A Study of M1/M2 Phase Synergy in the MoVTe(Nb,Ta)O Catalysts for Propane Ammoxidation to Acrylonitrile

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Abstract

The bulk mixed MoVTe(Nb,Ta)O catalysts containing nanoscale intergrowths of so-called M1 and M2 phases display uniquely high reactivity in propane ammoxidation to acrylonitrile (ACN) associated with the surface *ab* planes of the M1 phase. The current controversy surrounding this catalytic system is focused on the role of the M2 phase, which is unable to activate propane but was suggested in some studies to function in synergy with the M1 phase by efficiently converting the propylene intermediate to ACN. The present study systematically examined the catalytic behavior of pure M1 phases prepared by selective dissolution of the M2 phase in MoVTe(Nb,Ta)O catalysts in aqueous hydrogen peroxide. It confirmed that the MoVTe(Nb,Ta)O M1 phases are highly active and selective for propane and propylene ammoxidation, while the MoVTe(Nb,Ta)O M2 phases were active and selective in propylene ammoxidation only. Crucially, the present study of the pure MoVTe(Nb,Ta)O M1 and M2 phases in propylene ammoxidation revealed for the very first time that the M2 phases are

significantly less active than the corresponding M1 phases in propylene ammoxidation. The findings of this study do not support the existence of the synergy effect for the MoVTe(Nb,Ta)O M1 and M2 phases. Instead, the trends previously associated with the M1 and M2 phase synergy in propane ammoxidation can be explained by two effects that were unaccounted for previously: (i) the preferential loss of surface active TeO_x species from the M1 phase during the H_2O_2 treatment, and (ii) the generation of fresh *ab* planes via mechanical crushing of the H_2O_2 -treated M1 phase. These findings confirmed that the M1 phase is the only phase required for the activity and selectivity of the MoVTe(Nb,Ta)O catalysts in propane ammoxidation to ACN.

1. Introduction

The replacement of olefins and aromatics feedstocks employed in selective oxidation processes by natural gas-based alkanes that are more environmentally friendly and abundant, has received significant attention of the catalysis community in recent decades [1-6]. The ammoxidation of propane to acrylonitrile (ACN) is of particular interest as a possible alternative to the current industrial process of propylene ammoxidation providing a high-volume ACN intermediate for the manufacture of synthetic fibers, resins and rubbers [7-9]. Among different catalytic systems being investigated by academic and industrial research groups for one-step propane ammoxidation, the most promising system is the MoVTe(Nb,Ta) mixed metal oxide containing so-called M1 and M2 phases [6, 10-19].

The MoVTeNbO M1 phase was demonstrated to be responsible for propane activation and its selective transformation to ACN, while the MoVTeNbO M2 phase was proposed to play a secondary role by converting excess propylene intermediate that forms over the M1 surface into ACN [20, 21]. The M1 phase is capable of both propane oxidation to acrylic acid and propane ammoxidation to ACN, which were proposed to occur via the propylene intermediate [20, 22,

23]. While the M1 phase is the only active and selective phase in propane (amm)oxidation, the presence of the M2 phase was proposed to improve the selectivity to acrylic acid in propane oxidation [22] and the selectivity to ACN in propane ammoxidation [24]. The improvement in the ACN yield as a result of the MoVTeNbO M1 and M2 phase cooperation, or their synergy, was claimed in several studies [2, 19, 20, 24-26]. This synergy effect was explained by migration of the propylene intermediate desorbed from the M1 to the M2 phase where it is rapidly transformed to ACN [20].

Grasselli et al. [20] found that the synergy effect was only observed when the M1 and M2 phases, prepared separately, were crushed to particle size $< 5 \mu\text{m}$ and intimately mixed. The synergy effect was also claimed for propane oxidation to acrylic acid when the M1 and M2 phases were prepared independently and then physically mixed [22]. Two possible causes of the synergy effect in the oxidation of propane to acrylic acid were proposed by Baca et al. [22]: 1) highly efficient conversion of propylene desorbed from the M1 phase into acrylic acid over the M2 phase; and 2) the migration of Te from the M2 phase to the surface of the M1 phase, thus maintaining the Te concentration on the surface of the M1 which otherwise gradually decreases during the reaction causing the catalyst deactivation.

The earlier studies of the synergy effect in propane (amm)oxidation employed pure M1 phases obtained by the hydrogen peroxide treatment of as-synthesized catalysts to selectively dissolve the M2 phase, because as-synthesized catalysts contain both M1 and M2 phases [2, 19, 20, 24-26]. However, the impact of the hydrogen peroxide treatment on the surface chemistry and catalytic behavior of the resulting M1 phase has not been investigated. Moreover, the M1 and M2 phases were crushed in the earlier studies to increase their interfacial contact proposed to be important for the synergy effect. On the other hand, the as-synthesized MoVTe(Nb,Ta)O

catalysts are routinely crushed because it improves their catalytic activity in propane (amm)oxidation and the selectivity to ACN and acrylic acid [2, 19, 20, 24-26]. This improvement was explained by the rod-like crystal habit of the M1 phase that preferentially fractures along the *z*-axis exposing fresh *ab* planes that are proposed to contain the active and selective sites for propane (amm)oxidation [27]. Therefore, the studies of the synergy effect reported to date did not decouple the effects of hydrogen peroxide treatment and crushing of the M1 phase on its catalytic behavior from the catalytic behavior of the crushed M1/M2 phase mixtures.

