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DFT study of NO Reduction to N_2O assisted by a neutral silver atom

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Abstract

A density functional theory (DFT) study of NO reduction to N_2O in presence of a neutral silver atom is reported. The hybrid functional GGA-B3LYP combined with the effective core potential (ECP) LanL2DZ for $Ag^{(0)}$ and the extended basis set 6-311++G** for N and O were used. An elemental 6-step mechanism is proposed which starts with the coordination of two NO molecules to silver by means of the N atoms. Then, this first planar minimum (M1) is transformed into a second non planar one (M2). Afterwards, M2 breaks one of their Ag-N bonds through a transition state (TS) which has a three-member ring (Ag-N-N) and it is converted into M3, where the Ag is coordinated to only one N. Subsequently, a fourth cyclic minimum (M4) is obtained which after the breaking of the Ag-N bond is transformed into M5, where the silver is to coordinated to only one O. Finally, M5 breaks one of their N-O bonds to lead along the products AgO and N_2O. The global reaction studied is exothermic at the level of calculation employed (B3LYP/LanL2DZ/6-311++G**), nevertheless, the three last elemental steps with activation energies between 62 and 92 kJ mol^{-1} in the proposed mechanism difficult the reaction viability, however, the reaction is still possible at high temperatures. A brief comparative discussion between catalyst based in silver and catalyst based in copper is included.

Key words: B3LYP, NO reduction, LanL2DZ, 6-311++G**, silver.

Estudio DFT de la reducción de NO a N_2O asistida por un átomo de plata neutro

Resumen

Se reporta un estudio de la reducción de NO a N_2O en presencia de un átomo de plata neutro con la teoría del funcional de la densidad (DFT). Se usó el funcional híbrido GGA-B3LYP combinado con el potencial efectivo del "core" (ECP) LanL2DZ para $Ag^{(0)}$ y el juego de bases extendido 6-311++G** para el N y O. Se propone un mecanismo de seis pasos elementales el cual comienza con la coordinación de dos moléculas de NO a la plata por medio de los átomos de N. Luego, este primer mínimo plano (M1) es transformado en un segundo no plano (M2). Seguidamente, M2 rompe uno de sus enlaces Ag-N mediante un estado de transición que tiene un anillo de tres miembros (Ag-N-N) y este es convertido en M3, donde la Ag está coordinada sólo a un N.

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posteriormente, se obtiene un cuarto mínimo cíclico (M4) el cual después de la ruptura del enlace Ag-N es transformado en M5, donde la plata está coordinada sólo a un O. Finalmente, M5 rompe uno de sus enlaces N-O para conducir a los productos AgO y N_2O. Al nivel de cálculo empleado (B3LYP/LanL2DZ/6-311++G**) la reacción global estudiada es exotérmica, no obstante, los tres últimos pasos elementales en el mecanismo propuesto con energías de activación entre 62 y 92 kJ mol^{-1} dificultan la viabilidad de la reacción, sin embargo, la reacción es aún posible a altas temperaturas. Se incluye una breve discusión comparativa entre los catalizadores basados en plata y los basados en cobre.

Palabras clave: B3LYP, reducción de NO, LanL2DZ, 6-311++G**, plata.

Introduction

Nitrogen oxides (NO_x), including nitrogen dioxide (NO_2), nitric oxide (NO) and nitrous oxide (N_2O), are extremely harmful contaminants to the human health, the quality of the urban air, the living species (animal and vegetable ecosystems), and the environment (1, 2). The NO_x play an important role in atmospheric chemistry and in the climate system as precursor of tropospheric ozone. These nitrogen oxides are among the main responsible of the photochemical smog, greenhouse effect, acid rain and many respiratory diseases (3). Unfortunately, the NO_x level in atmosphere continues increasing year by year due mainly to anthropogenic activities; in particular to flue gasses emitted by stationary and mobile sources such as lean-burn automobiles, coal-fired power plants, electric power generators, nitric acid factories, biomass burning, among the other (4). Nowadays, because the enlargement in number of diesel engine cars, the amount of NO emission in urban areas increased significantly. The NO_x estimated global anthropogenic emission for 1990 is about 31 million tons of NO by year (5). Moreover, for the coming decades, combustion of fuels will remain an important source of energy. For these reasons, at present exits strict world trends to reduce the NO_x emissions and it is expected more stringent future legislations (6).

