The Structure, Stability and Reactivity of Mo-oxo species in H-ZSM5 Zeolites: Density Functional Theory Study

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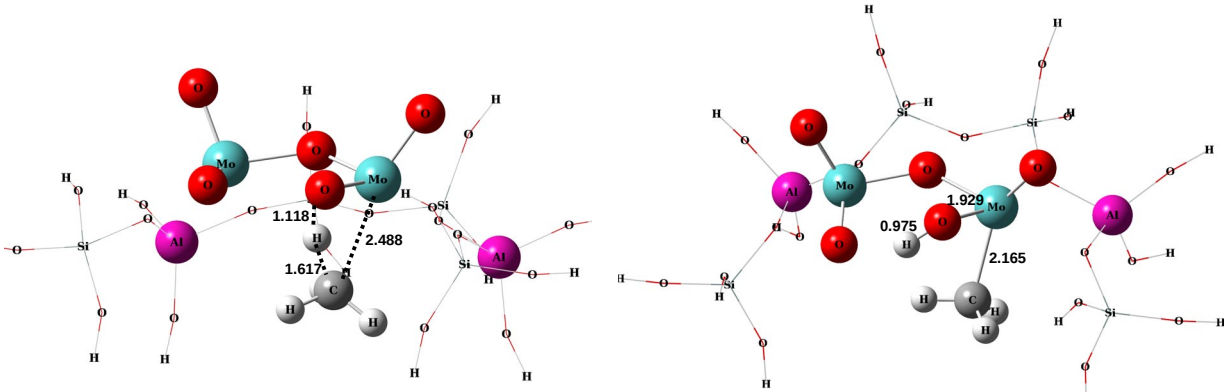
Supporting materials

TABLE S1: The Geometric Parameters of $Mo_2O_5^{2+}$ Dimer Located at Different Adjacent Brönsted Acidic Sites. Optimization were Performed at BLYP/DNP Level with 6T (10T) Cluster Model (Bond Length in Å, Bond Angle in Degree)

	T6T6	T6T9	T3T3	T3T12	T7T12–R	T7T12–L	Experimental Data
Mo≡O	1.733	1.731	1.733	1.735	1.734	1.726	Mo=O double bond: 1.69 ± 0.008; [12]
Mo≡O	1.732	1.731	1.732	1.731	1.727	1.738	1.73; [53]
Mo≡O	1.733	1.734	1.733	1.735	1.735	1.729	Mo–O single bond:
Mo≡O	1.732	1.731	1.732	1.731	1.728	1.736	1.78 ± 0.0009; [12,53]
Mo–O	1.926	1.888	1.928	1.886	1.939	1.944	Mo–O single bond in Mo–O–Mo:
Mo–O	1.926	1.974	1.928	1.975	1.939	1.936	1.84 ± 0.0009; [12,51]
Mo--Mo	3.570	3.553	3.554	3.523	3.500	3.477	Mo--Mo distance:
Mo–O_F	2.158	2.563	2.185	2.511	2.203	2.262	3.70 ± 0.0003; [12]
Mo–O_F	2.214	2.092	2.200	2.094	2.199	2.133	Mo--Al distance: 3.60 ± 0.0006;[12]
Mo–O_F	2.214	2.135	2.201	2.130	2.165	2.116	
Mo–O_F	2.158	2.156	2.182	2.174	2.240	2.296	
Mo--Al	3.065	3.298	3.055	3.118	3.096	3.107	
Mo--Al	3.065	3.039	3.053	3.034	3.116	3.084	
O_F–O_F	4.340	4.613	4.344	4.624	4.023	4.092	
Mo–O_F–Al	99.9	114.6	100.0	112.0	101.6	100.3	
Mo–O_F–Al	99.9	102.2	100.0	102.1	102.9	103.7	

TABLE S2: The potential energies of optimized reactant, transition state and product for methane C-H bond dissociation. (at B3LYP/6-31G**/LanL2DZ level).

Model	E_{tot}/a.u.
CH_4	-40.52402
Reactant	-3592.88784
Transition state	-3633.31097
Product	-3633.35126



(a) (b)

Figure S1. Optimized structure of transition state (a) and product (b) for methane C-H bond dissociation. The selected distances are in Å.