Supplementary Information

Theoretical Study of Induced Selective N\textsubscript{2} Binding under Electric Field in MOF-74: Application for N\textsubscript{2}/CH\textsubscript{4} Separations

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| M in M-MOF-74 | E-field (a.u.) | Bond length of N$_2$-CUS(Å) | B.E.(N$_2$) (kJ/mol) | B.E.(CH$_4$) (kJ/mol) | B.E.(CO$_2$) (kJ/mol) |
|---------------|----------------|----------------------------|---------------------|---------------------|---------------------|
| Mg            | −0.010         | 2.42                       | 32.1                | 24.1                | 40.7                |
|               | 0              | 2.40                       | 35.6                | 28.6                | 47.9                |
|               | +0.010         | 2.34                       | 44.3                | 37.2                | 59.1                |
| Mn            | −0.010         | 2.59                       | 27.5                | 25.1                | 33.1                |
|               | 0              | 2.59                       | 30.5                | 31.5                | 39.8                |
|               | +0.010         | 2.47                       | 40.9                | 41.8                | 51.6                |
| Fe            | −0.010         | 1.99                       | 51.9                | 24.4                | 32.5                |
|               | 0              | 2.24                       | 35.3                | 28.9                | 38.4                |
|               | +0.010         | 2.24                       | 42.7                | 36.1                | 47.1                |
| Co            | −0.010         | 1.91                       | 61.3                | 23.6                | 31.9                |
|               | 0              | 2.15                       | 35.4                | 27.9                | 38.3                |
|               | +0.010         | 2.16                       | 43.8                | 34.4                | 46.4                |
| Ni            | −0.010         | 2.23                       | 34.0                | 23.4                | 31.9                |
|               | 0              | 2.21                       | 35.8                | 29.6                | 43.9                |
|               | +0.010         | 2.15                       | 47.7                | 37.5                | 54.1                |
| Cu            | −0.010         | 2.19                       | 28.5                | 20.7                | 23.8                |
|               | 0              | 2.53                       | 21.0                | 22.6                | 27.6                |
|               | +0.010         | 2.46                       | 25.0                | 28.0                | 33.0                |
| Zn            | −0.010         | 2.63                       | 21.1                | 23.3                | 32.8                |
|               | 0              | 2.55                       | 26.0                | 26.8                | 36.7                |
|               | +0.010         | 2.41                       | 35.1                | 34.0                | 43.3                |

**Table S1.** Binding energy of N$_2$, CH$_4$, CO$_2$ and bond length of N$_2$-CUS in M-MOF-74 (M = Mg, Mn, Fe, Co, Ni, Cu, Zn)
Figure S1. Binding energy of $N_2$ and $CO_2$ in the system of M-MOF-74 (M=Mg, Mn, Fe, Co, Ni, Cu, Zn).

Figure S2. Visualization of NBOs corresponding to the $\sigma$ bond (lone pair electrons (donor) of N atom in $N_2 \rightarrow$ metal’s empty 3d orbitals (acceptor)) between $N_2$ and Co atom in Co-MOF-74 at negative, neutral, positive electric field. NBOs with largest stabilization energy for each case is visualized. Bond length between $N_2$ and Co atom is written together. Color code: Purple (Cobalt), Red (Oxygen), Blue (Nitrogen), Red mesh (positive surface), Green mesh (negative surface).
**Figure S3.** $N_2$ binding energy (orange circle) and its stretching frequency (blue triangle) in M-MOF-74 (M=Co, Fe) under external electric field.
Figure S4. (a) Energy diagram of d orbitals in octahedral coordination geometry and square pyramidal. (b) Coordination geometry of metal center in M-MOF-74. Purple: metal atom, blue: Nitrogen, red: Oxygen. (c) Description of orbital interaction in $\pi^*$ back-bonding and $\sigma$ bond. (d) Metal’s d electron configuration of M-MOF-74 system (M=Mn, Fe, Co, Ni, Cu, Zn) and number of electrons in specific d orbitals ($d_{x^2}$ and $d_{xy}$, $d_{yz}$).

Figure S4 shows coordination environment of metal center in M-MOF-74 and electron configuration of d electrons. Here we explain three key points to understand the extraordinary behavior of certain metals like Fe and Co.

