Electronic Supplementary Information

Theoretical Study of the CO_2 Hydrogenation into Formic Acid on Lewis Acidic Zeolites

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The energy changes of substituting Si with tetravalent atoms (Sn, Ge, Hf and Zr) and the formation energy of creating Si vacancy of zeolites are calculated based on equations below

1) Substitution energy

$$\text{Si-zeolite} + M(OH)_4 \rightarrow \text{M-zeolite} + Si(OH)_4$$
$$E_{substitution} = E(\text{M-zeolite}) + E(Si(OH)_4) - E(\text{Si-zeolite}) - E(M(OH)_4) \quad (1)$$

2) Desilication energy

$$\text{Perfect M-zeolite} + 4H_2O \rightarrow \text{Defect M-zeolite} + Si(OH)_4$$
$$E_{defect} = E(\text{Defect M-zeolite}) + E(Si(OH)_4) - E(\text{M-zeolite}) - E(H_2O)_4 \quad (2)$$

where E(M-zeolite), E(Si-zeolite), $E(Si(OH)_4)$, $E(M(OH)_4)$, E(Defect M-zeolite) are the total energies of the perfect M-zeolite (M= Sn, Ge, Zr and Hf), siliceous zeolite, silicon hydroxide, metals hydroxide and defect M-zeolite.

Table S1 Substitution energy and desilication energy of tetravalent metals substituted ZSM-5 zeolites

Zeolites	Substitution energy (kcal/mol)	Desilication energy (kcal/mol)
Sn-ZSM-5	81.3	-29.1
Ge-ZSM-5	73.6	-20.9
Zr-ZSM-5	83.4	-46.4
Hf-ZSM-5	83.3	-46.6

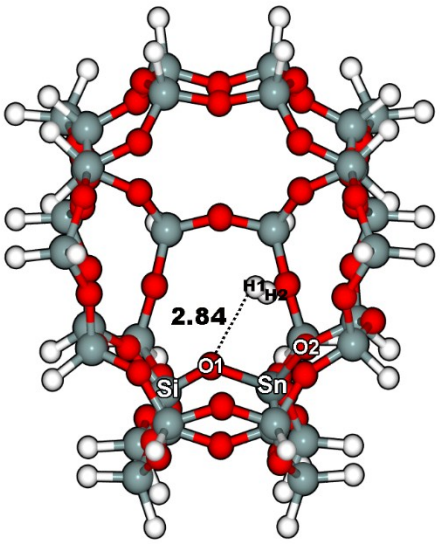
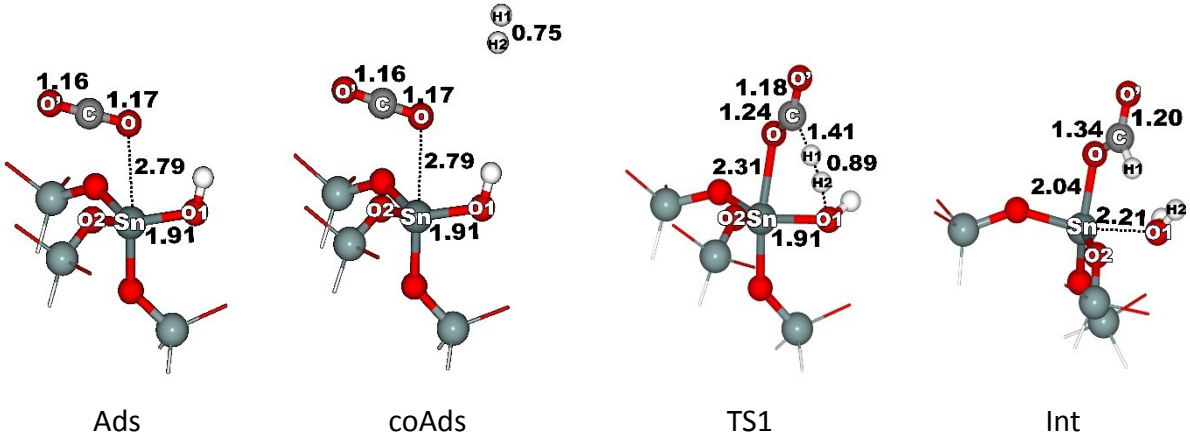
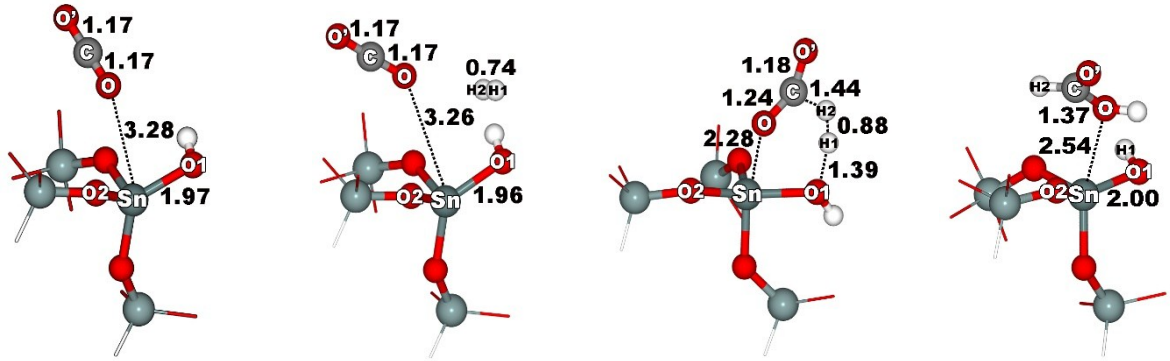


