

*Electronic Supplementary Information*

**DFT Exploration of Active Site Motifs in Methane  
Hydroxylation by Ni-ZSM-5 Zeolite**

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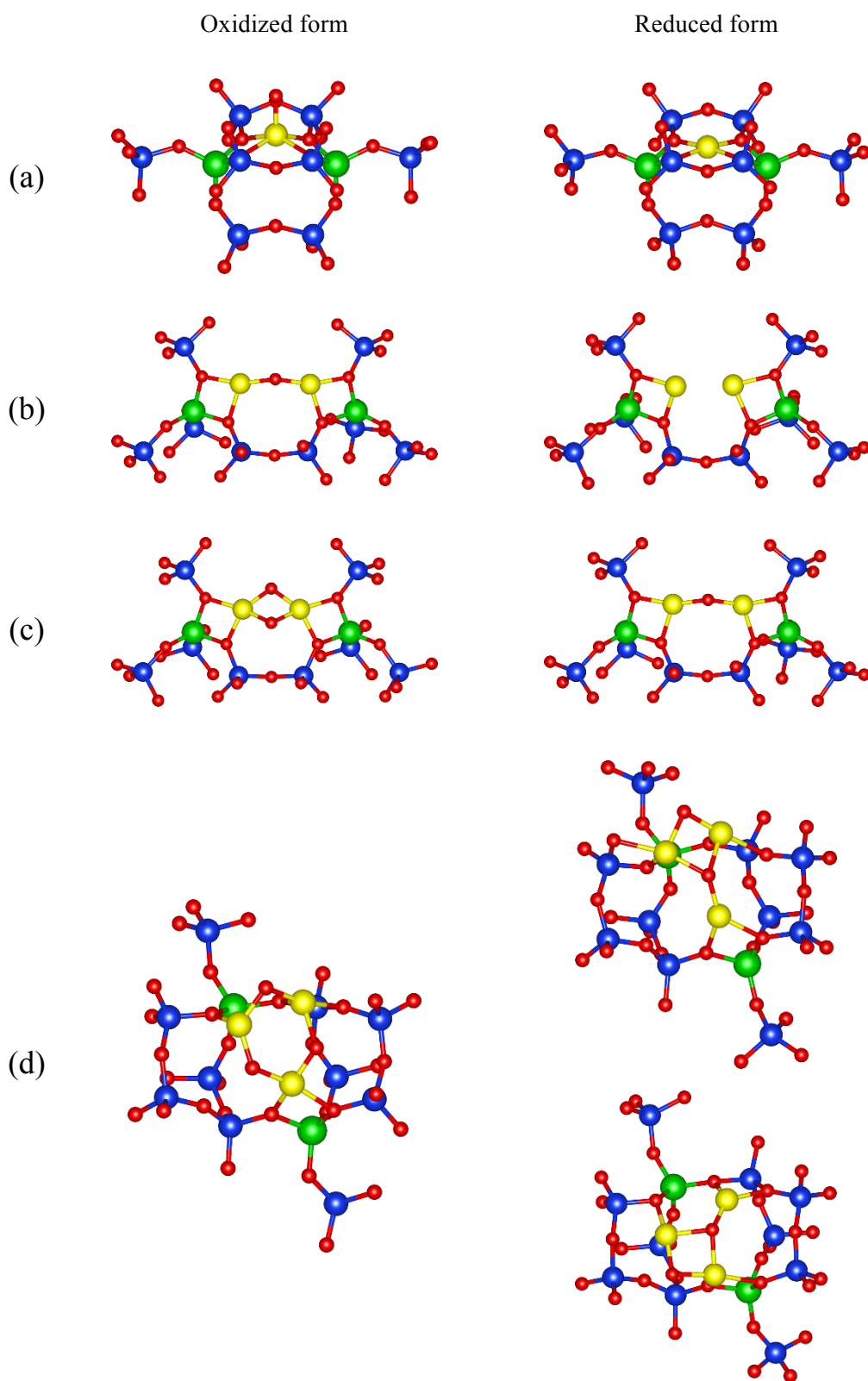
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**Figure S1.** Large cluster models of the oxidized and reduced active species: (a)  $[\text{NiO}]^{2+}$ - and  $\text{Ni}^{2+}$ -ZSM-5, (b)  $[\text{Ni}_2(\mu\text{-O})]^{2+}$ - and  $[2\text{Ni}]^{2+}$ -ZSM-5, (c)  $[\text{Ni}_2(\mu\text{-O})_2]^{2+}$ - and  $[\text{Ni}_2(\mu\text{-O})]^{2+}$ -ZSM-5, and (d)  $[\text{Ni}_3(\mu\text{-O})_3]^{2+}$ - and  $[\text{Ni}_3(\mu\text{-O})_2]^{2+}$ -ZSM-5. The terminating H atoms are omitted for clarity.

