ZnO@ZIF-8: stabilization of quantum confined ZnO nanoparticles by a zinc methylimidazolate framework and their surface structural characterization probed by CO₂ adsorption

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The microporous and activated zeolitic imidazolate framework (Zn(MeIM)₃; MeIM = imidazolate-2-methyl; ZIF-8) was loaded with the MOCVD precursor diethyl zinc [Zn(C₂H₅)₂]. Exposure of ZIF-8 to the vapour of the volatile organometallic molecule resulted in the formation of the inclusion compound [Zn(C₂H₅)₂]₀.₃₅@ZIF-8 revealing two precursor molecules per cavity. In a second step the obtained material was treated with oxygen (5 vol% in argon) at various temperatures (oxidative annealing) to achieve the composite material ZnO₀.₃₅@ZIF-8. The new material was characterized with powder XRD, FT-IR, UV-vis, solid state NMR, elemental analysis, N₂ sorption measurements, and transmission electron microscopy. The data give evidence for the presence of nano-sized ZnO particles stabilized by ZIF-8 showing a blue-shift of the UV-vis absorption caused by quantum size effect (QSE). The surface structure and reactivity of embedded ZnO nanoparticles were characterized via carbon dioxide adsorption at different temperatures monitored by ultra-high vacuum FTIR techniques. It was found that the surface of ZnO nanoparticles is dominated by polar O–ZnO and Zn–ZnO facets as well as by defect sites, which all exhibit high reactivity towards CO₂ activation forming various adsorbed carbonate and chemisorbed CO₂⁻ species.

Introduction

Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are novel hybrid inorganic–organic solid state compounds formed by the linking of single metal ions or multinuclear metal ion building units with oligotopic organic ligands. A huge variety of MOF systems has been reported with fascinating properties related to catalysis, chemical sensing, gas storage, gas separation, and drug delivery. The coordination space of the molecularly defined cavities inside the frameworks is of interest for adsorption of guest molecules or even size defined nanoclusters. As one first example, MOF-5 ([Zn₄O(bdc)₃] (bdc = benzene-1,4-dicarboxylate)) was loaded with different organometallic complexes [MLₙ] by means of a solvent-free gas phase infiltration technique which yields inclusion compounds of the general formula [MLₙ]@MOF-5, where a refers to the number of adsorbed molecules per formula unit MOF-5. These materials of the general formula [precursor]@MOF were of crucial importance for the further synthesis of nano-composite materials, known as “metal@MOFs”, which subject has been recently reviewed. For example, the stabilisation of homogeneously dispersed cavity-size matching gold nanoparticles inside functionalized zeolite imidazolate type metal–organic frameworks (ZIFs) was reported and a new concept of encapsulating metal nanoparticles inside MOFs was introduced. The elucidation of the actual microstructure of the obtained composites “nanoparticle@MOF” needs a combination of complementary analytical methods including Transmission Electron Microscopy (TEM). Obviously, such TEM studies involving MOF materials are quite sophisticated and must be done with great care using low dose techniques to rule out substantial and ill-defined changes of the sample during the measurement. Nevertheless TEM seems to be a powerful tool to determine the size and shape of the embedded “naked” metal nanoparticles.

In contrast to the variety of metal@MOF systems, reports dealing with the embedding of other types of nanoparticles, in particular metal oxides or compound semiconductors into porous MOF structures are extremely rare. Especially the caging of nanosized ZnO by MOFs may be interesting in terms of photocatalysis, photocatalysis and optoelectronic applications. Embedding of ZnO inside highly porous ordered silica materials, e.g. ZnO@MCM-48, influences the size and shape of the metal oxide particles by caging effect and...
was suggested to have an effect in photocatalytic reactions.\textsuperscript{22} Previously, we reported on the synthesis of nanometre-sized ZnO and TiO\textsubscript{2} host inside MOF-5, and on composite systems Cu/ ZnO@MOF-5 and Au/MO\textsubscript{x}@MOF-5 (M = Zn, Ti; x = 1, 2).\textsuperscript{23,24} However, MOF-5 is prone to be contaminated by intrinsic ZnO impurities depending on the synthesis conditions as was recently demonstrated by photoluminescence spectroscopy.\textsuperscript{25} We were thus led to choose the microporous zeolite imidazolate framework ZIF-8 (Zn(MeIM)\textsubscript{2}; MeIM = imidazolate-2-methyl; S(N\textsubscript{2}) = 1918 m\textsuperscript{2} g\textsuperscript{-1}) as host for ZnO nanoparticles (NPs). ZIFs exhibit zeolite network topologies, consisting of functionalized imidazolate groups linking tetra-coordinated Zn\textsuperscript{2+} or Co\textsuperscript{2+} metal ions and show exceptionally high thermal stability and chemical robustness.\textsuperscript{26} ZIF-8 in particular exhibits a sodalite-like structure with pore sizes of 1.2 nm and quite small pore windows of 3.5 Å. These features should restrain the growth of ZnO clusters and nanoparticles inside the cavities of the ZIF matrix.

