2 generation rate can be controlled as per the demand thereby avoiding the safety risks involved in high-pressure H_2 delivery systems.

Research activities on $NaBH_4$ based H_2 generation systems are increasing rapidly due to the potential feasibility for PEM fuel cell applications [6–14]. Many reports on the development of suitable catalysts for the hydrolysis of aqueous $NaBH_4$ solutions have appeared in recent years. The basic work was carried out by Schlesinger et al. [15] long ago where they have reported various transition metal catalysts for the hydrolysis of NaBH4 solutions. Amendola et al. [6] have reported a H_2 on demand system based on Ru impregnated on ion exchange resin beads. Kojima et al. [7] have developed various oxide-supported catalysts and reported Pt-$LiCoO_2$ as an excellent catalyst for H_2 generation from aqueous $NaBH_4$ solutions. They have also reported the development of a 10 kW scale H_2 generator based on $NaBH_4$ [8]. Kim et al. [9] have reported the filamentary nickel and cobalt catalysts for the hydrolysis of $NaBH_4$ solutions. The catalytic activity of carbon supported Pt catalysts [10], cobalt boride [11], nickel boride [13] and Ru(0) nanoclusters [14] are also reported recently. We have proposed PtRu-$LiCoO_2$ as an efficient catalyst for sodium borohydride hydrolysis and the results have been published in a preliminary communication [16]. We were further interested in examining the catalytic activity of PtRu alloy catalyst impregnated on various support materials to understand the superior performance of PtRu-$LiCoO_2$ catalyst. Preparation of various supported catalysts, characterization and performance evaluation studies carried out with the above objective are discussed in the present communication.

2. Experimental

2.1. Chemicals

Lithium nitrate ($LiNO_3$, 96.0 wt.%), lithium hydroxide hydrate ($Li(OH)\ H_2O$, 99.0 wt.%), manganese (II) nitrate hexahydrate ($Mn(NO_3)_2\,6H_2O$, 97.0 wt.%), nickel (II) hydroxide ($Ni(OH)_2$, 99.0 wt.%), nickel (II) oxide ((NiO), 99.0 wt.%), titanium dioxide (TiO_2, 98.0 wt.%), zirconium oxide (ZrO_2, 99.0 wt.%) all from Junsei Chemicals Co., Ltd., Japan, cobalt (II) nitrate ($Co(NO_3)_2$, 98.0 wt.%) and lithium cobalt oxide ($LiCoO_2$, 98.5 wt.%) from Sigma Chemicals, Pt-C (20 wt.%), Ru-C (10 wt.%), Pt-Black (99.90 wt.%) from Johnson Matthey, ruthenium chloride ($RuCl_3$) (99.90 wt.%), hexachloroplatinic acid (H_2PtCl_6 (99.90 wt.%), iridium (IV) oxide (IrO_2 99.99 wt.%), from Alfa-Aesar, Vulcan XC-72 from Cabot were used as received.

2.2. Preparation of catalyst supports

The cobalt oxide (Co_3O_4) was prepared from $Co(NO_3)_2$ by heating under the atmosphere of flowing air at 600 °C [17]. Lithium nickel oxide ($LiNiO_2$) was prepared from $Li(OH)H_2O$ and NiO [18]. The reactants in proper stoichiometric ratio were finely ground and heated at 650 °C for 10 h and then the temperature was raised to 700 °C for 15 h under oxygen flow. The lithium manganese oxide ($LiMnO_2$) was prepared from $LiNO_3$ and $Mn(NO_3)_2\ 6H_2O$ as the precursors [19]. The salts were dissolved in deionized (DI) water and heated to 110 °C in a convection oven to remove water. Then, the powder was uniformly mixed and calcined at 1000 °C in air atmosphere for 10 h. The PtRu-Black was prepared using $RuCl_3$ and H_2PtCl_6 as the precursors. Aqueous solutions of the precursors were mixed and reduced with 5 wt.% sodium borohydride solution. The precipitated PtRu-Black was filtered and washed with copious quantity of DI water for the complete removal of chlorides. Then, it was dried under vacuum at 110 °C and used for the H_2 generation experiments. The prepared supports as well as the supported catalysts were characterized by XRD and BET methods.

2.3. Preparation of supported PtRu catalysts

$RuCl_3$ and H_2PtCl_6 were used as precursors for catalysts preparation. The supported catalysts were prepared by the incipient wetness impregnation technique. The required amount of the support material was suspended in DI water and stirred with magnetic stirrer. The precursors were dissolved in sufficient quantity of DI water and added to the suspension containing the support material in a dropwise manner. Then, the suspension was stirred for 30 min, heated to 80 °C and reduced with 5 wt.% $NaBH_4$ solution. The catalysts were filtered using G4 sintered disc, washed and dried at 80 °C under vacuum. The PtRu-supported catalysts of NiO, Co_3O_4, $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, TiO_2, Vulcan-XC72, IrO_2 and ZrO_2 were prepared with 10 wt.% of catalyst loading. The atomic percentages (at.%) of Pt, Ru in the supported catalysts were calculated from ICP analysis and each was found to be ~50 at.% within the experimental error.

2.4. Characterization of the catalysts

2.4.1. BET analysis

Specific area, average pore radius and pore volume of the catalysts were determined by nitrogen adsorption–desorption isotherms at 77 k using the BET method in a Micromeritics Accusorb 2100E apparatus. Prior to the measurements, the samples were maintained at 250 °C under vacuum for 8 h to eliminate the adsorbed impurities.

2.4.2. X-ray diffraction measurements (XRD)

The powder XRD patterns were recorded in the 2θ range 10°–80° with a RIGAKU D/MAX-IIIC diffractometer using Cu Kα (λ = 1.4518 Å) radiation filtered through Ni.

2.4.3. X-ray photoelectron spectroscopy (XPS)

The XPS measurements were carried out on a VG scientific MultiLab ESCA2000 instrument. The spectra were recorded using monochromatic Al Kα radiation ($h\nu$ = 1486.6 eV) as the excitation source. Photoelectrons were selected in energy with a hemispheric electron analyzer. The sample in the form of a pellet was mounted on the sample plate. It was degassed in the pretreatment chamber at 110 °C for 3 h in vacuo and transferred to the analyzing chamber. Low-resolution survey spectra were