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Author(s): Kouva, Sonja; Honkala, Karoliina; Lefferts, Leon; Kanervo, Jaana

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Review: Monoclinic zirconia, its surface sites and their interaction with carbon monoxide

Sonja Kouva, a,b Karoliina Honkala, b Leon Lefferts, a,c and Jaana Kanervo a

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This review concerns monoclinic zirconia, its surface sites and their probing with carbon monoxide. The surface sites and their modifications using thermal treatments with vacuum or reactive gases are also included. In this work, we present information on the nature and manipulation of hydroxyl species and their quantities on the surface, the different types of cationic sites where CO is adsorbed linearly and their energetics, as well as the surface sites and dynamics of formate formation. We also compare the surface concentrations of the different surface species to better understand the extent and nature of the interactions. Finally, we discuss some of the remaining open questions and how to approach them.

1 Introduction

Zirconium oxide has gained interest both as a catalyst support and a catalyst on its own, mostly due to its weak acid and basic sites and stability under oxidizing and reducing atmospheres. It has been an interesting catalyst material especially for biomass-related reactions that are actively investigated, as the future is bright for non-fossil fuels and chemicals. Biomass-related reaction networks usually include carbon oxides, as both carbon and oxygen are largely abundant in the starting material.

Monoclinic zirconia (also known as baddeleyite) is an oxide typically covered with hydroxyl species, similar to many metal oxides used as catalysts and catalyst support materials. The structure of monoclinic zirconia provides a more versatile surface than the other polymorphs (cubic, tetragonal) due to a less symmetrical lattice. The surface sites on monoclinic zirconia include hydroxyls, oxygen vacancies, coordinatively unsaturated (c.u.s.) Zr–O pairs, and Lewis acid sites (Zr3+, Zr4+)8. The hydroxyl groups on the surface can be manipulated by thermal treatment in vacuum or in different atmospheres, which are often necessary for catalytic applications, e.g., in methanol synthesis. Additionally, monoclinic zirconia has been suggested as a support for water-gas shift reaction catalysts with gold, platinum and copper, and for reforming with platinum, nickel, cobalt and copper.

Since 2006, monoclinic zirconia has been prepared also in nanoshapes, including nanorods and nanosheets. Using the nanoshapes in catalysis might be beneficial due to their well-defined surface sites; thus their selectivity might be more easily linked to the exposed surfaces than those of traditional catalysts in polycrystalline form.

Carbon monoxide interacts with monoclinic zirconia both on the clean surface with few or no hydroxyls, as well as on the hydroxylated surface. The surface hydroxyl groups seem to play an important role in the interaction of CO with zirconia: as a site for forming formates and bicarbonates but also inhibiting the formation of adsorbed linear CO species. The main adsorbed CO species are linearly adsorbed CO at room temperature and below and formate species above 100°C, the first one desorbing reversibly and the second one decomposing both reversibly back to gas-phase CO and irreversibly to CO2 and H2.

The interaction of carbon monoxide with zirconium oxide has been studied actively since the 1970s. Due to differences in zirconia materials and their pretreatments, experimental setups and conditions, interpreting and comparing the obtained results is not straightforward. Most of the studies on the interaction with CO have been carried out using infrared spectroscopy, calorimetry, and gravimetry, as well as theoretical studies have been published.

The focus of this work is in the monoclinic polymorph of zirconia instead of the whole spectrum of zirconia materials: doped (including sulphated), tetragonal and cubic zirconia, to name the most significant zirconias excluded from this review. This choice is made for simplicity and clarity, as monoclinic and tetragonal zirconias differ in, e.g., surface hydroxyl species and acidity/basicity, further demonstrated in their interactions with CO and in their catalytic activity, e.g., in water-gas shift. More information can also be found in the reviews by Dyrek et al. and Hadžijivanov. Most of the pre-1993 works included in this paper were reviewed 20 years ago by Nawrocki et al. in the context of chromatography; this review is providing an update...
with work reported since 1993, from the perspective of catalysis.

2 Preparation, structure, and surfaces

2.1 Preparation

Zirconium oxide can be prepared, e.g., via hydrolysis from zirconium isopropylate (Zr(OCH(CH)2)2)4,18,27,38-40 or zirconium oxychloride (ZrOCl2)23,30,41-43, and also from zirconium oxynitrate (ZrO(NO3)2)42-44 and zirconium tetrachloride (ZrCl4)10,45. Yamaguchi introduces the processes starting from natural ores (zircon (ZrSiO4), baddeleyite) to zirconium oxide preparation2. Origin of the zirconia samples referred to in this review, with their preparation conditions and surface areas are presented in Table 1 to aid the reader by presenting the key properties of the materials used. Note that the applied pretreatment conditions might differ from the preparation conditions.

2.2 Crystal structure and surfaces

The unit cell of monoclinic zirconia is face-centered (space-group C2\(^h\)) consisting of 4 Zr atoms and 8 O atoms. In the bulk all Zr atoms are seven-fold coordinated to three-fold coordinated oxygen atoms and four four-fold coordinated oxygen atoms. Based on theory, the coordination numbers on the surface differ, e.g., on the (111) surface some of the zirconium atoms are only six-fold coordinated and some of the oxygen atoms are three- or two-fold coordinated instead of four- or three-fold coordination. On the (111) surface, some zirconium atoms can be even five-fold coordinated. The experimentally determined lattice parameters are \(a = 5.17\AA\), \(b = 5.23\AA\), and \(c = 5.34\AA\), and the angle \(\gamma = 99.3^\circ\).

Monoclinic zirconia has altogether nine inequivalent crystalline directions: [001], [100], [110], [011], [101], [110], [111] and [111]4. Warble reported (110), (100) and (111) surfaces to be exhibited in transmission electron microscopy (TEM)76. The (111)39,40, (001)39,40, and (011)40 planes have been reported based on high-resolution TEM (HRTEM) images. Theoretically, the most stable surface for monoclinic zirconia is the (111) surface4. The difference between the theoretically most stable surfaces and the experimentally observed surfaces might be due to inaccuracy in either method, and it is not clear whether the particle size or, e.g., the degree of surface hydration play a role. In nanocrystals, the (011) surface seems most abundant in TEM, while also (111) and (001) surfaces have been observed77. The ideal (111), (111), (001) and (011) surfaces are shown in Figure 1. The atom positions are those of the bulk structure assuming no reconstruction takes place.

![Image](image.png)

Fig. 1. Ideal surfaces of monoclinic ZrO\(_2\), top view, Zr atoms are grey and O atoms red. The atoms further in the lattice are shaded lighter than those on the surface. The surfaces were visualized using VESTA software78.

Jung et al. report that the crystallographic structure of zirconia, instead of crystallite size or calcination temperature, is the most significant factor for determining the nature and density of the surface sites suitable for CO\(_2\) and NH\(_3\) adsorption, i.e., the basic and acidic surface sites. Monoclinic zirconia has a higher CO adsorption capacity than tetragonal ZrO\(_2\), which is attributed to its higher Lewis acidity and basicity. The tetragonal structure is more symmetrical than the monoclinic one, leading to a smaller number of different surfaces and thus possibly also to less versatile surface site types.

Thermal treatment tends to increase the crystal size of monoclinic zirconia. Increasing the calcination temperature from 300 – 500\(^\circ\)C can lead to a particle size of three or even four times the original. Auger electron spectroscopy (AES)79 shows that the surface O/Zr ratio decreases from the stoichiometric 2 down to 1.1 with evacuation at 427\(^\circ\)C and 727\(^\circ\)C, respectively. The surface reduction is very fast, and extending the time to one hour in ultra-high vacuum (UHV) does not affect the surface79. With H\(_2\) the surface seems unreducible even at 900 Torr and 900\(^\circ\)C while atomic hydrogen reduces the surface already at 750\(^\circ\)C and H\(_2\) pressure of 5\(\mu\)Torr prior to atomization80. The ineffectiveness of H\(_2\) compared to UHV in surface reduction is rather unexpected, yet atomic hydrogen...
Table 1 Origin, preparation conditions and surface area of the zirconia samples

