

Multiscale, Multiphysics Computational Chemistry Methods Based on Artificial Intelligence Integrated Ultra-Accelerated Quantum Molecular Dynamics for the Application to Automotive Emission Control

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ABSTRACT

On the basis of extensive experimental works about heterogeneous catalysts, we developed various software for the design of automotive catalysts such as Ultra-Accelerated Quantum Chemical Molecular Dynamics (UA-QCMD), which is 10 million times faster than the conventional first principles molecular dynamics, mesoscopic modeling software for supported catalysts (POCO2), and mesoscopic sintering simulator (SINTA) to calculate sintering behavior of both precious metals (e.g., Pt, Pd, Rh) and supports (e.g., Al_2O_3 , ZrO_2 , CeO_2 , or $\text{CeO}_2\text{-ZrO}_2$). We integrated the previous programs in a multiscale, multiphysics approach for the design of automotive catalysts. The method was efficient for a variety of important catalytic reactions in the scope of the automotive emission control. We demonstrated the efficiency of our approach by comparing our data with experimental results including both simple laboratory experiments and chassis dynamometer exhaust gas emission control experiments. We also demonstrated that the UA-QCMD method is an efficient tool for the estimation of mesoscopic sintering activation energies for both precious metals and supports. On the basis of our successful applications of the UA-QCMD to various important chemical processes of exhaust emission controls and sintering predictions of both precious metals and support of automotive catalysts, we employed in the present study artificial intelligence to determine fundamental parameters from all electron density functional methods and thermodynamic results. This new technique was proven highly efficient for optimizing parameters necessary in our simulations.

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INTRODUCTION

Catalytic converters are widely used in the automotive industry to limit/control emissions of harmful species (carbon monoxide (CO), hydrocarbons, mono-nitrogen oxides (NO_x), particulate matter (PM)) contained in exhaust gases. However, performances of such devices are highly affected because of materials aging in high temperature conditions, reducing the lifetime of vehicle catalyst in maintaining low exhaust gas emissions. In that case, aging is characterized by a loss of active surface area in metal components as a result of sintering, causing a decrease in the catalytic activity. This is a longstanding problem that affects many other applications using highly dispersed metal nanoparticles (or nanoclusters). Experimentally, mid-life catalyst durability performances are examined through engine dyno evaluations. In such experiments, various kinds of catalyst prototypes are employed in continuous tests, implying the use of a large amount of fuel.

Usually, exhaust catalysts are made of a honeycomb structure where ceramic materials support clusters of precious metals used for the catalytic reaction (Fig. 1). Supported precious metals, like platinum

(Pt), rhodium (Rh), and palladium (Pd), are commonly employed to facilitate catalytic processes in the industry. In particular, Pt is found at the core of catalysts for three-way (CO and hydrocarbon oxidation/ NO_x reduction) conversions within car exhausts.

The most widely used ceramic materials as a support in Three-Way Catalysts (TWC) for the control of harmful emissions are alumina (Al_2O_3), ceria (CeO_2), and zirconia (ZrO_2). Al_2O_3 has a high hardness and wear resistance. Among different phases, $\gamma\text{-Al}_2\text{O}_3$ exhibits large surface area and a good thermal stability, making it widely used as a support material [1]. Ceria acts as an oxygen storage/release component by changing its stoichiometry between CeO_2 and CeO_{2-x} , x being a function of temperature and oxygen partial pressure, under reaction conditions due to high availability of surface oxygen. This allows the storage and the release of oxygen easily. However, for pure ceria, oxygen storage/release capacity (OSC) and durability remain inadequate for practical use in TWC. ZrO_2 has a lower surface area with respect to other compounds, but adding it to other ceramic materials increases their fracture toughness. In particular, addition of

ZrO₂ into the CeO₂ lattice (i.e., a Ce-Zr mixed oxide) has been found to be strongly effective in preventing ceria from sintering and promotes the OSC [2,3].

