

Rational design of sulfur-tolerant ruthenium catalysts for dry biomass derived CO methanation

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The process of methane production from dry biomass, called wood-to-Synthetic Natural Gas (SNG), consists of 4 main steps: biomass gasification, syngas cleaning to remove catalyst poisons such as H₂S, COS and C₄H₄S using “cold” gas cleaning technologies, methanation and upgrading to remove H₂O and CO₂.¹ To make SNG cost-competitive, the concept of integrating gas cleaning with methanation, which utilizes the ability of ruthenium-based catalysts to be regenerated under oxidizing atmosphere after sulfur poisoning is explored.²

However, a complete recovery of the catalytic activity after the regeneration cannot be achieved so far, probably because of a combination of several reasons. Firstly, Al₂O₃ support of the nanoparticles can “store” some of the sulfur poisons in the form of sulfate, which prevent efficient regeneration.² Secondly, TEM and XAS analysis evidences particle sintering upon recycling of originally 1 nm particle in Ru/Al₂O₃.

Here, we show that silica largely improve the regeneration process, because it is less prompt to sulfur storage (Fig. 1a). *Operando* XAS at the sulfur K-edge (Fig. 1b) and DRIFTS (Fig. 1c) showed that sulfate species formed on SiO₂ are unstable and could be removed by subsequent treatment with H₂. However, sintering still remains an issue. In addition, DRIFT spectroscopy revealed altered CO adsorption profile for the regenerated catalyst, implying that structural and/or electronic properties of the catalyst are changed after a poisoning-regeneration cycle.

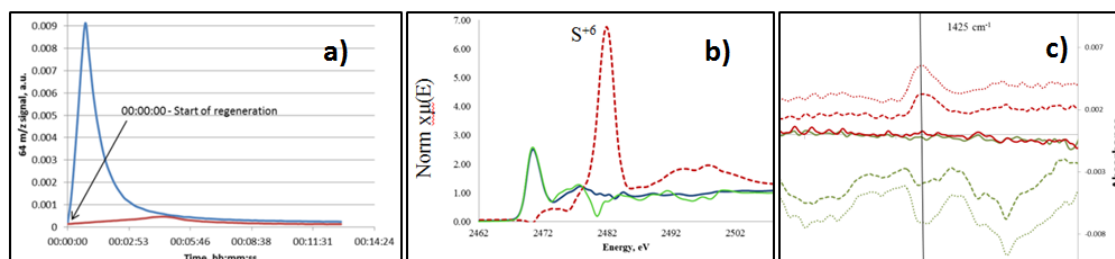


Figure 1: a) SO₂ detected at the reactor outlet for Ru/Al₂O₃ (red) and Ru/SiO₂ (blue) b) Sulfur K-edge XAS spectrum of Ru/SiO₂ catalyst taken during methanation with poisoning (blue), regeneration in 1% O₂ (red) and subsequent methanation (green); c) DRIFTS spectrum of Ru/SiO₂ showing sulfate (ca. 1425 cm⁻¹ band)⁴ formation (1% O₂ regeneration after catalyst poisoning, red) and decomposition (1% H₂, green) on SiO₂ surface

[1] C. F. J. König et al. in T. J. Schildhauer, S. M. A. Biollaz (Eds.), Synthetic Natural Gas from Coal, Dry Biomass, and Power-to-Gas Applications, John Wiley & Sons, **2016**.

[2] C. F. J. König et al., *Catalysis Today*, **2014**, 229, 56 – 63

[3] D. L. Trimm in G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, VCH Verlagsgesellschaft mbH, **1997**

[4] D. Bounechada, et al, *J. Phys. Chem. C*, **2014** pp. 29713–29723