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## 1. Introduction

Natural gas engines have the advantage of low  $NO_x$ ,  $SO_x$  and particulate emissions, which makes them interesting for applications such as maritime transport, but the slip of  $CH_4$  from lean-burn natural gas engines causes environmental problems due to the high greenhouse gas potential of  $CH_4$  (26–38 times that of  $CO_2$ ).<sup>1–3</sup> Mitigation of the  $CH_4$  slip by catalytic oxidation of  $CH_4$  in the exhaust gas is therefore necessary.

The exhaust gas from lean-burn natural gas fired engines is characterized by intermediate temperatures (350–540 °C), excess of O<sub>2</sub> (~10 vol%) and the presence of both H<sub>2</sub>O (5–10 vol%) and SO<sub>2</sub> (up to 1 ppm).<sup>4,5</sup> Complete removal of CH<sub>4</sub> under dry and sulfur-free conditions is facile using Pd-based catalysts, which are acknowledged as the most active catalysts for CH<sub>4</sub> oxidation.<sup>6–8</sup> However, the presence of H<sub>2</sub>O and



Yu Zhang, ம <sup>a</sup> Peter Glarborg, ம <sup>a</sup> Martin Peter Andersson, ம <sup>a</sup> Keld Johansen, <sup>b</sup> Thomas Klint Torp, <sup>b</sup> Anker Degn Jensen ம <sup>a</sup> and Jakob Munkholt Christensen 🛈 \*<sup>a</sup>

The role of the support in Rh-based catalysts for total oxidation of  $CH_4$  was investigated using both amorphous SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as well as ZSM-5 and SSZ-13 zeolites with varying SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. The methane oxidation activity was measured in both the presence and absence of 5 vol%  $H_2O$  and 20 ppm SO<sub>2</sub>. The support had a strong impact on Rh speciation (Rh<sub>2</sub>O<sub>3</sub> nanoparticles vs. single Rh atom sites), which was important for the activity, as the nanoparticle sites were found to be far more active than the single atom sites. A 2 wt% Rh/ZSM-5(SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 280) catalyst with Rh exclusively as Rh<sub>2</sub>O<sub>3</sub> nanoparticles was able to provide oxidation at a 75 °C lower temperature than an ion-exchanged 0.294 wt% Rh/ZSM-5(SiO<sub>2</sub>/  $Al_2O_3 = 30$ ) catalyst with Rh exclusively as single atoms despite a similar concentration of active sites in the two samples. All the catalysts were inhibited by the presence of water, but this inhibition was particularly strong for an amorphous SiO<sub>2</sub> support and for the most Al-rich zeolites and less severe for Si-rich zeolites. The inhibition from SO<sub>2</sub> was relatively stronger for the more Al-rich supports, which was attributed to an uptake of sulfur at Al sites that was detrimental to the performance of the active phase. In a realistic gas atmosphere containing both  $H_2O$  and  $SO_2$ , Si-rich ZSM-5(SiO\_2/Al\_2O\_3 = 280) therefore emerged as the best support. This was because the low acidity ensured minimal loss of Rh to the less active single atom sites, avoidance of the detrimental sulfur uptake by the support seen for more Al-rich supports, and avoidance of the strong water-induced inhibition that occurs for amorphous SiO<sub>2</sub> and Al-rich zeolites

> especially the combined presence of  $H_2O$  and  $SO_2$  are strongly detrimental to Pd-based catalysts.<sup>9–12</sup> Recent work found that Rh-based catalysts show better performance for CH<sub>4</sub> oxidation in atmospheres containing both  $H_2O$  and SO<sub>2</sub>.<sup>13</sup> The conversion of CH<sub>4</sub> over a Rh/ZSM-5(SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 280) catalyst could be maintained at 58–79% in the presence of 5 vol%  $H_2O$  and 1 ppm SO<sub>2</sub> at engine achievable exhaust gas temperatures (475–500 °C) and a high gas hourly space velocity (GHSV, 150 000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>).<sup>13–15</sup> The benefit of Rh was attributed to  $H_2O$  partly alleviating SO<sub>2</sub> poisoning by destabilizing the Rh sulfate hydrates, which allowed a partial sulfur release at low temperatures.

> Our previous work<sup>13</sup> identified  $Rh_2O_3$  nanoparticles to be the active phase for  $CH_4$  oxidation, which follows the Marsvan Krevelen type mechanism involving structural oxygen in the rhodium oxide surface.<sup>16</sup> In the optimization of the catalytic activity, which is of particular importance for catalysts relying on expensive noble metals, the identification of the optimal support is of central importance. It is therefore highly relevant to evaluate how the novel Rh-based oxidation catalysts depend upon the support. Previously, zeolite-based support materials with varying SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios have shown good performance in Cu catalysts for NH<sub>3</sub>-SCR as

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<sup>&</sup>lt;sup>a</sup> Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Søltofts Plads 229, 2800 Kgs. Lyngby, Denmark.

