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New insights in reactivity of hydroxyl groups in water gas shift reaction on Pt/ZrO_2

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ABSTRACT

The reactivity of mono- and multi-coordinated hydroxyl groups on Pt/ZrO_2 with CO was investigated with *in-situ* transmission FT-IR. It was found that mono-coordinated hydroxyl groups on the ZrO_2 support reacted with CO to formate. Multi-coordinated hydroxyl groups were needed for formate decomposition, producing H_2 and CO_2, taking place exclusively in the presence of Pt. The observed differences in reactivity of different types of OH groups are relevant for the WGS mechanism, assuming that formate is a reactive intermediate under the conditions used in this study (300–400 °C). The fact that Pt is needed for decomposition of formate indicates that the reactivity of formate depends on the position on the ZrO_2 surface, *i.e.* in close vicinity or remote from metal particles. Our results show that reduction of the support was limited to structural defective zirconia sites at edges and kinks, hosting the mono-coordinated hydroxyl groups. These sites can be re-oxidized with water, re-establishing the hydroxyl groups.

1. Introduction

Environmental issues and the depletion of crude oil stimulate the search for alternative energy carriers. Hydrogen based fuel cells were widely investigated as replacement for conventional combustion engines and showed to be very promising [1–4]. The expected increase in hydrogen demand has led to extensive research to optimize hydrogen production. At the moment, natural gas is the biggest source for hydrogen. Synthesis gas ($CO + H_2$) can be produced from natural gas via steam reforming, CO_2 reforming, catalytic partial oxidation and auto thermal reforming. Steam methane reforming (SMR) is the most common process for hydrogen production (1):

$$CH_4 + H_2O \rightarrow 3H_2 + CO \quad (\Delta H_0 = 206 \text{ kJ/mol}). \tag{1}$$

Carbon monoxide is also formed in addition to hydrogen and the mixture is used directly in numerous industrial applications [5]. If direct use of the hydrogen is desired, CO has to be removed from the synthesis gas mixture. Water gas shift (WGS) (2) is an interesting reaction for reducing CO concentrations, additionally producing more H_2. As fuel cell applications require CO-free hydrogen, further purification by selective oxidation of CO or methanation is necessary after water gas shift reaction [6–8].

$$CO + H_2O \rightleftarrows H_2 + CO_2 \quad (\Delta H_0 = -40.6 \text{ kJ/mol}). \tag{2}$$

Pt/ZrO_2 was studied as a promising catalyst for water gas shift reaction [9–11]. The reaction mechanism on noble metals is generally considered bifunctional, with essential roles for both the active metal and the support [12–15]. It has been reported that Pt cannot activate water under water gas shift reaction conditions [16], and therefore activation of water has to take place on the support. Two mechanisms for WGS are indicated in literature: the formate associative mechanism [9,17–19] and regenerative redox mechanism [12,15,20]. The regenerative redox mechanism requires a reducible support like CeO_2 or TiO_2.

A hydrid mechanism, so called "the associative mechanism with redox regeneration" was proposed for Pt/ZrO_2 [9]. In this mechanism, hydroxyls on the zirconia surface react with CO to form intermediate formate which can react/decompose into H_2 and CO_2. Afterwards the hydroxyl groups on zirconia are regenerated by water. Formate formation between CO and hydroxyl groups was also proposed earlier by Ma et al. [21]. Formate decomposition was suggested to be facilitated by water [10]. Azzam et al. [9] showed that CO_2 and H_2 could also be formed when CO was pulsed over Pt/ZrO_2 in the absence of water, using hydroxyl groups of the zirconia support and consequently removing oxygen from the zirconia support. Consequently the zirconia needs to be reactivated by decomposing water, thus filling the oxygen vacancy as well as generating OH groups. However, after regeneration of zirconia with N_2O instead of H_2O, resulting in the absence of OH-groups, CO is able to remove oxygen as well by forming CO_2. This confirms the ability of zirconia to provide oxygen under WGS conditions (300 °C),

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even in absence of OH groups. However, clear evidence exists that the formate mechanism is not relevant for Pt/ZrO_2 when operating at mild temperature (200 °C), based on DRIFT experiments in combination with isotopic transient experiments by Tibiletti et al. [11]. Nevertheless, the formate mechanism continues to be a valid hypothesis for higher temperatures of operation (300–400 °C).

Until now, the exact role of the hydroxyl groups in WGS has not been reported, while the presence of differently coordinated hydroxyl groups on the zirconia surface was already demonstrated with FT-IR in 1973 by Tsyganenko et al. [22]. In the following years, more studies were devoted to hydroxyl characterization on zirconia. Two different hydroxyl coordinations located at 3760 cm^{-1} and 3660 cm^{-1} in the FT-IR spectrum [23–26], respectively, were found on the surface of monoclinic zirconia. Mono-coordinated hydroxyls were assigned to IR signals at about 3760 cm^{-1} [26]. With increasing hydroxyl coordination number, the signal in FT-IR of the respective hydroxyl group shifts to lower wave number [22]. However, no consensus exists about the exact coordination of the hydroxyl peak located around 3660 cm^{-1}. Quintard et al. [26] assigned this peak to bi-coordinated hydroxyl groups, while others assigned it to tri-coordinated hydroxyl groups [22,27]. Korhonen et al. [28] concluded the presence of hydroxyl groups of mono, bi- and tri-coordination on monoclinic zirconia from a combined study by DFT and FT-IR spectroscopy. In this study the more general term multi-coordinated hydroxyl groups will be used for the peak located around 3660 cm^{-1}.

