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Sulfur poisoning and regeneration of Rh-ZSM-5 catalysts for total oxidation of methane

Yu Zhang (Conceptualization) (Methodology) (Investigation) (Writing - original draft), Peter Glarborg (Supervision) (Writing - review and editing) (Funding acquisition), Martin Peter Andersson (Writing - review and editing), Keld Johansen (Writing - review and editing), Thomas Klint Torp (Writing - review and editing), Anker Degn Jensen (Conceptualization) (Methodology) (Supervision) (Writing - review and editing), Jakob Munkholt Christensen (Conceptualization) (Methodology) (Supervision) (Writing - review and editing)



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Sulfur Poisoning and Regeneration of Rh-ZSM-5 Catalysts for Total Oxidation of Methane

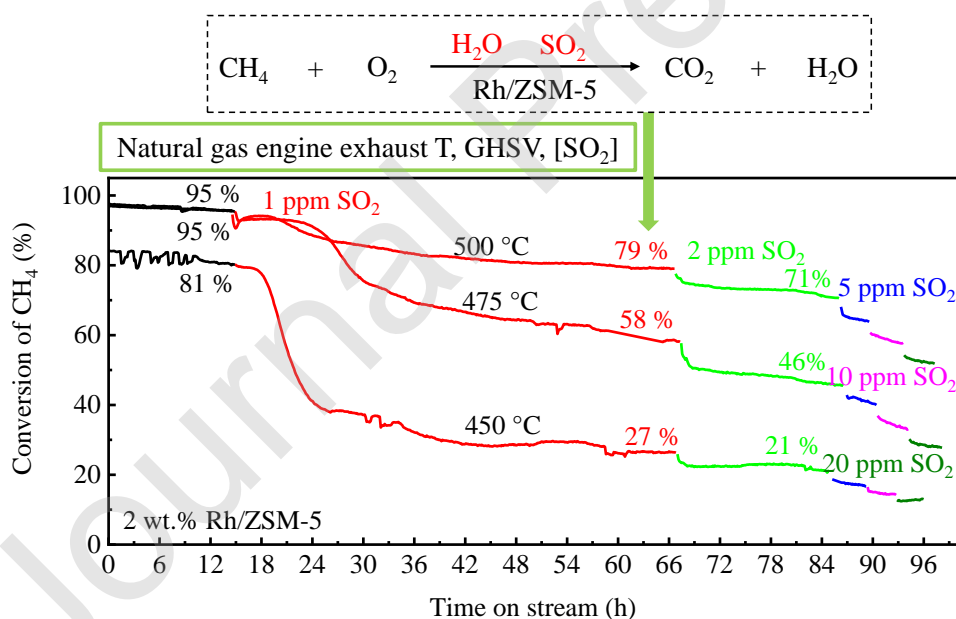
Yu Zhang¹, Peter Glarborg¹, Martin Peter Andersson¹, Keld Johansen², Thomas Klint Torp², Anker Degn Jensen¹, Jakob Munkholt Christensen^{1*}

¹DTU Chemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, DK-2800, Denmark

²Haldor Topsoe A/S, Haldor Topsøes Allé 1, Kgs. Lyngby, DK-2800, Denmark

* jmc@kt.dtu.dk

Graphical abstract



Highlights

- H₂O and SO₂ cause strong deactivation to Rh catalyst for CH₄ oxidation.
- Strong poisoning at low SO₂ concentration and levelling off at high concentrations.
- Temkin isotherm describes the deactivation caused by SO₂.
- Deactivation caused by SO₂ is partially reversible.
- Significant activity can be regenerated in SO₂-free gas.

Abstract

The activity of Rh/ZSM-5 catalysts for methane oxidation was investigated under conditions simulating the exhaust from lean burning, natural gas fueled engines to evaluate the influence of reaction atmosphere on catalytic activity. The Rh-catalysts yield high methane conversion at conditions achievable in real exhaust systems, despite the inhibiting effects of H₂O and SO₂. The influence of temperature and SO₂ concentration (1-20 ppm) on the activity were studied. The deactivation caused by SO₂ was intensified with decreasing temperature and increasing SO₂ concentration, and the SO₂-poisoning could be modeled as the occupation of active sites following a Temkin adsorption isotherm. At 400 °C essentially full coverage of S-species was reached with 1-2 ppm of SO₂, but at 500 °C the coverage had decreased significantly, and considerable catalytic activity was preserved in the presence of SO₂. Significant activity was regenerated in SO₂-free gas, but the nature of the SO₂-free regeneration atmosphere was unimportant.

Keywords: methane; catalyst; oxidation; rhodium; sulfur tolerance.

1. Introduction

Natural gas is an attractive alternative to diesel fuel in sectors such as maritime transport, as this could lower emissions of CO₂, NO_x and particulates [1]. However, the use of natural gas poses another environmental issue, namely the emission of unburnt methane, since methane is a greenhouse gas with an atmospheric warming potential 28-36 times that of CO₂ [2]. Thus, oxidative, catalytic removal of CH₄ in the exhaust from lean burning engines is a necessity for widespread introduction of natural gas as a fuel. The exhaust conditions of lean-burn natural gas fueled engines are characterized by low temperature (350-550 °C), 500-9000 ppm CH₄, around 10 vol.% O₂, 5-10 vol.% H₂O, and up to 1 ppm SO₂ [3,4]. A catalyst with a high activity and resistance to the H₂O and SO₂ present in the exhaust is thus needed for CH₄ mitigation from the exhaust gas.

Supported Pd catalysts are acknowledged as being highly active for CH₄ oxidation, relying on fully or partially oxidized Pd as active sites [5,6]. However, the activity of Pd catalysts is quite sensitive to H₂O and SO₂ in the exhaust gas [7,8,9,10]. The presence of H₂O leads to the formation of the less active Pd(OH)_x phase or blocking of the active sites, causing decreased CH₄ oxidation activity compared to dry conditions [7,11]. The inhibiting effect of water can be partly alleviated by using zeolite supports [11,12,13], but the combined presence of SO₂ and H₂O is highly detrimental and leads to a severe deactivation that renders the catalyst inactive for CH₄ oxidation [14,15,16]. The SO₂ poisoning can be postponed by using a sulfating support material like Al₂O₃, which can act as an SO₂ scavenger to prevent the formation of sulfur species directly on the active phase [17,18], but this does not provide a long-term solution. Gremminger et al. [16] investigated the sulfur poisoning of a Pd-Pt/Al₂O₃ catalyst for CH₄ oxidation in the presence of 12 vol.% H₂O. The conversion of CH₄ decreased from 100 % to 20 % after 25 h in the presence of 1 ppm SO₂ at 450 °C, and switching between CH₄ rich and lean conditions during operation was needed to keep the catalyst active in the presence of SO₂. Kinnunen et al. [20] also proposed to regenerate Pd-Pt catalysts by replacing O₂ with N₂ for 200 s every 30 min during operation to keep the average CH₄ conversion at 95 % at 450 °C. However, a catalyst that can remain active, with no need for regeneration, in the presence of SO₂ and H₂O is still being sought.

