Controlling the O-Vacancy Formation and Performance of Au/ZnO Catalysts in CO_2 Reduction to Methanol by the ZnO Particle Size

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ABSTRACT: In a systematic approach to control and improve the performance of Au/ZnO catalysts in methanol synthesis from CO_2, we have studied the effect of varying the ZnO particle size. We show that with increasing ZnO particle size (22 – 103 nm), while keeping the Au loading / Au particle size constant, the activity for methanol formation passes through a maximum in a volcano-shaped relation, while the selectivity increases steadily. This is explained by a competition between structural SMSI effects and electronic metal-support interactions (EMSIs): *In-situ* FTIR during CO adsorption at -140°C revealed a significant decrease of the accessible Au surface area, most likely due to partial overgrowth of the Au NPs by a layer of ZnO_x during reaction, which is more pronounced for smaller ZnO particle sizes. EPR spectroscopy indicates the formation of O-vacancy defects during reaction, whose concentration increases with increasing ZnO particle size, modifies the EMSIs via charge transfer to the Au NPs. Optimization of the support particle size is proposed as an attractive approach for controlling the performance of supported catalysts.

KEYWORDS: CO_2 hydrogenation, green methanol, O-vacancy, selectivity control, support particle size effect

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