Real-Time Facile Detection of the WO₃ Catalyst Oxidation State under Microwaves Using a Resonance Frequency

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ABSTRACT: Microwaves (MWs) are often used to enhance various heterogeneous catalytic reactions. Here, we demonstrate real-time monitoring of a catalyst’s oxidation state in a microwave catalytic reaction using a resonance frequency. The changes in the catalyst’s oxidation state during the reaction induced changes in the resonance frequency in the cavity resonator. The resonance frequency was not affected by 2-propanol adsorption, while the frequency decreased with the reduction of WO₃ → WO₃₋ₓ. That is, the redox state of the WO₃ catalyst could be detected using the resonance frequency. The oxidation state of the WO₃ catalyst was then directly observed by the resonance frequency during the dehydration reaction of 2-propanol by microwaves as a model reaction. Resonance frequency monitoring revealed that the enhanced dehydration of 2-propanol by microwaves was attributable to the reduction of the WO₃ catalyst. Moreover, the temporal changes in the oxidation state of the WO₃ catalyst detected by the resonance frequency coincided with that observed by operando Raman spectroscopy. Therefore, real-time resonance frequency monitoring allowed facile detection of the bulk catalyst oxidation state under microwaves without using any spectroscopic apparatus.

INTRODUCTION

Microwave (MW) heating is known to significantly accelerate heterogeneous gas–solid reactions.1–6 Understanding MW reaction enhancement mechanisms is useful for controlling catalytic reactions and applying them to various chemical industry processes. Many of the so-called “MW special effects” occur only during MW irradiation. Thus, in situ or operando (under catalytic working conditions) analyses are essential to directly observe the reaction enhancement phenomena by MWs and understand their mechanism.8

In fixed-bed flow reactions, MWs induce a complicated temperature gradient in the catalyst packed bed.9–11 Acceleration of the catalytic reaction occurs due to a localized high temperature (a “hot spot”). Using an infrared (IR) thermometer during the dehydrogenation of ethylbenzene via the Fe₃O₄ catalyst, Haneishi et al. revealed that the center of the catalyst bed was hotter than its surface.12 These authors further demonstrated that a local high-temperature region was formed by the concentration of the electric field near the contact points between the solid catalyst particles.13 Thus, MW irradiation can affect the structure, electronic state, and oxidation state of solid catalysts as well as specific thermal gradients.

We previously reported that MWs enhance the dehydration of 2-propanol over the WO₃ catalyst by 83% over that achieved through conventional heating with high selectivity to propylene (99.9%).14 Microwave operando Raman spectroscopy suggested that the reaction enhancement could be attributed to the surface reduction of WO₃. Formation of WO₃₋ₓ increased the Lewis and Brønsted acid sites at the surface defects and accelerated the dehydration of 2-propanol. However, spectroscopic monitoring of a specific area of the catalyst bed surface is not sufficient to understand the overall chemical changes in the bulk catalyst bed under MWs because of uneven gradients in both the electromagnetic field intensity and temperature. To understand the reaction enhancement by MWs, it is necessary to observe phenomena occurring in the entire catalyst bed.

Recently, complex dielectric constants were measured to analyze the oxidation state of the Pt/CeO₂ catalyst15 and carbon deposition of the zeolite catalyst.16 Changes in the complex dielectric constant correspond to chemical changes in the materials. For example, carbon deposition on zeolites leads to a low resonance frequency and Q-factor owing to the high conductivity of deposited carbon. Nishioka et al.17–20

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developed a frequency autotracking MW generator equipped with a semiconductor MW amplifier. This system enables efficient MW heating by periodically sweeping the incident MW frequency and monitoring the S21 output while autotracking the input MWs to the resonance frequency. The resonance frequency is used to detect features such as carbon deposition on the catalyst bed and carbonization of lignocellulose biomass during pyrolysis in real time. Catalá-Civera et al. developed a dynamic complex dielectric constant measurement system under MW irradiation. This system was applied to the real-time monitoring of the center temperature of solid materials by detecting the temperature-dependent changes in the dielectric properties of the materials. These methods measure the dielectric properties of the entire sample placed inside the resonator. Therefore, it can be used to monitor the chemical changes of the entire solid catalyst bed.

In this study, we report the facile detection of the oxidation state of a solid catalyst under MW heating by real-time resonance frequency monitoring. S-parameter measurement by a vector network analyzer (VNA) was used to verify the dependence of the resonance frequency on the oxidation state of the catalyst. Resonance frequency monitoring was applied to detect the oxidation state of the WO3 catalyst during the dehydration reaction of 2-propanol as a model reaction, in which we have recently reported the rate enhancement effect attributable to the changes in the oxidation state of WO3.

