QSTEM-based HAADF-STEM image analysis of Mo/V distribution in MoVTaO M1 phase and their correlations with surface reactivity

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Abstract

Three probability models (Model 1-3) were advanced and investigated in this study based on metal distributions determined by the QSTEM-based HAADF-STEM image analysis. The correlations between the Mo/V distributions in MoVTaO M1 phase catalysts and their catalytic behavior in propane ammoxidation were proposed for Model 1 (based on the probability of finding 1-2 V^{5+} cations in the proposed S3-S4-S4-S7-S7 catalytic center), Model 2 (based on the total V content in the S2-S4-S4-S7-S7 catalytic center), and Model 3 (based on the probability of finding more than 2 V cations in the S2-S4-S4-S7-S7 catalytic center). Model 1 suggested V^{5+} in S3 may activate propane. Model 2 and Model 3 emphasized the importance of total V content and multiple VO_x sites in the S2-S4-S4-S7-S7 catalytic center for catalytic reactivity in propane ammoxidation, respectively.

Keywords

MoVTaO M1 phase, probability model, propane ammoxidation, quantitative HAADF-STEM image analysis, aberration corrected HAADF-STEM,

1. Introduction

Direct ammoxidation of propane to acrylonitrile (ACN) has received significant attention of the scientific community in recent decades because propane is cheaper, more abundant and environmentally friendlier than the current propylene feedstock. Many catalytic systems have been researched, and the MoVTaNbO mixed metal oxide containing of two main crystalline phases, so-called M1 and M2, has emerged as the leading candidate for direct propane ammoxidation to ACN [1-12].

The M1 phase has an orthorhombic polyhedral molybdenum bronze structure with a framework similar to that of Mo_5O_{14} and $\text{Mo}_{17}\text{O}_{47}$. This phase can be described by the generic formula $\{\text{TeO}\}_{1-x}(\text{Mo}, \text{V}, \text{Nb})_{10}\text{O}_{28}$, where the $\{\text{TeO}\}$ component is interposed into framework channels [7, 9]. The M2 phase is an orthorhombically distorted hexagonal tungsten bronze (HTB) type structure, and the formula for M2 is written as $\{\text{TeO}\}_{2-x}(\text{Mo}, \text{V}, \text{Nb})_6\text{O}_{18}$ [13]. The surface *ab* planes of the M1 phase (Figure 1(a)) were proposed to be responsible for propane activation and its selective transformation to ACN, while the M2 phase was found to play a secondary role by converting excess propylene intermediate that forms over the M1 surface into ACN.

The bulk crystal structures of the M1 and M2 phase have been investigated by several groups in X-ray and neutron diffraction studies [7, 13, 14], which gave rise to several different versions of metal distribution in the M1 phase due to the complexity of refinement process [15]. However,

very little is known about their surface structure and chemical compositions that are critically important for understanding the catalytic behaviors of these phases.

High-Angle Annular Dark-Filed Scanning Transmission Electron Microscopy (HAADF-STEM) [16-18] emerged in recent years as a promising tool to study the structure and composition of crystalline multicomponent metal oxides with sub-angstrom resolution. Pyrz et al. [19-21] examined the HAADF-STEM images of the MoVTaNb(Ta)O M1 phases and found that the chemical composition of the M1 phase was in a good agreement with that reported in the earlier X-ray diffraction studies [14]. However, the local chemical compositions of the *ab* planes of the MoVTaTa M1 phase determined in previous HAADF-STEM studies were essentially bulk compositions based on average intensities of entire atomic columns corresponding to a large number of *ab* planes [19-21]. On the other hand, in our earlier study [22], we conducted the profile intensity analysis of the MoVTaTaO M1 phase oriented along the [hk0] directions and showed that the chemical composition of surface *ab* planes is very similar to that of bulk. Moreover, we prepared sectioned specimens with constant thickness (~50 nm) to avoid misinterpreting the HAADF-STEM image intensity, which is significantly influenced by the specimen thickness [22].

Based on the above-mentioned improvements, we presented the metal site distributions in the *ab* planes of the M1 phase determined by the HAADF-STEM image analysis of MoVTaTaO M1 and derived tentative relationships between the metal distributions in *ab* planes of M1 phase and its catalytic performance in propane ammoxidation to acrylonitrile [22]. However, the HAADF-STEM images analysis employed in our earlier study suffered from limited accuracy because of many simplifying assumptions made during the interpretation of the HAADF-STEM images of the M1 phases [22]. One of the most restrictive assumptions employed in the previous

study was that the atomic column intensity was proportional to Z^n (Z = atomic number), where n was taken to be 2 according to Rutherford scattering [23, 24]. However, previous studies established that n varies significantly ($1.5 < n < 2$) depending on the experimental parameters and contribution of the thermal diffuse scattering [25-27]. Therefore, the variation of n for Z^n under specific conditions of STEM image acquisition is expected to have a significant impact on the accuracy of metal distributions in the M1 phase. This conclusion is further supported by the results of a recent study by Blom et al. [28], which showed significant intensity changes in the simulated HAADF-STEM images depending on the M1 specimen thickness and detector angles. Therefore, an accurate analysis of HAADF-STEM data based on STEM image simulations is necessary to overcome limited accuracy and reliability of the previous approaches based on the assumption of $n=2$ for Z^n , which is denoted as Z^2 -based HAADF-STEM image analysis in this study .

