Passive NO_x Adsorption - Pd/ZSM-5

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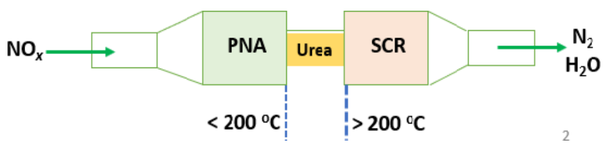
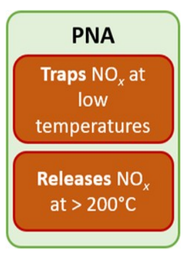
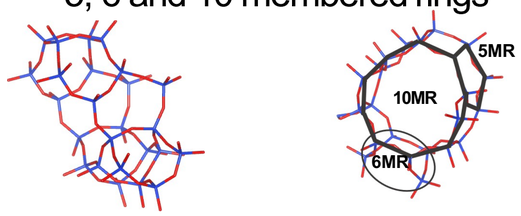
Background

- **NO_x comprises more than 50 %** of the diesel engine exhaust pollutant emissions.
- **Catalytic converters**
  - Reduce NO_x and oxidize CO and unburnt hydrocarbons before emission
  - Operate only at high temperatures (T > 200°C)
- **Cold-start** – time taken by the converter to reach its operating temperature
  - Majority of NO_x escapes Selective Catalytic Reduction (SCR) during cold-start
- **Passive NO_x Adsorbers** (PNA) can address the cold-start NO_x emission problem.





  - **Ion-exchanged zeolites** (SSZ-13, ZSM-5, BEA)
- **Pd-exchanged ZSM-5**
  - Medium pore zeolite.
  - ZSM-5 unit cell - 96 Silicon and 192 Oxygen atoms
  - **12 distinct** T-sites
  - 5, 6 and 10 membered rings

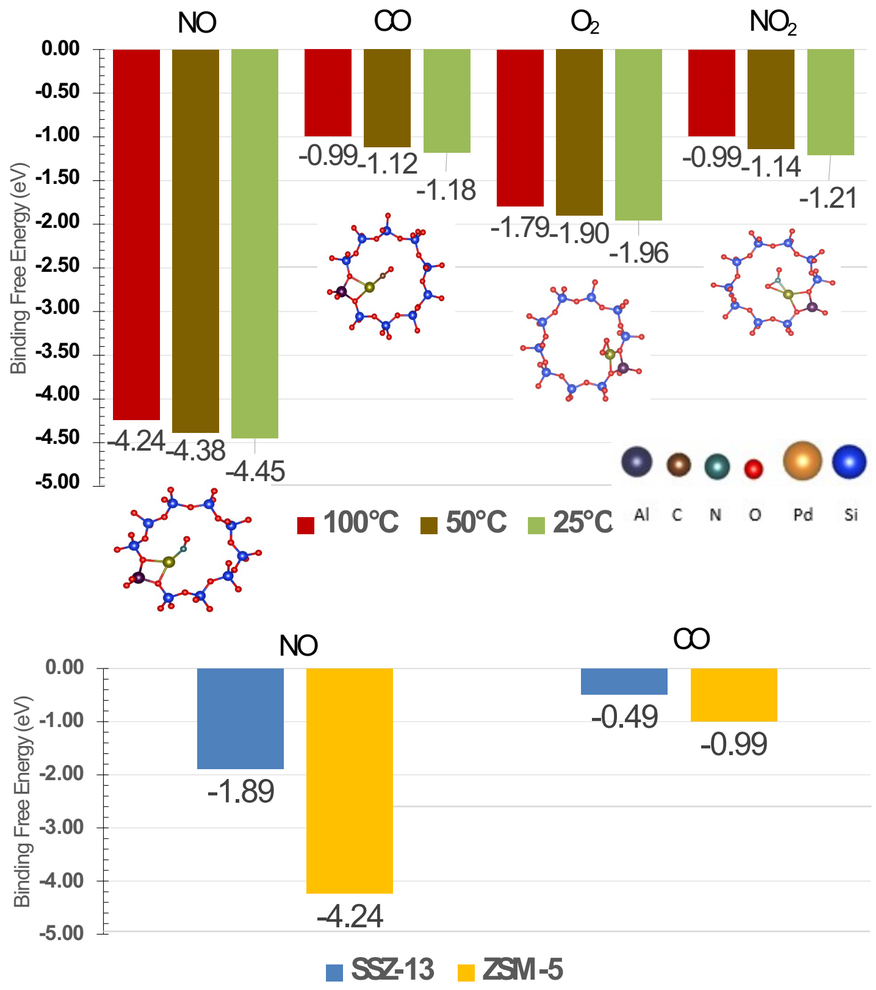


Methods

- **Density Functional Theory (DFT)** implemented in **VASP**
- Key parameters
  - **BEEF-vdW** functional
  - Brillouin zone sampling: Γ-point
  - Cut-Off Energy: **540 eV**
  - 10^{-5} *eV* for self-consistent field cycle
  - **< 0.02 eV/Å** for geometry optimizations

Results

- Simulations of PNA at different active sites of Pd/ZSM-5 and Pd/SSZ-13 were performed
- Adsorbates : **NO, CO, NO_2 and O_2**
- Binding Free Energy (BFE) for each adsorbate was determined at various temperatures and compared with those obtained with Pd/SSZ-13



Conclusions

- NO binding is **much stronger** than other gas-phase species for both zeolites (SSZ-13 and ZSM-5).
- Binding of adsorbates is **weaker at higher temperatures.**
- NO binding is **stronger for Pd/ZSM-5** than for Pd/SSZ-13

Future Work

- Identify transition states and calculate activation energies for NO oxidation on ZPd in presence of Oxygen
- Bader and Mulliken charge analysis on the active sites and adsorbates
- Investigate possible dimeric active sites
- Calculate BFE with a hybrid functional
- Investigate NO binding with other functionals

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References

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