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Investigation on the simultaneous removal of COS, CS_2 and O_2 from coke oven gas by hydrogenation on a Pd/Al_2O_3 catalyst

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The present study deals with the processing of coke oven gas mainly composed of H_2, CH_4, N_2 and CO to provide a feedstock for the synthesis of base chemicals. In this respect, the particular focus of this work is the simultaneous reduction of critical trace components like COS, CS_2 and O_2 by catalytic reaction with H_2. The investigations were performed in synthetic coke oven exhaust using a Pd/Al_2O_3 catalyst. The results of the hydrogenation tests showed complete conversion of COS, CS_2 and O_2 at 200 °C and above with selective formation of H_2S. However, below 200 °C the conversion of O_2 was markedly reduced and CH_3-SH appeared as a by-product. Mechanistic studies were performed by *in situ* diffuse reflectance infrared Fourier transform spectroscopy coupled with mass spectrometry. These investigations demonstrated dissociative adsorption of COS on the catalyst at 150 °C resulting in the formation of bridged CO adsorbates and probably elemental sulfur. It is assumed that these species predominate the active Pd surface under reaction conditions. Consequently, the adsorption of O_2 and the reaction to H_2O is suppressed thus substantiating the decrease in performance at low temperatures. However, increasing the temperature to 200 °C and above leads to desorption of CO and sulfur compounds restoring the efficiency of the catalyst.

1. Introduction

Deep desulfurization is widely used for the removal of sulfur from natural gas as well as refined petroleum products, for instance gasoline and diesel fuels. The reduction of sulfur is primarily required to avoid poisoning of downstream processes such as fuel cells or depollution catalysts of combustion engines. Although well-established in petrochemical industry, deep desulfurization is still a matter of R&D, particularly to meet future legislative regulations addressing the sulfur fraction of fuels.[1–6] Additionally, the reduction of sulfur is also considered for coke oven gases aiming sulfur contents below 10 mol ppm, whereas up to now no cost-efficient process exists. Coke oven gas is a by-product of the steel production and mainly consists of 60 vol% H_2, 20 vol% CH_4 and 6 vol% CO. Thus, the exhaust of coke ovens shows promising potential as a feedstock for basic chemicals, *e.g.* methanol.[7] However, the exhaust also contains critical sulfur components such as COS, CS_2 and mercaptans representing strong catalyst poisons, especially for Ni and Cu catalysts used in steam reforming and methanol synthesis, respectively.[7,8] Therefore, deep desulfurization is required, which is mostly realized by hydrodesulfurization (HDS). HDS implies hydrogenolysis of organosulfur compounds on CoMo or NiMo catalysts yielding sulfur-free hydrocarbons and H_2S. The H_2S produced can subsequently be removed by ZnO adsorbers or scrubbing processes.[9–11] As a result, HDS leads to drastic decrease in sulfur proportions down to 15–30 mass ppm as required for ultra-low sulfur fuels for instance.[12]

Furthermore, for deep desulfurization of diesel fuels, noble metal catalysts based on platinum and palladium were investigated with promising results.[13–17] But, only little is known on the HDS performance of noble metals in gaseous streams containing COS or mercaptans. Additionally, noble metals provide advantageous features, which are relevant for their use in gas oven exhaust, such as (i) enhancement of the removal of oxygen by reaction with hydrogen to water, since it can be harmful in downstream processes (*e.g.* due to safety issues or corrosion effects), (ii) suppression of coke formation by hydrogenation of olefins and (iii) their superior HDS activity as referred to traditional CoMo catalysts.[14] However, there is a debate in the literature on the stability of noble metal catalysts towards sulfur poisoning.[13–18] In this respect,

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some papers investigated the interaction of sulfur compounds with Pt and Pd catalysts. Bartholomew *et al.*[19] reported on the dissociative adsorption of COS, CS_2 and methyl mercaptan (CH_3SH) with strong sticking of the sulfur on the noble metals. Moreover, Reinhoudt *et al.*[14] studied the nature of the active sites on alumina–silica-supported Pt suggesting that the desulfurization takes place on vacancies present in small platinum particles. High activity was also attributed to the support acidity affecting the electron deficiency and weakening the noble metal–sulfur bond.[20] Additionally, Pt and Pd sulfides originated from HDS can effectively be regenerated by reaction with H_2 above 463 K.[17,21,22]

With the above background the present study is the first that deals with the simultaneous removal of organosulfur compounds and O_2 from coke oven gas by hydrogenation on a commercially available Pd/Al_2O_3 catalyst. The investigations were made in a synthetic exhaust using a laboratory test bench with fixed bed reactor. COS and CS_2 were taken as model components showing highest importance among the sulfur species in practice.[20] In addition to the evaluation of the catalytic performance, *in situ* diffuse reflectance infrared Fourier transform spectroscopy coupled with mass spectrometry was conducted to obtain some mechanistic insights into the complex reaction network, particularly at low temperatures.

