Multiscale, Multiphisics Computational Chemistry Methods for High Performance/Durability Automotive Catalysts

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日本再生 理論による新しいモノづくり
Miyamoto Laboratory

Multiscale, Multiphysics Computational Chemistry Methods for Industrial Innovations

1. Electronic Theory: Quantum Chemistry (QC), Quantum Mechanics (QM)

2. Atomistic Theory: Molecular Dynamics (MD), Molecular Mechanics (MM), and Monte Carlo (MC) Method

3. Quantum Molecular Dynamics Theory: *ab initio* MD, First-principles MD (Car-Parinello Method), UA-QCMD

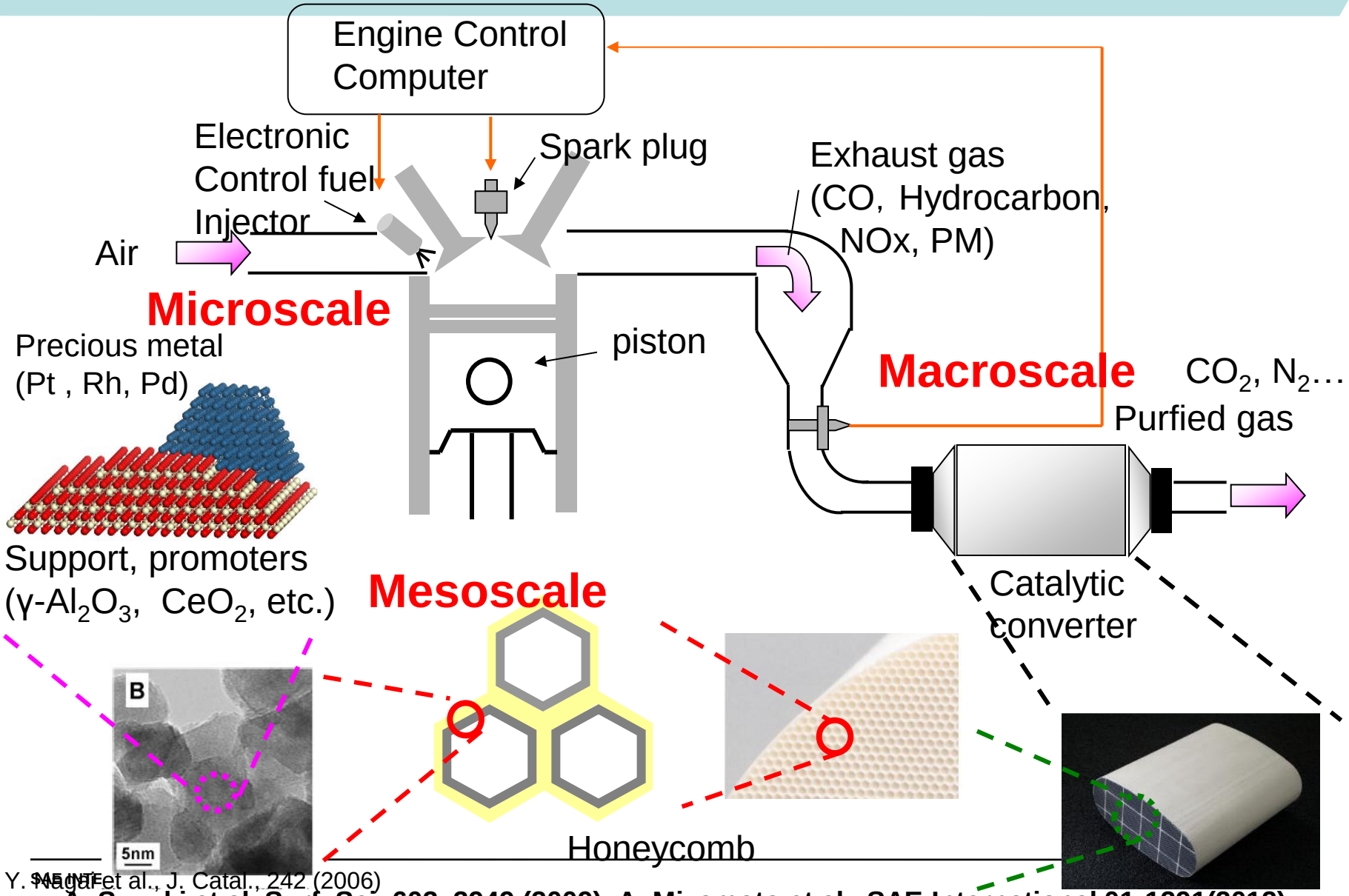
4. Informatics: Artificial Intelligence (AI), Neural Networks (NN), and Database (DB)

5. Mesoscopic and Macroscopic Theory: Kinetic Monte Carlo(kMC), Computational Fluid Dynamics(CFD), Finite Element Method(FEM)

6. Human Interface: Computer Graphics (CG) ,Virtual Reality (VR)

7. Experiments(Measurents) Integrated Computational Chemistry

Multiscale, Multiphysics Computational Chemistry Simulator for Automotive Catalysts