We recently observed that Rh supported on ZSM-5 was superior to Pd in an atmosphere containing both H₂O and SO₂ [21]. The active phase was found to be Rh₂O₃ nanoparticles that most likely work through a Mars van Krevelen mechanism [21]. The presence of SO₂ led to the formation of surface sulfate species and the relatively greater tolerance of Rh to the combined presence of H₂O and SO₂ was attributed to a partially destabilizing effect of water on the surface sulfates on the rhodium oxide phase. This discovery suggests that it is important to quantify the extent of SO₂-induced deactivation on Rh-based catalysts as a function of the Rh content and the reaction conditions, and this is the aim of the present work. Here 1-4 wt.% Rh on a zeolite support (ZSM-5 with SiO₂/Al₂O₃=280) was studied as a catalyst for CH₄ oxidation under simulated engine exhaust gas conditions where both H₂O and SO₂ were present. The influences of Rh loading, temperature, and SO₂ concentration in the inlet gas on the activity were investigated. The heat of SO₂ adsorption on 2 wt.% Rh/ZSM-5 was estimated from the activity data according to the Temkin isotherm [22]. Additionally, the regeneration of the sulfur poisoned catalyst was investigated by varying regeneration temperature (475-600 °C) and gas atmosphere (SO₂-free reaction gas, N₂ or 2 vol.% H₂ in N₂).

2. Experimental methods

2.1 Catalyst preparation

In this work, 1, 2, and 4 wt.% Rh-ZSM-5 catalysts were prepared by the incipient wetness impregnation method described elsewhere [21] using rhodium (III) nitrate hydrate Rh(NO₃)₃·xH₂O (~ 36 wt.% Rh, Sigma-Aldrich) as precursor and ZSM-5 (CBV 28014, Zeolyst International) with a Si/Al molar ratio of 140 (SiO₂/Al₂O₃=280) as support. The impregnated catalyst was calcined in flowing air at 600 °C for 6 h. Due to the texture change after calcination, the calcined catalyst was again pressed, crushed, and sieved to the size range of 150-300 μm for further test and this state is labeled as the fresh catalyst.

2.2 Catalyst characterization

The state of Rh was analyzed by X-ray diffraction (XRD) measurements of the fresh catalyst. Details of the XRD experiments are described elsewhere [21].

2.3 Catalytic activity measurement

The activity of the catalysts for CH₄ oxidation was measured in the form of fractionated 150-300 μm particles in a quartz fixed-bed plug flow reactor described in detail elsewhere [21]. For each experiment, 0.12 g of fresh catalyst was diluted with 1.08 g of sand and loaded into the reactor. The sand was pre-calcined at 900 °C in air for 9 h to remove any impurities. The activity of pure sand was measured by a blank test with only sand as bed material and visible conversion of CH₄ only occurred above 650 °C (see Figure S1 in Supporting Information). The different reaction and regeneration atmospheres are listed in Table 1. The reaction gas was achieved by mixing pure N₂, pure O₂, 5 vol.% CH₄ in N₂, and 50 or 500 ppm SO₂ in N₂. The total flowrate was 300 NmL/min (normal conditions: 0 °C, 1 atm), giving a gas hourly space velocity of 150,000 NmL/(g_{cat}·h). The pure N₂ and pure O₂ with purities of 99.999 % were supplied by Air Liquide Denmark. The 5 vol.% CH₄ in N₂ (± 0.1 %), 50 ppm (± 1 ppm), and 500 ppm SO₂ (± 10 ppm) in N₂ were obtained from AGA Industrial Gas Denmark.

After removal of moisture by a condenser, the effluent gas from the outlet of the reactor was analyzed by two IR NGA 2000 gas analyzers from Rosemount to monitor the concentrations of CO, CO₂, O₂, and SO₂, and a 3000A Micro GC from Agilent Technologies to measure the outlet concentration of CH₄ ([CH₄]_{out}). The inlet CH₄ concentration ([CH₄]_{in}) was measured before sending the reaction gas to the reactor. The conversion of CH₄ was calculated according to Eq.1.

$$X_{\text{CH}_4} = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100\% \quad \text{Eq.1}$$

In these experiments CO₂ and H₂O were the only products of the oxidation of CH₄. The carbon balance (CB) was calculated according to Eq.2 and was within ± 2 % for all the activity tests.

$$CB = \frac{[CH_4]_{in} - ([CH_4]_{out} + [CO_2]_{out})}{[CH_4]_{in}} \times 100\% \quad \text{Eq.2}$$

The conversion of CH₄ over the Rh/ZSM-5 catalysts in a specific reaction gas (see Table 1) was measured in light-off measurements in the temperature range of 250-600 °C with stepwise temperature increments of 25 or 50 °C. A fresh catalyst was loaded for the measurement in each reaction gas. At each temperature, the reaction was running under steady-state conditions for about 40 min for the conversion of CH₄ to stabilize. For conditions where both H₂O (5 vol.%) and SO₂ (1-20 ppm) were present, the conversion of CH₄ was measured under steady-state conditions both during heating from 250-600 °C and during the subsequent cooling. The heating run was labeled as ‘first run’ and the cooling run was labeled as ‘second run’. The conversion of CH₄ at 450 °C during heating and at 500 °C during cooling were maintained for 15 h to assess the stability of the catalyst. The detailed temperature program for the activity test in the presence of both H₂O and SO₂ is shown in Figure S2 in the Supporting Information.

2.4 Deactivation by SO₂

The deactivation of the 2 wt.% Rh/ZSM-5 catalyst in the presence of 5 vol.% H₂O and SO₂ was also tested in isothermal experiments at 450, 475, and 500 °C. Fresh catalyst was loaded for each isothermal deactivation test. Initially, a 15 h stability test was conducted in the absence of SO₂ (Rea-2 in Table 1). Then 1 ppm SO₂ was introduced to the feed stream and the concentration of SO₂ was raised in steps to 2, 5, 10, and 20 ppm awaiting an approximate steady state at each SO₂ concentration level. The degree of deactivation (*D*) of the catalyst by SO₂ was then calculated according to Eq.3.

$$D = \frac{k_f - k_d}{k_f} \times 100\% \quad \text{Eq.3}$$

Here k_f is the first-order rate constant of the fresh catalyst in the absence of SO_2 , $\text{L}/(\text{g}_{\text{Rh}}\cdot\text{s})$, and k_d is the rate constant of the deactivated catalyst.

