Zeolite-encapsulated single-atom catalysts for efficient CO$_2$ conversion

Gerard Alonso$^{a,b}$, Estefanía López$^b$, Fermín Huarte-Larrañaga$^a$, Ramón Sayós$^a$, Hector Prats$^{c,*}$, Pablo Gamallo$^{a, *}$

$^a$ Universitat de Barcelona and Institut de Química Teòrica i Computacional (IQTC), C / Martí i Franqués 1, 08028, Barcelona, Spain
$^b$ Departamento de Ingeniería Química, Universidad de Concepción, C / Edmundo Larenas 219, 4030000, Concepción, Chile
$^c$ Department of Chemical Engineering, University College London, Roberts Building, Torrington Place, London, WC1E 7JE, UK

A R T I C L E   I N F O
Keywords:
Single-atom catalysts
Zeolites
MFI
Heterogeneous catalysis
CO$_2$ conversion
Transition metals
Density functional theory

A B S T R A C T
Zeolite-supported single-atom catalysts (SACs) have emerged as a novel class of cheap and tuneable catalysts that can exhibit high activity, selectivity and stability. In this work, we conduct an extensive screening by means of density functional theory calculations to determine the usefulness of 3d, 4d and 5d transition metal (TM) SACs-supported in MFI-type Silicalite-1 zeolite for CO$_2$ conversion. Two reaction mechanisms are considered, namely the redox – direct CO$_2$ dissociation – and associative – hydrogen-assisted CO$_2$ dissociation – mechanisms. Early TM SACs exhibit the lowest energy barriers, which follow the redox mechanism. These energy barriers raise when going right in the periodic table up to group 10, where they become prohibitive and the associative mechanism should dominate. By also considering their resistance to aggregation, we support the use of Sc, Y, La, Ru, Rh, Ni, Pd and Pt as potentially active and stable catalysts for CO$_2$ conversion, given their low energy barriers and strong interaction with the zeolite framework.

1. Introduction
Proper control of atmospheric CO$_2$ content to fight climate change is one of the central challenges of mankind. Anthropogenic CO$_2$ is mainly produced via combustion of fossil fuels and is currently producing a notable environmental impact, such as in global warming [1]. Fortunately, CO$_2$ can be captured and transformed into other valuable chemicals (e.g., formaldehyde, methane, methanol or bicarbonate, among others [2–6]) with the help of transition metal (TM)-based catalysts [7], mainly through Au, Pd, Cu, Ru, Ni, Pt, Pd, Rh or Fe [8–14]. However, since some of these TMs are expensive and scarce, it is still imperative to develop better catalysts to increase the efficiency and reduce the cost of the CO$_2$ conversion.

In the last few years, single-atom catalysts (SACs) finely dispersed into different supports have emerged as new promising materials for catalysis [15,16]. SACs aim to combine the large activity and selectivity of homogeneous catalysts but with the separation and reutilization capabilities of a heterogeneous catalyst [17,18]. Supported SACs have a higher activity/mass relationship due to a better metal utilization than nanoparticles, which makes them also more cost-efficient for catalysis. Some of the early successful reactions were carried out in oxide and graphene supported SACs including CO oxidation [19], water-gas shift reaction [20,21], hydroformylation of olefins [22] and methanol and benzene oxidations [23,24]. The great activity of SACs is correlated to their low coordination numbers, which means they can be partially deactivated if they diffuse through the support and aggregate forming nanoparticles. For this reason, it is not only important to find a good SAC for a given application, but it is also critical to disperse it into a support that can stabilize it (i.e., prevent the metal atoms from clustering). In that sense, many efforts are devoted to preventing SAC surface migration by depositing the TM in surface vacancies [25–28], or spatially confining them in microporous materials (e.g., zeolites or metal-organic frameworks) [29–32].

