Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

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Computational Details

To validate our choice of freezing the bottom two layers in the adsorption calculations, we first checked the forces on the frozen layers of all the relaxed structures and found the maximum and minimum values of forces are 0.1 eV/Å for MgO (110) O-site and 0.005 eV/Å for MgO(111)-O terminated O-site, respectively. We further relaxed the MgO slab, with and without the CO_2 molecule, along with relaxing all the atomic layers. The adsorption energies, E_{ad}, changes by merely 0.003 eV in the case without the CO_2 adsorbate and 0.007 eV in the case with the CO_2 adsorbate (maximum forces on unrelaxed atoms). Since the difference in adsorption energy is in order of meV, the choice of freezing the bottom two layers is justified.

MgO (100) surface: Adsorption of CO_2 on bridge site

We found here significant structural transformation at 0.203 V/Å electric field with initial structure at 0 electric field. It is different from the relaxed structure even at 0.202 V/Å. Applying electric field of 0.203 V/Å on the relaxed structure at 0 or 0.202 V/Å leads to the structural change in CO_2 molecule (O-C-O bond angle changes from 133º to 169º). But the switch back to the structure of 0 electric field from a relaxed structure at 0.203 V/Å is not observed. The two metastable states are found here and the interaction of dipole moment with the AEEF is primarily responsible for the transformation.

Fig. S1. Change in structure of the MgO (100)-CO_2 adsorbed system on bridge site upon application of AEEF.

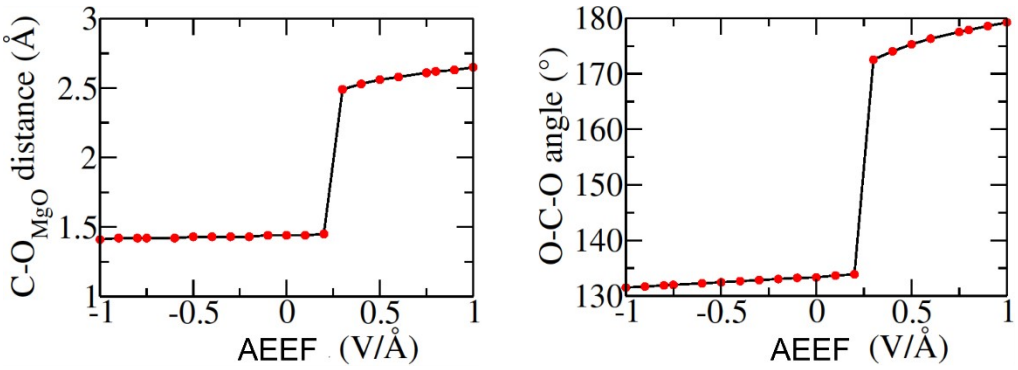

Fig. S2. Correlation plots of C-O(MgO) bond distance (on left) and O-C-O (CO_2) bond angle (on right) *versus* AEEF in case of MgO (100)-CO_2 adsorbed system on bridge site.

MgO (100) surface: Adsorption of CO_2 on Mg site

3 types of structures are found here. The relaxed structure at 0 electric field is mentioned as A_h with linear CO_2 molecule on hollow site. When electric field of -0.5 V/Å is applied CO_3^{2-} species is formed, which is classified as C. Considering type C structure as initial structure, relaxing with 0 electric field, switch to the A_h structure is not observed. Rather, C type structure is formed, but the E_{ad} is higher than C type structure. When B_{Mg} is relaxed with 0 electric field E_{ad} becomes slightly more stable but the structure remains same as B_{mg}.

