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SO_x storage- and release kinetics for ceria supported platinum

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Abstract

The SO_x storage- and release kinetics on CeO₂ have been studied by lean SO_x adsorption and temperature programmed desorption for different pairwise configurations of individual monolith samples, *i.e.*, Pt/CeO₂+SiO₂, Pt/SiO₂+CeO₂, CeO₂+Pt/SiO₂ and CeO₂+SiO₂. In the case of sole ceria, lean SO_x adsorption proceeds both via SO₂ and SO₃ adsorption although the latter channel is kinetically favored. Hence, the rate of SO₂ oxidation is crucial for the overall SO_x storage kinetics. It is found that physical contact between Pt and ceria is important for the storage process. This is attributed to efficient transport routes for SO_x (surface

diffusion and spill-over processes) and/or specific adsorption sites at the platinum-ceria interface. The main route for SO_x release is found to be thermal decomposition where the effect of platinum is minor, although, in similarity with the storage kinetics, an indirect role could be present. Different mechanistic scenarios for SO_x adsorption are addressed and discussed which may serve as a guide for future experiments.

Key words: sulfur trap, adsorption, desorption, SO_2 oxidation, noble metal-support interaction, CeO_2 , Pt

1 Introduction

Energy-efficient solutions for propulsion within the transportation sector are likely to involve oxygen excess (lean) combustion [1]. A possible concept to reduce the NO_x levels in the resulting (net-) lean exhausts is NO_x storage catalysis [2]. However, the NO_x storage catalyst (NSC) has a high affinity towards sulfur oxides (SO_x) which poison the storage sites and lead to severe deactivation. Thus, the NSC should not be exposed to even small amounts of SO_x originating from fuels and/or lubricants. It is challenging to find appropriate solutions to this durability issue as emission standards need to be fulfilled over an expected useful period [4]. One **strategy** is to prevent SO_x from reaching the NSC by including a, so-called, sulfur trap upstream the NSC in the aftertreatment system. Two different types of **upstream** sulfur traps have been proposed **earlier**, *i.e.*, disposable [3] and regenerable [5]. **Here, the latter is considered to be used under continuously lean conditions.**

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Other concepts based on, for example, incorporation of SO_x trapping materials in the NSC formulation that can store and release SO_x under lean and rich conditions, respectively, have also been reported [6,7]. Such systems, however, are not treated here.

In a previous study [5] it has been found that for **continuously** lean conditions, CeO_2 -based materials are suitable for regenerable SO_x traps. The design target in this case was to store SO_x by adsorption below 500°C and release stored SO_x by thermal desorption above 600°C . The addition of platinum was measured to significantly enhance the SO_x storage. However, the actual role of platinum was not clarified **although various scenarios were speculated on viz. importance of SO_2 oxidation and spill-over of SO_x species.** In the present work, the influence of SO_2 oxidation and noble metal-support interaction on SO_x adsorption- and desorption kinetics for Pt/ CeO_2 is studied in more detail.

2 Experimental section

2.1 Sample preparation and characterization

The supported platinum samples were prepared by impregnating ceria and silica, respectively, with halogen-free platinum precursors. Ceria (99.5 H.S.A. 514, Rhône-Poulenc) was dispersed in distilled water and an aqueous solution of platinum(II)nitrate ($\text{Pt}(\text{NO}_3)_2$, Heraeus GmbH) was gently added to the ceria slurry under continuous stirring. The slurry was, thereafter, instantly frozen with liquid nitrogen and freeze-dried. The resulting powder was calcined in air at 600°C for 1 h (heating rate of $4.8^\circ\text{C}/\text{min}$ from 25 to 600°C). The corre-

sponding procedure was used to prepare the Pt/SiO₂ sample by impregnating colloidal silica (20 nm spherical particles, Nyacol 2034DI, Eka Chemicals) with an aqueous solution of tetraammineplatinum(II)nitrate (Pt(NH₃)₄(NO₂)₂, Degussa AG). The platinum load was for both catalysts 5% by weight.

