

Electronic Supplementary Information

PREPARATION OF CATALYSTS

Synthesis of Mo/W-Nb-V mixed metal oxides (samples H1, H2, H3)

3.3 mmol of the corresponding heteropolyacid (Aldrich), 8.0 mmol of vanadyl sulphate (Aldrich) and 6.8 mmol of niobium oxalate (CBMM) are mixed in 62 g of deionized water at 80 °C, with stirring (800 rpm). Then, the gel is introduced in a teflon-lined, stainless steel autoclave and heat at 175 °C for 48 h. The obtained purple solid is filtered off, washed thoroughly with water and dried overnight at 80 °C, and then heat-treated at 700-800 °C in N₂ stream for 2 h. The XRD pattern of these catalyst is shown in Figure S1.

Synthesis of Mo/W-Nb-V-X (X=Te,Sb,Bi) mixed metal oxides (samples H1-T1, H1-T2, H1-S, H1-B, H2-T, H3-T, H4-T)

3.3 mmol of the corresponding heteropolyacid (Aldrich), 8.0 mmol of vanadyl sulphate (Aldrich), 6.8 mmol of niobium oxalate (CBMM) and 1.6-3.2 mmol of telluric acid (Aldrich), or 0.8 mmol of antimony III oxide (Fluka), or 0.8 mmol of bismuth III oxide (Fluka) are mixed in 62 g of deionized water at 80 °C, with stirring (800 rpm). Then, the gel is introduced in a teflon-lined, stainless steel autoclave and heat at 175 °C for 48 h. The obtained purple solid is filtered off, washed thoroughly with water and dried overnight at 80 °C, and then heat-treated at 700 °C in N₂ stream for 2 h. XRD patterns of these catalysts are shown in Figure S2.

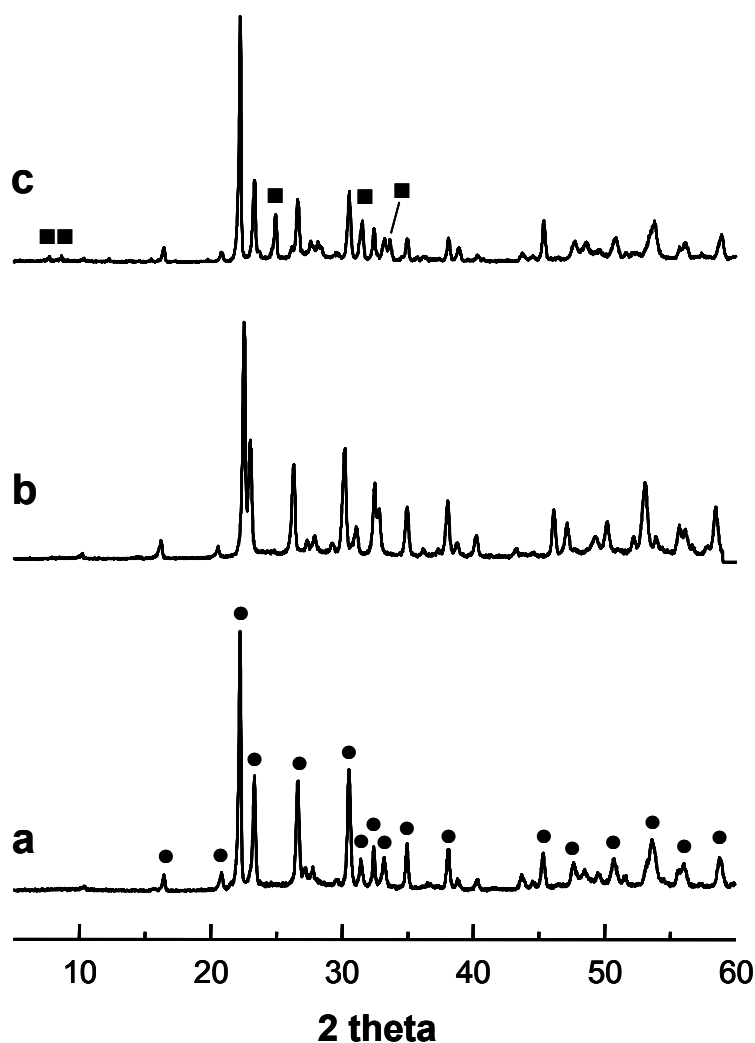


Figure S1 XRD patterns of TTB-structure based catalysts prepared by hydrothermal synthesis from different Keggin-type heteropolyacids. a) H1; b) H2; c) H3. Legend: (●) Main reflexions of the high purity TTB-related crystal phase present in H1 sample; (■) reflexions of M₅O₁₄-type phase (M= Mo, V, Nb) in Si-containing sample. The diffractogram of W-containing sample shows some reflections shifted with respect to the Mo-based tetragonal bronzes.

