Understanding the reaction mechanism of the CO₂ and cyclohexene oxide copolymerization catalyzed by zinc(II) and magnesium(II) catalysts: a DFT approach

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Abstract
The reaction mechanisms of carbon dioxide and cyclohexene oxide copolymerization catalyzed by four different zinc(II)-magnesium(II) (labeled as M1-M2) catalysts were computationally studied using density functional theory at the BP86-D3(BJ)/def2-TZVP/SMD/BP86-D3(BJ)/def2-SVP/SMD level of theory. The results showed that the most effective catalyst was the ZnMg system, in which poly(cyclohexene carbonate) was the preferred product, followed by the side product cis-cyclohexene carbonate. The QTAIM, NCI and ELF analysis performed to understand the role of metals in the reaction showed that ligands and substrates interact more strongly with zinc(II) centers compared to magnesium(II) centers. Furthermore, the Zn-I interaction at the M1 position was stronger than the Mg-I interaction at the same position. All these results indicate a synergism between the metals Zn and Mg, which makes Zn(II)Mg(II) the best combination for the reaction.

Keywords CO₂ · ROCOP · Bimetallic catalyst · DFT

Introduction
The industrialization process faced since the 18th century has generated social and environmental changes that have brought significant challenges, which is leading us to a climate that is increasingly less suitable for life on Earth. Due to the generation of energy based on the burning of fossil fuels, the concentrations of carbon dioxide (CO₂) in the atmosphere have increased c.a. 75% since the 18th century, scenario that contributed significantly with the rise in the average global surface temperature by 0.6 °C in the last century [10, 25, 39]. Aiming to find solutions to overcome this alarming situation, scientists around the world are trying to reduce CO₂ emissions into the atmosphere by different strategies. Among the viable alternatives of CO₂ conversion, the chemical conversion into valuable products is already a relevant industrial process that uses CO₂ to synthesize products like salicylic acid, methanol, cyclic carbonates, urea and polymers such as polyether carbonates and polycarbonates [10, 35]. Although the conversion of CO₂ into products will never be capable of compensating its emissions in the atmosphere, the conversion into materials that have large use in society such as polymers is an interesting alternative to mitigate the problem [25]. Polymers play a central role in modern societies in areas that have a wide range of uses, from personal uses, such as clothing, to materials used in the fabrication of water cleaners. The use of carbon dioxide as a reagent for the production of polymers has already reached the status of a commercial product, being an environmental alternative to polymers synthesized from petrochemical sources [43].

Ring opening and copolymerization reactions (ROCOP) employing CO₂ and a cyclic epoxide such as
cyclohexene carbonate (CHO) as a promising reaction to both use carbon dioxide as a reagent and to produce poly(cyclohexene carbonate) via a less harmful route than the traditional route that uses phosgene gas and trans-diols such as bisphenol A in synthesis [25]. Bimetallic homogeneous catalysts are being employed to promote the ROCOP of CO$_2$ and CHO. The use of bimetallic catalysts relies on the synergistic effects between metals that are used to activate chemical bonds that in a single metal catalyst would not happen [11].

In Fig. 1 is presented the general scheme of the ROCOP reaction and the catalyst used in this work. The main product of these reactions, as described in Fig. 1, is poly(cyclohexene carbonate), and a minor product is formed in a side reaction, the cis-cyclohexene carbonate. The catalyst employed in this reaction is composed by two metals described in Fig. 1 as metals 1 (M$_1$) and 2 (M$_2$), in which homo- or hetero-bimetallic combinations could be used [35]. Combinations such as Zn(II)Zn(II) [9], Mg(II)Mg(II) [12, 13], Ti(IV)Zn(II) [17], Fe(III)Fe(III) [8], Co(III)Co(II), Co(II)Co(II) [23], and Co(II)Mg(II) [12] were used at metal positions 1 and 2.

This work aims to study the reaction mechanism of the ROCOP catalyzed by bimetallic homogeneous catalysts composed of zinc(II) and magnesium(II) in homo- and hetero-bimetallic combinations (from now on named as MgMg, ZnMg, MgZn and ZnZn systems) by means of computational modeling employing the density functional theory (DFT) in calculations.

### Methods

#### Computational details

All geometry optimizations, vibrational frequencies, and single point calculations were performed with ORCA 4.2 software [30, 31] using the BP86 [6, 32, 33] density functional approximation (DFA) along with the def2-TZVP and def2-SVP basis set [42] for single point and geometry optimization/frequency calculations. Dispersion effects were accounted for using the D3 dispersion correction with Becke-Johnson damping [19, 20]. Solvation effects were modeled by the implicit solvation model SMD using the parameters for the dibutyl ether solvent [28]. To accelerate the calculation of Coulomb and exchange integrals, the resolution of identity (RI) approximation [1, 5, 14, 15, 24, 40], in which the def2/J auxiliary basis set [41] was used to perform the RI approximation. To reach this level of theory, a benchmark was made comparing the performance of ten selected DFAs, where the results of this study can be found in the supplementary material.

