

## Supporting Information

### Design and Catalytic Performance of Molybdenum Active Sites on MCM-41 Framework for the Aerobic Oxidation of 5- Hydroxymethylfurfural to 2,5-Diformylfuran

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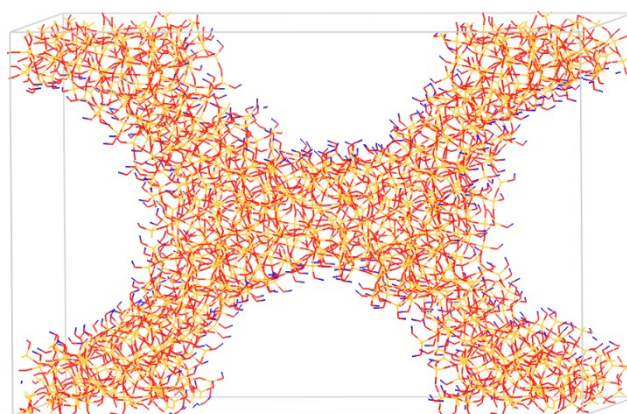
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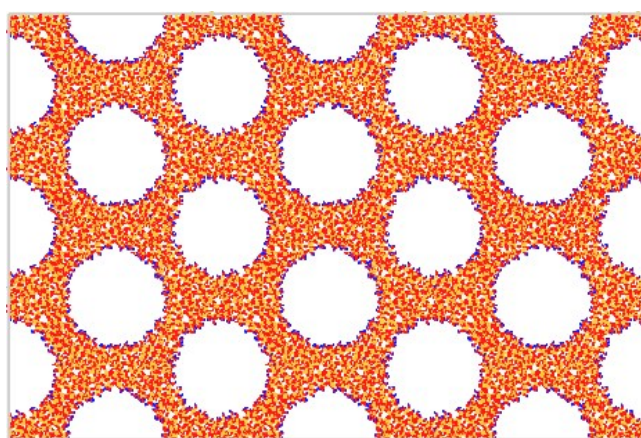
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## content

|      |                                                                                                                                                                                                                                                                                                                                                                                      |   |
|------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|
| i.   | Figure S1: (a) Final structure of MCM-41 after optimization; (b) The structure obtained by replicating the box. Color code: yellow, silicon; red, oxygen; blue, hydrogen. ....                                                                                                                                                                                                       | 1 |
| ii.  | Figure S2: Arrhenius plots of rate constants for the crucial reaction step 4-IM1 $\rightarrow$ 4-TS2b in the catalytic oxidation of HMF to DFF catalyzed over [Mo-4]. ....                                                                                                                                                                                                           | 2 |
| iii. | Figure S3: Arrhenius plots of rate constants for the crucial reaction step 5-IM1 $\rightarrow$ 5-TS2 in the catalytic oxidation of HMF to DFF catalyzed over [Mo-5]. ....                                                                                                                                                                                                            | 3 |
| iv.  | Figure S4: Arrhenius plots of rate constants for the crucial reaction step IM1 $\rightarrow$ TS2 in the catalytic oxidation of HMF to DFF catalyzed over [Mo-HPA]. ....                                                                                                                                                                                                              | 4 |
| v.   | Figure S5: Diagram (relative energies ([Mo-5]-[Mo-4]) vs. temperature) showing the stability ranges for the different molybdenum doped MCM-41 silica ....                                                                                                                                                                                                                            | 5 |
| vi.  | Table S1: Sum of electronic energies ( $E$ , hartree) and the relative energies ( $E_r$ , kJ mol <sup>-1</sup> ) of various species with respect to the reactants for the reaction of 2HMF + O <sub>2</sub> $\rightarrow$ 2DFF + 2H <sub>2</sub> O catalyzed over [Mo-4] at the hybrid quantum mechanics (QM, GGA-BP/DNP) and molecular mechanics (MM, Universal) calculations. .... | 6 |
| vii. | Table S2: Sum of electronic energies ( $E$ , hartree) and the relative energies ( $E_r$ , kJ mol <sup>-1</sup> ) of various species with respect to the reactants for the reaction of 2HMF + O <sub>2</sub> $\rightarrow$ 2DFF + 2H <sub>2</sub> O catalyzed over [Mo-4] at the hybrid quantum mechanics (QM, GGA-BP/DNP) and molecular mechanics (MM, Universal) calculations. .... | 7 |