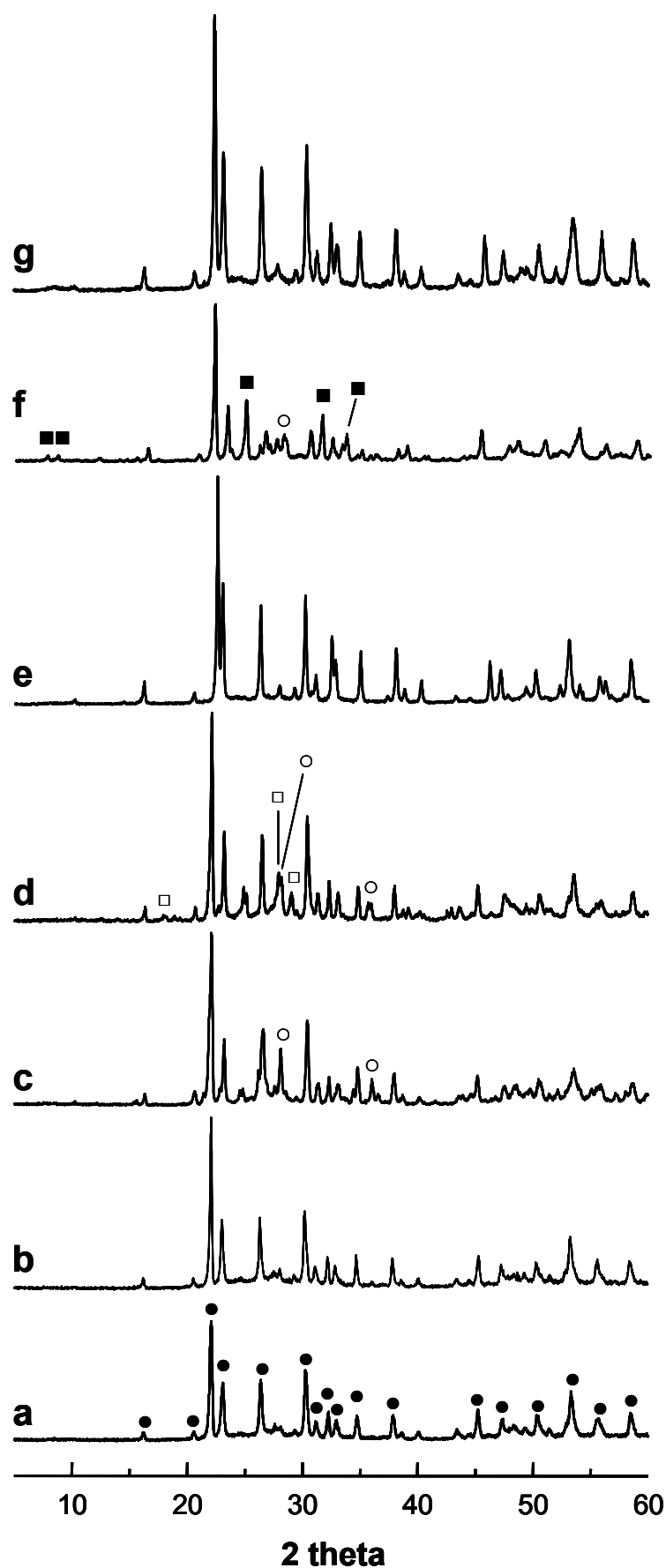


Figure S2 XRD patterns of TTB-structure based catalysts prepared by hydrothermal synthesis from different Keggin-type heteropolyacids and an element of group V or VI. a) H1-T1; b) H1-T2; c) H1-S; d) H1-B; e) H2-T; f) H3-T; g) H4-T. Legend: (●) Main reflexions of the high purity TTB-related crystal phase present in H1-T1 sample; (○) reflexions of the pseudo-hexagonal bronze $\text{Te}_{0.33}\text{MO}_{3.33}$ (M= Mo, V, Nb) or M2 crystalline phase in H1-S, H1-B and H3-T samples; (□) reflexions of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ in the H1-B sample; (■) reflexions of M_5O_{14} -type phase (M= Mo, V, Nb) in H3-T sample. The diffractogram of W-containing samples shows some reflections shifted with respect to the Mo-based tetragonal bronzes.

HREM/SAED STUDY

The structural characterization performed by means of Transmission Electron Microscopy has shown that the molybdenum (tungsten) bronzes obtained changed their microstructure depending on the final niobium content. Structural differences among the patterns arise mainly from the range of order between the niobium atoms allocated in the pentagonal tunnels of the basic TTB unit cell. When ordered, and for the lower niobium content in the corresponding crystal ($\text{Nb}/(\text{Mo}+\text{V}) \sim 0.22$), a threefold superstructure of TTB equivalent to that of $\text{Nb}_8\text{W}_9\text{O}_{47}$ (see Figure S3) is obtained. Increasing Nb ratios ($\text{Nb}/(\text{Mo}+\text{V}) \sim 0.4\text{--}0.5$) give rise to disordered occupation of the pentagonal tunnels or short range order microstructures (Figure S4).