The NO_x removal from the engine exhaust gases is only possible employing specific catalytic processes and these catalysts usually contain supported transition metals on a controlled pore size solid, such as diverse zeolites. There is a worldwide effort to elaborate improved catalyst capable to remove NO_x, however, until now there is no a suitable catalyst that can effectively convert NO into N_2 and O_2, although the chemical reaction is thermodynamically favorable at low temperature, is extremely slow kinetically. Since the 1980s intensive research is bringing about the production of highly efficient DeNOx catalysts to eliminate NO through reductive mechanism (7-9). To reach this goal, the catalytic activity, selectivity, stability and cost of catalytic active metal are important parameters to be considered. In this sense, several studies devoted to the development of catalysts capable to reduce the nitrogen oxides have been performed, and a considerable number of them have focused on the use of catalysts containing copper. The exceptional catalytic activity of copper ion-exchange on Y-type and ZSM-5 zeolites to the decomposition of NO were reported by Iwamoto and coworker (7, 8) in 1981 and 1986, and confirmed by Li and Hall (9) some time ago. Nevertheless, the Ag ion-exchanged zeolites catalyst (Ag^+/ZSM-5) displays comparable activity and selectivity towards the photocatalytic decomposition of NO into N_2 and O_2 (10). The selective catalytic reduction of NO by hydrocarbons (HC-SCR) employing Ag/Al_2O_3 has showed excellent activity and selectivity. The HC-SCR performance of supported Ag catalyst is very sensible to the reaction conditions, especially the type of hydrocarbons and the addition of H_2 (11). On the other hand, x-ray diffraction (XRD) and UV-Vis measurements on the Ag-H-ZSM5 systems show an evident relationship between the structure of the catalysts and their catalytic activities for the SCR of NO_x. (12). Moreover, the SCR of NO with Ag-Al_2O_3, Ag-H-ZSM5 and Ag-HY catalysts showed high selectivity to N_2 (around 95%), which is attributed to the same active phase of silver oxide (13).

The Cu and Ag atoms have the same electronic structure ($d^{10}s^1$) and the only differences are their principal quantum numbers of the valence shells. The dissimilar performance of the catalysts assisted by Cu and Ag may be explained by taking account the different in energy gap between 4d-5s for silver and 3d-4s for copper (14). It is customary in chemistry to associated analogous chemical behavior to the elements of the same periodic table group. So, copper, silver and gold must have similar responses in the NO reduction mechanism. Besides, silver and gold are considered among the IB group metals more active than Cu in many cases. On the other hand, usually, the heaviest elements inside a specific metal group present high activities; whereas, the lightest elements present low activities. Therefore, is reasonable to expect that the catalysts based on silver show better catalytic properties than the catalyst based on copper; although, is well known that the copper supported over several sieves has demonstrate to be an efficient catalyst to SCR of NO_x (15).

In this work, density functional theory (DFT) calculations were carried out to investigate the reaction paths for the NO reduction to N_2O in presence of a silver atom. Here, many efforts have been devoted to obtain the right connectivity between the transition state (TS) structures and their immediate neighbor on the proposed potential energy surface (PES) by mean of intrinsic reaction coordinate (IRC) calculations. All the transition structures proposed in this report present the fully connectivity with the corresponding immediate minimums on the PES. The energetic, electronic, vibrational and geometrical properties calculated may bring some insight on the mechanistic aspects of the NO reduction, and valuable recommendations for the catalyst manufacturers.

Computational details

All the calculations were carried out with the Gaussian-03 (G03) computational package (16). The hybrid functional B3LYP (17, 18) combined with the effective core potential (ECP) LanL2DZ (19) for $Ag^{(0)}$ and the extended basis set 6-311++G** (20) for N and O were used. A plausible reaction mechanisms, which include reactant and product, stable intermediates and transition states, for NO reduction to N_2O starting from two NO molecules interacting with a neutral silver atom were calculated at the level B3LYP/LanL2DZ/6-311++G** and their vibrational frequencies were obtained at the same level. These frequencies permit us to distinguish between the minimum (with all the vibrational frequencies positives) and the TS (with only one imaginary frequency). All the TS were obtained with the synchronous transit-guide quasi-Newton (STQN) methods (21), using the keyword QST2, QST3 and TS implemented in G03. Moreover, the IRC method (22), which examines the reaction paths going down from the TS on the PES was carefully analyzed to confirm the right connectivity between all transition structures and theirs immediate minimum.

