Activation of CO₂ by tBuZnOH species: efficient routes to novel nanomaterials based on zinc carbonates†

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We report on the activation of CO₂ by the well-defined alkylzinc hydroxide (tBuZnOH)₆ in the absence and presence of tBu₂Zn as an external proton acceptor. The slight modifications in reaction systems involving organozinc precursors enable control of the reaction products with high selectivity leading to the isolation of the mesoporous solid based on ZnCO₃ nanoparticles or an unprecedented discrete alkylzinc carbonate ([tBuZn]₂(µ₃-CO₃))₆ cluster with the Zn–C bond intact, respectively. The chemical fixation and activation of CO₂ has drawn long-standing interest as a means to mitigate global warming and utilize the captured CO₂ as an inexpensive chemical feedstock. Carbon dioxide is the most important and abundant C1-building block in Nature widely exploited by organisms (i.e. plants) for constructing larger carbohydrate-based building units. The most significant example of CO₂ activation by zinc complexes is represented by carbonic anhydrase (CA), a zinc-metalloenzyme that catalyzes the reversible hydration of CO₂ and is responsible for its fast metabolism. This process is based on Zn–OH type reaction systems patterned on the active centre of CA. Hence, a number of mono- or dinuclear zinc complexes supported by multidentate ligands and featuring terminal or bridging hydroxide ligation have been widely investigated as synthetic analogues of CA. However model studies mimicking the active Zn site in CA have so far failed to activate CO₂ beyond the bicarbonate complex due to the product inhibition effect that has been commonly observed in these systems. Undoubtedly, it is of particular significance to gain experience from biochemical model systems and utilize the bio-inspired approach in the development of more effective systems for CO₂ fixation as well as in the construction of new functional materials based on metal carbonate cores. Surprisingly, the latter issues are still essentially an unexplored area, and the use of well-defined alkylzinc compounds in this context is lacking.

The activation and conversion of CO₂ into useful products has also long been recognized by organometallic chemists as a desirable goal. Nevertheless simple homoleptic zinc allys are known to be essentially inactive toward CO₂, due to the more covalent nature of the Zn–C bond in comparison to other M–C systems. The introduction of supporting ligands and the tuning of the zinc coordination sphere allow the enhancement of the reactivity of Zn complexes toward CO₂ molecules. For example, the reaction of R-Zn–NR₂ compounds with CO₂ yields zinc-carbamates while the insertion of CO₂ into Zn–OR is a basic step in the alternating copolymerization of CO₂ with epoxides. In this regard, organozinc RZnOH-type compounds appear as very attractive model reagents due to the presence of both the CO₂-reactive ZnOH group and the proton-reactive Zn–C bond (Scheme 1a) in their structure. However, low-allyl RZnOH compounds are fairly unstable and only recently our group provided a well-defined alkylzinc hydroxide, i.e. [tBuZnOH]₆, (1) (Scheme 1b). Herein we report on the activation of CO₂ by 1 in the absence as well as in the presence of tBu₂Zn as a proton acceptor. We demonstrate that the reaction of 1 with CO₂ affords the unprecedented mesoporous material 2 based on ZnCO₃ nanoparticles of uniform size and shape, whereas tBu₂Zn promotes the formation of the unique discrete dodecanuclear alkylzinc carbonate cluster [[tBuZn]₂(µ₃-CO₃)]₆ (3).

The exposure of the freshly dissolved alkylzinc hydroxide 1 in toluene to a dry and oxygen-free CO₂ atmosphere at room
temperature afforded repeatedly the formation of a gel of zinc carbonate nanoparticles 2 (Scheme 2, path 1). After more detailed investigations we found that an excess of tBu₂Zn in the system involving 1 and CO₂ shifts the reaction course to the unprecedented dodecanuclear allylzinc carbonate cluster \([([\text{tBuZn}])_2(\mu_5-\text{CO}_3)]_6\) (3) with a moderate yield (isolated yield 38% for tBuZnOH : tBu₂Zn molar ratio 2 : 1), while the equimolar mixture of 1 and tBu₂Zn in toluene as a starting reaction system leads to the formation of 3 almost quantitatively (isolated yield 91%; Scheme 2, path 2).

The resulting zinc carbonate 2 in the form of a white gel (gelation of the post-reaction mixture occurs within 24 h), upon aging for two weeks under ambient conditions, transforms into a suspension of solid, which can be separated by decantation. The latter solid 2 with the bulk density as low as 0.24 g cm\(^{-3}\) with a moderate yield (isolated yield 38% for tBuZnOH : tBu₂Zn molar ratio 2 : 1), while the equimolar mixture of 1 and tBu₂Zn in toluene as a starting reaction system leads to the formation of 3 almost quantitatively (isolated yield 91%; Scheme 2, path 2).

The TEM micrographs of 2 show that the material consists of an interconnected network of essentially spherical (mean diameter of 8.0 nm) ZnCO₃ nanoparticles (Fig. 1b–d) as indicated by interplanar distances (d-values), 3.55 Å (±0.05) corresponding to the d-values of (102) planes of ZnCO₃ (Fig. 1d). The porosity of 2 was verified by N₂ adsorption at 77 K. Compound 2 adsorbs N₂ with a maximum uptake of 250 cm³ g⁻¹ and exhibits a type IV isotherm characteristic for mesoporous materials [Fig. S3 in the ESI†]. The calculated Brunauer–Emmett–Teller (BET) surface area for 2 is 91 m² g⁻¹ and Barrett–Joyner–Halenda (BJH) analysis shows that the average pore diameter falls in the range of 7–15 nm, which is a commonly observed value for xer- and aerogels of many semiconductors.\(^{11c-f}\) It is worth noting that the majority of known aerogels contain silica as the inorganic matrix and the development of this type of material based on other inorganic building blocks is still at an early stage.\(^ {11}\)

In conclusion, we have demonstrated for the first time that the alkylzinc hydroxides can be successfully utilized for the activation of CO₂ under mild conditions. Just by a slight modification of the reaction systems we isolated a mesoporous

![Scheme 2](image)

**Fig. 1** Images of the mesoporous solid 2: (a) SEM image showing meso- and macro-pores; (b) STEM image showing nanosized pores; (c) the same fragment in TEM mode; (d) HRTEM image of a single particle showing the crystalline nature of the nanoparticle architecture (lattice fringes corresponding to the (102) reflections of trigonal ZnCO₃).
solid 2 based on single ZnCO₃ nanoparticles or the unprecedented dendocenacarboxylalkyl zinc carbonate complex [(tBuZn)₂(μ₂-CO₃)₆]
(3). Thus, alkylzinc hydroxides appear to be interesting examples of organometallic Zn–OH-type compounds with reactive Zn–C bonds, where both functionalities can take part in sequential transformations. We believe that this approach shows the unique potential of simple organometallic precursors for post-synthetic modifications in order to design new functional materials based on biocompatible zinc carbonate components. Further studies on the effective fixation of CO₂ and other small molecules by organozinc hydroxides supported by organic ligands are in progress.

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Notes and references