**Table S1.** Relative energies and atomic spin densities ( $\rho$ ) for various motifs of Ni active site in ZSM-5 zeolite, comparing the results calculated by the hybrid B3LYP and semilocal PBE functionals in the cluster models and periodic structures, respectively. Comparisons to those calculated by the hybrid PBE0 functional are also given.

| Spin state <sup>a</sup>                                      | Cluster Model (PBE0)     |                   |                      | Cluster Model (B3LYP)    |                   |                      | Periodic Structure (PBE) |                          |                   |                      |                      |
|--|--------------------------|-------------------|----------------------|--------------------------|-------------------|----------------------|--------------------------|--------------------------|-------------------|----------------------|----------------------|
|  | $\Delta E$<br>(kcal/mol) | $\rho(\text{Ni})$ | $\rho(\text{O})$     | $\Delta E$<br>(kcal/mol) | $\rho(\text{Ni})$ | $\rho(\text{O})$     | $U_{\text{eff}}$<br>(eV) | $\Delta E$<br>(kcal/mol) | $\rho(\text{Ni})$ | $\rho(\text{O})$     |                      |
| [NiO] <sup>2+</sup> -Z                                       | Q                        | 0.0               | 1.85                 | 1.70                     | 0.0               | 1.84                 | 1.63                     | 3.0                      | 0.0               | 1.95                 | 1.46                 |
|  | T                        | 19.8              | 1.37                 | 0.37                     | 14.2              | 0.59                 | 1.37                     | 3.0                      | 16.8              | 1.25                 | 0.42                 |
|  | S                        | 37.6              | 0                    | 0                        | 30.7              | 0                    | 0                        | 3.0                      | 39.7              | 0                    | 0                    |
| [Ni] <sup>2+</sup> -Z  | Q                        | 118.5             | 3.17                 | -                        | 119.5             | 3.06                 | -                        | 0.0                      | 106.5             | 2.67                 | -                    |
|  | T                        | 0.0               | 1.75                 | -                        | 3.4               | 1.70                 | -                        | 0.0                      | 6.4               | 1.56                 | -                    |
|  | S                        | 3.9               | 0                    | -                        | 0.0               | 0                    | -                        | 0.0                      | 0.0               | 0                    | -                    |
| [Ni <sub>2</sub> ( $\mu$ -O)] <sup>2+</sup> -Z               | Q                        | 0.0               | 1.70, 1.70           | 0.40                     | 0.0               | 1.66, 1.65           | 0.46                     | 6.4                      | 2.9               | 1.75, 1.75           | 0.31                 |
|  | T                        | 29.1              | 1.05, 1.06           | 0.21                     | 14.9              | 0.99, 1.01           | -0.11                    | 6.4                      | 13.3              | 1.73, 0.02           | 0.15                 |
|  | S                        | 18.4              | 0, 0                 | 0                        | 14.7              | 0, 0                 | 0                        | 6.4                      | 0.0               | 1.71, -1.71          | 0                    |
