**Insight into the Reaction Mechanism of Ethanol Steam Reforming Catalyzed by Co-Mo6S8**

**[supporting information]**

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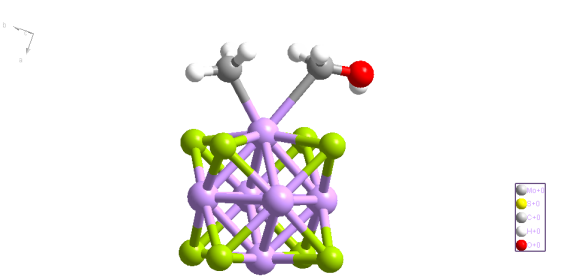
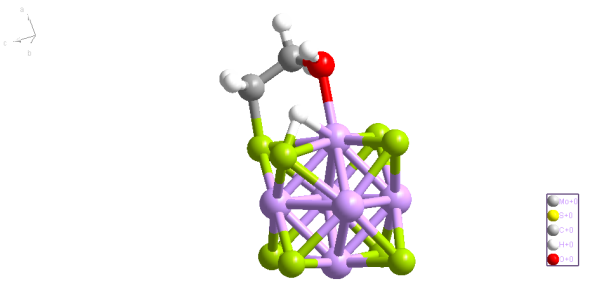
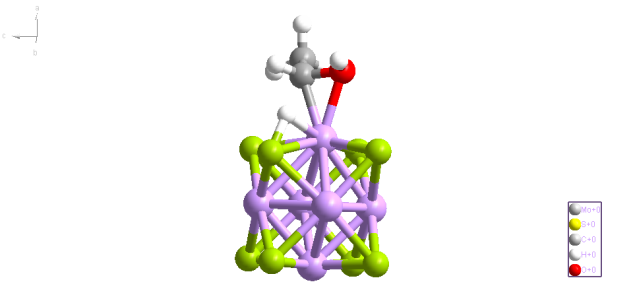
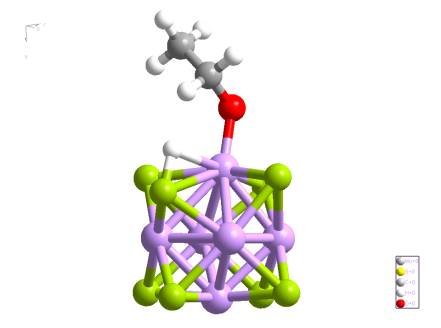
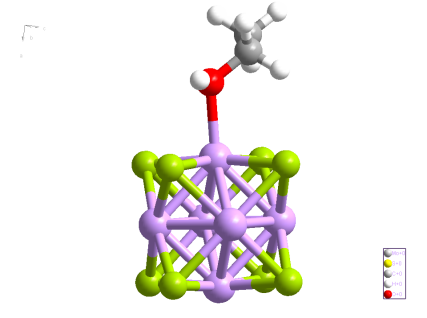
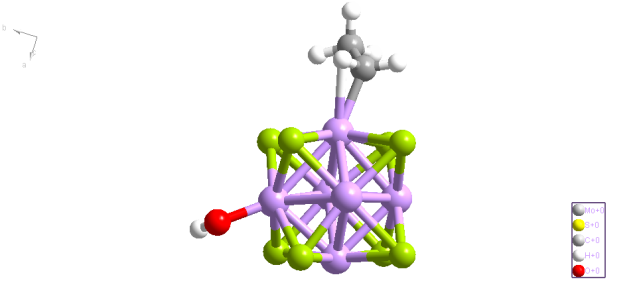
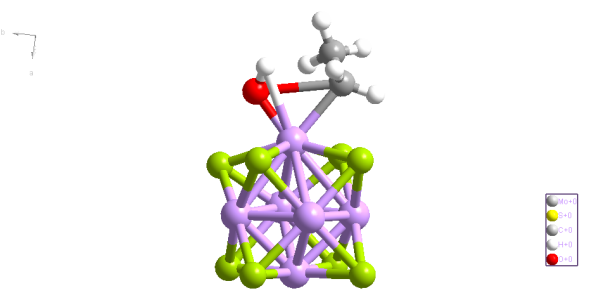
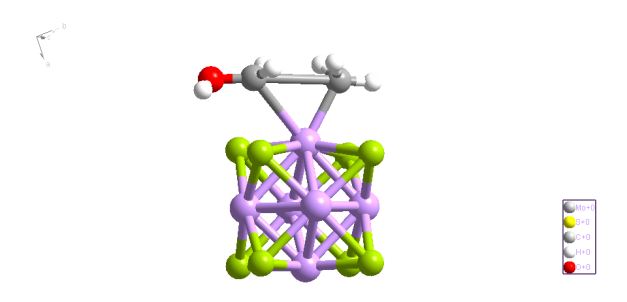
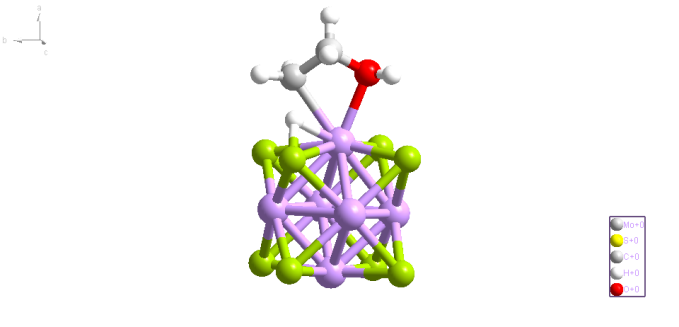
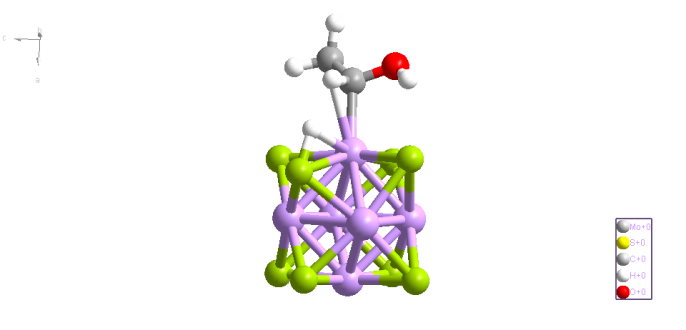
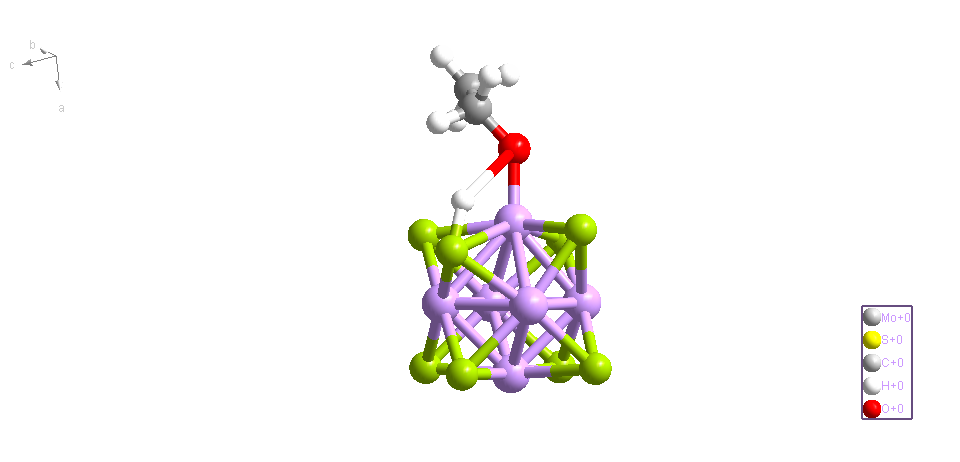
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**Fig. S1** Potential energy surfaces of CH3CH2OH\* decomposition catalyzed by Co-Mo6S8.