Four types of monolith samples were prepared by immersing bare cordierite monoliths ($\varnothing=20$ mm, length=18 mm, 400 cpsi) in water slurries containing a binder and, respectively, Pt/CeO₂, Pt/SiO₂, CeO₂ and SiO₂ material. A colloidal ceria sol (10-20 nm spherical particles, Nyacol CeO₂(Ac), Nyacol Nano Technologies) and colloidal silica sol (20 nm spherical particles, Nyacol 2034DI, Eka Chemicals) was used as a binder for the ceria and silica materials, respectively. The coated monolith samples were then dried in air at 90°C for 2 min and calcined at 600°C for 5 min also in air. By repeating this procedure, 1 g of the respective coating was attached to each sample. All samples were calcined in air at 600°C for 90 min and stabilized in a mixture of 1% CO, 0.15% C₃H₈ and 2% O₂ (Ar as balance) using a total flow of 3000 ml/min.

2.2 SO_x adsorption- and desorption experiments

The adsorption- and desorption experiments were carried out using a gas-flow reactor described elsewhere [5]. Briefly, it consists of a horizontal quartz tube surrounded by a metal coil for resistive heating of the gas flow and the samples. Gases are introduced via individual mass flow controllers and the gas temperature in front of the sample is controlled by a Eurotherm regulator. The reactor is equipped with a Fourier transform infrared spectrometer instrument (MultiGas 2030, MKS instruments) for simultaneous detection of gas phase SO₂ and SO₃ in the outlet stream.

Four different **sample** configurations as depicted in Figure 1 were evaluated by lean SO_x adsorption (100 vol.-ppm SO_2 and 7% O_2 in Ar) at 250°C for 1h followed by a lean temperature programmed desorption (7% O_2 in Ar) by ramping the temperature from 250 to 700°C with a ramp rate of 10°C/min. The total flow was in both cases 3500 ml/min. This adsorption-desorption sequence was repeated three times.

3 Results and discussion

In a previous investigation with the same conditions as the ones used here [5], it was observed that ceria based regenerable SO_x traps initially exhibit a certain (minor) degree of irreversible adsorption. **This has been observed also by other authors [refs]**. In order to concentrate on the regenerable and reproducible results, the same lean SO_x adsorption-desorption sequence was carried out three times. As the basis for the discussion we use here only the second and third sequence.

In Figure 2 the results for lean SO_x adsorption (third sequence) on the different sample configurations A-D are shown. It is clear that the adsorbed amount of SO_x is much higher for the Pt/ CeO_2 sample (A) as compared to bare CeO_2 (D). **Note that the A geometry is not even saturated during the time frame of the experiment.** Based on the second and third adsorption sequence, the average amount of adsorbed SO_x is 406 and 106 μmol for the Pt/ CeO_2 and CeO_2 , respectively. This is in accordance with previous observations [5] which intuitively were connected to different **routes whereby SO_x adsorbs on, respectively, Pt/ CeO_2 and bare CeO_2 .** However, based on previous results it is not clear whether or not the increased SO_x adsorption is

thanks to the formation of gaseous **SO₃ over Pt** and subsequent adsorption of SO₃ on ceria or if SO₃ (or some other sulfur species) is transported from the platinum crystallites to ceria via surface diffusion and spill-over processes. **Similarly diffusion and spill-over of oxygen to ceria may be important steps.** To study the influence of sulphur carrier, here SO₂ and SO₃, on the SO_x storage, we use as a starting point for the analysis the comparison of present results for SO_x adsorption for **the systems with** physically separated platinum *i.e.*, configurations B and C. **These results are in turn compared with the Pt free system (configuration D).**

It is found that the amount of adsorbed SO_x on ceria is higher in the case of the Pt/SiO₂ positioned upstream of the ceria (configuration B) as compared to either the downstream position (configuration C) **or, even more clearly, the configuration D without Pt.** For configuration B, SO_x is adsorbed during the entire 60 min period of SO₂ exposure, although the SO_x adsorption is minor at the end of the period, as reflected by increasing concentration of outlet SO₂. The average amount of adsorbed SO_x is 286 μmol. Contrary, for configuration C, the outlet SO₂ concentration reaches a steady level at about t=40 min. The total SO_x concentration (sum of SO₂ and SO₃) is close to the inlet SO₂ concentration of 100 vol.-ppm which indicates negligible SO_x adsorption at the end of the measurement. Here the average adsorbed amount of SO_x is 174 μmol. Similarly, for bare ceria (D) the outlet SO₂ concentration reaches a steady level even **earlier** at about t=30 min.

