**Supplementary Information**

**Study on CO methanation mechanism over Ni4/MCM-41 catalyst based on the density functional theory**

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1. Structures of C, O and CO adsorption

The O atom binds the Ni-1-Ni-3 bridge site with the O-Ni-1 and O-Ni-3 bond lengths of 1.684 and 1.732 Å, respectively. C atom is also located at the bridge sites of Ni4 and the bond lengths of C-Ni1 and C-Ni4 are 1.827 and 1.756 Å, respectively. CO is strongly present at the bridge site through C atom with with the C-Ni-1, C-Ni-2 and C-O bond length of 1.923, 1.842 and 1.267 Å, respectively.

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O C CO

Fig. S1 Most stable adsorption configuration of O, C and CO on Ni4/MCM-41 catalyst.

2. Structures of formyl (CHO) and hydroxyl methylidyne (COH)

CHO occupies the hollow site of Ni4 via C and O atoms with the C-Ni-1, C-Ni-3 and O-Ni-4 bond lengths of 1.822, 1.886 and 1.284 Å, respectively. H-C-O angel of CHO equals to 131° and the bond lengths of the C-H and C-O are 1.242 and 1.325 Å, respectively. COH binds the Ni-1-Ni-4 bridge site of Ni4 through C atom with the C-Ni-1 and C-Ni-4 bond length of 1.816 and 1.874 Å, respectively. The C-O-H angel of COH equals to 114° and the bond lengths of the O-H and C-O are 1.042 and 1.384 Å, respectively.

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CHO COH

Fig. S2 Most stable adsorption configuration of CHO and COH on Ni4/MCM-41 catalyst.

3. Structures of formaldehyde (CH2O) and hydroxyl methylene (CHOH)

CH2O binds to the top site of Ni4 via the C and O atoms with the C-Ni-1 and O-Ni-1 bond lengths of 2.017 and 1.938 Å, respectively. And the adsorption energy of CH2O is 116.7 kJ/mol, which is much lower than those of CHO and COH. The O-C-Ni-1 angel equals to 83° and bond lengths of C-O and C-H are 1.368 and 1.025 Å, respectively. CHOH is located at the bridge site of Ni4 via the C atom and the bond lengths of C-Ni-1 and C-Ni-2 are 1.8674 and 1.976 Å, respectively. The geometry of adsorbed CHOH on the Ni4/MCM-41 catalyst shows that the angles of Ni-1-C-O and C-O-H equal to 88° and 122°, respectively, with the bond lengths of C-H, C-O, and O-H of 1.034, 1.324, and 0.896 Å, respectively.

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CH2O CHOH

Fig. S3 Most stable adsorption configuration of CH2O and CHOH on Ni4/MCM-41 catalyst.

4. Structures of methoxy (CH3O) and hydroxy methylene (CH2OH)

CH3O occupies the top of Ni-1 atom of Ni4/MCM-41 catalyst via the O atom and the O-Ni bond length is 1.876 Å. The average bond lengths of the three C-H and C-O are 1.078 and 1.386 Å, respectively. CH2OH is also located at the top of Ni1 atom of the substrate via the C and O atoms with C-Ni-1 and O-Ni-1 bonds lengths of 1.862 and 2.132 Å, respectively. In the geometry structure of adsorbed CH2OH, the angle of C-Ni1-O equals to 56° and bonds lengths of the two C-H, C-O and O-H are 1.134, 1.641, and 0.965 Å, respectively.

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CH3O CH2OH

Fig. S4 Most stable adsorption configuration of CH3O and CH2OH on Ni4/MCM-41 catalyst.

5. Structures of CH3OH and CH4

CH3OH is located at the top site of the Ni-1 atom on the Ni4/MCM-41 catalyst with weak bonding force via the O atom. The bond length of O-Ni-1 is calculated to be 2.124 Å. The C-O-H angle is 108° and the bond lengths of C-O, the three C-H and O-H are 1.463, 1.108, and 0.968 Å, respectively. CH4 is also weakly adsorb at the top of the Ni4 atom on the Ni4/MCM-41 catalyst via the C atom with the adsorption energy of 67.8 kJ/mol and the C-Ni1 bond length is 2.012 Å. Like gas-phase CH4, adsorbed CH4 also shows a tetragonal structure with the average C-H bond length of 1.095 Å.

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CH3OH CH4

Fig. S5 Most stable adsorption configuration of CH3OH and CH4 on Ni4/MCM-41 catalyst.

6. Structures of CH, CH2 and CH3

CH is located at the Ni-1-Ni-2 bridge site of the Ni4 via the C atom with the C-Ni-1 and C-Ni-2 bond lengths of 1.821 and 1.786 Å, respectively and the C-H bond length is calculated to be 1.098 Å. CH2 adsorbed on Ni4/MCM-41 surface bonds to the Ni-1-Ni-2 bridge site of the Ni4 via the C atom and the bond lengths of C-Ni-1 and C-Ni-2 are calculated to be 1.885 and 1.843 Å, respectively. The average C-H bond length of adsorbed CH2 on the Ni4/MCM-41 surface is 1.104 Å. CH3 occupies the Ni-1 top site of the Ni4 through the C atom with the bond length of C-Ni-1 of 1.906 Å and the average bond length of the three C-H is calculated to be 1.102 Å.

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CH CH2 CH3

Fig. S6 Most stable adsorption configuration of CH, CH2 and CH3 on Ni4/MCM-41 catalyst.