A Density Functional Theory Study of NO Adsorption on Pd_4 and Pd_4/γ-Al_2O_3 Clusters

Letícia Maia Prates (PG), Maurício Tavares de Macedo Cruz (PQ)

Departamento de Química Geral e Inorgânica, Instituto de Química. Universidade do Estado do Rio de Janeiro, Rio de Janeiro, Brazil
leticiamaiapr@gmail.com

Keywords: γ-Al_2O_3, palladium cluster, nitric oxide, heterogeneous catalysis, DFT

INTRODUCTION

For the removal of nitric oxide, specifically, the heterogeneous catalysis using Pd particles supported on γ-Al_2O_3 has shown good results. Some studies show that the support plays an important hole in the reactivity of supported metals[1,2]. Therefore, is important to evaluate how the structure of γ-Al_2O_3 contribute for the process of interaction with the NO molecule. In this work, DFT calculations were performed to obtain geometric, electronic and energetic parameters involved in adsorption of NO on palladium clusters isolated and supported in alumina.

METHODS

As a first step, a molecule of NO has been optimized in several modes of adsorption on palladium clusters with both planar and tetrahedral arrangement with Pd—Pd distance fixed in 2.751 Å (bulk of palladium). To simulate the interaction between NO and palladium cluster supported, a planar Pd_4 with initial distance of palladium bulk (2.751) was optimized on an $Al_{18}O_{27}$ cluster. Following, the NO molecule was optimized on different sites containing palladium atom. All calculations were carried out with the Gaussian 03 program and performed with B3LYP method employing LANL2DZ and 6-311+G(d) basis sets to describe Pd_4 and $Pd_4/Al_{18}O_{27}$ clusters and NO molecule, respectively. The adsorption energy was calculated with equation 1 and its value was corrected using BSSE correction techniques.

$$E_{NO_{ads}} = E_{(NO/Pd_4/Al_{18}O_{27})} - [E_{(NO)} + E_{(Pd_4/Al_{18}O_{27})}] \quad (1)$$

RESULTS AND DISCUSSION

The NO molecule adsorbs on Pd_4 agglomerates with bridge mode on planar, and with atop mode on tetrahedral, with adsorption energies of –42.2 kcal.mol^{-1} and –30.6 kcal.mol^{-1}, respectively. When Pd_4 is supported ($Al_{18}O_{27}$), the NO molecule adsorbs preferentially in atop mode, with adsorption energy of -25.8 kcal.mol^{-1}, when the first layer of the $Al_{18}O_{27}$ cluster is relaxed.This result is in good agreement with experimental results (-27.2 kcal.mol^{-1})[3].

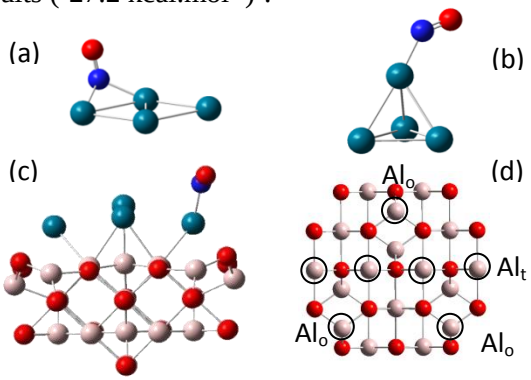

Figure 1. Preferential adsorption mode to NO molecule on (a) Pd_4 planar; (b) Pd_4 tetrahedral and (c) $Pd_4/Al_{18}O_{27}$ cluster. $Al_{18}O_{27}$ cluster (d).

For the NO adsorption on Pd_4 clusters isolated, NBO results show that the backdonation is very smaller than donation. However, the presence of alumina significantly increases the backdonation, especially when the molecule of NO adsorbed on Al hexacoordinated with higher coordination number.

CONCLUSIONS

The presence of alumina agglomerate increases palladium ability to transfer electrons to the molecule of NO, but this capability is greater in palladium bond to Al_o than palladium bound to Al_t.

ACKNOWLEDGMENTS

The authors are grateful for the support given from the CAPES, CNPQ and FAPERJ.

[1] J. W. M. Carneiro and M. T. M. Cruz, J. Phys. Chem. A, 112, 8929, (2008).
[2] K. A. Kacprzak, I. Czekaj, J. Mantzaras, Phys. Chem. Chem. Phys.,14, 10243,(2012).
[3] C. -B. Wang, T. -F. Yeh, H. -K. Lin, J. Hazard. Mater., 92, 241, (2002).