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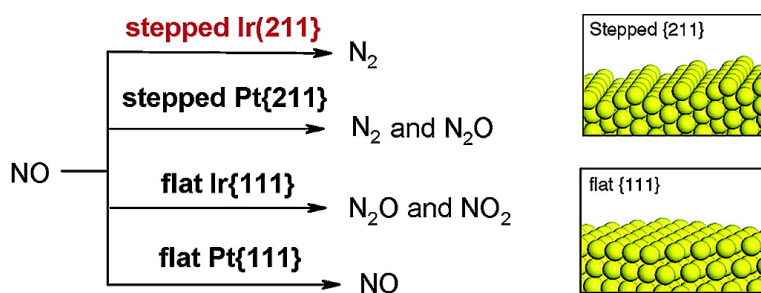
Communication

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Step-Enhanced Selectivity of NO Reduction on Platinum-Group Metals

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The chemistry of NO on transition metal surfaces has received considerable attention.¹ Technologically, it is involved in many catalytic processes. In the past decade, NO removal using hydrocarbon reductants under excess oxygen conditions has attracted much attention in respect to after-treatment systems for diesel and lean-burn gasoline engines.^{2–11} For this type of NO removal, platinum-group metals (PGMs) appear most promising as they can reduce NO to N₂. To control the selectivity of NO reduction, however, is very challenging as various undesired byproducts, mainly N₂O and NO₂, are also produced. In this communication, we aim to explain what determines the selectivity of NO reduction on platinum-group metals.

Recently, it has been reported that Ir-based catalysts have shown high selectivity and activities for NO reduction under excess oxygen conditions.^{2,5–7} Compared to Pt, another active metal for NO reduction, Ir has two advantages. First, at the temperatures required for activity, Ir selectively produces N₂, while Pt produces N₂ together with N₂O.⁸ Second, at high temperatures, when surfaces are dominated by excess O, Ir can still convert NO to N₂, while Pt cannot. The poisoning phenomenon has been explained in terms of a thermodynamic suppression of NO dissociation above a critical O adatom coverage.¹¹ Furthermore, it has also been found that the morphology of the Ir catalyst plays an important role: Ir nanocrystals are much more active and selective than bulk Ir metals.^{6,7} To understand the mechanism of NO reduction, extensive experimental studies have been conducted.^{2–11} The generally accepted mechanism in the literature² is as follows: (i) NO dissociation: NO → N + O; (ii) N₂ formation: N + N → N₂; (iii) byproducts, N₂O and NO₂ formations: NO + N → N₂O, NO + O → NO₂. Steps (i) and (ii) are diatomic reactions, and (iii) involves triatomic reactions. However, the reaction pathways and barriers for these reactions on different metal surfaces are generally unknown. Consequently, the factors that control the selectivity of NO reduction are not well identified. Since the selectivity of chemical reactions on transition metals is an important issue in heterogeneous catalysis, the questions raised here are of general interest.

In this work we have systematically studied the NO reduction processes on two important platinum-group metals, Ir and Pt, by density functional theory (DFT). Four elementary reactions, namely NO dissociation, N₂ formation, N₂O formation, and NO₂ formation were investigated on the flat {111} and the stepped {211} surfaces of the two metals. Details of the DFT calculations are described in ref 12. The {211} surface contains terraces of {111} facets that are separated by {100} monatomic steps. It should be mentioned that the close-packed {111} facet is generally the dominant face in real fcc metal catalyst particles and that the monatomic steps are possibly the most common defects. Experimental and theoretical studies have suggested that steps are very active for many reactions.^{13–16}

We determined the adsorption energies (E_{ad}) of NO, N, and O on Ir{211}, Ir{111}, Pt{211}, and Pt{111}, using first principles DFT-slab techniques.¹² It may be mentioned that the accuracy of

Table 1. Calculated Adsorption Energies (E_{ad})^a of NO, N, and O on the Most Stable Sites, and the Barriers (E_{a}) for the Elementary Reactions on Ir and Pt