E-mail: jmc@kt.dtu.dk

<sup>&</sup>lt;sup>b</sup> Haldor Topsoe A/S, Haldor Topsøes Allé 1, 2800 Kgs. Lyngby, Denmark

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#### Paper

well as in Pd catalysts for CH<sub>4</sub> oxidation.<sup>17-20</sup> A high concentration of zeolite exchange sites, obtained using low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio zeolites, was found to favor the dispersion of Pd into smaller nanoparticles, thereby improving the initial activity.<sup>6,21</sup> On the other hand, Pd supported on Si-rich zeolites was reported to be more stable and more sulfur tolerant.<sup>18,22</sup> The optimal acidity of the zeolite could thus be the one that strikes a balance between dispersion/initial activity at higher acidity and better stability/weaker interaction with inhibitors at lower acidity. The level of zeolite acidity giving the optimal performance for the Rhcatalyzed total oxidation of methane should therefore be identified. On a zeolite support, the active phase can take the form of both continuous phases and single atoms at the zeolite exchange sites. Among the continuous phases, it can be difficult to fully distinguish if the amorphous Rh<sub>2</sub>O<sub>3</sub> structure is in the form of nanoparticles or films. Here we have mainly used the term nanoparticles throughout the text. Rh on a zeolite support was studied for partial oxidation of CH4 to acetic acid and methanol, and single Rh atom sites were correlated to higher selectivity to the partial oxidation products.<sup>23,24</sup> The superiority of Rh catalysts with single atom sites was also reported for the water gas shift reaction.<sup>25,26</sup> Single Rh atom sites will provide the optimal utilization of the active phase, but their activity for total oxidation is unknown. To clarify the importance of single atom sites for total oxidation, it is important to study the influence of the support on the distribution between single Rh atoms and nanoparticles. This distribution can be characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements on chemisorbed CO, since CO binds differently to Rh single atom sites and nanoparticle sites.<sup>27-29</sup>

In this work, a variety of ZSM-5 MFI zeolites with Si/Al = 15-140 and an SSZ-13 CHA zeolite with Si/Al = 12 were studied as support materials for Rh in order to realize different Rh site distributions and compared to amorphous SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports. Rhodium was deposited by impregnation or ion-exchange techniques. The site distribution (i.e. single atom sites vs. nanoparticle sites) was analyzed by CO-DRIFTS and the presence of Rh<sub>2</sub>O<sub>3</sub> nanoparticles was also evaluated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The activity of the prepared Rh-based catalysts towards CH4 oxidation was tested in different reaction atmospheres in a fixed-bed plug flow reactor. The sulfur tolerance of the catalyst was correlated to the site distribution to identify the optimal Rh catalyst for CH<sub>4</sub> oxidation under realistic engine exhaust gas conditions where both H<sub>2</sub>O and SO<sub>2</sub> are present.

## 2. Experimental methods

#### 2.1 Materials

Rhodium(III) nitrate hydrate  $Rh(NO_3)_3 \cdot xH_2O$  (~36 wt% Rh basis, Sigma Aldrich) was used as a precursor for the catalyst preparation. ZSM-5 zeolites with Si/Al molar ratios of 140 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 280, CBV 28014), 40 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 80, CBV

8014), 25 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 50, CBV 5524G) and 15 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30, CBV 3014) were obtained from Zeolyst International. SSZ-13 with a Si/Al ratio of 12 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 24) was supplied by Haldor Topsoe. Presently, the zeolites are labelled ZSM-5(*X*) and SSZ-13(*X*) with *X* denoting the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. The amorphous support materials SiO<sub>2</sub> (SS 61138) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (SA 6175) were obtained from Saint-Gobain.

#### 2.2 Catalyst preparation

2 wt% Rh-based catalysts were prepared by the incipient wetness impregnation (IWI) method followed by calcination in flowing air at 600 °C for 6 h, as described elsewhere.<sup>13</sup> A catalyst with only single atom Rh sites was prepared by an ion exchange (IE) method with ZSM-5(30) zeolite as the support material. Here 0.1111 g rhodium(m) nitrate hydrate (giving 0.04 g Rh) was added to a beaker with 100 ml deionized water, and 1.96 g ZSM-5(30) powder was then added. The mixture was stirred at room temperature for 24 hours followed by washing with deionized water until the pH of the filtrate was neutral. The filter cake was then dried at 80 °C to remove the moisture. The sample was then subjected to a second, identical ion-exchange step followed by washing and drying. Finally, the ion exchanged catalyst was calcined in flowing air at 600 °C for 6 h. Because of texture changes after impregnation or ion exchange, the calcined catalysts were ground, pelletized, crushed, and sieved again to 150-300 µm. The catalysts prepared by IWI were denoted as 2 wt% Rh/support, e.g. 2 wt% Rh/ZSM-5(280), and the Rh catalyst prepared by ion exchange was labelled Rh/ZSM-5(30)-IE. The calcined samples were used for characterization and catalytic tests without any further degreening treatments. Tests of stability as a function of time on stream are presented in the ESI.<sup>†</sup>

#### 2.3 Catalyst characterization

The 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 the radiation source (1.54056 Å, 40 kV and 40 mA). The investigated  $2\theta$  range was 5–70° with a step size of 0.017°.

