

Steering the Selectivity in CO₂ Reduction on Highly Active Ru/TiO₂ Catalysts: Support Particle Size Effects

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ABSTRACT: The methanation of CO₂ is a highly attractive process both for reducing CO₂ levels in the atmosphere and for the chemical storage of electric energy from renewable sources. Using mixed rutile-anatase supported Ru/TiO₂ catalysts with similar Ru particle size and loading, but different specific surface areas (SSA) of the support and, for comparison, an anatase supported catalyst with similar structural characteristic, we show that the selectivity of Ru/TiO₂ catalysts for CH₄ formation can be controlled by the particle size / specific surface area of the TiO₂ support, which affects the phase stability, structural properties, chemical composition of the supports and O-vacancy formation. The low-SSA catalysts ($\leq 120 \text{ m}^2\text{g}^{-1}$) were 100% selective for CH₄ formation both before and after a temperature programmed reaction (TPR) procedure, while the high-SSA catalysts ($225 \text{ m}^2\text{g}^{-1}$) changed from 100% selective for CH₄ formation before to 100% CO formation after the TPR procedure. The TPR induced changes in reaction behavior are paralleled by significant modifications in the structural, chemical, and electronic properties of the catalysts, including the phase composition of the support, as derived by a comprehensive (surface) characterization of the catalysts before and after TPR. Careful comparison between the changes in reaction behavior and the changes in the physical and chemical properties of the catalyst revealed that this change in reaction behavior most likely results from a TPR-induced increase in O-vacancy formation, which is more pronounced for the high-SSA catalysts. Finally, we discuss the potential of varying the support particle size for controlling the reaction behavior as a general strategy for tailoring catalyst properties.

Keywords: Chemical energy storage, CO₂ methanation, reverse water gas shift (RWGS) reaction, O-vacancy, phase composition, Ru/TiO₂

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