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Possible reaction pathway in methanol dehydrogenation on Pt and Ag surfaces/clusters starting from O–H scission: Dipped adcluster model study

Takahiro Watanabe [a], Masahiro Ehara [a,c,*], Kei Kuramoto [a,1], Hiroshi Nakatsuji [a,b,c]

[a] *Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyou-ku, Kyoto 615-8510, Japan*
[b] *Quantum Chemistry Research Institute, Kyodai Katsura Venture Plaza 106, Goryo Oohara 1-36, Nishikyo-ku, Kyoto 615-8245, Japan*
[c] *JST, CREST, Sanbancho-5, Chiyoda-ku, Tokyo 102-0075, Japan*

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ABSTRACT

The mechanism of the methanol dehydrogenation reaction on a Pt surface has been investigated using the dipped adcluster model (DAM) combined with density-functional theory (DFT) calculations. Starting from O–H bond scission, methanol decomposes to form CO exothermically on the Pt surface, where the Pt-dσ orbital effectively interacts with the O–H antibonding orbital. The donative interaction of the Pt-dσ orbitals was found to be important for catalytic activation on the Pt surface. The reaction pathway starting from C–H bond scission has a larger activation barrier and, therefore, is less kinetically favorable. Electron transfer from the bulk, which is included in the present DAM calculation, plays an important role in the reaction pathway from O–H bond scission, in particular for the dehydrogenation of formaldehyde. On the other hand, the Ag surface has been shown to be effective for formaldehyde synthesis, because formaldehyde desorbs spontaneously from the Ag surface. The present reaction has also been examined and discussed in view of the nanoscale clusters and nanorods.

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1. Introduction

The oxidative reaction of methanol on a metal surface is one of the most important catalytic processes in the chemical industry. The production of formaldehyde has been conducted using Ag or Fe/Mo catalysts [1,2]. Recently, the methanol dehydrogenation reaction has received much attention because of its potential application in Direct Methanol Fuel Cells (DMFCs) [3–7]. DMFCs are superior to hydrogen-based fuel cells, because storage and conveyance is much easier for methanol than hydrogen. Taking advantage of these characteristics, DMFCs for mobile electrical products, such as mobile batteries, have been developed.

Many studies have been devoted to the development of DMFCs but commercialization has not been established yet, although prototypes of commercial DMFC units have been publicized. One of the reasons is that a practical catalyst for the oxidative reaction of methanol has not been established. Although it has been recognized that Pt catalysts show high activity for dehydrogenation of methanol to CO [3–5], more efficient decomposition is necessary to generate ample electric power. Poisoning by product CO is also a problem for commercial viability, although alloying with Ru is known to be one of the solutions [3–5]. The present work focuses on the methanol decomposition reaction on the Pt surface of DMFC, but the theoretical model mainly describes the reaction under vacuum condition, a solid/vacuum interface.

For the methanol dehydrogenation reaction, two types of reaction pathways have been proposed experimentally, as shown in Fig. 1. One possibility is a route that starts from scission of the O–H bond, followed stepwise by scission of the C–H bond [8]. The other possible route starts from C–H bond scission [9]. Many experiments, most of which are based on spectroscopic measurements, have been done to elucidate the mechanism of this reaction. However, the reaction mechanism is still unclear in particular for the first dehydrogenation step. This is partly because the high reactivity of the Pt catalyst prevents us from directly observing the intermediates and other related compounds. It has been reported that detection of the metastable intermediate species is difficult, except for methanol, CO, and H_2 on the metal surface, even under ultrahigh vacuum (UHV) conditions [10–15].

Many theoretical studies have been performed to clarify the reaction mechanism of methanol dehydrogenation on metal surfaces because of its importance in DMFCs. Kua and Goddard performed pioneering work by examining the thermostability of the intermediates on 2nd and 3rd row Group VIII metals [16]. They provided important and useful information by executing extensive calculations using a cluster model but the activation energies were not given. Ishikawa et al. have also reported a thermostability analysis by using quasirelativistic density-functional theory (DFT)

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[*] Corresponding author. Present address: Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan. Tel.: +81 564 55 7461; fax: +81 564 55 7025.
E-mail address: ehara@ims.ac.jp (M. Ehara).

[1] Present address: Toyota Central R&D Labs, Inc., Nagakute, Aichi 480-1192, Japan.

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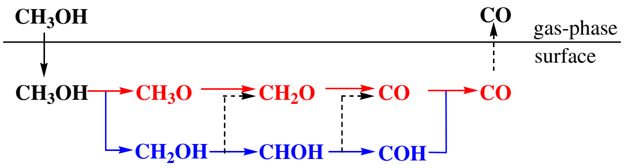

Fig. 1. Reaction pathways of the dehydrogenation reaction from CH_3OH to CO.

calculations of the Xα functional [17]. They also estimated the activation energies, as well as the adsorption and dissociation energies. Desai et al. examined the O–H and C–H bond activations of this reaction using a slab-model [18]. Okamoto et al. investigated this reaction using periodic slab-model DFT calculations, considering the hydrogen-bond network of the solvent water [19]. They reported that in the C–H scission mechanism, the solvent effect is about 0.7 eV for the exothermicity of complete dehydrogenation. Cao et al. [20] and Hartnig and Spohr [21] also studied the solvent effect of water using DFT calculations. Greeley and Mavrikakis performed slab-model DFT calculations to examine the reaction pathways starting with O–H [22] and C–H [23] scission and concluded that C–H scission is dominant, although O–H scission is another realistic route [22,23].

