Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary Information for

# N-H Bond Activation in Ammonia by TM-SSZ-13 (Fe, Co, Ni, Cu) Zeolites: A First-Principles Calculation

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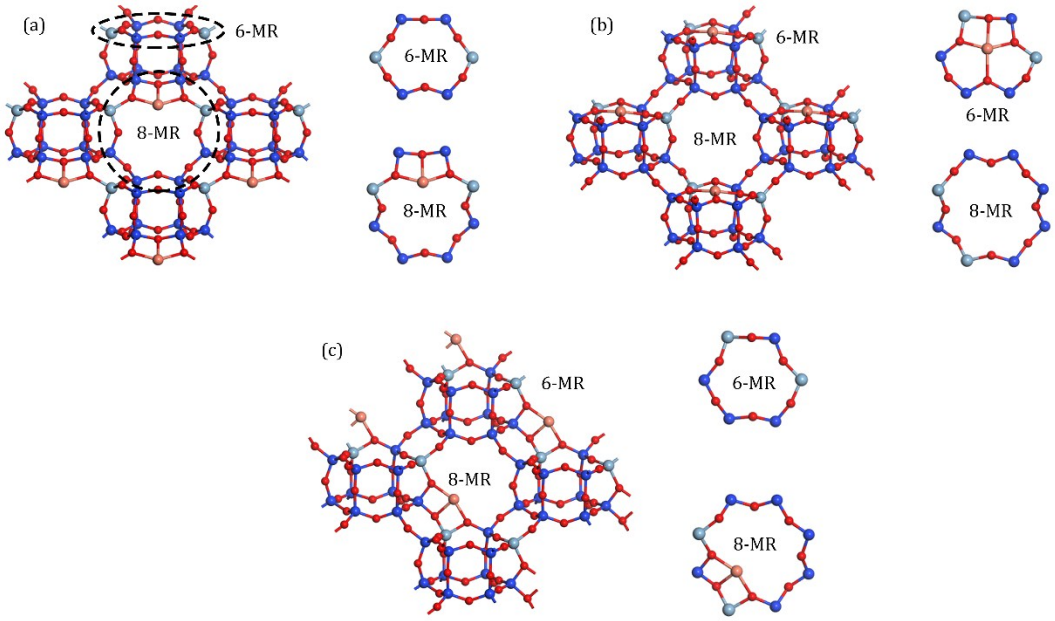


**Fig. S1** The structure schematic diagrams and corresponding 2-dimensional views of 6-MR and 8-MR (a) TM-pAl2-8MR (b) TM-mAl2-6MR (c) TM-mAl2-8MR