In this article, we report the reactivity of differently coordinated hydroxyl groups with CO. *In-situ* transmission FT-IR was used to characterize hydroxyl groups on both monoclinic ZrO_2 and Pt/ZrO_2. ZrO_2 supported catalysts were selected because of the relative simplicity, as compared to TiO_2 and CeO_2, of both the OH band region in the IR spectrum as well as minimal reducibility of the oxide. Additionally, the respective reactivity of the OH groups with CO was studied at different temperatures (240–400 °C). Gaseous product formation (CO_2 and H_2) during exposure to CO was monitored in a microreactor flow setup. The results provide mechanistic information on the water gas shift reaction on Pt/ZrO_2, under the assumption that the associative formate mechanism is operative under conditions used here, i.e. high temperature.

2. Material and methods

Monoclinic ZrO_2 obtained from Gimex Technical Ceramics (RC-100) was used as catalyst and as support for Pt. Zirconia, with particle sizes between 300 and 600 μm, was treated at 600 °C for 24 h under a helium flow. The structure of the zirconia was not changed by this pre-treatment and remained monoclinic, as detected by XRD. 0.5 wt% Pt/ZrO_2 was prepared by wet impregnation of 10 g of ZrO_2 with aqueous solution, obtained by dissolving H_2PtCl_6 (Alfa Aesar) in 25 ml of water. Pt/ZrO_2 was calcined at 600 °C in synthetic air (30 ml/min) for 24 h (ramp 5 °C min^{-1}).

Platinum loadings on zirconia and the exact composition of the zirconia support were determined using a Philips X-ray fluorescence spectrometer (PW 1480). Platinum dispersion was determined with pulse H_2 chemisorption at room temperature on 0.3 g of catalyst using a Micromeritics Chemisorb 2750, assuming a H/Pt ratio of 1. Before pulsing hydrogen, the catalyst was reduced in H_2 at 400 °C for 15 min and cooled in He to room temperature subsequently.

The transmission FT-IR measurements were recorded with a Bruker Vector 22 with MCT detector. A self supporting wafer was pressed of 15 mg of the sample and placed into a home made gold coated cell. Before measurements the samples were reduced in 5 vol% H_2 for 30 min (Linde Gas 5.0) at 400 °C (heating rate 10 °C/min, 40 ml/min) and subsequently cooled to reaction temperature in He.

Table 1
Catalyst composition.

Zirconia composition	Weight %
ZrO_2	98.1
HfO_2	1.7
TiO_2	0.1
Y_2O_3	0.1
Pt content Pt/ZrO_2	0.58

ZrO_2 was studied with FT-IR at 400 °C under He (Linde Gas 5.0) to investigate the different hydroxyl groups in the IR spectrum. Helium was dried with a Varian Chromopack CP17971 Gas Clean Moisture Filter. The resolution was 4 cm^{-1} and 256 scans were taken. The reactivity of hydroxyl groups on ZrO_2 and Pt/ZrO_2 towards CO was investigated by subjecting the catalysts to different CO (Hoekloos 4.7) concentrations in He (total flow 40 ml/min). No water was present during these experiments.

A microreactor flow setup was used in combination with a Balzers QMS 200 F mass spectrometer to study transient gaseous product formation during exposure to CO at different temperatures. The IR measurements were mimicked in the flow setup, as gas phase products in IR were not detectable because of too low concentrations. A detailed description of the microreactor flow setup is given in an earlier publication [29]. About 250 mg of 0.5 wt% Pt/ZrO_2 (0.3–0.6 mm) was inserted in a quartz microreactor with inner and outer diameter of respectively 4 and 6 mm, reduced with 5 vol% H_2 in Ar for 15 min at 400 °C (heating rate 10 °C/min, 100 ml/min) and flushed with Ar subsequently. CO (concentration: 8 vol%) in Ar (100 ml/min) was fed to the reactor at different temperatures (240 °C, 300 °C and 400 °C) and formation of gaseous products (i.e. CO_2 and H_2) was measured with MS detecting $M/z = 44$ and $M/z = 2$. The catalyst was treated with 6 vol% of water in Ar between experiments to regenerate hydroxyl groups.

3. Results

3.1. Characterization

The composition of the zirconia as determined with XRF is given in Table 1. The Pt content of Pt/ZrO_2 was 0.58 ± 0.01 wt%. Pt dispersion was 50% as determined with H_2 chemisorption, assuming a H/Pt ratio of 1.

Hydroxyl groups on ZrO_2 and Pt/ZrO_2 were studied under helium with transmission FT-IR. Fig. 1 shows the hydroxyl region (3900–3500 cm^{-1}) of the spectra obtained at 240 °C, 300 °C and 400 °C. Multiple peaks are found in the region between 3800 cm^{-1} and 3600 cm^{-1} with maxima at about 3745 cm^{-1} and 3658 cm^{-1}. Peaks in the 3800–3700 cm^{-1} region can be assigned to mono-coordinated hydroxyl groups, while the 3700–3600 cm^{-1} can be assigned to multi-coordinated hydroxyl groups [22]. Multiple smaller peaks are observed in addition to the maxima in both regions indicating hydroxyl groups with different interactions with zirconia. Stabilization of hydroxyl groups by hydrogen interactions between neighboring hydroxyl groups can induce a small shift to lower wavelengths, explaining the occurrence of multiple peaks [30].