2. Experimental

2.1. Catalytic studies

The performance of the commercial Pd/Al_2O_3 catalyst towards hydrogenation of COS and CS_2 combined with reduction of O_2 was studied in a coke oven model exhaust by employing a laboratory bench equipped with fixed bed reactor. The catalyst implied a Pd load of 0.3 wt% and was used in form of spheres with a diameter of 3 mm. According to Mears and Weisz–Prater criteria it was deduced that neither film nor pore diffusion limit the chemical kinetics.[23] The sample (68.6 g) was fixed in the stainless steel tube reactor (i.d. 30 mm) by quartz wool and a sieve resulting in a bed height of 15 cm. In front of the packed bed, glass beads (2.85–3.45 mm, Carl Roth) were placed to improve heating of the inlet gas. The temperature was recorded by two Pt100 shunts (type 27-7125, Bartec) directly located in front of and behind the catalyst bed. The catalyst was initially pre-treated at 350 °C for 1 h with 50% H_2 in N_2. Before the tests, the sample was heated up in N_2 flow (5.2 LN/min) to the specific test temperature and then the feed was adjusted until steady state conditions were reached. Each test point was held for 90 min. After this, temperature (120–400 °C) or feed composition was varied. The model feed consisted of 60–120 mol ppm COS, 55–120 mol ppm CS_2, 50 vol% H_2, 20 vol% CH_4, 1 vol% O_2 and N_2 as balance. The reactor pressure was regulated with a needle valve behind the reactor to 1.2 bara, whereas the total gas flow was kept at 5.2 LN/min corresponding to a space velocity of 3000 h^{-1}. All gases were purchased from Linde. Pure H_2 (5.0), CH_4 (2.5) and N_2 (5.0) were taken, while the sulfur compounds as well as O_2 were used as mixtures with N_2. Each volume flow rate was checked by independent mass flow controllers (Brooks Instruments). All electronic devices were controlled by Freelance 2013 software from ABB.

The gas analysis was carried out by gas chromatography (Compact GC 4.0, Global Analyser Solutions) using a pulsed flame photometric detector (PFPD) for COS, CS_2 and H_2S and a thermal conductivity detector (TCD) for O_2. Simultaneous measurement of organic sulfur components, H_2S and O_2 was not possible. Before entering the GC, the gas stream passed a condensate trap to reduce the amount of water in the columns. Furthermore, a pressure regulator was implemented to ensure a constant pressure at the inlet of the GC. With this set-up, reproducible results were achieved.

2.2. *In situ* DRIFTS and MS studies

The reaction of COS, O_2 and H_2 on the Pd/Al_2O_3 catalyst and the bare Al_2O_3 support was investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The analyses were performed on a FTIR Spectrometer Tensor 27 (Bruker) equipped with MCT detector (Internal) and Praying Mantis DRIFTS optics (Harrick), while gas phase was simultaneously checked by mass spectrometry (Cirrus 2, MKS Instruments). In each experiment, fresh catalyst sample was placed into the cell and was subsequently pre-reduced with a mixture of N_2 and H_2 (50 vol% each) at 300 °C for 15 min following the pre-treatment in the catalytic studies. DRIFTS data were recorded by accumulating 200 scans resulting in a time resolution of *ca.* 5 min. Background spectra were taken at 40 °C and 150 °C and under flowing N_2 (500 mL min^{-1}). Subsequently, the sample was exposed to COS (200 mol ppm) at 40 and 150 °C to investigate the resulting adsorbates. For temporal separation of the overall reaction, H_2 and O_2 were successively dosed after the pre-adsorption of COS at 150 °C. Additionally, the simultaneous conversion of the reactive gases was checked at the same temperature by exposing the catalyst and bare support to a mixture of 200 mol ppm COS, 60 vol% H_2, 1 vol% O_2. N_2 was used as balance. After the adsorption and reaction steps, the sample was flushed with 500 mL min^{-1} N_2 for 25 min to differentiate gas-phase and surface species, while each exposure was made until equilibrium or steady state. The overall gas flow was always kept at 500 mL min^{-1}. The DRIFT spectra are presented in form of the Kubelka Munk function defined as $F(R) = (1 - R)^2/(2R)$; R is the quotient of sample and background scans.

3. Results and discussion

3.1. Conversion of COS, CS_2 and O_2 on Pd/Al_2O_3 catalyst

At temperatures over 200 °C the conversion of organosulfur compounds (60 mol ppm COS and 55 mol ppm CS_2) as well as 1 vol% O_2 was complete and stable for the established time on stream of 90 min (Fig. 1). Additionally, the formation of 140 mol ppm H_2S was observed between 200 and 400 °C, which is the thermodynamically favored product under these

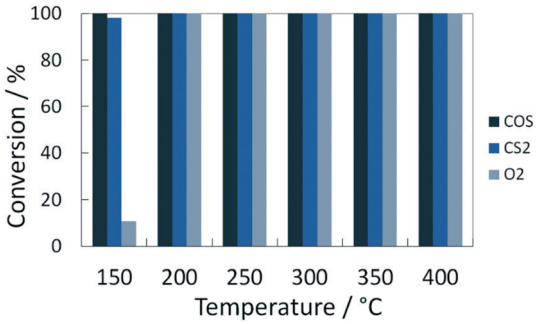

Fig. 1 Stationary conversion of COS, CS_2 and O_2 over temperature in model coke oven gas on Pd/Al_2O_3 catalyst. Conditions: 3000 1/h, 60 mol ppm COS, 55 mol ppm CS_2, 1 vol% O_2, 50 vol% H_2, 20 vol% CH_4, N_2 balance.

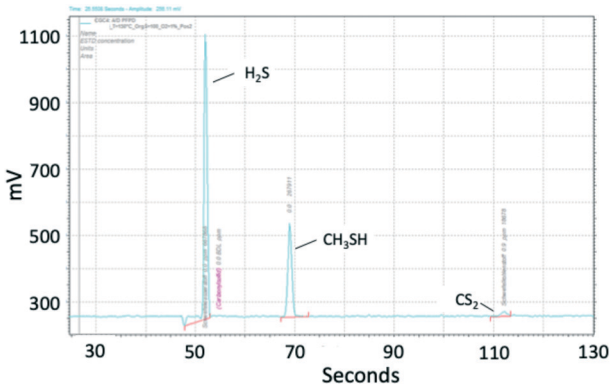

Fig. 3 Chromatogram of sulfur components, measured with PFPD. Conditions: 3000 1/h, 150 °C, 60 mol ppm COS, 55 mol ppm CS_2, 50 vol% H_2, 20 vol% CH_4, 1 vol% O_2, N_2 balance.

conditions. This proportion is in line with the stoichiometry of the conversion of COS and CS_2 according to eqn (1) and (2). Note that the discrepancy to the theoretical yield (170 mol ppm) is referred to influence of the condensate trap in front of the GC.

