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# Identification of C<sub>2</sub>–C<sub>5</sub> products from CO<sub>2</sub> hydrogenation over PdZn/TiO<sub>2</sub>–ZSM-5 hybrid catalysts†

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The combination of a methanol synthesis catalyst and a solid acid catalyst opens the possibility to obtain olefins or paraffins directly from CO<sub>2</sub> and H<sub>2</sub> in one step. In this work several PdZn/TiO<sub>2</sub>–ZSM-5 hybrid catalysts were employed under CO<sub>2</sub> hydrogenation conditions (240–360 °C, 20 bar, CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> = 1 : 1 : 3) for the synthesis of CH<sub>3</sub>OH, consecutive dehydration to dimethyl ether and further oxygenate conversion to hydrocarbons. No significant changes after 36 h reaction on the methanol synthesis catalyst (PdZn/TiO<sub>2</sub>) were observed by XRD, XAS or XPS. No olefins were observed, indicating that light olefins undergo further hydrogenation under the reaction conditions, yielding the corresponding alkanes. Increasing the aluminium sites in the zeolites (Si : Al ratio 80 : 1, 50 : 1 and 23 : 1) led to a higher concentration of mild Brønsted acid sites, promoting hydrocarbon chain growth.

## Introduction

The sustainable production of energy is one of the major challenges of modern society.<sup>1,2</sup> Several technologies have been developed to harvest renewable energy (e.g., solar panels, wind farms) in the form of electricity.<sup>2</sup> However, due to the intermittent nature of renewables, surplus produced electricity must be stored as chemical bonds to ensure a steady production of energy when electricity

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† Electronic supplementary information (ESI) available: XRD, pore size and surface area for commercial ZSM-5 after activation (550 °C, 6 h). CO<sub>2</sub> reaction metrics. CO<sub>2</sub> hydrogenation activity over PdZn/TiO<sub>2</sub> at different temperatures, CO<sub>2</sub> hydrogenation over ZSM-5 (23 : 1). Productivities and hydrocarbon selectivity based on MTH/DMTH over PdZn/TiO<sub>2</sub>–ZSM-5 hybrid catalysts. EXAFS fitting parameters. XRD and XPS post reaction PdZn/TiO<sub>2</sub> characterisation. Coke determination by TG-MS. See DOI: 10.1039/d0fd00135j



production is low.<sup>3</sup> The production of H<sub>2</sub> *via* water splitting is a route with a high renewable electricity storage capacity,<sup>4</sup> and is a possible energy vector for future technology.<sup>5,6</sup> However, energy decarbonisation is likely to occur in a subtle way.<sup>7</sup> Therefore, it is important to develop transitory routes that allow the use of current technology, but approach CO<sub>2</sub> neutrality.<sup>8</sup> This can be achieved by storing H<sub>2</sub> produced *via* water electrolysis through renewable electricity in the form of hydrocarbons, by its reaction with CO<sub>2</sub>.<sup>9–11</sup>

The production of CH<sub>3</sub>OH from syngas (CO/CO<sub>2</sub>/H<sub>2</sub>) over a CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is a mature process (250–300 °C, 50–100 bar), with an annual CH<sub>3</sub>OH production of 57 Mt,<sup>10</sup> and increasing. Hence, renewable H<sub>2</sub> could be easily incorporated in the CH<sub>3</sub>OH production cycle, however for the process to be CO<sub>2</sub> neutral, CH<sub>3</sub>OH must be obtained from recycled CO<sub>2</sub> and sustainably produced H<sub>2</sub>. Thermodynamically, CH<sub>3</sub>OH formation from CO<sub>2</sub> and H<sub>2</sub> is favoured at high pressure and low temperature. Nevertheless, a high temperature (>200 °C) is needed to activate CO<sub>2</sub>, which in turn results in the deactivation of Cu-based catalysts due to Cu sintering<sup>9–13</sup> and coke deposition.<sup>14</sup> Pd-based catalysts are employed in CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH as a stable alternative to Cu-based catalysts.<sup>15–19</sup>

Research on Pd/ZnO catalysts confirmed the  $\beta$ -PdZn alloy as the active phase for CH<sub>3</sub>OH synthesis.<sup>20–23</sup> Commercially sourced ZnO usually has a low surface area which results in large PdZn particles, and hence, to improve PdZn dispersion, supports with a higher surface area (*e.g.*, CeO<sub>2</sub>,<sup>18</sup> carbon nanofibers,<sup>22</sup> carbon nanotubes,<sup>24</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>25</sup> or TiO<sub>2</sub> (ref. 25 and 26)) are commonly used. The higher stability of PdZn alloy catalysts allows for higher reaction temperatures, however, then CH<sub>3</sub>OH productivity is limited by the thermodynamic equilibrium whilst CO formation is favoured through the reverse water gas shift (RWGS) reaction. To increase oxygenate productivity above the limited CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH dictated by the equilibrium, CH<sub>3</sub>OH can be simultaneously dehydrated to dimethyl ether (DME) by physically mixing a methanol synthesis catalyst with a solid acid catalyst.<sup>27–30</sup> ZSM-5 zeolites are commonly employed as solid acid catalysts to dehydrate CH<sub>3</sub>OH to DME due to their high resistance to water, high stability and the presence of Lewis and Brønsted acid sites.<sup>31</sup> The conversion of methanol or dimethyl ether to hydrocarbons (MTH or DMTH respectively) is a mature process that also employs ZSM-5 zeolites as catalysts (300–500 °C, 1 bar).<sup>32–34</sup> More importantly, it has been reported that using H<sub>2</sub> or H<sub>2</sub>O in the feed for the MTH process decreased the deactivation of several zeolites (HSAPO, HSSZ, HFER, HBEA, ZSM-5) by limiting coke deposition within structural pores, without significantly affecting the hydrocarbon chain distribution or the olefin-to-paraffin selectivity.<sup>35–37</sup> Water is produced as a by-product in CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH, moreover H<sub>2</sub> is present in the feed. Hence, the synthesis of hydrocarbons from CO<sub>2</sub> over a methanol synthesis catalyst combined with an acid catalyst with reduced coke deposition is achievable. Bonura *et al.*<sup>29</sup> studied different reactor bed configurations for the direct synthesis of DME from CO<sub>2</sub> by combining a methanol synthesis catalyst and a solid acid catalyst, and found that a physical mixture (also known as a hybrid catalyst) of Cu–ZnO–ZrO<sub>2</sub> and H-ZSM-5 gave the highest oxygenate (CH<sub>3</sub>OH + DME) productivity. Higher oxygenate productivity was also observed for a Pd/ZnO–ZSM-5 hybrid catalyst compared to a PdZn on ZSM-5 catalyst.<sup>38</sup> Ihm *et al.*<sup>39</sup> reported the direct synthesis of hydrocarbons from CO<sub>2</sub> + H<sub>2</sub> on CuO/ZnO/ZrO<sub>2</sub>–ZSM-5 (Si/Al = 22) hybrid catalysts. At 400 °C and 30