The distribution of Rh between Rh nanoparticle sites and single atom sites was determined by DRIFTS measurements of CO chemisorbed at 25 °C on the oxidized form of the catalyst. The details of the instrument have been described elsewhere.<sup>13,30</sup> The spectra were obtained by averaging 76 scans at a resolution of 4 cm<sup>-1</sup>. Catalyst samples in the fresh oxide form were diluted with KBr (FTIR grade, Sigma-Aldrich) particles and loaded into the chamber. Before dosage of CO, the background spectrum was collected in He at 25 °C. Then CO was introduced to the sample by mixing 9.5 vol% CO in Ar (AGA Industrial Gas Denmark) and He (Air Liquide Denmark), giving a CO concentration in the range of 0–5000 ppm. The spectra were collected during both CO chemisorption and He flush. The concentration of CO was increased stepwise until no changes in the spectra were observed, indicating saturation of the surface. After chemisorption the CO flow was switched off, the spectra were collected during He flush until no further change in the spectra occurred. On both isolated single atom sites and  $Rh_2O_3$  oxide nanoparticles, CO adsorption is expected to result in  $Rh(CO)_2$  dicarbonyl species.<sup>24,31–33</sup> The symmetric and asymmetric CO stretches of Rh carbonyls  $Rh(CO)_2$  on isolated Rh single atoms are labelled as  $a_s$  and  $a_a$ , and the symmetric and asymmetric CO stretches of  $Rh(CO)_2$  on  $Rh_2O_3$  nanoparticles are labelled as  $b_s$  and  $b_a$  throughout this work. The last spectrum during the He flush was used to determine the ratio between single atom Rh sites and nanoparticle Rh sites according to eqn (1).

$$\frac{\mathrm{Rh(CO)}_{2,\mathrm{SA}}}{\mathrm{Rh(CO)}_{2,\mathrm{NP}}} = \frac{A_{\mathrm{a}_{\mathrm{s}}}}{A_{\mathrm{b}_{\mathrm{s}}}} \tag{1}$$

Here  $A_{a_s}$  is the peak area of the symmetric stretch of Rh single atom bonded carbonyls, Rh(CO)<sub>2,SA</sub>, and  $A_{b_s}$  is the peak area of the symmetric stretch of Rh<sub>2</sub>O<sub>3</sub> nanoparticle bonded CO Rh(CO)<sub>2,NP</sub>. This analysis is based on the two strongest bands, which lowers uncertainty, and as the extinction coefficients of the two IR modes are not too dissimilar (less than a factor of 3),<sup>25</sup> this ratio should give a reasonable estimate of the site ratio.

The Rh loading of the Rh/ZSM-5(30)-IE catalyst was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an Agilent 720 ES ICP-OES. Here 0.1 g finely ground catalyst and 4 g finely ground  $Na_2O_2$  (pro analysis quality) were mixed thoroughly and transferred quantitatively into a zirconium crucible in duplicate. The sample was heated to 500 °C for 4 hours in a muffle furnace. After cooling, the fusion cake was dissolved in pure water (18.2 M $\Omega$ ) and the zirconium crucible was leached with 10 ml 37% HCl (pro analysis quality) three times with gentle heating. The sample solution was then transferred to a 200 ml volumetric flask and filled to the mark with pure water (18.2 M $\Omega$ ). The sample solution was analyzed by ICP-OES with two to five times further dilution and the emission signals from several Rh specific emission lines were compared to the signal from certified and matrix matched calibration standards containing 0-1 mg L<sup>-1</sup> Rh. The relative precision of the analysis is estimated to be  $\pm 5\%$ .

The morphology and distribution of Rh on fresh and spent Rh catalysts were analyzed with a Talos F200X analytical (S) TEM equipped with a new advanced energy dispersive X-ray spectrometer (EDS). A high angle annular dark field (HAADF) detector was used to acquire pictures. The EDS was complemented 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.

#### 2.4 CH<sub>4</sub> oxidation activity measurement

The activity of the Rh-based catalyst in the temperature range of 250–600  $^{\circ}\mathrm{C}$  in different atmospheres (as listed in Table 1)

Table 1 List of reaction atmospheres for oxidation of CH<sub>4</sub>

Atmospheres	Concentrations					
	CH <sub>4</sub> (ppm)	O <sub>2</sub> (vol%)	H <sub>2</sub> O (vol%)	SO <sub>2</sub> (ppm)	N <sub>2</sub> (vol%)	
Rea-1	2500	10	_	_	Rest	
Rea-2	2500	10	5	_	Rest	
Rea-3	2500	10	5	20	Rest	

was measured using a fixed-bed plug-flow quartz reactor placed in a furnace with three heating zones (top, middle, and bottom) described in more detail elsewhere.<sup>13</sup> A fresh catalyst sample was loaded for the measurement in each gas atmosphere. For each test, 0.12 g of catalyst was weighed and diluted with 1.08 g inert sand to give a total bed mass of 1.20 g. The catalyst and sand mixture was loaded between two layers of quartz wool. The gas flow rate was 300 N mL min<sup>-1</sup> (normal conditions for temperature and pressure: 0 °C, 1 atm), giving a gas hourly space velocity (GHSV) of 150 000 N mL  $g_{cat}^{-1}$  h<sup>-1</sup>. The effluent gas was measured using an online IR NGA 2000 gas analyzer from Rosemount to monitor the concentrations of CO<sub>2</sub>, CO and O2 and a Micro GC 3000A from Agilent Technologies for CH4, CO2, and O2 concentrations. The CH4 concentration measured by the Micro GC was used to calculate the conversion of  $CH_4$  as shown in eqn (2).

$$X_{\rm CH_4} = \frac{[\rm CH_4]_{in} - [\rm CH_4]_{out}}{[\rm CH_4]_{in}} \times 100\%$$
(2)

Here  $[CH_4]_{in}$  is the inlet  $CH_4$  concentration measured during bypass of the reactor and  $[CH_4]_{out}$  is the outlet  $CH_4$ concentration. In these experiments, the only products of  $CH_4$ oxidation were  $CO_2$  and  $H_2O$  and the carbon balance (CB) was within ±2% for all the activity tests.