Since some molecules in the catalytic cycle are non-rigid, a conformational analysis using CREST software [36] was performed prior to DFT geometry optimization and subsequent frequency calculation. The intermediaries Int3, Int6a, Int7a (Fig. 2) and the first monomer of the polymer produced in the reaction were submitted to this analysis and the structure with the lowest energy was taken as the initial structure for the DFT calculation.
Conformational analysis and thermal corrections for the DFT calculations were performed at 393.15 K, the temperature commonly held in experiments in analogous systems. The transition states were identified as having only one imaginary eigenvalue of the hessian and confirmed by the IRC algorithm [22].

The final Gibbs free energy ($G$) for each molecule was calculated using the expression:

$$G = E_{\text{elec}} + G_{\text{corr}} + \Delta G_{\text{solv}}^o$$  \hspace{1cm} (1)

where $E_{\text{elec}}$ is the electronic energy of the molecule at the BP86-D3(BJ)/def2-TZVP/SMD level of theory, the $G_{\text{corr}}$ is the thermal corrections from the frequency calculations at the BP86-D3(BJ)/def2-SVP/SMD level of theory and $\Delta G_{\text{solv}}^o$ is the correction to bring the molecules from the gas phase to solution at a concentration of 1 mol·L$^{-1}$ in which the calculated value for 393.15 K is 10.5 kJ·mol$^{-1}$.

QTAIM and ELF calculations and plots were performed using Multiwfn 3.8 software [27]. The NCI index analysis was performed using the NCIPLOT4 software [7]. Structure images were generated using ChimeraX software [18, 34] along with SEQCROW [21, 38] and in VMD 1.9.4a55 software [2].

**Results and discussion**

**Catalytic cycle**

In this article, two main products have their reaction mechanisms considered according to the experimental results on analogous systems [9, 13, 35]: (i) the catalytic cycle of poly(cyclohexene carbonate) formation (represented in Fig. 2 as the green path); and (ii) the catalytic cycle of cis-cyclohexene carbonate formation (represented as the orange path in Fig. 2). Both catalytic cycles have common steps that are represented as the black path, which comprehends the formation of intermediaries 1 (Int1), 2 (Int2), 3 (Int3) and 4 (Int4).
The first step of the reaction is due to the coordination of a CHO molecule with the catalyst, which forms Int1; after the formation of Int1, Int2 is formed through TS1 by opening the CHO epoxide ring. With the coordination of CO₂ in M₁ in Int2, Int3 is formed, subsequently forming Int4 by a nucleophilic attack of the oxygen bonded to M₂ in the CO₂ carbon atom passing through TS2. Up to this point, the reaction could take two different paths, forming the poly(cyclohexene carbonate) or cis-cyclohexene carbonate. The formation of the poly(cyclohexene carbonate) occurs by first coordinat- ing one more molecule of CHO, forming intermediary 5a (Int5a), and next forming intermediary 6a (Int6a) via a second CHO epoxide ring opening reaction passing through transition state 3a (TS3a), beginning the polymer propagation. Thus, to produce more monomers of the polymer, more molecules of CHO coordinate to M₁, subsequently reacting to open the CHO epoxide ring. In this work we restricted ourselves to only one propagation step since other propagation steps are similar to the first one. Finally, we proposed a termination step to the reaction in which one acetic acid molecule coordinates to M₂ forming the intermediary 7a (Int7a), and after a proton transfer reaction through transition state 4a (TS4a) forming the intermediary 8a (Int8a), eventually regenerating the catalyst and releasing the first monomer of poly(cyclohexene carbonate).

The formation of cis-cyclohexene carbonate proceeds by, firstly, a geometrical rearrangement of Int4a, forming thus the intermediary 5b (Int5b). After, by a backbiting reaction, the intermediary 6b (Int6b) is formed passing through the transition state 3b (TS3b). Finally, the catalyst is regenerated and the cis-cyclohexene carbonate molecule is released.

**Comparison between MgMg, ZnMg, MgZn and ZnZn energetic profiles**

The energetic profile for the MgMg, ZnMg, MgZn and ZnZn systems is represented in Fig. 3. As can be seen, the opening of the epoxide ring of the CHO molecule is a step in which all systems have similar energies and, on the other hand, the nucleophilic attack on the CO₂ carbon atom occurs with different energetic barriers in which the trends of the barriers are inversed in the second step of the reaction. A remarkable feature of the four catalytic systems is that all considered barriers are feasible to take place in the given temperature, which implies that the modeled catalytic systems determine only how fast the reaction could occur (for a further...
discussion on the energetic barriers in the modeled conditions, see the section S2 of the Supplementary Information).

The transition states 1 and 2 for the MgMg, ZnMg, MgZn and ZnZn systems are shown in Fig. 4. When analyzing the transition state structures, one can see that, especially for TS1, the structures are very similar, which is also reflected in the energetics of those molecules, as shown in Fig. 3. On the other hand, the structures for TS2 differ in two groups, in which the transition states of the molecules where the oxygen atom attacking CO₂ is bonded to Mg are earlier transition states than those bonded to Zn.

