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**Catalytic hydrogen production from dimethyl ether over CuFe_2O_4
spinel-based composites: hydrogen reduction and metal dopant effects**

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Abstract

Investigation of hydrogen reduction pretreatment and metal doping to Cu–Fe spinel catalyst coupled with γ -alumina was performed in dimethyl ether steam reforming for hydrogen production. The high activity and stability of the catalysts were achieved when the catalysts were reduced at or below 350 °C due to the stability of obtained Cu and Fe₃O₄ phases. Reduction at higher temperatures of 450 and 600 °C would bring about the decrease in activity and stability because the resultant Fe₃O₄ was further reduced to metallic Fe, and sintering of metallic Cu and Fe proceeded. Dopants (Mn, Cr, Co, and Al) could affect the reforming performance in terms of both activity and selectivity to products.

Keywords: Dimethyl ether; steam reforming; hydrogen reduction; copper spinel; doping

1. Introduction

Hydrogen has recently been recognized as an environmentally clean fuel for future energy systems. Utilization of hydrogen has been under investigation in the field of new energy, especially fuel cells [1]. Fuel cells are electrochemical devices that produce electricity directly from chemical energy by consuming fuel (generally hydrogen) and oxygen [2]. By this technique, hydrogen-fuelled fuel cells provide a high energetic efficiency without pollutant emission; only byproducts are heat and water. Fuel cells have been developed for a variety of applications in transportation and stationary uses. The primary routes of hydrogen production include steam reforming (SR), partial oxidation (PO), and autothermal reforming (ATR) that provide different features and merits [3].

Dimethyl ether (DME – CH₃OCH₃) is an oxyhydrocarbon with no C–C bonds and has a high hydrogen-to-carbon ratio. It has been used as a clean-burning fuel alternative to

liquefied petroleum gas (LPG) and diesel. The well-developed infrastructure of LPG can readily be adapted for DME because of their similar physical properties. DME and methanol (MeOH) are suitable for on-board reforming because they can catalytically be reformed at low temperatures of 200–350 °C for MeOH [4–9] and 200–400 °C for DME [10–22]. DME is less toxic and therefore is preferable to MeOH. DME SR proceeds via two reactions in sequence: hydrolysis of DME to MeOH and MeOH SR to hydrogen and carbon dioxide. Hydrolysis of DME takes place over acid catalysts, e.g. zeolite and alumina, while MeOH SR proceeds over Cu-, Pt-, or Pd-based catalysts. As a consequence, mixture of the acid catalysts and the metal-based catalysts is generally needed for DME SR. The Cu-based is promising in terms of cost effectiveness and activity. We have proposed the Cu-based spinel oxide catalysts mixed with γ -Al₂O₃ for hydrogen production via DME SR [12,19–22]. The Cu spinel exhibited excellent performance as compared with commercially available copper-based catalysts, including Cu/ZnO/Al₂O₃ and CuFe₂O₄ [12,15]. Various acid catalysts, such as H-mordenite, H-ZSM5, Y zeolite, and alumina, were proposed as DME hydrolysis catalysts [16, 17, 20]. Alumina is promising in terms of product quality and stability, especially in the reaction temperature range of 300 to 350 °C [20].

This work is a continuation of our recent researches that investigated the influences of type and preparation process of Cu spinels and solid-acid catalysts on DME SR activity [12, 15, 19, 20]. It is known that the catalyst preparation process can affect the catalytic performance. The catalytic activity of CuFe₂O₄ strongly depends on calcination temperatures that affect crystal properties and reducibility of the catalyst [19]. There is, however, no clear evidence for reduction pretreatment effect on catalysts activity and

stability so far, although the reforming catalysts are operated under reducing atmospheres in the practical applications. Addition (doping) of metal components is also known to enhance or inhibit the performance of catalysts in various reaction systems [23-24]. In the present work, the effects of reduction pretreatment of and metal dopants to CuFe_2O_4 spinel catalyst were investigated and discussed in DME SR in terms of product quality and catalyst stability. This effort was made to promote the catalyst performance by controlling the catalyst preparation process. The clear understanding of reduction effect was also obtained.