The solid line represents the PBE level with 6-31G (d, p) and LANL2DZ basis set and the dashed line represents the PBE-D3(BJ) level with 6-311++G (d, p) and SDD basis set.



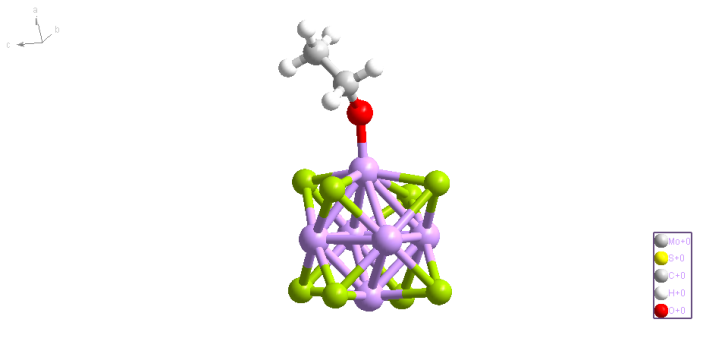
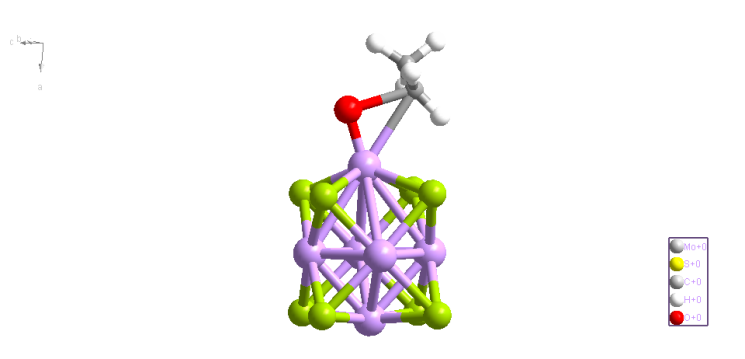
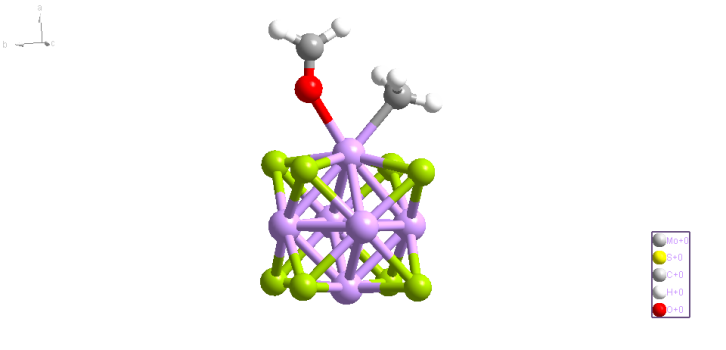
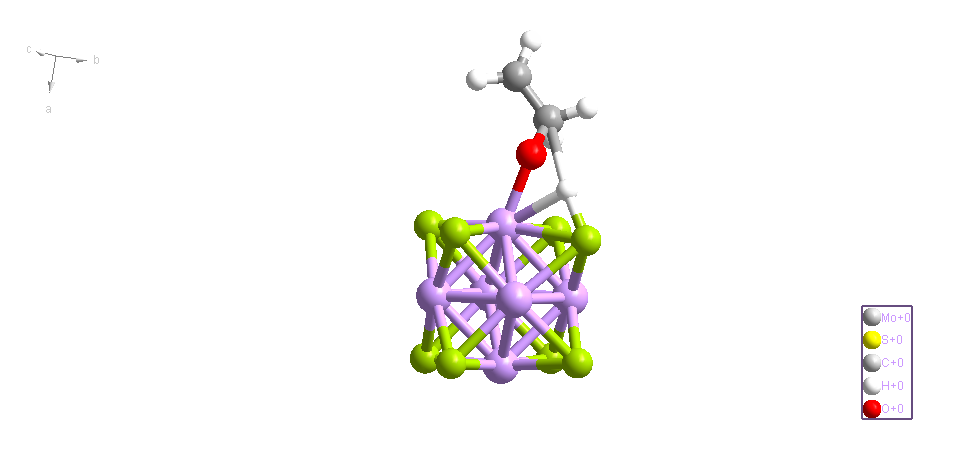
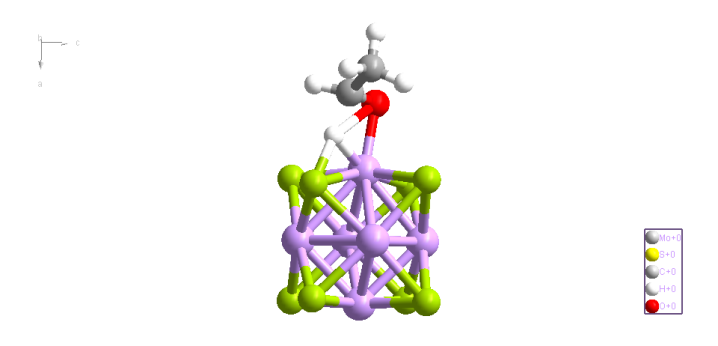
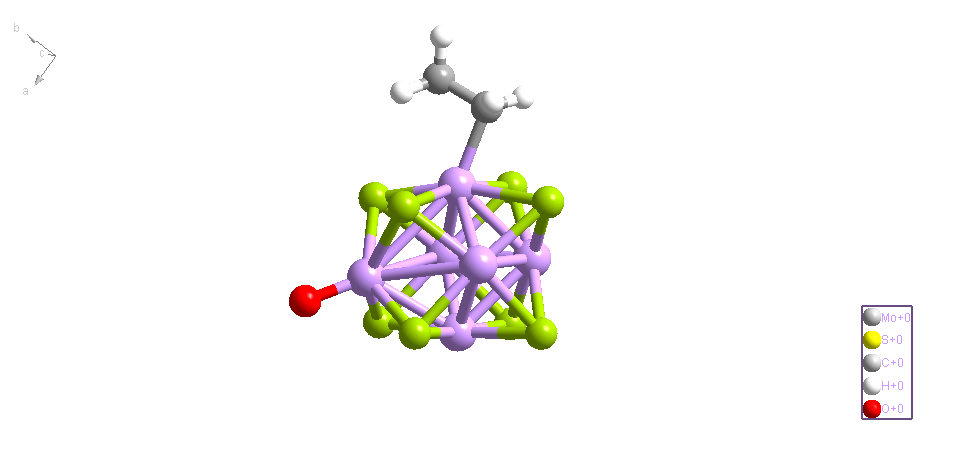
