



Effect of support's basic properties on hydrogen production in aqueous-phase reforming of glycerol and correlation between WGS and APR

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ARTICLE INFO

Article history:

Received 2 August 2011

Received in revised form 26 September 2011

Accepted 13 October 2011

Available online 29 November 2011

Keywords:

Hydrogen production

Aqueous phase reforming

Supports effect

Pt catalyst

Water–gas shift reaction

ABSTRACT

Pt loaded MgO, Al₂O₃, CeO₂, TiO₂ and SiO₂ catalysts were prepared by loading pre-synthesized Pt colloids on support and used for the aqueous-phase reforming (APR) of glycerol to investigate the influence of support properties on catalytic performance. The conversion of glycerol, rate of hydrogen production and composition of gaseous products were measured for the APR process of 5 wt.% glycerol. It was found that the overall catalytic activities for APR of glycerol decreased in the following order for Pt based catalysts: Pt/MgO > Pt/Al₂O₃ > Pt/CeO₂ > Pt/TiO₂ > Pt/SiO₂. The WGS reactions were also examined over these five catalysts. The relationship between WGS and APR was discussed and found that WGS played a key role in the process of APR, both are related to the surface properties: the basic sites are prefer for water–gas shift and further enhanced the APR process. Typical solid basic magnesium and alumina mixed oxides supporting Pt catalysts were also tested and exhibited the best APR activity.

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1. Introduction

Worldwide petroleum consumption has increased rapidly in the last decades, resulting in the problems of energy crisis and environmental pollution more and more serious. Transport sector accounts for some 60% of global oil consumption and produces one-fifth of global CO₂ emissions [1,2]. Thus, developing sustainable and clean sources as transportation fuels is of high interesting. As an alternative to petroleum-based transportation fuels, biodiesel has become one of the most common biofuels in the world [3]. Biodiesel can be generated from vegetable oils [4], and recently the production of biodiesel from microalgal becomes a newly emerging field [5]. The amount of glycerol (the main by-product of biodiesel production process) is increasing rapidly with the development of biodiesel industry. Its utilization is one of the main options to be considered to lower the overall cost of the biodiesel production [6–8]. It is worth to be considered to produce hydrogen from glycerol. In this sense, biodiesel would be fully integrated in the renewable fuel concept through its own use as biofuel, and that of the H₂ from the glycerol by-product, as clean fuel for fuel cell devices [9]. Several routes are available to produce hydrogen from glycerol, such as aqueous phase reforming (APR), steam reforming and autothermal reforming [10–13].

Among these processes, the APR process is thermodynamically and kinetically feasible in producing hydrogen with a low CO

concentration [14,15]. Moreover, the APR process is very high energy efficient as operating at relatively mild temperatures (150–250 °C) and elevated pressures (1.5–6.0 MPa) [16], comparing to the conventional reforming processes. So, many studies concerning on hydrogen production by APR, relating to the reaction conditions and new catalysts have been reported in the last few years [17–22]. The APR process involves the following two main reactions:

C–C cleavage leading to CO and H₂,



Water–gas shift (WGS),



The attractive catalysts for APR process should not only show high activity for the cleavage of C–C bond but also have high capability to promote the subsequent WGS reaction [23]. Furthermore, there is evidence that WGS reaction plays a key role in production hydrogen from APR [24]. Pt catalyst has been proved to be one of the most active and selective APR catalysts owing to its suitability to catalyze the WGS reaction and capability to break C–C bond [15]. Various supported Pt-based catalysts have been prepared and evaluated in the hydrogen production by APR of ethylene glycol and glycerol [25,26]. The nature of support has obvious effects on catalytic performance of APR of glycerol. However, the role played by support and the relation between WGS and APR on Pt catalysts are not very clear. Hence, it is important and necessary to study the correlation of WGS and APR process.

In this work, several catalysts with the same morphology of Pt colloids supported on different oxides (MgO, Al₂O₃, CeO₂, TiO₂ and

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SiO₂) were prepared and evaluated for hydrogen production by APR of glycerol. The effects of the support's basic properties on activity of Pt-based catalysts and relation between WGS and APR on Pt-based catalysts were studied. Besides, the possible mechanism of hydrogen production by APR of glycerol was also discussed.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of colloidal dispersions of PVP protected Pt clusters

The Pt colloids were prepared in a method with some modification [27]. In a typical synthesis, 0.5 g of polyvinylpyrrolidone (PVP $M_w = 40,000$) was added into 75 mL of ethylene glycol in a three-neck flask and treated ultrasonically for 30 min to dissolve PVP. To this solution, 2 mL of aqueous solution of hexachloroplatinic acid (H₂PtCl₆·6H₂O) containing a required amount of Pt was added dropwise under 400 r/min of stirring. Then, the pH was adjusted to ca. 10 by adding 0.1 M aqueous solution of sodium hydroxide. Finally, the system was heated to boiling temperature and kept refluxing for 3 h with a nitrogen flow passing through the reaction system. In this way, a dark-brown colloid was obtained.