The main difference in SO_x adsorption between configuration B and C is likely owing to the different SO₂ oxidation kinetics for Pt and CeO₂. Provided that the gas phase concentration of SO₃ is sufficiently stable (this assumption is supported by thermodynamic calculations not shown here), the present results

support the earlier suggestion in Refs. [5,13,14] that oxidation of SO_2 into SO_3 over Pt is important for the overall SO_x adsorption. **At the temperature used here, the SO_2 oxidation and subsequent sulphate formation on ceria are negligible** [5]. Based on results for configuration B and C, a few scenarios can be envisioned as depicted in Figure 3. For example, given that SO_2 and SO_3 compete for the same adsorption sites on ceria (scenario I versus scenario II), the present results indicate that SO_3 adsorption is kinetically favored. **Another explanation could be that the additional SO_x adsorption observed for configuration B occurs solely via the formation of SO_3 thanks to specific adsorption sites for SO_3 on the ceria.**

Consider again the SO_x adsorption onto the Pt/CeO₂ sample. Likely, the observed high adsorption is only partly explained by the formation of gaseous SO_3 . The comparison with the corresponding results for physically separated Pt and ceria (configuration B) shows the Pt/CeO₂ adsorbs significantly more SO_x . Assuming that the rate of SO_2 oxidation **into gaseous SO_3 is not too different** in the two cases (this is supported by the fact that the same amount of Pt was used in both cases) and that SO_3 is sufficiently stable in gas phase, the ceria is in both cases exposed to similar gas composition. Thus, the results indicate that physical contact between platinum and ceria is important for the overall SO_x adsorption process. Although the mechanistic details are difficult to deduce from the present results, we may speculate on different scenarios. If SO_3 is not stable in the gas phase under the conditions used here, then SO_2 oxidation close to the ceria is important (scenario III). However, as mentioned above, SO_3 is probably stable and, thus, a scenario where the SO_3 formed on Pt may diffuse on the Pt surface and spill-over to ceria (scenario IV) is possible. The SO_3 adsorbed on the ceria may then continue to diffuse

on the ceria surface as well as into the ceria bulk as was indicated by previous IR spectroscopy experiments [5]. In this case, the corresponding activation barriers for spill-over and diffusion are lower than the energy required for desorption. An expected crucial parameter in this respect is the length of the circumferential Pt-ceria interface. Another scenario that also involves the Pt-ceria interface as an important parameter, is the assumption of specific adsorption sites at the interface accessible for SO_x either directly from gas phase (scenario V) and/or via the platinum or ceria surface (scenario VI).

Hitherto it has been shown that the inclusion of Pt preferable in direct contact with ceria enhances the overall SO_x adsorption on ceria. Turning to the corresponding results for lean SO_x desorption (Figure 4), the role of Pt is not as pronounced. One obstacle is that for the four geometries the total amount of stored SO_x is different. This may influence the SO_x desorption spectra, especially the peak SO_x desorption. However, despite this issue, a few remarks can be made. The SO_x desorption starts at about 500°C for all samples indicating that thermal decomposition of SO_x adsorbed on ceria is important **for the release process**. Furthermore, comparing configuration A and B (and assuming that the effect of different stored amounts of SO_x is negligible) the peak SO_x desorption occurs at a temperature only about 20°C lower for Pt/ CeO_2 . This indicates that physical contact between Pt and ceria has a minor influence on the desorption and that, again, thermal decomposition of SO_x adsorbed on ceria is the main route. **The present results differ from our previous study [5] where SO_x desorption occurred at higher temperatures for ceria samples without Pt. The reason for this is probably due to different sample preparation in the two studies. In the previous study, ceria and Pt/ CeO_2 , respectively, was attached to monoliths**

