Supporting information

The role of surface basal planes of layered mixed metal oxides in selective transformation of lower alkanes: propane ammoxidation over surface *ab* planes of Mo-V-Te-Nb-O M1 phase

N. Raveendran Shiju*[a], Xinhua Liang[b], Alan W. Weimer[b], Chengdu Liang[c], Sheng Dai[c] and Vadim V. Guliants*[a]

[a] Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA
[b] Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80309-0424
[c] Chemical Sciences Division & Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN37831, USA

Experimental Section

The catalysts were synthesized by hydrothermal treatment of the slurry obtained by mixing appropriate amounts of source compounds, such as ammonium molybdate, vanadyl sulfate, niobium oxalate, and telluric acid (all chemicals from Alfa Aesar, USA) for the Mo-V-Te-Nb-O and tellurium oxide for Mo-V-Te-O compositions. Hydrothermal synthesis was carried out at 448 K for 72 and 48 h for the Mo-V-Te-O and Mo-V-Te-Nb-O M1 phases, respectively. The solids obtained were filtered, washed several times with deionized water and dried overnight at 353 K. The as-synthesized phases were calcined in a flow of ultra-pure N_2 at 773 K for Mo-V-Te-O and at 873 K for Mo-V-Te-Nb-O compositions to yield M1 phases, as confirmed by X-ray diffraction.

A fluidized bed reactor was used to deposit Al_2O_3 films on catalyst particles by atomic layer deposition (ALD). The system was operated at reduced pressures and under mechanical vibration. The vibration can help to improve the quality of fluidization by overcoming part of inter-particle forces of the fine particles. A detailed description of the fluidized bed reactor system for particle atomic layer deposition (ALD) may be found elsewhere.[1] Deionized water and trimethylaluminum (TMA) (97%, Sigma-Aldrich Co.) were used as reactants. Alumina ALD is carried out by splitting the reaction of TMA and H_2O into two self-limiting and self-terminating half-reactions:[1-5]

$$\text{(A) } AlOH^* + Al(CH_3)_3 \rightarrow [AlOAl(CH_3)_2]^* + CH_4 \qquad (1)$$

$$\text{(B) } Al(CH_3)^* + H_2O \rightarrow AlOH^* + CH_4 \qquad (2)$$

(Here the asterisks designate the surface species.) The TMA and H_2O half-reactions are performed in an ABAB…binary sequence to deposit low impurity content, pinhole-free, conformal and ultra-thin Al_2O_3 films. The growth rate of the Al_2O_3 films deposited at the reaction temperature of 450 K is nominally 0.11~0.13 nm per coating cycle.[4, 5]

In a typical run, ~ 10 g of catalyst particles are loaded into the reactor. The minimum fluidization velocity is 1.2 cm/s determined by measuring the pressure drop across the bed versus the N_2 superficial gas velocity. Precursors are fed separately through the distributor of the reactor using the driving force of their vapor pressures. The reaction temperature is 450 K. Before the reaction, the particles are out gassed at 450 K for about 4 hours. Each precursor is fed for enough time to make sure that all active sites are saturated. N_2 is then fed as the purge gas to help remove unreacted precursor and any by-

products formed during the reaction. The system is pumped down to 50 mtorr prior to the dose of the next precursor. In this manner, there is no overlap of two precursors and the undesirable chemical vapor deposition (CVD) is avoided.

Nitrogen sorption on M1 phases at 77 K was measured with a Micromeritics Tristar 3000. The M1 phase samples were degassed under flowing nitrogen at 423 K for 4 h before the measurement. The surface areas were calculated by the Brunauer-Emmet-Teller (BET) method. The SEM and Z-contrast TEM images of the M1 phase were collected by a Hitachi HD-2000 Scanning and Transmission Electron Microscope (STEM). The STEM unit was operated at an accelerate voltage of 200 KV and an electron current of 30 μA. The energy dispersive spectra (EDS) were collected at 30% of detector dead-time and 3 minutes of acquisition time.