$$COS_{(g)} + H_{2(g)} \rightleftharpoons H_2S_{(g)} + CO_{(g)} \quad \Delta_R H^0 = 7 \text{ kJ mol}^{-1} \quad (1)$$

$$CS_{2(g)} + 2H_{2(g)} \rightleftharpoons 2H_2S_{(g)} + C_{(s)} \quad \Delta_R H^0 = -158 \text{ kJ mol}^{-1} \quad (2)$$

$$O_{2(g)} + 2H_{2(g)} \rightleftharpoons 2H_2O_{(g)} \quad \Delta_R H^0 = -484 \text{ kJ mol}^{-1} \quad (3)$$

$$CS_{2(g)} + 3H_{2(g)} \rightleftharpoons CH_3SH_{(g)} + H_2S_{(g)} \quad \Delta_R H^0 = -160 \text{ kJ mol}^{-1} \quad (4)$$

Furthermore, when decreasing the temperature from 200 to 150 °C a strongly unsteady behavior of the catalyst appeared implying continuous decrease of O_2 conversion, which remained almost constant after 200 min at 150 °C (Fig. 2). The analysis of the sulfur components at 150 °C at the end of the experiment showed still high conversion of COS and CS_2. However, in addition to H_2S, CH_3SH was also formed (approx. 30 ppm), whereas both compounds totally amounted to 120 mol ppm (Fig. 3 and Table 1). For CoMo catalysts, Clark *et al.*[24] supposed that CH_3SH is originated from the hydrogenation of the C–S bond in line with the thermodynamics (eqn (4)). Furthermore, it cannot be excluded that some adsorbed sulfur still remained on the catalyst surface[25] and that another sulfur compound was produced, which could not be detected by PFPD. For example, the production of SO_2 is basically feasible when the reaction of S with O_2 is faster than that with H_2. Other organic sulfur components were not formed, they would have been detected by PFPD.

Moreover, the catalyst was exposed to a model coke oven gas with higher sulfur mole fractions, *i.e.* each 125 mol ppm for COS and CS_2, to evaluate the effect of sulfur on the catalytic performance. At 200 °C the conversion of O_2 and organic sulfur is complete. Subsequently, the temperature was lowered to 120 °C. This leads to a drop of oxygen conversion below 30% within less than 1 h (Fig. 4). Subsequently, it was heated again to 200 °C resulting in an immediate rise of the conversion to over 95%. Entire removal of O_2 was achieved by further increasing the temperature to 250 °C, whereas COS and CS_2 were also completely converted, *i.e.* the same performance was obtained than before (Fig. 2). Measuring the concentration of the sulfur components at the outlet showed the initially measured full conversions and solely a H_2S peak in the product stream; note that quantitative detection of H_2S was not available. This shows that sulfur, which inhibits the O_2 conversion below 150 °C, is released from the catalyst and therefore it can be regenerated by an increase of temperature.

Since the conversion of O_2 to H_2O is inhibited below 150 °C, while the sulfur compounds are still efficiently converted (<3 ppm), it can be concluded that COS, CS_2 and H_2 predominately chemisorb on the active sites of the catalyst. Furthermore, the higher fractions of the sulfur components obviously favor their adsorption as indicated by the stronger inhibition of the O_2 conversion (Fig. 4). This conclusion is in line with Bartholomew *et al.*,[19] who also observed preferential adsorption of sulfur compounds compared to O_2. Additionally, it is well known in the literature that sulfur forms strong bonds with metals of group 10 (Ni, Pd, Pt) due to unshared electrons. Therefore, it is assumed that in an

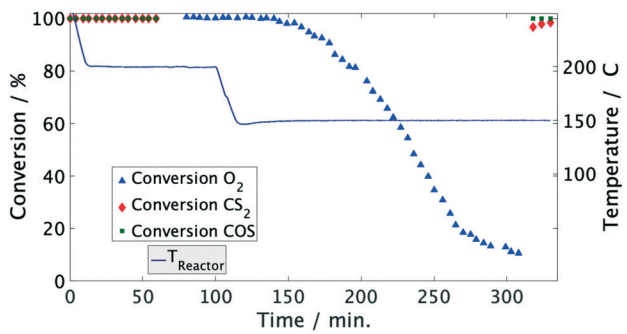

Fig. 2 Conversion of COS, CS_2 and O_2 over time in model coke oven gas on Pd/Al_2O_3 catalyst. Conditions: 3000 1/h, 60 mol ppm COS, 55 mol ppm CS_2, 50 vol% H_2, 20 vol% CH_4, 1 vol% O_2, N_2 balance.

Table 1 Conversion of COS, CS_2, CH_3SH and O_2 at steady-state at 200 °C and at 150 °C after 200 min. Conditions: 3000 1/h, 60 mol ppm COS, 55 mol ppm CS_2, 50 vol% H_2, 20 vol% CH_4, 1 vol% O_2, N_2 balance

	X(COS) in %	X(CS_2) in %	y(CH_3SH) in mol ppm	y(H_2S) in mol ppm	X(O_2) in %
200 °C	100	100	<3	≈140	100
150 °C	100	98	≈30	≈90	10.6

initial step COS adsorbs on at least one Pd atom followed by dissociation into CO and S adsorbates as described by eqn (5) and (6).[17,19,26–29] Obviously, the coverage of the Pd sites by S grows at lower temperatures (120 °C) thus suppressing the H_2–O_2 conversion as found in the experiments (Fig. 2 and 4). However, when re-increasing the temperature (>150 °C) the S adsorbates increasingly react with H_2 to yield Pd and H_2S,[21] which was detected in the gas-phase (eqn (7)). Consequently, the active Pd sites are regenerated and are again available in sufficient abundance for the conversion of O_2 as evidenced in Fig. 4.[14,17,28] Since this reaction is highly exothermic (eqn (3)), it probably leads to a self-acceleration of the reaction rate. This explains the rapid rise of the conversion to over 95% when heating up from 120 °C. Above that, the conversion rises slowly, but can be accelerated by increasing the temperature.