		Ir {211}	Ir {111}	Pt {211}	Pt {111}
E_{ad}	NO	3.14	2.10	2.44	2.05
	N	5.51	5.16	4.50	4.45
	O	5.39	4.73	4.31	4.00
E_{a}	NO → N + O	1.19	1.46	1.70	2.60
	N + N → N ₂	1.81	2.60	1.07	2.72
	NO + N → N ₂ O	2.31	1.33	1.66	1.78
	NO + O → NO ₂	2.56	1.46	1.95	1.52

^a The units are eV.

current DFT-slab calculations is consistently good and many of the calculated structures and energetics have been benchmarked against independent experimental results.¹⁷ Values for the most stable sites are listed in Table 1. It was found that steps can generally bond NO, N, and O more strongly. This can be attributed to the lower coordination of metal atoms at step edges than those at flat surfaces, favoring a higher bonding ability. It is noticed that on Ir the energy preference of adsorbates for the stepped {211} surface, compared to that for the flat {111} surface, is relatively large. For example, the NO adsorption energy on Ir{211} is 3.14 eV, much higher than that on Ir{111} (2.10 eV).

Next, we have located the *most stable transition states (TS)* for all the reactions. We found that the TS structure of a reaction on Pt is always very similar to that found on Ir. Furthermore, the TS structures between diatomic reactions (NO → N + O and N + N → N₂) are quite similar to each other, and the same is also true between the triatomic reactions (NO + N → N₂O and NO + O → NO₂). In Figure 1, we show the representative TS structures of a diatomic reaction, N + N → N₂, and a triatomic reaction, NO + N → N₂O, on Ir{111} and Ir{211}. The reaction barrier (E_{a}) for each reaction, which is defined with respect to the thermodynamically most stable initial state on each surface, is also listed in Table 1.

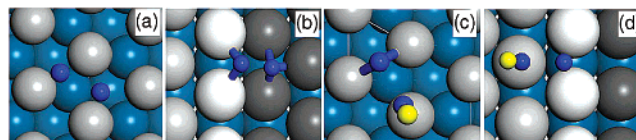


Figure 1. Calculated TS geometries of the N + N → N₂ (a and b) and NO + N → N₂O (c and d) reactions on Ir. (a) and (c) are on {111} surface; (b) and (d) are on {211} surface. Blue and yellow small balls represent N and O atoms, respectively.

On the basis of Table 1, we can address the activity and selectivity of NO reduction on the various surfaces. On the flat surfaces, Ir{111} and Pt{111}, the N + N → N₂ reaction has a high barrier (>2.5 eV), much higher than those of triatomic reactions. This certainly rules out Ir{111} and Pt{111} as good catalysts for NO reduction. Further comparing Pt{111} with

Ir{111}, it was found that NO dissociation on Pt{111} is more difficult ($E_a = 2.60$ eV) than on Ir{111} ($E_a = 1.46$ eV). Therefore, Pt{111} has little activity, while Ir{111} has very poor selectivity, since NO can be only converted to N_2O and NO_2 .

Moving to the stepped surfaces, both Ir and Pt become active for NO reduction. On the {211} surfaces the barriers for the $N + N \rightarrow N_2$ reaction are much reduced: 1.81 eV on Ir{211} and 1.07 eV on Pt{211}. In line with this, barriers to NO dissociation on steps are also lower than on flat surfaces. As for the N_2 selectivity, our results show that Ir{211} has a high selectivity, while Pt{211} has a poor selectivity, for the following reasons. On Ir{211} the barriers for the reactions studied follow the order: NO dissociation < N_2 formation < N_2O formation < NO_2 formation: *the barriers for diatomic reactions are much lower than those for the triatomic reactions*. Thus, on Ir{211}, high N_2 selectivity can be achieved by controlling the temperature so that only N_2 is produced. In contrast, on Pt{211}, the barrier to NO dissociation is higher than the barriers for N_2 and N_2O formation. This indicates that as soon as NO starts to dissociate on Pt{211}, both N_2 and N_2O will be produced. By kinetic analysis, we found that the $N_2:N_2O$ selectivity is not only dependent on the barriers for the $N + N$ reaction and $N + NO$ reactions, but also the barrier to NO dissociation, which determines the concentration of N atoms and NO molecules on the surface. Although on Pt{211} the barrier for N_2O formation is somewhat higher than for N_2 formation, the selectivity to N_2 is still poor due to the slow NO dissociation. Our results agree with the experimental findings that the selectivity to N_2O on a Pt catalyst can be over 50%.⁸