This study employed well-defined pure MoVTe(Nb,Ta)O M1, M2, M1/M2 physical mixtures, and as-synthesized catalysts to systematically probe the existence of the M1/M2 phase synergy in propane and propylene ammoxidation to acrylonitrile. The effects of crushing and hydrogen peroxide treatment were investigated for the pure MoVTeNbO M1 phase to elucidate the trends of catalytic behavior for the pure M1 phase and physical M1/M2 phase mixtures. Lastly, pure MoVTe(Nb,Ta)O M1 phases were crushed and treated by hydrogen peroxide in order to determine the nature of metal oxides species preferentially leached from the surface of the M1 phase.

2. Experimental

2.1 Catalyst synthesis

The MoVTeNbO catalyst with the synthesis molar ratio of Mo:V:Te:Nb = 1:0.3:0.17:0.12 was synthesized hydrothermally (HT) at 448 K for 48 h [23]. Ammonium molybdate (Alfa Aesar, 81-83% as MoO₃), vanadyl sulphate (Alfa Aesar, 99.9%), telluric acid (Alfa Aesar, 99%) and niobium (V) oxalate hexahydrate (Alfa Aesar) were used as the sources of respective elements.

After hydrothermal synthesis, the catalyst precursors obtained were filtered, washed and dried at 353 K overnight. Three MoVTaTaO catalysts, Mo:V:Te:Ta=1:0.31:0.22:(0.09, 0.12, 0.15), were prepared hydrothermally [23] and denoted as HT (0.09), HT (0.12) and HT (0.15). One more MoVTaTaO catalyst, Mo:V:Te:Ta=1:0.31:0.22:0.12, was made by the microwave assisted hydrothermal synthesis, MW [28]. The dry catalyst precursors obtained were calcined under ultra-high purity nitrogen flow (50 ml/min) at 873 for 2 h and crushed using a mortar and pestle for 10 min to yield as-synthesized MoVTa(Nb,Ta)O catalysts.

The selective dissolution of the M2 phase was carried out by stirring the calcined as-synthesized MoVTa(Nb,Ta)O catalysts in the aqueous 30% H₂O₂ for 3 h [29]. The resulting suspensions of pure M1 phase were filtered, washed with distilled water (200 ml) and dried overnight at 353K.

The MoVTaNb(Ta)O M2 phase catalysts were prepared by slurry evaporation (SE) method at the synthesis ratio of Mo:V:Te:Nb(Ta) = 1.00:0.31(0.3):0.27(0.37):0.08(0.06) as reported previously [25]. Physical M1/M2 mixtures denoted below as “M1/M2” were obtained by crushing the respective pure M1 and M2 phases in a 1:1 mass ratio for 10 min using a mortar and pestle. Finally, the pure MoVTa(Nb,Ta)O M1 phases after the H₂O₂ treatment were crushed for 10 min using a mortar and pestle and treated again by H₂O₂ as described above.

2.2 Characterization

Powder X-ray diffraction was recorded by a Siemens D500 diffractometer using the Cu K α radiation (tube voltage: 45kV, tube current: 40 mA). Scanning electron microscopy (SEM) and EDS analysis were conducted at the Advanced Materials Characterization Center at the

University of Cincinnati. SEM (FEI/Philips XL 30 FEG ESEM) has a resolution of 3.5 nm at 30 kV and is equipped with the Energy Dispersive X-ray Analyzer from EDAX.

2.3 ICP-MS elemental analysis

Elemental analysis was performed on an Agilent 7700 Inductively Coupled Plasma Mass Spectrometer (Agilent Technologies, Santa Clara, CA). Calibration curves were examined both with and without the use of collision cell (pressurized with He, 3 ml min⁻¹). However, no significant differences were noted and all data reported was acquired in no gas mode. Major isotopes of all analytes of interest were measured; quantitation was performed on the highest that contained no isobaric overlap with neighboring elements. Samples were introduced with Agilent integrated auto sampler. Specific instrument parameters are given in Table 1.

2.4 Reagents and standards

Calibration standards were purchased as 10 mg/L mixtures of Nb, Mo and Ta amongst other elements from Agilent Technologies (Agilent Technologies, Santa Clara, CA) and Spex CertiPrep (Spex CertiPrep, Metuchen, NJ). 1000 mg/L Specpure® standards for V and Te were purchased from Alfa Aesar (Alfa Aesar, Ward Hill, MA). Calibration standards were prepared by appropriate dilution of these standards with trace metal grade nitric acid (Fisher Scientific, Waltham, MA). Hydrogen peroxide, 30% was also used (Fisher Scientific, Waltham, MA). The MoVTe(Nb,Ta)O M1 phases (20 mg) were digested for 3 days at room temperature in a mixture of 49% HF (0.9 g) and 69.4% HNO₃ (2.5 g) and then diluted as needed for the ICP-MS analysis.

2.5 Propane and propylene ammoxidation

The catalytic behavior of the MoVTe(Nb,Ta)O M1, M2, M1/M2, and as-synthesized catalysts prepared by HT and SE synthesis methods was investigated in both propane and propylene ammoxidation using a fixed bed micro-reactor equipped with an on-line GC under steady-state conditions at atmospheric pressure and 613–733K. Among the four MoVTeTaO catalysts synthesized, the catalyst with the synthesis molar ratio of Mo:V:Te:Ta = 1:0.3:0.17:0.12 (Table 2) was characterized in propane and propylene ammoxidation. The feed was composed of C₃H₈ (C₃H₆)/NH₃/O₂/He in the molar ratio of 5.7(5.7):8.7:17.1:68.4 at the total flow rate of 26.3 mL/min. The reactants and products were analyzed by an on-line GC system (Shimadzu 14A) equipped with a flame ionization detector and a thermal conductivity detector. The total carbon balances agreed within $\pm 5\%$.