$$\mathrm{COS} + x\mathrm{Pd} \rightleftharpoons \mathrm{COS{-}Pd}_x \quad (5)$$

$$\mathrm{COS{-}Pd}_x \rightleftharpoons \mathrm{CO{-}Pd}_y + \mathrm{S{-}Pd}_z \quad (x = y + z) \quad (6)$$

$$\mathrm{S{-}Pd}_z + \mathrm{H_2} \rightleftharpoons \mathrm{H_2S} + \mathrm{Pd}_z \quad (7)$$

On the other hand, the complete inhibition of the hydrogen–oxygen reaction upon cooling from 200 to 120 °C is also fast within a narrow temperature window. Hence, it can be concluded that at temperatures below 200 °C the formation of elemental sulfur from COS or CS_2 decomposition is faster than its reaction with hydrogen. The continuous chemisorption of sulfur on active Pd sites leads to decreasing levels of oxygen conversion which initiates further cooling of the catalyst internally and therefore increases chemisorption of sites with sulfur even more.

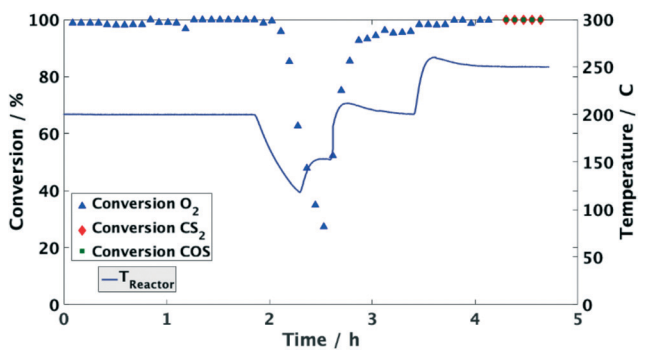

Fig. 4 Conversion of O_2 and inlet temperature over time using a Pd/Al_2O_3 catalyst. 3000 1/h, 125 mol ppm COS, 125 mol ppm CS_2, 50 vol% H_2, 20 vol% CH_4, 1 vol% O_2, N_2 balance. Decrease and increase of O_2 conversion upon change in reaction temperature.

As shown by other groups, the supports' acidity has a positive effect on the regeneration of the catalyst: firstly, the number of active sites is increased because of stabilization of small noble metal particles.[17,28] Secondly, acid support material weakens the Pt–S bond and therefore promotes the formation vacant sites.[30,31]

In this series of experiments no other side reactions were observed. However, it was previously described that metals of group 10 can catalyze the methanation reaction in this temperature range.[33]

3.2. Mechanistic studies

In situ DRIFTS measurements were conducted with both Pd/Al_2O_3 as well as Al_2O_3 to evaluate the role of sulfur in the inhibition of the O_2 conversion at low temperatures. In these studies, COS was taken, as it represents the most prominent organic sulfur compound present in real coke oven gas.[32] The DRIFTS studies were conducted by subsequently exposing the sample to O_2, H_2 and COS as well as by simultaneously supplying the gases.

3.2.1. Successive exposure to COS, H_2 and O_2. The DRIFT spectra of Pd/Al_2O_3 recorded after COS exposure at 40 °C exhibit predominant bands in the range between 1200 cm^{-1} and 1700 cm^{-1} (Fig. 5). Features at 1658 ($\nu_{as}(CO_2)$) and 1435 cm^{-1} ($\nu_s(CO_2)$) are associated with HCO_3^- surface species present on Al_2O_3.[34] Furthermore, the bands at 1578 (ν_{as}(OCS)) and 1330 cm^{-1} (ν_s(OCS)) are assigned to $HSCO_2^-$ coordinated to Al_2O_3. The weak bands located at 2050 and 2070 cm^{-1} are referred to molecularly adsorbed COS,[35,36] while the weak feature at 2586 cm^{-1} is ascribed to the stretching vibration of

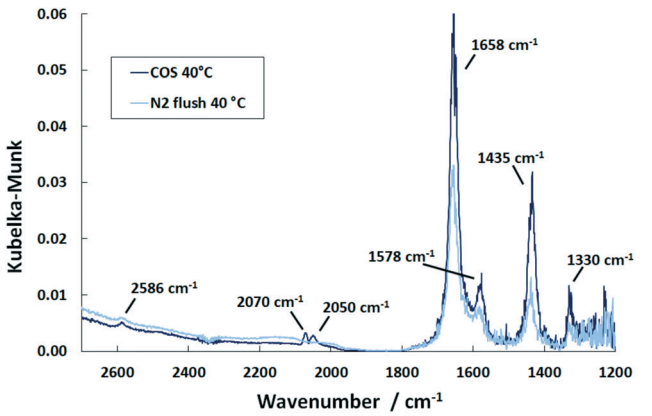

Fig. 5 DRIFT spectra of the Pd/Al_2O_3 catalyst after saturation with COS at 40 °C and upon subsequent flushing with N_2 (500 ml min^{-1}, 500 ppm COS, N_2 balance).

HS species.[37,38] Since reference tests with pure Al_2O_3 provided the same DRIFTS bands, all features are assigned to the chemisorption of COS on the Al_2O_3 support. OH stretching bands of the support appear and increase over time in the range from 2700 to 3700 cm^{-1}. Subsequent flushing with nitrogen leads to disappearance of the band referred to molecularly adsorbed COS and to a slight decrease in the feature of HCO_3^- associated with desorption. During the entire time a small and decreasing amount of CO_2 is detected by MS in the outlet stream.