Subsequently, in our recent study [29], a novel method for the accurate determination of metal distributions in the M1 phase was developed by matching the normalized atomic column intensities in simulated [30] and experimental HAADF-STEM images [22]. This method, QSTEM-based HAADF-STEM image analysis, provided accurate metal distributions in the M1 phase and, furthermore, indicated a significantly lower V occupancy in linking sites, S1, 2, 3, 4, and 7 and higher Ta occupancy in S9 as compared to the results of the Z^2 -based HAADF-STEM image analysis [22]. The results of this study demonstrated that the QSTEM-based HAADF-STEM image analysis is more reliable and accurate as compared to the Z^2 -based HAADF-STEM image analysis [29]. The knowledge of accurate metal site occupancies in the linking sites S2, 4, and 7 is very crucial because these sites form an integral part of the proposed catalytic center (S2-S4-S4-S7-S7) for propane ammoxidation [9, 31] shown in Figure 1(b). Therefore, findings

of our recent study [29] strongly suggested that the probability models presented in our earlier study need to be revised in light of more accurate and reliable metal site occupancies in the M1 phase catalysts determined by QSTEM-based HAADF-STEM image analysis.

Therefore, the main objective of this study was to employ the metal site occupancies of Mo, V, and Ta in the MoVTeTaO M1 phase catalysts obtained by QSTEM-based HAADF-STEM image analysis [29] in order to explore the correlations between the composition of the proposed catalytic centers present in the surface *ab* planes of the M1 phase and its catalytic behavior in propane ammoxidation.

2. Experimental

2.1 Synthesis of MoVTeTaO M1 phase catalysts

The MoVTeTaO M1 phase was prepared by the hydrothermal synthesis (HT) [32] and microwave-assisted synthesis (MW) [33] methods at the synthesis ratio of Mo:V:Te:Ta=1.00:0.31:0.22:0.09, 0.12, and 0.15 with two different Ta precursors, tantalum(V) ethoxide and tantalum oxalate complex [22, 34]. The M1-Ta HT catalysts made using different Ta concentrations during synthesis are denoted as M1-Ta HT (0.09), M1-Ta (0.12), and M1-Ta (0.15), respectively, where the numbers in parentheses indicate the synthesis Ta/Mo ratios. The M1-Ta HT synthesized using the Ta oxalate complex is labeled below as M1-Ta HT(P). In order to obtain pure M1 phases, the M2 phase impurity initially present in all calcined as-synthesized catalysts was selectively removed by a hydrogen peroxide treatment [35].

2.2 Experimental HAADF-STEM imaging and its analysis

Detailed information for the analysis of experimental HAADF-STEM images of M1 phases and their analysis was described in our earlier study [22].

2.3 HAADF-STEM image simulation by QSTEM and its data extraction

The HAADF-STEM image simulation was performed using the QSTEM simulation software [30]. The detailed parameters for HAADF-STEM image simulation by QSTEM and information regarding data extraction from simulated HAADF-STEM images were described in our recent study [29].

3. Results and Discussion

3.1 QSTEM-based metal site occupancies of MoVTeTaO M1 phases

As demonstrated in our recent study [29], the QSTEM-based HAADF-STEM image analysis provided accurate metal occupancies of the MoVTeTaO M1 phase catalysts. The Mo, V, and Ta occupancies in 11 crystallographic sites of the MoVTeTaO M1 phase catalysts determined by QSTEM-based HAADF-STEM image analysis are shown in Table 1.

The M1-Ta HT(0.12) showed the highest Ta occupancy among all catalysts shown in Table 1 [22]. The Ta occupancy in S9 decreased as follows: M1-Ta HT(0.12) > M1-Ta MW > M1-Ta HT(0.15) > M1-Ta HT(P) > M1-Ta HT (0.09). This order is similar to that observed in our earlier study based on the Z²-based HAADF-STEM image analysis where Ta occupancy in S9 did not correlate with synthesis Ta concentration [22]. A similar conclusion was reached for Ta occupancies in S9 determined by the QSTEM-based HAADF-STEM image analysis. Those findings suggested that kinetic factors governing the Ta incorporation during hydrothermal synthesis of M1-Ta are poorly understood at present. Lastly, the metal site occupancies of the MoVTeTaO M1 phase catalysts determined by the QSTEM-based HAADF-STEM image analysis were subsequently employed to build detailed surface molecular structure - catalytic

reactivity relationships for propane ammoxidation to ACN over these M1 phase catalysts. These fundamental structure-catalytic reactivity relationships were discussed in detail below.

3.2 Propane ammoxidation over MoVTaO M1 catalysts

3.2.1 Catalytic performance of MoVTaO M1 catalysts

The M1-Ta HT(0.09), HT(0.12), HT(0.15), MW, and HT(P) were tested in propane ammoxidation reaction. The reaction data for propane ammoxidation for all catalysts can be found in our earlier study [22], and also reproduced in this study as Table 1 of Supporting Information. The catalytic behavior reported in Table 1 of Supporting Information is further discussed below on the basis of QSTEM-based metal occupancies in M1 phase catalysts.

