Supplementary Information

# Role of the Heptagonal Channel of Crystalline $Mo_3VO_x$ Catalyst for the Selective Oxidation of Acrolein and Methacrolein

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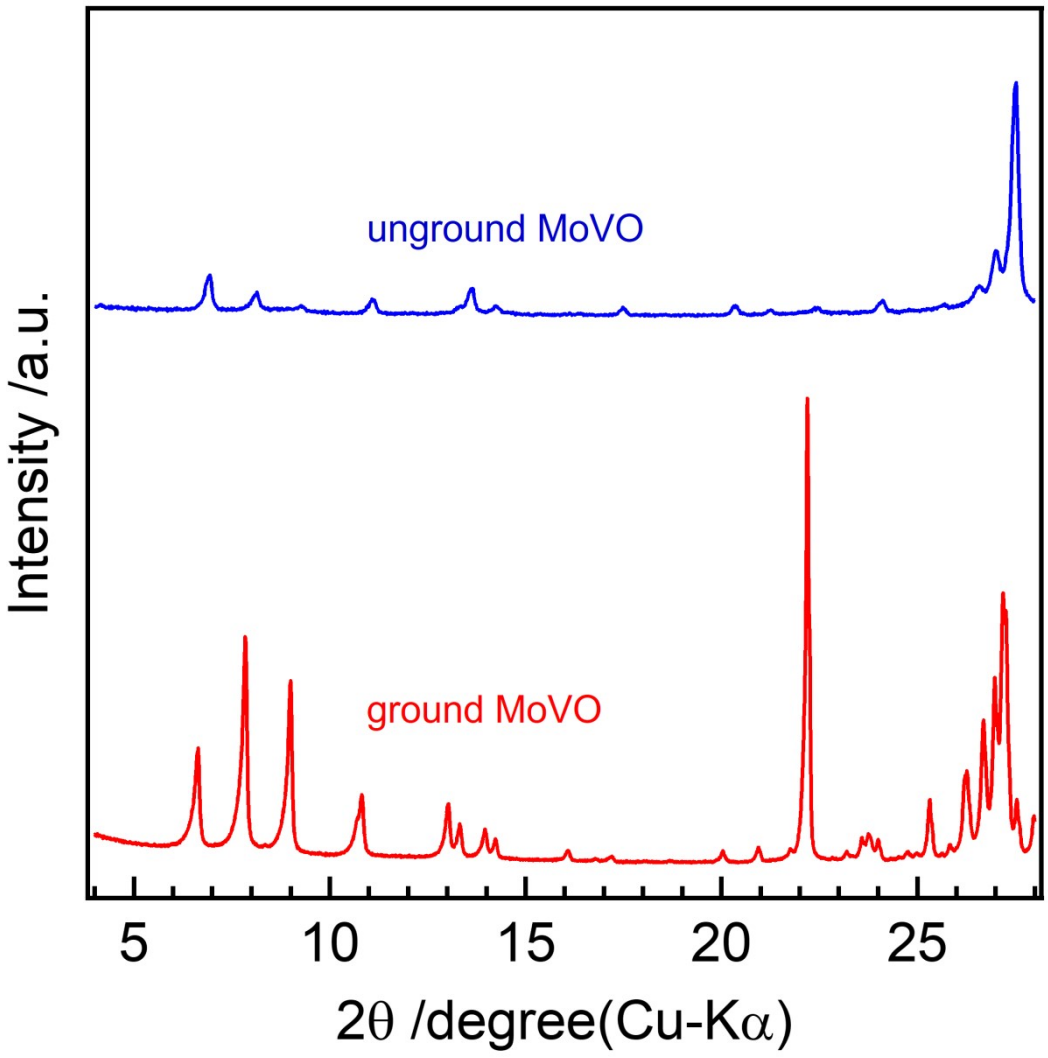


Fig. S1. XRD patterns of ground and unground MoVO.

