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Phosphate functionalization of CeO_2-ZrO_2 solid solutions for the catalytic formation of dimethyl carbonate from methanol and carbon dioxide

Iuliia Prymak,[a] Oleg Prymak,[b] Junhui Wang,[a,c] Venkata Narayana Kalevaru,[a] Andreas Martin,[a]
Ursula Bentrup*[a] and Sebastian Wohlrab*[a]

Abstract: Phosphate surface groups on CeO_2-ZrO_2 solid solutions were generated by treating Ce-Zr-hydroxide precursors with phosphoric acid. In the catalytic formation of dimethyl carbonate from methanol and CO_2 the performance of P-modified samples is markedly affected compared to unmodified ones: The phosphate treatment has caused remarkable changes in phase composition, acid-base properties and the ability to form monodentate methoxy intermediates. The DMC yield (1.6%) was successfully improved from 0.24% to 1.6% by phosphate modification of CeO_2-ZrO_2 (Ce/Zr = 4.7, P/Zr = 0.13) running the reaction at 170 °C and 65 bar for 1 h.

Alternative routes towards “green” dimethyl carbonate (DMC) are intensively under study due to the unique application potential of this compound: DMC can be used as a solvent,[1] as raw material for polycarbonate resins,[2] electrolyte solvent,[3] or in pharmacy.[4] Among different possibilities for DMC synthesis, the most desirable, environmentally attractive and direct route is from CO_2 and methanol. However, the reaction is thermodynamically difficult due to equilibrium limitations, and hence, the yield of DMC reported so far is relatively low.[5] Attempts to use dehydrating agents for removing the formed water from the product stream to shift the equilibrium towards product side still remain challenging.[6] Nevertheless, concerted efforts of various research groups are underway to develop efficient catalyst compositions to produce DMC in an attractive way. Among others, ZrO_2, CeO_2, and their solid solutions are widely used as catalysts for this reaction.[5, 7] The catalytic properties of these CeO_2-ZrO_2 solid solutions can be adjusted by tuning the Ce/Zr ratios. Due to the different charges and radii of the cations, the acid strength of the resulting oxides may be altered. Hence, Zr^{4+} with the smaller ionic radius exhibits a more acidic nature in solid solution.[8] But, for an efficient synthesis of dialkyl carbonates from CO_2, a balance of basic and acidic centers on the catalyst surface is needed.[9] Moreover, Ikeda et al. have performed surface modifications of ZrO_2 with phosphoric acid.[10] These modified ZrO_2 catalysts exhibited remarkably improved catalytic activities for DMC formation, in particular at lower temperatures. It was found that both, ZrO_2 and ZrO_2/H_3PO_4, have Lewis acid sites (Zr^{4+}), whereas only ZrO_2/H_3PO_4 with P/Zr = 0.05 has additional weak Brønsted acid sites.[11] The authors claimed that Brønsted acid sites can contribute to MeOH activation and enhances the catalytic activity.

Inspired by these results, we extended this approach to CeO_2-ZrO_2 catalysts. Based on initial tests of the catalytic conversion of carbon dioxide with methanol over several CeO_2-ZrO_2 catalysts (Table SI1, maximal DMC yields ~ 0.24%), which were in good agreement with previous findings,[5a, 12] the CeO_2-ZrO_2 solid solution catalyst with a theoretical Ce/Zr ratio of 4 (C80Z) was chosen and used in subsequent runs especially for modification with H_3PO_4 to boost the yield of DMC beyond 0.24%. The promoting effect of H_3PO_4 was then investigated by varying the P-contents in C80Z with the aim to identify efficient catalyst compositions for achieving enhanced DMC yields. Furthermore, the key catalyst properties should be explored which play a pivotal role for an improved catalytic performance.

In Table 1 the elemental ratios, surface areas, and DMC yields of the unmodified C80Z and three P-modified C80Z samples obtained from H_3PO_4 pretreatment of a Ce-Zr hydroxide precursor (C80ZP1-3, P/Zr = 0.03-0.3) are compared. In addition the data of another catalyst are included (C80ZP*) which was prepared by post-treatment of C80Z with H_3PO_4.

Table 1 Effect of the H_3PO_4 modification of CeO_2-ZrO_2 catalysts on the overall molar Ce/Zr and P/Zr ratios, the surface areas as well as the DMC yields (Reaction conditions: catalyst weight 50 mg, CH_3OH = 247 mmol, T = 170 °C, p = 65 bar, t = 1 h).

Sample	Ce/Zr (ICP)	P/Zr (ICP)	BET-SA [m^2g^{-1}]	Y_{DMC} [mol%]
C80Z	5.5	-	46	0.24
C80ZP-1	4.6	0.04	73	0.24
C80ZP-2	4.7	0.13	63	1.62
C80ZP-3	4.6	0.47	74	0.11
C80ZP*[a]	1.5	0.13	22	0.004

[a] post-treated sample (H_3PO_4-addition to already calcined solid).

