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Reaction characteristics of dimethyl ether (DME) steam reforming catalysts for hydrogen production

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ABSTRACT

The purpose of this study was to develop new catalysts for dimethyl ether (DME) steam reforming (SR) in the absence of a carrier gas for hydrogen fuel cell vehicles and to find the optimal reaction conditions for said process. The steam reforming catalysts were prepared by impregnation of Cu, the active material, with Ce and Ni additives using mordenite (MOR) and alumina as supports. The prepared catalysts were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), and inductively coupled plasma – optical emission spectrometer (ICP-OES). The catalysts were prepared in honeycomb and pellet form. The hydrogen yield with the pellet Cu₁₀MOR₁₀/γ-Al₂O₃ catalyst was 80% at 400 °C, higher than that obtained with the honeycomb catalyst under the same experimental conditions (50%). The ratio of H₂O/DME, one of the most important parameters among the experimental conditions, afforded the best hydrogen yield at a value of 6, higher than the theoretical ratio of 3. Space velocity (SV) values in the range of 340–510 h⁻¹ afforded hydrogen yields of ~80%. The hydrogen yield was similar at temperatures in the range of 300–550 °C although, at 400–450 °C, higher DME conversions and lower CH₄ production were observed. The addition of Ni to the catalyst resulted in the inhibition of the deposition of hydrocarbons, and the Ce additive was found to increase the DME conversion. Finally, it was found that the best catalyst for DME steam reforming was Cu₁₀Ce₄MOR₁₀/γ-Al₂O₃. The optimum reaction conditions for H₂ production were determined as SV = 340 h⁻¹, H₂O/DME ratio = 6, the pellet-type catalyst, and a catalytic reaction temperature range of 400–450 °C.

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Introduction

Hydrogen fuel cell vehicles (FCVs) are environmentally friendly automobiles that generate electricity using hydrogen as fuel, which does not result in harmful emissions [1].

Hydrogen FCVs use fuel cells to generate electricity. At present, the supply of hydrogen in hydrogen FCVs suffers from problems of stability in the hydrogen tank and the insufficient establishment of a hydrogen supply infrastructure [2–4].

As an alternative, a variety of reforming reactions of hydrocarbon fuels for hydrogen production have been studied.

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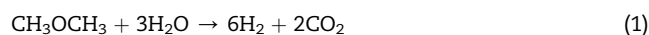
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Among them, research on dimethyl ether (DME) steam reforming (SR) reactions as an efficient hydrogen storage medium is gaining momentum [5]. Reforming methods can be divided into partial oxidation, autothermal reforming, and steam reforming. Among them, DME steam reforming has the advantage of having the highest theoretical hydrogen yield [6]. Unlike methanol, which is used in conventional reforming, DME is not corrosive, harmless to the human body, and has a high H/C ratio [5]. It would also be easy to convert the existing infrastructure facilities into this new technology because DME has similar physical properties of liquefied petroleum gas (LPG).

A variety of DME steam reforming catalysts have been reported [7–11], but there are only a few studies in which they have actually been applied to hydrogen fuel cell automobiles. Conventional studies employ nitrogen and water, as well as carrier gases, for DME steam reforming [2–8]. The presence or absence of a carrier gas affects the DME conversion and the hydrogen yield by changing the space velocity. Steam reforming catalysts for hydrogen production should be studied under the same conditions than the actual working conditions of FCV systems.

The DME steam reforming Reaction (1) involves the hydrolysis of DME (Reactions (2)) and methanol steam reforming (Reaction (3)).



During DME steam reforming, Reactions (2) and (3) occur simultaneously. Therefore DME steam reforming catalyst need to be bifunctional catalyst that has acidic part (for DME hydrolysis) and metallic part (for MeOH steam reforming). The hydrolysis of DME (2) is an endothermic reaction with an enthalpy of 388 kJ mol⁻¹ that requires a reaction temperature of 350–500 °C in order to achieve acceptable reaction rates [11–13]. Copper catalyst is widely used for the methanol steam reforming reaction due to their high activity and selectivity but it suffered from thermal sintering in the temperature range of 300–350 °C [14,15]. Coke is also formed during the DME hydrolysis. Acid catalysts with high acidity can cause serious coke deposition in the DME hydrolysis. This reduces the active surface area and the catalyst performance [15–20]. Besides DME decomposition can be occurred in the case strong acidic catalyst or high reforming temperatures are employed [6]. Therefore, the use of suitable additives and supports is essential. In our previous work, we developed and reported a Cu/ γ -Al₂O₃ + mordenite (MOR) catalyst as a DME reforming catalyst [21]. Unfortunately, the catalytic performance of Cu/ γ -Al₂O₃+MOR deteriorated due to coke formation during

DME hydrolysis at long reaction times. In order to suppress the sintering of copper catalysts, methods of adding Ni or CeO₂ [22,23] and Cu-spinel oxide catalysts are used to increase the Cu dispersion in Cu-based catalyst supported on γ -Al₂O₃ [24]. The preparation method could be effect on performance of reforming catalyst. Various preparation method were reported such as the citric acid complex method [12], deposition-precipitation [23], sol-gel method [18,25], impregnation [9,18]. Furthermore, various methods have been reported as methods for forming certain nanostructures of inorganic materials such as TiO₂, ZnO, MnO₂ on the surface [26–28]. The purpose of this study was the development of new catalysts for DME SR for hydrogen fuel cell vehicles in the absence of a carrier gas and the identification of the optimal reaction conditions. The steam reforming catalysts were prepared by impregnation of Cu (the basic active material) with Ce and Ni as additives, using MOR and alumina as supports.

Experimental

Catalysts preparation

Catalyst powder

The DME steam reforming catalyst was prepared in powder form by the impregnation method. The precursors of the metallic materials are shown in Table 1 and the composition of the catalysts is shown in Table 2. γ -Al₂O₃(the support) and MOR were added to distilled water (500 mL) at 60 °C, and the mixture was stirred for 30 min. Each precursor was added and stirred for 6 h, followed by drying at 80 °C for 12 h. The dried reforming catalyst was milled for 2 h and calcined in air atmosphere at 500 °C for 2 h at a rate of 4 °C/min.

Honeycomb type catalyst

The catalyst powder (2 g) was added to distilled water (500 mL) at 60 °C, and the mixture was stirred for 2 h. The substrate (honeycomb type, cordierite, 400 cpsi (cell per square inch), diameter: 19 mm, length: 19 mm) was dried at 80 °C for 30 min. The initial weight of the dried substrate was recorded. The dried substrate was dipped into the distilled water containing the catalyst, and the resulting supported catalyst was dried at 80 °C. The weight of the dried catalyst on the substrate was determined and the above procedure was repeated until the amount of supported catalyst reached 70 g/L. The substrates coated with the different catalysts were calcined in air atmosphere at 500 °C (4 °C/min) for 2 h. The prepared catalysts were subjected to a reduction process under H₂/N₂ (10%/balance) flow at 500 °C for 2 h.

Table 1 – Precursor of various catalysts and supports.

Metal	Precursor	Manufacturer
Cu	Cu(NO ₃) ₂ × 2.5H ₂ O	Sigma Aldrich
Ce	Ce(NO ₃) ₃ × 6H ₂ O	Sigma Aldrich
Ni	Ni(NO ₃) ₂ × 2H ₂ O	Sigma Aldrich
γ -Al ₂ O ₃	–	Umicore
Mordenite (MOR)	–	Umicore

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