Electronic Supplementary Material (ESI) for RSC Advances.

Hydrothermally Synthesized Poorly Crystalline Binary Oxides with ZrW_2O_8 composition: Preparation, Structural Analysis, and Catalytic Activity for the Alkylation of Anisole with Benzyl Alcohol

Takashi Yamamoto[1,2,*], Sena Heiuchi[2], Maki Kondo[2], Kei Tabusadani[1], and Atsushi Sakaki[3]

[1] Department of Science and Technology, Tokushima University, Tokushima 770-8506, Japan

[2] Department of Mathematical and Material Sciences, Tokushima University, Tokushima 770-8502, Japan

[3] Nichia Corporation, Anan, Tokushima 774-8601, Japan

*Corresponding author; E-mail: takashi-yamamoto.ias@tokushima-u.ac.jp

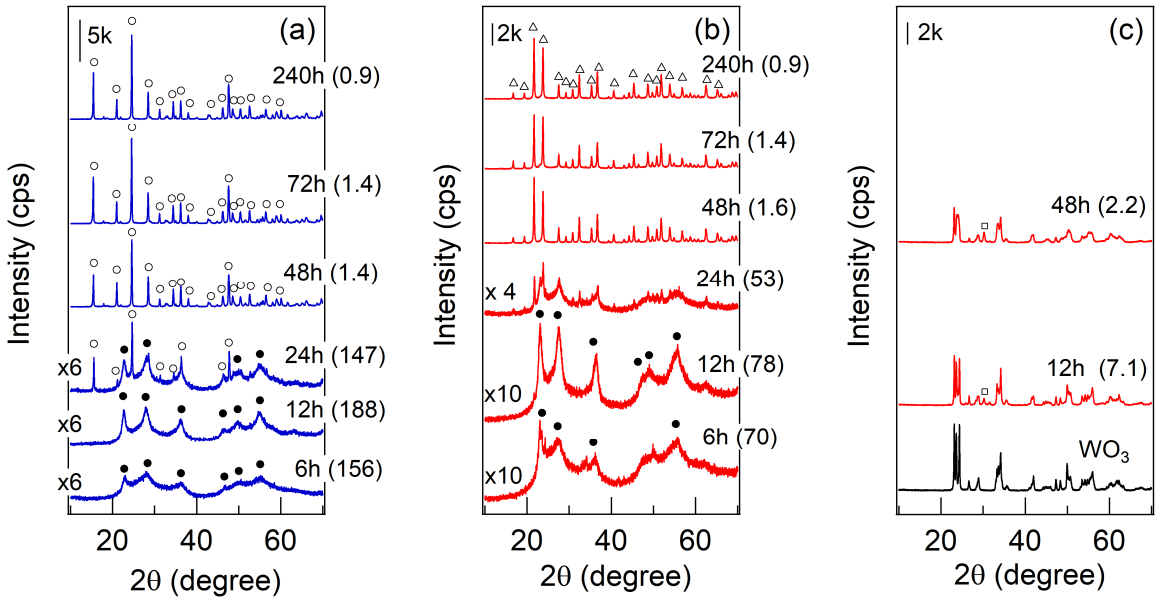

Fig. S1: Crystalline phases of zirconium tungsten binary hydroxide with different hydrothermal treatment time at 453 K: (a) as-synthesized, calcined at (b) 873 K, and (c) 1073 K. HCl concentration: 6 M. The values in parentheses show the BET specific surface area. ○: $ZrW_2O_7(OH)_2 \cdot 2H_2O$, ●: ZWO-I, △: ZrW_2O_8, □: tetragonal- or cubic-ZrO_2.