| [2Ni] <sup>2+</sup> -Z                                       | Q                        | 0.0               | 1.70, 1.70           | -                        | 4.2               | 1.81, 1.97           | -                        | 0.0                      | 6.9               | 1.80, 1.80           | -                    |
|  | T                        | 2.0               | 1.01, 0.89           | -                        | 0.0               | 0.98, 0.91           | -                        | 0.0                      | 0.0               | 0.94, 0.93           | -                    |
|  | S                        | 24.8              | 0, 0                 | -                        | 22.8              | 0, 0                 | -                        | 0.0                      | 1.2               | 1.17, -1.16          | -                    |
| [Ni <sub>2</sub> ( $\mu$ -O) <sub>2</sub> ] <sup>2+</sup> -Z | Q                        | 0.0               | 0.69, 1.72           | 0.64, 0.79               | 3.5               | 0.69, 1.70           | 0.66, 0.75               | 4.0                      | 3.2               | 1.00, 1.73           | 0.52, 0.52           |
|  | T                        | 4.8               | 1.17, 1.08           | -0.22, -0.14             | 2.2               | 0.76, 0.64           | 0.33, 0.20               | 4.0                      | 1.6               | 1.12, 1.12           | -0.27, -0.09         |
|  | S                        | 1.3               | -1.06, 1.01          | 0.03, -0.04              | 0.0               | -1.01, 1.00          | 0.03, -0.01              | 4.0                      | 0.0               | -1.02, 1.02          | -0.01, 0.00          |
| [Ni <sub>3</sub> ( $\mu$ -O) <sub>3</sub> ] <sup>2+</sup> -Z | Sp                       | 0.0               | 0.74, 1.73,<br>1.62  | 0.45, 0.85,<br>0.41      | 0.0               | 0.65, 1.68,<br>1.60  | 0.53, 0.82,<br>0.51      | 4.0                      | 0.0               | 0.76, 1.68,<br>1.69  | 0.43, 0.74,<br>0.47  |
|  | Q                        | 5.3               | 0.93, 1.66,<br>1.53  | 0.13, 0.23,<br>0.65      | 7.5               | 1.56, 0.68,<br>0.14  | 0.21, 0.78,<br>0.47      | 4.0                      | 6.3               | 1.65, 0.75,<br>0.76  | 0.24, 0.09,<br>0.33  |
|  | T                        | 3.8               | -1.13, 1.65,<br>1.56 | 0.41, 0.10,<br>0.68      | 6.4               | -0.63, 1.55,<br>1.20 | -0.22, 0.07,<br>-0.09    | 4.0                      | 1.6               | -0.99, 1.48,<br>1.21 | 0.28, 0.04,<br>-0.12 |
| [Ni <sub>3</sub> ( $\mu$ -O) <sub>2</sub> ] <sup>2+</sup> -Z | Sp                       | 1.0               | 1.74, 1.61,<br>1.57  | 0.43, 0.43               | 0.7               | 1.70, 1.55,<br>1.51  | 0.50, 0.50               | 6.4                      | 2.5               | 1.76, 1.65,<br>1.67  | 0.37, 0.35           |
|  | Q                        | 8.3               | 1.71, 0.01,<br>1.61  | 0.17, 0.33               | 11.6              | 1.37, 0.20,<br>1.29  | 0.46, 0.59               | 6.4                      | 10.0              | 1.74, 0.12,<br>1.66  | 0.10, 0.23           |
|  | T                        | 0.0               | 1.73, -1.57,<br>1.56 | -0.13, 0.40              | 0.0               | 1.69, -1.51,<br>1.48 | -0.17, 0.48              | 6.4                      | 0.0               | 1.74, -1.62,<br>1.65 | -0.09, 0.20          |

<sup>a</sup> Sp, Q, T, and S stand for septet, quintet, triplet, and singlet states, respectively.