In this situation, we believe that the mechanism of this reaction should be examined, taking into account the electron transfer from the bulk metal and calculating activation energies by locating the transition states (TS). Thus, in the present work, we have investigated the overall reaction pathways of the dehydrogenation reaction of CH_3OH on the Pt surface, using the dipped adcluster model (DAM) [24–26]. The DAM can describe electron exchange between adsorbates and bulk metal (usually electron flows from bulk metal to adsorbates), which is relevant in reactions on metal surfaces. Previously, we investigated the reaction mechanism of CO_2 hydrogenation on the Cu(100) surface, which is related to the present reaction, using the DAM [27]. In this work, we examine the reaction pathway starting from O–H bond scission and compare it with that from C–H bond scission. We have also studied the possibility of methanol dehydrogenation on an Ag surface. We have also examined the cluster size dependence of the results using DAM model.

Recently, the reactions on the nanoscale clusters and nanorods have also been paid much attentions and focused because of their characteristic reactivities [28,29]. The present results are also of interest in view of the reactions on the nanoscale clusters and nanorods. We have also discussed the present reaction in this aspect by examining the standard cluster model.

2. Computational details

The DAM [24,25] was adopted to describe electron exchange between adsorbates and the metal surface. DFT calculations using the B3LYP functional were executed according to the DAM. We also included energy correction due to the image force on the metal surface [26]. We assumed the highest spin coupling model and one-electron transfer from the bulk metal to the adcluster. In the present case, the paired spin coupling is more suitable since the spin-polarization is not experimentally observed for the Pt and Ag surfaces. We adopted, however, the highest spin coupling since it provides stable energy and is computationally simple compared to the paired spin coupling. In the calculations, the spin state of the adcluster was taken as singlet or doublet depending on the step of the reaction.

For the computational model of the Pt surface, we adopted a linear Pt_4 DAM cluster to represent the Pt(111) surface. For the first step which is relevant for the reaction mechanism, we examined the larger clusters for DAM, that is Pt_{10} and Pt_{15} models. The Pt–Pt distance was fixed to 2.772 Å on the basis of the lattice constant of the Pt(111) surface [30]. Most of the structures of the intermediates and transition states have been restricted to C_s symmetry, except for the transition state between CH_2O_a and CHO_a (subscript 'a' indicates a surface-adsorbed species). It was confirmed that all the intermediates are true local minima, and vibrational analysis showed that all the transition states have only one imaginary frequency, except for some states noted. Similarly, the computational model of the Ag surface was also an Ag_4 DAM cluster and the Ag–Ag distance was fixed to 2.892 Å [30]. All calculations were performed using the Gaussian03 suite of programs [31]. The basis set of the Pt atom was (8s6p3d)/ [3s3p2d] and the [Xe] $4f^{14}$ core was replaced by the effective core potential [32]. For carbon, oxygen, and hydrogen atoms, we adopted the Huzinaga–Dunning double zeta polarization [33] plus diffuse s, p functions, that is, (10s6p1d)/[3s3p1d] for C and O atoms, and (5s1p)/[3s1p] for H atoms. The exponents of the diffuse s, p functions were taken from Dunning [34]. For all the steps, we calculated the reaction paths with the standard cluster model to examine the present dehydrogenation reaction on the nanoscale clusters and nanorods. These calculations also show the effect of the electron transfer from bulk metal to the adcluster region.

3. Results and discussion

3.1. Reaction of methanol to form CO starting from O–H bond scission

Fig. 2a shows the energy diagram for the reaction of methanol, from adsorption to dissociation of the O–H bond, producing adsorbed methoxy. The structures of the adsorbed methanol, transition state, and the adsorbed methoxy are also shown. Methanol adsorbs with oxygen at a on-top site of the Pt surface, which agrees with the previous works [18,22]. The adsorption energy of methanol on the Pt surface was calculated to be 11.7 kcal/mol, which is in

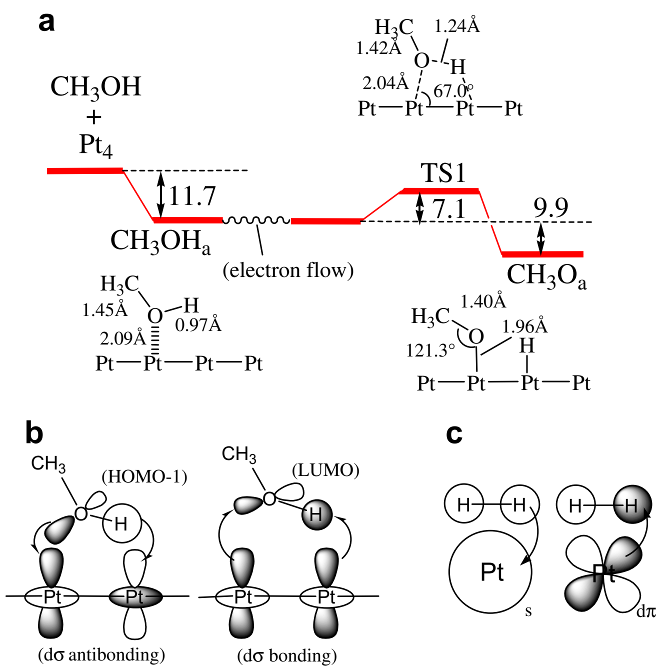

Fig. 2. (a) Energy diagram and optimized geometries for the reaction step from methanol to adsorbed methoxy on the Pt surface (energy in kcal/mol), (b) orbital interaction between methanol and the Pt surface, and (c) orbital interaction in the dissociation of H_2 on the Pt surface [34].

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