

# On the Stability of Single Cluster Catalysts in MFI Zeolites

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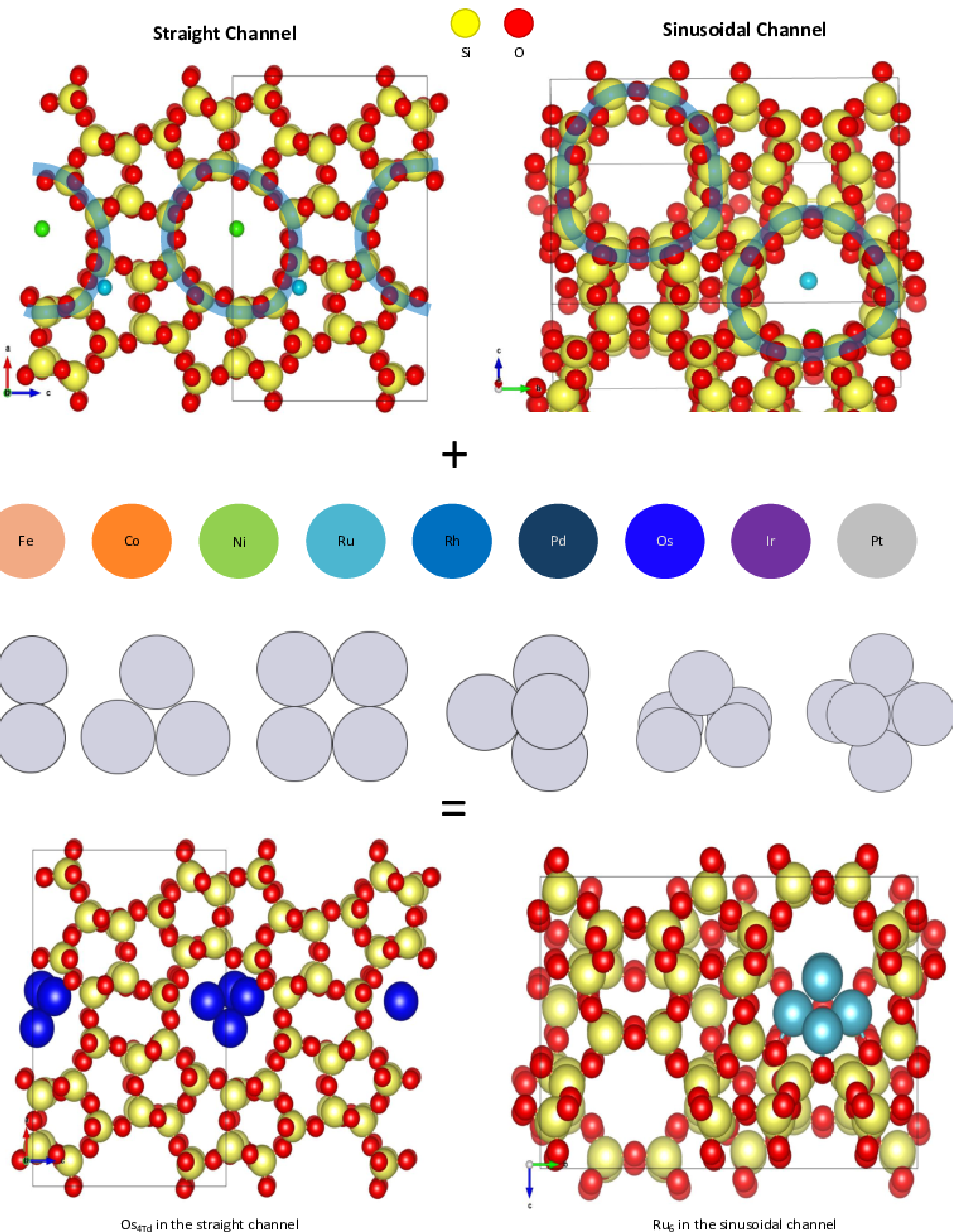
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## Introduction

Transition metal (TM) clusters in the sub-nanometric regime (typically 2 to 6 atoms) exhibit catalytic properties that differ significantly from their bulk counterparts at the cost of thermodynamic instability. Encapsulation of TM clusters within zeolites as Single Cluster Catalysts (SCC) has emerged as a particularly effective approach to overcome this expense. This thorough study abords the stability of a series of clusters formed by 9 different TM (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) inside the MFI zeolite. This work aims to deliver an energetic, structural and magnetic threshold for future SCCs cluster encapsulations inside zeolites.