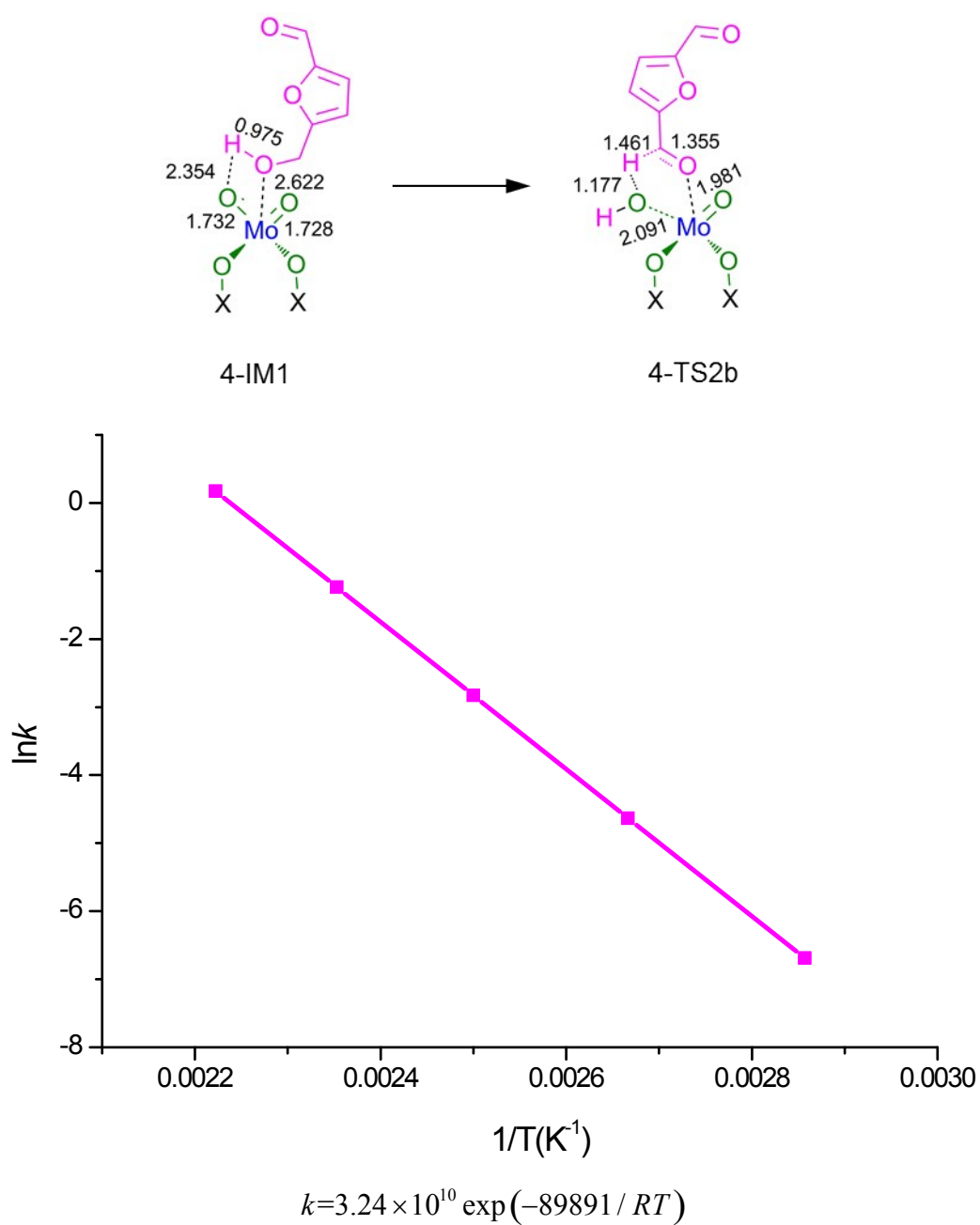


(a)

