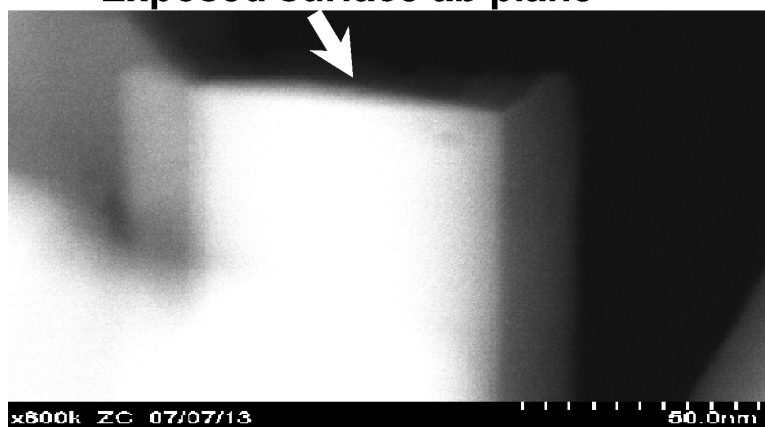## Communication

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, Xinhua Liang, Alan W. Weimer, Chengdu Liang, Sheng Dai, and Vadim V. Guliants

Exposed surface *ab* plane

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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

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The rational assembly of layered mixed metal oxides and understanding their structure−reactivity relationships remains one of the most difficult challenges of today's catalytic materials science. Many of the layered mixed oxides exhibit strong structure sensitivity in which only one of the possible phases or a set of particular planes are both catalytically active and selective. A typical example is the vanadium−phosphorus−oxide (VPO) system for the selective oxidation of *n*-butane to maleic anhydride. It has been proposed that the basal (100) planes of layered vanadyl(IV) pyrophosphate, the dominant crystalline phase present in the VPO catalysts, contain the active and selective surface sites for this reaction.[1] Recently, much attention has been paid by the scientific community to the layered M1 phase present in the Mo−V−Te−Nb−O mixed oxide, which is a highly promising candidate catalyst for the selective (amm)oxidation of propane.[2] This catalyst is unique because it showed high activity and selectivity in both ammoxidation and oxidation of propane as well as the oxidative dehydrogenation of ethane, whereas other mixed metal oxide catalysts, such as the VPO and V−Sb−Al mixed oxides, are only active and selective in a single alkane transformation reaction.[3] It was recently reported that the M1 phase is characterized by a layered, orthorhombic structure, consisting of a network of MO_6 octahedra (M = Mo, V, Nb) forming pentagonal, hexagonal, and heptagonal channels.[4] These octahedra are suggested to be stabilized and structurally isolated by Nb^{5+} pentagonal bipyramidal sites. The M1 phase catalyst particles are rodlike crystals, as evidenced by the electron microscopy studies, where the long axis is coincident with the *c*-direction. The *ab* (basal) planes are oriented perpendicular to this long axis, suggesting fast M1 crystal growth in the *c*-direction perpendicular to the *ab* planes which probably possess the highest surface energy.[5] The catalytic performance of the M1 phase catalyst is significantly improved after the rodlike crystals of the M1 phase are crushed before reaction and it is postulated that this improvement is due to increased exposure of surface *ab* planes which contain the active and selective surface sites.[4] Assuming that crushing the catalyst particles increases the exposed surface area of the *ab* planes, it may be suggested that the spatial arrangement and distribution of the various elements on the basal plane of the M1 phase is of great importance for achieving desired product selectivity. The surface of the basal plane is suggested to contain
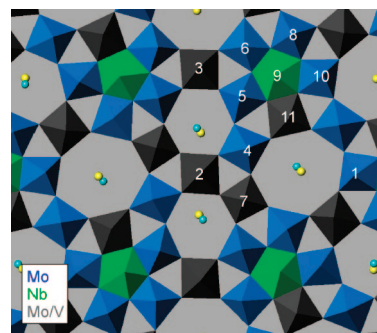

Figure 1. The proposed model of the surface basal (*ab*) plane of Mo−V−Te−Nb−O M1 phase. Mo, V, and Nb are present in the framework showing pure Mo and mixed occupancy Mo/V sites, while Te is present in the hexagonal and heptagonal channels.

Mo^{6+}, Mo^{5+}, V^{5+}, V^{4+}, and Te^{6+} which are stabilized and isolated by Nb^{5+} sites (Figure 1).[4] According to the statistical analysis of the various distribution probabilities of the key catalytic metal ions at the basal *ab* plane of M1 based on the bulk chemical composition of this phase, 44% of the sites are active and selective for propane ammoxidation, 46% are inactive, and 10% are waste-forming, leading to the prediction of the maximum selectivity to acrylonitrile of 81 mol %.[6]

We have investigated this concept using a novel surface modification approach which enables probing selectively the catalytic properties of surface *ab* planes. In this approach the entire surface of the M1 crystals is passivated initially via the atomic layer deposition (ALD) of alumina followed by crushing the M1 crystals to preferentially expose the *ab* planes. The catalytic behavior of the M1 phase catalyst before the ALD step, after ALD, and after crushing the passivated M1 phase was evaluated in propane ammoxidation. We believe this technique to be of general utility in the field of heterogeneous catalysis as it allows studying selectively the catalytic behavior of surface planes in layered mixed metal oxides.

