The effect of support and reaction conditions on aqueous phase reforming of polyol over supported Pt–Re bimetallic catalysts

Ho-Dong Kim [a,b], Hyun Ju Park [a], Tae-Wan Kim [a], Kwang-Eun Jeong [a], Ho-Jeong Chae [a], Soon-Yong Jeong [a], Chang-Ha Lee [b], Chul-Ung Kim [a,*]

[a] Petroleum Displacement Technology Research Center, Green Chemistry Research Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Sinseongno 19, Yuseong, Daejeon 305-600, Republic of Korea
[b] Department of Chemical and Biomolecular Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, Republic of Korea

ARTICLE INFO

ABSTRACT

The effect of support and reaction conditions on the aqueous phase reforming of polyol over supported Pt–Re bimetallic catalyst has been investigated. Catalysts were characterized by XRD, N_2 sorption analysis, XPS and H_2 chemisorption. It was found that the activity of supported 3 wt% Pt–Re catalysts was given as follows: Al_2O_3 < SiO_2 < activated carbon < CMK-3. CMK-3 supported catalyst showed good catalytic activity for APR reaction due to its easy accessibility of liquid reactant to metal catalytic active sites, and easy escape of product gas in addition to the alloy formation of Pt–Re, and a high metal dispersion. The effect of reaction conditions such as reaction temperature, weight hourly space velocity (WHSV), and kinds of polyol was also studied. The conversion of carbon to gas and hydrogen yield increased in proportion to the reaction temperature and corresponding system pressure, whereas low WHSV was favorable for hydrogen yield and conversion of carbon to gas without decreasing the selectivity of hydrogen and alkane. Moreover, the hydrogen production rate tended to increase with the increase of reaction temperature and WHSV, as well as with the decrease of the feed carbon number.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Concerns about the depletion of fossil fuel reserves and the pollution caused by continuously increasing energy demands make hydrogen as an attractive alternative energy source [1]. Currently, hydrogen can be generated from renewable biomass sources. Recently, an aqueous phase reforming (APR) process, one of the effective reactions for hydrolysis of biomass, has drawn the attention in specific application fields like production of hydrogen from oxygenated hydrocarbons (e.g. ethylene glycol, glycerol, sorbitol) [2]. Based on the previous result [3,4], an addition of Re to Pt increases the rate of C–C cleavage and water-gas shift reaction as well as alkane formation rates. Specifically, carbon supported Pt–Re bimetallic catalysts showed the highest catalytic activity in the carbon conversion of oxygenated hydrocarbons. However, the conventional carbon supports can limit hydrogen production because of their textual natures such as irregular pore arrangement, broad distribution of pore size, and high microporosity.

In supported metal catalyst, the support not only modifies the metal dispersion, but there are also metal–support interactions due to physical and chemical properties of both. The nature of the support would have remarkable influence on the activity as well as the gas distribution of the products. Carbonaceous supports such as activated carbon [4,5] and single wall carbon nanotube (SWCNT) [6] were specifically investigated for hydrogen production via APR process in the previous several works. However, despite promising hydrothermal stability with high surface area, platinum loaded activated carbon supports show limited activity and selectivity of hydrogen production because of the textual nature of carbon support (e.g. irregular pore arrangement, broad distribution of pore size, and high microporosity). The properties of activated carbon support lead to a significant pore resistance that prevents the transportation of liquid-phase reactants to catalytic active sites [7,8]. In addition, resultant gas products from catalytic active sites fill in micropores and block the catalytic reaction between reactant and catalyst particles in the micropores [8,9].

The pore resistance and blocking active site may significantly affect the activity and selectivity in liquid-phase and gas–liquid multi-phase reactions. In our previous results [10], we studied a series of the ordered mesoporous carbon (OMC), CMK-3, supported platinum catalysts with a different Pt loading amount. The Pt/CMK-3 catalysts that were investigated showed their catalytic activity and selectivity of the hydrogen production in aqueous phase reforming of 10 wt% of ethylene glycol along with a study of textual properties of the carbon support and amount of metal loading. The ordered mesoporous carbon (OMC) materials may provide

a good diffusion of reactants, and an easy contact between reactants and catalytic active sites to demonstrate the removal of gas products. As well, due to a uniform pore size distribution and ordered pore structure, the OMC materials could play a role as reference support materials for providing information for the behavior of a carbonaceous catalyst during the chemical reaction.

In this work, we have extended on the liquid phase reforming reaction of ethylene glycol to bimetallic catalyst and Pt–Re metals supported on CMK-3 support. Various polyols were also tested in order to understand the relationship between feed nature and catalyst structure. The interaction of bimetal active material and CMK-3 for catalytic activity and selectivity was discussed in depth. All the catalysts were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), N_2-sorption, temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), and CO chemisorption techniques.

2. Experimental

2.1. Preparation of CMK-3 supported Pt–Re catalyst

SBA-15 was prepared under a low HCl concentration condition according to the procedure reported by Choi et al. [11]. Ordered mesoporous carbon CMK-3 was prepared using Al-SBA-15 as a hard template and furfuryl alcohol as a carbon precursor. The synthesis for CMK-3 (2-D hexagonal structure composed of carbon nanorods) is used by a complete filling of mesopores in SBA-15 with a carbon precursor [12].

