**Supporting Information for**

**Probing the Distinct Roles of Zeolite-Confined and External Rh Sites by Selective Poisoning in 1-Hexene Hydroformylation Regioselectivity**

Rui Feng 1,[[1]](#footnote-1), Wei Wang 1, Tianbo Li 1，Feifei Yang 1, Xiaoyan Hu 1, Xinlong Yan 1, Lianming Zhao 2, Shijian Lu 3,[[2]](#footnote-2)

1. *China University of Mining and Technology; School of Chemical Engineering,* *Xuzhou 221116*

*2. China University of Petroleum, School of Science, Qingdao, 266580*

3. *China University of Mining and Technology; Carbon Neutrality Institute,* *Xuzhou 221116*

**Computational methods**

DFT calculations were performed using the DMol3 module in Materials Studio software.[1] The exchange correlation energy was calculated using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional.[2] Long-range dispersive interactions were corrected using Grimme’s PBE-D3 method, with deviations typically within 10% of CCSD(T) reference values for both molecular and solid systems.[3] To account for relativistic effects, the density functional semi-core pseudopotential (DSPP) method was employed.[4] Double numerical plus polarization (DNP) basis sets augmented with diffuse polarization functions were selected as the basis set for all calculations. Fermi smearing of 0.005 Ha was applied to ensure numerical accuracy and convergence. Based on the convergence tests, the global orbital cutoff radius was set to 5.2 Å, while the Brillouin zones were sampled with 6×6×1 k-point meshes. During geometry optimization, we established convergence criteria (energy: 1×10-5 Ha, force: 2×10-3 Ha·Å-1, and displacement: 5×10-3 Å). Transition states of the elementary reaction were located using the linear synchronous transit/quadratic synchronous transit (LST/QST) method and verified by vibrational frequency analysis.

The adsorption free energy (Δ*G*) of the adsorbed species (e.g., DMBT (C8H10S), and TPMT (C9H16S)) on the surface was calculated by the equation:

in which Δ*E* was calculated by , where *E*absorbate/substrate, *E*absorbate, and *E*substrate are the total energy of the catalyst system with the adsorbed species, the gas phase adsorbate, and the isolated catalyst substrate, respectively. Δ*ZPE* is the difference in zero-point energy, and Δ*S* is the entropy correction at T = 298 K.



Figure S1. Schematic illustration (a) and Gibbs free energy profiles (b) of different reaction pathways for the hydroformylation of 1-hexene over the Rh@MFI catalyst, calculated using the DMol3 module.