The reaction energies ($\Delta E_{A\rightarrow B}$) and the activation energies ($\Delta E_{A\rightarrow TSA}$) for the elemental step $A\rightarrow TSA\rightarrow B$ were calculated using the equations:

$$\Delta E_{A\rightarrow B} = (E_{el,B} + ZPE_B) - (E_{el,A} + ZPE_A) \quad (1)$$

$$\Delta E_{A\rightarrow TSA} = (E_{el,TSA} + ZPE_{TSA}) - (E_{el,A} + ZPE_A) \quad (2)$$

where: $E_{el,A}$, $E_{el,TSA}$ and ZPE_A are the electronic energy of A, of TSA and the zero point energy of A, respectively.

Results and discussion

A 6-step mechanism is proposed with one reactant, five minimum, five TS and the products. The minimum and the TS hereafter will be referred as M*n* and TS*n*, *(with* $n=1\rightarrow5$*)*, respectively. The total energies ($E_{el} + ZPE$) and the relative energies (ΔE) calculated at the level B3LYP/LanL2DZ/6-311++G** for the all participating species in the NO reduction to N_2O are in figure 1, which shows the reaction diagram of the minimal path way on the PES for the studied reduction reaction in presence of a neutral silver atom. All the ΔE values of figure 1 are energies relative to the reactants ($Ag^{(0)}$ + *2NO*). The figure 2 and 3 show the optimized structures with their geometrical parameters for the minima and TS structures, respectively. The structures of figure 2 and 3 are all in their ground states and have spin multiplicities equal to two (2S+1=2).

The first step of the proposed mechanism start with the coordination of two NO molecules to one $Ag^{(0)}$ atom, both by means of N atoms, forming the first minimum (M1 structure, see figure 2), which is planar, symmetric (C_{2V}) and look like a claw. The M1 formation is an exothermic step ($\Delta E_{R\rightarrow M1}$ = –22.8 kJ mol^{-1}) due to the formation of two Ag-N bonds. Then, in a second step, M1 is converted exothermically in M2 ($\Delta E_{M1\rightarrow M2}$ = –32.7 kJ mol^{-1}), passing through TS1, which has very little activation energy ($\Delta E_{M1\rightarrow TS1}$ = 4.0 kJ mol^{-1}). TS1 is symmetry (C_{2V}), look like a claw too, but is non planar (see figure 3). Two changes can be observed going from M1 to M2, the lost of planarity and the decreasing in the N-Ag-N angle value, from 84.5° in M1 to 42.3° in M2, logically, TS1 show an intermediate value (70.0°). On the other hand, M1 and TS1 are totally symmetric, but M2 is slightly asymmetric (see figure 2).

The third step is a slightly endothermic process ($\Delta E_{M2\rightarrow M3}$ = 0.3 kJ mol^{-1}) and several changes occur to reach the M3 structure. Initially, the passage from M2 to TS2 implies