In the cases of [Ni<sup>IV</sup>O]<sup>2+</sup>-Z and [Ni<sup>II</sup>]<sup>2+</sup>-Z, the use of  $U_{\text{eff}} = 3.0$  and  $0.0$  eV, respectively, results in the same relative-energy trend as that calculated by the B3LYP functional in the cluster model and predicts the same ground state, i.e. the quintet and closed-shell singlet states, respectively. Comparing the spin densities for Ni and O atoms of [NiO]<sup>2+</sup>-Z, we found that the use of  $U_{\text{eff}} = 3.0$  eV can correctly result in similar numbers to those

calculated by B3LYP, except for those in the triplet state, due to the characteristics of PBE functional (see also results calculated by PBE0 in the triplet state). For  $[\text{Ni}]^{2+}\text{-Z}$ , in contrast, the PBE0 and B3LYP functionals predict different ground states, i.e. triplet and closed-shell singlet states, respectively, which are very close in energy. As many researchers (e.g. Bachler et al. *Inorg. Chem.* **2002**, *41*, 4179–4193) suggested the singlet state as the ground state for square planar Ni complexes, we choose  $U_{\text{eff}} = 0.0$  eV, which can also predict the singlet state as the ground state. Thus, in the periodic DFT calculations, we consider the quintet, triplet, and closed-shell singlet states both for the first and second half of the reaction.

In the cases of  $[\text{Ni}^{\text{II}}_2(\mu\text{-O})]^{2+}\text{-Z}$  and  $[2\text{Ni}^{\text{I}}]^{2+}\text{-Z}$ , while the PBE+U method predicts that the open-shell singlet state is the ground state, both the PBE0 and B3LYP functionals fail to predict the open-shell configuration (instead, the closed-shell singlet state is predicted).  $U_{\text{eff}} = 6.4$  eV for  $\text{Ni}^{\text{II}}\text{O}$  was originally reported by Wang et al. (*Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 195107). The use of  $U_{\text{eff}} = 6.4$  eV for  $[\text{Ni}_2(\mu\text{-O})]^{2+}\text{-Z}$  can reproduce similar values of Ni-atom and O-atom spin densities to those calculated by both of the PBE0 and B3LYP functionals, except for those in the triplet state. Thus, in the periodic DFT calculations, we consider only the quintet and open-shell singlet states for the first half of the reaction. On the other hand, the use of  $U_{\text{eff}} = 0.0$  eV for  $[2\text{Ni}]^{2+}\text{-Z}$  in the quintet and triplet states can predict correctly the Ni-atom and O-atom spin densities. Thus, we consider all possible spin states (quintet, triplet, and open-shell singlet states) for the second half of the reaction.

In the case of  $[\text{Ni}^{\text{III}}_2(\mu\text{-O})_2]^{2+}\text{-Z}$ , the use of  $U_{\text{eff}} = 4.0$  eV results in the same relative-energy trend as that calculated by the B3LYP functional in the cluster model and predicts the same ground state, i.e. the open-shell singlet state. However, it fails to reproduce the triplet-state Ni spin densities predicted by the B3LYP functional, due to the characteristics of PBE functional (see also Ni spin densities calculated by PBE0 in the triplet state). In the quintet state, on the other hand, the use of  $U_{\text{eff}} = 4.0$  eV is unable to predict the same spin density distribution as that predicted by both of the PBE0 and B3LYP functionals. Thus, in the periodic DFT calculations, we consider only the triplet and open-shell singlet states for the first half of the reaction and the quintet and open-shell singlet states for the second half of the reaction.