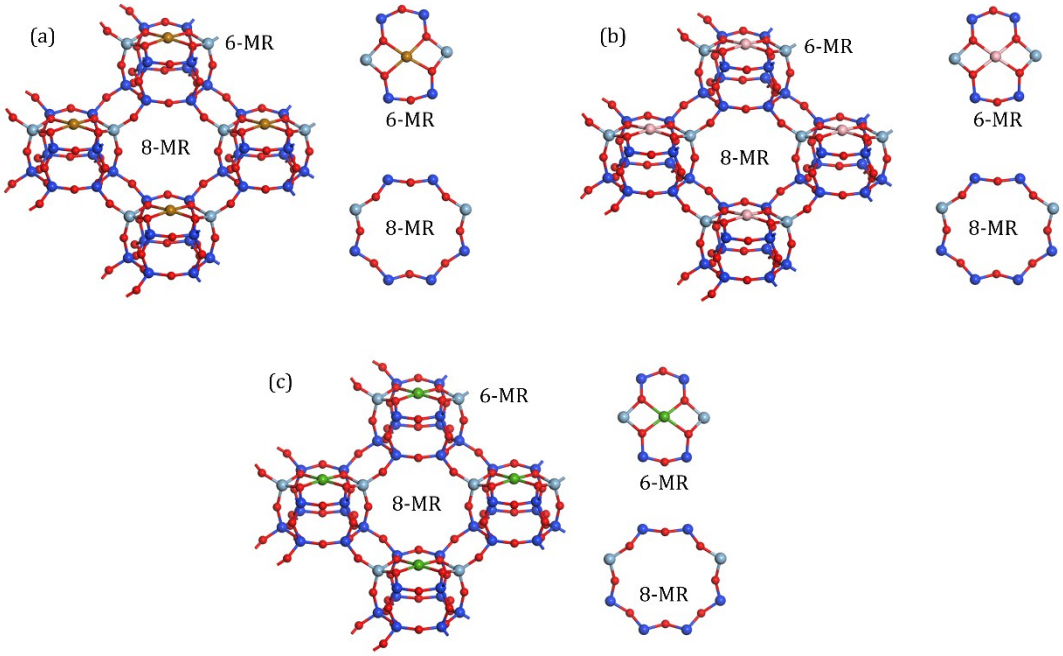


**Fig. S2** The structure schematic diagrams and corresponding 2-dimensional views of 6-MR and 8-MR (a) Fe.Sym-SSZ-13 (b) Co.Sym-SSZ-13 (c) Ni.Sym-SSZ-13

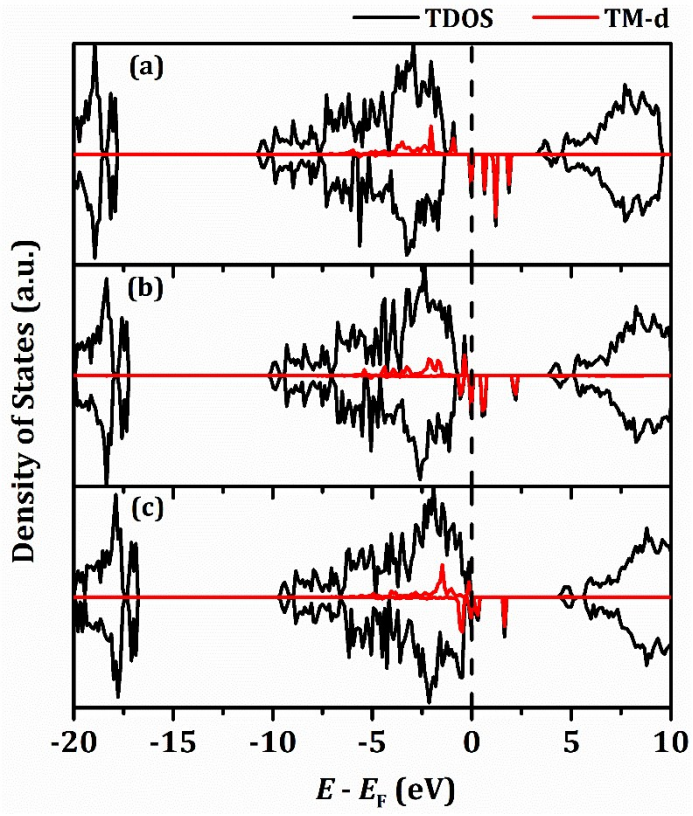


**Fig. S3** Density of states (DOS) for (a) Fe.Sym-SSZ-13 (b) Co.Sym-SSZ-13 and (c) Ni.Sym-SSZ-13. The vertical dashed line indicates the position of the Fermi level ($E_F$) which is set equal to zero.