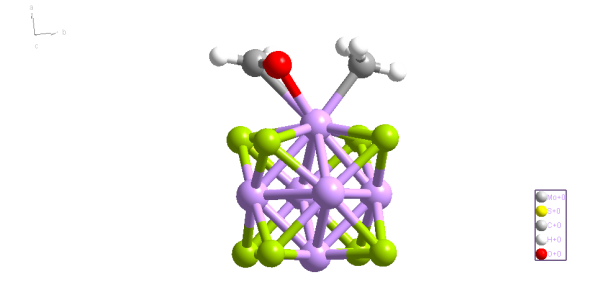
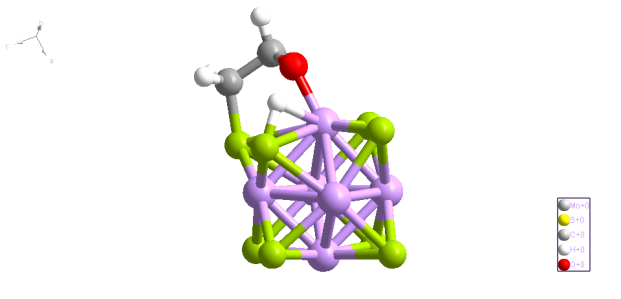
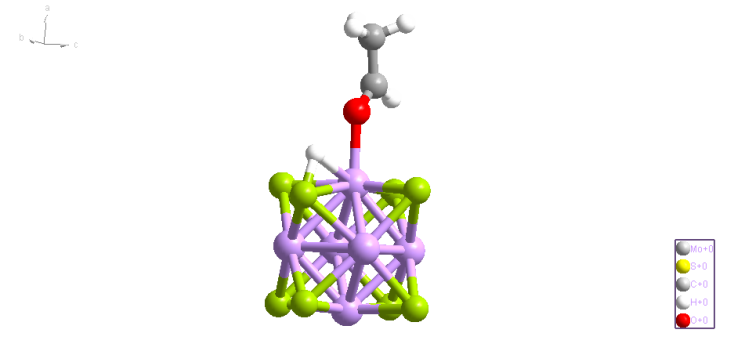


TS1’ TS2’ TS3’ TS4’ TS5’

CH3CH2OH\* CH3CH2O\*+H\* CH3CHOH\*+H\* CH2CH2OH\*+H\* CH3\*+CH2OH\*  CH3CH2\*+OH\*

**Fig. S2** Potential energy surfaces and geometrical structures of CH3CH2OH\* decomposition catalyzed by Mo6S8. Atom colors are Mo (pink), S (green), O (red), C (black), and H (white).



