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Abstract
An emerging application for the WGS reaction is on-board purification and production of $H_2$ for fuel cell powered vehicles. Existing commercial LTS catalyst are unsuitable for transportation applications because of their large volume and size, and the deactivation of the copper-based catalyst under the severe conditions encountered in an automotive system. To develop a high performance WGS catalyst, we have studied the WGS reaction over transition metal carbides and Pt supported cerium oxide catalysts. Molybdenum carbide ($Mo_2C$) was demonstrated to be highly active for the WGS of a synthetic steam reformer exhaust steam. This catalyst was more active than a commercial LTS catalyst. It was found that Pt supported catalyst was more active than the LTS catalyst at a high temperature more than 250°C.

Introduction
The WGS reaction is used industrially to produce $H_2$ for petroleum refining, chemicals production, and in processes that require synthesis gas with high $H_2/CO$ ratios. Since the reaction is exothermic, the equilibrium CO conversion is highest at low temperatures. Consequently a two-stage process in often used [1–3]. In industrial reactors, $Fe_3O_4-Cr_2O_3$ catalyst was used for the high temperature shift (HTS) and $Cu-Zn/Al_2O_3$ catalyst was used for the low temperature shift (LTS) reaction. The exiting commercial LTS catalyst are unsuitable for transportation applications because of their large size and weight, and the deactivation tendency of the copper-based catalysts under the severe conditions encountered in an automotive system. These copper-based catalysts degrade by a thermal cycling mechanisms such as hydrothermal sintering during operation and oxidation when exposed to air. Copper-based catalysts
also cannot be used at temperatures above about 250°C, which further limits their utility. The goal of the research was to develop a high performance WGS catalysts for integration with PEM fuel cells. In this work, we have studied the WGS reaction over the transition metal carbides and the platinum supported cerium oxide catalysts. The performance of the prepared catalysts were compared with the commercial LTS catalyst.

**Experimental**

1. Preparation of Catalyst

Molybdenum carbide catalysts were synthesized by the carburization of molybdenum oxide [1-3]. A standard molybdenum oxide sample was obtained from Aldrich Chemicals. Carburization of the oxide was done in a temperature-programmed method using an equimolar mixture of CH₄ and H₂ flowing at 400 cm³ min⁻¹. Approximately 5g of the oxide was loaded into the quartz straight tube reactor. The temperature program for carburization consisted of heating the oxide at a rate of 600°C h⁻¹ to 300°C, then at 60°C h⁻¹ to the final carburization temperature. Following a 2 h soak period at the final temperature, the product was quenched to room temperature and passivated for 4 h in a mixture of 1% O₂ in He following at 30 cm³ min⁻¹ [1].

Platinum supported cerium oxide catalysts were prepared by the impregnation method. The ceria support (cerium oxide 99.9%, Aldrich Chemicals) was calcined in air for 2-4 h at 600°C or at 900°C. The ceria was impregnated with a solution of chloroplatinic acid (H₂PtCl₆), dried for 24 h at 120°C and then calcined for 2 h at 550°C [2].

2. Characterization of catalyst

BET surface area and pore size distributions of catalysts were measured by N₂ physisorption. The active metal surface area of the prepared catalysts were measured by CO chemisorption using a sorption analyzer [Quantachrome Autosorb-1C]. The carburization temperature of molybdenum oxide was determined via thermal gravimetric analysis (TGA).

3. Low temperature shift reaction

The catalytic activity WGS reaction were measured at atmospheric pressure and temperatures between 200 and 300°C in a fixed bed reaction system. The Cu-Zn/Al₂O₃ catalyst was reduced at 200°C in a mixture of 2% H₂ in N₂ for 4.5 h. The MoₓC catalyst was reduced at 400°C in H₂ for 4.5 h. The Pt/ceria catalyst was first reduced in 40ml/min of 5% H₂ in Ar at 400°C for 1 h, and then oxidized in 50ml/min of 2% O₂ in Ar at 500°C for 20 min. The reductive
pretreatment consisted of exposure to 40 ml/min of 5% H₂ in Ar at 200°C for 30 min. The reactant gas contained 62.5% H₂ (99.99% pure), 31.8% deionized H₂O and 5.7% CO (99.99% pure). The gas effluent was analyzed by on-line gas chromatography (HP–5890 Series II) equipped with TCD which use a carbosphere column (10" × 1/8" SS, 80/100 meshes).

Results and discussion
The characteristics of the used catalysts are summarized in Table 1. The different calcination temperatures of ceria sample resulted in a high surface area at 600°C and low surface area at 900°C. It was found that the Pt/ceria-A catalyst displayed better activity than the Pt/ceria-B catalyst in the LTS reaction.

It was observed that the activity of the carbide systems greatly depending on the carburization temperature (see Fig. 1). As the temperature reaches 580°C, Mo₂C converts to Mo₂C. The formation of carbide phase begins at 615°C and completes at 650°C. For temperatures in excess of 650°C, excess of carbon deposits on the carbide systems, thereby giving low activity. Comparison of the prepared catalysts with commercial Cu–Zn/Al₂O₃ catalyst is shown in Figure 2. It was found that transition metal carbide showed higher activity than the commercial LTS catalyst at a temperature range of 200°C to 300°C and the catalytic activity increased progressively with increasing reaction temperature. Maximum activity of Mo₂C and Pt/ceria-A were observed at 280–300°C with a total CO conversion more than 85%. The Cu–Zn/Al₂O₃ catalyst displayed the highest activity in the temperature range of 270–280°C with a CO conversion nearly 70%.

The results demonstrate that transition metal carbides are attractive candidates for development as WGS catalysts for automotive applications. The development of these materials could lead to substantial reductions in the size, weight and cost of WGS reactors.

Reference


Table 1. Characteristics of the prepared catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pretreatment temperature (°C)</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cc/g)</th>
<th>Active metal surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Zn/Al₂O₃</td>
<td>-</td>
<td>60</td>
<td>0.08025</td>
<td>1.035×10⁻¹</td>
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<tr>
<td>Mo₂C</td>
<td>-</td>
<td>640</td>
<td>0.03594</td>
<td>1.285×10⁻¹</td>
</tr>
<tr>
<td>1%Pt/ceria-A</td>
<td>600</td>
<td>550</td>
<td>131</td>
<td>0.05383</td>
</tr>
<tr>
<td>1%Pt/ceria-B</td>
<td>900</td>
<td>550</td>
<td>58</td>
<td>0.05159</td>
</tr>
</tbody>
</table>

Fig. 1 Catalytic activity as a function of the carburization temperature of the molybdenum carbides prepared. (with the commercial Cu–Zn/Al₂O₃ catalyst for the LTS reaction; Space Velocity=10,000h⁻¹, Feed molar ratio=H₂(62.5%), H₂O(31.8%), CO(5.7%).

Fig. 2 Comparison of the catalytic activity of the various prepared catalysts with commercial Cu–Zn/Al₂O₃ Reaction temperature 300°C, Space Velocity=10,000h⁻¹, Feed molar ratio=H₂ (62.5%), H₂O (31.8%), CO (5.7%).