Fig. S1 Optimized structures of the H_2 adsorption complexes on Sn-ZSM-5.

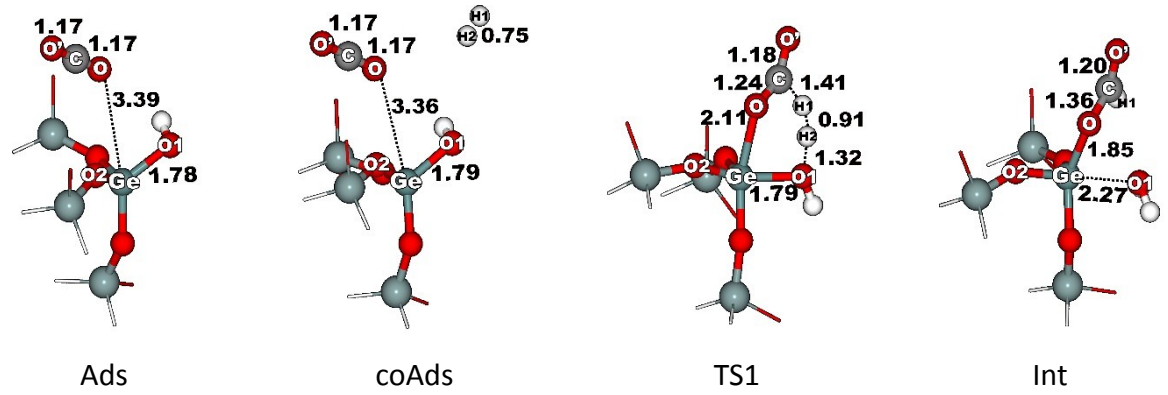


(a)

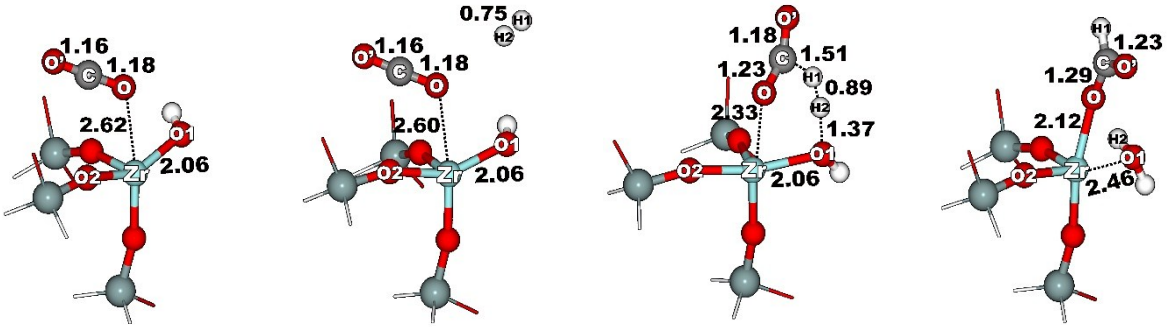


(b)