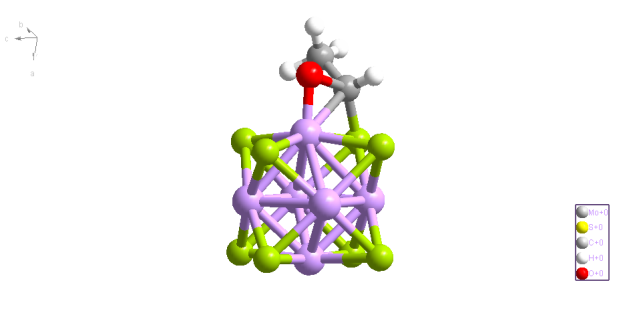
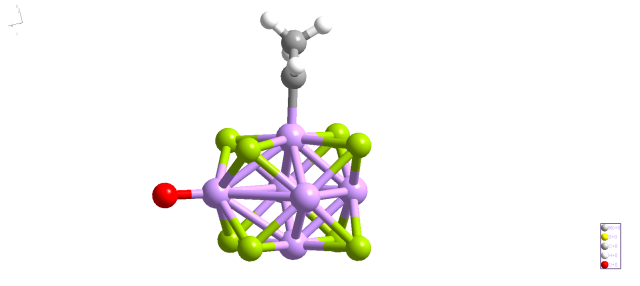
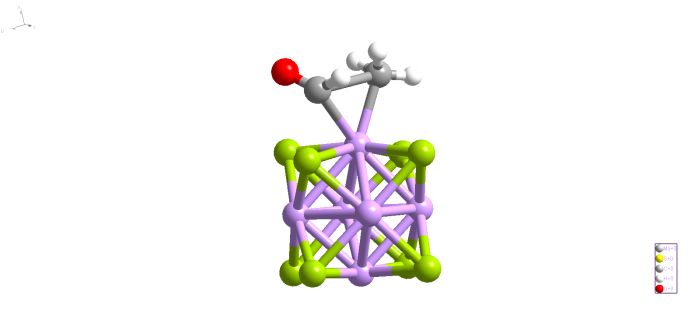
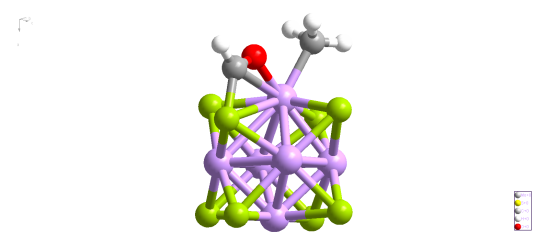
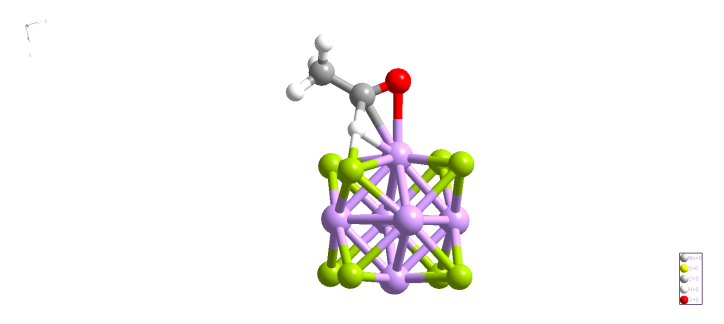
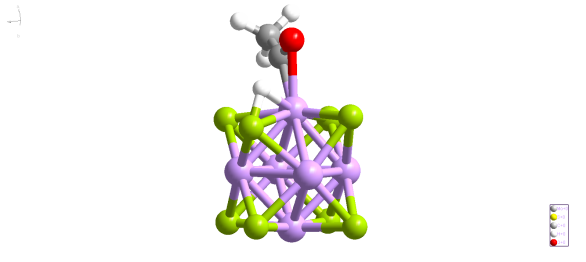
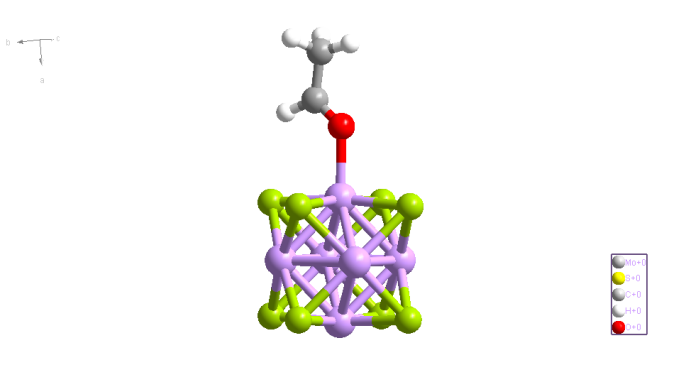
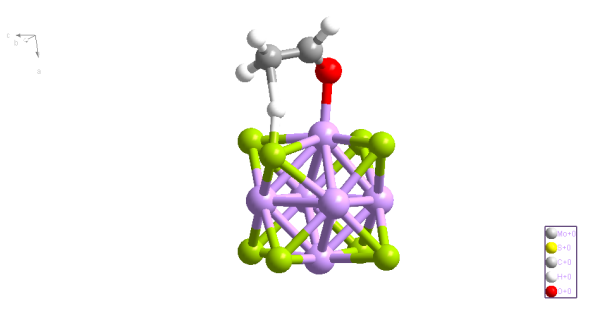
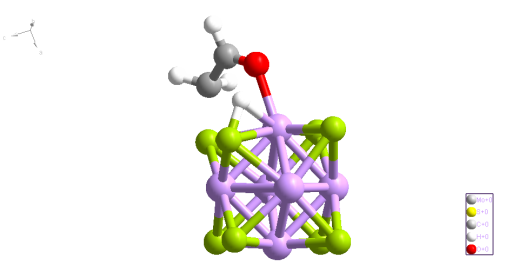


TS6’ TS7’ TS8’ TS9’

CH3CH2O\* CH3CHO\*+H\* CH2CH2O\*+H\* CH3\*+CH2O\* CH3CH2\*+O\*

**Fig. S3** Potential energy surfaces and geometrical structures for CH3CH2O\* decomposition catalyzed by Mo6S8. Atom colors are Mo (pink), S (green), O (red), C (black), and H (white).



