N₂O Decomposition on TiO₂ (110) from Dynamic First-Principles Calculations

J. Oviedo* and J. F. Sanz

Physical Chemistry Department, Chemistry Faculty, University of Seville, c/ Prof. García González, 41012 Sevilla, Spain

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We have carried out a systematic study of N₂O dissociation on a TiO₂ (110) surface by means of plane-wave pseudopotential density-functional theory calculations. We have made use of both static and dynamic calculations in order to elucidate N₂O decomposition mechanisms. We find that dissociation is not favorable on the stoichiometric surface. On the other hand, the presence of oxygen bridging vacancies make the N₂O decomposition possible. The role of the defective surface is to provide electrons to the adsorbed molecule. We find two channels for decomposition, depending on whether the molecule is adsorbed with the O or the N end of the molecule on a vacancy. The first case is energetically downhill and proceeds spontaneously, leading to N₂ ejection from the surface and vacancy oxidation. The second case relies on the formation of an intermediate bridging configuration of the adsorbed molecule and is hindered by a small energy barrier. In this case, molecule breaking produces N₂ in the gas phase and leaves oxygen adatoms on the surface. We relate our results to recent experimental findings.

Introduction

Conversion of N₂O to form N₂ is the key step in the elimination of potentially dangerous NO$_x$,[1] responsible for acid rain and greenhouse warming.[2] In recent years, there has been a considerable effort expended in understanding N₂O decomposition mechanisms that could help to design better catalysts for NO$_x$ removal.[1,3−12] Among the candidates, TiO₂ (110) has been extensively studied as a metal oxide surface prototype.[13] Recent experimental work[1] shows that N₂O partially decomposes when adsorbed at 90 K on defective TiO₂ (110) in a vacancy mediated process. The mechanism is composed of two channels. The first channel occurs instantaneously at 90 K and results in N₂ ejection from the surface and vacancy oxidation. The second channel results upon heating from an adsorbed state of the N₂O molecule, which decomposes at 170 K giving rise to N₂ in the gas phase and oxygen atoms at nondefect Ti^{4+} sites. It has been proposed that the two channels correspond to adsorption of the N₂O molecule with the N-end or the O-end of the molecule bound to an oxygen vacancy. A detailed mechanism for the process is still unclear, although the existence of an intermediate state on the surface has been suggested, since decomposition depends on adsorption temperature and is not observed at 220 K. In addition, there has been some previous theoretical work,[14,15] and several optimized adsorption geometries have been reported. Specifically, linear molecules are found to adsorb weakly on the defective surface, whereas there are other configurations with adsorption energies up to 20 kcal/mol. However, these results are insufficient to clarify the role of the surface in decomposition mechanisms.

Theoretical Calculations

There are two major difficulties in doing suitable comparisons between theoretical and experimental results. First, computational resources are limited, and realistic models are not feasible. We recall here that in typical TiO₂ experiments the vacancy concentration is about 10%.[1] The surface model used in this study is a (4 × 1) unit cell that corresponds to a 25% vacancy concentration and contains vacancies separated by ∼6 Å. Results taken from these calculations constitute our best approximation to the behavior of an isolated vacancy. However, we showed in previous work that this is enough to make vacancy−vacancy interaction almost negligible.[16] The second difficulty is related to surface dynamics. Most of the previous theoretical work has been done in static conditions (i.e., geometry optimization that implies no temperature effect). However it is evident that temperature plays a critical role in desorption−decomposition processes.

In the present work, we use the implementation of density functional theory (DFT) with pseudopotentials and plane waves.[17] The calculations were performed with the Vienna ab initio simulation package (VASP) code. We use the generalized gradient approximation (GGA) from Perdew et al.[18,19] and the standard ultrasoft pseudopotentials included in the code.[20−22] An energy cutoff of 396 eV and a Monkhorst−Pack[23] 4 × 4 × 1 *k*-point set including the Γ-point were used.