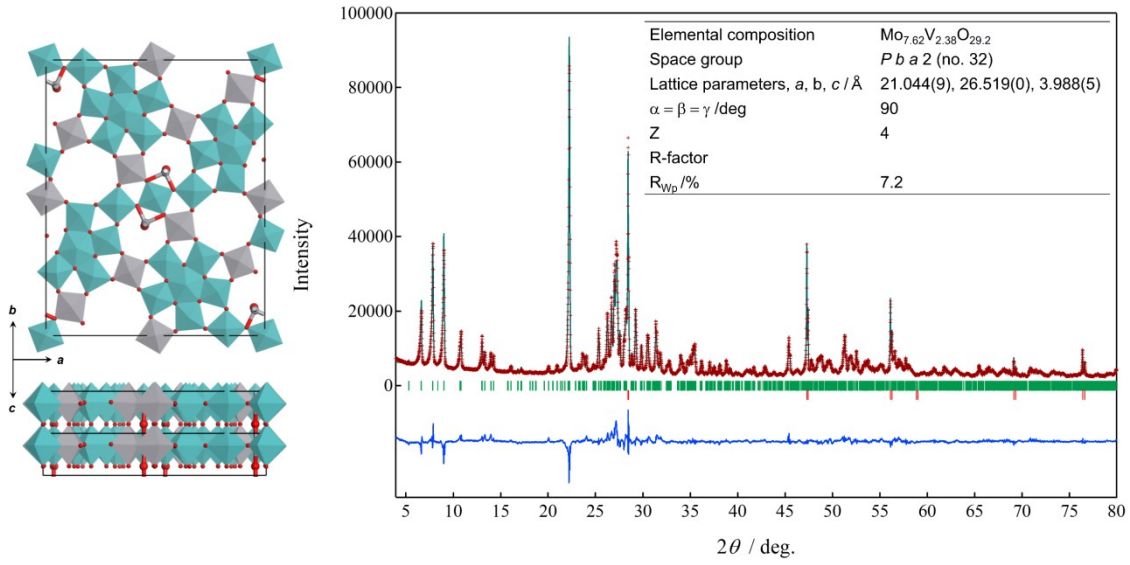


Fig. S2. Results of Rietveld refinement for MoVO. Initial structural model was obtained by single crystal analysis.[1] Mo, green; V, gray; O, red. Observed (red), calculated (light blue), and difference (blue) patterns resulting from Rietveld analysis are shown in right. The green and purple vertical bars indicate the Bragg positions for MoVO and Si, respectively. NIST SI powder (SRM640D) was mixed with the sample as an internal standard to improve the accuracy of the lattice constants, and a two-phase Rietveld analysis was performed.

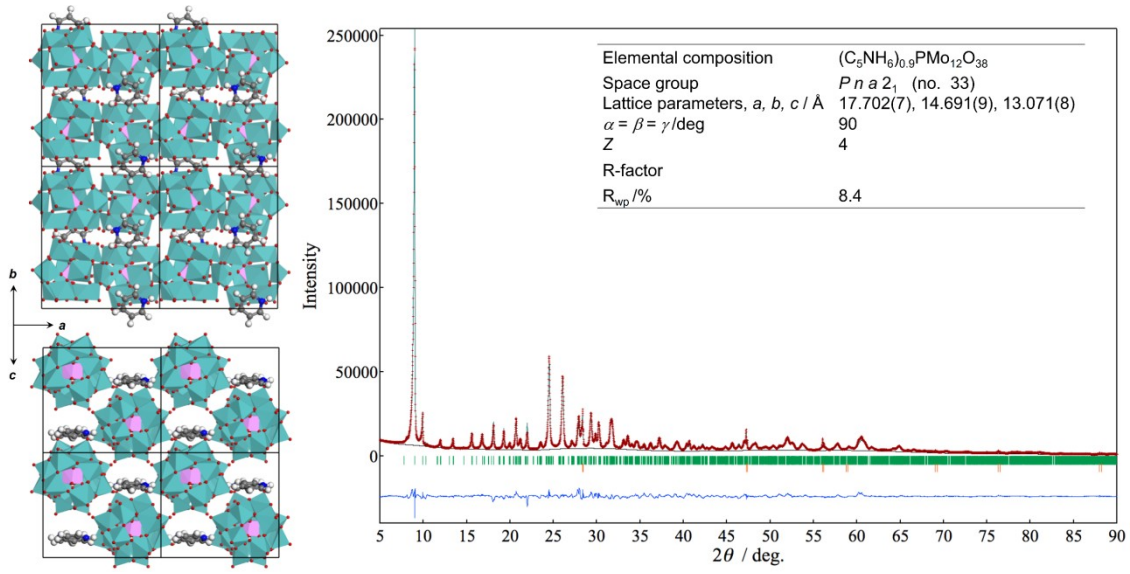


Fig. S3. Results of Rietveld refinement for PyPMo-420. Initial structural model was obtained by single crystal analysis.[2] Mo, green; P, pink; O, red; C, gray; N, blue; H, white. Observed (red), calculated (light blue), and difference (blue) patterns resulting from Rietveld analysis are shown in right. The green and purple vertical bars indicate the Bragg positions for PyPMo-420 and Si, respectively. NIST SI powder (SRM640D) was mixed with the sample as an internal standard to improve the accuracy of the lattice constants, and a two-phase Rietveld analysis was performed.

