

Calcium Oxide Supported on Monoclinic Zirconia as a Highly Active Solid Base Catalyst

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Calcium oxide supported on ZrO_2 is a highly active catalyst for base-catalyzed reactions such as aldol-type reactions and transesterification reactions. The role of key parameters during preparation, that is, impregnation versus precipitation, heat treatment, and metal oxide loading on the basicity and catalytic activity were investigated for CaO supported on ZrO_2 . An impregnation of 10 wt% CaO on monoclinic zirconia followed by heat treatment at 600 °C resulted in high activity for the selfcondensation reaction of acetone. An evaluation of a series of CaO/ZrO₂ samples with different loadings showed that the activity increased for impregnated amounts per gram catalyst of 0–10 wt% CaO, and at higher loading the activity decreased as a result of a decrease in dispersion. The number of strong base sites (calculated from CO₂ desorbed at temperatures higher than 625 °C) correlated with the activity. For MgO, CaO, SrO, and BaO on zirconia the catalytic activity increased as the ionic radius of the metal cation increased, suggesting the impact of base strength on catalytic performance.

Introduction

Base catalysis is currently gaining in interest owing to its relevance in the field of biomass conversions such as transesterification and aldol condensation reactions.^[1–4] Compared to homogeneous base catalysts solid base catalysts offer several advantages such as easy regeneration and separation and lower corrosivity.^[5–7] One drawback of bulk solid bases is, however, that the number of active sites per unit mass is generally low. This drawback can be overcome by dispersing the active phase as nanosized particles on a support.^[8,9]

Alkaline earth metal oxides (MgO, CaO, SrO, and BaO) have been investigated as base catalysts for multiple different reaction such as isomerization reactions,^[10,11] Claisen–Schmidt condensations,^[12,13] Knoevenagel condensation,^[14] Michael additions,^[15] Tishchenko reactions,^[16] aldol condensations,^[17] and transesterification reactions.^[18] For more examples and details we refer to a landmark review by Corma and Iborra.^[1]

It is well known that not only the number of actives sites but also the base strength of the sites are important for the catalytic performance of bulk solid base catalysts.^[19-22] As MgO and CaO are readily available, cheap, and environmentally benign, these are most promising candidates among the alkaline earth metal oxide for catalytic applications. CaO is gaining a lot of interest because it is a stronger base than MgO and thus expected to be more catalytically active in reactions requiring a strong base. $^{\left[23-25\right] }$

Previously it has been demonstrated that supporting CaO on carbon nanofibers (CNF) resulted in small particles of approximately 3 nm that are active as a solid base catalyst for aldol reactions and transesterification reactions.^[26] The advantage of using a carbon support is that the interaction between the support and the active phase is kept as low as possible. Therefore, it is expected that the catalysis of nanosized CaO will not be affected by the support (see below).

The inert nature of carbon support makes it possible to gain fundamental insight on the properties of nanoparticles. It is, for example, possible to investigate the role of the cation in basic oxides. By using CNF as a support, nanosized alkaline earth metal oxide particles containing the same number of active sites could be prepared,^[26] and the catalytic activity of such nanosized particles correlated directly with the base strength, which again correlates with, for example, the ionic radius of the alkaline earth metal ion.

If using traditional oxide supports, there is a possibility of strong interaction between the support and the active phase, that is, formation of a mixed oxide that often exhibits lower basicity than the active phase itself.^[27,28] The influence of mixed oxide formation on catalysis has, to the best of our knowledge, not been reported in the literature for solid base catalysts. Therefore, we performed an initial screening study on the role of the support (CNF, SiO₂, TiO₂, Al₂O₃, and ZrO₂) on the activity of supported CaO for the base-catalyzed self-condensation of acetone (Scheme 1).

From this screening, the ZrO_2 support provided the most active catalysts and, therefore, this support was selected for further studies. Zirconia has already been shown to be a good choice as a catalyst support material in the processing of biomass in liquid-phase reactions.^[29,30] Zirconia as a support for

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Scheme 1. Self-condensation of acetone to diacetone alcohol (DAA).

