

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

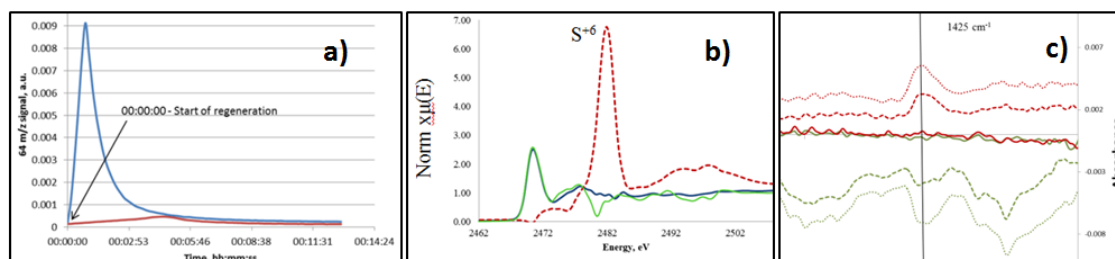
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The process of methane production from dry biomass, called wood-to-Synthetic Natural Gas (SNG), consists of 4 main steps: biomass gasification, syngas cleaning to remove catalyst poisons such as H<sub>2</sub>S, COS and C<sub>4</sub>H<sub>4</sub>S using “cold” gas cleaning technologies, methanation and upgrading to remove H<sub>2</sub>O and CO<sub>2</sub>.<sup>1</sup> 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.<sup>2</sup>

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<sub>2</sub>O<sub>3</sub> support of the nanoparticles can “store” some of the sulfur poisons in the form of sulfate, which prevent efficient regeneration.<sup>2</sup> Secondly, TEM and XAS analysis evidences particle sintering upon recycling of originally 1 nm particle in Ru/Al<sub>2</sub>O<sub>3</sub>.

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<sub>2</sub> are unstable and could be removed by subsequent treatment with H<sub>2</sub>. 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<sub>2</sub> detected at the reactor outlet for Ru/Al<sub>2</sub>O<sub>3</sub> (red) and Ru/SiO<sub>2</sub> (blue) b) Sulfur K-edge XAS spectrum of Ru/SiO<sub>2</sub> catalyst taken during methanation with poisoning (blue), regeneration in 1% O<sub>2</sub> (red) and subsequent methanation (green); c) DRIFTS spectrum of Ru/SiO<sub>2</sub> showing sulfate (ca. 1425 cm<sup>-1</sup> band)<sup>4</sup> formation (1% O<sub>2</sub> regeneration after catalyst poisoning, red) and decomposition (1% H<sub>2</sub>, green) on SiO<sub>2</sub> surface

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