

Computational studies on poisoning of Ni catalyst in Methane Steam Reforming

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Introduction

Poisoning of catalysts due to carbon-based species is a major impediment to the productivity of industrial operations. Chemical industries spend billions of dollars annually to replace or regenerate deactivated catalysts. Ni catalysts used in Methane Steam Reforming (MSR) are highly susceptible to carbon poisoning due to formation of graphite layers. Although, numerous experimental investigations have been carried out, there is a lack of comprehensive understanding on the carbon poisoning of Ni at the molecular level. It is thus imperative to gain deeper insight into poisoning mechanisms to reduce the rate of deactivation of Ni catalysts.

Graphene (a single layer of graphite) is a representative model for carbon poison. Previous studies have shown that graphene binds on Ni (111) in a commensurate manner under the influence of van der Waals forces.¹ However, the detailed mechanism of graphene formation (within the MSR pathways) is unclear. Our ultimate aim is to develop a computational model that can capture the MSR reaction and the poisoning by graphene, including the important van der Waals interactions between the Ni catalyst and the adsorbed species (including graphene).

Methods

Spin-polarized Density Functional Theory (DFT) calculations have been performed to understand the formation of graphene on Ni(111). A thorough investigation was conducted to select an appropriate DFT functional for the MSR-graphene system. The binding energies of graphene and MSR species - CO, C, H₂O, H, O and OH - were computed using different DFT functionals. The latter include PBE and RPBE (GGA functionals), PBE-D3 and RPBE-D3 (GGA functionals with a posteriori dispersion corrections), optB86b-vdW and optB88-vdW (van der Waals – DFT functionals). The predictive accuracy of these functionals has been evaluated by consistent benchmarking with the data available in literature.

Results and Discussion

The predictions of the DFT functionals (which include van der Waals interactions) for graphene-Ni(111) has been benchmarked against a published value for the binding energy (BE) obtained using Random-Phase Approximation (RPA) method. The RPA estimates the BE of graphene and C-Ni distance to be 0.067 eV per carbon atom and 2.17 Å, respectively (experimental C-Ni distance has been reported to be 2.11 ± 0.07 Å).^{1,2} As shown in figure 1, optB86b-vdW, PBE-D3 and optB88-vdW predict the binding energy of graphene on Ni(111) with reasonable accuracy. The RPBE-D3 functional fails to predict the minimum between graphene and Ni(111).

Table 1 summarizes the performance of DFT functionals in estimating the binding energies of representative species of the MSR reaction. The DFT predictions were benchmarked using the experimental evidence obtained from the literature (TPD and calorimetric studies). The RPBE functional deviates significantly from experimental predictions. The PBE functional has an overall acceptable performance; however, it does not capture the van der Waals interactions.¹ The optB86b-vdW and optB88-vdW functionals predict the adsorption energies of certain species such as H₂O and H well; however they fail in the cases of CO and O. In addition, optB88-vdW exhibited convergence issues in estimating the total DFT energy of gas O₂. Although

RPBE-D3 performs well, as illustrated in figure 1, it does not predict the binding energy of graphene on Ni(111). Overall, the PBE-D3 functional predicts the adsorption energies of most MSR species reasonably well (excluding CO, all the deviations with respect to experimental data are well within 0.3 eV), it also captures the adsorption energy and geometry of graphene-Ni(111) system with good accuracy (refer to Figure 1). Hence, it is the functional of choice for this system. The PBE-D3 functional has been used to perform transition state calculations for different reaction pathways of MSR.

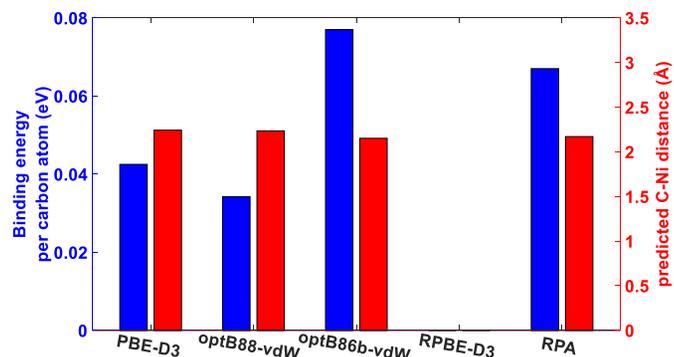


Figure 1. The blue bars and red bars indicate the binding energy and C-Ni distance, respectively.

Table 1. Performance evaluation of DFT functionals.

Functional	Deviation between functional prediction and experimental data of MSR species (eV)					
	C	CO	H ₂ O	H	O	OH
PBE	0.129	0.639	-0.198	0.016	0.095	-0.306
PBE-D3	0.196	0.821	0.033	0.225	0.147	-0.213
RPBE-D3	-0.184	0.546	-0.035	-0.059	-0.312	-0.488
RPBE	-0.329	0.238	-0.401	-0.339	-0.458	-0.653
optB88-vdW	0.146	0.705	-0.019	-0.056	-	-0.199
optB86b-vdW	0.264	0.880	0.026	0.066	0.610	-0.042

Note: Deviation = Experimental value – DFT predicted value. Colour code: |Deviation| < 0.1 eV - value is coloured to green, |Deviation| > 0.3 eV - value is coloured to red, 0.1 eV ≤ |Deviation| < 0.3 eV - value is coloured to yellow

Significance and future work

A systematic screening study has been conducted to use a reliable DFT model for understanding the poisoning of Ni catalyst in Methane steam reforming. The rate constants of MSR pathways obtained from the DFT studies will be used as an input to develop a Kinetic Monte Carlo model. These computational investigations can provide qualitative insights to control and mitigate the poisoning rate of Ni catalyst at MSR conditions.

References

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