Higher intensity of mono hydroxyls around 3760 cm^{-1} was found on Pt/ZrO_2 as compared to ZrO_2 at 240 °C. The intensities of mono hydroxyl groups on both materials are similar at 300 °C and 400 °C and are hardly affected by temperature increase above 300 °C. In contrast, the intensity of multi-coordinated hydroxyl groups clearly decreases with increasing temperature on both ZrO_2 and Pt/ZrO_2. The multi-coordinated hydroxyls show similar intensities under all conditions on both. In general, the intensities of the hydroxyl groups on ZrO_2 and Pt/ZrO_2 are quite similar.

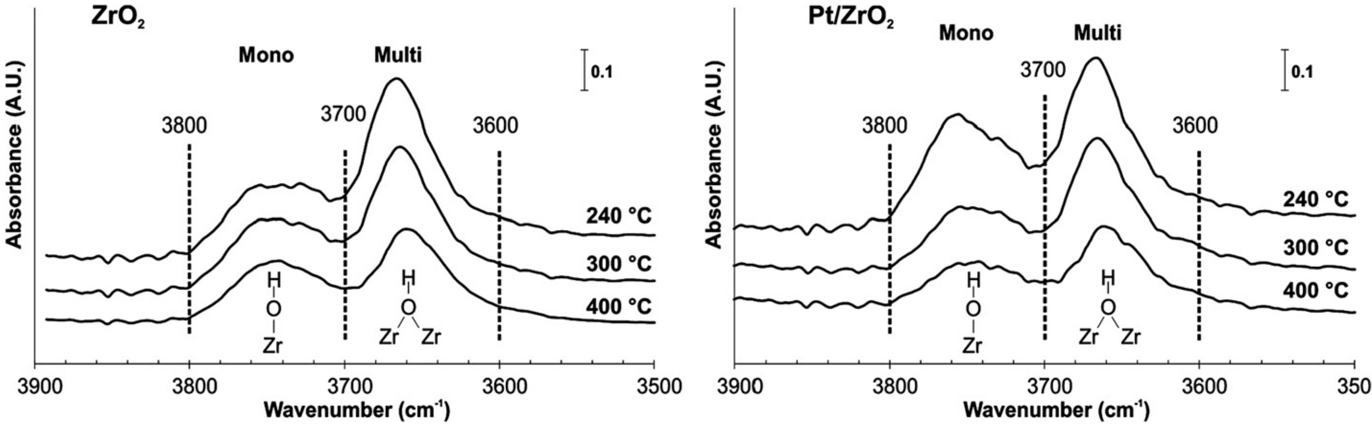


Fig. 1. IR spectrum of ZrO_2 (left) and Pt/ZrO_2 (right) at 400 °C under He.

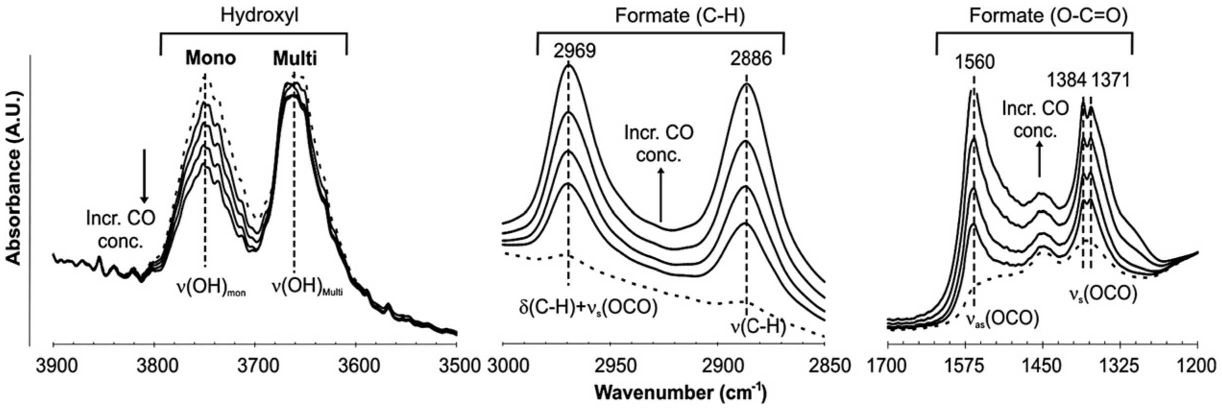


Fig. 2. FT-IR spectra of addition of CO concentrations of 0, 8, 15, 37, 65 vol% on ZrO_2 at 400 °C. Hydroxyl region (3900–3500 cm^{-1}), formate region (3000–2850 cm^{-1}) and (1700–1200 cm^{-1}). Reference spectrum taken in He (dotted line).

3.2. Reactivity of hydroxyl groups with CO on ZrO_2

Fig. 2 shows close up spectra of the hydroxyl region (3900–3500 cm^{-1}) and C–H and O–C=O formate regions (3000–2850 cm^{-1})/(1700–1200 cm^{-1}) when ZrO_2 was subjected to CO at 400 °C. The dotted lines represent the spectrum under helium, used as a reference. Addition of CO resulted in a decrease of the intensity of mono-coordinated hydroxyl peak (3800–3700 cm^{-1}), while the multi-coordinated hydroxyl peak (3700–3600 cm^{-1} region) was hardly influenced.

As a result of CO addition new peaks appeared on ZrO_2 at 2969 cm^{-1}, 2886 cm^{-1}, 1560 cm^{-1}, 1384 cm^{-1} and 1371 cm^{-1}. The peaks in the 3000–2850 cm^{-1} and 1700–1200 cm^{-1} region can be assigned to C–H bending and O–C=O stretching vibrations respectively and are representing surface formate [10].

