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Transmission electron microscopic observation on reduction process of copper–iron spinel catalyst for steam reforming of dimethyl ether

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Abstract

The reduction process of copper–iron spinel oxide, which is active for steam reforming of dimethyl ether after mixing with alumina, has been investigated by a transmission electron microscope (TEM), scanning TEM (STEM), and energy dispersive X-ray (EDX) analyzer. The catalyst preparation was started from formation of well-sintered $CuFe_2O_4$ by calcination in air at 900 °C. After reduction of $CuFe_2O_4$ with hydrogen at 250 °C, metallic copper grains were developed on reduced spinel surface by the phase separation from the oxide. Strong chemical interaction between deposited Cu and reduced spinel oxide was expected from their intimate interfacial contact and lattice matching. The reduced sample contained metallic Cu, reduced spinel, and spinel oxide with super-lattice structure. Partial elimination of Cu and lattice oxygen resulted in formation of pores in and between the oxide grains. The size of the deposited Cu particle and Cu grain was largely distributed. After heating at higher temperature of 350 °C, the large spinel oxide particles are decomposed into small particles via formation of cracks. The resultant catalyst powder was very porous and consisted of very small particles of Cu, iron oxide, and spinel oxide. STEM–EDX analyses clarified the phase separation process of metallic Cu and iron oxide from host $CuFe_2O_4$ upon reduction.

Keywords: TEM; EDX; $CuFe_2O_4$ spinel; Reduction; Dimethyl ether; Steam reforming

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been regarded as clean and highly efficient power generators for stationary and mobile use [1–3]. Recently, dimethyl ether (DME) has attracted much attention as a H_2 source as well as an alternative fuel for diesel engine with clean exhaust. Catalytic hydrogen production from dimethyl ether has been proposed by Amoco Corp. in 1996 as hydroshift reaction [4]. Dimethyl ether can be reformed at lower temperatures than hydrocarbons [5,6]. Dimethyl ether shows a good potential to be used as a H_2 source for automotive PEFC system [7], since this fuel molecule can be reformed at lower temperatures than hydrocarbons [8–17]. As DME molecules possess no C–C bond, carbon deposition can be avoided easily by adding water in the reaction system. It was suggested that sufficiently low cost should be achieved by producing in a large scale, though the cost problem is still controversial. As for the safety to toxicity, DME is preferable to methanol [10,12]. Production of hydrogen from DME can be achieved through catalytic reactions, such as steam reforming, partial oxidation, and autothermal reforming [17–19].

Steam reforming of DME can be expressed as a combination of hydrolysis of DME (reaction (1)) and steam reforming (SR) of methanol (reaction (2)):

$$(CH_3)_2O + H_2O \rightarrow 2CH_3OH \tag{1}$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{2}$$

From reactions (1) and (2), overall DME steam reforming can be expressed as follows:

$$(CH_3)_2O + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{3}$$

Copper-based catalysts have been known to be active for reforming of methanol (step (2)), while solid-acid catalysts

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are commonly used for hydrolysis of DME (step (1)) [8–17]. We have proposed copper-based spinel catalysts for a series of reactions; i.e., water gas shift reaction (WGSR) and steam reforming of methanol and DME [13,17,20,21]. For the application to steam reforming of DME copper–iron spinel mixed with γ-alumina was the most active in the temperature range of 350–450 °C among the spinel oxide-based catalysts investigated. The activity was found to be higher than the commercial $Cu/ZnO/Al_2O_3$ catalysts when the $CuFe_2O_4$ catalyst was mixed with γ-alumina [22]. In this temperature range, on weakly acidic sites of γ-alumina, the reaction (1) proceeds without significant formation of decomposition products such as methane or carbonaceous compounds [13]. Zeolite or acidic catalysts were more active for this step, but the strong acidity gave rise to unselective decomposition to methane and carbonaceous species at the temperature desirable for the second step [22]. The second reaction is conducted on Cu which is deposited by phase separation from the spinel oxide in the proposed catalyst. This Cu-spinel catalyst attained the sufficient activity for complete conversion of methanol in the temperature range of 350–450 °C. For the DME reforming at lower temperatures, Cu catalysts do not exhibit enough activities, whereas at higher temperature range unselective decomposition and sintering of Cu led to deactivation of catalysts [17,22].