The temperature programs for the activity measurement for CH<sub>4</sub> oxidation in different atmospheres are shown in Fig. 1. Measurements were made during both heating and subsequent cooling, and throughout the text the heating is termed the 1st run, whereas the subsequent cooling is termed the 2nd run. Under dry and SO<sub>2</sub>-free conditions (Rea-1), the activity during the 1st run was measured under steady-state conditions at each temperature and during the 2nd run it was measured under transient conditions as shown in Fig. 1(a). In the presence of 5 vol%  $H_2O$  (Rea-2), an extra stability test at 475 °C for 15 h was carried out in the 2nd run during cooling (Fig. 1(b)). With both 5 vol%  $H_2O$ and 20 ppm SO<sub>2</sub> present (Rea-3), both the 1st and 2nd runs were measured under steady-state conditions, and extra 15 h stability tests were carried out at 450 °C during heating and at 500 °C during cooling (Fig. 1(c)).

# 3. Results and discussion

### 3.1 Characterization of the fresh catalysts

The results of XRD analyses for the supported Rh catalysts and the pure support materials are shown in Fig. 2(a)–(f).



**Fig. 1** Temperature programs for the CH<sub>4</sub> oxidation activity test in (a): 2500 ppm CH<sub>4</sub> + 10 vol% O<sub>2</sub>, (b): 2500 ppm CH<sub>4</sub> + 10 vol% O<sub>2</sub> + 5 vol% H<sub>2</sub>O, and (c): 2500 ppm CH<sub>4</sub> + 10 vol% O<sub>2</sub> + 5 vol% H<sub>2</sub>O + 20 ppm SO<sub>2</sub>, balanced with N<sub>2</sub>, GHSV = 150 000 N mL  $g_{cat}^{-1}$  h<sup>-1</sup>. Figure reproduced with permission from Zhang *et al.*<sup>13</sup> Copyright 2020, American Chemical Society.



**Fig. 2** XRD patterns of the pure supports and 2 wt% Rh catalysts on (a):  $SiO_{2r}$  (b):  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (c): ZSM-5(280), (d): ZSM-5(80), (e): ZSM-5, and (f): SSZ-13(24). Data for Rh/SiO<sub>2</sub>, Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Rh/ZSM-5(280) from Zhang *et al.*<sup>13</sup>

The XRD patterns of the pure supports confirmed the MFI structure of all the ZSM-5 samples, the CHA structure of SSZ-13(24), and the amorphous nature of SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The impregnation of Rh did thus not change the structure of the support. The Rh catalysts contain well-dispersed Rh<sub>2</sub>O<sub>3</sub>, which is largely amorphous on all the supports. Previous analyses of spent catalysts have also suggested that this oxide form is the working state of the catalyst under the presently used oxygen-rich reaction conditions.<sup>13</sup> The XRD pattern of Rh/ZSM-5(30)-IE is shown in Fig. S1 in the ESI† and it is identical to that of the pure ZSM-5(30) support, but ICP-OES does reveal a Rh content of 0.294 ± 0.015 wt%, indicating that Rh is in a highly dispersed state invisible to XRD.

The HAADF-STEM images of 2 wt% Rh/ZSM-5(280) and Rh/ZSM-5(30)-IE are shown in Fig. 3 and the corresponding EDS maps are shown in Fig. 4.  $Rh_2O_3$  nanoparticles (~20 nm) as a separate phase outside the zeolite structure could be observed for 2 wt% Rh/ZSM-5(280) (Fig. 3(a)). Oppositely, no

continuous Rh<sub>2</sub>O<sub>3</sub> phase could be clearly identified on the Rh/ ZSM-5(30)-IE sample, as shown in Fig. 3(b). The EDS mapping



**Fig. 3** HAADF-STEM images of (a): 2 wt% Rh/ZSM-5(280) and (b): Rh/ZSM-5(30)-IE. The red lines in (a) represent 20 nm. Fig. 3(a) reproduced with permission from Zhang *et al.*<sup>13</sup> Copyright 2020, American Chemical Society.



Fig. 4 HAADF-STEM-EDS of (a): 2 wt% Rh/ZSM-5(280) and (b): Rh/ZSM-5(30)-IE. Fig. 4(a) reproduced with permission from Zhang et al.<sup>13</sup> Copyright 2020, American Chemical Society.

of Rh/ZSM-5(30)-IE shown in Fig. 4(b) also confirmed the high dispersion of Rh in the ion exchanged sample. The Rh loading determined from EDS of the measured crystal is  $0.44 \pm 0.21$  wt% which is in reasonable agreement with the result from ICP-OES (0.294  $\pm$  0.015 wt%). This suggests that the highly dispersed state seen in Fig. 3(b) and 4(b) is representative of the entire Rh/ZSM-5(30)-IE sample.