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Although no correlation was found between catalytic performance and surface area, the yield of DMC significantly increases with increasing P/Zr ratio and reaches a maximum at composition of P/Zr=0.13 (C80ZP-2; Y_{DMC} = 1.62%). A greater P/Zr of 0.47 resulted in a significant decrease of the DMC yield. Similar findings were also reported for the ZrO_2/H_3PO_4 system by Ikeda et al. but to a much lower efficiency: catalysts with low P/Zr ratio (0.025-0.1) were more effective for DMC formation compared to un-phosphated ZrO_2.[11] For the post-treated C80ZP* a considerably lower yield of DMC was obtained. This suggests, that *i)* the method of H_3PO_4 treatment plays a crucial role on the catalyst properties and *ii)* a certain amount of phosphorus in the C80Z catalyst (P/Zr = 0.13) is essential for proper catalyst formation.

HAADF-STEM images of C80Z and C80ZP-2, shown in Fig. SI1, revealed nano-sized irregular particles densely agglomerated in all cases in the range of 7-15 nm. This was in a good agreement to the crystallite sizes calculated by XRD (see Table SI3). The sizes of pores measured by nitrogen adsorption (3.7 and 4.5 nm, Table SI1) are in good agreement with those obtained from TEM images (~ 5 nm). However, energy dispersive X-Ray microanalysis (EDX) showed that the distribution of cerium and zirconium concentrations differ on the nanometer scale within the samples (Table SI2). The X-ray diffraction patterns of samples with a Ce content ≥ 60 mol% generally reveal the coexistence of a tetragonal and a cubic phase, which is in accordance to results of Alifanti et al.[13] (Fig. SI2 and Table SI3). Thus, the unphosphated C80Z sample contains a tetragonal Ce-rich $Ce_{0.62}Zr_{0.38}O_2$ phase (24%) besides a cubic $Ce_{0.93}Zr_{0.07}O_2$ phase (76%). In contrast, the formation of a Zr-rich tetragonal $Ce_{0.22}Zr_{0.78}O_2$ phase (13%) besides the cubic $Ce_{0.93}Zr_{0.07}O_2$ phase (87%) is observed in the phosphated C80ZP-2 sample (Figs. 1, SI3 and SI4). Crystalline P-containing phases were not detected in the phosphated samples.

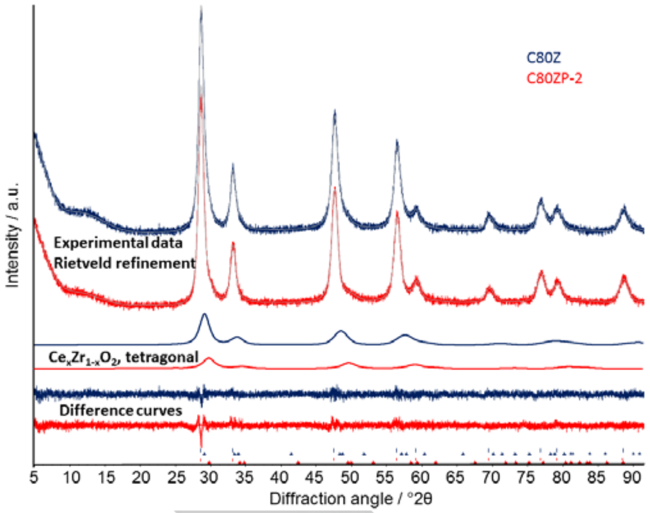

Figure 1. Representative X-ray powder diffractograms with Rietveld refinement of the samples C80Z and C80ZP-2 with additionally highlighted tetragonal $Ce_xZr_{1-x}O_2$ phases.

Temperature-programmed desorption (TPD) of NH_3 is a suitable characterization technique to estimate the total acidity of the catalysts (Table SI4). The respective NH_3-TPD profiles are displayed in (Fig. 2a). Depending on desorption temperature range the presence of acid sites can be classified as weak, moderate and strong.[14]. Both, unmodified Ce-Zr mixed oxides as well as P-modified solids, exhibit mainly weak (<180 °C) and moderate (180-410 °C) acid sites (Table SI5). When CO_2 is used as acidic TPD probe molecule basicity of surface hydroxyl (forms hydrogen carbonate species) or oxygen ions (forms carbonate species) on metal oxides can be studied[15] (Fig. 2b, Table SI5). C80Z exhibits a broad range of CO_2 desorption temperature indicating the presence of three different types of basic sites such as weak (<230 °C), moderate (230-500 °C) and strong (above 500 °C).[16]