Taking the energetics from the intermediary 1 (local minimum) to the energetics of the transition states, the two main barriers of this part of the catalytic cycle can be determined: (i) the barrier to reach TS1 from Int1 (ΔG₁); and (ii) the barrier from Int1 to TS2 (ΔG₂). Taking the Boltzmann weight ratio \( p_2/p_1 = e^{-(ΔG_2-ΔG_1)/RT} \), the relative populations of each transition states can be calculated. This ratio is important to show how fast the reaction would proceed in the nucleophilic attack step on CO₂ compared to the opening of the epoxide ring of the CHO molecule because the barriers for the first part of the reaction are close to each other, and thus the second step of the reaction determines the best catalytic system. In Table 1 the calculated values of ΔG₁, ΔG₂, and \( p_2/p_1 \) are shown.

The values shown in Table 1 show that although the ZnMg system has the second highest value ΔG₁, ΔG₂ compensates by providing a faster reaction than the other systems, as can be seen from the relative populations of \( p_2/p_1 \). The general trend for the systems is ΔG₁ < ΔG₂ for systems with Mg at M₁ position and ΔG₂ < ΔG₁ for systems with Zn at M₁.

**Topological analysis**

Once the TS2 presented such large difference between activation energies for distinct combinations of M₁-M₂, it was performed an AIM analysis of TS2 and its previous intermediate (Int3) in order to evaluate the effect of metal changes (M₁ and M₂) in the strength of some highlighted chemical bonds (or interactions) beyond its influence on the reactivity.

| Catalytic system | ΔG₁ / kJ·mol⁻¹ | ΔG₂ / kJ·mol⁻¹ | \( p_2/p_1 \) |
|------------------|----------------|----------------|--------------|
| MgMg             | 62.0           | 73.6           | 2.88 × 10⁻²  |
| ZnMg             | 68.0           | 40.2           | 4.94 × 10³  |
| MgZn             | 58.7           | 90.5           | 5.96 × 10⁻⁵ |
| ZnZn             | 69.0           | 58.7           | 2.34 × 10¹  |

Fig. 4 Transition states 1 and 2 for the MgMg, ZnMg, MgZn and ZnZn systems. Golden bonds are those formed or broken in the reaction step, in which the bond lengths are given in angstroms.
of such systems. The quantum theory of atoms in molecules (QTAIM) was developed by Richard Bader [3, 4] and has been widely applied in the evaluation and characterization of chemical bonds and noncovalent interactions [26, 29]. This theory is based on the topological evaluation of the electronic density $\rho(r)$ to characterize the atoms in the properties of the molecules and their interactions. In broad terms, a chemical bond (or an interaction between atoms) can be investigated through the evaluation of its AIM properties at its Bond Critical Points (BCPs). The BCP is a critical point formed by the encounter of vector path lines of the electronic density gradient $\nabla^2 \rho_{CP}$ that come from two distinct attractors (commonly atoms in a molecule). These path lines that connect two attractors through the same BCP are called Bond Path (BP). The presence of a BP connecting two attractors between a BCP features the presence of a chemical bond or a noncovalent interaction between them. The strength of such interactions can be estimated through the AIM properties at its respective BCP.

The AIM molecular graphs of Int3 and TS2 (MgMg, ZnMg, MgZn, and ZnZn, respectively) revealed several covalent and noncovalent interactions between catalysts and substrates (Figs. 5 and 6). Some interactions in these systems were highlighted to evaluate their AIM properties in detail, and the main interactions are displayed in Tables 2 and 3. The AIM properties for all the BCPs studied are shown in Tables S5–S12.

In general, the AIM analysis of Int3 and TS2 in the MgMg, ZnMg, MgZn, and ZnZn systems shows that Zn atoms have stronger interactions with O and N atoms (from the ligand). The electronic density $\rho(r)$ values of Zn-O and Zn-N bonds for Int3 and TS2 ranging between 0.05 and 0.07 $e/\text{Bohr}^3$ (BCPs for MgMg, BCPs for MgZn, BCPs for ZnMg, and BCPs for ZnZn) that

![Int3-MgMg](image1)
![Int3-ZnMg](image2)
![Int3-MgZn](image3)
![Int3-ZnZn](image4)

Fig. 5 AIM molecular graphs for Int3 in the MgMg, ZnMg, MgZn and ZnZn systems. Other visualization angles can be found in the supplementary material.
are higher than equivalent $\rho(\tau)$ values for Mg-O and Mg-N bonds which ranged between 0.03 and 0.05 ($e$/Bohr$^3$) (BCPs f, g, h, i, j, k, l, and m for MgMg, BCPs f, k, l, and m for ZnMg, and BCPs f, g, h, and i for MgZn) as can be verified at Tables S5–S12. In addition to that, the Zn-O and Zn-N bonds showed $\|V_{cr}\|/G_{cr} > 1$, which indicates that these interactions are covalent [16], while the Mg-O and Mg-N bonds showed $\|V_{cr}\|/G_{cr} < 1$, which indicates that these interactions are noncovalent. This behavior demonstrates that Zn atoms interact with the ligand more strongly than Mg atoms, and the strength of such interactions is reflected in the stability of the complexes and their reactivity.

