Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for

Investigation of the Formation Process of Zeolite-like 3D Frameworks Constructed with ε-Keggin-type Polyoxovanadometalates with Binding Metal Ions and Preparation of a Nano-crystal.

*Zhenxin Zhang [1], Masahiro Sadakane [*2, 3], Toru Murayama [1], and Wataru Ueda [*1]*

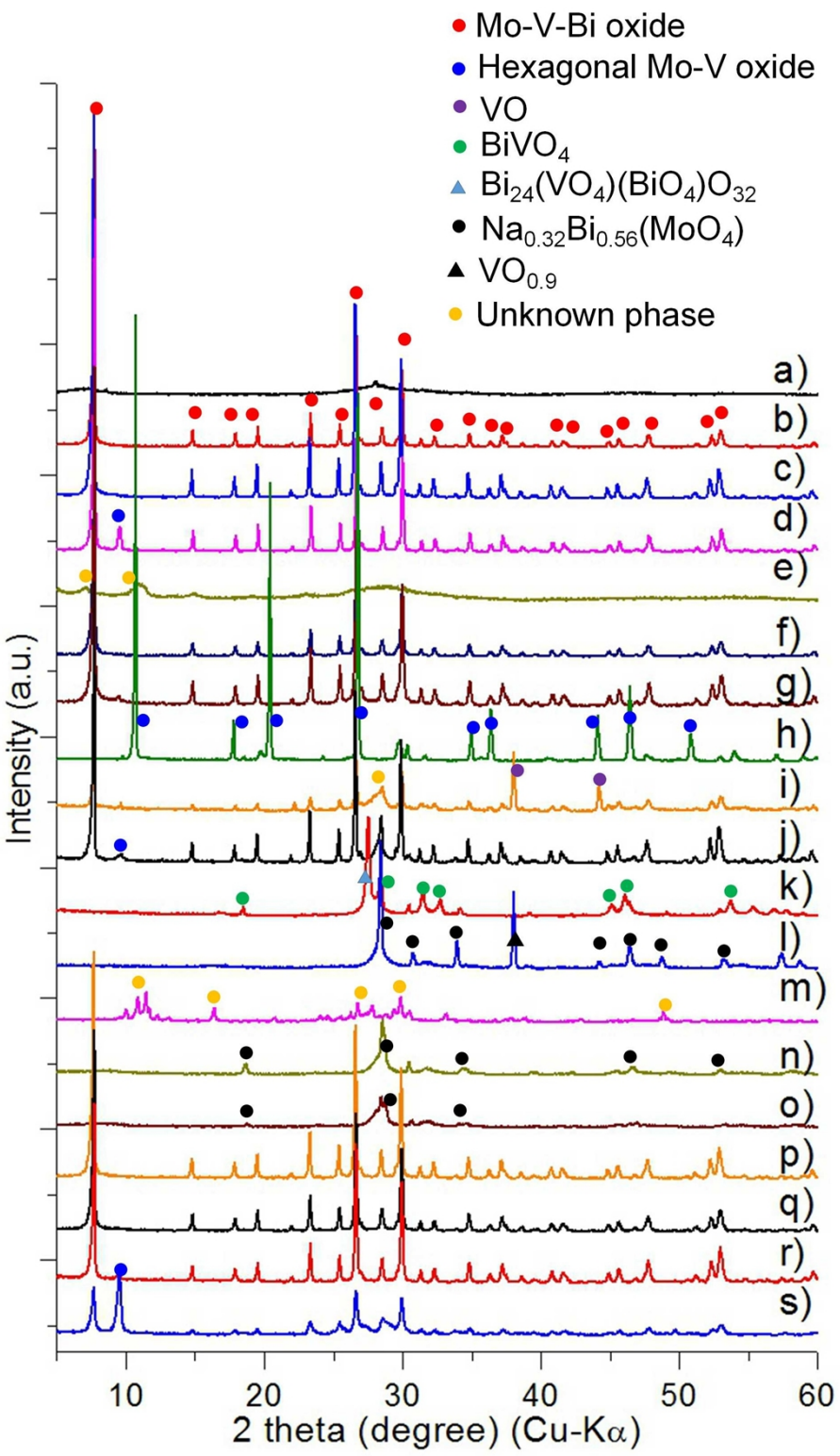

Fig. S 1. XRD patterns of resulting materials synthesized under different conditions shown in Table 1: (a) entry 1, (b) entry 2, (c) entry 3, (d) entry 4, (e) entry 5, (f) entry 6, (g) entry 7, (h) entry 8, (i) entry 9, (j) entry 10, (k) entry 11, (l) entry 12, (m) entry 13, (n) entry 14, (o) entry 15, (p) entry 16, (q) entry 17, (r) entry 18, and (s) entry 19, PDF numbers, hexagonal Mo-V oxide: 00-021-0569, VO: 03-065-2896, $BiVO_4$: 00-048-0744, $Bi_{24}(VO_4)(BiO_4)O_{32}$: 01-080-0837, $Na_{0.32}Bi_{0.56}(MoO_4)$: 01-079-2241, and $VO_{0.9}$: 01-078-0721.