3 wt% Pt–Re (1:1 molar ratio) supported on the CMK-3 catalyst were prepared by a simple incipient wetness method with aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (Acros, 99.9%) and $HReO_4$ (Acros, 99.99%), respectively. After impregnation, the samples were dried at 100 °C overnight. For comparison, Pt–Re supported on commercial activated carbon (Aldrich), γ-alumina (γ-Al_2O_3, Strem Chemical), and silica (SiO_2, Aldrich) were also prepared by the incipient wetness method and denoted as Pt–Re/AC, Pt–Re/Al_2O_3, and Pt–Re/SiO_2, respectively.

2.2. Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiplex instrument using Cu Kα radiation (λ = 0.15406 nm), operated at 40 kV and 40 mA (1.6 kW). Transmission electron microscopy (TEM) images were taken from thin edges of particles supported on a porous carbon grid, using Philips Tecnai G220 equipment operated at 200 kV. Nitrogen adsorption isotherms were measured at −196 °C on a Micromeritics Tristar 3000 volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed at 300 °C in the degassing station. The Brunauer–Emmett–Teller (BET) equation was used to calculate the apparent surface area from adsorption data obtained at P/P_0 between 0.05 and 0.2. The total volume of micro- and mesopores was calculated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$, assuming that adsorption on the external surface was negligible compared to adsorption in pores. The pore size distributions (PSD) were calculated by analyzing the adsorption branch of the N_2 sorption isotherm using the Barret–Joyner–Halenda (BJH) method. CO chemisorption was carried out using a BELCAT-B (BEL Japan Inc.). Samples were first heated at 120 °C (rising temperature rate = 10 °C/min) for 15 min under He flow. After the gas was changed from He to O_2, that sample was maintained for 15 min at 120 °C and then heated again at 300 °C for 30 min under He flow. Complete reduction of PtO_x sites was then achieved by exposing the samples to 100% H_2 for 60 min at 300 °C. Subsequently, the samples were cooled down to 50 °C under He flow. Before the TPR

measurements, the samples were treated in a He stream at 110 °C for 30 min, cooled to 50 °C, and then reduced in a mixture gas stream of 10% H_2/N_2 at a flow rate of 30 mL/min and at a heating rate of 10 °C/min to 800 °C, using an instrument of Micromeritics AutoChem II 2920 analyzer. Hydrogen consumption during reduction was detected using a thermal conductivity detector (TCD). X-ray photoelectron spectroscopy (XPS) spectra were carried out using a Kratos AXIS NOVA analyzer equipped with a Mg source (1253.6 eV). The binding energy of samples was calibrated using the binding energy of the C 1s peak (284.8 eV) as a reference.

2.3. Catalytic test

Aqueous phase reforming of 10 wt% ethylene glycol was performed in a lab made fixed bed reactor system as shown in Fig. 1. The reactor was made of 3/8 in. inner diameter and 14 in. high stainless steel tube and up-flow liquid feeding system. The reaction temperature was controlled by a type-K thermocouple (Omega) and PID controller. A liquid feed of 10 wt% ethylene glycol in deionized water was fed into the catalytic reactor at 0.1 mL/min with a high-performance liquid chromatography (HPLC) pump. The catalyst was loaded in the middle of the stainless steel tube and quartz wool was used to fill the length of the catalyst. Before performing an aqueous phase reforming reaction, the catalyst goes through H_2 reduction step in 50 mL/min flow at 260 °C (heating rate: 1.0 °C/min) for 2 h [6]. After reduction, the temperature of the reactor was cooled down to room temperature for removing adsorbed H_2 gas using N_2 as a sweep gas. This reforming reaction was performed with 2.0 h^{-1} of weight hourly space velocity (WHSV) at 250 °C under 45 atm. The effluent gas products were measured by a gas chromatograph (6100GC, Young Lin Instrument Co.) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). H_2, CO, CO_2, and CH_4 content in the effluent gas were detected by TCD using packed Carboxen column (1/8 in. id × 4.57 m), and hydrocarbons were detected by the FID using a capillary GS-GASPRO column (1/8 in. id × 15 m).

The H_2 yield, H_2 and alkane selectivities, and carbon conversion to gas were calculated by the following equations [13]:

$$H_2 \text{ yield } (\%) = \frac{H_2 \text{ produced experimentally}}{H_2 \text{ calculates according to theoretical quantity}} \times 100$$

$$H_2 \text{ selectivity } (\%) = \frac{H_2 \text{ produced experimentally}}{C \text{ atoms produced in gas products}} \times n \times 100$$

n is reciprocal of H_2/CO_2 reforming ratio for polyol (ethylene glycol: 2/5, glycerol: 3/7, propylene glycol: 2/4, sorbitol: 6/13)

$$\text{Alkane selectivity } (\%) = \frac{C \text{ atoms in alkane produced}}{\text{total C atoms produced in gas products}} \times 100$$

$$\text{Carbon conversion } (\%) = \frac{C \text{ atoms in the gas-phase product}}{\text{total C atoms in the feedstock}} \times 100$$

3. Results and discussion

3.1. Properties of CMK-3 supported Pt–Re/CMK-3 catalysts

The physicochemical properties of a series of mesoporous carbon CMK-3 supported platinum, rhenium, and platinum–rhenium bimetallic catalysts were characterized by X-ray diffraction pattern (XRD), transmission electron microscopy (TEM), nitrogen physisorption, hydrogen temperature programming reduction (TPR), and CO chemisorption. Fig. 2 shows wide-angle powder XRD patterns of the CMK-3 support and CMK-3 supported Pt, Re, and Pt–Re catalysts. The XRD patterns of the single metallic 3 wt% Pt/CMK-3 catalyst do not clearly exhibit distinct X-ray diffraction peaks for platinum metal. However, the XRD patterns of the