The In-situ XANES Study of Hydrogen Production from Methanol on $Cu_{30}Mn_{20}$/ZnO Catalyst in the PEMFC

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The methanol reformer is a good candidate as hydrogen generator for fuel cell. Among the methanol reforming reaction, partial oxidation of methanol (POM) can be catalyzed at lower temperature. The most common catalyst for partial oxidation of methanol (POM) is the Cu-based catalyst. However, a long start-up time (ts > 4 mins) and the less stability at high temperature would restrict the application of Cu-based catalysts.

The catalytic activities of CuMn/ZnO-C0.6 and CuMn/ZnO-C2 parepared by sol-gel method in the partial oxidation of methanol (POM) are shown in Fig. 1. The main products, hydrogen and carbon dioxide, and the minor product, carbon monoxide, were detected. Due to the exothermic property, the POM reaction can be initiated at a low reaction temperature. The methanol conversion (C_{MeOH}) in the catalytic POM reaction over CuMn/ZnO-C0.6 and CuMn/ZnO-C2 increased with temperature. The profiles presented that the catalytic activity of CuMn/ZnO-C0.6 was better than CuMn/ZnO-C2 catalyst during POM reaction. The main reason might excess citric acid release a lot of heat during clcaination and result in reduction of surface area. (Surface area test by BET). The larger surface area of catalyst provided more active sites on the surface of catalyst. The C_{MeOH} over the CuMn/ZnO-C0.6 catalyst was almost the same as the CuMn/ZnO-C2 catalyst at T > 275℃ but the CuMn/ZnO-C2 catalyst performed lower S_{H2} and higher S_{CO} than the CuMn/ZnO-C0.6 catalyst.

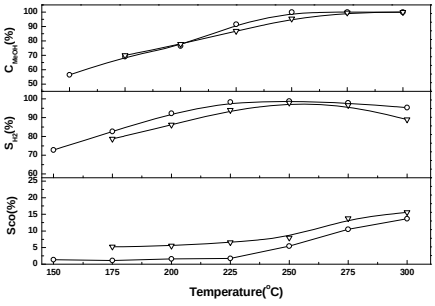

Fig. 1: The temperature profiles of catalytic performances in the POM reaction over CuMn/ZnO-C2 (▽) and CuMn/ZnO-C0.6 (○) catalysts.

The component fits of XANES spectra of reduced CuMn/ZnO-C0.6 catalyst (see Fig. 2 (a)) showed that more than 87% of Cu (II) (see Fig. 2 (b)) were reduced to Cu^0 or Cu^I during the reduction process. For POM reaction, notice that, Cu (I) and Cu (II) oxides constituted the major copper bulk phase species at 250℃ and the composition of the former compound was changed to 27% of Cu(0), 70 % of Cu (I) and 3 % of Cu (II) species (see Fig. 2 (c)). Under the POM reaction, it seems that Cu (0) and Cu (I) are the main activity sites on the surface of catalysts. Redox of Cu_2O probably was the rate-determining step for POM reactions over Cu-based catalysts. The larger surface area of catalyst might provide more active sites (Cu (0) and Cu (I)) on the surface of catalyst. Evidently, CuMn/ZnO-C0.6 catalysts could exhibit high activity at 250℃.

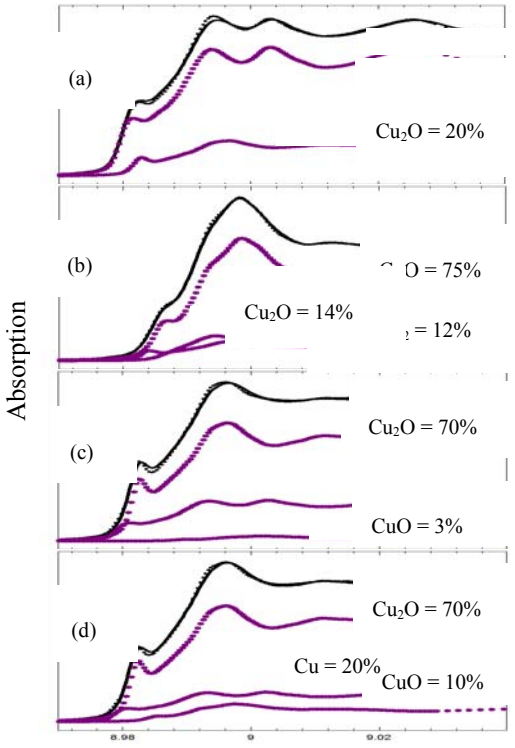

Fig. 2: The component fits of in-situ XANES spectra of (a) reduced CuMn/ZnO-C0.6 (b) oxidated CuMn/ZnO-C0.6, and during the catalytic POM reaction (c) CuMn/ZnO-C0.6 at 250℃ (d) CuMn/ZnO-C2 at 250 ℃.The dotted line denotes the best fits of XANES spectra.

The in-situ XANES spectra also presented that oxygen could rapid adsorb on the reduced copper and oxidized to Cu (I) (70%) and Cu (II) species (3%). However, more of active Cu (0) (70%) and Cu (I) species (27%) existed on the CuMn/ZnO-C0.6 might cause the higher catalytic activity at 250℃.