3. Results and Discussion

3.1 Bulk characteristics of the MoVTe(Nb,Ta)O catalysts

XRD patterns of the as-synthesized MoVTe(Nb,Ta)O catalysts made by the HT method revealed the presence of both the M1 and M2 phases (Figure S1). Their M1/M2 phase ratios were estimated using the pure MoVTeNbO M1 and M2 phases, and three physical phase mixtures containing different mass fractions, M1:M2 of 1:3, 1:1, and 3:1, as XRD standards. The characteristic peak areas at $2\Theta = 27.1^\circ$ for the M1 phase and $2\Theta = 36.1^\circ$ for the M2 phase in as-synthesized catalysts were determined by the PANalytical X'Pert HighScore software. The calibration curve thus obtained was employed to estimate the M1 and M2 phase content in as-synthesized catalysts shown in Table 2.

The XRD patterns of the as-synthesized MoVTe(Nb,Ta)O catalysts after the H₂O₂ treatment (Figure S2) show the presence of pure M1 phase with its the characteristic peaks at

$2\Theta=6.7, 7.8, 8.9, 22.1, 27.2,$ and 45° (PDF 01-073-7574) without any impurities. The XRD patterns of the MoVTe(Nb,Ta)O M2 phases (Figure S3) displayed peaks at $2\Theta=22, 28, 36, 45$ and 50° corresponding to those of the pure M2 phase (PDF 01-073-7575). The morphology, crystal shape and size of the MoVTe(Nb,Ta)O M1 and M2 phases were characterized by SEM. The SEM images of the MoVTe(Nb,Ta)O M1 phase catalysts in Figure 1 show the rod-like morphology for all synthesis compositions. The crystal morphology of the M2 phases is different from that of the M1 phases (Figure 2). This result is in good agreement with the results of a previous study [25] where the M2 phase particles were found to have platelet morphology.

3.2 Propane and propylene ammoxidation over MoVTe(Nb,Ta)O M1 and M2 phase catalysts

3.2.1 MoVTe(Nb,Ta)O M1 phase catalysts in propane ammoxidation

The ACN selectivity of MoVTe(Nb,Ta) M1 phase catalysts is plotted against propane conversion as a function of reaction temperature in Figure 3. Interestingly, the MoVTeTaO M1 phase showed even higher selectivities to ACN than the MoVTeNbO M1 phase at propane conversion $< 20\%$. However, the MoVTeNbO M1 phase showed a superior selectivity to ACN at propane conversion $> 30\%$ (Figure 3).

The kinetic studies of the MoVTe(Nb,Ta)O M1 phase catalysts were conducted in order to further understand their catalytic behavior in propane ammoxidation to acrylonitrile. According to previous kinetic studies of the MoVTeNbO M1 phase, the propane consumption over the MoVTeNbO M1 phase under propane ammoxidation conditions was found to be a *first-order irreversible* reaction [23, 30]. The linear nature of Arrhenius plots of the first-order irreversible reaction rate constant, $k''(\text{C}_3\text{H}_8)$, for MoVTe(Nb,Ta)O M1 phase catalysts confirmed that propane consumption over these M1 phase catalysts during propane ammoxidation is the 1st

order reaction (Figure 4). The activation energies of propane consumption estimated from these plots to be 103 and 126 kJ/mol for the MoVTaNbO and MoVTaTaO M1 phases, respectively, are in good agreement with reported values for these and other M1 phase compositions [23]. The MoVTaNbO M1 phase is a more active catalyst than the MoVTaTaO M1 phase (Figure 4), while the latter catalyst is somewhat more selective to ACN (Figure 3).

3.2.2 Propylene ammoxidation over MoVTe(Nb,Ta)O M1 and M2 catalysts

The MoVTaNbO M1 and M2 phases were previously shown to be active for propylene (amm)oxidation [1, 19, 20, 22]. However, few studies directly compared the catalytic performance of the M1 and M2 phases in propylene ammoxidation [20, 31], whereas the MoVTaTaO composition has not been investigated. Therefore, MoVTe(Nb,Ta)O M1 and M2 phase catalysts were systematically investigated in propylene ammoxidation in this study.

The ACN selectivity of MoVTe(Nb,Ta)O M1 and M2 phase catalysts was plotted against propylene conversion at various reaction temperatures in Figures 5 and 6, respectively. The MoVTe(Nb,Ta) M1 phase catalysts were found to be selective to ACN indicating that the M1 phase contained the active surface sites capable of both propane and propylene activation to ACN, which is in a good agreement with the results of previous studies [1, 2, 32]. The MoVTe(Nb,Ta)O M2 phase catalysts displayed relatively high selectivity toward ACN (~ 80 mol. %) at low propylene conversion (~15%).

