Molecular-level Understanding of Support Effects on the Regenerability of Ru-based Catalysts in the Sulfur-poisoned Methanation Reaction

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Abstract

The production of synthetic natural gas – SNG – from dry biomass currently involves a costly and energy inefficient low temperature gas cleaning step, needed to remove various sulfur-containing poisons from syngas generated from wood gasification before the sulfur sensitive methanation step. Here we explore the use of Ru-based methanation catalysts in an alternative process, where the low temperature gas cleaning step is omitted and the syngas from the gasifier is directly used for methanation. In this process, methanation is carried out in the presence of organic and inorganic sulfur species and is followed by a periodic oxidative regeneration of the poisoned catalyst. *In situ* diffuse reflectance infra-red Fourier transform (DRIFTS) and Ru K-edge X-ray absorption (XAS) spectroscopy were employed to understand the deactivation mechanism of Ru nanoparticles on two different supports: Al₂O₃ and SiO₂. The efficiency of the regeneration is better when Ru nanoparticles are supported on SiO₂, on which only a small amount of unstable sulfate species is formed and Ru nanoparticles are shown to be somewhat more stable against sintering during the oxidative regeneration due to a “passivation” effect of adsorbed sulfur poison.

Keywords: Sulfur poisoning, Oxidative Regeneration, CO methanation, in situ X-ray absorption, in situ diffuse reflectance infra-red Fourier transform spectroscopy, support effect

Introduction

Synthetic natural gas (SNG) produced from dry biomass is a sustainable alternative to natural gas by lowering CO₂ emissions associated with SNG produced, in particular, from coal. Furthermore, using hydrogen, produced by electrolysis using renewable electricity, significantly increase the methane output while decreasing the environmental footprint of SNG production. The flexibility of the process is particularly tailored to balance the needs of the electricity grid when using intermittent renewable sources (e.g. wind, light).¹ The production of methane from dry biomass, called wood-to-SNG, consists of four main steps: i) biomass gasification, ii) syngas cleaning to remove catalyst poisons such as sulfur-containing compounds (H₂S, COS and thiophene), iii) methanation and iv) removal of H₂O and CO₂.¹ The largest wood-to-SNG producing plants utilize cold gas cleaning technologies: low-temperature scrubbers in the 1 MW_{SNG} process development unit (PDU) of the EU project BioSNG and complex combinations of catalytic steps and wet scrubbers in case of the 20 MW_{SNG}-

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GoBiGas plant in Sweden.¹ The overall process energy efficiency is low because cooling of syngas to ambient temperature is required between gasification ($\sim 850^\circ\text{C}$) and methanation ($\sim 400^\circ\text{C}$) steps. The reason of the preferred use of organic sorbents operating at low temperature in place of inorganic high temperature sorbents (e.g. ZnO) is that the latter mostly remove H_2S but not organic sulfur-containing poisons.¹ Alternatively, performing methanation without removing sulfur poisons could make the wood-to-SNG process significantly more efficient by strongly simplifying the gas cleaning step (process intensification). This approach would either require a sulfur resistant methanation catalyst (SRM), or a methanation catalyst that can be efficiently regenerated after sulfur poisoning. The former approach has been explored extensively in the past. However, all SRM catalysts, e.g. MoS_2 , have much lower activity than these based on supported metals and have been mostly applied to convert coal-derived gas with very high hydrogen partial pressures (>10 bars); their applicability to biomass is not economically viable given the relatively small capacities of biomass-based plants (few ten MW) compared to coal-based plants (several 100 MW to GW scale).¹ The alternative approach suggests a methanation catalyst that is periodically regenerated upon sulfur-poisoning. The most effective methods to regenerate the catalyst is by using an oxidizing atmosphere, i.e. diluted O_2 or air.^{2, 3} However, this method is not applicable to the widely used $\text{Ni}/\text{Al}_2\text{O}_3$ methanation catalyst since regenerating a sulfur poisoned $\text{Ni}/\text{Al}_2\text{O}_3$ with O_2 at an industrially relevant partial pressures range results in the formation of NiSO_4 , which can only be reduced back to the active Ni at high temperatures, leading to significant particle sintering and dramatic loss of activity.⁴