CaO has been reported in the literature as a suitable catalyst for transesterification reactions in preliminary studies.^[31-33] Wang et al.^[31] compared precipitated CaO–ZrO samples with samples in which the calcium was introduced on tetragonal zirconia, t-ZrO₂, by impregnation, or in which CaO and t-ZrO₂ were physically mixed. For the precipitated sample, no calcium-containing phase could be observed in XRD analyses, which was taken as an indication that a solid solution was formed. For the impregnated sample, a mixed-oxide CaZrO₃ with very low basicity was formed. A CaO phase was only observed for the physical mixture of CaO and t-ZrO₂. The precipitated sample was found to be the most active catalyst.

Herein, we investigated in detail the role of the preparation methods of calcium oxide–zirconia samples on their catalytic performance and their base properties. Catalysts prepared by impregnation on a monoclinic (m) ZrO₂ support were compared with precipitated samples, tetragonal (t) ZrO₂. The calcination temperature and calcium oxide loading was evaluated for CaO on m-ZrO₂. Amount and strength of the base sites were evaluated by using temperature-programmed desorption (TPD) of CO₂. The catalytic activity correlated with the amount of strong base sites (desorption of CO₂ > 625 °C). For different alkaline earth metal oxides on zirconia, the catalytic activity paralleled the increase of the ionic radius within the group from Mg²⁺ to Ba²⁺.

Results and Discussion

Screening of support materials for calcium oxide based catalysts

In a screening study, preparations of CaO on different supports (CNF, Al₂O₃, m-ZrO₂, SiO₂, and TiO₂) prepared by incipient wetness impregnation and activated by heat treatment at 600 °C in N₂ were compared for their performances as a base catalyst in the self-condensation reaction of acetone to diacetone alcohol (DAA). The catalysts were handled in inert atmosphere to avoid exposure to CO₂ in the air. The results are shown in Figure 1 and Table 1.

CaO on TiO₂ or SiO₂ displayed no activity whereas CaO/ZrO₂-600 showed superior activity compared to the other catalysts, with the activity following the order CaO/ZrO₂-600 > CaO/CNF-600 > CaO/Al₂O₃-600. Only with the CaO/ZrO₂-600 catalyst the thermodynamic maximum concentration of DAA (1.4 m, at 0 °C) was reached within 7 h. TEM images of the three active samples, before reaction, can be found in the Supporting Information (S1).

To rule out homogeneous catalytic activity, as a result of CaO leaching, an experiment was performed in which the CaO/ZrO₂-600 was filtrated off after 1 h. The continuation of the reaction in the filtrate (if present) was monitored for an additional 6 h. As the filtrate exhibited no activity, that is, no



Figure 1. DAA concentration from the self-condensation of 100 g acetone at 0 °C using 1 g of 5 wt % CaO/support-600, support = $SiO_{2^{2}}$ TiO₂, Al₂O₃, CNF, and m-ZrO₂.

Catalysts	CO_2 uptake [μ mol g ⁻¹]	Specific surface area [m ² g ⁻¹]	Initial rate [mmol _{DAA} g ⁻¹ _{cat} h ⁻¹]
CNF-600	9	190	0
CaO/CNF-600	154	143	33
Al ₂ O ₃ -600	76	150	0
CaO/Al ₂ O ₃ -600	419	147	10
m-ZrO ₂ -600	459	91	0
CaO/ZrO ₂ -600	504	69	149 ^[a] /152 ^[b]
CaO/ZrO ₂ -800	423	-	26
t-ZrO ₂ -600	224	111	0
p-CaO–ZrO ₂ -600	371	106	0.1
p-CaO-ZrO ₂ -800	-	-	0.1
MgO/ZrO ₂ -600	411	-	10
SrO/ZrO ₂ -600	609	-	175
BaO/ZrO ₂ -600	450	-	265

change in concentration of DAA, it can be concluded that the observed performance of CaO/ZrO₂-600 was solely the result of heterogeneous catalysis. The zirconia supports, m-ZrO₂ and t-ZrO₂, showed negligible activities.