Herein we report on a two-step synthesis of ZnO NPs inside ZIF-8 by the chemical vapour infiltration (CVI) of diethyl zinc, followed by oxidative annealing of [Zn(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}]\textsubscript{26} as host for ZnO nanoparticles (NPs). ZIFs exhibit zeolite network topologies, consisting of functionalized imidazolate groups linking tetra-coordinated Zn\textsuperscript{2+} or Co\textsuperscript{2+} metal ions and show exceptionally high thermal stability and chemical robustness.\textsuperscript{26} ZIF-8 in particular exhibits a sodalite-like structure with pore sizes of 1.2 nm and quite small pore windows of 3.5 Å. These features should restrain the growth of ZnO clusters and nanoparticles inside the cavities of the ZIF matrix.

Experimental techniques
General techniques, materials and methods
All manipulations were carried out under inert conditions using Schlenk-line and glove-box techniques (O\textsubscript{2}, H\textsubscript{2}O, below 1 ppm). Solvents were purified, dried and saturated with Ar using an automatic catalytic Solvent Purification System (MBraun, Garching). The MOCVD precursor [Zn(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}]\textsubscript{26} was purchased from ABCR and stored at 8 °C.

Transmission electron microscopy was only applicable in a restricted way because of the low contrast between the host framework and embedded ZnO particles. Therefore, the accessibility and microstructural composition of the ZnO NPs were characterized via CO\textsubscript{2} gas adsorption, observed with ultra-high vacuum FTIR spectroscopy (UHV-FTIR).\textsuperscript{27} This technique allows determination of the interaction of CO\textsubscript{2} with differently oriented ZnO surfaces by activation of carbon dioxide,\textsuperscript{28} leading to the formation of different types of chemisorbed carbonate species which data give hints to the surface structure of the embedded ZnO NPs.

Elemental analyses. Measurements were performed in the Microanalytical Laboratory of the Department of Analytical Chemistry at the Ruhr-University Bochum. For Zn determination an AAS apparatus by Vario CHNSO EL (1998) instrument.

Infrared spectroscopy. Spectra were recorded inside a glove-box on a Bruker Alpha-P FT-IR instrument in the ATR geometry with a diamond ATR unit.

UV-vis. Spectra were measured with a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer in diffuse reflectance mode using BaSO\textsubscript{4} as reference.

Solid-state NMR. \textsuperscript{1}H and \textsuperscript{13}C-CP-MAS NMR spectra were measured with a Bruker DSX, 400 MHz spectrometer under MAS conditions in 2.5 mm ZrO\textsubscript{2} rotors with a sample volume of 12 µl. The rotation frequency was 20 kHz. All spectra were measured applying pulse programs written by H.-J. Hauswald at the Department of Analytical Chemistry of the Ruhr-University Bochum. For the proton MAS NMR measurements a ZG4PM pulse program was used. The carbon NMR measurements were carried out using the pulse program CP4C (cross-polarization) and were referenced to adamantane at 38.56 ppm.

Powder X-ray diffraction (PXRD). Measurements of the samples were recorded on a D8-Advance Bruker AXS diffractometer with Cu K\textalpha;-radiation (\(\lambda = 1.5418 \text{ Å}\)) and a focused Göbel mirror in \(\theta - 2\theta\) geometry with a position sensitive detector in a 2θ range from 5–90° at a scan speed of 10 s per step. The experimental set-up was in capillary mode. For data accumulation, the samples were filled under inert gas (glove-box) into 0.7 mm capillaries which were then sealed.

\(N_2\)-Sorption. Measurements were performed using a Quantachrome Autosorp-1 MP instrument and optimized protocols.

