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A Rhodium-Based Methane Oxidation Catalyst with High Tolerance to H₂O and SO₂

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Abstract

Increased use of natural gas as a fuel in efficient, lean-burning engines could offer environmental advantages, but this necessitates a catalytic oxidation of methane escaping from the engine. The challenge for the catalytic oxidation of CH₄ is that the catalyst must operate in the exhaust, which contains H₂O (5-15 vol.%) and SO₂ (~1 ppm), and both components cause a severe inhibition of the catalyst. Here we report that a 2 wt.% Rh/ZSM-5 catalyst offers great promise by showing that high methane conversion can be reached at practically achievable conditions and high space velocities also in the presence of H₂O and SO₂. Rh-based catalysts, which are in the form of Rh₂O₃ under reaction conditions, become superior to the state of the art Pd-based catalysts in an atmosphere with both H₂O and SO₂. Although both H₂O and SO₂ inhibit Pd- and Rh-catalysts, water is found to have a destabilizing effect on rhodium sulfate that enables a partial decomposition of the sulfate below 400 °C. We propose that this partly alleviates the sulfur poisoning of Rh-catalysts, wherefore the combined inhibition from H₂O+SO₂ is weaker for Rh than for Pd.

Key words: methane, catalyst, oxidation, rhodium, SO₂ tolerance

Introduction

Catalysis is an enabling technology for the transition to cleaner and more sustainable fuels. A clear example of this is the transition to less polluting fuels in the shipping industry. Shipping accounts for approximately 2 % of global CO₂ emissions, up to 30 % of total global NO_x emissions and 9 % of SO_x emissions.¹ Major reductions in these emissions could be achieved by replacing traditional diesel and heavy fuel oil with engines running on natural gas.^{2,3} However, natural gas engines emit significant amounts of unburnt methane (so-called methane slip),^{4,5,6,7,8} and due to the high greenhouse gas potential of methane⁹ this is a potential showstopper for the otherwise beneficial technology. Mitigation of unburnt CH₄ in the engine exhaust gas is thus a necessity for the use of natural gas as a marine fuel.^{10,11} Low-temperature CH₄-oxidation is facile with noble metal catalysts under dry and sulfur free conditions.^{12,13} The main challenge is that H₂O (typically 5-15 vol%) and SO₂ (typically 1 ppm)^{14,15,16}

in the exhaust gas cause severe deactivation to the currently known catalysts,^{17,18} which leads to a low CH₄ removal efficiency. The temperature that can be achieved in such exhaust gas systems is at most 495-540 °C, if the catalyst can be placed upstream of the engine's turbocharger.^{19,20} To offer a practically applicable solution a catalyst should thus be able to offer high conversion at a temperature of about 500 °C with as high a space velocity as possible to keep costs and equipment volume to a minimum. The state of the art Pd or Pd-Pt based catalysts are the most studied systems for CH₄ oxidation and exhibit good activity in the absence of H₂O and SO₂.^{21,22} However, the presence of water is highly detrimental to Pd-based catalysts,^{23,24} although this inhibition can be partly alleviated using zeolite-based supports, which offer improved stability.^{25,26,27,28} An even larger issue is the combined presence of H₂O and SO₂. Whereas Pd-based catalysts are relatively sulfur tolerant under dry conditions,^{28,29} the simultaneous presence of H₂O and SO₂ causes a severe inhibition of the catalytic activity.^{18,30}

Rh is far less studied for CH₄ oxidation,^{31,32} but it is an important component of the three-way-catalyst (TWC), where it yields improved catalytic activity and stability.^{33,34} Here we report that a rhodium-based 2 wt.% Rh/ZSM-5 catalyst can achieve high methane conversion at practically achievable temperatures and high space velocities even in the combined presence of H₂O and SO₂. Although the high cost of Rh should be considered, when evaluating the business case for Rh-catalysts, the identification of a catalyst that provides high conversion at realistically achievable conditions is a fundamental advance that offers great promise for the development of solutions to the methane slip problem.