3.2.2 Probability models for propane ammoxidation over M1 phase

Grasselli et al. [36] recently discussed four probability models, i.e., ORIG-1, ORIG-2, REV-1, and REV-2, and their predictions of ACN and propylene yields during propane ammoxidation based on the probabilities of the metal site distributions in the proposed catalytic center. They found that the expected maximum yield of ACN (predicted ACN yield plus propylene yield assuming all propylene is consecutively converted to ACN) of REV-2 differed from ORIG-1 and ORIG-2, while ORIG-1, ORIG-2, and REV-2 predicted similar ACN yield (41~43 mol. %). The expected maximum yield of ACN (59 mol. %) predicted by REV-2 is similar to the optimal ACN yield (62 mol. %) observed for the M1/M2 phase mixtures by Grasselli et al. [9]. Therefore, the REV-2 model represented an improvement over earlier models (ORIG-1 and ORIG-2) [36].

Beside the probability models proposed by Grasselli et al. [29], Pyrz et al. [20] determined the metal site occupancies in the MoVTaO, MoVTaNbO, MoVTaO M1 phase

catalysts by employing the HAADF-STEM image analysis and then estimated the probabilities of finding 0-5 V cations in the proposed S2-S4-S4-S7-S7 catalytic center. They estimated that ~86 % of the MoVTaNbO, ~97 % of the MoVTaTaO, and 64 % of the MoVTaO M1 phases would have S2-S4-S4-S7-S7 centers containing less than 3 V cations. They further stated that the increasing V concentration in the catalytic center (S2-S4-S4-S7-S7) corresponded with the decreasing selectivity to ACN when the MoVTaO M1 catalyst was compared to the MoVTaNbO and MoVTaTaO M1 phase catalysts. However, no clear correlation between the probability of finding less than 3 V cations in the S2-S4-S4-S7-S7 catalytic center and the ACN yield over the MoVTe, MoVTaNbO, and MoVTaTaO catalysts in propane ammoxidation was suggested by the ACN yield data [20]. It should be noted that the probabilities of finding vanadium cations in the proposed catalytic center (S2-S4-S4-S7-S7) calculated by Pyrz et al. [20] did not consider vanadium oxidation state, whereas the ORIG-1 model described by Grasselli et al. [37] accounted for the oxidation states of vanadium by explicitly calculating the probability of V^{5+} in the proposed catalytic center (S2-S4-S4-S7-S7).

As stated in our earlier study [22], we employed the same approach as described by Pyrz et al. [20] for predicting the catalytic performance of the MoVTaTaO M1 phase catalysts in propane ammoxidation because we obtained accurate metal site occupancies from the QSTEM-based HAADF-STEM image analysis but lacked the oxidation state information. The QSTEM-based metal distributions in the catalytic center (S2-S4-S4-S7-S7) and the probabilities of finding 0-5 vanadium in the catalytic center (S2-S4-S4-S7-S7) are listed in Tables 2 and 3, respectively, according to the probability approach described by Pyrz et al. [20]. In our previous study [22], calculation of the probabilities, P, of finding different numbers of V cations in the catalytic center was described in detail.

According to the approach described by Pyrz et al. [20], nearly 100% of the M1-Ta HT(0.12) and HT(0.15) would have S2-S4-S4-S7-S7 centers containing less than 3V cations, while only 80% of M1-Ta HT(0.09) would have such compositions. However, no clear correlation was observed between the observed maximum selectivity to ACN and the probability of finding less than 3 V cations in the proposed catalytic center (S2-S4-S4-S7-S7). In conclusion, we could not find the relationship between the QSTEM-based metal distributions of the MoVTaTaO M1 phase catalysts and their catalytic performance employing the approach of Pyrz et al. [20].

3.2.3 New probability models of propane ammoxidation over MoVTaTaO M1 phase catalysts

In our earlier study [22], we proposed and examined three probability models (Models 1-3) to correlate the metal site occupancies in the MoVTaTaO M1 phases with their catalytic behavior in propane ammoxidation. Model 1 was modified based on the ORIG-1 model proposed by Grasselli et al. [37]. In Model 1, the vanadium 4+ and 5+ oxidation states were considered on the basis of the recent study of Li et al. [38] where they suggested that only linking sites S3, S4, and S7 contained V^{5+} , while S2 contained V^{4+} . Furthermore, recent theoretical DFT studies from our group also supported the view that S2 contains V^{4+} [39-42]. These findings suggested that vanadium present in S2 might be inactive due to its 4+ oxidation state, while vanadium in S3 can activate propane due to its 5+ oxidation state. Therefore, S2 was replaced by S3 in the new catalytic center (S3-S4-S4-S7-S7) in Model 1 shown in Figure 1(b). Moreover, the absence of V^{5+} in the new center (S3-S4-S4-S7-S7) was considered to correspond to the lack of catalytic activity in this Model 1. The following assumptions were further made in order to calculate the probability of V^{5+} in the new S3-S4-S4-S7-S7 center: (1) the isolated V^{5+} cations present in S3 only convert propane to propylene; (2) single V^{5+} cations in the S4-S4-S7-S7 catalytic center

convert not only propane to propylene, but also the propylene intermediate further to ACN; (3) the presence of more than two V^{5+} cations in the S4-S4-S7-S7 is responsible for combustion activity. First assumption that an isolated V^{5+} in S3 can only produce propylene was made on the basis of recent studies of Grasselli et al. [36, 43] who proposed that a propylene forming site only needed a single V^{5+} adjacent to a Te^{4+} , while the ACN forming sites needed V^{5+} adjacent to a Te^{4+} as well as a pair of vicinal Mo^{6+} sites. Site 3 meets the requirement for a propylene-forming site, but does not meet the requirements as an ACN forming site due to the lack of a pair of vicinal Mo^{6+} .