The CO-DRIFTS results illustrating the distribution of the Rh sites (i.e. Rh<sub>2</sub>O<sub>3</sub> nanoparticles or single Rh atoms) on the various supports are shown in Fig. 5. Fig. 5 shows that dicarbonyls, Rh(CO)2, were formed on both isolated single Rh atoms ( $a_s$  and  $a_a$  at 2115 cm<sup>-1</sup> and 2048 cm<sup>-1</sup>)<sup>24,31</sup> and oxidized  $Rh_2O_3$  nanoparticles (b\_s and b\_a, at 2084–2089  $\mbox{cm}^{-1}$ and 2010-2016 cm<sup>-1</sup>).<sup>29,32,33</sup> Fig. 5(a) shows that the ion exchanged Rh/ZSM-5(30)-IE catalyst only contains isolated single Rh atoms at the exchange sites, in good agreement with the high dispersion evident from the XRD and TEM results. Oppositely, Fig. 5(b-d) show that the fresh Rh/SiO<sub>2</sub> and Rh/y-Al<sub>2</sub>O<sub>3</sub> catalysts and the Rh/ZSM-5(280) catalyst on a ZSM-5 support with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 280 only contain Rh<sub>2</sub>O<sub>3</sub> particles as evidenced by the symmetric and asymmetric stretches of Rh dicarbonyl Rh(CO)<sub>2</sub> on oxide nanoparticles (b<sub>s</sub> and b<sub>a</sub>). This is in good agreement with the XRD results in Fig. 2(c) and the STEM results in Fig. 3(a) and 4(a). For ZSM-5 zeolites with lower SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios and hence more exchange sites, the IR data in Fig. 5(e-g) show that more Rh is dispersed as single atoms at the exchange sites and that Rh exists as a mixture of nanoparticles and isolated Rh atoms. Fig. 5(d-f) show an increased relative intensity of single Rh atoms at exchange sites  $(a_s \text{ and } a_a)$ relative to Rh<sub>2</sub>O<sub>3</sub> nanoparticle sites (b<sub>s</sub> and b<sub>a</sub>) with decreasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the ZSM-5 zeolites. By using an Al-rich CHA structure zeolite, SSZ-13(24), Rh was also mainly

dispersed as single Rh atoms at exchange sites with small amounts of nanoparticles as shown in Fig. 5(g). To quantify



Fig. 5 CO-DRIFTS spectra obtained in He flush after CO chemisorption at 25 °C. (a): Rh/ZSM-5(30)-IE; (b): 2 wt% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; (c): 2 wt% Rh/SiO<sub>2</sub>; (d): 2 wt% Rh/ZSM-5(280); (e): 2 wt% Rh/ZSM-5(80); (f): 2 wt% Rh/ZSM-5(50); (g): 2 wt% Rh/SSZ-13(24). Data for Rh/SiO<sub>2</sub>, Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Rh/ZSM-5(280) from Zhang *et al.*<sup>13</sup>

the ratio of single atoms to nanoparticle sites, the area ratios between the IR band for the symmetric CO stretch at single atom sites  $(Rh(CO)_{2,SA}, a_s)$  and the band for the symmetric CO stretch at nanoparticles  $(Rh(CO)_{2,NP}, b_s)$  were calculated according to eqn (1) and are shown in Fig. 6. The linear relationship between the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the zeolite and the Rh(CO)<sub>2,SA</sub>/Rh(CO)<sub>2,NP</sub> ratio in Fig. 6 illustrates that the dispersion of Rh atoms to exchange sites is directly correlated to the availability of exchange sites in the zeolite which scales with the Al content of the zeolites.

The characterization of the Rh-based catalysts by XRD, HAADF-STEM-EDS, and CO-DRIFTS thus provides a relatively consistent picture. For SiO2, y-Al2O3 and the most Si-rich ZSM-5(280) zeolite, rhodium only exists in the form of Rh<sub>2</sub>O<sub>3</sub> nanoparticles. For the ZSM-5 samples with higher Al-content, rhodium exists as a mixture of oxide nanoparticles and single Rh atoms at exchange sites, and the relative amount of Rh at exchange sites scales with the number of available exchange sites. Based on the absence of a continuous Rh<sub>2</sub>O<sub>3</sub> phase in STEM-EDS investigations (Fig. 4(b)) and the exclusive identification of single atom sites in DRIFTS measurements (Fig. 5(a)), it is concluded that Rh/ZSM-5(30)-IE only contains single Rh atoms at the exchange sites of the zeolite. Using the active site density on Rh<sub>2</sub>O<sub>3</sub> estimated from methanol chemisorption by Badlani and Wachs,<sup>34</sup> and the Rh<sub>2</sub>O<sub>3</sub> nanoparticle size of 10-20 nm in the 2 wt% Rh/ZSM-5(280) sample as determined from the STEM results in Fig. 3(a), the concentration of active sites in this sample should be in the order of 15–29  $\mu$ mol g<sub>cat</sub><sup>-1</sup>. The ion-exchanged Rh/ZSM-5(30) catalyst contains only 0.294 ± 0.015 wt% Rh, but Rh is exclusively present as single atom sites. Taking each single Rh atom as an active site, this translates into a concentration of active sites of 29  $\mu$ mol g<sub>cat</sub><sup>-1</sup>. Given the similarity in site concentration, the differences in activity between the two samples should therefore reflect the differences in turnover



Fig. 6 The area ratio of the symmetric stretch of the CO bonded to the single atom Rh site  $Rh(CO)_{2,SA}$  to the symmetric stretch of the CO bonded to the  $Rh_2O_3$  nanoparticle site  $Rh(CO)_{2,NP}$  as a function of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the zeolite support in the fresh 2 wt% Rh samples determined from Fig. 5.

frequencies of the two types of sites – *i.e.*  $Rh_2O_3$  nanoparticle sites and single atom sites.

