

Pd/TiO₂ 촉매를 이용한 HCO₂K 광 분해 반응

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Photocatalytic Dehydrogenation of Potassium Formate Over Pd/TiO₂

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Abstract >> A Pd/TiO₂ catalyst was prepared by a conventional impregnation method, and further characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and UV-Vis spectroscopy. The as-prepared material was employed to accelerate dehydrogenation of potassium formate in the presence of light at different temperatures. The Pd/TiO₂ catalyst showed distinct dehydrogenation activities, and particularly, the material exhibited a higher turnover frequency (TOF) of 2,097 h⁻¹ at 80°C after 10 minutes in the presence of light compared to that (TOF of 1,477 h⁻¹) obtained in the absence of light. Numerous analytical techniques suggest that the increased dehydrogenation activity likely originates from light-excited electron and hole at the photocatalyst, i.e., TiO₂, in conjunction with metal-support interaction.

Key words : Palladium(팔라듐), TiO₂(이산화타이타늄), Photolysis(광반응), Potassium formate(포름산칼륨), Dehydrogenation(탈수소화)

1. Introduction

Hydrogen has been considered as an alternative energy carrier to fossil fuels because of its high gravimetric energy density^{1,2)}. To realize hydrogen economy, it is necessary to develop innovative and economically feasible technologies for hydrogen production, storage, and utilization. However, these key

technologies have still several technical obstacles for commercialization, and particularly, an efficient and safe hydrogen storage method with high storage densities is needed.

To address the issues, numerous chemical hydrogen storage materials including NaBH₄^{3,4)}, NH₃BH₃⁵⁻⁷⁾, and HCO₂H^{8,9)} have been proposed. Owing to its relatively high volumetric hydrogen storage capacity (53 g/L) as

well as physical nature, formic acid (FA, HCO₂H) has recently attracted increasing attention among the studied materials. In addition, the chemically stored hydrogen atoms in FA can readily be released on demand in the presence of palladium based heterogeneous catalysts even at room temperature, producing hydrogen (H₂) and carbon dioxide (CO₂) gases¹⁰. Likewise, structurally similar compounds, metal formate (MCO₂H; M = Na, K, or an alkali metal) based materials have also proved to be potential hydrogen carriers, although their hydrogen storage densities are relatively low.

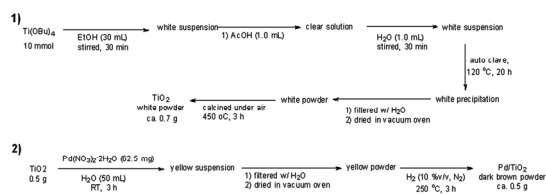
For a chemical hydrogen storage material to be valuable for practical applications, it is necessary to accelerate the rate of dehydrogenation by providing energy required to overcome a kinetic barrier. In general, thermal energy is employed to activate relevant chemical bonds from the hydrogen storage materials (e.g., FA) with a heterogeneous catalyst. For instance, FA dehydrogenation was proceeded in the presence of Pd catalysts at temperatures ranging from room temperature to 60°C. In contrast to the thermal induced dehydrogenation, light can be employed as a energy source. For example, photolysis of formic acid was recently reported using pure, N-doped and Au-promoted TiO₂¹¹); the N-doped Au/TiO₂ catalyst with visible light showed enhanced photocatalytic activity by lowering the band gap of TiO₂.

We report here on the preparation and characterization of Pd catalysts supported on the photo-active TiO₂ material. In addition, their photo-induced dehydrogenation activities of potassium formate are further assessed using simulated sun light, demonstrating that photocatalytic H₂-release activity was significantly improved by charge transfer to Pd active sites.

2. Results and discussion

2.1. Catalyst preparation and characterization

TiO₂ support and Pd/TiO₂ catalyst were synthesized according to scheme 1. TEM and STEM images revealed that Pd nanoparticles (NPs) were well dispersed over the prepared TiO₂ support with an average size of ca. 2.2 nm (Fig. 1). XRD patterns of TiO₂ showed the clear peaks attributed to anatase phase were presented while no peaks were observed for rutile or other phases (Fig. 2). After immobilization of Pd NPs on TiO₂, no phase transition was observed on the XRD pattern. In addition, no peaks attributed to metallic Pd species were observed presumably due to the small-sized Pd NPs.



