Electronic Effect in Methanol Dehydrogenation on Pt Surfaces: Potential Control during Methanol Electrooxidation

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S Supporting Information

ABSTRACT: Establishing a relationship between the catalytic activity and electronic structure of a transition-metal surface is important in the prediction and design of a new catalyst in fuel cell technology. Herein, we introduce a novel approach for identifying the methanol oxidation reactions, especially focusing on the effect of the Pt electronic structure on methanol dehydrogenation. By systematically controlling the electrode potential, we simplified the reaction paths, excluding other unfavorable effects, and thereby obtained only the methanol dehydrogenation activity in terms of the electronic structure of the Pt surface. We observed that the methanol dehydrogenation activity of Pt decreases when the position of the d-band center relative to the Fermi level is lower, and this fundamental relation provides advanced insight into the design of an optimal catalyst as the anode for direct methanol fuel cells.

SECTION: Energy Conversion and Storage; Energy and Charge Transport

Fuel cells are promising alternative power generation sources to conventional combustion-based ones, capable of environmentally friendly energy conversion. Polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) are the key technologies of low-temperature cells for various applications such as electric vehicles, portable electronic devices, and so forth.^{1–7}

Unfortunately, current state-of-the-art catalysts are mainly platinum-based, often too expensive for large-scale commercialization.^{8–13} To overcome this barrier, researchers have tried to establish the fundamental rule governing the activity of catalysts. With progresses in density functional theory (DFT) calculations, Nørskov and several co-workers proposed the d-band center relative to the Fermi level as a descriptor for the reactivity of a transition-metal surface.^{14–20} According to this model, the bond strength is characterized by the filling of the antibonding states formed between adsorbate states and metal d states. Because this filling is given by the energy of the antibonding states relative to the Fermi level, the position of the d-band center relative to the Fermi level is directly related to the adsorption energies and activation barriers in catalytic reactions. The higher the position of the d-band center relative to the Fermi level, the more vacant the antibonding states, which leads to a stronger bond between the adsorbate and the metal surface.^{14,15,17,20} Actually, this model has successfully represented various catalytic reactions, and on the basis of experimentally measured values, many approaches have directly linked catalytic activity with the electronic structures of transition-metal surfaces.^{21–29}

However, in the case of the methanol oxidation reaction (MOR), the access to the pure electronic effect has been blocked due to many limitations such as the disturbance of the bifunctional mechanism,^{30–33} complex reaction paths,^{34–39} ensemble-site requirements,^{31,40–42} and so forth. These limitations originate from the intrinsic complexity of methanol oxidation mechanisms. By conventional approaches, it is impossible to observe the electronic effect on the catalytic activity in methanol oxidation.

In this research, we introduce a new strategy for understanding catalytic reactions in terms of electronic structures. Generally, the MOR on Pt can be described by three steps^{30,34,38,43} when passing through the CO_{ad} intermediate

Because the CO oxidation processes (eqs 2 and 3) are mainly governed by bifunctional effects and not by the electronic structure when a second component is used with Pt,^{44,45} these processes were separated by sensitive potential control. To focus on the methanol dehydrogenation reaction (eq 1), the

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voltage was held at 0.3 V (versus the reversible hydrogen electrode (RHE)), where methanol is decomposed to CO without any other reactions. Further reaction does not occur because Pt is unable to activate water (eq 2), and CO₂ cannot be formed until ~0.45 V.^{41,46–48} Also, in the potential range below 0.35 V, the reaction path can be simplified as a sole reaction pathway forming CO_{ad} on the Pt surface without other possible routes that lead to the formation of soluble product species.³⁴ Therefore, we can successfully obtain the adsorbed CO as the final product, not as the reaction intermediate, in this case.

