Reforming Catalysts

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Effect of Thermal Treatment on Activity and Durability of $CuFe_2O_4$–Al_2O_3 Composite Catalysts for Steam Reforming of Dimethyl Ether**

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Dedicated to the Catalysis Society of Japan on the occasion of its 50th anniversary

Fuel cells are promising power generators for both mobile and residential uses because of their environmental friendliness and high electric efficiency. In a typical fuel cell, gaseous fuels and oxidants are fed to the electrodes where electrochemical reactions proceed to produce electricity. Hydrogen is the most common fuel utilized in fuel cells; development of hydrogen-generating processes has been widely implemented through catalytic reactions to support and commercialize the fuel-cell systems.[1–4]

Spinel oxides (AB_2O_4) with cations that occupy the tetrahedral and octahedral holes in a dense cubic packing of oxygen anions are one of the most important and interesting oxides owing to their wide variety of applications in sensors, electronics, and catalysts.[5,6] Spinel oxides have long played an important role in various catalytic applications, such as abatement of gaseous pollutants[7] and the water gas shift reaction.[8] Recently, copper-based spinels have been proposed as a reforming catalyst for hydrogen production from oxygenated hydrocarbons.[9,10] Steam reforming of dimethyl ether (DME SR: $CH_3OCH_3 + 3\,H_2O \rightarrow 6\,H_2 + 2\,CO_2$) has been regarded as an efficient hydrogen production method, and has attracted much attention. DME SR is a two-step reaction, namely, DME hydrolysis over acid catalysts, such as zeolite and alumina, to produce methanol (DME hydrolysis: $CH_3OCH_3 + H_2O \rightarrow 2\,CH_3OH$), and subsequent methanol steam reforming over copper-based catalysts to produce hydrogen (MeOH SR: $CH_3OH + H_2O \rightarrow 3\,H_2 + CO_2$).[11] The bifunctional composite containing acidic and copper sites is generally required for DME SR.

Development of composite catalysts for DME SR has been extensively studied in recent years. Various acid catalysts, such as H-ZSM5, H-mordenite, WO_3/ZrO_2, and γ-Al_2O_3, were proposed for DME hydrolysis, which is an equilibrium-limited reaction and is considered as the rate-determining step of overall DME SR.[10,12] Although the high activity of zeolites and WO_3/ZrO_2 for the hydrolysis was achieved at lower hydrolysis temperatures (limited to not exceed 300 °C) because of their high acid strength, considerable catalyst degradation was observed owing to coking. Alumina with a low acid strength led to less carbon formation; however, the reaction generally requires a high temperature (more than 300 °C) to effectively hydrolyze DME. Copper-based catalysts, including Cu/ZnO and Cu/ZnO/Al_2O_3, are generally used as methanol reforming catalysts. However, deactivation by sintering of copper could be significantly accelerated at temperatures above 300 °C.[13,14] In addition, the high temperatures bring about lower reformate quality, namely, a high yield of CO and CH_4. We recently found that copper ferrite spinel ($CuFe_2O_4$) was the most promising catalyst in MeOH SR at high temperatures among various copper-based spinels and Cu/ZnO/Al_2O_3, whereas γ-Al_2O_3 was highly stable in DME hydrolysis.[15] The $CuFe_2O_4$–Al_2O_3 composite catalyst showed excellent performance for DME SR over the temperature range 300–450 °C.[16,17] Nevertheless, copper-based spinels were still required to improve their thermal stability and catalytic activity in DME SR, leading to lower reaction temperatures and longer catalyst life. Herein, we propose a simple thermal treatment method to remarkably enhance the activity and durability of $CuFe_2O_4$–Al_2O_3 composite catalysts. Various thermal treatment conditions were systematically investigated to originate their roles on treated catalysts.

Figure 1 shows the effect of calcination temperature of the $CuFe_2O_4$–Al_2O_3 composite catalyst on DME conversion in DME SR. Over the as-prepared composite without thermal treatment, DME conversion increased with increasing temperatures from 275 to 375 °C. At 375 °C, the activity gradually decreased with time on stream of 55 h. The stability was improved slightly over the samples heat-treated at 350 and 500 °C, though their activity was not significantly improved. It turned out that the heat treatment at 700 and 800 °C was highly effective in enhancing the activity and stability of the composite catalyst, whereas calcination at 900 °C degraded the catalyst completely, possibly owing to deterioration of the acid sites on Al_2O_3. The lower activity of samples treated at 700 °C and 800 °C at a reforming temperature of 300 °C was