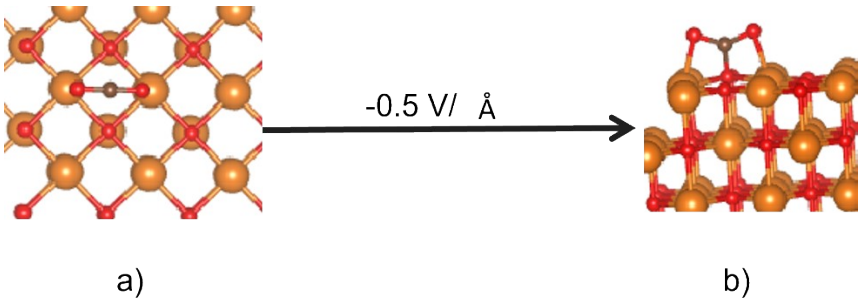

Fig. S3. Change in structure of the MgO (100)-CO_2 adsorbed system on Mg site upon application of AEEF.

MgO (100) surface: Adsorption of CO_2 on O site

Qualitatively we found here two class of structures which are mentioned as Region I and Region II with E_{ad} value of ~ -0.6 eV. With onset of electric field 0.2 V/Å on the ground state optimized structure at 0.0 V/Å, a structural transformation is found where CO_2 is desorbed from the adsorbed state at 0 electric field. When this desorbed structure is relaxed at 0 electric field no transformation is observed but E_{ad} becomes more stable by 0.18 eV, almost same as 0 electric field relaxed structure. With the relaxed structure at -0.8 V/Å, which is found lowest in energy among all, when relaxed with 0 electric field, E_{ad} increases slightly, and the structure is relatively unchanged compared to the reactant structure.

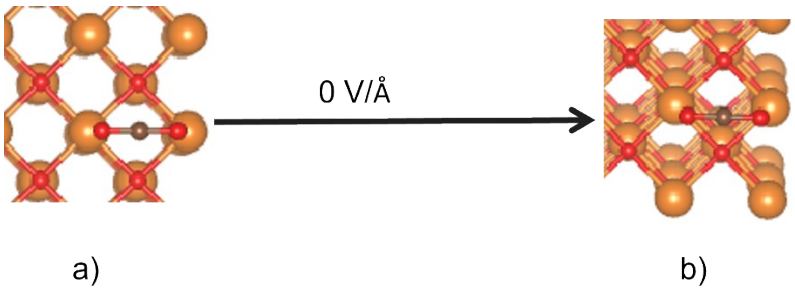

Fig. S4. Change in structure of the MgO (100)-CO_2 adsorbed system on O site upon application of AEEF.

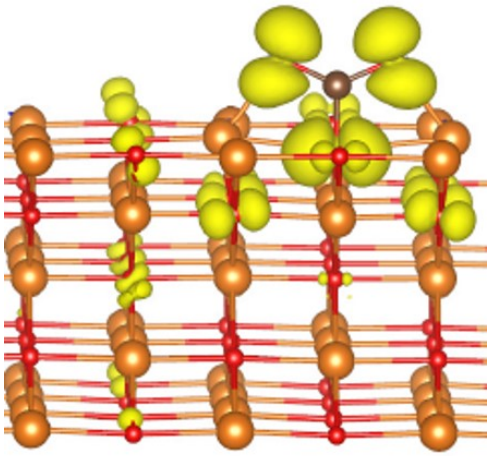

Fig. S5. Isosurface of the charge density associated with an occupied state at Y-point in the configuration of CO_2 interacting with MgO (110) surface, adsorbing on O-site, at AEEF of 0.1 V/Å.

MgO (110) surface: Adsorption of CO_2 on Mg site

3 metastable states are found here with structural transformation at electric field -0.1 V/Å, -0.5 V/Å and at -0.8 V/Å. We found CO_2 adsorption at 0 electric field relaxed structure and when electric field -0.1 V/Å is applied CO_2 is desorbed. With this desorbed structure, when 0 electric field is applied and relaxed CO_2 does not get adsorbed, but the E_{ad} becomes stable by 1.2 eV. On application of electric field -0.5 V/Å, the relaxed structure at 0 electric field remains the same. When this relaxed structure at -0.5 V/Å is relaxed with -0.1 V/Å, E_{ad} increases by 0.12 eV, while the structure remains relatively same.