In the case of  $[\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}_2(\mu\text{-O})_3]^{2+}\text{-Z}$ , because the  $\text{Ni}^{\text{III}}$  cation can only be reasonably treated by using  $U_{\text{eff}} = 4.0$  eV, whereas the  $\text{Ni}^{\text{II}}$  cation can be treated reasonably by using  $U_{\text{eff}} = 6.4$  or  $4.0$  eV (see Tables S2 and S3 below), we choose  $U_{\text{eff}} = 4.0$  eV for the first half of the reaction. For the second half of the reaction, on the other hand, as it involves only  $\text{Ni}^{\text{II}}$  cation in the reduced  $[\text{Ni}^{\text{II}}_3(\mu\text{-O})_2]^{2+}\text{-Z}$ , we choose  $U_{\text{eff}} = 6.4$  eV. These  $U_{\text{eff}}$  values can reproduce very well the Ni-atom spin densities and ground states predicted by the PBE0 and B3LYP functionals, except for  $[\text{Ni}_3(\mu\text{-O})_3]^{2+}\text{-Z}$  calculated in the quintet state. Thus, in the periodic DFT calculations, we consider only the septet and open-shell triplet states for the first half of the reaction, while the septet, quintet, and open-shell triplet states for the second half of the reaction.

**Table S2.** Relative energies and atomic spin densities ( $\rho$ ) for  $[\text{Ni}^{\text{IV}}\text{O}]^{2+}$ - and  $[\text{Ni}^{\text{II}}]^{2+}$ -ZSM-5 in the high-spin and low-spin states calculated by using different  $U_{\text{eff}}$  values.

| $U_{\text{eff}}$ (eV) | Spin state | [NiO] <sup>2+</sup> -ZSM-5 |                   |                  | [Ni] <sup>2+</sup> -ZSM-5 |                   |
|-----------------------|------------|----------------------------|-------------------|------------------|---------------------------|-------------------|
|                       |            | $\Delta E$<br>(kcal/mol)   | $\rho(\text{Ni})$ | $\rho(\text{O})$ | $\Delta E$<br>(kcal/mol)  | $\rho(\text{Ni})$ |
| 0.0                   | Q          | 0.0                        | 1.92              | 1.44             | 106.5                     | 2.67              |
|                       | T          | 18.9                       | 0.90              | 0.77             | 6.4                       | 1.56              |
|                       | CSS        | 33.8                       | 0                 | 0                | 0.0                       | 0                 |
| 2.0                   | Q          | 0.0                        | 1.94              | 1.45             | 103.1                     | 2.63              |
|                       | T          | 17.9                       | 1.52              | -0.01            | 0.0                       | 1.64              |
|                       | CSS        | 49.5                       | 0                 | 0                | 1.8                       | 0                 |
| 3.0                   | Q          | 0.0                        | 1.95              | 1.46             | 65.8                      | 2.65              |
|                       | T          | 16.8                       | 1.25              | 0.42             | 0.0                       | 1.67              |
|                       | CSS        | 39.7                       | 0                 | 0                | 1.5                       | 0                 |
| 4.0                   | Q          | 0.0                        | 1.96              | 1.47             | 100.6                     | 2.67              |
|                       | T          | 16.6                       | 1.72              | -0.08            | 0.0                       | 1.70              |
|                       | CSS        | 18.4                       | 0                 | 0                | 4.9                       | 0                 |
| 6.4                   | Q          | 0.0                        | 1.98              | 1.52             | 99.4                      | 2.70              |
|                       | T          | 37.8                       | -0.06             | 1.52             | 0.0                       | 1.77              |
|                       | CSS        | 35.2                       | 0                 | 0                | 13.6                      | 0                 |

Q, T, and CSS stand for quintet, triplet, and closed-shell singlet states, respectively.

The use of  $U_{\text{eff}} = 0.0, 2.0, 3.0,$  and  $4.0$  eV for  $[\text{Ni}^{\text{IV}}\text{O}]^{2+}$ -Z in the quintet state results in reasonable Ni-atom and O-atom spin densities, but we choose  $U_{\text{eff}} = 3.0$  eV because it can predict a reasonable C $\cdots$ H distance of **TS1** (see the main text). The use of  $U_{\text{eff}} = 0.0$  eV for  $[\text{Ni}]^{2+}$ -Z result in the same ground state as that predicted by the B3LYP functional (see Table S1).