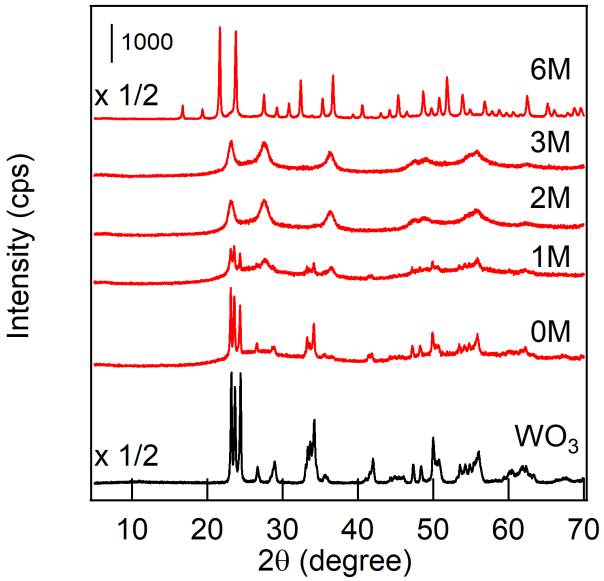

Fig. S2: XRD patterns of calcined zirconium tungsten binary hydroxides ZWOH_*X*M_72h_873 prepared with different HCl concentration (X = 0–6 M). Hydrothermal treatment: 453 K, 72 h. Calcination temperature: 873 K.

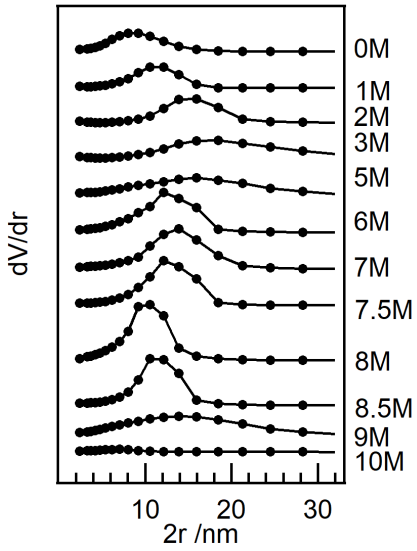

Fig. S3: Pore size distribution curves of calcined binary oxides ZWOH_*X*M_12h_873 prepared with different HCl concentration (*X* = 0–10 M).

