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Effect of the Metal–Support Interaction on the Adsorption of NO on $Pd_4/\gamma\text{-}Al_2O_3$

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Introduction: Strong metal−support interaction (SMSI)[1] is a term coined to describe an effect that hinders or even suppresses the chemisorption process in a catalyst, altering its efficiency. Nonetheless, it has been reported that the SMSI effect can be related to electronic and morphological contributions, which can favor or not the chemisorption process.[2-4] The $\gamma\text{-}Al_2O_3$ support, one of the most employed oxides in supported catalysts, displays a structure with octahedral and tetrahedral aluminum cations occupying the interstices between oxygen anions.[5] Due to the different coordination environments, these sites can influence in different manners the metal–support electronic flux, depending on where the metal atom sits.[6] However, despite of a large amount of research developed to understand the SMSI effect, the rationalization of its origin is still under debate. In this work, we performed DFT/B3LYP calculations to evaluate the nature of the metal–support interaction effect in a $Pd_4/\gamma\text{-}Al_2O_3$ catalyst model and its influence in the adsorption of a molecular prototype, the NO molecule.

Key-words: $\gamma\text{-}Al_2O_3$, palladium, NO, metal–support interaction, DFT

Methodology: A planar Pd_4 cluster was deposited and optimized on (110C) surface of a $\gamma\text{-}Al_2O_3$ model ($Al_{14}O_{24}H_6$). On the resulting $Pd_4/Al_{14}O_{24}H_6$ structure (Fig. 1), several adsorption modes were tested for NO molecule, allowing only this last to relax during optimization. The NO adsorption energies (E_{ad}) and the cohesion energy (E_{coh}) between palladium atoms were computed. The effect of metal-support interaction on NO adsorption was evaluated by means of two contributions: *electronic* ($\Delta E_{(E)} = E^{*}_{ad(NO_{(sp)}/Pd_4)} - E_{ad(NO/Pd_{4(sup)})}$) and *geometric* ($\Delta E_{(G)} = E_{ad(NO/Pd_4)} - E^{*}_{ad(NO_{(sp)}/Pd_4)}$). The DFT B3LYP methodology was employed using Gaussian 03 program. The electrons of $\gamma\text{-}Al_2O_3$, palladium clusters and were described by 6-31G(d,p), LANL2DZ and 6-311+G(d), respectively. All computed energies were corrected by the basis set superposition error (BSSE), calculated by the counterpoise method. The atomic charges were calculated by the Natural Bond Orbital (NBO) approach.

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*NO adsorption energy on isolated Pd_4 in the same coordinates of $NO/Pd_{4(sup)}$.
(Obs: $Pd_{4(sup)} = Pd_4/Al_{14}O_{24}H_6$).

Results and discussion: Pd_4 adsorbs on $Al_{14}O_{24}H_6$ in a distorted arrangement (Fig. 1a,b). The Pd−alumina interaction leads to a reduction of 39.1 kcal.mol^{-1} in the cohesion energy among palladium atoms, when comparing with the same distorted Pd_4 arrangement isolated. This decrease corresponds to an electronic contribution of 48.9%. Tab. 1 shows that as the NO coordination on palladium increases, the N–O distance elongates and the charge transfer to NO increases, which is relevant to the catalytic process. However, in the presence of support, these parameters are less modified, the adsorption energy decreases and the preferential adsorption mode changes from hollow (–52.0 kcal.mol^{-1}) to on-top (−25.4 kcal.mol^{-1}, in accordance with experimental result[7]). These results suggest the existence of SMSI effect. It can be observed that at the sites where the electronic contribution promoted by Pd–alumina interaction is higher, the decrease in the adsorption energy is greater. On Pd(2) is verified the lowest NO adsorption energy (–5.4 kcal.mol^{-1}) and an electronic effect of 57.0% (Fig. 1d). On Pd(3), however, the smallest decrease in the NO adsorption occurs and the electronic contribution is the lowest (2%, Fig. 1e). For the bridge mode, the metal–support interaction promotes the highest electronic effect (91.1%, Fig. 1f), an indicative that as the NO coordination increases, the electronic component becomes higher, even suppressing the mode (hollow) that could better favors the catalysis.

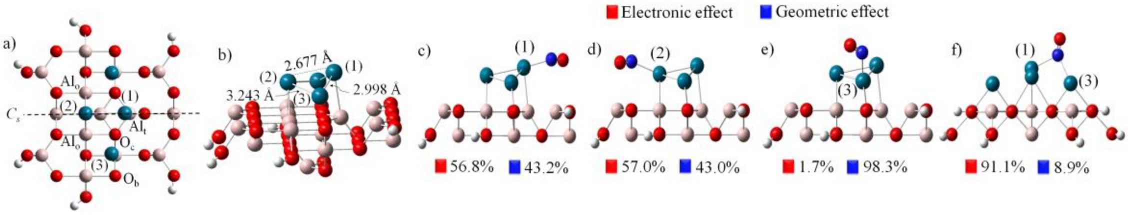

Figure 1. (a) Superior and (b) lateral views of $Pd_4/Al_{14}O_{24}H_6$ unit. (c–f) Lateral views of $NO/Pd_4/Al_{14}O_{24}H_6$ structures and electronic and geometric effects (%) involved in NO adsorption.

Table 1. Adsorption energy (E_{ad}, kcal.mol^{-1}), NBO charge density (ē) and bond distance (Å) for NO adsorbed on distorted isolated Pd_4 and $Pd_4/Al_{14}O_{24}H_6$.

	Supported					Isolated				
	On-top			Bridge	Hollow	On-top			Bridge	Hollow
Pd	(1)	(2)	(3)	(1)–(3)	(1)–(2) (3)	(1)	(2)	(3)	(1)–(3)	(1)–(2) (3)
N–O	1.151	1.156	1.156	1.182	convert to bridge	1.158	1.165	1.157	1.185	1.205
q_{NO}	+0.070	+0.011	+0.072	–0.106		–0.012	–0.019	–0.032	–0.236	–0.410
E_{ad}	–17.55	–5.37	–25.36	–14.47		–26.81	–25.78	–31.93	–42.75	–51.98

Conclusion: The presence of γ-Al_2O_3 support decreases the cohesion energy between palladium atoms. The Pd–alumina interaction promotes an important electronic contribution, capable to weak the NO molecule adsorption. However, this contribution depends on the γ-alumina site at which the palladium atom interacts and also the adsorption mode of the adsorbate molecule.

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