As CaO/ZrO₂-600 displayed a very high activity in the screening study, only half the catalyst amount was used in the rest of the study to avoid comparing catalysts at conversions too close to those predicted by thermodynamics.

Zirconia as a support for CaO

The role of the preparation method (impregnation vs. precipitation) and heat-treatment temperature (600 vs. 800° C) on the catalytic activity was studied first (Figure 2, Table 1).

The impregnated CaO/ZrO₂-600 was far more active than precipitated p-CaO–ZrO₂-600. The catalytic activity after activation at 600 $^{\circ}$ C was compared to activities after heat treatment at 800 $^{\circ}$ C. The precipitated p-CaO–ZrO₂ sample exhibited simi-

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Figure 2. Impact of the preparation method on the catalytic activity in the self-condensation reaction of 100 g acetone at 0 °C with 0.5 g of catalysts CaO/ZrO₂ and p-CaO-ZrO₂, after heat treatment at 600 °C and 800 °C.

lar low activity after activation at 800 °C to after activation at 600 °C. The impregnated samples CaO/ZrO₂ were significantly less active after heat treatment at 800 °C than after heat treatment at 600 °C.

The catalytic performances of CaO/ZrO₂ and p-CaO–ZrO₂ after heat treatment at 600 °C was also evaluated in the transesterification reaction between triacetine and methanol. The product formation was evaluated after 30 min reaction time. CaO/ZrO₂-600 exhibited 100% conversion of the triacetin whereas the p-CaO–ZrO₂-600 converted less than 1%. This shows that the trend in performance for the two catalysts is the same for both the aldol coupling and the transesterification reaction. Furthermore it demonstrates the applicability of CaO/ZrO₂-600 as a catalyst for biomass-related conversions.

The samples were characterized to understand the differences in catalytic performance. XRD patterns of the materials after different preparation methods were evaluated (Figure 3) to gain insight into the structure of the different catalysts.

No peaks originating from CaO were observed in any of the XRD patterns of the materials displayed in Figure 3. The precipitated t-ZrO₂ and coprecipitated p-CaO–ZrO₂ exhibited only diffractions from a tetragonal zirconia phase (marked with t in



Figure 3. XRD patterns of p-CaO–ZrO₂-600, t-ZrO₂-600, CaO/ZrO₂-800, CaO/ZrO₂-600, and m-ZrO₂-600.

the Figure). The impregnated CaO/ZrO₂ and the m-ZrO₂ after heat treatment at 600 °C exhibited diffractions from a monoclinic zirconia phase (marked with m in the Figure) along with traces of tetragonal zirconia, identified by the low intensity peak at $2\theta = 36^{\circ}$. If heat treating the impregnated sample at higher temperature, CaO/ZrO₂-800, the peak at $2\theta = 36^{\circ}$ increased whereas the peaks originating from monoclinic ZrO₂ decreased. This shows that a partial phase transformation of monoclinic zirconia into tetragonal zirconia took place. This increase in the amount of tetragonal zirconia (Figure 3) corresponds to a decrease in the catalytic activity as is observed in Figure 2. This suggests that either the monoclinic zirconia phase is advantageous for catalytic performance, or that base sites from the calcium oxide are lost, for example, by incorporation in the support during the transformation from monoclinic to tetragonal ZrO₂.

The CaO/ZrO₂-600 and p-CaO–ZrO₂-600 were examined with SEM (Figure 4a and 4b, respectively) and with TEM (Figure 4c and 4d, respectively) to gain insight in their morphology.



Figure 4. SEM images of a) CaO/ZrO_2-600 and b) $p-CaO-ZrO_2-600$, and TEM images of c) CaO/ZrO_2-600 and d) $p-CaO-ZrO_2-600$.