bar the selectivity towards CO, oxygenates and hydrocarbons observed was 93.4, 1.8 and 4.8% respectively. C<sub>5+</sub> products were detected, although C<sub>1</sub> and C<sub>2</sub> products accounted for 95.4% of the hydrocarbon product distribution. Over a ZnZrO<sub>2</sub>/SAPO catalyst at 380 °C and 20 bar (~18% CO<sub>2</sub> conversion), the CO selectivity was reduced to 47%, whilst C<sub>2</sub>–C<sub>4</sub> olefins accounted for 80% of the total hydrocarbon distribution, and the remaining hydrocarbons were assigned to C<sub>2</sub>–C<sub>4</sub> alkanes (14%), C<sub>1</sub> (3%) and C<sub>5+</sub> (3%).<sup>40</sup> Light olefins synthesised on hybrid catalysts from CO<sub>2</sub> can also undergo further reduction to their corresponding alkanes on the methanol synthesis catalyst, which effectively acts as a hydrogenation catalyst. Park *et al.*<sup>41</sup> reported ethane (76.4%) as the main hydrocarbon product over a CuZnOZrO<sub>2</sub>–ZSM-5 catalyst (28 bar, 400 °C), with little formation of C<sub>3</sub> (4.5%), C<sub>4</sub> (0.8%) and C<sub>5+</sub> (0.2%) products. However, as reported by Giordano, Frusteri and co-workers<sup>42,43</sup> for CO<sub>2</sub> conversion to DME over CuZnZr/ferrierite hybrid catalysts, Cu remains prone to severe sintering under the reaction conditions (260 °C, 30 bar). This makes catalyst stability the bottle neck of this process.

To the best of our knowledge, reports on PdZn hybrid catalysts for CO<sub>2</sub> hydrogenation focus on DME,<sup>27,38</sup> but no detailed attention has been paid to the produced hydrocarbons. We therefore assessed the activity and stability of diverse PdZn/TiO<sub>2</sub>–ZSM-5 hybrid catalysts under CO<sub>2</sub> hydrogenation conditions (20 bar, <360 °C) and identified produced hydrocarbons derived from MTH and DMTH.

## Experimental section

### Materials

All ZSM-5 zeolites used in this work were purchased from Alfa Aesar (NH<sub>4</sub><sup>+</sup>-form of ZSM-5, Si/Al = 23, 50 and 80); Pd acetylacetonate (Pd(acac)<sub>2</sub>, 99%) and Zn acetylacetonate (Zn(acac)<sub>2</sub>, 99%) were supplied by Sigma-Aldrich; titanium oxide (TiO<sub>2</sub>-P25) was ordered from Aeroxide.

### PdZn/TiO<sub>2</sub> catalyst synthesis

The synthesis of PdZn/TiO<sub>2</sub> by chemical vapour impregnation (CVI) was reported previously.<sup>25–27</sup> For the synthesis of 3 g of PdZn/TiO<sub>2</sub> catalyst with a 5 wt% Pd loading and a 1 : 5 palladium to zinc molar ratio, Pd(acac)<sub>2</sub> (0.43 g, 1.40 mmol), Zn(acac)<sub>2</sub> (2.06 g, 6.93 mmol) and TiO<sub>2</sub> (2.39 g) were physically mixed in a glass vial until homogeneous. The mixture was then transferred into a Schlenk flask, evacuated (10<sup>−3</sup> bar) and heated (145 °C, 1 h). The as prepared materials were recovered and annealed in static air (10 °C min<sup>−1</sup>, 500 °C, 16 h). PdZn/TiO<sub>2</sub> characterisation was performed on a portion of catalyst reduced in flowing 5% H<sub>2</sub>/Ar (400 °C, 5 °C min<sup>−1</sup>, 1 h).

### PdZn/TiO<sub>2</sub>–ZSM-5 hybrid catalyst preparation

The as received (NH<sub>4</sub>)–ZSM-5 zeolites were annealed in static air (550 °C, 10 °C min<sup>−1</sup>, 6 h) to obtain the H-ZSM-5 form prior to reaction. 0.5 g of PdZn/TiO<sub>2</sub> and 0.5 g of treated ZSM-5 were physically mixed in a vial until homogeneous. The mixture was pelleted (10 ton) and crushed (425–600 μm) to obtain the hybrid catalyst. Zeolites are named in the text according to their Si/Al ratio, for instance ZSM-5 with a Si/Al ratio of 23 : 1 will be referred to as ZSM-5(23).



