

# Furfuryl 알코올의 선택적 산화 전환에 대한 수화 이산화망간 나노와이어의 One-pot 합성

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## One-pot Synthesis of Hydrus MnO<sub>2</sub> Nanowires for Selective Oxidative Transformation of Furfuryl Alcohol

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### 초 록

간단한 불-밀 방법에 의한 one-pot 합성법을 통해 수화된 이산화망간 나노와이어가 합성되었다. 이렇게 준비된 이산화망간 나노와이어는 주사 전자 현미경(SEM), 투과 전자 현미경(TEM), X-선 회절(XRD) 및 Brunauer-Emmett-Teller (BET)로 특성화되었고, 적당한 크기(4-5 nm)와 형태에서 좋은 촉매적 활성을 보였다. 기질 Furfuryl 알코올을 선택하여 톨루엔 용매를 사용하고 산소 1기압 및 온도 100 °C에서 반응시켰다. 이산화망간 나노와이어 촉매는 뛰어난 선택성과 전환성을 보이며 월등한 furfural 수율을 나타내었다. 또한 재사용 촉매 성능 테스트에서, 5번 이상 재실험 중 촉매 활성의 손실이 거의 없어 좋은 기계적 강도를 보여주었다.

### Abstract

Hydrus MnO<sub>2</sub> nanowires were easily synthesized by a one-pot synthesis with a simple hydrothermal method. As prepared hydrus MnO<sub>2</sub> nanowires were characterized with scanning emission microscopy (SEM), transmit emission microscopy (TEM), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET). They showed a good catalytic activity with the suitable nano-size of 4-5 nm and morphology. The furfuryl alcohol was selected as a substrate and the reaction was carried out in a toluene solvent at 100 °C under the atmospheric pressure of oxygen. The hydrus MnO<sub>2</sub> nanowire catalyst exhibited an excellent yield of furfural with the first-rate selectivity and conversion. The catalytic performance during recycle tests was also carried out and the catalyst showed a good mechanical strength with a negligible loss in the activity over five reaction cycles.

**Keywords:** One-pot synthesis, Hydrus MnO<sub>2</sub> nanowires, Furfuryl alcohol, Furfural

## 1. Introduction

The selective oxidation of alcohols to their corresponding aldehydes and ketones is a crucial transformation in organic synthesis[1-3]. Furfural is a significant precursor as a potential biomass platform for biofuels[4]. Furfural with high selectivity can be produced by the dehydrogenative oxidation of furfuryl alcohol under the environmentally friendly conditions. From the viewpoint of both laboratory and industry, a range of oxidizing approaches such as pyridinium chlor ochromate (PCC), pyridinium dichromate (PDC), and swern oxidation have been

considered so as to carry out the oxidation transformation[5]. Dess-martin periodate, 2-azaadamantane *N*-oxyl (AZADO), 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO), and tetrapropylammonium perruthenate (TPAP) oxidations are recently used for the alcohol oxidation[6]. However, the issues of cost effectiveness and environment threats are accompanied with these stoichiometric oxidants[7]. Although many supported noble metal catalyst systems have been developed so far for the furfuryl alcohol oxidation[8-11], the development of efficient catalytic procedure to avoid expensive noble metals in molecular oxygen is still required.

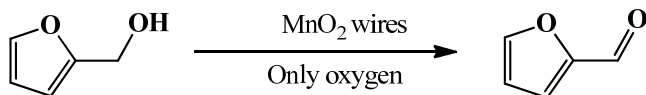
Manganese oxides have been proven as an efficient class of oxidants in catalytic organic reactions owing to their exclusive features; availability, low density, cost effectiveness, enhanced activity, rich structures, high specific capacitance, good permeability and varying morphology[12-15]. These characteristics make manganese oxides as a competitive candidate for use in the fields of catalysis, electrochemical

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**Table 1. Catalytic Performance of Different Catalysts for Furfuryl Alcohol Oxidation<sup>[a]</sup>**

Entry	Catalyst	Temperature (°C)	Time (hr)	Yield (%)
1	Wire MnO <sub>2</sub>	100	10	> 97
2	Wire MnO <sub>2</sub> <sup>[b]</sup>	100	10	> 60
3	Bulk MnO <sub>2</sub>	100	10	25
4	<i>alpha</i> -Al <sub>2</sub> O <sub>3</sub>	100	10	2
5	TiO <sub>2</sub>	100	10	3
6	ZrO <sub>2</sub>	100	10	5
7	<i>beta</i> -Al <sub>2</sub> O <sub>3</sub>	100	10	-