Results and discussion

Rh and Pd catalysts supported on both γ -Al₂O₃, SiO₂ and ZSM-5 (SiO₂/Al₂O₃=280) were prepared for this work. Characterization by XRD, HAADF-STEM and DRIFTS spectroscopy on adsorbed CO revealed that the active phase was primarily in the form of oxide (Rh₂O₃) nanoparticles outside the zeolite micropores rather than dispersed as single metal atoms at zeolite exchange sites (Figure S3-S8 in the supporting information). Among the Rh-based catalysts an Si-rich ZSM-5 zeolite support offered the best activity (Figure S9). This is attributed to weaker interactions with the support compared to γ -Al₂O₃ (see Figure S8) and to the avoidance of a particularly strong H₂O inhibition that occurred for both

Rh and Pd on the amorphous SiO₂ support.^{35,36} For Pd-based catalysts one of the advantages of a zeolite support is reported to be a greater tolerance towards water,^{26,27} and part of the benefit of the ZSM-5 support for Rh may also be an alleviation of the inhibiting effects of water. Among the Pd-based catalysts Pd/ZSM-5 was initially less active than Pd/Al₂O₃, but Pd/ZSM-5 was far more stable in the presence of H₂O (Figures S10-S13 in the supporting information) in good agreement with observations in the literature.²⁷ On this basis the comparisons in the main text are made in terms of the more stable ZSM-5 supported catalysts. Figure 1a shows light off curves for CH₄-oxidation in the presence of 5 vol.% H₂O and 20 ppm SO₂ to provide a severe test of water and sulfur tolerance. Figure 1a shows that Rh is clearly superior to Pd under these conditions. Despite being tested at a higher space velocity the stabilized CH₄ conversion achieved here with Rh/ZSM-5 in the presence of 5 vol.% H₂O and 20 ppm SO₂ at 450 °C was higher than recently reported conversions at the same temperature for a Pd-Pt/Al₂O₃ catalyst in the presence of 5 ppm SO₂ and for Pd/Al₂O₃ or Pd/zeolite catalyst in the presence of 10 ppm SO₂.^{18,28} This illustrates that the present Rh/ZSM-5 catalyst not only compares favorably to the Pd-catalysts synthesized in this work, but also outperforms Pd-based catalysts reported in the literature.

Figure 1. (a) Conversion of CH₄ on 2 wt.% Rh/ZSM-5 (squares) and 2 wt.% Pd/ZSM-5 (circles) in the presence of 5 vol.% H₂O and 20 ppm SO₂. Full line 1st run during heating, dashed line 2nd run during cooling. (b) Conversion of CH₄ on 2 wt.% Rh/ZSM-5 catalyst in the presence of 5 vol.% H₂O and 1 ppm SO₂ at 450, 475, and 500 °C. Conditions: 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O, 1 or 20 ppm SO₂, balanced with N₂. GHSV=150,000 Nml/(g_{cat}·h).

Figure 1b illustrates that with 5 vol.% H₂O and 1 ppm SO₂, conditions characteristic of real exhaust gases,¹⁴ the Rh/ZSM-5 catalyst was able to achieve a conversion of 27 % at 450 °C and a high conversion of 79 % at 500 °C. This occurred at a relatively high space velocity corresponding to GHSV=7500 NL/(g_{noble metal}·h), which compares favorably to field tests with catalyst coated monoliths that typically apply space velocities in the range of 3500-7000 NL/(g_{noble metal}·h).^{18,37} Figure 2 shows light-off curves for the CH₄ oxidation in various gas atmospheres to investigate the origins of the superiority of Rh compared to Pd. The curves for conversion of CH₄ during cooling are shown in Figure S9-S14 in the supporting information. Figure 2 shows that the presence of SO₂ or H₂O individually caused a significant deactivation and a reasonably similar performance for both Rh and Pd. The relative activity loss caused by SO₂ in a dry feed was in fact smaller for Pd compared to Rh, which is in line with previous reports²⁸ of good SO₂ tolerance of Pd under dry conditions. Figure 2 shows that the superiority of Rh emerges in an atmosphere containing both H₂O and SO₂, where the combined inhibition was far stronger for Pd than for Rh.