## CO<sub>2</sub> hydrogenation and consecutive MTH/DMTH catalyst testing

Catalytic activity for CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH, DME, olefins and hydrocarbons was achieved in a stainless steel fixed-bed (50 cm length, 0.5 cm internal diameter) continuous flow reactor. 0.5 g of hybrid catalyst without diluent (or 0.25 g of pelleted PdZn/TiO<sub>2</sub> with 0.25 g of SiC as diluent) were secured in the reactor tube using quartz wool. Prior to reaction, the hybrid catalysts were pre-reduced in 5% H<sub>2</sub>/He (400 °C, 5 °C min<sup>-1</sup>, 1 h). Subsequently, the reactor was cooled down to 50 °C, the 5% H<sub>2</sub>/He flow was switched to the reaction mixture (CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> = 1 : 1 : 3, 30 ml min<sup>-1</sup>), and the reactor was pressurised to 20 bar and heated to the desired reaction temperature (240, 270, 300, 320, 340 and 360 °C, 5 °C min<sup>-1</sup>, 6 h dwell). To avoid product condensation, post reactor lines and valves were heated to 130 °C. Products were analysed *via* online gas chromatography (Agilent 7890, fitted with FID and TCD detectors). Details of how CO<sub>2</sub> conversion, product selectivity and productivities were calculated can be found in the ESI (eqn (S1–S11†)).

## Catalyst characterisation

X-ray absorption spectroscopy (XAS) was carried out in transmission mode at the Pd K-edge, at the B18 beamline of the Diamond Light Source, Harwell, UK, and a Pd foil was examined simultaneously with the sample and used as a reference. Three spectra were averaged to minimise the noise signal. The X-ray absorption fine structure (EXAFS) was analysed with the Demeter software package (Athena and Artemis).<sup>44</sup> X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra-DLD fitted with a monochromatic Al K $\alpha$  (75–150 W) source and analyser, using a pass energy of 40 eV. The XPS data were analysed using Casa XPS software. Powder X-ray diffraction (XRD) patterns were obtained on a ( $\theta$ – $\theta$ ) PANalytical X'pert Pro powder diffractometer fitted with a hemispherical analyser using a Cu K $\alpha$  radiation source (40 keV, 40 mA). The pore sizes and BET surface areas of the ZSM-5 zeolites were obtained through N<sub>2</sub> adsorption isotherms using a 3-flex Micromeritics instrument. Samples were degassed *in situ* at 250 °C for 10 h prior to analysis. Coke deposition during CO<sub>2</sub> hydrogenation was measured through thermogravimetric analysis on a PerkinElmer TL9000 with a TG-IR-MS interface.

## Results and discussion

### PdZn/TiO<sub>2</sub>–ZSM-5 hybrid catalysts for direct CO<sub>2</sub> conversion to hydrocarbons

In addition to PdZn/TiO<sub>2</sub> employed as a CH<sub>3</sub>OH synthesis catalyst,<sup>20–23</sup> commercial ZSM-5 zeolites with various Si/Al ratios (23, 50 and 80) were used as solid acid catalysts to promote consecutive CH<sub>3</sub>OH dehydration to DME<sup>27–30</sup> and further MTH/DMTH.<sup>32–34</sup> XRD patterns, pore sizes and BET surface areas for the commercial ZSM-5 zeolites after annealing (static air, 550 °C, 10 °C min<sup>-1</sup>, 6 h) can be found in the ESI (Fig. S1 and Table S1,† respectively). Thorough characterisation of PdZn/TiO<sub>2</sub> synthesised by chemical vapour impregnation (CVI) with 5 wt% Pd and a Pd/Zn molar ratio of 1 : 5 was previously reported.<sup>25–27</sup>

Firstly, the catalytic activity of PdZn/TiO<sub>2</sub> (0.25 g catalyst diluted with 0.25 g of SiC) for CO<sub>2</sub> hydrogenation was assessed (20 bar, CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> = 1 : 1 : 3, 240–360 °C). As observed in Table S2,† raising the reaction temperature from 240 to



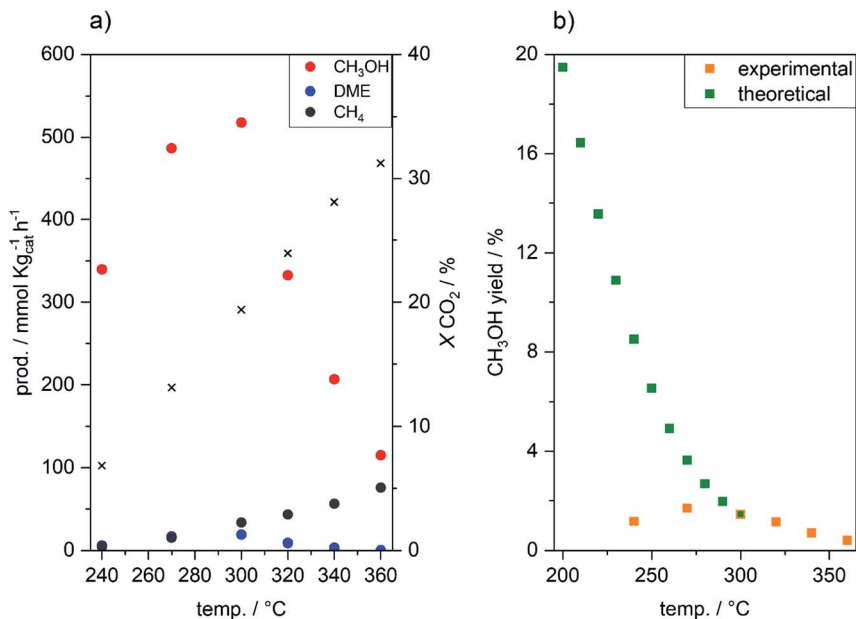


Fig. 1 (a)  $\text{CH}_3\text{OH}$ , DME and  $\text{CH}_4$  productivities and  $\text{CO}_2$  conversion for  $\text{CO}_2$  hydrogenation (20 bar,  $30 \text{ ml min}^{-1}$ ,  $\text{CO}_2/\text{H}_2/\text{N}_2 = 1 : 3 : 1$ , 240–360  $^{\circ}\text{C}$ , 6 h dwell) over  $\text{PdZn}/\text{TiO}_2$ . (b) Theoretical  $\text{CH}_3\text{OH}$  yield obtained from Shen *et al.*<sup>45</sup> compared to experimental  $\text{CH}_3\text{OH}$  yield with temperature over  $\text{PdZn}/\text{TiO}_2$ .