Y. Nagai et al., J. Catal., 242 (2006)

A. Suzuki et al, Surf. Sci. 603, 3949 (2009); A. Miyamoto et al., SAE International 01-1291(2012)

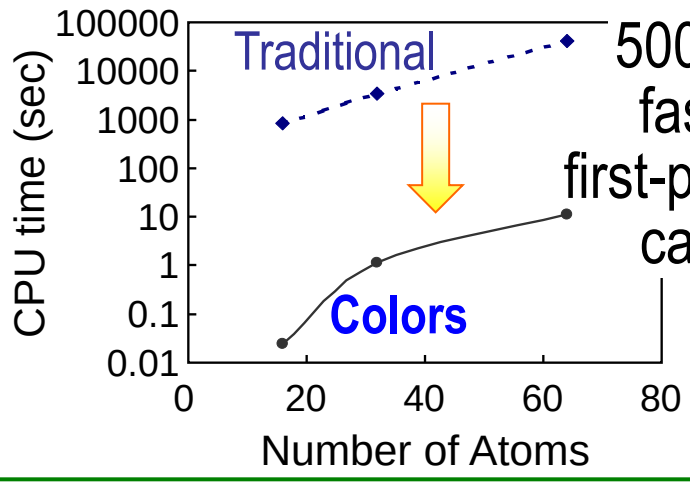
Ultra Accelerated QCMD Method

New Scheme based on Tight-Binding Quantum Chemistry Method

Quantum Chemistry Calculation

Colors

Original Tight-Binding Approximation



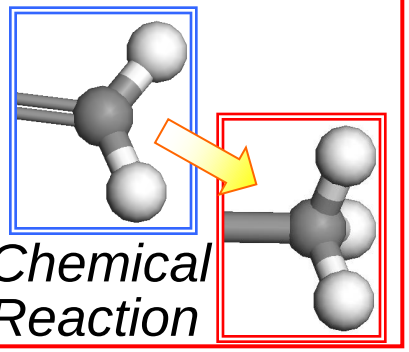
5000 times faster than first-principles calculation

Potential Function Determination

$$E=\Sigma D_{ij}(1-\exp(\beta(r_{ij}-r_0))^2+\Sigma H_{ijk}(\theta_{ijk}-\theta_0)^2$$
$$+\Sigma H_{ijkl}(1+\cos(n\phi-\phi))$$
$$+\Sigma(A_{ij}/r_{ij}^{12}-B_{ij}/r_{ij}^{6})+\Sigma(Z_iZ_je^2/r_{ij})$$

Chemical Nature:
Quantum Chemistry
Bond E, Charge, etc.

Atomic Motion:
Potential Function



Chemical Reaction

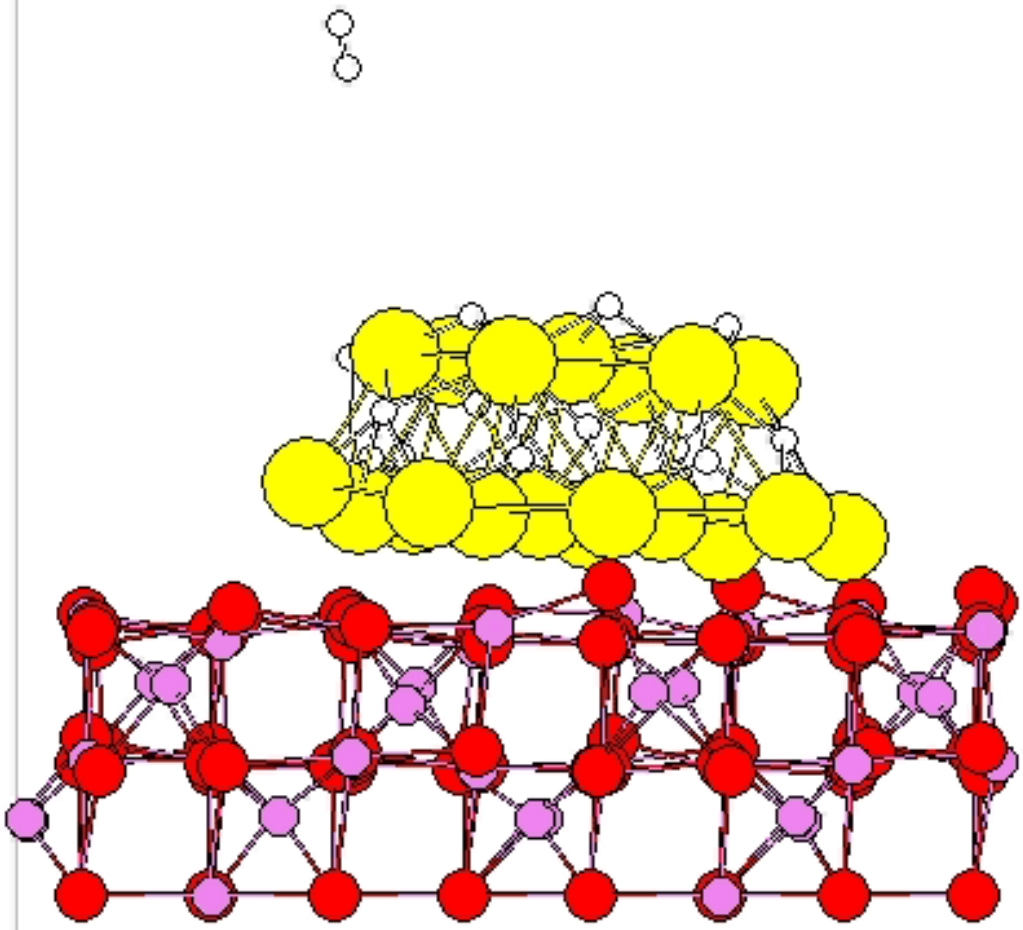
Time Evolution (Quantum Chemistry-based Molecular Dynamics)