The surface was represented by means of four-layered slabs made of (2 × 1) and (4 × 1) unit cells, although we report on results for the (4 × 1) unit cell only. For defective surfaces, this represents a 25% vacancy concentration. Convergence tests and full technical details can be found in a previous work.[16] We have made some calculations and estimate that the error caused by using a four-layered slab is about 1−2 kcal/mol. In addition, there are other sources of error such as the high

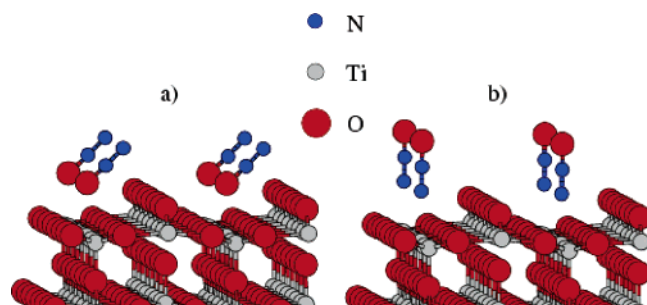* Corresponding autor. E-mail: jol@us.es. Fax +34954557174.

Figure 1. Optimized adsorption geometries for N_2O on the stoichiometric TiO_2 (110) surface: (a) case O, (b) case N.

coverage of adsorbed N_2O molecules when compared with experimental conditions, numerical errors, and the intrinsic DFT precision as well. For this reason, we regard our results as "semiquantitative", and we have tried to be very careful when making statements. The situation is somehow alleviated since we are comparing energies obtained in exactly the same conditions, and therefore, some error cancellation is expected. However, it is important to stress that comparison with experimental data might not be as favorable.

To study surface dynamics, we performed molecular dynamic calculations in the canonical (NVT) ensemble using the Nosé algorithm with a Nosé parameter of $1.3 \cdot 10^{14}$ s^{-1} that roughly corresponds to 160 time steps. The time step was 3 fs, and typical simulation lengths ranged from 1 to 4 ps. The precision during the simulations was lowered, and only the Γ-point was used.

Results and Discussion

We started studying adsorption of the N_2O molecule on the stoichiometric TiO_2 (110) surface, with the molecule vertical over a Ti atom, with both the oxygen and nitrogen ends of the molecule closer to the surface (from here on, we call these configurations case O and case N, respectively). We find that in all cases the N_2O molecule remains linear and does not dissociate, even after long molecular dynamics (MD) simulations at 150 K, confirming that dissociation must be vacancy-mediated. We show the optimized geometries in Figure 1. Remarkably, the optimized configuration for case O is tilted, which seems to be related to the presence of the lone pair of electrons around the oxygen. Adsorption energies in both cases are relatively small (2.8 and 4.2 kcal/mol), which is indicative of a physisorption and would give rise to an adsorption/desorption process at low temperature, which is confirmed by temperature-programmed desorption (TPD) experiments that show a peak at 130 K.[1] Our adsorption energies are in good agreement ($\sim$1 kcal/mol) with previously reported ones,[15] despite the fact there are significant differences in surface models and technical conditions.

The presence of bridging vacancies does not significantly change the adsorption on nondefect Ti^{4+} sites even when they are located adjacent to the vacancies. Optimized geometries are similar, and adsorption energies are only slightly reduced.

The scenario for adsorption on vacancy sites is far more complex. We carried out geometry relaxations for the adsorbed linear molecule in cases O and N, starting from positions with the molecule vertical on a bridging vacancy. We obtained in both cases weak adsorption energies and little changes with respect to the isolated molecule (Table 1); a tilted geometry is again preferred for case O. However, after some trials, we realized that, in fact, the molecules were constrained to maintain their linearity because of the initial geometry. Actually, when
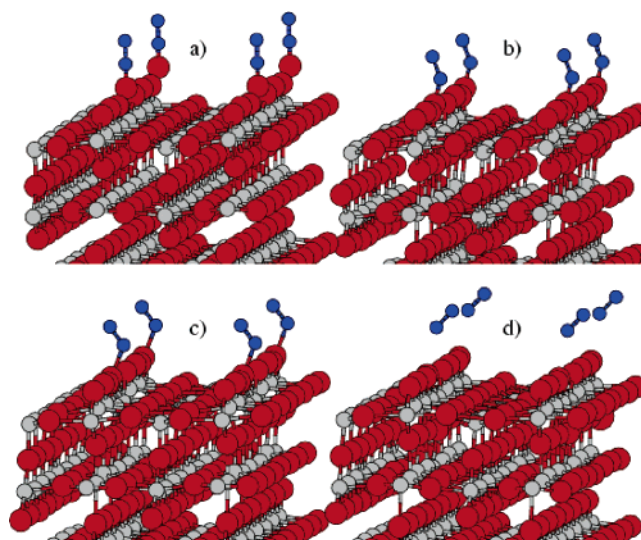