**Table S3.** Relative energies and atomic spin densities ( $\rho$ ) for  $[\text{Ni}^{\text{II}}_2(\mu\text{-O})]^{2+}$ - and  $[2\text{Ni}^{\text{I}}]^{2+}$ -ZSM-5 in the high-spin and low-spin states calculated by using different  $U_{\text{eff}}$  values.

| $U_{\text{eff}}$ (eV) | Spin state | $[\text{Ni}_2(\mu\text{-O})]^{2+}$ -ZSM-5 |                   |                  | $[2\text{Ni}]^{2+}$ -ZSM-5 |                   |
|-----------------------|------------|---|-------------------|------------------|----------------------------|-------------------|
|                       |            | $\Delta E$<br>(kcal/mol)                  | $\rho(\text{Ni})$ | $\rho(\text{O})$ | $\Delta E$<br>(kcal/mol)   | $\rho(\text{Ni})$ |
| 0.0                   | Q          | 4.5                                       | 1.52, 1.52        | 0.63             | 6.9                        | 1.80, 1.80        |
|                       | T          | 0.0                                       | 0.81, 0.81        | 0.23             | 0.0                        | 0.94, 0.93        |
|                       | S          | 4.8                                       | 0, 0              | 0                | 1.2                        | 1.17, -1.16       |
| 4.0                   | Q          | 4.1                                       | 1.67, 1.67        | 0.42             | 0.0                        | 1.89, 1.88        |
|                       | T          | 22.9                                      | 1.73, 0.02        | 0.15             | 1.8                        | 0.95, 0.96        |
|                       | S          | 0.0                                       | 1.60, -1.60       | 0                | 1.7                        | 0.98, -0.98       |
| 6.4                   | Q          | 2.9                                       | 1.75, 1.75        | 0.31             | 0.0                        | 1.92, 1.92        |
|                       | T          | 13.3                                      | 1.73, 0.02        | 0.15             | 0.3                        | 0.97, 0.97        |
|                       | S          | 0.0                                       | 1.71, -1.71       | 0                | 0.2                        | 0.97, -0.97       |
| 7.0                   | Q          | 2.6                                       | 1.77, 1.77        | 0.28             | 0.0                        | 1.93, 1.93        |
|                       | T          | 13.7                                      | 1.75, 0.02        | 0.13             | 0.4                        | 0.97, 0.97        |
|                       | S          | 0.0                                       | 1.73, -1.73       | 0                | 0.3                        | 0.97, -0.97       |

Q, T, and S stand for quintet, triplet, and singlet states, respectively.

The  $U_{\text{eff}} = 6.4$  eV for  $\text{Ni}^{\text{II}}\text{O}$  has been suggested previously by Wang et al. (*Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, 73, 195107). Although calculations of  $[\text{Ni}^{\text{II}}_2(\mu\text{-O})]^{2+}$ -ZSM-5 by using  $U_{\text{eff}} = 4.0, 6.4,$  and  $7.0$  eV result in the same ground state and atomic spin densities, we decided to choose  $U_{\text{eff}} = 6.4$  eV for calculating the first half of the reaction. On the other hand, calculations of  $[2\text{Ni}^{\text{I}}]^{2+}$ -ZSM-5 can only be performed by using  $U_{\text{eff}} = 0.0$  eV to predict the correct ground state and Ni-atom spin densities.