The propane ammoxidation reaction was carried out in a fixed bed tubular flow reactor at atmospheric pressure using 0.2 g of the calcined catalyst. Whenever necessary, the catalyst was gently crushed in an agate mortar prior to catalytic tests. The catalyst was placed into the reactor, heated to the desired temperatures under He flow and exposed to the reaction feed. The feed was composed of C_3H_8, NH_3, O_2 and He in the molar ratio of 6:7:17:70 at the total flow rate of 20 ml/min. The reactants and products were analyzed by an on-line GC system (Shimadzu 14A) equipped with FID and TCD. The total carbon balances agreed within ±5 %.

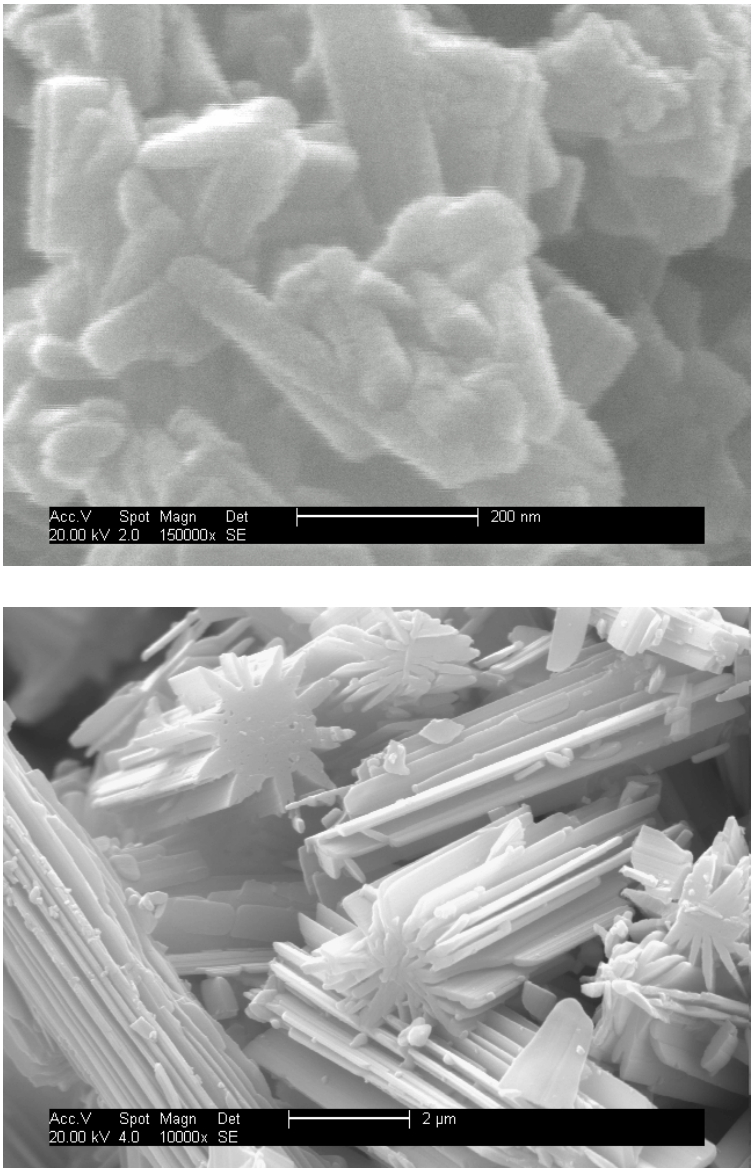
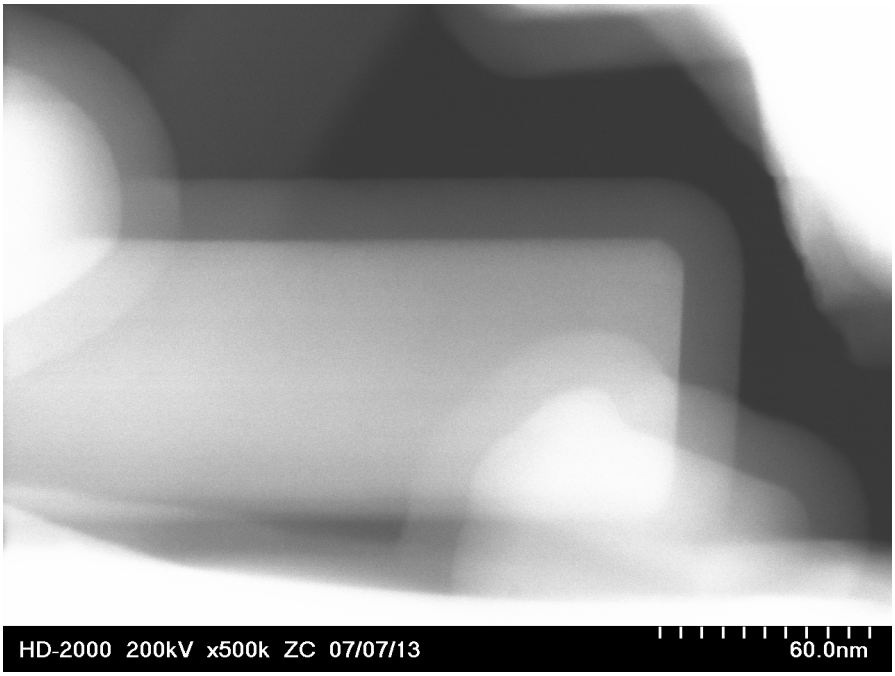


