Supporting Information

Operando Raman spectroscopy of the microwave-enhanced catalytic dehydration of 2-propanol by WO_3

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(1) Temperature profiles of the core of the catalyst bed.

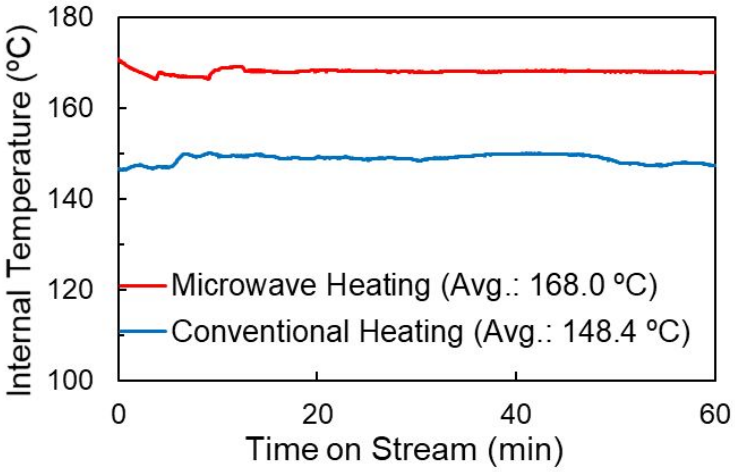

Figure S1. Temperature profile at the center of the catalyst bed as monitored using a fiber-optic thermometer during the dehydration of 2-propanol via MW heating and CH. In both cases, the temperature at the surface of the catalyst bed was controlled to 150 °C. Carrier gas: air.

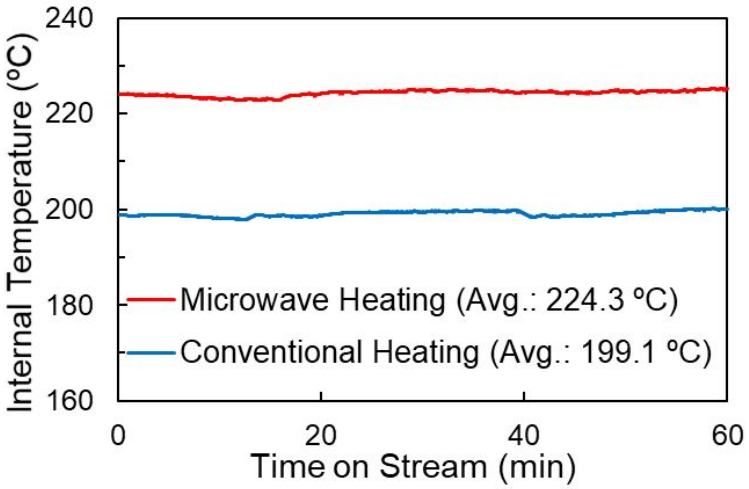

Figure S2. Temperature profile at the center of the catalyst bed as monitored using a fiber-optic thermometer during the dehydration of 2-propanol via MW heating and CH. In both cases, the temperature at the surface of the catalyst bed was controlled to 200 °C. Carrier gas: air.

(2) Post characterization of WO_3 catalysts.

The post-reaction oxidation state of the bulk WO_3 catalyst was further characterized using CHN, XPS and UV-vis DRS. Significant coke deposition occurred under MW as compared to CH. Figure S4 indicate the color change in the surface of the catalyst bed after dehydration of 2-propanol under MW in air and argon flow conditions.

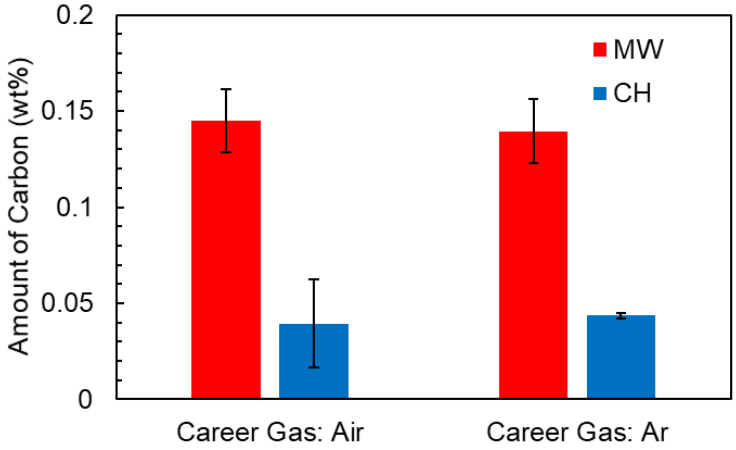

Figure S3. The amount of carbon deposited on the WO_3 catalyst after the dehydration of 2-propanol via MW heating or CH under an air or argon gas flow.

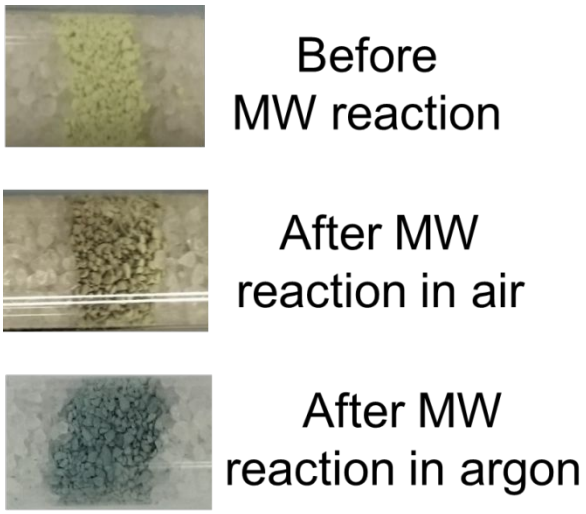

Figure S4. Photograph of catalyst bed before and after MW reaction in air and argon atmospheres.

