Encapsulation of Ru Nanoparticles: Modifying the Reactivity Toward CO and CO\textsubscript{2} Methanation on Highly Active Ru/TiO\textsubscript{2} Catalysts

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Aiming at a better understanding of the complex interactions between metal nanoparticles and support, which may range from purely electronic metal-support interactions (EMSIs) up to (additional) structural modifications associated with strong metal-support interactions (SMSIs), we have investigated the impact of a temperature programmed reduction treatment (T\textsubscript{max}: 350°C) of highly active Ru/TiO\textsubscript{2} catalysts on their physical properties and their CO / CO\textsubscript{2} methanation performance by kinetic and \textit{in situ} diffuse reflectance FTIR (DRIFTS) measurements, in combination with high resolution electron microscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XP spectra resolved a significant shift of the Ru 3d core levels to lower binding energies after the TPR treatment, which goes along with a significant red-shift of the CO\textsubscript{ad} related IR bands. This indicates an increase of the local charge density on the Ru nanoparticles (NPs), which we suggest to result from a charge transfer from O-vacancy defects to the Ru NPs. This results in changes in the electronic interactions between metal and support. Furthermore, CO adsorption measurements revealed a substantial decrease of the free Ru surface area after reaction at high temperature, which, supported also by microscopy and XPS measurements, is attributed to a structural modification, to a partial encapsulation of the Ru NPs by a TiO\textsubscript{x} layer. Possible reasons for the observed decrease / increase in CO/CO\textsubscript{2} methanation activity at rather low temperature (190°C) and mechanistic implications are discussed.

\textbf{Keywords:} Methanation, encapsulation of Ru nanoparticles, EMSI, SMSI, in situ DRIFTS, HAADF-STEM, CO adsorption, XPS.

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