Figure S1: SEM images of Mo-V-Te-Nb-O (top) and Mo-V-Te-O (bottom) M1 phases.



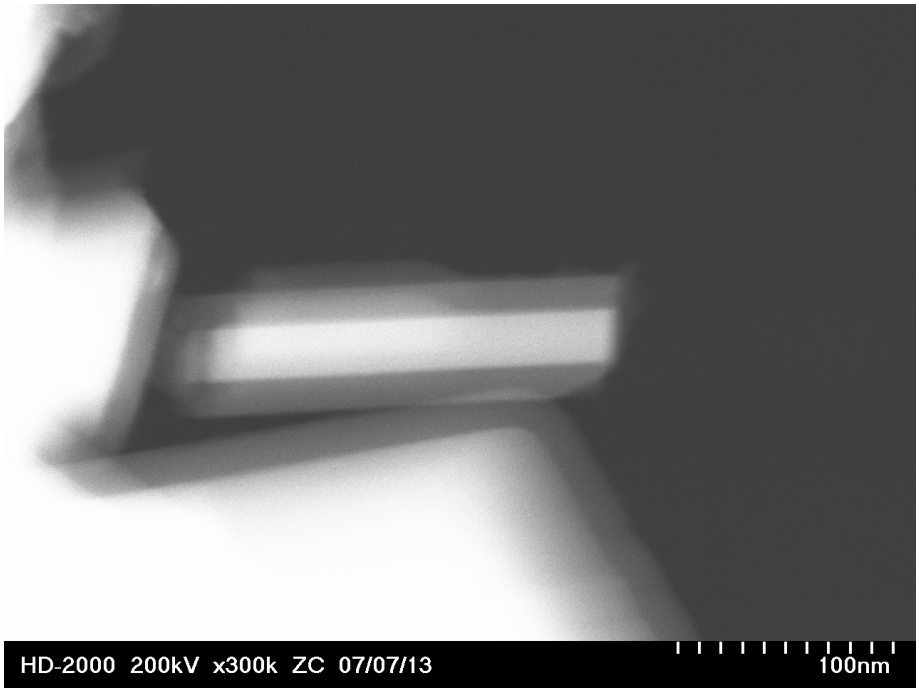


Figure S2: Z-contrast TEM images of Mo-V-Te-Nb-O M1 phase catalyst coated with alumina before crushing (top) and after crushing (bottom).