Based on these assumptions, the probabilities of 0-1 V^{5+} in S3 and 0-4 V^{5+} in the S4-S4-S7-S7 center were calculated (Table 2 of Supporting Information). According to our assumptions stated above, cases 1 and 5 shown in Table 2 of Supporting Information were considered to be only selective for propylene formation, while cases 2 and 3 were regarded to be selective for both propylene and acrylonitrile. As a result, the sums of probabilities for cases 1 and 5, assumed to form only propylene, and for cases 2 and 3, assumed to form both propylene and ACN, for the MoVTaTaO M1 phases are shown in Table 4. The predicted maximum selectivities to ACN for all MoVTaTaO M1 phase catalysts, calculated by the method of Grasselli et al. [37], were also listed in Table 4. For example, the predicted maximum selectivity for M1-Ta HT(0.12) was calculated as $0.42/(0.42+0.32) \times 100\%$. It is important to note that the predicted maximum selectivities shown in Table 4 were calculated based on another assumption that propylene formed over the S4-S4-S7-S7 center is completely converted to ACN. Assuming 100% propane conversion over M1 phase catalysts, the maximum theoretical ACN yield is in the range of 50 ~ 60 mol. %, which is similar to the expected maximum yield of ACN (59 mol. %) based on the REV-2 model proposed by Grasselli et al. [36] for propane ammoxidation over the MoVTaNbO

M1 phase. The range of the maximum theoretical acrylonitrile yield (50 ~ 60 mol. %) predicted by Model 1 is in good agreement with the highest yield of acrylonitrile (43 ~ 52 mol. %) observed experimentally for propane ammoxidation over the MoVTaNbO M1 phase catalyst, structurally similar to MoVTaTaO M1 phase catalysts [44, 45].

To illustrate this point further for Model 1, the combined yield of propylene and ACN was plotted in Figure 2 as a function of the probability of finding 1-2 V^{5+} cations in the newly proposed S3-S4-S4-S7-S7 center, since an isolated V^{5+} in S3 can only activate propane to propylene, while a single V^{5+} in S4-S4-S7-S7 not only converts propane to propylene but also propylene to ACN according to Model 1. A correlation between the probability of finding 1-2 V^{5+} in the newly proposed S3-S4-S4-S7-S7 center and the combined yield of propylene and ACN was observed (Figure 2). It is important to note that this correlation was not observed in our previous study [22]. This result suggested that the vanadium in S3 may activate propane because of its 5+ oxidation state suggested by the earlier findings of Li et al. [38]. This result also suggested that the predictive ability of Model 1 reported in our previous study [22] suffered from the limited accuracy of metal occupancies determined by the Z^2 -based HAADF-STEM image analysis.

In our previous study [22], we described a correlation between the propane consumption rate constants, k'' , for the MoVTaTaO M1 phases and the total V content in the catalytic center (S2-S4-S4-S7-S7), when k'' was normalized to the surface ab plane areas of these M1 phases estimated by the statistical size analysis of M1 phase crystals in their SEM images to yield k''_{ab} . We further explored the relationship between k''_{ab} for the MoVTaTaO M1 phase catalysts and the probability of finding 1-2 V^{5+} in the newly proposed catalytic center (S3-S4-S4-S7-S7). It is also important to note that propane consumption over the MoVTaTaO M1 phase catalysts during

its ammoxidation was assumed to be a first-order irreversible reaction for a plug flow reaction model [32, 46]. This assumption was confirmed by straight line fits observed for the Arrhenius plots of the first-order irreversible reaction rate constant for propane consumption, k'' , for MoVTaTaO M1 phase catalysts reported in our previous study [22]. In addition, the activation energies determined from these Arrhenius plots were also consistent with the activation energy reported in the previous study of propane ammoxidation over a MoVTaNbO M1 phase [32].

The reaction rate constants, k''_{ab} , of the MoVTaTaO M1 phase catalysts were plotted against the probability of 1-2 V^{5+} in the S3-S4-S4-S7-S7 center in Figure 3, which showed the general trend of increasing k''_{ab} along with $P(1-2 V^{5+})$ in the S3-S4-S4-S7-S7 center. Therefore, it was concluded that Model 1 could predict catalytic performance of the MoVTaTaO M1 phase catalysts in propane ammoxidation to ACN based on their metal distributions determined by the QSTEM-based HAADF-STEM image analysis.