10,000,000 Times Acceleration Compared with First-Principles MD

M.K. Alam et al, J. Phys. Chem. C113 7723 (2009); F. Ahmed et al., J. Phys. Chem. C113 15672 (2009)

Role of Pt: Formation of Atomic H from H_2 demonstrated by UA-QCMD

Understanding roles of Pt, Pd, or Rh is highly important to decrease or replace the use of precious metals



H_2

Pt_{19} cluster

Al_2O_3

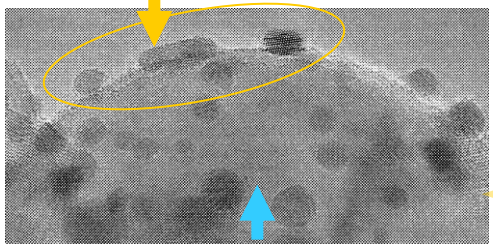
573K

F. Ahmed et al., J. Phys. Chem. C113 15672 (2009)

Experimental Try & Error Manufacturing flow of Automotive Catalyst

Potential Catalysts

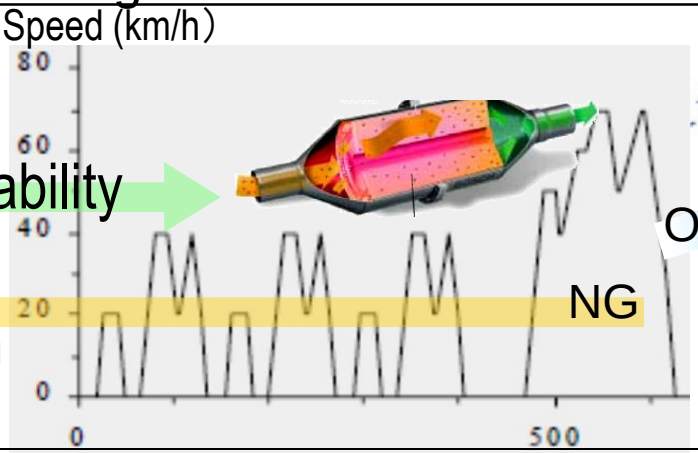
PGM Pt Pd Rh



Supports γ-Al_2O_3, CeO_2, ZrO_2

Check Durability

Re-Design



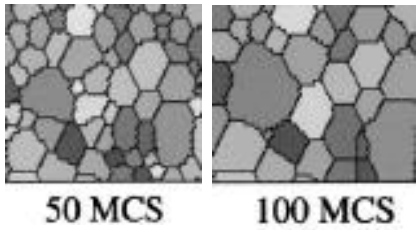
OK

Sale

Theoretical Works Background

Static Monte-Carlo

Non real-time



Acta materialia 47-3, 1007, 1999

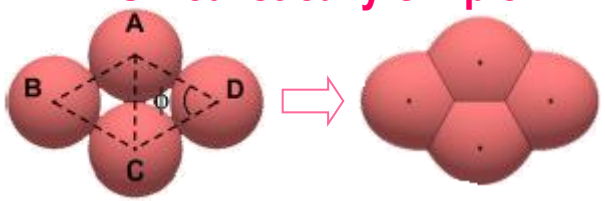
Molecular Dynamics

Too short "ps" for aging simulation

Computational Materials Science 14, 125, 1999

Surface Evolving Dynamics

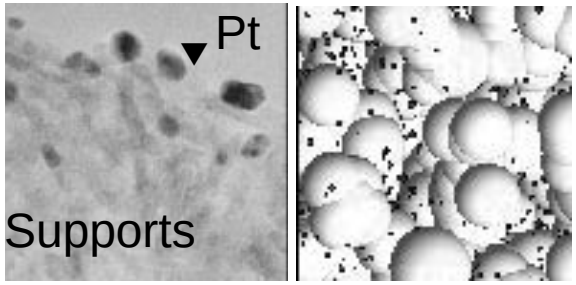
Unrealistically-simple



Acta Materialia 55, 4553, 2007

Aim

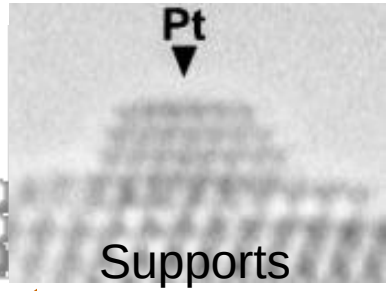
Multi-scale Simulation is applied for theoretical study on durability of catalyst.



