



The effects of stepped sites and ruthenium adatom decoration on methanol dehydrogenation over platinum-based catalyst surfaces



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ABSTRACT

A density functional theory study of methanol dehydrogenation over stepped Pt(2 1 1) surfaces without and with Ru modification was carried out to understand fuel catalytic reactions on Pt-based catalysts. Two main pathways of the CH₃OH dehydrogenation were examined: the O–H pathway which was initiated by O–H bond scission to form the methoxy (CH₃O) intermediate followed by sequential cleavage of C–H bonds to CO, and the C–H pathway which was initiated by C–H bond scission to form the hydroxymethyl (CH₂OH) followed by two C–H bond cleavages to COH and then CO. Possible crossover reactions between the O–H and C–H pathways were also computed. Compared to flat Pt(1 1 1), stepped Pt(2 1 1) increases the adsorption energies of intermediates, making no significant contribution to decreasing the reaction barriers of most elementary steps involved, except in the first hydrogen scission. However, on the Ru-modified surface, a significant reduction was found in reaction barriers for the first step of the C–H bond scission and a number of further dehydrogenation steps crossing over to the O–H pathway, with the most facile paths identified. Our data reveals the complexity of methanol catalytic reaction processes at the atomic level and contributes to a fundamental understanding of fuel reactions on Pt-based catalysts.

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1. Introduction

Liquid methanol has significant advantages over gaseous hydrogen, such as ease of handling, transportation and storage, and in particular it has a much higher energy density [1–5], methanol is becoming a promising alternative fuel to hydrogen in fuel cell applications, for example in direct methanol fuel cells (DMFCs) [1–11]. Ideally, methanol can be electro-catalytically oxidized on platinum anode catalysts to produce CO₂ with six electrons released per CH₃OH molecule [1,2,9–11]; however, the methanol oxidation reaction may also produce partial oxidation products such as formaldehyde and formic acid [10], yielding only two and four electrons, respectively.

Numerous efforts have been made aimed at understanding the mechanism of methanol oxidation on various platinum electrode surfaces. Sun and Clavilier [12] studied methanol oxidation at low index planes of platinum, Pt(1 1 1) and Pt(1 0 0), in perchloric acid solution, and Herrero et al. [13] studied catalytic decomposition

of methanol on Pt(1 1 1), Pt(1 1 0) and Pt(1 0 0) in perchloric, sulphuric and phosphoric acids at room temperature. These studies investigated the effect of surface morphology of Pt catalysts and the composition of electrolyte (anions) on the reactions regarding reducing the surface poisoning by CO adsorbates (CO_{ads}) formed from methanol dissociation adsorption. In addition to the surface poisoning species CO_{ads}, the formation of other intermediates during the successive dehydrogenation of methanol have also been identified, for example soluble byproducts, such as formaldehyde and formic acid [10,14–18], and adsorbed species including CHO (formyl) and COH [14–16,19].

Modification of the Pt surface with the addition of a second and even a third metal, such as Ru [20–24], Sn [20,23], Rh [25,26] and Au [27], as well as exploration of surfaces to improve platinum catalysts towards the activity and the CO₂ selectivity of methanol oxidation have also been performed extensively. To date, PtRu catalysts [20–24,28–30] have been experimentally shown the highest reactivity towards methanol oxidation reaction and also the best tolerance with respect to CO poisoning. For pure Pt, CO adsorbs strongly on the surface (e.g., –2.09 eV binding energy on Pt(2 1 1), see Table 1), and at lower potentials, there is little active oxidant (OH) formation from water on the Pt surface, so CO poisons the

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Table 1Adsorption energies E_{ads} (eV) and geometrical adsorption sites of intermediates for methanol decomposition on Pt(2 1 1), Ru decorated Pt(2 1 1) (Ru/Pt(2 1 1)) and Pt(1 1 1).

| Species | Pt(2 1 1) | | Ru/Pt(2 1 1) | | Pt(1 1 1) |
|--------------------|-----------------------|-------------------|-----------------------|-----------------------|---|
| | E_{ads} (eV) | Adsorption site | E_{ads} (eV) | Adsorption site | E_{ads} (eV) |
| CH ₃ OH | −0.52 | e-top via O | −0.26 | e-top via O | −0.33 ^a ; −0.46 ^b |
| CH ₃ O | −2.36 | e-bri via O | −2.62 | bri Pt–Ru via O | −1.54 ^a ; −1.67 ^b |
| CH ₂ O | −0.97 | e-bri via C and O | −1.13 | bri Pt–Ru via C and O | −0.50 ^a ; −0.5 ^b |
| CHO | −2.83 | e-bri via C and O | −2.53 | bri Pt–Ru via C and O | −2.36 ^a ; −2.46 ^b |
| CH ₂ OH | −2.45 | e-bri via C and O | −2.37 | bri Pt–Ru via C and O | −1.98 ^a ; −2.17 ^b |
| CHOH | −3.45 | e-top via C | −3.67 | top Ru via C | −3.24 ^a |
| COH | −4.66 | e-bri via C | −4.85 | hollow Pt–Ru via C | −4.45 ^a |
| CO | −2.09 | e-bri via C | −2.04 | bri Pt–Ru via C | −1.82 ^a ; −1.74 ^b |
| O | −1.52 | e-bri via O | −2.2 | bri Pt–Ru via O | −1.36 |
| OH | −3.27 | e-bri via O | −3.94 | top Ru via O | −2.12 ^a ; −2.46 |
| H | −2.89 | e-bri via H | −2.86 | e-bri via H | −2.71 ^a ; −2.79 ^b |

^a Ref. [42].^b Ref. [40].