Scheme 1. The procedure for TiO₂ support (1) and Pd/TiO₂ catalyst (2)

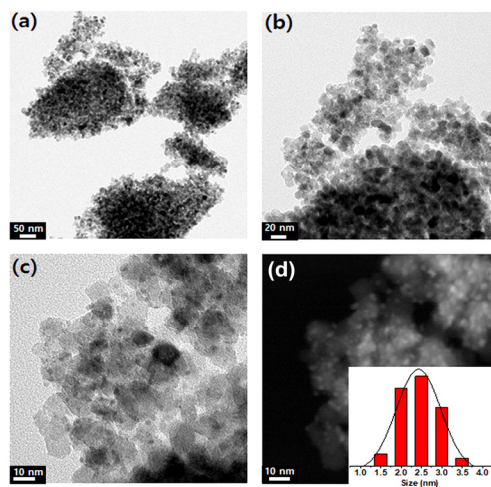


Fig. 1. TEM (a- c) and STEM (d) images of Pd/TiO₂. Pd particle size distribution was presented in Fig. 1(d) (inset)

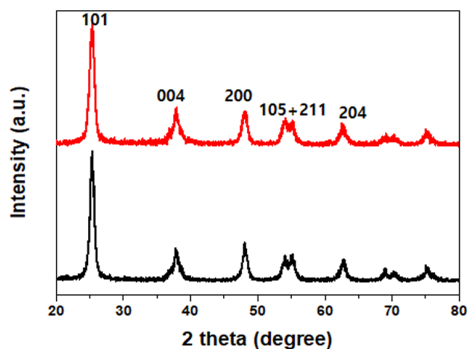


Fig. 2. XRD spectra of Pd/TiO₂ (red) and TiO₂ (black)

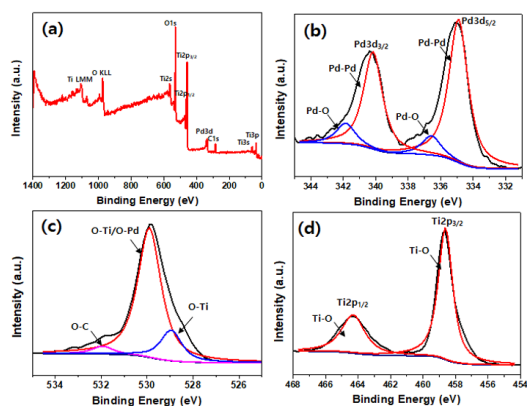


Fig. 3. XPS spectra of Pd/TiO₂: (a) survey peaks, (b) Pd3d, (c) O1s, and (d) Ti2p

To elucidate chemical states of Pd, Ti, and O species, XPS analyses were conducted (Fig. 3). The Pd, Ti and O species was clearly appeared in the XPS survey spectrum (Fig. 3(a)). In addition, as depicted in Fig. 3(b) and 3(c), the Pd3d and O1s peaks attributed to Pd-O bond were observed, indicating interactions between Pd (metal) and O (from TiO₂, support). The interaction could occur in way that activated electrons of TiO₂ by irradiation of light were transferred into Pd active sites, which enhanced the catalytic activity of formate dehydrogenation (see below). UV-vis absorption spectroscopy was additionally employed to determine electronic structures of the TiO₂ and Pd/TiO₂ materials (Fig. 4). Compared to that of TiO₂, the absorption peak of Pd/TiO₂ was red

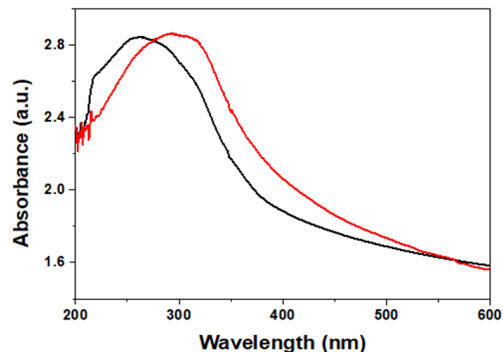


Fig. 4. UV-Vis absorption spectra of TiO₂ (black) and Pd/TiO₂ (red)

shifted by the interaction of Pd with the TiO₂ support. Pd NPs is known to show the surface plasmonic resonance absorption dependent on the NP size¹²⁾. The enhanced light absorption clearly displays a synergistic interaction of Pd NPs and TiO₂ where the Pd NPs improves both reactions kinetics of FA dehydrogenation (vide infra) and light absorption of TiO₂ photocatalyst, the two most important factors determining the efficiency of photocatalysis.