#### 3.2 Activity for CH<sub>4</sub> oxidation

The catalytic activity of the Rh-based catalysts for CH<sub>4</sub> oxidation in different reaction atmospheres is shown in the form of light-off curves in Fig. 7, and the temperature for 50%  $CH_4$  conversion ( $T_{50}$ ) for the catalysts under different conditions is listed in Table 2. A fresh catalyst sample was loaded for the activity measurement in each atmosphere. For the feeds without SO<sub>2</sub>, only the conversion during heating (the so-called 1st run) is shown in Fig. 7, while the conversion during cooling is shown in Fig. S2 and S3 in the ESI.† For the SO<sub>2</sub>-containing feed, the data for both heating (1st run) and cooling (2nd run) are shown. Fig. 7(a and b) and Table 2 show the catalytic activity in the absence of SO<sub>2</sub> and here the most active sample is Rh/ZSM-5(280), which according to Fig. 5 only has Rh in the form of Rh<sub>2</sub>O<sub>3</sub> particles. The least active sample is the ion-exchanged Rh/ZSM-5(30)-IE sample, where rhodium initially is exclusively present in the form of Rh atoms at zeolite exchange sites. As Rh/ZSM-5(280) and Rh/ZSM-5(30)-IE are estimated to have a similar concentration of surface sites, this strongly suggests that the sites on Rh<sub>2</sub>O<sub>3</sub> particles are far more active than single Rh atoms. The remaining zeolite supported samples, which initially have rhodium in a mixture of nanoparticle and single atom forms, exhibit intermediate activity. The difference in activity between particle and single atom sites is likely to arise from the underlying differences in electronic structure. The single atom sites are likely to be oxygen-deficient under reaction conditions, possibly because they are occupied by stable CO species,<sup>35</sup> and this is likely to lower their activity in a Mars-van Krevelen type reaction mechanism. The lower activity of the Rh single atom sites may contribute to their higher selectivity to partial oxidation products such as methanol under certain conditions.<sup>24</sup> The significantly lower activity of single atom sites compared to nanoparticle sites for CH4 oxidation was also reported for Pd catalysts.<sup>18,36,37</sup> The conversion for the Rh/ZSM-5(30)-IE catalyst is improved significantly during the subsequent cooling (2nd run), and the conversion is shifted ca. 25 °C down in temperature (Fig. S2 in the ESI<sup>†</sup>). Characterization of the spent Rh/ZSM-5(30)-IE catalyst by HAADF-STEM (Fig. 8 and S6<sup>†</sup>) clearly illustrates that agglomeration of the Rh single atoms into small (<5 nm) nanoparticles has occurred during operation. The higher activity during cooling (2nd run) compared to heating (1st run) for this sample is attributed to a higher activity of the Rh<sub>2</sub>O<sub>3</sub> particles that have formed by agglomeration of single Rh atoms during the heating (1st run). These results indicate a tendency to partial agglomeration during operation that can explain why the activity of the zeolite supported samples with a mixture of particle and single atom sites does not correlate fully to the initial dispersion illustrated in Fig. 6.

Fig. 7(b) and Table 2 show that in the presence of 5 vol%  $H_2O$  there is a lower activity for all the supports, and  $T_{50}$  is

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**Fig. 7** Conversion of CH<sub>4</sub> on Rh-based catalysts in different atmospheres. (a): 1st run in CH<sub>4</sub> + O<sub>2</sub>; (b): 1st run in CH<sub>4</sub> + O<sub>2</sub> + H<sub>2</sub>O; (c): 1st run in CH<sub>4</sub> + O<sub>2</sub> + H<sub>2</sub>O + SO<sub>2</sub>; (d): 2nd run in CH<sub>4</sub> + O<sub>2</sub> + H<sub>2</sub>O + SO<sub>2</sub>. 1: Rh/ZSM-5(30)-IE (orange), 2: 2 wt% Rh/γ-Al<sub>2</sub>O<sub>3</sub> (blue), 3: 2 wt% Rh/SiO<sub>2</sub> (black), 4: 2 wt% Rh/ZSM-5(280) (red), 5: 2 wt% Rh/ZSM-5(80) (light green), 6: 2 wt% Rh/ZSM-5(50) (gray), 7: 2 wt% Rh/SSZ-13(24) (dark green). 2500 ppm CH<sub>4</sub>, 10 vol% O<sub>2</sub>, 5 vol% H<sub>2</sub>O when present, 20 ppm SO<sub>2</sub> when present, balanced with N<sub>2</sub>, GHSV = 150 000 N mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. Data for 2 wt% Rh/ZSM-5(280) from Zhang *et al.*<sup>13</sup>