We also excluded the ensemble site effect that hinders the investigation of the electronic effect in an alloy system like PtRu by using amorphous metal phosphate (FePO₄) as the support material in the modification of the electronic structure according to the Fermi energy difference.⁴⁹ In our previous research, we have observed that core-level binding energies of Pt or Au nanoparticles vary with the nearby amorphous metal phosphate, and this material is also known as a suitable transfer medium for protons, hydroxyl ions, water, methanol, and oxygen.^{50–56}

Although Ru or other components are alloyed with Pt to enhance the CO oxidation process,^{1,3,9,30–33,41} the methanol dehydrogenation rate is still insufficient for the practical application of DMFCs. Therefore, optimum catalysts should be designed by optimizing each aspect, methanol dehydrogenation and CO oxidation. In this Letter, our approach focuses on the methanol dehydrogenation reaction that leads to the formation of CO_{ad}, and the results are discussed in terms of the d-band center model.^{14–17} Other reactive intermediates (HCOO* or HCHO*) or soluble species are not significant in the potential range of interest.³⁴ This is the first experimental report on the direct correlation between dehydrogenation activity and the d-band center of a transition metal during the MOR. Our novel finding for the electronic effect in CO production from methanol can furnish valuable insight into the development of a new catalyst for DMFC.

Pt nanoparticles having different positions of the d-band center were prepared by varying the sputtering rate of FePO₄ with the sputtering rate of Pt fixed (cosputtering). Before measuring the methanol dehydrogenation activity, we first identified the crystal structure, grain size, and surface orientation of each sample. X-ray diffraction (Figure S2, SI) confirmed polycrystalline Pt phases embedded in the amorphous FePO₄. From the Scherrer equation of Δk versus k (the scattering vector $k = (4\pi/\lambda) \sin \theta$), the grain size of Pt was in the range of 6.8–12.7 nm for the pure Pt and Pt/FePO₄ nanocomposites (Table 1). The size decreased with the increased sputtering power of FePO₄. However, these are beyond the range where the catalytic activity is strongly sensitive to the Pt nanoparticle size.^{57–64}

Table 1. Grain Size of Crystalline Pt at Various Sputtering Powers of FePO₄, Obtained from the Δk versus k Plot of Figure S2 (SI)

sample	grain size (nm)
Pt	12.3 ± 1.7
Pt/FePO ₄ (30 W)	12.7 ± 1.2
Pt/FePO ₄ (60 W)	7.6 ± 0.4
Pt/FePO ₄ (90 W)	6.8 ± 0.4

From the adsorption and desorption of hydrogen, we measured the active surface areas of Pt and also confirmed no significant change in Pt orientation (Figure S1, SI). Furthermore, it was observed that the amorphous FePO₄ does not participate in the MOR (Figure S3, SI), only acting as an electronic-tuning component for Pt by the Fermi energy difference.

To investigate the methanol dehydrogenation activity, the coverage of adsorbed CO on Pt was measured from the methanol dehydrogenation reaction (eq 1). Wieckowski's group showed that the amount of CO_{ad} formed from methanol decomposition can be measured without changing the electrolyte solution by combining chronoamperometry and fast-scan cyclic voltammetry (CV)^{34,46,65} under potential control (Figure 1).

Figure 1. Schematic figure representing the potential control and the corresponding function of each step during methanol electro-oxidation. The time for chronoamperometry (methanol dehydrogenation) is changed from 0.1 to 150 s to measure the CO coverage as a function of reaction time.

This technique consists of three steps, cleaning, methanol dehydrogenation, and CO stripping. During the chronoamperometry step, methanol is decomposed into CO, which is strongly adsorbed on Pt until stripped through the fast-scan CV. This is possible because at a fast scan rate, Pt is insensitive to the presence of methanol in the solution, and only the adsorbed CO is stripped during the fast CV (Figure 2).

The coverage of CO was measured by varying the chronoamperometry time (0.1–150 s). Previous research has shown that the rate of CO_{ad} formation from methanol on a Pt surface can be modeled by the Elovich equation (eq 4), which assumes a linear dependence of the activation barrier for methanol dehydrogenation on CO coverage.^{66–69} Figure 3 shows the CO coverage behavior as a function of reaction time and is fitted by

$$\frac{d\theta_{\text{CO}}}{dt} = k_a C_m \exp(-\alpha \theta_{\text{CO}}) \quad (4)$$

where k_a is the rate constant for methanol dehydrogenation, C_m is the methanol concentration (0.1 M in this experiment), and α reflects the effect of repulsive CO interactions on the rate of methanol dehydrogenation. The CO coverage was measured from the charges corresponding to the oxidation of the adsorbed CO, which can be obtained by integrating the CO stripping peak of Figure 2 after background subtraction.