Figure 2. Conversion of CH₄ on (a) 2 wt.% Rh/ZSM-5 and (b) 2 wt.% Pd/ZSM-5 under CH₄+O₂ (red), CH₄+O₂+H₂O (blue), CH₄+O₂+SO₂ (green), and CH₄+O₂+H₂O+SO₂ (black) conditions. 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).

Figure 3 (a) shows that the deactivation of Rh/ZSM-5 caused by addition of 500 ppm-5 vol.% H₂O in the presence of 20 ppm SO₂ occurred very rapidly and was completely reversible. The stability test in the absence of SO₂ at 450 °C during 0-12 h is shown in Figure S15 in the supporting information. This suggests that the H₂O inhibition is a kinetic effect from competitive adsorption and the resulting site blocking. Figure 3 (b) shows that the deactivation by 20 ppm SO₂ in the presence of 5 vol.% H₂O was partially reversible, as indicated by a slow, partial recovery of activity after removal of SO₂ from the feed. This suggests that the sulfur poisoning is also due to site blocking, but related to a more stable surface species. The advantage of Rh-catalysts must therefore be a lower coverage of the competitively adsorbed species formed from H₂O and SO₂ than present on Pd-catalysts.

Figure 3. Reversibility of (a) H₂O deactivation in the presence of SO₂ at 450 °C and (b) SO₂ deactivation in the presence of H₂O at 475 °C. The stability test in the absence of SO₂ at 450 °C during 0-12 h for (a) is shown in Figure S15 in the supporting information. A-G in (a) represent the concentration of H₂O in the reaction gas varies in the range of 500 ppm-5 vol.% as stated in the figure. Conditions: 2500 ppm CH₄, 10 vol.% O₂, 500 ppm-5 vol.% H₂O when present, 20 ppm SO₂ when present, balanced with N₂. GHSV=150,000 Nml/(g_{cat}·h).

Figure 4. (a) Rh 3d XPS spectra of poisoned 2 wt.% Rh/ZSM-5 catalyst, fresh 2 wt.% Rh/ZSM-5 and bulk rhodium sulfate on ZSM-5 as a reference; (b)-(g) HAADF-STEM-EDS results of 2 wt.% Rh/ZSM-5 catalyst after poisoning in SO₂. Poisoning conditions: 475 °C for 15 h, 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O, 20 ppm SO₂, balanced with N₂, GHSV=150,000 Nml/g_{cat}·h.

Ex situ XPS analyses of Rh catalysts in Figure 4(a) and Pd catalyst in Figure S16 in the supporting information suggested that the working state of the catalyst is the oxide state. The correspondence between the Rh and S in the elemental maps by ex-situ HAADF-STEM-EDS in Figure 4(b-g) indicates that the deactivation was caused by the formation of sulfur species on Rh sites. Figure 4 (a) shows that the Rh 3d binding energy in the poisoned Rh/ZSM-5 catalyst is slightly shifted towards that of a bulk sulfate. This could suggest that the poisoning species is surface sulfate in agreement with previous studies of sulfur poisoning of methane oxidation catalysts.³⁸ However, Figure 4 (a) also shows that the Rh 3d binding energy in the spent, poisoned catalyst remains closer to the binding energy of Rh₂O₃, which is the state in the fresh catalyst. This suggests that the working catalyst surface is not completely sulfated and that the rhodium oxide surface is partially free of sulfur at the applied poisoning conditions (5 vol.% H₂O and 20 ppm SO₂ at 475 °C). Based on CH₄-pulsing experiments with Rh/γ-Al₂O₃ by Buyevskaya et al.³⁹ we surmise that the CH₄ oxidation mechanism is of the Mars-van Krevelen type involving structural oxygen in the rhodium oxide surface. The sulfation of the Rh₂O₃ surface sites is expected to prevent the exposure of the active structural oxygen in the oxide surface, and this is expected