The O-M$_2$ interaction between M$_2$ and O atoms of the CHO molecule (BCP a) was verified to be stronger when M$_2$=Zn ($\rho_{CP}$ about 0.097 ($e$/Bohr$^3$) for Int3 and $\rho_{CP}$ about 0.075 ($e$/Bohr$^3$) for TS2) than when M$_2$=Mg ($\rho_{CP}$ about 0.057 ($e$/Bohr$^3$) for Int3 and $\rho_{CP}$ about 0.05 ($e$/Bohr$^3$) for TS2). Additionally, the interaction O-M$_2$ with Zn showed $\|V_{cr}\|/G_{cr} > 1$ (indicating covalence), whereas the interaction with Mg showed $\|V_{cr}\|/G_{cr} < 1$ (indicating noncovalence). The O-M$_2$ strength difference between Int3 and TS2 is substantially higher for Zn as M$_2$ than for Mg (that barely had the strength of its O-M$_2$ interaction changed).

Besides that, the interaction M$_2$-CO$_2$ (BCP b) is stronger for Zn as M$_2$ then for Mg as M$_2$ either for CO$_2$ adsorbed on CHO (Int3) and for TS2 in which the O-C chemical bond between O of CHO and C of CO$_2$ is being formed. The O-CO$_2$ interaction is particularly stronger for Zn as M$_2$ ($\rho_{CP}$ is about 0.15 ($e$/Bohr$^3$) at BCP b for M$_2$=Zn) than for Mg ($\rho_{CP}$ about 0.08 ($e$/Bohr$^3$) at BCP b for M$_2$=Mg) in the TS2 structures. These results agree with the O-CO$_2$ bond distances and the ELF analysis presented in Fig. 7 that shows higher concentration of electron density in Mg than in Zn centers, and consequently, smaller interaction between the atoms of the forming bond. The strength of the O-CO$_2$ interaction directly affects the bond strength of C-O bonds.
of CO₂ (BCPs c and d), particularly in the TS2. The ρ_{CP} at the BCPs c and d in the TS2 is about 0.43 (e/Bohr³) when M₂=Mg and ρ_{CP} is about 0.42 (e/Bohr³) when M₂=Zn. Although this difference can seem low, by evaluating the difference between potential energy density (V_{CP}) at the BCPs c and d for M₂=Mg and M₂=Zn we can achieve a difference about 0.13 Hartree/Bohr³ (or 80 kcal/mol) between TS2 in the MgMg and in the MgZn systems that is substantial.

Finally, the AIM analysis indicates that the I-M₁ interaction is considerably stronger for M₁=Zn than for M₁=Mg.

### Table 2 QTAIM data for Int3 of the MgMg, ZnMg, MgZn and ZnZn systems

| Structure | Bond     | BCP | ρ_{CP} | (V²ρ_{CP}) | V_{CP} | (‖V_{CP}/G_{CP}‖) |
|-----------|----------|-----|--------|------------|--------|-----------------|
| MgMg      | M₂-O     | a   | 0.0559 | 0.4269     | -0.0869| 0.8979          |
| ZnMg      | M₂-O     | a   | 0.0579 | 0.4471     | -0.0915| 0.9003          |
| MgZn      | M₂-O     | a   | 0.0973 | 0.4954     | -0.1692| 1.1547          |
| ZnZn      | M₂-O     | a   | 0.0965 | 0.4909     | -0.1672| 1.1534          |
| MgMg      | M₂-CO₂   | b   | 0.0163 | 0.0632     | -0.0109| 0.8177          |
| ZnMg      | M₂-CO₂   | b   | 0.0141 | 0.0467     | -0.0082| 0.8275          |
| MgZn      | M₂-CO₂   | b   | 0.0192 | 0.0653     | -0.0124| 0.8651          |
| ZnZn      | M₂-CO₂   | b   | 0.0197 | 0.0664     | -0.0128| 0.8703          |
| MgMg      | C-O      | c   | 0.4428 | 0.0151     | -1.6248| 1.9954          |
| ZnMg      | C-O      | c   | 0.4484 | 0.0613     | -1.6647| 1.9818          |
| MgZn      | C-O      | c   | 0.4484 | 0.0682     | -1.6667| 1.9797          |
| ZnZn      | C-O      | c   | 0.4489 | 0.0725     | -1.6702| 1.9785          |
| MgMg      | C-O      | d   | 0.4576 | 0.1892     | -1.7395| 1.9471          |
| ZnMg      | C-O      | d   | 0.4493 | 0.0797     | -1.6727| 1.9764          |
| MgZn      | C-O      | d   | 0.4477 | 0.0556     | -1.6595| 1.9834          |
| ZnZn      | C-O      | d   | 0.447 | 0.0458    | -1.6539| 1.9862          |
| MgMg      | I-M₁     | e   | 0.0191 | 0.0566     | -0.0147| 1.0202          |
| ZnMg      | I-M₁     | e   | 0.0497 | 0.0901     | -0.0422| 1.3035          |
| MgZn      | I-M₁     | e   | 0.0226 | 0.0706     | -0.0183| 1.0176          |
| ZnZn      | I-M₁     | e   | 0.0461 | 0.082     | -0.0378| 1.2962          |