Similar to the catalytic activity of the MoVTe(Nb,Ta)O M1 phases in propane ammoxidation, the propylene consumption over the M1 and M2 of the MoVTe(Nb,Ta)O catalysts under propylene ammoxidation was assumed to be the *first-order irreversible* reaction for a plug flow reactor model [33]. The linear nature of the Arrhenius plots of the first-order

irreversible reaction rate constant, $k''(\text{C}_3\text{H}_6)$, for the MoVTe(Nb,Ta)O M1 and M2 phases further supported the assumption that propylene consumption over the MoVTe(Nb,Ta)O M1 and M2 phases in propylene ammoxidation is indeed a 1st order reaction.

Figure 7 shows a comparison of the reaction rate constants for propylene consumption, $k''(\text{C}_3\text{H}_6)$, over MoVTe(Nb,Ta)O M1 and M2 phases in propylene ammoxidation at 613-713 K. The $k''(\text{C}_3\text{H}_6)$ values for MoVTe(Nb,Ta)O M1 phase catalysts in propylene ammoxidation showed some dependence on the chemical composition, as did the $k''(\text{C}_3\text{H}_6)$ values for MoVTe(Nb,Ta)O M2 phases (Figure 7). However, the $k''(\text{C}_3\text{H}_6)$ values of MoVTe(Nb,Ta)O M1 phases were significantly higher than those of corresponding M2 phases at the same reaction temperature (e.g., 673K), whereas the MoVTeNbO M1 phase was investigated at lower temperatures due its much greater activity than that of the MoVTeNbO M2 phase. The $k''(\text{C}_3\text{H}_6)$ values of the MoVTeNbO M1 at higher temperatures were estimated by the Arrhenius fit (Figure 4), indicating that it was ca. 65 times higher at 673K than that of the M2 phase.

These findings strongly indicated that all M1 phases are much more active than all corresponding M2 phases in converting propylene to ACN at the same reaction temperature. These results are further supported by the earlier findings of Ishchenko et al. [34], which showed the MoVTeNbO M1 phase to possess much higher activity as compared to the MoVTeNbO M2 phase in propylene oxidation reaction.

3.3 Propane and propylene ammoxidation over MoVTe(Nb,Ta)O M1, M1/M2, and as-synthesized catalysts

3.3.1 MoVTeNbO M1, M1/M2, and as-synthesized catalysts in propane ammoxidation

The improvement of the yield of acrylic acid and ACN in propane (amm)oxidation over a mixture of the MoVTaNbO M1 and M2 phases were reported by several groups [2, 19, 22, 24, 25]. The yield enhancement of acrylic acid in propane oxidation was explained by superior catalytic activity of the M2 phase in converting propylene to acrylic acid [21]. In a subsequent study, Holmberg et al. [20] suggested that symbiotic increase in the ACN yield is explained by the conversion of unreacted propylene intermediate migrating from the M1 to M2 phase [1, 2]. Baca et al. [22] also proposed the M2 phase participation in transforming propylene formed on M1 phase as one of the origins of the synergy effect.

However, the MoVTaNbO M1 phase was shown to be the only active and selective phase in propane ammoxidation to ACN [31]. This conclusion is based on the findings that the MoVTaNbO M1 phase was more efficient in propylene ammoxidation at longer reactor residence times and higher propane conversion [31]. In addition, Ishchenko et al. [34] proposed that the M1 phase is sufficient for the oxidation of propane to acrylic acid while the M2 phase is undesirable due to its lower activity and selectivity as compared to the M1 phase.

Therefore, a systematic study of propane and propylene ammoxidation over (1) pure M1, (2) pure M2, (3) M1/M2 physical mixtures, and (4) as-synthesized MoVTaNbO catalysts was conducted in order to probe the existence of the synergy effect for this catalytic system. The M1/M2 catalyst is a physical mixture of the M1 and M2 phases (M1:M2=1:1 mass ratio) described in the experimental section. The M1:M2 content (wt. %) in the as-synthesized MoVTaNbO catalyst was estimated to be 0.75:0.25 (Table 2). The selectivities to ACN for the MoVTaNbO M1, M1/M2, and as-synthesized catalysts in propane ammoxidation are plotted as a function of propane conversion in Figure S4. These results suggested higher selectivity to ACN

for the M1/M2 and as-synthesized catalysts as compared to the pure M1 at low propane conversion (< 20 %) during propane ammoxidation (Figure S4).

However, the selectivity to ACN of all catalysts became similar at propane conversion > 50%. This result is similar to that observed in our earlier study [31] where the as-synthesized MoVTaNbO catalyst (75% M1 and 25% M2) was found to be more efficient at low to moderate propane conversion (~ 50%), but the pure M1 phase became more efficient as propane conversion increased above 50% during its ammoxidation. Therefore, these results suggested that the pure M1 phase is sufficiently active in propane ammoxidation, while some improvement in the selectivity to ACN was observed for the M2-containing catalysts at low propane conversion.