The impregnated CaO/ZrO₂-600 sample consisted of 1–5 μ m lumps, built up from clusters of approximately 10 nm primary particles (Figure 4a). The precipitated sample p-CaO-ZrO₂-600 was more inhomogeneous and consisted of both large lumps (\approx 50 μ m) with flat surfaces and smaller (1–5 μ m) lumps on top. In Figure 4b an example of one such large lump is displayed with smaller parts of the material deposited on the surface. Electron dispersive X-ray (EDX) analysis revealed that the composition of Zr and Ca is the same for both the large and the small lumps in the precipitated sample. The morphologies of m-ZrO₂ and t-ZrO₂ resembled those of CaO/ZrO₂-600 and p-CaO-ZrO₂-600, respectively (see the Supporting Information, S2). The presence of calcium was verified with EDX but individual CaO particles were not observed. In TEM the two materials, CaO/ZrO₂-600 and p-CaO-ZrO₂-600 (Figure 4 c-d) looked comparable, and again the materials were found to be indistinguishable in morphology to zirconia reference samples. In TEM the calcium oxide could thus also not be observed directly but

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Figure 5. SEM and element mapping of Ca, Zr, and O for CaO/ZrO₂-600.

EDX analysis confirmed that for both preparation methods the element ratios corresponded to the expected loadings of calcium.

In Figure 5 element mapping by SEM of CaO/ZrO₂-600 is shown. From this it can be seen that the Ca is well distributed over the zirconia within the boundaries of the resolution obtainable with SEM. The same held true for the coprecipitated sample (see the Supporting Information, S3). This is in accordance with EDX line profile scans in TEM analysis, which showed that the calcium and zirconium were always in close proximity. The fact that the calcium could not be visualized indicated that the CaO is present either in form of a thin film over the surface, as very small particles (<1 nm), incorporated in the structure of the zirconia, or forming a solid solution as suggested in the literature.^[31,32]

To gain more insight into the location of calcium in CaO/ ZrO₂-600 and p-CaO–ZrO₂-600, XPS was performed. A difference was found between CaO/ZrO₂-600 samples having a Ca/ Zr ratio of 0.29 and p-CaO–ZrO₂-600 samples having a Ca/Zr ratio of only 0.17 (see the Supporting Information, S4). As the two samples have the same nominal Ca/Zr composition this shows that part of the calcium has been incorporated in the structure in the precipitated sample. The higher calcium content on the surface of the impregnated sample might play a role in the higher activity displayed by this sample. It suggests that CaO is well dispersed (e.g., as a film) on the zirconia surface meaning that there are more sites available but potentially also sites of a different nature, for example, different base strength compared to the precipitated sample.

The specific surface area and number of base sites were evaluated by using BET and CO_2 chemisorption techniques, respectively; these results are summarized in Table 1. The numbers of base sites are difficult to compare, which is owing to the amount of base sites already present in zirconia itself. However, the CaO/ZrO₂-600 sample (504 µmol g⁻¹; m-ZrO₂-600

459 μ mol g⁻¹) has more base sites than the p-CaO–ZrO₂-600 (371 μ mol g⁻¹; t-ZrO₂ 224 μ mol g⁻¹), whereas the specific surface area follows the opposite trend, larger for p-CaO–ZrO₂-600 (106 m²g⁻¹) than for CaO/ZrO₂-600 (69 m²g⁻¹). The difference in number of base sites is consistent with the XPS results revealing that more calcium is present on the surface for the impregnated sample than on the precipitated sample. The number of base sites alone cannot account for the difference in catalytic activity between the impregnated and coprecipitated samples, indicating that base strength also plays an important role. The base strengths of CaO/ZrO₂-600 and p-CaO–ZrO₂-600 were thus evaluated by using CO₂ TPD as displayed in Figure 6 and compared to those of m-ZrO₂-600 and t-ZrO₂-600.



Figure 6. CO $_2$ TPD results for CaO/ZrO $_2$ -600, p-CaO–ZrO $_2$ -600, m-ZrO $_2$ -600, and t-ZrO $_2$ -600.