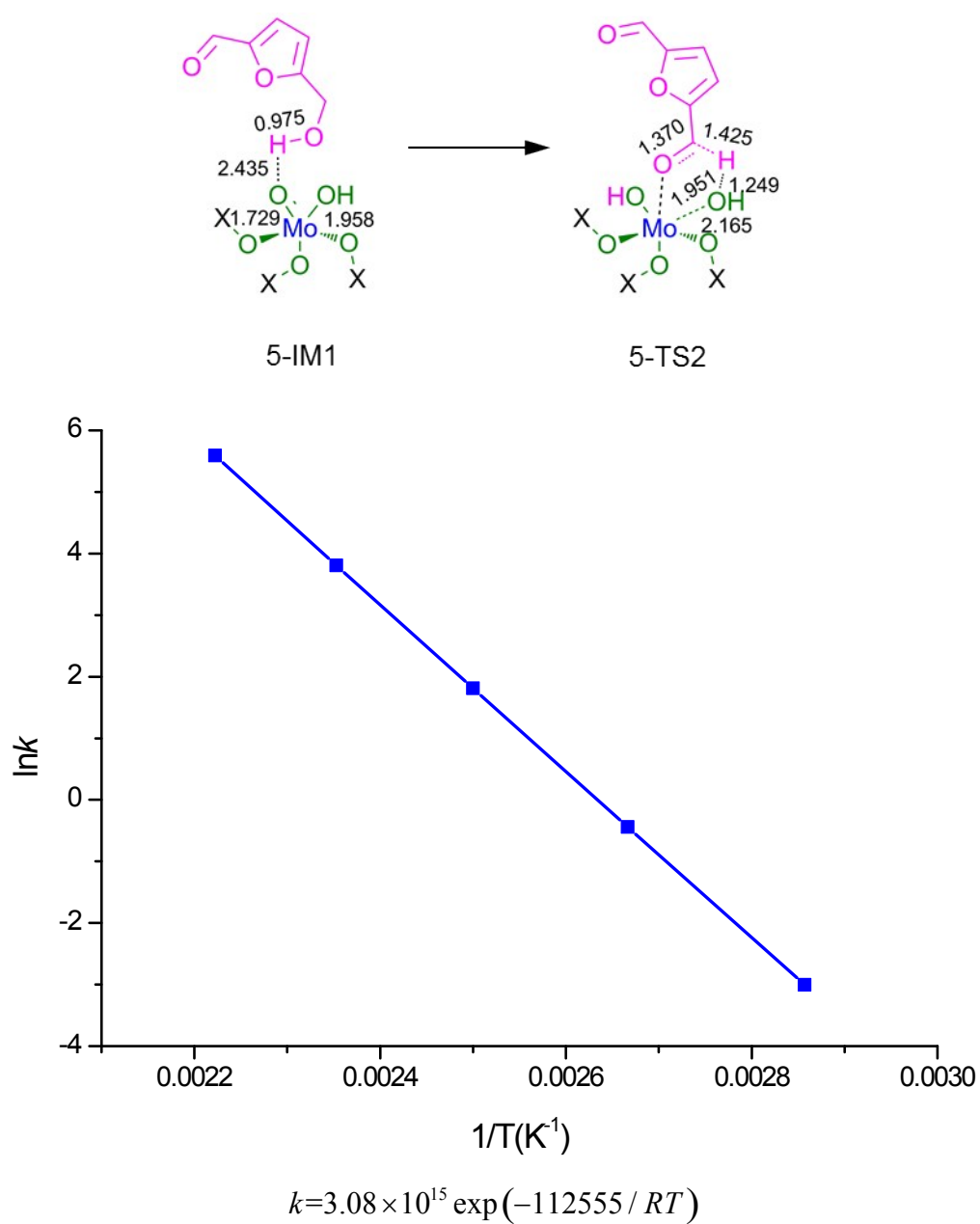


(b)