## 1. Studied Structures

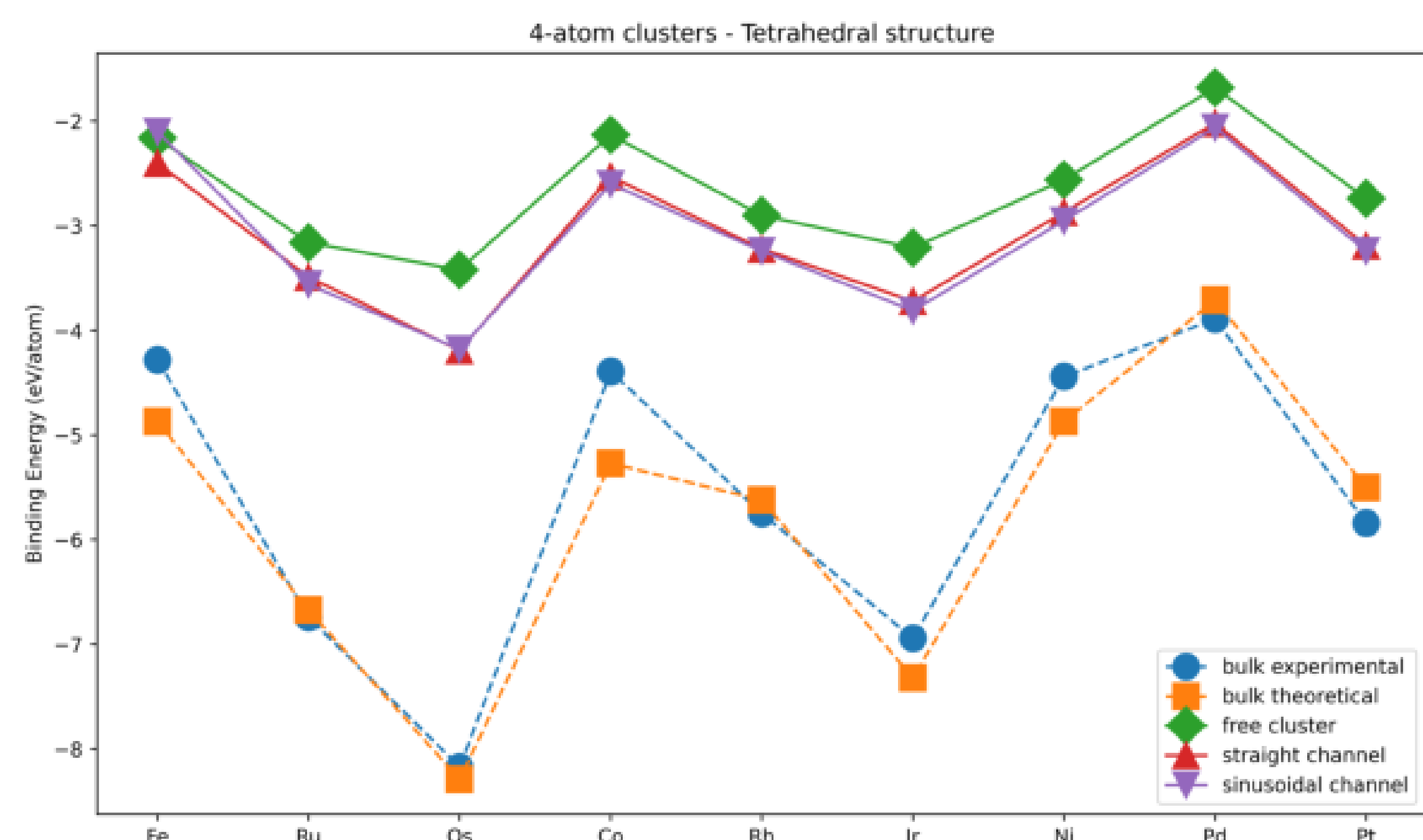


## Computational Details

- Plane waves basis set
- PBE functional
- D3 dispersion correction
- $\Gamma$  point only
- Spin correlated optimisations
- Optimised zeolite parameters: a = 20.31 Å, b = 19.86 Å, c = 13.37 Å