From the CO₂ TPD data it can be seen that both zirconia samples (m-ZrO₂ and t-ZrO₂) display one broad desorption peak with a maximum at approximately 200°C. This peak can be ascribed to weak basic sites intrinsically present on a zirconia surface. For the CaO/ZrO₂-600 this low-temperature peak is shifted to higher temperature with a desorption maximum at 375 °C. This suggests that part of the calcium has been incorporated in the structure in form of a solid solution with stronger sites than those intrinsic to the zirconia support. Additionally, a peak with a maximum at approximately $775\,^\circ\text{C}$ is observed, indicating that the sample contains some very strong base sites most likely associated to the presence of highly dispersed CaO on the ZrO₂ surface. For the precipitated p-CaO-ZrO₂-600 sample, the low-temperature peak is also shifted towards higher temperature, 250°C, but to a lesser extent that for the impregnated sample, which could be explained by part of the calcium dissolving in the zirconia lattice structure. A very broad but low-intense peak is observed at 600-900 °C for p-CaO-ZrO₂-600. The fact that this high temperature peak has so low intensity indicates that only few strong base sites are present, compared to in CaO/ZrO2-600. The p-CaO-ZrO2-600 and CaO/ZrO₂-600 have thus very different properties with respect to base strength, dependent on the preparation method and the calcium-support interaction. We propose that the su-

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perior activity of CaO/ZrO₂-600 is owing to the present of strong base sites, as the acetone self-condensation reaction requires strong base to deprotonate acetone ($pK_a = 20$) and perform the coupling. The importance of base strength for the catalytic activity for zirconia-based catalysts was further demonstrated by comparing samples containing alkaline earth metal oxides MgO, CaO, SrO, and BaO with molar loadings corresponding to 5 wt% CaO/ZrO₂.



Figure 7. Catalytic activities of 0.5 g MgO/ZrO₂, CaO/ZrO₂, SrO/ZrO₂, and BaO/ZrO₂ after heat treatment at 600 °C in the self-condensation reaction of 100 g acetone at 0 °C.

As shown in Figure 7, the activity increased in the order $MgO/ZrO_2 < CaO/ZrO_2 < SrO/ZrO_2 < BaO/ZrO_2$. The number of base sites (Table 1) did not correlate with the observed activity. The activities, however, followed the same trend as the ionic radius of the alkaline earth metals Mg < Ca < Sr < Ba and thus the base strength. It can thus be concluded that the activity is increasing with increasing basicity.

For the most active calcium oxide catalyst (i.e., the CaO/ ZrO_2 -600) the impact of the CaO loading on catalytic activity was investigated (Figure 8).



Figure 8. Impact of CaO loading on the activity of impregnated zirconia samples after heat treatment at 600 $^{\circ}$ C.

A maximum in the catalytic performing measured in formation of DAA per gram of catalyst per hour was found for the 10 wt% CaO catalyst. From 0 to 10 wt%, the increase in initial rate with loading is almost linear meaning that the activity per gram of CaO is constant in this region. At higher loadings than 10 wt%, the activity decreases, indicating that there is a maximum in the amount of calcium that can be deposited in a monodispersed manner on the zirconia. One monolayer CaO on m-ZrO₂ was calculated to correspond to 7 wt% CaO. As there are indications, based on the positions of the CO₂ desorption peaks, that some of the CaO is dissolved in the structure (Figure 6), it is likely that a slightly higher loading, that is, 10 wt% can be deposited on ZrO₂ before losing activity per gram CaO. At loading more than 10 wt% (not shown) an increase was observed in the XRD pattern at $2\theta = 36^{\circ}$, which indicates the appearance of crystalline CaO particles. This was not observed at lower loadings at which atomic/ionic dispersion was expected. The presence of strong base sites was evaluated for the samples with different CaO loading using CO₂ TPD (Figure 9).



Figure 9. CO₂ desorption versus temperature for CaO/ZrO₂ samples with different loadings (0, 2, 5, 10, and 15 wt%) after activation at 600 $^\circ$ C.