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{calc}}$ (°C)</th>
<th>Atmosphere</th>
<th>$A_s$ (m²/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition of ZrO(NO$_3$)$_2$ · xH$_2$O</td>
<td>300 &amp; 300</td>
<td>air &amp; 10% H$_2$</td>
<td>20</td>
<td>4,243</td>
</tr>
<tr>
<td>Hydrolysis of ZrOCl$_2$</td>
<td>600</td>
<td>air, 4h</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Hydrolysis of ZrOCl$_2$</td>
<td>300 &amp; 700</td>
<td>O$_2$, 5h</td>
<td>110 &amp; 19</td>
<td>25,30</td>
</tr>
<tr>
<td>Hydrolysis of ZrOCl$_2$</td>
<td>700 &amp; 300 – 550</td>
<td>calc. &amp; vacuum, air (1h), H$_2$, vacuum</td>
<td>44</td>
<td>29</td>
</tr>
<tr>
<td>Hydrolysis of ZrOCl$_2$</td>
<td>800 &amp; 1000</td>
<td>vacuum, 10 min &amp; air, 6h</td>
<td>-</td>
<td>46</td>
</tr>
<tr>
<td>Hydrolysis of ZrO(NO$_3$)$_2$</td>
<td>500 &amp; 800</td>
<td>air, 5h &amp; vacuum, 5h</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td>Hydrolysis of ZrO(NO$_3$)$_2$</td>
<td>700 &amp; 500 &amp; 700</td>
<td>calc., 3h &amp; O$_2$, 10h &amp; vac., 20 min</td>
<td>58</td>
<td>48</td>
</tr>
<tr>
<td>Hydrolysis of ZrO(NO$_3$)$_2$</td>
<td>500 &amp; 500 &amp; 730</td>
<td>calc., 3h &amp; O$_2$, overnight &amp; vac., 20 min</td>
<td>-</td>
<td>49</td>
</tr>
<tr>
<td>Hydrolysis of ZrO(NO$_3$)$_2$</td>
<td>530 / 710</td>
<td>air, 3h</td>
<td>70 / 58</td>
<td>26</td>
</tr>
<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>447</td>
<td>calcination</td>
<td>81</td>
<td>50</td>
</tr>
<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>447 &amp; 597</td>
<td>calcination &amp; vacuum, 2h</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>447 &amp; 397 – 397</td>
<td>calc. &amp; vac., 2h + 50 torr O$_2$, 30 min</td>
<td>36</td>
<td>27</td>
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<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>447 &amp; 400 &amp; RT &amp; 250 – 600</td>
<td>calc. &amp; vac., + O$_2$ &amp; H$_2$O vapor &amp; vac., 2h</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>397 &amp; 100 – 600</td>
<td>air &amp; vacuum, 2h + O$_2$</td>
<td>-</td>
<td>8</td>
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<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>397 &amp; e.g. 597 &amp; e.g. 597</td>
<td>calc. &amp; vacuum, 2h &amp; O$_2$, 30 min</td>
<td>-</td>
<td>51</td>
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<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>597 &amp; 197 – 597</td>
<td>calc. &amp; vacuum</td>
<td>78</td>
<td>39</td>
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<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>997 &amp; 197 – 597</td>
<td>calc. &amp; vacuum</td>
<td>10</td>
<td>39</td>
</tr>
<tr>
<td>Hydrolysis of Zr isopropylate</td>
<td>600 / 800 / 900 &amp; 27 – 800</td>
<td>air, 3h &amp; vacuum</td>
<td>55 / 35 / 20</td>
<td>40</td>
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<tr>
<td>Hydrolysis of Zr propylate</td>
<td>400 &amp; 400</td>
<td>calcination &amp; vacuum</td>
<td>84</td>
<td>52</td>
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<tr>
<td>Hydrolysis of Zr propylate</td>
<td>400</td>
<td>O$_2$ &amp; vacuum</td>
<td>200 – 220</td>
<td>53</td>
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<tr>
<td>Hydrolysis of Zr propylate</td>
<td>400</td>
<td>O$_2$, 1h &amp; He 30 min</td>
<td>200</td>
<td>20</td>
</tr>
<tr>
<td>Hydrolysis of Zr propylate</td>
<td>440</td>
<td>O$_2$, 2h</td>
<td>200 – 220</td>
<td>54</td>
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<tr>
<td>Hydrolysis of Zr propylate</td>
<td>440</td>
<td>air, 12h</td>
<td>120</td>
<td>55</td>
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<td>Microemulsion from ZrOCl$_2$</td>
<td>500 – 1200</td>
<td>annealing</td>
<td>1.6 – 44.9</td>
<td>31</td>
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<tr>
<td>NH$_3$ hydrolysis of ZrOCl$_2$</td>
<td>120 &amp; 400</td>
<td>drying &amp; preheating</td>
<td>-</td>
<td>56</td>
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<tr>
<td>NH$_3$ hydrolysis of ZrOCl$_2$</td>
<td>550 &amp; 550</td>
<td>air, 2h &amp; N$_2$, 7h</td>
<td>70</td>
<td>57</td>
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<tr>
<td>NH$_3$ hydrolysis of ZrOCl$_2$</td>
<td>550</td>
<td>air, 1h</td>
<td>56</td>
<td>58</td>
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<tr>
<td>NH$_3$ hydrolysis of ZrOCl$_2$</td>
<td>500</td>
<td>air, 6h</td>
<td>57</td>
<td>59,60</td>
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<tr>
<td>NH$_3$ hydrolysis of ZrOCl$_2$</td>
<td>600</td>
<td>vacuum</td>
<td>41</td>
<td>7</td>
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<tr>
<td>NH$_3$ hydrolysis of ZrOCl$_2$</td>
<td>100 &amp; 700</td>
<td>O$_2$, 5h</td>
<td>19</td>
<td>41</td>
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<tr>
<td>NH$_3$ hydrolysis of dissolved ZrCl$_4$</td>
<td>600 – 900</td>
<td>air, 2 – 6h</td>
<td>8.2 – 30</td>
<td>45</td>
</tr>
<tr>
<td>NH$_3$ hydrolysis of dissolved ZrCl$_4$</td>
<td>600</td>
<td>O$_2$</td>
<td>30 – 36</td>
<td>10</td>
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<tr>
<td>NH$_3$ hydrolysis of Zr(NO$_3$)$_4$</td>
<td>500</td>
<td>air, 2 – 3h</td>
<td>80</td>
<td>44</td>
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<td>PICA process</td>
<td>700</td>
<td>air, 2h</td>
<td>33</td>
<td>34</td>
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<tr>
<td>ZrO(NO$_3$)$_2$ precipitation with hydrazine</td>
<td>1450 &amp; 800</td>
<td>air &amp; vacuum</td>
<td>1.0</td>
<td>32</td>
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<tr>
<td>A.D Mackay / nuclear grade</td>
<td>500</td>
<td>vacuum</td>
<td>23.7</td>
<td>33,61</td>
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<tr>
<td>Alfa Aesar</td>
<td>&gt; 1200 &amp; 800</td>
<td>air &amp; vacuum</td>
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<td>32</td>
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<td>Alfa Aesar</td>
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<td>air</td>
<td>10.4</td>
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<td>Alfa-Ventron</td>
<td>620</td>
<td>O$_2$, 0.5 h &amp; He, 0.25 h &amp; H$_2$, 0.5 h</td>
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<td>21</td>
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<tr>
<td>Alfa-Ventron</td>
<td>500</td>
<td>O$_2$, overnight</td>
<td>5.8</td>
<td>19</td>
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<td>Criceram / ZrCl$_4$ + H$_2$O vapor</td>
<td>877/903</td>
<td>air, 24h / 30% O$_2$ + 70% H$_2$O, 24h</td>
<td>6 / 4.2</td>
<td>63</td>
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<tr>
<td>Daiichi Kigenso Kagaku Kogyo (RC100)</td>
<td>400</td>
<td>air, 15h</td>
<td>71</td>
<td>64</td>
</tr>
<tr>
<td>Degussa / flame hydrolysis</td>
<td>600 – 800</td>
<td>air or vacuum</td>
<td>37 ± 1</td>
<td>65</td>
</tr>
<tr>
<td>Degussa</td>
<td>450</td>
<td>air, 4h</td>
<td>40</td>
<td>66</td>
</tr>
<tr>
<td>Gimex Technical Ceramics (RC-100)</td>
<td>600 &amp; 400</td>
<td>He, 24h &amp; H$_2$, 30 min</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>Magnesium Elektron (E-10 powder)</td>
<td>-</td>
<td>vacuum</td>
<td>14</td>
<td>24</td>
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<tr>
<td>MEL EC0100</td>
<td>580</td>
<td>O$_2$, 2h</td>
<td>47</td>
<td>22,67</td>
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<tr>
<td>MEL Zr(OH)$_4$</td>
<td>RT/150/300/500</td>
<td>vacuum</td>
<td>66.6 – 537</td>
<td>68</td>
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<tr>
<td>MEL Zr(OH)$_4$</td>
<td>450 &amp; 600</td>
<td>air, 16h &amp; O$_2$/inert, 2h</td>
<td>90</td>
<td>28</td>
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<tr>
<td>Nanotek</td>
<td>-</td>
<td>-</td>
<td>78</td>
<td>6</td>
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<td>Saint-Gobain NorPro</td>
<td>-</td>
<td>-</td>
<td>52</td>
<td>69</td>
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<tr>
<td>Commercial Zr(OH)$_4$</td>
<td>700</td>
<td>calcination, 6h</td>
<td>12</td>
<td>70</td>
</tr>
</tbody>
</table>

$^a$ Details about their zirconium oxide material.

$^b$ Surface area value reported prior to calcination.

$^c$ Surface area value reported prior to wafer pressing.
seems to be a better reductant than molecular hydrogen. Based on the literature, the mechanism for oxygen removal remains unclear; is it removed as O₂ or perhaps through dehydroxylation via multicoordinated OH groups, as shown in Eq. 1:

\[
\text{multi-OH} + \text{multi-OH} \leftrightarrow O_{\text{lattice}} + \text{ vacancy} + \text{H}_2\text{O}. \quad (1)
\]

The presence of Zr³⁺ sites has been proposed based on electron paramagnetic resonance (EPR) \(\text{8,46,51,57}\). The Zr surface cations have been probed with \(\text{N}_2\text{O}\), it decomposes on Zr³⁺ already at room temperature but also at higher temperatures, and reversibly adsorbs on Zr⁴⁺ sites \(\text{6}\). Vacuum treatment at above 600°C is sufficient to initiate formation of oxygen vacancies \(\text{81}\) and reduction of cations from Zr⁴⁺ to Zr³⁺ \(\text{6,81}\). Hydrogen treatment at 700°C also transforms some of the Zr³⁺ sites to Zr³⁺ sites \(\text{81}\), but with hydrogen treatment at 600°C, the amount of Zr³⁺ sites does not increase \(\text{9}\) in agreement with the low reducibility with H₂ mentioned previously. If the sample has been vacuum-activated at 400°C, hydration quenches the defect centers (Zr³⁺) and the defects have to be re-created with evacuation \(\text{8}\). If the sample has been vacuum-activated at 800°C, there are two options: (1) the defect centers are quenched but they are easier to re-create on a sintered surface, or (2) the defect centers are not quenched, rather coordinately saturated with water and dehydration restores their coordinatively unsaturated state \(\text{8}\). Based on EPR, the most exposed Zr³⁺ are transformed to Zr⁴⁺ when in contact with water (200°C, 18 torr \(\text{H}_2\text{O}\)) but the others are coordinately saturated with water and remaining Zr³⁺\(\text{8}\).

Syzgantseva et al. have calculated the formation energies for oxygen vacancies, and based on those the zirconia (T11) surface is less reducible than the (T01) surface \(\text{82}\), in line with the stability observation by Christensen and Carter \(\text{4}\). When comparing to other oxides, the oxygen vacancy formation energy on the zirconia surface is 820 – 880 kJ/mol and in the bulk ca. 860 kJ/mol, whereas those for titania, which is considered a reducible oxide, are 530 – 580 kJ/mol on the surface and 670 kJ/mol in the bulk \(\text{82}\). Syzgantseva et al. have also predicted the conditions necessary to create oxygen vacancies with surface hydrogenation followed by desorption of water (temperature above 927°C and \(\text{H}_2\text{O}/\text{H}_2\) pressure ratio below 10⁻⁸) \(\text{82}\). They conclude that water desorption takes place already at milder conditions, thus the simplifications in their computations required for, e.g., surface models might cause the discrepancy between theory and experiments \(\text{82}\).

The oxygen mobility, dissociation and recombination on zirconia among other oxide materials were probed by Martin and Duprez \(\text{66}\). Isotopic oxygen exchange experiments between \(^{16}\text{O}_2\) and \(^{18}\text{O}_2\) showed surface oxygen exchange at 380 – 780°C \(\text{66}\). The maximum O-exchange rate was at 530°C and the exchange rate was further expedited in the presence of Rh or Pt on the surface \(\text{66}\). The exchange is attributed to c.u.s. Zr³⁺ centers created by vacuum thermal treatment and their ability to dissociate molecular oxygen \(\text{66}\). The number of exchanged oxygens on ZrO₂ was found to be greater than the theoretical number of surface oxygen species implying that bulk oxygen atoms participated in the exchange \(\text{66}\).

### 3 Hydroxyl species and the interaction of water and hydrogen on monoclinic zirconia

Dissociative adsorption of water on monoclinic zirconia is exothermic, occurring already at room temperature \(\text{31,69}\). Therefore the surfaces of zirconia are hydroxylated under ambient and in most reactive atmospheres. In this section, different types of OH groups are discussed, followed by methods of manipulating the hydroxyl species on the surface of zirconia.