In the COS exposure at the reaction temperature of 150 °C (Fig. 6), the DRIFT spectra of the Pd/Al_2O_3 catalyst also show the features of HCO_3^- and $HSCO_2^-$. However, the intensities of the HCO_3^- band decline with time, whereas that of the $HSCO_2^-$ entities increase. Also, molecularly adsorbed COS and the HS surface species are again observed. This result is in contrast to Jackson *et al.*[39] who did not observe COS adsorption on Pt/Al_2O_3. Nevertheless, since Al_2O_3 is used as a catalyst for the hydrolysis of COS in Claus plants, the mechanism was widely investigated.[25,40] It is generally accepted that in the initial step COS adsorbs on a OH^- surface group of Al_2O_3 leading to the formation of $HSCO_2^-$. According to George,[41] $HSCO_2^-$ further reacts with water, originated from surface OH groups and H present on Pd, and subsequently dissociates to CO_2, H_2O and SH^-. Finally, SH^- is converted with H_2O into H_2S while OH^- is reformed. This mechanism explains the formation of HCO_3^- on the surface, which increases at 40 °C. Since at this temperature only traces are detected by MS, most CO_2 formed is adsorbed on the surface as indicated by the DRIFTS features at 1658 and 1435 cm^{-1} (Fig. 5). The decreasing peak at 150 °C (Fig. 6) shows that HCO_3^- is decomposed at higher temperatures and CO_2 is released to the gas phase. Contrary, SH^- remains on the catalyst surface, which is shown by the band located at 2586 cm^{-1} (ν(HS)), (not shown in Fig. 6).

In contrast to 40 °C, a double band with maxima at 1890 and 1810 cm^{-1} is obtained upon COS exposure at 150 °C. According to the literature,[42,43] the band at 1890 cm^{-1} refers to bridged Pd_x–CO (with x = 2–3) moieties, whereas the feature at 1810 cm^{-1} is likely due to threefold hollow binding CO (Pd_3–CO).[42,44–47] The presence of CO adsorbates is ascribed to the dissociation of COS on Pd sites in line with the literature.[39] However, the proof of resulting Pd–S species is difficult, as the corresponding stretching vibration is expected below 600 cm^{-1},[48] which is not accessible by the DRIFTS cell used.

Compared to 40 °C a higher partial pressure of CO_2 is detected in the outlet stream at 150 °C decreasing over time (Fig. 7). This effect is referred to the above mentioned HCO_3^- decomposition. Additionally, it is likely that the adsorbed CO reacts with surface oxygen of the support to yield CO_2 which is released in the gas phase. When the excessive oxygen is consumed, CO remains on Pd as demonstrated by the growing DRIFTS bands between 1800 and 2000 cm^{-1} (Fig. 6). This leads to increased absorption of COS on the support (growing bands at 1578 and 1330 cm^{-1} in Fig. 6). Flushing the catalyst afterwards with nitrogen leads stable adsorbates. However, it has little influence on the HCO_3^- and $HSCO_2^-$ deposits. The weakly adsorbed COS is removed immediately from the catalyst surface upon N_2 flushing.

The COS adsorption on bare Al_2O_3 performed at 150 °C provides no CO bands indicating that Pd is necessary for COS dissociation. Besides that, all the other features appear which confirms that they are surface species formed on Al_2O_3 and not on the active sites of the catalyst (Fig. 8).

When supplying H_2 to the catalyst at 150 °C after COS adsorption and N_2 flushing all the DRIFTS bands decrease and disappear with the exception of the feature of the HCO_3^- species (Fig. 9). Considering the outlet stream, the MS trace showed strong release of water upon addition of H_2 referred to the reaction with some surface oxygen species of the support.[49] Simultaneously, the MS signal with m/z = 32 increased sharply followed by slow decay (inlay in Fig. 9). Since no oxygen has been added, it is presumably ^{32}S derived from small amounts of H_2S which were removed from the catalyst by reduction of sulfur species. This is confirmed by small and noisy signals of mass 33 and 34 that were also detected. Since the catalyst reveals little load of Pd (0.3 wt%),

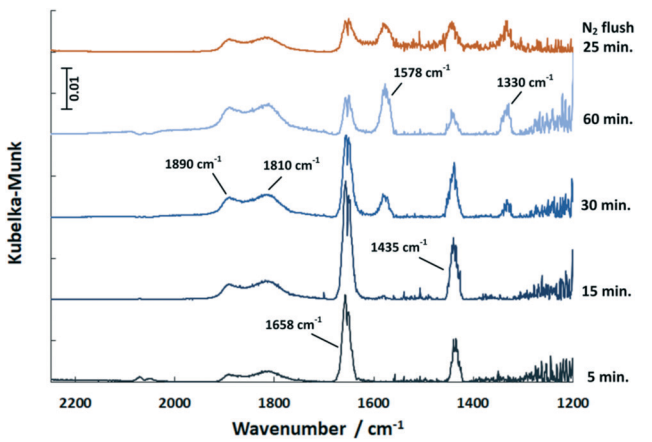

Fig. 6 DRIFT spectra of the Pd/Al_2O_3 catalyst exposed to COS at 150 °C over time and upon subsequent flushing with N_2 (500 ml min^{-1}, 500 ppm COS, N_2 balance).

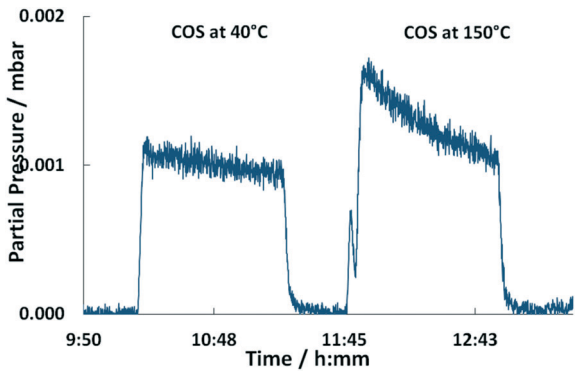

Fig. 7 MS traces of m/z = 44 upon COS exposure of the Pd/Al_2O_3 catalyst at 40 °C and 150 °C over time (500 ml min^{-1}, 500 ppm COS, N_2 balance).

