Water-Gas Shift Reaction over Cu-Based Mixed Oxide Catalysts

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ABSTRACT

A series of Cu-based mixed oxides was investigated for the development of active Cu catalysts for the water gas shift reaction (WGSR). Tri-metallic catalysts active for WGSR were obtained after high temperature calcination at 900 ºC and subsequent reduction. The results were compared with commercial Cu/ZnO/Al₂O₃ catalyst and prepared Ru/TiO₂/Al₂O₃ catalyst. The prepared catalysts were characterized by temperature programmed reduction, XRD, and sorption analyzer. Near equilibrium conversion of CO was achieved by the prepared catalysts around 250 ºC. The Ru-based catalyst showed maximum CO conversion around 300 ºC with some methanation activity. Whereas Cu-based catalysts produced negligible amount of methane in the product stream.

1. INTRODUCTION

Water-gas shift is an old and established technology that may find new applications in fuel cell and coal processing systems. Water gas shift is a reversible, exothermic reaction that is thermodynamically unfavorable at elevated temperatures. In order to achieve high conversions, the reaction is typically run in multiple adiabatic stages, with lower inlet temperatures in the later stages. Additionally excess steam is used to drive the reaction thermodynamically. Carbon monoxide reacts with water to yield carbon dioxide and water

\[ \text{CO} (g) + \text{H}_2\text{O} (g) = \text{CO}_2 (g) + \text{H}_2 (g) \] (1)

The stoichiometric equation is well known as water gas shift reaction (WGSR). A higher content of carbon monoxide is expected in the reformed fuel from hydrocarbons. For the application of polymer electrolyte fuel cell (PEFC) for electricity generation for vehicles and portable applications, CO must be reduced to less than 10 to 20 ppm before feeding a gas mixture of the reformates to the Pt electrode of PEFC [1,2]. Water gas shift reaction is a preferable reaction for CO removal with a moderate exothermic reaction ($\Delta H = -41.1 \text{ kJ/mol}$), and thus appropriate for controlling temperature. The equilibrium conversion of carbon monoxide is dependent largely on the reaction temperature: since WGSR is an exothermic reaction, lower temperature is favored for higher CO removal. On the other hand, from the viewpoint of kinetics, the reactant gases are not active enough to reach the chemical equilibrium at low temperatures. Therefore, there exists an optimum temperature for WGSR; in general, the optimum temperature is between 200 and 280 ºC. In addition, CO₂ in the reformed gases suppresses WGSR according to Le Chatelier’s principle. The WGSR is very desirable for fuel processing as it
provides two benefits. In addition to effectively reducing the CO concentration, a mole of H₂ is produced for every mole of CO that is converted in the WGS reaction (equation 1). The WGS reaction increases the fuel cell efficiency by generating H₂ from water. From a thermodynamic perspective, the efficiency of the WGSR is maximized at low temperature, high water and a low hydrogen concentration. However, under some conditions the catalysts available today are kinetically limited at low temperatures needed for high CO conversion while striving to minimize reactor volumes.

The Cu/ZnO/Al₂O₃ catalyst is well known as a CO shift catalyst and is widely used in industrial field [3-6]. In this work some Cu-based spinel-type oxide catalysts for WGSR activity in comparison with commercial Cu/ZnO/Al₂O₃ and prepared Ru/TiO₂/Al₂O₃ are reported.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Copper iron chromium and copper iron manganese oxide catalysts were prepared by mixing the nitrates of the respective salts of the metal required. Ruthenium was impregnated on a titanium modified alumina support. The detailed procedures of the catalysts preparation are given in the following sub sections.

2.1.1. Preparation of CuFeCr Catalyst Following amounts of nitrates of the respective metals were dissolved in distilled water to make 300 ml solution:

i) Cu(NO₃)₂·3H₂O  12.142 g  
ii) Fe(NO₃)₃·9H₂O  30.600 g  
iii) Cr(NO₃)₃·9H₂O  10.22 g

The solution was stirred at 60 °C for 2 h and then 46.22 g of citric acid monohydrate was added to the solution further mixing for 1 h was carried out at 60 °C and then the temperature was raised to 90 °C. The solution remained on hot plate until complete removal of water. After dryness the solid was heated further at 140 °C for four hours. Finally the solid was calcined up to 900 °C for 10 h at a heating rate of 3 °C per minute.