#### 3.1 Nature, density and probing of hydroxyl species

Typical hydroxyl sites reported on monoclinic zirconia include terminal OH groups (also known as monocoordinated OH) and tribridged OH groups, first assigned by Tsyganenko and Filimonov as a part of a wider study on different oxides including cerium, hafnium, magnesium, nickel, cobalt and several other oxides \(\text{3,71}\). Schematic drawings of the hydroxyl groups are presented in Fig. 2. The latter species has been assigned either tribridged \(\text{7,25,70,71}\), bibridged \(\text{29,53,61,63}\) or simply presumed as multicoordinated OH groups \(\text{18,19,23,59}\). In this work, the term multicoordinated is generally used to refer to this species.

**Fig. 2** Terminal and tribridged hydroxyl species.

The terminal and multicoordinated hydroxyl species are usually observed in IR spectroscopy at 3780 – 3760 cm⁻¹ and 3690 – 3650 cm⁻¹, respectively \(\text{7,19,50,61,71}\), as shown in Table 2 and Figure 3. Jacob et al. assign the bands to OH groups related to trigonally coordinated O²⁻ anions (ca. 3774 cm⁻¹) and to tetrahedrally coordinated O²⁻ anions (ca. 3668 cm⁻¹) \(\text{65}\), however, without further evidence. Yamaguchi et al. suggested that the bands at 3780 cm⁻¹ and 3680 cm⁻¹ would be isolated hydroxyls (as opposed to hydrogen-bonded ones) of bridged and terminal type adapting the interpretation for rutile, a type of TiO₂ \(\text{59}\). The occurrence of a band at 3740 – 3720 cm⁻¹ is typically interpreted as a sign of tetragonal phase and its bibridged hydroxyl. Yet the band of terminal OH (typically at 3780 – 3760 cm⁻¹) shifts towards lower
wavenumbers (even down to 3680 cm\(^{-1}\)) with increasing degree of hydration due to hydrogen bonding\(^{18}\) and at that point the multicoordinated OH band is even below 3600 cm\(^{-1}\)\(^{40}\), as suggested already by Tret’yakov \textit{et al.}\(^{44}\). Thus interpreting the hydroxyl band position must be done carefully, considering the possibility of hydrogen bonding at higher degrees of hydration. Tsyganenko and Filimonov also report an IR band at 3380 cm\(^{-1}\), assigned to hydrogen-bonded polynuclear water species\(^{61}\), based on the IR spectra of hydrogen bonding of water\(^{83}\). The hydrogen bonding is suggested to occur between molecularly adsorbed water and the hydroxyl groups\(^{18,33,42,53}\). The OH wavenumber and thermal stability depend on the crystalline phase of zirconia\(^{9}\); thus impurities in the crystalline phase can lead to misinterpretations.

**Table 2** Experimentally and theoretically determined \(\nu(\text{OH})\) wavenumbers

<table>
<thead>
<tr>
<th>Terminal</th>
<th>Bibridged</th>
<th>Tribridged</th>
<th>H-bonded</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{cm}^{-1})</td>
<td>(\text{cm}^{-1})</td>
<td>(\text{cm}^{-1})</td>
<td>(\text{cm}^{-1})</td>
<td></td>
</tr>
<tr>
<td>3770</td>
<td>3670</td>
<td>3380</td>
<td>371</td>
<td></td>
</tr>
<tr>
<td>3776</td>
<td>3667</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3772</td>
<td>3681 &amp; 3660</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3775</td>
<td>3675 – 3668</td>
<td>3600 – 2800</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>(\approx 3775)</td>
<td>3695 – 3662</td>
<td>(&lt; 3600)</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>3778</td>
<td>3680 – 3675</td>
<td>3455 – 3450</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>3779 – 3771</td>
<td>3738 – 3727</td>
<td>(\approx 3400)</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>3740</td>
<td>3675</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3760</td>
<td>3660</td>
<td>3600 – 2800</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>3770</td>
<td>3680</td>
<td>53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3769</td>
<td>3688</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3774</td>
<td>3668</td>
<td>65.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Experimental**

| 3822 – 3743         | 3755 – 3568| 3647 – 3498| 67       |
| 3778                | 3550       | 3475       | 84       |
|                     | 3750       | 3700       | 74       |

**Theoretical**

Terminal hydroxyls are bound directly to a single cation at oxygen lattice sites whereas the multicoordinated hydroxyls are located at low-index faces\(^{61}\). The former are able to accommodate a water molecule to hydrogen-bond on an edge or a corner site of the oxide particle while the latter are incapable of hydrogen bonding due to steric factors\(^{61}\). The assignment of multicoordinated hydroxyls to low-index faces\(^{61}\) and the observed decrease in the relative amount of terminal OH species with vacuum treatment at 500 – 1000\(^\circ\)C\(^{65}\) are in line with the observation that the regularity of sintered crystals is higher\(^{39}\).

**Table 2**

Based on IR spectroscopy, the tribridged OH species (at 3690 – 3681 cm\(^{-1}\) and at 3670 – 3660 cm\(^{-1}\)) on zirconia are suggested to be actually two species\(^{7,40}\), and signs of multiple tribridged species are also seen both at high\(^{18,28}\) and low\(^{18}\) degrees of hydration. The OH species differ slightly in their acidic character\(^{40}\) and their behavior with calcination at 600 – 900\(^\circ\)C suggests that the low-frequency band (3670 – 3660 cm\(^{-1}\)) should be assigned to tribridged species at crystallographic defects selectively annealed during sintering\(^{40}\). However, in our recent investigations for reduced zirconia with no visible H-bonding effect, both terminal and multi-coordinated bands shift down in wavenumber with increasing temperature\(^{28}\).

The nature of the multicoordinated OH species has also been considered at the atomic level. The ZrO\(_2\)(111) surface is suggested to have too small a distance between the c.u.s. O\(^{2-}\) and the c.u.s. Zr\(^{4+}\) site (only 2 \(\text{Å}\))\(^{40}\), that is not enough space to dissociate a water molecule to form terminal and bibridged OH groups. The corresponding distance between Zr\(^{4+}\) and tribridged oxygen is \(\approx 2.3 \text{ Å}\), allowing formation of a terminal and a tribridged hydroxyl via dissociation\(^{40}\). Based on theory, both bibridged and tribridged species exist\(^{67,74}\). Korhonen \textit{et al.} report that at low coverages (\(\theta = 0.25\) ML), there are only bibridged hydroxyls on the (111) and (101) surfaces\(^{67}\). Bibridged hydroxyls are also claimed to form following dissociative adsorption on the (001) surface until a full coverage (\(\theta = 1\) ML) is obtained\(^{85}\).

The hydroxyl IR vibrations have been determined computationally\(^{67,74,84}\) as shown in Table 2. It demonstrates the large variation of calculated frequencies which span, e.g., over 200
wavenumbers for tribridged OH species. Diversity of calculated frequencies for adsorbed OH is not unique to ZrO₂ but also reported on CeO₂. The overall discrepancy between calculated and experimental frequencies can follow from three different origins. First, frequencies are typically calculated using a so-called harmonic approximation, which specifically leaves out possible anharmonic effects leading, in part, to errors in calculated frequencies. Secondly, discrepancies can also originate from the inability of density functional theory (DFT) to reliably describe the electronic structure of a given system. Thirdly, for polycrystalline oxide nanostructures, the discrepancy of calculated frequencies compared to the experimental ones can stem from the fact that an active surface site cannot experimentally be identified definitely. This may lead to an inaccurate computational adsorption site model, which differs from the real adsorption site. Moreover, the application of a cluster model to simulate ZrO₂ surfaces can impact on the calculated frequencies.

Hydroxyl densities can be estimated based on the amount of water removed from zirconia, water adsorbed on zirconia, or on quantification via 1H MAS NMR, and these estimates are presented in Table 3. In the table, the scaled values represent OH density regardless whether it has been measured directly or by water adsorption (each water molecule is assumed to form two surface hydroxyls).

The observed amount of adsorbed water decreases with increasing temperature, as expected. Based on an estimated number of Zr atoms on the ZrO₂ surface (ca. 12 µmol/m²) and water adsorption leading to formation of two OH groups, one on Zr cation and one on a surface oxygen, the estimated hydroxyl densities seem reasonable in magnitude. Nawrocki et al. report a theoretical maximum OH concentration of ca. 25 µmol/m² based on the average surface Zr concentration of ca. 12.2 µmol/m². The amount of induced hydroxyls (20.2 µmol/m² desorbed above 200°C) seems to be in agreement with the estimated total OH capacity, also Piskorz et al. have reported similar theoretical OH site densities.

The energetics of water adsorption have been investigated both with an experimental and a theoretical approach. Piskorz et al. have studied the effect of surface hydration on the stability of the crystal planes using DFT calculations. A hydroxylated surface is favored over the clean surface on very small crystallites (< 20 Å), whereas hydration does not enhance the stability of the surface on crystallites between 500 Å and 2000 Å, and the authors claim that the transformation from clean to hydrated surface is attenuated. However, this is not in line with experimental observations suggesting the hydroxylated surface to be the prevalent one. Based on microcalorimetry, the integral enthalpy of adsorption for a half-layer coverage of water (3.65 µmol/m²) is −142 kJ/mol on monoclinic ZrO₂ nanoparticles (crystal size 100 – 500 Å, specific surface area 1.6 – 27.2 m²/g). This is in agreement with the values measured for powder zirconias (1.0 – 1.6 m²/g) giving a range from −110 kJ/mol to −170 kJ/mol. Theoretical adsorption energy values typically range from −80 kJ/mol to −190 kJ/mol on (001), (T11), (111), and (T01). We have recently reported dissociative adsorption energies for the first adsorbing water molecule ranging from −106...−119 kJ/mol up to −297 kJ/mol, for flat, stepped and corner adsorption sites. The calculated values demonstrate the structure sensitivity of dissociative adsorption of water, which is clearly most favorable on a c.u.s. site such as a corner site suggested by our DFT calculations.

3.2 Manipulation of hydroxyl species

The intensity ratio of terminal and multicoordinated hydroxyls varies according to temperature, used atmosphere and pretreatment. Hydroxyl species can be added to the surface with water or hydrogen treatments and removed using heat together with inert gas or evacuation. The initial state of zirconia can usually be restored with evacuation or flushing with inert at the same temperature as before rehydration.

Sample hydration is typically carried out by adsorbing water vapor, either by letting the sample adsorb moisture from air (virgin material in), equilibrating in a closed vessel with water vapor in nitrogen (to avoid CO₂ adsorption), or by feeding water vapor to the sample. The rehydrated sample can be used as such or after further dehydration with vacuum and/or elevated temperature. Rehydration has also been carried out by exposing the sample to hydrogen at room temperature, or by contacting the zirconia sample with water-saturated hydrogen for 10 min at 50°C. Unfortunately, rehydration is often described vaguely, omitting time, water vapor concentration or temperature, all relevant in controlling the degree of hydroxylation.