For CH_4 oxidation under excess oxygen conditions in a plug-flow reactor, taking the reaction to be first order in CH_4 and zero order in O_2 [23], the rate constant can be calculated by Eq.4 [24].

$$k = -\frac{v}{W} \times \ln(1 - X) \quad \text{Eq.4}$$

v is the volumetric flow rate of the feed stream, L/s ; W is the weight of Rh metal in the catalyst, g ; and X is the conversion of CH_4 calculated from Eq.1.

2.5 SO_2 adsorption isotherm

In order to quantify the activity loss as a function of the exposure to SO_2 , the inhibition from SO_2 was modeled as being purely due to a loss of active sites on the Rh_2O_3 active phase. In this model the adsorption of SO_2 was assumed to occupy free sites in a 1:1 ratio, and the coverage of other species was assumed negligible compared to the sulfur species. This leads to the site balance in Eq. 5.

$$\theta_{\text{SO}_x} + \theta_* = 1 \quad \text{Eq.5}$$

Here θ_* is the remaining fraction of free sites and θ_{SO_x} is the fraction of sulfur poisoned sites. The model makes no assumption regarding the nature of the adsorbed sulfur species, which are simply termed SO_x species. However, based on previous work sulfate species are the most likely candidates [21]. If assuming that the poisoning is only due to a loss of active sites (i.e. remaining free sites are unaffected by the presence of sulfur covered sites), and that other causes of deactivation, such as sintering, are insignificant compared to the sulfur poisoning, then k_d/k_f represents the fraction of free sites, and the experimentally measured sulfur coverage $\theta_{\text{SO}_x, \text{Exp}}$ can be calculated by:

$$\theta_{\text{SO}_x, \text{Exp}} = 1 - \frac{k_d}{k_f} \quad \text{Eq.6}$$

Comparison of Eq. 3 and Eq. 6 shows that $\theta_{\text{SO}_x, \text{Exp}}$ is equal to the degree of deactivation, D . At steady state, where the SO_2 adsorption has reached equilibrium, the relationship between sulfur coverage and concentration of SO_2 is given by Eq.7.

$$\theta_{\text{SO}_x} = \frac{K \cdot [\text{SO}_2]}{1 + K \cdot [\text{SO}_2]} \quad \text{Eq.7}$$

Here $[\text{SO}_2]$ is the molar concentration of SO_2 in the gas phase, and K is the adsorption equilibrium constant, which is given by the Arrhenius type equation shown in Eq.8.

$$K = A \cdot \exp\left(\frac{-\Delta H_{\text{ads}}}{RT}\right) \quad \text{Eq.8}$$

Here ΔH_{ads} is the heat of adsorption, kJ/mol, A is the pre-exponential factor; R is the gas constant, J/(mol·K), and T is the temperature in K. The heat of adsorption is determined according to the Temkin isotherm, where the heat of adsorption decreases linearly with coverage due to the sorbate/sorbate interactions as shown in Eq.9.

$$-\Delta H_{\text{ads}} = \Delta H^0 (1 - B \cdot \theta_{\text{SO}_x}) \quad \text{Eq.9}$$

Here B is the Temkin parameter describing the linear dependence of the heat of adsorption on coverage, and ΔH^0 is the adsorption enthalpy at zero sulfur coverage, kJ/mol. By fitting A , ΔH^0 and B to the experimentally obtained sulfur coverages from Eq.6 it was possible to obtain a theoretical framework for quantifying the inhibition as a function of SO_2 concentration and temperature.

2.6 Catalyst regeneration

The regeneration efficiency was evaluated based on the remaining deactivation after regeneration. The influence of temperature and gas atmosphere on the catalyst regeneration was investigated for the catalyst poisoned by SO₂ at 475 °C.

2.6.1. Regeneration temperature

The influence of temperature on the regeneration was investigated by removing SO₂ from the reaction gas and observing the recovery of activity in the SO₂ free feed (Reg-1 in Table 1). The catalysts deactivated in the presence of 5 vol.% H₂O and 1-20 ppm SO₂ at 475 °C in Section 2.4 were regenerated by removal of SO₂ from the reaction gas at 475 °C and further heating to 500, 550, and 600 °C in the SO₂-free feed. The regeneration at 475 °C started with the removal of SO₂ and lasted for 14 h before a steady state was achieved. The time period for regeneration at higher temperatures was 2 h. After regeneration at each temperature, the conversion of CH₄ was measured in the SO₂-free reaction gas (Rea-2 in Table 1) at 475 °C for comparison.

2.6.2. Regeneration atmosphere

The influence of atmosphere (Reg-2: pure N₂, and Reg-3: 2 vol.% H₂ in N₂) on regeneration was investigated. The regeneration temperature was chosen to be 600 °C and the regeneration time was 2 h. For these tests, two batches of fresh catalyst were pre-poisoned at 475 °C for 12 h by addition of 20 ppm SO₂ to the reaction gas containing 5 vol.% H₂O. Then SO₂ was removed from the reaction gas, and the poisoned catalyst was heated to 600 °C in SO₂-free reaction gas (Reg-1). The atmosphere was then switched to pure N₂ (Reg-2) or 2 vol.% H₂ in N₂ (Reg-3), respectively. The regenerated catalyst was then cooled to 475 °C to measure the conversion of CH₄ in SO₂-free reaction gas (Rea-2) for comparison.

3. Results and discussion

3.1 Characterization

The X-ray diffraction patterns of the fresh 1, 2 and 4 wt.% Rh/ZSM-5 catalysts and the ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=280$) support are shown in Figure 1. The XRD patterns confirmed the MFI structure of the zeolite support and that the impregnation of Rh did not influence the main structure of the ZSM-5 support (see Figure 1 (a)). The main form of Rh was a highly amorphous Rh_2O_3 phase and only broad feature can be seen at the major reflections from Rh_2O_3 (indicated by the diamond in Figure 1 (a) and (b)). Figure 1 (b) shows that the Rh_2O_3 features primarily are visible for the 4 wt.% samples which indicates a significantly larger particle size for this sample. Previous studies [21] have suggested that this Rh_2O_3 phase is composed of continuous films/particles at the external surface of the zeolite grains and that Rh_2O_3 is also the state of Rh during the CH_4 oxidation reaction.