2.1.2. Preparation of Pt/oxide catalysts

The catalysts of Pt@PVP supported on MgO, Al₂O₃, CeO₂, TiO₂ and SiO₂ were prepared. Commercial grade MgO, TiO₂ and SiO₂ were used as received, Al₂O₃ was obtained by calcining commercial pseudo boehmite alumina at 550 °C and CeO₂ was synthesized by hydrothermal method according to our previous work [28]. After refluxing the above solution (preparing for Pt colloid) for 3 h, calculated amount of support (MgO, Al₂O₃, CeO₂ or TiO₂) was added into the pre-synthesized Pt colloidal system and further refluxed for 2 h to load Pt@PVP clusters on the supports. Then, the system was cooled down to room temperature. The resultant dark-grey solid product was separated by centrifugation and washed with deionized water, absolute ethanol for several times and dried at 60 °C overnight in a vacuum oven. For preparation of Pt@PVP/SiO₂ catalyst, incipient wetness impregnation method was adopted. After the Pt@PVP clusters were separated from the colloid suspension and dispersed into deionized water for the removal of any salts produced in the reaction, it was precipitated by pouring large amount of acetone. After that, ethanol was added and a new colloidal Pt clusters were obtained. The Pt@PVP/SiO₂ catalyst was achieved after adding SiO₂ into the colloid suspension and dried in air for 10 h at room temperature, then further dried under vacuum overnight at 60 °C.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 Advance X-ray diffractometer (Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$), operated at 40 kV and 40 mA, respectively. Pt nanoparticles were collected for XRD characterization. Before pouring the Pt colloid suspension to 300 mL of acetone in a glass beaker, a piece of coverglass was put on the bottom of beaker. After 12 h, the solution was colorless and the dark-brown precipitates of Pt@PVP appeared on the coverglass. Thus, it is feasible and convenient for sample preparation for XRD analysis.

Fig. 1 shows the characterizations of Pt nanoparticles. As shown in Fig. 1A and B, Pt nanoparticles were dispersed in a very homogeneous fashion in the colloidal system with a narrow particle size distribution within the range from 0.5 to 4 nm with (an average diameter is ca. 2 nm). Fig. 1C displays that the synthesized Pt nanoparticles have an fcc structure, since the diffraction peaks of (1 1 1),

(2 0 0) and (2 2 0) of Pt (JCPDS 65-2868) can be observed in the pattern. Moreover, all peaks are very broad, indicating that Pt crystallites have smaller size which is consistent with the TEM data.

The textural properties of catalysts were measured at $-196 \text{ }^\circ\text{C}$ on a NOVA 4200e surface area & pore size analyzer. Before the measurements, the samples were degassed at 180 °C in vacuum for 6 h. TEM images were obtained with FEI Tecnai 20 S-TWIN operating at 200 kV. The compositions of the catalysts were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS Intrepid spectrometer. The basic properties of supports were probed by temperature programmed desorption of CO₂ (CO₂-TPD). Before CO₂ adsorption, the samples were treated at 500 °C in a helium stream for 1 h to remove moisture and impurities on the surface and then cool down to 30 °C. After that, a flow of pure CO₂ was introduced into the reactor and kept for 0.5 h. Finally, the system was purged with pure helium. The desorption analysis were detected in a Pfeiffer Omnistar 200 mass spectrometer. The temperature was increased linearly at a rate a 10 °C/min from 30 to 600 °C.

2.3. Activity test

The catalytic activity test was performed in a fixed bed reactor system (Scheme 1). 1.0 g of catalyst with 40–60 mesh size distribution was loaded in the stainless steel tubular reactor with an inner diameter of 6 mm. 5 wt.% of glycerol in water was introduced into the reactor at a flow rate of 3.6 mL/h by an HPLC pump. The reforming was conducted at 225 °C and 2.76 MPa. Gaseous products were analyzed by an on-line gas chromatogram equipped with a methanizer and FID and TCD detectors.

The selectivities to H₂ and alkane are defined as:

$$\text{H}_2 \text{ selectivity} = (\text{molecules of H}_2 \text{ produced/C atoms in gaseous phase}) \times (7/3) \times 100\%$$

$$\text{Alkane selectivity} = (\text{C atoms in gaseous alkanes/total C atoms in gaseous product}) \times 100\%$$

$$\text{C conversion to gas} = \text{C in the gaseous products/ C fed into reactor} \times 100\%$$

It should be indicated that H₂ and alkane selectivities do not add to 100%, because they are calculated based on the independent H and C balances, respectively.

Water-gas shift reaction was conducted in a fixed bed reactor at 225 °C and atmospheric pressure. 0.2 g of catalyst (sieved 40–60 mesh size) was used for testing. The mixture of CO/N₂ containing 5.2% of CO was supplied through mass-flow controller at 4.2 mL/min and the deionized water was fed into a vaporizer where it was vaporized and heated to 150 °C in a flow rate of 0.012 mL/min by an HPLC pump. The weight hourly space velocity of CO (WHSV (volume flow rate of CO)/(weight of catalyst)) of 65.5 mL g⁻¹cat h⁻¹, is equivalent to the half of total CO produced in the APR of glycerol if and only if all of the C atoms in glycerol are converted to CO. The WHSV of water is approximately same with that adopted in the APR of glycerol.

3. Results and discussion

In order to investigate the influence of support properties on the APR process and lessen the effect of Pt active site, Pt colloid was prepared first and characterized above (see Fig. 1).

The XRD patterns of different supports before and after loading of Pt nanoparticles are shown in Fig. 2. Commercial grade MgO is identified as a pure cubic periclase phase, while after refluxing of prepared Pt/MgO catalyst, all of the peaks become weak and broad, indicating that the crystallites of MgO became smaller. Besides, a

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