Reaction conditions: [a] furfuryl alcohol (0.5 mmol), wire MnO<sub>2</sub> (1.2 mmol), toluene (3 mL), [b] calcinated at 400 °C

**Scheme 1. Oxidation of furfuryl alcohol with hydrous MnO<sub>2</sub> wires.**

supercapacitor, ion exchange, chemical sensing, adsorption and Li-ion battery[16,17]. The different phase structures of manganese oxides such as MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, MnOOH, Mn<sub>3</sub>O<sub>4</sub>, and MnO<sub>6</sub> showed significantly different catalytic activity for various reactions. A number of complex methods have been described in the literature to synthesize the numerous shaped and structured MnO<sub>2</sub> (nanoparticles, nanowires, and nanorods etc.)[18-20]. In this study, we have developed a facile one-pot method for the preparation hydrous MnO<sub>2</sub> nanowires for the aerobic selective alcohol oxidation. The scanning and transmission electron microscopy (SEM and TEM) and X-ray diffraction (XRD) have been applied to estimate the morphology, structure, and phase of the hydrous MnO<sub>2</sub> nanowires. As synthesized hydrous MnO<sub>2</sub> nanowires were successfully applied for the selective aerobic oxidation of the furfuryl alcohol to produce the corresponding furfural, an important platform compound for the biofuel derivatives under the environmentally benign conditions in scheme 1.

## 2. Experimental

### 2.1. Preparation of catalyst

Hydrous MnO<sub>2</sub> wires were synthesized by the following experimental procedure. A mixture of KMnO<sub>4</sub> (0.507 g) and MnSO<sub>4</sub> (0.218 g) was dissolved in deionized (DI) water and then stirred for 30 min at room temperature (RT). The resultant was put into the reactor and sealed. The reactor was left under mild hydrothermal treatments at 140 °C for 8 h. The hydrous MnO<sub>2</sub> wire sample was obtained after washing several times with DI water and anhydrous ethanol and finally dried under vacuum at RT.

### 2.2. Catalyst characterization

The morphologies of hydrous MnO<sub>2</sub> wires were examined by scanning electron microscopy (SEM, FEI Nova 200 Nanolab) and transmit emission microscopy (TEM, JEM-2100F HR-TEM, 200 kV). X-ray diffraction (XRD) was used to investigate crystalline structure of hy-

drous MnO<sub>2</sub> wires using a Rigaku D/max IIIc (3 kW) with a q/q goniometer equipped with a Cu K $\alpha$  radiation generator. To analyze specific surface area and pore size distributions, N<sub>2</sub> adsorption/desorption was performed by Brunauer-Emmett-Teller (BET) measurements using an ASAP-2010 surface area analyzer.

### 2.3. Catalytic activity test

Hydrous MnO<sub>2</sub> nanowires (1.2 mmol) was loaded in the reactor tube with toluene (3 mL) and stirred for few minutes at 100 °C following the addition of furfuryl alcohol (0.5 mmol). The reaction mixture was continuously stirred for 10 h and the samples were taken at regular intervals. The productivity of the reaction was analyzed by gas chromatography (Yonglin GC-6500 instrument using a flame ionization detector (FID) equipped with an HP-INNOWAX capillary column having internal diameter of 0.25 mm and length of 30 mm). In order to do a comparison of catalytic activities, the reaction was also performed with bulk MnO<sub>2</sub> and calcinated MnO<sub>2</sub> (400 °C) along with some other catalysts (Table 1). It is clear from the table that only the hydrous wire MnO<sub>2</sub> is efficient enough to give > 97% yield of furfural. The other two forms of MnO<sub>2</sub> also showed some conversion but not at a desired rate. Catalysts in entries 4-7 showed negligible conversion.

### 2.4. Recycling test

Recycle test was performed in a glass tubular shaped reactor with 1.2 mmol of hydrous MnO<sub>2</sub> nanowire catalyst, 0.5 mmol of furfuryl alcohol (substrate), and 3 mL of toluene. The reaction mixture was stirred at 100 °C under 1 atmospheric pressure of O<sub>2</sub>. After the reaction, the catalyst was separated from the reaction mixture by the simple filtration process and washed repeatedly with de-ionized water. It was then air dried completely before being recycled.

