

ZrO₂ Acting as a Redox Catalyst

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Published online: 11 April 2016

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Abstract Surface defects are discussed and reviewed with regards to the use of ZrO₂ in applications involving interactions with CO, H₂, CH₄, CO₂, water and hydrocarbons. Studies of catalytic partial oxidation of methane reveal that part of the surface lattice oxygen in terraces can be removed by methane at high temperatures (e.g. 900 °C). The reaction proceeds via a surface confined redox mechanism. The studies presented here also highlight that defects play a decisive role in the water–gas-shift reaction, since the reaction is likely carried out via OH groups present at defect sites, which are regenerated by dissociating water. Hydroxyl chemistry on ZrO₂ is briefly reviewed related to the studies presented. Finally, new density functional theory calculations were conducted to find out how H₂S interacts with ZrO₂ surface (defect sites), in order to explain enhancement of activity in naphthalene and ammonia oxidation by H₂S. Molecularly adsorbed H₂S as well as terminal SH species (produced by dissociation of H₂S) cannot be responsible for enhanced reactivity of surface oxygen. In contrast, multi-coordinated SH induced

a relatively weak increase of the reactivity of neighboring OH groups according to thermodynamic calculations. Probably, the right active site responsible for the observed H₂S-induced enhancement of oxidation activity on ZrO₂ is yet to be discovered.

Keywords ZrO₂ · CPOM · WGS · Tar oxidation · H₂S · Hydroxyl groups · Redox

1 Introduction

This review presents an overview of research performed at Aalto University and the University of Twente on studies on ZrO₂ catalyzed oxidation over the past 10 years. The reactions studied all targeted production of hydrogen and synthesis gas (syngas, a mixture of H₂ and CO), via partial oxidation of methane (CPOM), water–gas-shift (WGS) and tar decomposition as part of clean-up of biomass gasification gas.

Pure ZrO₂ is a stable oxide that cannot be reduced under the conditions relevant for catalysis. However, it is claimed that surface oxygen can be removed in vacuum at temperatures above 700 °C [1, 2]. Reduction of ZrO₂ has been suggested to follow a mechanism according to which surface OH groups formed by dissociatively activated hydrogen react to form water, and therefore the role of OH groups in directing the catalytic properties of the oxide should be considered [2]. So, reactivity of surface oxygen on ZrO₂ is connected to the formation of OH groups, which will always be present on the surface under conditions relevant to catalysis. Part of the surface oxygen (coordinatively unsaturated O²⁻) on ZrO₂ can also be reduced with H₂ producing water and leaving an oxygen vacancy, which is again quenched in the presence of water [3].

Electronic supplementary material The online version of this article (doi:10.1007/s11244-016-0556-4) contains supplementary material, which is available to authorized users.

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Water can also dissociate to yield OH groups on the surface, so it seems that there is an equilibrium between H_2 , H_2O , surface hydroxyl groups and oxygen vacancies depending on the reaction conditions.

The data discussed in this review include ZrO_2 with and without yttrium doping, as well as different crystal structures. Despite the fact that doping will have an important influence on the properties of ZrO_2 , we do not make systematic distinction because generally the properties discussed here are not influenced qualitatively. The goal of this short review is to combine information available now on ZrO_2 catalyzed reactions (CPOM, WGS and tar decomposition) in which redox cycles at the surface of ZrO_2 are involved, focusing on the role of specific surface sites including OH groups. In addition, and connected to this we will present new results on DFT calculations in order to explain the improved performance of ZrO_2 in tar decomposition in the presence of H_2S .

2 Partial Oxidation of Methane

Syngas is traditionally produced via steam-reforming of methane (SR), which yields a H_2 -rich syngas. However, if the syngas is targeted to Fischer–Tropsch (FT) synthesis, a more favorable H_2/CO -ratio is attained by CPOM [4]. FT technology has become very important since it provides an alternative route to liquid fuels based on e.g. natural gas [5]. Another advantage of CPOM is the fact that the reaction ($\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2$) is mildly exothermic, in contrast to the extremely endothermic SR reaction.

Two mechanisms for CPOM are considered, the indirect mechanism and the direct mechanism. In the indirect mechanism methane is first combusted to CO_2 and H_2O , and the following reforming reactions, i.e. SR and dry-reforming (DR) of unconverted methane, generate CO and H_2 . This, however, creates large temperature gradients, the demand for high operation temperatures and a risk for hotspots in the reactor since exothermic deep oxidation and endothermic reforming reactions proceed in different zones in the reactor. The direct mechanism yields CO and H_2 directly from methane without deep oxidation, requiring high temperatures and usually a noble metal catalyst. Metallic catalysts suffer from sintering and metal loss via evaporation at high temperatures, which can be simply prevented by avoiding the presence of the metal. ZrO_2 is a potential alternative catalyst, with the disadvantage of a significantly lower activity [4].

Formaldehyde (CH_2O) had been considered a reaction intermediate in CPOM [6], however, it was questioned whether it was the only source of CO and H_2 . Zhu et al. conducted a study in order to complete the reaction

scheme of CPOM over yttrium-stabilized ZrO_2 (YSZ) catalyst [4]. Catalytic experiments with methane and formaldehyde in transient as well as in steady-state operation were conducted and CPOM was also studied with in situ FTIR. The major products formed during CPOM over YSZ were CO, H_2 , CO_2 and H_2O . Figure 1 shows that there is a linear relationship between their yields and methane conversion at 600 °C. The product selectivities are independent of methane conversion indicating that CO, H_2 , CO_2 and H_2O are all primary products of CPOM. This implies that, surprisingly, methane is better activated on YSZ than CO or H_2 [4]. Also, ZrO_2 apparently allows running CPOM partly via the direct mechanism. In the study YSZ was used, however, the general trends observed here are also valid for un-doped ZrO_2 .