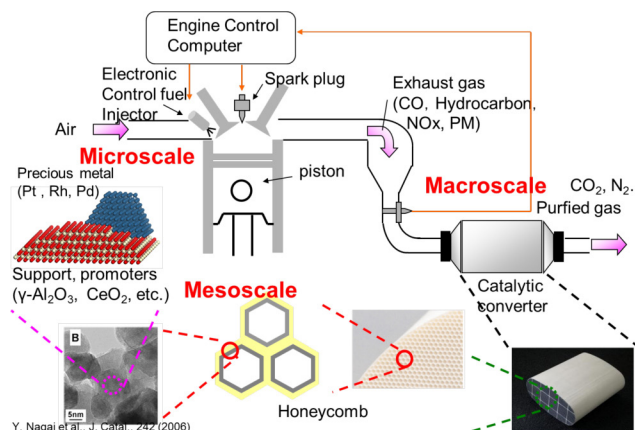


Figure 1. Cartoon showing steps encountered in an engine from combustion in the piston to the treatment of exhaust gases via a catalytic converter. In this work, we focused on the latter device and we applied simulations involving various scales (microscale, mesoscale, and macroscale) and various physical phenomena (multiphysics).

To design automotive catalysts with sustainable performances, the development of more efficient and durable TWC necessitates investigating and clarifying more the relationship between supported precious metal and support material. For such work, some of us previously employed a multiscale, multiphysics computational approach [4,5,6], which was proven useful and highly effective for various industrial systems and is well suited for analyzing automobile catalytic reactions. This bottom-up approach relied on quantum chemical calculations at the smallest scale (atomic-scale; microscopic) and was used in combination with the ceramic grain-scale (mesoscopic simulations). The approach was applied to Pt/γ-Al₂O₃, Pt/ZrO₂, and Pt/CeO₂ systems at a temperature condition (1073 K) where durability of materials is important.

From microscopic simulations (Fig. 1), authors [4] found that adsorption energies of Pt³⁷ on supports decreased as follows; Pt/CeO₂ (445.37 kJ/mol), Pt/ZrO₂ (363.83 kJ/mol), and Pt/γ-Al₂O₃ (296.55 kJ/mol). They also found that the magnitude of the binding energy of Pt atoms with oxygen atoms of the substrate play a role on the diffusion of Pt nanoclusters. Indeed, while Pt diffuse easily on γ-Al₂O₃ substrates, diffusion of Pt nanoclusters is reduced with respect to γ-Al₂O₃ substrates. This is due to the stronger binding energy for Pt-O bonds observed in Pt/ZrO₂ systems. For Pt/CeO₂ systems, authors observed almost no diffusion in the course of the simulation, because Pt clusters are strongly anchored on the CeO₂ substrate through Pt-O-Ce bonds. Binding energies for the three systems follow the same order as the one for adsorption energies; Pt-O(-Al) < Pt-O(-Zr) < Pt-O(-Ce). It also revealed that Pt becomes gradually cationic.

From mesoscopic simulations, authors first built catalyst models that exhibit specific surface area consistent with experimental values [7] obtained using the BET (Brunauer-Emmett-Teller) method. Initial Pt nanoclusters had a size of ~1.0 nm and represent 2.0 wt. % of the model, considering the mass density of each phase, 7.132 g/cm³ for

CeO₂, 5.68 g/cm³ for ZrO₂, and 3.9 g/cm³ for γ-Al₂O₃. After simulating sintering at constant temperature (1073 K) and for 5 hours with the Kinetic Monte Carlo method (Fig. 2), authors found that the size of ceramic grains for the γ-Al₂O₃ model remained small (1-5 nm) rendering the porous structure thermally stable. Thus, Pt nanoclusters at the surface of ceramic grains stay in a fine porous structure environment and their average size was found to be ~2.27 nm using the cluster size distribution. However, when agglomeration occurs, clusters can reach sizes up to 23 nm, which is in the range given by Ref. [7,8]. For the Pt/ZrO₂ system, the cluster size of Pt atoms after aging was in the range 11-18 nm with an average ~14.83 nm, which is in good agreement with the experimental value (~15 nm) obtained using the CO pulse method [7]. For the Pt/CeO₂ system, clusters of Pt atoms remained highly dispersed on the CeO₂ support and their average size was ~1.24 nm, which agrees well with experiments showing that Pt in the CeO₂ catalyst did not sinter at all [8].