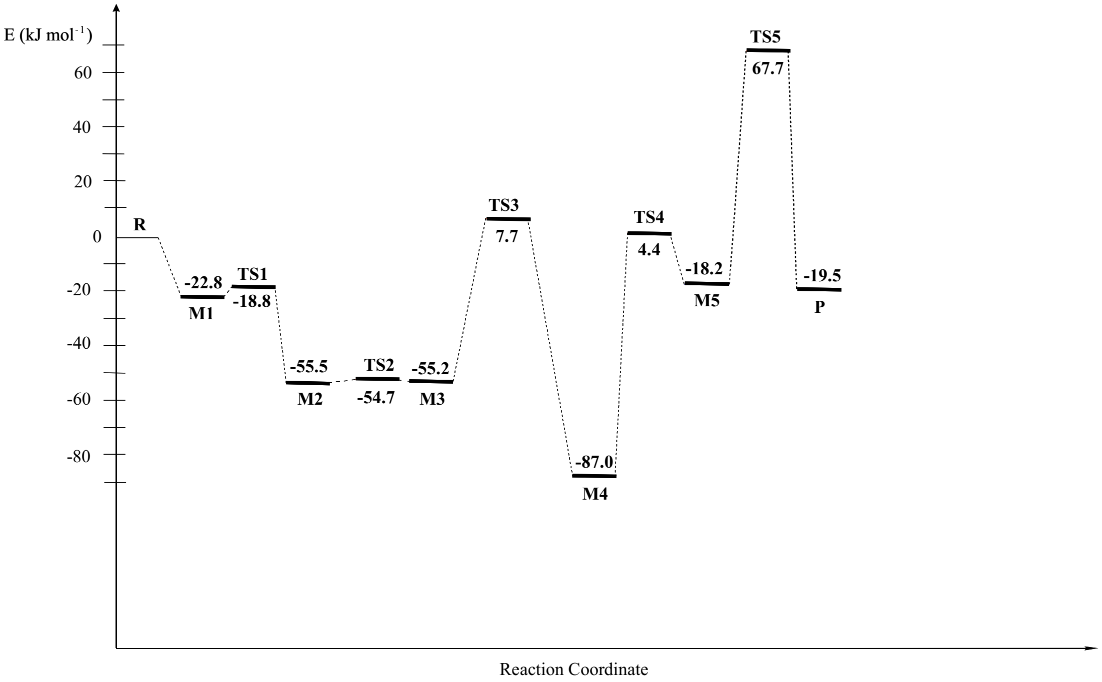

Figure 1. PES of NO reduction to N_2O in the presence of Ag calculated at the level B3LYP/LanL2DZ/6-311++G**.

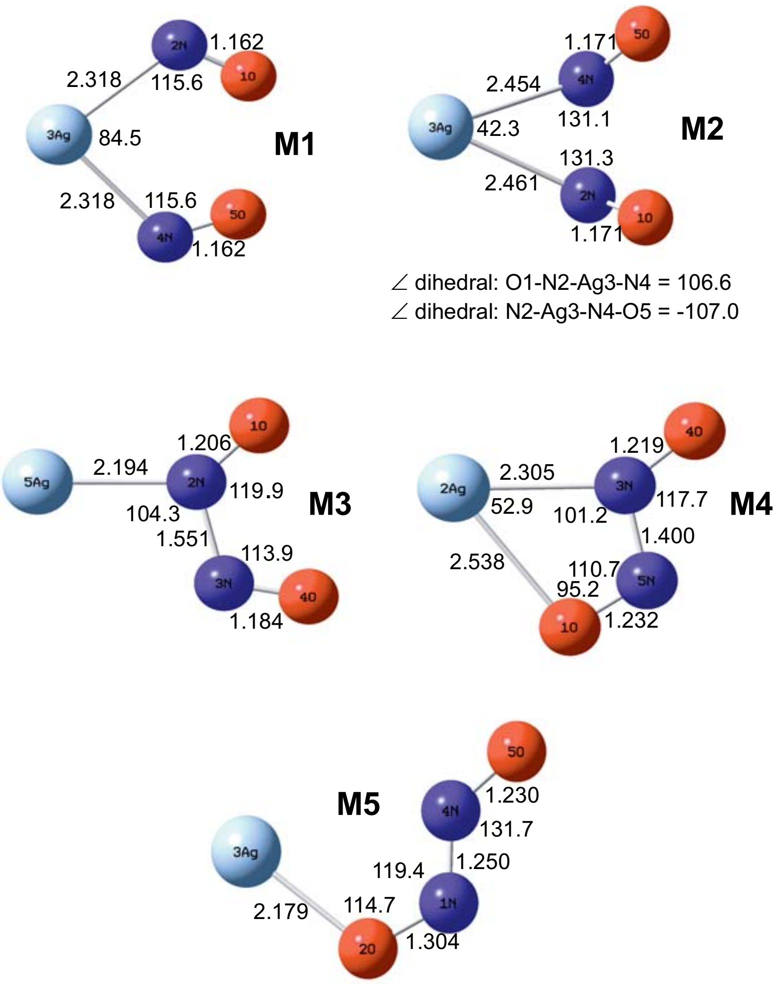

Figure 2. Geometries of the minimum optimized at the level B3LYP/Lanl2DZ/6-311++G**. (Bond distances in Å and bond angles in degree, with three and one decimals, respectively).

an additional diminution of the N-Ag-N angle until the N-N distance is enough short to form a new weak bond between these atoms in the TS2, which is a hindered structure due to the N-Ag-N angle and the Ag-N distances. The height barrier for the TS2 formation is very small ($\Delta E_{M2\rightarrow TS2}$ = 0.8 kJ mol^{-1}). Afterward, the large Ag-N bond is broken for obtain the M3 structure, where the Ag$^{(0)}$ is coordinated to only one N atom. Summarizing, the two initial steps are exothermic and the third is only slightly endothermic, beside, the barriers energies are moderately low. So, the arrival to M3 structure from the reactants is highly favored.