Commonly used methods for dehydration are vacuuming or flushing at elevated temperatures. Undissociated water adsorbed at room temperature is completely removed in vacuum by 127°C and after evacuation at 200°C only two distinct OH bands at ca. 3775 cm⁻¹ and 3665 cm⁻¹ remain. Köck et al. pretreated the zirconia in air at 900°C to completely dehydroxylate the sample, and only very weak OH bands remained. Evacuation at 500°C is reported to be insufficient for complete dehydroxylation, but already at 550°C spectra with no trace of surface hydroxyls after evacuation are shown. The conditions necessary for total OH removal are at ca. 550 – 750°C in vacuo, in agreement with the enthalpies for water adsorption discussed earlier in this paper in Section 3.1. As most pretreatments and processes do not reach these conditions, the presence of these OH groups on the zirconia surface in process conditions is practically inevitable, especially in biomass-based processes, where water is present.
Table 3 Hydroxyl densities reported in literature

<table>
<thead>
<tr>
<th>Measurement</th>
<th>As reported</th>
<th>Scaled to µmol OH/m²</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH concentration (SA = 19 m²/g)</td>
<td>6.2 OH/nm²</td>
<td>10.30</td>
<td>25</td>
</tr>
<tr>
<td>OH concentration (SA = 110 m²/g)</td>
<td>9.4 OH/nm²</td>
<td>15.61</td>
<td>25</td>
</tr>
<tr>
<td>Induced hydroxyls (desorbed above 200°C) after 48h in humid N₂ at RT</td>
<td>20.2 µmol OH/m²</td>
<td>20.2</td>
<td>34</td>
</tr>
<tr>
<td>OH coverage calc. from H₂ evolution after standardization (400°C, O₂, 1h)</td>
<td>2.1·10⁻²⁰ OH/cm²</td>
<td>0.35</td>
<td>20</td>
</tr>
<tr>
<td>Estimated full OH coverage before standardization</td>
<td>7.2·10⁻¹⁰ OH/cm²</td>
<td>1.2</td>
<td>20</td>
</tr>
<tr>
<td>Estimated chemisorption capacity at 25°C</td>
<td>5.7 mg H₂O/g</td>
<td>26.7</td>
<td>33</td>
</tr>
<tr>
<td>Irreversibly adsorbed water at 25°C</td>
<td>4.8 mg H₂O/g</td>
<td>22.5</td>
<td>33</td>
</tr>
<tr>
<td>Surface hydrogen after H₂O adsorption at 200°C</td>
<td>4.20 H/nm²</td>
<td>6.97</td>
<td>69</td>
</tr>
<tr>
<td>Surface hydrogen after H₂O adsorption at 300°C</td>
<td>3.62 H/nm²</td>
<td>6.01</td>
<td>69</td>
</tr>
<tr>
<td>Surface hydrogen after H₂O adsorption at 400°C</td>
<td>3.22 H/nm²</td>
<td>5.51</td>
<td>69</td>
</tr>
<tr>
<td>Full coverage of water (2x half-layer coverage)</td>
<td>4.4 H₂O/nm²</td>
<td>14.6</td>
<td>31</td>
</tr>
<tr>
<td>Theoretical H₂O adsorption capacity at θ = 1 ML on (T11) surface</td>
<td>8.9 H₂O/nm²</td>
<td>29.6</td>
<td>77</td>
</tr>
<tr>
<td>Theoretical H₂O adsorption capacity at θ = 1 ML on (111) surface</td>
<td>7.1 H₂O/nm²</td>
<td>23.6</td>
<td>77</td>
</tr>
<tr>
<td>Theoretical H₂O adsorption capacity at θ = 1 ML on (011) surface</td>
<td>5.2 H₂O/nm²</td>
<td>17.3</td>
<td>77</td>
</tr>
<tr>
<td>Theoretical H₂O adsorption capacity at θ = 1 ML on (001) surface</td>
<td>7.5 H₂O/nm²</td>
<td>24.9</td>
<td>77</td>
</tr>
</tbody>
</table>

The partial dehydration method\(^{18,44,53,65}\) can be used to vary the concentration of several types of OH groups on zirconia. Depending whether the amount of adsorbed water results from dehydration or rehydration, the surface species distribution might be different as demonstrated by Bolis et al.\(^{27}\) by heating the sample in a closed vessel and analyzing the OH distribution on the sample before and after. Based on their findings, dehydration is systematic even in terms of the surface effects whereas rehydration is more blotchy as the water collides and dissociates on the surface as hydrogen-bonded pairs\(^{27}\). Thus allowing the system to approach equilibrium leads to a more even surface distribution. All in all, the method chosen to adjust the amount of hydroxyls influences their distribution on the zirconia surface.

Cerrato et al. suggest based on theory that water dissociates forming a tribridged OH at a tricoordinated c.u.s. oxygen and a terminal OH on a c.u.s. cation, leaving a c.u.s. monocoordinated oxygen in the same sphere unsaturated\(^{40}\). The presence of the suggested c.u.s. monocoordinated oxygen is in agreement with CO₂ adsorption experiments on a fully hydrated surface, yielding monodentate and bidentate carbonate species requiring the presence of basic, c.u.s. oxygen ions\(^{40}\).

Based on theory, dissociative adsorption for the first adsorbed water molecule of a unit cell (θ = 0...0.25 ML) has been reported on (T11)\(^{67,77}\), (T01)\(^{67}\), and (111)\(^{67}\) surfaces. The second H₂O molecule adsorbs molecularly on (T11)\(^{67,77}\) and (111)\(^{67}\), and dissociatively on (T01)\(^{67}\) surfaces. The additional H₂O molecules adsorb molecularly\(^{67,77}\). For both (T11) and (T01) surfaces already the first water molecule forming two hydroxyls is hydrogen-bonded\(^{67}\). Iskandarova et al. have reported both dissociative and molecular adsorption enthalpies resulting in coverages of 0.5 ML and 1 ML on a (001) surface, the dissociative adsorption is favored by 45 – 75 kJ/mol in both cases\(^{85}\). Our recent investigations suggest that at θ = 0.25 ML, there is hydrogen bonding between the hydroxyl groups on the (T11) surface but not on the hydroxylated (112) edge and corner sites\(^{28}\). Cerrato et al. point out that the hydrogen bonding at high hydroxyl coverages only takes place between OH species and coordinated undissociated water whereas hydrogen bonding between OH pairs is unlikely\(^{40}\).

Morterra et al. hypothesize that if all surface oxygens on a (111) surface are transformed into hydroxyls to maintain electrical neutrality, and then dehydration takes place via desorbing terminal hydroxyls and hydrogen atoms from bridging OH groups (shown in Fig. 4), only bridging oxygens are left behind, and thus highly uncoordinated Zr\(^{4+}\) sites are achieved\(^{39}\). The intensity of the terminal hydroxyl species decreases more than that of the multicoordinated OH when the zirconia sample is thermoevacuated at 500 – 600°C after calcination at 600°C\(^{70}\). Dehydration in vacuum at 500 – 1000°C followed by hydration caused the relative amount of terminal OH to decrease significantly compared to multicoordinated OH, whereas oxygen treatment (500 – 750°C) before hydration had the opposite effect\(^{65}\). The decrease in terminal hydroxyls with high-temperature vacuum treatment is assigned to increasing amount of tetragonal zirconia, as the tetragonal phase is stabilized by oxygen vacancies\(^{65}\).

One approach to hydroxyl studies is to replace hydrogen with its heavier isotope deuterium using D₂ or D₂O, or to replace \(^{16}\)O with \(^{18}\)O, all of which are easily observable in both IR and mass spectrometry. OD groups, known as deuteroxyls, have been investigated by many groups\(^{19,21,24,42,44,56,59,61,87}\) while oxygen-labeling studies are more scarce\(^{66,69,81}\).

Observed deuteroxyl IR wavenumbers are collected in Table 4. Erkelens et al. report that the ratios of the frequen-
cies between the OH bands (3732 cm\(^{-1}\), 3660 cm\(^{-1}\), and 3584 cm\(^{-1}\)) and the OD bands (2758 cm\(^{-1}\), 2702 cm\(^{-1}\), and 2651 cm\(^{-1}\)) are ca. 1.36, in agreement with the expected isotopic substitution\(^{56}\). Similar results with additional OH band at 3738 \(-\) 3727 cm\(^{-1}\) (OD at 2757 \(-\) 2748 cm\(^{-1}\)) were reported also by Guglielminotti\(^{29}\). A spectrum showing the changes in OH/OD groups is shown in Fig. 5.

Table 4 Experimentally determined \(\nu(\text{OD})\) wavenumbers

<table>
<thead>
<tr>
<th>Terminal cm(^{-1})</th>
<th>Multicoordinated cm(^{-1})</th>
<th>Other cm(^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2780</td>
<td>2703</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>2758</td>
<td>2702</td>
<td>2651</td>
<td>56</td>
</tr>
<tr>
<td>2770</td>
<td>2695</td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>2785 (-) 2779</td>
<td>2713 (-) 2701</td>
<td>2757 (-) 2748</td>
<td>29</td>
</tr>
<tr>
<td>2780</td>
<td>2710</td>
<td></td>
<td>59</td>
</tr>
<tr>
<td>2783</td>
<td>2713 (-) 2710</td>
<td></td>
<td>63</td>
</tr>
<tr>
<td>2760</td>
<td>2706</td>
<td></td>
<td>48</td>
</tr>
<tr>
<td>2760</td>
<td>2710</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>2782</td>
<td>2705</td>
<td></td>
<td>81</td>
</tr>
</tbody>
</table>

Repeated treatments with, e.g., 10 torr of D\(_2\)O vapor\(^{44}\) at room temperature almost completely replace hydrogen with deuterium in both terminal and multicoordinated OH, resulting in corresponding OD groups\(^{19,24,44,56,59,61}\). The terminal species seem to exchange more easily than the multicoordinated species\(^{24,59}\).

Ignatchenko \textit{et al}. propose that the hydrogen–deuterium exchange mechanism would proceed \textit{via} hydroxyl/deuteroxyl exchange so that a deuterated water absorbs adjacent to an existing terminal hydroxyl species and a hydrogen bond is formed between the D\(_2\)O and the OH species\(^{69}\). Then the hydrogen-bonding deuterium atom and the original OH group desorb as HDO species, leaving the OD species on the surface. The mechanism is shown in Fig. 6.