From all those promising supports, we have turned our attention to zeolites [33], where important successes were achieved in the last years by encapsulating different TM atoms in structures with different Si/Al ratio to carry out CO oxidation [34], methane conversion to higher hydrocarbons [35], to methanol and to acetic acid [36] or n-hexane isomerization [37], among others [16]. PD SACs were also anchored to mesoporous silica SBA-15 [38] and used to hydrogenate alkenes. Finally, Ru and Rh SACs were recently encapsulated in the fully silicated MFI structure (i.e., TM@Silicalite-1 or simply TM@S-1) [39,40] and the resulting catalysts were promising for H$_2$ production from ammonia borane hydrolysis and ammonia synthesis, respectively. The
encapsulation of metal atoms in zeolites requires a strict control of experimental conditions, since high pH and/or temperature might lead to particle aggregation [41]. Available synthesis techniques include direct synthesis from inorganic or ligand-assisted metal precursors, multistep post-synthesis encapsulation (e.g., two-step dry-gel-conversion) or ion-exchange followed by reduction, as described by Chai et al., [42]. From the very large number of potential SAC + support combinations, only less than 10 TMs have actually been synthesized as SACs. Such a small number evidences the need of a systematic screening for catalysts with large activity whilst still being stable at operative conditions. In a previous study [43], we computationally assessed the structure and stability of all period IV-VI TM SACs. Such a small number evidences the need of a systematic screening study and the large amount of possible reaction products, it was not feasible to build the full reaction profiles for each SAC. Instead, we focus on the first steps of CO₂ activation, which involve the adsorption of reactants (CO₂ and H₂), direct CO₂ dissociation through the redox mechanism (CO₂ → CO + O), H₂ dissociation (H₂ → H + H) and hydrogen-assisted CO₂ dissociation through the associative mechanism, either via formate (CO₂ + H → HCOO) or carbonyl (CO₂ + H → COOH) intermediates.

Herein, we evaluate the potential activity of this set of SACs for CO₂ conversion. Due to the large number of systems included in this screening study and the large amount of possible reaction products, it was not feasible to build the full reaction profiles for each SAC. Instead, we focus on the first steps of CO₂ activation, which involve the adsorption of reactants (CO₂ and H₂), direct CO₂ dissociation through the redox mechanism (CO₂ → CO + O), H₂ dissociation (H₂ → H + H) and hydrogen-assisted CO₂ dissociation through the associative mechanism, either via formate (CO₂ + H → HCOO) or carbonyl (CO₂ + H → COOH) intermediates.

Note that the experimental viability of TM @ S-1 synthesis was already proven for Rh@S-1 and Ru@S-1 [39,40], so the results from this study will serve to assess how adequate are those catalysts in comparison to other non-synthesized TM @ S-1 and for proposing novel catalysts capable of adsorbing and converting CO₂. The results obtained here will provide a solid theoretical background from which potential catalytic activity can be predicted, paving the road for further experimental and computational studies on this topic.

2. Computational details

The MFI Silicalite-1 has a microporous Si₉₀O₁₉₂ unit cell composed by SiO₄ tetrahedra (T) units positioned at 12 non-equivalent T sites (i.e., T₁-T₁₂). The framework O atoms are located at 26 distinct O sites (i.e., O₁ – O₂₆). This arrangement leads to a 3D pore system with straight ten-membered-ring (10-MR) channels in the [010] direction intersected by sinusoidal 10-MR channels in the [100] direction, as shown in Fig. 1. The most stable structures of each one of the 29 TM @ S-1 SACs were taken from our previous study [43]. In summary, we employed Density Functional Theory (DFT) calculations to find the most stable site to adsorb each TM in the pristine S-1 structure by optimizing the geometry of each TM placed in all possible non-equivalent positions of all pores. With this procedure, we located only 6 preferred sites in S-1 by the entire set of TM adatoms. Most TM atoms adsorb via van der Waals (vdW) interactions into the sinusoidal 10-MR channels at distances larger than 2.7 Å. Among all possible positions in these channels, only 3 specific adsorption sites are preferred by the TM atoms, which are denoted as Channel X (X=A, B or C) sites (see Fig. 1). The only exceptions are group 3 T Ms (i.e., Sc, Y and La), which prefer to adsorb in the middle of the quadrilaterals formed by two O₁₆ and two O₂₅ atoms (i.e., O₁₆(× 2) – O₂₅(× 2) site); Group 10 T Ms (i.e., Ni, Pd and Pt) and Ru atoms, which are found closely coordinated with O₁₈ and O₂₃ atoms (i.e., O₁₈ – O₂₃ site) and weakly coordinated to O₁₆(× 2); and finally, Rh atoms, which are located in the middle of the quadrilaterals formed by O₁₈, O₁₁, O₁₈ and O₂₆ atoms (i.e., O₁₈ – O₁₁ – O₁₈ – O₂₆ site). In all these systems the porous support provides protection against SAC sintering via 3D confinement, except in group 3 TMs where the S-1 also accepts part of their electron density changing their electronic structure. Notice that, Ru and Rh are the only TMs experimentally encapsulated in Silicalite-1, and their coordination according to EXAFS fittings agree with our DFT-based predictions, both suggesting TM coordination with four O atoms. However, DFT results slightly overestimates the average Ru – O distance (r (DFT) = 2.15 Å) by a 7% [40] and the Rh – O distance (r (DFT) = 2.40 Å) by a 18% [39] with differences in TM–O bonds lower than 0.01 Å between DFT and DFT-D3 geometries. For a more complete description of those sites, the reader is referred to the original work [43]. Additionally, images of each TM location are compiled in Fig. 1.