As an alternative to Ni-based catalysts, methanation in the presence of sulfur poisons with $\text{Ru}/\text{Al}_2\text{O}_3$ has been previously explored,⁴ because ruthenium display high activity in CO methanation and is not expected to form bulk RuSO_4 even at a high O_2 partial pressure according to thermodynamic phase stability diagrams.⁴ However, it was shown that SO_2 produced during oxidative treatment generated $\text{Al}_2(\text{SO}_4)_3$ species, which were shown to partially reduce under methanation conditions and re-poison the Ru methanation catalyst.⁴ In this study, we explore the corresponding silica-supported Ru-catalyst and compare it with the alumina-supported analogue, paying specific attention to deactivation and activation mechanisms upon methanation/poisoning-regeneration cycles by using a combination of characterization methods: *in situ* diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS), *ex situ* TEM/XRD and *in situ* X-ray absorption spectroscopy (XAS) at the Ru K-edge.

2. Experimental

2.1. Catalyst preparation and characterization

SiO₂ (Aerosil Degussa, 200 m².g⁻¹) and Al₂O₃ (Puralox SASOL, 140 m².g⁻¹), used as catalyst supports, were compacted by adding distilled water, dried in an oven at 120 °C for 2 days, sieved to select particles in the size fraction of 250-400 µm and calcined at 500 °C in a flow of synthetic air for 2 h to remove any organic impurities. An aqueous solution of [Ru(NO)(NO₃)₃] was added dropwise to the pre-treated support while stirring. Impregnated samples were dried in a flow of synthetic air at 120 °C (1 °C/min) for 6h and subsequently reduced at 500 °C (0.5 °C/min) in a flow of pure hydrogen. Then, the samples were cooled down in hydrogen to ambient temperature and brought in contact with air.⁷

Ruthenium content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). Ru dispersion was determined by H₂ and CO chemisorption carried out on a Belsorb-Max device (BEL Japan). The measurements were carried out at 25 °C after pretreatment at 10⁻⁶ mbar and 350 °C (ramp rate 1 °C/min) for 3 h (more details in ESI). Transmission electron microscopy of selected samples was performed on a Tecnai F30 ST with 300 kV acceleration voltages. After exposure to ambient air, the as-prepared samples were placed on a lacey carbon grid. The particle size distribution was estimated by statistical analysis on ca. 100 particles. Powder X-ray diffraction (XRD) patterns in the 2θ range from 30° to 60° were recorded on a Bruker D8 Advance AXS diffractometer with Cu Kα radiation. Match! software with ICSD/Retrieve database (release 1993-2002) was used for reference diffraction patterns. The crystallite size was estimated using the Scherrer equation, with shape factor taken as 0.9, assuming particles are spherical (eq. 1).

$$D = \frac{0.9\lambda}{FWHM(2\theta) \cos\theta} \quad (1)$$

2.2. Catalytic testing

The catalysts (16 mg Ru/SiO₂ and 24 mg Ru/Al₂O₃) were placed in a quartz tube (6 mm outer diameter, 2 mm wall thickness) between two quartz wool plugs, heated to 430°C at 10°C/min under Ar, and subsequently reduced in 10 vol% H₂ in Ar for 10 minutes. After pre-treatment, the catalyst methanation activity was tested during fourteen poisoning-regeneration cycles with the following gas sequence: methanation with poisoning (2 vol% CO/10 vol% H₂/48 ppm H₂S/10 ppm COS/5 ppm C₄H₄S) for 1200 seconds, Ar flushing for 180 seconds, oxidative regeneration (1 vol% O₂) for 600 seconds. These steps were followed by three sulfur-free cycles consisting of the following sequence: methanation without poisoning (2 vol% CO/10 vol% H₂) for 1200 seconds, Ar flushing for 180 seconds, oxidative regeneration (1 vol% O₂) for 600 seconds. For comparison, also completely sulfur-free methanation-regeneration cycles were conducted where methanation consisted of feeding only 2 vol% CO/10 vol% H₂ for 1200 seconds. The total flow rate was held constant at 25 mL/min. The gases were dosed with mass flow meters (Bronkhorst) and analyzed with a quadrupole mass spectrometer (Max 300-LG, Extrel). All stainless steel tubes outside the reactor were coated with quartz to minimize sulfur adsorption (Restek).