Labeling the oxygen of water (H\(_{18}\)\(_2\)O) reveals that the oxygens of hydroxyls are thoroughly exchanged by 400\(^\circ\)C, yet at 200\(^\circ\)C the findings of Ignatchenko \textit{et al}.\(^{69}\) disagree with the suggested mechanism in Fig. 6. It appears that already at 200\(^\circ\)C the terminal hydroxyls can be exchanged but for the multicoordinated ones higher temperatures (closer to 400\(^\circ\)C) are required\(^{69}\), and the presented mechanism should be modified to also apply for the multicoordinated hydroxyls. Based on these findings, it seems that the hydrogen scrambling follows the suggested mechanism\(^{69}\) (see Fig. 6). The terminal OH species are completely exchanged \textit{via} the normal (de)hydroxylation mechanism involving also multicoordinated OH groups and labeled H\(_{18}\)\(_2\)O as deduced from the applied temperature range (200 \(-\) 400\(^\circ\)C). The exchange of multicoordinated hydroxyls requires a new mechanism hypothesis and we propose that multi-OH groups are removed as water, leaving behind one oxygen atom and an oxygen vacancy (see Eq. 1). This mechanism may be predominating only at high temperatures when terminal OH species have already been desorbed.

In addition to water or its deuterated counterpart, also H\(_2\) or D\(_2\) can be used to create surface OH or OD groups on monoclinic zirconia. He and Ekerdt have suggested that gas-phase hydrogen is able to replenish OH groups\(^{21}\), the hydroxyl IR bands emerge at 200 \(-\) 600\(^\circ\)C\(^{9,48,53}\) for both terminal and multicoordinated hydroxyl species\(^{53}\).

Hydroxyl formation mechanism by molecular hydrogen can be either homolytic, resulting in two hydroxyl species and two electrons\(^{9}\), or heterolytic, resulting in IR-inactive Zr–H (H\(^+\) type) species and a hydroxyl (OH) species\(^{49}\). At temperatures above 100\(^\circ\)C, large amounts of hydroxyl species are formed likely due to homolytic dissociation of hydrogen\(^{48}\), whereas hydrogen contact at room temperature induces heterolytic dissociation\(^{48}\). Heterolytic dissociative adsorption of H\(_2\) at room
temperature seems to require unhydroxylated c.u.s. Zr sites, as pretreatment above 600°C is necessary to remove adsorbed water from the zirconia surface.\(^{26,49}\) Even though Bianchi et al. have observed increasing hydroxyl species intensities in IR during H\(_2\) treatment, they report no adsorption or desorption of hydrogen at 25–400°C, and no water evolution during H\(_2\)-TPR from 25°C up to 700°C.\(^{53}\) Assuming no reoxidation process concerning the Zr cations, a hydrogen desorption mechanism is postulated for Zr–H and Zr–OH sites leading to Zr and Zr–O sites, as hydrogen adsorbed at 550°C is desorbed from m-ZrO\(_2\) at 600°C.\(^{9}\)

According to Syzgantseva et al., hydrogen dissociates on Zr\(^{3+}\) with a neighboring oxygen vacancy (\(v_o\)), leading to formation of Zr–H hydrides and the transformation of Zr cations into Zr\(^{4+}\) species.\(^{82}\) The proposed mechanism is presented in Fig. 7. Addition of gas-phase oxygen to the Zr–H hydrides, produced by gas-phase H\(_2\) at room temperature, increases the OH intensity at 3668 cm\(^{-1}\) (generally considered as multicoordinated OH), creates the 3774 cm\(^{-1}\) OH intensity at 3668 cm\(^{-1}\) and decreases the intensity of the Zr–H species at 550°C is desorbed from m-ZrO\(_2\) at 600°C.\(^{9}\)

The hydrogen dissociation mechanism proposed by Syzgantseva et al.\(^{82}\) is illustrated in Fig. 7. Substitution of regular oxygen (\(^{16}O_2\)) with isotopically labeled oxygen (\(^{18}O_2\)) does not affect the position of the OH bands (expected shift 11 cm\(^{-1}\)) in IR spectra, thus OH formation seems to occur on lattice oxygen rather than the gas-phase originating oxygen species.\(^{81}\)

Fig. 7 The hydrogen dissociation mechanism proposed by Syzgantseva et al.\(^{82}\) Reproduced from ref.\(^{82}\) with permission. Copyright 2012, American Chemical Society.

Treatment with deuterium gas at 200°C (1h, 18 torr) and 250°C (1h, 250 torr), is sufficient to exchange virtually all hydrogen of hydroxyl groups to deuterium.\(^{56}\) He and Ekerdt report that the deuterium in OD groups is replaced by hydrogen already at 200°C with hydrogen dissociating on the zirconia surface.\(^{19}\) At 150°C in 488 kPa of D\(_2\), half of the hydrogen in surface OH species is changed to deuterium within 30 seconds.\(^{42}\) The H/D exchange takes place already at 100°C with D\(_2\) in the gas phase, however, at 200°C the exchange rate increases considerably.\(^{26}\) The activation energies of the H/D exchange reaction with D\(_2\) are similar for both terminal and multicoordinated hydroxyls, and they seem to increase with the progress of the reaction.\(^{26}\) This is interpreted to be due to the overall exchange (migration and replacement of atomic hydrogen by deuterium) being limited by D migration on the surface, subject to heterogeneity of potential barriers to various sites.\(^{26}\)

Merle-Méjean et al. have found that on an air-calcined zirconia the hydroxyl species are H/D exchanged in contact with D\(_2\) (507°C, 100 hPa) so quickly that it gives reason to believe the OH species are on the surface only.\(^{63}\) Conversely, on the steam-calcined zirconia there are some hydroxyls exchanged to deuterium-containing species so slowly (during several hours), if at all, that they must be elsewhere in the oxide, likely in the bulk.\(^{63}\)

The presence of formate species is suggested to decrease the number of available sites for H\(_2\)/D\(_2\) dissociation as well as partially block the path for surface transport of H or D atoms.\(^{42}\) If there are formates on the surface, the H/D exchange between OH and OD species at 150°C is 4–36 times slower depending on the formate coverage (0.3 or 0.8 times the maximum coverage).\(^{42}\) The overall extent of the H/D exchange of multicoordinated OH to OD is limited to 9% with formate and 2% with methoxy species as compared to normal ZrO\(_2\) surface.\(^{26}\)

4 Interaction with CO

Upon contact with monoclinic zirconia, CO tends to form several surface species: at low temperatures up to ca. 100°C the preferred species is linearly adsorbed CO, at higher temperatures the dominating surface species is formate. In addition to these, also carbonate and carboxylate-type species have been observed.

4.1 Linear CO species, formation and stability

CO adsorption at room temperature leads to the formation of linear CO species on cationic sites of the zirconia surface (see Fig. 8), the corresponding bands in IR spectra are located at ca. 2200 – 2170 cm\(^{-1}\).\(^{15,18,48,50}\) Spectra of the linear CO species as a function of CO pressure and with two differently prepared samples are shown in Fig. 9. The presence of a weak band at 2112 cm\(^{-1}\) is reported after CO adsorption at room temperature.\(^{48}\) With adsorption below room temperature, e.g., at \(-173\ldots-195\)°C, the range of adsorbed linear CO species extends to ca. 2200 – 2140 cm\(^{-1}\) at varying CO pressures (from 10\(^{-4}\) to 40 torr).\(^{39,58}\)

Fig. 8 Linearly adsorbed CO species.

Morterra et al. report that the linearly adsorbed CO species seen in IR at room temperature are at wavenumbers 2198 –
2187 cm\(^{-1}\) and 2188 – 2174 cm\(^{-1}\), named (CO)\(_{H}\) and (CO)\(_{L}\) after the high-frequency and low-frequency bands.\(^{18}\) Also Guglielminotti has adsorbed CO to zirconia at room temperature, and his results for either reduced (550 \(^{\circ}\)C) or oxidized (400 – 550 \(^{\circ}\)C) and vacuum-activated (400 \(^{\circ}\)C) samples show strong bands at around 2200 cm\(^{-1}\).\(^{29}\) For samples reduced at 300 \(^{\circ}\)C and/or vacuum-activated at 500 \(^{\circ}\)C after oxidation, adsorbed CO is observed also at 2110 cm\(^{-1}\).\(^{29}\)

The IR bands at ca. 2200 – 2190 cm\(^{-1}\) are interpreted as CO adsorbed on Zr\(^{4+}\).\(^{6,27,29}\) and the band at ca. 2120 – 2110 cm\(^{-1}\) is assigned to CO on Zr\(^{3+}\) surface ions,\(^{6,7,9,29,81}\) whereas ESR (electron spin resonance spectroscopy) results are interpreted so that Zr\(^{3+}\) surface ions do not interact with CO at room temperature.\(^{27}\) The appearance of IR bands assigned to adsorbed CO at higher wavenumbers than gas-phase CO (at 2202 cm\(^{-1}\)) is attributed to polarization of the CO molecule on the surface.\(^{38}\) At room temperature the OH groups are not modified during CO adsorption.\(^{54}\)

The (CO)\(_{H}\) and (CO)\(_{L}\) species are suggested to be on two types of Lewis-acidic centers,\(^{18}\) both types assigned as Zr\(^{4+}\) ions.\(^{27}\) For CO chemisorption, these centers are suggested to be caused by differences in crystallography and/or coordinative configurations as the (CO)\(_{L}\) intensity increases while the (CO)\(_{H}\) intensity declines with increasing activation temperature as a result of the beginning sintering process.\(^{18}\) The (CO)\(_{L}\) sites are therefore assigned to flat sites whereas the (CO)\(_{H}\) sites are thought to be on rougher (high-index) planes or structural defects: steps, kinks, or corners.\(^{57}\) Sintering the surface indeed causes a sharp relative decline on (CO)\(_{H}\) intensity (at ca. 2190 cm\(^{-1}\)) in IR, and the sintered surface seems to have more extended and regular flat surface sites based on HRTEM images.\(^{39}\)

Linear CO is reversibly adsorbed on the surface at room temperature as removing the CO from gas phase results in the disappearance of its IR band.\(^{20,27,54,55}\) CO adsorption at room temperature at constant CO pressure shows constant intensity against time on stream if measured by the band at ca. 2192 cm\(^{-1}\).\(^{20,54}\), indicating unactivated adsorption. Jung and Bell present an interesting scheme (see Fig. 10) relating linearly adsorbed CO and its interactions with the zirconia surface.\(^{25}\) In the scheme they show two differently coordinated adsorbed CO molecules with bicarbonate and bidentate carbonate as transformation intermediates: in the former case the Zr\(^{4+}\) cation will have a lower Lewis acidity in the vicinity of an OH group, leading to a lower displacement value of the IR wavenumber compared to the gas-phase CO IR band than with the bidentate carbonate intermediate in a c.u.s. oxygen environment.\(^{25}\)

Increasing the CO partial pressure increases the adsorbed CO band intensity.\(^{20,52}\) The intensity ratio for the two adsorbed CO species favors (CO)\(_{H}\) at low coverages and (CO)\(_{L}\) at high CO pressures.\(^{18,27}\) An increase in the CO partial pressure shifts the IR band position down from ca. 2195 cm\(^{-1}\) to 2188 cm\(^{-1}\).\(^{18,27,30,52,54}\), and the overall surface area of the band indicates adsorption according to Langmuir’s adsorption model with increasing CO partial pressure.\(^{54}\)

Increasing the adsorption temperature shifts the main band at ca. 2190 cm\(^{-1}\) downwards to higher wavenumbers.\(^{18,55}\) This shift is attributed to inductive effects, as the charge-release mechanism of the adsorbed CO is affected by those, as well as the influence of other surface species (e.g. OH) on the adsorbed CO.\(^{18}\) The temperature range with detectable linear CO bands extends typically to ca. 100 – 150 \(^{\circ}\)C.\(^{46,54,55}\) but it has been reported even at 250 \(^{\circ}\)C\(^{23}\) at 2184.9 cm\(^{-1}\) (CO pressure not
reported). Ma et al. observed a band at 2109 cm$^{-1}$ during CO adsorption at 350$^\circ$C, linked to CO adsorption on c.u.s. Zr$^{3+}$.