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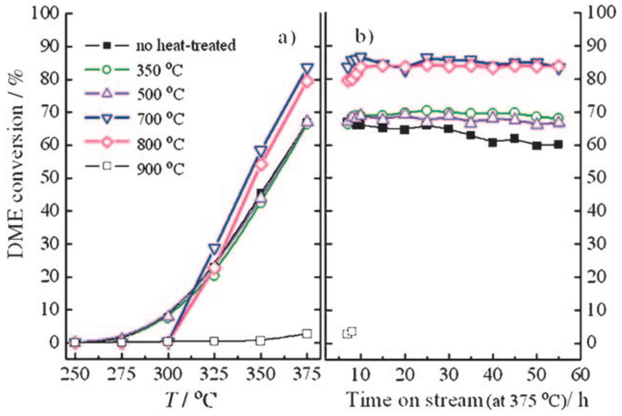


Figure 1. a) Temperature dependence of DME conversion in DME SR over composite catalysts heat-treated at various temperatures (0–900 °C), and b) time on stream at 375 °C. Reaction conditions: Steam-to-carbon ratio S/C = 2.5, Gas hourly space velocity (GHSV) = 9100 h^{-1}.

due to their lower reducibility after the heat treatment. The activation process (in situ reduction) of those treated catalysts requires longer times. With a pre-reduction process, those samples showed improved activity throughout the reaction temperature range studied. The heat-treated $CuFe_2O_4$–Al_2O_3 catalyst provided excellent stability in DME SR compared to composite catalysts of Cu/ZnO/Al_2O_3-Al_2O_3 (see Supporting Information), Cu/ZnO/Al_2O_3-ZSM5,[18] CuO/CeO_2-WO_3/ZrO_2,[12] and $CuFe_2O_4$-mordenite.[19]

Table 1: BET surface area and crystalline phases of catalyst samples before and after thermal treatment at various temperatures.

Catalyst	BET surface area [$m^2\,g^{-1}$]	Crystalline phase
$CuFe_2O_4$	0.5	$CuFe_2O_4$
Al_2O_3	137.5	γ-Al_2O_3 (or amorphous)
$CuFe_2O_4$–Al_2O_3	48.2	$CuFe_2O_4$, γ-Al_2O_3
$CuFe_2O_4$–Al_2O_3 treated at 350 °C	43.5	$CuFe_2O_4$, γ-Al_2O_3
treated at 500 °C	42.5	$CuFe_2O_4$, γ-Al_2O_3
treated at 700 °C	34.2	$CuFe_{1.5}Al_{0.5}O_4$, Fe_2O_3, $CuFe_2O_4$, γ-Al_2O_3
treated at 800 °C	23.9	$CuFe_{1.5}Al_{0.5}O_4$, Fe_2O_3, $CuFe_2O_4$, γ-Al_2O_3
treated at 900 °C	1.9	$CuFe_{1.5}Al_{0.5}O_4$

Brunauer–Emmett–Teller (BET) surface areas of $CuFe_2O_4$, Al_2O_3 (ALO8), and their composites are given in Table 1. Composite samples treated at 350 and 500 °C had a slightly lower BET surface area, whereas those treated at 700, 800, and 900 °C had significantly lower surface areas at 21, 45, and 96 %, respectively. The decrease in BET surface area was assigned to shrinkage of the alumina phase. Despite the decrease in BET surface area, the catalytic performance was improved remarkably. To clarify the effect of thermal treatment on the change of crystal property, XRD analysis was carried over samples treated at various temperatures (350–1000 °C). The crystalline phases detected by XRD are given in Table 1, and XRD patterns of treated samples are depicted in Figure 2. The crystalline phases of copper-iron spinel and alumina are the tetragonal $CuFe_2O_4$ spinel phase and γ-Al_2O_3, respectively; both phases remained stable after mechanical mixing. The XRD pattern did not change significantly if the calcination temperature was increased up to 500 °C. The crystalline phases were systematically transformed when the temperature increased from 700 to 1000 °C. The new phases appeared in the samples calcined at temperatures of 700 and 800 °C, which can be assigned to $CuFe_{1.5}Al_{0.5}O_4$ and Fe_2O_3, whereas $CuFe_2O_4$ and γ-Al_2O_3 coexisted in the samples. The new phase of $CuFe_{1.5}Al_{0.5}O_4$ spinel at 2θ of ca. 31°, 36°, 44°, 58°, and 64° was formed after partial solid-state reaction of $CuFe_2O_4$ and Al_2O_3 at their interface, whereas the peaks at 2θ of ca. 24°, 33°, and 49° are assigned to Fe_2O_3. An increase in the calcination temperature above 800 °C completely transformed $CuFe_2O_4$ and γ-Al_2O_3 to $CuFe_{1.5}Al_{0.5}O_4$. The new active phase of $CuFe_{1.5}Al_{0.5}O_4$ and the original phase of $CuFe_2O_4$ were considered to synergistically contribute to the enhanced reforming performance.