Figure 2. Snapshots from an MD simulation of N_2O (case O) adsorbed on the defective TiO_2 (110) surface at 100 K: (a) the starting vertical linear position, (b) the bent geometry, (c) NO bond stretches, (d) NO bond beaks leading to N_2 desorption and healing the vacancy.

TABLE 1: Geometrical Parameters (Å and deg) and Adsorption Energies (kcal/mol) for the Optimized N_2O Molecule on a Bridge Vacancy, Case N

model	Ti–O	O–N	N–N	N–Ti	O–N–N angle	E_{ads}
free N_2O		1.20	1.14		180°	
linear		1.19	1.14	2.68	180°	6.46
bent		1.23	1.36	1.97	118°	2.77
bridge	2.10	1.30	1.28	2.07	119°	15.00

we performed geometry optimizations starting with the molecule slightly deviated from the straight line, we found stable bent configurations as shown in Figures 2b and 3a. This is indicative of a charge transfer from the surface to the molecule. We recall that the equilibrium geometry of the isolated N_2O^- molecule is bent,[24] and electron attachment to N_2O is well-known in gas phase or solution.[25] There has also been previous evidence that shows N_2O behaves on the TiO_2 surface as an electron scavenger in photocatalysis experiments.[12]

The time evolution of the adsorbed molecule differs substantially depending on the configuration. We find that, in case O, the intermediate bent molecule is unstable and the optimization procedure spontaneously leads to N_2O dissociation, followed by desorption of an N_2 molecule and vacancy healing. Since the entire process is energetically downhill, we were able to reproduce it in a single MD simulation at 100 K as shown in Figure 2. We assign this N_2 ejection to the reported instantaneous dissociation channel at low temperature (90 K). The primary role of the surface in the process is therefore to provide electrons that are located on the adsorbed molecule through an irreversible linear to bent geometry transformation.

In case N, the situation is quite different. From experiments, it seems that a fraction of initially adsorbed molecules desorbs, whereas the rest decomposes at about the same temperature (170 K). Our calculated adsorption energies are higher for adsorption on vacancy sites as compared to adsorption on the stoichiometric surface. We tentatively assign the TPD peak at 170 K to desorption of intact N_2O molecules from vacancy sites. In Table 1, we show that the linear molecule is more stable than the bent molecule. This fact means that the linear to bent transformation is hindered by a small energy barrier, which can only be surmounted if temperature is high enough. This result may help to explain why decomposition depends on temperature.
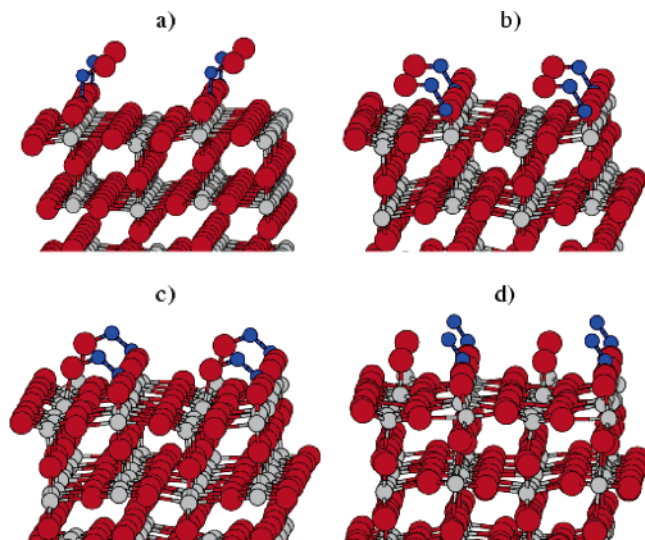
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J. Phys. Chem. B, Vol. 109, No. 34, 2005 **16225**

Figure 3. Snapshots from an MD simulation of N$_2$O (case N) adsorbed on the defective (110) surface at 150 K: (a) the bent molecule, (b) N$_2$O feels an adjacent Ti atom, (c) the bridge geometry, (d) NO bond breaking leading to an N$_2$ molecule that desorbs and an oxygen adatom over a Ti site.