Fig. 3 shows the integrated intensities of FT-IR signals of the mono-coordinated and the formate representing C–H region (3000–2850 cm^{-1}) as a function of CO concentration. It is shown that the intensity of the formate peak increased steadily with increasing CO concentration, accompanied by increased consumption of mono-coordinated hydroxyl groups. The experiments presented here were mimicked experimentally in the microreactor flow setup to check the formate decomposition to CO_2 and H_2. However, no gas phase products were detected with mass spectrometry when exposing ZrO_2 to CO between 240 °C and 400 °C.

It was found that formate formation was completely reversible: reducing CO concentration led to a decrease of surface formate and a simultaneous increase of mono-coordinated hydroxyl groups. Complete removal of CO led to the disappearance of surface formate and complete recovery of mono-coordinated hydroxyl groups (not shown).

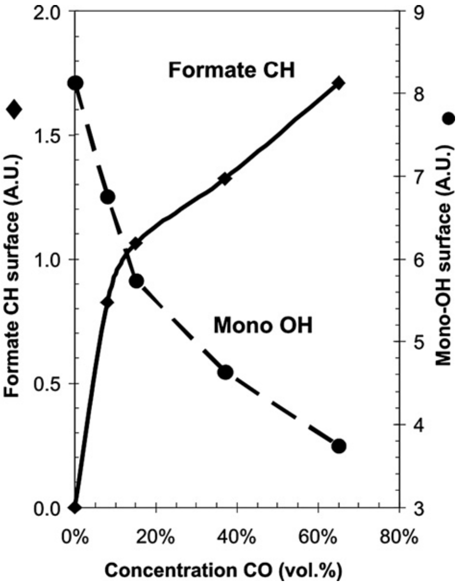


Fig. 3. Integrated FT-IR regions of mono-coordinated hydroxyls (●) (3745 cm^{-1}) and formate (◆) (2886 cm^{-1}) as function of CO concentration at 400 °C.

The effect of temperature to formate formation on zirconia is shown in Fig. 4, showing the FT-IR spectra of ZrO_2 of the hydroxyl region (3850–3550 cm^{-1}) and formate region (3025–2825 cm^{-1}/1750–1150 cm^{-1}) at 240 °C, 300 °C and 400 °C after exposure to 8 vol% CO (solid line). Temperature was increased under continuous presences of CO. The dashed lines in Fig. 4 represent

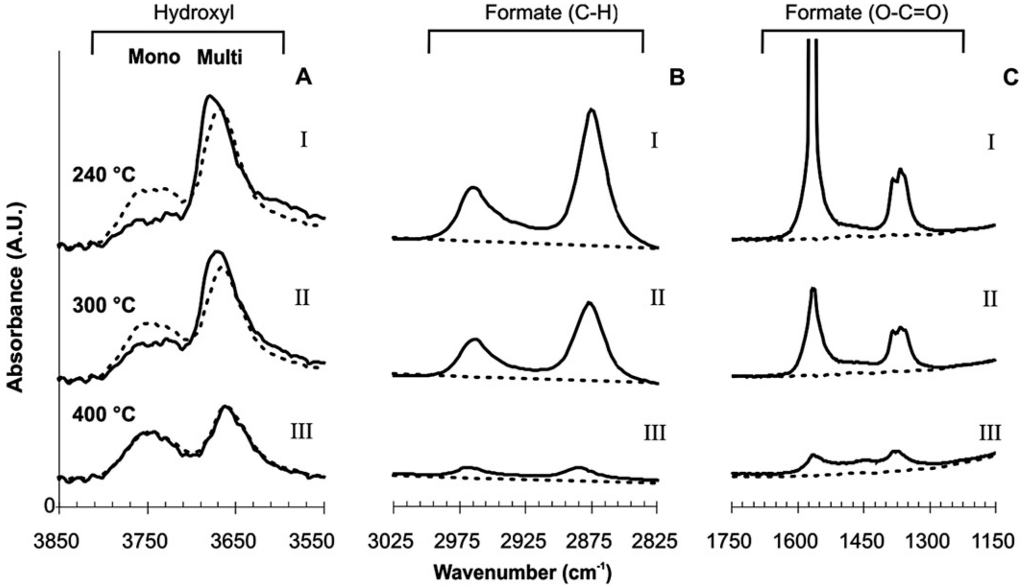


Fig. 4. FT-IR spectra of ZrO_2 subjected to 8 vol% CO (solid lines) at 240 °C (I), 300 °C (II) and 400 °C (III). Hydroxyl region (3850–3550 cm^{-1}) (A), formate region (C–H, 3025–2825 cm^{-1} (B), O–C=O, 1750–1150 cm^{-1} (C)). Reference spectra under helium (dashed lines).