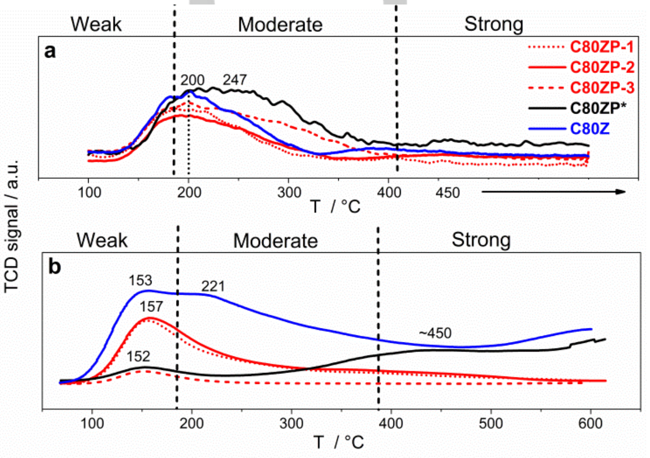

Figure 2. Normalized NH_3-TPD (a) and CO_2-TPD profiles (b) of C80Z and all C80ZP samples.

The C80ZP1-3 samples exhibit CO_2 desorption peak at around 150 °C that indicated the presence of only weak basicity, whereas this feature is distinctly reduced for C80ZP-3. This suggests that P-modification from hydroxide derived catalyst suppresses the concentration of both moderate and strong basic sites which is not the case for C80ZP*. From previous investigations, we have observed that CeO_2-ZrO_2 solid solutions with balanced concentration of acid-base sites performed the best in the continuous esterification of CO_2 to dialkyl carbonates.[9] Obviously, it is possible to reduce moderate and strong basic sites to a higher extent by H_3PO_4 treatment which in turn causes enhanced activity.

For further inspecting the surface properties, hydroxyl groups and possible carbonate surface species FTIR spectra of the pretreated samples (synthetic air, 400 °C) at 170°C were recorded (Fig. 3). Compared to C80Z, the C80ZP-2 catalyst shows additional bands at 3671 cm^{-1} (νZr–OH)[17] and 3510 cm^{-1}, besides of a band at 3649 cm^{-1} (νCe–OH)[17]. The latter can be assigned to a νOH band from a cerium hydroxide microphase.[18] The (νC–H) bands at 2935, 2844, and 2723 cm^{-1} in C80Z stem from formate species[19], the respective $\nu_{as}/\nu_{s}COO^{-}$ bands of which appear at 1546 and 1372/1358 cm^{-1}. These formate bands are missing at C80ZP-2, instead, bands at 1542/1523 cm^{-1} and 1253/1220 cm^{-1} can be seen pointing to surface bidentate carbonate species.

For studying the influence of H_3PO_4 modification on the surface properties, *in situ* FTIR experiments were performed in which $MeOH/CO_2$ gas mixtures were adsorbed exemplarily on C80Z and C80ZP-2 solids at 170°C (Fig. 4).

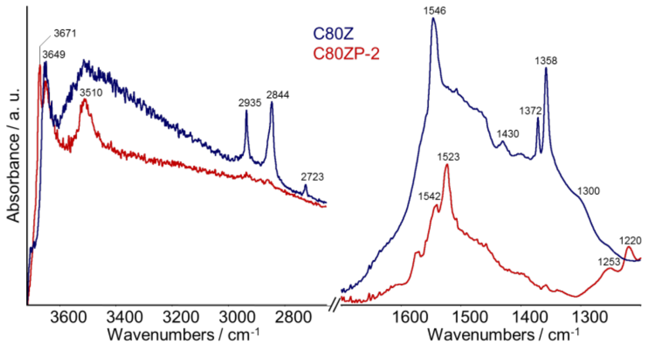

Figure 3. *In situ* FTIR spectra of C80Z and C80ZP-2 recorded at 170°C after pretreatment in synthetic air at 400°C.

Under these conditions both catalysts are also active in the conversion of CO_2 with methanol (see ESI). The bands in the νC–H region around 2940, 2915, and 2810 cm^{-1} can be assigned to C–H stretching vibrations of methoxy species, while those in the frequency range of 1200-1000 cm^{-1} are due to νC–O vibrations.[20] Depending upon the νC–O band positions the nature of surface methoxides can be estimated. Hence, bands around 1150 and 1100 cm^{-1} are related to monodentate methoxy species while the bands around 1050/1030 cm^{-1} are characteristic for bidentate methoxy species adsorbed on Zr^{4+} or/and Ce^{4+}.[17, 21] From the band positions of the monodentate methoxy species, it is possible to distinguish between Ce^{4+}–OCH_3 (1103 cm^{-1})[21] and Zr^{4+}–OCH_3 (1148 cm^{-1}).[17] The spectrum of C80Z is characterized by a strong band of Ce^{4+}–OCH_3 and only a weak band of Zr^{4+}–OCH_3 species, while the latter is essentially more intensive over C80ZP-2 (Fig. 4).