## RESULTS AND DISCUSSION

The S21 changes of the WO3 catalyst were first studied using a VNA. WO3 catalyst particles (150–600 μm) were packed in a quartz tube (φ 7 mm) and inserted into the cylindrical cavity resonator (TM011 mode). The S-parameter was measured using an input port and a field sensor equipped within the cavity. Figure 1A shows the S21 of WO3 during 2-propanol gas flow at different partial pressures at room temperature of approximately 20 °C. The resonance frequency can vary the adsorption of 2-propanol because it is a dipolar molecule. However, there was no obvious change in S21 by 2-propanol.

![Figure 1A](image1.png)  
**Figure 1A.** Resonance frequency monitoring of the WO3 catalyst during the dehydration reaction of 2-propanol at different partial pressures. (A) S21 of WO3 under 2-propanol flow at different partial pressures. (B) S21 of mixtures with different ratios of WO2 and WO3 and calculated dielectric constant values of these mixtures.

The S21 changes of WO3 during 2-propanol gas flow at different partial pressures are shown in Figure 1B. The dielectric constant values of these mixtures are calculated using the cavity perturbation method. The decrease in WO3 concentration by MW irradiation is nearly 72.9 MHz, which was attributable to the reduction in WO3. The S21 profile of WO3 (100%) is shown in Figure 1B, which is lower than the Industrial, Science, and Medical (ISM) band for 2.45 ± 0.05 GHz cavity. Therefore, WO3 (100%) is not an appropriate sample for the present resonance frequency measurement. This system is applicable to the sample with a resonance frequency of around 2.45 ± 0.05 GHz. The resonance frequency of slightly reduced in WO3 is nearly 2.45 GHz; therefore, these are adequate for this measurement using the present cavity resonator. Then, the relative permittivities (ε′) of the mixtures of WO3 and WO2 were calculated using the cavity perturbation method indicated in eq 1 as the changes in the resonance frequency were correlated to ε′.

\[
\varepsilon' = 1 - \frac{1}{\alpha} \left( \frac{f_L - f_0}{f_0} \right) V_C \quad (1)
\]

where \(f_L\) and \(f_0\) represent the resonance frequencies with and without load, volumes of the cavity resonator and sample, and the constant that is determined by a mode, respectively. The dielectric loss (ε″) was not monitored in this study because the present system does not provide the Q-factor. The changes in the resonance frequency are attributable to the changes in the oxidation state of WO3 when the V_C value is constant. As the dielectric properties of materials change depending on their oxidation state, resonance frequency monitoring can be used to detect the oxidation state of the WO3 catalyst. Figure 1B also shows the ε′, values of the WO3–WO2 mixtures. An increase in the proportion of WO2 increases the relative permittivity, which can be used to detect the reduction of WO3.

Subsequently, the real-time resonance frequency was monitored during the dehydration of 2-propanol using a frequency autotracking MW reactor equipped with a gallium nitride (GaN) amplifier. This MW reactor monitored the resonance frequency in the cavity every 1 s through the field sensor and fed back the optimum MW frequency for the efficient heating of irradiated materials. The temperature of the catalyst bed was precisely maintained by a proportional–integral–differential (PID) program using a quartz transparent IR thermometer and a control PC. Figure 2A shows the temperature and resonance frequency profiles before, during, and after the introduction of vaporous 2-propanol (960 Pa) through a saturator with N2 carrier gas (10 mL min⁻¹). The increase in temperature upon MW heating decreased the resonance frequency owing to the change in the dielectric property of WO3 at elevated temperatures (Figure S1). A steep reduction in the resonance frequency occurred soon after the introduction of 2-propanol vapors. When the 2-propanol flow was stopped, the resonance frequency recovered very slightly. Figure 2B shows the ε′, calculated from the resonance frequency.
frequency. The $\varepsilon'_r$ values increased upon introducing 2-propanol. As the temperature of the catalyst bed was kept constant by PID control, the changes in $\varepsilon'_r$ were attributed to the reduction of $\text{WO}_3 \rightarrow \text{WO}_3^{-x}$.

Next, we used operando Raman spectroscopy to verify the oxidation state of the WO$_3$ catalyst. Figure 3A shows the Raman spectra of mixtures with different ratios of WO$_3$ and WO$_2$. Raman peaks of 1 (lattice), 2 ($\delta$(O–W–O)), 3 ($\nu$(W–OH$_2$)), 4 and 5 ($\nu$(O–W–O)) were identified and the peaks were clearer than that at 785 nm. An increase in the WO$_2$ ratio lowered the Raman intensity because WO$_3$ is Raman-active and WO$_2$ is Raman-inactive. Next, the operando Raman spectra of WO$_3$ were obtained during the dehydration of 2-propanol at a constant temperature of 150 °C using a PID to avoid temperature-induced spectral changes (Figure S3A).