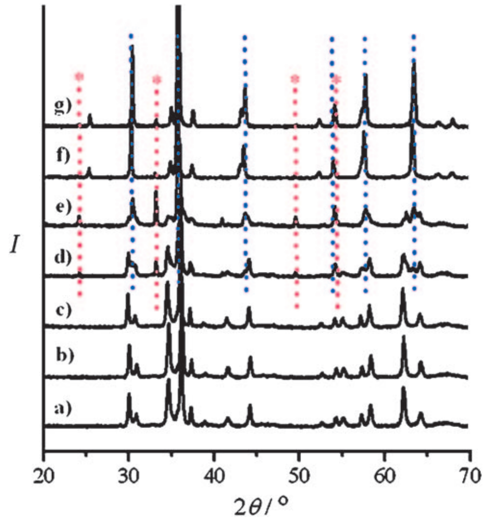
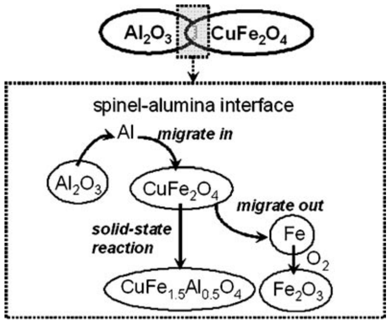


Figure 2. XRD patterns of $CuFe_2O_4$–Al_2O_3 composite catalysts heat-treated at various temperatures: a) as-prepared; b)–g) treated at b) 350, c) 500, d) 700, e) 800, f) 900, and g) 1000 °C. Peaks marked with * are due to Fe_2O_3, others marked are due to $CuFe_{1.5}Al_{0.5}O_4$.

The proposed mechanism of temperature-induced solid-state reaction of $CuFe_2O_4$ and γ-Al_2O_3 is shown in Scheme 1. The solid-state reaction did not occur at temperatures below 500 °C. In the temperature range of 700 to 800 °C, aluminum atoms migrated to the spinel structure and replaced iron atoms in the lattice to form CuFeAl spinel, and subsequently the migrated iron atoms formed hematite.

Increasing the temperature above 800 °C would expedite the solid-solid interaction between $CuFe_2O_4$ and γ-Al_2O_3, whereas the crystalline phase of remaining γ-Al_2O_3 would



Scheme 1. Proposed mechanism of formation of new active phases formed by thermal treatment of $CuFe_2O_4$–Al_2O_3 composites.

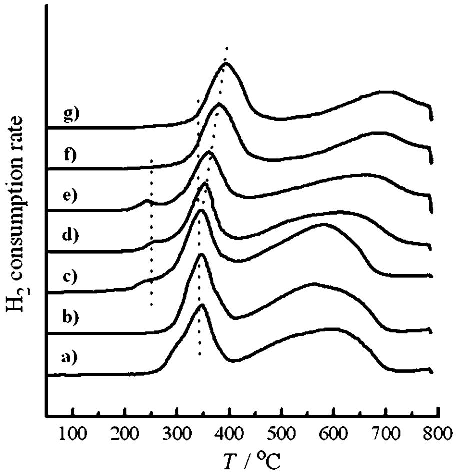


Figure 3. TPR patterns of $CuFe_2O_4$–Al_2O_3 composite catalysts heat-treated at various temperatures: a) as-prepared; b)–g) treated at b) 350, c) 500, d) 700, e) 800, f) 900, and g) 1000 °C.

change to the delta phase, leading to the significant decrease in the surface area.

It was confirmed that the promoting effect of the heat treatment was evident only for the samples calcined after mixing the spinel and alumina, but not for those mixing the spinel and alumina calcined separately at the same temperature. These results indicate that by the calcination process of the composite catalysts, a new active spinel phase was produced at the interface of the spinel and alumina, and that new copper species would contribute to the improvement in the catalytic activity for DME SR. The influence of heat-treatment time was also investigated. A time of 1 h was not long enough to enhance the activity and stability of the composite catalyst. The catalysts treated for 5, 10, and 20 h exhibited comparable performance with high activity and stability for 55 h.