### Table 3 QTAIM data for TS2 of the MgMg, ZnMg, MgZn and ZnZn systems

| Structure | Bond     | BCP | ρ_{CP} | (V²ρ_{CP}) | V_{CP} | (‖V_{CP}/G_{CP}‖) |
|-----------|----------|-----|--------|------------|--------|-----------------|
| MgMg      | M₂-O     | a   | 0.0501 | 0.3688     | -0.0733| 0.8859          |
| ZnMg      | M₂-O     | a   | 0.0493 | 0.3607     | -0.0715| 0.8844          |
| MgZn      | M₂-O     | a   | 0.0745 | 0.3712     | -0.1158| 1.1104          |
| ZnZn      | M₂-O     | a   | 0.0744 | 0.3698     | -0.1155| 1.1107          |
| MgMg      | M₂-CO₂   | b   | 0.0824 | 0.1099     | -0.0718| 1.4464          |
| ZnMg      | M₂-CO₂   | b   | 0.0841 | 0.1087     | -0.0737| 1.4611          |
| MgZn      | M₂-CO₂   | b   | 0.1513 | -0.0156    | -0.1704| 2.047           |
| ZnZn      | M₂-CO₂   | b   | 0.1489 | -0.008     | -0.166 | 2.0243          |
| MgMg      | C-O      | c   | 0.4266 | -0.2272    | -1.499 | 2.0788          |
| ZnMg      | C-O      | c   | 0.4268 | -0.2283    | -1.4999| 2.0791          |
| MgZn      | C-O      | c   | 0.4108 | -0.4663    | -1.3679| 2.1863          |
| ZnZn      | C-O      | c   | 0.4121 | -0.4542    | -1.3771| 2.1797          |
| MgMg      | C-O      | d   | 0.4304 | -0.1605    | -1.5319| 2.0538          |
| ZnMg      | C-O      | d   | 0.4295 | -0.1715    | -1.5251| 2.0579          |
| MgZn      | C-O      | d   | 0.4178 | -0.3672    | -1.4249| 2.1377          |
| ZnZn      | C-O      | d   | 0.4177 | -0.3652    | -1.4247| 2.1369          |
| MgMg      | I-M₁     | e   | 0.0023 | 0.0721     | -0.0188| 1.0204          |
| ZnMg      | I-M₁     | e   | 0.0468 | 0.0828     | -0.0384| 1.3             |
| MgZn      | I-M₁     | e   | 0.0227 | 0.071     | -0.0184| 1.0174          |
| ZnZn      | I-M₁     | e   | 0.0466 | 0.0832     | -0.0383| 1.2963          |
and this interaction contributes to the stabilization of Int3 and TS2 in the ZnMg and ZnZn systems. This behavior agrees with NCI finds that showed stronger interactions between 1-Zn than 1-Mg as can be verified in Fig. 8 and helps to understand its stabilization. Meanwhile, the stability exchange between ZnMg and ZnZn in TS2 could be related to the energetic balance between the two half-broken strong C-O bonds (BCPs c and d) to make a new single O-C bond (BCP b). The noncovalent interactions (presented in Fig. 8) between catalyst, CHO and CO2 showed weak in comparison to the interactions highlighted and should not had great role on the stabilization of systems. The AIM and NCI analysis demonstrated that the interaction between Zn and I stabilizes the system. Beyond that, the Mg as M2 favors the reaction because low O-M2 interaction strength and the slightly difference between O-CO2 interactions strength for Int3 and TS2 which reflects on a lower difference between Int3 and TS2 and a lower activation barrier, which also can be observed by the results of the ASM analysis presented in the Supplementary Information. Such synergy between M1=Zn and M2=Mg make the ZnMg a better candidate to catalyze this reaction, as verified through the other analyzes.

ZnMg full energetic profile

The full catalytic energetic profile of the ZnMg system is presented in Fig. 9. As expected by the experimental results [13], the formation of the first monomer of poly(cyclonexene carbonate) is both a thermodynamic and a kinetic product. An important feature of the energetic profile is that the steps that involve the opening of the CHO epoxide ring have larger barriers compared to the reaction with CO2, especially the opening of the first CHO epoxide ring, that is, $\Delta G^\ddagger_{TS1}$ configures the highest barrier to polymer formation. This trend of opening the first ring being the most energetic step in the reaction is in agreement with the experiments [12] and can be explained as being more energetic demanding than the $\Delta G^\ddagger_{TS3a}$ because the TS3a is more stabilized by the term $T\Delta S$ due to the higher number of degrees of freedom than TS1. The termination step proposed for this reaction seems to be a good suggestion because $\Delta G^\ddagger_{TS4a}$ is a feasible barrier and also because it configures an irreversible step, as there is no documented expressive formation of side products from the polymer monomers.

Fig. 7 ELF plots for Int3, TS2, and Int4 in the ZnMg and MgZn systems. Length units are given in angstrom. ELF analysis was plotted only around CO2, the O atom that attacks the CO2 C atom and M2, where the complete plot can be found in the supplementary material.
Fig. 8 Noncovalent interaction plots for TS2 in the MgMg, ZnMg, MgZn and ZnZn systems.

