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Predicting the Activity of Nano Transition Metal DeNox Catalysts

Ismail Can Oğuz¹, Hazar Guesmi^{1,*}, Dominique Bazin^{2,*}, Frederik Tielens^{3,*}

¹ Institut Charles Gerhardt Montpellier, CNRS/ENSCM/UM, 240, Avenue du Professeur
Emile Jeanbrau, 34090 Montpellier, France

² CNRS, LCP, Bat349, Université Paris-11, 91405 Orsay, France

³ General Chemistry (ALGC), Vrije Universiteit Brussel (Free University Brussels-VUB),
Pleinlaan 2, 1050 Brussel, Belgium

Corresponding authors:

dominique.bazin@u-psud.fr, frederik.tielens@vub.be, hazar.guesmi@enscm.fr

Abstract

With the aim to rationalize the reactivity of transition metal (TM) clusters, the model reaction of NO dissociation on TM_{13} clusters was investigated on a set of seven TMs. The adsorption energy and the activation energy for NO dissociation were calculated for each TM and discussed within the findings of Boudart in his article “Model catalysts: reductionism for understanding”. In this work we focused on selected TM cluster calculations instead of surface science slab-type calculations, which have been performed for some TMs and focus on the electronic structure to investigate and rationalize the TM reactivity. Besides the electronic and spin properties of the TM we discuss the reactivity trends using also qualitatively the chemical hardness and softness. We conclude that the combination of these reactivity parameters will be necessary to fine tune TM clusters reactivity with the scope of multi-metallic TM clusters.

Keywords: Nitrous oxide; metallic nanoparticles ; DFT ; activation energies; model catalyst

A rational design of catalyst is based on deep understanding of the interaction between the different actors of the chemical reaction. Regarding DeNox catalysis, it encompasses the interaction of the different molecules and nanometer scale metallic particles as well as the support. Following an approach defined and discussed by Boudart in his article “Model catalysts: reductionism for understanding”¹, a possible first step consists to focus on the main molecule which is related to the chemical process i.e. nitrous oxide (NO). Then, a simple model able to take into account all the transition metals which can be selected to build nanometer scale monometallic clusters is proposed. Such model which has to be obviously in line with experimental data has then to be addressed from a theoretical point of view. In parallel, the case of more complex chemical reactions (with several molecules e.g.) on supported clusters, as used in reaction or in close to industrial conditions, has to be discussed. Such an approach allows a fine optimization of the chemical process through theory which can then be considered as a fully integrated tool.

Here, the model we want to complete by electronic structure calculations is based on a relationship between the interaction of NO and the behavior of nanometer scale metallic particles (sintering or disruption) in response to this interaction²⁻⁴. Such bridge between surface science and nanoscience is based on a set of experimental data regarding several 3d, 4d and 5d nanometer scale transition metals clusters deposited on various supports, such as: copper⁵, ruthenium⁶, rhodium⁷⁻⁹, palladium^{10,11}, iridium¹² and platinum¹³⁻¹⁵.

Regarding surface science, the different investigations focusing on the adsorption of NO on 2-D metallic surfaces made of transition metals (TM) clearly distinguish two families of metals following the adsorption mode which can be either dissociative or molecular. The projection of this experimental fact in nanoscience shows that these two families of metals correspond to two different behaviors of the clusters i.e. sintering or disruption. From a catalytic point of view, the line which separates the two groups defines an ideal catalyst, being its structural characteristics stable.

Let us recall some basic notions related to the model discussed here. The starting point is given by the different behavior of Pt and Ru nanometer scale metallic particles regarding the adsorption of NO molecules. Even if these two metals are deposited on the same support, that the metallic clusters of both metals have the same size and that when the experimental

procedure is similar, X-ray absorption spectroscopy, a technique using synchrotron radiation as a probe, give very different data^{6,15}. For Pt metallic clusters, a sintering process is observed while for ruthenium, an oxidation process of the metallic clusters occurs. The simplicity of the chemical reaction allows the opportunity to use surface concepts to understand this apparent contradiction. At this point, and based on the initial model of G. Broden et al.¹⁶, where the tendency of different metal surfaces to dissociate NO was discussed depending on the position of the substrate in the Periodic Table, W. Brown and D.A. King¹⁷ have suggested a revised picture where the variation of the melting points as the direct measure of the cohesive energies could include a line which separate dissociative and non-dissociative mode of NO on metallic surfaces.