Transmission electron microscopy (TEM). Samples were analyzed at the University of Antwerp, Belgium. A FEI Tecnai G2 operated at 200 kV was used for bright field (BF) imaging. Electron diffraction (ED) patterns were obtained on a Philips CM20 microscope also operated at 200 kV. High resolution transmission electron microscopy (HRTEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) experiments were performed on a FEI Titan 80–300 “cubed” microscope fitted with an aberration-corrector for the imaging lens and the probe forming lens as well as a monochromator, yielding a resolution in STEM mode around 80 pm and a resolution in TEM mode around 50 pm. An HAADF camera length of 91 mm (a detector inner-angle of \(\sim 50\) mrad) was used for the STEM measurements. For the BF techniques low intensity beam conditions (lowest possible magnification, low beam intensity and shortest possible exposure times) were used as much as possible. In STEM mode the dwell time and dose were minimized to avoid possible beam damage of the metal–organic framework.\textsuperscript{15}

Chemical vapour infiltration of ZIF-8 with [Zn(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}]

The loading of ZIF-8 with the volatile [Zn(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}] (\(\rho_{\text{vap}} = 2.1 \times 10^0 \text{ Pa at 293 K}\))\textsuperscript{29} followed the general procedure of loading metal–organic frameworks described in a previous publication.\textsuperscript{11} Typical amounts of 100 mg ZIF-8 were placed together with the selected amount of the precursor, both contained in small glass vials, in a glass tube under Ar atmosphere. Gas phase infiltration
of [Zn(C2H5)2] into ZIF-8 was performed in static vacuum (10^-3 mbar) at 298 K for 8 h. After the loading procedure the tube was opened and the obtained material [Zn(C2H5)2]0.38@ZIF-8 (1) was stored under Ar atmosphere at -30 °C. Elemental analysis (wt%): C, 30.5; H, 4.0; N, 16.6; Zn, 35.8.

Preparation of ZnO@ZIF-8

The obtained sample [Zn(C2H5)2]0.38@ZIF-8 was placed in a glass tube under Ar atmosphere (H2O and O2 below 1 ppm). Oxidative annealing was performed passing a stream of oxygen (5 vol% in argon, 1 sccm s^-1) over the sample at temperatures varying from 250 °C to 150 °C for 6 h and further annealing under dynamic vacuum at 200 °C for 12 h. The obtained material [ZnO]0.38@ZIF-8 (2) was stored under argon atmosphere. The new material was characterized with powder XRD, FT-IR, UV-vis, solid state NMR, elemental analysis, N2 sorption measurements, and transmission electron microscopy. Elemental analysis (wt%): C, 30.5; H, 4.0; N, 16.6; Zn, 35.8.

Ultra-high vacuum FTIR spectroscopy

UHV-FTIRS experiments on [ZnO]0.38@ZIF-8 materials were carried out using a UHV apparatus, which combines a state-of-the-art vacuum IR spectrometer (Bruker, VERTEX 80v) with a novel UHV system (Prevac). (For details, please see ref. 27.) The powder samples were first pressed into a gold covered stainless steel grid and then mounted on a sample holder that was particularly designed for the FTIR transmission measurements under UHV conditions. The base pressure in the measurement chamber was 2 × 10^-10 mbar. The optical path inside the IR spectrometer and the space between the spectrometer and UHV chamber was evacuated to avoid atmospheric moisture adsorption, thus resulting in a high sensitivity and long-term stability. The samples pure ZnO, pure ZIF-8 and [ZnO]0.38@ZIF-8 were cleaned in the UHV chamber by heating to 800 K in order to remove all the adsorbed species such as carbon-containing and hydroxyl groups.28,30 Prior to each exposure, a spectrum of the clean powder samples was used as a background reference. All UHV-FTIR spectra were collected with 1024 scans at a resolution of 4 cm^-1 in transmission mode.

Results and discussion

Preparation and analytical characterisation of [Zn(C2H5)2]0.38@ZIF-8 (1)

The gas phase loading of ZIF-8 was performed choosing an excess of [Zn(C2H5)2] to achieve a saturation loading of ZIF-8 at the chosen conditions. A typical sample of 100 mg (0.44 mmol) of activated ZIF-8 was placed together with an excess (0.8 ml, 7.8 mmol) of colourless, liquid diethyl zinc, contained in small glass vials, in glass tube under inert gas conditions (Ar). The zinc precursor is extremely moisture and temperature sensitive (pyrophoric!), thus experiments were done under strict exclusion of air. The loading was performed by allowing the adsorption of diethyl zinc vapour under static conditions at room temperature for 8 h (298 K; base pressure of the sealed vial, 0.1 Pa). No colour change of ZIF-8 was visible during the loading procedure and the amount of the diethyl zinc compound in the precursor boat vanished almost completely after chemical vapour infiltration. The obtained inclusion “compound” [Zn(C2H5)2]0.38@ZIF-8 (1) is very air sensitive and rather unstable at ambient temperatures because of slow desorption of diethyl zinc (very weak physisorption). The obtained material reveals a zinc amount of 36.3 wt%, leading to an average number of 2 molecules [Zn(C2H5)2] per ZIF-8 cavity or 0.38 diethyl zinc molecules per formula unit Zn(MeIM)2.