2.2. Photolysis of potassium formate over Pd/TiO₂

The photocatalytic dehydrogenation activity of Pd/TiO₂ towards potassium formate was assessed at different temperature with and without light. In a typical reaction, 150 W Xenon lamp was used as a light source to provide a simulated sun light with light intensities ranged from 100 to 300 mW/cm². Compared to that obtained under dark conditions, the Pd/TiO₂ catalyst showed a higher activity at each temperature in the presence of light (Fig. 5(a)); e.g., Pd/TiO₂ displayed a turnover frequency (TOF) of 2,097 h⁻¹ at 80°C after 10 min in the presence of light but exhibited a TOF of 1,477 h⁻¹ without light source. In order to determine the extent of light effect as a function of temperature on catalytic activity, the TOF val-

ues obtained at each temperature were normalized by the TOFs of corresponding reactions conducted in the absence of light (Fig. 5(b)). The result show that the normalized TOFs were found to decrease with increasing temperature although the apparent TOFs increased with temperature, indicating that the light effect decreased as temperature increased. In other words, thermal effect is dominant at high temperatures for the catalytic dehydrogenation of potassium formate over Pd/TiO₂ while light effect seems to be favored at relatively low temperatures. Next, we further examined the influence of light intensity on the photocatalytic activity (Fig. 6). The catalytic activity increased as light intensity increased, whereas the TOF under 300 mW/cm² of light was not sig-

nificantly improved compared to that obtained under 200 mW/cm² of light.

3. Experimental

3.1. Catalyst preparation

Photo-active TiO₂ support was prepared by a conventional hydrolysis method¹³. First, a titanium containing precursor (Ti(OBu)₄, 1.0 g) was added into ethanol (30 mL) upon vigorous stirring, followed by addition of acetic acid (CH₃COOH, 1.0 mL) after 30 min. Deionized water (1.0 mL) was then added into the solution sequentially and further stirred for 30 minutes. The resultant white suspension was transferred into an autoclave reactor, followed by hydrolysis at 120°C for 20 hours. The formed white precipitation was filtered, washed several times with deionized water, and dried in a vacuum oven for 12 hours. Finally, the resulting material was calcined at 450°C for 3 hours, yielding white powder (0.7 g).

The prepared TiO₂ powder (0.5 g) was then used as a support for a desired catalyst. The TiO₂ material was added into the aqueous solution (50 mL) of Pd(NO₃)₂ · 2H₂O (62.5 mg), which was stirred at room temperature for 3 hours. The heterogeneous re-

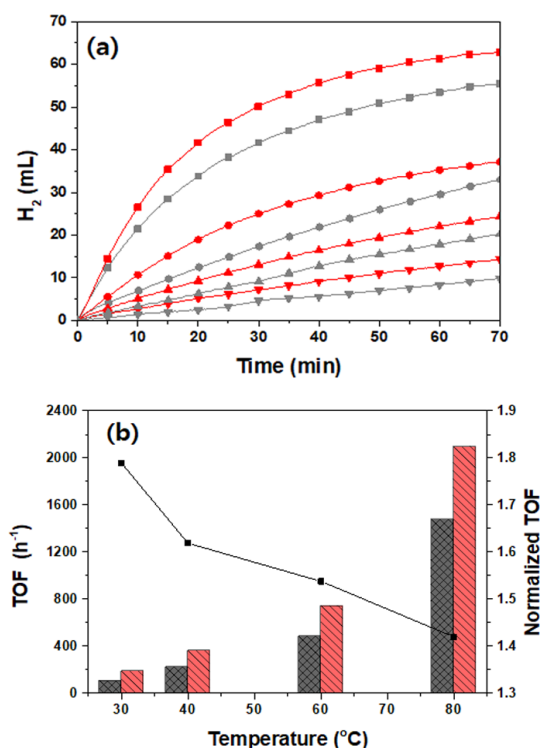


Fig. 5. Catalytic dehydrogenation of potassium formate over Pd/TiO₂ at different temperature: (a) 80°C (light, ■; dark, □), 60°C (light, ●; dark, ○), 40°C (light, ▲; dark, △), and 30°C (light, ▼; dark, ▽) and (b) TOFs (light, ▨; dark, ▩) and normalized TOFs at each temperature. The light intensity was 300 mW/cm²