2. Experimental

2.1 Catalyst preparation and characterization

Cu-based spinels were prepared by a citric acid complex method [19, 20]. An aqueous solution of corresponding nitrates was stirred at 60 °C for 2 h, followed by addition of citric acid. The solution was continued to be kept at 60 °C for 1 h to make it homogeneous. The solution was then heated up to 90 °C to evaporate water. The precipitate obtained was heated up to 140–200 °C until oxide powders were attained. Next, the powders were calcined in air at 900 °C for 10 h. Gamma-alumina (ALO8) provided by the Catalyst Society of Japan was calcined in air at 700 °C for 0.5 h prior to mixing with Cu-based spinel. The Cu spinel was mechanically mixed with the alumina at a fixed weight ratio of 2:1. The mixture was then pressed, crushed, and sieved to particle sizes of 0.85 to 1.7 mm.

Temperature-programmed reduction (TPR) measurements were carried out in a quartz tube reactor, and the amount of consumed hydrogen was measured by a thermal conductivity detector (TCD). A 25-mg catalyst sample was reduced in a gaseous mixture of

5% H₂–95% Ar at a flow rate of 30 ml min⁻¹ (at 25 °C; 1 atm) in a heating process at a rate of 10 °C min⁻¹. The crystalline phase of the catalysts was determined by X-ray diffraction (XRD) using Rigaku RINT1400 with Cu K_α radiation source. The crystallite size of copper ferrite and metallic copper was calculated by XRD–line broadening using Scherrer equation. The specific surface area of the catalysts was determined by the conventional BET method with N₂ adsorption using a BEL Japan Bellsorp–miniII instrument.

2.2 Catalytic performance tests

Catalytic activity of the catalysts in DME SR was evaluated in a conventional flow reactor under atmospheric pressure. Prior to the evaluation of the catalytic activity, the catalyst was reduced by hydrogen at a designed reduction temperature for 3 h in 10% H₂/N₂. A mixture of DME and steam was supplied to a pre-heater at temperature of ca. 150 °C, and then to the catalyst bed at a designed reaction temperature. Compositions of influent and effluent gas were analyzed by online gas chromatographs equipped with a flame ionization detector (Shimadzu, GC-9A) and a thermal conductivity detector (VARIAN, CP-4900). The steam in the feed and reformat was trapped by a condenser at ca. 3 °C before the gas analysis. A Poraplot U column was used for separation of DME, MeOH, and CO₂, and a molecular sieve 5A column for separation of H₂, O₂, N₂, CH₄, and CO. DME conversion and selectivity to C₁ species are defined as follows:

$$DME\ conversion(\%)=100\left(\frac{F_{CO} + F_{CO_2} + F_{CH_4} + F_{MeOH}}{F_{CO} + F_{CO_2} + F_{CH_4} + F_{MeOH} + 2F_{DME}}\right)$$

$$Selectivity\ to\ C_1\ species=100F_{C_1} / \sum F_{C_1}$$

where F_{DME} and F_{C_1} are the effluent molar flow rates of DME and C₁-containing products (CH₄, CO, CO₂, and MeOH), respectively.

3. Results and discussion

DME SR comprises two reactions in sequence: DME hydrolysis and MeOH SR, as expressed in reaction (1) and (2), respectively.

The combination of them gives DME SR as expressed in reaction (3)

Feeding DME and steam over either copper-iron spinel or alumina could not produce hydrogen via direct DME SR (reaction (3)). On the other hand, over the present composite catalysts DME hydrolysis followed by MeOH SR is a dominant process. Besides DME SR, reverse water gas shift reaction (r-WGSR) generally takes place over Cu catalysts during the reforming process. Additionally, methane would be generated via DME decomposition over alumina, especially when high reforming temperatures are employed. Carbon monoxide could be produced via r-WGSR and DME decomposition, while some reports demonstrated that CO could also be formed via CO hydrogenation and direct

decomposition of methanol [19,25]. It is worth noting that CO formation over the present catalysts is relatively low – CO concentration below 2% at reaction temperature of 350 °C.