360  $^{\circ}\text{C}$  resulted in an increase in the  $\text{CO}_2$  conversion from 6.8 to 31.2%, accompanied by an increase in the CO selectivity (from 74.6 to 97.9%) at the expense of  $\text{CH}_3\text{OH}$  selectivity (from 24.3 to 1.3%), in accordance with the reaction thermodynamics.<sup>45</sup> Below 300  $^{\circ}\text{C}$ ,  $\text{CH}_3\text{OH}$  synthesis proceeded in the kinetic regime (Fig. 1a), as shown by the increase in the  $\text{CH}_3\text{OH}$  productivity with temperature up to 518  $\text{mmol kg}_{\text{cat}}^{-1} \text{h}^{-1}$ . At 300  $^{\circ}\text{C}$ , the  $\text{CH}_3\text{OH}$  yield reached equilibrium (1.45%  $\text{CH}_3\text{OH}$  yield),<sup>45</sup> and hence, above 300  $^{\circ}\text{C}$   $\text{CH}_3\text{OH}$  synthesis is controlled by the thermodynamic equilibrium (Fig. 1b), as shown by the sharp decrease in  $\text{CH}_3\text{OH}$  productivity. Low selectivity toward  $\text{CH}_4$  (<0.8%) and DME (<1.0%), produced by  $\text{CH}_3\text{OH}$  decomposition on  $\text{TiO}_2$  (ref. 46 and 47) and  $\text{CH}_3\text{OH}$  dehydration,<sup>27</sup> respectively, was observed. Nevertheless, in the absence of ZSM-5 solid acid catalysts, no other hydrocarbons were detected.

Comparable  $\text{CO}_2$  conversion and CO productivity to  $\text{PdZn}/\text{TiO}_2$  were observed for all  $\text{PdZn}/\text{TiO}_2$ -ZSM-5 hybrid catalysts (Fig. 2), indicating that the activity of the methanol synthesis catalyst is not altered by the proximity of solid acid zeolites, and that ZSM-5 zeolites are not active towards the RWGS. To ensure that ZSM-5 zeolites do not act as RWGS or as  $\text{CH}_3\text{OH}$  synthesis catalysts, blank ZSM-5(23) was employed for the  $\text{CO}_2$  hydrogenation reaction (Table S3†), and negligible  $\text{CO}_2$  conversion was observed at 270  $^{\circ}\text{C}$ . The efficient dehydration of  $\text{CH}_3\text{OH}$  to DME occurred over all  $\text{PdZn}/\text{TiO}_2$ -ZSM-5 hybrid catalysts. The highest oxygenate productivity ( $\text{CH}_3\text{OH} + \text{DME}$ ) was obtained at 270  $^{\circ}\text{C}$ . At this temperature almost no methanol to olefins (MTH) or dimethyl ether to olefins (DMTH) conversion takes place, with only small traces of ethane detected over hybrid catalysts with



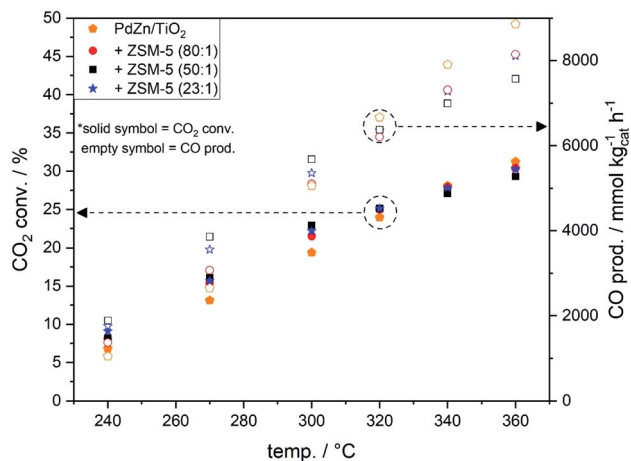


Fig. 2  $\text{CO}_2$  conversion and CO productivity over  $\text{PdZn/TiO}_2$  and  $\text{PdZn/TiO}_2$ -ZSM-5 hybrid catalysts during  $\text{CO}_2$  hydrogenation (20 bar,  $30 \text{ ml min}^{-1}$ ,  $\text{CO}_2/\text{H}_2/\text{N}_2 = 1 : 3 : 1$ , 240–360 °C, 6 h dwell).