Fig. 9 Full energetic profile for the ZnMg system. In black, the common steps between both products are represented, in which the energetics for the formation of the first monomer of poly(cyclohexene carbonate) are represented in green, and the energetics for the formation of cis-cyclohexene carbonate are represented in orange. Calculations at the BP86-D3(BJ)/def2-TZVP/SMD//BP86-D3(BJ)/def2-SVP/SMD level of theory.
The backbiting reaction occurs first by the formation of intermediary 5b (Int5b) which is more favorable than intermediary 5a (Int5a); however, $\Delta G^\ddagger_{TS5b}$ is 22.6 kJ mol$^{-1}$ greater than $\Delta G^\ddagger_{TS5a}$ and becomes the determining step of the formation of cis-cyclohexene carbonate. Since the barrier to TS3b is overcome, the formation of intermediary 6b (Int6b) is favorable and, like in the termination step of the polymerization reaction, the formation of Int6b is an irreversible step in the reaction. A notable characteristic of this path is that Int6b is more stable than the formation of the reaction product and the regeneration of the catalyst. Once TS3b became the rate-determinant step of the cyclohexene carbonate formation it was performed AIM and NCI analysis of TS3a and TS3b to investigate the influence of covalent and noncovalent interactions on their energetic differences. The AIM analysis (Table S13 and Figure S29) demonstrated that the interactions between the substrate and the metals (Zn and Mg, respectively) through the BCPs a and e (interactions M$_2$-O and M$_1$-O, respectively) are stronger for TS3a ($\rho_{CP} = 0.038$ e/Bohr$^3$ and $\rho_{CP} = 0.079$ e/Bohr$^3$, respectively) than TS3b ($\rho_{CP} = 0.032$ e/Bohr$^3$ and $\rho_{CP} = 0.066$ e/Bohr$^3$, respectively) while the interaction regarding the bond in formation (BCP b, interaction O-C) for TS3a ($\rho_{CP} = 0.054$ e/Bohr$^3$) is weaker than for TS3b ($\rho_{CP} = 0.068$ e/Bohr$^3$). In addition to this, the NCI analysis (Figure S30) indicated the presence of stronger repulsive interactions in the new ring formation in the TS3b compared to the ring opening in the TS3a. These repulsive interactions, together with the weaker interactions between substrate and metals revealed by the AIM analysis, should be related to the higher energy of TS3b regarding TS3a. This behavior indicates that the interactions between substrate and catalyst can affect the energetic profile of the reaction. Therefore, better catalysts can be designed by understanding these interactions to optimize them employing different substituents to tune the interaction between metal and substrate molecules.

In summary, the reaction catalyzed by the ZnMg system proceeds with the formation of the first monomer of poly(cyclohexene carbonate) because this product is more stable than the cis-cyclohexene carbonate and also because since the reaction reaches Int4, passing through TS3a is faster than passing through TS3b, although Int5b is more stable than Int5a. A note about both paths is that all involved barriers are feasible to take place under experimental conditions; however, a key point, especially for path A, is that the more monomers are added to the substrate, the more the $T \Delta S$ term in $\Delta G$ contributes to stabilizing the product, and consequently, the polymer formation establishes as the most favorable product.

Taking into account the other three systems studied in this work and the reactivity presented up to the formation of Int4, the features of the energetic trend presented to the ZnMg systems would be similar, especially in the ZnZn system. However, in a system having both the ZnMg and the MgZn catalysts, the preferable route would be the reaction being catalyzed by ZnMg system because of the faster passage of this catalyst through TS2.

Conclusions

The reaction mechanism of the ring opening and copolymerization of CHO and CO$_2$ was studied at the BP86-D3(BJ)/def2-TZVP/SMD//BP86-D3(BJ)/def2-SVP/SMD level of theory for the MgMg, ZnMg, MgZn and ZnZn systems using a model system. The characteristic that makes the ZnMg catalyst better than other studied catalysts is that the ratio $r_p/r_i$ is smaller for this system than for the other ones, and consequently, in reaction media that initially contained the ZnMg and MgZn system, the most probable catalyst that acts in the reaction is ZnMg. The metal in position 2 has a key role in CO$_2$ activation since this metal influences directly the electron density of the oxygen atom that is attacking CO$_2$ carbon atom; the metal 1, on the other hand, works in the stabilization of Int2, and therefore the energetic demand to distort both Int2 and CO$_2$ to the geometry of TS2.

Poly(cyclohexene carbonate) formation involves four transition states, in which the opening of the CHO epoxide ring that passes through the TS1 is the bottleneck of the reaction, especially for ZnMg and ZnZn systems that share similar reactivities up to CO$_2$ activation. Already at the formation of the first monomer of poly(cyclohexene carbonate) we could observe that this is the most preferable product in the reaction and the main factor that influences in the formation of cis-cyclohexene carbonate is the barrier to overcome the TS3b. One point that is still unclear in the studied systems is how the stereoselectivity of the polymer produced is controlled in the reactions catalyzed by the studied bimetallic catalysts. Reddi and Cramer [37] have recently studied the ROCOP of CHO and CO$_2$ catalyzed by an indium(III) phosphasalen catalyst and described the intricacies that promote RR as the preferred product in the reaction. Therefore, we believe that promoting a better understanding of the features that promote possible poly(cyclohexene carbonate) enantiomers would be of great importance in rationalizing the stereochemistry of this polymer.