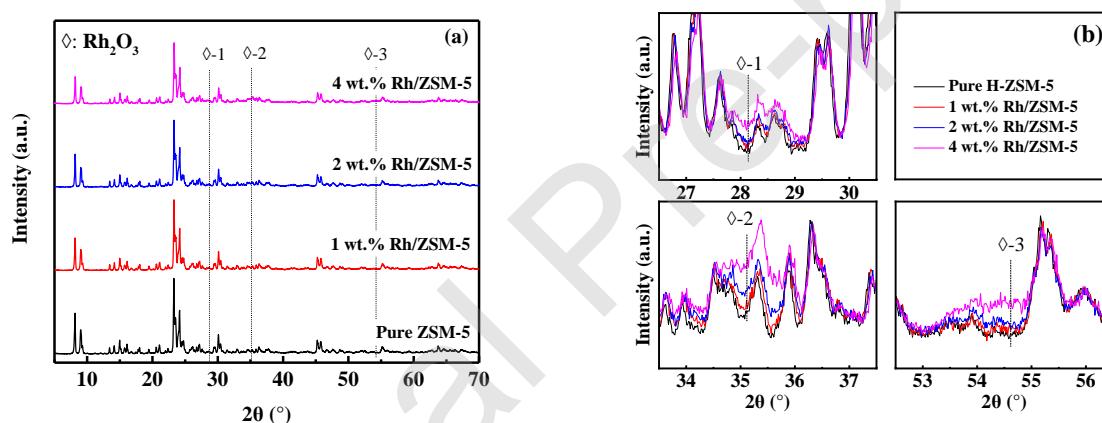


Figure 1. XRD spectra of fresh 1, 2, and 4 wt.% Rh/ZSM-5 catalysts and pure ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=280$) zeolite. The diamonds in (a) indicate Rh_2O_3 and are shown in detail in (b). Data for 2 wt.% Rh/ZSM-5(280) from Zhang et al.[21].

3.2 Influence of Rh loading

The activity for CH_4 conversion over 1, 2, and 4 wt.% Rh/ZSM-5 catalysts in the absence of H_2O and SO_2 (Rea-1 in Table 1), in the presence of 5 vol.% H_2O (Rea-2), and in presence of 5 vol.% H_2O + 20 ppm SO_2

(Rea-3) are compared in the temperature range of 250-600 °C in Figure 2. Fresh catalyst was loaded for the activity measurement in each atmosphere. In the absence of both H₂O and SO₂, oxidation of CH₄ started at 250 °C on all Rh/ZSM-5 catalysts. The conversion of CH₄ decreased significantly after addition of 5 vol.% H₂O and decreased even more after further addition of 20 ppm SO₂, and the qualitative behavior is the same for all weight loadings. The temperatures for reaching 10 %, 50 %, and 90 % conversion of CH₄ (T₁₀, T₅₀, and T₉₀) under the three reaction atmospheres are summarized in Table 3. As shown in Figure 2, the oxidation temperature decreases significantly from 1 wt.% to 2 wt.% Rh, which is attributable to the larger content of active material, but the effect of an additional increase to 4 wt.% is considerably smaller. The XRD results in Figure 1 suggest that the Rh₂O₃ particles are significantly larger in the 4 wt.% sample, and the relatively similar activity for the 2 wt.% and 4 wt.% samples are attributed to the lower dispersion of the 4 wt.% sample nearly outbalancing the increased Rh content. Given that the 4 wt.% catalyst was only slightly more active than the 2 wt.% catalyst the 2 wt.% Rh/ZSM-5 sample was selected as the most promising catalyst and used in the further studies.

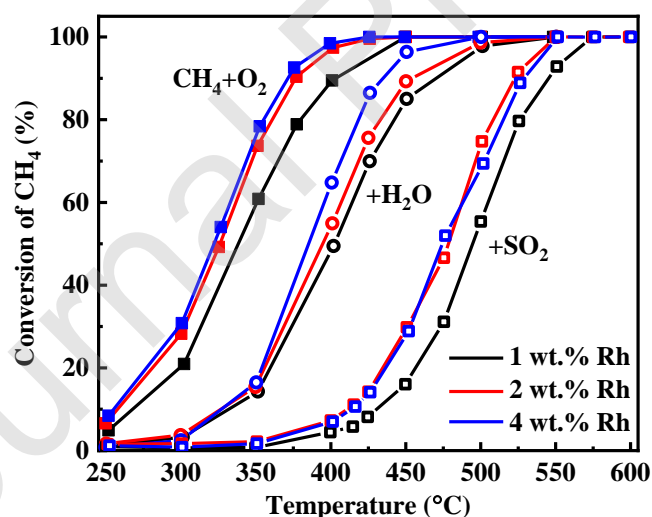


Figure 2. Activity of Rh/ZSM-5 catalyst with a Rh loading of 1 wt.% (black), 2 wt.% (red) and 4 wt.% (blue) under Rea-1: CH₄ + O₂ (closed square), Rea-2: CH₄ + O₂ + H₂O (open circle), and Rea.3: CH₄ + 10 vol.% O₂ + H₂O + SO₂ (open square). Test conditions: 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O when

present, 20 ppm SO₂ when present, balanced with N₂, GHSV=150,000 NmL/(g_{cat}·h). Data for 2 wt.%

Rh/ZSM-5(280) from Zhang et al.[21]

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3.3 Influence of temperature and SO₂ concentration