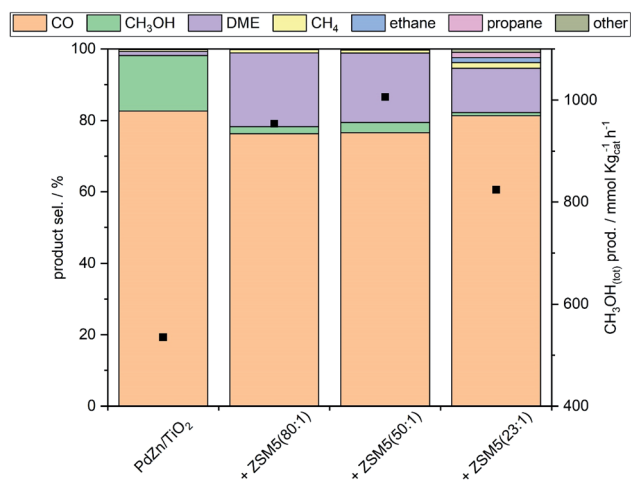


Fig. 3 CO, oxygenate and hydrocarbon selectivity and total  $\text{CH}_3\text{OH}$  productivity for  $\text{CO}_2$  hydrogenation (20 bar, 270 °C,  $\text{CO}_2/\text{H}_2/\text{N}_2 = 1 : 3 : 1$ ) over  $\text{PdZn/TiO}_2$  and  $\text{PdZn/TiO}_2$ -ZSM-5 hybrid catalysts.

ZSM-5(50 and 80), and small amounts of higher hydrocarbons observed for  $\text{PdZn/TiO}_2$ -ZSM-5(23). DME is the major oxygenate product with a selectivity close to 20%. Moreover, the total methanol productivity ( $\text{CH}_3\text{OH}_{(\text{tot})}$ ), considering that all hydrocarbons originate from  $\text{CH}_3\text{OH}$  by either dehydration to DME or through the MTH/DMTH process, was higher for all hybrid catalysts compared to  $\text{PdZn/TiO}_2$  (Fig. 3).

The hydrocarbon productivities and  $\text{CH}_3\text{OH}_{(\text{tot})}$  over  $\text{PdZn/TiO}_2$ -ZSM-5 hybrid catalysts can be found in Table S4.† At 300 °C, the hybrid catalysts showed higher

$\text{CH}_3\text{OH}_{(\text{tot})}$  compared to  $\text{PdZn}/\text{TiO}_2$ , thus overcoming the theoretical  $\text{CH}_3\text{OH}$  yield dictated by the equilibrium. Increasing the alumina ratio in the zeolite promoted the formation of longer hydrocarbons. The presence of aluminium sites is related to Brønsted acid sites with mild acidity, and hence, a higher concentration of Brønsted acid sites promotes chain growth *via* the hydrocarbon pool mechanism.<sup>33,48</sup> Light olefins produced as intermediates in MTH<sup>49</sup> undergo further hydrogenation over  $\text{PdZn}/\text{TiO}_2$ , yielding the corresponding alkanes (ethane and propane); a mixture of *n*-butane and 2-butene was observed, whilst only olefins were detected in the  $\text{C}_5$  fraction (1-pentene and 2-*cis/trans*-pentene). Thus, when  $\text{PdZn}$  alloys are used for the synthesis of hydrocarbons from  $\text{CO}_2$  *via* a methanol mediated route over hybrid catalysts, they behave as methanol synthesis catalysts but also as olefin hydrogenation catalysts, limiting hydrocarbon chain growth as also reported for Cu-based catalysts.<sup>49–51</sup>  $\text{CH}_3\text{OH}_{(\text{tot})}$  over hybrid catalysts is higher compared to  $\text{PdZn}/\text{TiO}_2$  at any temperature, with total  $\text{CH}_3\text{OH}$  productivity surpassing the equilibrium yield above 300 °C. The highest total  $\text{CH}_3\text{OH}$  productivity for hybrid catalysts was observed in the 270–300 °C range; hybrid catalysts with ZSM-5(80 and 50) gave the highest oxygenate productivity ( $\text{CH}_3\text{OH}$  and DME), while ZSM-5(23) led to higher hydrocarbon productivity (Fig. 4) *via* faster MTH/DMTH. Although the total  $\text{CH}_3\text{OH}$  productivity was higher than the equilibrium yield, above 300 °C, the hydrocarbon productivity is limited by  $\text{CH}_3\text{OH}$  availability which leads to a decrease in the total  $\text{CH}_3\text{OH}$  productivity at higher temperatures. The hydrocarbon selectivity based on MTH/DMTH showed that increasing the aluminium concentration in ZSM-5 in the hybrid catalyst resulted in improved selectivity towards higher hydrocarbons (Table S5†). In the 320–340 °C temperature range ethane and propane accounted for 50% of MTH/DMTH product selectivity for all hybrid catalysts. Note that the real  $\text{CH}_4$

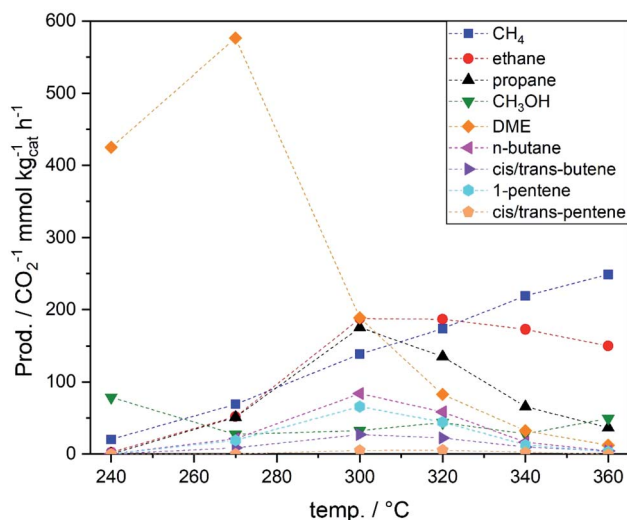


Fig. 4 Productivities based on carbon (e.g., two molecules of  $\text{CO}_2$  converted per ethane molecule and three molecules of  $\text{CO}_2$  converted per propane molecule) during  $\text{CO}_2$  hydrogenation (20 bar, 30 ml min<sup>-1</sup>,  $\text{CO}_2/\text{H}_2/\text{N}_2 = 1 : 3 : 1$ ) over the  $\text{PdZn}/\text{TiO}_2$ -ZSM-5(23) hybrid catalyst.





