



In situ XANES study of methanol decomposition and partial oxidation to syn-gas over supported Pt catalyst on SrTiO₃ nanocubes



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ABSTRACT

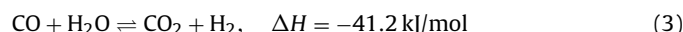
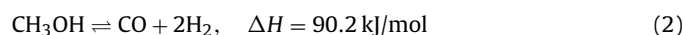
A catalyst of Pt nanoparticles was prepared by atomic layer deposition on SrTiO₃ nanocuboids and tested for methanol decomposition and partial oxidation. The catalyst had uniform nanoparticle size of 1.58 ± 0.37 nm and a Pt (1 1 1) surface. *In situ* X-ray absorption near-edge spectroscopy (XANES) measured in a temperature-programmed reduction showed that the Pt particles were easily reduced. However, the as-received catalyst, a reduced catalyst, and an oxidized catalyst all had catalytic activity, differing slightly in methanol conversion and product selectivity. *In situ* XANES also revealed that CO adsorbed on the Pt sites was the only observed surface species during both methanol decomposition and partial oxidation. It seemed that the breakage of CH and OH bonds overwhelmingly occurred once methanol was adsorbed, forming H₂ and adsorbed CO. The latter was then released from the catalyst surface or was oxidized to CO₂ when O₂ was present.

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1. Introduction

The Institute of Atomic-Efficient Chemical Transformations (IACT) led by Argonne National Laboratory researchers focuses on key catalytic conversions that could improve the efficiency of producing fuels from biomass resources. Catalytic conversion of methanol (MeOH) into hydrogen or other value-added chemicals or energy forms plays an important role in biomass utilization because methanol can be produced from renewable sources such as lignocellulosic biomass and sugar, as well as from starch crops via biochemical or chemical processes [1].

Because of its high H-to-C ratio and absence of C–C bonds, methanol is an ideal onboard liquid hydrogen carrier for H₂ fuel cell vehicles. Hydrogen can be produced at relatively low temperatures by steam reforming and other reforming reactions:



Two major groups of catalysts, Cu-based alloys and Group VIII metals, have been used in investigations of steam reforming of methanol by Sá et al. [2]. Supported Cu catalysts must be reduced to form Cu metallic particles on the catalyst. Catalyst preparation must yield high values of Cu metal dispersion and surface area but small metallic particle size. Catalytic deactivation occurs mostly because of Cu oxidation and sintering, carbon formation, and/or formation of poisoning gases in the feed. Catalytic deactivation also results from CO formed during the reforming reactions. The reaction mechanism can involve one or two adsorbed molecules, depending on the support materials and preparation method. In the dual-molecule mechanism, two adsorbed methanol molecules form methyl formate. In the single-molecule mechanism, an adsorbed methanol forms formaldehyde on the catalyst surface. Either methyl formate or formaldehyde on the surface is hydrolyzed to form formic acid, and then the formic acid is decomposed to form hydrogen and CO₂. A reverse water-gas shift reaction is blamed for the formation of CO, which is harmful to the

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anodic catalyst in the low-temperature H_2 fuel cell. The Group VIII–X metal-based catalysts for the steam reforming of methanol are also reviewed in this paper, among which Pd supported on ZnO is the most commonly used [2]. Even for other supports, the addition of Zn greatly improves the catalytic selectivity and H_2 production rate. When used in steam reforming, the Pd metallic particles and PdZn alloy exhibit different reaction mechanisms. On the metallic Pd particles, the dehydrogenated formaldehyde is adsorbed on two sites with C and O atoms, and then is decomposed into CO and H_2 . On the PdZn alloy particles, the dehydrogenated formaldehyde is adsorbed on one site with an O atom, followed by nucleophilic addition of water, formation of formic acid, and its decomposition. Compared with Cu-based catalysts, Pd–Zn catalysts are more stable due to their resistance to sintering and easy recovery from oxidation.

Because use of a direct methanol fuel cell for vehicle propulsion is simpler than converting methanol to hydrogen in a reformer and then hydrogen to electricity in a fuel cell [3], researchers have widely studied the decomposition of methanol on transition metal catalysts or supported transition metal catalysts, among which Pt is the most widely examined. Desai et al. used a periodic density functional theory (DFT) calculation to determine the methanol decomposition mechanism on the Pt (1 1 1) surface; in particular, they analyzed the interactions of the possible radicals such as molecular methanol, methoxide, hydroxymethyl, formaldehyde, formyl, CO, and H on an ideal and defect Pt (1 1 1) surface [4]. They concluded that methanol molecules are not activated by the ideal Pt (1 1 1) surface; while on the defect surface, an OH bond is likely to be broken to form methoxide, followed by its dehydrogenation via the formation of formaldehyde and formyl. After dehydrogenation, adsorbed CO and H are formed on the surface. The latter further desorbs to form H_2 but the former stays on the surface as a poisonous species. Niu et al. employed DFT with general gradient approximation to study the methanol decomposition mechanism on five surfaces: flat Pt (1 1 1), Pt defect, Pt step, Pt (1 1 0) (1×1), and Pt (1 1 0) (2×1) [5]. They observed that the decomposition of methanol on these surfaces begins with the activation and breakage of the OH bond, followed by the consecutive dehydrogenation of the methoxide, formaldehyde, and formyl on the Pt surfaces and ending with the formation of adsorbed CO and H. They also reported that the stereochemical configuration and bond length of the adsorbed species and the energy of the pathway change according to the different catalyst surface structures. Experimental studies do not always entirely agree with theoretical calculations, however. For example, using soft X-ray synchrotron photoelectron spectroscopy, Matolin et al. studied the methanol desorption on Pt particles supported on Ce (1 1 1)/Cu (1 1 1) and on an ion-eroded Pt (1 1 1) single crystal [6]. They found that the chemisorbed methoxy formed on both surfaces, which is consistent with the theoretical calculations. However, they also detected the partial C–O bond scission and the carbon formation. The same group extended their research to the Pt (1 1 0) (2×1) single crystal [7]. They observed CO adsorption as molecules form on the surface, but no trace of carbon on the crystal.

