DFT Approach of CO and NO Adsorption on LaFeO$_3$ Perovskite Doped with Pd and Co

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INTRODUCTION

The sintering of metal particles in conventional automotive catalysts is an inherent process which affects its efficiency and increases the demand for precious metals. Studies have proposed that the intelligent catalyst suppresses this problem through a self-regeneration mechanism as response to redox fluctuations in the atmosphere of automobile engine exhaust gases, during fuel combustion. Experimental studies[1] show that LaFeO$_3$ perovskite doped with Pd, when exposed to reductive atmospheres, Pd particles segregate out of the perovskite structure. As the oxidative atmosphere become, the palladium atoms return to the perovskite structure as cations.[2] The objective of this study is to evaluate the relationship between composition and catalytic activity of the perovskite LaFeO$_3$ through DFT calculations for the adsorption of CO and NO on a LaFeO$_3$ cluster doped with a Pd atom, and, adding a Co atom in different positions.

METHODS

A cubic perovskite an arrangement (LaFe$_{0.94}$Pd$_{0.06}$O$_3$) was simulated by a set of four unit cells containing one atom of Pd doped in the center of the surface (Figure 1a). Then, using the same structure, a Fe atom has been replaced by an atom of Co. As a first step, the two complexes were fully optimized. Next, a CO molecule and a NO molecule were optimized over the Pd atom on the surface of the perovskite clusters, individually. All calculations were described with the PBEV5LYP/LANL2DZ/6-311+G(d) method, where 6-311+G(d) basis sets was used to describe the electrons of NO and CO molecules. During optimization of the complexes, NO and CO were optimized keeping the atoms of perovskite frozen, except the palladium atom.

RESULTS AND DISCUSSION

It was obtained opposite behaviors, comparing the results obtained to adsorption of CO and NO molecules. The CO adsorption is favored with the presence of cobalt whereas the NO adsorbs strongly when the structure is doped only with palladium. Analyzing the bonding energy for the Pd atom, the Co acts maintaining the Pd atom more fixed in the agglomerate.
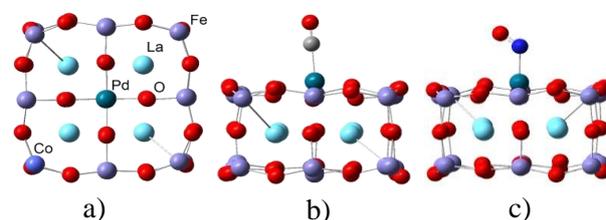

Figure 1. LaFeO$_3$ perovskite structure optimized doped with Pd and Co: a) pure, b) with CO adsorption, c) with NO adsorption.

Table 1. CO and NO adsorption energy (E$_{ad}$, kcal.mol^{-1}) and bonding energy for the Pd (E$_b$, kcal.mol^{-1}) with and without Co.

Perovskite		E$_{ad}$	Perovskite	E$_b$
NO	Pd	-41.80	Pd	-140.02
	Pd/Co	-19.60		
CO	Pd	-16.40	Pd/Co	-168.33
	Pd/Co	-28.60		

CONCLUSIONS

The perovskites doped with Pd and Pd/Co present opposite behaviors, comparing the results obtained to adsorption of molecules of CO and NO molecules. The presence of Co increases the bonding energy of the palladium atom.

ACKNOWLEDGMENTS

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