Solid state NMR characterisation of 1 (Fig. 1) was performed using the magic angle spinning technique at 20 000 Hz and standard cross-polarization pulse sequences as mentioned above. The 1H MAS NMR spectrum shows in addition to the framework signals new proton peaks at 0.86 and 0.03 ppm, indicating the presence of diethyl zinc in the composite material. 13C CP-MAS NMR data also confirm the successful loading of ZIF-8 as seen from the appearance of the ethyl-group carbon signals of [Zn(C2H5)2] at 10.45 and 6.76 ppm.

Fig. 2 shows the FT-IR spectra of pure [Zn(C2H5)2] (a), activated ZIF-8 (b), [Zn(C2H5)2]0.38@ZIF-8 (1, c), and [ZnO]0.38@ZIF-8 (2, d). The material 1 shows new IR bands at 2929, 2898, 2862, 618, and 563 cm^-1 in addition to characteristic ZIF-8 framework vibrations, indicating the presence of [Zn(C2H5)2]. These bands are slightly shifted to higher wave numbers as compared to pure diethyl zinc (Fig. 2a). X-Ray powder diffraction measurements (capillary mode) were performed on the samples and empty ZIF-8 as the reference substance. The PXRD pattern of 1 shows the characteristic reflections of the host lattice, revealing an intact ZIF-8 structure after chemical vapour infiltration (Fig. 3). The relative intensities

![Fig. 1](image-url) 1H and 13C CP-MAS NMR spectra of [Zn(C2H5)2]0.38@ZIF-8. Framework signals are marked with an asterisk.
of the first two reflections of ZIF-8 at low 2θ angles of 7.3° and 10.3° are inverted in comparison to guest-free, activated ZIF-8. As reported earlier in related cases, e.g. [Ru(COD)(COT)]@MOF-5,31 the intensity ratio of the low index reflection of a porous coordination polymer corresponds to the presence of adsorbed and disordered guest molecules.32 This observation of 1 again substantiates the presence of [Zn(C2H5)2] inside the framework cavities.

Preparation and analytical characterisation of [ZnO]0.35@ZIF-8 (2)

A typical sample [Zn(C2H5)2]0.38@ZIF-8 (1) was placed in a glass tube for gentle oxidative annealing in an oxygen stream (5 vol% in argon, 1 sccm s⁻¹) and temperatures varying from 25°C to 150°C for 6 h to obtain [ZnO]0.35@ZIF-8 (2). Subsequently, the new material was annealed in dynamic vacuum at 200°C (10⁻³ mbar) to get rid of any volatile by-products. From the elemental analysis a loading of 9 wt% ZnO, corresponding to 0.35 ZnO units per formula unit ZIF-8, was deduced. Only a very small fraction of the adsorbed precursor molecules were lost by desorption from the framework in the gaseous stream before oxidation takes place. The BET surface area dropped from 1918 m² g⁻¹ for the activated ZIF-8 to 988 m² g⁻¹ for 2, indicating that the pores are still accessible and not blocked by large ZnO agglomerates, which may be formed and would be primarily located at the outer surface of the host matrix. The FT-IR spectrum of 2 (Fig. 2d) does not show any adsorption bands of diethyl zinc suggesting quantitative conversion of diethyl zinc to ZnO. The very broad band in the region of 450 cm⁻¹ is assigned to the ν(Zn–O) lattice vibration of zinc oxide,33 indicating additionally the conversion of [Zn(C2H5)2] to ZnO. Powder X-ray diffraction analysis of 2 (Fig. 3c) shows an intact framework structure after oxidative annealing. Now, only a small relative intensity decrease of the reflection at 7.3° 2θ is visible, not as pronounced as in 1, but still a difference to the activated compound is present. This corresponds with only a small fraction of the pores (<5%) being filled with ZnO nanoparticles after oxidative annealing. Note that each ZnO nanoparticle will contain many ZnO units. The characteristic reflections for hexagonal ZnO are, however, not observed in the PXRD pattern of 2 (typical reflections at 2θ = 31.8° [100], 34.4° [002], 36.3° [101]).34 This is attributed to the small size of ZnO nanoparticles in the composite material.