Figure 2. Fast scan (3 V/s) CV of Pt showing the CO_{ad} stripping peak (first cycle) and subsequent three cycles (total of four cycles), measured from potential control (Figure 1) in 0.1 M HClO_4 + 0.1 M CH_3OH (red solid line). The second and subsequent scans are almost identical and also similar to the CV curve in 0.1 M HClO_4 (dotted line), except for a slight current at around 0.7 V from the methanol decomposition process forming soluble species.⁴⁶ Thus, the second scan of CV was used as a background to obtain the charge corresponding to the oxidation of CO_{ad} .

Figure 3. CO coverage versus time for each Pt surface prepared by different sputtering powers of FePO_4 . The CO_{ad} coverage was obtained from a CV scan at the rate of 3 V/s in 0.1 M HClO_4 + 0.1 M CH_3OH (Figure 2) and fitted from eq 4.

With the initial condition of $\theta_{\text{CO}} = 0$ at $t = 0$, we obtained the rate constant for methanol dehydrogenation of each sample. Before this process, we obtained α from each sample, and the average value of α was used to acquire a more reliable rate constant k_a for methanol dehydrogenation (see Figure S4, SI).

Figure 4 clearly exhibits the trend that the methanol dehydrogenation activity k_a decreases with the downshift of the d-band center (from the valence band spectra of Figure S5, SI). On the Pt surface, the dissociative adsorption of methanol involving first-hydrogen extraction by O–H or C–H bond scission is regarded as the rate-determining step of methanol dehydrogenation.^{16,70,71} Because the methanol desorption barrier is less than that for the O–H or C–H scission,^{70,72} methanol desorption is often observed on Pt surfaces in ultrahigh vacuum.^{73–75} From this point of view, a stronger adsorption of methanol on Pt may induce a higher methanol dehydrogenation rate by increasing the likelihood of O–H or C–H scission and finally lead to very stable CO_{ad} through subsequent exothermic reactions. Therefore, the

Figure 4. Rate constant for methanol dehydrogenation on Pt surfaces as a function of the d-band center, as measured from the valence band spectra in Figure S5 (SI) (relative to pure Pt).

decrease in the rate constant can originate from direct methanol desorption without bond scission and following catalytic reactions because the downshift of the d-band center implies a weaker adsorption of reactant molecules on the Pt. It should be noted that these kinds of arguments can be more systematically described when the changes of the activation barrier and the adsorption energy of each reaction step are calculated according to the d-band shift of Pt by considering the scaling properties in the adsorption energies of adsorbed reaction intermediates or by considering the Brønsted–Evans–Polanyi relationships, which have been established between activation barriers and reaction energies for surface reactions.^{18,20,76–80}

In addition, the higher position of the d-band center relative to the Fermi level not only results in the strong binding of a reactant on Pt but also the strong binding of spectator species in the electrolyte, such as specifically adsorbed anions, underpotentially deposited hydrogen (H_{upd}), OH_{ad} , and other nonreactive molecular species that block the available Pt sites for methanol adsorption.^{24,41,81} Therefore, an optimum point of the reaction rate would exist at a suitable position of the d-band center, and the so-called volcano-type relation should appear.²⁴ However, in this experiment, because we covered only the downshift of the d-band center, further study is needed on the region of the higher d-band center relative to pure Pt by opposite metal–phosphate selection to establish the overall trend of methanol dehydrogenation.