using Boehmite as a binder. During sample calcination Boehmite forms alumina which is known to store SO_x also at relatively high temperatures [5]. Thus in the case of the ceria sample where a low amount of SO_x was stored, SO_x desorbed from ceria at low temperatures could be temporarily adsorbed on the alumina until higher temperatures was reached. In the case of Pt/CeO₂, this effect is likely negligible due to the much higher amounts of stored SO_x . In the present study a ceria sol was used instead of Boehmite in order to prepare ceria samples with as few components as possible. It should be noted, however, that an indirect effect of Pt on the SO_x release kinetics for platinum-ceria systems could be observed in the present results. The desorption spectra for configuration A and B **as well as for C and D are similar**. For A and B, SO_x was stored mainly via SO_3 adsorption, whereas for C and D, storage proceeds mainly via SO_2 adsorption. Intuitively, adsorption of SO_3 may lead to formation of SO_4 species whereas SO_2 adsorption may lead to formation of SO_3 species in the ceria structure [5]. This indicates that the route for SO_x adsorption is important for the corresponding desorption and, thus, inclusion of platinum has an indirect effect on the SO_x release kinetics for platinum-ceria systems.

4 Concluding remarks

In summary we have shown that lean SO_x storage on platinum-ceria systems occurs both via adsorption of SO_2 and SO_3 , where the latter is kinetically favored. Thus, the rate of SO_2 oxidation is important for the overall SO_x storage kinetics. Moreover, physical contact between platinum and ceria is important

for the overall SO_x storage kinetics possibly by providing new transport routes (diffusion and spill-over) and/or adsorption sites at the platinum-ceria interface for SO_x . Thermal decomposition of SO_x species seems to be the main route for SO_x desorption and thus platinum plays a minor role. However, platinum may play an indirect role as the route for SO_x storage, *i.e.*, via SO_2 or SO_3 adsorption, seems to influence the SO_x desorption kinetics.

Acknowledgments

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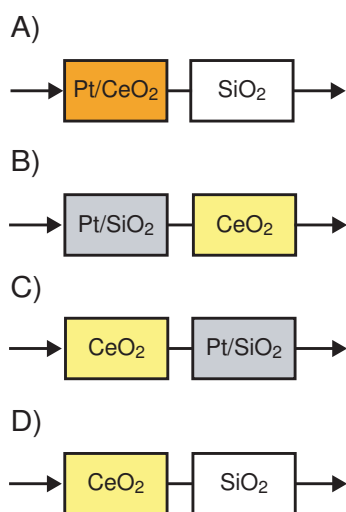


Fig. 1. Schematic picture of the four (A-D) pairwise configurations 5%Pt/CeO₂, 5%Pt/SiO₂ and bare CeO₂ and SiO₂ monolith samples used to study SO_x adsorption- and desorption kinetics.