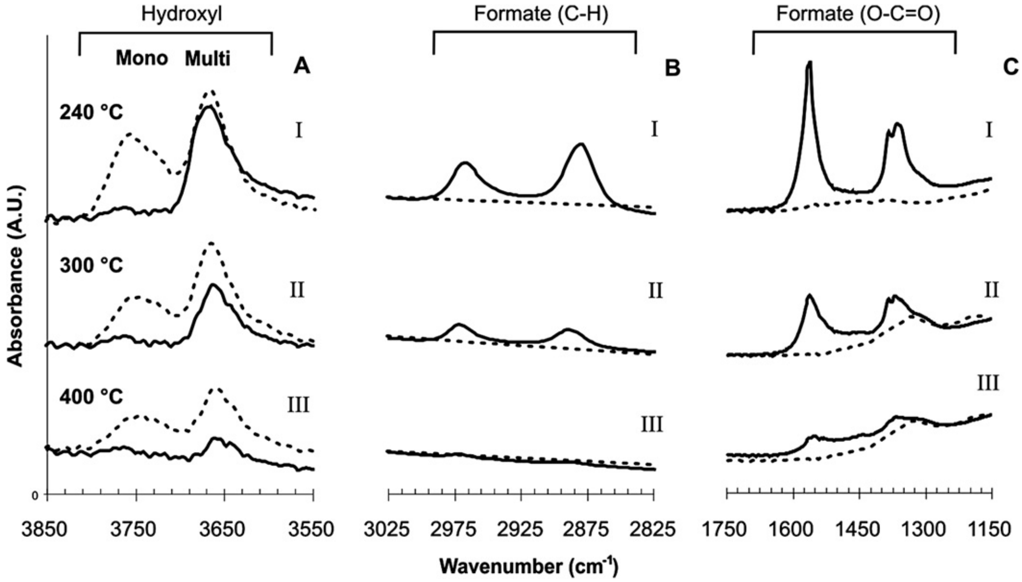


Fig. 5. FT-IR spectra of 0.5 wt%Pt/ZrO_2 subjected to 8% CO (solid lines) at 240 °C (I), 300 °C (II) and 400 °C (III). Hydroxyl region (3850–3550 cm^{-1}) (A), formate region (C–H, 3025–2825 cm^{-1} (B), O–C=O, 1750–1150 cm^{-1} (C)). Reference spectra under helium (dashed lines).

the spectra under He at the respective temperature (as shown in Fig. 1). Two well defined hydroxyl peaks were observed at 240 °C under helium (dashed) with maxima around 3745 cm^{-1} (mono-coordinated hydroxyls) and 3658 cm^{-1} (multi-coordinated hydroxyls). The mono-coordinated hydroxyl peak (3745 cm^{-1}) at 240 °C decreased instantaneously when ZrO_2 was treated with 8 vol% CO (Fig. 4A-I, solid line). Simultaneously, large quantities of formate were formed (Figs. 4B-I and 4C-I, solid line).

The amount of adsorbed formate decreased when the temperature was increased to 300 °C (Figs. 4B-II and 4C-II, solid line) and mono-coordinated hydroxyls (3700–3800 cm^{-1}) partly recovered (Fig. 4A-II, solid line). Further increase of temperature to 400 °C caused the amount of formate to decrease even more (Figs. 4B-III and 4C-III, solid line). Simultaneously, the intensity of mono-coordinated hydroxyl groups increased further, becoming similar to the level obtained in helium at 400 °C in the absence of CO (Fig. 4A-III, solid line).

The intensities of multi-coordinated hydroxyl groups did not change as a result of CO addition during the experiments on ZrO_2, as similar intensities of multi OH groups were found in presence and absence of CO between 240 °C and 400 °C. No gaseous products were detected on ZrO_2 between 240 °C and 400 °C when this experiment was mimicked in experiments in the microreactor flow setup.

3.3. Reactivity of hydroxyl groups with CO on Pt/ZrO_2

Fig. 5 shows transmission FT-IR spectra, obtained by treating Pt/ZrO_2 with 8% CO (solid lines) at 240 °C, 300 °C and 400 °C, compared to reference spectra under helium (dashed lines, identical with results in Fig. 1). Complete consumption of mono-coordinated hydroxyls was observed at 240 °C (Fig. 5A-I, solid line). Only marginal changes in the amount of multi-coordinated hydroxyls were observed at 240 °C. Simultaneously, formate was

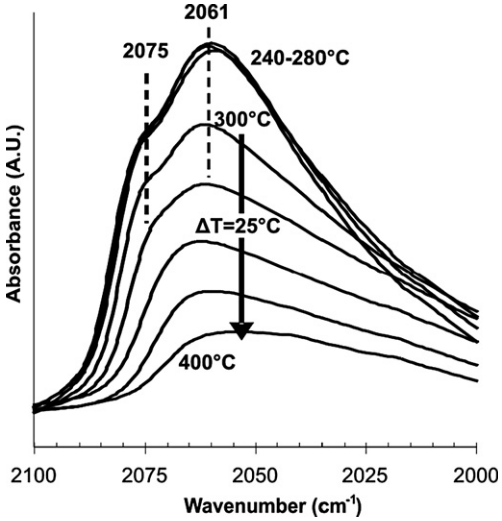


Fig. 6. FT-IR spectra of CO adsorption on Pt/ZrO_2 at different temperatures.

formed (Figs. 5B-I and 5C-I, solid line). The formate formation is still reversible: removal of CO leads to disappearance of formate species (not shown). A decrease of multi-coordinated hydroxyls was observed when the temperature was increased to 300 °C. Also, the amount of formate on Pt/ZrO_2 decreased as compared to the amount of formate observed at 240 °C.