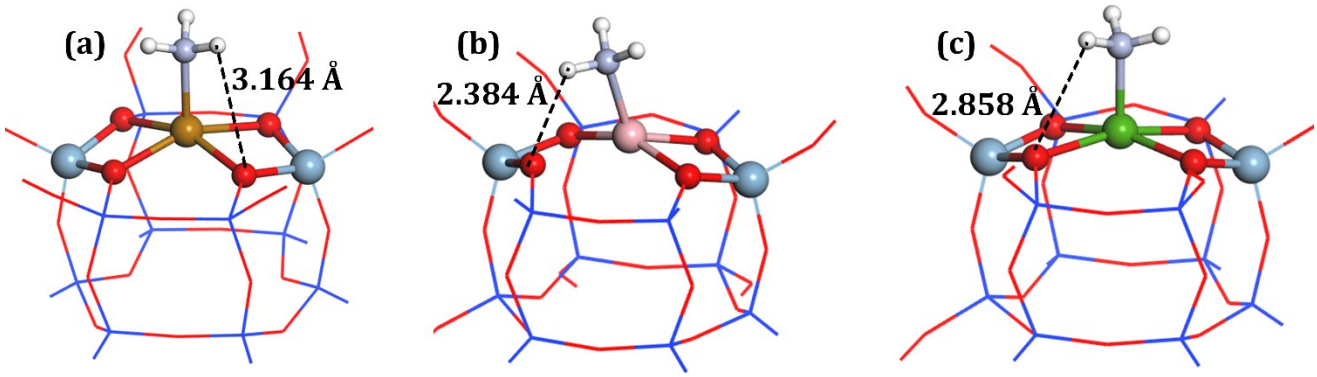


**Fig. S4** The structures of $NH_3$ adsorption on (a) Fe.Sym-SSZ-13 (b) Co.Sym-SSZ-13 (c) Ni.Sym-SSZ-13.

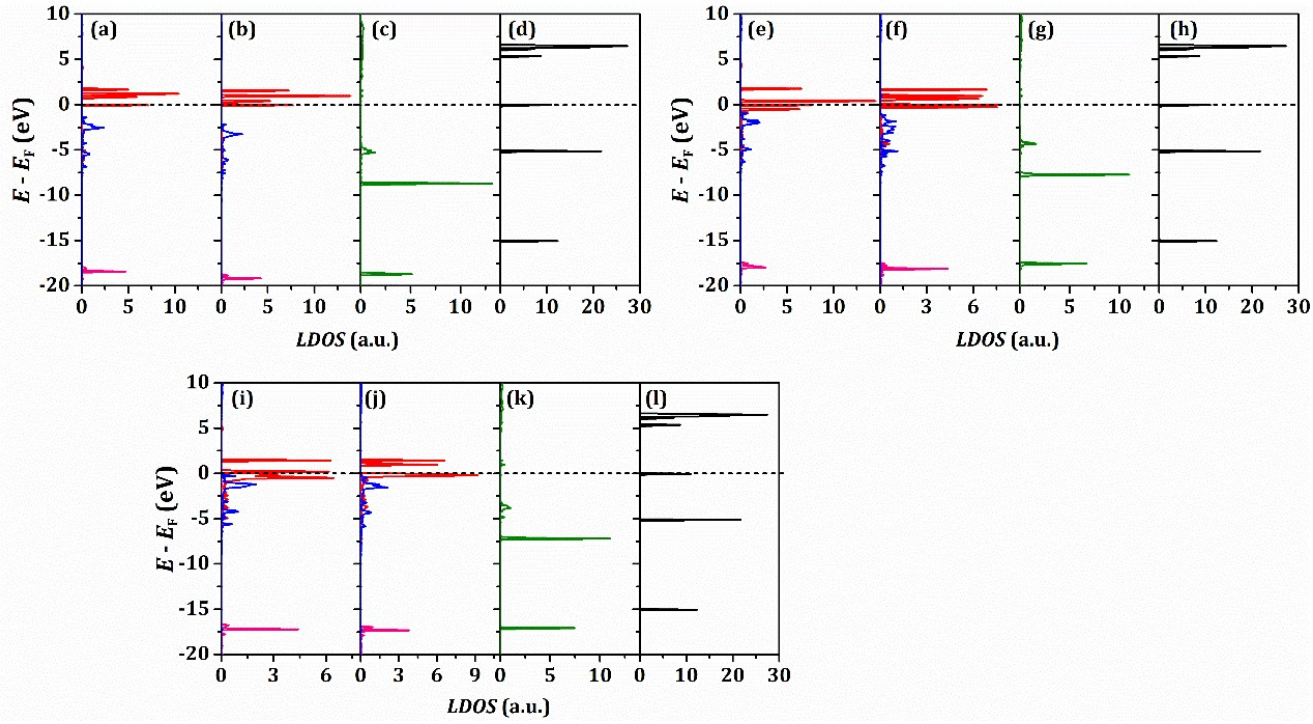


**Fig. S5** PDOS for $NH_3$ adsorption (a-d) Fe-SSZ-13 (e-h) Co-SSZ-13 (i-l) Ni-SSZ-13: red solid line, d-projected PDOS of TM; pink and blue solid line, 2s, 2p-projected PDOS for the neighboring oxygen atom of $NH_3$. (a, e, i) without $NH_3$ adsorption, (b, f, j) with $NH_3$ adsorption. (c, g, k) $NH_3$ in the adsorbed state; (d, h, l) $NH_3$ in gas phase.

