Reply to: On the role of metal cations in CO2 electrocatalytic reduction

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Reply to: On the role of metal cations in CO_2 electroreduction reduction

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REPLYING TO: D. Le et al. *Nature Catalysis* https://doi.org/10.1038/s41929-022-00876-2 (2021)

In our recent publication[1], we demonstrate the absence of CO_2 electroreduction on copper, gold and silver electrodes without alkali metal cations in solution through unequivocal experimental evidence. Additionally, we propose a mechanism for CO_2 electroreduction in which the metal cation is key to stabilizing CO_2 adsorption, thus enabling its activation and reduction. This last finding is supported by ab initio molecular dynamics (AIMD) simulations on Au/solvent/cation/CO_2 supercells. In their Matters Arising[2], Le and Rahman point out a constraint included in our computational setup, suggesting that it may affect our main conclusions. We here confirm that, although our computational framework was minimal, it is robust enough to support the proposed mechanism and thus our main conclusions.

In our study[1], we carried out density functional theory (DFT) simulations to compare the thermodynamic, structural and electronic properties of an activated CO_2 molecule on Au(111) with and without metal cations in solution (Fig. 7a,b in ref. [1]). At that stage, we primarily aimed at investigating whether metal cations enable the electrochemical reduction of CO_2 on polycrystalline copper, gold and silver, as found in our experiments. We did this by following a divide-and-conquer approach, where different degrees of complexity are included in the simulations step by step. First, we focused on the effect of short-term interactions by alkali metal cations on the activation of CO_2, disregarding concurrent effects by mean electric field and surface charging. We employed a minimal computational setup to tackle our research question, highlighting the need to further improve the model. To allow other researchers to build upon our study[1], we provided full open access to the DFT datasets generated[2]. We very much appreciate the efforts by Le and Rahman in this direction and we hope that future datasets related to the topic will be equally made available, as we typically do for all our DFT datasets through the ioChem-BD repository[3].

Our initial setup included no electric field, low cation coverage, a neutral solvation layer, an alkali cation, a compensating hydroxide and the Au(111) supercell. During the AIMD simulations, we fixed the C–Au surface distance (d_{Au-C}) to a value of 2.16 Å to prevent CO_2 from desorbing, as evident from the supplementary videos[1] and open-access DFT datasets[2] related to the study. Le and Rahman suggest that this last assumption was instrumental to our conclusions since they could not reproduce cation–CO_2 coordination nor CO_2 activation when allowing the carbon atom to move. In fact, AIMD simulations on Au(111) with explicit solvation and a K^+ cation confirmed desorption of CO_2 within less than 100 fs if the C–Au distance was not fixed. Besides, they performed an ionic optimization of the initial bidentate $\eta_{C,O}^2$ CO_2 configuration (without explicit solvation and cation), which equally desorbs. In this regard, the key message of our study[1] is indeed that CO_2 activation does not occur without the presence of a metal cation on gold, thus the instability of CO_2 on Au without cation is consistent with our findings. We note that ΔG for CO_2 chemisorption is around 1 eV in the absence of a metal cation[1], and the optimized structure is typically achieved by converging CO_2H and removing the H with the C fixed[4]. Allowing the O-C-O angle to bend to 120° without electron transfer or any external support by cations requires more than 3 eV (ref. [5]). Thus, it is not surprising that the ionic optimization or AIMD simulation of such an endergonic structure is difficult and requires electric field, excess electrons and cations to prevent desorption of a fully relaxed CO_2. In our original work[1], we fixed the C–Au distance to compute the thermodynamics of CO_2 activation in the absence and presence of cations and compare both cases. Such a comparison would have been impossible without fixing such a distance, as, in line with our main conclusions, CO_2 activation does not occur unless a cation is present. Finally, by highlighting the limitations of our approach, the authors indicate that more accurate modelling protocols must include electrode potential (grand-canonical DFT) with excess electrons within the simulation cell[6]. In a successive study published at the end of last year[5], we included explicit electric field effects and higher cation concentrations. In this short reply, we demonstrate that the minimal setup employed in our original study[1] was sufficiently accurate to support our previous conclusion: without metal cation, CO_2 activation does not occur. We have run additional simulations that support this conclusion[7], which are freely and openly accessible in the ioChem-BD database[3].