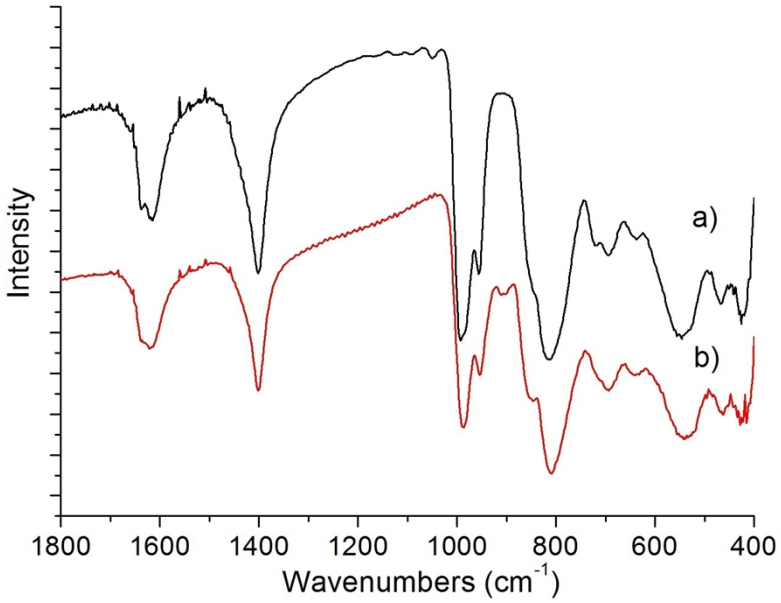

Fig. S 2. FT-IR spectra of (a) Mo–V–Bi oxide and (b) nano-Mo–V–Bi oxide.

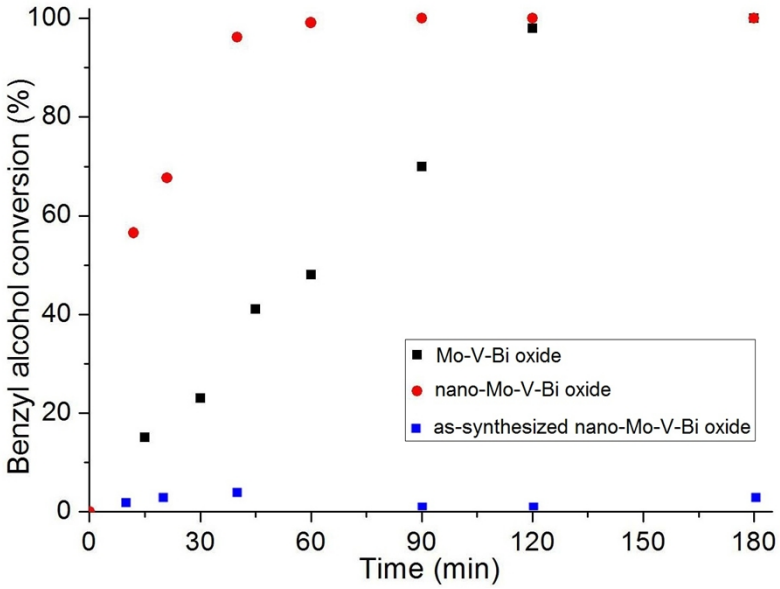

Fig. S 3. Benzyl alcohol etherification catalyzed by Mo–V–Bi oxides. Reaction conditions: 20 mg of Mo–V–Bi oxide, 10 mmol of benzyl alcohol, 1 mmol of tridecane added as an internal standard, 403 K, 3 h.