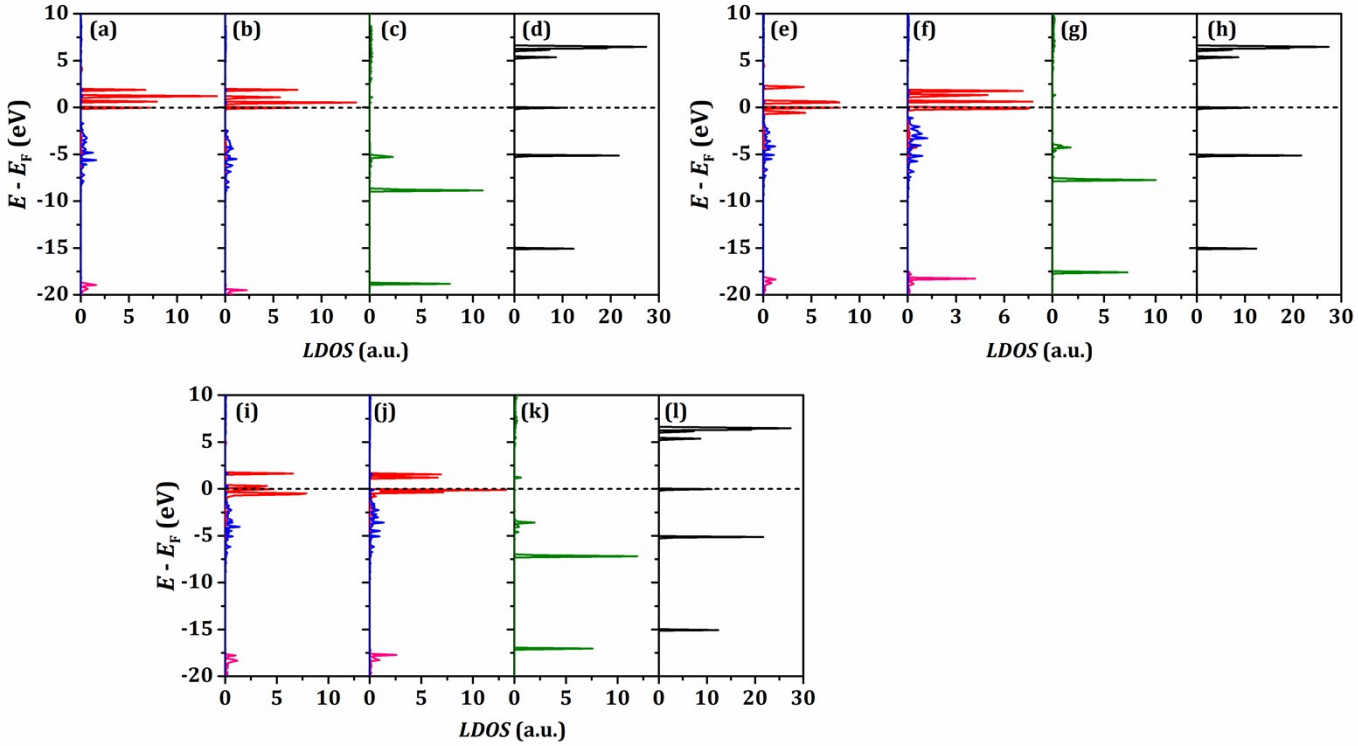


**Fig. S6** PDOS for $NH_3$ adsorption (a-d) Fe.Sym-SSZ-13 (e-h) Co.Sym-SSZ-13 (i-l) Ni.Sym-SSZ-13: red solid line, d-projected PDOS of TM; pink and blue solid line, 2s, 2p-projected PDOS for the neighboring oxygen atom of $NH_3$. (a, e, i) without $NH_3$ adsorption, (b, f, j) with $NH_3$ adsorption. (c, g, k) $NH_3$ in the adsorbed state; (d, h, l) $NH_3$ in gas phase.