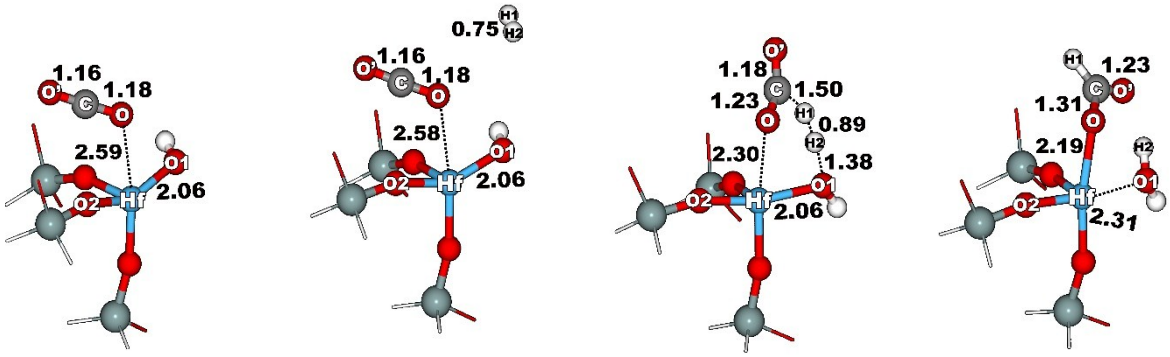
Fig. S2 Optimized structures of the intermediate adsorption and the transition state of the CO2 hydrogenation on defect Sn-BEA (a), and defect Sn-FAU.



(a)



(b)



(c)

Fig. S3 Optimized structures of the intermediate adsorption and the transition state of the CO_2 hydrogenation on defect Ge-ZSM-5 (a), defect Zr-ZSM-5 and defect Hf-ZSM-5.

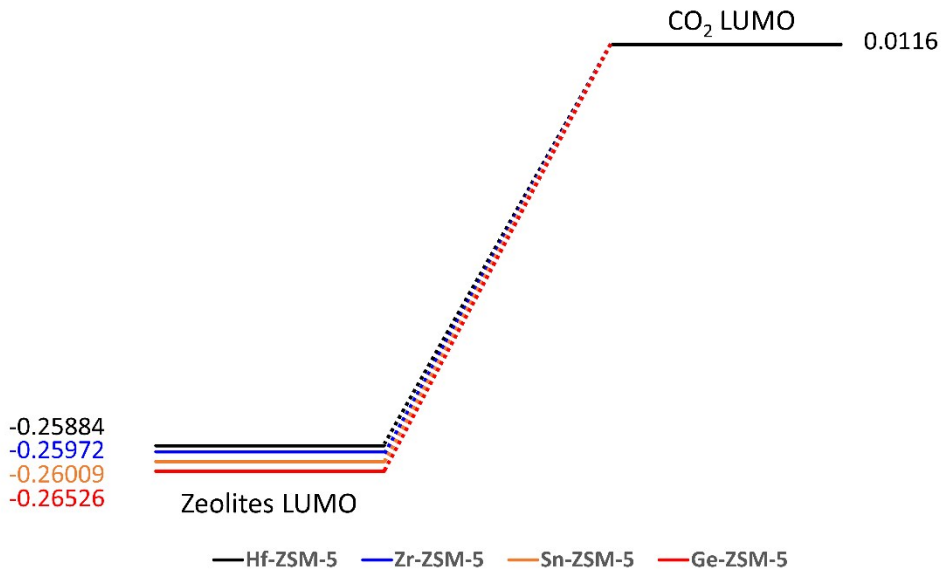


Fig. S4. Energy levels of the frontier molecular orbitals (FMOs) of zeolites and CO_2 (energies are in atomic unit).