The proposed reaction scheme for methane oxidation includes dissociation of methane on O sites at the surface, finally forming surface formate, as observed by in situ IR, which technique was unfortunately limited to relatively mild temperatures (400–470 °C). CH_2O was indicated as an intermediate product, which is fast transformed to rather stable surface formate. Formate is decomposed to CO_2 and H_2 , but also to CO and H_2O . CO and H_2 are formed via both decomposition of adsorbed formaldehyde and formate, whereas CO_2 forms mainly via decomposition of formate. Some CO_2 is also produced via oxidation of formate to carbonates, which decomposes to yield CO_2 . This is a minor pathway that may be relevant at high temperatures [4]. The influence of surface hydroxyl species on formaldehyde conversion to formate was studied by Zhu et al. [7]. It was concluded that water improves the selectivity to CO and H_2 by increasing surface hydroxyl coverage, suppressing oxidation of formaldehyde to formate on the surface. Surface hydroxyls were suggested to partially block the lattice oxygen anions needed for oxidation of formaldehyde [7].

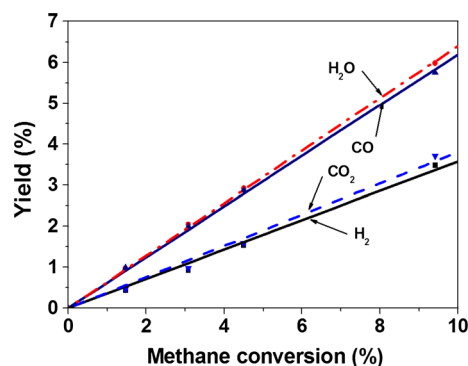


Fig. 1 Yields of CO, H_2O , CO_2 and H_2 as a function of methane conversion at 600 °C (different conversion levels at steady state were reached by varying the amount of catalyst). Reprinted from Ref. [4], Copyright (2004), with permission from Elsevier

Methane activation at high temperature was studied further on ZrO_2 and YSZ with transient pulse experiments concentrating especially on the role of surface lattice anions [8]. CH_4 was pulsed over pre-oxidized YSZ (and ZrO_2) at 900 °C and a mixture of CO , H_2 , CO_2 and H_2O was produced during pulsing. This is in line with the product mixture in steady-state experiments and is the result of CH_4 reacting with active oxygen species on the catalyst surface [8]. On continuing methane pulsing, it was noted that CO_2 and H_2O were formed only during the first four pulses, whereas formation of CO and H_2 continued during methane pulses until the 22nd pulse. After that, CO formation ceased and CH_4 decomposed to H_2 and carbon deposits on the catalyst surface. Thus, part of the surface oxygen was indeed available to oxidize CH_4 to CO_2 and H_2O at 900 °C. The amount of surface oxygen that can be extracted by methane on ZrO_2 and YSZ corresponded to approx. 14 and 8.5 % of a monolayer of oxygen atoms on the surface, respectively. During subsequent O_2 pulsing, after methane pulsing, CO was formed exclusively during the first 12 pulses. Thereafter also CO_2 was detected in the products. This was due to oxidizing of carbon deposits on the surface. After pulse 17 constant oxygen signals were observed, indicating no further consumption of oxygen. Figure 2 shows the amounts of oxygen atoms in the pulses leaving the reactor on YSZ; the dotted line indicates the amount of oxygen contained in each pulse. The difference between the amount of oxygen pulsed and the amount of oxygen detected in the product pulse allows calculation of the amount of oxygen consumed by re-oxidation of the ZrO_2 . The amounts of oxygen restored in the materials during re-oxidation were similar to the amounts extracted by CH_4 , in the order of 10 % of the monolayer capacity [8]. It was ensured that these properties are not due to any redox-active contamination, based on careful analyses with LEIS [9].

To summarize, the study by Zhu et al. [8] revealed that CPOM over ZrO_2 and YSZ proceeds via Mars-van Krevelen mechanism [10], be it that this is confined to a minor fraction of surface lattice oxygen. Originally, the reactive

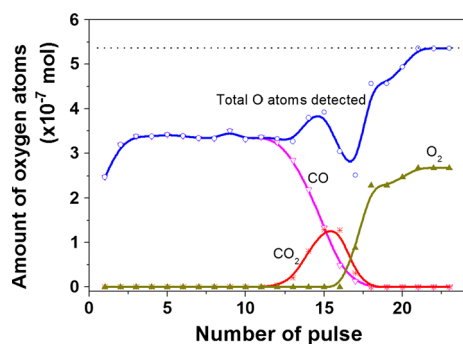


Fig. 2 Oxygen pulses over 0.3 g YSZ; amount of oxygen contained in the products of each pulse. Reprinted from Ref. [8], Copyright (2005), with permission from Elsevier

O species were assumed to be surface lattice oxygen species, however, it is conceivable that OH groups at the ZrO_2 surface are involved.