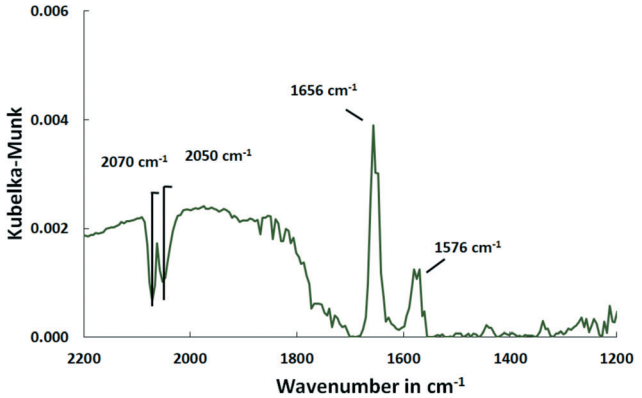

Fig. 8 DRIFT spectra of the Al_2O_3 support after saturation with COS at 150 °C (500 ml min^{-1}, 500 ppm COS, N_2 balance).

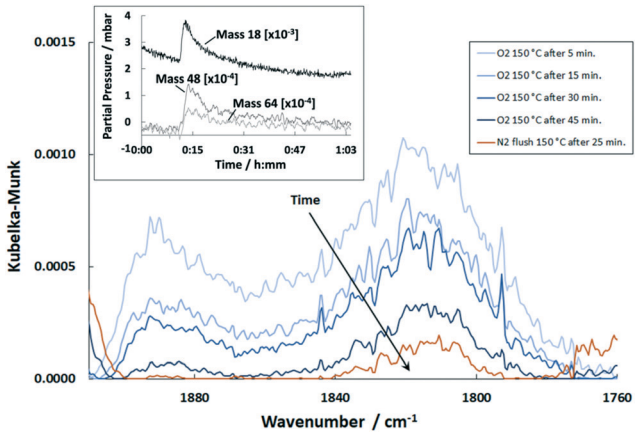

Fig. 10 DRIFT spectra of the Pd/Al_2O_3 catalyst exposed to O_2 at 150 °C over time and upon subsequent flushing with N_2 (500 ml min^{-1}, 1 vol% O_2, N_2 balance). Inlay shows the simultaneous MS trace of m/z = 18, m/z = 48 and m/z = 64.

the amount of H_2S is expected to be very small and hence hard to detect.

During the addition of H_2 the bands in the region above 3000 cm^{-1} correlated to stretching vibrations of OH groups increase in intensity (Fig. 9), which is associated with the adsorption of H_2O. Additionally, the formation of H_2O enhances the hydrolysis of COS leading to the reaction of SH^- and H_2S, respectively. This is confirmed by detection of mass 32 that appears due to ionization and decomposition of COS into CO and S inside the mass spectrometer. Mass 60, that would indicate appearance of COS in the outlet stream was not detected. As shown in Fig. 9, the addition of H_2 to the catalyst led to further but not complete reduction of the CO peak(s). It is presumed that it is thermally desorbed due to the exothermic reaction of H_2 with surface oxygen species (eqn (3)). Flushing with N_2 had no effect on the CO bands.

Continuing with 1 vol% O_2 after exposure of the catalyst with COS and H_2 induced a slow but almost complete removal of CO (Fig. 10). A small band of threefold bound CO was still observed at 1807 cm^{-1} after 45 min. Additionally, MS indicates signals with m/z ratios of 33 and 34, which are clearly more pronounced as compared to the natural abundance of $^{16}O^{17}O$ and $^{17}O_2$. Due to the relatively high partial pressure these masses are unlikely to be HS^- or H_2S. Instead they are probably different combinations of H and O atoms and hence of a minor importance of the catalytic activity.

Furthermore, the exposure of O_2 lead to weak MS peaks 64 (SO_2^+) and 48 (SO^+) associated with SO_2 (inlay in Fig. 10). Hence, residues of sulfur were still present on the catalyst surface after H_2 treatment. Since SO_2 is produced on Pd/Al_2O_3 and Al_2O_3, it can be assumed that remaining sulfur existed on the Al_2O_3 support.[50,51] It was shown by Hoyos *et al.*[52] that H_2S adsorbed on Al_2O_3 can be completely

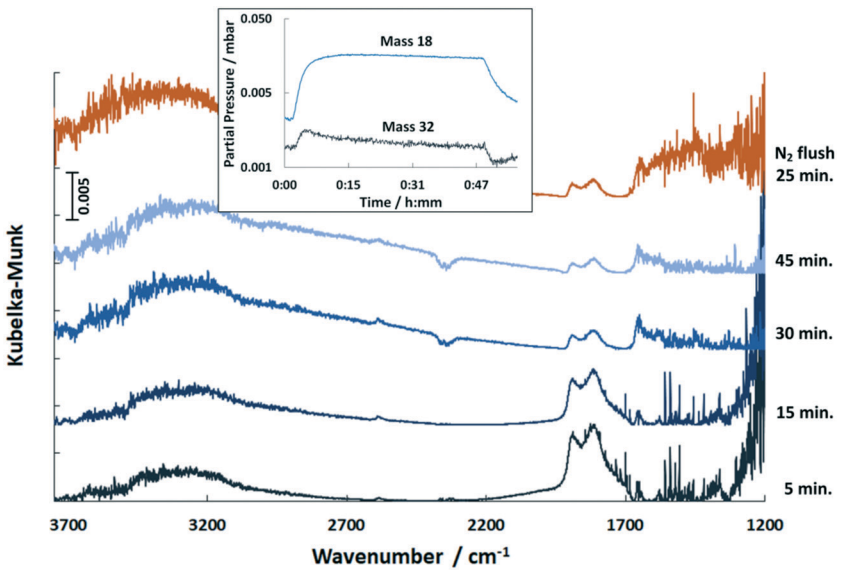

Fig. 9 DRIFT spectra of the Pd/Al_2O_3 catalyst exposed to H_2 at 150 °C over time and upon subsequent flushing with N_2 (500 ml min^{-1}, 60 vol% H_2, N_2 balance). Inlay shows the simultaneous MS traces of m/z = 18 and m/z = 32.