To be consistent with our previous study [43], the Vienna Ab Initio Simulation Package (VASP) [44] was used to perform all periodic DFT calculations by employing the Perdew-Burke-Ernzerhof [45] exchange-correlation functional, plus the Grimme D3 dispersion correction (PBE-D3) [46]. The valence electron density was expanded in a 600 eV kinetic energy plane-wave basis set, which gave total energy variations below 0.01 eV. The effect of core electrons on the valence electron density was accounted through the Projected Augmented Wave
and free energy barriers were calculated by correcting the respective indicated. Additionally, the Gibbs free energy of adsorption, reaction

\[ \Delta E_{\text{ads}} = E_{\text{SAC}} - E_{\text{g}} \]

(1)

where \( E_{\text{SAC}} \) is the total energy of adsorbed species in the TM@S-1 SAC, \( E_{\text{g}} \) is the energy of the clean SAC (i.e., the relaxed pristine TM@S-1 structure) and \( E_{\text{g}} \) is the energy of species \( i \) in gas-phase and in its ground electronic state. With this definition, negative values of \( \Delta E_{\text{ads}} \) indicate favorable adsorption. The latter term was calculated in a simulation cell with the same parameters than the TM@S-1 using only the \( \Gamma \)-point. The energy barriers (\( \Delta E^f \)) and reaction energies (\( \Delta E_r \)) were calculated as:

\[ \Delta E^f = E_{\text{TS-SAC}} - E_{\text{R-SAC}} \]

(2)

\[ \Delta E_r = E_{\text{F-SAC}} - E_{\text{R-SAC}} \]

(3)

where \( E_{\text{TS-SAC}} \) is the energy of the transition state (TS), \( E_{\text{R-SAC}} \) is the energy of the initial configuration (i.e., adsorbed reactants), and \( E_{\text{R-SAC}} \) the energy of final configuration (i.e., adsorbed products). All TSs were located by using the Climbing-Image Nudged Elastic Band (CI-NEB) method [49]. The initial guesses for the employed intermediate images were created through the Image Dependent Pair Potential (IDPP) interpolation procedure [50] as implemented in the Atomic Simulation Environment (ASE) [51]. All adsorption minima and TSs were characterized through frequency calculations by computing the elements of the Hessian matrix as finite differences of 0.03 Å length and considering the harmonic oscillator model for all degrees of freedom [52].

The most stable site for the adsorbed species was obtained by screening several initial geometries with different positions and orientations. The tolerance for the conjugate gradient algorithm to minimize its ground electronic state. With this definition, negative values of \( \Delta E_{\text{ads}} \) is calculated by

\[ \Delta E_{\text{ads}} = E_{\text{SAC}} - E_{\text{g}} \]

(1)

1.46 Å and the \( O - C - O \) angle is bent from 180° to 120° – 150°. This activated configuration leads to a significantly strong adsorption energy (i.e., \( \Delta E_{\text{ads}} < -1 \) eV). In general, the binding strength of \( CO_2 \) on the supported TMs decreases along a period and moving up along a group (Fig. 2a), with a limit on group 11 and 12 TMs, where \( CO_2 \) weakly physisorbs with no noticeable perturbation from its gas-phase geometry. Other exceptions are those TMs with semi-occupancy of \( d \) orbitals (i.e., \( Mn \) and \( Re \) with \( s^2d^3 \)) and group 4 TMs, where \( CO_2 \) does not have a stable configuration (i.e., \( Hf \)) or where it binds in a \( \eta (CO) \) configuration instead of \( \eta (CO) \) (i.e., \( Ti \) and \( Zr \)). Notice that, for \( Hf \), \( \Delta E_{\text{ads}} \) is calculated by considering \( O + CO \) as the adsorbed state.