When temperature is increased to 400 °C, most multi-coordinated hydroxyls on Pt/ZrO_2 were consumed and formate almost disappeared. In contrast to ZrO_2, mono-coordinated hydroxyls on Pt/ZrO_2 did not reappear. Titration experiments of Pt/ZrO_2 with CO in the microreactor flow setup with MS analysis revealed formation of CO_2 and H_2 at 300 °C and 400 °C. Exposure of Pt/ZrO_2 to CO at 240 °C, however, did not result in any formation of CO_2 and H_2. The formation of CO_2 and H_2 at 300 °C and 400 °C stopped after a few seconds, indicating that surface hydroxyl groups were exhausted (as shown in Figs. 5A-II and 5A-III). Treating Pt/ZrO_2 with water restored the activity, regenerating hydroxyl groups (not shown).

3.4. *CO adsorption on platinum*

CO adsorption on platinum was studied on Pt/ZrO_2 during the treatments with CO. Fig. 6 shows transmission FT-IR spectra between 2100 cm^{-1} and 2000 cm^{-1} of 0.5 wt% Pt/ZrO_2 when subjected to 8 vol% CO in a temperature range of 240 °C to 400 °C. At 240 °C, two peaks with a maximum at 2061 cm^{-1} and a shoulder at 2075 cm^{-1} are observed in the FT-IR spectrum and can be assigned to CO linearly adsorbed on platinum [31]. The intensity of both peaks was independent of temperature up to 280 °C. A further increase to 300 °C decreased the amount of adsorbed CO. At 400 °C, CO adsorption on Pt reduced significantly.

4. Discussion

4.1. *Characterization of ZrO_2 and Pt/ZrO_2*

Transmission FT-IR characterization of monoclinic zirconia and Pt/ZrO_2 revealed two peaks that can be assigned to mono- and multi-coordinated hydroxyl groups respectively (Fig. 1) in agreement with literature [23–26]. Only marginal differences in intensities of mono- and multi-coordinated hydroxyl groups were observed between ZrO_2 and Pt/ZrO_2 above 300 °C under He. Thus, the differences observed in reactivity of hydroxyl groups are not due to differences in the initial amount of OH groups, and must be must be due to the presence of Pt as discussed below.

4.2. *Hydroxyl reactivity on ZrO_2 towards CO*

It was demonstrated in Fig. 2 that mono-coordinated hydroxyls on ZrO_2 reacted with CO, resulting in formation of surface formate on ZrO_2. Formate formation as a result of CO addition can be concluded based on the appearance of peaks at 2969 cm^{-1}, 2886 cm^{-1}, 1560 cm^{-1}, 1384 cm^{-1} and 1371 cm^{-1}. The peaks at 1560 cm^{-1}, 1384 cm^{-1} and 1371 cm^{-1} can be assigned to symmetric and asymmetric stretching vibrations of O–C–O species. The presence of O–C–O is an indication for surface formate, but also surface carbonate could be responsible for O–C–O peaks [10]. However, the presence of C–H species is clear from the peaks at 2969 cm^{-1} and 2886 cm^{-1}. The combined presence of C–H and O–C–O vibrations indicate formate formation [10]. However, additional presence of surface carbonate cannot be ruled out. Several studies in literature claim the involvement of CO adsorbed on Pt in the formation of formate [9,10]. However, formate was also formed on zirconia without any Pt in our experiments, demonstrating that Pt is not necessary on the present catalyst. This view is supported by Ma et al. [21], who also reported formate formation between hydroxyls on ZrO_2 and CO in the absence of platinum. In exact agreement with our results, formate formation in absence of Pt between CO and mono-coordinated hydroxyl groups on monoclinic zirconia was also reported in a recent paper by Korhonen et al. [32].

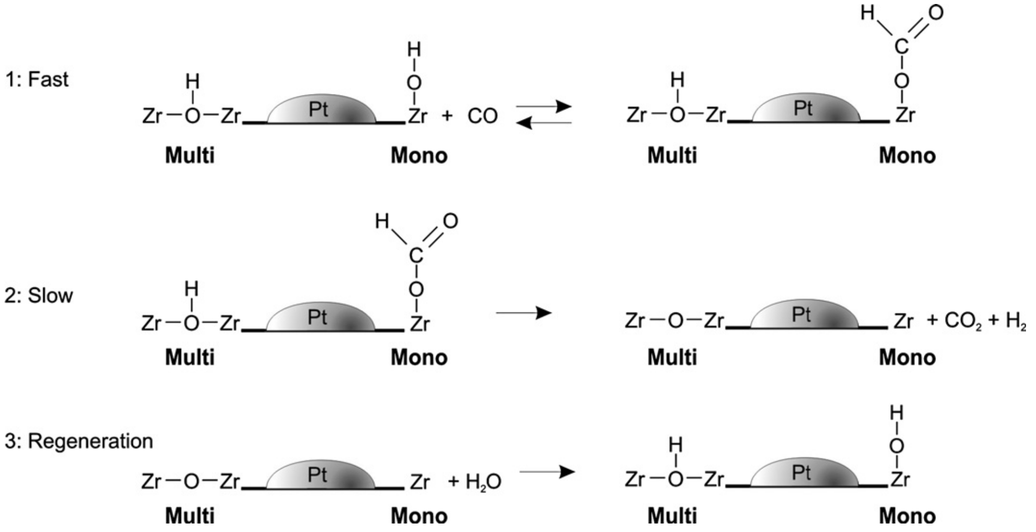
It was observed that increasing CO concentration resulted in increased consumption of mono-coordinated hydroxyls as well as formation of larger amounts of formate (Fig. 2). This formate did not decompose into gaseous products. Formate formation proved to be reversible as removal of CO resulted in total recovery of mono-coordinated hydroxyl groups and disappearance of formate species on ZrO_2 (Fig. 3). Large amounts of formate were observed at 240 °C but the amount decreased upon increasing the temperature to 400 °C, also accompanied by recovery of mono-coordinated hydroxyls (Fig. 4). This shows that formate is thermodynamically favored at low temperature, at higher temperatures the equilibrium is shifted to gas phase CO and mono-coordinated hydroxyl groups, obviously because of high entropy of CO in gas phase. Multi-coordinated hydroxyls on ZrO_2 were not reactive towards CO. From these observations, we conclude that formate can be formed on ZrO_2 through an equilibrium reaction between CO and mono-coordinated hydroxyl groups as shown in Scheme 1 (step 1).