The reported linear CO coverages are scaled to $\mu$mol/m$^2$ and collected in Table 5. The amount of adsorbed CO depends on the adsorption temperature, the coverage at $-173^\circ$C is significantly higher than the coverage at room temperature. As can be seen in Table 5, dehydroxylation increases the linear CO adsorption capacity$^{20}$, as dehydroxylated surfaces have a higher number of bare zirconium cations. Increasing activation temperature results in increasing monolayer capacities for both (CO)$_L$ and (CO)$_H$ according to the literature$^{27}$, as expected due to lower hydroxyl coverage with increasing activation temperature. It has been estimated that 50% of the dehydroxylated sites can absorb CO reversibly$^{20}$. The capacity for the (CO)$_L$ species is significantly lower than for the (CO)$_H$ species, the latter almost fourfold compared to the former$^{27}$.

Dulaurent and Bianchi have assumed Langmuir adsorption, calculated adsorption coefficients from IR data and used them with statistical thermodynamics to extract heats of adsorption, and their results range from 55 kJ/mol to 42 kJ/mol (at zero surface site coverage, respectively)$^{55}$. Molar heat of adsorption determined with microcalorimetry is reported to be 65 $\pm$ 2 kJ/mol for (CO)$_H$ and 44 $\pm$ 5 kJ/mol for (CO)$_L$ according to the literature and for Lewis-acidic sites at vanishing coverages at 60 kJ/mol. Based on theory, the adsorption energy of linearly adsorbed CO was determined to be 45 $\pm$ 5 kJ/mol$^{28}$. To give an idea of the strength of the CO adsorption on the Zr$^{3+}$ sites, CO on Zr$^{4+}$ (at ca. 2200 cm$^{-1}$) can be removed by evacuation at room temperature and CO on Zr$^{4+}$ (at ca. 2110 cm$^{-1}$) is slightly more strongly bound to the zirconia surface, yet also possible to evacuate at room temperature$^{29}$. The observed IR band intensities of the (CO)$_H$ and (CO)$_L$ species with increasing CO pressures are in line with their heats of adsorption: the (CO)$_H$ with a higher heat of adsorption has a higher intensity at low pressures and vice versa at higher pressures$^{27}$.

As shown in Table 5, the linear CO adsorption capacity on dehydroxylated surfaces is higher than on hydroxylated surfaces. The hydroxyl species has an adverse effect on CO adsorption as linear CO$^{20,27,28}$, completely suppressing CO adsorption at room temperature already at a surface concentration of 2.4 $\mu$mol/m$^2$ H$_2$O$^{27}$, corresponding to a 20% surface coverage. The more strongly adsorbed linear CO species, (CO)$_H$, seems to be suppressed more than the more weakly adsorbed species when the sample is changed from a dehydroxylated one to one with a low OH coverage$^{27}$, suggesting that the site for (CO)$_H$ is the preferred site for hydroxyl formation. Four irreversibly held water molecules are required to eliminate one acidic site based on adsorption capacity experiments at varying degrees of hydration$^{27}$. This 4:1 ratio between water and CO suggests that adsorption sites for linearly adsorbed CO represent only a minority of the sites available for water adsorption. This division is also reflected in the adsorbed amounts of water or OH groups (Table 3) and linearly adsorbed CO (Table 5).

In addition to increasing the adsorption capacities, dehydroxylation seems to shift the bands of the adsorbed CO species up in wavenumber, once full dehydroxylation has been carried out by evacuation at 597$^\circ$C, the bands only decrease in intensity: especially the (CO)$_H$ band intensity decreases as is expected due to the sintering process first affecting the minority sites$^{27}$. Morterra et al. indicate that on a highly hydrated surface, local interactions among hydroxyls exceed the adsorbate-adsorbate interactions caused by CO, i.e., the ordered CO oscillator network is interfered with the hydroxyls present$^{39}$.

Morterra et al. have looked at CO adsorption to cationic Zr sites after rehydration and they report that the CO species adsorbing at 2145 cm$^{-1}$ (assigned to CO adsorbed to Zr$^{4+}$ centers via a $\sigma$ bond) are quickly suppressed with water, but the lower wavenumber band tends to downshift from 2112 cm$^{-1}$ to 2102 cm$^{-1}$ (proposed to be c.u.s. cationic center Zr$^{4+}$, where $n < 4$) and increase in intensity$^8$. The overall surface coverage of charge-releasing CO species inductively affect also the position of the adsorbed CO band$^8$.

Even though hydroxylation decreases the linear CO adsorption capacity$^{27,58}$, surface hydroxyls are an important surface site for CO adsorption as formate species$^{5,21}$. Linearly adsorbed CO intensities during room-temperature adsorption have been compared before and after CO adsorption at elevated temperature$^{54,55}$. Dulaurent and Bianchi report that after CO adsorption at 85$^\circ$C or 152$^\circ$C, cooling to 27$^\circ$C and another CO adsorption, the absorbance of the linear CO band is reported to decrease by 12% or 35%, respectively$^{55}$. Mugniery et al. show spectra where formate preadsorption at 300$^\circ$C shifts the linear CO bands from 2192 cm$^{-1}$ to 2177 cm$^{-1}$$^{54}$. When these bands are compared to the spectra of Morterra et al.$^{38}$ we note that the (CO)$_H$ species is suppressed by formates, linking the formate and the (CO)$_H$ to the same Zr$^{4+}$ surface site. As mentioned earlier, when investigating the CO pressure effect on the band, (CO)$_L$ is the preferred species at high coverages. However, it is not clear whether that applies also to the increasing formate coverage (or coverage of any species) or if the (CO)$_H$ site is occupied or otherwise hindered due to the adsorbed formate species.

### 4.2 Formates, formation and decomposition

Formate species consists of a HCOO$^-$ unit connected to a surface zirconium cation from oxygen atom(s). Two different surface configurations have been proposed for the formate species: a bidentate formate$^{20,22,30,42}$ and a monodentate formate$^{22,42}$ shown in Fig. 11. Main IR bands of formate species on monoclinic zirconia are observed typically (see Fig. 12) at ca. 2965 cm$^{-1}$, 2880 cm$^{-1}$, 1565 cm$^{-1}$, 1387 cm$^{-1}$,
Table 5  Linear CO coverages reported in literature

<table>
<thead>
<tr>
<th>Measurement</th>
<th>As reported</th>
<th>Scaled to $\mu$mol/m$^2$</th>
<th>$T_{ads}$</th>
<th>$P_{CO}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed quantities of CO$^a$</td>
<td>up to 220$\mu$mol/g</td>
<td>up to 2.7</td>
<td>RT</td>
<td>N/A</td>
<td>50</td>
</tr>
<tr>
<td>Monolayer (ML) capacity for (CO)$_H$</td>
<td>0.12 – 0.24 molec./nm$^2$</td>
<td>0.2 – 0.4</td>
<td>RT</td>
<td>70 or 20 torr $^b$</td>
<td>27</td>
</tr>
<tr>
<td>Monolayer (ML) capacity for (CO)$_L$</td>
<td>0.5 – 0.8 molec./nm$^2$</td>
<td>0.8 – 1.3</td>
<td>RT</td>
<td>N/A $^c$</td>
<td>27</td>
</tr>
<tr>
<td>Monolayer coverage for CO</td>
<td>0.65 CO sites/nm$^2$</td>
<td>1.1</td>
<td>RT</td>
<td>60 torr</td>
<td>52</td>
</tr>
<tr>
<td>ML capacity for fully dehydroxylated sample</td>
<td>1.04 molec./nm$^2$</td>
<td>1.73</td>
<td>RT</td>
<td>N/A</td>
<td>27</td>
</tr>
<tr>
<td>$Zr^{+\delta}$ sites available for linear CO adsorption</td>
<td>$8 \cdot 10^{13}$ sites/cm$^2$</td>
<td>1.33</td>
<td>RT</td>
<td>N/A</td>
<td>55</td>
</tr>
<tr>
<td>Total CO coverage on a hydroxylated surface</td>
<td>2.7 molec./nm$^2$</td>
<td>4.5</td>
<td>$-173^\circ$C</td>
<td>260 Pa</td>
<td>58</td>
</tr>
<tr>
<td>Total CO coverage on a dehydroxylated surface</td>
<td>3.8 molec./nm$^2$</td>
<td>6.3</td>
<td>$-173^\circ$C</td>
<td>260 Pa</td>
<td>58</td>
</tr>
</tbody>
</table>

$^a$ Assuming full adsorption on the surface from fed known amount of CO. IR band in the presence of CO gas at 800 Pa is thrice as intensive as the one with 2.7$\mu$mol/m$^2$.

$^b$ Saturation pressure, 70 torr for samples activated at 397$^\circ$C and 597$^\circ$C, 20 torr for sample activated at 797$^\circ$C.

$^c$ Estimated to be 30% higher than adsorption capacity at 130 torr.

1379 cm$^{-1}$ and ca. 1365 cm$^{-1}$$^{15,19,22,23,88}$, listed with their originating vibrations as well as theoretical IR bands in Table 6. Unlike for the linearly adsorbed CO species, formate formation (see Eq. 2) is an activated process, and its rate expression is shown in Eq. 3.

$$CO + OH* \leftrightarrow COOH*$$ (2)

$$r_f = k \cdot P_{CO} \cdot [OH*]$$ (3)

Due to the activated formation process, at low temperatures (e.g. $T < 200^\circ$C) the adsorption time affects the amount of formate formed, whereas at high temperatures the system quickly reaches equilibrium, however, the equilibrium coverage is also temperature-dependent. The activated nature of the process is demonstrated with increasing intensity of the formate IR bands at different temperatures ($25 – 350^\circ$C) with adsorption times ranging from 30 min up to 18 h$^{19,42,54}$. Formate formation requires rearrangement of at least three bonds, the cleavage of the O–H bond, and the formation of the O–C and the C–H bonds$^{28}$. The theory-based estimate for the activation energy of formate formation is 154 kJ/mol$^{28}$, which is in agreement with the experimental observations, yet no experimental value for the activation energy has been reported.