The fourth step, the M4 formation, requires overcome a very high energy barrier ($\Delta E_{M3\rightarrow TS3}$ = 62.9 kJ mol^{-1}) passing through TS3. The M4 is the most stable structure of our mechanism and has cyclic 4-member ring structure. TS3 is also a cyclic structure and has positive relative energy. The geometries of TS3 and M4 structures are very similar except for two interatomic distances, the N-N distance is greater in M4 and the Ag-O distance is lower in M4. Thus, going from TS3 to M4 the N-N distance increase and the Ag-O decrease; whereas the Ag-N distance remains practically unchanged. The M4 for-

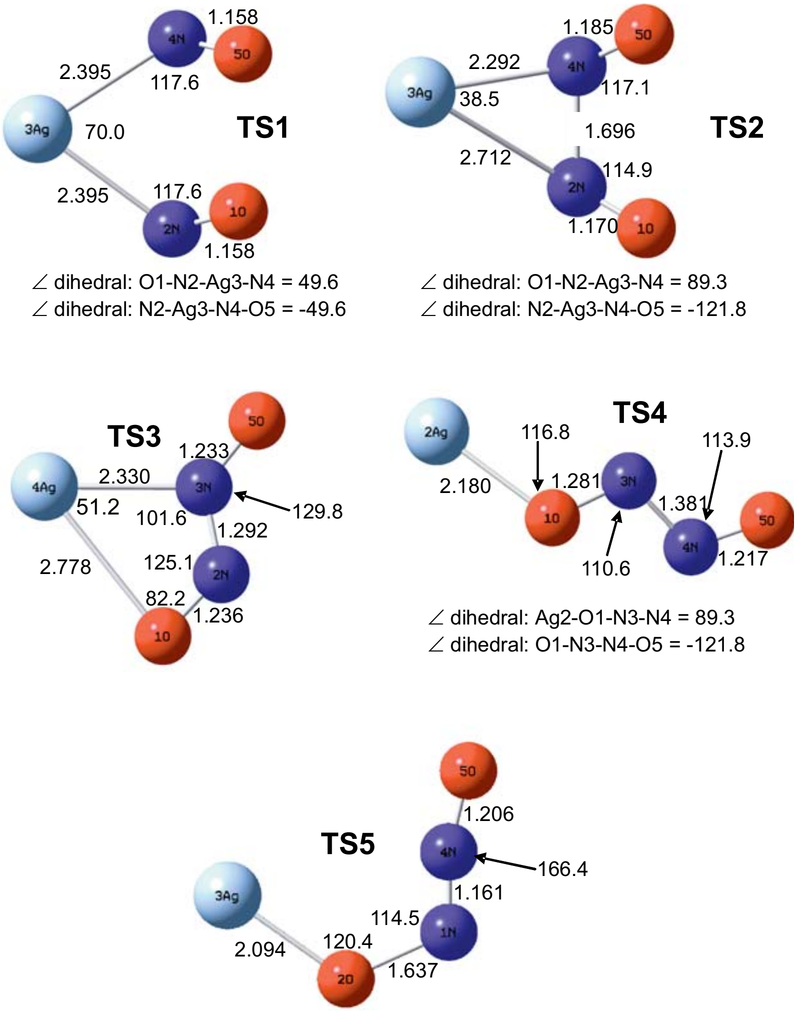

Figure 3. Geometries of the TS optimized at the level B3LYP/Lanl2DZ/6-311++G**. (Bond distances in Å and bond angles in degree, with three and one decimals, respectively).

mation is an exothermic step ($\Delta E_{M3\rightarrow M4}$ = –31.8 kJ mol^{-1}). The M4 structure exhibit high similarity with one structure reported by Citra and Andrews (23) obtained from infrared spectroscopy and density functional calculations of $Ag_x(NO)_y$ (x, y = 1,2). Citra and Andrews proposed four structural isomers for $Ag(NO)_2$. Our M4 structure is equivalent to the trans isomer, which is the main responsible of the vibrational frequency taken in neon matrix. Our calculated vibrational frequency for the Ag-O stretching is 1383.4 cm^{-1}, which is in worthily agreement with the experimental value reported of 1387.5 cm^{-1}. The narrow difference between the experimental and theoretical values for this vibrational frequency is a good indicial about the exactitude of the calculation combinations employed. Additional comments may be achieve for other vibrational frequencies reported by Citra and Andrews for the simple Ag-NO and Ag-ON systems. The vibrational frequencies differences between the experimental and the calculated values with the combination B3LYP/LanL2DZ/6-311++G** are always lower than 18 cm^{-1}.