4.3. *Hydroxyl reactivity on Pt/ZrO_2 towards CO*

Identical to ZrO_2, formation of formate through mono-coordinated hydroxyls was also observed on Pt/ZrO_2 at 240 °C (Fig. 5A). The formate peaks were located at the same wave numbers on Pt/ZrO_2, indicating that the formate species on ZrO_2 and Pt/ZrO_2 are identical. Apparently formate species on Pt/ZrO_2 do not interact significantly with the Pt particles. No H_2 and CO_2 formation occurred at 240 °C on Pt/ZrO_2. This demonstrates that step 1 in Scheme 1 is also valid in case of Pt/ZrO_2.

Increasing the temperature to 300 °C resulted in a decrease of surface formate and multi-coordinated hydroxyl groups on Pt/ZrO_2 (Fig. 5). At 400 °C hardly any multi-coordinated hydroxyls and surface formate were present on Pt/ZrO_2 (Fig. 5). On Pt/ZrO_2 mono-coordinated hydroxyl groups were not recovered at temperatures above 300 °C in contrast to ZrO_2, which excludes formate decomposition to CO and mono-coordinated OH groups, i.e. the reverse reaction 1 in Scheme 1 (comparing Figs. 5A-I and 5A-III). Production of gas phase products (CO_2 and H_2) on Pt/ZrO_2 was observed, starting at 300 °C. This shows that formate on Pt/ZrO_2 decomposes to CO_2 and H_2 at temperatures above 300 °C.

It was found that next to H_2 and CO_2 formation, simultaneous decrease of both surface formate and especially multi-coordinated



Scheme 1. Water gas shift reaction mechanism for Pt/ZrO_2. 1: Formate formation through reaction between CO and mono-coordinated hydroxyls. 2: Formate decomposition involving Pt and multi-coordinated hydroxyls. 3: Hydroxyl regeneration with water.

hydroxyl groups occurred above 300 °C on Pt/ZrO_2 (Fig. 5). This suggests that multi-coordinated hydroxyl groups on Pt/ZrO_2 are involved in formate decomposition to H_2 and CO_2. Furthermore, this study showed that formate decomposition to gas phase products only occurs in the presence of Pt. Step 2 in Scheme 1 schematically depicts formate decomposition into H_2 and CO_2 by consumption of multi-coordinated hydroxyl groups in the presence of Pt.

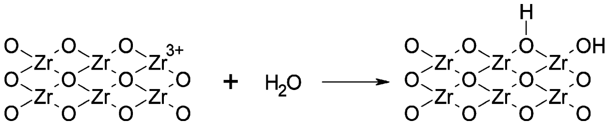
The relevance of these observations for the mechanism of WGS will now be discussed, assuming that formate is the relevant intermediate species at the relatively high temperatures used in this study. Formate formation proved to be an equilibrium reaction depending on the gas phase concentration of CO (Fig. 2) and temperature (Figs. 4 and 5). It was demonstrated that formate was already formed at 240 °C. As higher temperatures were required for formate decomposition, it seems likely that the decomposition is rate determining. This is in agreement with Pigos et al. who identified C–H bond breaking in formate as the rate determining step in WGS mechanism [10]. Pigos et al. [10] proposed that platinum assists in abstracting H from the formate C–H bond to enable the complex to dissociate into H_2 and CO_2, based on hydrogen–deuterium exchange experiments in formate over ZrO_2 and Pt/ZrO_2. H–D exchange in formate hardly occurred without Pt, whereas Pt increased the exchange rate significantly. Our results confirm that Pt is required for the formate decomposition and additionally demonstrate the involvement of multi-coordinated hydroxyl groups in the decomposition of formate. However, hydrogen abstraction from formate and subsequent recombination of this hydrogen atom adsorbed on Pt with a hydrogen atom of a multi-coordinated hydroxyl group seems not very likely, as the O–H bond is very strong. Therefore, we suggest that a concerted mechanism occurs in formate decomposition. The multi-coordinated OH group and the Pt surface both interact with the formate complex simultaneously, breaking the C–H bond in the formate and the O–H bond in the multi-coordinated OH group, forming CO_2 and H_2 in one concerted step.

The experimental observation that decomposition of formate to CO_2 and H_2 takes place exclusively in the presence of platinum, would suggest that formate species located close to a metal particle decompose faster than a formate species positioned remotely from metal particles. This would seriously complicate the interpretation of the experimental result reported by Tibiletti et al. [11], showing a much slower response of the formate IR signals when feeding labeled CO in DRIFT measurements as compared to the kinetics of the reaction. Based on this, it was concluded that formate is not involved in the rate determining step and instead is a spectator in water gas shift reaction at 200 °C. However, a slow response of formate species can also be explained by assuming that part of the formate species are located far away from Pt particles and surface diffusion is required for formate decomposition at the Pt particles. Relatively slow surface diffusion of formate could well result in slow response of the formate IR signals to the isotopic step change. It should be noted that mono-coordinated hydroxyl groups were almost completely converted (Fig. 5), when treating Pt/ZrO_2 with CO above 300 °C. This demonstrates the mobility of both formate species as well as bridged OH groups in order to interact with Pt on the zirconia surface, eventually resulting in consumption of all available mono-coordinated surface OH-groups. Unfortunately, our experiments did not allow accurate determination of the dynamics of those events.