Increasing the crystal size by calcining at high temperature was found to increase the number of active sites per m^2 [9]. In general, large crystals obtained by treatment at high temperature contain less low coordination sites and structural defects. Since large crystals are more active per m^2 at high temperature [9, 11] the redox mechanism seems structure sensitive. The surface confined redox mechanism in CPOM apparently proceeds on sites on flat terrace on YSZ. Structural defects, such as Zr^{3+} cations on corners, edges, and kinks, seem not responsible for CPOM at high temperature [11].

ZrO_2 and YSZ show relatively low but significant activity for CPOM. CPOM on ZrO_2 proceeds via direct partial oxidation of methane, which results in milder temperature profiles in the reactor compared to deep oxidation. However, selectivity is far from complete and hence reforming reactions do contribute, like in the indirect mechanism.

3 WGS; Formate Chemistry and Reactivity of Hydroxyl Groups on ZrO_2

WGS ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$) process is key technology for production of hydrogen. Complete conversion of CO is desired when pure H_2 is targeted. High CO conversion can be achieved by combining high-temperature-shift (350–500 °C) and low-temperature-shift (200–250 °C) using Fe-based and Cu-based catalysts, respectively, in the well-established two-staged process. On the other hand, in gas to liquids (GTL) or biomass to liquids (BTL) applications the goal is to achieve a suitable H_2/CO ratio for FT-synthesis, which can be adjusted by carrying out the WGS reaction to the required extent. The role of formates in the mechanism of WGS has been and is being discussed intensively in literature. This might be relevant also considering CPOM, since formate has been observed with IR on ZrO_2 during CPOM at relatively low temperatures (approx. 400 °C) [4].

The study by Graf et al. showed that CO reacts with terminal hydroxyls (t-OH) to surface formate on pure ZrO_2 [12]. Those formates were found to be in equilibrium as CO was reversibly released into the gas phase on flushing with inert gas. The multi-coordinated hydroxyls (m-OH) present on ZrO_2 surface were found not to interact with CO at temperatures studied, i.e. 240–400 °C. On Pt/ZrO_2 catalyst, the formation of surface formate was found to occur similarly via interaction with t-OH. However, decomposition of formate at temperatures between 200 and 400 °C results in formation of gas-phase CO_2 and H_2 , consuming m-OH and requiring the presence of Pt. Furthermore, Pt

also provides a site to linearly bind CO, which is easily observed in FTIR. Thus, formate was found to be a reactive intermediate in WGS on the Pt/ZrO₂ at 300–400 °C. The WGS reaction mechanism was presented on Pt/ZrO₂ by Graf et al. (Figure 3), where the decomposition of formate (step 2) is suggested to be rate-determining [12].

Based on CO pulsing experiments performed earlier by Azzam et al. [13] and steady-state WGS experiments, Graf et al. noted that partial reduction of the support takes place during WGS. The role of water in WGS mechanism was concluded to be regeneration of the OH groups and re-oxidation of the surface (step 3 in Fig. 3) [12]. This is in line with the study by Azzam et al., establishing the role of the oxide support in activating water as well as its role in the WGS mechanism (redox step) [13]. Azzam et al. demonstrated that CO could be transformed to formate and further to CO₂ and H₂ on a hydroxylated Pt/ZrO₂ surface, whereas if the surface was regenerated by N₂O and thus leaving virtually no reactive OH groups on the surface, only CO₂ was formed. Therefore, WGS reaction can not be carried out on the non-hydroxylated surface, but CO can still be oxidized with lattice oxygen. Also, some lattice oxygen could be removed from Pt/ZrO₂ either via reaction with hydroxyls (when ZrO₂ was regenerated with H₂O) or reaction with lattice oxygen (when ZrO₂ is oxidized with N₂O) even at 300 °C [13]. These results confirm that part of the surface lattice oxygen on ZrO₂ is reactive, as was already observed by Zhu et al. [8] and that N₂O gives rise to particular active surface oxygen species [11].

It was suggested by Graf et al. [12], based on data in [11, 13], that the redox step (step 3) is limited to structural defects on ZrO₂. Furthermore, Graf et al. proposed that the regeneration of the surface with water occurs by dissociation of water on Zr³⁺ ions on structural defects producing two hydroxyl groups, t-OH and m-OH. Thus, the WGS reaction mechanism was proposed to involve defect sites (edges and kinks) on the support [12]. The apparent reactivity of formate was suggested to depend on the distance

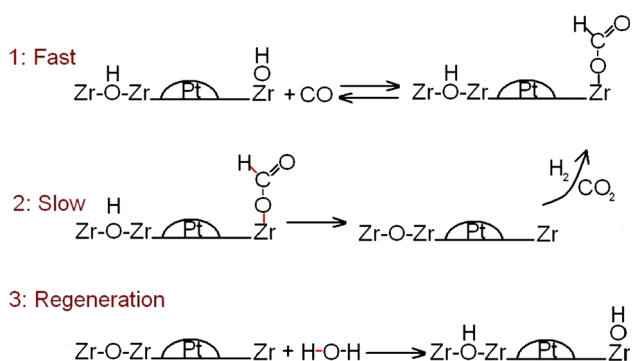


Fig. 3 WGS mechanism on Pt/ZrO₂. Reprinted from Ref. [12], Copyright (2008), with permission from Elsevier

to Pt particles [12], implying that the reaction proceeds on, or close to, the metal-support interphase and the role of metal is to promote the reaction occurring on ZrO₂.