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Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were
performed by Lucas W. de Lima, Sara Figueirêdo de Alcântara Morais and Atualpa A.C. Braga. The first draft of the manuscript was written by Lucas W. de Lima and Sara Figueirêdo de Alcântara Morais, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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**Code and data availability** Inputs and outputs files of the calculations presented in the article are available in ioChem-BD and NOMAD repositories. The Python script used to perform ASM calculations is available in GitHub repository.

**Declarations**

**Conflict of interest** The authors declare no competing interests.

**References**

1. Eichkorn K, Teutler O, Öhm H, Häser M, Ahlrichs R (1995) Auxiliary basis sets to approximate Coulomb potentials. Chem Phys Lett 240(4):283–290. https://doi.org/10.1016/0009-2614(95)00621-A

2. Humphrey W, Dalke A, Schulten K (1996) VMD: Visual molecular dynamics. J Mol Graph 14(1):33–38. https://doi.org/10.1016/0263-7855(96)00018-5

3. Bader RFW (1994) Atoms in Molecules: A Quantum Theory. International series of monographs on chemistry. Claredon Press, Oxford

4. Bader RFW (1991) A quantum theory of molecular structure and its applications. Chem Rev 91(5):893–928. https://doi.org/10.1021/cr00005a013

5. Baerends E, Ellis D, Ros P (1973) Self-consistent molecular Hartree-Fock-Slater I. The computational procedure. Chem Phys 2(1):41–51. https://doi.org/10.1016/0301-0104(73)80059-X

6. Becker AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 38:3098–3100. https://doi.org/10.1103/PhysRevA.38.3098

7. Boto RA, Pecci F, Laplaza R, Quan C, Carbone A, Piqueul MP, Maday Y, Contreras-Garcia J (2020) NCIPLOT4: Fast, Robust, and Quantitative Analysis of Noncovalent Interactions. J Chem Theory Comput 16(7):4150–4158. https://doi.org/10.1021/acs.jctc.0c00063

8. Buchard A, Kember MR, Sandeman KG, Williams CK (2011) A bimetallic iron(III) catalyst for CO2/epoxide coupling. Chem Commun 47:212–214. https://doi.org/10.1039/COC02205E

9. Buchard A, Jutz F, Kember MR, White AJP, Rzepa HS, Williams CK (2012) Experimental and Computational Investigation of the Mechanism of Carbon Dioxide/Cyclohexene Oxide Copolymerization Using a Di锌c Catalyst. Macromolecules 45(17):6781–6795. https://doi.org/10.1021/ma300830b

10. Burkart MD, Hazari N, Tway CL, Zeitler EL (2019) Opportunities and Challenges for Catalysis in Carbon Dioxide Utilization. ACS Catal 9(9):7937–7956. https://doi.org/10.1021/acscatal.9b02113

11. Campos J (2020) Bimetallic cooperation across the periodic table. Nat Rev Chem 4:696–702. https://doi.org/10.1038/s41570-020-00226-5

12. Deacy A, Kilpatrick A, Regoutz A, Williams CK (2020) Understanding metal synergy in heterodinuclear catalysts for the copolymerization of CO2 and epoxides. Nat Chem 12(4):372–380. https://doi.org/10.1038/s41577-020-0450-3

13. Deacy AC, Durr CB, Garden JA, White AJP, Williams CK (2018) Groups 1, 2 and Zn(II) Heterodinuclear Catalysts for Epoxide/CO2 Ring-Opening Copolymerization. Inorg Chem 57(24):15575–15583. https://doi.org/10.1021/acs.inorgchem.8b02923

14. Dunlap BI, Connolly JWD, Sabin JR (1979) On first-row diatomic molecules and local density models. J Chem Phys 71(12):4993–4999. https://doi.org/10.1063/1.438313

15. Eichkorn K, Weigend F, Teutler O, Ahlrichs R (1997) Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. Theor Chem Acc 97:119–124. https://doi.org/10.1007/s002100050244

16. Espinosa E, Alkorta I, Elguero J, Molins E (2002) From weak to strong interactions: A comprehensive analysis of the topology of the electronic and energetical properties of the electron density distribution involving X-HF-Y systems. J Chem Phys 117(12):5529–5542. https://doi.org/10.1063/1.1501133

17. Garden J, White A, Williams CK (2017) Heterodinuclear titanium/zinc catalysis: synthesis, characterization and activity for CO2/epoxide copolymerization and cyclic ester polymerization. Dalton Trans 46:2532–2541. https://doi.org/10.1039/C6DT04193K

18. Goddard TD, Huang CC, Elaine Meng EF, Pettersen C, Couch GS, Morris JH, Ferrin TE (2018) UCSF ChimeraX: Meeting modern challenges in visualization and analysis. Protein Sci 27(1):14–25. https://doi.org/10.1002/pro.3235

19. Grimme S, Ehrlich S, Goerigk L (2011) Effect of the damping function in dispersion corrected density functional theory. J Comput Chem 32(7):1456–1465. https://doi.org/10.1002/jcc.21759

