



# Adsorption and dissociation of molecular hydrogen on Pt/CeO<sub>2</sub> catalyst in the hydrogen spillover process: A quantum chemical molecular dynamics study

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## ABSTRACT

Ultra accelerated quantum chemical molecular dynamics method (UA-QCMD) was used to study the dynamics of the hydrogen spillover process on Pt/CeO<sub>2</sub> catalyst surface for the first time. The direct observation of dissociative adsorption of hydrogen on Pt/CeO<sub>2</sub> catalyst surface as well as the diffusion of dissociative hydrogen from the Pt/CeO<sub>2</sub> catalyst surface was simulated. The diffusion of the hydrogen atom in the gas phase explains the high reactivity observed in the hydrogen spillover process. Chemical changes, change of adsorption states and structural changes were investigated. It was observed that parallel adsorption of hydrogen facilitates the dissociative adsorption leading to hydrogen desorption. Impact with perpendicular adsorption of hydrogen causes the molecular adsorption on the surface, which decelerates the hydrogen spillover. The present study also indicates that the CeO<sub>2</sub> support has strong interaction with Pt catalyst, which may cause an increase in Pt activity as well as enhancement of the metal catalyst dispersions and hence increasing the rate of hydrogen spillover reaction.

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## 1. Introduction

Supported noble metal catalysts such as Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Pt/CeO<sub>2</sub> show special peculiarities of hydrogen adsorption, the extent of which is increased by hydrogen spillover [1]. The hydrogen spillover mechanism has earned intensive interest in the past decades as it plays a vital role in emerging technologies for the reduction of NO<sub>x</sub> in automobile exhausts [2]. Hydrogen spillover has been defined as the dissociative chemisorption of hydrogen on one site, such as a metal particle, and the subsequent transport of atomic hydrogen onto another substrate, which by itself has little or no activity for hydrogen dissociative adsorption [3–10]. Spillover of hydrogen consists of several elementary steps of reactions, namely: adsorption, dissociation, diffusion and finally desorption. Central to this potentiality is the hydrogen spillover effect by means of which dissociated hydrogen chemisorbed on the surface of the metal particle moves on a surface of the support metal oxide, the latter having little or no activity for atomic hydrogen adsorption [3–10].

Temperature dependency of catalytic activity will reveal some information on these mechanisms. An earlier analysis by Levy and Boudart [11] indicated that temperature greater than 800 K would be required for the formation of free hydrogen atom in typical catalytic system. Ekstrom et al. [12] and Batley et al. [13] concluded that in the case of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, gas phase diffusion of hydrogen is significant at temperatures above 623 K. These results indicate that high temperature is needed for the formation of spillover hydrogen. Kramer and Andre [14] reported a temperature programmed desorption (TPD) peak for H atoms on Al<sub>2</sub>O<sub>3</sub> by spillover from Pt at 753 K. They observed that the rate of hydrogen spillover increases with increasing temperature and pressure and that the amount of spilled-over hydrogen is proportional to the square root of adsorption time. Theoretical studies for hydrogen spillover have only been performed marginally. Chen et al. [15] studied the mechanisms of hydrogen spillover using a Pt<sub>6</sub> supported on the MoO<sub>3</sub> (0 1 0) surface using density functional theory (DFT) calculations. They showed that hydrogen initially undergoes a sequential dissociative chemisorption upon interacting with the Pt<sub>6</sub> cluster and energy of 35.66 kJ/mol is required for hydrogen atom to flow onto the surface of the selected materials.

We have recently undertaken a quantum chemical molecular dynamics study [16] on hydrogen spillover mechanisms in the well-known Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst surface. In that study, we have investigated the temperature effects on hydrogen spillover mech-

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anism, and suggested that a transfer of kinetic energy during the hydrogen dissociation is important for the even distribution of hydrogen over the support surface. Different experimental studies generally conclude that at room temperature a spillover hydrogen diffuses along the support surface; at high temperatures, however, spilled-over hydrogen diffuses in the gas phase [17–23]. Despite extensive experiments and a few theoretical studies on the hydrogen spillover systems on  $\text{Al}_2\text{O}_3$  and Pt, some problems remain about the underlying mechanism including metal/support interaction and the effect of temperature [24,25]. These studies indicated that adsorption and catalytic properties of hydrogen spillover depend on the operating conditions as well as interactions with the metal support. Their dynamics is furthermore related to the diffusion of the dissociated hydrogen atom. The UA-QCMD computational procedure was utilized here to investigate the hydrogen spillover mechanism on the Pt/ $\text{CeO}_2$  catalyst system. In our previous study, simulations were carried out at 873 K. In realistic systems, however, the actual temperature for such hydrogen spillover reaction to occur in automotive three-way catalyst is more than 1073 K.