Pt surface. However, on PtRu surface, CO binding energy decreases slightly (e.g., from −2.09 eV on Pt(2 1 1) to −2.04 eV on Ru/Pt(2 1 1), see Table 1) due to electronic effect of Ru; more importantly, Ru can provide active oxidant (OH, from water) at a much lower potential (about 300 mV) than that on Pt, thus can oxidize CO at lower potential than that on pure Pt [31–37]. This is so called “bi-functional mechanism” in which OH on Ru reacts with CO on Pt, rather than OH on Pt reacts with CO on Pt that require much higher potential [31,32,38].

Theoretical analyses of methanol dehydrogenation to CO and further oxidation to CO₂ have also been performed. Zhang and Hu [39] showed that methanol decomposition occurred via both O–H and C–O scission on Pd(1 1 1) surface. They suggested that the O–H bond scission pathway is more energetically favourable than the C–O bond scission pathway. Desai et al. [40] performed periodic DFT calculations on the dehydrogenation of methanol to CO over Pt(1 1 1) and reported the chemisorption energies of some intermediates as well as methanol and showed that methanol adsorbs weakly at the top site of Pt(1 1 1). Greeley and Mavrikakis [41,42] conducted DFT work by investigating the thermo-chemistry and reaction barriers of the elementary steps for methanol decomposition to CO on Pt(1 1 1). In addition, three well-defined low index platinum single crystal planes have been studied using a combination of experimental and theoretical methods by Cao et al. [43]. Yuan et al. [44] also examined the decomposition pathways of methanol on PtAu(1 1 1) bimetallic surface. Notably, all the above studies were performed on the close-packed flat (1 1 1) surfaces and few theoretical investigations have been conducted on defective stepped surfaces.

In fact, it is known that surface defects may play an important role in heterogeneous catalysis and electrocatalysis as well

[29,45–48]. Therefore, to uncover the mechanism of methanol dehydrogenation on surface defects is vital to understand the real systems. In this work, the dehydrogenation of methanol on Pt(2 1 1), a typical stepped surface with defects [45–48], has been investigated together with the further oxidation to CO₂ in the presence of oxidants O/OH using periodic DFT calculations. In addition, the effect of Ru adatoms has also been studied. By mapping out the whole reaction network and the rate-determining step, a clear picture of methanol dehydrogenation and oxidation on Pt(2 1 1) and Ru-modified Pt(2 1 1) surfaces has been revealed.

2. Computational details

Total energy calculations within the DFT framework were carried out. The Perdew–Burke–Ernzerhof (PBE) [49,50] functional of generalized gradient approximation (GGA) [50–52] implemented in the Vienna ab initio simulation package (VASP) [53–55] was used for the exchange and correlation term. Ionic cores were described by projector augmented-wave (PAW) pseudo-potentials [56]. The Kohn–Sham orbitals were expanded in a plane wave basis set with the cut-off energy of 400 eV. The cut-off energy of 500 eV was tested, which showed small energy differences (within 0.01 eV). The atomic positions were relaxed until the forces were smaller than 0.05 eV/Å.

The super-cell approach to model the periodic geometry was employed. Surfaces were modelled by $p(1 \times 4)$ super cells with four layers, in which the top two layers were allowed to relax and the bottom two fixed [57]. The step notation of the Pt(2 1 1) surface is $[3(1 1 1) \times (1 0 0)]$ as shown in Fig. 1(a), which consists of three-atom-wide terraces with (1 1 1) structure and one-atom-high steps exhibiting (1 0 0) arrangement. The vacuum region between

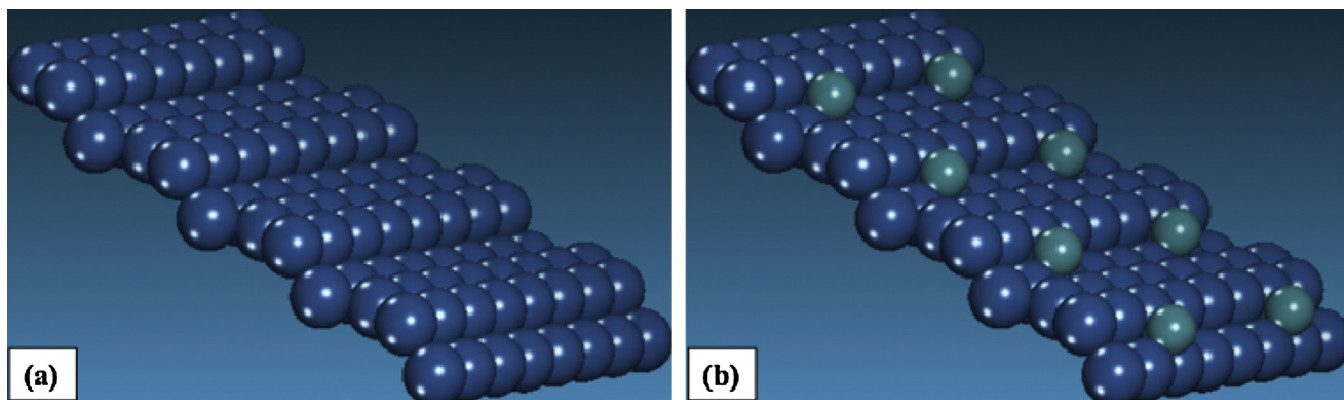


Fig. 1. Surface structures of the stepped Pt(2 1 1) without (a) and with Ru-modification (b).

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