Macro ⟷ Micro

Sintering Behavior

Diffusivity



Kinetic Monte-Carlo

Ultra Accelerated Quantum Chemical Molecular Dynamics

Sintering Simulator of Supported Metals and Supports

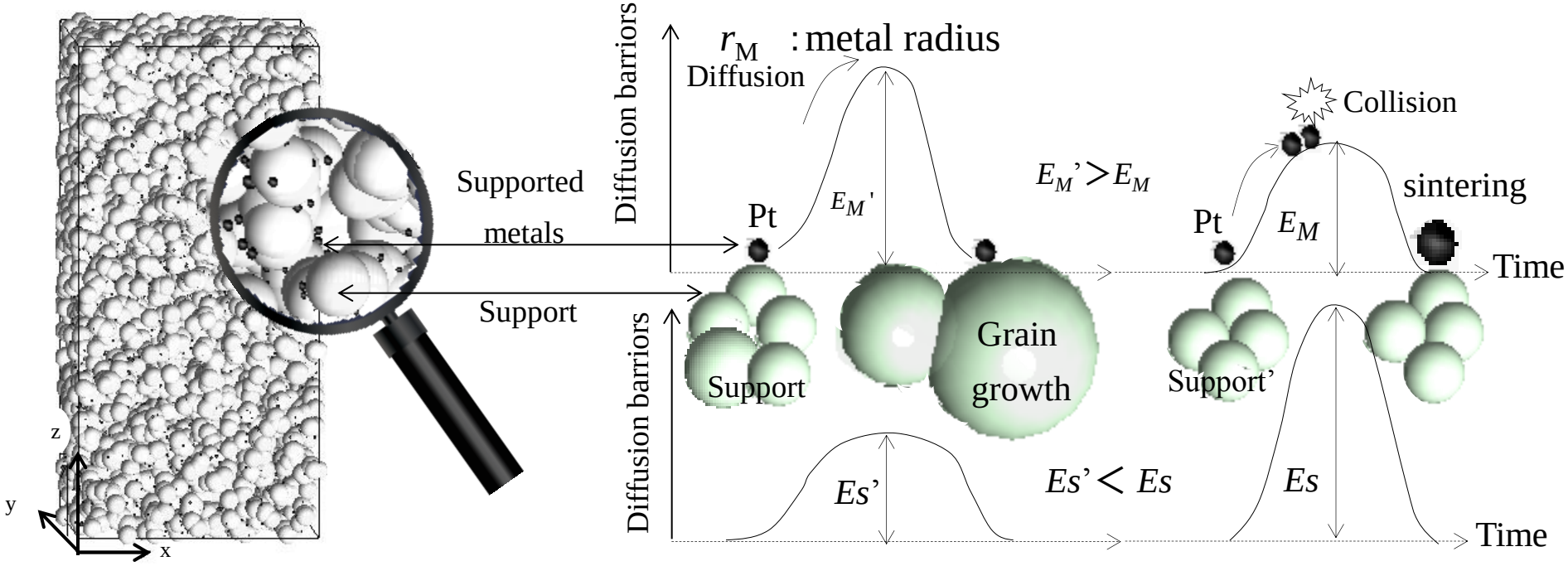
Diffusion of Supported Metals: Pt, Pd, Rh

$$D_M(r) = D_{M0}(2r_M)^{-n}\exp(-\frac{E_M}{RT})$$

D_{M0} : Diffusion coefficient of supported metals

E_M : Activation energy for sintering of metals

r_M : metal radius



Diffusion of Supports: Al_2O_3, ZrO_2, CeO_2

$$D_S(r) = D_{S0}(2r_S)^{-n}\exp(-\frac{E_S}{RT})$$

D_{S0} : Diffusion coefficient of supports

Es : Activation energy for grain growth of supports

r_S : support radius

n : Grain-size exponent R : Universal gas constant T : Absolute temperature

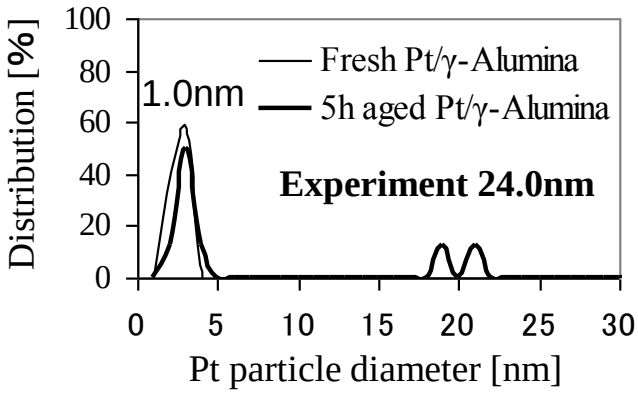
A. Suzuki et al, Surf. Sci. 603, 3949 (2009); A. Suzuki et al., SAE Int. J. Fuel. Lub. 2(2) (2010)

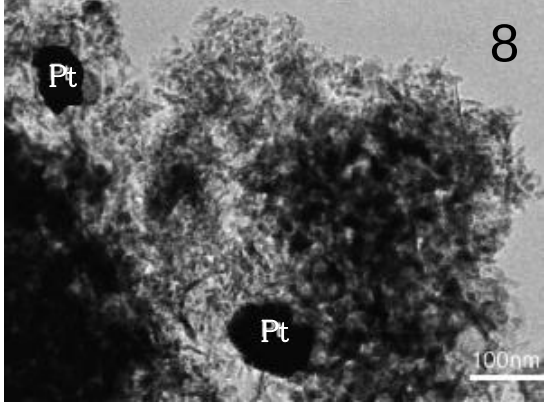
$Pt/\gamma\text{-}Al_2O_3$ Sintering Behavior

800.0 ℃ ⊿t 0.01 s/step

cell size[um]