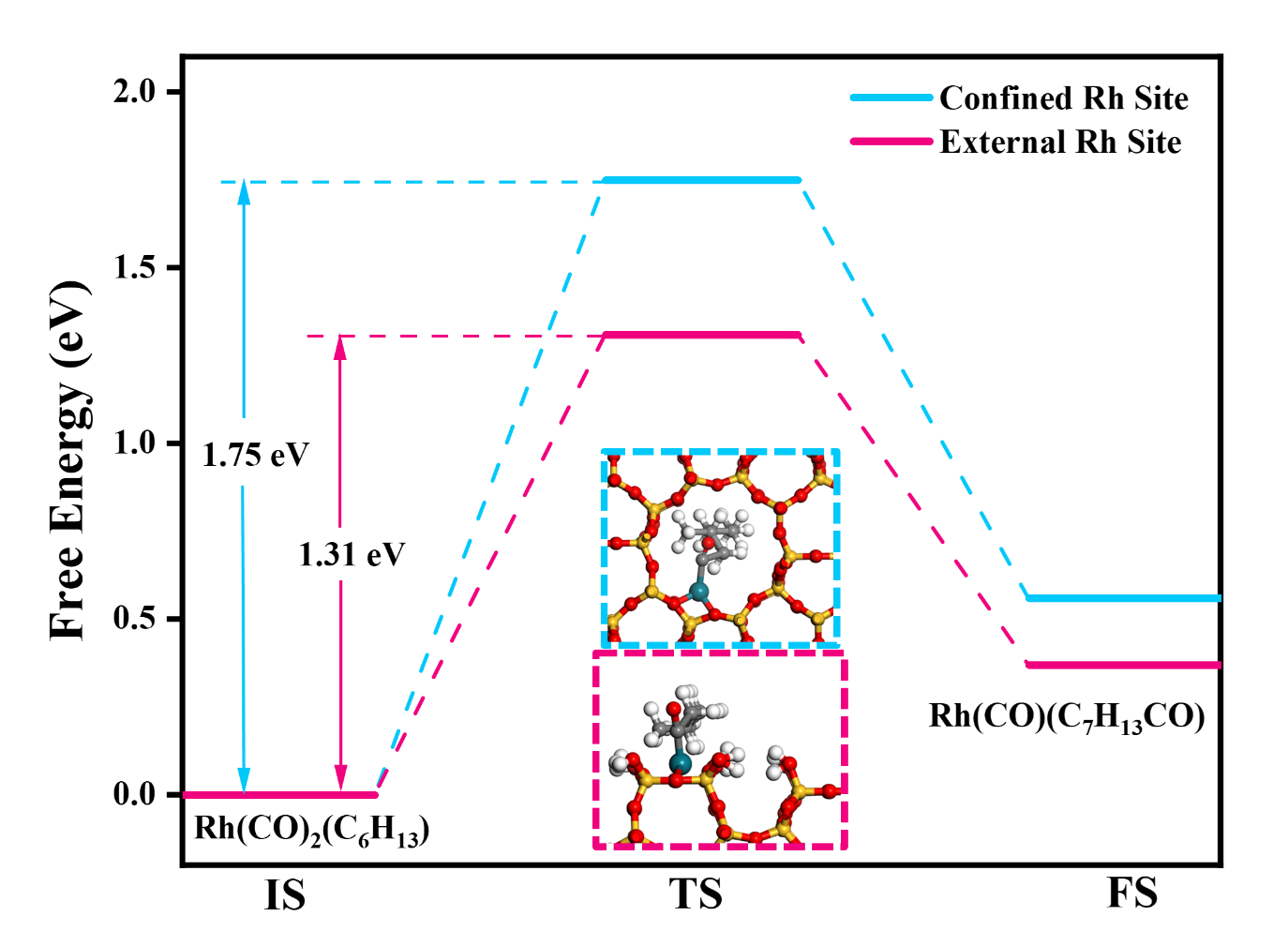


Figure S2. Calculated energy barriers for the key CO insertion step to form n-heptanal catalyzed by Rh sites located inside and outside the zeolite pores.

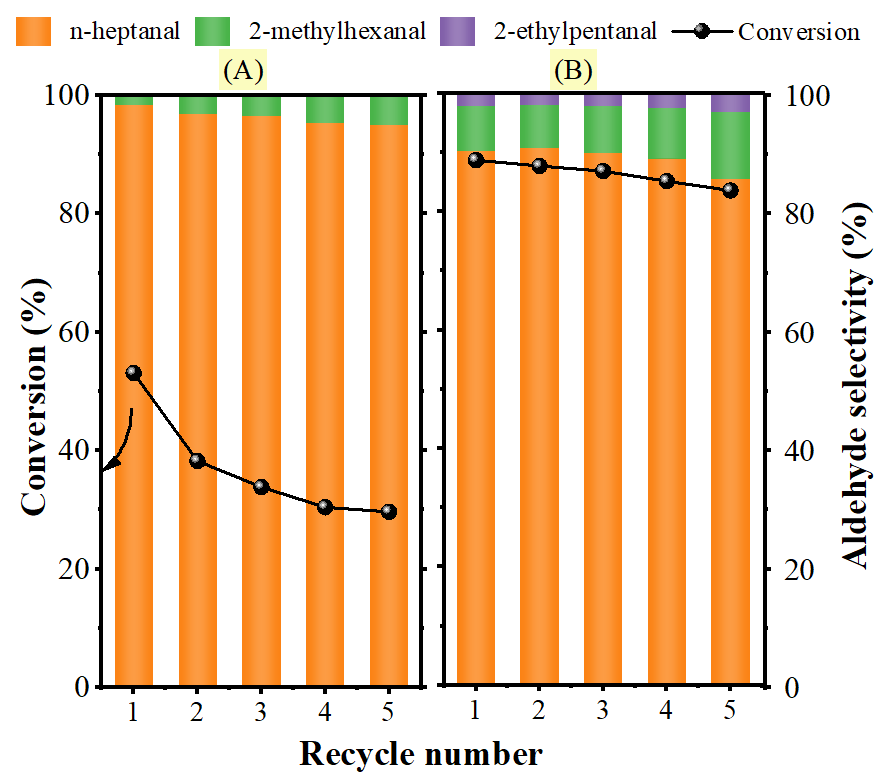


Figure S3. Stability of 0.5%Rh@S-1 catalysts evaluated with (A) DMBT and (B) TPMT, which was added added in each cycle of the test. Reaction conditions: 0.05 g catalyst, 5 mL toluene, 4 MPa CO/H 2 = 1/1, 70 °C for 6 h. 0.8 mmol (100 μL) 1-hexene



Figure S4. The S2p XPS spectra of poisons on (a) S-1; (b & c) 0.5%Rh@S-1. The specific sample treatment procedure was as follows: each sample was stirred in ethanol, followed by the addition of the corresponding poisoning agent. The mixture was then stirred at room temperature for adsorption over 6 h. Afterward, the suspension was separated by high-speed centrifugation, washed with ethanol, and the solid residue was collected and dried in an oven at 50 °C before XPS measurement.