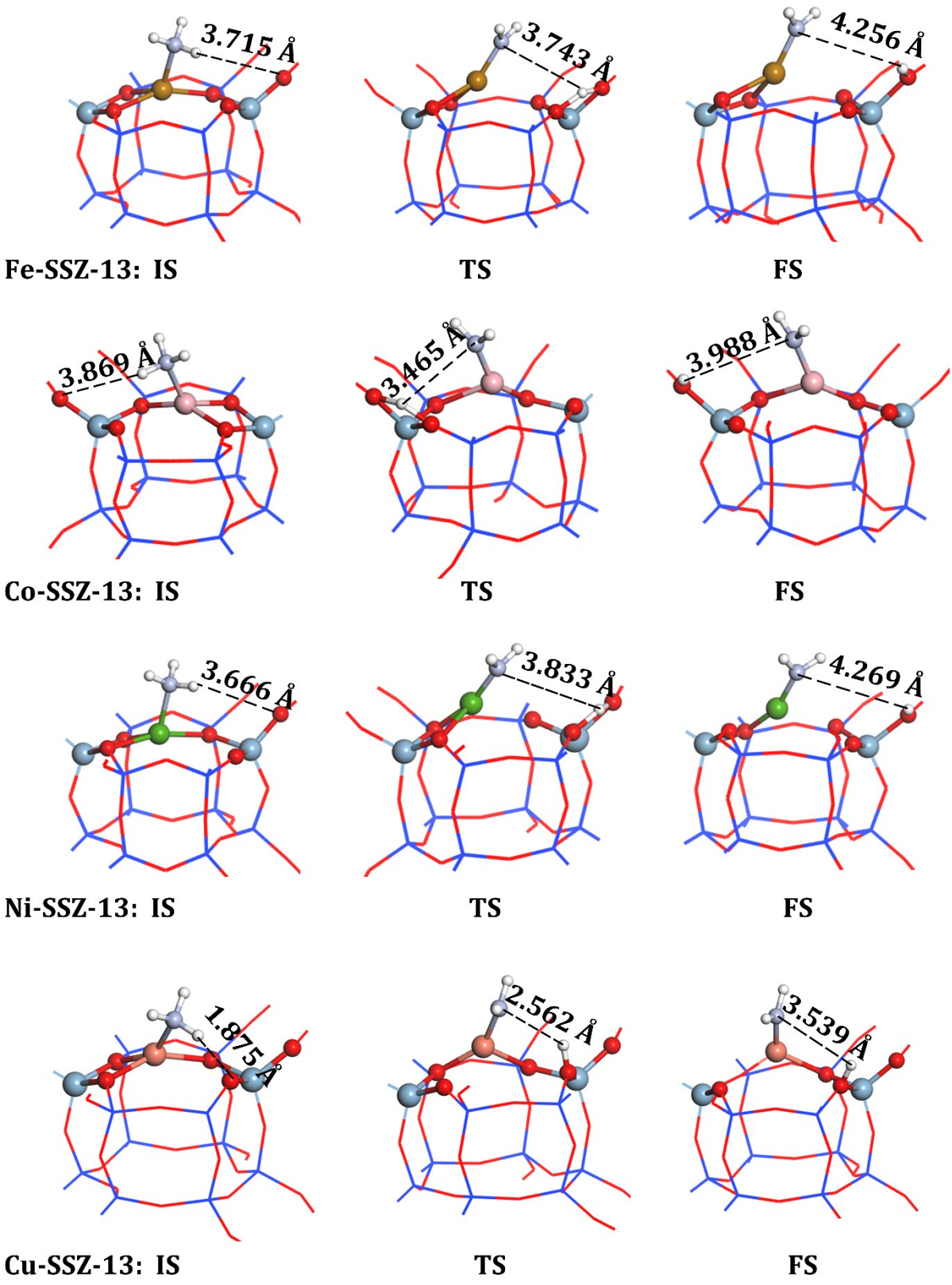


**Fig. S7** Calculated structures of the initial, final, and transition states for $NH_3$ activation in Fe, Co, Ni, Cu-SSZ-13.