The kinetic studies of the MoVTaNbO M1, M1/M2, and as-synthesized catalysts were conducted to further understand the observed improvement of the ACN selectivity at low propane conversion reported in Figure S4. The propane reaction rate constants, $k''(\text{C}_3\text{H}_8)$, of the MoVTaNbO M1, M1/M2, and as-synthesized catalysts are plotted against the reaction temperature in Figure 8. If one assumes that the M2 phase is inactive towards propane and only converts propylene to ACN, then the pure M1 phase was expected to display the highest reaction rate constant, $k''(\text{C}_3\text{H}_8)$, as compared to the M1/M2 and as-synthesized catalysts, which contained a significant fraction of the inactive M2 phase. For instance, the M1/M2 catalyst contained 50 wt. % M2, while the as-synthesized catalyst contained 25 wt. % M2 (Table 2). However, $k''(\text{C}_3\text{H}_8)$ of the M1/M2 catalyst was higher than that of the M1 catalyst at temperatures above 653 K as shown in Figure 8, which is against this expectation. This higher $k''(\text{C}_3\text{H}_8)$ of the M1/M2 catalyst as compared to that of the pure M1 phase suggested three possible scenarios responsible for the observed trends in catalytic behavior: (1) the M2 phase

participation in propane activation; (2) a detrimental impact of the H_2O_2 treatment on the surface chemistry and catalytic behavior of the pure M1 phase; and (3) enhanced catalytic activity of the M1 phase due to preferential exposure of fresh *ab* planes as a result of crushing the M1/M2 phase mixture to improve its interfacial contact. The results of the previous [20-22, 35-37] and present study clearly demonstrated that the M2 phase is not capable of propane activation. Therefore, the only reasonable explanations for the observed trends of $k''(\text{C}_3\text{H}_8)$ values for the MoVTaNbO M1, M1/M2, and as-synthesized catalysts are scenarios 2 and 3 above.

While the pure M1 phase after the H_2O_2 treatment was not crushed prior to its catalytic testing, this pure M1 was thoroughly ground together with the M2 phase to prepare the M1/M2 catalyst because the synergy effect was previously claimed only when these phases were mixed on micro-scale to improve their interfacial contact (for particles $<5\ \mu\text{m}$) [20]. It is well known that this crushing preferentially exposes fresh *ab* planes of the M1 phase, which are proposed to contain active and selective surface sites for propane ammoxidation [24, 38, 39]. A study of the MoVTaNbO M1 phase that selectively exposed *ab* planes also provided additional evidence that the *ab* planes may contain the active and selective sites for propane ammoxidation [27]. The higher BET surface area of the M1/M2 catalyst than the pure M1 phase reported in Table 2 further supports the proposal that the M1/M2 crushing increased the surface area of freshly exposed *ab* planes of the M1 phase. Therefore, high $k''(\text{C}_3\text{H}_8)$ of the M1/M2 catalyst for propane ammoxidation (Figure 8) can be explained by the additional *ab* planes exposed by crushing as reported previously [31]. This crushing effect can explain the improved selectivity to ACN over the M1/M2 catalyst at low propane conversion (Figure S4), while the removal of some surface active species from the M1 surface by H_2O_2 may explain lower catalytic activity of the pure M1 phase thus obtained.

3.3.2 MoVTenbO M1, M2, M1/M2, and as-synthesized catalysts for propylene ammoxidation

The kinetic studies of the MoVTenbO M1, M2, M1/M2, and as-synthesized catalysts were performed in order to further understand their catalytic behavior in propylene ammoxidation. The propylene consumption rate constants, $k''(\text{C}_3\text{H}_6)$, of the M1, M2, M1/M2, and as-synthesized catalysts were plotted against the reaction temperature in Figure 9. It appeared that all M1-containing phases are more active toward propylene than the pure M2 even though the reaction temperature ranges do not overlap under the reaction conditions of this kinetic study (Figure 9). Furthermore, the $k''(\text{C}_3\text{H}_6)$ values of the M1, M2, M1/M2, and as-synthesized catalysts were estimated based on Arrhenius fits at the same temperature, 673 K, and these $k''(\text{C}_3\text{H}_6)$ values, normalized to the $k''(\text{C}_3\text{H}_6)$ value of the M2 phase, were compared; M1 : M1/M2 : as-syn : M2 = 65 : 44 : 31 : 1.

These results indicated that the MoVTenbO M2 phase is significantly less active than the MoVTenbO M1 phase although the M2 phase may be somewhat more selective than the M1 phase toward ACN in propylene ammoxidation (Figures 5 and 6). Slightly lower selectivity of the pure M1 phase during propylene ammoxidation as compared to the pure M2 phase may be also explained by the partial removal of some surface active species, such as TeO_x , from the M1 surface after the H_2O_2 treatment. Most importantly, these findings strongly suggested the absence of the M1/M2 synergy effect because the M2 phase is inactive in propane ammoxidation and significantly less active than the M1 phase in propylene ammoxidation. Moreover, the improved selectivity to ACN observed for the MoVTenbO M1/M2 catalyst in propane ammoxidation can instead be explained by crushing the M1 phase, which selectively exposes fresh surface *ab* planes proposed to be active and selective in propane (amm)oxidation [24, 38, 39].

3.3.3 MoVTaTaO M1, M1/M2, and as-synthesized catalysts in propane ammoxidation

The selectivities to ACN during propane ammoxidation over the MoVTaTaO M1, M1/M2, and as-synthesized catalysts are plotted as a function of propane conversion in Figure S5. The M1/M2 and as-synthesized catalysts showed slightly higher selectivity to ACN than the M1 phase similar to that observed for the MoVTaNbO system.

