

# Sulfur Poisoning and On-Stream Regeneration of a Ru/C Catalyst for Hydrothermal Biomass Reforming

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## Introduction

The catalytic supercritical water gasification (SCW-G) of wet biomass is a highly efficient way of producing methane-rich synthetic natural gas (SNG) from various types of biomass. However, catalyst deactivation due to poisoning and fouling (coking) severely limits the lifetime of catalysts used in this process, making the development of regeneration protocols imperative [1]. Particularly, catalyst poisoning mechanisms by sulfur, a major obstacle in catalytic biomass conversion, need to be understood in order to design sulfur resistant catalysts and regeneration procedures.

## Materials and Methods

The dynamic structural changes of a Ru/C catalyst (2 wt% Ru nanoparticles on coconut carbon) during the conversion of biomass model compounds to methane in supercritical water (400°C, 24.5 MPa) were studied in a continuous flow reactor. The structural analysis via in-situ EXAFS was combined with electronic structure calculations and isotope labeling in order to establish structure-reactivity relationships for both active and sulfur poisoned catalysts. The efficiency of on-stream regeneration of poisoned/deactivated catalysts, achieved by an oxidative treatment, was studied with in-situ XANES and isotope labeling. Results from these methods are accompanied by analysis of catalyst samples via electron microscopy, chemisorption and physisorption as well as MS and GC analysis of product gas samples.

## Results and Discussion

The active catalyst phase under supercritical conditions is metallic Ru<sup>0</sup>. Sulfur poisoning of the catalyst occurs due to surface adsorption of sulfur atoms instead of bulk sulfidation. For complete sulfur poisoning, a surface coverage of about 40% was determined experimentally by in-situ EXAFS, suggesting that only the active sites of the catalyst are blocked by sulfur whereas the less active parts of the Ru surface most likely remain free. Using a combination of DFT calculations and direct chemical probing via isotope labeling, the pathway of the methanation reaction under hydrothermal conditions was resolved. Under SCW conditions, methanation proceeds via direct hydrogenation of (hydro-) carbon adsorbates on the Ru surface instead of the classic methanation pathway via carbon monoxide and hydrogen. On an active catalyst, organic molecules are predominantly broken down and dehydrogenated to surface bound C *before full hydrogenation to methane occurs*. *Upon sulfur poisoning, stripping of hydrogen from the hydrocarbon adsorbates proceeds at a much lower rate and leads to the preferential formation of CH instead of C\*.* The change in the free energies of the (hydro-) carbon adsorbates on an S-poisoned Ru surface explains both the lower overall activity as well as the change in composition of isotope-labeled methane.

Through a liquid-phase oxidation of the S-poisoned catalyst at mild conditions, the original state of the catalyst was restored, both in terms of surface reaction pathways as well as catalyst structure. This treatment does not seem to lead to Ru particle sintering or corrosion of the carbon support. Our current efforts are concentrated on finding optimal regeneration conditions that guarantee long term stability of the catalyst.

## Significance

This work not only offers for the first time a mechanistic insight into hydrothermal biomass conversion –a new and challenging process –but also opens new pathways for performing and studying chemistry under conditions that go beyond the capabilities of most spectroscopic techniques and analytical setups. The presented results will enable a better understanding of reactions and catalysts under hydrothermal conditions and offer an incentive for the further development of biomass-to-SNG conversion processes.

## References

1. Elliott, D.C. Biofuels, Bioprod. Bioref. 2, 254 (2008)

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