to be the reason for the inhibition by SO₂. The extent to which the surface is sulfated will thus depend upon the stability of the sulfate, and the very different performance of Rh and Pd in the combined presence of H₂O and SO₂ can be correlated to the properties of their sulfates. For a completely anhydrous sulfate, the decomposition of bulk Rh₂(SO₄)₃ starts at 475 °C and finishes at 750 °C.⁴⁰ By contrast, the decomposition of anhydrous bulk PdSO₄ starts at 460 °C and finishes at a lower temperature of 580 °C (Figure S17b in the supporting information). The relatively higher SO₂ tolerance of Pd catalysts under dry conditions without H₂O in the feed thus correlates to the lower decomposition temperature (Figure S17 in the supporting information) and hence lower stability of the dry Pd-sulfate, which will lead to a lower sulfate coverage at a given temperature compared to Rh. In the presence of water, the decomposition temperature of bulk PdSO₄ was only shifted slightly down in temperature (Figure S17b in the supporting information), which suggests a limited effect of H₂O upon the stability of PdSO₄. However, the effect of water on the sulfate stability is very different for Rh. The highly hydrophilic Rh₂(SO₄)₃ forms hydrated compounds of the type [Rh(H₂O)_x]₂(SO₄)₃·yH₂O,^{41,42} and Figure 5a shows that temperature programmed desorption (TPD) of SO₂ from moist, bulk rhodium sulfate yielded a bimodal sulfur desorption with a partial release of sulfur at a relatively low temperature of 300-400 °C. The TPD results are in good agreement with TGA investigations of the hydrated rhodium sulfate in Figure S17a, where the [Rh(H₂O)_x]₂(SO₄)₃·yH₂O partially decomposed at around 300 °C and where a second release of sulfur occurred above 450 °C. The integrated sulfur release shows that the low-temperature release corresponds to one of the three sulfate groups in the molecule (Figure S18 in the supporting information). Such a low-temperature release does not take place for anhydrous Rh₂(SO₄)₃,⁴⁰ and it must therefore be associated with the hydrated state of the sulfate. Figure 5b illustrates that TPD of the SO₂-poisoned Rh/ZSM-5 catalyst showed the same bimodal sulfur release as the moist bulk sulfate, and the relatively weak low temperature peak in the TPD from the catalyst suggests that the sulfur, which can be removed at low temperature, is largely removed under reaction conditions. The destabilizing effect of water on rhodium sulfate is expected to facilitate the partial removal of surface sulfate species from the rhodium oxide phase and thereby lessen the severity of the sulfur poisoning. Although both water adsorption and sulfation block free sites and thus inhibit the catalyst, water thus also partly alleviates the sulfur poisoning, and we propose that this is an important

aspect of the superiority of Rh in the combined presence of H₂O and SO₂. Additionally, the qualitative similarities between the TPD spectra in Figure 5 for both the bulk sulfate and the Rh/ZSM-5 catalyst also suggest that it is valid to use the properties of the bulk sulfates in the interpretation of the qualitative effects of SO₂ on the real catalysts.

Figure 5. TPD of (a) moist bulk rhodium sulfate impregnated on sand from an aqueous solution, see Supplementary Figure S18a for comparison to palladium sulfate, and (b) the 2 wt.% Rh/ZSM-5 catalyst poisoned during 96 hours on stream in SO₂-containing gas. TPD conditions: N₂ (carrier gas), 300 Nml/min; heating rate: 5 °C/min. Poisoning conditions: T=475 °C, 96 h, 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O, 20 ppm SO₂, balanced with N₂. GHSV=150,000 Nml/(g_{cat}·h).

In conclusion, 2 wt.% Rh/ZSM-5 was able to reach a high CH₄-conversion under simulated exhaust conditions – achieving 79 % conversion at 500 °C and GHSV=150,000 Nml/(g_{cat}·h) in the presence of 1 ppm SO₂ and 5 vol.% H₂O. This ability to reach a high methane conversion at conditions achievable in the exhaust system of a natural gas fired engine offers promise by showing that catalytic methane oxidation at realistically achievable conditions is technically feasible. The results also provide an example of how the chemistry of the active phase can alleviate the inhibition from catalyst poisons and illustrate how catalytic exhaust gas rectification will be able to help facilitate the introduction of less polluting natural gas fuels in sectors such as maritime transport.