This suggestive correlation between the propensities of TM for the dissociation of the NO molecule and their melting points is based on the thought that the higher the metal cohesive energy of TM, the stronger is the NO metal bond and thus the weaker is the N-O bond. Nevertheless, it should be noted that bulk properties, such as melting temperature, might not follow cluster-type properties, and that exceptions exist to the above mentioned behavioral models. The TM clusters are indeed expected to have more molecular-like electronic structures and consequently should confirm the particularity of nanochemistry contrasted with bulk chemistry.

Based on this model, a logical link with heterogeneous catalysis materials is the investigation of the nanoparticle reactivity instead of the surface reactivity. Indeed, the vast majority of the NO/TM studies in the literature have been done for close-packed TM surfaces¹⁸⁻²⁰ where atomistic understanding obtained for the adsorption of NO on surfaces cannot be directly transferred to NO on nanoclusters. As reported by D. Silva et al.⁴ the atomic relaxation and thus, the absence of symmetry constraints, leads to a lowering in the total energy of the system upon NO adsorption, which plays an important role in the adsorption properties. For instance, the general relationship based on the d-band model between adsorption energy and the center of gravity of the occupied d-states does not hold for the TM₁₃ clusters, in particular, for clusters with low symmetry. Similarly, finite size effect in chemical bonding was demonstrated to exist for many monometallic (ref: A,B,C) and bimetallic systems (ref :D).

So far, most of the Density Functional Theory (DFT) studies devoted to the NO interacting with small TM clusters focused on just one or a few particular systems¹⁸⁻²⁰. To our knowledge, no comparative study that includes many clusters that could be of interest for the

community of catalysis has been performed. In addition, the interaction of NO was generally limited to the adsorption mechanisms and adsorption sites and no evaluation of the activation energy of NO dissociation reaction depending on the TM cluster has been performed.

In this work, we report the first confirmation of the reliability of this model where in first instance seven different TM clusters are investigated using DFT to elucidate the fundamental adsorptive properties and interactions of NO on nanometer scale monometallic catalysts.

In the present study spin polarized calculations were performed to investigate the adsorption behavior of NO and its dissociation reaction on monometallic clusters of 13 atoms (TM_{13}). 3d (Ni_{13} , Cu_{13}), 4d (Ru_{13} , Rh_{13} , Pd_{13}) and 5d (Ir_{13} , Pt_{13}) MT clusters were considered. In line with several previous works [3], the optimization of a set of structural configurations show that the non-compact structures are always more stable than the compact Mackay Icosahedron. For each structure, the spin moment modes were fixed and the space of possible magnetic structures was scanned. Several systems have nonzero magnetic moments, even when their bulk phases do not show magnetism, e.g., Cu_{13} , Pd_{13} and Pt_{13} . These findings were attributed to the low dimension and lower coordination of the non-compact structures, which have been known to enhance the magnetic properties of surfaces²¹. The description of spin states of different gas phase metallic clusters and comparison with the data in the literature was largely debated and is out of the scope of this work. All details concerning magnetic states of M_{13} clusters could be found elsewhere²¹. In Table 1, all calculated adsorption energies of NO on M_{13} clusters and NO elongations are presented. The overall calculated values are consistent with the literature²¹. Results show the top-to-edge site as the favorable adsorption site for NO on Pt, Ir, Rh, and Ru, and the fcc site as the favorable adsorption site on Ni, Cu, and Pd. Over this latter site, the NO bond distance is found to be much more elongated than on top-to-edge sites. Note that the NO bond distance in the gas phase is calculated to be of 1.17 Å, within the doublet ground state.