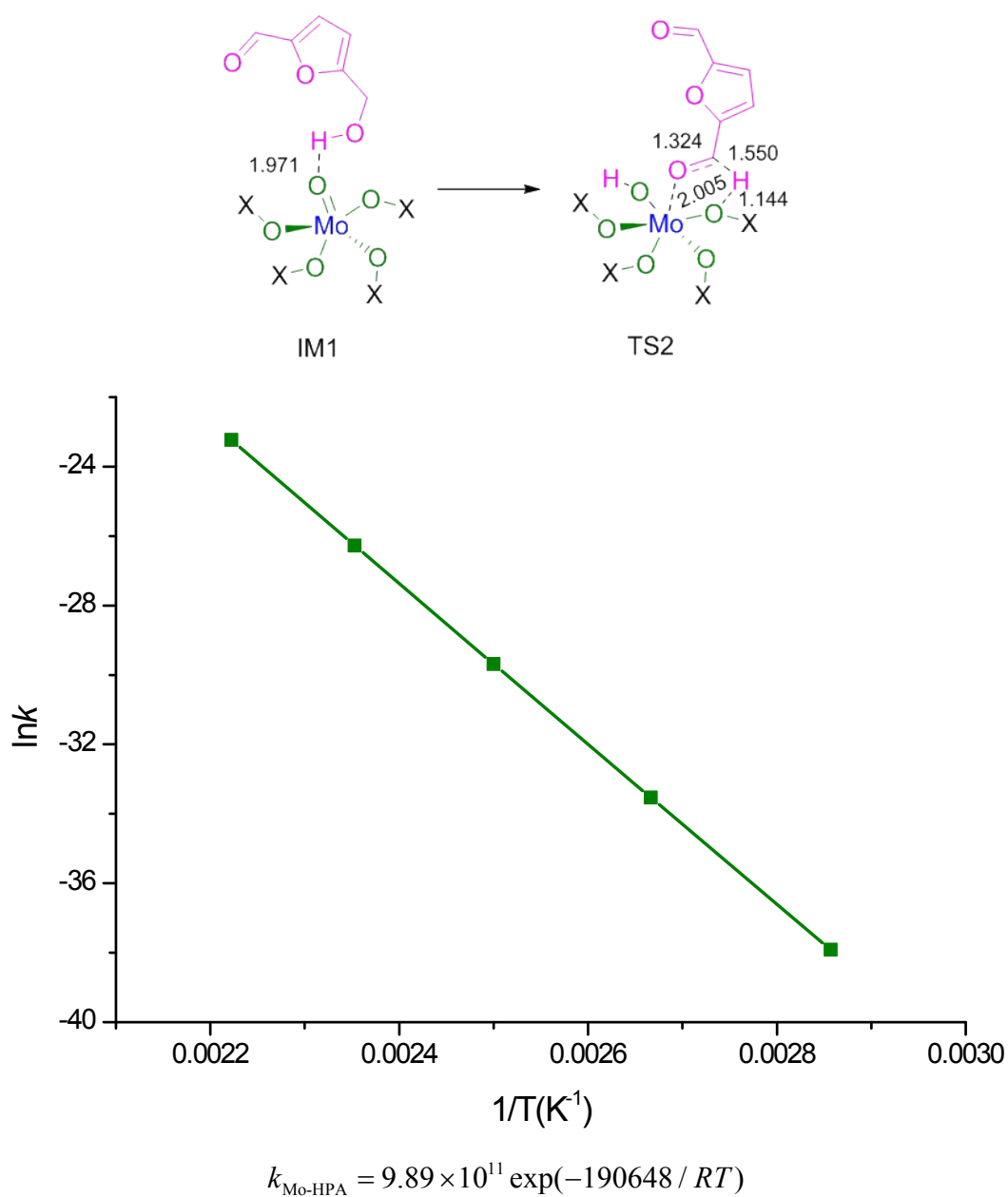
**Figure S1:** (a) Final structure of MCM-41 after optimization; (b) The structure obtained by replicating the box. Color code: yellow, silicon; red, oxygen; blue, hydrogen.



