H₂ production from water-gas shift reaction over supported platinum catalysts using simulated waste-derived syngas

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1. Introduction

Although fuel cell is an attractive technology to produce clean energy, it requires pure H₂ as a fuel for its operation. Currently, the requirement is being fulfilled by the fuel processors, which generate hydrogen from hydrocarbons through reforming reactions [1–3]. However, the CO level present in the reformed gas (ca.10%) is sufficient enough to poison the Pt electrode in fuel cell [4]. Hence, the CO level should be below 10 ppm before entering the fuel cell system. This triggered an immense interest towards water-gas shift (WGS) reaction (CO (g) + H₂O (g) → CO₂ (g) + H₂ (g), ΔH=−41.2 KJ/mol). Due to the exothermic and reversible nature of WGS reaction, higher CO conversion is favorable at lower temperatures. But at lower temperatures the reactant gases are not active enough to reach the chemical equilibrium. In another word, the reaction is kinetically limited. Hence, in general, WGS reaction is carried out at two different temperature ranges; high temperature shift (HTS, 350–500 °C) using Fe₂O₃–Cr₂O₃ catalyst and low temperature shift (LTS, 190–250 °C) using CuO–ZnO–Al₂O₃ catalyst [5].

Recently, waste to energy has attracted substantial attention due to the depletion of fossil fuels and environmental issues [6, 7]. In general, based on the organic nature, the waste consists of wide range of gases including CO₂, CH₄, N₂ and H₂ etc. Therefore, production of hydrogen from the waste through catalytic reactions such as steam reforming of methane (SRM) and/or WGS requires more active and robust catalysts to withstand severe conditions. In the last few years, novel catalyst compositions have been intensively investigated to overcome the limits of the available catalysts. Together with gold [8], platinum supported on ceria [9–11], titania [12], zirconia [13] or mixed oxide of ceria-zirconia [14], have been intensively studied. Especially, supported Pt catalysts have received much interest during last decades due to their outstanding catalytic performance for WGS reaction.

To the best of our knowledge, there are a few reports available on the WGS reaction study using simulated waste-derived synthesis gas. Compared to a typical synthesis gas, the waste-derived synthesis gas consists of CO, CH₄, CO₂, and H₂. The presence of higher concentration of CO together with other gases makes the system more severe. Therefore, it is important to develop a stable and active WGS catalyst. Hence, the objective of the present study is to prepare highly active supported Pt catalysts and to screen the support to get the maximum CO conversion with 100% selectivity to CO₂ in WGS of simulated waste-derived synthesis gas under severe conditions. The effect of support on the catalyst properties have been characterized and related to the activity results in WGS.

2. Experimental

2.1. Catalyst preparation

Supports employed in this study were MgO–Al₂O₃ (MgO = 30 wt%, SASOL), Al₂O₃ (99%, SASOL). CeO₂ and ZrO₂ were prepared by a precipitation method using Ce(NO₃)₃·6H₂O (99%, Aldrich) and zirconyl nitrate solution (20 wt% ZrO₂ basis, MEL Chemicals), respectively. The prepared supports were calcined at 500 °C for 6 h. MgO was prepared by pre-calcination of Mg(NO₃)₂·6H₂O (99%, Aldrich) at 500 °C for 6 h. Supported Pt catalysts (1.0 wt%) were prepared by an incipient wetness impregnation method with Pt(NH₃)₄(NO₃)₂ (99%, Aldrich). The prepared catalysts were calcined at 500 °C for 6 h. A commercial catalyst (Fe–Cr) for HTS was also tested as a reference catalyst.

2.2. Characterization

Temperature programmed reduction (TPR) experiments were carried out in a BEL–CAT (BEL JAPAN INC.). Typically, 0.1 g of sample was loaded into a quartz reactor. TPR was performed using 10% H₂ in Ar with a heating rate of 10 °C/min, from 20 to 500 °C. The sensitivity of the detector was calibrated by reducing the known weight of NiO.
2.3. Catalytic Reaction