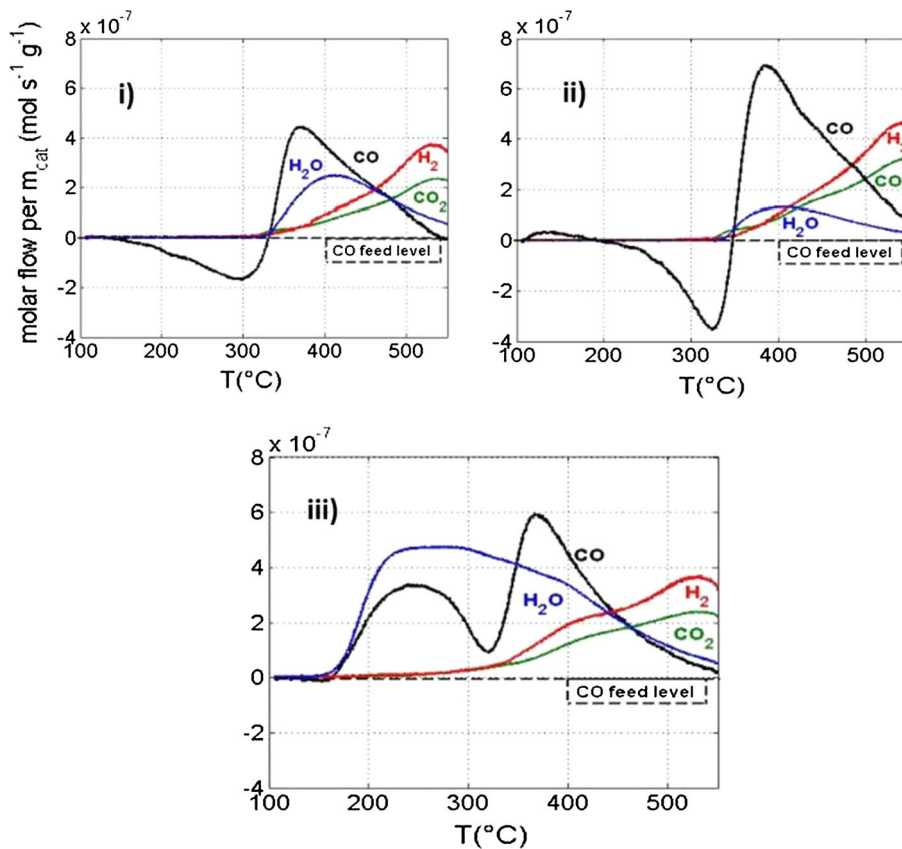
Thus, further studies on pure ZrO₂ are needed for further insight. Kouva et al. performed a study utilizing a combination of surface characterization techniques, i.e. DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) and temperature programmed reaction [14]. The type of the experiment, i.e. continuous CO feed with temperature rise, was of paramount importance in the recovery of the interactions between carbon oxides and surface OH groups, allowing observations of surface reactions of surface formate species at temperatures under which thermodynamics is favoring decomposition of these species [14].

In this study, the properties and quantity of hydroxyl groups on ZrO₂ were changed by the pre-treatment method so that sample (i) was calcined and reduced with 5 % H₂ at 600 °C and cooled to 100 °C in He flow, sample (ii) was calcined 600 °C and re-hydroxylated with water (0.1 vol%) during cooling down to 100 °C, and (iii) was calcined and reduced with 5 % H₂ at 600 °C followed by cooling down under H₂O-continuing flow. The obtained degrees of hydration were: (i) 0.15, (ii) 0.25, and (iii) 0.50 fractions of a ML. These surfaces were further characterized via CO- and CO₂-temperature-programmed surface reaction (CO- and CO₂-TPSR) which were also performed under DRIFTS.

Figure 4 presents the results of CO-TPSR experiments (gas-phase) on ZrO₂ samples with varied degrees of hydration [14]. It can be noted how samples (i) and (ii) behave qualitatively similarly, only the adsorption of CO is somewhat higher on the more hydrated (ii) sample at around 300 °C. On the sample (iii), i.e. the sample with the highest degree of hydration, a new low-temperature release of water and CO is observed. Finally, all samples release concurrently CO and H₂O at around 400 °C, as well as CO₂ and H₂ at above 500 °C. It can be noted that the effect of surface hydration is mainly seen in the low temperature window since the high-temperature processes do not differ greatly [14].

CO adsorption in the temperature window up to 300 °C (Fig. 4) is indicative of activated formate formation and was not found to be affected by surface hydration. The adsorption of CO during flushing the sample with CO at 100 °C (not shown in Fig. 4), before starting the temperature program, is thus kinetically limited. Full adsorption is not achieved, but adsorption is significant, explaining the seemingly imbalance between the amounts of CO adsorption and desorption in Fig. 4. The effect is masked to some extent by the low temperature desorption that is observed exclusively on the most hydrated surface (iii). The release of CO and water at low temperature observed on sample (iii) remarks a new weakly bound CO adsorption state. Surprisingly, this state cannot be detected with IR

Fig. 4 CO-TPSR as a function of temperature on ZrO₂ samples with varied hydroxyl coverages, (i) 0.15, (ii) 0.25, (iii) 0.50 of a ML. Level 0 refers to the feed level of CO. Reproduced from Ref. [14] with permission from the PCCP Owner Societies



spectroscopy and more research would be required to understand this phenomenon [14].