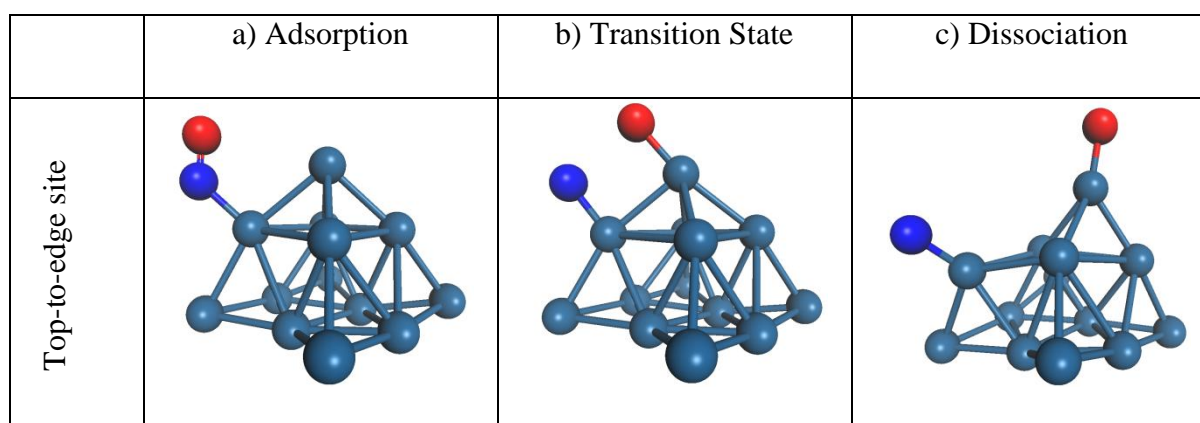
Table 1. Adsorption energies and NO bond distances on onefold (top-to-corner, top-to-edge), twofold (bridge-edge, top-bridge-terrace), and threefold (fcc terrace) sites of Mt_{13} clusters.

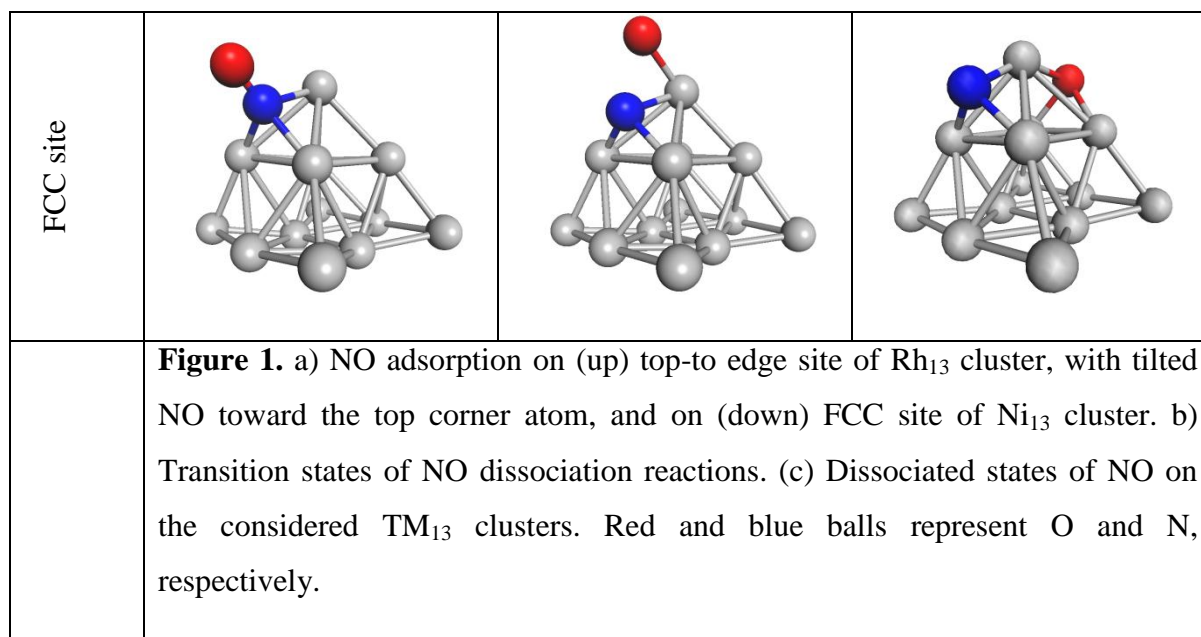
	Adsorption energy, ΔE_{ads} (eV)	dN-O (Å)