2.1.2. Preparation of CuFeMn Catalyst Following amounts of nitrates of the respective metals were dissolved in distilled water to make 300 ml solution:

i) Cu(NO₃)₂·3H₂O  12.142 g  
ii) Fe(NO₃)₃·9H₂O  30.60 g  
iii) Mn(NO₃)₂·6H₂O  7.32 g  
iv) Citric acid (anhydrous)  42.27 g

All solids were added to distilled water to make 300 ml solution. The solution was stirred at 60 °C for one hour and then the temperature was raised to 90 °C until dryness. Finally, the temperature was raised to 140 °C to decompose citrates. The sample was calcined following the same procedure mentioned above.

2.1.3. Preparation of Ru/TiO₂/Al₂O₃ Catalyst First TiO₂/Al₂O₃ support was prepared as follows:
Commercial alumina supplied by Sumitomo Chemicals (AKP-GO15) with BET surface area of 148 m$^2$/g and average particle size of 2.2 µm was used to support Ti. 7.3 grams of alumina was added to a solution of containing 1.877 g of Ti(IV) isopropoxide in 70 ml of isopropanol. The addition was conducted in Ar glove box. The mixture was stirred in the glove box for 30 min. After removing the sample from glove box 0.5 g of water was added to the mixture to hydrolyze the isopropoxide. Isopropanol was evaporated at 60 °C on a hot plate with constant stirring. The sample was dried at 120 °C over night in oven. The support was calcined at 500 °C for 1 h in muffle furnace in air.

2% Ru was loaded on this support by impregnation method. 2.709 g of 25% Ru(NO$_3$)$_3$ solution corresponding to 0.1 g Ru and 4.9 g of the Ti modified alumina were mixed with appropriate amount of distilled water. The excess of water was evaporated over a steam bath set at 80 °C. The partially dried sample was placed in an oven for complete dryness at 120 °C overnight. Finally, the catalyst was calcined at 400 °C for 1 h in air.

### 2.1. Catalyst Characterization

Surface area of the catalysts was measured by the BET method with N$_2$ adsorption using a Quantachrom NOVA1200. Temperature-programmed reduction (TPR) was carried out by supplying 10% H$_2$ in Ar to 150 mg of catalyst sample in a quartz tube flow reactor without oxidation treatment prior to measurements. The flow rate of the reducing gas was set at 20 ml/min. The temperature of the reactor was raised from room temperature to 1030 °C at the rate of 10 °C/min. The rate of hydrogen consumption was determined by using a thermal conductivity detector and recorded on an on-line personal computer.

### 2.2. Catalyst Evaluation

All catalysts were pretreated in 10% H$_2$ in N$_2$ stream at 250 °C for 1 h at a heating rate of 1 °C/min except for Ru-based catalyst that was reduced at 400°C for 1h prior to the activity evaluation. Initially, the catalyst was treated under N$_2$ flow up to 120 °C and then hydrogen was introduced. The catalyst activity was measured using a conventional flow reactor at atmospheric pressure in the temperature range from 120 to 300 °C and at a constant space velocity of 6400/h, using 1.5 ml of catalyst. The temperature range for Ru-based catalyst was from 150 to 450 °C. A model gas after hydrocarbon steam reforming containing H$_2$, CO, H$_2$O, CO$_2$ and N$_2$ was supplied to the catalyst bed through mass flow controllers (STEC, SEC–400MK3). The standard composition of the reaction gas was 37.5% H$_2$, 5.0% CO, 25.0% H$_2$O, 12.5% CO$_2$ and N$_2$ (balance). The gas composition before and after the reaction was measured by gas chromatograph with a thermal conductivity detector (Shimadzu, GC–8A) using Ar (60 ml/min) gas as a carrier. A molecular sieve 13X column was used for the separation of H$_2$, N$_2$ and CO; and a Porapak Q column for CO$_2$. Since Ru based catalyst was expected to produce CH$_4$ gas, therefore another GC with similar configuration as mentioned above with 13X column and He gas as a carrier (40 ml/min) was used.