During the adsorption process, there is a significant TM-to-\( CO_2 \) charge transfer, which is evidenced by the final oxidation state of the metal atom (i.e., \( Q_{\text{TM}} > 0 \)) and the negative net charge on \( CO_2 \), as shown...
in Fig. 2b. The atomic Bader charges on the TM atoms decrease along a period, which in part can be rationalized due to the higher electronegativity of the metal atom. On group 11 and 12 TMs, the charge transfer is negligible, due to the weak CO
2
activity of the metal atom. On group 11 and 12 TMs, the charge transfer -
Fig. 3. Characteristic reaction pathways for direct CO
2
 dissociation, H
2
 dissociation and H-assisted CO
2
 dissociation. Optimized geometries for the initial, transition and final states are shown in the left, middle and right panels, respectively. SiO
4
 units are represented by blue tetrahedra with yellow Si and red O atoms. TM atoms are shown either as cyan or purple spheres (consistent with the site colour coding presented in Fig. 1) and C, O and H are shown as brown, red and white spheres, respectively. All panels corresponding to the same reaction path share the same orientation, as shown by the lower-right hand axis where red, green and blue arrows represent the a, b and c directions, respectively.

It is worth noting that for TM SACs adsorbed very close to the S-1 zeolite wall (i.e., group 3, group 10, Ru and Rh SACs) the CO
2
 adsorption typically promotes a small surface reconstruction, where the TM + CO
2
 pair separates slightly from the zeolite wall to reduce the repulsive CO
2
–zeolite interactions. Similarly, the H~2~ adsorption only promotes a small surface reconstruction on top of Ni and Pd TM SACs due to the H~2~ smaller size and weaker H~2~–zeolite repulsion. However, the cleavage to H + H leads to an equivalent reconstruction of group 3, Rh and Pt TMs. For a more precise picture of the surface reconstruction the reader is referred to Section S4 of the SI, where the original TM@S-1 structure and the deformation caused by CO
2
/H~2~ is compiled for the full set of TMs. Also, all geometry files for each stationary point characterized in this work have been uploaded to a public repository (see Appendix A).

3.2. Redox mechanism

The redox mechanism involves the C–O bond breaking by direct CO
2
 dissociation to CO + O. The calculated reaction energies and energy barriers for this step are compiled in Fig. 2e–f and Table S1 in the SI. For the un-aided CO
2
 dissociation in the pristine S-1 with no TM, the weak interactions among the support, the reactants and the products lead to a gas-phase-like highly endoergic reaction with a prohibitive energy barrier (\(\Delta E^r > 6 \text{ eV}\)). However, the presence of single TM atoms stabilizes the reaction products, yielding to affordable reaction barriers and even barrierless dissociations in a few cases.

\(\Delta E\) and \(\Delta E^r\) follow a similar trend than the \(\Delta E_{\text{ads,CO}}\) along the periodic table, meaning that the reaction is more favourable in TM SACs from the bottom left of the periodic table and less favourable when moving right along a period and up along a group. As shown in Fig. 2e, the reaction is highly exoergic (i.e., high negative values up to –2.8 eV) for early TMs, and proceeds with very low reaction barriers (i.e., 11
TM$_1$@S-1 catalysts belonging to groups 3 – 8 break CO$_2$ with $\Delta E^r < 0.30$ eV, 5 of them with $\Delta E^r < 0.10$ eV). These values contrast with the typical $\Delta E^r$ ranging from 0.38 eV to 0.90 eV reported for other catalysts [58], such as flat metal surfaces [59–61] or supported metal clusters [62–64], placing many TM$_1$@S-1 from groups 3 – 8 as extremely active towards direct C – O bond cleavage. In those TMs, CO$_2$ is expected to be transformed via redox pathway, because it follows a single unimolecular step with a very low reaction energy barrier. In contrast, TM$_1$@S-1 of groups 10 – 12 are poor catalysts for the direct CO$_2$ dissociation, with prohibitive energy barriers due to their inability to stabilize the reaction products and their weak interaction with CO$_2$. This implies that hydrogen-assisted associative pathways could dominate in these cases.

