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Nanodeposit of metallic copper in spinel oxides and its catalytic behavior in steam reforming of methanol and dimethyl ether

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Abstract – The spinel catalysts have been developed for hydrogen production from steam reforming (SR) of methanol (MeOH) and dimethyl ether (DME). The mophology, crystal structure, and surface species were characterized by means of SEM, TEM, the BET method, X-ray diffraction, and X-ray photoelectron spectroscopy. Well-crystallized spinel nanostructures of $CuFe_2O_4$ and $CuMn_2O_4$ were highly active and stable when employed in the reforming reactions. Copper nanodeposit formation in the matrix of oxides from the spinel structures has been observed during the reduction/reaction process. The spinel structure could be reconstruced by heat-treatment of the reduced spinels.

Hydrogen production from catalytic reforming of oxygenated hydrocarbons, e.g. methanol and dimethyl ether has been recognized as an efficient process for fuel cell application. Recently, copper-based spinel was proposed as a highly active catalyst for MeOH SR and DME SR [1,2]. In this study, MeOH SR and DME SR were investigated over Cu-based spinels, solid acids, and/or the mixture of them. The morphology, crystal property and surface species of the catalysts were investigated.

The CuFe₂O₄ and CuMn₂O₄ spinels were prepared via a gel-combustion method [2]. The powders obtained after the gel-combustion were calcined in air at 900 °C for 10 h. After H₂ reduction of the catalysts, MeOH SR tests were carried out over the spinels and DME SR were over the spinels mixed with γ -Al₂O₃.

The BET surface area of the spinels was so low at 0.4–0.7 m² g⁻¹, while that of γ -Al₂O₃ was relatively high at 137 m² g⁻¹. The CuFe₂O₄ and CuMn₂O₄ were reduced to Cu and Fe₃O₄ (CuFe₂O₄) or MnO (CuMn₂O₄), whilst the Cu crystallite size of the reduced spinels was comparable at 27 nm. The Cu¹⁺-rich surface was observed over the reduced spinels, whereas a commercial Cu/Zn/Al had the low proportion of Cu¹⁺ on the surface. The CuFe₂O₄ and CuMn₂O₄ showed high activity in MeOH and DME SR as compared with Cu/Zn/Al (Fig.1). The Cu¹⁺-rich surface was considered to correspond to the high reforming activity. The copper nanodeposit after reduction/reaction process was clearly demonstrated in Fig.2. Reformation of the spinel structure by heat treatment was confirmed by XRD analysis. The excellent performance and the reversibility of the spinel structure formation make it very promising for the actual application to fuel cells.

Catalyst	Crystalline phase (-)	Crystallite size ^b (nm)	Cu ¹⁺ / (Cu ¹⁺ +Cu ⁰) ^c (%)
CuFe ₂ O ₄	CuFe ₂ O ₄ (Cu, Fe ₃ O ₄) ^a	42 (27) ^a	70
CuMn ₂ O ₄	CuMn ₂ O ₄ , Cu _{1.5} Mn _{1.5} O ₄ (Cu, MnO)	31 (27)	65
Cu/Zn/Al	CuO, ZnO, Al ₂ O ₃ (Cu, ZnO, Al ₂ O ₃)	n/c (20)	10
γ -Al ₂ O ₃	not calculated (n/c)	n/c	-

Table 1: Crystal property and surface species of catalyst samples.

^a samples reduced in 10% H₂/N₂ at 350 °C for 3 h; ^b determined from XRD-line broadening; ^c determined from surface species detected by XPS (The amount of Cu^{2+} is negligible)





Figure 1: MeOH SR and DME SR over the catalysts. Reaction conditions: MeOH SR – GHSV = 24000 h^{-1} ; S/C = 1.2, DME SR – GHSV = 2000 h^{-1} ; S/C = 2.5.

Figure 2: (a) SEM image of CuFe₂O₄, (b) SEM image of the reduced CuFe₂O₄ and (c) TEM image of the reduced CuFe₂O₄. Reduction condition: 350 °C 3 h in 10% H₂/N₂.



[1] K. Faungnawakij, T. Fukunaga, R. Kikuchi, K. Eguchi, J. Catal. 256 (2008) 37-44.

[2] K. Faungnawakij, R. Kikuchi, N. Shimoda, T. Fukunaga, K. Eguchi, Angew. Chem. Int. Ed. 120 (2008) 9454-9457.