Overall the temperature range of formate observations is wide, ranging from ca. 85$^\circ$C up to 550$^\circ$C$^{7,20,24,25,28,48,55}$. The formate intensity maximum is at ca. 300 – 400$^\circ$C$^{23,28}$, depending on the pretreatment and measurement conditions, with increasing intensities reported at lower temperatures$^{48}$. All in all, the formate coverage depends on the adsorption conditions (temperature, CO pressure) and the contact time with CO. With increasing temperature (240 – 400$^\circ$C) the formate coverage decreases$^{23}$ while formate intensity increases with increasing CO concentration in the gas phase$^{23}$. Silver et al. have adsorbed CO on pure ZrO$_2$ at 500$^\circ$C and they only discovered formates on the surface, no (bi)carbonates or adsorbed CO species$^{35}$.

![Fig. 11 Monodentate and bidentate formate species.](image)

![Fig. 12 Formate and linear CO spectra at (a) 25$^\circ$C, (b) 150$^\circ$C, (c) 250$^\circ$C, and (d) 350$^\circ$C in 5% CO/He. Reprinted from ref. 20 with permission. Copyright 1993, Elsevier.](image)
the monodentate case and 300 cm\(^{-1}\) into two bands at 1589 cm\(^{-1}\) following time-on-stream (CO at 250 °C) mates at high surface concentrations.

Bidentate formates is due to repulsion among the bidentate for-

formation process, and that the shift from bidentate to mono-
dentate complex. They state that based on DFT calculations
the formate is likely in a bidentate configuration as the mono-
dentate is unlikely to be stable. Our investigations indicate
a bridging bidentate formate configuration as the most stable
geometry on all the tested surfaces.

At 250°C the monodentate formate has a maximum at
1589 cm\(^{-1}\) and bidentate formate has maxima at 1568 cm\(^{-1}\),
1388 cm\(^{-1}\) and 1371 cm\(^{-1}\). The authors also suggest that
the formation of monodentate formate is intensified with in-
creasing time in contact with CO, in agreement with activated
formation process, and that the shift from bidentate to mono-
dentate formates is due to repulsion among the bidentate for-
mates at high surface concentrations as shown with increasing
time-on-stream (CO at 250°C) at 1568 cm\(^{-1}\) separating
into two bands at 1589 cm\(^{-1}\) and 1556 cm\(^{-1}\).

According to Bianchi \textit{et al.}, the formate species would be
probably a bidentate as the difference between the observed
bands at 1567 cm\(^{-1}\) (\(v_{ads}(OCO)\)) and 1367 cm\(^{-1}\) (\(v_{ads}(OC)\)) is
200 cm\(^{-1}\), and the same deduction has been used by Ma
\textit{et al.} for formate bands at 1570 cm\(^{-1}\) and 1361 cm\(^{-1}\), both
assigning the species based on the band separation. For car-
bonates, the typical difference should be \textit{ca.} 100 cm\(^{-1}\) in
the monodentate case and 300 cm\(^{-1}\) in the bidentate case.
Bianchi \textit{et al.} also state that another formate species might
cause the band at 1382 cm\(^{-1}\); however, it should also have a
dooublet band near 1570 cm\(^{-1}\), close to the one of the bidentate
formate.

Korhonen \textit{et al.} have suggested a reaction scheme where the
bidentate formate formation proceeds via an activated mono-
dentate complex. They state that based on DFT calculations
the formate is likely in a bidentate configuration as the mono-
dentate is unlikely to be stable. Our investigations indicate
a bridging bidentate formate configuration as the most stable
geometry on all the tested surfaces.

Formate forms on a surface hydroxyl species. Pozdnyakov
and Filimonov stated already in 1972 that the formate is
formed due to CO reacting with the surface hydroxyls. Ya-
maguchi \textit{et al.} in 1978 have shown formation of formate and
disappearance of terminal OH and multicoordinated OH bands
following the adsorption of deuterated acetone-\(^{18}D\), the termi-
nal OH being more reactive toward formates than the multico-
ordinated one. Amount of formate formed is dependent on
the surface hydroxyls, a decrease in formate formation shown
by Jackson and Ekerdt by removing water from CO/H\(_2\) feed
and by Bianchi \textit{et al.} by dehydroxylating the surface. He
and Ekerdt suggested that formate formation proceeds via gas-
phase CO and surface OH group.

Formate formation has been reported at low temperatures
(25°C and 160°C) on terminal OH (IR band at 3770 cm\(^{-1}\)) in
addition to the terminal OH site, formate formation on mul-
ticoordinated OH (band at 3680 cm\(^{-1}\)) has been reported at
higher temperatures (250 – 350°C), however, some experi-
mental and theoretical results do not support the par-
ticipation of the multicoordinated OH species. Jung and Bell suggested that the primary route for formate formation is via gas-phase CO and an OH group, after 9 hours at 250°C and 162 kPa CO, all terminal hydroxyl species are consumed to formate formation as well as 38% of the bridged hydroxyl species. Based on their spectral evidence, it seems that the consumption of terminal OH species is faster than that of multicoordinated OH species, yet whether all bridged hydroxyls can be consumed is unclear based on the evidence.

Jackson and Ekerdt suggested that formate formation in methanol synthesis involves an oxygen vacancy and an adjacent bridged hydroxyl site so that there is a terminal CO intermediate, the scheme is shown in Fig. 13. However, their suggestion is in contradiction with some more recent results reporting that indeed the terminal hydroxyls participate in the formate formation.

Formate decomposition has been proposed to take place by two different pathways: dehydrogenation producing CO₂ and H₂, and dehydration releasing CO and H₂O, to follow the naming of He and Ekerdt. Similar decomposition pathways have been proposed by Bianchi et al. suggesting the release of CO and restoring the OH groups, and in our investigations suggesting that the dehydration is two separate reactions: first reversible formate decomposition to CO resuming surface hydroxyls and then dehydroxylation to produce H₂O, as the dehydroxylation process is observed at a similar temperature range also without CO present in the gas phase. A lower limit estimate for the activation energy for the dehydrogenation reaction is its reaction energy at 178 – 363 kJ/mol based on theory. The typical temperature range for formate decomposition is above 300°C, a desorption maximum has been reported at 410°C. The activated formate formation (increasing uptake rate up to 300°C) and the formate decomposition pathways are demonstrated in Figure 14, where the zirconia sample is linearly heated from 100°C to 550°C in the presence of 2% CO, the y-axis corresponds to release/uptake from the sample.

Bianchi et al. have reported amounts of CO, CO₂ and H₂ that have adsorbed/desorbed during temperature-programmed desorption (TPD) after CO adsorption. Not all carbon species are recovered, suggesting that the surface is not empty of formate (ca. 10% of the CO adsorbed at 350°C unaccounted for) by the end of the desorption process with T_max at 410°C. Based on the observed CO₂/H ratio the surface species is claimed to be formate. The decomposition routes of formate have been reported to be either completely reversible decomposition resulting in restoring the terminal hydroxyls or that only about 20...40% of formate decompose forming hydrogen while the rest is decomposed reversibly. For ceria-based catalysts, the presence of co-adsorbed water on the catalyst significantly increased the decomposition rate of formate to CO₂ and H₂, presumably by associating hydrogen (analogous to water-gas shift reaction), enabling a reasonable temperature window instead of 500°C or more.

The adsorption temperature has a significant effect on the
amount of CO desorbed from the surface as CO$_2$ during TPD, yet the overall profile of the CO$_2$ desorption curve remains qualitatively similar\textsuperscript{30}. CO desorption was clearly observable only after adsorption at 200°C or 250°C. At 250°C there are formates on the surface according to IR\textsuperscript{30}, thus the CO desorption is likely due to decomposition of surface formate species and the CO$_2$ originates from formates or, especially after low-temperature adsorption of CO, (bi)carbonate species. The temperature of maximum desorption was in the range of 330°C for CO$_2$ and 330 – 430°C for CO desorbing after CO adsorption.

Köck \textit{et al.} have adsorbed CO on ZrO$_2$ from room temperature up until 600°C, yet their pretreatment (annealing at 900°C and thereafter oxidation at 600°C) of the sample has quenched most of the surface hydroxyls, leaving formate formation negligible and thus supporting the formate formation mechanism based on surface hydroxyl species\textsuperscript{62}.

If CO adsorption at 85 – 250°C is followed by cooling down to 25°C, the intensity of the linear CO band at 2190 cm$^{-1}$ is smaller (by 12% with $T_{ads}$ at 85°C, 35% at 152°C) with increasing preadsorption temperature compared to room temperature preadsorption\textsuperscript{20,55}. This is assigned to the formation of formate species at cationic Zr sites\textsuperscript{32} which are thought to be the sites where CO adsorbs linearly\textsuperscript{6,18,27,29}. When combined with our observations that formate formation at 100°C in the presence of CO in the gas phase is accompanied by decreasing linear CO intensity (see Figure 15)\textsuperscript{28}, it is suggested that site competition takes place and that linear CO facilitates formate formation compared to gas-phase CO. Assuming a bidentate formate species formed on a terminal OH and bound to a Zr cation (see Fig. 11), the cation site necessary for linear CO adsorption is blocked by the formate.

Measured adsorbed or desorbed CO amounts reported in literature are collected in Table 7. Increasing adsorbed/desorbed amounts of CO are reported with increasing adsorption temperature up to 350°C\textsuperscript{20,30}. Both Bianchi \textit{et al.}\textsuperscript{20} andPokrovski \textit{et al.}\textsuperscript{30} have applied a similar TPD method, where adsorption is carried out at elevated temperature ($T_{ads}$ in the table) followed by cooling to room temperature, and thereafter temperature-programmed heating begins. The desorbed amount of CO$_2$ reported by Bianchi \textit{et al.}\textsuperscript{20} (0.12 $\mu$mol/m$^2$) is significantly lower than those reported by Pokrovski \textit{et al.}\textsuperscript{30} (0.35/1.34 $\mu$mol/m$^2$) after adsorption at 250°C, while the specific surface areas are ca. 200 m$^2$/g and 19/110 m$^2$/g, respectively. The values reported in our recent work\textsuperscript{28} seem to be larger than those by others; this might be explained with a different experimental procedure, where weakly bound CO is not removed from the surface prior to temperature-programming.

As mentioned previously, the terminal OH group is the active species concerning formate or bicarbonate formation on the zirconia surface after gas-phase adsorption of CO at elevated temperature (240 – 400°C)\textsuperscript{23}. The activity of the terminal OH group has been further investigated using isotope-labeled experiments with D$_2$O and D$_2$. When deuteronated formates were formed via CO adsorption to OD (deuteroxyl) species, they could be transformed back to HCOO with contact to hydrogen at 200°C\textsuperscript{19}. H/D isotope exchange of the surface formates with gas-phase D$_2$ seems to be possible, yet slow and competing with formate decomposition already around 300°C\textsuperscript{26}. Only 2 – 3% of the surface formate species are exchanged to DCOO species at 150°C in 488 kPa D$_2$\textsuperscript{42}. The necessity of gas-phase D$_2$ for formate scrambling was demonstrated as the H/D exchange did not proceed between formates and surface deuteroxyls\textsuperscript{26}. However, as formates can form on surface deuteroxyls achieved by surface treatment with D$_2$O\textsuperscript{19}, it is implied that once formed, formates are stable and do not scramble with each other via cleavage of the O$_{support}$–C bond.

