



Catalytic behavior toward oxidative steam reforming of dimethyl ether over CuFe₂O₄-Al₂O₃ composite catalysts

Kajornsak Faungnawakij*, Nawin Viriya-empikul

National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency, 111 Thailand Science Park, Paholyothin Rd., Patumthani 12120, Thailand

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ABSTRACT

Oxidative steam reforming of dimethyl ether (DME OSR) for hydrogen production was studied over CuFe₂O₄-Al₂O₃ composite catalysts. The catalytic behaviors of the catalysts were investigated in terms of DME conversion, H₂ production rate, and selectivity to CO₂, CO, and CH₄ as well as the catalyst temperature and gaseous concentration profiles along the catalyst bed. The catalysts exhibited good reforming activity and low CO formation (<2.5 vol.%) with trace amounts of other byproducts in the temperature range of 275–375 °C, steam/DME of 2.5, and O₂/DME of 0–1. The increase in O₂/DME resulted in improved DME conversion, but lower selectivity to H₂. The catalyst was essentially stable in DME OSR in the 200 h stability test in the temperature range of 317–335 °C, while H₂ concentration was stably obtained at ca. 62 vol.%. Oxygen was rapidly consumed in the beginning zone of the catalyst bed where the exothermic partial oxidation of DME along with CO oxidation would preferentially occur. The majority of reactions in the remaining zone was endothermic steam reforming of DME together with water gas shift reaction.

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1. Introduction

So far, primary energy production in the world has come from combustion of fossil fuels which releases green house gases (CO₂). Global warming due to the increased emissions of CO₂ along with CH₄, CFCs, and N₂O is a focus of serious concerns due to its effects [1,2]. Besides that, declining fossil fuel stocks have led to searching for alternative energy sources. A fuel cell is a clean and efficient power generator, since it can generate electrical energy directly from chemical energy without pollutant emission [3]. Typically, an electrochemical reaction of a fuel at an anode (generally H₂) and of an oxidant at a cathode (generally O₂) generates electricity through a fuel cell, where only water is produced onsite as a single chemical product.

Catalytic hydrogen production has been intensively developed for exploiting in fuel-cell system [4–11]. Catalytic reforming is one of the important methods to produce hydrogen from hydrocarbon fuels on small to large scales. In industrial scale, steam reforming of natural gas is presently the preferred process for producing of hydrogen. It is a fact that natural gas is a fossil fuel and is considered an unsustainable energy source due to an unbalance of demand and supply. As more sustainable energy sources, biomass and biomass-derived fuel, such as bioethanol, biogas, and dimethyl

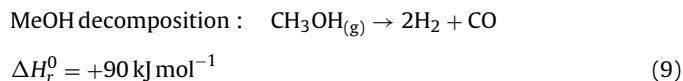
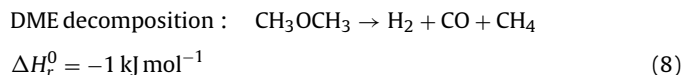
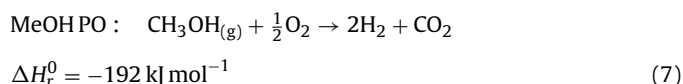
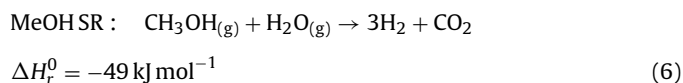
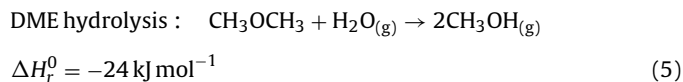
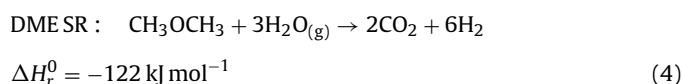
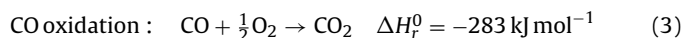
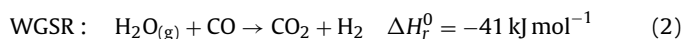
ether (DME), have attracted considerable attention as a clean fuel due to the merit of being CO₂ neutral. Nowadays, DME has become a promising candidate as a hydrogen source for the reforming process, because it has a high hydrogen-to-carbon ratio and a high energy density. DME can be easily handled, stored, and transported. Furthermore, the infrastructure of LPG can readily be adapted for DME due to their similar physical properties. DME is preferable to methanol (MeOH) due to its non-toxicity. DME can be catalytically reformed at relatively lower temperatures than ethanol and methane [4–6].

Steam reforming (SR), partial oxidation (PO), and oxidative steam reforming (OSR) also called autothermal reforming (ATR) or combined reforming are three major methods for production of H₂ fuel-cell feeds [12]. Steam reforming can provide a H₂-rich feed with low CO concentrations to fuel cells; however, endothermicity, slow start-up time, and the steam need make it unsuitable for mobile uses. Partial oxidation uses oxygen (typically from air) instead of steam, and is an exothermic reaction, providing fast response time. However, drawbacks are hot spot formations in a catalyst bed and a lower reformat quality. The most energy efficient and dynamic method of producing hydrogen is the OSR process, that combines the merits of both SR and PO reactions. The OSR running at suitable condition could provide a high quality feed to fuel cells, though addition of oxygen to an SR system would theoretically lower the reformat quality [9]. The gaseous reactions potentially involved in DME OSR are shown below:



* Corresponding author. Tel.: +66 2 564 7100x6638; fax: +66 2 564 6981.