It is natural to ask why it is only on Ir{211} that the barriers for diatomic reactions are much lower than those for triatomic reactions, since this is the key to achieving high selectivity for NO reduction to N_2 . By comparing the electronic and geometric structures of Ir{211} with other surfaces, we found two major reasons. First, the difference in the electronic structure of Ir and Pt determines that NO dissociation on Ir is always easier than it is on Pt.¹ Theoretically, it has been found that the barrier to a dissociation reaction is largely dependent on the reaction enthalpy.¹⁸ As Ir can bond N and O more strongly compared to Pt (Table 1), the NO dissociation barrier on Ir is consequently lower. As shown in Table 1, the only problem for Pt{211} to selectively reduce NO is its high barrier to dissociate NO. This problem may be solved if NO dissociation can be promoted. The experiment by Konsolakis et al.,⁹ has indeed shown that N_2 selectivity can be greatly improved when alkali metals are used as promoters. Second, compared to flat surfaces, stepped surfaces lower the barriers for diatomic reactions but generally increase the barriers for triatomic reactions. The former phenomenon is mainly due to the geometric effect at steps, and the latter is due to the electronic effect at steps. For diatomic reactions, the geometry of the TS at flat surfaces (Figure 1a) is very different from that on the steps (Figure 1b). Specifically, the TS on the flat surface requires the two reacting atoms to share bonding with one metal atom, which incurs an extra energy cost due to the so-called bonding competition effect, hence increasing the barrier.^{14–16} On the other hand, triatomic reactions are less affected by the surface geometries as their TSs are rather similar on flat and stepped surfaces (see Figure 1, c and d): on both surfaces three metal atoms are involved in bonding with the TS complex, and no surface atom is shared by the reactants. However, because NO, N, and O are more strongly bonded at steps than on flat surfaces, which leads to them being more chemically inert, the recombination reactions between them require higher activation

energies. This effect is particularly evident on Ir{211} as NO on that surface is very strongly bonded indeed, which gives rise to the barriers to the $NO + O$ and $NO + N$ reactions being very high.

From our results, *stepped structures are crucial for both the activity and selectivity of NO reduction*. This is in line with the observed structure sensitivity of NO reduction on Ir.⁷ One would expect that any factors that affect steps would lead to changes in the catalytic performance. Under excess O_2 conditions, O adatoms will pre-occupy stepped sites as the steps also bond O atoms more strongly than terraces. As a consequence, N_2 formation is slowed, and NO dissociation may also be poisoned.¹¹ In contrast, NO_2 production is little affected as it can well occur on flat surfaces. Thus, the formation of NO_2 is accompanied by the decrease of N_2 production, as observed in experiment.^{2–7} One way to increase the N_2 selectivity in an oxidizing environment is to use small metal particles,^{6,7} where a large amount of surface defects, like steps, are expected to be present. This increases the concentration of stepped sites but reduces the concentration of terrace sites, and thus can increase the N_2 selectivity.

To summarize, this work represents the first systematic study of the selectivity of NO reduction on Ir and Pt within the first-principles framework. A stepped-Ir surface is found to possess high selectivity for NO reduction, which is attributed to both the electronic and geometric structures of the Ir steps. The results presented here provide insight into the physical origin of reactivity differences between the metals, which is valuable to assist the design of new catalysts.

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