We further plotted $k''(\text{C}_3\text{H}_8)$ of the MoVTaTaO M1, M1/M2, and as-synthesized catalysts in propane ammoxidation in Figure 10 in order to understand the greater ACN selectivity of the M1/M2 and as-synthesized catalysts as compared to pure M1 phase (Figure S5). Similar to the MoVTaNbO M2 phase, the MoVTaTaO M2 phase was also found to be inactive for propane ammoxidation in this study, which agrees well with the results of Grasselli et al. [25]. The high $k''(\text{C}_3\text{H}_8)$ values of the MoVTaTaO M1/M2 catalyst for propane ammoxidation (Figure 10) can be also explained by the additionally exposed *ab* planes produced by crushing as reported previously [31]. This crushing effect can explain the improved selectivity to ACN over the M1/M2 catalyst (Figure S5), while the removal of some surface active species from the M1 surface by H_2O_2 may explain lower catalytic activity of the pure M1 phase thus obtained.

3.3.4 MoVTaTaO M1, M2, M1/M2, and as-synthesized catalysts in propylene ammoxidation

The kinetic studies of the MoVTaTaO M1, M2, M1/M2, as-synthesized catalysts in propylene ammoxidation were conducted in order to understand somewhat higher selectivity to ACN for the MoVTaTaO M1/M2 and as-synthesized catalysts as compared to pure M1 phase (Figure S5). The propylene consumption rate constants, $k''(\text{C}_3\text{H}_6)$, for the MoVTaTaO catalysts were plotted against the reaction temperature in Figure 11. Similar to that observed for the MoVTaNbO catalysts, the MoVTaTaO M1, M1/M2, and as-synthesized catalysts showed similar

propylene consumption rate constants. At the same reaction temperature (e.g., 653K), the k'' (C_3H_6) of the M2 phase is lower than that of all M1-containing catalysts. This result indicated that the M2 phase would produce ACN at a lower yield than the M1 phase due to the low activity of the M2 phase in propylene ammoxidation, even though it is somewhat more selective. Therefore, these results indicated that the MoVTeTaO M1 phase is significantly more efficient than the MoVTeTaO M2 phase in terms of converting the propylene intermediate to ACN. This conclusion further suggests the lack of the synergy effect for the MoVTeTaO M1/M2 phases in propane ammoxidation to ACN.

3.4 Effects of H_2O_2 treatment and crushing on catalytic behavior of M1 phase

The results of our kinetic studies indicated the lack of the synergy effect for the MoVTe(Nb,Ta)O M1/M2 system and suggested instead that the H_2O_2 treatment and mechanical crushing may be responsible for the observed reactivity trends in propane ammoxidation. The decrease of $k''(C_3H_8)$ of pure MoVTe(Nb,Ta)O M1 catalysts is consistent with H_2O_2 partially removing surface components from the M1 phase that are important for its activity in propane ammoxidation. Given the labile nature of the TeO_x species in this catalytic system, it may be further proposed that the H_2O_2 treatment may selectively remove some surface TeO_x species that are known to be important for the catalytic activity and selectivity of the M1 phase towards propane (amm)oxidation. It was previously demonstrated that the catalytic activity and selectivity of the two-component MoVO M1 phase was significantly enhanced when it was promoted with a submonolayer TeO_x species introduced by the incipient wetness impregnation [40]. Our recent theoretical studies further indicated that the surface TeO_x species participates in both propane and propylene activation through α -hydrogen abstraction during propane (amm)oxidation [41]. Therefore, the partial Te loss from the surface of the M1 phase may

explain decreased activity and selectivity of the H₂O₂-treated M1 phase in propane ammoxidation. On the other hand, the recovery of catalytic activity after crushing the M1/M2 phase mixtures coincides with the generation of fresh surface *ab* planes of the M1 phase proposed to contain active and selective sites for propane ammoxidation [27].

The effect of the H₂O₂ treatment and subsequent grinding of the M1 phase was recently further investigated by our group for the MoVTaNbO system [42]. The reaction rate constants, $k''(\text{C}_3\text{H}_8)$, of propane consumption for the as-synthesized MoVTaNbO catalyst containing a mixture of the M1 and M2 phases, pure MoVTaNbO M1 phase after the H₂O₂ treatment, and MoVTaNbO M1 phase *crushed* after the H₂O₂ treatment are shown in Figure 12. The detailed information about these catalysts is summarized in Table S1. The activity of the M1 phase decreased after the H₂O₂ treatment as compared to the as-synthesized catalyst. On the other hand, crushing of the M1 phase after the H₂O₂ treatment not only restored the catalytic activity, but further enhanced it as compared to the as-synthesized catalyst. The activation energies of propane consumption estimated from the Arrhenius plots of $k''(\text{C}_3\text{H}_8)$ of these three catalysts were in the 103-108 kJ/mol range indicating the similar nature of propane-activating sites in these catalysts.

The crushed MoVTaNbO M1 phase catalyst was further treated by aqueous 30% H₂O₂ as described in the experimental section in order to elucidate the nature of metal oxide species removed from the M1 phase by H₂O₂. The pure MoVTaTaO M1 catalysts (HT 0.09, HT 0.12, HT 0.15 and MW) were also crushed and treated by H₂O₂. The detailed catalytic properties and behaviors of the MoVTaTaO M1 catalysts (HT 0.09, HT 0.12, HT 0.15 and MW) in propane ammoxidation can be found in our recent study [43]. The H₂O₂ solutions after this treatment were separated from the solid catalyst by centrifugation and analyzed by ICP-MS (Table 3).