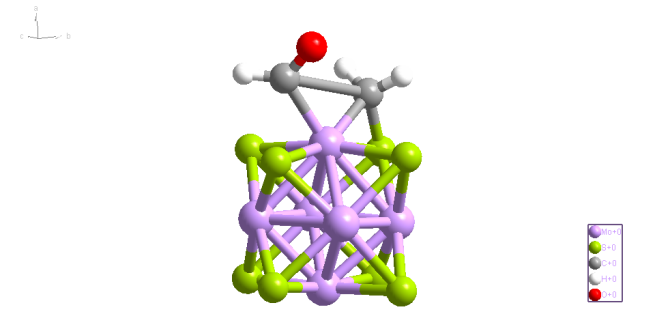
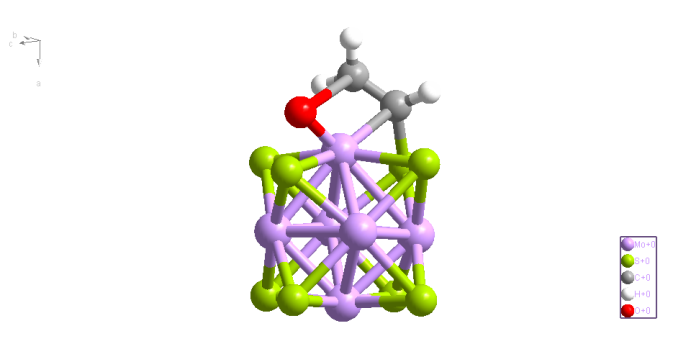
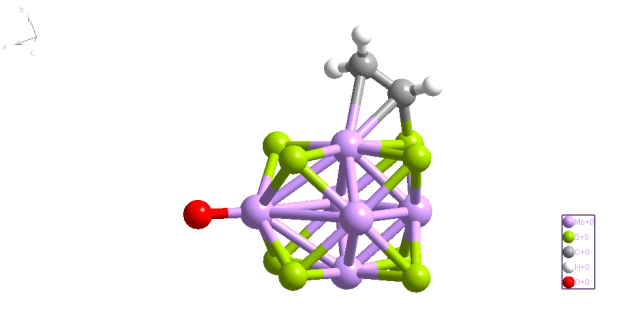
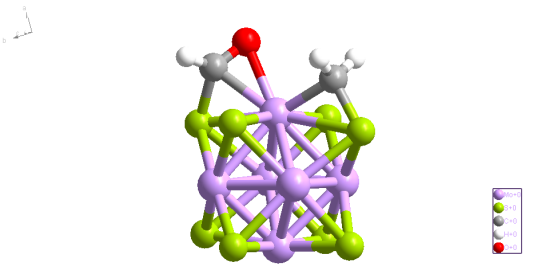
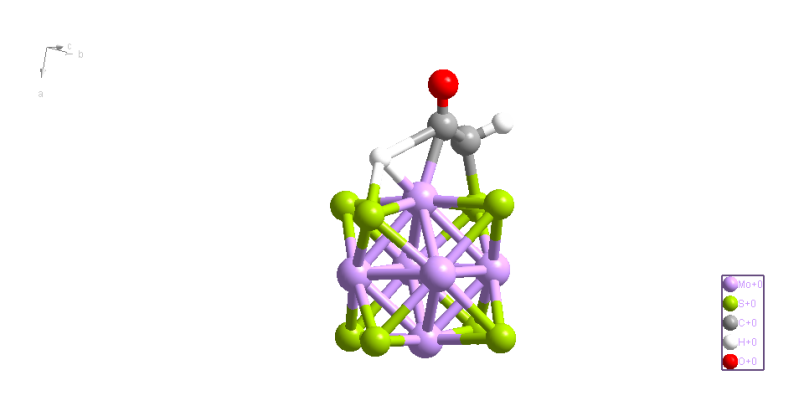
