



Methane synthesis and sulfur removal over a Ru catalyst probed in situ with high sensitivity X-ray absorption spectroscopy



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ABSTRACT

Catalytic conversion of natural feedstocks, such as wood, into synthetic natural gas (SNG) has much potential for sustainable energy supply. Sulfur, which is present in virtually all biomass – albeit in low quantities, needs to be removed from the gas to protect catalysts. Current technology using wet scrubbing to remove sulfur species between the gasification and the catalytic conversion decreases overall efficiency and therefore impedes commercialization. We show that sulfur removal from the gas stream with integrated methane synthesis at high temperatures is possible over many cycles, using supported Ru catalysts. The sensitivity of in situ X-ray absorption spectroscopy was improved by using a “modulated excitation” approach, showing that the catalyst is poisoned by sulfur, and it can be fully regenerated. The proposed mechanism for sulfur removal highlights the role of the support for sulfur poisoning and efficient regeneration. The integrated process of methanation and sulfur removal can make the biomass-to-SNG process significantly more efficient by replacing wet scrubbing.

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1. Introduction

Future energy demands require sustainable feedstocks to replace fossil fuels, such as coal, oil, or natural gas [1–3]. Biomass is a sustainable, CO₂-neutral feedstock, which can be converted to heat, electricity, or fuels. Gasification of dry biomass (such as wood), cleaning of the producer gas (i.e. the raw gas after gasification), and subsequent methanation generate synthetic natural gas (SNG) [4], which can be distributed in the existing gas grid and thus facilitate biomass logistics by eliminating the need for long transportation distances. Gas cleaning is required after the gasification step, since biomass, like coal, contains significant amounts of sulfur that form compounds such as H₂S, COS, or thiophenes upon gasification, which are known to poison the methanation catalyst downstream of the gasifier [5–9]. For the biomass-to-SNG process to be cost-effective and thus competitive, it needs to be energy efficient. Currently, gas cleaning is done after the high-temperature gasification step by low-temperature scrubbers, causing water condensation, while the gas needs to be heated to 300–400 °C afterward, for catalytic methanation [4]. Techno-economic analysis of a biomass-to-ethanol process indicated that current technology for gas cleaning (tar reforming, acid gas, and sulfur removal) represents 31% of the minimum selling price of the produced ethanol [10]. Improving the gas-cleaning efficiency is

therefore essential to make biomass-derived fuels competitive with other energy sources. High-temperature sulfur-cleaning processes work at a temperature between those of the gasifier (800 °C) and the methanation reactor (300–400 °C) and have been proposed to overcome energy inefficient scrubbing. Options are primary sulfur removal by adding a sorbent to the gasifier, and/or secondary cleaning, by a dedicated reactor between the gasifier and the methanation reactor [11–13]. So far, the proposed high-temperature gas-cleaning processes lead to complete removal of H₂S; however, it remains challenging to reduce the more refractory organic sulfur compounds, such as thiophene, benzothiophene, and dibenzothiophene, to the necessary sub-ppm level.

If the sulfur removal step is not complete or fully omitted, the challenge is to regenerate sulfur-poisoned methanation catalysts, of which Ni-based catalysts are mostly used commercially. Regeneration can be performed under reductive, oxidative, steam, or inert environment [14]. Oxidative regeneration, typically in air, removes large amounts of sulfur from the catalyst [15,16]. However, oxidation of Ni catalysts poisoned with sulfur forms NiSO₄, which is stable up to ~800 °C [17]. Regeneration at these temperatures is not only costly, but also leads to irreversible sintering of catalyst nanoparticles and therefore to loss of activity [14].

Ruthenium-based catalysts are also known to be good methanation catalysts [7]. In contrast to Ni, stability diagrams show that Ru-based catalysts do not form sulfates upon oxidation (see Fig. S1). This suggests that regeneration of sulfur-poisoned Ru catalysts by O₂ is feasible without the detrimental formation of

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sulfates. In this work, we successfully explored an integrated process, where the Ru-based catalyst is poisoned over time during methanation by the sulfur species in the producer gas from the gasifier and subsequently regenerated in an oxygen-containing gas stream. This could for example be realized in a swing-reactor design, or a dual fluidized bed, similar to chemical looping reactors [18]. Accordingly, the energetic and economic efficiency of the overall wood to SNG process is expected to be significantly improved by skipping the low-temperature gas-cleaning step.

Obtaining structure–performance relationships of a catalyst under operating conditions is of utmost importance for their knowledge-based development [19]. To probe the catalyst structure, time-resolved X-ray absorption spectroscopy (XAS) at the Ru K-edge was employed to decipher the structure of the active, the poisoned and the regenerated sites of the catalyst. Periodic, reproducible changes in the catalyst's state allow extracting the local structure of the sites/atoms that change structure upon excitation using the newly developed modulated excitation XAS method [20–22]. This method increases the sensitivity of XAS significantly, and it was extended for this study, to quantify minute structural changes of the catalyst during methanation, poisoning, and regeneration. The performance of the materials was monitored with online mass spectrometry.

