## Supporting Information

## Novel Mechanistic Insights into Methane Activation over Fe and Cu Active Sites in Zeolites: A Comparative DFT Study Using Meta-GGA Functionals

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**Figure S1.** Complete energy diagrams of methane activation over [FeO]<sup>2+</sup>-MFI in the quintet (blue lines) and triplet (red lines) states. Energies are in kcal/mol.



**Figure S2.** Projected density of states (PDOS) for **RC** of [FeO]<sup>2+</sup>-MFI in the quintet state, calculated by the TPSS-D2 (top) and MS0-D2 (bottom) functionals.

- Both of the TPSS-D2 and SCAN-D2 functionals show the presence of an unoccupied Fe-d orbital both in the  $\alpha$  and  $\beta$  spins near the Fermi level (at about 0.2~0.5 and 0.7~1.0 eV, respectively for the  $\alpha$  and  $\beta$  spins), which indicates the characteristic of Fe<sup>IV</sup> electronic structure.
- The  $\alpha$ -LUMO (i.e. the Fe–O  $\sigma^*$  orbital) predicted by the MS0-D2 functional is lower in energy than that predicted by the TPSS-D2 functional, thus causing the [FeO]<sup>2+</sup> predicted by the MS0-D2 functional to be more reactive toward methane.



**Figure S3.** Complete energy diagrams of methane activation over  $[Cu_2(\mu-O)]^{2+}$ -MFI in the triplet (blue lines) and open-shell singlet (red lines) states. Energies are in kcal/mol.



**Figure S4.** Projected density of states (PDOS) for **RC** and **RI** of  $[Cu_2(\mu-O)]^{2+}$ -MFI in the triplet state, calculated by the MS2-D2 and SCAN-D2 functionals.

- In RC, both of the MS2-D2 and SCAN-D2 functionals show the presence of two occupied Cu-d orbitals (α spin) at about -0.4 and -0.7 eV and two unoccupied Cu-d orbitals (β spin) at about 0.2 and 0.7 eV. This indicates two singly occupied molecular orbitals (SOMOs), which characterize the involvement of two Cu<sup>2+</sup> ions in the active species.
- A slight stabilization of the whole  $\alpha$  orbitals is observed when comparing the PDOSs of **RC** calculated by the SCAN-D2 and MS2-D2 functionals. As a result, the  $\alpha$  electron of •CH<sub>3</sub> in **RI** calculated by the SCAN-D2 functional is slightly more stable.



**Figure S5.** Complete energy diagrams of methane activation over  $[Cu_3(\mu-O)_3]^{2+}$ -MOR in the quartet (blue lines) and doublet (red lines) states. Energies are in kcal/mol.



**Figure S6.** Projected density of states (PDOS) for **RC** and **RI** of  $[Cu_3(\mu-O)_3]^{2+}$ -MOR in the quartet state, calculated by the MS2-D2 and SCAN-D2 functionals.

- In RC, both of the MS2-D2 and SCAN-D2 functionals show a pair of unoccupied Cu1-d orbitals in the α and β spins near the Fermi level (at about 0.3 and 0.6 eV, respectively for the α and β spins), indicating a Cu<sup>3+</sup> ion, which is different from Cu<sup>+</sup> ion that would result in all occupied Cu-d orbitals. At the same time, the presence of two unoccupied Cu2-d and Cu3-d orbitals as well as one unoccupied O2-p orbital in the β spin near the Fermi level indicates two Cu<sup>2+</sup> ions and one O<sup>•</sup> radical. The Cu1-d and O2-p orbitals in the β spin are not hybridized with each other since the Cu1 and O2 atoms are located away from each other.
- The presence of unoccupied O1-p orbital in the  $\beta$  spin is due to a hybridization between Cu2 and O1 atoms. The same description also applies for O3 atom (i.e. Cu3-d and O3-p hybridization).
- In **RI**, there seems only one unoccupied Cu-d orbital in the  $\beta$  spin. However, there are actually three unoccupied Cu-d orbitals, which are energetically very close to each other.

**Table S1.** Comparison of CH<sub>4</sub> Adsorption Energies ( $E_{ads}$ ) on [FeO]<sup>2+</sup>-ZSM-5 Calculated with and without the D2 or D3 Method of Dispersion Correction.

	RTPSS	RTPSS-D2	RTPSS-D3	MS0	MS0-D2	MS0-D3
E <sub>ads</sub> (kcal/mol)	0.4	-5.4	-6.6	-2.4	-8.5	-9.3

- As shown in this table, dispersion correction is essential for correctly predicting the CH<sub>4</sub> adsorption energy inside the microporous of zoolites. This suggests that dispersion correction still should be included even for meta-GGA functionals.
- This table also shows that even without the dispersion correction, the MS0 functional already predicts a negative value of  $E_{ads}$  (exothermic), which is in contrast to  $E_{ads}$  predicted by the RTPSS functional. This indicates how weak interactions except the van der Waals dispersive interactions are well treated by the MS functionals.



**Figure S7.** Visualization of atomic spin densities (yellow and blue isosurfaces correspond to positive and negative spin densities, respectively) and C–H bond length for **RC**, **TS**, and **RI** of [FeO]<sup>2+</sup>-ZSM-5 in the corresponding ground state.



**Figure S8.** Visualization of atomic spin densities (yellow and blue isosurfaces correspond to positive and negative spin densities, respectively) and C–H bond length for **RC**, **TS**, and **RI** of  $[Cu_2(\mu-O)]^{2+}$ -ZSM-5 in the corresponding ground state.



**Figure S9.** Visualization of atomic spin densities (yellow and blue isosurfaces correspond to positive and negative spin densities, respectively) and C–H bond length for **RC**, **TS**, and **RI** of  $[Cu_3(\mu-O)_3]^{2+}$ -MOR in the corresponding ground state.