The Mo−V−Te−Nb−O M1 phase used in this study was prepared by hydrothermal synthesis at 448 K and calcined in ultrapure N_2 at 873 K (Supporting Information). The X-ray diffraction pattern of this phase shows characteristic Bragg peaks of the M1 phase at $2\theta < 10°$, as well as sharp peaks at $2\theta \approx 22°$ and 45° and a broad peak at ∼27°. The SEM images confirmed the rod-shaped morphology of the M1 phase catalyst (Figure S1, Supporting Information).

These M1 crystals prior to crushing were subjected to atomic layer deposition (ALD)[7] by the surface reaction with alternate

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%) at moderate propane conversion (30%) was close to the maximum value of 81 mol % predicted for the *ab* surface of the M1 phase.[4] Moreover, the selectivity to CO_x (8 mol %) was similar to the value of 10 mol % predicted for the waste-forming sites. Therefore, the observed selectivity pattern indicated the highly selective nature of the exposed *ab* plane surface. The majority of propene intermediate formed over the M1 phase is converted to acrylonitrile by the adjacent selective sites while some propene is desorbed from the surface without undergoing combustion probably because of the limited number of waste-forming sites on the surface of *ab* planes.

Similar results were observed for the Mo−V−Te−O M1 phase possessing similar rodlike crystal habit (Table 1). No acrylonitrile was observed when alumina-coated Mo−V−Te−O M1 phase was studied in propane ammoxidation, while the combined selectivity to acrylonitrile and propene was 78 mol % after this phase was crushed. The selectivity for the desired products was slightly lower and that of CO_x was higher than that observed for the Mo−V−Te−Nb−O M1 phase, probably because the active surface sites are not isolated in Mo−V−Te−O M1 phase due to the lack of niobium in the structure.

In summary, this study of selectively exposed *ab* planes of the M1 phase demonstrated the importance of these surface planes for the activity and selectivity of the intriguing M1 phase in propane ammoxidation. This approach may be extended to the studies of surface planes in other layered mixed metal oxides with similar crystal morphologies in which the active and selective planes are perpendicular to the long crystal axis.

Supporting Information Available: Experimental details, SEM, TEM, and EDS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 2. Z-contrast TEM images of Mo−V−Te−Nb−O M1 phase catalyst coated with alumina before crushing (top) and after crushing (bottom). The former image shows the complete coverage of the particle by alumina and the latter shows the exposure of *ab* plane at the top side of the particle after crushing.

Table 1. Catalytic Behavior of M1 Phases in Propane Ammoxidation

catalyst	BET[a] m²g⁻¹	X_{C_3}[b]	S_{ACN}	S_{C3H6}	S_{MCN}	S_{CO_x}
MoVTeO crushed	7.3	43	50	6	5	39
MoVTeO ALD	1.1	15	0	0	0	100
MoVTeO ALD/crushed	7.1	13	52	26	4	18
MoVTeNbO crushed	11.8	64	61	3	4	32
MoVTeNbO ALD	0.2	12	0	1	1	98
MoVTeNbO ALD/crushed	9.5	30	69	14	9	8
Al₂O₃	272	13	0	1	8	91
SiC-ALD	0.5	12	0	1	0	99

[a] BET = BET surface areas. [b] C_3H_8 conversion. S = selectivities in mol %; ACN = acrylonitrile; MCN = acetonitrile.

doses of trimethylaluminum and water, which results in a deposition of ultrathin and conformal alumina nanolayers, as confirmed by TEM (Figures 2 top and S2). The thickness of the alumina layer was ∼22 nm. The signal from Al only was observed by the EDS analysis of the edges of the coated sample, thus confirming that the M1 crystals were covered by a thin layer of alumina (Figure S3). The alumina-coated M1 phase was tested in propane ammoxidation at 693 K. No acrylonitrile or propene were observed as products confirming the complete coverage of the active surface by alumina nanolayer (Table 1). The alumina-coated M1 phase exhibited some propane combustion activity typical of alumina surfaces (Al₂O₃ and SiC coated by alumina ALD in Table 1). This M1 phase was crushed gently in a mortar and TEM showed that the *ab* plane surfaces were exposed after crushing while the side planes of the M1 crystals were still covered by the alumina layer (Figures 2 bottom and S2). The EDS analysis of the crushed M1 phase showed the signals due to Mo, V, and Te, besides Al (Figure S3). The crushed M1 phase displayed significant increase in the selectivity to acrylonitrile and propene under the same reaction conditions (Table 1). The observed selectivities to acrylonitrile, propene, and carbon oxides (CO_x) were 69, 14, and 8 mol %, respectively. The combined selectivity to acrylonitrile and propene (83 mol