UV-vis measurements of 2 (Fig. 4) give an additional hint for the presence of ZnO NPs as seen from the characteristically blue shifted adsorption edge at 362 (±0.5) nm in comparison to bulk ZnO (385 nm). This blue shift is expected and relates to the increase of the band gap in correlation to particle size (quantum-size-effect).33,35 From the UV-vis data typical particle diameters of approx. 2 (±0.5) nm are deduced.35,36 The ZnO NPs seem to be...
slightly larger as ZIF’s cavity size (1.2 nm), indicating a partial distortion of the host framework at the sites of the NPs. This effect is already known for metal@MOF materials and relates to diffusion processes of metal (metal oxide) nuclei upon precursor decomposition.\textsuperscript{13,14} However, this effect can in principle be reduced by introduction of anchoring groups at the linkers with surfactant like properties as binding sites for the precursors and also to control the growth and stabilise the nanoparticles inside the cavities as we have recently demonstrated in the case of Au@ZIF-90.\textsuperscript{14}

Bright field TEM images (see Fig. 5a) of 2 show a homogenous material and reveal the absence of larger ZnO agglomerates on the outer MOF surface, in good agreement with UV-vis data. Electron diffraction patterns of the ZnO loaded material reveal intact ZIF-8 crystals. High-resolution images of 2 (Fig. 5b) clearly demonstrate the presence of small, crystalline (wurtzite) ZnO nanoparticles close to the surface of the ZIF-8 host, with diameters varying from 2–3 nm. The inset to Fig. 5b shows a ZnO nanoparticle imaged along the [011] zone axis orientation, as evidenced by the inset FFT. As the contrast between the extremely small nanoparticles and the ZIF-8 host was minimal in the (HR)TEM images, Z-contrast (HAADF-STEM) imaging was also performed, to gain extra insight into the positioning of the nanoparticles within the ZIF-8 host. We have previously shown that small, individual (not agglomerated or sintered) (~1 to 5 nm) metal nanoparticles are likely to be present both at the surface of a porous host as well as throughout the host matrix in this type of hybrid system.\textsuperscript{14,45}

The contrast in HAADF-STEM images is known to be mass-thickness sensitive. Fig. 5c–e are Z-contrast images of 2. Fig. 5c shows that some ZIF-8 crystals have a clear enrichment of ZnO near to the surface. Other crystals show a more uniform contrast distribution in low magnification, but exhibit a “speckled” contrast upon investigation at higher magnification. Fig. 5d shows a ZIF-8 crystal with regions of surface enrichment (enlarged in Fig. 5e), showing the presence of 2–3 nm ZnO nanoparticles. Small nanoparticles can also be made out away from the ZIF-8 surface (speckle contrast of the bulk ZIF-8 in Fig. 5d), an indication of the dispersion of extremely small particles throughout the ZIF matrix. Unfortunately, the contrast

**Fig. 5**  (a) BF-TEM image of a large [ZnO]_{0.35}@ZIF-8 (2) crystal showing a homogeneous composite material. Inset: the ED pattern of 2 evidencing the cubic crystal structure of the ZIF-8 matrix after loading with ZnO nanoparticles. (b) HRTEM image of 2 showing small ZnO nanoparticles on the surface of ZIF-8. Insets: the magnified image of area marked by the white box in (b) showing a ZnO nanoparticle (scale bar = 2 nm) imaged along the [011] axis orientation as evidenced by the inset FFT. (c, d and e) HAADF-STEM images of 2. The mass–thickness contrast reveals accumulated ZnO nanoparticles at the surface of the ZIF-8 crystal. (d) ZIF-8 crystal showing the presence of individual ZnO nanoparticles and (e) magnified image of the region indicated in (d); the ZnO nanoparticles are approximately 1–3 nm in diameter.
difference between the ZnO nanoparticles and the ZIF-8 framework remains too small to perform a full 3D analysis (3D electron tomography), meaning the HAADF-STEM results need to be backed-up by another technique that can provide insight into the 3D ZnO nanoparticle distribution. At a given ZnO bulk density of 5.61 g cm\(^{-1}\), an estimated cluster size of 2 nm and the assumption of spherical metal oxide nanoparticles 175 formula units ZnO are present in one crystallite. Note that the HRTEM data only show crystalline particles on the outer ZIF-8 surface and do not give any information about imbedded ZnO species.

