

Phase-pure MoVTeNbO M1 catalysts for propane oxidation: particle dimension and catalytic properties

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Enabling the oxidation of low-cost propane to acrylic acid, M1 ($\text{Mo}_{7.8}\text{V}_{1.2}\text{Te}_{0.94}\text{NbO}_{28.9}$, orthorhombic, *Pba2*, $a = 21.134 \text{ \AA}$, $b = 26.658 \text{ \AA}$ and $c = 4.015 \text{ \AA}$) MoVTeNbO oxides have been proposed as a promising catalyst, ascribed to its exceptional catalytic performance [1]. Since there is a close correlation between the particle size of catalysts and their catalytic reactivity and selectivity [2], it will be necessary to explore this relationship for M1 catalyst, which is critical for the development of new and improved multicomponent MoVTeNbO catalysts. However, such investigations are seldom reported to date. Recently we successfully synthesized phase-pure M1 phase catalysts exhibiting various particle dimensions. This enables us to explore the effect of M1 particle sizes and morphology on the catalytic performance, allowing the establishment of an important reference for designing and preparing high-performance M1 catalysts for the selective oxidation of propane to acrylic acid.

A series of highly crystalline phase-pure powdered M1 catalysts (confirmed by XRD) with various particle sizes have been prepared by applying a hydrothermal-based route, purification of two-phase M1&M2 oxide system and a method utilizing superheated-water vapor treatment, referred thereafter to as HT-M1, W-M1-a/W-M1-b, and SH-M1, respectively, keeping the chemical composition of M1 nearly constant (Mo $63.6 \pm 1.2 \text{ at.}\%$, V $16 \pm 0.7 \text{ at.}\%$, Te $6.4 \pm 0.3 \text{ at.}\%$ and Nb $14 \pm 1.3 \text{ at.}\%$, as confirmed by EDX). A Hitachi S-4800 SEM and a Philips CM200-FEG TEM were employed to characterize microstructure of samples.

The good bulk crystallinity was confirmed for the M1 crystals growing along $\langle 001 \rangle$ direction, as shown in Fig. 1a and b. Mo, V, Te, Nb and O maps (see Fig. 1c) highlight very homogeneous distribution of the constituent elements inside the W-M1-b particles, and reveal no local fluctuation at this microscopic scale, similar to other three samples. Whereas the overall morphology of the four M1 catalysts is similar, only dimensional variations are observed, as shown in Fig. 2. Typically, the M1 particles in each sample can be approximately regarded as a cylindrical shape with (001) plane termination at basal surfaces and other (hk0) planes termination at lateral surfaces. The particle size distributions of each sample are obtained by statistical evaluation of approximately more than 350 particles for each item (length and width) of particle, as shown in Fig. 3.

The particle sizes are largest for the HT-M1. The average length of HT-M1 particles is 418 nm and 212 nm in width. The particles sizes are similar for W-M1-a and W-M1-b particles. The average length 194 nm of W-M1-a particles is slightly larger than that of W-M1-b 189 nm while the average width 91 nm of the former is smaller than that of the latter 111 nm. Quite different from the aforementioned 3 samples, the dominant SH-M1 particles are very tiny together with a minority of exceptional large ones. The width of particles is only 61 nm with an average length of 197 nm. As shown in Table. 1, the W-M1-b sample shows the highest conversion 72%. Similar conversion 68% is confirmed in W-M1-a sample with

the similar particle dimensions. Their selectivity for the formation of acrylic acid is also similar. Similar selectivity to acrylic acid of about 60% is observed at a propane conversion of approximate 50% for the catalysts HT-M1 and W-M1-b, provided that the latter underwent a high total flow during the catalytic reaction. That is to say, for the M1 particle dimensions larger than or around 100nm, there will be no obvious differences on the selectivity for the oxidation from propane into acrylic acid if the similar conversion exists. However, it was found that one order of magnitude lower for the selectivity of the catalysts SH-M1, with particle dimensions of much less than 100nm. HT-M1 shows high selectivity to acrylic acid, whereas nanostructured M1 turned out to catalyze the total combustion of propane to carbon oxides. The selectivity for the acrylic acid decreases with the decrease of particle size, i.e., in the order of HT-M1 > W-M1-b > W-M1-a > SH-M1.

In summary, particle size of M1 has a significant impact on the catalytic performance. The selectivity to acrylic acid decreases drastically with decreasing particle size of M1 catalysts.

1. R.K. Grasselli et al., Top. Catal. **23** (2003) p5.
2. I. Lee et al., Nature mater. **8** (2009) p132.
3. The authors thank Dr. Yu V. Kolen'ko for the preparation of one of the catalysts.

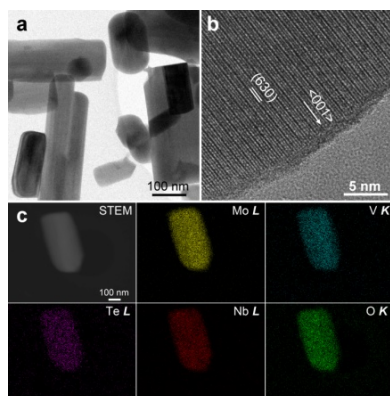


Figure 1. (a) TEM and (b) HR-TEM images of the W-M1-b M1 particles. (c) STEM image together with EDX maps.

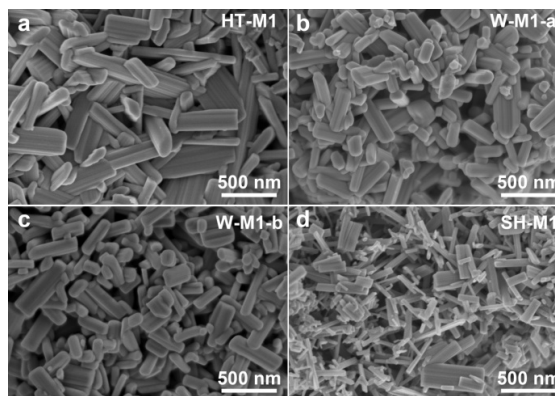


Figure 2. Typical SEM images of samples (a) HT-M1, (b) W-M1-a, (c) W-M1-b and (d) SH-M1.

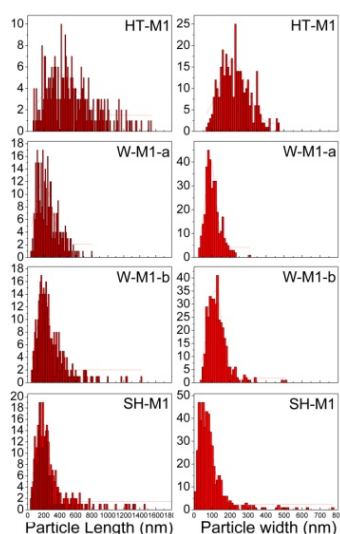


Figure 3. The distribution of length and width of catalyst particles.

Table 1. Catalytic properties of the various M1 catalysts in selective oxidation for propane to acrylic acid. The condition is $T = 400^{\circ}\text{C}$ and $\text{C}_3\text{H}_8/\text{O}_2/\text{H}_2\text{O}/\text{N}_2 = 3/6/40/51$ vol % (*at higher total flow).

Catalyst	$X_{\text{C}_3\text{H}_8}$ [%]	$S_{\text{C}_3\text{H}_6\text{O}_2}$ [%]
HT-M1	52	58
W-M1-a	68	34
W-M1-b	72 47*	40 62*
SH-M1	56	5