 Table 2
 T<sub>50</sub> of Rh-based catalyst in different atmospheres

Catalysts	$T_{50}^{b}$ (°C)					
	$CH_4 + O_2$	$CH_4 + O_2 + H_2O$	$CH_4 + O_2 + H_2O + SO_2$			
	1st run	1st run	1st run	2nd run		
Rh/ZSM-5(30)-IE(0.294 wt%) <sup>a</sup>	404	445	531	567		
2 wt% Rh/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	358	418	509	515		
2 wt% Rh/SiO <sub>2</sub>	361	460	>600	>600		
2 wt% Rh/ZSM-5(280)	326	395	478	483		
2 wt% Rh/ZSM-5(80)	355	412	570	574		
2 wt% Rh/ZSM-5(50)	330	401	495	513		
2 wt% Rh/SSZ-13(24)	357	433	520	540		

<sup>*a*</sup> The weight loading of Rh/ZSM-5(30)-IE was determined by ICP-OES. <sup>*b*</sup> The  $T_{50}$  was calculated by interpolation between the CH<sub>4</sub> conversions at two adjacent temperatures.

shifted *ca.* 60 °C up in temperature. Such inhibition by  $H_2O$  has also been observed previously for both Rh and Pd catalysts.<sup>13,14,38</sup> This is partly attributable to a competitive adsorption by OH formed from  $H_2O$ . For Si-rich Rh/ZSM-5(280), the water inhibition is completely reversible,<sup>13</sup> and no gradual deactivation was seen here during a stability test at 475 °C for 15 h (Fig. S4 in the ESI†). However, for the Al-rich zeolites the stability is also affected (Fig. S4†) with a clear

continuous deactivation over time, especially for the Rh/ZSM-5(30)-IE and Rh/SSZ-13(24) catalysts with the highest Al-content in the zeolite. The stronger inhibition for Al-rich zeolite supports has also been observed for zeolite-supported Pd catalysts and has been attributed to changes in hydrophobicity with proton content, which makes more proton-rich zeolites more hydrophilic and thus more susceptible to the adverse effects of water.<sup>18-20,22</sup> Given that the single atom sites are



**Fig. 8** HAADF-STEM images of spent Rh/ZSM-5(30)-IE. (a): after CH<sub>4</sub> oxidation in CH<sub>4</sub> + O<sub>2</sub> atmosphere; (b) after CH<sub>4</sub> oxidation in CH<sub>4</sub> + O<sub>2</sub> + H<sub>2</sub>O atmosphere. EDS analysis can be seen in Fig. S6 and S7 in the ESI.† The red lines represent 5 nm. The STEM picture of the fresh catalyst can be seen in Fig. 3(b).

found to be less active and favored by a higher Al content, this gradual loss of activity for Al-rich zeolites could be due to a water-mediated dispersion into single atom species. The results in Fig. 7(a and b) show that Rh/y-Al<sub>2</sub>O<sub>3</sub> and Rh/SiO<sub>2</sub> are of intermediate activity despite having rhodium entirely in the more active nanoparticle form, which would indicate that there is a beneficial support effect of the structured zeolite support. Rh/SiO<sub>2</sub> exhibits a modest activity in the absence of H<sub>2</sub>O (Fig. 7(a)), but is strongly inhibited by the presence of  $H_2O$  in the feed and becomes the least active catalyst when water is present. The strong inhibition by H<sub>2</sub>O for SiO<sub>2</sub> as a support was also reported for CH<sub>4</sub> oxidation on Pd.<sup>39</sup> This suggests the existence of specific interactions between water and the amorphous silica support that are highly detrimental to the catalytic activity. The Rh/SiO2 catalyst also experienced a continuous gradual deactivation in the presence of H<sub>2</sub>O, which was not seen for the Si-rich zeolite supports (ESI<sup>+</sup> Fig. S4). A Sirich zeolite support is thus able to avoid the stronger inhibition occurring for both amorphous SiO<sub>2</sub> and Al-rich zeolites.

In the presence of both 5 vol%  $H_2O$  and 20 ppm  $SO_2$ , the catalytic activity is lowered further, and the oxidation is shifted to a higher temperature as shown in Fig. 7(c) and (d). This is attributed to the formation of sulfate-type species on the active phase that block the active sites.<sup>13</sup> In the initial period of SO<sub>2</sub> exposure during the 1st run, the more Al-rich samples, particularly Rh/y-Al<sub>2</sub>O<sub>3</sub> and Rh/ZSM-5(50), are more active. It is well-established that the surface of Al<sub>2</sub>O<sub>3</sub> takes up SO<sub>2</sub> and becomes sulfated.<sup>12,40-45</sup> The higher initial activity on the Al<sub>2</sub>O<sub>3</sub> support is attributed to this initial SO<sub>2</sub> uptake by the Al<sub>2</sub>O<sub>3</sub> sites that protects the active phase from SO<sub>2</sub> until the support is saturated. During cooling (2nd run in Fig. 7(d)), a stable activity level (Fig. S5(b)<sup>†</sup>) indicates that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support has been saturated, whereby the full impact of SO<sub>2</sub> on the active phase becomes visible, and here a strong deactivation is also observed for the Rh/y-Al2O3 sample. Fig.7(d) shows that the more Al-rich zeolites are relatively more affected by the presence of SO<sub>2</sub>. This is most clearly seen for the Rh/ZSM-5(50) sample, which is almost as active as Rh/ZSM-5(280) in the SO<sub>2</sub>-free atmospheres, but significantly less active in the presence of SO<sub>2</sub>. An

explanation could be that some sulfation occurs for the more Al-rich zeolites in the same way as for the amorphous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and that this sulfation has negative implications for the performance of the active phase.<sup>18,45</sup> Previous EDS mapping of the elemental distribution in Rh/ZSM-5 after operation in a SO<sub>2</sub>-containing atmosphere did indicate some correlation between Al and sulfur, which could suggest that sulfur uptake occurs at the Al sites.<sup>13</sup> More Al-rich zeolites are thus likely to take up greater amounts of sulfur on the support.