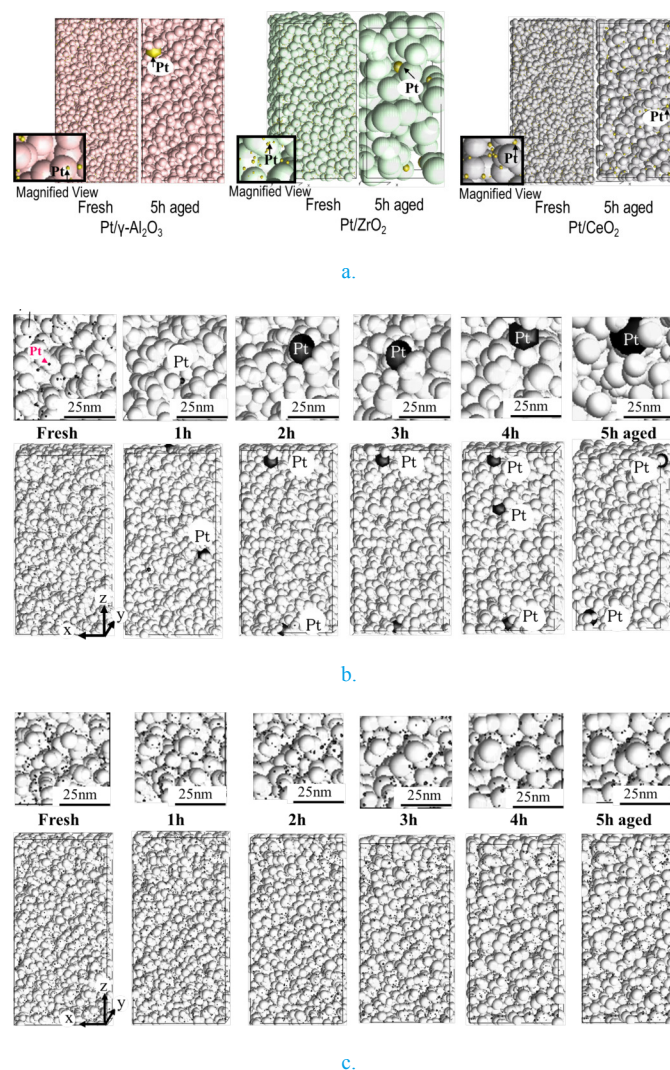


Figure 2. Snapshot at the mesoscale (ceramic grain scale) showing (a) the fresh and the 5h-aged structures of systems of Pt/Al₂O₃ (left), Pt/ZrO₂ (middle), and Pt/CeO₂ (right); and the detailed evolution of the ceramic grain structure and Pt nanocluster agglomeration over aging for the Pt/Al₂O₃ system (b) and the Pt/CeO₂ system (c).

To go beyond the previously mentioned preliminary theoretical work, we refined our multiscale, multiphysics computational approach by adding a third level of simulation, i.e., the reactor-scale (macroscopic chemical kinetics simulations), we provided results directly comparable with chassis dynamometer and engine dynamometer experiments (i.e., macroscopic results). Furthermore, the use of a human-based approach for the derivation of fundamental parameters for microscopic simulations is tedious, time consuming limiting simulations to a few cases, and subject to errors. Here, we employed artificial intelligence (AI) to overcome these problems. With these two improvements to our original approach we were able to simulate the exhaust catalyst in a more realistic way. In the remainder of this technical article, we first present methods employed to simulate our systems. Then, we showed results obtained with our macroscopic simulator, microscopic simulation of various catalytic supports for the prediction of sintering parameters at higher scales, and first outcomes and validations of AI-aided derivation of fundamental parameters for microscopic simulations.

