The mechanism of CO$_2$ hydration: a porous metal oxide nanocapsule catalyst can mimic the biological carbonic anhydrase role†‡

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The mechanism for the hydration of CO$_2$ within a Keplerate nanocapsule is presented. A network of hydrogen bonds across the water layers in the first metal coordination sphere facilitates the proton abstraction and nucleophilic addition of water. The highly acidic properties of the polyoxometalate cluster are crucial for explaining the catalysed hydration.

Concerns about global warming, together with the incoming necessity to find alternative feedstocks to fossil fuels,$^1$ have boosted interest in the capture and use of CO$_2$ as a chemical analogues$^{10}$ has afforded major bio-inspired catalytic routes for catalyst. The exploration of carbonic anhydrase$^6–9$ and related molecules in the proximity of the enzyme site makes the hydration reaction possible, which is rather slow in the absence of a catalyst. The presence of an electrophilic Zn center together with a network of water hydration to carbonic acid, in an easy manner. The presence of an electrophilic Zn center together with a network of water molecules in the proximity of the enzyme site makes the hydration reaction possible, which is rather slow in the absence of a catalyst. The exploration of carbonic anhydrase$^6–9$ and related analogues$^{10}$ has afforded major bio-inspired catalytic routes for CO$_2$ fixation over the past few decades. On the other hand, synthetic chemistry afforded new transition metal based catalysts that can convert CO$_2$ into other chemical entities, for instance CO$_2$ reduction to methanol,$^{11}$ coupling with oxiranes to produce cyclic carbonates,$^{12–14}$ or other value added chemicals.$^{15,16}$

Some of us reported recently$^{17}$ a novel way to sequestrate and transform CO$_2$ into carbonate by encapsulation within unique molybdenum oxide nanocapsules. This novelty hinges on the fact that the approach uses only aqueous, room temperature and open air chemistry. These capsules, belonging to the Keplerate family, are nano-sized molecular metal oxide spheres with the general formula $[[[(M^{VI})M^{VII}O_2]_3(H_2O)_6]_{12}[(M^{II}O_2X_2(\mu^2-Y)]_{30}]^{2–}$ ($M = Mo, W; M' = Mo, X = O, Si; Y = bridging ligand, e.g. RCOO$^–$, SO$_4^{2–}$.)$^{18}$ This sort of capsule contains 12 pentagonal $\{Mo^{VI}\}$ units placed at the vertices of an icosahedron and linked by 30 binuclear $\{Mo^{II}\}$ units. This arrangement leads to the formation of capsules (Fig. 1) with twenty $\{M_2Mo_3O_8\}$-type pores and a cavity where a large quantity of water molecules, anions or other species can be confined.$^{19,20}$ By bubbling CO$_2$ in an aqueous solution of (NH$_4$)$_3[(Mo^{VI})Mo^{VII}O_2(H_2O)_6]_{12}[(Mo^{II}O_2(\mu^2-CH_3COO)]_{30}]^{2–}$ ca. 10 CH$_3COONH$_4 ca. 300 H$_2$O $\equiv$ (NH$_4$)$_{42}$ Anion 1a ca. 10 CH$_3COONH$_4 ca. 300 H$_2$O $\equiv$ Compound 1$^{21}$ at pH 7 the carbonate derivative (NH$_4$)$_2[[[(Mo^{VI})Mo^{VII}O_2(H_2O)_6]_{12}[(Mo^{II}O_2(\mu^2-CH_3COO)]_{30}]^{2–}$ ca. 260 H$_2$O $\equiv$ (NH$_4$)$_2$ anion 2a ca. 260 H$_2$O $\equiv$ Compound 2 was obtained.$^{22}$ The pictorial representation of the $\{Mo_{132}\}$ Keplerate capsule is displayed in Fig. 1.

The characterisation of Compound 2 prompted the major question of whether the carbonate anion formed in solution (in minute amounts at pH 7) was captured by the Keplerate cluster by diffusion into the inner cavity or, more interestingly, whether the carbonate anion formation took place in situ inside the capsule, either at the Mo$^V$ or Mo$^{VI}$ coordination sites, by a metal catalysed nucleophilic addition of water to a solubilised CO$_2$ molecule, likewise the accepted mechanism of carbonic anhydrase.

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† Dedicated to the memory of Tom Ziegler (1945–2015).

‡ Electronic supplementary information (ESI) available: Computational details and methodology. See DOI: 10.1039/c5cc06423f
The CO₂ transformation is also reversible via acidification of the aqueous solution of Compound 2.¹⁷ The results of the theoretical study presented herein suggest that this transformation of CO₂ to carbonate is actually the third example²²,²³ known to date of a catalytic process occurring inside the {Mo₁₃₂} capsule, where the Mo⁵ and also the Mo⁶ sites play a role.