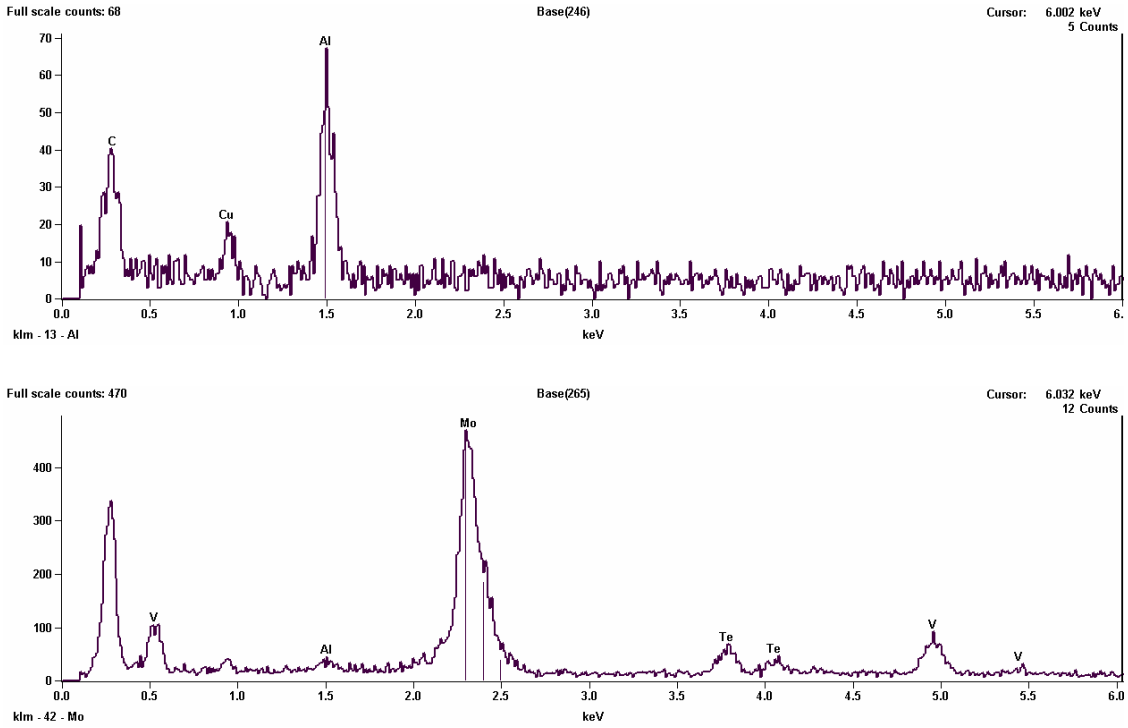


Figure S3: EDS analysis of alumina-coated Mo-V-Te-Nb-O M1 phase catalyst before crushing (top) and after crushing (bottom).

Additional references:

(1) X. H. Liang, S. M. George, A. W. Weimer, N. H. Li, J. H. Blackson, J. D. Harris, P. Li, Chem. Mater. 2007, 19, 5388.

(2) J. R. Wank, S. M. George, A. W. Weimer, Powder Tech. 2004, 142, 59.

(3) L. F. Hakim, C. L. Vaughn, H. J. Dunsheath, C. S. Carney, X. H. Liang, P. Li, A. W. Weimer, Nanotech. 2007, 18, 345603/1.

(4) L. F. Hakim, J. Blackson, S. M. George, A. W. Weimer, Chem. Vapor Dep., 2005, 11, 420.

(5) J. W. Elam, Z. A. Sechrist, S. M. George, Thin Solid Films, 2002, 414, 43.