3.3.1 CH₄ conversion

The influences of temperature and SO₂ concentration on the activity of the 2 wt.% Rh/ZSM-5 catalyst were investigated in light-off tests. For each test a fresh batch of catalyst was loaded, and the activity was measured during heating (first run) and subsequent cooling (second run) with a fixed SO₂ concentration (1 to 20 ppm) in the feed. The temperature procedure of the experiment is shown in Figure S2 in the Supporting Information. The outlet concentrations of SO₂ during the activity tests in the presence of 10 and 20 ppm SO₂ are shown in Figure S4 and S5 in the Supporting Information. With the lowest SO₂ concentration of 1 ppm the deactivation occurred so slowly that a steady state was not reached during heating (Figure S3 in the Supporting Information). For this reason focus is on the cooling (second run), where steady state was achieved. Figure 3 (a) shows the conversion of CH₄ in the second run as a function of temperature with varying concentrations of SO₂ in the feed and illustrates that the major loss of activity occurs already with a concentration of 1 ppm SO₂, while higher concentrations only cause a limited additional deactivation. The conversions of CH₄ in the presence of 10 ppm and 20 ppm SO₂ seem so close that any differences between these two experiment is purely due to experimental uncertainties. The same observation was made for Rh/ZSM-5 catalysts with 1 and 4 wt.% Rh shown in Figure S6 in the Supporting Information. That the conversion at the highest temperatures in Figure 3 (a) are higher in the presence of 20 ppm SO₂ than in the presence of 10 ppm SO₂ is therefore simply attributed to uncertainty. Generally the results in Figure 3 suggest that already from 2 ppm SO₂ the coverage of SO_x species approaches saturation – especially at the lower temperatures. Figure 3 (b) shows the conversion as a function of time at 500 °C during the second run for the various SO₂ concentrations to illustrate the stability. The minor change of CH₄ conversion at 500 °C over 15 h in the presence of 1-20 ppm SO₂ indicates that the poisoning by SO₂ had reached equilibrium in all five SO₂ concentrations in the second run. The sulfur adsorption capacity of the catalyst was determined from the SO₂ uptake upon introduction of 20 ppm SO₂ at low temperature (250 °C) and yielded 27.25 μmol/g_{cat}, which corresponds to a mass rise of 0.22 wt.%, if the

sulfur is fully converted to sulfate species (Figure S8 (b) in the Supporting Information). For comparison full sulfation of the rhodium phase corresponds to a mass rise of 2.33 wt.%. The sulfur capacity of the catalyst is thus relatively limited, and any sulfation of the active phase must be limited to the outer surface. Measurements of the SO₂ concentration in the effluent during the experiments in Figure 3 (Figures S4 – S8 in the Supporting Information) revealed significant SO₂ conversion and at higher SO₂ concentrations condensed sulfuric acid could be detected in the reactor effluent suggesting that H₂SO₄ is the product of the SO₂ conversion.

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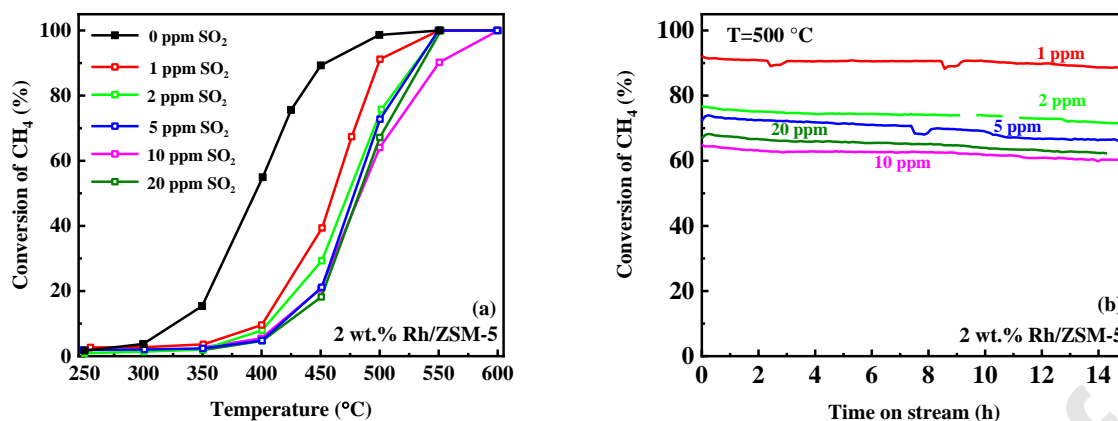


Figure 3. Influence of SO₂ concentration (0, 1, 2, 5, 10, 20 ppm) on the activity of 2 wt.% Rh/ZSM-5 catalyst (a) conversion in the second run during cooling down from 600 to 250 °C, (b) conversion at 500 °C during the second run. The points in Figure 3(a) represent the conversion of CH₄ at different temperatures under steady-state conditions at each temperature. The SO₂ concentrations in the effluent gas for tests with SO₂ present are shown in Figures S4-S8 in the Supporting Information. Test conditions: 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O, 1, 2, 5, 10, or 20 ppm SO₂ when present, balanced with N₂. GHSV=150,000 NmL/(g_{cat}·h).

Data for 0 and 20 ppm SO₂ from Zhang et al.[21].

The dynamic changes in CH₄ conversion due to addition of progressively increasing concentrations of SO₂ to the feed at a fixed temperature are shown in Figure 4. Before the addition of SO₂ to the feed the activity is stable, and the conversion then declines with progressively increasing SO₂ concentration. Figure 4 illustrates that the approach to a stabilized activity level occurs more rapidly with higher concentrations and lower temperatures. Figure 4 also emphasizes that the deactivation is intensified with decreasing temperature and with increasing SO₂ concentration. This conclusion is also illustrated by Figure 5, which summarizes the degree of deactivation as a function of temperature and SO₂ concentration determined at the end of each segment with a certain SO₂ concentration in Figure 4.

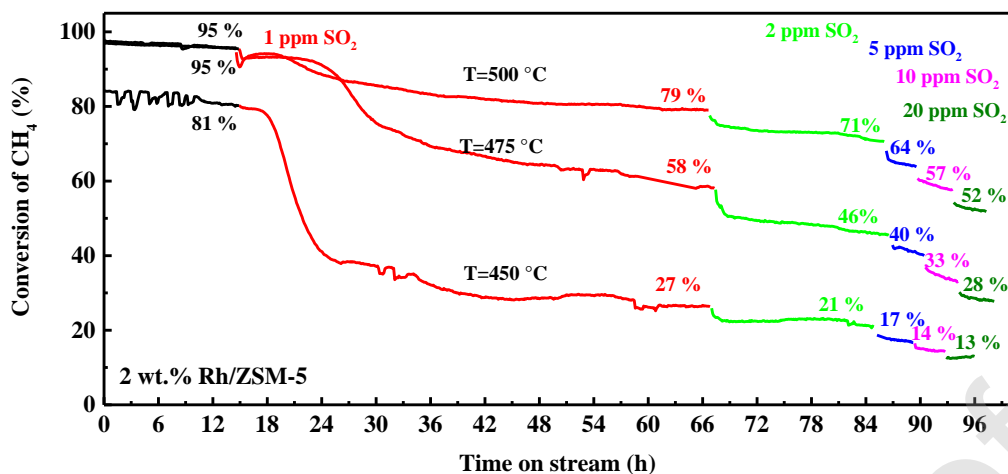


Figure 4. Influence of operation temperature (450, 475, and 500 °C) on the activity of 2 wt.% Rh/ZSM-5 catalyst in the presence of 0-20 ppm SO₂. Test conditions: 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O, 1, 2, 5, 10, or 20 ppm SO₂ when present, balanced with N₂. GHSV=150,000 NmL/(g_{cat}·h). Data for 1 ppm SO₂ from Zhang et al.[21].