It was observed that linear adsorption of CO on Zr⁴⁺ cations becomes possible when the OH-coverage on the oxide is decreased; it was suggested this may provide a favourable pathway for forming formates. Formation of formate via linear CO interacting with t-OH and its further decomposition on ZrO₂ is presented in Fig. 5. On the other hand, high degree of hydration blocks the adsorption sites for linear CO, but creates hydroxyl sites allowing formate formation directly from gas phase CO. This, however, is a route with a higher activation barrier as compared to the route via CO linearly adsorbed on Zr⁴⁺ cations, based on

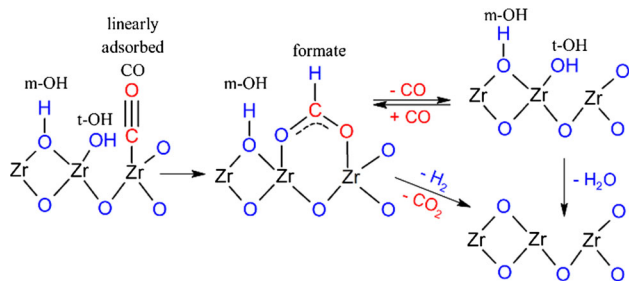


Fig. 5 Formation and decomposition of formates on pure ZrO₂. Reproduced from Ref. [14] with permission from the PCCP Owner Societies

DFT calculations. The formation of CO₂ and H₂ can be connected to reductive decomposition of surface formate via reducing the ZrO₂ surface. This was proven to be a valid reaction pathway also on pure ZrO₂ without the metal, at high temperatures (above 500 °C) however [14].

Based on density functional theory (DFT) model calculations presented in the study by Kouva et al. it was indicated that both carbonates and hydroxyl groups preferably form on low-coordinated sites. This is in agreement with the observation that t-OH is required for the formation of formate. Carbonates could be a possible reaction intermediate in CO oxidation on ZrO₂ even at high temperatures [14]. Also Zhu et al. concluded that carbonate might play a role in methane oxidation. [4] The effect of the surface area and thus the amount of structural defects on the surface chemistry described above is currently subject of further studies.

4 H₂S Adsorption on ZrO₂ and the Effect on its Redox Properties

Many industrial gas-mixtures of CO, CH₄, CO₂ and H₂ contain also varying amounts of H₂S, coal-derived syngas even 2000 ppm. H₂S is well known to poison especially metal catalysts. However, also beneficial effects are known,

which occur typically on metal oxide catalysts. For example, methane oxidation was found to be promoted by H₂S on YSZ, which was studied as a sulfur-tolerant catalyst to be used in solid oxide fuel cell applications [15]. Also sour water gas shift, i.e. WGS in the presence of H₂S tolerant catalyst, has been investigated recently with regards to converting H₂S-containing streams in integrated gasification combined cycle (IGCC) plants [16]. It can be noted that catalysts tolerating H₂S offer possibilities to simplify upstream processes, reducing capital as well as operating cost.

Biomass gasification yields a syngas mixture, which is complex and needs treatment before further use [17]. Tars are a major challenge in utilization of the gas. ZrO₂-based catalysts have been proven competent in oxidizing tars during biomass gasification gas clean-up [18], where also H₂S is present. Moreover, it has been shown that the redox/oxidative properties of ZrO₂ are enhanced by H₂S [19]. H₂S (100 ppm) improved naphthalene and ammonia oxidation activity in biomass gasification gas clean-up experiments on ZrO₂ (and on YSZ), under conditions where carbon oxides, hydrogen, and water are also present at 600 and 700 °C [19]. Oxidation of organic compounds often involves redox cycles during which the organic molecule is oxidized by surface lattice oxygen leaving a reducing center (the Mars-van Krevelen mechanism), and its occurrence requires the catalysts' ability to generate oxygen vacancies [10, 20]. Therefore, it is suggested that H₂S improves the reactivity of surface lattice oxygen or increases the amount of sites able to participate in the redox cycles.

Later studies targeted understanding how H₂S influences the reactivity of surface oxygen on ZrO₂ [21]. Temperature-programmed reduction with CO (CO-TPR) was performed on five samples sulfided to different extent via temperature-programmed sulfiding (TPS). The results were compared with those on pure ZrO₂ to study how adsorbed H₂S changes the CO reactivity of the samples (Fig. 6). H₂S was adsorbed on the samples isothermally at 30 °C, and in a temperature-programmed manner between 30 and 100, 200, 300, or 400 °C (samples labeled as H₂S_{ads} 30 °C, TPS₃₀₋₁₀₀₋₃₀ °C, TPS₃₀₋₂₀₀₋₃₀ °C, TPS₃₀₋₃₀₀₋₃₀ °C or TPS₃₀₋₄₀₀₋₃₀ °C), respectively.