**Table S4.** Relative energies and atomic spin densities ( $\rho$ ) for  $[\text{Ni}^{\text{III}}_2(\mu\text{-O})_2]^{2+}$ -ZSM-5 in the high-spin and low-spin states calculated by using different  $U_{\text{eff}}$  values.

| $U_{\text{eff}}$ (eV) | Spin state | $[\text{Ni}_2(\mu\text{-O})_2]^{2+}$ -ZSM-5 |                   |                  |
|-----------------------|------------|---|-------------------|------------------|
|                       |            | $\Delta E$<br>(kcal/mol)                    | $\rho(\text{Ni})$ | $\rho(\text{O})$ |
| 0.0                   | Q          | 9.3   | 0.94, 1.54        | 0.57, 0.64       |
|                       | T          | 0.0   | 0.60, 0.60        | 0.40, 0.31       |
|                       | S          | 2.7   | -0.01, -0.01      | -0.39, 0.41      |
| 3.0                   | Q          | 3.9   | 0.98, 1.72        | 0.55, 0.53       |
|                       | T          | 3.1   | 0.55, 0.56        | 0.44, 0.36       |
|                       | S          | 0.0   | -0.90, 0.90       | 0.00, 0.00       |
| 3.5                   | Q          | 3.6   | 0.98, 1.75        | 0.53, 0.52       |
|                       | T          | 5.7   | 0.54, 0.54        | 0.45, 0.37       |
|                       | S          | 0.0   | -0.95, 0.95       | 0.00, 0.00       |
| 4.0                   | Q          | 3.2   | 1.00, 1.73        | 0.52, 0.52       |
|                       | T          | 1.6   | 1.12, 1.12        | -0.27, -0.09     |
|                       | S          | 0.0   | -1.02, 1.02       | -0.01, 0.00      |
| 5.0                   | Q          | 2.5   | 1.05, 1.75        | 0.50, 0.50       |
|                       | T          | 0.7   | 1.25, 1.27        | -0.25, -0.36     |
|                       | S          | 0.0   | -1.19, 1.22       | -0.02, -0.01     |
| 6.4                   | Q          | 0.0   | 1.71, 1.71        | 0.22, 0.19       |
|                       | T          | 20.2  | 1.42, 1.44        | -0.42, -0.48     |
|                       | S          | 19.2  | -1.41, 1.57       | -0.14, -0.04     |

Q, T, and S stand for quintet, triplet, and singlet states, respectively.

The use of  $U_{\text{eff}} = 4.0$  eV can correctly predict the ground state and atomic spin densities of  $[\text{Ni}^{\text{III}}_2(\mu\text{-O})_2]^{2+}$ -ZSM-5 in the triplet and open-shell singlet states. However, calculations in the quintet state cannot result in similar atomic spin densities to those calculated in the cluster models (see Table S1).



**Table S5.** Relative energies and atomic spin densities ( $\rho$ ) for  $[\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}_2(\mu\text{-O})_3]^{2+}$ - and  $[\text{Ni}^{\text{II}}_3(\mu\text{-O})_2]^{2+}$ - ZSM-5 in the high-spin and low-spin states calculated by using different  $U_{\text{eff}}$  values.

| $U_{\text{eff}}$ (eV) | Spin state | $[\text{Ni}_3(\mu\text{-O})_3]^{2+}$ -ZSM-5 |                      |                        | $[\text{Ni}_3(\mu\text{-O})_2]^{2+}$ -ZSM-5 |                       |                  |
|-----------------------|------------|---|----------------------|------------------------|---|-----------------------|------------------|
|                       |            | $\Delta E$<br>(kcal/mol)                    | $\rho(\text{Ni})$    | $\rho(\text{O})$       | $\Delta E$<br>(kcal/mol)                    | $\rho(\text{Ni})$     | $\rho(\text{O})$ |
| 4.0                   | Sp         | 0.0   | 0.76, 1.68,<br>1.69  | 0.43, 0.74,<br>0.47    | 2.0   | 1.69, 1.54,<br>1.57   | 0.52, 0.44       |
|                       | Q          | 6.3   | 1.65, 0.75,<br>0.76  | 0.24, 0.09,<br>0.33    | 0.0   | 1.64, 0.07,<br>1.53   | 0.24, 0.33       |
|                       | T          | 1.6   | -0.99, 1.48,<br>1.21 | 0.28, 0.04, -<br>0.12  | 16.7  | 1.66, 0.07, -<br>0.07 | 0.26, -0.04      |
| 6.4                   | Sp         | 0.3   | 1.58, 1.76,<br>1.76  | 0.13, -0.22,<br>0.80   | 2.5   | 1.76, 1.65,<br>1.67   | 0.37, 0.35       |
|                       | Q          | 0.0   | 1.64, 1.67,<br>1.60  | -0.34, -0.30,<br>-0.44 | 10.0  | 1.74, 0.12,<br>1.66   | 0.10, 0.23       |
|                       | T          | 3.6   | 1.74, -1.60,<br>1.53 | 0.64, -0.25, -<br>0.17 | 0.0   | 1.74, -1.62,<br>1.65  | -0.09, 0.20      |

