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## Operando X-ray absorption spectroscopy (XAS) study of the selective CO methanation on Ru/TiO2 catalysts: TiO2 surface morphology effects

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Metal-support interactions in Ru/TiO2 catalysts have a decisive impact on their catalytic activity and selectivity for CO methanation. These effects and the catalytic performance of the catalysts were found to change upon varying the surface area of the support, which is not yet well understood. One approach to explain this change would be a change in the surface morphology of the TiO2 crystallites. In this study, we investigated Ru/TiO2 catalysts with different TiO2 morphologies for the selective CO methanation, employing anatase TiO2 nanocrystals with preferentially {001}, {100}, and {101} oriented facets. The results indicate a significant impact of the TiO2 surface morphology on the initial activation phase of the catalyst and its long-term stability. The Ru/TiO2-{001} catalyst reached its highest activity already in 5 min, then it started to continuously deactivate. For Ru/TiO2-{101} and Ru/TiO2-{100}, the activation was much slower, taking 150 and 300 min, respectively. Furthermore, these catalysts were very stable during >1000 min on stream. Based on operando XANES measurements, it could be demonstrated that under reaction condition ~ 95% of the Ru NPs on TiO2-{001} become metallic in 10 min, while it takes up to 80 min to reach the same state for TiO2-{100}. These observations indicate strong effects of the TiO2 surface morphology on the electronic properties of the supported Ru NPs.

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