Characterisation of the ZnO nanoparticle surface structure of [ZnO\(_{0.35}\)]@ZIF-8 by CO\(_2\) adsorption and UHV-FTIR spectroscopy

Since transmission electron microscopy can in this instance not provide a direct 3D distribution of the ZnO nanoparticles in 2, further investigations were carried out to characterise the ZnO nanostructures. For this purpose, a UHV-FTIRS study on CO\(_2\) adsorption was selected as a technique to probe the surface structure of the ZnO nanoparticles. Adsorption and activation of carbon dioxide on different faces of single crystalline ZnO and as well on polycrystalline ZnO nanoparticles leading to various forms of carbonate species is well understood and documented.\(^{28,37}\) We were thus led to characterise 2 using a novel UHV-FTIRS instrument, which allows to record high-quality IR data in transmission mode.\(^{27,28,30,39,40}\)

In the first place the thermal stability of ZIF-8 was studied under UHV-conditions in order to ensure the feasibility of cleaning as-synthesised 2 prior to the subsequent CO\(_2\) adsorption studies. The corresponding UHV-FTIRS data (not shown) reveal that the structure of ZIF-8 remains unchanged during thermal treatment up to 800 K. After exposing the clean, adsorbate-free sample 2 to CO\(_2\) at 300 K, a number of IR bands show up in the frequency range 1800–800 cm\(^{-1}\) (Fig. 6). They increase in intensity with increasing the CO\(_2\) pressure. For comparison, we have performed the UHV-FTIRS experiments of CO\(_2\) adsorption on pure ZIF-8 at 300 K. In the corresponding spectra no any new IR bands show up, indicating that the CO\(_2\) activation does not occur on the surfaces of pure ZIF-8. On the basis of the vibrational data of CO\(_2\) on pure ZnO nanoparticles,\(^{28}\) we can provide a consistent assignment of the IR bands observed on 2 which are related to the different carbonate groups formed via activation of CO\(_2\) on the various exposed facets of ZnO.

The intense vibrational bands at 1619, 1292, 974 and 870 cm\(^{-1}\) are characteristic for the formation of a bidentate carbonate species on the polar O-terminated ZnO(0001) surface and are assigned to the three C–O stretching modes \(\nu(C=O)\), \(\nu_{as}(OCO)\) and \(\nu(C=O)\) as well as the out-of-plane deformation mode \(\tau(OCO)\), respectively.\(^{28}\) It is known that the polar ZnO(0001) surface is electrostatically unstable because of uncompensated surface charges and exhibits a (1 \times 3) reconstruction for the clean adsorbate-free surface, in which every third surface oxygen atom is missing.\(^{41,42}\) This (1 \times 3) O–ZnO surface contains a high density of O vacancies (33\%) and is highly reactive in CO\(_2\) activation. As a result, a bidentate carbonate species is formed via the interaction of CO\(_2\) with oxygen vacancies on O–ZnO(0001) surfaces.

A second group of major IR bands is detected at 1545 and 1330 cm\(^{-1}\) (see Fig. 6). They are also indicative for the formation of carbonate species and are assigned respectively to the asymmetric \(\nu_{as}(OCO)\) and symmetric \(\nu(C=O)\) stretching vibrations of a monodentate carbonate species, as evidenced by the relatively small splitting of the two modes.\(^{43}\) According to the UHV-FTIRS results of CO\(_2\) on pure ZnO nanoparticles,\(^{28}\) we can further identify that this carbonate species results from the activation of CO\(_2\) at defect sites (e.g. steps, kinks and edges) on ZnO nanoparticles embedded inside ZIF-8.

In addition to the intense IR bands observed in Fig. 6, two shoulders are resolved at 1600 and 1343 cm\(^{-1}\). These frequencies are in good agreement with those for carbonate species formed on the mixed-terminated ZnO(10\(\overline{1}0\)) facet and are assigned to the \(\nu_{as}(OCO)\) and \(\nu(C=O)\) modes, respectively.\(^{35}\) In contrast to the polar surfaces, the nonpolar ZnO(10\(\overline{1}0\)) is the energetically most favorable surface and consists of coordinatively unsaturated Zn–O ion pairs.\(^{44}\) It was found that the perfect ZnO(10\(\overline{1}0\)) surface exhibits also high reactivity for chemisorption.\(^{38}\) The activation of CO\(_2\) on this surface occurs even at temperatures below 100 K and leads to the formation of an unusual tridentate carbonate species, in which the carbon atom binds to a surface oxygen atom and both O atoms of the CO\(_2\) molecule interact with the neighboring Zn atoms.\(^{37}\)