NO adsorption site	Top-to-corner	Top-to edge	Bridge-edge	Top-bridge-top	fcc terrace	
Pt ₁₃	-2.03	-2.24	-1.83	-1.88	-1.42	1.19
Ir ₁₃	-2.53	-2.42*	-2.00	-1.92	-1.87	1.19
Rh ₁₃	-2.42	-2.41*	----	-1.86	-2.59	1.19
Ru ₁₃	-2.45	-2.21*	-2.24	-1.80	-2.24	1.19
Pd ₁₃	-1.64	-1.89	-2.07	-1.52	-2.26	1.22
Cu ₁₃	-1.65	---	-1.84	-1.79	-2.01	1.24
Ni ₁₃	-2.05	-1.99	----	-2.19	-2.36	1.24

*top-to edge with NO tilted toward the top corner atom, vertical adsorption values are -2.87, -2.69 et -2.62 for Ir, Rh et Ru, respectively.

On Pt₁₃ cluster, the NO stabilizes on the top to-edge site (See **Figure S1**) with adsorption energy of -2.24 eV (see **Table 1**). From this configuration, the NO can tilt or rotate toward the top corner Pt atom without any energy barrier (see **Figure 1a (up)**) and stabilizes within the same energy minima on the triplet ground state. This tilted NO geometry is also found for Ir, Rh, and Ru, but exists after the system overcome a small activation barrier of 0.5 eV where O of nitrous oxide rotate from vertical position toward the nearest top corner metallic atom. (See **Figure S2**) Thus, the top to-edge adsorptions with vertical NO are found to occur with energy values of -2.87 eV, -2.69 eV, and -2.62 eV for Ir, Rh, and Ru, respectively. The NO adsorption on top to-edge adsorptions with tilted geometry are found to occur with energy values of -2.42 eV, -2.41 eV, and -2.21eV for Ir, Rh, and Ru, respectively. Singlet ground state is predicted for NO on Rh cluster while doublet ground state is predicted for NO on Ir and Ru.





On the Pd, Cu and Ni clusters NO adsorbs preferentially on the fcc site (see **Figure 1a** (down)). The predicted ground states are the sextet, the doublet and the decuplet for Pd, Cu and Ni, respectively. The highest spin states are calculated from Pd₁₃ and Ni₁₃. The adsorption energy (ΔE_{ads}) of NO on TM₁₃ evolves from 2.01 to 2.87 eV, from Cu to Ir, respectively.

In **Figure 2** are represented the variations of calculated NO adsorption energies ΔE_{ads} and activation energies (E_{act}) of dissociation reaction. As it can be seen, the adsorption energies on TM₁₃ vary from -2.01 eV/atom to -2.42 eV/atom, which ranges in a window of 0.41 eV with an average adsorption energy of -2.27 eV/atom (see horizontal blue line in Figure 2). No specific trend concerning these calculated energies could be directly found following any atomistic or chemical property such as, the atom number or the position in the Periodic Table. However, the predicted activation energies of NO dissociation E_{act} are found to vary from 0.63 eV to 2.88 eV for the 7 metals investigated (see **Table 2**). Thus, when the E_{act} is plotted versus the metal with increasing magnitude, as it is depicted in **Figure 2**, 2 groups can be distinguished a) Ru, Ir, Rh and Ni, and b) Pt, Cu and Pd, separated by a line (vertical black line) which correspond to the NO dissociation activity on metal surfaces.