Effect of reduction pretreatment on the catalytic activity of the composite catalysts of CuFe_2O_4 and $\gamma\text{-Al}_2\text{O}_3$ for DME SR was examined under the reaction conditions of $\text{S/C} = 2.5$, reaction temperature = 350 °C, and $\text{GHSV} = 2000 \text{ h}^{-1}$. Prior to DME SR reaction, the composites were reduced in 10% H_2/N_2 for 3 h at 250, 350, 450, and 600 °C. **Figure 1** shows DME conversion over the reduced and unreduced composite catalysts at reaction time of 1 and 25 h. At reaction time of 1 h, DME conversion over the catalysts unreduced and reduced at 250 and 350 °C was comparable, suggesting the *in situ* reduction of CuFe_2O_4 in the working condition of DME SR [19]. A slight decrease in the activity was seen over these samples in the reaction time of 25 h. On the other hand, the catalytic activity was decreased considerably by increasing the reduction temperature to 450 and 600 °C, and more rapid drop in the activity was observed over the catalyst reduced at 600 °C. Degradation of the catalytic activity proceeded significantly over both catalysts during DME SR for 25 h, and more severely over the sample reduced at 600 °C.

Figure 2 shows hydrogen concentration and selectivity to MeOH in DME SR test over unreduced and reduced composite catalysts. The H_2 -rich feed reformat was generated with H_2 concentration of ca. 70-73% from DME SR over all catalysts at reaction time of 1 h. Over the catalysts reduced at temperatures below 350 °C, H_2 concentration exhibited no

significant drop after reaction test of 25 h, whereas it decreased to 68 and 60% over the catalysts reduced at 450 and 600 °C, respectively, corresponding well with the changes of DME conversion, as shown in Fig. 1. Selectivity to MeOH was negligible at 1 h and dramatically increased over the catalysts reduced at 450 and 600 °C after reaction test of 25 h. The increase in MeOH selectivity indicated degradation of the catalysts in Cu phase since they lost catalytic activity for MeOH SR. The γ -Al₂O₃ was known to be highly stable in DME SR [15].

H₂ TPR profiles of CuFe₂O₄ and γ -Al₂O₃ are depicted in **Fig. 3**. The CuFe₂O₄ sample exhibited two distinct peaks showing maximum at 330 °C and 580 °C. The peaks appearing in the temperature range of 240 to 400 °C were ascribed to the reduction of CuFe₂O₄ to metallic Cu and Fe₂O₃, and to the subsequent reduction of Fe₂O₃ to Fe₃O₄. It is hard to define a clear boundary between each of the reduction steps. The iron oxides continued to be reduced to metallic Fe via FeO, according to the peak appearing at higher temperature. In general, the Al₂O₃ was not reducible at temperatures below 800 °C.

The XRD patterns of the composites of CuFe₂O₄ and γ -Al₂O₃ reduced at different temperatures are depicted in **Fig. 4**. The fresh composite before reduction shows a highly crystallized copper-ferrite spinel phase together with small crystal or amorphous alumina ($2\theta = 68$ - 69°). The composites reduced at 250 and 350 °C composed of two phases of metallic Cu and Fe₃O₄. The main peaks for Cu at $2\theta = 43.3^\circ$ and 50.4° correspond to [1 1 1] and [2 0 0] crystal planes, respectively. There is no Cu₂O or CuO present in the sample, which indicates all CuFe₂O₄ has been reduced to Cu metal and Fe₃O₄ or Fe. Fe₃O₄ was fully reduced to Fe after high temperature reduction at 450 and 600 °C. The Cu crystallite

size calculated using Scherrer formula at the respective Cu[1 1 1] reflections revealed that the crystallite size increased in keeping with the reduction temperature: 24, 27, 51, and 60 nm for the catalysts reduced at 250, 350, 450, and 600 °C, respectively. The greater size of Cu would result in smaller active surface areas, and subsequently in the lower catalytic activity, in agreement with the result in **Fig. 1**. The catalysts reduced at the high reduction temperatures, which displayed two metallic phases of Cu and Fe, were not stable in DME SR likely due to Cu sintering. The iron oxides are indispensable in preventing metallic Cu from sintering. It should be noted that all composite catalysts had BET surface area of ca. 135 to 145 m² g⁻¹.