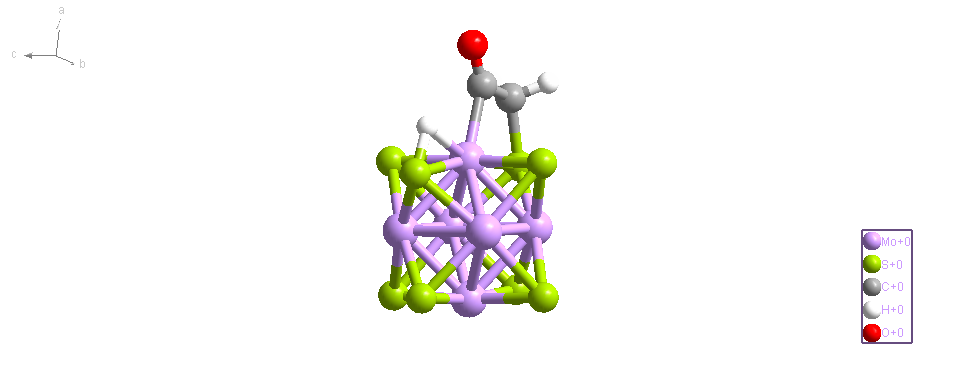
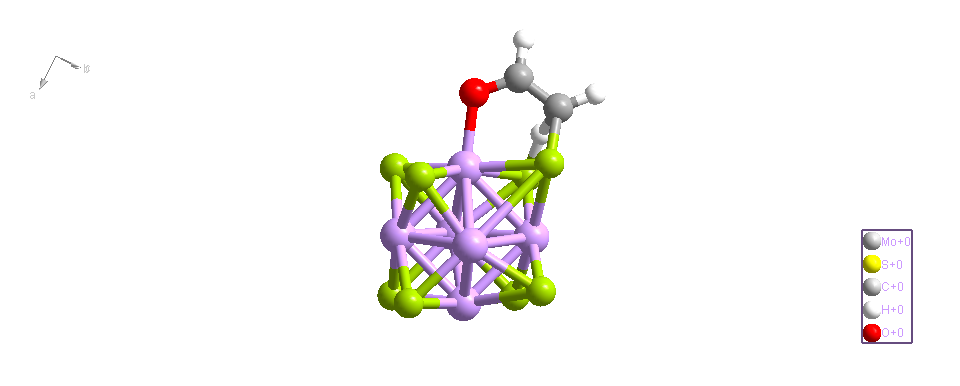
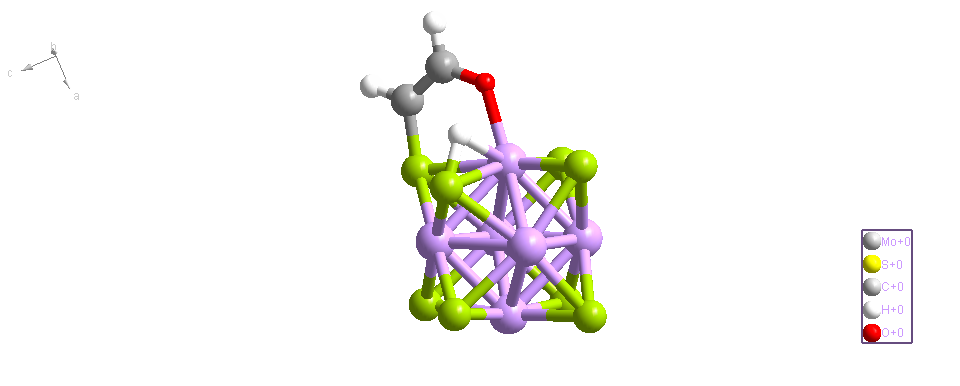
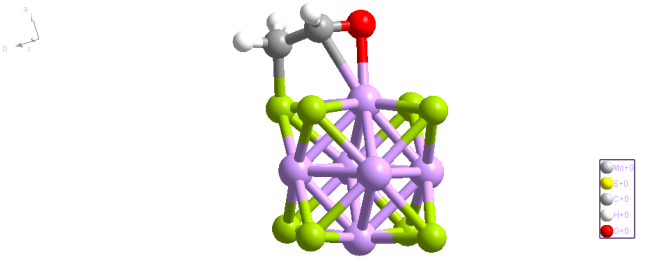


