The chemistry of NO on transition metal surfaces has received considerable attention. 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. To understand the mechanism of NO reduction, extensive studies have been conducted. 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. 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. 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. 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. To understand the mechanism of NO reduction, extensive experimental studies have been conducted. The generally accepted mechanism in the literature 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.

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. It may be mentioned that the accuracy of current DFT-slab calculations is consistently good and many of the calculated structures and energetics have been benchmarked against independent experimental results. 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 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.

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

![Figure 1](image-url)

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.

**Table 1. Calculated Adsorption Energies (E_ad) of NO, N, and O on the Most Stable Sites, and the Barriers (E_a) for the Elementary Reactions on Ir and Pt**

<table>
<thead>
<tr>
<th></th>
<th>Ir {211}</th>
<th>Ir {111}</th>
<th>Pt {211}</th>
<th>Pt {111}</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_ad</td>
<td>NO</td>
<td>N</td>
<td>O</td>
<td>NO → N + O</td>
</tr>
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<td></td>
<td>3.14</td>
<td>5.51</td>
<td>5.39</td>
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</tr>
<tr>
<td></td>
<td>2.05</td>
<td>4.45</td>
<td>4.00</td>
<td>2.60</td>
</tr>
</tbody>
</table>

*The units are eV.*
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 only be converted to N\textsubscript{2}O and NO\textsubscript{2}.

Moving to the stepped surfaces, both Ir and Pt become active for NO reduction. On the [111] surfaces the barriers for the N + N \rightarrow N\textsubscript{2} reaction are much reduced: 1.81 eV on [111] and 1.07 eV on Pt[111]. In line with this, barriers to NO dissociation on steps are also lower than on flat surfaces. As for the N\textsubscript{2} selectivity, our results show that Ir\{111\} has a high selectivity, while Pt\{111\} has a poor selectivity, for the following reasons. On Ir\{111\} the barriers for the reactions studied follow the order: NO dissociation < N\textsubscript{2} formation < N\textsubscript{2}O formation < NO\textsubscript{2} formation: the barriers for diatomic reactions are much lower than those for the triatomic reactions. Thus, on Ir\{111\}, high N\textsubscript{2} selectivity can be achieved by controlling the temperature so that only N\textsubscript{2} is produced. In contrast, on Pt\{111\}, the barrier to NO dissociation is higher than the barriers for N\textsubscript{2} and N\textsubscript{2}O formation. This indicates that as soon as NO starts to dissociate on Pt\{111\}, both N\textsubscript{2} and N\textsubscript{2}O will be produced. By kinetic analysis, we found that the N\textsubscript{2}:N\textsubscript{2}O 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\{111\} the barrier for N\textsubscript{2}O formation is somewhat higher than for N\textsubscript{2} formation, the selectivity to N\textsubscript{2} is still poor due to the slow NO dissociation. Our results agree with the experimental findings that the selectivity to N\textsubscript{2}O on a Pt catalyst can be over 50%.

It is natural to ask why it is only on Ir\{111\} 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\textsubscript{2}. By comparing the electronic and geometric structures of Ir\{111\} with other surfaces, we found two major reasons. First, the difference in the electronic structure of Ir and Pt determines that the barriers for N reaction and N + O reaction are very high. As NO reactions being very high.

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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References