Methods

Catalyst preparation. The catalyst precursors rhodium (III) nitrate hydrate $\text{Rh}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (~ 36 wt.% Rh basis) and palladium (II) nitrate dihydrate $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (~ 40 wt.% Pd basis) were obtained from Sigma-Aldrich. The support material ZSM-5 with a Si/Al molar ratio of 140 ($\text{SiO}_2/\text{Al}_2\text{O}_3=280$) was obtained from Zeolyst International, γ -alumina ($\gamma\text{-Al}_2\text{O}_3$) (SA 6175) and silica (SiO_2) (SS 61138) were provided by Saint-Gobain. The 2 wt.% Rh and Pd catalysts were prepared via the incipient wetness impregnation (IWI) method followed by calcination in an air flow at 600 °C for 6 h. The impregnation on zeolite support was carried out on the NH_4 -form of the zeolite. The calcined catalysts were pelletized, ground, and sieved to particles with a size range of 150-300 μm . This state is denoted as the fresh catalyst.

XRD. X-Ray Diffraction (XRD) patterns of the fresh catalysts were measured using a Panalytical XPert Pro instrument system in Bragg-Brentano geometry working in reflectance mode with Cu $K\alpha$ as radiation source (1.54056 Å, 40 kV and 40 mA). The 2θ range was 5-70 ° with a step size of 0.017 °. The particle size was determined by a Rietveld analysis method.

Microscopy characterization. The morphology and distribution of Rh and Pd supported on ZSM-5 were analyzed with a Talos F200X analytical Scanning Transmission Electron Microscopy (STEM) equipped with advanced energy dispersive X-ray spectroscopy (EDS). The High Annular Angle Dark Field (HAADF) detector was used to acquire pictures. The EDS was complimented by an Electron Energy Loss Spectroscopy (EELS) system with 0.7 eV energy resolution for image filtering (EFTEM) and quantitative analysis of the sample elements.

CO-DRIFTS. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) measurements after CO chemisorption at 25 °C with and without a H_2 pre-reduction were carried out to study the type of Rh sites on the support by using a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with a Harrick Scientific Praying Mantis DRIFTS unit and a high temperature reaction chamber. The spectra were obtained by averaging 76 scans at a resolution of 4 cm^{-1} . Catalyst samples were diluted with potassium bromide (KBr, FTIR grade, Sigma-Aldrich) particles and loaded into the chamber. The gas

dosage system for the IR setup is described elsewhere.⁴³ The H₂ pre-reduction was carried out in-situ in 5 vol.% H₂ in N₂ at 200 °C (5 °C /min to 190 °C then 2 °C /min to 200 °C) for 60 min with further removal of residual H₂ by heating to 210 °C in He for 20 min. Before dosage of CO, the cell was cooled down to 25 °C in He and background spectrum was collected. Then CO was introduced to the sample by mixing the 9.5 vol.% CO in Ar and He, giving the CO concentration in the range of 0-5000 ppm. The 9.5 vol.% CO in Ar was obtained from AGA Industrial Gas Denmark and He with a purity of 99.999 % was obtained from Air Liquide Denmark respectively. The spectra were collected during both CO chemisorption and He flush. The concentration of CO was increased stepwise until no change in the last two spectra occurred. After chemisorption, the CO flow was then switched off and the spectra were collected in He until there was no further change in the spectrum.

