

### The role of $ZrO_2$ in $Cu/ZnO/Al_2O_3$ catalysts in Methanol Synthesis

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The structure sensitivity of Cu based catalysts has been an important issue in methanol synthesis. It was claimed that the methanol synthesis was structure-insensitive by showing that methanol synthesis rates were linearly proportional to Cu surface areas using  $Cu/ZnO/Al_2O_3$ . On the other hand, the formate species and hydrogen spillover from Cu to ZnO and  $ZrO_2$  were also observed and it was suggested that the formate species were hydrogenated on ZnO and  $ZrO_2$ . The observation of hydrogen spillover shows that methanol synthesis can occur on  $ZrO_2$ . The Cu surface areas of  $Cu/ZnO/Al_2O_3$  catalysts were 10.6, 13.0, 22.6, 27.9, 30.6, 27.7 and 21.9  $m^2/g$ , depending on the aging time of 6, 12, 18, 24, 36, 42 and 72 h. The Methanol TOF (MeOH mmol/Cu- $m^2/h$ ) for seven catalysts was within  $2.67 \pm 0.27$  MeOH mmol/Cu- $m^2/h$ , indicating that methanol synthesis on  $Cu/ZnO/Al_2O_3$  catalysts is structure-insensitive. On the other hand, MeOH TOF increased with a  $ZrO_2$  addition to  $Cu/ZnO/Al_2O_3$ . This experimental results suggests that  $ZrO_2$  can afford active sites for methanol synthesis.