



# Lattice oxygen assisted room-temperature catalytic process: Secondary alcohol dehydrogenation over Au/birnessite photocatalyst

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## ABSTRACT

Au-based catalysts were widely applied in photocatalytic areas owing to Au local surface plasmon resonance (LSPR), especially in the reactions of secondary alcohol dehydrogenation. However, there were rare cases reporting Au catalysts to dehydrogenate secondary alcohols under dark condition at room temperature. In this work, basic semiconductor birnessite, with easily extractable lattice oxygen in its lattice structure, was employed as support of Au catalyst and it was found that the Au/birnessite catalyst could dehydrogenate iso-propanol (IPA) to acetone under dark condition (3.7  $\mu\text{mol}$  acetone was produced within 5 h). With the utilization of lattice oxygen in the reaction under dark condition, oxygen vacancies were instantaneously formed which enhanced the light absorbing properties of Au/birnessite and further improved its photocatalytic activity (13.6  $\mu\text{mol}$  acetone production within 5 h). The synergistic effects between lattice oxygen and oxygen vacancies enhanced the performance of Au-based catalyst in IPA dehydrogenation and this work provides a synthesis tactic for effective catalysts in the dehydrogenation of various secondary alcohols.

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## 1. Introduction

Due to the relentless environmental concerns and risky demands for the fossil fuels, iso-propanol (IPA) dehydrogenation has overwhelmed the other methods (such as Wacker oxidation [1] and Cumene process [2]) and become the most economical one for acetone generation [3,4]. According to the energy employed to initiate the reaction, there are two major routes for IPA dehydrogenation, one is IPA dehydrogenation reaction driven by the external heat supply [3,4], and another one is photo induced photocatalytic systems [5–7]. For the thermal catalytic process, IPA could be dehydrogenated over the Cu-based catalysts at about 100 °C [3,4], whereas the high temperature requirement hindered its wide application. With the entry of photocatalysis era [8,9], semiconductors, such as TiO<sub>2</sub> and SrTiO<sub>3</sub>, were employed as catalysts to photo-catalytically transformed IPA to acetone at room

temperature [5], however the utilizable ultra-violet light constitutes less than 5% of the whole solar light spectrum [10]. Catalysts prepared by loading metal with local surface plasmon resonance (LSPR) in visible light region (Au) on white semiconductors (such as TiO<sub>2</sub> and SrTiO<sub>3</sub>) were reported to be able to adsorb visible light and improve the photocatalytic performance [6,7], nevertheless the solar energy utilization efficiency was quite low [11]. Therefore, it's meaningful to prepare a catalyst which is robust under versatile conditions, such as at low temperature without light irradiation, and the conditions with visible light introduction.

To prepare such a robust catalyst, it is of critical importance to search for a catalyst which is effective in IPA dehydrogenation at room temperature. It has been reported that, for the reactions with oxygen as one of the reactants, lattice oxygen would participate in the reactions and facilitate the reaction occurrence via Mars-van Krevelen mechanism [12]. Selecting a support with easily extractable active lattice oxygen might be a possible tactic for this issue.

Birnessite (Na<sub>x</sub>MnO<sub>2</sub>·H<sub>2</sub>O), a semiconductor which could absorb visible light, was recently extensively studied in various photocatalytic reactions with the irradiation of abundant visible light (43% of the whole solar light spectrum) [13,14], and birnessite

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supported Au catalyst Au/birnessite was also studied previously in the reaction of oxygen evolution from water [15]. More importantly, the lattice oxygen in manganese oxide was reported to be extractable easily at room temperature [16,17], birnessite, a kind of existing states of manganese oxide, might exhibit a similar character. Up to now, there were almost no reports on Au/birnessite in IPA photocatalytic dehydrogenation reaction yet. In this paper, Au/birnessite was synthesized and first adopted as catalyst in IPA dehydrogenation, and the effects of lattice oxygen and the instantaneously generated oxygen vacancies were studied in detail.

## 2. Experimental

### 2.1. Catalyst preparation

Commercial anatase  $\text{TiO}_2$ ,  $\text{HAuCl}_4$ ,  $\text{KMnO}_4$ ,  $\text{MnCl}_2$ ,  $\text{NaOH}$  and  $\text{CH}_3\text{OH}$  were purchased from Wako pure chemical industries Ltd., and used as raw materials.

Preparation of birnessite: birnessite was prepared by the reduction of  $\text{KMnO}_4$  with  $\text{MnCl}_2$  in high concentration  $\text{NaOH}$  solution [16,17]. Typically, the aqueous solution of  $\text{MnCl}_2$  was added dropwise into the highly alkaline  $\text{NaOH}$  solution of  $\text{KMnO}_4$ . Then it was stirred for 1 h and aged for 24 h at R.T., and the resultant black precipitate was washed with water, dried at  $70^\circ\text{C}$  overnight to get the sample birnessite.

Preparation of Au/ $\text{TiO}_2$  and Au/birnessite: Au was loaded on the supports  $\text{TiO}_2$  and birnessite by photoreduction method with  $\text{CH}_3\text{OH}$  as the reductant, and the theoretical loadings of Au were kept as 2.0 wt.%.