2.3 *In situ* Ru K-edge XAS

Ru K-edge quick XAS spectra were acquired in transmission mode at the SuperXAS beamline at the Swiss Light Source which operated at 2.4 GeV and 400 mA. The polychromatic X-ray beam from a 2.9 Tesla bending magnet was collimated using a Pt-coated collimating mirror at 2.5 mrad and

monochromatized with a Si (111) channel-cut crystal monochromator. The beam was subsequently focused with a Pt coated toroidal mirror to a spot size of 0.5 by 0.1 mm². The Si (111) channel crystal was rotated at a frequency of 0.5 Hz around the Ru K-edge (22117 eV) resulting in one spectrum per second, and the signals of the 15 cm long ionization chambers (filled with 2 bars of a 1:1 Ar/N₂ mixture) and the angular encoder were sampled with 2 MHz.¹¹ Each spectrum measured was aligned to a Ru mesh that was measured simultaneously between the second and third ionization chamber.

Ru/Al₂O₃ and Ru/SiO₂ (ca. 13 mg) were placed in a 2.8 mm inner diameter (0.1 mm wall thickness) quartz capillary between two quartz wool plugs. The loaded catalyst was heated with a hot air blower at 10°C/min rate under He and subsequently reduced in 10 vol% H₂ in He for 10 minutes. The methanation reaction was carried out at 430°C as measured by the thermocouple at the start of the experiment at the beginning of the catalyst bed. Each poisoning-regeneration cycle consisted of the following gas sequence: reduction (1.2 vol% H₂), methanation (2 vol% H₂, 0.4% CO) for 600 seconds, methanation with poisoning (2 vol% H₂, 0.4 vol% CO, 50 ppm H₂S) for 1500 seconds and oxidative regeneration (1 vol% O₂) for 600 seconds. Eight poisoning-regeneration cycles in total were performed with each catalyst. The total flow rate was kept constant at 25 mL/min. In a separate experiment, both catalysts were poisoned for a longer period (over 35 minutes) to more clearly observe spectroscopic evidence for sulfur adsorption. EXAFS spectra were background corrected and normalized using Athena of the iFEffit software suite^{29, 30}, converted to the photo-electron wave vector by setting the inflection point of the absorption edge to 22117 eV and subsequently Fourier transforming the resulting spectra from 2.8 to 15.8 Å⁻¹, EXAFS spectra were fitted with using the Artemis program from the iFEffit software suite and using the structures of Ru, RuO₂ and RuS₂.^{33, 37, 38} The amplitude reduction factor was set to 0.76, as determined by fitting a Ru metal foil spectrum.

2.4 *In situ* DRIFTS

DRIFTS experiments were performed on a Bruker Vertex 70 spectrometer equipped with a liquid nitrogen cooled HgCdTe detector and a Praying Mantis mirror unit (Harrick). Spectra were acquired in the 4000 to 600 cm⁻¹ range at 4 cm⁻¹ resolution and 80 kHz scanner velocity. The catalysts (ca. 7 mg) were diluted with a natural diamond powder (40-60 µm, Alfa Aesar) at a diamond-to-catalyst weight ratio of 4:1 in order to reduce the absorption of infra-red light in the region below 1650 cm⁻¹ (due to bulk Si-O stretching). 50 mg of this mixture were placed on top of 150 mg of the diamond powder in the sample cup of the homemade *in situ* spectroscopy cell based on the commercial Harrick cell but with reduced dead volume¹⁰ and equipped with a flat CaF₂ window and a thermocouple. The cell was SilcoTek coated to prevent H₂S adsorption. After heating the sample to 400°C (10°C/min ramp rate) in Ar, the catalyst was exposed to the following gas pulses sequence: reduction (1.2 vol% H₂), methanation (0.4 vol% CO, 1.2 vol% H₂), methanation with sulfur poisons (0.4 vol% CO, 1.2 vol% H₂, 24 ppm H₂S) and oxidative regeneration (0.5-5 vol% O₂). Argon was used as a diluent, total gas flow was 50 mL/min. All spectra are plotted in absorbance units. The spectrum collected in argon immediately before exposing the catalyst to the reactive gas mix was taken as background spectrum and subtracted from the spectra obtained in the reactive feed.