XPS. X-ray photoelectron spectroscopy (XPS) experiments on the fresh and poisoned catalysts as well as reference sulfates were performed ex-situ in a ThermoScientific XPS-instrument using an Al K-Alpha source with flood gun to avoid the influence of charging during the measurement. Before measurement, the sample was outgassed in a preparation chamber until passing the pressure check of the analysis chamber ($<1 \cdot 10^{-7}$ mbar). The pass energy was 50.0 eV with an energy step size of 0.100 eV. The spectrum was collected in the binding energy ranges for Rh 3d and Pd 3d. The carbon C1s was also measured and compared with the standard 284.8 eV for the charging shift correction. The Avantage software was used for XPS measurements and data treatment. The binding energy of Rh metal and Rh oxides, Pd metal and Pd oxides was referenced to the XPS Knowledge Database in the Avantage software with binding energy of C1s at 284.8 eV.

Catalytic activity measurements. The oxidation of methane under different reaction atmospheres (Table S1 in the supporting information) was carried out in a fixed-bed plug-flow reactor (Figure S1 in the supporting information) in the temperature range of 250-600 °C at near atmospheric pressure. The fresh catalyst was tested in powder form in the size range of 150-300 µm. For each experiment, a bed consisting of 0.12 g of catalyst and 1.08 g inert sand was loaded into the reactor tube. A K-type thermal couple, inserted to the central position of the reactor tube and below the plate that holds the catalyst bed, was used to measure the downstream temperature. During methane oxidation, the catalyst bed was

exposed to the reaction gas composed of 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O when present and 20 or 1 ppm SO₂ when present at a total flowrate of 300 Nml/min (Standard temperature and pressure: 0 °C, 1 atm). The reaction gas was achieved by mixing pure N₂ (99.999 %, Air Liquide Denmark), pure O₂ (99.999 %, Air Liquide Denmark), 5 vol.% CH₄ in N₂ ($\pm$ 0.%, AGA Industrial Denmark), 50 ppm SO₂ in N₂ ($\pm$ 1 ppm, AGA Industrial Denmark), and 500 ppm SO₂ in N₂ ($\pm$ 10 ppm, AGA Industrial Denmark). The gas hourly space velocity (GHSV) for the experiment was 150,000 Nml/(g_{cat}·h), which is equivalent to a noble metal mass based GHSV of 7,500 NL/(g_{noble metal}·h⁻¹). The temperature programs for the different gas atmospheres are shown in Figure S2 in the supporting information. As shown in Figure S2a, in the reaction gas containing only CH₄ and O₂ (Rea-1 in Table S1 in the supporting information), the activity was measured under steady-state conditions at each temperature during heating from 250 to 600 °C with an increment of 50 or 25 °C as 1st run and under transient conditions during cooling as 2nd run. When also 5 vol.% H₂O was present (Rea-2 in Table S1 in the supporting information), see supporting information Figure S2b, an extra stability test at 475 °C for around 15 h was carried out during cooling. When 20 ppm SO₂ was present (Rea-3 and Rea-4 in Table S1 in the supporting information), see supporting information Figure S2c, a 15 h stability test was carried out both at 450 °C in the first run during heating and at 500 °C in the 2nd run during cooling. The activity under conditions of real exhaust gases, where 5 vol.% H₂O and 1 ppm SO₂ are present (Rea-5 in Table S1 in the supporting information), was tested by addition of 1 ppm SO₂ when the conversion of CH₄ was stable in the 5 vol.% H₂O containing reaction gas at 450, 475, and 500 °C. The gas product was analyzed by an online IR NGA 2000 gas analyzer from Rosemount for CO, CO₂, and O₂ concentrations, and a 3000 A Micro GC from Agilent Technologies for the concentration of CH₄, CO, O₂ and CO₂. The CH₄ concentrations measured by the micro GC were used to calculate the conversion of CH₄. In this work, CH₄ was completely oxidized to CO₂ and H₂O. The carbon balance for the activity measurement was evaluated as the difference between the inlet CH₄ concentration and the sum up of the outlet CH₄ and CO₂ concentrations relative to the inlet CH₄ concentration. The carbon balance in this work was always within $\pm$ 2%.