## 2. Binding energies

$$E_{b/n} = \frac{E_{\text{structure}} - n \cdot E_{\text{reference}}}{n}$$
$$E_{b/n} = \frac{(E_{\text{clu@MFI}} - E_{\text{MFI,vac}}) - n \cdot E_{\text{reference}}}{n}$$



- MFI structure provides support to the SCCs, but far from their bulk cohesion level
- $E_{b/n}$  trends in the bulk and free-cluster spectra are preserved for encapsulated SCCs

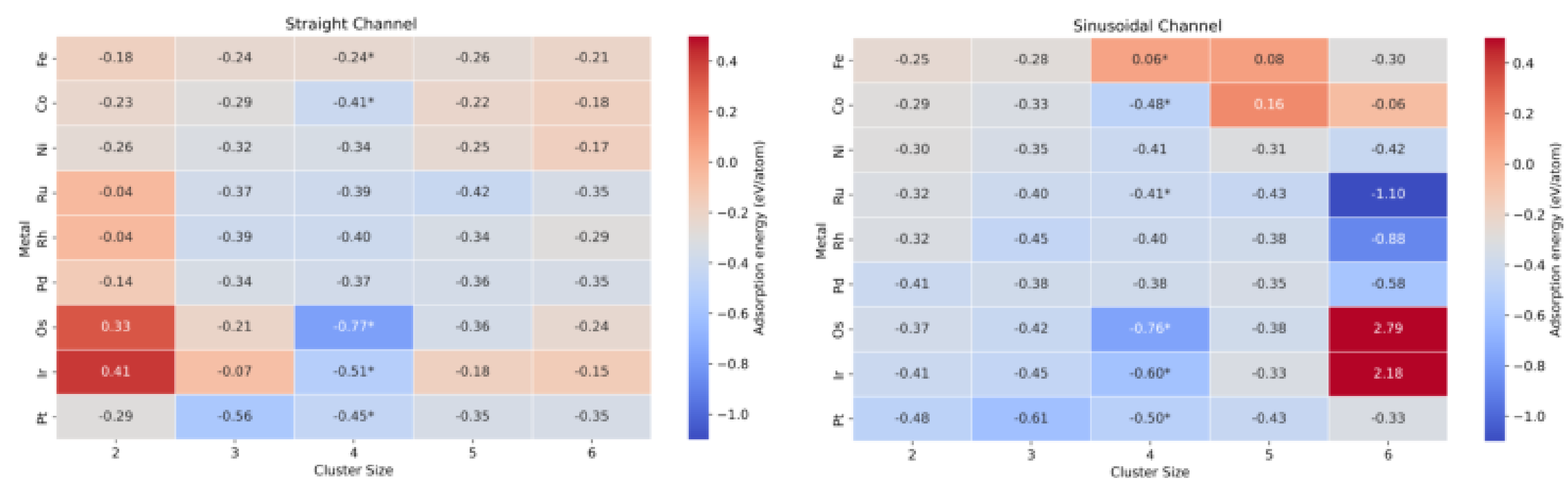
## Acknowledgments

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## 3. Adsorption Energies

$$E_{ads/n} = \frac{E_{clu@MFI} - (E_{MFI,vac} + E_{clu,vac})}{n}$$



- Notable channel differences
- Tetrahedral 4-atom SCC → most stable structure
- Steric effects for sinusoidal channel
- Good candidates as SCC begin to appear (Os<sub>4Td</sub>, Ru<sub>6</sub>, Rh<sub>6</sub>, Pt<sub>3</sub>, ...)