This creates a situation, where the most silica-rich zeolites, particularly the 2 wt% Rh/ZSM-5(280) catalyst, provide the best performance. The activity of 2 wt% Rh/ZSM-5(280) was found to be stable over time in the presence of SO<sub>2</sub> and H<sub>2</sub>O as indicated by a limited (5 °C) shift for  $T_{50}$  between the 1st and 2nd runs after time on stream in SO<sub>2</sub> for around 20 h (Table 2 and Fig. 7(c) and (d)) as well as the stable conversion of CH<sub>4</sub> during the 15 h stability test at 450 °C and 500 °C (Fig. S5 in the ESI†). The relatively sulfur-tolerant behavior of Rh-catalysts for methane oxidation has previously been correlated to the ability of moist, bulk Rh sulfates to release part of their sulfur at lower temperatures.<sup>13</sup>

In a realistic reaction atmosphere containing  $H_2O$  and  $SO_2$ , the Rh/ZSM-5(280) catalyst thus emerges as the most active sample. As discussed, this can be attributed to the silica-rich zeolite, which minimizes the formation of less active Rh single atom sites, minimizes the water inhibition that occurs for amorphous  $SiO_2$  and the more Al-rich supports and avoids the negative effects of  $SO_2$  that occur for both Al-rich zeolites and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

## 4. Conclusion

The influence of the support has been investigated for Rhbased catalysts employed for total oxidation of CH<sub>4</sub> using both amorphous SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 280, 80, and 50) and SSZ-13 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 24) zeolites. A series of 2 wt% Rh catalysts on the various supports were prepared by incipient wetness impregnation and a catalyst containing 0.294 ± 0.015 wt% Rh was prepared by ion exchange. The support was found to have a strong impact on both the speciation of Rh and the catalytic activity, as the support influences the distribution of Rh between Rh<sub>2</sub>O<sub>3</sub> nanoparticle sites and single atom sites. On SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the most Sirich ZSM-5(280) zeolite, Rh is only present as Rh<sub>2</sub>O<sub>3</sub> particles, but on the more Al-rich zeolite supports a fraction of Rh is dispersed as single atoms on the zeolite exchange sites. The fraction of Rh at exchange sites in the fresh catalyst scales with the Al-content of the zeolites as expected from the increased number of exchange sites. However, the ionexchanged sample clearly shows that there is a tendency for agglomeration of single atom sites into particles during methane oxidation. This means that the site distribution of the working catalyst may differ from that of the fresh catalyst.

For  $CH_4$  oxidation with and without the presence of 5 vol%  $H_2O$ , the highest catalytic activity is obtained for the Rh/ZSM-5(280) sample containing only rhodium in the

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nanoparticle form and the lowest activity occurs for the ion exchanged sample with Rh exclusively in the single atom form. The zeolite-supported samples containing a mixture of nanoparticle and single atom sites exhibit an intermediate activity. This tendency clearly illustrates that the oxide nanoparticles are the most active form of Rh for total oxidation of methane. The presence of water is inhibiting to all the catalysts, but most inhibiting for Rh2O3 on an amorphous SiO<sub>2</sub> support, where the T<sub>50</sub> is shifted 100 °C up in temperature by the presence of 5 vol% H<sub>2</sub>O. The lower activity of Rh/SiO<sub>2</sub> despite Rh being in the more active nanoparticle form is attributed to this particularly strong inhibition from water that must be associated with the SiO<sub>2</sub> support. With both amorphous SiO<sub>2</sub> and Al-rich supports, water also affects the stability resulting in slow protracted deactivation, whereas Si-rich ZSM-5 zeolite supports do not yield this instability in the presence of water.

In the presence of both H<sub>2</sub>O and SO<sub>2</sub>, the most Al-rich supports are initially more active, but once a steady state has been reached the inhibition is stronger for the more Al-rich supports. This is most likely because the more Al-rich supports take up sulfur. This uptake delays the poisoning of the active phase, but at the steady state the sulfur uptake by the more Al-rich supports appears to be detrimental to the performance of the active phase. These findings provide a basis for design of catalysts to be used under real engine exhaust gas conditions where both H<sub>2</sub>O and SO<sub>2</sub> are present. The results illustrate that the optimal support is one that minimizes the interaction with both the reaction atmosphere and the active phase. Too strong interactions with the active phase causes more Rh to be lost to the less active single atom sites and too strong interaction with the atmosphere causes the support to undergo interactions with H<sub>2</sub>O or SO<sub>2</sub> that are detrimental to the performance of the active phase. The Sirich ZSM-5(280) zeolite emerges as the best support because the low number of exchange sites ensures that Rh is present in the more active oxide nanoparticle form, the low Al content prevents the sulfur uptake by the support that inhibits the active phase at the steady state and the structuring of the support prevents the particularly strong water-induced inhibition that occurs with an amorphous SiO<sub>2</sub> support.

## Conflicts of interest

There are no conflicts of interest to declare.

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