The promoting effect of the heat treatment could also be obtained for the $CuFe_2O_4$–Al_2O_3 composite catalysts pre-reduced at 350 and 600 °C, or even a reacted catalyst. The composites reduced or reacted at 350 °C were composed of Cu, Fe_3O_4, and γ-Al_2O_3, whereas those reduced at 600 °C contained Cu, Fe, and γ-Al_2O_3. After thermal treatment at 700 to 800 °C, the catalytic activity was recovered to the same level as the freshly treated composites. XRD analysis revealed that all treated composites had identical XRD patterns (see Supporting Information).

Figure 3 shows temperature-programmed reduction (TPR) profiles of composite catalysts of $CuFe_2O_4$ and ALO8 treated at various temperatures of 0 to 1000 °C. For the as-prepared sample, the profile exhibited two distinct peaks with maxima at 330 and at 580 °C. The peaks appearing in the temperature range of 240 to 400 °C were ascribed to the reduction of $CuFe_2O_4$ to metallic copper and Fe_2O_3, and the subsequent reduction from Fe_2O_3 to Fe_3O_4. It is hard to define a clear boundary between the two reduction steps. The iron oxides continued to be reduced to metallic iron via FeO, ascertained from the peak appearing at a higher temperature. A small peak was present at circa 250 °C for the composites treated at 500, 700, and 800 °C. This peak would be attributed to reduction of the new phases, $CuFe_{1.5}Al_{0.5}O_4$ and/or Fe_2O_3. The peaks showing maxima at 330 and at 580 °C were shifted to the higher reduction temperature when the calcination temperature increased from 500 to 1000 °C, which suggests that the catalyst calcined at higher temperature contains more hardly-reducible species. Note that γ-alumina will not be reducible at temperatures below 800 °C.

The thermal treatment is effective to significantly enhance the reforming performance of $CuFe_2O_4$–Al_2O_3 composite. Interestingly, the treatment is also effective for the $CuFe_2O_4$-$Al(OH)_3$ composite, but not for $CuFe_2O_4$-ZSM5, $CuFe_2O_4$-mordenite, and $CuFe_2O_4$-TiO_2 composites. The results indicate that the alumina phase is a key species in the heat-treatment process for a mechanical mixture of copper spinel and alumina. Moreover, $Cu/ZnO/Al_2O_3$ catalysts with or without Al_2O_3 added are able to promote the reforming activity by thermal treatment as well (see Supporting Information). Work is being carried out to evaluate the thermal treatment effect on other catalyst systems.

Experimental Section

$CuFe_2O_4$ spinel was prepared by a citric acid complex method. A homogeneous aqueous solution of corresponding nitrates and citric acid was heated up to 90 °C to evaporate the water, and subsequently up to 300 °C to decompose the citric acid. The resultant powder was then calcined in air at 900 °C for 10 h. This spinel powder and alumina (ALO8, provided by the Catalysis Society of Japan) were physically mixed at a fixed-weight ratio (2:1), and then the $CuFe_2O_4$–Al_2O_3 composite catalyst was calcined again in air at a designed heat-treatment temperature for 10 h, unless otherwise stated. Catalytic activity was evaluated using a conventional flow reactor under atmospheric pressure. A mixture of DME and steam at a steam-to-carbon ratio (S/C) of 2.5 was supplied to a pre-heater at ca. 150 °C, and then to the catalyst bed at a designated reaction temperature. No pre-reduction treatment was done before reaction test, unless otherwise stated. Influent and effluent gas compositions were analyzed by online gas chromatographs equipped with an FID (Shimadzu, GC-9A) and a TCD (VARIAN, CP-4900). The steam in the reformate gas was trapped by a condenser at circa 3 °C before the gas analysis.

Catalyst specific surface areas were determined by the conventional BET method with N_2 adsorption using a BEL Japan Bellsorp-miniII instrument. Temperature-programmed reduction (TPR) was conducted using a CHEMBET-3000. The 25 mg catalyst sample was reduced in 5 % H_2/Ar at a flow rate of 30 mL min^{-1} (25 °C, 1 atm) in a heating process at a rate of 10°C$\,$min^{-1}. X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT-2200, equipped with $Cu_{K\alpha}$ radiation source.

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