3. Results and Discussion

Al₂O₃ and SiO₂ supported Ru catalysts with Ru weight loading of 2.3 and 3.6 wt % (ICP-OES) respectively were prepared by incipient wetness impregnation. Table 1 presents the results of H₂ and CO chemisorption experiments and TEM measurements (Figure 1) and shows that Ru particles on Al₂O₃ have a smaller average particle size (ca. 1 nm) compared to Ru particles supported on SiO₂ (2.5 nm). Overall, the nanoparticle sizes determined from H₂ and CO chemisorption and TEM are in good

agreement. However, smaller nanoparticles were formed on Al_2O_3 , preventing to obtain an accurate particle size distribution.

Catalyst	Chemisorption		TEM
	Dispersion	Particle size, nm	
Ru/ Al_2O_3	0.93^a	0.95^a	< 1 nm
	0.89^b	1.0^b	
Ru/ SiO_2	0.39^a	2.6^a	2.5 ± 0.8
	0.39^b	2.6^b	

Table 1: Particle size for Ru/ Al_2O_3 and Ru/ SiO_2

^a H_2 chemisorption ($2\text{H}/\text{Ru}$ stoichiometry¹²), ^b CO chemisorption ($1.5\text{CO}/\text{Ru}$ stoichiometry¹²). All adsorption isotherms and fitted Langmuir adsorption isotherm parameters can be found in ESI (Table S1 and Figures S1 and S2).

Figure 1: Ru/ Al_2O_3 (left) and Ru/ SiO_2 (right) TEM images, the inset shows a particle size histogram

To test the methanation activity recovery after each methanation-regeneration cycle under industrially relevant conditions, methanation was carried out with a mixture of organic and inorganic sulfur species. Fourteen poisoning-regeneration cycles were performed on both catalysts, followed by three subsequent sulfur-free methanation-regeneration cycles to test whether or not the full initial methanation activity can be recovered in the absence of sulfur species in the feed. In a separate experiment, methanation-regeneration cycles were also conducted under completely sulfur-free conditions. The integrated CH_4 output per cycle as detected by MS under sulfur-rich and sulfur-free conditions is summarized in Figure 2.

Initially, in the sulfur-free feed, both catalysts showed equilibrium CO conversion ($>99\%$) at 430°C (a value set to one in Figure 2 for ease of comparison). During the first poisoning cycle, the CH_4 production for Ru/ SiO_2 reaches ca. 85% of this observed under sulfur-free condition, while there is no difference for Ru/ Al_2O_3 (open vs closed symbols for cycle 1 in Figure 2). This difference can be explained by: i) the higher dispersion of Ru in Ru/ Al_2O_3 (see Table 1) and ii) the Al_2O_3 support can adsorb significant amounts of H_2S ³⁴ thereby protecting Ru nanoparticles further downstream from poisoning in the initial cycles. Both would lead to delaying the observation of sulfur poisoning that will eventually happen.

Figure 2: Relative CH₄ output per cycle: during poisoning-regeneration (■ - Ru/SiO₂, ◆ - Ru/Al₂O₃), and completely sulfur-free methanation-regeneration (□ - Ru/SiO₂, ◇ - Ru/Al₂O₃). Figures S3-8 show selected mass spectrometer signals for the 1st, 14th and 17th cycle of the poisoning-regeneration experiment.

In contrast, after 14 poisoning-regeneration cycle, Ru/SiO₂ is more active (see also the MS trace plots in Figures S4 and S7) and shows better catalytic recovery when operating under sulfur-free conditions (Cycles 15-17, see also MS trace plots in Figures S5 and S8). Noteworthy, with Ru/SiO₂, the methanation activity is higher after 14 poisoning-regeneration cycles followed by sulfur free conditions than upon purely sulfur-free methanation-regeneration (Figure 2, open vs. closed squares). For Ru/Al₂O₃ nanoparticles, 17 sulfur-free methanation-regeneration cycles did not result in any observable deactivation (Figure 2, open diamonds).