Figure 2B shows the operando Raman spectra of WO$_3$. In our previous paper, using the Raman spectroscopy probe at 785 nm, the WO$_3$ Raman shifts were hindered by the strong emission. In contrast, the 532 nm microscopic Raman spectroscopy in the current study was effective in suppressing the light emission and quantitatively tracing the intensity of the Raman shifts during WO$_3$ surface reduction. The peak intensity decreased sharply in the initial 10 min, decreasing gradually thereafter. This decrease in the Raman peak intensity suggests a reduction in the WO$_3$ catalyst surface. The peak intensity was still small even after stopping the 2-propanol flow. Figure 3C shows the superimposed temporal changes in the resonance frequency and Raman intensity at 817 cm$^{-1}$ for WO$_3$. The reduction in the resonance frequency exactly matched the reduction in the Raman intensity. Therefore, we can confirm that real-time resonance frequency monitoring can be applied to trace the oxidation state of the WO$_3$ catalyst.

Then, the reaction products were monitored by electron ionization mass spectrometry (EI-MS) coupled with resonance frequency and Raman spectroscopy monitoring (Figure 4).

The m/z values of 45 (2-propanol), 41 (propylene), 43 (acetone), 18 (water), and 2 (hydrogen) were monitored as the representative fragment ion peaks of each compound. Diisopropyl ether was not separately characterized as it overlapped with m/z 45 and 43. Formation of propylene and water occurred via the dehydration reaction soon after introducing 2-propanol. Acetone and hydrogen were produced simultaneously via the dehydrogenation of 2-propanol. During the first 10 min, the formation of these products strongly correlated with a decrease in the intensity of the Raman spectra. These behaviors are in line with our previous study, which used GC analysis (every 20 min). Meanwhile, the present MS system allowed time-resolved product analysis (every 3 s), which was useful for tracking the changes in the product distribution along with the oxidation state of the WO$_3$ catalyst. The production of these compounds gradually decreased after stopping the 2-propanol flow, indicating that the reaction products were monitored by electron ionization mass spectrometry (EI-MS) coupled with resonance frequency and Raman spectroscopy monitoring (Figure 4).
the 2-propanol adsorbed on the WO3 surface still facilitated the reaction. Upon stopping the MW irradiation, the m/z 45 and 43 peaks increased during the cooling process. This could be attributed to the formation of diisopropyl ether by intermolecular dehydration of 2-propanol, which proceeded at a lower temperature than intramolecular dehydration.

From the resonance frequency results, together with Raman spectroscopy and MS, we concluded that the WO3 surface was reduced in tandem with the enhanced dehydration of 2-propanol. Moreover, these results strongly agreed with our previous report on operando Raman spectroscopy (785 nm) of the same reaction.14 The Raman peak intensity and resonance frequency profiles strongly coincided with the formation of propylene. Approximately 10% of WO3 was reduced during the dehydration of 2-propanol; the degree of reduction of WO3 was estimated from the Raman peak intensity and S21 operated at room temperature (Figures S3 and 4). Resonance frequency monitoring revealed that WO3 reduction occurred in the entire catalyst bed. This reduction occurred along with the dehydrogenation of 2-propanol to form acetone and hydrogen. The defect sites of WO3 acted as Lewis acids. Moreover, Brønsted acid sites (H\textsubscript{2}WO\textsubscript{3−x}) were formed by water generated during the dehydration of 2-propanol. Enhanced formation of both Lewis and Brønsted acid sites under MWs contributed to the acceleration of the dehydration of 2-propanol.26,27

### CONCLUSIONS

This study demonstrated that real-time resonance frequency is effective for facile monitoring of the oxidation state of the WO3 catalyst during the dehydration of 2-propanol under MW irradiation. The resonance frequency was significantly affected by the reduction of WO3 but was not affected by the adsorption of 2-propanol. It was confirmed that the reduction of the WO3 catalyst occurred soon after the introduction of 2-propanol. The formation of surface defects increased the Lewis and Brønsted acid sites on WO3, which enhanced the isotope transport and dehydrogenation of 2-propanol to form acetone and hydrogen. Moreover, these results strongly agreed with our previous report on operando Raman spectroscopy and MS. Microwave heating was conducted using a TM\textsubscript{110}-mode cylindrical cavity resonator and a GaN semiconductor MW generator (Ryowa Electronics Co., Ltd., Sendai, Japan). The TM\textsubscript{110}-mode cavity resonator equipped with a frequency autotracking MW reactor provided more efficient MW heating than our previous TM\textsubscript{110}-mode reactor,15 owing to the higher Q factor of the cavity as well as the continuous input of optimum frequency MWs. The cavity resonator was equipped with five windows at the top (1), bottom (1), side (2), and front (1) of the cavity. The top and bottom windows were used for Raman spectroscopy and temperature monitoring by an infrared thermometer, respectively. Side windows were used to place the quartz tube with the WO3 sample that passed through the cavity. The front window was used to tune the sample position. The cavity resonator and MW were connected by a coaxial cable. The impedance matching was performed using a slug tuner and frequency-auto-tracking system. Every second, the field sensor monitored the resonance frequency of the cavity containing the WO3 sample. The resonance frequency was fed back to apply this frequency for heating the WO3 sample at a frequency of 2.45 ± 0.05 GHz. The temperature of the WO3 sample was monitored using a quartz transparent infrared thermometer (TMHX-STM0050; Japan Sensor Co., Tokyo, Japan) using 0.83 as the emissivity of WO3. The forward and reflected MW powers, temperature, and resonance frequency were recorded with a control PC.