As suggested by Pallasana and Neurock [65] and popularized by Norskov et al. [66], the correlation between reaction energies and energy barriers in heterogeneous catalysed reactions is expected to follow the Bronsted-Evans-Polanyi (BEP) relationship. Specifically, the transition state energy ($E_{TS}$) and the dissociative reaction energy ($E_d$) defined by Wang et al. [69] as Eqs. 4 and 5 (without ZPE) are used to compare with the universal BEP relation for extended TM surfaces.

\[
E_{TS} = E_{TS-SAC} - E_{SAC} - E_d
\]  

\[
E_d = E_{P-SAC} - E_{SAC} - E_d
\]

As mentioned above, many TMs exhibit extremely low reaction energy barriers to convert CO$_2$ through the redox pathway. Since the dissociation is a unimolecular step, it is not expected that bimolecular steps (such as hydrogenations in the associative pathway) will be kinetically relevant, even in the case of low energy barriers. For this reason, we have decided to consider this alternative pathway only in a subset of TM$_1$@S-1 in which the redox mechanism has a significant energy barrier. This includes the late TMs in group 10 (i.e., Ni, Pd and Pt), where CO$_2$ adsorbs strongly but it is hard to break, and also Ru and Rh, which have been already synthesized experimentally, proven to be highly active catalysts, and can dissociate H$_2$ spontaneously.

In those five TMs, CO$_2$ adsorbed as $\eta$(CO) can react with a coadsorbed H species by forming an O – H bond leading to the carboxyl intermediate (i.e., COOH), which is bonded to the TM via the C atom (see Fig. 3). Alternatively, the H atom can react with the C atom forming a C – H bond leading to the formate intermediate (i.e., HCOO), which is first produced in its monodentate configuration (m–HCOO), bonded to the metal through one of its O atoms. Then, m–HCOO rearranges itself leading to the lower energy bidentate configuration (b–HCOO), in which the formate is bonded to the metal through both its O atoms. The reaction energies and energy barriers for both pathways (plus the redox for comparison) are compiled in Fig. S4 and Table S3 in the SI. To compare those pathways in actual operative conditions, the Gibbs free energy diagrams at 600 K and 1 atm were built and shown in Fig. 5. To our knowledge, CO$_2$ conversion in TM$_1$@S-1 is currently not assessed experimentally, so those conditions were selected as they are generally used in similar systems [40,70] or other CO$_2$ conversion catalysts [71]. Finally, the geometry for each minimum and TS are shown in Section S4 of the SI.

### 3.3. Associative mechanism

As mentioned above, many TMs exhibit extremely low reaction energy barriers to convert CO$_2$ through the redox pathway. Since the dissociation is a unimolecular step, it is not expected that bimolecular steps (such as hydrogenations in the associative pathway) will be kinetically relevant, even in the case of low energy barriers. For this reason, we have decided to consider this alternative pathway only in a subset of TM$_1$@S-1 in which the redox mechanism has a significant energy barrier. This includes the late TMs in group 10 (i.e., Ni, Pd and Pt), where CO$_2$ adsorbs strongly but it is hard to break, and also Ru and Rh, which have been already synthesized experimentally, proven to be highly active catalysts, and can dissociate H$_2$ spontaneously.

In those five TMs, CO$_2$ adsorbed as $\eta$(CO) can react with a coadsorbed H species by forming an O – H bond leading to the carboxyl intermediate (i.e., COOH), which is bonded to the TM via the C atom (see Fig. 3). Alternatively, the H atom can react with the C atom forming a C – H bond leading to the formate intermediate (i.e., HCOO), which is first produced in its monodentate configuration (m–HCOO), bonded to the metal through one of its O atoms. Then, m–HCOO rearranges itself leading to the lower energy bidentate configuration (b–HCOO), in which the formate is bonded to the metal through both its O atoms. The reaction energies and energy barriers for both pathways (plus the redox for comparison) are compiled in Fig. S4 and Table S3 in the SI. To compare those pathways in actual operative conditions, the Gibbs free energy diagrams at 600 K and 1 atm were built and shown in Fig. 5. To our knowledge, CO$_2$ conversion in TM$_1$@S-1 is currently not assessed experimentally, so those conditions were selected as they are generally used in similar systems [40,70] or other CO$_2$ conversion catalysts [71]. Finally, the geometry for each minimum and TS are shown in Section S4 of the SI.