TS10’ TS11’ TS12’ TS13’

CH3CHO\* CH2CHO\*+H\* CH3CO\*+H\* CH3\*+CHO\* CH3CH\*+O\*

**Fig. S4** Potential energy surfaces and geometrical structures for CH3CHO\* decomposition catalyzed by Mo6S8. Atom colors are Mo (pink), S (green), O (red), C (black), and H (white).





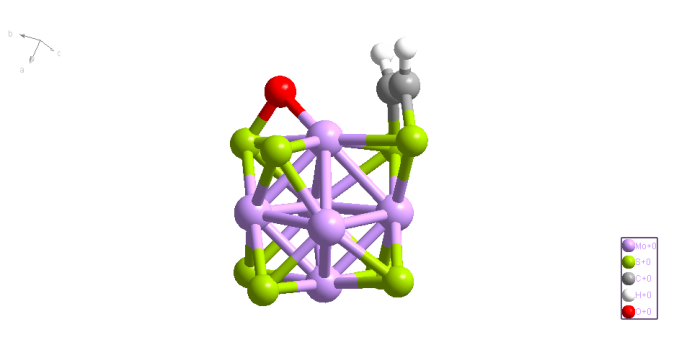
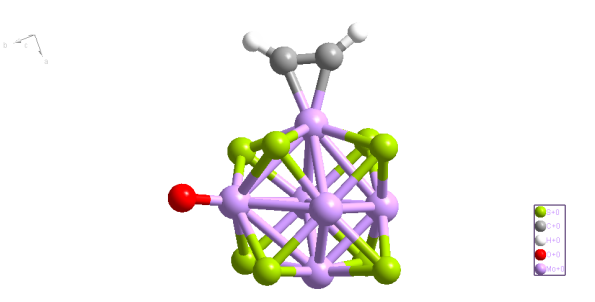
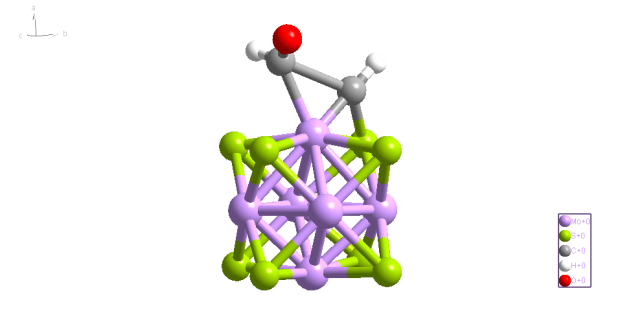
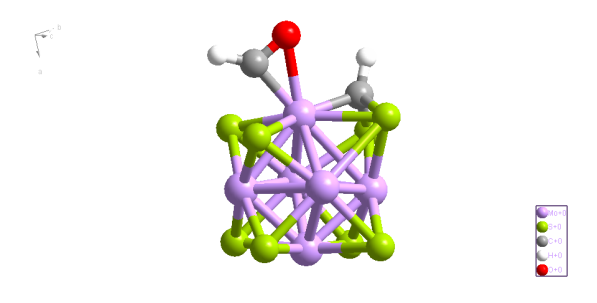
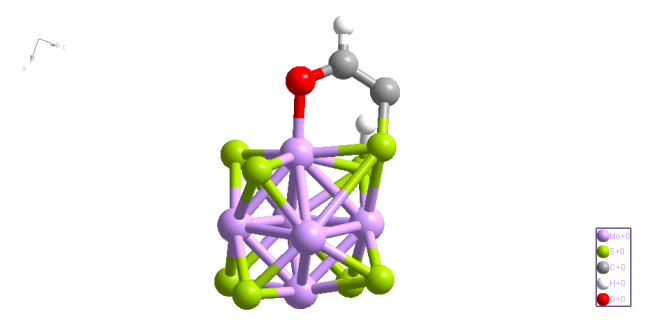
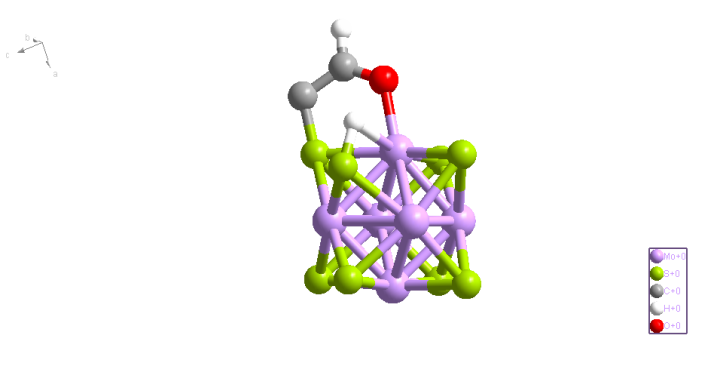
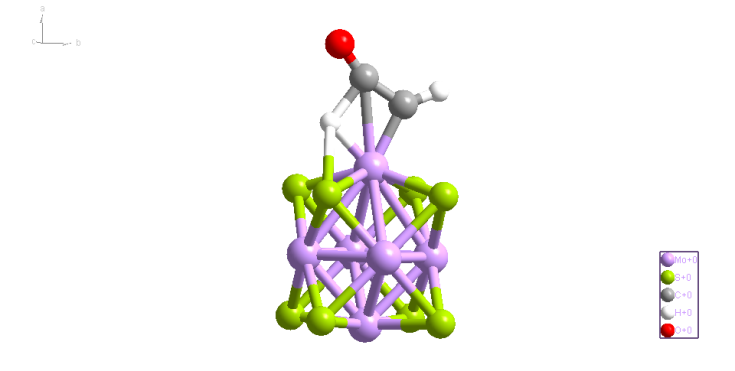
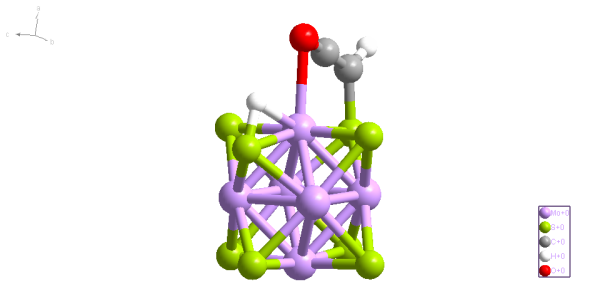
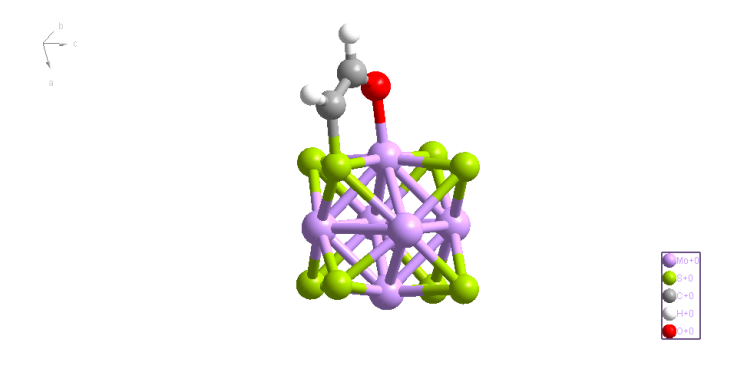
TS14’ TS15’ TS16 ’ TS17’

CH2CHO\* CHCHO\*+H\* CH2CO\*+H\* CH2\*+CHO\* CH2CH\*+O\*

**Fig. S5** Potential energy surfaces and geometrical structures for CH2CHO\* decomposition catalyzed by Mo6S8. Atom colors are Mo (pink), S (green), O (red), C (black), and H (white).

