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 H_2S, COS and C_4H_4S using "cold" gas cleaning technologies, methanation and upgrading to remove H_2O and CO_2.[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, Al_2O_3 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/Al_2O_3.

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 SiO_2 are unstable and could be removed by subsequent treatment with H_2. 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.

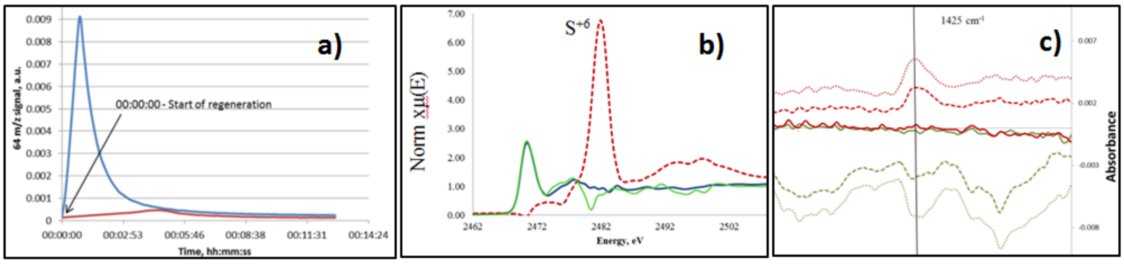

Figure 1: a) SO_2 detected at the reactor outlet for Ru/Al_2O_3 (red) and Ru/SiO_2 (blue) b) Sulfur K-edge XAS spectrum of Ru/SiO_2 catalyst taken during methanation with poisoning (blue), regeneration in 1% O_2 (red) and subsequent methanation (green); c) DRIFTS spectrum of Ru/SiO_2 showing sulfate (ca. 1425 cm^{-1} band)[4] formation (1% O_2 regeneration after catalyst poisoning, red) and decomposition (1% H_2, green) onSiO_2 surface

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