The present results suggest that CO$_2$ conversion steps on group 10 TMs (i.e., Ni, Pd and Pt) should follow the associative mechanism via COOH or HCOO intermediates, as the free energy barrier for their formation are much lower than for the direct CO$_2$ dissociation (Fig. 5). In the case of Ni, the HCOO pathway is much more favoured than the COOH pathway. However, after H$_2$ dissociation, the H + H recombination is barrierless, implying that the activity of the associative mechanism will be limited by the small amount of H species present in the catalyst. For Pd and Pt, the dissociation of H$_2$ is very favoured and there will be a strong competition between the HCOO and COOH pathways, as both exhibit similar free energy barriers. For this reason, kinetic modelling techniques such as kinetic Monte Carlo [61] or microkinetic modelling should be employed to truly identify which pathway is more dominant. However, developing an accurate model for the TM$_1$@S-1 catalysts requires further study due to their uncommon 3D morphology and is out of the scope for this work. Finally, we show that
Rh and Ru would follow the redox mechanism, since, apart from being unimolecular, have lower free energy barriers compared to COOH or HCOO associative pathways.

4. Conclusions

CO₂ adsorption and subsequent activation have been investigated by means of periodic DFT calculations for the full set of 3d, 4d, and 5d TM SACs supported on zeolite S-1, namely TM₁@S-1. The steps considered include adsorption and dissociation of CO₂ and H₂ species, as well as CO₂ reaction with adsorbed H to produce COOH or HCOO intermediates. The catalytic properties are mainly controlled by the encapsulated TM atoms, since CO₂ and H₂ interact very weakly with the S-1 framework structure. In general, CO₂ binds strongly to TM atoms and receives electron density from the TM, ending up being negatively charged. These effects are particularly strong for those TMs in the bottom left of the periodic table and become less pronounced when moving right along a period or up in a group. On the other hand, H₂ chemisorbs on TMs from groups 3, 4, 5, 9, 10 and Os with negligible charge transfer from the TM. Noticeably, TMs from groups 11 – 12 hardly interact with CO₂ and H₂, where both species are physisorbed. TMs in groups 3 – 9 exhibit very low energy barriers for direct CO₂ dissociation, suggesting that CO₂ conversion reactions on these SACs would follow the redox mechanism. However, the COOH—or HCOO—mediated associative mechanism is more favoured in group 10 TMs, according to the free energy profiles. Finally, we predict group 11 – 12 TMs SACs to have a very poor catalytic activity for CO₂ conversion, due to their weak interaction with CO₂ and H₂ as well as high energy barriers.

Combining the present results with the stability assessment of supported TM SACs in our previous contribution [43], we conclude that groups 3 and 10 TM SACs, as well as Rh₁@S-1 and Ru₁@S-1 are very promising candidates for CO₂ conversion reactions. All these catalysts exhibit low energy barriers and are predicted to have a strong resistance to aggregation/sintering due to their strong interactions with the zeolite wall. These results are in agreement with experimental observations stating that Ru and Rh were encapsulated in S-1 and used in different catalytic processes [39,40] with good stability and superior catalytic activity. With this contribution, we hope to narrow down the materials space for novel CO₂ conversion SACs and provide a solid theoretical background from which observed experimental features can be interpreted, understood, and discussed.

CRediT authorship contribution statement

Gerard Alonso: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. Estefanía López: Methodology, Investigation, Writing - review & editing. Fermín Huarte-Larranaga: Methodology, Investigation, Writing - review & editing. Ramón Sayos: Project administration, Funding acquisition, Writing - review & editing. Hector Prats: Conceptualization, Methodology, Formal analysis, Writing - review & editing. Pablo Gamallo: Supervision, Methodology, Investigation, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Support to this research is granted by the Spanish Ministry of Science, Innovation and Universities (Grants RTI2018-094757-B-I00, MCIU/AEI/FEDER, UE and MDM-2017-0767) and by the Generalitat de Catalunya (Grant 2017SGR0013 and P.G. Serra Hunter Associate Professorship). Authors thank to the Red Española de Supercomputación (RES) for the supercomputing time granted (QS-2021-1-0035 and QS-2020-3-0023).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jcou.2021.101777.

References

[1] C.P. Morice, J.J. Kennedy, N.A. Rayner, P.D. Jones, Quantifying uncertainties in global and regional temperature change using an ensemble of observational...