### METHODS

#### Materials.

Tungsten oxides (WO3 and WO2) were supplied by Kojundo Chemical Laboratory Co., Ltd. (Saitama, Japan). WO3 catalyst particles were prepared by pelletizing WO3 powder and reforming these pellets into secondary particles approximately 250–600 μm in size. The complex dielectric constants of WO3 and WO2 at 2.45 GHz were measured by a cavity perturbation method using a VNA (ZND; Rohde & Schwarz GmbH & Co. München, Germany; Table 1).

#### Table 1. Complex Dielectric Constants of WO3 and WO2 at 2.45 GHz

|          | ε′  | ε″ | tan δ |
|----------|-----|----|-------|
| WO2      | 15.7| 1.24| 0.0790|
| WO3      | 2.94| 0.0672| 0.0228|

#### Microwave (MW) Heating.

Figure 5 shows the MW heating system equipped with resonance frequency monitoring.
The resonance frequency was monitored using the same MW setup (Figure S5A,B). The resonance frequency was monitored using a field sensor (S$_2$1). The S$_2$1 was also monitored using a VNA at room temperature. S$_2$1 was used to monitor the effects of 2-propanol adsorbed on WO$_3$ and reduction of WO$_3$ on the resonance frequency. The amount of adsorbed 2-propanol was controlled by its partial pressure in the flowing N$_2$ carrier gas by changing the temperature of the saturator from 0 °C (960 Pa) to 10 °C (2.16 kPa) and 30 °C (7.88 kPa). S$_2$1 was recorded after the partial pressure of 2-propanol became stable.

For the dehydration reaction of 2-propanol, WO$_3$ catalyst particles (0.4 g) were packed in a quartz tube (φ 7 mm) and placed in the cavity through the side windows. First, the packed WO$_3$ catalyst was heated by MWs to 150 °C in air. The fragment ions with m/z of 45, 41, 43, 18, and 2 were used to estimate the amount of 2-propanol, propylene, acetone, water, and hydrogen, respectively. These m/z values were selected to avoid overlap in the fragment ion peaks of each compound according to the NIST Chemistry WebBook.

Operando Raman Spectroscopy under MW Irradiation. We improved our Raman spectroscopy methodology from that used in our previous report, which used 785 nm probe Raman spectroscopy. 14 Here, Raman spectra were obtained using a 532 nm laser (Cobolt 06-01, 100 W; HÜBNER GmbH & Co. KG, Kassel, Germany), microscope unit (Seishin Trading Co., Ltd., Kobe, Japan), and imaging spectrometer (iHR320; Horiba Ltd., Kyoto, Japan) equipped with a CCD detector (Syncerity; Horiba Ltd., Kyoto, Japan). The present system was effective in suppressing light emission from the WO$_3$ sample during the reaction and obtaining fine Raman spectra. The incident light was applied from the top of the WO$_3$ sample through a long-working-distance objective lens (M Plan Apo 10×; Mitutoyo Co., Kanagawa, Japan). The laser spot size was 38 μm when a 200 μm pinhole was used. Temperature-dependent Raman spectra were recorded using an electrical furnace designed for in situ spectroscopy (SAP0694; Sakaguchi E.H VOC Co., Tokyo, Japan) at room temperature, 50, 100, 200, 300, 400, and 500 °C in air. The Raman spectrum of the WO$_3$ and WO$_2$ mixture was obtained without heating in air. The operando Raman spectrum of WO$_3$ was recorded using a cylindrical cavity resonator placed on the stage in the microscope Raman unit. The intensity of the Raman spectrum was maximized by adjusting the focal length and pinhole (200 μm). The Raman spectra were recorded every minute for 30 min simultaneously with resonance frequency monitoring and MS, as indicated above.

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04862.

Additional results including resonance frequency depending on the temperature, shift in resonance frequency depending on the different ratios of WO$_3$ and WO$_2$, and temperature-dependent Raman spectra of WO$_3$ (PDF).

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**Notes**

The authors declare no competing financial interest.

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