Sp, Q, and T stand for septet, quintet, and triplet states, respectively.

The  $[\text{Ni}_3(\mu\text{-O})_3]^{2+}$  species involves  $\text{Ni}^{\text{II}}$  and  $\text{Ni}^{\text{III}}$  cations. Because the  $\text{Ni}^{\text{III}}$  cation can only be correctly described by using  $U_{\text{eff}} = 4.0$  eV, while the  $\text{Ni}^{\text{II}}$  cation can be correctly described by using  $U_{\text{eff}} = 4.0$  or 6.4 eV (see Table S3), we decided to use  $U_{\text{eff}} = 4.0$  eV for the first half of the reaction on  $[\text{Ni}_3(\mu\text{-O})_3]^{2+}$ -ZSM-5. For the second half of the reaction, on the other hand,  $U_{\text{eff}} = 6.4$  eV is used because the reduced  $[\text{Ni}_3(\mu\text{-O})_2]^{2+}$ -ZSM-5 involves only  $\text{Ni}^{\text{II}}$  cation and this value can correctly predict the ground state.

**Table S6.** Reaction energies of methane hydroxylation to methanol on various active site motifs of Ni-ZSM-5 calculated by B3LYP functional in large cluster models.

|  | Ground state | $\Delta E$ (kcal/mol) | remarks |
|--|--------------|-----------------------|---------|
| $[\text{NiO}]^{2+}\text{-Z} + \text{CH}_4$                           | Q            | 0.0                   |         |
| $[\text{Ni}]^{2+}\text{-Z} + \text{CH}_3\text{OH}$                   | CSS          | -49.1                 |         |
| $[\text{Ni}_2(\mu\text{-O})]^{2+}\text{-Z} + \text{CH}_4$            | Q            | 0.0                   |         |
| $[\text{Ni}_2]^{2+}\text{-Z} + \text{CH}_3\text{OH}$                 | T            | 43.9                  |         |
| $[\text{Ni}_2(\mu\text{-O})_2]^{2+}\text{-Z} + \text{CH}_4$          | OSS          | 0.0                   |         |
| $[\text{Ni}_2(\mu\text{-O})]^{2+}\text{-Z} + \text{CH}_3\text{OH}$   | Q            | -34.6                 |         |
| $[\text{Ni}_3(\mu\text{-O})_3]^{2+}\text{-Z} + \text{CH}_4$          | Sp           | 0.0                   |         |
| $[\text{Ni}_3(\mu\text{-O})_2]^{2+}\text{-Z} + \text{CH}_3\text{OH}$ | T            | -29.3                 | Oxo: O1 |
| $[\text{Ni}_3(\mu\text{-O})_2]^{2+}\text{-Z} + \text{CH}_3\text{OH}$ | T            | -25.6                 | Oxo: O2 |

Sp, Q, T, CSS, and OSS stand for septet, quintet, triplet, closed-shell singlet, and open-shell singlet states, respectively.