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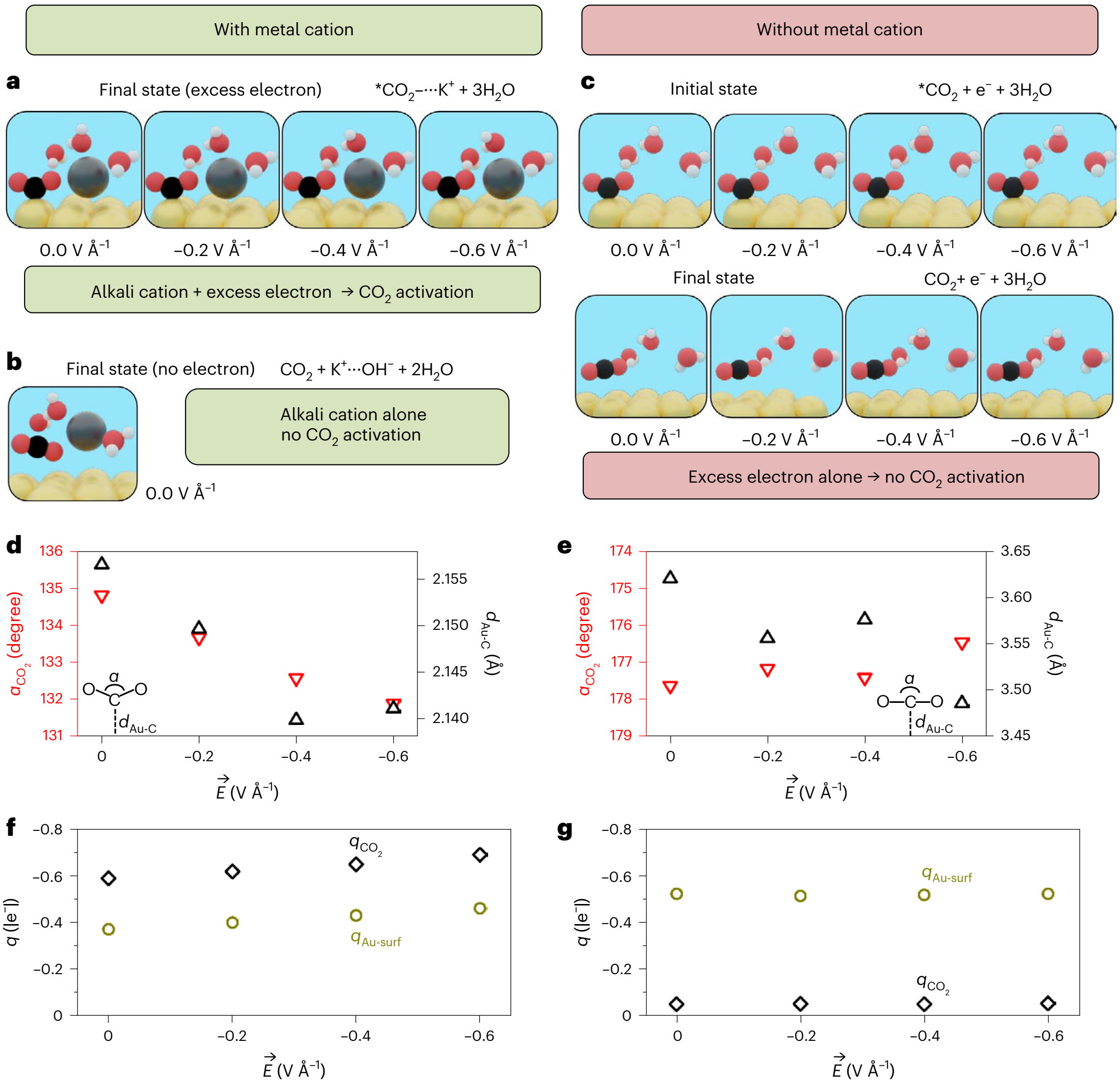

Fig. 1 | CO_2 activation with and without alkali cations and excess electrons. **a**–**g**, Ionic optimization of adsorbed CO_2 on Au(111) (3 × 3) with (**a**,**b**,**d**,**f**) and without (**c**,**e**,**g**) metal cation K^+. α_{CO_2} corresponds to the activation angle; q_{CO_2} and $q_{Au\text{-}surf}$ stand for the Bader charges of CO_2 and the first Au surface layer and all of them are presented as a function of the external electric field, $\vec{E}$.