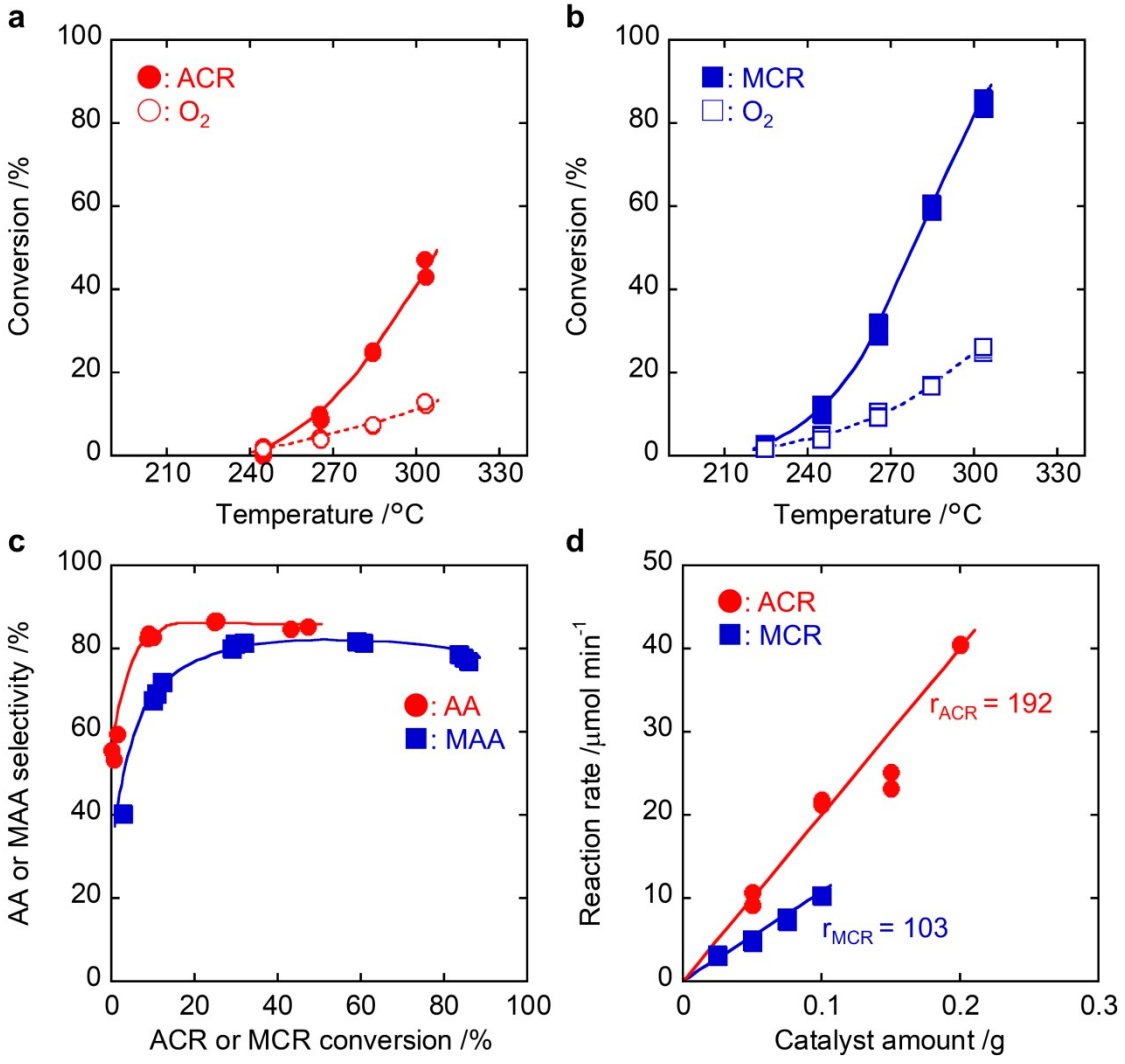


Fig. S4. **a**–**b** ACR and $O_2$ conversions (**a**) and MCR and $O_2$ conversions (**b**) as a function of reaction temperature over PyPMo-420. Reaction conditions: reactant gas, ACR/$O_2$/($N_2$+He)/$H_2O$ = 1.5/4.0/31.8/12.0 mL $min^{-1}$ (**a**) and MCR/$O_2$/($N_2$+He)/$H_2O$ = 0.7/1.7/18.3/4.5 mL $min^{-1}$ (**b**); catalyst amount, 0.50 g. **c** Relationship between ACR or MCR conversion and AA or MAA selectivity obtained from **a** and **b**. **d** Reaction rates of ACR and MCR conversion as a function of catalyst amount at 300 °C over PyPMo-420. Reactant gas compositions are the same as in **a** and **b**. ACR conversion range, 2.8%–34.2%; MCR conversion range, 11.8%–53.3%. The numbers shown in **d** indicate conversion rates based on gram of catalyst (μmol $min^{-1}$ $g_{cat}^{-1}$).

## References

(1) M. Sadakane, K. Kodato, N. Yasuda, S. Ishikawa and W. Ueda, *ACS Omega*, 2019, **4**, 13165−13171.

(2) S. Ishikawa, T. Ikeda, M. Koutani, S. Yasumura, K. Amakawa, K. Shimoda, Y. Jing, T. Toyao, M. Sadakane, K.-i. Shimizu and W. Ueda, *J. Am. Chem. Soc.*, 2022, **144**, 7693−7708.