For a direct comparison, Fig. 7 presents the UHV-FTIR spectra obtained after CO\(_2\) adsorption on the clean 2 and pure ZnO nanoparticles at 300 K. The appearance of the similar IR bands on both powder samples confirms the presence of different active sites on ZnO nanoparticles loaded in ZIF-8, where CO\(_2\) can be activated yielding various carbonate species as discussed above in detail. The intensity of the carbonates formed on 2 is lower than those on pure ZnO powder samples, which is expected.
from the relatively low loading of ZnO in ZIF-8 (i.e. dilution of ZnO by ZIF-8). In addition, it was found that the major species formed on pure ZnO nanoparticles is the tridentate carbonate on mixed-terminated ZnO(10\(\overline{1}\)/C\(_{22}\)10) surfaces, as evidenced by the characteristic dominant bands at 1584, 1331, 1002 and 850 cm\(^{-1}\) (Fig. 7b). This finding is consistent with the fact that polycrystalline ZnO nanoparticles mostly exhibit the nonpolar (10–10) facets as supported by detailed XRD and TEM studies. 45

Interestingly, in contrast with the observation on pure ZnO nanoparticles, the present IR data at 300 K show that the major species formed on [ZnO]\(_{0.35}@\)ZIF-8 (2) are bidentate carbonates on O–ZnO surfaces and monodentate carbonates on defects, indicating that the embedded ZnO nanoparticles exhibit a high density of polar ZnO(000\(\overline{1}\)) facets and defect sites.

To gain more insight into the surface structures of ZnO nanoparticles loaded in ZIF-8 as well as the CO\(_2\) activation on them, we also carried out the corresponding UHV-FTIRS experiments on 2 at lower temperatures. Fig. 8a shows again the presence of a clean, adsorbate-free powder sample 2 prepared by heating in the UHV chamber to 800 K in order to remove contaminants.

In addition to the carbonate-related IR bands, Fig. 8 presents a new intense band at 1714 cm\(^{-1}\) which is not visible in the IR spectra recorded at room temperature (see Fig. 6). Simultaneously, a second band at 1192 cm\(^{-1}\) is resolved at the low-frequency side. These bands are characteristic for the formation of a chemisorbed CO\(_2\) species and are assigned to two C–O

![Fig. 7 UHV-FTIR spectra obtained after CO\(_2\) exposure at room temperature in a UHV chamber; (a) 1 \(\times\) 10\(^{-4}\) mbar CO\(_2\) on clean [ZnO]\(_{0.35}@\)ZIF-8, and (b) 1 \(\times\) 10\(^{-4}\) mbar CO\(_2\) pure ZnO nanoparticles. Samples were prepared via heating in the UHV chamber to 800 K in order to remove contaminants.](image)

![Fig. 8 UHV-FTIR spectra obtained after exposing the [ZnO]\(_{0.35}@\)ZIF-8 powder particles to various amounts of CO\(_2\) at 100 K in an UHV chamber. Prior to CO\(_2\) adsorption the clean [ZnO]\(_{0.35}@\)ZIF-8 sample was prepared via heating in the UHV chamber to 800 K in order to remove all the adsorbed species: (a) clean surface, and exposure to CO\(_2\): (b) 5 \(\times\) 10\(^{-6}\) mbar, (c) 1 \(\times\) 10\(^{-5}\) mbar, (d) 5 \(\times\) 10\(^{-5}\), and (e) 1 \(\times\) 10\(^{-4}\) mbar.](image)
stretching modes.\textsuperscript{43} The chemisorption of CO\textsubscript{2} involves charge transfer from the substrate to the molecule yielding a CO\textsubscript{2}\textsuperscript{−} anionic species on metal cation sites. This process is accompanied by the structure change of the CO\textsubscript{2} molecule from the linear to a bent configuration.\textsuperscript{44,46} According to the recent experimental and theoretical studies,\textsuperscript{41,47–49} the polar Zn-terminated ZnO(0001) surface exhibits coordinatively unsaturated Zn cations and has essentially a (1 × 1) structure, which is stabilized by triangular-shaped islands with a high density of steps. The activation of CO\textsubscript{2} on Zn–ZnO(0001) is expected to give rise to a CO\textsubscript{2}\textsuperscript{−} species chemically bound to the surface Zn cations.