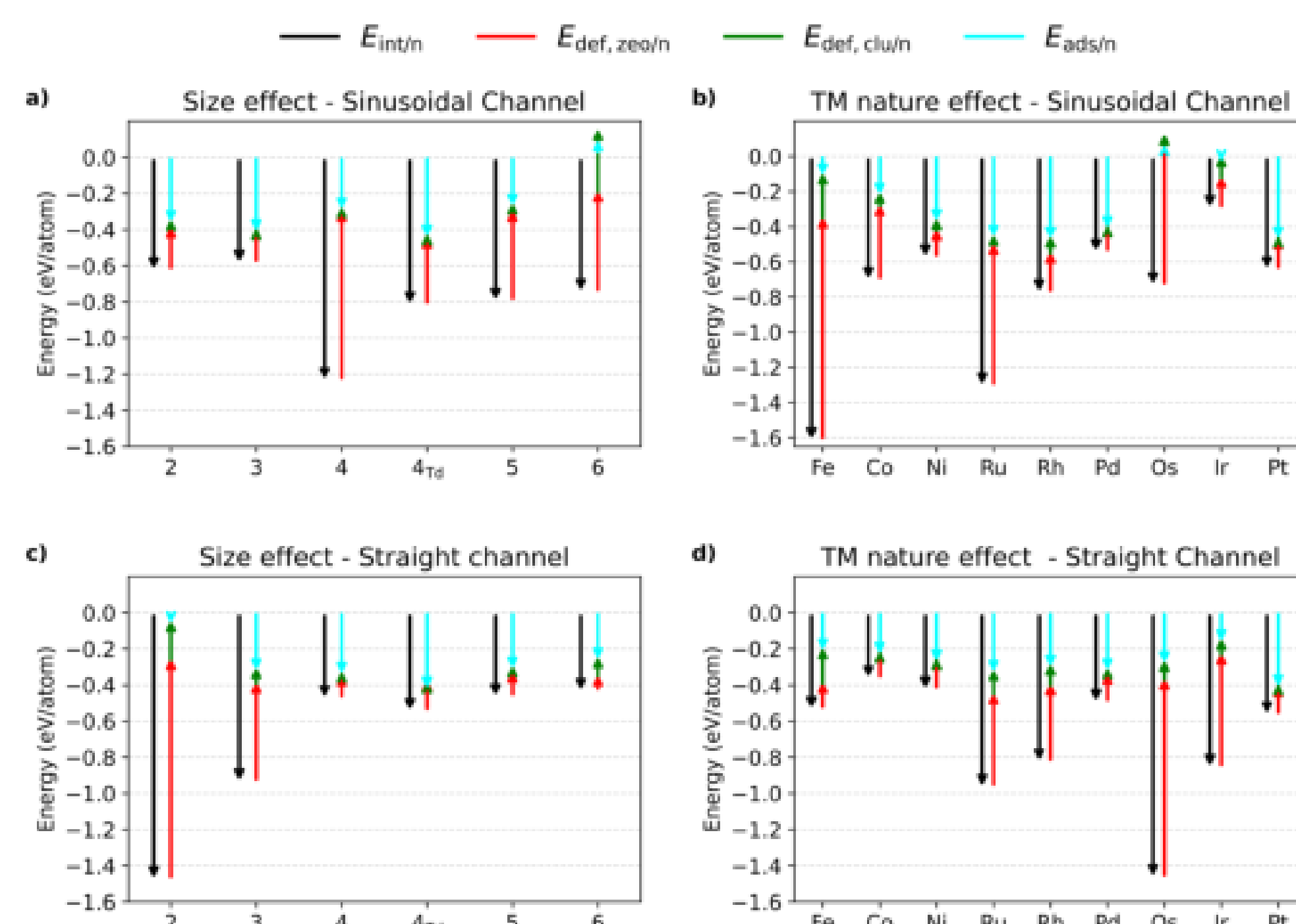
## 4. Interaction and Deformation Energies