selectivity *via* the MTH and DMTH process is lower than the reported values, since  $\text{CH}_4$  is also produced as a by-product in  $\text{CH}_3\text{OH}$  decomposition on  $\text{PdZn}/\text{TiO}_2$ .<sup>47</sup>

### Catalytic stability of $\text{PdZn}/\text{TiO}_2$ under the reaction conditions

The higher stability of  $\text{PdZn}$  alloy catalysts compared to their Cu-based counterparts was proven under methanol reforming conditions,<sup>15,52–54</sup> which is the opposite reaction to the intended  $\text{CO}_2$  hydrogenation to  $\text{CH}_3\text{OH}$ . Copper sinters in the presence of water at elevated temperatures, and hence, due to the higher water content when the feed is  $\text{CO}_2$  instead of  $\text{CO}$ ,  $\text{PdZn}$  alloys are employed as stable alternatives to Cu-based catalysts for the synthesis of  $\text{CH}_3\text{OH}$  from  $\text{CO}_2$ .<sup>15–19</sup> According to the Pd–Zn phase diagram developed by Massalski<sup>55</sup> and Vizdal *et al.*,<sup>56</sup> the  $\beta$ - $\text{PdZn}$  alloy is thermally stable up to 1200 °C. However, in the presence of oxygen at 300 °C, the surface of the  $\text{PdZn}$  alloy segregates into  $\text{ZnO}$  and metallic Pd,<sup>53</sup> whilst under  $\text{H}_2$ , the  $\beta$ - $\text{PdZn}$  alloy was experimentally proven to be stable up to 600 °C.<sup>57</sup> Chen *et al.*,<sup>58</sup> based on DFT calculations, suggested that Zn segregates from the  $\text{PdZn}$  alloy when the alloy is supported on  $\text{ZnO}$ . Nevertheless, Ahoba-Sam *et al.*<sup>38</sup> reported no changes in the  $\text{PdZn}$  phase and no formation of extra Pd-phases through *operando* XAS during  $\text{CO}_2$  hydrogenation to  $\text{CH}_3\text{OH}$  (8 bar, 350 °C).

The stability of the  $\text{PdZn}$  phase in the  $\text{PdZn}/\text{TiO}_2$  methanol synthesis catalyst was assessed through XAS, XRD and XPS characterisation pre- and post-reaction

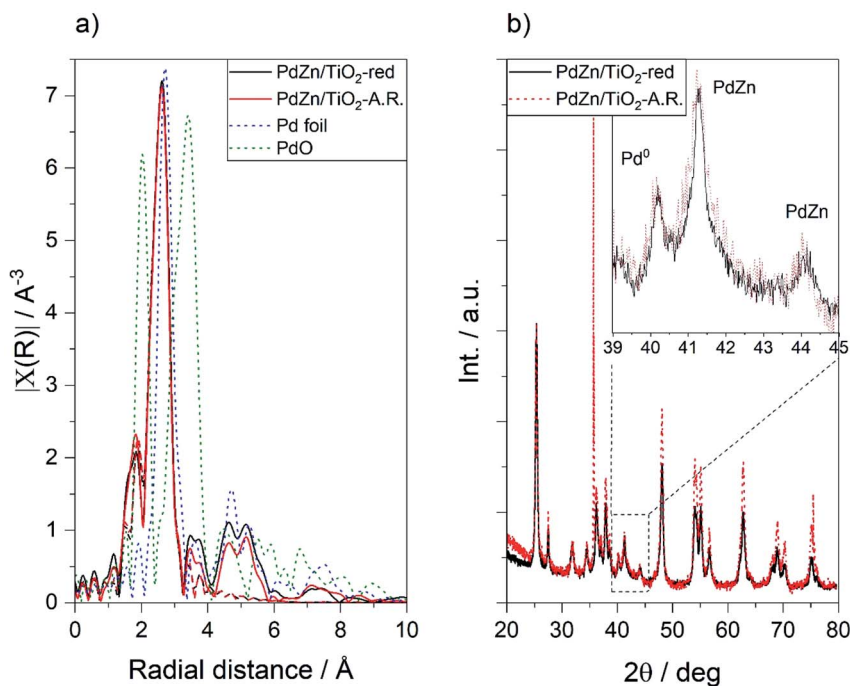


Fig. 5 (a) EXAFS spectra of  $\text{PdZn}/\text{TiO}_2$  after reduction and  $\text{PdZn}/\text{TiO}_2$  after reaction (240–360 °C). Recorded spectra and fits (window 1.8–3.5 Å) are represented by solid and dashed lines, respectively. Spectra of Pd foil and PdO are included for comparison; (b) XRD patterns recorded for  $\text{PdZn}/\text{TiO}_2$  after reduction and  $\text{PdZn}/\text{TiO}_2$  after reaction.