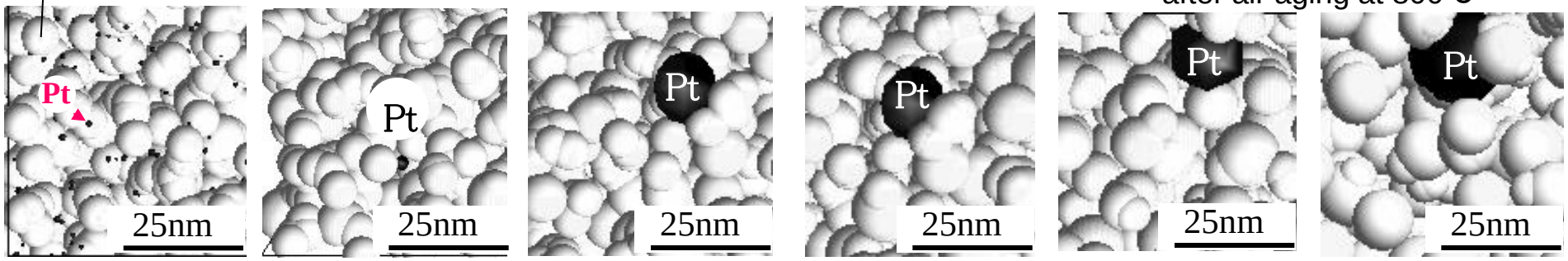
x=0.1, y=0.2, z=0.2



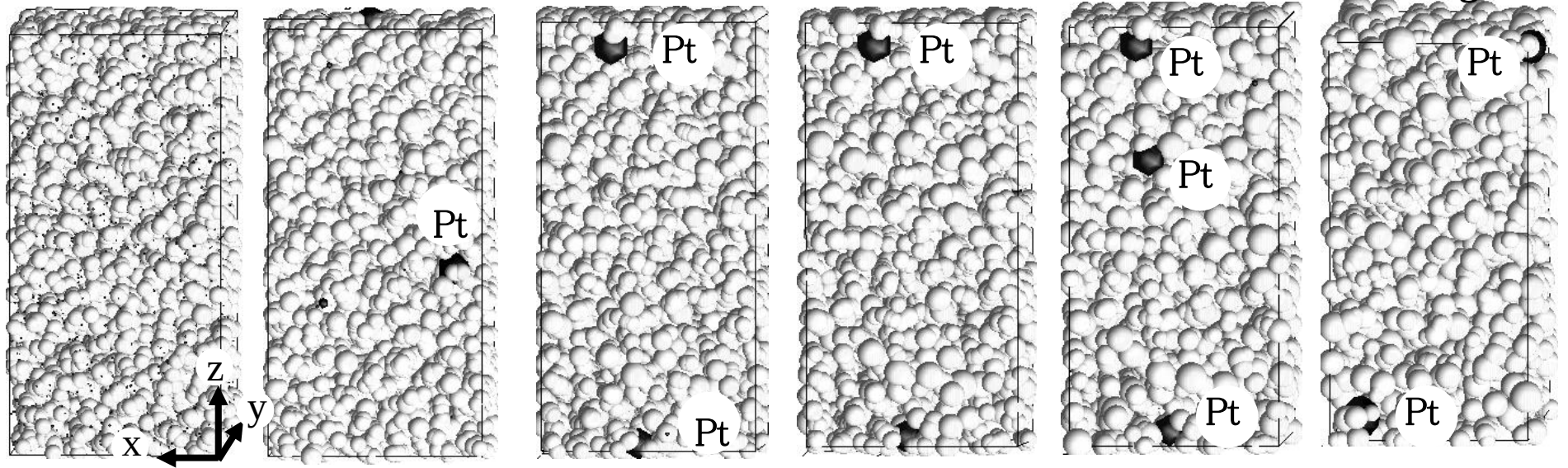


TEM images of Pt/γalumina after air aging at 800℃

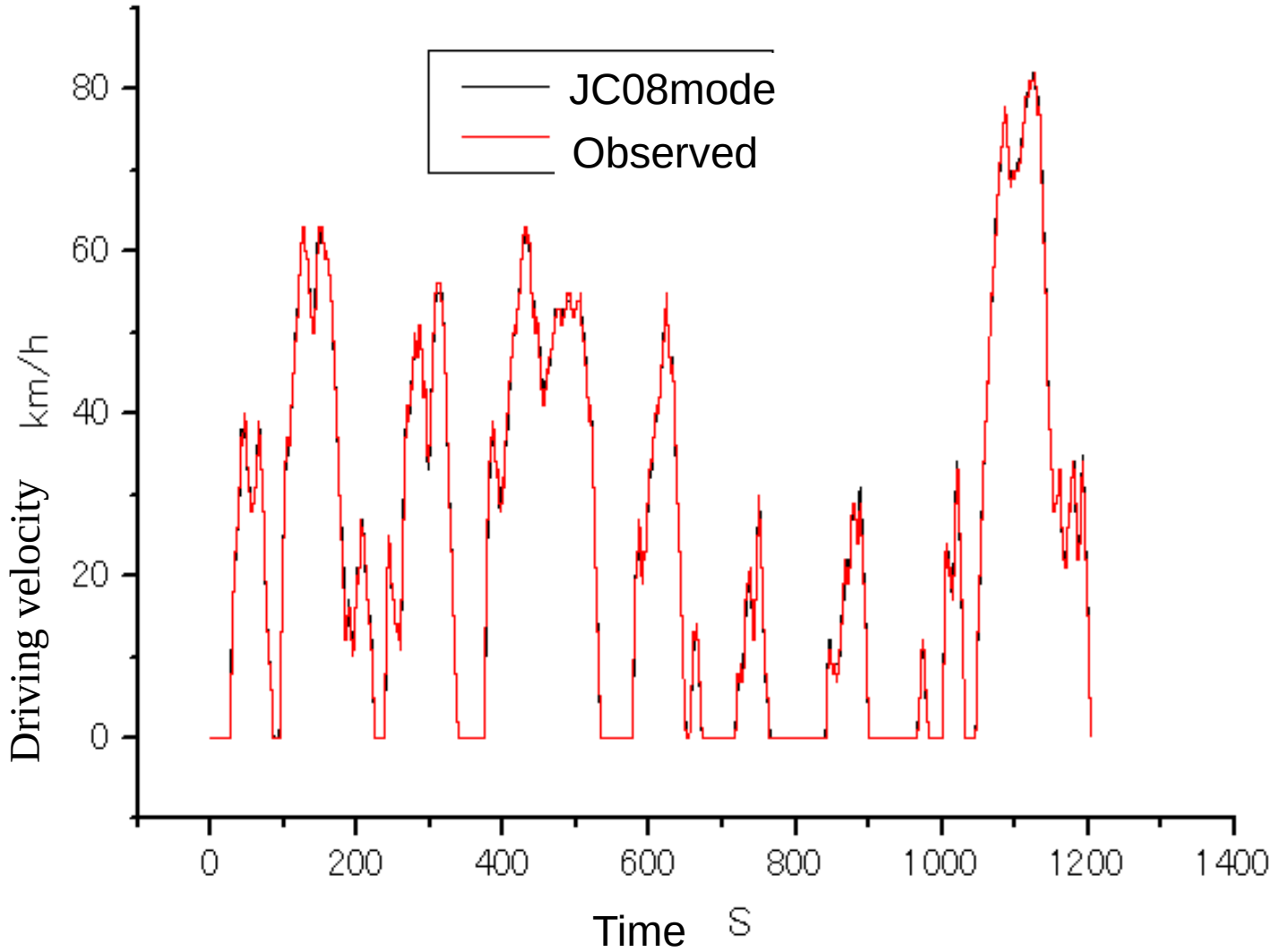
γ-Alumina



Fresh **1h** **2h** **3h** **4h** **5h aged**



Chassis Dynamometer Driving Velocity: Comparison between JC08 mode and Observed one



Elementary reactions on precious metal

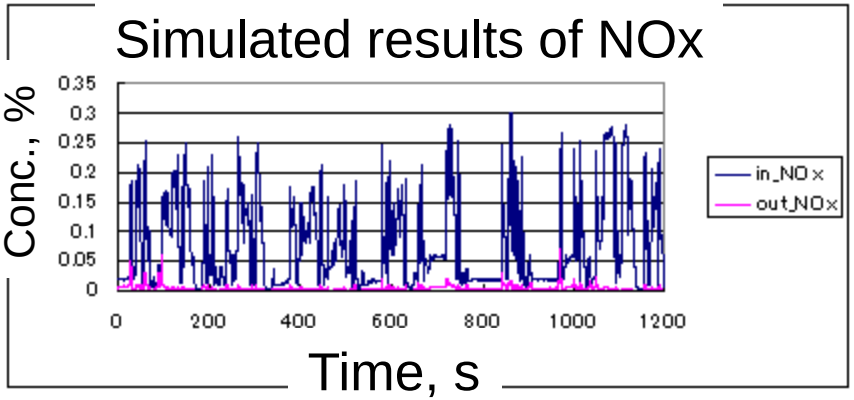
Reaction
NO(g)+th_V_Pt → NO(a-Pt)
NO(g)+th_V_Pt ← NO(a-Pt)
O2(g)+2th_V_Pt → 2O(a-Pt)
O2(g)+2th_V_Pt ← 2O(a-Pt)