The mechanism of the hydration of CO₂ to form the carbonic acid has been a subject of theoretical studies over the past few decades.²⁴,²⁵ The challenge lies in the accurate description of the explicit water molecules participating in the reaction as was shown by the latest work of Yamabe and Kawagishi.²⁶ The uppermost energy barrier of carbon dioxide hydration is always the initial step of water addition.²⁷ The arrangement of this initial transition state²⁴–²⁶,²⁸ is a cyclic three water molecular arrangement as depicted in Fig. 2. We will adopt this model as a benchmark to compare with our own calculations on the catalytic sequestration of CO₂ and its conversion into the carbonate form.

In a recent study we demonstrated that by using a cluster model of the {Mo₁₃₂} nanocapsule, the reaction pathway of the reversible cleavage of methyl-tert-butyl ether was successfully unravelled. The model assembly was defined to mimic the nature of the active sites of the Keplerate and it was formulated as [(Mo⁶)Mo⁶O₁₃(OH)₈]₂{Mo⁵₂O₄}⁶⁺ containing two pentagonal {(Mo⁶)Mo⁶}²⁻ units and one linker unit of the type {Mo⁵₂O₄}.

It fully retained the essential characteristics of the {Mo₁₃₂} reactive sites and therefore we have selected that model for the present study. Since the formation of the carbonate anion takes place in aqueous media, the presence of water molecules inside the Keplerate sphere must play an essential role in the reaction and therefore it is essential that the cluster model should incorporate a sufficiently large number of water molecules. Thus we included 13 additional water molecules explicitly in this study, so the model used is formulated as [(Mo⁶)Mo⁶O₁₃(H₂O)₆(OH)₈]₂{(Mo⁵₂O₄)(H₂O)}⁶⁺, which leaves one vacant coordination site reserved for the incoming CO₂ molecule at one of the two Mo⁵ sites, while the second one bears a water molecule which is supposed to undergo nucleophilic addition.

As expected the CO₂ molecule, being nonpolar, does not coordinate in the initial stage to an Mo⁵ centre either in an η¹ or η² fashion. Notwithstanding, we could characterize a weakly bound stationary point structure in which CO₂ is hydrogen-bonded to the water molecule in one Mo⁵ centre and to a water molecule on Mo⁶, thus located in the vicinity of the reactive centre. This will be our starting point (named Reactants) for the reaction path studies defining the zero of energies.

The highest energy reaction path explored TS1 (Fig. 2) is perhaps the most intuitive pathway involving a concerted nucleophilic addition of an aqua ligand to CO₂ followed by the subsequent proton rejection and formation of a local Zundel cation.

**Fig. 2** Several mechanistic pathways for CO₂ hydration: in red the uncatalysed reaction is presented; in green the iso-charge pathway leading to the formation of a local H₃O⁺ cation; in blue is the route with direct Mo⁶ intervention in the formation of bicarbonate; in black the proposed catalytic pathway. Electronic energies and Gibbs free energies in parentheses are evaluated using a partial Hessian. All energies in kJ mol⁻¹.
The bicarbonate intermediate undergoes further deprotonation resulting in 2d. The release of a proton from 2d to 2e has a negligible energy barrier (for TS2d, 2 kJ mol⁻¹ in electronic or + 8 kJ mol⁻¹ in free energy). The carbonate intermediate 2e is approximately iso-energetic with its parent bicarbonate 2d but can be easily converted to 2f with lower free energy. The intermediate 2f has one non-coordinated water molecule which stabilises the carbonate ligand \( \text{via} \) hydrogen bonding. The Mo-carbonate bond lengths in 2e are 2.392 and 2.329 Å, which are within the error limits of the experimentally determined values.¹²

The higher acidity of the Mo VI centre prompted us to explore another possible mechanistic route in which the direct nucleophilic addition to the CO₂ molecule takes place directly by the hydroxo group coordinated to the Mo VI sites while the vacant coordination site of Mo V is utilized to stabilize the transition state. A subsequent backflip of bicarbonate or carbonate to the \( \{\text{Mo}^\text{VI}\} \)-linker would be necessary to be consistent with the final carbonate adduct. The initial steps of this pathway are sketched in blue as shown in Fig. 2. The transition state TS3 has a similar energy value to TSw (the uncatalysed transition state) but intermediate 3a is not sufficiently stable to be considered a viable route (see ESI, for these additional structures).