Reversibility of the deactivations caused by H₂O and SO₂. The reversibility of the deactivation caused by 500 ppm – 5 vol.% H₂O in the presence 20 ppm SO₂ was tested at 450 °C by varying the H₂O feed concentration through adjustment of the N₂ flow that passed through the saturator/evaporator used to dose water. The reversibility of the deactivation caused by 20 ppm SO₂ in the presence of 5 vol.% H₂O was tested at 475 °C by switching on/off 20 ppm SO₂. When varying the dosage of H₂O/SO₂ the change in the flow was compensated by an extra N₂ flow to keep the total flow constant.

Poisoned catalysts and reference sulfates for XPS and TEM. The poisoned Rh and Pd catalysts for the XPS analyses in Figure S16 were produced by removal of SO₂ from the reaction gas at 250 °C and cooling down to room temperature after activity test in the presence of 5 vol.% H₂O and 20 ppm SO₂ (Rea-3 in Table S1 in the supporting information) according to the experimental procedure shown in Figure S2c. An additional poisoned Rh catalyst for the TEM and XPS analyses in Figure 4 was prepared by poisoning in the presence of 5 vol.% H₂O and 20 ppm SO₂ (Rea-3 in Table S1 in the supporting information) at 475 °C for 15 h, followed by removal of SO₂ from the reaction gas at 475 °C and cooling to room temperature. The reference sulfates used for XPS measurements were prepared by incipient wetness impregnation of ZSM-5(SiO₂/Al₂O₃=280) with rhodium sulfate tetrahydrate Rh₂(SO₄)₃·4H₂O or palladium sulfate dihydrate PdSO₄·2H₂O (both obtained from Alfa Aesar) followed by drying at 45 °C for 48 h to remove the moisture.

Temperature programmed desorption (TPD) of sulfates. Thermal Gravimetric Analysis (TGA): A NETZSCH STA 449 F1 Jupiter ACS was used to study the decomposition of the sulfates in different gas atmospheres: pure N₂, 10 vol.% O₂ in N₂, and 5 vol.% H₂O in N₂ in the temperature range of 30-1050 °C at a heating rate of 5 °C/min. The palladium sulfate dihydrate PdSO₄·2H₂O and rhodium sulfate tetrahydrate Rh₂(SO₄)₃·4H₂O were obtained from Alfa Aesar. TPD in flow reactor: Temperature programmed desorption (TPD) in N₂ was carried out for bulk sulfates and SO₂ poisoned 2 wt.% Rh/ZSM-5 catalyst in the flow reactor shown in Figure S1 in the supporting information. The bulk sulfates were prepared by impregnation of rhodium sulfate (rhodium(III) sulfate solution, ~8 wt.% Rh basis, Sigma Aldrich) and palladium sulfate (palladium sulfate dihydrate PdSO₄·2H₂O, Alfa Aesar) on sand. About 0.0008 mol metal sulfate was used giving a total S amount of 2.4×10⁻⁴ mol and 0.8×10⁻⁴

mol for Rh sulfate and Pd sulfate respectively. An MKS 2030 FTIR analyzer was used to measure the SO₂, SO₃, and H₂SO₄ concentrations in the exhaust gas during the bulk sulfates TPD measurements. The SO₂ poisoned 2 wt.% Rh/ZSM-5 catalyst was achieved by aging in 5 vol.% H₂O and 20 ppm SO₂ containing reaction gas (Rea-3 in Table S1 in the supporting information) at 475 °C for 96 hours. For the TPD of the poisoned catalyst, an online IR NGA 2000 gas analyzer from Rosemount was used and only the SO₂ concentration was measured. The flowrate of the carrier gas was 300 Nml/min and the heating rate was 5 °C/min. The highest temperature achievable for TPD was 750-780 °C. The gas analyser was calibrated with a calibration gas with 450±2 ppm SO₂ in N₂ obtained from AGA Industrial gases.

Supporting information

S1. Experimental methods

S2. Characterization of fresh catalysts

S3. Activity and stability for CH₄ oxidation in different gas atmospheres

S4. XPS analysis of the spent catalysts

S5. TGA and TPD study on the stability of Rh sulfate and Pd sulfate

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