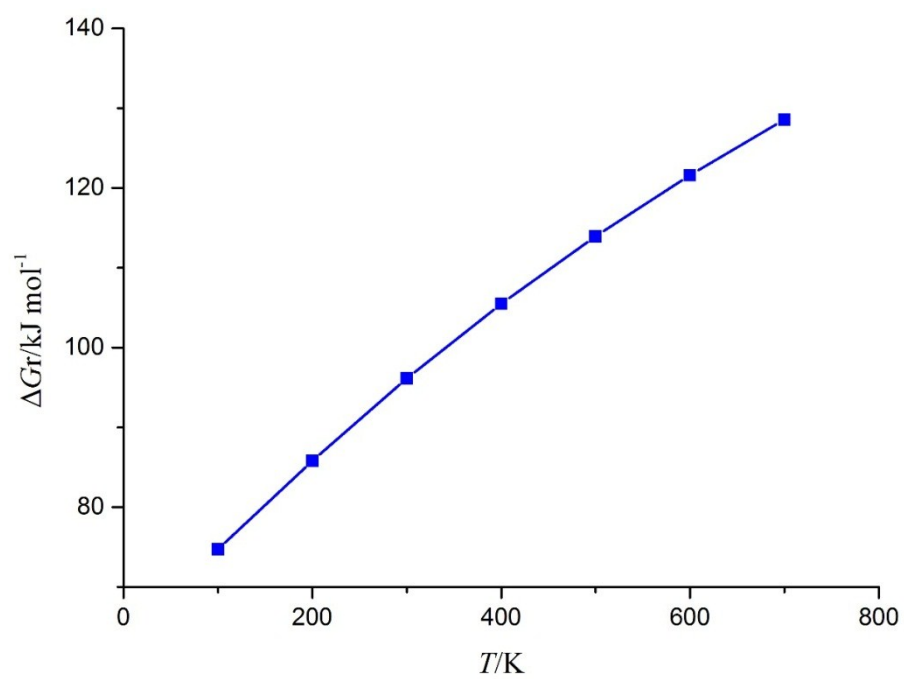
**Figure S2:** Arrhenius plots of rate constants for the crucial reaction step 4-IM1 → 4-TS2b in the catalytic oxidation of HMF to DFF catalyzed over [Mo-4].



**Figure S3:** Arrhenius plots of rate constants for the crucial reaction step 5-IM1  $\rightarrow$  5-TS2 in the catalytic oxidation of HMF to DFF catalyzed over [Mo-5].



**Figure S4:** Arrhenius plots of rate constants for the crucial reaction step  $\text{IM1} \rightarrow \text{TS2}$  in the catalytic oxidation of HMF to DFF catalyzed over [Mo-HPA].



**Figure S5:** Diagram (relative energies ([Mo-5]-[Mo-4]) vs. temperature) showing the stability ranges for the different molybdenum doped MCM-41 silica

**Table S1:** Sum of electronic energies ( $E$ , hartree) and the relative energies ( $E_r$ , kJ mol<sup>-1</sup>) of various species with respect to the reactants for the reaction of 2HMF + O<sub>2</sub> → 2DFF + 2H<sub>2</sub>O catalyzed over [Mo-4] at the hybrid quantum mechanics (QM, GGA-BP/DNP) and molecular mechanics (MM, Universal) calculations.