2



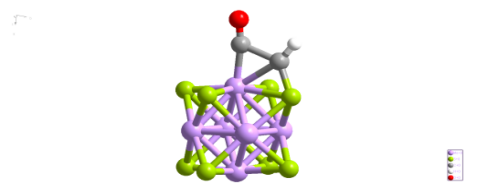
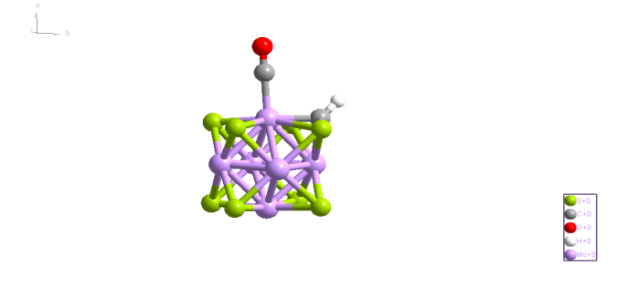
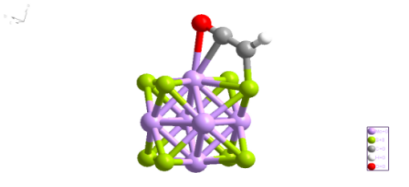
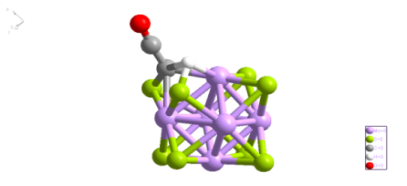
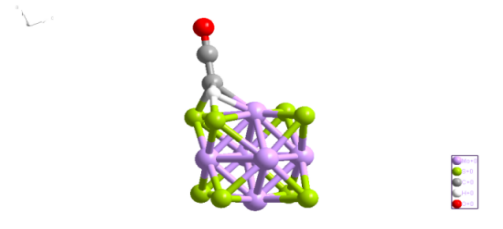


TS21’ TS22’ TS23’ TS24’

CHCHO\* CHCO\*+H\* CCHO\*+H\* CH\*+CHO\* CHCH\*+O\*

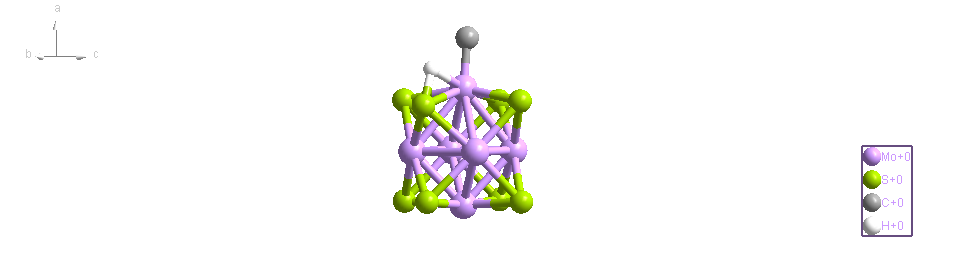
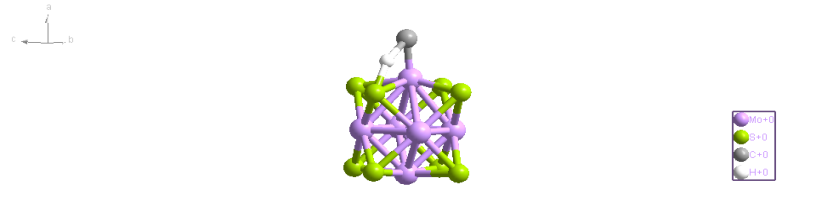
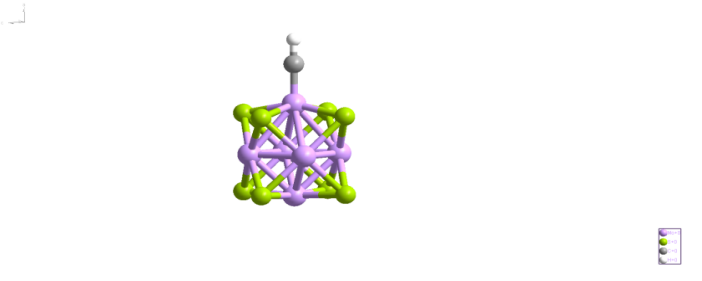
**Fig. S6** Potential energy surfaces and geometrical structures for CHCHO\* decomposition catalyzed by Mo6S8. Atom colors are Mo (pink), S (green), O (red), C (black), and H (white).





**Fig. S7** Potential energy surfaces and geometrical structures for CHCO\* decomposition catalyzed by Mo6S8. Atom colors are Mo (pink), S (green), O (red), C (black), and H (white).





**Fig. S8** Potential energy surfaces and geometrical structures for CH\* decomposition catalyzed by Mo6S8. Atom colors are Mo (pink), S (green), and H (white).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Elementary reactions | PBE PBE-D3(BJ)  6-31G (d , p) and LANL2DZ 6-311++G (d, p) and SDD | | | |
| Ea  (kcal/mol) | ΔE  (kcal/mol) | Ea  (kcal/mol) | ΔE  (kcal/mol) |
| CH3CH2OH\* → CH3CH2O\* + H\* | 15.69 | 12.24 | 13.56 | 10.47 |
| CH3CH2OH\* →CH3CHOH\*+ H\* | 31.6 | 27.83 | 27.79 | 24.98 |
| CH3CH2OH\*→CH2CH2OH\*+ H\* | 25.70 | 18.64 | 22.99 | 18.49 |
| CH3CH2OH\* → CH3\* +CH2OH\* | 54.38 | 32.85 | 51.23 | 30.18 |
| CH3CH2OH\* → CH3CH2\* +OH\* | 26.72 | 21.95 | 22.68 | 18.32 |

**Table S1** Possible elementary reactions involved in CH3CH2OH\* decomposition catalyzed by Co-Mo6S8 together with the activation energies (*Ea*), reaction energies (*ΔE*).

**Table S2** Optimized structures and relative energetics with respect to the most stable for Mo6S8 and Co-Mo6S8. Atom colors are Co (blue), Mo (pink), and S (green).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Mo6S8 | Co-Mo6S8 | | |
| Mo-S-S-Mo 4-fold site | Mo top site | S-S bridge site |
| Structure  bond length (Å) |  |  |  |  |
| Energy (Hartree) | -3590.113548 | -3735.227828 | -3734.967875 | -3735.197779 |
| Adsorption energy (kcal/mol) | \_ | -73.39 | 89.33 | -54.93 |