The fifth step, the M5 formation is the slowest step of the whole mechanism with the highest activation energy ($\Delta E_{M4 \rightarrow TS4}$ =91.4 kJ mol^{-1}). The silver atom in the cyclic M4 structure is bonded to one O atom and to one N atom. For obtain M5 structure is necessary the breaking of the strong Ag-N bond leading to planar and elongated TS4 structure. In both, TS4 and M5 species, the silver atom is coordinated to only one O atom; however, the O-N-N angle is radically different. For obtain M5 from TS4 the O-N-N angle must vary in about 130° leading to a non elongated structure M5. The fifth step is quite endothermic ($\Delta E_{M4 \rightarrow M5}$ = 68.8 kJ mol^{-1}) and the relative energy of TS4 is positive. The M5 formation is difficult due to three aspects: First, the high stability of M4 (the most stable structure of the mechanism), second, the enormous high barrier that involve a positive TS and, third, the step is endothermic. Finally, the M5 structure must overcome a new high energy barrier ($\Delta E_{M5 \rightarrow TS5}$ = 85.9 kJ mol^{-1}) to reach the products. This last step is slightly exothermic ($\Delta E_{M5 \rightarrow P}$ = –1.3 kJ mol^{-1}). From M5 to TS5 we can noted that the N-N-O angle increase to adopt the linear geometry of the product N_2O.

In summary, our mechanistic proposal for the global reaction is exothermic (–19.5 kJ mol^{-1}); however, it contains three steps with very high energy barriers. Moreover, three TSs have positive relative energies. The presence of three unstable TSs with positive relative energy complicates the viability of our mechanism; however, the half-life of these three TSs are extremely short (femtoseconds) and the large energy barriers can be surmounted when the reaction is carried out at high temperature.

The same reaction was studied in the presence of a Cu atom at the B3LYP/ LanL2DZ level by Zhang and coworkers (24). They proposed three mechanistic routes to convert NO to N_2O; however, we found that some TSs structures proposed by Zhang are not connected with theirs intermediate minimum on the PES, as shown the IRC calculations. To avoid that, in the present work, the calculations of the reaction paths going down from all the TSs on the PES were carefully analyzed. Independently of the problems related with the Zhang structures, they suggest two decomposition channels, where the energetically favored has a maximum activation energy of 61.1 kJ mol^{-1}. Instead, our only route presents three high activation energies (62.9, 91.4 and 85.9 kJ mol^{-1} for the steps M3→TS3, M4→TS4 and M5→TS5, respectively). Clearly, this fact makes our mechanistic proposal very difficult; however, at high temperatures such mechanism it would possible. On the other hand, additional calculations made by us on copper-based catalyst exhibits lower energy barriers than the silver based catalyst (25). This assertion obtained from theoretical calculations by both Zhang and ourselves, is in agreement with the supported cooper catalyst reported by Iwamoto (7, 8) are better than the supported silver catalyst reported by Anpo and coworkers (4, 10, 25).

A theoretical study of the NO interaction with neutral and charge silver cluster reported by Zhou and coworker (26) show that the vibrational frequencies of NO diminish when the electronic charge of silver change from +1 to 0; whereas, the N-O distance increase and the adsorption energy is reduce to half. So, the positive silver atom produces more stable species, which are less reactive and difficult the NO reduction. For this reason, we make our calculation with a neutral silver atom.

Concluding remarks

A 6-step mechanism for NO reduction to N_2O is proposed, which include three high activation barriers and three TS with positive relative energies. So, the catalytic processes assisted by silver will be more realizable at high temperature. The stability of M4 specie with respect to AgO + N_2O point out the feasibility to uses silver oxide as strong

N_2O adsorbent and offer the possibility to design systems as clean air sponges.

The selection of the combination B3LYP/LanL2DZ/6-311++G** in ours calculations result very suitable as indicated the narrow differences between the experimental and calculated vibrational frequencies for the species Ag-NO, Ag-ON and $Ag(NO)_2$. Beside this work show the importance to use the IRC methodology to confirm the right connectivity between TS and the relative minimum. If not, an intermediate in the reaction mechanism could be assigned wrong.

In accordance to the actual results, the catalysts based on copper are more active for the NO decomposition than the catalyst based on silver. This topic will be the central goal of our future investigations.

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