oxidized to SO_2 or SO_3. Furthermore, Ordóñez *et al.*[53] showed little desorption of SO_2 below 200 °C when conducting temperature programmed oxidation of SO_2-poisoned Pd/Al_2O_3. Hence, it is derived that although H_2 was shown to release sulfur from the support material, residues still remain on Al_2O_3 subsequently oxidized by O_2 to produce SO_2. Additionally, the MS signal with m/z = 18 (H_2O) increased sharply upon exposure to O_2 and decreased afterwards (inlay in Fig. 10). This indicates that adsorbed hydrogen is still present on the Pd sites even after N_2 flushing which reacts with O_2 to form H_2O.[54]

3.2.2. Simultaneous exposure to COS, H_2 and O_2 to Pd/Al_2O_3 or Al_2O_3. In another DRIFTS investigation, COS, H_2 and O_2 were simultaneously fed to mimic practical reaction conditions, whereas the temperature of the catalyst was set to 150 °C (Fig. 11). This approach led to an initial but weak formation of HCO_3^- within the first 5 min, continued by a decrease over the remaining 120 min until only a small peak at 1658 cm^{-1} remained. The previously identified CO peak on Pd (bridged Pd_x–CO (with x = 2–3) moieties) appeared as a shoulder at around 1866 cm^{-1}. Reference experiments made with the bare Al_2O_3 support basically shows very similar DRIFT spectra with exception of the CO shoulder, which again only appeared with Pd present (Fig. 12).

Considering that the catalyst is plain and active sites are free until the gas mixture is exposed to it, it can be assumed that initially all substances bind to it. Hence, besides the formation of CO–Pd and S–Pd by dissociation of COS, it is likely that oxygen and hydrogen also chemisorb to Pd.[54] Consequently, CO can be oxidized in a Langmuir–Hinshelwood mechanism to CO_2 and in addition H_2O is formed. The initial increase of HCO_3^- bands indicate an adsorption of CO_2 on Al_2O_3. At the same time, CO_2 is detected in the MS with a decreasing trend that coincides with the removal of HCO_3^- deposits. Therefore, the adsorption is an intermediate phenomenon. In addition, the MS data show a peak of H_2O in the beginning of the experiment, hence a release into the gas phase, that is more pronounced with Pd present. This is plausible, since Pd enhances the oxygen–hydrogen reaction.

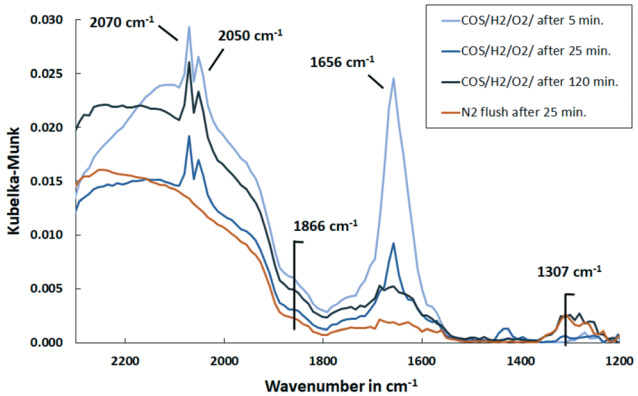

Fig. 11 DRIFT spectra of Pd/Al_2O_3 support exposed to synthetic coke oven gas at 150 °C over time and upon subsequent flushing with N_2 (500 ml min^{-1}, 500 ppm COS, 60 vol% H_2, 1 vol% O_2, N_2 balance).

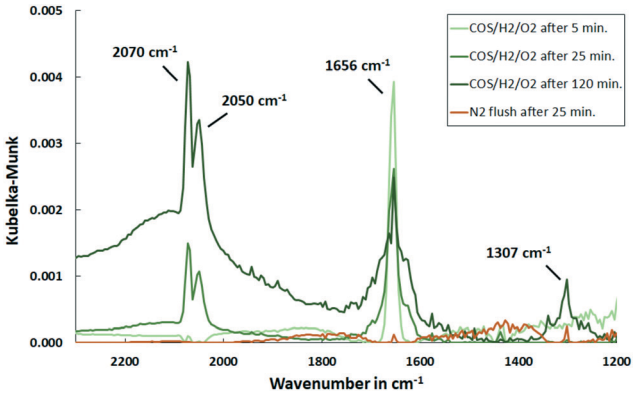

Fig. 12 DRIFT spectra of Al_2O_3 support exposed to synthetic coke oven gas at 150 °C over time and upon subsequent flushing with N_2 (500 ml min^{-1}, 500 ppm COS, 60 vol% H_2, 1 vol% O_2, N_2 balance).

At 150 °C CO is favorably adsorbed over O_2, so in the steady state Pd is preferably covered with CO and S, which inhibits O_2 adsorption and hence CO_2 formation. As investigated by Klauck *et al.*[55] and also shown in this work, for the same reason, the oxygen–hydrogen reaction is inhibited.