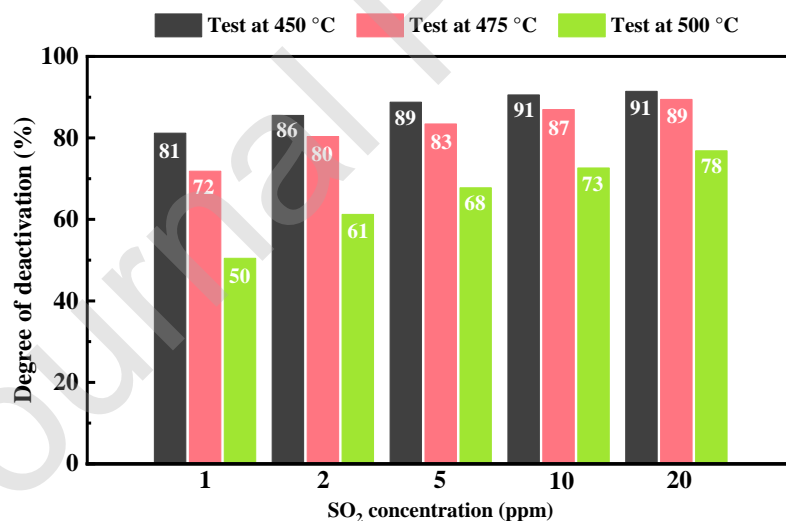


Figure 5. Degree of deactivation of 2 wt.% Rh/ZSM-5 catalyst as the SO₂ concentration increased from 1 to 20 ppm at 450 (gray), 475 (pink), and 500 (green) °C. Calculated from Figure 4.

3.3.3 SO₂ adsorption isotherm

As a tool for quantifying the deactivation caused by SO₂, the results were described by a sulfur adsorption isotherm as presented in Section 2.5. Initially, a Langmuir isotherm, with the assumption of a uniform surface and no interaction between adsorbates, was used but did not provide a satisfactory fit to the experimental results as shown in Figures S10 and S11 in the Supporting Information. For this reason a Temkin isotherm, assuming a linear dependence of the heat of adsorption on the sulfur coverage due to sorbate/sorbate interactions, was adopted and provided a reasonable description of the data. The SO₂ coverage on the 2 wt.% Rh/ZSM-5 catalyst at 400-500 °C and SO₂ concentrations of 0-20 ppm was calculated from both the light-off data in Figure 3 (a) and the approximately stabilized conversion levels in Figure 4. The determined sulfur coverages are close for the two data series (Table S2 in the Supporting Information), which indicates a reasonable reliability of this approach. Figure 6 shows the determined SO_x coverages as functions of temperature and SO₂ concentration. Figure 6 also shows a Temkin isotherm fitted to the data, which yields a heat of adsorption at zero coverage of 274.6 kJ/mol and a Temkin parameter of 0.195. The quality of the fit shows that the present sulfur adsorption model is a practically useful way of quantifying and predicting the inhibiting effect of a certain set of reaction conditions. The quality of the fit may also suggest that the assumption of attributing the loss of activity simply to a loss of active sites due to deposition of SO_x species could provide a realistic description of the physical phenomena despite the significant simplifying assumptions in the model.

The Temkin isotherm model predicts that the heat of adsorption is in the range of 221-274.6 kJ/mol depending on the SO_x coverage. There are relatively few measurements of the stability of surface sulfur species on Rh or RhO_x with which to evaluate the validity of this quantification of the heat of adsorption. Ku and Wynblatt [25] studied SO₂ adsorption on a Rh(110) single crystal and found that the heat of desorption exceeds 225 kJ/mol, which is in reasonable agreement with the presently obtained value. Previous TPD measurements [21] on this Rh/ZSM-5 catalyst yielded a bimodal desorption with two peaks at 364 °C and 637 °C. In a Redhead analysis with the commonly applied pre-factor of 10¹³ s⁻¹ those two desorption peaks correspond to

heats of desorption of 194 kJ/mol and 270 kJ/mol, respectively, and the currently derived heat of adsorption also falls in this range. So the approach of modeling the activity loss as a coverage of inhibiting species leads to a heat of adsorption for the SO_x species that is in reasonable agreement with previous determinations of the stability of such species on Rh based samples.

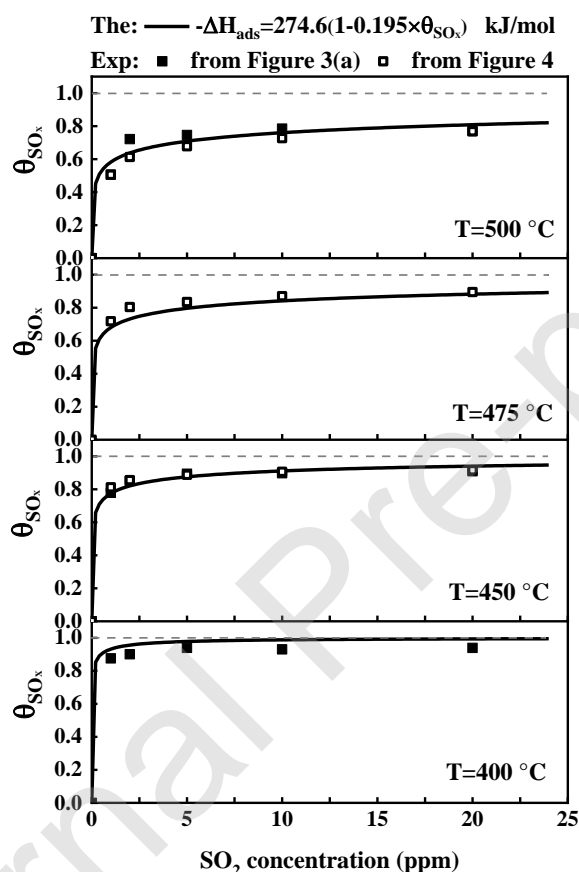


Figure 6. Theoretical (lines) and experimental (points) sulfur coverage as SO_2 concentration increases from 1 to 20 ppm at 400, 450, 475, and 500 °C. The solid points at 400, 450, and 500 °C are calculated from steady-state CH_4 conversion in the 2nd run shown in Figure 3(a), while the open points at 450, 475, and 500 °C are calculated from the stabilized CH_4 conversion shown in Figure 4. Dashed lines represent the sulfur coverage of 1.

