

# FIRST-PRINCIPLES-BASED KINETIC MONTE CARLO SIMULATION OF NITRIC OXIDE REDUCTION OVER PLATINUM NANOPARTICLES UNDER LEAN-BURN CONDITIONS

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## Summary

The kinetics of NO reduction over platinum nanoparticles under lean-burn conditions has been investigated by kinetic Monte Carlo (KMC) simulation. Platinum nanoparticles are represented by a truncated octahedron model that consists of one {100} facet and eight {111} facets. Density functional theory calculations are used to determine the intrinsic kinetic parameters that are fed into KMC simulations. NO reduction to N<sub>2</sub> occurs only on the {100} facet while NO can be oxidized to NO<sub>2</sub> on both {100} and {111} facets. The effects of size and shape on the kinetics of NO reduction under oxygen excess conditions are studied.

## Keywords

Computational Catalysis, Diesel Emission Control

## Introduction

The reactivity of structure-sensitive reactions over the supported nanosized metal catalyst particles usually depend on particle size and morphology. Various factors such as different exposed surface structures (facets) and interplay between different facets of nanoparticles make it extremely difficult to interpret the underlying microscopic kinetics and probe the reaction mechanism on the basis of measured macroscopic kinetics under experimental conditions. The kinetics of both NO decomposition and NO oxidation over supported Pt catalyst are particle size dependent.<sup>1,2</sup> To investigate the effects of particle size and morphology on the NO reduction kinetics under lean-burn conditions, a first-principles-based KMC simulation study of NO reduction reaction over three-dimensional Pt nanoparticles with different sizes and shapes is presented. Density functional theory calculations are used to provide an intrinsic kinetics database that is fed into the explicit-site variable time KMC simulations.

## Simulation Methodology

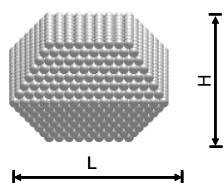
For Pt particles, the most common shape is the cubo-octahedral structure consisting of {111} and {100} facets. Due to low surface energy, the {111} facet dominates the

exposed surface structure of Pt particle.<sup>3</sup> As such, a three-dimensional model Pt catalyst consisting of one {100} facet and eight {111} facets with truncated octahedral shape has been selected. The size of Pt model catalyst particles, which is designated as the H×L, is represented by the total number of atoms along with widest side (L) and the total number of height layers (H) shown in Figure 1. Different sizes and shapes of Pt nanoparticles have been obtained by varying the H and L values. The intrinsic kinetics database used as input for KMC simulation was built by carrying out a comprehensive set of DFT calculations for NO dissociation and oxidation, as well as NO coupling reaction on the flat {100} and {111} surfaces, and the stepped {211} Pt surfaces using the VASP code. The structural, electronic and energetic properties calculated from DFT for the intermediates were used as inputs for the simulation. This includes the binding energies and molecular structures of the adsorbates at all of the possible adsorption sites, van der Waals radii (physical size) for all of the reactants, the intermediates and products along with the reaction energies and activation barriers for elementary surface processes. This intrinsic kinetic database is subsequently combined with the lateral interaction models and incorporated into the core reaction

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kinetic model in the simulation. The details of the KMC simulation have been described in our previous publication.<sup>4</sup>



**Figure 1.** Three-dimensional Model Pt Catalyst.

## Results and Discussion

Kinetic Monte Carlo simulation can be used to track actual catalytic chemical transformations over the well-defined model catalysts at experimental operating conditions. We carried out a series of KMC simulations of NO reduction under lean-burn conditions over the three-dimensional Pt model nanoparticle with different sizes and shapes. For direct comparison with experiments, the partial pressures of NO and O<sub>2</sub> in the gas phase are set to be 0.468 torr and 60.8 torr respectively. The temperature range examined here varies from 500 K to 900 K. The TOFs of products (N<sub>2</sub>, NO<sub>2</sub> and N<sub>2</sub>O) are calculated by counting the number of product molecules which desorb from the particle surfaces as a function of time. As expected, the TOF for N<sub>2</sub> increases with the increasing temperature. However, the TOF of NO<sub>2</sub> passes through a maximum around 800 K with the increasing temperature. Compared to N<sub>2</sub> and NO<sub>2</sub> production, N<sub>2</sub>O formation rate is relatively low. The rates of N<sub>2</sub>O formation are about two or three orders of magnitude lower than the rates of N<sub>2</sub> and NO<sub>2</sub> formation. The simulated apparent activation energy for N<sub>2</sub> formation is 45 kJ/mol, which is consistent with the measured apparent activation energy of 31 kJ/mol for N<sub>2</sub> formation in high-throughput experiments.<sup>5</sup> The apparent activation energy of NO<sub>2</sub> formation by extracting TOF data from 500 to 800 K is 42 kJ/mol, which is in agreement with the reported value of 40.8 kJ/mol was reported by Olsson et al. using kinetic modeling calculations.<sup>6</sup> Mulla et al. have investigated the inhibition effect of NO<sub>2</sub> on NO oxidation over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the temperature range of 510 to 592 K with 300 ppm NO and 10% O<sub>2</sub> in the feed gas.<sup>7</sup> An apparent activation energy of 39  $\pm$  6 kJ/mol without NO<sub>2</sub> in the feed was reported. By adding NO<sub>2</sub> in the feed, the apparent activation energy was increased to be 82  $\pm$  9 kJ/mol. The simulated reaction orders of NO and O<sub>2</sub> were also in agreement with experimental measurements. We note that the reactivities of NO reduction and oxidation change with the available active sites of the corresponding facets over the exposed particle surface. The more {111} facet fraction with the increasing particle size, the higher NO oxidation activity; on the other hand, the increase in {100} facet fraction over the particle surface with

increasing particle size will increase the activity of NO reduction.

## Conclusions

In this work, we present a study of NO reduction kinetics over three-dimensional Pt nanoparticle catalysts using a first-principles-based kinetic Monte Carlo simulation method. The kinetics of NO reduction over both the {111} and the {100} facets of Pt particles under lean-burn condition have been investigated. It has been found that only the {100} facet of Pt particles is capable of reducing NO to N<sub>2</sub> under lean-burn conditions while NO dissociation and NO coupling are hindered because of higher activation barriers. NO oxidation to form NO<sub>2</sub> is predominant on the {111} facets of the Pt particles. As the temperature increases, the TOFs of N<sub>2</sub> and NO<sub>2</sub> increase. With increasing particle size, the activities for NO reduction and NO oxidation depend on the available active sites of the corresponding facets over the exposed Pt particle while the specific activities on both the {100} and the {111} facets for NO dissociation and oxidation remain the same.

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