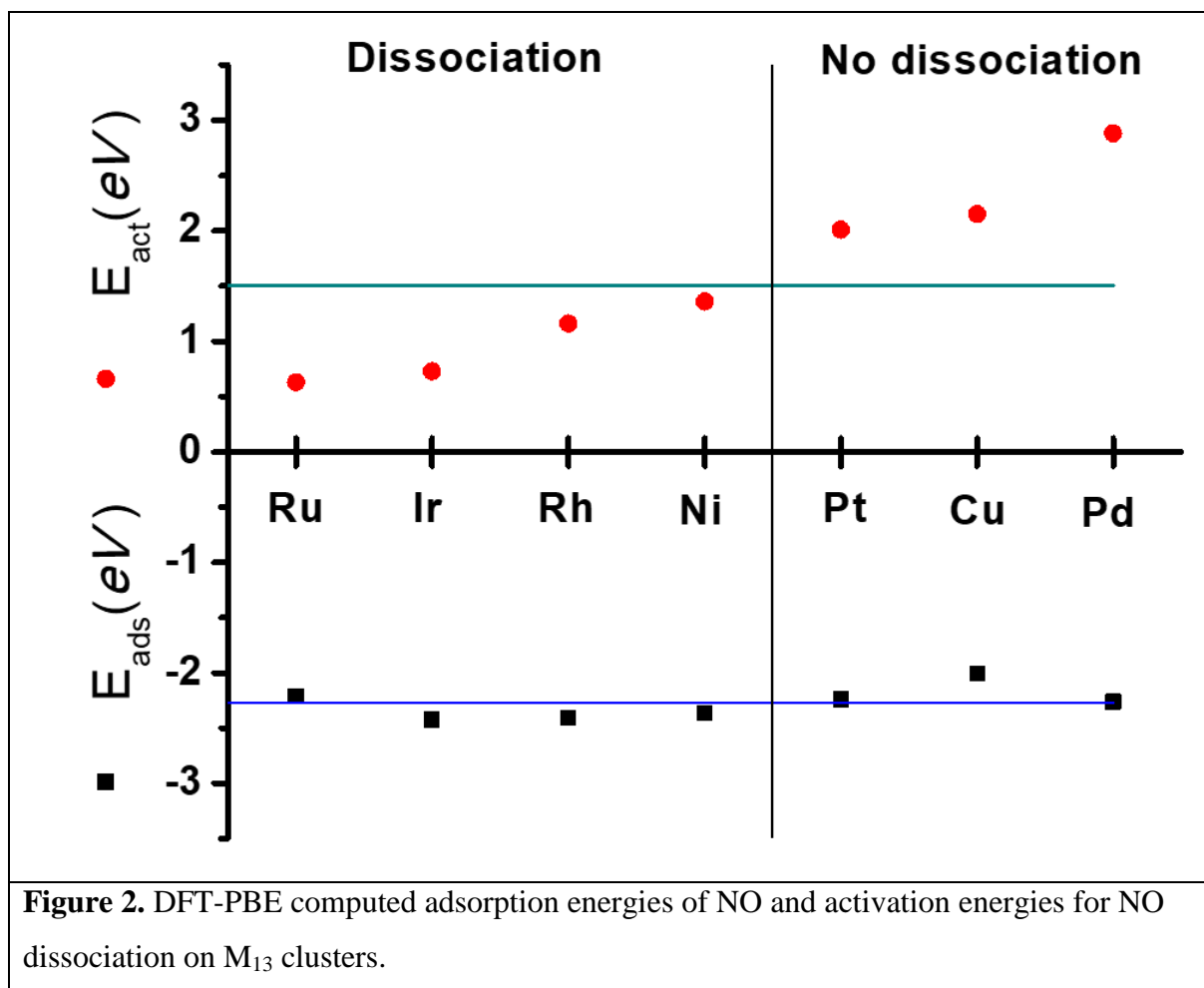
Now, if we consider NO a hard molecule, we can see that the ΔE_{ads} becomes more negative (i.e. stronger adsorption) with increasing TM hardness (see Table 2), which is in line Pearson's HSAB principle²². Interesting to note also is that the E_{act} for NO dissociation

increases with increasing number of d electrons of the metal, i.e. from Ru(4d⁷5s¹) to Pd(4d¹⁰). This trend is in line with the maximal hardness principle²³, which states that the harder the transition state, the lower the activation energy. This principle is recovered if one plots the hardness of the TM versus the E_{act} , without taking into account Pd.