Qualitatively the intensity of the peak at 775 °C follows the activity—it increases from 0 to 10 wt% CaO. For the 15 wt% sample this peak decreases, correlating with a decrease in catalytic activity, whereas a more distinguished peak is arising at lower temperature of approximately 540 °C. The CO₂ desorption temperature can be used as a measure for the base strength. In Figure 6 three distinct contributions were observed that we ascribe to weak, medium, and strong base sites. We defined the amount of strong sites based on the amount of CO₂ desorbed at temperatures higher than 625 °C. The resulting quantitative TPD results are summarized in Table 2.

One interesting observation from Table 2 is that the number of strong base sites in CaO/ZrO₂-800 is considerably lower than in CaO/ZrO₂-600 (25 vs. 63 μ mol_{CO₂}g⁻¹). This explain the lower catalytic activity observed (Figure 2) and is most likely owing to the change in material properties related to the phase transformation observed in XRD analysis (Figure 3).

In Figure 10, the relation between the number of strong base sites and the catalytic activity for the CaO samples is sum-

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Table 2. C	O ₂ uptake,	specific	surface	area,	and	activity	of	supports	and
catalysts.									

Catalysts	Tetel	CO_2 uptake [μ mol g ⁻¹]				
	lotal	(>625 °C)	(>450 °C)	(<450°C)		
m-ZrO ₂ -600	115	13	0	102		
(5%)CaO/ZrO ₂ -600	142	63	6	73		
CaO/ZrO ₂ -800	192	25	0	167		
2% CaO/ZrO ₂ -600	118	17	0	101		
10% CaO/ZrO ₂ -600	184	68	25	91		
15% CaO/ZrO ₂ -600	131	41	13	77		
t-ZrO ₂ -600	54	7	0	47		
p-CaO–ZrO ₂ -600	69	9	0	60		



Figure 10. Correlation between the number of strong base sites (defined as CO_2 desorption above 625 °C) and initial activity for CaO/ZrO₂-600 samples with different loadings, CaO/ZrO₂-800, and p-CaO–ZrO₂-600.

marized. Even though the optimal base strength is unknown, the initial catalytic activity for the calcium-based zirconia catalysts as shown in Figure 10 correlates with the total number of strong base sites.

The deviation from a linear relationship between the initial rate and the number of strong base sites is explained by the differences in the distribution of these strong base sites for the various catalysts. This is, for example, witnessed by a shift in the position of the peak maximum from 725 to 800° C for the 2–15 wt% samples (see Figure 9). The importance of strong base sites for catalytic performance and the correlation between activity and number of strong base sites is, however, clear.

As it is expected that the CaO leaching is negligible in acetone at 0°C in contrast to transesterification conditions, the recyclability of the CaO/ZrO₂-600 catalyst was investigated for the acetone self-condensation reaction. No activation step was performed in between the tests. The initial rates were comparable for the first and the second run, 149 mmol_{DAA} $g_{cat}^{-1}h^{-1}$ and 164 mmol_{DAA} $g_{cat}^{-1}h^{-1}$, respectively. After four tests, however, the activity was reduced to 61 mmol_{DAA} $g_{cat}^{-1}h^{-1}$, likely owing to exposure to air (CO₂, water) during the handling procedure. One possible way to re-gain activity is by heat treatment at high temperatures which needs further investigation.

Conclusions

CaO/ZrO₂ is a highly active base catalyst. Impregnation of calcium nitrate into monoclinic zirconia resulted in a highly active catalyst, owing to the high amount of strong basic sites. Precipitation resulted in less active catalysts because Ca was incorporated in the ZrO_2 structure leading to sites of lower basicity. The number of strong base sites present in CaO samples prepared in different ways and with different loadings correlated with the initial catalytic activity. The impact of base strength was also shown by comparing CaO/ZrO₂ with other alkaline earth metal oxides introduced to zirconia. It is concluded that base strength is of crucial importance for catalytic performance of zirconia-supported solid base catalysts.

Experimental Section

Chemicals

Magnesium nitrate hexahydrate (99+%) was obtained from Acros, and acetone (HPLC grade) was obtained from Fluka. Calcium nitrate tetrahydrate (99%), strontium nitrate (p.a.), barium nitrate, isooctane (99%), and ZrO(NO₃)₂·2H₂O (99%) were obtained from Sigma–Aldrich.