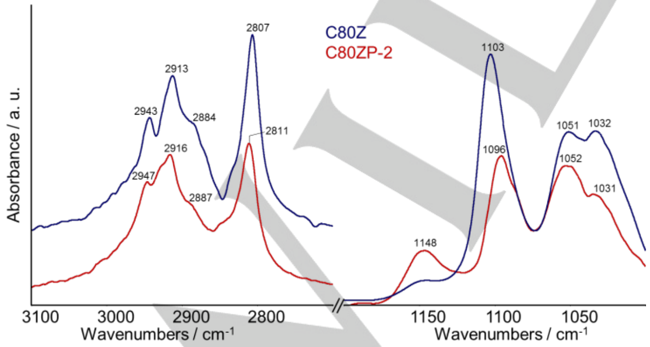

Figure 4. *In situ* FTIR of C80Z and C80ZP-2 recorded after 30 min exposure to $MeOH/CO_2$ at 170 °C and subsequent flushing with He.

Although the overall intensities of the methoxy bands is decreased for C80ZP-2, the intensity ratio of the Ce^{4+}/Zr^{4+}–OCH_3 bands changes dramatically by H_3PO_4 modification in favour of Zr^{4+}–OCH_3 (Table 2). This goes along with an increasing Lewis acidity caused by higher percentage of unsaturated surface Zr^{4+} cations in the modified C80ZP-2 sample. In parallel, the total basicity drops by modification while the overall acidity does not change significantly (Table 2). Considering the findings of Tomishige et al.[22] intermediate methoxy carbonate species over ZrO_2 catalysts are easily formed by reaction of adsorbed monodentate methoxy species with CO_2. Based on these results, it can be concluded that the favoured formation of Zr^{4+}–OCH_3 species is responsible for the enhanced yield of DMC over C80ZP-2 catalyst.

Table 2. Surface properties of the unmodified and modified C80Z samples as examined by $MeOH/CO_2$ and pyridine adsorption (FTIR) as well as NH_3-TPD and CO_2-TPD.

Sample	Methoxy formation Ce^{4+}/Zr^{4+}[a]	Lewis acid. (py. ads.)[b]	Total acidity NH_3 uptake (μmol m^{-2})	Total basicity CO_2 uptake (μmol m^{-2})
C80Z	40/1	15.9	2.0	2.2
C80ZP-2	2/1	30.5	1.7	0.5

[a] Ratio of νC–O band intensities (~1100 cm^{-1} and ~1150 cm^{-1}), normalized to BET-SA. [b] Band intensity ×10^{-3} (1440 cm^{-1}), normalized to BET-SA.

In summary, the phase composition of a Ce rich CeO_2-ZrO_2 solid solution changed considerably after phosphoric acid pretreatment leading to Ce rich cubic and Zr rich tetragonal $Ce_xZr_{1-x}O_2$ nanophases with intimate contact on the nanoscale. Crucial for the increased activity are the specific surface properties such as surface composition (Ce/Zr and P/Zr ratios) and acid-base properties. The H_3PO_4 modification caused a decrease of moderate and strong basic sites and an increase of Lewis acidic sites from most likely unsaturated surface Zr^{4+} cations which are responsible for an enhanced ability to form monodentate methoxy species as an intermediate of the catalytic cycle.

Experimental Section

Experimental details are provided in the accompanying Supporting Information.

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Keywords: Ce-Zr mixed oxides • *in situ* FTIR • crystal phases • acid-base properties • dimethyl carbonate

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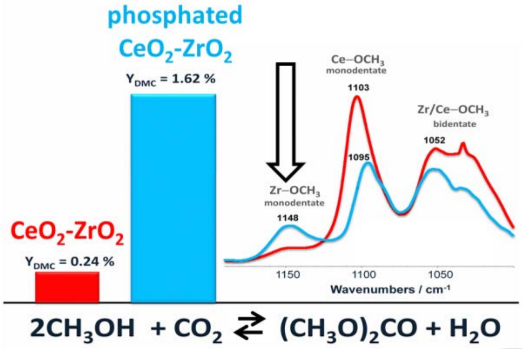
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Esterification of CO_2 with methanol over phosphate functionalized CeO_2-ZrO_2 solid solutions results in more than 6 times higher yields of dimethyl carbonate (DMC) compared to the untreated mixed oxides. Changed surface properties of the phosphated catalysts lead to a decrease of moderate and strong basic sites and an increase of Lewis acidic sites which are responsible for an enhanced ability to form Zr-OCH_3 species – an intermediate of the aimed product DMC.



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Phosphate functionalization of CeO_2-ZrO_2 solid solutions for the catalytic formation of dimethyl carbonate from methanol and carbon dioxide