In summary, to identify the electronic effect during a MOR, we separated the CO oxidation process by introducing an elaborate potential control. With this approach, we could systematically study the electronic effect on methanol dehydrogenation without concern for any unfavorable effects. We confirmed that the dehydrogenation activity of the Pt surface decreases with the downshift of the d-band center. Through further incorporation of CO oxidation properties or the bifunctional effect, advanced designs of methanol oxidation catalysts can be achieved. Also, this kind of potential control strategy can be applied to other catalytic reactions, such as ethanol oxidation or formic acid oxidation, to resolve otherwise-complicated catalytic reactions with the proper tuning of the electronic structure.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed experimental procedures, additional electrochemical analysis, structural characterizations, and XPS spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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Supporting Information

Electronic Effect in Methanol Dehydrogenation on Pt Surfaces: Potential Control during Methanol Electrooxidation

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Experimental Procedure

Pt/FePO₄ nanocomposite electrodes were fabricated by rf magnetron co-sputtering on indium-tin oxide (ITO) glass using Pt and FePO₄ targets at room temperature (RT) by varying the sputtering rate of FePO₄ at a fixed power of Pt. Thin films were annealed at 300°C for 30 min to enhance their adhesion onto the ITO surface as well as to synthesize well-connected Pt nanocrystals in the amorphous FePO₄ matrix.

X-ray diffraction (XRD, New D8 Advance: Brucker) was used to characterize the crystal structures of Pt, Pt/FePO₄ and FePO₄, and to determine the grain size of Pt in the nanocomposite. The electronic structure of the Pt valence-band was analyzed by x-ray photoelectron spectroscopy (XPS, AXIS-HSI: KRATOS) with 1253.84-eV incident photon.

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The Shirley background was subtracted from each measured spectrum, and the position of the *d*-band center was obtained from $\int N(\varepsilon)\varepsilon d\varepsilon / \int N(\varepsilon) d\varepsilon$, where $N(\varepsilon)$ is the density of states or the XPS intensity after background correction [1-6].

The Pt/FePO₄ nanocomposite, Pt wire, and Hg/Hg₂Cl₂ (SCE) as the working, counter, and reference electrodes, respectively, were used with a computer-controlled potentiostat (CHI 604A: CH Instrumental Inc.). All of the potentials in this article were converted to RHE. The cyclic voltammetry (CV) was carried out in a 0.1 M HClO₄ solution at a scan rate of 50 mV/s, to determine the available Pt sites by integrating the hydrogen adsorption/desorption curves and to confirm the surface orientation of Pt. For the CO-coverage measurement, a set of programmed potential steps, chronoamperometry, and fast-scan CV (Fig. 1) were performed in a 0.1 M CH₃OH + 0.1 M HClO₄ solution. The potential steps for cleaning the Pt surfaces were attained by several 1.0 V (oxidation) - 0.01 V (reduction) steps with 1-s holding time for each step. Time for chronoamperometry (methanol dehydrogenation) was varied in the range of 0.1 - 150 s to measure the amount of adsorbed CO at different reaction times. Fast CV was performed at a scan rate of 3 V/s to strip the CO_{ad}. Each electrochemical measurement was carried out in a N₂-purged solution at RT.

Fig. S1. Cyclic voltammograms of the Pt and Pt/FePO₄-nanocomposite electrodes with various sputtering powers of FePO₄ in 0.1 M HClO₄.

Fig. S2. X-ray diffraction of Pt and Pt/FePO₄ nanocomposites to determine the grain size of Pt nanocrystals from the Δk vs. k plot.

Fig. S3. Cyclic voltammograms of Pt and FePO₄ in 0.1 M HClO₄ + 0.1 M CH₃OH at a scan rate of 50 mV/s.

Fig. S4. Plot of α as a function of FePO₄ sputtering power. In Eq. (4), α reflects the effect of repulsive CO interactions on the rate of methanol dehydrogenation; we did not find any considerable variations or tendency in α for different samples. So, α was obtained from each data, and the average value of α (19.2 ± 0.9 ML⁻¹) was used to obtain the rate constant k_a for methanol dehydrogenation with the fitting from Fig. 3.

Fig. S5. The valence-band spectra for Pt and Pt/FePO₄ composites with various sputtering powers of FePO₄.

Fig. S6. XPS spectra in the Pt 4f region for the Pt and Pt/FePO₄ nanocomposites with various sputtering powers of FePO₄. The peak positions of pure Pt are represented by dashed lines, and the peak shift in the nanocomposites is clearly toward higher binding energies.

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