Support materials

 γ -Al₂O₃ (Engelhard), ZrO₂ (Degussa), TiO₂ (Alfa Aesar, Johnson Matthey), SiO₂ (Grace-Davidson), and oxidized CNF were used as supports. The CNF were prepared by a vapor deposition method using a 5 wt% Ni/SiO₂ growth catalyst prepared by deposition precipitation synthesis at 90 °C as reported before.^[8] After calcination (600 °C) and reduction (700 °C), CNF were grown from the growth catalyst (5 g) by using syngas (H₂/CO/N₂ 102/266/450 mLmin⁻¹) at 550 °C and 3.8 bar pressure. The fibers were purified by heating in 1 m KOH at reflux (1.5 h) to remove the silica and, after washing, subsequent heating in concentrated HNO₃ at reflux (1.5 h) to remove nickel and functionalize the fibers. An amount of 30 g oxidized CNF was typically obtained after the washing of the material.

CaO at 5 wt% introduced to different supports by impregnation

CaO/ZrO₂: The zirconia was dried in static air for 2 h at 120 °C. Dried ZrO₂ (2.5 g), denoted m-ZrO₂, (pore volume of 0.68 mL g⁻¹) was placed in a 50 mL impregnation flask and kept under vacuum for 30 min. Calcium nitrate was introduced by incipient wetness impregnation using 1.93 M aqueous Ca(NO₃)₂·4H₂O solution (1.7 mL). The sample was allowed to equilibrate for 1 h, followed by drying at 120 °C for 12 h in static air.

CaO on the other supports were prepared by the same procedure and are named CaO/support.

Samples with different loadings were prepared by using different concentration of calcium nitrate solutions. The loading will be stated in the text if different than 5 wt%, which is the standard loading if studying support effects.

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Alkaline earth metal oxide supported on zirconia

MgO (3.4 wt%), CaO (5.0 wt%), SrO (8.8 wt%), and BaO (13 wt%, same molar amount of the alkaline earth metal ion) were introduced to ZrO_2 by incipient wetness impregnation as described above for CaO/ZrO₂. In the case of the BaO sample, five impregnation cycles with barium nitrate were needed to obtain the required loading.

Precipitated samples

Coprecipitation of CaO–ZrO₂ (containing 5% CaO) was performed as follows: ZrO(NO₃)₂·2H₂O (7.00 g) and Ca(NO₃)₂·4H₂O (0.72 g) were dissolved in water (100 mL). This solution was added dropwise to 50 mL of water in a double-walled thermostated batch glass reactor at 40 °C in which the pH had been adjusted to 10 with NH₃ (aq.). While adding the metal salt solution (duration 30 min), the pH was kept constant at 10 by adding a 2.8 m NH₃ solution dropwise under vigorous stirring. After 4 h of ageing at 40 °C, the formed, white precipitate was isolated by centrifugation and washed three times with water (50 mL). The sample was dried overnight at 120 °C. An amount of 2.8 g (85% yield) of pale orange product could be collected. The sample is denoted p-CaO–ZrO₂.

A sample of ZrO_2 precipitated without calcium was synthesized in the same way, by omitting the adding of calcium nitrate in the synthesis. This sample is denoted t- ZrO_2 .

Activation of catalysts

All materials were crushed and sieved to particles of 25–150 μm size. The samples were heat-treated in N_2 at 30 mLmin $^{-1}$ at 600 $^\circ C$ as the standard (800 $^\circ C$ in specific cases) for 3 h (5 $^\circ Cmin^{-1}$) immediately prior to the catalytic test. The activation temperature is indicated at the end of the sample code.