Although Model 1 showed the importance of V distributions in the new catalytic center (S3-S4-S4-S7-S7) for predicting the catalytic behavior of the MoVTaTaO M1 phase catalysts in propane ammoxidation above, it did not probe the importance of the total V content in the S2-S4-S4-S7-S7 center of the M1 phase for the catalytic activity and selectivity in propane ammoxidation. Recently, Naraschewski et al. [47, 48] showed the existence of a linear relationship between the initial rate of propane conversion and the total V content in MoVTaNbO catalysts during propane oxidation to acrylic acid. Similarly, Model 2 reported in our earlier study [22] demonstrated the existence of a correlation between the yield of ACN during propane ammoxidation over the MoVTaTaO M1 phase catalysts and the total V content in the S2-S4-S4-S7-S7 center. However, the V content in the S2-S4-S4-S7-S7 center employed in our earlier study [22] was determined by the Z^2 -based HAADF-STEM image analysis, which

is characterized by limited accuracy as compared to the QSTEM-based HAADF-STEM image analysis method [29]. Therefore, it is necessary to revisit Model 2 employing accurate metal distributions determined by the QSTEM-based HAADF-STEM image analysis. The catalytic center proposed in Model 2 is shown in Figure 1(b). The yield of ACN was plotted in Figure 4 as a function of total V content in the catalytic center (S2-S4-S4-S7-S7) determined by the QSTEM-based HAADF-STEM image analysis. We observed a correlation between the yield of ACN and the total V content in the catalytic center (S2-S4-S4-S7-S7) of the MoVTaO M1 phase catalysts. This correlation is similar to that observed in our earlier study [22] except that the outlier in this case is M1-Ta MW, which is discussed further below.

We further attempted to establish the relationship between the Mo/V distributions of the MoVTaO M1 phase catalysts and their propane consumption activity. The reaction rate constants of propane consumption, k''_{ab} , of the MoVTaO M1 phase catalysts were plotted against the total V content in the S2-S4-S4-S7-S7 center in Figure 5. The reaction rate constant, k''_{ab} , was found to increase with the total V content in the S2-S4-S4-S7-S7 center of M1 phase catalysts (Figure 5), with one exception of M1-Ta MW, which is discussed further below. This observation is consistent with the results of recent studies that showed a linear relationship between the initial rate of propane consumption and the bulk vanadium content of the MoVTaNbO M1 phase during propane oxidation to acrylic acid [47, 48].

Model 2 indicated a correlation between the yield of ACN and the total V content in the catalytic center of M1 phase (Figure 4) and a correlation between the reaction rate constant, k''_{ab} , and the total V content in the catalytic center of M1 phase (Figure 5). Interestingly, the outlier observed in this study is M1-Ta MW for both correlations mentioned above, while the outlier reported in our earlier study [22] was M1-Ta HT(P).

We observed the change of the outlier catalyst from M1-Ta HT(P) to M1-Ta MW when Model 1 and 2 were explored using the metal site occupancies determined by the QSTEM-based HAADF-STEM image analysis. Therefore, we also re-examined Model 3, which showed in our earlier study [22] a tentative correlation between the probability of finding more than 2 V cations, $P(V>2)$, in the S2-S4-S4-S7-S7 center and their catalytic reactivity during propane ammoxidation.

Model 3 was proposed on the basis of previous studies where multiple surface V cations present in the M1 phase and other vanadium-based catalysts were indicated to be more active towards propane than isolated V cations [47-52]. Indeed, an earlier experimental study of propane oxidation to acrylic acid combined with chemical probe chemisorption and low energy ion scattering (LEIS) demonstrated that multiple VO_x sites present in M1 phases were more efficient in selective propane oxidation than isolated VO_x species [49]. Therefore, we proposed that more than one V cations present in the S2-S4-S4-S7-S7 center may be associated with high reactivity in propane ammoxidation. The catalytic center proposed in Model 3 is shown in Figure 1(b). In Model 3, the catalytic reactivity in propane ammoxidation was correlated with: (1) $P(V=2)$, the probability of 2 V cations in the catalytic center; (2) $P(V=2)+P(V=3)$, the probability of 2-3 V cations in the catalytic center; (3) $P(V=2)+(V=3)+P(V=4)$, the probability of 2-4 V cations in the catalytic center. The probability of 5 V cations in the catalytic center is theoretically possible, but since the $P(V=5)$ is less than 0.1 for all MoVTaTaO M1 phase catalysts, this case was not considered in this study.

The probabilities of $P(V>2)$ according to three different cases mentioned above are reported in Table 5. The probabilities of V for $P(V=2)$, $P(V=2)+P(V=3)$, and $P(V=2)+(V=3)+P(V=4)$ for all MoVTaTaO M1 phase catalysts are plotted against the yield of

ACN in Figure 6. The increase of ACN yield with increasing $P(V>2)$ in the catalytic center was observed in Figure 6 except for M1-Ta MW. Furthermore, the reaction rate constants, k''_{ab} , normalized to the geometric estimates of surface ab plane areas were plotted against the $P(V>2)$ in the S2-S4-S4-S7-S7 center (Figure 7). A correlation between k''_{ab} and the probabilities of $V>2$ in S2-S4-S4-S7-S7 center was observed in Figure 7, further supporting the view that multiple VO_x redox sites present in the surface ab planes of the M1 phase are more active in propane (amm)oxidation [49, 50, 53].