2. Materials and methods

2.1. Catalyst

The Ru/Al₂O₃ (2 wt.% Ru) catalyst was prepared by wet impregnation of Ru(III) nitrosyl nitrate solution (Aldrich) and was calcined at 500 °C. Fig. S2 shows transmission electron microscopy (TEM) images of the fresh catalyst sample, indicating a particle size of 10–30 nm.

2.2. In situ experiments

In situ methanation, poisoning and regeneration experiments were conducted in a capillary reactor. The total cycle time was 1800 s for the non-isothermal experiments and 1200 s for the isothermal experiments, and the total flow rate was always kept at 20 ml min⁻¹. Prior to the methanation/poisoning/regeneration experiments, identical experiments were performed without sulfur and without sulfur and CO, respectively. The plug-flow micro-reactor (quartz capillary with 2.8 mm ID, 3.0 mm OD) was filled with ca. 15 mg of the catalyst, kept in place by plugs of quartz wool.

The reactor was heated with a hot air blower, and the temperature was measured with a thermocouple inside the reactor. All gas lines were sulfonert coated to prevent sulfur adsorption (Restek). The pressure in the reactor was kept at 0.5 bar overpressure by a pressure-controlling valve. The temperatures during the methanation and poisoning (T_m) and the temperature during regeneration (T_r) were varied between 300 °C and 550 °C or all kept at 430 °C. During heating, the catalyst was purged with He (quality 4.6). The gas composition at the inlet and the outlet of the reactor was measured with a quadrupole mass spectrometer (Extrel, USA). The gas composition at the reactor inlet was varied according to the following scheme:

1. 120 s H₂ (2.5%) in He.
2. 240 s H₂ (2.5%), CO (0.25%) in He.
3. 300 s H₂ (2.5%), CO (0.25%), H₂S (60 ppm), COS (6 ppm), C₄H₄S (12 ppm) (in Ar).
4. 120–360 s He.
5. 360–420 s O₂ (0.25%) in He).
6. 60–360 s He.

For the isothermal experiments, the He flushing was 120 s and 60 s before and after the 360 s long oxidation, respectively. For the experiments where the oxidation was performed at elevated temperatures for 420 s, the flushing duration was 360 s before and after oxidation to allow for heating and cooling. The mass spectrometer was not calibrated before the in situ XAS experiment. Accordingly, the results shown in Figs. 2 and 4 only have qualitative character.

2.3. Offline experiments

In addition to the in situ experiments, reactivity was studied offline (i.e., without X-ray beam) in a steel tube reactor with 1/4" outer diameter, which was sulfonert coated like the other gas lines (Restek). The sequence of gas exposure was similar to the one described above, only with longer exposure to sulfur, higher H₂, CO, and O₂ concentration, and N₂ added to O₂, to simulate regeneration with air or diluted air. The detailed conditions were as follows:

1. 120 s H₂ (33.3%) in He.
2. 300 s H₂ (33.3%), CO (6.7%) in He.
3. 840 s H₂ (33.3%), CO (6.7%), H₂S (60 ppm), COS (6 ppm), C₄H₄S (12 ppm) in Ar.
4. 180 s He flushing.
5. 180 s O₂ (5%), N₂ (17%) in He.
6. 180 s He flushing.

The catalyst was identical to the one used in the XAS experiments, of which ~75 mg was used. The temperature was set to 430 °C, and the pressure was 2 bar absolute during all offline experiments. For all offline experiments, the same mass spectrometer as for the in situ experiments was used. The mass spectrometer was calibrated by a two-point calibration. First, the background signal for all masses was measured when the gas lines were purged with He to determine the background signal. Subsequently, gas bottles with calibration gases were connected, and the mass spectrometer was calibrated with the known concentrations of the gases.

2.4. XAS setup

Ru K-edge quick XAS spectra were acquired at the SuperXAS beamline at the Swiss Light Source in transmission mode [23]. The X-ray beam from the bending magnet was monochromatized with a Si(1 1 1) channel-cut crystal in the QuickXAS monochromator [24]. The Si(1 1 1) crystal was rotated at a frequency of 0.2 Hz around the Ru K-edge (22,117 eV), and the signals of the ionization chambers and the angular encoder were sampled with 2 kHz. The edge energy was calibrated by a Ru foil after the sample.

2.5. Generalized method for the demodulation of data with more than 2 states and non-equidistant excitation

Modulated excitation spectroscopy describes a method where a sample (e.g. a catalyst) is periodically excited by an external stimulation, such as a change in gas atmosphere, and the state of the sample is monitored by a spectroscopic technique [25]. The measured data are then filtered with the known excitation frequency, removing contributions to the signal that either occur at lower frequencies (i.e. static species), or at higher frequencies (i.e. noise). This procedure is called demodulation or phase-sensitive detection, and it generates difference spectra between the different states of excitation with a significantly improved signal to noise ratio. Modulated excitation XAS was introduced as a method to increase sensitivity of XAS to small changes in a sample's state

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