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Limiting mechanisms in catalytic steam reforming of dimethyl ether

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ABSTRACT

The limiting mechanisms in dimethyl ether steam reforming (DME SR) are experimentally investigated over the nanocomposite catalysts of Cu spinel and alumina. The dominant reactions involved in DME SR are proved to be DME hydrolysis to methanol over acidic sites of alumina and subsequent methanol steam reforming to H_2 and CO_2 over Cu sites, followed by reverse-water gas shift reaction. The contribution of other side reactions is also clearly evaluated. DME hydrolysis is limited by the equilibrium, and the hydrolysis rate was much slower than the methanol SR rate, and thus was a rate-determining step in DME SR. The deactivation of Cu spinel was significantly faster than that of alumina, and would determine the lifetime of the composite catalysts. With varied superficial velocities up to 5.2 cm s^{-1} (25 °C, 1 atm), the evidence of mass transfer-limiting mechanism and reaction-limiting mechanism was observed in the low flow rate and the high flow rate regions, respectively.

1. Introduction

Steam reforming (SR) is a method of producing hydrogen from hydrocarbon fuels. It is a distinguished process to produce hydrogen on an industrial scale, and is a current attractive route to provide hydrogen to fuel cells on a small/medium scale. Unlike combustion engine, hydrogen fuel cells generate electricity with only water as a single chemical product and therefore benefit the environment. Using fuel cells can also diminish a dependence on fossil fuels. Some hydrogen sources, e.g. liquefied petroleum gas (LPG), ethanol, methanol (MeOH), and dimethyl ether (DME), have been used in SR [1–4]. Among them, steam reforming of dimethyl ether is currently recognized as a promising process for catalytic hydrogen production [5]. A biomass-derived DME is an oxygenated hydrocarbon without C–C bonds that provides a high hydrogen-to-carbon ratio. It has been used as a clean-burning fuel alternative to LPG and diesel. DME and MeOH are suitable for on-board reforming; they can catalytically be reformed at low temperatures of 200–350 °C for MeOH [6–9] and 200–400 °C for DME [10–15]. DME is harmless and less explosive, and therefore is preferable to MeOH. The utilization of LPG infrastructures to handle DME can be possible due to their similar physical properties, making DME attractive for residential use as well. In addition, autothermal reforming of DME over Pd-based catalysts has also been developed for automobile uses [16].

DME SR ($(CH_3)_2O + 3H_2O_{(g)} \rightarrow 6H_2 + 2CO_2$, $\Delta H_r^0 = 122\ kg\ mol^{-1}$) proceeds via two moderately endothermic reactions in sequence: hydrolysis of DME to MeOH and steam reforming of MeOH 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. Therefore, bi-functional catalysts containing both acidic and metallic sties are generally needed for DME SR. The Cu-based catalysts are promising in terms of cost effectiveness and activity. We have proposed the Cu-based spinels mixed with γ-Al_2O_3 for DME SR [17–20]. The Cu spinels exhibited excellent performance as compared with Cu/ZnO and Cu/ZnO/Al_2O_3. A sizable number of solid acid catalysts such as H-mordenite, Y-zeolite, and alumina have been proposed as DME hydrolysis catalysts. As compared to strong acids such as H-mordenite and H-ZSM5, γ-alumina possesses relatively weak acid sites and therefore provides lower hydrolysis activity. Nevertheless, a high durability along with inhibition of side reactions was observed from the weak acids [19]. A high temperature above 300 °C is required for effective hydrolysis of DME over γ-Al_2O_3. The high temperature brings about, however, severe sintering of copper [21,22]. Limiting mechanisms in catalytic reaction are the important aspects to understand, design, and develop the catalysts and systems for the reaction processes. There is however no evident report on limiting mechanisms in DME SR so far.

In this work, we explored the limiting mechanisms in DME SR over Cu-based spinel and alumina. The parameters studied were

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reaction temperature, gas flow rate, and configuration of catalyst bed which strongly affected the catalyst performance and reaction behaviors. The reaction and limiting mechanisms were discussed based on the experimental measurements of structural characteristics and reaction behaviors of the catalyst.

2. Experimental

2.1. Catalyst preparation and characterization

Cu-based spinel used in this work was copper-ferrite spinel oxide ($CuFe_2O_4$) which was prepared by a citric acid complex method as described elsewhere [17,18,23]. The different cations can effectively be accommodated in the complex, providing uniform mixing of the cations [23–26]. An aqueous solution of corresponding nitrates and citric acid was heated to 90 °C to evaporate water until viscous gel was formed. The precipitate obtained was then heated to 140–200 °C until fine powders were achieved. Subsequently the calcination of the powder was conducted in air at 900 °C for 10 h. Gamma-alumina (ALO8) provided by the Catalysis Society of Japan was calcined in air at 700 °C for 0.5 h prior to investigation. 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 0.85–1.7 mm. In addition, the Cu spinel and alumina were separately pelletized to the same particle size. For the limiting mechanism tests, the particles were placed randomly or as layers in the reactor.