The activation of the Cu-based spinel catalyst is indispensable for the use in WGSR and DME reforming; i.e., the pretreatment composed of calcination in air at around 900 °C and subsequent reduction with H_2 or in reaction gases at around 250–350 °C [17,21]. The initial calcination in air is for the complete formation of spinel phase, and the following reduction treatment for the deposition into active Cu^0 species and pore formation. The oxidation state of copper in spinel is divalent, whereas reduction to metallic state was observed for spent catalysts by X-ray diffraction. This suggests that the reduction process as well as reduced state of copper in the spinel catalyst is important in elucidating the catalytic properties of the copper-based spinel catalysts. The present investigation focused on the structural analysis of $CuFe_2O_4$ spinel that demonstrated high activity for DME reforming after mixing with γ-alumina. Reduction process of the spinel oxide and subsequent deposition of active copper species were observed by high resolution transmission electron microscope (HR-TEM). A composition and dispersion on nm scale was analyzed by scanning TEM (STEM) with energy dispersive X-ray (EDX) analysis.

2. Experimental

2.1. Catalyst preparation

The spinel-type oxide catalyst, $CuFe_2O_4$, was prepared from corresponding nitrate mixture and subsequent solid state reaction with the citrate process. The atomic ratio of Cu to Fe was fixed at 1:2 which is stoichiometric for the formation of spinel-type oxide. An aqueous solution of $Cu(NO_3)_2$ and $Fe(NO_3)_3$ (Nacalai Tesque, Analytical Grade) was stirred at 60 °C for 1 h and heated to 90 °C to evaporate H_2O. The precipitate was heated to 140–200 °C to decompose citric acid until fine oxide powders were obtained. The obtained powders were calcined in air at 900 °C for 10 h for Cu-based spinel-oxide type catalysts. The heat treatment at high temperature and complete formation of spinel phase was indispensable in deriving high activity for water gas shift reaction [21] as well as DME reforming [17]. Reduction treatment of catalyst was carried out at 250 °C or 350 °C for 1 h in 10% H_2/N_2 in a flow system.

The catalytic reforming of DME is carried out at 350 °C and a little higher temperature over $CuFe_2O_4 + \gamma\text{-}Al_2O_3$ and $Cu/ZnO/Al_2O_3$ catalysts, respectively [13]. Thus, the catalyst after reduction treatment at 350 °C may reflect the working state. The effect of reduction treatment on the catalytic activity will be explained in Section 3. The catalyst for steam reforming of DME was prepared by mechanical mixing of spinel oxide, $CuFe_2O_4$, with γ-alumina (ALO-8, Catalysis Soc., Japan), since the spinel-based catalyst does not possess acidic center for hydrolysis (reaction (1)). The Cu spinel was physically mixed with the γ-alumina catalyst at a fixed weight ratio of 2:1 [22]. However, the present TEM observation was focused on the phase transformation and microstructural change of the spinel oxide in a reduced state. Therefore, the observation was made only for reduced $CuFe_2O_4$ samples without alumina.

2.2. Catalytic performance measurement

Catalytic activities for steam reforming of DME were evaluated under atmospheric pressure in a packed bed reactor. Prior to the evaluation, reduction of the catalyst composed of the mixture of $CuFe_2O_4$ and γ-alumina was carried out at 250 °C and 350 °C in the following manner [22]. A catalyst was heated in the N_2 flow; then the reduction was performed in 10% H_2/N_2 at 250 °C or 350 °C for 0.5 h. The reduced catalyst was then set at the reaction temperature in N_2 flow prior to the reaction tests. A mixture of steam, DME, and N_2 at a desired steam-to-carbon ratio (S/C) was supplied through mass flow controllers to a pre-heater at temperature of 150 °C, and then to the catalyst bed at 350 °C. For the time-on stream measurement, the gas analysis was periodically carried out. Compositions of influent and effluent gas were analyzed by on-line gas chromatographs equipped with FID (Shimadzu, GC-9A) and TCD (VARIAN, CP-4900). The steam in the feed and reformate was trapped by a condenser before the gas analysis. A Poraplot U column was used for separation of DME, MeOH, and CO_2, and a molecular sieve 5A column was used for separation of H_2, N_2, CH_4, and CO.

2.3. TEM observation

The spinel catalyst powder thus obtained was embedded in a resin. The bulky resin sample containing the catalyst powder was sliced and thin flaky sample was mechanically ground. The thin specimen preparation was followed by ion milling with GATAN, Dual Mill 600. The samples were mounted on Mo grid for the TEM, STEM–EDX observation.