H₂S adsorption on ZrO₂ can be considered to occur molecularly, dissociatively, or by exchange of sulfur with surface lattice oxygen [21–23]. During TPS experiments, H₂S adsorption at 30 °C was observed to be partly reversible via molecular adsorption, and partly irreversible suggesting dissociative adsorption. At elevated temperatures H₂S adsorption caused water desorption. It was suggested that exchange of sulfur with lattice oxygen occurs at elevated temperatures, resulting in water generation as observed, indicating surface reaction of H₂S with ZrO₂ via an activated process. The amount of H₂S adsorbed at 30 °C was 5.8 % of

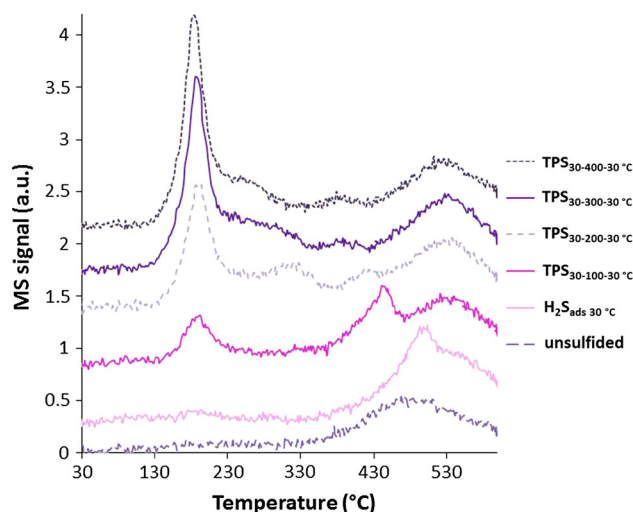


Fig. 6 CO₂ generation on unsulfided and differently sulfided ZrO₂ during CO-TPR from 30 to 600 °C (10 °C/min, 5 vol% CO in He). Reprinted from Ref. [21], Copyright (2014), with permission from Elsevier

a ML and the additional amounts, i.e. activatedly adsorbed H₂S at elevated temperatures, were 0.7, 2.3, 4.3, and 5.4 % of a ML on the samples TPS₃₀₋₁₀₀₋₃₀ °C, TPS₃₀₋₂₀₀₋₃₀ °C, TPS₃₀₋₃₀₀₋₃₀ °C or TPS₃₀₋₄₀₀₋₃₀ °C, respectively. The sub-ML amounts of adsorbed/reacted H₂S indicated that minority sites, i.e. defects such as edges, steps or kinks, are involved in interactions between H₂S and ZrO₂ [21].

After the sulfidation step the catalysts were treated with CO with increasing temperature from 30 to 600 °C and the outlet was analyzed with MS. During these CO-TPR experiments, CO₂ was generated on the sulfided ZrO₂ samples at lower temperatures than on the pure oxide (Fig. 6). Furthermore, it was noted that the amount of CO₂ generated at approx. 200 °C increased with increasing amount of activatedly adsorbed sulfur species. The reaction with H₂S at temperatures of 100 °C and higher apparently modified the ZrO₂ surface so that CO could be oxidized to CO₂ at remarkably lower temperatures than on the unsulfided ZrO₂. This is in agreement with the results in [14]. It was further suggested that reaction of H₂S with defective sites increases the reactivity of surface lattice oxygen on ZrO₂ [21]. However, it could not be ruled out that molecularly and dissociatively adsorbed species, without reacting with the lattice, also might change the reactivity.

The CO₂-peak evolving at higher temperatures (approx. 500 °C), which is also observed on pure ZrO₂ but at somewhat lower temperature, is the only one accompanied by H₂ generation (not shown in Fig. 6). Kouva et al. attributed this to decomposition of surface formates to yield CO₂ and H₂ with consumption of t-OH and m-OH on the surface [14]. It was suggested that the sites for formate generation and their reductive decomposition (t-OH and

m-OH) were modified by sulfur. Moreover, the sites to adsorb carbonates were blocked on the sulfided surface, since CO_2 could be formed and released to gas-phase at low temperature ($\sim 200\text{ }^\circ\text{C}$) [21].

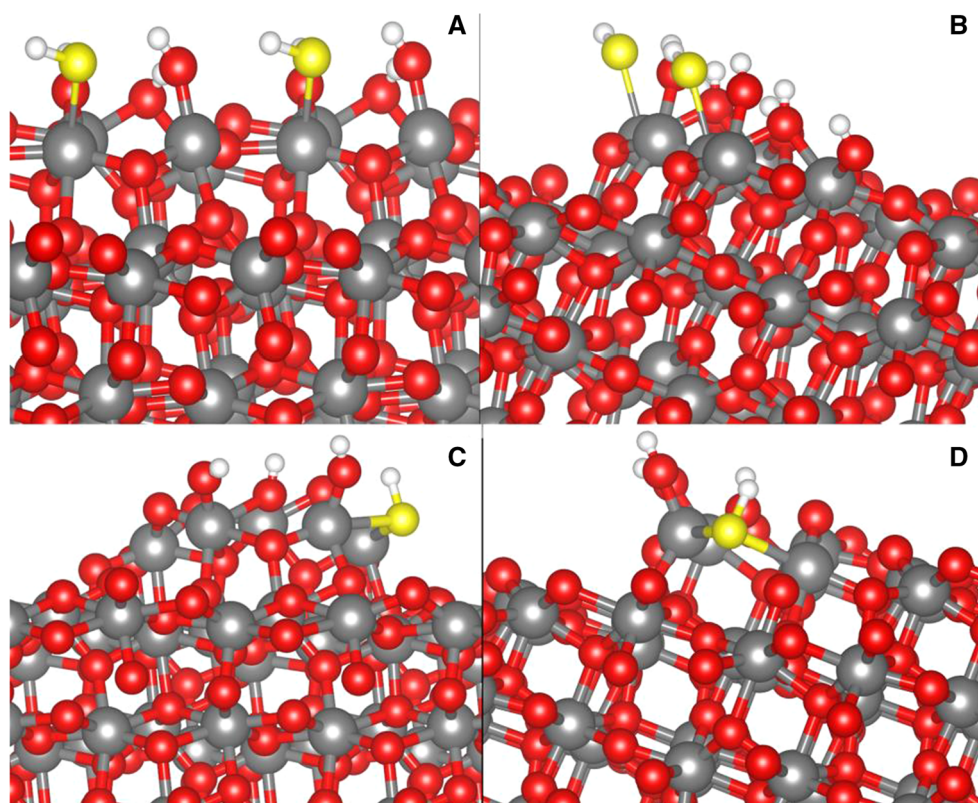
The obtained CO-TPR results call for better understanding of the interaction between H_2S and ZrO_2 . Despite IR-spectroscopy can be and has been used to study H_2S adsorption on oxides [22, 23], the information obtained is rather limited due to low extinction coefficients of S–H stretching vibrations. Unfortunately, surface lattice sulfur species could not be detected and it is not possible to distinguish between molecular and dissociative adsorption. Density functional theory (DFT) calculations could be employed to obtain atomic level information on the interaction between H_2S and ZrO_2 . Similar calculations have been previously employed to study H_2S on CeO_2 [24] and on YSZ [25, 26] but, to the best of our knowledge, no computational study of H_2S adsorption on ZrO_2 has been published to date.