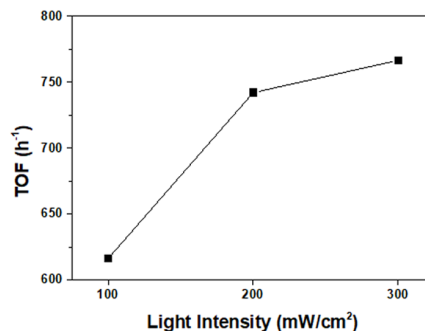


Fig. 6. TOF values of formate dehydrogenation using Pd/TiO₂ under different light intensity. The reaction was conducted at 60°C

action mixture was filtered, washed several times with deionized water, and dried in a vacuum oven for 12 hours. The obtained yellowish powders were reduced under a H₂ flow (10 v/v%, N₂) at 250°C for 3 hours, yielding dark brown powders (0.5 g, 4.75 wt% Pd).

3.2. Catalyst characterization

The morphology of the as-prepared Pd/TiO₂ catalyst was analyzed by high-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) using a field emission, FEI Tecnai microscope G2 F20 operating at 200 kV. X-ray diffraction (XRD) studies of the catalyst was carried out using a Rigaku Mini Flex II instrument operating with Cu K α X-ray source at 40 kV and 20 mA. XPS spectra were acquired with an XPS instrument equipped with a PHI50000 Versa Probe operating with an Al K α X-ray beam at a background pressure of 6.7×10^{-8} Pa. The spectra were calibrated by using peak of C1s at 284.6 eV. UV-Vis absorption of the catalyst was measured by Cary 100 UV-Vis instrument (Agilent Technologies).

3.3. Photocatalytic dehydrogenation of potassium formate

Catalytic dehydrogenation of potassium formate (HCO₂K) was performed as follows: First, Pd/TiO₂ (12.5 mg) was added into an aqueous solution of potassium formate (5.0 mL, 1.0 M). The reaction mixture was purged with N₂ at room temperature, which was then stirred at various temperatures (30, 40, 60, and 80°C) for 70 minutes. A photocatalytic dehydrogenation was carried out under the irradiation of 150 W of Xenon lamp (USHIO) equipped with Model 10500 Low Cost Solar Simulator with a

10513 90° Uniform Illumination Accessory with Manual Shutter (ABET technologies). The power of light source was calibrated by a light power meter prior to a reaction. The amount of a generated gaseous product, H₂, was measured by a gas burette equipped with a real-time recording system after passing through a NaOH (10 M) trap to remove a small amount CO₂ byproduct. To analyze the purity of gaseous products, in situ Fourier transformed infrared spectroscopy (FT-IR) was performed using a Nicolet iS10 instrument (Thermo Scientific) equipped with a smart OMNI-transmission accessory. In a spectrum, neither CO₂ nor CO peak was observed, indicating the formation of H₂ only during a dehydrogenation reaction.

4. Conclusions

A Pd/TiO₂ catalyst was synthesized and further characterized using a number of analyses. The as-prepared Pd/TiO₂ material proved to be a potentially feasible catalyst for potassium formate, which is a chemical hydrogen storage material. The H₂-release properties of potassium formate over Pd/TiO₂ were determined as a function of temperature in the presence of light. The Pd/TiO₂ catalyst showed increased TOFs at every temperature in the presence of light, compared to those without light. Further studies revealed that light-driven enhancement for the activity was dominant at low temperatures but the extent of improvement decreased with increasing temperature. The enhanced H₂-release properties particularly at low temperatures were proposed by light-driven photocatalysis at TiO₂/Pd active sites in conjunction with metal-support interaction. On the basis of the results, Pd supported on photo-active supports are thus potentially promising as catalysts for the photolysis of potassium formate particularly at low temperatures.

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