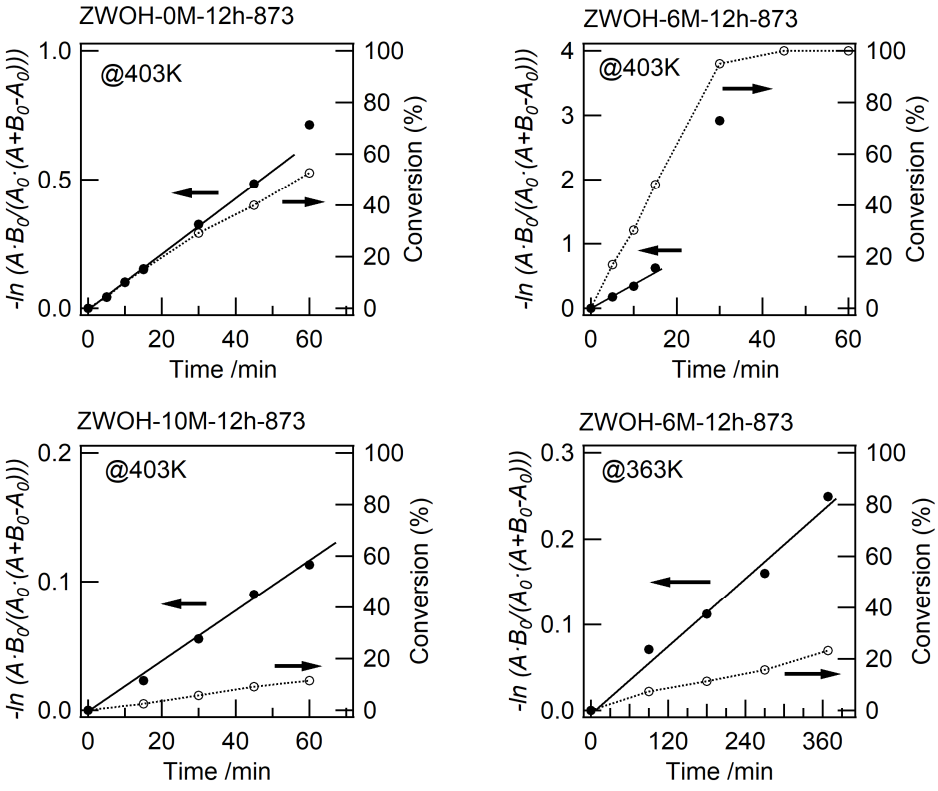

Fig. S4: Typical results of the alkylation of anisole with benzyl alcohol analyzed with second-order kinetic model. Catalyst: 0.1 g; benzyl alcohol: 0.64 mL; anisole: 10 mL; reaction temperature: 363 or 403 K.
A: benzyl alcohol concentration, B: anisole concentration. X_0: initial concentration of substrate *X*.

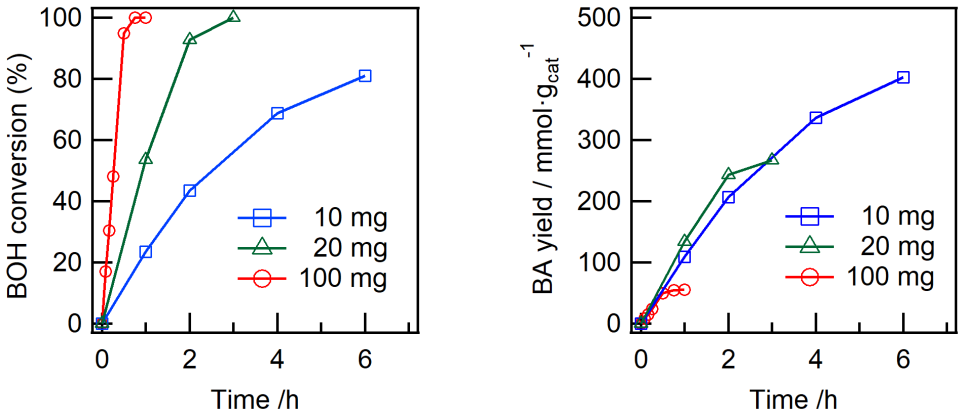

Fig. S5: Results of anisole alkylation with benzyl alcohol with different catalyst amounts. Catalyst: ZWOH_6M_12h_873, 0.01- 0.10 g; benzyl alcohol: 0.64 mL; anisole: 10 mL; reaction temperature: 403 K. BOH: benzyl alcohol; BA: benzyl anisoles.

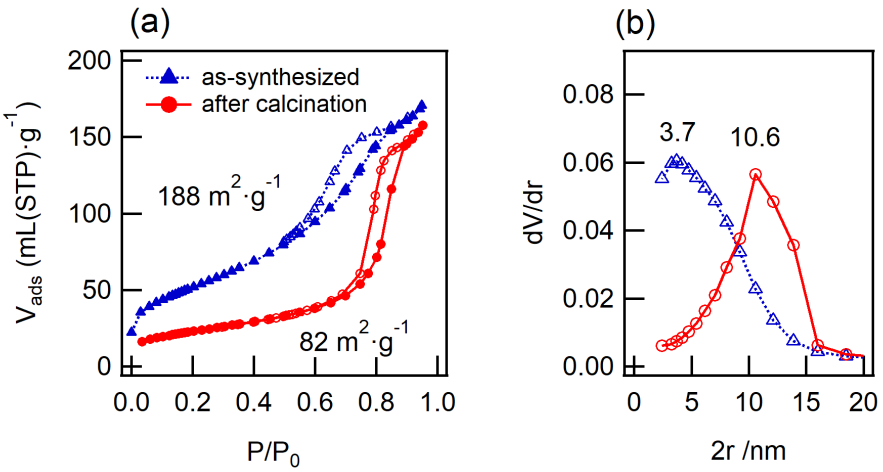

Fig. S6: Pore structural changes of as-synthesized ZWO-1 sample (ZWOH_6M_12h) by calcination. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution curves. Calcination temperature: 873 K.