E-mail addresses: kajornsak@nanotec.or.th, jw037@yahoo.com (K. Faungnawakij).



In DME OSR, DME is reacted with oxygen in air and steam, so that the combination of the endothermic steam reforming and the exothermic partial oxidation could simultaneously proceed to give rise to better energetic efficiency and faster start-up time as compared with the SR process. These functions make DME OSR attractive for automotive and residential applications, for example, in intermediate temperature proton-exchange-membrane fuel cells (IT-PEMFCs) operative at 100–300 °C [13–15] and intermediate temperature solid oxide fuel cells (IT-SOFCs) operative at 500–800 °C [16,17]. DME PO has been investigated over various metal catalysts such as Pt, Ni, Co, and Rh supported on different oxide supports such as Al₂O₃, YSZ, LaGaO₃-based, and MgO at a high reaction temperature ranging from 400 to 700 °C [18,19]. In

DME OSR condition, DME PO (reaction (1)) may first proceed to produce CO and H₂, followed by water gas shift reaction (reaction (2)) and CO oxidation to produce CO₂ (reaction (3)). DME SR (reaction (4)) comprises two reactions in sequence: hydrolysis of DME to MeOH (reaction (5)) and steam reforming of MeOH to hydrogen and carbon dioxide (reaction (6)). Generally, DME hydrolysis is catalyzed over solid-acid catalysts such as zeolites and alumina [20–22], while MeOH SR is catalyzed over Cu or Pd catalysts [9,22]. Partial oxidation of methanol (MeOH PO) could also occur over Cu or Pd catalysts (reaction (7)) [23,24]. In addition, DME/MeOH decomposition could concurrently occur over solid acids and copper-iron catalyst [25–27]. The catalyst required for DME OSR must be active and stable in both DME SR and DME PO. It is known that the Cu-based catalyst is superior in MeOH SR due to the cost effectiveness and the activity, though its thermal stability is poor when one employs it at a reaction temperature above 300 °C. We have previously developed the composite catalysts of copper-ferrite spinel oxide coupled with γ-Al₂O₃ for DME SR at the temperature range of 300–375 °C. The composite exhibited excellent activity and stability in DME SR at the high reforming temperatures [8]. Gamma-alumina outperformed strong acid catalysts (e.g. zeolites) in DME hydrolysis in terms of stability and selectivity [21].

In the present work, we aimed at investigating the performance of CuFe₂O₄-Al₂O₃ composite catalysts in oxidative steam reforming of dimethyl ether. Effects of inlet steam-to-DME ratios, inlet oxygen-to-DME ratios, and reaction temperature on catalytic behavior were evaluated in a fixed bed reactor where catalyst temperature profiles and concentrations of gaseous species were monitored. Middle-term stability (200 h) over the catalyst was also tested.

2. Experimental

2.1. Preparation of catalysts

The Cu-based spinel was prepared by a sol-gel combustion based on citric acid complexation. The method can effectively accommodate different cations in the complex, resulting in uniform mixing of the cations. 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 the water. The precipitate obtained was heated up to 140–200 °C until fine powders were achieved. Next, cal-

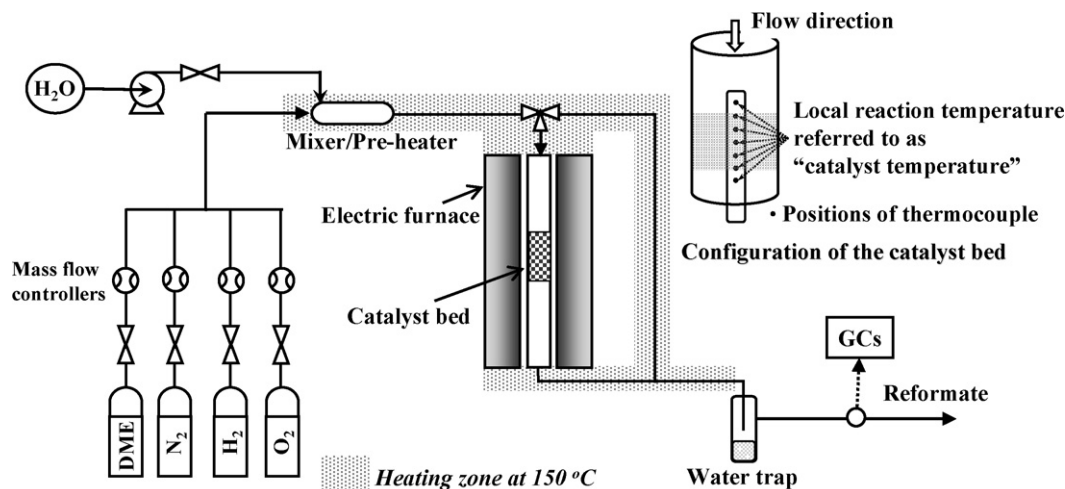


Fig. 1. Experimental apparatus and configuration of reactor.

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