Activity tests were carried out from 240 to 360 °C under atmospheric pressure in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm. The catalyst charge was 45 mg. T-union was employed at the exit of quartz reactor to install a thermocouple. A thermocouple was inserted into the catalyst bed to measure the reaction temperature. Unless otherwise mentioned, prior to each catalytic measurement, the catalyst was reduced in 5% H\textsubscript{2}/N\textsubscript{2} from room temperature to 400 °C at a heating rate of 3.1 °C/min and then the temperature was maintained for 1 h. Afterwards, the temperature was decreased to 240 °C. The simulated reformed gas consisted of 38.0 vol% CO, 21.3 vol% CO\textsubscript{2}, 2.3 vol% CH\textsubscript{4}, 29.3 vol% H\textsubscript{2}, and 9.1 vol% N\textsubscript{2}, which represents a typical syngas from waste gasifier that might enter the WGS reactor in a waste gasification system. The feed H\textsubscript{2}O/(CH\textsubscript{4} + CO + CO\textsubscript{2}) ratio was intentionally fixed at 2.0 to avoid coke formation [15, 16]. A gas hourly space velocity (GHSV) of 40,206 h\textsuperscript{-1} was used to screen the catalysts in this study. Water was fed using a syringe pump and was vaporized at 180 °C upstream of the reactor. The product gas was chilled, passed through a trap to condense the residual water, and then analyzed on-line using an Agilent micro-gas chromatograph (Agilent 3000).

3. Results and Discussion

3.1. TPR study

Fig. 1 TPR patterns of supported Pt catalysts.

TPR patterns of supported Pt catalysts are depicted in Fig. 1. The TPR patterns of supported Pt catalysts are characterized by a lower temperature peak and two medium temperature peaks located at ca. 200 °C and ca. 400 °C, respectively. It is known that lower temperature peaks are assigned to the reduction of the surface PtO\textsubscript{x} species [24]. Pt/CeO\textsubscript{2} shows three reduction peaks around 70, 160 and 450 °C. The first peak, appearing at 70 °C, is attributed to the reduction of surface PtO\textsubscript{x} species. The peak, appearing at 160 °C, is assigned to the reduction of PtO\textsubscript{x} species, which have interaction with CeO\textsubscript{2}. The third peak, appearing at 450 °C, corresponds to the reduction of bulk CeO\textsubscript{2} [17]. According to results in the literature, Pt/CeO\textsubscript{2} has a reduction peak around 100 ~ 250 °C due to the reduction of surface PtO\textsubscript{x} species [18]. Thus, it should be noted that the Pt/CeO\textsubscript{2} catalyst prepared by a precipitation method in this study has easier reducibility of PtO\textsubscript{x} species. As a consequence, it is expected that this catalyst should have higher CO conversion than others for WGS. For Pt/Al\textsubscript{2}O\textsubscript{3} and Pt/ZrO\textsubscript{2} catalysts, the first reduction peak appears at 165 and 180 °C, respectively and the second reduction peak is present at 344 and 350 °C, respectively. The first peak is due to the reduction of surface PtO\textsubscript{x} species. The second peak is possibly assigned to the reduction of PtO\textsubscript{x} species, which have interaction with the support. In the case of Pt/MgO, the first peak appears at 260 °C and the second peak at 390 °C. Pt/MgO-Al\textsubscript{2}O\textsubscript{3} shows the first peak at 220 °C and the second peak at 350 °C.

3.2. Reaction results

To develop a catalyst for WGS, we have tested supported Pt catalysts at the GHSV of 40,206 h\textsuperscript{-1}, which is 15 times higher than that of the typical experimental condition of WGS. Fig. 2 shows the CO conversion with reaction temperature over supported Pt catalysts. It is obvious that Pt/CeO\textsubscript{2} exhibited the highest CO conversion within the temperature range from 240 to 360 °C. On the contrary, the commercial catalyst showed the lowest CO conversion among the catalysts tested in this study. This is mainly due to the fact that the commercial catalyst is optimized at the GHSV of 3,000 h\textsuperscript{-1} for WGS. Thus, the commercial catalyst is not suitable for WGS in simulated waste-derived synthesis gas. At the reaction temperature of 240 °C, only Pt/CeO\textsubscript{2} exhibited significant CO conversion (23.5%). At 280 °C, Pt/CeO\textsubscript{2} exhibited 58.5% CO conversion, while the others showed less than 20%. At the reaction temperature range