| Species                     | $E$         | $E_r$  |
|-----------------------------|-------------|--------|
| HMF                         | -458.02462  |        |
| DFF                         | -456.82137  |        |
| <sup>3</sup> O <sub>2</sub> | -150.38903  |        |
| O <sub>2</sub>              | -150.34313  |        |
| H <sub>2</sub> O            | -76.45648   |        |
| [Mo-4]                      | -7058.17368 | 0.0    |
| 4-IM1                       | -7516.20059 | -6.0   |
| 4-TS1                       | -7516.16618 | 84.3   |
| 4-IM2                       | -7516.18688 | 30.0   |
| 4-TS2a                      | -7516.15152 | 122.8  |
| 4-IM3a                      | -7516.16384 | 90.5   |
| 4-TS2b                      | -7516.15766 | 106.7  |
| 4-IM3b                      | -7516.18517 | 34.5   |
| [Mo-4+2Ha]                  | -7059.32141 | 145.8  |
| [Mo-4+2Hb]                  | -7059.32862 | 126.8  |
| <sup>3</sup> 4-IM4a         | -7209.74869 | 45.3   |
| 4-IM4a                      | -7209.77235 | -16.4  |
| 4-TS3a                      | -7209.75879 | 19.2   |
| 4-IM5a                      | -7209.78396 | -47.3  |
| 4-TS4a                      | -7209.73084 | 92.2   |
| 4-TS3b                      | -7059.28247 | 248.0  |
| 4-IM5b                      | -7209.79430 | -74.4  |
| <sup>3</sup> 4-IM5b         | -7209.75413 | 31.1   |
| 4-IM6a                      | -7209.79025 | -63.8  |
| [Mo-4+O]                    | -7133.32780 | -48.1  |
| [ <sup>3</sup> Mo-4+O]      | -7133.28935 | 52.9   |
| 4-IM7                       | -7591.35264 | -48.7  |
| 4-TS5                       | -7591.33832 | -11.1  |
| 4-IM8                       | -7591.34422 | -26.6  |
| 4-TS6a                      | -7591.31348 | 54.1   |
| 4-IM9a                      | -7591.33083 | 8.6    |
| 4-TS6b                      | -7591.29942 | 91.0   |
| 4-IM9b                      | -7591.45610 | -320.3 |
| 4-IM10a                     | -7134.61737 | -274.7 |
| 4-TS7a                      | -7134.59537 | -217.0 |
| [Mo-4]+ H <sub>2</sub> O    | -7134.63201 | -313.2 |
| [Mo-4]                      | -7058.17368 | -308.3 |

**Table S2:** Sum of electronic energies ( $E$ , hartree) and the relative energies ( $E_r$ , kJ mol<sup>-1</sup>) of various species with respect to the reactants for the reaction of 2HMF + O<sub>2</sub> → 2DFF + 2H<sub>2</sub>O catalyzed over [Mo-4] at the hybrid quantum mechanics (QM, GGA-BP/DNP) and molecular mechanics (MM, Universal) calculations.

| Species  | $E$         | $E_r$  |
|----------|-------------|--------|
| [Mo-5]   | -7865.57214 | 0.0    |
| 5-IM1    | -8323.61608 | -50.7  |
| 5-TS1    | -8323.58013 | 43.7   |
| 5-IM2    | -8323.59769 | -2.4   |
| 5-TS2    | -8323.56803 | 75.4   |
| 5-IM3    | -8323.60520 | -22.2  |
| 5-IM4    | -7866.78414 | -23.0  |
| [Mo-5+O] | -7790.30288 | 42.1   |
| 35-IM5   | -7940.71844 | -27.6  |
| 5-IM5    | -7940.74120 | -87.3  |
| 5-TS3    | -7940.73011 | -58.2  |
| [Mo-5+O] | -7940.75340 | -119.4 |
| 5-IM6    | -8398.76884 | -95.3  |
| 5-TS4    | -8398.74356 | -28.9  |
| 5-IM7    | -8398.76280 | -79.4  |
| 5-TS5    | -8398.71781 | 38.7   |
| 5-IM8    | -8398.86530 | -348.5 |
| [Mo-5]   | -7865.57214 | -308.3 |