NO(a-Pt)+O(a-Pt)→NO2(a-Pt)+ th_V_Pt
NO(a-Pt)+O(a-Pt)←NO2(a-Pt)+ th_V_Pt
CO(a-Pt)+O(a-Pt) → CO2(a-Pt)+th_V_Pt
CO(a-Pt)+O(a-Pt) ← CO2(a-Pt)+th_V_Pt
CO2(g)+th_V_Pt → CO2(a-Pt)
CO2(g)+th_V_Pt ← CO2(a-Pt)
H2O(g)+th_V_Pt → H2O(a-Pt)
H2O(g)+th_V_Pt ← H2O(a-Pt)
C3H6(g)+th_V_Pt → C3H6(a-Pt)
C3H6(g)+th_V_Pt ← C3H6(a-Pt)
C3H6(a-Pt)+9O(a-Pt) → 3CO2(a-Pt)+3H2O(a-Pt)+4th_V_Pt
NO(a-Pt)+th_V_Pt → N(a-Pt)+O(a-Pt)
NO(a-Pt)+th_V_Pt ← N(a-Pt)+O(a-Pt)
NO(a-Pt)+N(a-Pt) → N2(g)+O(a-Pt)+th_V_Pt
2N(a-Pt) → N2(g)
NO(a-Pt)+O(a-Pt)→NO2(a-Pt)+ th_V_Pt
NO2(g)+th_V_Pt ← NO2(a-Pt)