A nitrogen adsorption system (BEL Japan Bellsorp–max) was employed to determine adsorption–desorption isotherms. The Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) approaches were employed to determine the surface area and pore size distribution of the samples, respectively. The crystalline bulk phase of the catalysts was measured by powder X-ray diffraction (XRD) technique using a Rigaku RINT1400 and a JEOL JDX-3530 with Cu Kα radiation source. The crystallite size was calculated by XRD-line broadening using the Scherrer equation. Scanning electron microscope (SEM, Hitachi S-3400N TypeII) was used to observe morphology of the catalysts. Transmission electron microscope (TEM, Hitachi H-9000UHR III) was used for the observation of microstructure, high resolution TEM image, and diffraction image. Temperature-programmed oxidation (TPO) was employed to analyze the carbon deposition on catalyst surface. A 50 mg catalyst sample was oxidized in 5% O_2/He at a flow rate of 30 ml min^{-1} (25 °C, 1 atm) at a heating rate of 10 °C min^{-1}. The product gases were monitored by online mass spectrometer. X-ray photoelectron spectroscopy (XPS) was performed using a Shimadzu ESCA-850 with a Mg Kα radiation source ($h\upsilon$ = 1253.6 eV) and operated at 8 kV and 30 mA. Each binding energy was referenced to the C 1s peak (284.3 eV).

2.2. Evaluation of catalytic performance

The evaluation of catalytic activity was carried out using a conventional flow reactor under atmospheric pressure. Prior to the evaluation of catalysts, reduction of the catalyst was carried out at 350 °C for 3 h in 10% H_2/N_2. The reaction was attained at each condition for 1 h to achieve a steady state prior to the gas analysis, except in the time-on-stream test. Mass flow controllers were used to adjust the gas feed rate and a low pressure gradient pump to control the water feed rate. A mixture of DME and steam at a steam-to-carbon ratio (S/C) was supplied to a pre-heater at temperature of 150 °C, and then to the catalyst bed at reaction temperature.

The analysis of influent and effluent gaseous compositions was carried out by using online gas chromatographs equipped with a thermal conductivity detector (VARIAN, CP-4900). The steam in the gas stream was trapped by a condenser at ca. 3 °C before the gas analysis. A PoraPLOT Q column was used for the separation of DME, MeOH, and CO_2 and a molecular sieve 5A column for separation of H_2, O_2, N_2, CH_4, and CO. DME conversion and selectivity to gaseous products (S_i) are defined as follows:

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

$$S_i(\%) = 100\left(\frac{F_i}{F_{CO}+F_{CO_2}+F_{CH_4}+F_{H_2}}\right)$$

where F stands for the effluent molar flow rate of each chemical species, and i stands for gaseous products (CO, CO_2, CH_4, or H_2). The deviation of the conversion and the gaseous product distribution (concentration) was typically within ±1% in the duplicated experiments. The reported results were calculated based on the average value obtained by triple gas analyses at each condition.

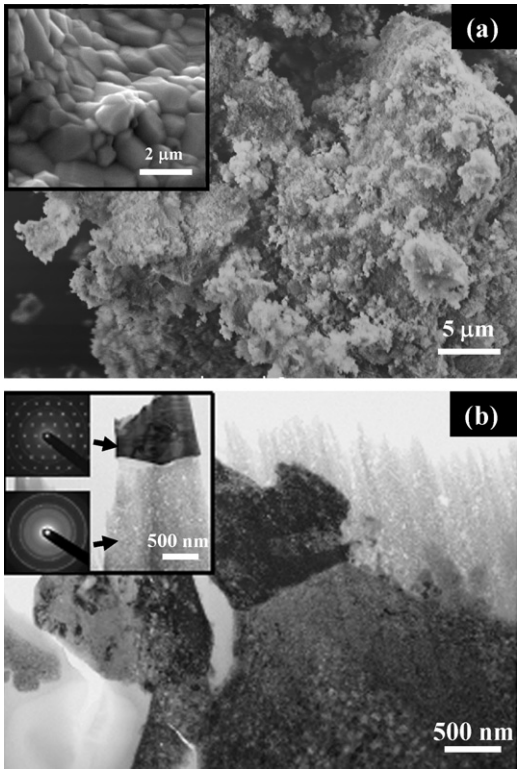

Fig. 1. Typical SEM and TEM micrographs of composite of $CuFe_2O_4$ and Al_2O_3. (a) SEM image with a highly magnified image of $CuFe_2O_4$ (as an inset); (b) TEM image with its zoomed-in image and corresponding SAED (as an inset).

3. Results and discussion

3.1. Characteristics of catalyst

The SEM and TEM images of composite catalyst of $CuFe_2O_4$ and γ-Al_2O_3 are shown in Fig. 1. As seen in Fig. 1(a), the well-mixed state between Cu spinel and alumina was observed in a microscopic scale, while the clean surface of Cu spinel is shown as an inset. The BET surface area of alumina is 141 m^2 g^{-1}, while spinel $CuFe_2O_4$ was a less-porous catalyst with a surface area of 0.5–1 m^2 g^{-1}. The close contact of spinel and alumina is demonstrated in nano-scale by TEM analysis in Fig. 1(b). The SAED images (as an inset) revealed that the Cu spinel is highly crystallized, whereas alumina is almost in amorphous phase. The crystallite size of $CuFe_2O_4$ was ca. 40–45 nm. XRD analysis confirmed that $CuFe_2O_4$ was well crystallized in tetragonal