We apply DFT to shed light on the nature of sulfur species present on ZrO_2 and secondly to determine how different sulfur species modify the redox properties of ZrO_2 , as observed experimentally. We note that sulfur species must be relatively strongly bound to ZrO_2 to be able to modify the reactivity of neighboring oxygen atoms. Therefore, the first aim of calculations is to identify the structure of stable sulfur species on ZrO_2 .

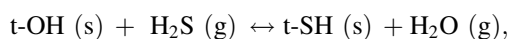
Calculations are performed on minority sites on ZrO_2 , since the TP-experiments indicated that H_2S adsorption is limited to such sites. These sites are modelled employing edge and corner site models. The edge sites are presented with a four-layer thick stepped ($2\bar{1}2$) ZrO_2 surface with a (1×2) unit cell. The highly uncoordinated corner sites were modeled by doubling the unit cell of the ($2\bar{1}2$) surface in the x direction and removing atoms from the step to form a corner site. We also assume that low coordinated sites are partially hydroxylated under reaction conditions and thus one t-OH and one m-OH species are placed on the model surfaces. The models are shown in Fig. 7 and the details of calculations are presented in Supplementary information.

To start with, the adsorption of molecular H_2S at the hydroxylated edge of ZrO_2 ($2\bar{1}2$) is addressed. According to calculations, H_2S resides on a Zr ion at a distance of 4.3 Å. The adsorption is weakly exothermic with adsorption energy of -14.5 kJ/mol , confirming that molecularly adsorbed H_2S cannot be held responsible for modifying redox properties of the surface. Moreover, due to the weak binding, molecular H_2S cannot be significantly present on the surface at temperatures where increased reactivity has been observed. Weak interaction between H_2S and ZrO_2 is also in line with experimental findings [21, 23, 27] and calculations on H_2S adsorption on CeO_2 [28] and on YSZ (111) [25].

Fig. 7 SH adsorption on the edge model (ZrO_2 ($2\bar{1}2$)) a front and side view (a and b) and on the corner model a front and side view (c and d). Zr atoms are grey, oxygen is red, sulfur is yellow and hydrogen is white. Here, the SH group binds to a Zr atom which is missing one oxygen



Dissociative adsorption of H_2S has been suggested to take place on the strong Lewis acid–base pair site [22, 23]. Moreover, H_2S can also undergo a dissociation process, where lattice oxygen is exchanged with sulfur and water is released. The other possible process is that H titrates a terminal OH (t-OH) group and forms a water molecule and a terminal SH (t-SH) group as follows



where (s) refers to surface species and (g) to gas-phase species. Computed reaction enthalpy for the above-described exchange process is +28 kJ/mol on a hydroxylated edge model. In the case that lattice oxygen is replaced with sulfur upon H_2S dissociation, the computed reaction enthalpy is nearly thermo-neutral being only 8 kJ/mol endothermic for the hydroxylated edge model. Considering the general accuracy of DFT calculations, this interaction may also be mildly exothermic.

Next we addressed H_2S dissociation on an oxygen vacancy at the hydroxylated edge, where no water is released but a new m-OH forms together with a t-SH group, filling the vacancy. This process is strongly exothermic having a reaction enthalpy of -69.5 kJ/mol. These results demonstrate that the thermodynamics of dissociation depends strongly on the nature of the site. The fact that the dissociation is energetically more favorable on oxygen deficient ZrO_2 is in line with recent DFT calculations on ZnO [29] and CeO_2 (111) [28] surfaces.

If it is assumed that ZrO_2 is partly reduced and a corner model is applied, the dissociative adsorption of H_2O is computed to be exothermic by -216 kJ/mol on a vacancy site at the edge, while the dissociative adsorption of H_2S to the same site is exothermic only by -140 kJ/mol. This indicates that from a thermodynamical point of view oxygen vacancies are easily mended under water atmosphere. However, temperature and pressure might have an effect which is not predicted with the calculated model, since experiments in [21] indicate that during H_2S adsorption at elevated temperatures H_2O is indeed released.