### 2.2. Material characterization

The crystalline structures of the supports and Au-based catalysts were analyzed by X-ray diffraction (XRD) method, on an X-Pert diffractometer equipped with graphite monochromatized  $\text{Cu-K}\alpha$  radiation. The specific surface areas were determined with a surface area analyzer (BEL Sorp-II mini, BEL Japan Co., Japan) by the Brunauer-Emmett-Teller (BET) method. The morphology was observed on transmission electron microscope JEM-2100 (TEM, JEOL, USA). The diffuse reflection spectra of the catalysts were measured by UV–visible spectrophotometer (UV-2600, SHIMADZU Co., Japan) from 200 nm to 800 nm. The contents of Au on the catalysts were analyzed by inductively coupled plasma optical

emission spectrometry (ICP-OES, SPS3520UV-DD, SII nano technology Inc., Japan). The oxygen vacancies were analyzed by electron spin resonance (ESR) on JEOL JES-FA-200. The basic properties of the catalysts were characterized by  $\text{CO}_2$  temperature programmed desorption method ( $\text{CO}_2$ -TPD, Autochem II 2920). The photocurrents and the Fermi levels of the catalysts were performed on the CHI electrochemical analyzer (ALS/CH model 650A) using a standard three-electrode mode with 0.5 M  $\text{Na}_2\text{SO}_4$  solution as the electrolyte. For the photocurrent analysis, HA30 and L42 cut-off filters were employed to remove ultraviolet and infrared light.

### 2.3. Catalyst evaluation

In a typical IPA dehydrogenation reaction, 0.15 g catalyst was uniformly dispersed on the bottom surface of a vessel ( $5.6\text{ cm}^2$ ) which was placed in a glass reaction cell of 500 mL. The catalyst temperature was probed by a digital thermometer (CT-1200D, CUSTOM Co., Japan). The cell was totally covered by tinfoil and then IPA was injected into the cell through an installed inlet/outlet port. For the reaction carried out at room temperature without light illumination, 30 min was required to ensure the adsorption-desorption equilibrium of the gaseous reactants. After that the concentrations of IPA, acetone, and  $\text{CO}_2$  were measured using a gas chromatograph (GC-14B, Shimadzu) equipped with a flame ionization detector (FID). Porapak Q and PEG-1000 columns were used to detect  $\text{CO}_2$  and the two organic gases (IPA and acetone), respectively. Isotope experiment was also conducted with  $^{18}\text{O}_2$  and IPA as the reactants, with the labeled products analyzed by gas chromatography–mass spectrometry (GC-MS, JMS-K9, JEOL Co., Japan). As to IPA dehydrogenation reaction with visible light irradiation, HA30 and L42 cut-off filters were employed to remove ultraviolet and infrared light. The reaction cell was also kept in dark for 30 min before turning on the 300 W Xe arc lamp.

## 3. Results and discussion

### 3.1. Physicochemical properties of the catalysts

The successful syntheses of these catalysts were confirmed by XRD patterns in Fig. 1a and  $\text{N}_2$  adsorption-desorption isotherms in Fig. 1b. For birnessite, the diffraction peaks at about  $12.0^\circ$ ,  $24.0^\circ$  and  $36.0^\circ$  showed a basal spacing of about 0.7 nm [14,16,17] (Fig. 1a), together with the  $\text{H}_3$  type of hysteresis loop in the  $\text{N}_2$  adsorption-

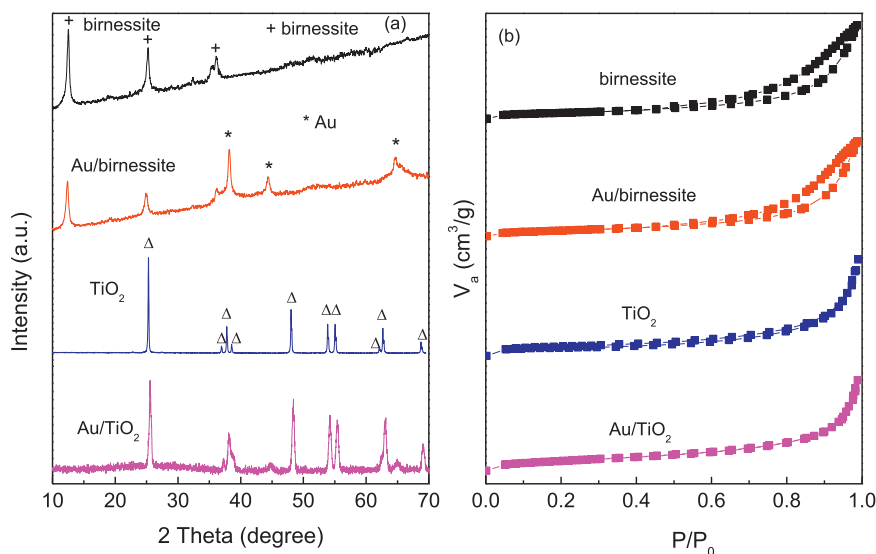


Fig. 1. (a) XRD patterns of the supports and Au-based catalysts. (b) Adsorption-desorption isotherms of the supports and Au-based catalysts.

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