Density functional theory screening of metal nanocatalysts for activity and selectivity toward water pollutants

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Introduction

Providing clean water for human consumption and to sustain ecosystems is one of the biggest challenges facing society today. The water demand continually increases, and the number and amount of substances that are released into water increases concomitantly. Current water treatment strategies in the US can barely keep up, and the problem is worse in less developed nations.

Catalysts are a promising strategy for improving water quality. Indeed, palladium catalysts are presently used to decompose some contaminants in drinking water. In order for catalysts to significantly impact water quality, they must be modified to target a wider variety of contaminants. In this work we use density functional theory (DFT) calculations to screen transition metal nanocatalysts for activity and selectivity toward nitrate, which is a persistent water pollutant, and δ -valerolactone, which we use as a model for lactone-based pharmaceuticals. Our preliminary calculations employ Au-based catalysts for three related reasons. First, nanosized Au is well-known to be catalytically active. Second, like its periodic table neighbor Pt, Au obeys the Sabatier Principle, in that Au catalysts adsorb reaction intermediates, but not so strongly as to become poisoned by them. Third, catalytic energies can be tuned by altering the Au particle size and/or composition, providing a relatively large degree of control over these catalysts. We hypothesize that we can harness this control to design catalysts to selectively decompose the contaminants of interest.

Materials and Methods

DFT calculations were performed with the periodic boundary condition, planewave basis set VASP code.¹ Valence electron exchange and correlation were calculated using the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA),² and ionic cores were modeled using the projector augmented wave (PAW) method.³ Spin polarization was included because of the magnetic natures of some of the metals. The nanocatalysts were modeled using thirteen atom icosahedral clusters.

Results and Discussion

As a first step, we screened for activity toward nitrate reduction to nitric oxide, i.e., $NO_3^* \rightarrow NO_2^* \rightarrow NO^*$ on $Au_{12}X$ catalysts, where X = Fe, Cu, Pd, and In, which were chosen due to their different electronic properties, possibility to alloy or mix with Au, cost, and toxicity. Results are shown in **Table 1**. From those results, X = Fe and Pd showed the most promising reduction energies, so we also computed the reduction energies on $Au_{11}XY$ models, where X, Y = Fe and/or Pd. Those results are given in Table 1 as well.

All catalyst models show exothermic behavior for NO₃ reduction, while NO₂ reduction is widely variable, spanning from -0.99 to +1.42 eV. We find that the NO₂ reduction energy correlates to the adsorption energy of NO, i.e., NO (g) + $* \rightarrow$ NO^{*}. These results are

shown in **Figure 1**. Thus, we hypothesize that NO is a descriptor of activity for nitrate reduction. We are currently calculating the kinetics of this reaction to test this hypothesis.

Table 1. NO_3^* and NO_2^* reduction energies (in eV, 1 eV = 100 kJ/mol) on Au-based catalysts.

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	$NO_3^* \rightarrow NO_2^* + O^*$	$NO_2^* \rightarrow NO^* + O^*$
Au ₁₃	-0.09	0.79
Au ₁₂ Pd	-0.21	0.15
Au ₁₂ Fe	-0.14	-0.07
Au ₁₂ Cu	-0.40	0.28
Au ₁₂ In	-0.15	1.42
Au ₁₁ Fe ₂	-0.08	-0.99
Au ₁₁ FePd	-0.34	-0.81



Figure 1. Reaction energy for $NO_2^* \rightarrow NO^* + O^*$ versus NO adsorption energy.

Within the next three months, we will apply the techniques discussed in this work to the decomposition of δ -valerolactone, i.e., $C_5H_8O_2$. We will also work on calculating the kinetics of nitrate reduction in order to initiate rational catalyst design for nitrate reduction.

Significance

Nitrate is a persistent contaminant and the most common contaminant in groundwater aquifers. Lactones are primary components in an emerging class of pharmaceutical contaminants, which are increasing in wastewater, in part because remediation strategies have not been developed for these chemically recalcitrant structures.

References

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