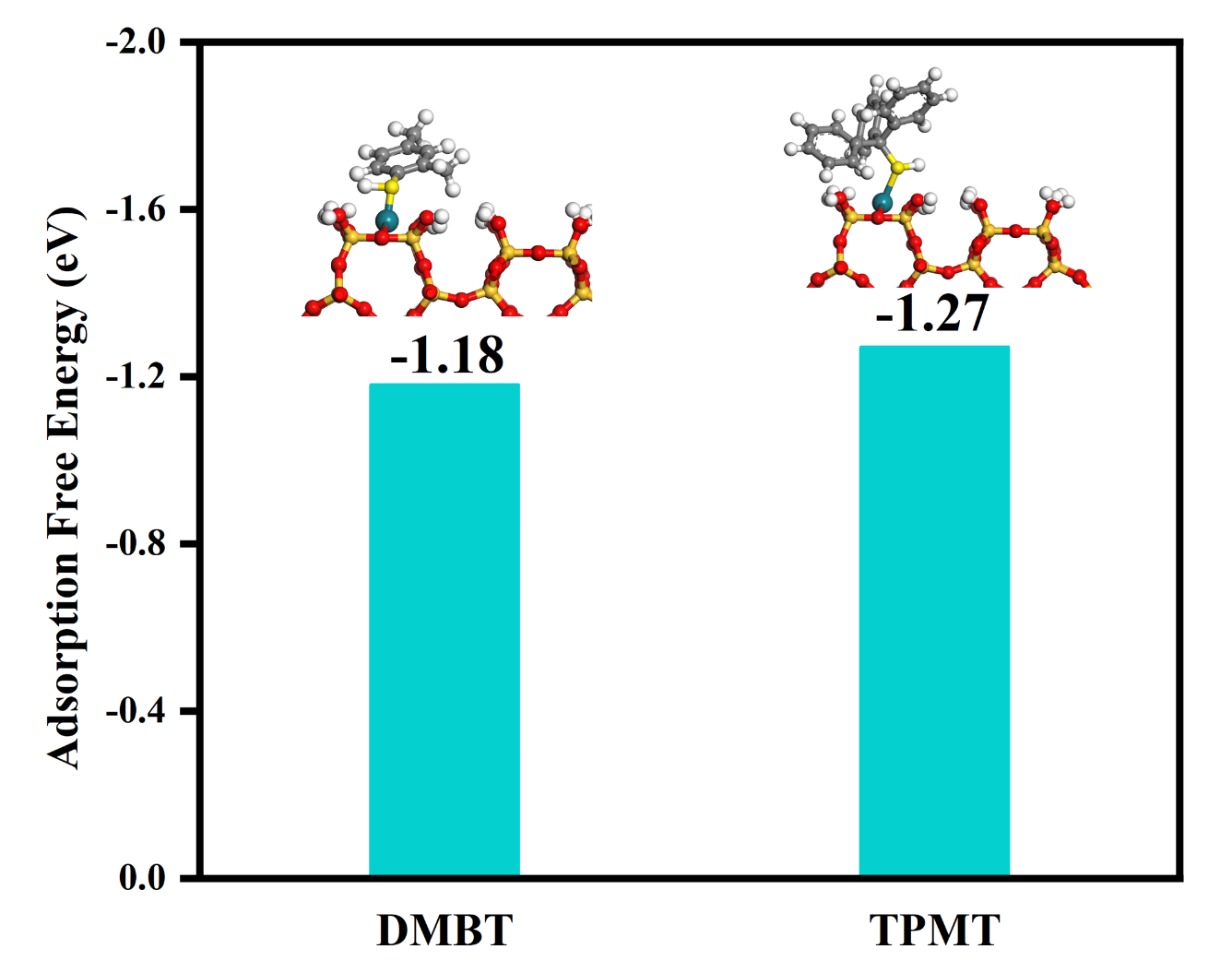


Figure S5. The calculated adsorption energy of DMBT and TPMT on Rh site.

**References**

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1. E-mail: fengrui@cumt.edu.cn [↑](#footnote-ref-1)
2. E-mail: lushijian@cumt.edu.cn [↑](#footnote-ref-2)