In Fig. 1 we report the structural and electronic properties of a CO_2 molecule adsorbed on Au(111) (3 × 3) at different external electric fields in the presence of a partially solvated K^+ with three H_2O molecules in its solvation shell (Supplementary Methods). As shown in Fig. 1a, CO_2 does adsorb on Au(111) in a bent configuration with or without applied electric field, provided that the alkali metal donates its extra electron to the surface. Instead, if we impose charge neutrality (as in our original AIMD simulations), CO_2 desorbs towards the non-activated, linear configuration (Fig. 1b). Thus, increasing charge separation through excess electrons within the simulation cell (and thus the cation-induced local electric field) is crucial for the accurate assessment of cation effects in CO_2 activation. By contrast, excess electrons or an external electric field alone does not enable CO_2 activation if K^+ is absent (Fig. 1c). Remarkably, CO_2 activation angles (α), C–Au distances and CO_2 Bader charges for optimized $^*CO_2$ (* indicates adsorbtion) configurations in the presence of K^+ are in line with the ones achieved in our previous AIMD study (Fig. 1d,f). All these parameters confirm that, without a metal cation, even an initially activated CO_2 molecule deactivates towards the linear configuration (Fig. 1c,e). As shown in Fig. 1g, although the extra electron increases the excess electronic density at the surface ($q_{Au\text{-}surf}$), the electron transfer to CO_2 does not occur without metal cation (q_{CO_2} ~ 0 |e|$^-$). Thus, CO_2 activation on Au(111) does not occur without a metal cation, even if an excess electron is added to the system.

Taking all the previous considerations into account, the complementary findings that we report here highlight that our previous insights on thermodynamic, structural and electronic properties of CO_2 activation with and without a metal cation in solution hold true for more accurate simulations including electrode charging through excess electrons and electric field (as shown independently in ref. [8]). Additionally, we observe that an external homogeneous electric field up to −0.6 V Å^{-1} (~1.6 V vs SHE, Supplementary Methods) does not enable CO_2 activation alone, since to increase charge separation through excess electrons and high cation-induced electrostatic fields are needed to assist the electron transfer to adsorbed CO_2. Thus, although higher level (grand canonical) modelling approaches are desirable to achieve realistic modelling of cation effects, simplified simulations without applied electric potential may be representative enough under specific and well-motivated assumptions. This is was the case of our original study[1], where we showed that alkali cations enable adsorption of short-lived CO_2 species on Au(111) prone to fast desorption or protonation. We highlight that modelling choices should be validated by robust experimental evidence, as we exercise in our studies[1,5].

We agree with Le and Rahman that a generalized protocol to fully assess cation effects in electrochemical CO_2 reduction should include electrode charging through excess electrons and electric field, but also mass transfer effects, as shown recently[9]. Indeed, the state of the art is evolving fast in this research area (see the very recent work on CO_2 activation and C_2 selectivity[8]). As a last remark, we call the community for a shared effort toward the development of an ultimate protocol to assess cation effects in electrochemical CO_2 reduction and other electrocatalytic reactions. Such a protocol should integrate electrode potential and excess charge, cation accumulation, local pH, local solvent structure, mass transfer effects and their mutual dependences[10]. All the data and models related to them should be open to ensure that all researchers can validate and reuse them, as it was in our original study.

Data availability

Computational details are available in the Supplementary Information. The new datasets generated through DFT simulations and analysed during the current study are available in the ioChem-BD database[3] at https://doi.org/10.19061/iochem-bd-1-243[7].

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Author contributions

All authors contributed to this study (PLACEHOLDER).

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Competing interests

The authors declare no competing interests.

Additional information

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