$$E_{ads} = E_{def} + E_{int}$$

$$E_{int/n} = \frac{E_{clu@MFI} - [E_{clu,sp} + E_{MFI,sp}]}{n}$$

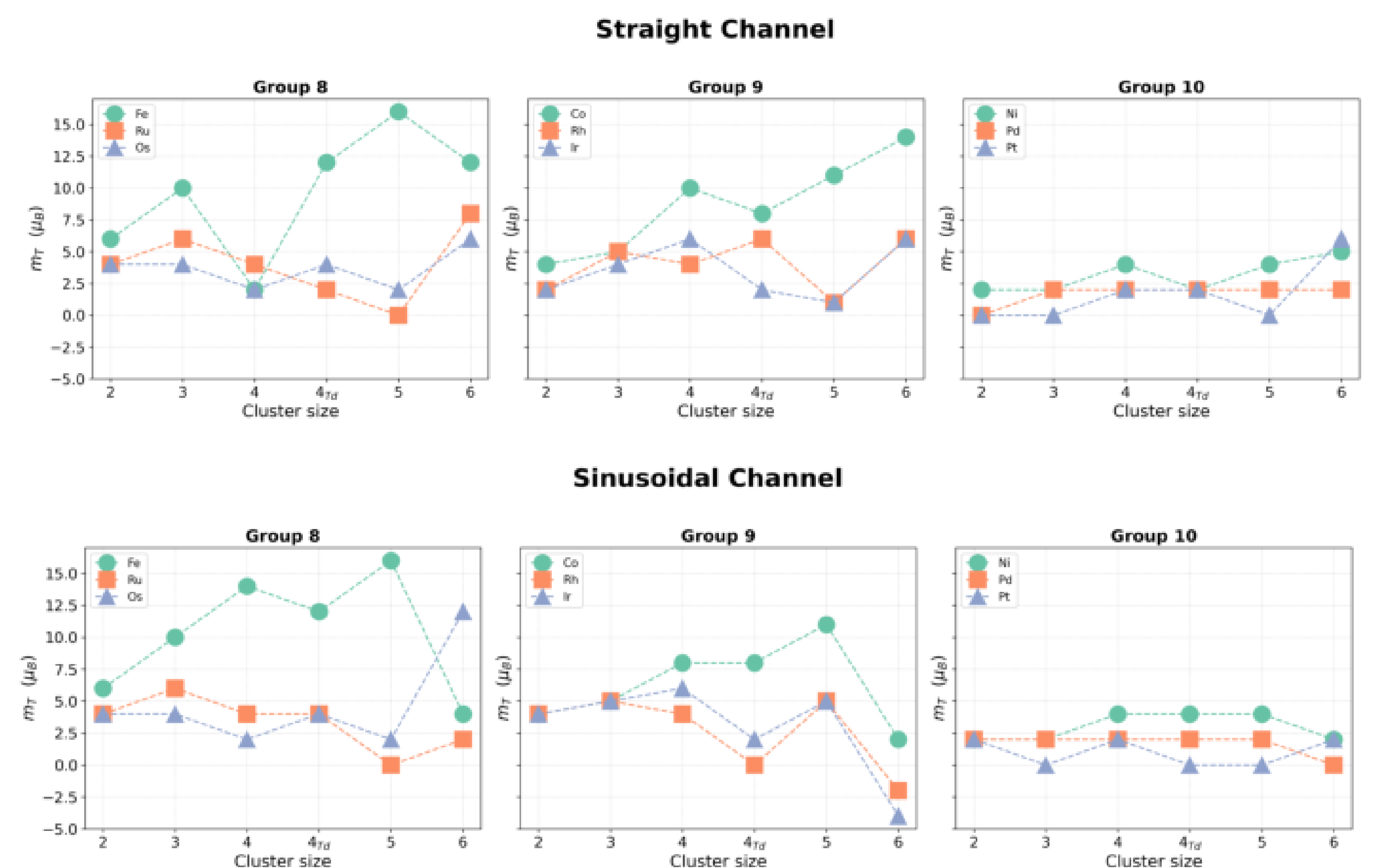
$$E_{def,zeo/n} = \frac{E_{MFI,sp} - E_{MFI,vac}}{n}$$

$$E_{def,clu/n} = \frac{E_{clu,sp} - E_{clu,vac}}{n}$$



- Deeper understanding of  $E_{ads/n}$
- $E_{int}$  → Energy change due to the variation in electronic structure.
- $E_{def}$  → Energy cost of distorting the geometry of either cluster or zeolite.