20. Grimme S, Antony J, Ehrlich S, Krieg H (2010) A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J Chem Phys 132(15):154104. https://doi.org/10.1063/1.3382344

21. Ingman VM, Schaefer AJ, Andreola LR, Wheeler SE (2021) QChASM: Quantum chemistry automation and structure manipulation. WIREs Comput Mol Sci 11(4):e1510. https://doi.org/10.1002/wcms.1510

22. Ishida K, Morokuma K, Komornicki A (1977) The intrinsic reaction coordinate. An ab initio calculation for HNC→HCN and H+CH4→CH4+H. J Chem Phys 66(5):2153–2156. 10.1063/1.434152

23. Kember MR, White AJP, Williams CK (2010) Highly Active Di- and Trinuclear Cobalt Catalysts for the Copolymerization of CHO and CO2 at Atmospheric Pressure. Macromolecules 43(5):2291–2298. https://doi.org/10.1021/ma902582m

24. Kendall RA, Früchtl HA (1997) The impact of the resolution of the identity approximate integral method on modern ab initio algorithm development. Theor Chem Acc 97:158–163. https://doi.org/10.1007/s002100050249

25. Klaus S, Lehenmeier MW, Anderson CE, Rieger B (2011) Recent advances in CO2/epoxide copolymerization-New strategies and cooperative mechanisms. Coord Chem Rev 255(13):1460–1479. https://doi.org/10.1016/j.ccr.2010.12.002
26. Kumar PSV, Raghavendra V (2016) Bader’s Theory of Atoms in Molecules (AIM) and its Applications to Chemical Bonding. J Chem Sci 128(10):1527–1536. https://doi.org/10.1007/s12039-016-1172-3

27. Lu T, Chen F (2012) Multiwfn: A multifunctional wavefunction analyzer. J Comput Chem 33(5):580–592. https://doi.org/10.1002/jcc.22885

28. Marenich AV, Cramer CJ, Truhlar DG (2009) Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. J Phys Chem B 113(18):6378–6396. https://doi.org/10.1021/jp810292n (PMID: 19366259)

29. Mounssef B Jr, de Alcântara Morais SF, de Lima Batista AP, de Lima LW, Braga AAC (2021) DFT study of H2 adsorption at a Cu-SSZ-13 zeolite: a cluster approach. Phys Chem Chem Phys 23:9980–9990. https://doi.org/10.1039/D1CP0422K

30. Neese F (2012) The ORCA program system. WIREs Comput Mol Sci 2(1):73–78. https://doi.org/10.1002/wcms.81

31. Neese F (2018) Software update: the ORCA program system, version 4.0. WIREs Comput Mol Sci 8(1). https://doi.org/10.1002/wcms.1327

32. Perdew JP (1986) Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Phys Rev B 33:8822–8824. https://doi.org/10.1103/PhysRevB.33.8822

33. Perdew JP (1986) Erratum: Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Phys Rev B 34:7406. https://doi.org/10.1103/PhysRevB.34.7406

34. Pettersen EF, Goddard TD, Huang CC, Meng EC, Couch GS, Croll TI, Morris JH, Ferrin TE (2021) UCSF ChimeraX: Structure visualization for researchers, educators, and developers. Protein Sci 30(1):70–82. https://doi.org/10.1002/pro.3943

35. Plajer AJ, Williams CK (2022) Heterocycle/Heteroallene Ring-Opening Copolymerization: Selective Catalysis Delivering Alternating Copolymers. Angew Chem Int Ed 61(1):e202104495. https://doi.org/10.1002/anie.202104495

36. Pracht P, Bohle F, Grimme S (2020) Automated exploration of the low-energy chemical space with fast quantum chemical methods. Phys Chem Chem Phys 22:7169–7192. https://doi.org/10.1039/C9CP06869D

37. Reddy Y, Cramer CJ (2021) Mechanism and Design Principles for Controlling Stereoselectivity in the Copolymerization of CO2/Cyclohexene Oxide by Indium(III) Phosphasalen Catalysts. ACS Catal 11(24):15244–15251. https://doi.org/10.1021/acscatal.1c04619

38. Schaefer AJ, Ingman VM, Wheeler SE (2021) SEQCROW: A ChimeraX bundle to facilitate quantum chemical applications to complex molecular systems. J Comput Chem 42(24):1750–1754. https://doi.org/10.1002/jcc.27600

39. Service RF (2004) The Carbon Cunundrum. Science 305(5686):962–963. https://doi.org/10.1126/science.305.5686.962

40. Van Alesonoy C (1988) Ab initio calculations on large molecules: The multiplicative integral approximation. J Comput Chem 9(6):620–626. https://doi.org/10.1002/jcc.26700

41. Weigend F (2006) Accurate Coulomb-fitting basis sets for H to Rn. Phys Chem Chem Phys 8:1057–1065. https://doi.org/10.1039/B515623H

42. Weigend F, Ahlrichs R (2005) Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Phys Chem Chem Phys 7:3297–3305. https://doi.org/10.1039/B508541A

43. Zhu Y, Romain C, Williams CK (2016) Sustainable polymers from renewable resources. Nature 540(7633):354–362. https://doi.org/10.1038/nature21001

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