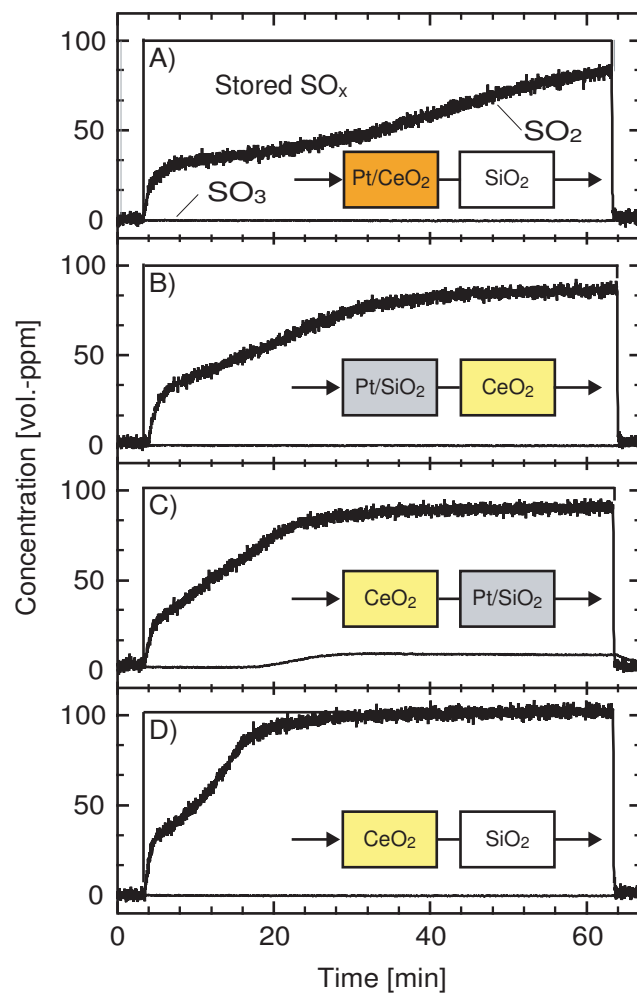


Fig. 2. Outlet SO₂ and SO₃ concentration traces during lean SO_x adsorption (100 vol.-ppm SO₂/7%O₂/N₂) at 250°C for different sample configurations.

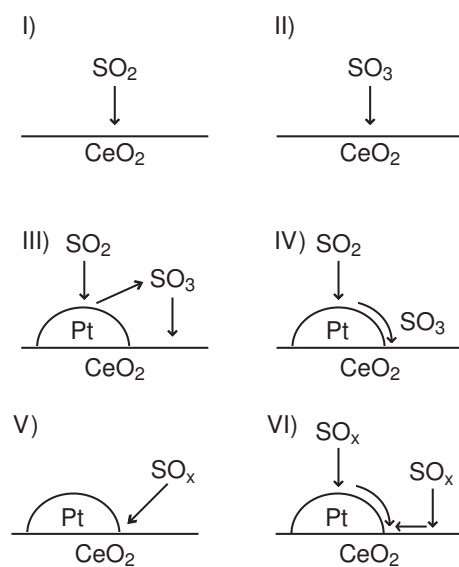


Fig. 3. Schematic picture showing possible routes for adsorption of SO_x on bare ceria and platinum-ceria systems.

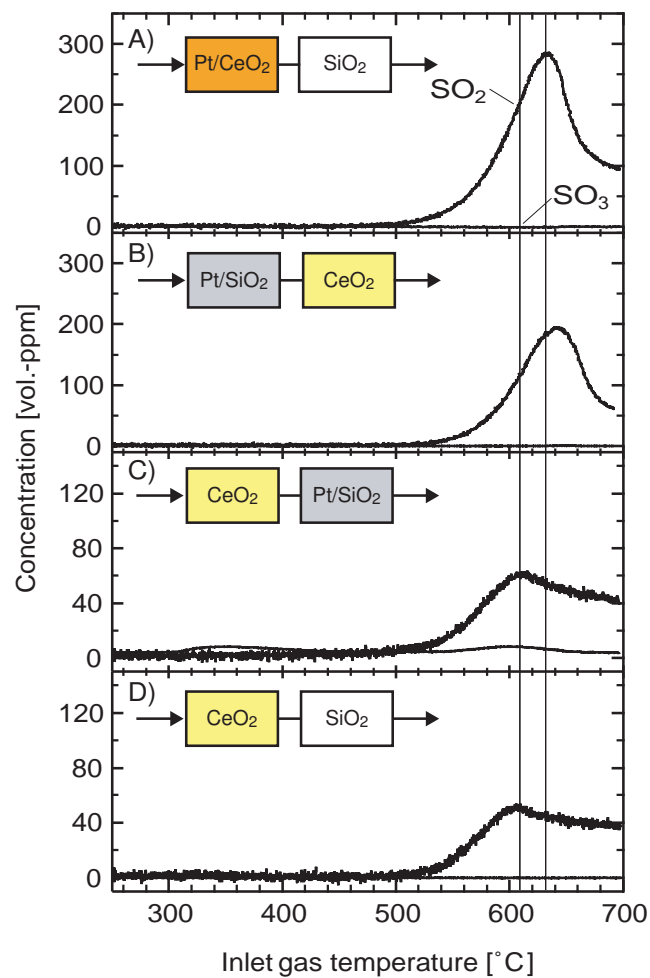


Fig. 4. Outlet SO₂ and SO₃ concentration traces during lean temperature programmed desorption of SO_x (7% O₂/N₂) for different sample configurations. Ramp rate 10°C/min. The two vertical lines show the SO₂ peak desorption for configuration A and C, respectively.