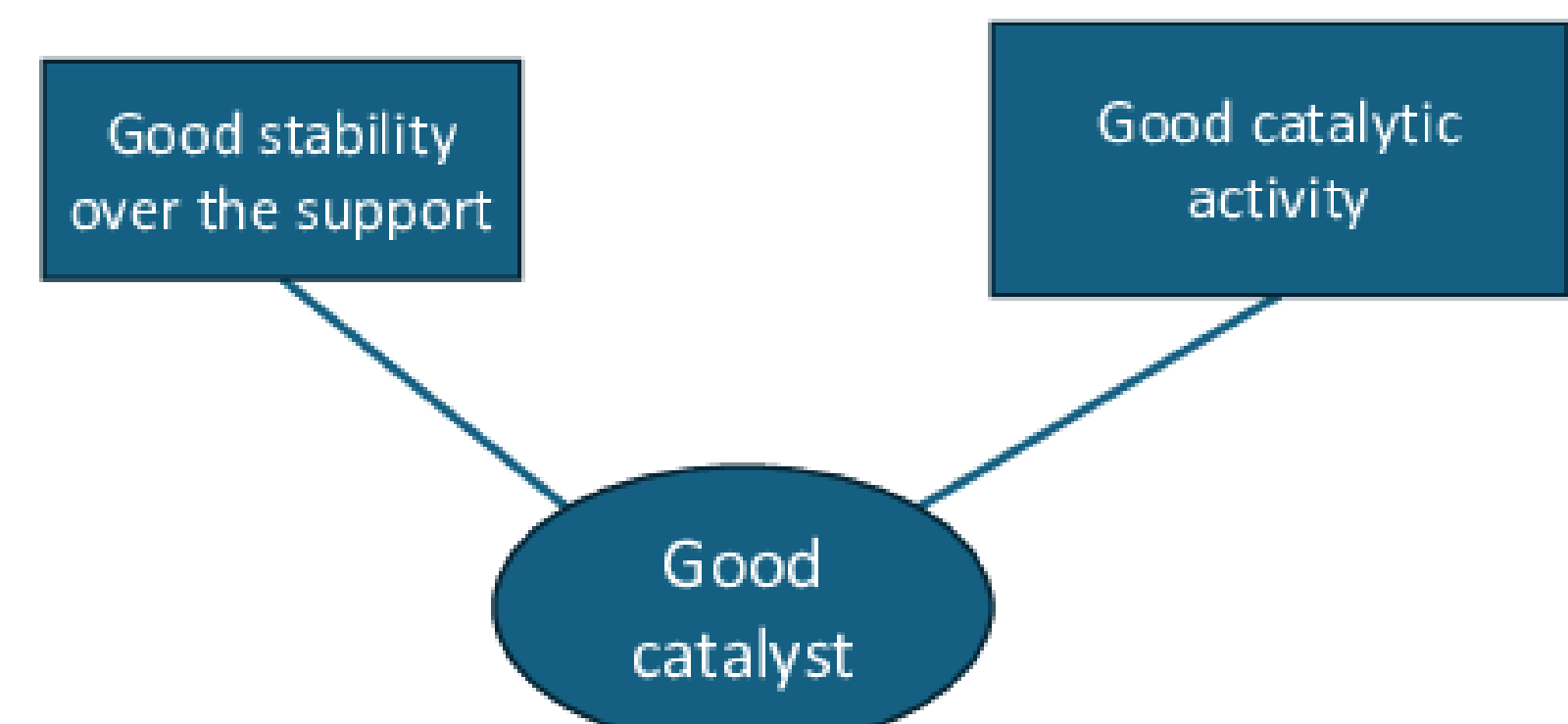
## 5. Magnetic Properties



- Magnetic moment properties mostly preserved from free-cluster structures
- Exceptions → Charge transfer with zeolitic O
- Magnetic moment trends in the bulk and free-cluster spectra are preserved for encapsulated SCCs

## Take-Home Message and Future Work

- MFI zeolite provides support to the SCCs
- Trends in the bulk and free-clusters are mostly conserved for encapsulated SCCs@MFI
- Steric effects start to appear for structures as small as 6 atoms
- Good candidates as SCC begin to emerge (Os<sub>4Td</sub>, Ru<sub>6</sub>, Rh<sub>6</sub>, Pt<sub>3</sub>, ...)



## References

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