Therefore, these findings suggested that the activity and selectivity of the M1 phase in propane ammoxidation may not be explained entirely by the presence of single, site-isolated redox sites in the surface ab planes. Specifically, the presence of multiple V cations present in the proposed catalytic center, which were previously regarded as wasting forming sites [54], was indicated to correlate with catalytic reactivity of the M1 phase in propane ammoxidation to ACN. The importance of multiple sites is stressed appears to be supported by the findings of recent studies, e.g., a combined experimental and theoretical DFT study [55], which suggested that a binuclear Au complex is better than a mononuclear Au site in a gold-catalyzed alkene heteroarylation reaction.

It should be noted that the approach adopted in this study treated the surface structure of the M1 phase as static and did not account for its dynamic characteristics under reaction conditions. Moreover, the QSTEM-based HAADF-STEM image analysis was not capable of providing information about metal oxidation states. Accordingly, several assumptions were made for the probability models presented here in order to develop the relationships between the Mo/V distributions in MoVTaO M1 phase and its catalytic reactivity in propane ammoxidation. For

example, one S3, two S4, and two S7 (S3-S4-S4-S7-S7) (Figure 1(b)) were proposed to comprise the catalytic center in the case of Model 1, because these sites were indicated to contain V^{5+} according to Li et al. [38]. The following assumptions were additionally made for Model 1: (1) that the isolated V^{5+} cation in S3 only converts propane to propylene; (2) one V^{5+} cation in the S4-S4-S7-S7 center converts propane (and the propylene intermediate) to ACN; (3) while two and more V^{5+} cations in the S4-S4-S7-S7 center are propane combustion sites; (4) the S3-S4-S4-S7-S7 centers lacking V^{5+} are unable to inactivate propane. In the case of Model 2, it was assumed that the catalytic reactivity correlated with the total V content in the catalytic center (S2-S4-S4-S7-S7), which did not take its oxidation state into consideration. For Model 3, it was hypothesized that the reactivity in propane ammoxidation correlated with probability of finding more than one V in the catalytic center (S2-S4-S4-S7-S7), which did not consider the V oxidation state.

It is important to note that Models 1-3 employed in this study revealed the same outlier, i.e., M1-Ta MW, when they were applied to predict the catalytic behavior on the basis of metal distributions determined by the QSTEM-based HAADF-STEM image analysis. The outlier nature of M1-Ta MW might be understood in terms of its crystallinity. As described in the experiment section, M1-Ta HT (0.09, 0.12, and 0.15) and HT(P) were prepared by the same hydrothermal (HT) synthesis method, while the M1-Ta MW, the outlier in this study, was prepared by microwave-assisted (MW) synthesis method. It is well known that synthesis methods can have a significant impact on the chemical composition and catalytic properties of mixed metal oxide catalysts. Furthermore, heat transfer, wall effects, homogeneity, and crystallization behavior during synthesis are significantly affected by such experimental parameters as the wall material, vessel size, the type of a stirring system, oven heating and

cooling programming, etc. [56]. There are many crucial differences between these experimental parameters for HT and MW synthesis methods. For instance, the MW method took 2 h for the synthesis of the M1 phase catalysts, while HT method took 48 h for the M1 phase catalysts. In the case of HT synthesis, once the oven reached the target temperature of 448 K, it was maintained for 48 h within ± 5 K. Unlike HT synthesis method, synthesis temperature for MW method is controlled by the microwave-accelerated MARS 5 reaction system (CEM, USA) depending on the signal of a temperature probe located inside a sealed teflon tube. The significant temperature fluctuations (± 20 K) were observed during entire MW synthesis. We believe that these differences had a pronounced impact on the crystallinity of M1 phase catalysts prepared by HT and MW, thereby resulting in different catalytic behaviors.

Moreover, this hypothesis is further supported by the recent findings of Sanfiz et al. [56] who prepared MoVTaNbO M1 phases by the HT method and investigated the influence of various synthesis parameters on the structure and morphology of MoVTaNbO M1 phases. They demonstrated that synthesis temperature and time are very crucial parameters to form a pure M1 phase. Both lower synthesis temperatures and shorter synthesis times resulted in more extensive formation of the M2 phase as well as other impurity phases, e.g., Mo₅O₁₄, V_{0.95}Mo_{0.97}O₅, and TeMo₅O₁₆. These latter impurities are known to be inactive for propane ammoxidation, but unlike the M2 phase, and they cannot be removed by the H₂O₂ treatment. Similar to the findings of Sanfiz et al. [56], we also detected much greater levels of various impurity phases in M1-Ta MW as compared to MoVTaTaO M1 phases made by the HT method.

The presence of impurity phases in M1-Ta MW is suggested by its representative SEM image shown together with those of the M1-Ta HT(0.12) and M1-Ta HT(P) in Figure 8. Unlike M1-Ta HT(0.12) and M1-Ta HT(P) that show the presence of typical rod-shaped M1 crystals, a

heterogeneous mixture of different crystal morphologies is observed in the SEM image of the M1-Ta MW. Furthermore, the presence of impurity phases in the M1-Ta (MW) was further suggested by its XRD pattern, which is shown in Figure 8 along with that of M1-Ta HT(0.12).