At low temperatures, N$_2$O molecules get trapped on the surface and only when the temperature rises can transform to the bent geometry that leads to dissociation. However, if adsorption temperature is high, the residence time for linear molecules on the surface is short, and transformations are not possible.

We speculate that a fraction of adsorbed linear molecules transform irreversibly to the bent geometry, gaining some electron charge from the surface. Although we tried to reproduce either the linear to bent transformation or the desorption of linear molecules by means of MD simulations (4 ps at 150 K), we did not succeed. We must recall, however, that a major shortcoming of current MD simulations is that they span a very short period of time (around the picosecond order) compared to experiments, which make direct simulations unfeasible unless conditions are favorable. We have made a serious effort in finding the transition state between the linear and bent con-figurations. Algorithms for finding transition states are not as robust as those for finding stationary points, so the initial guess geometry is essential. Basically, we tried several different minimum energy paths (in VASP, this is controlled by "images" that determine the energy path). The algorithm works on several images in parallel, so calculations are very demanding. We were forced to reduce our precision and use only the Γ-point in the *k*-space. From these calculations, our estimation for the transition barrier was 7 kcal/mol. Since the calculations were necessarily at a low precision, we prefer to be cautious and not speculate about this result. We plan to report on this important issue soon.

To follow the time evolution of the molecules, we also performed MD simulations starting from the bent geometry (Figure 3a), which is stable for long simulations at an equilib-rium angle of about 118°. It slowly rotates until the upper end of the molecule (the O atom) points to a nearby Ti site. When this happens, the oxygen feels an attraction and moves until the N$_2$O molecule adopts another stable geometry, forming a bridge between the vacancy site and an adjacent Ti atom (Figure 3c). It seems that there must be almost no energy barrier for this transformation, since we were able to reproduce it in MD calculations, if simulations were long enough, even at low temperature (100 K).

A similar geometry has been reported previously[15] and corresponds to a large adsorption energy. Despite important

differences in modeling the surface and technical parameters, our adsorption energy agrees reasonably well with the previous one (15 and 20.5 kcal/mol, respectively), and the optimized geometrical parameters are also quite similar (119° and 118° for the N−N−O angles, respectively), which is indicative of the same configuration.

The bridge geometry is not stable when MD temperature rises. The NO bond is stretched (Table 1), and after relatively short simulations, the N$_2$O molecule dissociates. In fact, we were able to obtain (Figure 3) in a single simulation at 150 K the successive transformation from a bent N$_2$O molecule to a bridge geometry and finally the dissociation of the molecule into an N$_2$ molecule that is ejected out of the surface and an oxygen adatom over a fivefold Ti. There have been previous experi-mental reports that show evidence of the presence of oxygen adatoms, which show interesting catalytic activity on subsequent adsorbed molecules.[26,27] We assign this route to the reported decomposition channel at 170 K. In this case, the role of the surface in decomposition is not only to provide electrons but to promote NO bond breaking because of the presence of different adsorption sites on the oxide.

Conclusions

In summary, we have elucidated two different mechanisms for N$_2$O decomposition on defective TiO$_2$ (110) and related them to experimental findings. We have clarified the role of the metal oxide surface as a provider of electrons and pointed out the fact that, from a methodological point of view, dynamical effects are essential. We plan to extend our study to precursors of N$_2$O such as NO and NO$_2$ and possibly to other metal oxides.

Supporting Information Available: Optimized geometrical parameters and adsorption energies for the models described in the text.[28] This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Molecular dynamics movies that show N_2O decomposition mechanisms for several illustrative situations are available upon request.