These metal concentrations were converted to metal ratios by normalizing them to their Mo concentrations, which were in turn divided by their content in the bulk M1 phases in order to determine the nature of metal species preferentially leached by H_2O_2 . These normalized ratios are shown in Figure 13 indicating that V and especially Ta and Nb were relatively depleted in the H_2O_2 solution as compared to Te. The average elemental $\text{M(s)}/\text{M(b)}$ ratio for the four MoVTeTaO M1 phases were 1.39 for Te, 0.79 for V, and only 0.36 for Ta. These conclusions are further supported by the ICP-MS analysis of three other MoVTeTaO M1 phases shown in Table 3 that were treated similarly. The average elemental $\text{M(s)}/\text{M(b)}$ ratio for the four MoVTeTaO M1 phases were 1.39 for Te, 0.79 for V, and only 0.36 for Ta. These findings confirmed the hypothesis that the H_2O_2 treatment indeed removes metal oxides species from the M1 phase and does so preferentially towards the TeO_x , which is detrimental for its catalytic activity and selectivity in propane (amm)oxidation.

4. Conclusions

In this study, we systematically explored the catalytic activity and selectivity of MoVTe(Nb,Ta)O M1 and M2 phase catalysts prepared by hydrothermal synthesis (HT) and slurry evaporation (SE) methods, respectively, in propane ammoxidation. This study confirmed that the MoVTe(Nb,Ta)O M1 phases are highly active and selective for propane and propylene ammoxidation, while both MoVTe(Nb,Ta)O M2 phases were active and selective in propylene ammoxidation only.

Crucially, the present study of the MoVTe(Nb,Ta)O M1 and M2 phases in propylene ammoxidation revealed for the very first time that the M2 phases are significantly less active than the corresponding M1 phases in propylene ammoxidation. The findings of this study do not support the existence of the synergy effect for the MoVTe(Nb,Ta)O M1/M2 system. Instead, the

observed trends for the MoVTe(Nb,Ta)O catalysts in propane ammoxidation are consistent with preferential loss of surface TeO_x species from the M1 phase during the H₂O₂ treatment and generation of fresh *ab* planes of the M1 phase via mechanical crushing of the H₂O₂-treated M1 phase. These findings provided further strong evidence that the M1 phase is the only phase required for the activity and selectivity of the MoVTe(Nb,Ta)O catalysts in propane ammoxidation to ACN.

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Supporting Information Available: XRD patterns of the M1 and M2 phases and as-synthesized catalysts as well as the selectivity plots for these catalysts as a function of propane conversion.

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Legends for Tables

Table 1. ICP-MS operating conditions.

Table 2. Elemental compositions, surface areas, and phase ratios of MoVTe(Nb,Ta)O catalysts.

Table 3. Elemental compositions and BET surface areas of the MoVTe(Nb,Ta)O M1 phase catalysts and elemental compositions of used H₂O₂ treatment solutions.

Table 1. ICP-MS operating conditions.

Plasma gas	Argon
Carrier gas	Argon
Carrier gas flow rate	1.05 L min ⁻¹
RF Power	1550 W
RF matching	1.80 V
Sample depth	10 mm
Nebulizer	MicroMist
Nebulizer Pump	0.10 rps
Spray chamber temperature	275K
Make up gas flow rate	0.12 L min ⁻¹
Total Acquisition Time	67.584 sec
Replicates	3
Sweeps/Replicates	10
Integrated Time/Mass	0.09 sec

Table 2. Elemental compositions, surface areas, and phase ratios of MoVTe(Nb,Ta)O catalysts.

Catalysts	Synthesis Ratio	Elemental Analysis	Surface area (m ² /g) ^c		M1:M2
	Mo/V/Te/(Ta,Nb)	Mo/V/Te/(Ta,Nb)	Before H ₂ O ₂ treatment	After H ₂ O ₂ treatment	
M1 Nb HT	1.00/0.3/0.17/0.12	1/0.36/0.11/0.13 ^a	5.7	15.3	
M1 Ta HT	1.00/0.31/0.22/0.12	1/0.45/0.13/0.24 ^a	4.3	14.1	
M2 Nb SE	1.00/0.31/0.27/0.08	1/0.45/0.31/0.17 ^b	1.7		
M2 Ta SE	1.00/0.3/0.37/0.06	1/0.4/0.35/0.28 ^b	2.1		
M1/M2 Nb			10.2		
M1/M2 Ta			17.9		
Nb HT as-syn	1.00/0.3/0.17/0.12		11.2		0.75:0.25
Ta HT as-syn	1.00/0.31/0.22/0.12		15.1		0.48:0.52

^a determined by ICP-MS; ^b determined by EDS; ^c measured by the BET method; HT (Hydrothermal); SE (Slurry evaporation); as-syn (as-synthesized).

Table 3. Elemental compositions and BET surface areas of the MoVTe(Nb,Ta)O M1 phase catalysts and elemental compositions of used H₂O₂ treatment solutions.