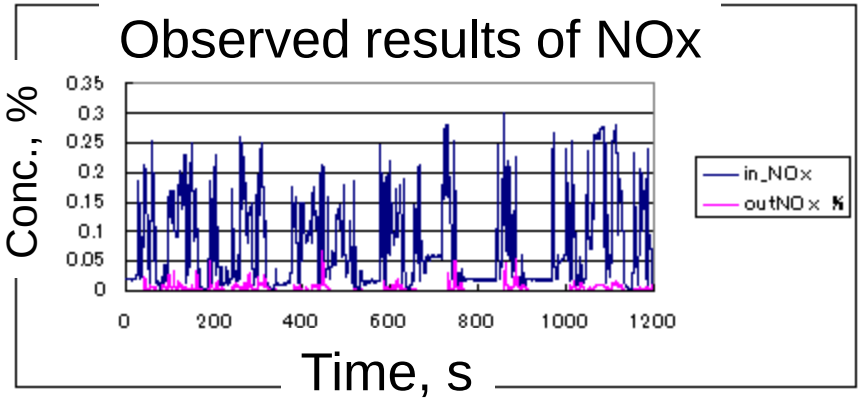
(g) : Gas phase

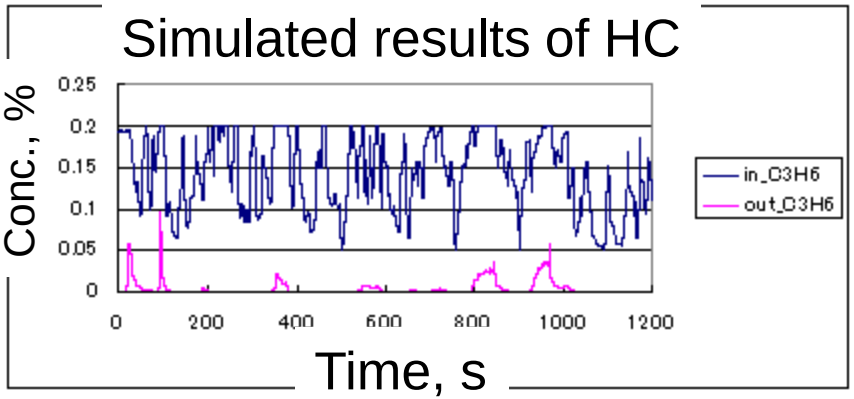
(a-Pt) : Adsorbed site on Pt

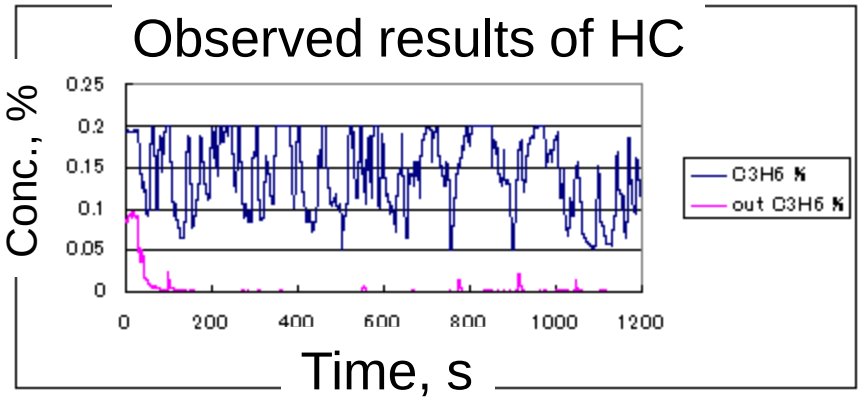
th_V_Pt : Vacant site on Pt

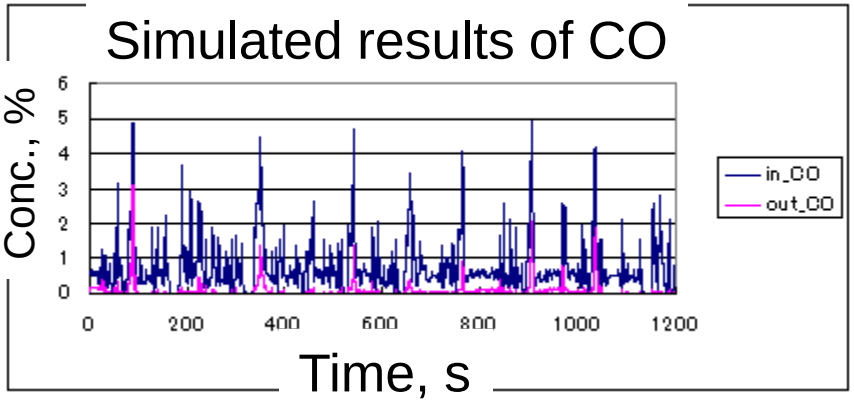
Macroscopic Simulation of Chassis Dynamometer Automotive Catalytic Performance