Figure S5A shows the XPS spectra of the WO_3 catalyst before and after the reaction. The peaks at 35.0 eV, 37.2 eV, and 40.5 eV were attributed to the $W4f_{7/2}$, $W4f_{5/2}$, and $W5p_{3/2}$ levels of WO_3, respectively.[1] No obvious changes in these peaks were observed after reaction under air, while the peaks due to $W4f_{7/2}$ and $W4f_{5/2}$ were shifted to lower energies of -34.8 eV and -37.0 eV after the reaction under argon, respectively. The decreases in the binding energies suggested the reduction of the WO_3 surface due to a decrease in the valence of W. No clear differences were observed between the MW and CH spectra, because the XPS spectra were obtained in bulk while the Raman spectra were obtained at the surface of the WO_3 catalyst under the working conditions.

UV-vis DRS spectra were also obtained after the MW reaction under the different gas flow conditions (Figure S5B). The absorption above 400 nm gradually increased after reaction under argon; this phenomenon was not observed before the reaction or after the reaction under air. The reduction of WO_3 can be observed as an absorption in the near infrared (NIR) originated from the generation of a mid-gap level in the bandgap formed by oxygen vacancies and coincide with the formation of blue color at the surface.[2] The NIR absorption should also be responsible for the broad light emission, as the 785 nm wavelength of the incident laser during operando Raman spectroscopy overlaps the WO_3 peaks. No differences were observed in the XRD patterns obtained after the MW and CH reactions also suggest that the bulk WO_3 structure was maintained (Figure S5C).

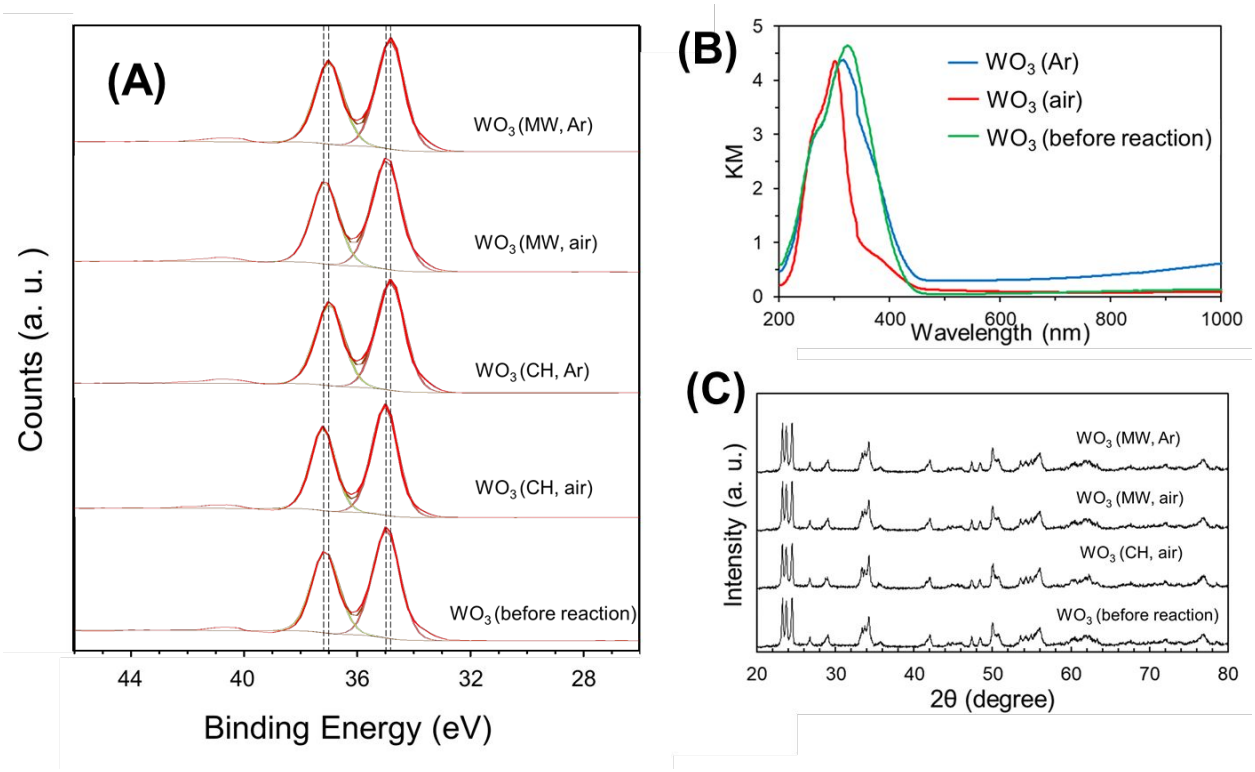

Figure S5. Characterization of the bulk of WO_3 catalyst after the dehydration of 2-propanol using MW heating or CH under a flow of air or argon: (A) XPS spectra, (B) UV-vis DRS spectra, and (C) XRD patterns.

References

(1) Xie, F. Y.; Gong, L.; Liu, X.; Tao, Y. T.; Zhang, W. H.; Chen, S. H.; Meng, H.; Chen, J. XPS Studies on Surface Reduction of Tungsten Oxide Nanowire Film by Ar+ Bombardment. *J. Electron Spectrosc.* **2012**, *185*, 112–118.

(2) Chakrapani, V.; Brier, M.; Puntambekar, A.; DiGiovanni, T. Modulation of Stoichiometry, Morphology and Composition of Transition Metal Oxide Nanostructures through Hot Wire Chemical Vapor Deposition. *J. Mater. Res.* **2016**, *31*, 17–27.