(20 bar,  $\text{CO}_2/\text{H}_2/\text{N}_2 = 1 : 3 : 1$ , 30 ml  $\text{min}^{-1}$ , 240–360 °C, 6 h dwell, 36 h reaction). Extended X-ray absorption fine-structure spectroscopy (EXAFS) at the Pd K-edge was employed to detect structural and electronic changes in the PdZn phase after reaction. No noticeable differences were observed between the EXAFS spectra up to 3.5 Å of PdZn/TiO<sub>2</sub> after pre-reduction (5% H<sub>2</sub>, 400 °C, 1 h) and after CO<sub>2</sub> hydrogenation at up to 360 °C (Fig. 5a). Bulk Pd has a cubic structure with a Pd–Pd bond distance of 1.75 Å, whilst the  $\beta$ -PdZn alloy has a tetragonal structure. As expected for the intercalation of a Zn atom between two Pd atoms, on average shorter bond distances for the first coordination shell compared to bulk Pd were observed (shorter Pd–Zn bond distance compared to the Pd–Pd distance in Pd foil).<sup>59</sup> Moreover, comparison with a PdO standard could suggest the presence of a Pd–O bond at 2.02 Å, with the concomitant but lower intensity Pd–O–Pd bond at 3.41 Å in the second coordination shell.<sup>60</sup> This could be attributed to oxidation of the first atomic layer of the PdZn alloy in contact with air.<sup>53</sup> Peak fitting using Artemis<sup>44</sup> allowed us to obtain the Pd–Pd and Pd–Zn bond distances and the Pd coordination environment (Table 1). Details of the fitting can be obtained from Table S6.† Based on previous reports, PdZn alloy formation begins at the surface of Pd nanoparticles *via* hydrogen spillover to adjacent ZnO, and the alloy grows inwards, generating a PdZn layer over a Pd core.<sup>53,57</sup> Therefore, the incorporation of bulk Pd–Pd bond distances was necessary to obtain a good fit. No differences in the Pd–Zn or Pd–Pd bond distances or coordination number were observed, suggesting high bulk structural stability of the PdZn alloy under reaction conditions, as also reported by Olsbye and co-workers.<sup>38</sup> Despite the apparent bond distance at 2.02 Å, no good fit was obtained after the introduction of the Pd–O scattering path, indicating that this contribution can be attributed to noise or to marginal PdO content.

Phase changes in the  $\beta$ -PdZn alloy during reaction were investigated by recording the XRD pattern of PdZn/TiO<sub>2</sub> after reduction (400 °C, 1 h) and after reaction (240–360 °C, 20 bar, 36 h). In agreement with the EXAFS analysis, no changes were observed in the (111) and (200)  $\beta$ -PdZn reflections at 41.2° and 44.1° respectively,<sup>15,19,27</sup> showing the high thermal stability of bulk PdZn under the reaction conditions (Fig. 5b). Moreover, no significant changes were observed in the XRD peak at 40.1° assigned to metallic Pd (PDF 00-046-1043), which presumably is protected underneath a PdZn layer.<sup>53,57</sup> Unincorporated Zn in the

**Table 1** Bond distances and coordination numbers for PdZn/TiO<sub>2</sub> after reduction and PdZn/TiO<sub>2</sub> after reaction obtained from EXAFS fitting

PdZn/TiO <sub>2</sub>	Bond	Distance	CN	$\sigma^2$	$R_f$
Reduced	Pd–Zn <sub>(alloy)</sub>	2.59	2.62–0.21	0.0047–0.0014	0.019
	Pd–Pd <sub>1(alloy)</sub>	3.06	7.58	0.0217–0.0055	
	Pd–Pd <sub>2(alloy)</sub>	3.35	3.79	0.0215–0.0111	
	Pd–Pd <sub>(metal)</sub>	2.75	12 (fixed)	0.0238–0.0030	
A.R.	Pd–Zn <sub>(alloy)</sub>	2.60	2.71	0.0050–0.0015	0.020
	Pd–Pd <sub>1(alloy)</sub>	3.03	7.52	0.0216–0.0068	
	Pd–Pd <sub>2(alloy)</sub>	3.31	3.76–0.2	0.0218–0.0115	
	Pd–Pd <sub>(metal)</sub>	2.74	12 (fixed)	0.0220–0.0030	
Pd foil	Pd–Pd <sub>1</sub>	2.75	12 (fixed)	0.0055–0.0002	0.016
	Pd–Pd <sub>2</sub>	3.89	6 (fixed)	0.0097–0.0022	



PdZn alloy is observed as ZnO at  $31.7^\circ$ ,  $34.4^\circ$  and  $36.3^\circ$  (PDF 00-036-1451). In line with PdZn and Pd, no changes in the ZnO reflections were observed after reaction. Nevertheless, the  $\text{TiO}_2$ -related reflections become more intense after reaction, suggesting an increase in the particle size of the support (Fig. S2†).

EXAFS and XRD are averaging techniques sensitive to bulk changes. Catalysis, however, is a surface process, and hence small changes at the surface greatly affect the catalytic activity. To follow surface changes in the PdZn alloy composition, the Pd(3d) and Zn(LM<sub>2</sub>) orbitals of the PdZn/TiO<sub>2</sub> catalyst before and after reaction were analysed by X-ray photoelectron spectroscopy (XPS). The Zn(2p) orbital is not sensitive towards chemical changes (*e.g.* the binding energies for Zn<sup>0</sup> and Zn<sup>2+</sup> are reported at 1021.7 and 1022 eV, respectively),<sup>61</sup> and as observed by XRD, the unalloyed zinc remained as ZnO, hence the Pd(3d) and Zn(LM<sub>2</sub>) orbitals were calibrated against the Zn(2p) orbital at 1022 eV. The Pd(3d) peak for PdZn/TiO<sub>2</sub> after reduction and after reaction was centred at 335.6 eV (Fig. 6), between the binding energy values reported for metallic Pd (334.8–335.4 eV)<sup>62–64</sup> and the PdZn alloy (335.6–336.7 eV).<sup>64–66</sup> Peak fitting using finite Lorentzian line shapes for the Pd and PdZn peaks (including satellites) and Gaussian line shapes for the PdO peaks and satellites with a Shirley background as described previously<sup>47</sup> indicated the presence of Pd, PdZn and PdO at 335.0, 335.9 and 337.2 eV, respectively (Fig. S3a†).<sup>54,64</sup> The presence of Pd and PdZn was confirmed by the XRD and EXAFS bulk characterisation techniques, however bulk PdO was not observed. The broadening of the Pd(3d) peak after reaction indicated an increase in the proportion of surface PdO, suggesting that surface PdZn phase separation into ZnO and Pd occurred, with concomitant palladium passivation when in contact with air.<sup>53</sup> No significant changes were observed in the Zn(LM<sub>2</sub>) Auger electron spectra before and after reaction (Fig. S3b†); the main peak at 998 eV with a minor satellite contribution at 991 eV was attributed to the presence of ZnO.<sup>67</sup>