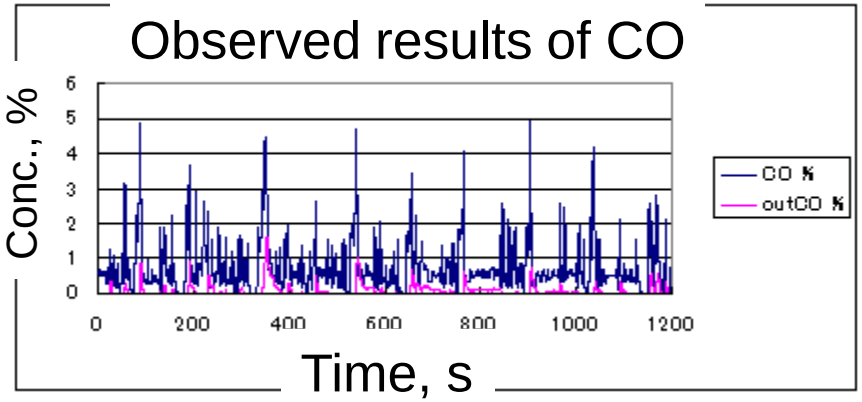




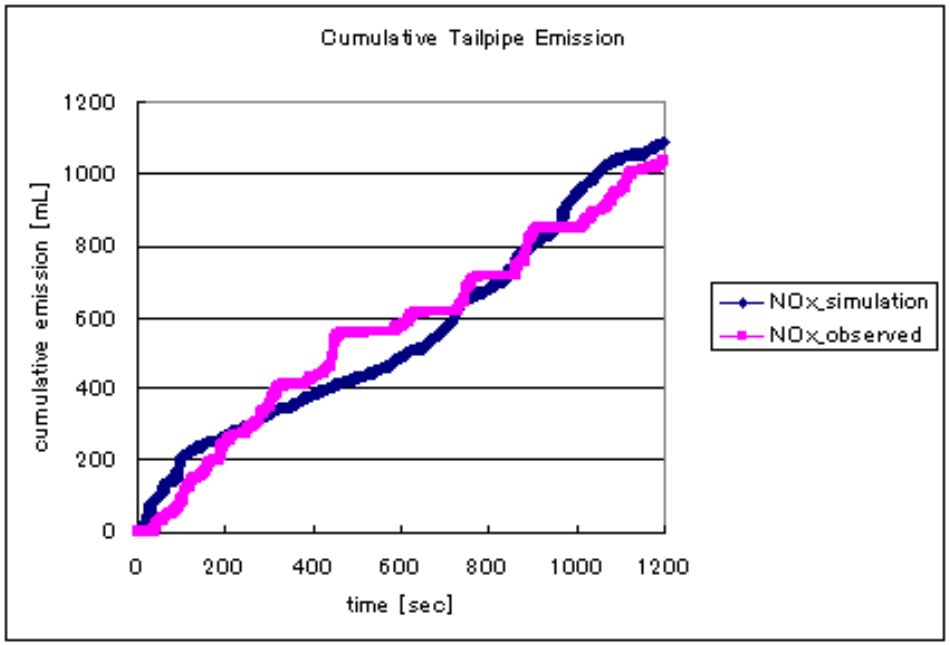


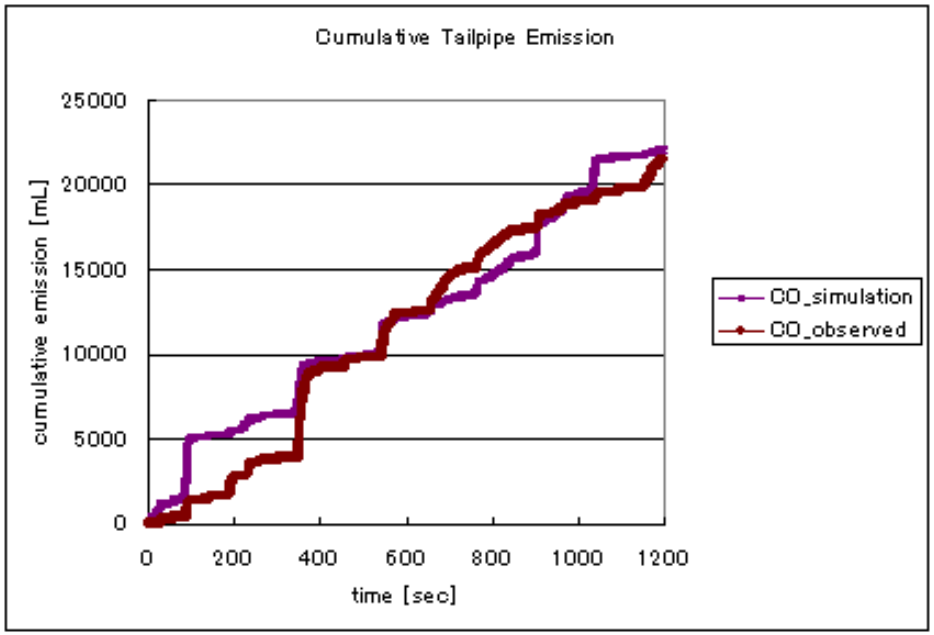






Comparison of Cumulative Tailpipe Emission in the Simulation and the Experiment: NOx and CO





Multiscale, Multiphysics Simulator is Effective for the Analysis/Simulation of Chassis Dynamometer Results of Automotive Catalysts