In Pt-based catalyst development for methanol decomposition to produce syn-gas, Brown and Gulari synthesized Pt/ Al_2O_3 catalyst and a ceria-promoted Pt/ Al_2O_3 catalyst using a single-step sol-gel method [8]. The optimum Pt and CeO_2 loading was found to be 9 and 10 wt %, respectively. The addition of ceria improved both methanol conversion and selectivity for H_2 and CO. The best catalyst completely avoided the methanation reaction. Although Brown and Gulari evaluated Pt/ Al_2O_3 and Pt/ CeO_2 - Al_2O_3 catalysts of various compositions and compared their performance with commercial catalysts and other catalysts with other metals, they did not perform a mechanism study. Croy et al. investigated the pretreatment effect on methanol decomposition and oxidation over a catalyst of Pt nanoparticles supported on ZrO_2 , which was synthesized using

a so-called “micelle method,” where the Pt precursor was first dissolved in self-prepared nano-cages of a polymer solution and then loaded onto ZrO_2 nanoparticles (NPs) [9]. The size of the Pt NPs was controlled by the size of the cages, and the latter was controlled by the functional groups of the polymer. It was interesting to observe that the catalyst pretreated in O_2/H_2 mixture resulted in the best activity for methanol decomposition, followed by the catalyst pretreated in O_2 and He. The catalyst pretreated in H_2 did not show good activity. The pretreatment did not affect the activity of the oxidation reaction. Croy et al. believe that the Pt oxide is of help in the maintenance of clean, stable, and active Pt NPs [9]. But the oxide is easily reduced with the formed H_2 and facilitates the decomposition reaction. The same group extended the studies to include the decomposition of other alcohols [10]. Ubago-Perez et al. prepared a Pt catalyst supported by activated carbon by adsorbing Pt precursor solutions onto self-made activated carbon particles followed by solvent removal and drying [11]. A linear relationship was found between the turn-over frequency of methanol decomposition and the Pt NP size, which can be controlled by the pretreatment gases used. Helium-treated catalyst had NPs with narrower particle size distribution and smaller average size and higher surface Pt dispersion, which led to lower decomposition activity. Hydrogen-treated catalyst, however, had NPs with broader particle size distribution and greater average size and lower surface Pt dispersion, which led to higher activity. Ubago-Perez et al. concluded that larger particles facilitated higher activity to methanol decomposition and that the formed CO suppressed the smaller Pt particles.

The IACT researchers earlier developed a Pt/ $SrTiO_3$ -nanocuboid catalyst. The catalyst support consists of single-crystal nanocubes of $SrTiO_3$ with an edge length of 60–120 nm. It was synthesized using sol-precipitation coupled with a hydrothermal procedure or a molten salt procedure [12]. The platinum was introduced onto the support by atomic layer deposition (ALD), such that the Pt particles are evenly distributed and their size is controlled by the number of ALD cycles [13]. Because of the unique properties of the catalyst, *i.e.*, nonporous single-crystal support and evenly dispersed Pt nanoparticles with known surface structure, we use it as a model for the study of methanol decomposition and partial oxidation. By combining catalytic performance tests and the results of *in situ* X-ray absorption near-edge spectroscopy (XANES), we hope to deepen the understanding of the mechanism of methanol decomposition and partial oxidation over the Pt/ $SrTiO_3$ -nanocuboid catalyst made by ALD. This paper reports the result of this study.

2. Experimental

2.1. Catalyst preparation

$SrTiO_3$ nanocuboids were synthesized by using sol-precipitation combined with hydrothermal treatment [12]. About 80 mL of an aqueous solution containing stoichiometric amounts of Sr and Ti was prepared from $Sr(OH)_2 \cdot 8H_2O$ and $TiCl_4$ as metallic precursors. Co-precipitation of $SrTiO_3$ was induced by adding about 5 g of NaOH pellets to the above bimetallic precursor solution. Dissolution of the NaOH pellets produced a highly viscous suspension, which was subsequently transferred to a 125 mL Teflon-lined autoclave and heated at 240 °C for 36 h. The solution was filtered, and the product washed thoroughly with double-deionized water and dried at 80 °C for 24 h, yielding $SrTiO_3$ nanocuboids.

The Pt atoms were deposited onto the $SrTiO_3$ nanocuboids using ALD [13–15]. About 0.25 g of the $SrTiO_3$ nanocuboids powder was spread in a stainless steel tray. The powder was covered by a stainless steel mesh that allowed easy access by the ALD precursors and contained the powder while being cleaned *in situ* with a 400 mL/min flow of an ozone-oxygen (10% ozone) mixture

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