MgO (110) surface: Adsorption of CO_2 on bridge site

We found here two metastable states with structural transformation at 0.3 V/Å. The relaxed structure at 0 electric field is an adsorbed state where a carbonate-like species is formed. Considering the relaxed structure at 0 electric field as the initial one, when relaxed with 0.3 V/Å, the structure changes and the E_{ad} becomes more stable by 0.78 eV. On the other hand, when the relaxed structure at 0.3 V/Å is relaxed at 0.2 V/Å electric field, energy becomes unstable by 0.079 eV but the structure remains relatively unchanged. E_{ad} becomes unstable by 0.093 eV when the relaxed structure at 0.3 V/Å is further relaxed with 0 electric field.

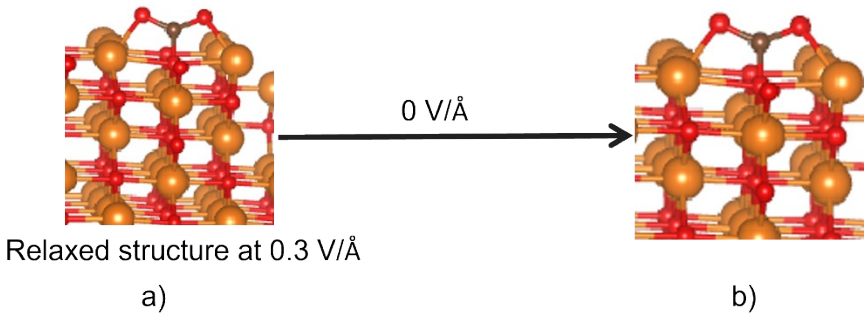

Fig. S6. Change in structure of the MgO (110)-CO_2 adsorbed system on bridge site upon application of AEEF

MgO (111-Mg terminated) surface: Adsorption of CO_2 on Mg site

2 metastable states are found with structural transformation on application of electric field -0.7 V/Å. The linear CO_2 molecule is weakly adsorbed at 0 electric field. The structure remains almost unaltered in the electric field range from -0.6 V/Å to 1 V/Å. On application of electric field -0.7 V/Å to the relaxed structure at 0 electric field, carbonate-like species is formed by the interaction of CO_2 with two O atoms and one Mg atom on the surface. This process is irreversible, i.e, the carbonate-like structure upon application of 0 electric field does not relax to the 0 electric field structure.

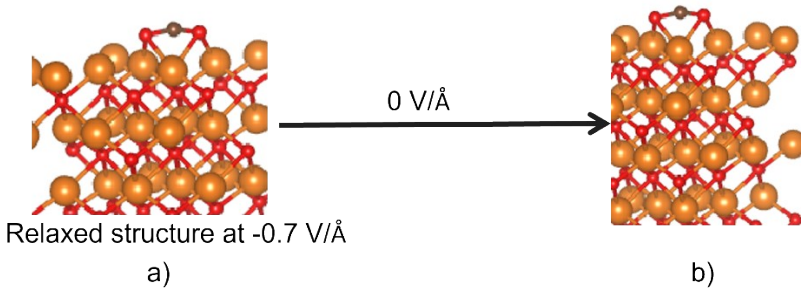

Fig. S7. Change in structure of the MgO (111)-CO_2 Mg-terminated adsorbed system on Mg site upon application of AEEF

MgO (111-Mg terminated) surface: Adsorption of CO_2 on bridge site

3 types of states are found here with significant structural transformations. Upon application of 0.5 V/Å electric field, dissociative adsorption was observed where CO fragment is bonded perpendicularly with the MgO slab. This dissociative adsorption is not reversible. The dissociated CO_2-like structure is irreversible as the structure remains unaltered upon application of 0 electric field.