In three-way catalyst (TWC) precious metals (Pt, Pd, Rh) are active sites that remark harmful components from automotive exhaust, such as nitrogen oxide ( $\text{NO}_x$ ), carbon monoxide and unburned hydrocarbons (HC). When a TWC is exposed to a high temperature (about 1073 K or greater) the precious metal will agglomerate and sinter, thus reducing the active surface area of the catalyst [26–29]. One of the biggest issues for three-way catalysts is the degradation of catalytic activity caused by sintering of the noble metals. It has been trying by using many methods to improve the catalytic activity after ageing of the catalysts; improving noble metal dispersion with high surface area supports, adding some promoters, and improving the thermal stability of supports and promoters [30–33]. It was experimentally established that Pt particles in Pt/ $\text{CeO}_2$  based catalysts did not sinter at all during high temperature ageing in an oxidizing atmosphere, in contrast with conventional Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalysts. It has been reported that a Pt–ceria complex was formed under oxidizing atmosphere [34–37]. In case of Pt/ $\text{Al}_2\text{O}_3$ , since the interaction between Pt and  $\text{Al}_2\text{O}_3$  is weak, Pt particles migrate across the surface of the  $\text{Al}_2\text{O}_3$  support and sinter during 1073 K ageing treatment in an oxidizing atmosphere [27,38,39]. In contrast, the ceria-based support stabilizes the high-oxidation state of Pt, and the formed Pt–O–Ce bond on the support suppresses the Pt sintering. Experimental studies proved that the Pt–O–Ce bond, which is the Pt-oxide support interaction, functioned as an anchor and inhibited the sintering of Pt particles on ceria-based oxides [26–29,40,41]. It is considered that the highly dispersed Pt-oxide on the surface of ceria-based oxide support under oxidizing condition is more stable since the Pt–O bond energy is greater than that of the Pt–Pt bond energy in Pt crystallite. Diwell et al. [36] reported that the formation of Pt–Ce complexes under oxidizing conditions could prevent Pt from sintering. In addition, Murrell et al. [37] showed by using a Laser Raman technique that the precious metal oxide structure interacts strongly with the ceria surface.

In this study, we introduce ultra accelerated quantum chemical molecular dynamics (UA-QCMD) program as a versatile tool to investigate the adsorption dynamics of hydrogen spillover in Pt/ $\text{CeO}_2$  catalyst surface. Comparison of different electronic properties, chemical changes and dynamics of adsorption states of hydrogen in Pt/ $\text{Al}_2\text{O}_3$  and Pt/ $\text{CeO}_2$  catalyst surfaces are necessary to elucidate the effect of temperature and supports in hydrogen spillover process. The purpose of this paper is to investigate the effect of supports and temperatures in hydrogen spillover reaction. The simulations also enable the visualization of the electronic and structural changes as well as dynamics behavior in this system.

## 2. Computational methods

### 2.1. Ultra accelerated quantum chemical molecular dynamics method

We used our in house code for ultra accelerated quantum chemical molecular dynamics (UA-QCMD) [16,42,43] to investigate the electronic and structural change of supported Pt cluster as well as diffusion characteristics of Pt on the different supported metal oxides. Quantum chemical molecular dynamics program UA-QCMD, is based on a self-consistent charge (SCC) tight binding theory (TB-QC), which belongs to our in house program “Colors” [44–47] and a classical molecular dynamics program “New-Ryudo” [48]. UA-QCMD enables one to perform quantum chemical molecular dynamics calculation which provides binding energies and atomic charges based on quantum chemistry calculations. The program allows the study of systems including both covalent and ionic interactions, e.g., Pt/ $\text{Al}_2\text{O}_3$ , Pt/ $\text{CeO}_2$ . Also, the original tight binding approximation introduces several parameters to accelerate computation, permitting faster computation than the conventional first principles calculation method.

Dynamics of atoms were carried out using the following potential functions, which were employed to consider the ionic, covalent, and weak Van der Waals interactions among atoms.

$$U = \sum_i \sum_{j>i} \left[ \frac{Z_i Z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp \left( \frac{a_i + a_j - r_{ij}}{b_i + b_j} \right) \right] + \sum_i \sum_{j>i} D_{ij} \{ \exp[-2\beta_{ij}(r_{ij} - r_0)] - 2 \exp[-\beta_{ij}(r_{ij} - r_0)] \} \quad (1)$$

The first term corresponds to the Coulomb potential, and the second term corresponds to the short-range exchange repulsion potential ( $f_0$  is the constant for unit adjustment,  $a$  is the size, and  $b$  is the stiffness), which gives a good account of the repulsive interactions arising from the overlap of electronic clouds. The third terms in Eq. (1) correspond to the Morse-type potential which represents covalent interactions, where  $D_{ij}$  is the bond energy,  $\beta_{ij}$  is the form factor, and  $r_0$  is the bond length at minimum energy. Using these potentials determined by the above-mentioned scheme, a classical molecular dynamics (MD) simulation was performed. This system can solve the motion of equation for large set of atoms [49,50]. In this MD simulator, a Verlet algorithm [51] is employed to integrate equation of motion. Moreover, the temperature scaling method implemented in the system is similar to the Woodcock algorithm [52]. Hydrogen is the lightest atom in the periodic table. The vibrational frequency of hydrogen is very high even at room temperature. So that MD simulations were carried out with a 0.1 fs of integration time for the equations of motions.

Using tight binding calculations,  $Z_i$  and  $D_{ij}$  in Eq. (1) were determined for the conformation of atoms at certain steps of molecular dynamics. Further MD develops a new atomic configuration to update  $Z_i$  and  $D_{ij}$  parameters. This combination of TB-QC and MD was repeated to calculate the time development of the system. MD consists of the numerical, step-by-step, solution of the classical equations of motion. In the TB-QC, an electronic structure calculation was performed by solving the Schrödinger equation ( $H C = \epsilon S C$ ;  $H$ ,  $C$ ,  $\epsilon$ , and  $S$  refer to the Hamiltonian matrix, eigenvectors, eigenvalues, and overlap integral matrix, respectively) with the diagonalization condition ( $C^T S C = I$ ;  $I$  refers to the identity matrix). In the TB-QC, the double- $\zeta$  Slater-type basis set was employed and long-range Coulombic interactions were computed by the Ewald method. In order to determine the off-diagonal elements of  $H$ ,  $H_{rs}$ , the corrected distance-dependent Wolfsberg–Helmholz

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