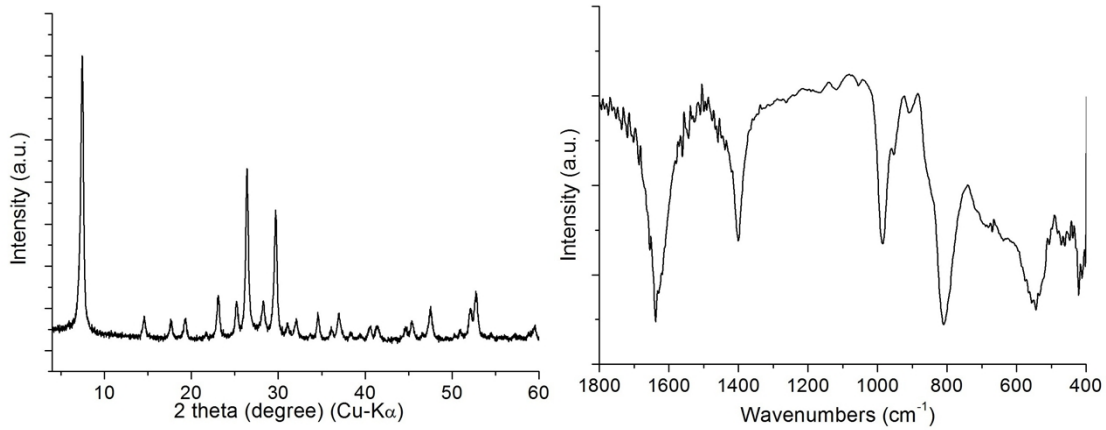

Fig. S 4. (left) XRD patterns and (right) FT-IR spectra of the solid obtained under the following conditions: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$: 8.33 mmol based on Mo, $VOSO_4\cdot 5H_2O$: 2.08 mmol, 1.4 mmol of $Bi(NO_3)_3\cdot 5H_2O$ in 1.7 mL of water-glycerol (1:1), 40 mL of water, 373 K, 150 min, pH adjusted to 3.4 by NH_3 solution (28%).

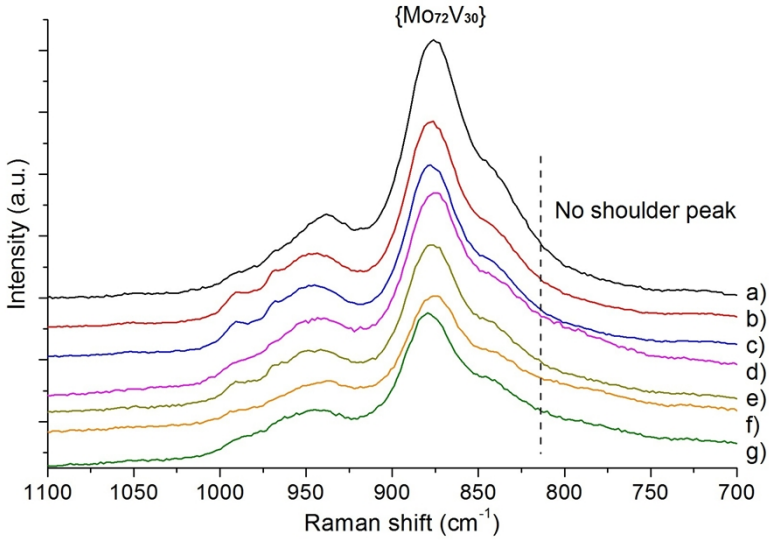

Fig. S 5. Raman spectra of solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $VOSO_4\cdot 5H_2O$ under the following conditions: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$: 8.33 mmol based on Mo, $VOSO_4\cdot 5H_2O$: 2.08 mmol, 40 mL of water, 1.7 mL of solution (water: glycerol = 1: 1), pH of 3.4, 373 K, synthesis time, (a) 0 min, (b) 7 min, (c) 15 min, (d) 20 min, (e) 30 min, (f) 60 min, and (g) 150 min.

Table S 1. Solubility of bismuth compounds determined by elemental analysis. [a)]

entry	Materials	Material amount (mmol based on metal)	Water amount (mL)	Ion concentration (mmol/L)
1	$Bi(OH)_3$	0.281	40	2.54×10^{-5}
2	Bi_2O_3	0.281	40	4.93×10^{-5}
3	BiOCl	0.281	40	0
4	$Bi_2(SO_4)_3$	0.281	40	0.0288
5	$Bi(NO_3)_3$	0.281	40	5.41
6	$Bi(NO_3)_3$	1.402	40	7.91
7 [b)]	$Bi(NO_3)_3$	1.402	40	9.98
8 [c)]	AHM	8.33	40	208
9 [c)]	$VOSO_4$	2.08	40	52

[a)] Materials were added to water and stirred for 10 min. The solutions were filtered with a membrane filter before ICP measurement. [b)] 0.85 mL of glycerol was added to 40 mL of water. [c)] AHM and $VOSO_4$ can be dissolved completely in this condition and theoretical values are shown.