We turn next to calculations on reactivity of ZrO_2 in the presence of sulfur employing again an edge model. For comparison, we first consider the case, where hydrogen is used as reducing agent to form water on a hydroxylated ZrO_2 surface without sulfur. For this process reaction enthalpy is +205 kJ/mol. Next, we replace one t-OH at the edge with a t-SH group (Fig. 7a, b). This leads to a configuration, where m-OH, which is to be reduced with H_2 , and t-SH share one Zr atom. The computed reaction enthalpy for m-OH reduction to H_2O is slightly higher in the presence of -SH (+217 kJ/mol) as compared to +205 kJ/mol in the absence of -SH. This result suggests that t-SH groups on the edge of the ZrO_2 ($2\bar{1}2$) are not

responsible for enhanced reducibility. Increasing the coverage of SH groups at a step edge has no significant influence. Thus, the observed discrepancy between calculations and experimental results is not due to -SH coverage.

As a next step, we considered how a multi-coordinated SH (m-SH) group, present on a corner model (Fig. 7c, d), would destabilize lattice oxygen (m-OH) and t-OH. m-SH might modify the electronic properties of ZrO_2 as it binds to two Zr atoms and is thus more integrated into the oxide lattice. Moreover, some Zr atoms at the corner are less coordinated than Zr atoms at the edge of a ($2\bar{1}2$) surface, presenting higher structural flexibility. Again, the reactivity of oxide is studied employing H_2 as a reducing agent. We consider the removal of both t-OH and m-OH species but one species at the time. On a non-sulfided surface, the reduction of m-OH to H_2O with gas-phase hydrogen costs +273 kJ/mol while the reduction of t-OH is slightly more favorable with reaction enthalpy of +239 kJ/mol. The presence of m-SH decreases the reduction enthalpies with 36 and 31 kJ/mol for m-OH and t-OH species, respectively. These findings agree with experiments in a sense that the presence of m-SH slightly improves the reactivity. However, if we compare the absolute values, the edge model without SH still gives the highest reducibility among the computed systems.

In general, the calculations suggest that minority sites are needed to adsorb H_2S dissociatively but we cannot solely determine the composition and geometry of the site from the present results. One of the main reasons why computational results only partially support experimental findings could be that the structure of the active site and the ZrO_2 surface structure remain unresolved. Throughout this study, we employed edge and corner models based on a ZrO_2 ($2\bar{1}2$) surface to mimic a minority site on a ZrO_2 nanoparticle. However, these systems apparently do not represent the minority sites correctly. This, together with the fact that the exact concentration of OH groups and oxygen vacancies is unknown, as well as uncertainty about the bulk structure of ZrO_2 , might be responsible for the observed discrepancies. Without knowing the properties of active sites more precisely, one way to proceed with calculations would be to explore a variety of models for the surface of ZrO_2 nanoparticles, varying concentrations of oxygen vacancies and OH/SH groups using first principles atomistic thermodynamics [30].

The calculations demonstrate that the interaction of molecular H_2S or t-SH with ZrO_2 is too weak to increase the reactivity of surface oxygen on ZrO_2 . Thermodynamics does not favour the formation of the bulk sulfide but since some sites are able to bind H_2S the nature of these sites is different. Furthermore, calculations suggest that possibly m-SH species, but more likely a minority site with a so far unknown structure, is needed to explain enhanced oxidation activities observed during CO-TPR [21] and tar oxidation in the

gasification gas media [19]. Limited interaction with H₂S can also be seen as a benefit for oxidation catalysis, since the catalysts' sulfur tolerance is improved.

5 Conclusions

This review discusses the catalytic properties and surface chemistry of ZrO₂ in catalytic partial oxidation of methane (CPOM), water–gas-shift reaction (WGS), and tar decomposition. The catalytic properties are discussed in terms of (sub-monolayer) redox capacity of the ZrO₂ surface.

A fraction of the surface lattice oxygen on ZrO₂ was revealed to be involved in redox cycles, part of the cycle being formation of oxygen vacancies at terraces (comprising ~ 10 % of the monolayer capacity) during CPOM. Reduction of the surface via decomposition of formates to H₂ and CO₂ was presented to proceed involving t-OH and m-OH surface species. DFT calculations revealed a relatively weak enhancing effect of m-SH on the reactivity of neighboring t-OH and m-OH sites. The effect is too small to account for the significant enhancement of the reducibility of the ZrO₂ surface by the presence of sulfur. We therefore conclude that the structure of the actual active site is yet to be discovered.

ZrO₂ is clearly not just a catalyst support, but provides intrinsic catalytic activity. Application of ZrO₂ as a catalyst, mitigating disadvantages of metallic catalysts i.e. activation by sulfur instead of deactivation as well as thermal stability, or as a reactive catalyst support is therefore promising for practical applications.

Acknowledgments The authors are grateful for all contributions of Ph.D. students and postdocs that have contributed over the years, resulting in many references in this manuscript. Financial support of the Foundation of Applied Sciences (STW), Netherlands Organisation for Scientific Research (NWO), Advanced Chemical Technologies for Sustainability (ACTS) as well as the FiDiPro program of the Finnish Funding Agency for Innovation (Tekes) is gratefully acknowledged. The computer resources were provided by the Finnish IT Centre for Science (CSC) Finland.

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