In Situ Observation of 2-propanol Dehydration over WO_3 Catalyst under Microwave Irradiation

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Abstract: *In situ* Raman spectroscopy was used for direct observation of the solid catalyst during microwave irradiation to study the mechanism of rate enhancement due to microwaves. Dehydration of 2-propanol over WO_3 catalyst was used as a model reaction. We designed an *in situ* Raman analysis system by assembling a fix bed flow reactor, microwave apparatuses, and Raman spectrometer. By *in situ* Raman analysis during the reaction, we observed a difference in the Raman spectra between conventional heating and microwave heating originating from bonding state changing and coke forming. This would be caused by non-equilibrium local heating at the vicinity of the catalyst.

Keywords: microwave chemistry, *in situ* Raman spectroscopy, microwave local heating

1. Introduction

Microwave heating has been used for various chemical reactions to shorten reaction time and improve the reaction rate.[1] Especially in the heterogeneous catalytic reactions, non-equilibrium local heating formed in the packed bed under microwaves is important to exhibit rate enhancement under microwaves.[2] Our group previously found that the local high temperature region was formed at the contact points between the catalyst particles due to concentrated microwave electric field using electromagnetic wave simulation.[3] Furthermore, at the local high temperature region, the reaction progress rate should be enhanced. Direct observation of the solid catalyst is required to gain a deeper understanding of reaction enhancement by microwave heating, therefore, *in situ* observation of the catalyst bed during microwave reaction was conducted using Raman spectroscopy. Raman spectroscopy provides information of the surface structure of the solid catalyst. In addition, local temperature of the catalyst particle can be determined from the intensity ratio of Stokes to anti-Stokes lines since they are strongly dependent on the temperature. Previously, Tsukahara et al., used Raman spectroscopy to clarify the existence of microwave-induced non-equilibrium local heating at the Co particle dispersed in a DMSO solution[4], so it is expected that the local high temperature region could also be directly observed by Raman spectroscopy in the solid-gas reaction system.

In this study, we designed a fixed bed reactor equipped with a laser Raman spectrometer placed in a single-mode microwave apparatus for direct analysis of solid catalysts under microwaves (Figure 1). WO_3 was used as a catalyst because WO_3 exhibited clear Raman spectrum under microwaves. By using this system, we conducted dehydration of 2-propanol using WO_3 catalyst as a model reaction. We discuss the effects of microwaves on generation of non-equilibrium local heating as well as surface structural changes of the solid catalyst of WO_3 during microwave heating.

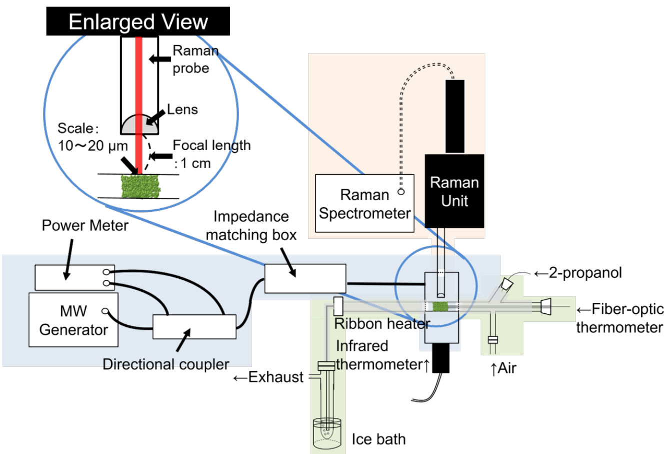

Figure 1. The microwave *in situ* Raman spectroscopy system

2. Experimental

WO_3 catalyst (0.5 g) was added to a quartz reaction tube which was placed at the focal point of an elliptical single-mode (TM110) microwave cavity (2.45 GHz). 2-propanol (23.4 mmol/h) was continuously fed to the reaction tube and reacted at 150 °C or 200 °C. As a conventional heating, we used an electric tube furnace. All the reactions were conducted under air flow at 20 mL/min. The amounts of 2-propanol, propylene and diisopropyl ether as the products were determined by gas chromatography. During all the reactions, the catalyst layer was analyzed by the Raman spectroscopy (785 nm, 120 mW) every 20 minutes.

3. Results and discussion

Figure 2 shows the yields of propylene and diisopropyl ether in dehydration reaction of 2-propanol over WO_3 at 150 °C. By microwave heating, the reaction exhibited diisopropyl ether yield of about 5%, while by conventional heating the reaction hardly proceeded. We also conducted the reaction at 200 °C and observed propylene yield of about 80%. These results suggest the occurrence of the local high temperature region promoting dehydration reactions in the packed bed, which cannot be measured by general thermometers such as a fiber-optic thermometer, or a pyrometer due to their low resolution.

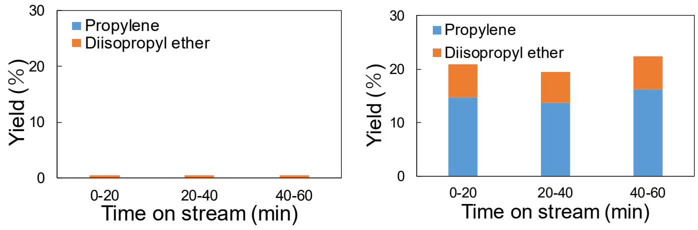

Figure 2. Yields of 2-propanol dehydration. 2-propanol (23.4 mmol/h) and air (20 mL/min) were continuously fed to the reaction tube at 150 °C. (left: conventional heating, right: microwave heating)

Figure 3 shows Raman spectra of WO_3 catalyst under the reaction condition. From Raman spectra, the differences in the surface structure of WO_3 between microwaves and electric furnace were observed. Raman spectra were almost unchanged due to low reaction activity by conventional heating at 150 °C. While in microwave heating, the peaks of WO_3 gradually became smaller after the initiation of the reaction, showing the reaction was more promoted by microwave heating than by conventional heating. Raman spectra after the reaction gave the new peaks at 1310 cm^{-1} and 1550 cm^{-1}, which can be assigned to cokes generated at the surface of the catalyst.

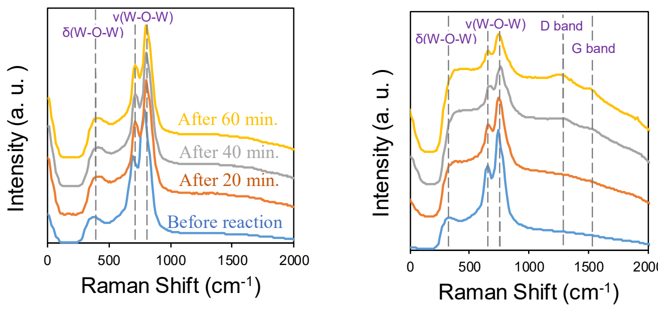

Figure 3. Raman spectra of the catalyst. Spectra are before the reaction and after 20, 40, 60 min. (left: conventional heating, right: microwave heating)

4. Conclusions

We demonstrated that the microwaves enhance the dehydration of 2-propanol on WO_3 catalyst. The surface of the catalyst was directly observed by using *in situ* Raman spectroscopy. The results suggested that surface structure such as amounts of WO_3 and/or cokes is different between conventional heating and microwave heating, and it would lead to the difference of reaction activity. We will challenge to directly observe the local high temperature region in the catalyst bed, so we are developing a new *in situ* Raman analysis system containing a microscopic Raman spectrometer.

References

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