3.4 Regeneration

The deactivation of the catalyst in the presence of SO_2 is inevitable, and the possibilities for regeneration were therefore also investigated. Previous work has shown that a substantial recovery of activity could be achieved at $475\text{ }^\circ\text{C}$ by simply removing the SO_2 from the feed, but that study did not provide any information about the role of temperature or of the regeneration atmosphere [21]. Here the sample deactivated in SO_2 -containing gas for 80 h at $475\text{ }^\circ\text{C}$ in Figure 4 was first exposed to SO_2 -free reaction gas for 14 h at $475\text{ }^\circ\text{C}$. The catalyst was then in the same atmosphere heated to progressively higher regeneration temperatures for 2 h before returning to $475\text{ }^\circ\text{C}$ to measure the activity. Figure 7 shows the conversion of CH_4 measured at $475\text{ }^\circ\text{C}$ as a function of this regeneration temperature. The results illustrate that a significant activity recovery can be attained by removing SO_2 from the feed. The results also show that the recovery of activity increases with increasing temperature, which is consistent with the conclusion from Figure 6, namely that the SO_x adsorption/desorption equilibrium is displaced towards a lower coverage at higher temperatures. Figure 7 also shows that not all of the initial activity is recovered even with the highest regeneration temperature applied. This is most likely due to irreversibly bound sulfur species that cannot be removed with the temperature and duration of the current regeneration treatments, but a contribution from other sources of deactivation such as sintering of the Rh-phase or degradation of the zeolite cannot be fully excluded [7,24,25].

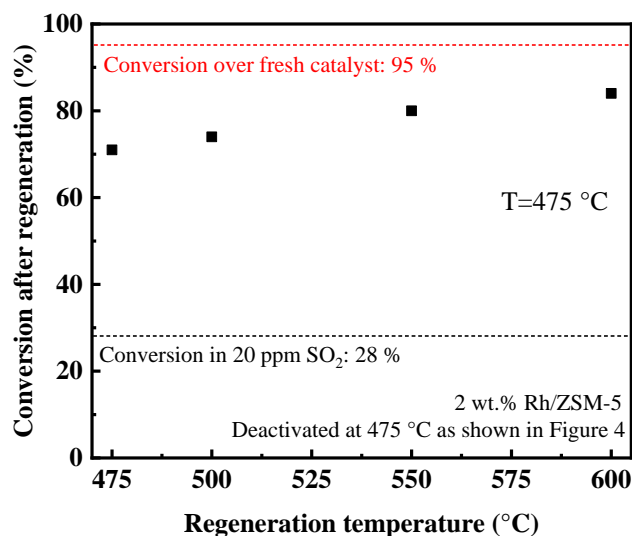


Figure 7. Conversion of CH₄ at 475 °C in SO₂-free reaction gas after regeneration at various temperatures (14 h at 475 °C and 2 h at higher temperatures). The red dashed line represents the conversion of CH₄ over the fresh catalyst, the black dashed line represents the conversion of CH₄ in the presence of 20 ppm SO₂ from Figure 4. Test conditions: 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O balanced with N₂. GHSV=150,000 NmL/(g_{cat}·h).

The role of the regeneration atmosphere was also investigated. A 2 wt.% Rh/ZSM-5 sample was poisoned by operation at 475 °C for around 10 h in the presence of 20 ppm SO₂. The catalyst was then regenerated for 2 h at 600 °C in different atmospheres (Reg-2: N₂, Reg-3: 2 vol.% H₂ in N₂). Figure 8 shows the CH₄ conversion during stabilization, during poisoning and after regeneration (conversion levels and degrees of deactivation at the states marked with 1-4 in Figure 8 are summarized in Table S2 in the Supporting Information). The change in CH₄ conversion after regeneration shows that the recovery of activity after regeneration in N₂ and 2 vol.% H₂ in N₂ is similar to the recovery after regeneration in the SO₂-free reaction gas (conversion around 80% after regeneration at 600 °C in both Figures 7 and 8). This would indicate that among the tested regeneration atmospheres there is no major advantage to regenerate in an inert or mildly reducing atmosphere compared to regeneration in the oxidizing reaction gas. This suggests that the stability of the surface sulfate on the Rh₂O₃

phase is such that temperature alone is the primary factor for its decomposition and that the reactive atmosphere is less crucial to the conversion of the sulfate. This is in reasonable agreement with the results for Si-rich zeolite supported Pd catalysts found by Friberg et al. [15]. The temperature is thus the most important parameter for the restoration of activity.

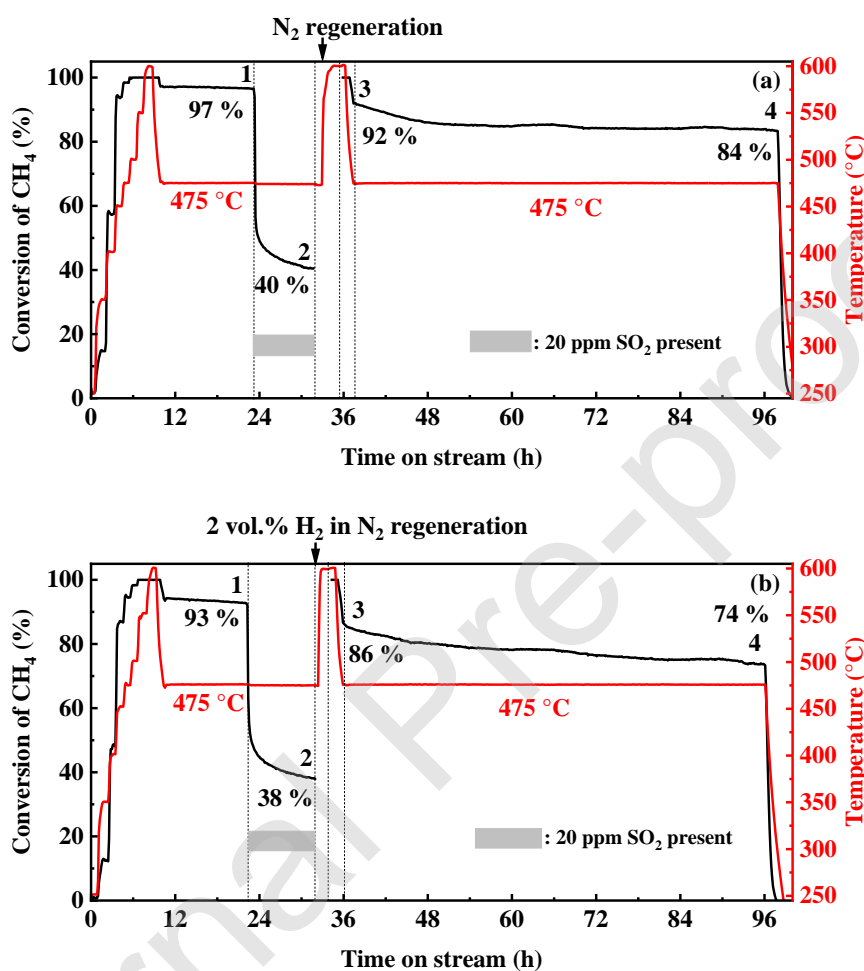


Figure 8. CH₄ conversion change and temperature program for the influence of regeneration atmosphere test.