## 3. Results and Discussion

### 3.1. Structural and textural properties of the catalyst

Figure 1 shows low-and high-resolution SEM and TEM images of hydrous MnO<sub>2</sub> nanowires. Although it is hard to conclude the exact aspect ratio because of random aggregation of hydrous MnO<sub>2</sub> nanowires, it can be determined that the hydrous MnO<sub>2</sub> nanowires have a width of ~50 nm and lengths of several micrometers, giving high aspect ra-

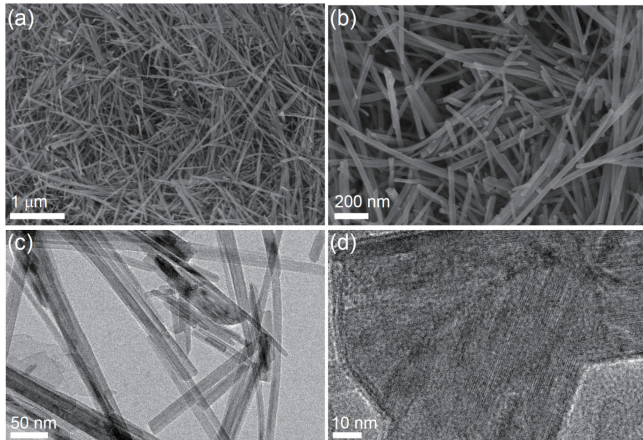


Figure 1. SEM images of hydrous  $\text{MnO}_2$  nanowires at different resolutions, (a) 1  $\mu\text{m}$ , (b) 200 nm, (c) TEM images at 50 nm and (d) 10 nm.

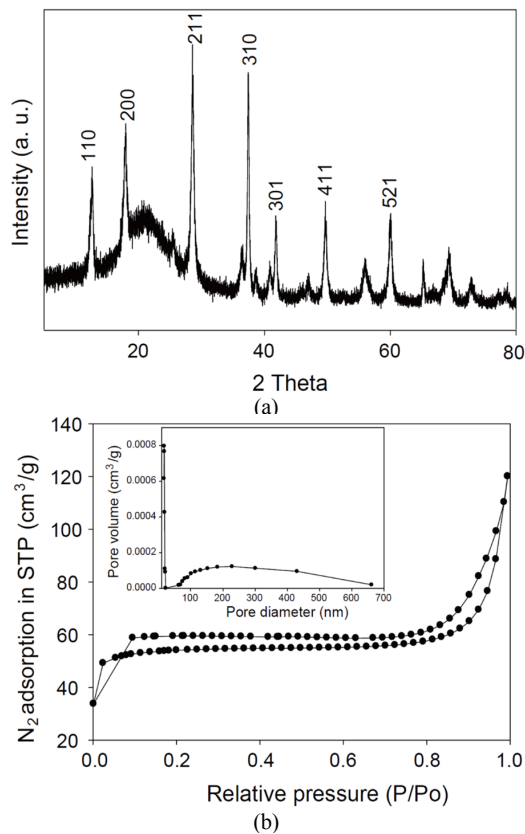


Figure 2. (a) XRD pattern of hydrous  $\text{MnO}_2$  nanowires, (b)  $\text{N}_2$  adsorption/desorption isotherms and pore size distribution of hydrous  $\text{MnO}_2$  nanowires.

tios in a range of 20-40 (Figure 1a, 1b). TEM characterization further confirms the nano-wired structure of hydrous  $\text{MnO}_2$  catalyst (Figure 1c). In addition, high-resolution TEM images exposed the crystallinity of the  $\text{MnO}_2$  nanowires. These results indicate that one-pot hydrothermal method developed in this work enables to an effective synthesis of hydrous  $\text{MnO}_2$  nanowires. To confirm the phase structure of

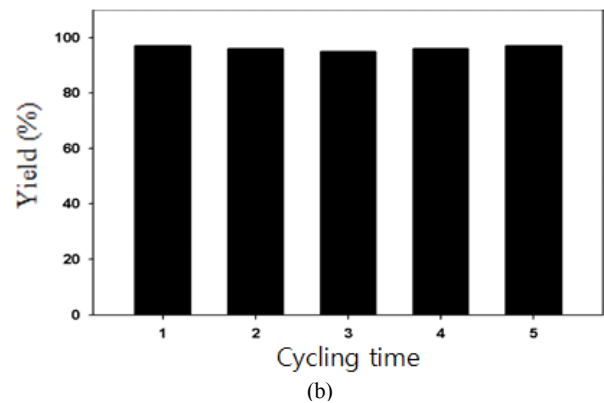
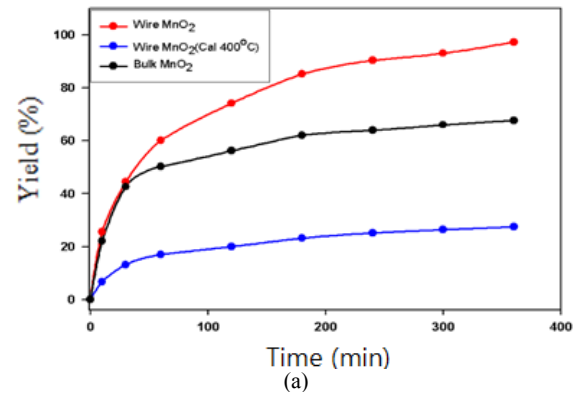