Although both M1-Ta HT(0.12) and M1-Ta MW showed the presence of M1 as the dominant phase in Figure 9, the XRD pattern of the M1-Ta (MW) showed the presence of additional peaks at 23.5, 24.7, and 31.5° 2 θ corresponding to (V_{0.07}Mo_{0.93})₅O₁₄ (PDF 00-031-1437). We further compared the intensities of main peaks of this impurity phase at 23.5, 24.7, and 31.5° 2 θ for M1-Ta HT(0.12) and M1-Ta MW. These peaks were approximately twice as intense for M1-Ta MW than M1-Ta HT(0.12) further suggesting that M1-Ta MW contained more (V_{0.07}Mo_{0.93})₅O₁₄ impurity proposed to be responsible for the poor catalytic performance of this catalyst and making M1-Ta MW an outlier in this study.

4. Conclusions

In this study, the accurate metal distributions of the MoVTaO M1 phase catalysts determined by the QSTEM-based HAADF-STEM image analysis were employed to validate several probability models described previously in our earlier study, where these models were investigated based on the metal distributions determined by the Z²-based HAADF-STEM image analysis [22].

The correlations between the QSTEM-based Mo/V distributions in MoVTaO M1 phase catalysts and their catalytic behavior in propane ammoxidation was proposed on the basis of Model 1 (the probability of finding 1-2 V⁵⁺ in the S3-S4-S4-S7-S7 center), Model 2 (the total V content in the S2-S4-S4-S7-S7 center), and Model 3 (the probability of finding V over 2 in the S2-S4-S4-S7-S7 center). Specifically, the ACN yield and 1st order irreversible reaction rate

constants for propane consumption normalized to the *ab* plane areas, k''_{ab} , correlated with (1) the probability of 1-2 V^{5+} in the S3-S4-S4-S7-S7 center (Model 1); (2) total V content in the S2-S4-S4-S7-S7 center (Model 2); and (3) the probability of more than 2 V cations in the S2-S4-S4-S7-S7 center (Model 3). The observed relationship between the probability of finding 1-2 V^{5+} cations in the S3-S4-S4-S7-S7 center of M1 phase and its catalytic behavior according to Model 1 suggest that V^{5+} in S3 may also be an active site for propane activation. The correlations observed from Model 2 and 3 emphasized the importance of total V content (Model 2) and multiple VO_x sites (Model 3) in the S2-S4-S4-S7-S7 center for the catalytic activity and selectivity in propane ammoxidation. Moreover, the fundamental relationships elucidated in this study are promising for the development of general rules of rational design of improved mixed metal oxide catalysts for propane ammoxidation and other selective oxidation reactions.

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Legends for Tables

Table 1. Metal occupancies of the M1 phase catalysts determined by QSTEM-based HAADF-STEM image analysis.

Table 2. QSTEM-based Mo and V occupancies in the proposed catalytic center (S2-S4-S4-S7-S7) of M1-Ta HT(0.09), M1-Ta HT(0.12), M1-Ta HT(0.15), M1-Ta MW, and M1-Ta HT(P).

Table 3. The probabilities of finding 0-5 V cations in the proposed catalytic center (S2-S4-S4-S7-S7) in M1-Ta HT(0.09), M1-Ta HT(0.12), M1-Ta HT(0.15), M1-Ta MW, and M1-Ta HT(P).

Table 4. The sums of probabilities for cases that are assumed to form only propylene and ACN M1-Ta HT(0.09), M1-Ta HT(0.12), M1-Ta HT(0.15), M1-Ta MW, and M1-Ta HT(P).

Table 5. The probability of the number of V cations in proposed catalytic center (S2-S4-S4-S7-S7) of M1-Ta (0.09), M1-Ta (0.12), M1-Ta (0.15), M1-Ta MW, and M1-Ta HT(P).

Table 1. Metal occupancies of the M1 phase catalysts determined by QSTEM-based HAADF-STEM image analysis [22].

	M1-Ta HT(0.09)		M1-Ta HT(0.12)		M1-Ta HT(0.15)		M1-Ta MW		M1-Ta HT(P)	
	Mo	V(Ta)	Mo	V(Ta)	Mo	V(Ta)	Mo	V(Ta)	Mo	V(Ta)
site 1	0.35	0.65	0.76	0.24	0.65	0.35	0.77	0.23	0.79	0.21
site 2	0.61	0.39	0.74	0.26	0.70	0.30	0.58	0.42	0.70	0.30
site 3	0.65	0.35	0.73	0.27	0.66	0.34	0.67	0.33	0.72	0.28
site 4	0.80	0.20	0.90	0.10	0.90	0.10	0.83	0.17	0.95	0.05
site 5	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00
site 6	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00
site 7	0.56	0.44	0.73	0.27	0.85	0.15	0.70	0.30	0.85	0.15
site 8	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00
site 9	0.88	(0.12)	0.28	(0.72)	0.60	(0.40)	0.51	(0.49)	0.65	(0.35)
site 10	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00
site 11	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00

Table 2. QSTEM-based Mo and V occupancies in the proposed catalytic center (S2-S4-S4-S7-S7) of M1-Ta HT(0.09), M1-Ta HT(0.12), M1-Ta HT(0.15), M1-Ta MW, and M1-Ta HT(P).

