Supplementary Materials

Mechanistic investigation of benzene esterification by K_2CO_3/TiO_2 : the catalytic role of the multifunctional interface

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Supplementary Information:

- 1. C_6H_6 deprotonation on K_2CO_3/TiO_2 and bare defective TiO_2
- 2. Slab model of K₂CO₃/TiO₂
- 3. Electronic structure analysis of C₆H₆COO*
- 4. Electronic structure analysis of $C_6H_5COOCH_3^*$ and H_2O^*



Figure S1. Optimized structure of K_2CO_3 supported on defective anatase TiO₂ (101) surface (K_2CO_3/TiO_2). (a) and (b) are top view and side view, respectively.



 C_6H_6 deprotonation on K_2CO_3/TiO_2 and bare defective TiO_2

Figure S2 Reaction energy diagrams for (a) C_6H_6 deprotonation without CO_2^* on K_2CO_3/TiO_2 , (b) C_6H_6 deprotonation with CO_2^* on K_2CO_3/TiO_2 , (c) C_6H_6 deprotonation without CO_2^* on bare defective TiO_2 , and (d) C_6H_6 deprotonation with CO_2^* on bare defective TiO_2 , and (d) C_6H_6 deprotonation with CO_2^* on bare defective TiO_2 .

The experimental study hypothesised that the benzene carboxylation mechanism can proceed via benzene deprotonation followed by rapid reaction with CO_2 to produce a surface-bound carbonate.¹ K₂CO₃ should then be responsible for the deprotonation reaction, as observed in other hydrocarbon

carboxylation reactions promoted by homogeneous catalysts.^{2, 3} An alternative mechanism involves a direct C-H bond carboxylation via electrophilic attack by pre-activated CO₂, which has also been considered in a number of earlier studies as a viable reaction path.^{4,5} Herein, both reaction pathways were considered by DFT calculations and the respective computed energetics are shown in Figure S2. We found that the deprotonation of C₆H₆ (Figure S2(a)) is an endothermic reaction with a rather higher activation barrier ($\Delta E = 1.07 \text{ eV}$, Ea = 1.41 eV). The alternative reaction starts with a much more favourable addition of an activated CO₂* to C₆H₆ ($\Delta E = 0.46 \text{ eV}$, Ea = 0.72 eV) followed by an exothermic C-H bond dissociation (Figure S2(b)) ($\Delta E = -1.37 \text{ eV}$, Ea = 1.19 eV). The same trend is also observed in the case of bare defective TiO2 (Figure S2(c) and Figure S2(d)). These results indicate that the C₆H₆ deprotonation that Kanan et al.¹ proposed as an initial reaction step for the benzene carboxylation is both thermodynamically and kinetically less favourable than the direct carboxylation route facilitated by TiO₂ catalyst.

Electronic structure analysis of C₆H₆COO*



Figure S3. Charge density difference plots of $C_6H_6COO^*$ adsorbed on (a) K_2CO_3/TiO_2 and (b) bare defective TiO_2 . The green and yellow regions represent enriched and depleted electron density, respectively. The isosurface values are 0.005 e/Bohr³.

For the 1st step, which represents carboxylation of benzene with CO₂ forming benzoic acid, the C₆H₆COO* is the first intermediate. The detailed geometries of this intermediate on K₂CO₃/TiO₂ and bare TiO₂ surface are shown in Fig. 2 and Fig. 3. The formation of the meta-stable C₆H₆OO* species on the surface of the catalyst is facilitated by the interaction of the CO₂ moiety with the Ti³⁺ and K⁺ species (with two Ti³⁺ in case of bare TiO₂). The reaction is formally a nucleophilic aromatic substitution reaction, which is facilitated by the increased nucleophilicity of CO₂ adsorbed to the defect Ti³⁺ sites. This mechanistic proposal is supported by the anionic nature of the C₆H₆COO* intermediate on K₂CO₃/TiO₂ and bare TiO₂ catalysts as follows from the charge density difference plots.



Figure S4. The spin density difference of (a) K_2CO_3/TiO_2 , (b) defective TiO_2 , (c) $C_6H_6COO^*$ on K_2CO_3/TiO_2 , (d) $C_6H_6COO^*$ on TiO_2 , (e) $C_6H_5COO^*$ on K_2CO_3/TiO_2 , and (f) $C_6H_5COO^*$ on TiO_2 . Isosurface values are 0.01 e/Bohr³.

Spin density difference was used to investigate the electronic property of the $C_6H_6COO^*$ intermediate. Defect was introduced to the surface of TiO₂ by removing an oxygen atom from the top layer (O-vacancy). This leads to the formation of Ti³⁺ site next to the O-vacancy. Figure S3a-b show that the unpaired electron is localized on Ti³⁺ site for both bare TiO₂ and K₂CO₃/TiO₂ catalysts. After C₆H₆COO^{*} intermediate was formed (Figure S3c-d), redistribution of the unpaired electrons on the benzene ring indicating the formation of a sigma complex. In the next step, Hydride transfer from the benzene ring to the surface forming C₆H₅COO^{*} intermediates lead to spin density relocalized to the surfaces (Figure S3e-f).

Electronic density analysis of $C_6H_5COOCH_3^*$ and H_2O^*



Figure S5 Charge density difference of (a) $C_6H_5COOCH_3$ adsorption on K_2CO_3/TiO_2 , (b) $C_6H_5COOCH_3$ adsorption on defective TiO₂, (c) H_2O adsorption on K_2CO_3/TiO_2 , and (d) H_2O^* adsorption on defective TiO₂. Green region indicates electrons accumulation whereas yellow region indicates electron depletion. Isosurface values are 0.005 e/Bohr³.

The electron density difference plots for $C_6H_5COOCH_3$ and H_2O adsorption on K_2CO_3/TiO_2 and defective TiO₂ are shown in Figure S4. Upon adsorption, it can be seen that electron transfer takes place between the adsorption sites (Ti³⁺ and K⁺) and the oxygen atoms of the adsorbates ($C_6H_5COOCH_3$ and H_2O). For the adsorption of $C_6H_5COOCH_3$, it is obvious that the electron transfer between $C_6H_5COOCH_3$ and TiO₂ is much more significant than that between $C_6H_5COOCH_3$ and K_2CO_3/TiO_2 , accounting for the stronger intereaction and higher desorption barrier demonstrated in Figure 3 in the main text. For the adsorption of H_2O on defective TiO₂, the accumulation of electrons is observed at both Ti³⁺-O_{H2O} bonds. In the case of H_2O adsorbed on K_2CO_3/TiO_2 , the accumulation of electrons on the surface is only observed at Ti³⁺ site while that on K⁺ is negligible. These results indicate the stronger interaction of $C_6H_5COOCH_3$ and H_2O on the defective TiO₂ which is in agreement with the calculated desorption energy.

References

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