The effect of dopants (Mn, Cr, Co, and Al) to the CuFe₂O₄ on DME SR performance was investigated. The catalyst CuFe_{1.8}B_{0.2}O₄, where *B* is Mn, Cr, Co, or Al, was prepared by the citric acid method using the corresponding metal nitrate solution at stoichiometric ratio. The as-synthesized catalyst was then calcined in air at 900 °C for 10 h. According to XRD analysis, all catalyst comprised mainly a spinel-type oxide phase (results not shown here). No other metallic or oxide phases were distinctly observed. Thus, the dopants could be incorporated into the spinel lattice or stay as an amorphous form. **Figure 5** depicts the temperature dependence of DME conversion and selectivity to CO₂, CO, and CH₄ over the doped spinel catalysts mixed with γ -alumina. The DME conversion over all doped catalysts was lower than that over the un-doped one. Even doping small amount of the metal additives to copper-iron spinel suppressed DME SR activity. The conversion over Mn-, Cr-, and Co-doped catalysts was comparable, while that over Al-doped catalyst was the lowest. The highest CO₂ and the lowest CO selectivities were found over Mn-doped catalyst. Cr-doped catalyst gave the highest CO selectivity, indicating that

r-WGSR was expedited over Cr species. CH₄ selectivity over Co-doped catalyst was significantly higher than the others. Cobalt is generally known as a methanation catalyst and would produce CH₄ under the reforming condition. Partial substitution of Mn, Cr, Co, or Al would decrease the amount of iron oxide formed and would promote side reactions, resulting in low DME SR activity.

4. Conclusions

DME SR over composite catalysts of CuFe₂O₄ and γ -Al₂O₃ was carried out to investigate the effect of hydrogen reduction pretreatment and metal doping to CuFe₂O₄ spinel. The composites reduced at 250 and 350 °C and even unreduced were highly active and stable in DME SR reaction for 25 h due to stability of the reduced phases of composites, Cu and Fe₃O₄. The higher reduction temperatures would result in continuous reduction of Fe₃O₄ to metallic Fe as well as in sintering of metallic Cu and Fe, leading to decrease in activity and stability of the catalysts. Dopants, including Mn, Cr, Co, and Al, to CuFe₂O₄ could all inhibit the activity of the catalyst.

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Figure captions

Figure 1. DME conversion in DME SR over composite catalysts of CuFe_2O_4 and $\gamma\text{-Al}_2\text{O}_3$ reduced at various reduction temperatures. Reaction conditions: $\text{S/C} = 2.5$; $\text{GHSV} = 2000 \text{ h}^{-1}$; temperature = 350°C , reaction time = 1 and 25 h.

Figure 2. Hydrogen concentration and selectivity to MeOH in DME SR over composite catalysts of CuFe_2O_4 and $\gamma\text{-Al}_2\text{O}_3$ reduced at various reduction temperatures. Reaction conditions: $\text{S/C} = 2.5$; $\text{GHSV} = 2000 \text{ h}^{-1}$; temperature = 350°C , reaction time = 1 and 25 h.

Figure 3. TPR patterns of CuFe_2O_4 and $\gamma\text{-Al}_2\text{O}_3$. TPR conditions: $10^\circ\text{C min}^{-1}$ in 5% H_2/Ar .

Figure 4. XRD patterns of composite catalysts of CuFe_2O_4 and $\gamma\text{-Al}_2\text{O}_3$ reduced at various reduction temperatures: (a) fresh (unreduced), (b) 250°C , (c) 350°C , (d) 450°C , and (e) 600°C .

Figure 5. Temperature dependence of (a) DME conversion and selectivity to (b) CO_2 , (c) CO , and (d) CH_4 for DME SR over doped catalysts $\text{CuFe}_{1.8}\text{B}_{0.2}\text{O}_4$ ($\text{B} = \text{Fe, Mn, Cr, Co, and Al}$) coupled with $\gamma\text{-Al}_2\text{O}_3$. Reaction conditions: $\text{S/C} = 1.75$; $\text{DME} = 15\%$, steam = 52.5%, N_2 balance; $\text{GHSV} = 6000 \text{ h}^{-1}$. Equilibrium data calculated by minimization of Gibbs free energy assuming no CH_4 and carbon formation.

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