It is known that there exist different adsorption structures of chemisorbed CO\textsubscript{2}\textsuperscript{−}, which can be distinguished by the frequency of the C–O stretching modes as well as the magnitude of their splitting.\textsuperscript{43,46} On the basis of the corresponding vibrational data reported in the literature,\textsuperscript{43} the present IR bands (1714 and 1192 cm\textsuperscript{−1}) indicate the presence of chemisorbed CO\textsubscript{2}\textsuperscript{−} species with a side-on configuration, in which the CO\textsubscript{2} molecule is bound to the surface Zn cations \textit{via} both C and O atoms. However, it should be noted that so far no vibrational data are available for CO\textsubscript{2} adsorption on the single crystalline Zn–ZnO(0001) surface. Further research is needed to elucidate the precise nature of chemisorbed CO\textsubscript{2}\textsuperscript{−} species on ZnO.

Finally, upon CO\textsubscript{2} adsorption on 2 at 100 K two additional dominant bands appear at 2335 and 653 cm\textsuperscript{−1} (Fig. 8). They originate from the physisorbed CO\textsubscript{2} and are assigned to the asymmetric stretching $\nu_{as}(\text{OCO})$ and the degenerate bending mode $\delta$(OCO), respectively. The frequencies are very close to the values for gas phase CO\textsubscript{2}, revealing the presence of a linear CO\textsubscript{2} species which is very weakly bound to the surface $\textit{via}$ electrostatic interaction. In addition, the IR spectra show a broad band centered at 1233 cm\textsuperscript{−1}, which is attributed to a Fermi resonance between the symmetric stretching mode $\nu_{s}(\text{OCO})$ and the first overtone of the $\delta$(OCO) mode.\textsuperscript{43}

In summary, the present UHV-FTIRS data obtained using CO\textsubscript{2} as a probe molecule provide deep insight into the structure and reactivity of ZnO nanoparticles supported by ZIF-8, which characteristically differ from that of pure polycrystalline ZnO nanoparticles. The ZnO NPs exhibit a high population of both polar surfaces as well as defect sites, which are all very reactive for CO\textsubscript{2} activation yielding various carbonates and chemisorbed CO\textsubscript{2}\textsuperscript{−} species. This finding could be related with the reduced size of ZnO NPs and the caging effect of ZIFs. Further studies are in progress to elucidate the influence of different ZIFs on the structure and reactivity of ZnO NPs. However, we like to note that the above CO\textsubscript{2} adsorption studies of course do not provide direct information about the location of the ZnO NPs at the ZIF-8 matrix.

Conclusions

ZIF-8 was loaded with ZnO nanoparticles \textit{via} chemical vapour infiltration followed by oxidative annealing. It was shown that ZIF-8 is able to influence the size and surface structure of the metal oxide particles \textit{via} a caging effect. HRTEM and HAADF-STEM images of $[\text{ZnO}]_{0.35}@\text{ZIF-8}$ show the presence of small ZnO particles at/close to the MOF surface as well as a local surface enrichment of ZnO on some ZIF-8 crystals, probably caused by drag-out of precursor molecules during passing a stream of oxygen over the sample. Further work is directed to minimize this effect and to stabilize even smaller, cavity size matching ZnO particles by using anchoring groups at the linkers similar to our work on Au@ZIF-90.\textsuperscript{14} The speckled contrast in the HAADF-STEM images appears to indicate dispersion of the ZnO nanoparticles throughout the whole ZIF-8 matrix, although this cannot be confirmed by 3D techniques as the contrast between the ZnO nanoparticles and the ZIF-8 matrix is too low. Therefore, the surface structure and reactivity of the ZnO NPs supported by ZIF-8 were characterized by UHV-FTIRS using CO\textsubscript{2} as a probe molecule. Whereas the pure ZnO NPs are dominated by the non-polar mixed-terminated (1010) facet, the loading of ZnO at ZIF-8 leads to a large increase of the population of both polar surfaces, O-terminated (0001) and Zn-terminated (0001), which becomes the dominant ones within $[\text{ZnO}]_{0.35}@\text{ZIF-8}$. All the polar and nonpolar facets of ZnO exhibit high activity towards CO\textsubscript{2} activation at temperature as low as 100 K. On Zn–ZnO(0001) a chemisorbed CO\textsubscript{2}\textsuperscript{−} species is formed \textit{via} the interaction of CO\textsubscript{2} with surface Zn cations, while on ZnO(1010) and O–ZnO(0001) surfaces CO\textsubscript{2} reacts with both coordinatively unsaturated Zn and O atoms giving rise to tridentate and bidentate carbonates, respectively. In addition, ZnO nanoparticles supported or caged by ZIF-8 exhibit a high density of defects which also serve as active sites for CO\textsubscript{2} activation.

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