**Table S1** The cation stabilities respect to the most stable configuration, $\Delta E_{stab}$ in eV, for various locations of Al and associated counter-cations.

| | $\Delta E_{stab}$ | | $\Delta E_{stab}$ | | $\Delta E_{stab}$ | | $\Delta E_{stab}$ |
|---|---|---|---|---|---|---|---|
| Fe-pAl2-6MR | 0 | Co-pAl2-6MR | 0 | Ni-pAl2-6MR | 0 | Cu-pAl2-6MR | 0 |
| Fe-pAl2-8MR | 1.320 | Co-pAl2-8MR | 1.335 | Ni-pAl2-8MR | 1.187 | Cu-pAl2-8MR | 1.307 |
| Fe-mAl2-6MR | 0.606 | Co-mAl2-6MR | 0.341 | Ni-mAl2-6MR | 0.238 | Cu-mAl2-6MR | 0.323 |
| Fe-mAl2-8MR | 0.965 | Co-mAl2-8MR | 0.893 | Ni-mAl2-8MR | 0.761 | Cu-mAl2-8MR | 0.912 |

**Table S2** The cation stabilities, $E_{stab}$ in eV, charge transfer of TM, $\Delta Q_{TM}$ in e, total magnetic moments, $M_{total}$ in $\mu_B$, magnetic moments of TM site, $M_{TM}$ in $\mu_B$, for TM.Sym-SSZ-13 (TM: Fe, Co, Ni). Numbers in parentheses are corresponding values for TM-SSZ-13 (i.e. the distorted square planar configuration).

| | $E_{stab}$ | $\Delta Q_{TM}$ | $M_{total}$ | $M_{TM}$ |
|---|---|---|---|---|
| Fe.Sym-SSZ-13 | -1.082(-0.969) | +1.335(+1.320) | 3.864(3.858) | 3.605(3.580) |
| Co.Sym-SSZ-13 | -0.922(-0.703) | +1.236(+1.241) | 2.903(2.889) | 2.586(2.579) |
| Ni-Sym-SSZ-13 | -0.545(-0.334) | +1.151(+1.154) | 1.923(1.920) | 1.555(1.555) |

**Table S3** The adsorption energy, $E_{ads}(NH_3)$ in eV, charge transfer $\Delta Q_{NH3}$ in e, bond length in Å and bond angle in degree of $NH_3$ adsorption on the TM.Sym-SSZ-13 (TM: Fe, Co, Ni). Numbers in parentheses are corresponding values for TM-SSZ-13 (i.e. the distorted square planar configuration).

| | $E_{ads}(NH_3)$ | $\Delta Q_{NH3}$ | N-H(1) | N-H(2) | N-H(3) | H-O | N-TM | H(1)NH(2) | H(2)NH(3) | H(3)NH(1) |
|---|---|---|---|---|---|---|---|---|---|---|
| Fe.Sym-SSZ-13 | -1.369 (-1.510) | +0.156 (+0.151) | 1.025 | 1.025 | 1.025 | 3.164 | 2.114 | 106.78 | 106.93 | 106.85 |
| Co.Sym-SSZ-13 | -1.518 (-1.772) | +0.186 (+0.187) | 1.024 | 1.024 | 1.026 | 2.384 | 2.051 | 107.26 | 107.50 | 108.21 |
| Ni-Sym-SSZ-13 | -1.752 (-1.785) | +0.226 (+0.224) | 1.024 | 1.024 | 1.024 | 2.858 | 2.016 | 107.94 | 107.59 | 108.17 |