For both properties (ΔE_{ads} and E_{act}), governing the TM clusters reactivity, Pt and Pd appears to the exception, when its reactivity is described using atomic hardness. This finding points into the direction that hardness alone is not sufficient to rationalize the TM clusters reactivity, and that another property modulates it. The other possible descriptors are the electronic spin states or magnetism which were shown to highly affect the properties of small Pd clusters (ref :E) . However, descriptors such as spin and density of states cannot be ruled out to obtain a complete understanding of the TM clusters reactivity, as it has been shown already for other TM systems.^{18–20}

Table 2. DFT calculated adsorption energies and dissociation activation barriers of NO on M₁₃ clusters. (Energy in eV/atom). Hardness values of elements are added for discussion.

M ₁₃	ΔE_{ads}	E_{act}	<i>Hardness</i>
Pt	-2.24	+2.01	3.5
Ir	-2.42	+0.73	6.5
Rh	-2.41	+1.16	6.0
Ru	-2.21	+0.63	6.5
Pd	-2.26	+2.88	4.75
Cu	-2.01	+2.15	3
Ni	-2.36	+1.36	4



Nevertheless, the best descriptor here is the E_{act} of NO dissociation, which intrinsically contains the electronic information of the system. For $E_{\text{act}} < 1.5$ eV/atom the dissociation of NO is predicted (see green line in **Figure 2**).

This leads us to the following thought²³: Is it possible to select some bimetallic catalysts with synergistic properties? This purely energetic model leads to a complete rejection of some bimetallic systems. For example, if we consider the RhRu bimetallic cluster (or a RhIr as well as RuIr bimetallic), the NO adsorption process leads probably to the formation of a metal oxide i.e. the dissociation of NO will stop. On the other hand, if we consider a PtCu system, it is probable that the NO adsorption will lead to large clusters. A guideline for the choice of the bimetallic system for interesting DeNox activity would be to add to platinum a second metal such Rh, Ir or Ru. It is obvious that such guideline should be accompanied by a rigorous consideration of the alloy properties as mixing and segregation enthalpies of the two elements [ref: G] as well as structural and composition of the nanoalloys .

While the literature regarding DFT calculation on the adsorption process of small molecules on metallic surface is well studied, very few papers deal with the adsorption of NO molecules

on TM clusters. The goal of this investigation was to valid a simple model (melting point/reactivity) in which a relationship exists between the adsorption mode of NO molecules and the behavior of the metallic cluster during reaction with NO. To attain this goal, a set of seven metals namely Ru, Ir, Rh, Ni, Pt, Cu, and Pd has been selected which correspond to the ones for which experimental data exist. For each one, different adsorption sites for the NO molecules have been considered, while the structural parameters of the metallic clusters have been fixed by the use of a TM_{13} cluster.

The complete set of simulations is in line with the initial model based on experimental data. Indeed, the dissociation of NO on Ru, Ir, Rh and Ni, which lead to the formation of an oxide, was recovered. At the opposite, the DFT calculations indicate no NO dissociation for Pt, Cu and Pd.

At our best knowledge, this work paves the way to a deep understanding of NO adsorption. Works are in progress to consider other TM as well as bi or tri metallic systems, which enable to fine tune the model and propose an optimized multi-metallic catalysts (containing even more than two TMs).

Considering the selection of the transition metals that were tested on their behavior to dissociate NO on TM_{13} , one could observe that the activation energy of the NO dissociation reaction increases with the number of d electrons in the metal valence. Metals with less filled d orbitals (less noble) are better candidates for the promotion of NO dissociation and the oxidation of the TM_{13} cluster. Nevertheless, Pd element, was found to show a more complex behavior, and that beside absolute atomic hardness, more electronic and spin based properties are important in the description of the NO dissociation reaction.

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