Conversions of CO and H$_2$ as well as CH$_4$ yield were defined as follows:

\[
\begin{align*}
\text{CO conversion (％)} & = \frac{F_{\text{CO}}^{\text{in}} - F_{\text{CO}}^{\text{out}}}{F_{\text{CO}}^{\text{in}}} \times 100 \\
\text{H}_2 \text{ conversion (％)} & = \frac{F_{\text{H}_2}^{\text{in}} - F_{\text{H}_2}^{\text{out}}}{F_{\text{H}_2}^{\text{in}}} \times 100 \\
\text{CH}_4 \text{ yield (％)} & = \frac{F_{\text{CH}_4}^{\text{out}}}{F_{\text{CO}}^{\text{in}} + F_{\text{CO}_2}^{\text{in}}} \times 100
\end{align*}
\]
where $F_{i}^{in} - F_{i}^{out}$ denote the flow rates of species $i$ at the inlet and outlet of the reactor, respectively.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical properties

Table 1 shows the BET surface area of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Stoichiometric composition</th>
<th>BET surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFeCr</td>
<td>Cu:Fe:Cr 2:3:1</td>
<td>0.83</td>
</tr>
<tr>
<td>CuFeMn</td>
<td>Cu:Fe:Mn 2:3:1</td>
<td>0.83</td>
</tr>
<tr>
<td>Ru/TiO$_2$/Al$_2$O$_3$</td>
<td>Ru 2 wt%</td>
<td>152</td>
</tr>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$</td>
<td>--</td>
<td>70</td>
</tr>
</tbody>
</table>

As it can be noted from the results of BET surface area measurements that the Cu–based spinel type oxide catalysts have very low surface area as compared with that of the commercial and Ru based alumina catalysts. Despite very low surface area spinel type catalysts showed activity comparable to that of the commercial catalyst.

Figure 1 shows the results of the TPR measurements. The chromium containing catalyst showed relative broader reduction peak with a maximum temperature at 240 °C and a broad peak with a maxima at 740 °C. The lower temperature peak is related to the reduction of mixed CuO and Fe$_2$O$_3$ whereas higher temperature reduction could be attributed to the presence of Cr in the catalyst. Similarly a sharp TPR peak was observed in manganese containing catalyst with strong peak at 224 °C and a small peak at 274 °C. Again the major peak is due the reduction of CuO and Fe$_2$O$_3$ mixed phase and small peak is due to the reduction of Mn$_2$O$_3$ to MnO. Since the composition of the copper based commercial catalyst was not known therefore it is difficult to analyze the TPR profile. However the sharp peak at 165 °C could be attributed to the reduction of CuO present in the catalyst. The Ru impregnated titanium modified alumina catalyst should a peak at 130 °C with a shoulder around 170 °C. The profile is 16 times enlarged to show a clear comparison the peak shape and position. The Ru is well known as a methanation catalyst [7] and having very high hydrogenation activity reduced at a lower temperature in comparison to other catalysts studied.

3.2. Evaluation of catalytic activity

The activities of the prepared catalysts are compared with a reference commercial catalyst based on Cu and Zn oxides with Al$_2$O$_3$ for water gas shift reaction. At 200 °C or higher temperatures, the conversion of CO over Cu based spinel type catalysts were comparable and reached the thermodynamic equilibrium. CuFeMn catalyst showed activation at slightly higher temperature as compared with CuFeCr and commercial catalysts. However, Ru–based catalyst showed highest CO conversion at 300 °C but CH$_4$ yield was substantially high at this temperature. The results are shown in Figure 2. The equilibrium conversion shown in the figure is only valid for the copper based WGSR catalyst. Since Ru based catalyst produced a substantial amount of methane in the product gas stream, the equilibrium calculation are not performed also the CO conversion was approaching near 100% around 300 °C.

Maximum CO conversion achieved by the various catalysts is in the inverse order of the TPR peak temperature position. The catalyst reduced at lowest temperature gave highest CO conversion at certain
temperature. Similar trend was observed in metal supported hydrotreating catalysts studied in our laboratory [8-9].

4. CONCLUSIONS

Investigations of Cu-based mixed oxides for WGSR showed that the spinel-type oxides have comparable CO conversion than well-known Cu/ZnO/Al2O3. Precious metal based WGSR catalyst showed higher CO conversion with substantially higher yield of methane. The Ru–based catalyst showed highest CO conversion around 300 °C achieving over 99% CO conversion. A trend was found between the TPR peak maxima of the major peak and the maximum CO conversion achieved by respective catalysts.

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REFERENCES

Figure 1. TPR profiles of WGSR catalysts.

Figure 2. Temperature dependence of WGSR activity over prepared and commercial catalysts. Reaction conditions: H₂, 37.5%; CO, 5%; H₂O, 25.0%; CO₂, 12.5%; space velocity, 6400 h⁻¹.