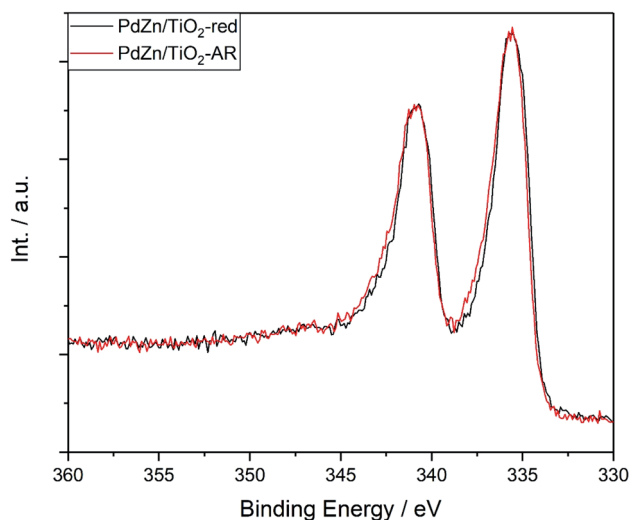


Fig. 6 Pd(3d) XPS analysis for PdZn/TiO<sub>2</sub> after reduction (5% H<sub>2</sub>, 400 °C, 1 h) and after reaction (20 bar, 240–360 °C, 36 h, CO<sub>2</sub> : H<sub>2</sub> : N<sub>2</sub> = 1 : 3 : 1).



No significant changes in the PdZn phase were detected by EXAFS or XRD, confirming the bulk thermal stability of PdZn under reaction conditions (20 bar, 240–340 °C,  $\text{CO}_2/\text{H}_2/\text{N}_2 = 1 : 3 : 1$ , 36 h). However some surface PdZn phase separation into Pd and ZnO was suggested by the XPS characterisation. Coke deposition is often reported as the main deactivation mechanism for MTH over acid zeolite catalysts. Coke inhibits  $\text{CH}_3\text{OH}$  diffusion to the acid active sites by either filling zeolite cavities or blocking pores.<sup>34</sup> Zeolites can be regenerated at high temperature (500–600 °C) by oxidising deposited coke to  $\text{CO}_2$  with oxygen.<sup>68</sup> To assess the extent of coke deposition during  $\text{CO}_2$  hydrogenation (20 bar, 240–340 °C,  $\text{CO}_2/\text{H}_2/\text{N}_2 = 1 : 3 : 1$ , 36 h) over PdZn/ $\text{TiO}_2$ -ZSM-5 hybrid catalysts, TGA-MS was performed on fresh and spent catalysts (Fig. S4†). The mass loss observed below 200 °C can be assigned to physis/chemisorbed water. Just above 200 °C, an extra 1 wt% mass loss compared to the fresh samples was observed for the PdZn/ $\text{TiO}_2$ -ZSM-5(80 and 50) hybrid catalysts with a corresponding release of  $\text{CO}_2$ , which could be assigned to coke deposits with high oxygen content as reported for  $\text{CH}_3\text{OH}$  conversion to olefins over ZSM-5.<sup>69</sup> No additional mass loss at higher temperature, which would be assigned to coke deposits with low oxygen and hydrogen content (e.g. aromatics), was detected.<sup>69</sup> No coke deposition was detected for PdZn/ $\text{TiO}_2$ -ZSM-5(23). This should not be interpreted as ZSM-5(23) being less sensitive to coke deposition, since a higher concentration of acid sites generally leads to faster deactivation,<sup>70</sup> but instead the initial rate of coke formation might be slower in this system. This might be attributed to the presence of  $\text{H}_2\text{O}$  and  $\text{H}_2$  in the feed<sup>35–37</sup> as well as the low concentration of  $\text{CH}_3\text{OH}$  throughout the catalyst bed.<sup>69</sup>

## Conclusions

The combination of a PdZn/ $\text{TiO}_2$  methanol synthesis catalyst with solid acid ZSM-5 zeolites in the form of a hybrid catalyst allowed for consecutive  $\text{CO}_2$  hydrogenation to  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OH}$  dehydration to DME, and MTH/DMTH in a one-pass single bed reactor. Thus, the total  $\text{CH}_3\text{OH}$  productivity from  $\text{CO}_2$  hydrogenation over PdZn/ $\text{TiO}_2$ -ZSM-5 hybrid catalysts was higher compared to PdZn/ $\text{TiO}_2$ . The synthesised light olefins undergo further hydrogenation to the corresponding alkanes (ethane, propane and butane) as also reported for Cu-based catalysts, which limit hydrocarbon chain growth. Hence, future research using PdZn alloys for the synthesis of hydrocarbons *via* the methanol route should focus on limiting the activity towards olefin hydrogenation whilst maintaining good selectivity for  $\text{CH}_3\text{OH}$ . Increasing the concentration of aluminium sites in ZSM-5, correlated with mild Brønsted acid sites, resulted in the production of higher hydrocarbons. The bulk stability of the PdZn/ $\text{TiO}_2$  catalyst up to 360 °C under the reaction conditions (20 bar,  $\text{CO}_2/\text{H}_2/\text{N}_2 = 1 : 3 : 1$ , 30  $\text{ml min}^{-1}$ , 36 h) was confirmed by XAS and XRD. However XPS suggests that some surface PdZn separation into Pd and ZnO occurred during the reaction.

## Dataset available

Data information can be found at <http://doi.org/10.17035/d.2021.0129194354>.

## Conflicts of interest

There are no conflicts to declare.



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