We thus investigated in more details the possible cause of deactivation for the two methanation catalysts: i.e. incomplete sulfur removal by oxidative treatment, “carry-over” of sulfur from the support to Ru metal and particle sintering. Figure 3 shows the relative amount of SO₂ ($m/z=64$) released during the second poisoning-regeneration cycle for both catalysts. For Ru/Al₂O₃, no SO₂ could be detected at the reactor outlet, while a large SO₂ peak during oxidative regeneration (labeled 2) and a smaller peak during methanation (labeled 1) are observed with Ru/SiO₂. Peak 2 is most likely the result of the surface oxidation of Ru-S_x by O₂ giving SO₂ and RuO₂, while peak 1 could be due to the reduction of a SO₄²⁻ species during the reducing conditions of methanation, formed on the catalyst support during oxidative regeneration or SO₂ desorption. Overall, during the oxidative regeneration cycle, more sulfur, in the form of SO₂, is released in the case of Ru/SiO₂ than Ru/Al₂O₃.

Figure 3: SO₂ MS signal during the oxidative stage of the 2nd poisoning-regeneration cycle for Ru/SiO₂ and Ru/Al₂O₃

Diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS) was then employed to investigate the speciation at 430°C of sulfur *in situ* on both supported Ru catalysts. Figure 4a shows DRIFTS spectra recorded *in situ* at several times during oxidative regeneration of H₂S poisoned Ru/Al₂O₃ catalyst (treated for 25 mins with 0.4 vol% CO, 1.2 vol% H₂, 24 ppm H₂S poisoning mix). Figure 4b shows the spectra recorded during subsequent H₂ treatment of this oxidatively regenerated catalyst. A growth of various S-containing species is observed when a H₂S-poisoned Ru/Al₂O₃ is exposed to diluted O₂, which corresponds to surface sulfate (1391 cm⁻¹),^{27, 28} sulfite (1346 and 1068 cm⁻¹)^{25, 27} and to a smaller extent bulk sulfate (1200 cm⁻¹)^{25, 26}; the deconvolution is shown in Figure S9 and Table S2. The subsequent treatment in H₂ leads to a conversion of these species (Figure 4b): the surface sulfite/adsorbed SO₂ is fully removed (1345 cm⁻¹, 998 cm⁻¹), while the surface sulfate (1402 cm⁻¹) are only partially removed (deconvolution shown in Figure S10 and Table S3). For Ru/SiO₂ (Figure 4c), the formation of surface sulfate occurred (1425 cm⁻¹)^{24, 29} on SiO₂ only after a prolonged exposure to O₂ at a concentration (5%) higher than used for the oxidative regeneration treatment of the catalytic tests (1%, Figure 2). Moreover, H₂ treatment decomposes all generated sulfate species during methanation, most likely by reducing it to gaseous SO₂. Overall, DRIFTS data show that deactivation is in part due to Ru metal “re-poisoning” because slow reduction of the sulfate present on the support probably yields H₂S that can poison Ru/Al₂O₃ as previously hypothesized⁴ and now demonstrated. This “re-poisoning” is less likely to occur on Ru/SiO₂ since sulfate species on SiO₂ are removed easily as observed by DRIFTS.

Figure 4: *In situ* DRIFTS spectrum of Ru/Al₂O₃ a) during oxidative regeneration and b) the subsequent reduction, c) Ru/SiO₂ during oxidative regeneration (top) and the subsequent reduction (bottom)

In addition, monitoring *in situ* CO adsorption provide further information about the availability of Ru surface sites for methanation. CO adsorption in the presence of hydrogen (CO:H₂=1:5) on a pre-reduced Ru/SiO₂ catalyst show that oxidation and subsequent reduction of the catalyst did not affect the CO adsorption region significantly (“Fresh” vs. “After oxidation” in Figure 5), while H₂S addition leads to a complete disappearance of the CO adsorption band (labelled “Poisoned” in Figure 5). Ru/SiO₂ after methanation in the presence of sulfur-poison and oxidative regeneration alone only shows a small fraction of the original CO adsorption band (“Regenerated” in Figure 5), indicating that S species blocks Ru active sites even after an oxidizing treatment, which is likely one of the causes for deactivation.