It should be noted that the conclusions drawn so far were obtained in experiments with surface hydroxyl groups, without any gas phase water present. Two possible roles for water in the reaction mechanism are proposed in literature [8]. The role of water is either decomposition of formate (and simultaneous reoxidation of zirconia and regeneration of hydroxyl groups) or regeneration of the zirconia support exclusively. It was demonstrated in transient experiments that CO_2 and H_2 could be formed on hydroxylated Pt/ZrO_2 during titration studies with CO, in the absence of water. As described extensively in earlier work by our group [9], product formation of Pt/ZrO_2 stopped when the hydroxyl groups were exhausted. After pulsing water to the "exhausted" catalyst, complete regeneration of hydroxyl groups on Pt/ZrO_2 was accomplished, demonstrated by complete recovery of the reactivity of the catalyst in reaction with CO to CO_2. We therefore conclude that the exclusive role of water is regeneration of the hydroxyl groups and simultaneous re-oxidation of the support.

DFT calculations [28,33] showed that the dissociation of water involves adsorption of water on a zirconium ion, resulting in the formation of one mono-coordinated and one multi-coordinated hydroxyl group. We showed that one mono-coordinated and one multi-coordinated hydroxyl groups are consumed during water gas shift reaction of one CO molecule. Regeneration of both hydroxyl groups with one water molecule leads to a stoichiometrically balanced reaction for water gas shift.

Our current experiments with continuous presence of CO and earlier results with CO pulsing experiments by Azzam et al. [9] demonstrated that oxygen of the support was consumed during reaction with CO and thus partial reduction of the zirconia takes



Scheme 2. Proposed regeneration of surface hydroxyl and simultaneous reoxidation of ZrO_2, taking place on structural defects.

place. It was shown by Azzam et al. that after regeneration of an "exhausted" zirconia surface with N_2O, also reaction of CO to CO_2 was possible. It was found by Zhu [34] that activation of N_2O on zirconia takes place at structural defect sites (i.e. low coordinated Zr-cations located edges and corners). Zhu also showed that the structural defects did not react with O_2. Based on the fact that the amount of CO_2 formed during exposure to CO is similar after re-oxidation with H_2O compared to N_2O [9], it follows that reduction of zirconia under WGS reaction conditions is limited to the structural defect sites. Scheme 2 illustrates the regeneration step with water on a defective Zr^{3+}-cation. Water dissociation creates a mono-coordinated OH-group on the structural defect site and a multi-coordinated OH-group on a neighboring oxygen atom. It is proposed that in case of regeneration with water, the formed mono-coordinated OH-group on the defect site can react with CO to form formate. The surface formate can be converted with use of the multi OH group to H_2 and H_2O, assisted by Pt. To summarize, we need to precise our previous conclusion on the reaction pathway for WGS on Pt/ZrO_2 via "formate and redox regeneration" [9], in the sense that the redox step is limited to structural defect sites on zirconia.

The regeneration of the hydroxyl groups on ZrO_2 is also depicted more schematically in Scheme 1 (step 3). This leads to the following overall reaction steps in WGS: First, CO reacts with one mono hydroxyl group to form formate which is subsequently converted with a multi-coordinated hydroxyl group to H_2 and CO_2 in the presence of Pt. Finally, the hydroxyl groups on the ZrO_2 surface are regenerated by water dissociation.

In this mechanism CO activation on Pt is not required to produce formate on ZrO_2 (Figs. 2, 3 and 4). Identical formate species were detected in presence of Pt (Fig. 5). Fig. 6 shows that high CO coverage on Pt can be expected below 300 °C. Starting at 300 °C, the intensity of adsorbed CO on Pt decreased, indicating a lower surface coverage. Exactly at the same temperature, formation of gas phase products was initiated. This demonstrates that adsorption of carbon monoxide on platinum could have a negative influence on water gas shift reaction, occupying Pt sites and preventing formate decomposition below 300 °C. At temperatures above 300 °C, the lower CO coverage on Pt increases accessibility of Pt sites, enhancing formate decomposition to H_2 and CO_2.

5. Conclusion

The main goal of this study was to determine the reactivity of hydroxyl groups on Pt/ZrO_2 in the water gas shift reaction. It was shown in this paper that two types of hydroxyl groups are present on monoclinic zirconia: mono- and multi-coordinated hydroxyls. Mono-coordinated hydroxyls are involved in formate formation, while multi-coordinated hydroxyls are needed for formate decomposition. Platinum is not involved in the formation of formate, in contrast, Pt is needed to enable formate decomposition, resulting in formation of CO_2 and H_2. These results imply that the apparent reactivity of formate species depend on the distance to Pt particles.

In addition to the formate mechanism with redox regeneration proposed earlier for WGS on Pt/ZrO_2 by Azzam [9], it was found in this study that reduction of the support was limited to structural defective zirconia sites at edges and kinks. These sites can be regenerated with water, implying that the role of water in the WGS mechanism is regeneration of hydroxyl groups and simultaneous re-oxidation of ZrO_2.

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