Catalyst testing

Acetone self-condensation reaction: The self-condensation of acetone was performed at 0 °C in a 200 mL double-walled thermostated batch glass reactor. The reactor was loaded with acetone (100 g), isooctane (6 g, as an internal standard) and catalyst (0.5 or 1 g). Prior to the experiment, the reactor was flushed with nitrogen and during the entire experiment a nitrogen atmosphere was kept over the reaction mixture to avoid exposure to air. The reactor mixture was mechanically stirred at 1700 rpm. Aliquots of 1 mL solution were taken at specific times during a total of 7 h reaction time. The samples were filtrated over hyflo (Sigma-Aldrich) to remove traces of catalyst before GC analysis. The samples were analyzed by using a Chrompack CP 9001 gas chromatograph equipped with an flame ionization detector. Only traces of other products than DAA were observed, which made it possible to evaluated the catalytic activity by the formation of DAA. Initial rates are evaluated after 15 min reaction time, in terms of DAA formation in this time period normalized to the amount of catalyst.

In the experiments in which the catalyst was reused, the reaction mixture was decanted after sedimentation of the catalyst. The catalyst was washed with acetone (25 mL), which was decanted after which the catalyst was dried at RT in a nitrogen flow. A new batch of acetone (100 g) and isooctane (6 g) was then added and the reaction was continued for 7 h at 0 °C.

Transesterification reaction: Triacetine (10 g) and methanol (11.7 mL) were mixed in a 100 mL round-bottom flask. Toluene (0.3 mL) was added as a GC reference. CaO/ZrO₂ or p-CaO-ZrO₂ (500 mg) heat-treated at 600 °C was added. The reaction mixture was heated to 60 °C and a sample was taken after 30 min to evaluate the performance of the catalysts.

Characterization

 N_2 physisorption experiments were performed at -196 °C by using a Micrometrics Tristar Surface Area and Porosity analyzer to determine pore volumes and specific surface areas of the catalysts.

Volumetric CO₂ adsorption was performed with a Micromeritics ASAP 2010C. The samples were heat-treated as before the catalytic tests (ex situ), followed by an in situ drying at 450 °C in vacuum for at least 20 h prior to the measurements in the setup. The adsorption measurements were performed by dosing CO₂ and measuring the uptake versus the absolute pressure at 0 °C. The total number of base sites was determined by extrapolation the linear part of the isotherm (100–250 mbar) to zero pressure.

CO₂ TPD was measured by using a Micromeritics ASAP 2920 using 100 mg of sample. The samples were pretreated in a He heat flow of 30 mLmin⁻¹ at 600 °C for 1 h (5 °Cmin⁻¹). The samples were cooled to 40 °C and CO₂ was loaded with pulses of 10% CO₂/He (loop size 0.5311 mL) until saturation. The TPD was performed by heating the sample to 1000 °C with 10 °Cmin⁻¹ in He (30 mLmin⁻¹).

Electron microscopy (TEM) was performed by using an FEI Tecnai 12 or an FEI Technai 20F. The samples were placed on holy carbon grids and both bright-field and dark-field TEM images were recorded.

SEM micrographs were obtained by using a Philips XL30FEG electron microscope equipped with an energy dispersive X-ray detector for elemental analysis. The samples were placed on a carbon grid and coated with platinum before measurements to prevent charging.

XPS measurements were performed by using a Kratos AXIS Ultra spectrometer, equipped with a monochromatic X-ray source and a delay-line detector. The samples were heat-treated ex situ and stored in a glovebox before they were loaded onto the sample holder and transferred to the spectrometer chamber. The samples were outgassed before they were transferred into the measurement chamber. The background pressure was 2×10^{-9} mbar. Spectra were obtained by using an aluminum anode (Al_{Ka} = 1486.6 eV) operating at 150 W. Survey scans were measured at a constant pass energy of 160 eV and region scans (O1s, Ca 2p, Zr 3p, and C1s regions) at 40 eV.

To compensate for charging effects, the binding energies were referenced by C1s photoemission line of the adventitious hydrocarbon (285.0 eV). The areas of each contribution were computed by using CASA XPS by fitting the experimental spectra to Gaussian/ Lorenzian curves (GL30) after removal of the background (Shirley function). Atomic ratios were calculated by using Scofield relative sensitivity factors.

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