Figure 5: *In situ* DRIFTS spectrum of fresh, oxidized, poisoned and regenerated Ru/SiO₂ during methanation (CO:H₂=1:5).

Further examining the catalysts by XRD and TEM (Figure 6) shows an increase in Ru particle size for both catalysts after both poisoning-regeneration and sulfur free methanation-regeneration, i.e. in presence and absence of sulfur species, respectively. For Ru/Al₂O₃ sintering took place to about the same extent (Figures 6e vs 6f) whether or not the catalyst was exposed to cycles that include sulfur poisoning. The absence of decreased activity (decrease conversion shown in Figure 2) is most likely due to the catalyst test is run at equilibrium conversion, thus prevented the observation of deactivation. For Ru/SiO₂, the increase of particle size was much smaller upon cycling with vs. without sulfur poisoning (Figures 6b vs 6c), suggesting that adsorption of sulfur onto the surface of nanoparticles could make Ru nanoparticles more resistant towards sintering under oxidizing atmosphere. In fact, Ru/SiO₂ exposed to only methanation-regeneration deactivated more than Ru/Al₂O₃ (Figure 2), even if both catalysts have similar particle size according to XRD (ca. 28 nm,

Figure 6). However, it is likely that, after methanation-regeneration, small and very active Ru particles on Ru/Al₂O₃, which are not detected by XRD, are present and efficiently catalyze methane production.

Figure 6: Left: XRD pattern of a) fresh Ru/SiO₂; b) Ru/SiO₂ after poisoning-regeneration; c) Ru/SiO₂ after completely sulfur-free methanation-regeneration; d) fresh Ru/Al₂O₃; e) Ru/Al₂O₃ after poisoning-regeneration; f) Ru/Al₂O₃ after completely sulfur-free methanation-regeneration. Top right: TEM of e), bottom right: TEM of b). The Scherrer equation was used to estimate the particle size.

To understand why sintering is not decreased upon exposure of Ru/Al₂O₃ to cycles with sulfur poisoning in contrast to Ru/SiO₂, we further studied these catalysts by X-ray absorption spectroscopy (XAS) at the Ru K-edge. The Fourier Transformed EXAFS spectra for Ru/SiO₂ and Ru/Al₂O₃ catalysts after being treated under H₂/CO/50 ppm H₂S for 35 minutes are shown in Figure 7, and Table 2 presents the best fit structural parameters for both catalysts under H₂/CO and after H₂/CO/50 ppm H₂S for 35 minutes. These fitted structures show that there is no bulk sulfide formation, suggesting that sulfur adsorption takes place mostly on the surface of the nanoparticles, since the Ru-Ru coordination number and bond distance is the same before and after 35-minutes of S-poisoning. Note that the fit include Ru-S neighbors, whose distance for both catalysts is slightly smaller than for bulk Ru-S (2.35 Å).³³ The proposed formation of surface rather than bulk sulfur adsorption is consistent with previously reported data obtained under similar conditions.^{19, 36} The additional small peak at 3.5 Å observed for Ru/SiO₂ can be attributed to the second shell Ru-Ru scattering in both Ru metal and RuS₂ and thus cannot be used to distinguish surface sulfur adsorption from bulk sulfide formation. After oxidative regeneration, mostly Ru-O and hardly any Ru-Ru contribution at ca. 2.7 Å can be seen for both catalysts (Figures S11-12). If only surface and no bulk sulfur adsorption takes place as suggested above, one can estimate a sulfur surface coverage from the fitted Ru-S coordination number.³⁶ Since the bulk RuS₂ standard has a Ru-S coordination number of 6, the Ru-S coordination numbers of 1.2 and 0.6 for Ru/SiO₂ and Ru/Al₂O₃ respectively allow an average catalyst composition to be evaluated, i.e. RuS_{0.4} and RuS_{0.2}, respectively. Taking into account this stoichiometry and the dispersion of ca. 40 (Ru/SiO₂) and 90% (Ru/Al₂O₃) obtained from H₂ and CO chemisorption measurements (see Table 1), a sulfur surface coverage is around 50 and 20 per cent for Ru/SiO₂ and Ru/Al₂O₃ respectively.³⁶ From the XAS data we propose that adsorption of sulfur on the surface of Ru nanoparticles could be responsible for stabilization of Ru nanoparticles under oxidative condition, explaining why smaller particles are observed when Ru/SiO₂ is exposed to poisoning-regeneration cycles compared to when it is exposed to sulfur-free methanation-regeneration cycles (Figure 6). The same effect is not observed for Ru/Al₂O₃ most likely because sulfur coverage of