Since CO–Pd is formed by dissociation of COS, it can be once more assumed that in addition S–Pd is formed. While a high concentration of H_2 is present in the gas stream, it can be concluded that this bound sulfur reacts with dissociatively adsorbed H_2 on Pd to H_2S and is removed from the surface.[17] It was previously described that this reduction of metal sulfides such as Pd–S is catalyzed by the adsorption of H_2 molecules on Pd and their subsequent dissociation into atoms.[17,21]

The conversion of COS to H_2S catalyzed by Pd is confirmed by the MS spectra. A comparison of the outlet streams of simultaneous gas exposure on the catalyst and the support shows that with Pd/Al_2O_3 the partial pressure of mass 60 (COS) is lower (Fig. 13). In addition, comparing the spectra reveals that the masses 34, 33 and 32 showed steady signals in both cases, but with Pd/Al_2O_3 the partial pressure is higher compared to the support only. This indicates the formation of H_2S, HS^- and ^{32}S, the latter derived from splitting of H_2S in the MS.

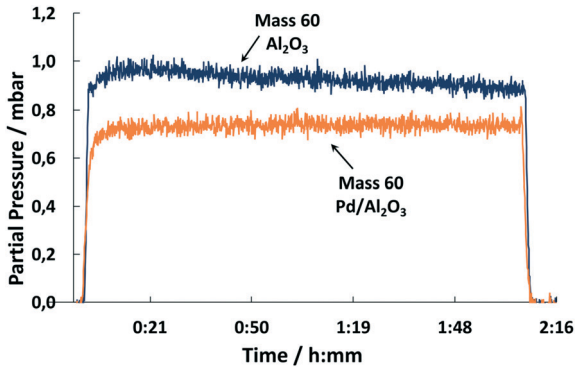

Fig. 13 MS trace of m/z = 60 upon exposure of Pd/Al_2O_3 and Al_2O_3 to synthetic coke oven gas (150 °C, 500 ml min^{-1}, 500 ppm COS, 60 vol% H_2, 1 vol% O_2, N_2 balance).

Moreover, the DRIFT spectra show that CO is bound to Pd over the entire duration. Therefore, it can be concluded that COS adsorption is not inhibited by CO, sulfur or H_2, hence all four can adsorb on the active sites under these conditions.

Furthermore, $HCSO_2^-$ appeared as a shoulder in the DRIFT spectra at 1578 cm^{-1} only in the beginning and exhibits a lower amount compared to initial COS dosing. This indicates that it is removed by hydrogen as shown before (Fig. 9). Moreover, a small feature at 1307 cm^{-1} was detected that increased with time and showed a smaller intensity with Pd present. A peak in that range was previously assigned to be physisorbed or chemisorbed SO_2 on Al_2O_3.[50,56] This accumulation of sulfates on Al_2O_3 were smaller when Pd is present. It was explained by Luo *et al.*[21] that sulfates in proximity to noble metal particles are reduced stepwise to H_2S by activated H_2 and are subsequently released. This reduction is temperature dependent, since higher temperatures increase the mobility of absorbed sulfates to the region where reduction is possible.

Again, small and noisy signals of mass 64 and 48 were detected with both catalyst and support present. This confirms the formation of SO_2. However, over time the signals decreased, which leads to the assumption that in the steady state H_2S is the predominant sulfur species that is released into the gas phase. It this assumed that this again originates in the inhibited adsorption and therefore reactivity of oxygen molecules. In addition, COS molecularly adsorbed on Al_2O_3 was present that was again instantly removed by flushing with N_2.

4. Conclusions

The performance of a Pd/Al_2O_3 catalyst was evaluated for the simultaneous hydrogenation of organosulfur compounds and conversion of O_2, while some mechanistic investigations were made by DRIFT spectroscopy coupled with MS. The catalyst was tested between 120 and 250 °C in a model coke oven gas consisting of H_2, CH_4, O_2, COS and CS_2. The results showed that at 200 °C and above the organosulfur compounds are almost completely converted to H_2S. Simultaneously, O_2 entirely reacted with H_2 to H_2O. Upon lowering the reactor temperature below a critical point, the O_2 conversion is strongly inhibited, whereas COS and CS_2 are still completely converted. Also, the selectivity towards H_2S is decreased and CH_3SH appears as additional product. This altered performance is rapidly reversed by increasing the temperature just to 200 and 250 °C, respectively.

The mechanistic examinations of the Pd/Al_2O_3 catalyst as well as the bare Al_2O_3 support were conducted by (I) successive gas dosage of COS, H_2 and O_2 and (II) simultaneous exposure to all the reactive gases at 150 °C. It was shown that COS dissociates on the Pd sites to form CO and S adsorbates. These surface species located on the Pd sites prevent the adsorption of O_2 and they therefore strongly inhibit the oxygen–hydrogen reaction as observed in the catalytic performance tests. In addition, it was demonstrated that CO was removed from Pd due to displacement at 150 °C and it is assumed that desorption is accelerated at higher temperatures. Furthermore, the presence of H_2 leads to a removal of bound sulfur to H_2S.

Moreover, it was shown that COS also adsorbs on the Al_2O_3 support resulting in the formation of $HSCO_2^-$. Subsequently, $HSCO_2^-$ reacts with OH^- surface groups to CO_2 and H_2S, which can re-adsorb to yield HCO^-_3 species. However, $HSCO_2^-$ plays a rather minor role in the conversion of COS to H_2S.

To conclude, the strong blockage of the catalytically active Pd sites by CO and S inhibits side reactions. It is reversible by two effects: firstly, the increase of temperature that leads to the desorption of CO and secondly, by the presence of H_2 in the feed stream that removes bound sulfur to form H_2S.

Finally, this study shows that commercially available Pd/Al_2O_3 catalysts can be effectively taken for the removal of organosulfur compounds and oxygen from coke oven model gas. Also, the high amount of H_2 simply facilitates the catalyst regeneration. Consequently, HDS by Pd/Al_2O_3 catalysts is considered as a suitable method for the deep desulfurization of coke oven gas to supply synthesis gas for the chemical industry.

Conflicts of interest

There are no conflicts to declare.

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