There are structural differences between the catalysed and uncatalysed systems namely with regard to each transition state which are summarised in Fig. 3. The Mayer–Mulliken bond orders¹⁰ (MBOs) were also analysed in the present case which reflect the bond strength between the different atoms in any given system. The most striking difference between TSw and TS2b is that the latter is a slightly "lesser bound" transition state with a reaction coordinate (C–O) bond order 0.377 whereas in TSw it is 0.557 in line with Hammond’s postulate. The \( \angle \text{O–C–O} \) angles are also considerably different between TSw (139°) and TS2b (152°) consistent with a larger electron cloud of the incoming O(–C) and consequently a lower angular distortion of CO₂. The leaving proton is also more bound to the oxygen atom in TSw (MBO = 0.430) than in TS2b (MBO = 0.250). In the latter case the outgoing proton from the aqua ligand is already at a large distance (1.535 Å, see Fig. 3). Interestingly the Mo V–OH bond in 2a (x-hydroxo isomer) is stronger (MBO = 0.450) than the Mo VI–OH bond in 2b (MBO = 0.219). This causes a vibrational stiffness in the 2a isomer decreasing its entropy and increasing the free energy difference with respect to 2b.

Finally to predict the potential reactivity of related systems, additional calculations were carried out on model analogues of the \{W72Mo60\} and \{W132\} nanocapsules. The former nanocapsule has been characterised¹¹ experimentally although the latter is still unknown. Since the key point in the mechanism is the generation of the nucleophilic hydroxo species coordinated to the star-shaped M VI moieties, the relative thermodynamic stability of 2a and 2b species was determined. The calculated \( \Delta E(2a \rightarrow 2b) \) is \( -65 \text{ kJ mol}^{-1} \) for the mixed W/Mo oxo-cluster model and \( -85 \text{ kJ mol}^{-1} \) for the hypothetical full W system. This points to a likely enhanced reactivity of the heavier metal Keplerates in the order \{Mo132\} < \{W72Mo60\} < \{W132\}. These results also indicate that W VI centres are less (Lewis) acidic with respect to Mo VI in relation to Mo VI.

DFT based calculations enabled unravelling the CO₂ hydration reaction pathway as evidenced involving Compound 1 by considering the known mechanism in the aqueous solution.
The \textit{in situ} bicarbonate formation, promoted by the Mo\textsuperscript{VI} centres, inside the capsule is kinetically more favourable than direct carbonate uptake from aqueous solution. Three trials were performed in the present work, which can be summarised as follows:

(i) A neutral charge pathway with aqua ligand nucleophilic addition to CO\textsubscript{2} results in a high kinetic barrier $\Delta E^\ddagger = +81$ kJ mol\textsuperscript{-1} and a product of exceedingly high energy.

(ii) A hydroxo ligand pathway in which the nucleophilic attack takes place on a Mo\textsuperscript{V} site. This is a high energy process requiring $+44$ kJ mol\textsuperscript{-1} at the calculation level to form a product.

(iii) A hydroxy ligand pathway where the hydroxy group in an Mo\textsuperscript{VI} centre will act as a proton acceptor in tandem with the nucleophilic addition of CO\textsubscript{2} to an aqua ligand at the Mo\textsuperscript{V} sites. The activation energy $\Delta E^\ddagger = +36$ kJ mol\textsuperscript{-1} is the lowest of all the trials, even lower than the uncatalysed hydration reaction, and the ensuing product assembly is 28 kJ mol\textsuperscript{-1} more stable than the reactant assembly.

Therefore the most plausible mechanism for the formation of Compound 2 will be the latter based on comparison of computed energies with respect to a comparable micro-solvated CO\textsubscript{2} hydration. The resemblance of the mechanism with that operating in the carbonic anhydrase enzyme is remarkable. The subtle differences lie in the first steps of the latter mechanism: the rate-limiting step is the protonation of the aqua ligand in (His)\textsubscript{3}Zn–OH\textsubscript{2}\textsuperscript{b} which is then followed by a lower energy nucleophilic addition to CO\textsubscript{2} whereas the Keplerate acts in a concerted single step for both. These results pave the way for defining a new application of Keplerate anionic capsules as CO\textsubscript{2} storage nanodevices.

While the Mo\textsuperscript{V} sites still remain the active catalytic host in Keplerate catalysis there is a clear involvement of the adjacent Mo\textsuperscript{VI} centres as promoters of Bronsted acidity and proton relay.

This work was funded by the Spanish Ministerio de Economía y Competitividad (MINECO) through project CTQ2014-52824-R, by the Generalitat de Catalunya project 2014SGR409, and by the ICIQ Foundation. The Severo Ochoa Excellence Accreditation (SEV-2013-0319) and the COST Action CM1203 “Polyoxometalate Chemistry for Molecular Nanoscience (PoCheMoN)” are gratefully acknowledged. NAGB gratefully acknowledges COFUND/Marie Curie action 291787-ICIQ-IPMP for funding. A.M. acknowledges continuous financial support by the Deutsche Forschungsgemeinschaft and the ERC (Brussels) for an Advanced Grant.

Notes and references