	MoVTeTa HT(0.09)		MoVTeTa HT(0.12)		MoVTeTa HT(0.15)		MoVTeTa MW		MoVTeTa HT(P)	
	Mo	V(Ta)	Mo	V(Ta)	Mo	V(Ta)	Mo	V(Ta)	Mo	V(Ta)
Site										
site 2	0.61	0.39	0.74	0.26	0.70	0.30	0.58	0.42	0.70	0.30
site 4	0.80	0.20	0.90	0.10	0.90	0.10	0.83	0.17	0.95	0.05
site 7	0.56	0.44	0.73	0.27	0.85	0.15	0.70	0.30	0.85	0.15
Sum	1.97	1.03	2.37	0.63	2.45	0.55	2.11	0.89	2.50	0.50

Table 3. The probabilities of finding 0-5 V cations in the proposed catalytic center (S2-S4-S4-S7-S7) in M1-Ta HT(0.09), M1-Ta HT(0.12), M1-Ta HT(0.15), M1-Ta MW, and M1-Ta HT(P).

# of V atoms in the active center	M1-Ta HT (0.09)	M1-Ta HT(0.12)	M1-Ta HT (0.15)	M1-Ta MW	M1-Ta HT(P)
0	0.12	0.32	0.41	0.20	0.46
1	0.33	0.42	0.41	0.39	0.40
2	0.34	0.21	0.15	0.29	0.12
3	0.16	0.05	0.03	0.10	0.02
4	0.04	0.00	0.00	0.02	0.00
5	0.00	0.00	0.00	0.00	0.00

Table 4. The sums of probabilities for cases that are assumed to form only propylene and ACN M1-Ta HT(0.09), M1-Ta HT(0.12), M1-Ta HT(0.15), M1-Ta MW, and M1-Ta HT(P).

Catalyst	selective (Propylene)	selective (ACN)	*Predicted maximum selectivity to ACN, %
M1-Ta HT(0.09)	0.20	0.42	0.48
M1-Ta HT(0.12)	0.16	0.42	0.61
M1-Ta HT(0.15)	0.23	0.34	0.55
M1-Ta MW	0.19	0.43	0.55
M1-Ta HT(P)	0.20	0.30	0.56

* calculated as $100\% \times \Sigma \text{ selective centers to ACN} / \Sigma [\text{selective centers to ACN} + \text{waste centers}]$.
It is assumed that all propylene, formed from the selective centers to ACN, is converted to ACN.

Table 5. The probability of the number of V cations in proposed catalytic center (S2-S4-S4-S7-S7) of M1-Ta (0.09), M1-Ta (0.12), M1-Ta (0.15), M1-Ta MW, and M1-Ta HT(P).

Cases	M1-Ta HT (0.09)	M1-Ta HT(0.12)	M1-Ta HT (0.15)	M1-Ta MW	M1-Ta HT(P)
Case 1) P(V=2)	0.34	0.21	0.15	0.29	0.12
Case 2) P(V=2)+P(V=3)	0.51	0.26	0.18	0.40	0.14
Case 2) P(V=2)+P(V=3)+P(V=4)	0.54	0.26	0.18	0.41	0.14

Legends for Figures

Figure 1. (a) The structure of the *ab* plane of the MoVTaO M1 phase; (b) catalytic centers proposed in probability Models 1, 2, and 3.

Figure 2. Combined yield of propylene and acrylonitrile, $Y(C_3H_6+ACN)$, as a function of probability of 1-2 V^{5+} in the newly proposed catalytic center (S3-S4-S4-S7-S7) of MoVTaO 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: 693 K.

Figure 3. Reaction rate constants of propane consumption, k''_{ab} , vs. probability of 1-2 V^{5+} in the newly proposed catalytic center (S3-S4-S4-S7-S7) of MoVTaO 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: 693 K.

Figure 4 Yield of acrylonitrile, $Y(ACN)$, as a function of total V content in the catalytic center (S2-S4-S4-S7-S7) of MoVTaO 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: 693 K.

Figure 5. Reaction rate constants of propane consumption, k''_{ab} , normalized to the estimated *ab* planes surface area vs. total V content in the catalytic center (S2-S4-S4-S7-S7) of MoVTaO 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: 693 K.

Figure 6. Yield of acrylonitrile, $Y(ACN)$, as a function of probability of $V>2$ in the catalytic center (S2-S4-S4-S7-S7) of MoVTaO 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: 693 K.

Figure 7. Reaction rate constants, k''_{ab} , based on the estimated *ab* planes surface area plotted as a function of probability of $V>2$ in the catalytic center (S2-S4-S4-S7-S7) of MoVTaO 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: 693 K.

Figure 8. SEM images of M1-Ta catalysts; a) M1-Ta HT(0.12), b) M1-Ta MW, c) M1-Ta HT(P).

Figure 9. Enlarged area of 2θ from 22 to 38 in the XRD patterns of M1-Ta HT(0.12) (blue) and M1-Ta MW(red); ▲M1 phase, ■ $(V_{0.07}Mo_{0.93})_5O_{14}$.

Figure 1. TIFF

Figure 2. Excel

Figure 3. Excel

Figure 4. Excel

Figure 5. Excel

Figure 6. Excel

Figure 7. Excel

Figure 8. TIFF

Figure 9. TIFF

Mo
V
Te
Ta

Mo
V
Te