Samples	Preparative ^a	ICP-MS	S.A. (m ² /g) ^b	
	Mo/V/Te/Ta	Mo/V/Te/Ta	Before H ₂ O ₂ treatment ^c	After H ₂ O ₂ treatment ^d
M1 Nb HT H ₂ O ₂		1/0.28/0.13/0.07 ^c		
M1 HT (0.09)	1.00/0.31/0.22/0.09	1/0.32/0.11/0.22	22.4	37.2
M1 HT (0.09) H ₂ O ₂		1/0.28/0.14/0.00		
M1 HT (0.12) H ₂ O ₂		1/0.26/0.09/0.04 ^c		
M1 HT (0.15)	1.00/0.31/0.22/0.15	1/0.38/0.13/0.23	4.9	12.3
M1 HT (0.15) H ₂ O ₂		1/0.25/0.20/0.20		
M1 MW	1.00/0.31/0.22/0.12	1/0.25/0.14/0.35	3.1	17.7
M1 MW H ₂ O ₂		1/0.26/0.29/0.14		

^a Synthesis compositions; ^b S.A. = BET surface areas; ^c for as-synthesized catalysts; ^d for pure M1 phases; ^e corresponding M1 phase composition shown in Table 2; MW (Microwave-assisted hydrothermal synthesis); HT (Hydrothermal synthesis)

Legends for Figures

Figure 1. SEM images of the (a) MoVTenbO and (b) MoVTetaO M1 phase catalysts.

Figure 2. SEM images of the (a) MoVTenbO and (b) MoVTetaO M2 phase catalysts.

Figure 3. Selectivity to ACN as a function of propane conversion over the MoVTenbTaO M1 phase catalysts in propane ammoxidation; Reaction conditions: $C_3H_8:NH_3:O_2:He=5.7:8.6:17.1:68.6$ (%); total flow rate, $26.3\text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst; reaction temperature: 623-733 K.

Figure 4. Arrhenius plots of k'' of propane consumption over the MoVTenbTaO M1 phase catalysts in propane ammoxidation; Reaction conditions: $C_3H_8:NH_3:O_2:He=5.7:8.6:17.1:68.6$; total flow rate, $26.3\text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst.

Figure 5. Selectivity to ACN as a function of propylene conversion over the MoVTenbTaO M1 phase catalysts in propylene ammoxidation; Reaction conditions: $C_3H_6:NH_3:O_2:He=5.7:8.6:17.1:68.6$ (%); total flow rate, $26.3\text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst; reaction temperature: 613-673 K.

Figure 6. Selectivity to ACN as a function of propylene conversion over the MoVTenbTaO M2 phase catalysts in propylene ammoxidation; Reaction conditions: $C_3H_6:NH_3:O_2:He=5.7:8.6:17.1:68.6$ (%); total flow rate, $26.3\text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst; reaction temperature: 653-713 K.

Figure 7. Reaction rate constant of propylene consumption, $k''(C_3H_6)$, vs. reaction temperature of the MoVTenbTaO M1 and M2 in propylene ammoxidation; Reaction conditions: $C_3H_6:NH_3:O_2:He=5.7:8.6:17.1:68.6$; total flow rate, $26.3\text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst.

Figure 8. Reaction rate constants of propane consumption, $k''(C_3H_8)$, vs. reaction temperature of the MoVTenbO M1, M1/M2, and as-synthesized catalysts in propane ammoxidation; Reaction conditions: $C_3H_8:NH_3:O_2:He=5.7:8.6:17.1:68.6$; total flow rate, $26.3\text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst.

Figure 9. Reaction rate constant of propylene consumption, $k''(C_3H_6)$, vs. reaction temperature of the MoVTenbO M1, M2, M1/M2, and as-synthesized catalysts in propylene ammoxidation; Reaction conditions: $C_3H_6:NH_3:O_2:He=5.7:8.6:17.1:68.6$; total flow rate, $26.3\text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst.

Figure 10. Reaction rate constants of propane consumption, $k''(C_3H_8)$, vs. reaction temperature for the MoVTetaO M1, M1/M2, and as-synthesized catalysts in propane ammoxidation;

Reaction conditions: $\text{C}_3\text{H}_8:\text{NH}_3:\text{O}_2:\text{He}=5.7:8.6:17.1:68.6$; total flow rate, $26.3 \text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst.

Figure 11. Reaction rate constants of propylene consumption, $k''(\text{C}_3\text{H}_6)$, vs. reaction temperature of the MoVTaTaO M1, M2, M1/M2, and as-synthesized catalysts in propylene ammoxidation; Reaction conditions: $\text{C}_3\text{H}_6:\text{NH}_3:\text{O}_2:\text{He}=5.7:8.6:17.1:68.6$; total flow rate, $26.3 \text{ mL}\cdot\text{min}^{-1}$; 0.2 g catalyst.

Figure 12. Reaction rate constants of propane consumption, $k''(\text{C}_3\text{H}_8)$, vs. reaction temperature of the as-synthesized MoVTaNbO [as-syn], the M1 after the H_2O_2 treatment [M1(H_2O_2)], and M1 crushed after H_2O_2 treatment [M1(H_2O_2 /crushed)] in propane ammoxidation; Reaction conditions: $\text{C}_3\text{H}_8:\text{NH}_3:\text{O}_2:\text{He}=6:7:17:70$; total flow rate, $20 \text{ mL}\cdot\text{min}^{-1}$; 0.2 – 0.4 g catalyst.

Figure 13. Elemental ratios in H_2O_2 solutions (s) referenced to elemental ratios in the H_2O_2 -treated M1 phases (b) (Tables 2 and 3).

Figure 1. TIFF

Figure 2. TIFF

Figure 3. EXCEL

Figure 4. EXCEL

Figure 5. EXCEL

Figure 6. EXCEL

Figure 7. EXCEL

Figure 8. EXCEL

Figure 9. EXCEL

Figure 10. EXCEL

Figure 11. EXCEL

Figure 12. TIFF

Figure 13. EXCEL