**Key 1:** d electrons will be filled in the order of ($d_{xy}$, $d_{yz}$)→$d_{x^2}$→$d_{y^2}$→$d_{x^2-y^2}$.

Coordination geometry of the metal center in M-MOF-74 can be considered as octahedral or
square pyramidal. In Figure S4 (b), CUS forms octahedral coordination with N\textsubscript{2} molecule, but its energy state cannot be perfect octahedral coordination (e.g. Figure S4 (a) left). Because the bond between the metal and oxygen atom (in Figure S4 (b)) will be tighter than the bond between the metal and N\textsubscript{2} molecule, there will be less electron density interruption toward z-direction. Therefore, the energy state of d orbitals along the z-direction will be more stable, and d electrons will be filled in the order of (d\textsubscript{xz} d\textsubscript{yz})\rightarrow d\textsubscript{xy} \rightarrow d\textsubscript{z}\textsuperscript{2} \rightarrow d\textsubscript{x}\textsuperscript{2}−y\textsuperscript{2} similar to square pyramidal coordination. From this order, d orbitals in M-MOF-74 in high spin state will be filled like Figure S4 (d).

**Key 2:** The more electron in ( ), the stronger the \pi* back-bonding.

**Key 3:** The less electron in , the stronger the \sigma bond.

The description of which orbitals are involved in each bond (\pi* back-bonding and \sigma bond) is in Figure S4 (c). In the case of \pi* back-bonding, (d\textsubscript{xx}, d\textsubscript{yy}) orbitals act as donor. The more electron in (d\textsubscript{xx}, d\textsubscript{yy}), the stronger the \pi* back-bonding. For stronger \sigma bond, it requires empty d\textsubscript{z}\textsuperscript{2} because spare electron in d\textsubscript{z}\textsuperscript{2} will be located in antibonding state when N\textsubscript{2} molecule donates its lone pair electrons to the metal. All things considered, more electrons in (d\textsubscript{xx}, d\textsubscript{yy}) orbitals and less electrons in d\textsubscript{z}\textsuperscript{2} orbital are required to have strong N\textsubscript{2} binding.

Figure S4 (d) shows electron configurations in d orbitals for each M-MOF-74 and which of them satisfy the two keys (Key 2 and 3) to have strong N\textsubscript{2} binding. Co and Ni satisfy two keys the most and Fe also satisfies them moderately. In Figure 2, Co-MOF-74 shows better performance enhancement under electric field compared to Fe-MOF-74. Another interesting point is that these promising candidates (Co, Ni, and Fe-MOF-74) have higher carbon monoxide adsorption capacity among M-MOF-74 systems.\cite{1} (Since carbon monoxide can also form \pi* back-bonding with the metal atom, it has similarity with N\textsubscript{2} molecule.)

However, Ni-MOF-74 doesn’t show such strong binding with N\textsubscript{2} under electric field. It appears that increased occupancy in d\textsubscript{z}\textsuperscript{2} orbital causes the weak N\textsubscript{2} binding (see Figure S5). Under negative electric field, d\textsubscript{z}\textsuperscript{2} occupancy of Ni atom in Ni-MOF-74 increased. The increased d\textsubscript{z}\textsuperscript{2} occupancy (i.e. increased electron density at antibonding state) interrupt strong \sigma bond, and it will result in weak N\textsubscript{2} binding with Ni atom. Slightly decreased d\textsubscript{z}\textsuperscript{2} occupancy of Cu under negative electric field appears to be related with increased N\textsubscript{2} binding in Figure 2.
**Figure S5.** $d_{z^2}$ occupancy of metal center in M-MOF-74 from natural population analysis.
Figure S6 shows NBO stabilization energy plots regarding the \( \sigma \) bond between the transition metal and small gas molecules (CH\(_4\) and CO\(_2\)). In both plots, the stabilization energy monotonically increases regardless to the metal type, and such result agrees with our hypothesis that these small gas molecules has \( \sigma \) bond dominance.
Figure S7. Visualization of NBOs corresponding to $\sigma$ bond of (a) Co-CH$_4$ and (b) Co-CO$_2$ at negative, neutral, positive electric field in Co-MOF-74 system. Central transition metal of the cluster and its first coordination shell (5 oxygen atoms) are only visualized for simplicity. Color code: Purple (Cobalt), Red (Oxygen), Blue (Nitrogen), Red mesh (positive surface), Green mesh (negative surface).

Reference

1. E. D. Bloch, M. R. Hudson, J. A. Mason, S. Chavan, V. Crocellà, J. D. Howe, K. Lee, A. L. Dzubak, W. L. Queen, J. M. Zadorozny, S. J. Geier, L.-C. Lin, L. Gagliardi, B. Smit, J. B. Neaton, S. Bordiga, C. M. Brown and J. R. Long, *Journal of the American Chemical Society*, 2014, **136**, 10752-10761.