Ru/Al₂O₃ after being exposed to the same amount of S poisons is smaller than for Ru/SiO₂. As mentioned before, this is likely due to H₂S adsorption on Al₂O₃³⁴, while it is not the case on SiO₂.

Figure 7: Data (solid line) and fit (dashed) of Fourier Transform magnitude and imaginary part of the Ru/SiO₂ (top) and Ru/Al₂O₃ (bottom) after 35-minute methanation with poisoning

Catalyst	Gas composition	Ru-Ru			Ru-S			ΔE_0 , eV	R-factor
		N	σ^2 , Å ²	R, Å	N	σ^2 , Å ²	R, Å		
Ru/SiO ₂	H ₂ +CO	8.1 ± 0.6	0.0095 ± 0.0007	2.64 ± 0.006				1.4 ± 0.6	0.016
	H ₂ +CO+H ₂ S	8.3 ± 0.7	0.0097 ± 0.0008	2.65 ± 0.005	1.2 ± 0.4	0.003 ± 0.004	2.29 ± 0.021	1.9 ± 0.6	0.007
Ru/Al ₂ O ₃	H ₂ +CO	6.6 ± 0.4	0.0099 ± 0.0007	2.63 ± 0.005				2.4 ± 0.5	0.016
	H ₂ +CO+H ₂ S	6.3 ± 0.3	0.0096 ± 0.0004	2.63 ± 0.003	0.6 ± 0.2	0.004 ± 0.003	2.30 ± 0.013	1.2 ± 0.3	0.004

Table 2: Structural parameters obtained from best fitting the FT EXAFS spectra of Ru/SiO₂ and Ru/Al₂O₃ under H₂/CO and after H₂/CO/50 ppm H₂S for 35 minutes. N – number of nearest neighbors, σ^2 - pseudo Debye-Waller factor, R – bond distance, ΔE_0 – edge energy correction, R-factor indicates the degree of mismatch between the fit and the data. Amplitude reduction factor set to 0.76.

In situ Ru K-edge XAS is also consistent with particle size growth during oxidative regeneration as evidenced by an increase in the Ru-Ru coordination number (Figures S13-14).^{21, 22} Figure S17 shows the proportion of oxidized (Ru⁺⁴) to reduced (Ru⁰) ruthenium obtained from the Linear Combination Fitting (LCF) of the XANES part of the spectrum. There is always a certain proportion of Ru⁰ present during oxidative treatment meaning that surface rather than bulk Ru oxidation takes place. Since only

surface of the nanoparticle is oxidized and the bulk of nanoparticle remains reduced, the ratio of Ru^{+4} to Ru^0 during oxidative treatment is proportional to the surface-to-bulk ratio, with a higher ratio being an indication of a higher surface-to-bulk ratio. Starting from the second cycle, Ru/SiO₂ has a higher Ru^{+4} to Ru^0 ratio, suggesting that it has a higher surface-to-bulk ratio and thus a smaller particle size compared to Ru/Al₂O₃ (in agreement with *ex situ* XRD and TEM see Figure 6).