### 4.3 Other species formed during interaction with CO

In addition to linear CO and formates also other species have been observed during CO adsorption. These species reveal the diversity of the interaction between CO and monoclinic zirconia although the number of reported observations remains low. The observed species include bidentate carbonates\textsuperscript{48}, probably also carboxylylate species as the band at 1416 cm$^{-1}$ and its symmetric counterpart at 1560 cm$^{-1}$ have been confirmed via difference spectra\textsuperscript{20}. Monodentate carbonate (1469 cm$^{-1}$) and ion carbonate bands (1303 cm$^{-1}$ and 1442 cm$^{-1}$) were observed after CO adsorption at 350°C\textsuperscript{7}. Similarly, ionic carbonate and carboxylylate species have been suggested, their bands disappear when CO is removed from the gas phase at 400°C while the formate species remain intact\textsuperscript{54}. When comparing CO adsorption at 350°C on hydroxylated and dehydroxylated samples, the latter shows less intense formate bands but more intense bands at 1440 cm$^{-1}$ and 1416 cm$^{-1}$ as well as new bands at 1540 cm$^{-1}$ and 1317 cm$^{-1}$, suggesting carbonates present on the surface and perhaps also carboxylylate species\textsuperscript{20}. Also bidentate carbonates have been reported from high-temperature adsorption (above 250°C) of CO\textsuperscript{48}. Ma \textit{et al.} have suggested that bicarbonate and carbonate species could be formed on ZrO$_2$ from CO via carboxylylate surface species\textsuperscript{7}. He and Ekerdt have suggested that CO is adsorbed on the metal oxide oxygen forming a [COO] intermediate and then reacting further to carbonate or formate\textsuperscript{21}. All these species require the participation of one or two surface oxygen atoms.

CO adsorption followed by carbonate formation and CO$_2$ desorption leads to surface reduction as oxygen is removed from the surface. During temperature-programmed surface reaction (TPSR) in CO, CO$_2$ amounts detected correspond to 10 – 14% of surface oxygen atoms depending on pretreat-
Fig. 15 Decreasing linearly adsorbed CO intensity (at 2192 – 2185 cm\(^{-1}\)) and increasing formate intensity (at 1569 cm\(^{-1}\), 1538 cm\(^{-1}\), 2975 – 2965 cm\(^{-1}\) and 2884 cm\(^{-1}\)) with time in contact with CO at 100°C. Reproduced from ref. 28 with permission from the PCCP Owner Societies.

iment of the zirconia\(^{28}\). Pulse oxidation experiments show that estimating the monolayer coverage based on assuming a ZrO\(_2\)(100) surface, 13.6% of the surface oxygen atoms can be removed by CH\(_4\) at 900°C.\(^{92}\)

During static adsorption of CO at 200°C and above, CO\(_2\) formation was observed in the IR spectra, originating either from formate decomposition or from CO oxidation via lattice oxygen species.\(^{62}\) Ionic carbonate was observed during CO adsorption at 150°C and above on rehydrated zirconia, and it was released as CO\(_2\) instead of CO\(_2\).\(^{20}\)

Silver et al. reported a small bicarbonate desorption peak during temperature-programmed heating in CO (25 – 620°C), however, no gas-phase CO\(_2\) or IR bands of carbonates or bicarbonates were observed during CO exposure at 500°C.\(^{45}\) These observations suggest that formation of bicarbonates takes place below 500°C, as expected based on the knowledge of bicarbonate species (for more information, see\(^{28}\) and references therein).

5 Future perspectives

As both monoclinic zirconia and its interaction with CO have been investigated for more than 40 years, in some regions knowledge is still lacking. The surface configuration is one of the remaining questions, as the most stable surfaces according to density functional theory are different from those assumed based on HRTEM, yet the amount of independent experimental observations on clearly monoclinic samples remain few. The stability of the surface structure in the reaction conditions and during the reaction should be investigated carefully. Also the IR designation of terminal and multicoordinated hydroxyls (or any of the other interpretations) remains without irrefutable evidence, even though the multi-oxide studies by Tsyganenko and Filimonov\(^{3,71}\) were very thorough in providing comparable information of several oxides with presumably different OH groups due to their crystal structure. Especially in the light of theoretical calculations suggesting mostly terminal and bridged hydroxyl species, further confirmation of the assignment would provide more clarity. The Zr cations (Zr\(^{3+}\), Zr\(^{4+}\)) have also caused some confusion: the basis for the IR assignment is unclear, yet the trivalent species have
could elucidate the interaction. Advanced methods similar to promoters and dopants without changing its crystalline phase also tailoring the properties of monoclinic zirconia by using e.g. ther information on surface vacancies and also surface defects, Zr−Adsorbed CO (gravimetric) 3

Desorbed CO

Desorbed CO

Desorbed CO

Desorbed CO

Desorbed CO

Desorbed CO

Desorbed CO

µ

Adsorbed CO (MS) 37 µmol/g

Desorbed CO2 (MS) 6.5 µmol/g

Desorbed CO2 (MS) 23 µmol/g

Desorbed CO2 (MS) 33.6 µmol/g

Desorbed CO2 (MS) 0.09 µmol/m2 (SA=19 m2/g)

Desorbed CO2 (MS) 0.17 µmol/m2 (SA=19 m2/g)

Desorbed CO2 (MS) 0.22 µmol/m2 (SA=19 m2/g)

Desorbed CO2 (MS) 0.35 µmol/m2 (SA=19 m2/g)

Desorbed CO2 (MS) 0.51 µmol/m2 (SA=110 m2/g)

Desorbed CO2 (MS) 0.46 µmol/m2 (SA=110 m2/g)

Desorbed CO2 (MS) 0.59 µmol/m2 (SA=110 m2/g)

Desorbed CO2 (MS) 1.34 µmol/m2 (SA=110 m2/g)

Adsorbed CO (gravimetric) 3

Net desorbed CO2 at 100 – 550°C (MS) 240 – 530 µmol/mol/g

a Depending on sample preparation temperature (600 – 900°C).

b Depending on pretreatment (hydration, reduction, reduction and hydration). CO contact first 90 min at 100°C, then continuing during heating up to 550°C.

been successfully probed with N2O6. The EPR assignment of Zr3+ species has also been under discussion.8,46,47,51,57 Further information on surface vacancies and also surface defects, e.g. at the surface boundaries could give a more thorough look at the surface interaction with hydroxyl and CO species. Also tailoring the properties of monoclinic zirconia by using promoters and dopants without changing its crystalline phase could elucidate the interaction. Advanced methods similar to Raman in the case of ceria might also provide surprisingly rich information.

With the adsorbed CO species the knowledge on especially the formate species deserves more investigation. The surface configuration of the species (monodentate, chelating or bridging bidentate) is unclear based on experimental observations, although bidentate species has been speculated and theoretical calculations suggest both chelating and bridging bidentate species. Also the enthalpy of formation for formate species has only been estimated theoretically, an experimental confirmation for it, e.g. with microcalorimetry, would be welcome. Some clarity on the kinetics of formate formation on terminal and multicoordinated hydroxyls or even the extent of the reaction on both types of hydroxyls could provide new insights related to catalysis. Operando-style experiments with combined surface and gas-phase quantification would provide valuable input on all of the surface species with CO and hydroxyls. Observing the surface species in the same setup under vacuum might enlighten the mechanism of surface reduction via oxygen removal and why evacuation is a more efficient reduction method than hydrogen treatment.

To improve the modeling of carbon oxides, a better understanding of an active surface site is highly important to be able to set up more accurate computational surface models to better describe the complexity of the ZrO2 support/catalyst. This would not only impact on calculation of adsorption energies but would also influence on calculated frequencies. As long as the nature of an active site is not known exactly, a systematic approach, where, e.g. different surface models are investigated side by side, is a natural choice to obtain information of adsorption characteristics. To discover the active surface sites and to further improve the selectivity of catalysts, nanoshaped supports and catalysts with their surface regularity have proven an interesting alternative. The better the control over the surface sites, the better the catalyst selectivity. However, the control is only to be reached through monocrystalline nanoshapes as in polycrystalline shapes the surfaces are not controlled.

Growing monoclinic zirconia in the shape of nanofibres and nanorods has become gained some attention during the last 15 years, yet most of the shapes are polycrystalline. The preparation methods differ from traditional wet chemistry to prepare monoclinic zirconia powders. Nanorods have been prepared hydrothermally in an autoclave, resulting in nanorods of various sizes, the diameter in general some tens of nanometers and the length a few hundred nanometers, and the length—
Exposed faces of the nanoshapes should be characterized with advanced electron microscopy techniques (e.g. aberration-corrected TEM as in \(^94\)) to determine the orientation of the exposed surfaces. Boucher \(^95\) et al. have tested different shapes of metal oxides with gold catalysts for steam reforming of methanol and water-gas shift, and they conclude that the different shapes show somewhat different activities. Li and Shen \(^96\) discuss widely the oxide shape effects in nanocatalysis, and they mention some of the unknown issues with metal deposition on oxide nanoshapes: whether the metal atoms are located on a single type of surface only. They also bring up that the nanoshapes might not be stable under the reaction conditions, this might also affect the metal–support interface, often considered to be the active site \(^96\).

### 6 Conclusions

Monoclinic zirconia surface has three kinds of coordinatively unsaturated cationic sites, two types of Zr\(^{4+}\) and one type of Zr\(^{3+}\), coordinately unsaturated Zr\(^{4+}\)-O\(^2-\) pairs, oxygen vacancies, terminal hydroxyls, and two types of multicoordinated hydroxyl species. The ratios of these sites can be modified with pretreatments by removing or adding oxygen and hydrogen to the surface through applying heat, vacuum or reactive atmospheres. The cationic sites are responsible for the linearly adsorbed CO species while formates are suggested to form preferably on a site where an unshielded zirconium ion is paired with a terminal hydroxyl species, assuming a bidentate formate. This would provide an explanation for the submonolayer quantities of formate on zirconia. The concentrations of active sites for linear CO and formate formation are of similar magnitude, corresponding to ca. 5% of a monolayer or less, whereas the amount of hydroxyl species on the surface is roughly tenfold. The formates as well as hydroxyl species prefer the defect type of Zr\(^{4+}\) sites. The specific roles for Zr\(^{3+}\) and the terrace-type Zr\(^{4+}\) remain unclear. Other open questions include confirming the nature of the multicoordinated hydroxyls, the surface configuration of the formate species, and the energetics of formate formation. Nanoshapes might be a valuable tool in exploring the surface aspects related to formates and hydroxyls.

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**References**