(a): Regeneration in N₂ at 600 °C; (b): Regeneration in 2 vol.% H₂ in N₂ at 600 °C. 1: stabilized catalyst; 2: SO₂ poisoned catalyst; 3: regenerated catalyst; 4: regenerated catalyst after prolonged test. The conversion of CH₄ as well as the extent of deactivation at the four states are summarized in Table S2 in the Supporting Information. The gray boxes represent 20 ppm SO₂ was present in that period. Test conditions: 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O, 20 ppm SO₂ when present, balanced with N₂. GHSV=150,000 NmL/(g_{cat}·h).

4. Conclusions

Rh/ZSM-5 based catalysts (nominal loading 1, 2 and 4 wt.%) were synthesized and tested for complete oxidation of CH₄ in various flue gases, including under demanding conditions containing both water (5 vol.%) and SO₂ (1-20 ppm). XRD results showed that rhodium was present as relatively amorphous Rh₂O₃ in the freshly synthesized Rh/ZSM-5 catalyst. Catalytic activity was observed at 250 °C and conversion reached 100 % at 450 °C in the absence of H₂O and SO₂ (GHSV of 150,000 NmL/(g_{cat}·h)) indicating the high activity of this catalyst. The presence of H₂O and SO₂ in the reaction stream caused strong deactivation to the catalyst. By addition of 5 vol.% H₂O to the reaction stream, T₅₀ shifted approximately 60 °C up in temperature. Further addition of 20 ppm SO₂ decreased the conversion of CH₄ even more with T₅₀ shifted further by >70 °C. 2 wt% Rh/ZSM-5 catalyst was chosen as the most promising candidate for further tests based on the similarity in activity between the 2 wt.% and 4 wt.% samples, which is attributed to a larger particle size/decreasing dispersion nearly outbalancing the increased amount of active material in the 4 wt.% sample. The performance of the 2 wt.% Rh/ZSM-5 catalyst was found to be dependent on the temperature and SO₂ concentration with the deactivation being intensified at lower temperatures and higher SO₂-concentrations. The SO₂-induced inhibition could be described well as the coverage of sites blocked by sulfur species (and loss of free sites available for reaction) according to a Temkin adsorption isotherm. The adsorption energy at zero sulfur coverage was found to be 274.6 kJ/mol and the Temkin parameter was 0.195, which means that the heat of adsorption is in the range of 221-274.6 kJ/mol depending on the coverage – values that were in reasonable agreement with prior studies of the stability of sulfur species on Rh-based materials. It is consistent with this picture that the sulfur adsorption/desorption equilibrium is shifted towards a lower sulfur coverage at higher temperatures, which results in a relatively weaker inhibition. When operating at an elevated temperature of 500 °C and low SO₂ concentration of 1 ppm the catalyst can retain a high CH₄ removal efficiency (79 % CH₄ conversion). The activity of the SO₂ poisoned catalyst could be partly recovered by regeneration in SO₂-free reaction gas, pure N₂, and 2 vol.% H₂ in N₂. Increase in regeneration temperature in the range of 475-600 °C increased the regeneration efficiency. Regeneration in inert and reducing atmospheres was found to yield no major improvement compared with the SO₂-free reaction gas, which suggests that within the regeneration

programs investigated in this work the temperature is the most important factor for the recovery of activity. The present results provide data and tools for quantification of the SO₂-inhibition of Rh₂O₃ based oxidation catalysts and emphasize the relatively good sulfur tolerance of Rh-based catalysts, which could make such catalyst systems valuable for oxidative removal of methane in the exhaust from lean burning engines.

Credit Author Statement

Yu Zhang: Conceptualization, Methodology, Investigation, Writing – Original Draft

Peter Glarborg: Supervision, Writing – Review&Editing, Funding acquisition

Martin Peter Andersson: Writing – Review&Editing

Keld Johansen: Writing – Review&Editing

Thomas Klint Torp: Writing – Review&Editing

Anker Degn Jensen: Conceptualization, Methodology, Supervision, Writing – Review&Editing

Jakob Munkholt Christensen: Conceptualization, Methodology, Supervision, Writing – Review&Editing

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1. List of the reaction and regeneration atmospheres.

Atmosphere		Gas composition					
		CH ₄ (ppm)	O ₂ (vol.%)	H ₂ O (vol.%)	SO ₂ (ppm)	H ₂ (vol.%)	N ₂ (vol.%)
Reaction	Rea-1	2500	10	/	/	/	Rest
	Rea-2	2500	10	5	/	/	Rest
	Rea-3	2500	10	5	20	/	Rest
	Rea-4	2500	10	5	10	/	Rest
	Rea-5	2500	10	5	5	/	Rest
	Rea-6	2500	10	5	2	/	Rest
	Rea-7	2500	10	5	1	/	Rest
Regeneration	Reg-1	2500	10	5	/	/	Rest
	Reg-2	/	/	/	/	/	100
	Reg-3	/	/	/	/	2	Rest

Table 3. T₁₀, T₅₀, and T₉₀ of Rh/ZSM-5 catalysts in different reaction atmospheres. Rea-1: 2500 ppm CH₄ + 10 vol.% O₂; Rea-2: 2500 ppm CH₄ + 10 vol.% O₂ + 5 vol.% H₂O; Rea-3: 2500 ppm CH₄ + 10 vol.% O₂ + 5 vol.% H₂O + 20 ppm SO₂.

Rh loading (wt.%)	Rea-1 /Rea-2 /Rea-3		
	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
1	268/333/430	338/402/495	403/470/546
2	258/325/412	327/395/478	377/453/522
4	255/325/415	322/384/474	371/435/530

These values were calculated based on an interpolation method from the data in Figure 2.