To estimate if sulfur poisoning is reversible, i.e. if adsorbed sulfur can be removed from the surface via oxidative treatment during the later cycles where the amount of methane per cycle for Ru/SiO₂ tended to stabilize (see Figure 2), the spectra of the poisoned and reduced regenerated catalysts have to be compared. Figure 8 shows the Fourier transformed Ru K-edge EXAFS spectra of an active Ru/SiO₂ catalyst under H₂/CO and after poisoning for 25 minutes under H₂/CO/H₂S for cycles 6 and 7. Table 3 below summarizes the fitted structural parameters, which shows that S adsorbed on the Ru surface during the poisoning part of cycle 6 is removed by an oxidative treatment since no Ru-S contribution could be fitted for a catalyst in the sulfur-free H₂+CO methanation feed of cycle 7. The reversible changes were also observed in the XANES region (Figures S15-16). Note however that XAS is a bulk-averaging technique hence the absence of Ru-S scattering paths does not necessarily indicate that the absence of sulfur on the Ru nanoparticle surface, but that the amount of S adsorbed is below the detection limit of this technique. The same analysis was attempted for Ru/Al₂O₃ but no difference was observed between the spectrum of an active and poisoned catalyst, possibly due to the larger particle size of Ru/Al₂O₃ as confirmed by TEM and XRD (see Figure 6).

Figure 8: Fourier transformed magnitude Ru K-edge EXAFS spectra of Ru/SiO₂ exposed to H₂/CO during cycle 6 (green dashed line) and cycle 7 (purple solid line), after poisoning for 25 minutes with H₂/CO/H₂S during cycle 6 (blue dotted line) and cycle 7 (red dash-dotted line). The inset shows the magnification of the region corresponding to Ru-S scattering.

Cycle	Gas composition	1 st Ru-Ru			1 st Ru-S			ΔE_0	R factor
		N	σ^2	R	N	σ^2	R		
6	H ₂ +CO	10 ± 0.7	0.008 ± 0.0006	2.66 ± 0.004				3.0 ± 0.6	0.014
	H ₂ +CO+H ₂ S	9.6 ± 0.5	0.008 ± 0.0004	2.67 ± 0.004	0.6 ± 0.1	0.0005 ± 0.002	2.31 ± 0.01	4.2 ± 0.4	0.004
7	H ₂ +CO	10.4 ±	0.008 ±	2.66 ±				2.1 ± 0.5	0.013

		0.7	0.00 06	0.004					
	H ₂ +CO+ H ₂ S	9.6 ± 0.4	0.00 8 ± 0.00 03	2.67 ± 0.004	0.6 ± 0.1	0.001 ± 0.002	2.30 ± 0.01	1.5 ± 0.5	0.004

Table 3: Structural parameters obtained from best fitting the FT EXAFS spectra of the for the 6th and 7th poisoning-regeneration cycle for Ru/SiO₂; N – number of nearest neighbors, σ^2 - pseudo Debye-Waller factor, R – bond distance, ΔE_0 – edge energy correction, R-factor indicates the degree of mismatch between the fit and the data. Amplitude reduction factor set to 0.76.

4. Conclusions

In summary, we have investigated the deactivation of Ru/SiO₂ and Ru/Al₂O₃ during several poisoning-regeneration cycles. In contrast to Al₂O₃, SiO₂ is mostly inert to “sulfur” with only weak interaction with sulfur species such as SO₂ and H₂S. Ru/SiO₂ is less sulfur-resistant than Ru/Al₂O₃ in the first cycles, most likely due to the ability of Al₂O₃ to react with H₂S. This explains a larger loss of methanation activity and a higher S surface coverage observed by XAS for Ru/SiO₂ compared to Ru/Al₂O₃ after being exposed to the same amount of sulfur poisons. However, the higher S surface coverage in Ru/SiO₂ appears to reduce the extent of sintering when a poisoned catalyst is exposed to oxygen leading to less sintering than for Ru/Al₂O₃ after multiple poisoning-regeneration cycles. In addition, based on the SO₂ signals of the MS and *in situ* DRIFTS data we have shown that Ru/SiO₂ compared to Ru/Al₂O₃ has a much smaller sulfur storage capacity in the form of sulfate during oxidative regeneration. We propose that the diminished sintering of Ru nanoparticles in Ru/SiO₂ catalyst and reduced sulfur storage explains higher methane production of Ru/SiO₂ after multiple poisoning-regeneration cycles. Another important deactivation mechanism is the incomplete S removal which is inferred by comparing the CO adsorption of a fresh and regenerated Ru/SiO₂ using DRIFTS. Further research therefore should focus on improved S-removal from Ru/SiO₂, e.g. by increased temperatures during regeneration, while minimizing sintering.

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