Liquid-phase partial oxidation of methane with hydrogen peroxide over Cu-Fe/ZSM-5

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With an upsurge of shale gas production, the direct conversion of methane into valuable chemical feedstocks has attracted increasing attention compared with conventional multi-step processes including syngas production through methane steam reforming. Methanol, which is commercially produced from syngas over $Cu/ZnO/Al_2O_3$ catalyst and an important feedstock for olefin and gasoline, can be synthesized via partial oxidation of methane at low temperatures in the presence of strong oxidants including hydrogen peroxide [1].

Hammond *et al.* reported that a direct oxidation of methane into methanol could be achieved over copper-promoted Fe/ZSM-5 catalysts with hydrogen peroxide with a high efficiency [2]. However, a systematic study on the catalyst composition has not been disclosed in detail. In this study, the effects of catalyst composition in the Cu-Fe/ZSM-5 catalyst system on the catalytic activity are probed.

Various catalysts with different compositions were prepared by solid-state ion-exchange (SSIE) method in which copper (Ⅱ) acetylacetonate (Sigma Aldrich) and iron (III) acetylacetonate (Sigma Aldrich) were mixed with NH_4-ZSM-5 (Zeolyst, CBV3024E) in a mortar for 20 min. Then, it was calcined in a static air at 550 ℃ for 3 h. The catalysts with different ion-exchange orders were also prepared by SSIE method, in which copper (II) acetylacetonate or iron (III) acetylacetonate was ion-exchanged with NH_4-ZSM-5 first and the other metal precursor was sequentially ion-exchanged, and then the catalyst was calcined. The catalytic reaction was carried out in a batch reactor with a total volume of 125 mL. 30 mL of 0.1 wt% H_2O_2 aqueous solution and 50 mg of catalyst were loaded and methane was pressurized at a pressure of 31 bar at room temperature. The slurry was stirred vigorously at 900 rpm at 70 ℃ for 1 h.

Fig. 1 shows that the product yield is strongly dependent on the catalyst composition. The highest product yield was obtained over Cu-Fe/ZSM-5 in which a mass ratio of Cu/Fe is 1. Besides catalyst composition, the ion-exchange sequence also appears to be important to affect the catalytic activity, as shown in Fig. 2. The product yield decreased in the following order: Cu-Fe/ZSM-5 > Fe/Cu/ZSM-5 > Cu/Fe/ZSM-5.

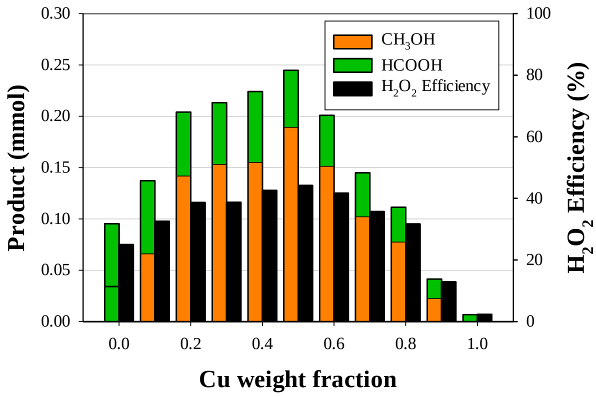

Fig.1. Product distribution during partial oxidation of methane with hydrogen peroxide over Cu-Fe/ZSM-5 catalysts with different mass fractions of Cu.

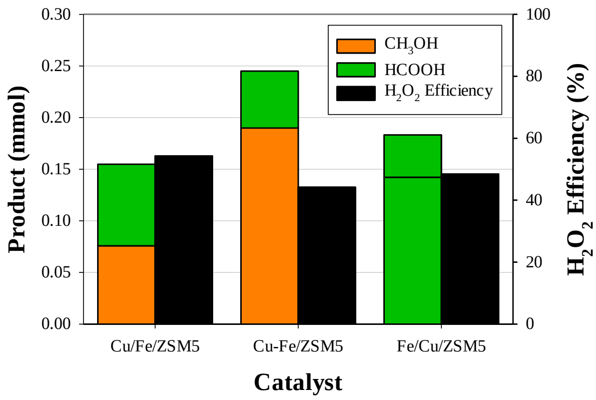

Fig. 2. Product distribution during partial oxidation of methane with hydrogen peroxide over Cu/Fe/ZSM-5, Cu-Fe/ZSM-5, and Fe/Cu/ZSM-5 catalysts.

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