

# X-ray absorption spectroscopy as a tool for in situ investigating sulfur poisoning and regeneration of ruthenium supported nanoparticles for dry biomass derived syngas methanation

J. Kuzmenko<sup>1</sup>, T. Schildhauer<sup>1</sup>, C. Coperet<sup>2</sup>, M. Nachttegaal<sup>1</sup>

<sup>1</sup>Paul Scherrer Institute, 5232, Villigen, Switzerland

<sup>2</sup>ETH, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland

**Background:** Sulfur-containing compounds, such as H<sub>2</sub>S, COS and C<sub>4</sub>H<sub>4</sub>S, are often present as impurities at part per million (ppm) level in syngas produced by the gasification of biomass and are one of the causes of the methanation catalysts deactivation. Hence sulfur-containing species should be either removed from the stream before reaching the catalyst by a separate gas cleaning step or a poisoned catalyst should be efficiently regenerated, the latter is preferred since it simplifies the process and reduces the total cost.<sup>1</sup>

**Methods:** In this work, the oxidative regeneration after sulfur poisoning of the supported ruthenium catalysts (Ru/Al<sub>2</sub>O<sub>3</sub> and Ru/SiO<sub>2</sub>) was investigated and improved using *in situ* X-ray absorption spectroscopy (XAS). *In situ* XAS measurement at Ru K-edge was employed to detect adsorption and removal of sulfur from Ru surface while XAS at S K-edge allowed determining the speciation of sulfur in a catalyst under relevant operating conditions.

**Results:** Firstly, Ru K-edge XAS data suggested that adsorbed sulfur can be removed from the Ru surface via oxidative treatment during several consecutive poisoning-regeneration cycles. In addition, particle sintering due to an oxidative treatment was detected by XAS and confirmed with TEM. Using XAS at the S K-edge, we have established that the formation of S<sup>+6</sup> (~ 2482 eV) species is taking place during oxidative regeneration of sulfur-poisoned catalyst both on alumina and to a smaller extent also on silica support. These sulfate-like species can be fully decomposed with H<sub>2</sub> from SiO<sub>2</sub> but only partially from Al<sub>2</sub>O<sub>3</sub>. Simultaneous measurement of the reactor outlet composition using a mass spectrometer (MS) showed a) higher SO<sub>2</sub> concentration during oxidative regeneration for Ru/SiO<sub>2</sub> and b) a decrease in methanation activity for both catalysts. However, Ru/Al<sub>2</sub>O<sub>3</sub> deactivated very quickly in the subsequent sulfur-free feed whereas Ru/SiO<sub>2</sub> remained stable suggesting reduction of the stored sulfates on the Al<sub>2</sub>O<sub>3</sub> support that subsequently re-poison the catalyst.<sup>2</sup> In addition, in a separate off-line test, Ru/SiO<sub>2</sub> showed a higher methane production per cycle after 14 poisoning-regeneration cycles.

**Conclusion:** Our data suggest that sulfur adsorbed on the Ru surface is removed by an oxidative regeneration as SO<sub>2</sub>, which interacts with the support forming sulfates. Using SiO<sub>2</sub> as a catalyst support improves the regeneration efficiency which could be attributed to its lower sulfur storage as compared to Al<sub>2</sub>O<sub>3</sub>. However, sintering of Ru on both supports still remains an issue lowering the activity with each oxidative regeneration.

## References

1. Rhyner, U. in Schildhauer, T.J. and Biollaz, S. (Eds), Synthetic Natural Gas from Coal, Dry Biomass, and Power-to-Gas Applications, Hoboken, New Jersey: John Wiley & Sons, pp. 43, 57, (2016)
2. König C. F. J., et al., Catal. Today, 229, 56 – 63, (2014).