Figure 3. (a) Yield of furfural with hydrous wire  $\text{MnO}_2$ , calcinated hydrous  $\text{MnO}_2$  (400  $^{\circ}\text{C}$ ), and bulk  $\text{MnO}_2$ , (b) recycling results of hydrous wire  $\text{MnO}_2$  for oxidative transformation of furfuryl alcohol.

hydrous  $\text{MnO}_2$  nanowires, XRD measurements were performed (Figure 2). All XRD patterns of hydrous  $\text{MnO}_2$  nanowires were matched with the formation of  $\text{MnO}_2 \cdot 0.3\text{H}_2\text{O}$  (ICDD Ref. No. 44-0140, Figure 2a). Figure 2b displays the  $\text{N}_2$  adsorption/desorption isotherms and pore size distribution of hydrous  $\text{MnO}_2$  nanowires. The hydrous  $\text{MnO}_2$  nanowire exhibited the hysteresis loop of the type IV isotherm, indicating the existence of mesoporous structure. Particularly, hydrous  $\text{MnO}_2$  nanowires had a high surface area of 209  $\text{m}^2/\text{g}$ , which was calculated from the BET equation. When observing pore size distribution of hydrous  $\text{MnO}_2$  nanowires, a narrow pore size distribution of 17 nm and broad pore size distribution in a range of 100-600 nm was exhibited. This hierarchical pore distribution was attributed to the formation of the randomly interconnected network as a consequence of aggregation of high aspect ratio of hydrous  $\text{MnO}_2$  nanowires, as confirmed in Figure 1.

### 3.2. Oxidation of furfuryl alcohol to furfural

The activation process of  $\text{MnO}_2$  having mild oxidizing character requires particular care to the efficiency of oxidant[21]. For instance, a small amount of water of crystallization can increase the catalytic activity of oxidant as the -OH group of water acts as the active site for the substrate, so if it is lost during activation then completely dried  $\text{MnO}_2$  is futile for oxidation[22]. Moreover, surface morphology plays a pivot role in determining the catalytic activity. Nanoscale metal oxide

particles are considered to be more functional as they are featured by extremely high surface-to-volume ratios of the active species[23]. Taking this fact into consideration, the furfuryl alcohol substrate was subjected to three types of MnO<sub>2</sub> catalysts as described (bulk, calcinated and nanowires). The calcination was done by heating the catalyst at 400 °C to remove all bonded water. The efficiency of all three catalysts and reusability of our reported catalyst can be seen in the reaction profile (Figure 3). It is evident that the reaction was well completed in 10 h with more than 97% yield of our desired furfural with hydrous wire MnO<sub>2</sub>. The calcinated hydrous MnO<sub>2</sub> showed only 25% yield in the same time period but the bulk MnO<sub>2</sub> exhibited about 60% (Figure 3a). Moreover, the hydrous MnO<sub>2</sub> wire catalyst was successfully separated from the mixture after finishing the reaction. Washing and drying of the wire catalyst was followed by recycling test and it is shown that there was no noteworthy loss in the original activity of the used catalyst even after several runs of furfuryl alcohol oxidation reaction (Figure 3b).

#### 4. Conclusion

In summary, a facile synthesis of hydrous MnO<sub>2</sub> nanowires was carried out under ordinary conditions of temperature and pressure. The as synthesized catalyst was characterized by using SEM, TEM, XRD, and BET analysis techniques. The catalyst was then subjected to the selective oxidative transformation of furfuryl alcohol to furfural in the presence of molecular oxygen as only oxidant at 100 °C. The surface morphology of hydrous wire MnO<sub>2</sub> was observed to play an important role in this transformation due to the presence of a well-coordinated surface and more oxygen vacancies as compared to the calcinated hydrous MnO<sub>2</sub> and bulk MnO<sub>2</sub>. The catalyst produced excellent yield of furfural (> 97%) within 10 h and retained its catalytic activity when recycled for 5 times under the same reaction conditions for the furfuryl alcohol.

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