METHODS

Ultra-Accelerated Quantum Chemical Molecular Dynamics

To estimate mesoscopic sintering activation energies for both precious metals and supports, we used Ultra-Accelerated Quantum Chemical Molecular Dynamics (UA-QCMD). This technique is based on a Tight-Binding Quantum Chemical (TB-QC) approach to compute electronic structures of materials, which is implemented in our in-house computer code COLORS that can calculate energies, charges, and bond populations for large-scale systems [4,5,9,10]. COLORS is used to periodically evaluate pair potential energy functions in the course of classical molecular dynamics (MD) simulations performed with our code NEW-RYUDO. The period between each update of pair potentials is chosen so that considerable changes in the atomic structure occur, which also modify strongly the electronic structure of the system. Using this scheme, the simulation time is accelerated by about 10^7 times with respect to conventional molecular dynamics density functional theory (DFT) computations. The basic idea of this approach is summarized in Fig. 3 and details of the scheme are given below.

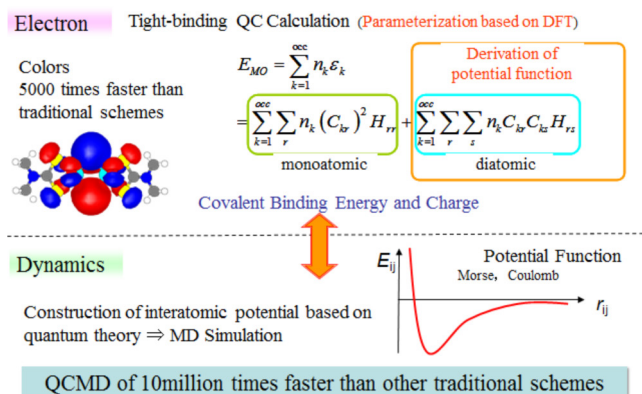


Figure 3. Sketch of the underlying physics and methodology employed in Ultra-Accelerated Quantum Chemical Molecular Dynamics (UA-QCMD) for microscopic simulations.

In COLORS, the electronic structure was obtained through the resolution of the Schrödinger equation ($H^e C = \epsilon S C$; where H^e , C , ϵ , and S refer to the electronic Hamiltonian matrix, eigenvectors, eigenvalues, and the overlap integral matrix, respectively) with the diagonalization condition ($C^T S C = I$; I being the identity matrix). To determine H^e and S , we needed exponents of Slater-type atomic orbital (AO), noted ζ_r , and valence state ionization potentials (VSIPs) for the considered atomic species in this work, i.e., the 1s AO of hydrogen atoms as well as the 2s and 2p AOs of carbon atoms. The relationship between diagonal elements H_{rr}^e and VSIP of the r^{th} AO of the i^{th} atom (i_r) was: $H_{rr}^e = -I_{i_r}$. In our approach, ζ_r and H_{rr}^e were finally approximated using polynomial functions of atomic charges:

$$\zeta_r = a_0 + \sum_{k=1}^5 a_k (Z_i)^k \quad (1)$$

and

$$H_{rr}^e = b_0 + \sum_{k=1}^5 b_k (Z_i)^k \quad (2)$$

where Z_i is the charge of the atom i , and a_0 , a_k , b_0 , and b_k are polynomial coefficients. The previous a and b parameters were determined using DFT calculations as provided by DMol³ [11] and CASTEP [12] codes. DFT energies were computed in the frame of the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Since parameters are obtained using DFT calculations, they implicitly include exchange and correlation effects. They are tuned to reproduce ground state energies, but not band gaps. Parameters are summarized in Ref. [13]. The determination of off-diagonal elements (H_{rs}^e) in the Hamiltonian matrix (H) was obtained using the corrected distance-dependent Wolfsberg-Helmholtz formula [14]:

$$H_{rs}^e = \frac{K}{2} S_{rs} (H_{rr}^e + H_{ss}^e), \quad (3)$$

where r and s are matrix indices and K is a parameter related to the Wolfsberg-Helmholtz constant (~ 1.75) in the extended Hückel molecular orbital theory.

On the basis of previous electronic structure calculations and in the frame of the Born-Oppenheimer approximation, the total energy of the system is computed as follow:

$$E_{tot} = \sum_{k=1}^{occ} n_k \epsilon_k + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{Z_i Z_j e^2}{r_{ij}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N E_{ij}^{repulsion}(r_{ij}) \quad (4)$$

where first, second, and third terms on the right-hand side are the molecular orbital (MO) energy, the Coulomb energy, and the exchange-repulsion energy, respectively. The MO energy on the right-hand side of Eq. (4) can be written as follows: