

Mg₃(VO₄)₂: Insight Into Catalytic Behavior Through Single Crystal Studies

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Mg₃(VO₄)₂ is known as an active catalyst for the oxidative dehydrogenation (ODH) of butane and propane [1,2]. In our previous studies, Mg₃(VO₄)₂ demonstrated remarkable turn over frequencies for the ODH of propane to propene. It was shown that when the catalytic operation was under reducing conditions (O₂ from the feed stream was completely consumed), the reaction became significantly more selective towards propylene [3]. Interestingly, Mg₃(VO₄)₂ and its reduced phase, Mg₃V₂O₆, are structurally very similar [5], as Mg₃(VO₄)₂ has a cation-deficient spinel-type structure [4] and Mg₃V₂O₆ has a cation-stuffed spinel-type structure. A single crystal of Mg₃(VO₄)₂ can undergo a topochemical reduction reaction to become a single crystal of Mg₃V₂O₆. It is the goal of this work to increase our understanding of the bulk and surface properties of Mg₃(VO₄)₂ under oxidizing and reducing conditions in order to gain insight into the observed catalytic behavior. In this study, transmission electron microscopy (TEM) is used to characterize synthetically grown Mg₃(VO₄)₂ single crystals of known orientation.

Transmission electron microscopy of various orientations of Mg₃(VO₄)₂ annealed at 750°C in O₂ showed formation of MgO islands on the surface of the sample (Fig. 1). The possibility of manipulating the surface stoichiometry of [010] samples was tested by adding V₂O₅ powder into the system during the annealing. Nucleation of MgO was not seen on the surface after annealing at 600°C, suggesting that annealing with V₂O₅ powder (thus increasing V₂O₅ partial pressure in the system) can prevent significant surface enrichment in MgO. Annealing an [010] sample with V₂O₅ at 700°C (above the melting temperature of V₂O₅) caused the sample to coarsen and become contaminated with V₂O₅.

Mg₃V₂O₆ samples of [20-1] orientation were reduced by annealing for 30 minutes at 560°C in a flow of 7% H₂ in N₂. After reduction, the samples were black in color and transmission electron diffraction revealed that the sample was composed of Mg₃V₂O₆. The zone axis (that is, the direction normal to the plane of the sample) was determined to be the [111] direction (Fig 2). Therefore we have observed that [20-1] Mg₃(VO₄)₂ transforms to [111] Mg₃V₂O₆. This result is very interesting since both the [111] direction in Mg₃V₂O₆ and the [20-1] direction in Mg₃(VO₄)₂ are perpendicular to the close-packed oxygen planes of their respective spinel-type structures. We have therefore shown that the reduction of bulk Mg₃(VO₄)₂ to Mg₃V₂O₆ occurs with the orientation of the close-packed oxygen planes remaining constant with respect to the sample geometry.

In conclusion, we have used TEM to study oriented single crystals of Mg₃(VO₄)₂ under oxidizing and reducing conditions in order to gain insight into the catalytic behavior of Mg₃(VO₄)₂. The TEM observations showed that upon heating in an oxidizing environment, the surface of Mg₃(VO₄)₂

becomes covered with MgO islands. As a result, we suggest that MgO enrichment occurs at the surface of $\text{Mg}_3(\text{VO}_4)_2$ during practical catalytic operation. This enrichment caps the catalyst with a non-reactive layer, effectively poisoning the ODH reaction. This proposed phenomenon agrees well with the observed catalytic performance of $\text{Mg}_3(\text{VO}_4)_2$ in oxidizing environments: with excess O_2 present in the gaseous feed stream the catalytic activity progressively decreases with time/temperature. Furthermore we have observed the single crystal to single crystal phase transformation of $\text{Mg}_3(\text{VO}_4)_2$ to $\text{Mg}_3\text{V}_2\text{O}_6$. We conclude by noting that this reduction is extremely facile and occurs with the close-packed oxygen network remaining constant with respect to the sample geometry [6].

References

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- [6] This research is supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, Grant No. DE-FG02-03ER15457.

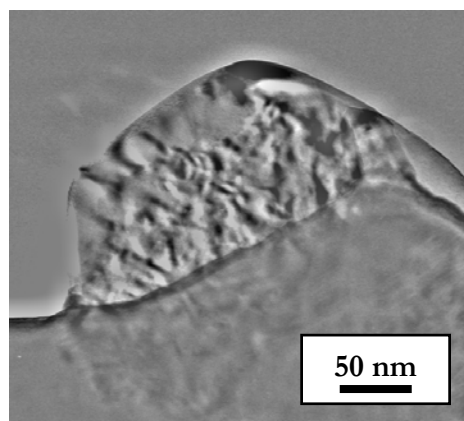


Figure 1: Bright field image of $\text{Mg}_3(\text{VO}_4)_2$ after 2 hour O_2 anneal at 750°C showing formation of MgO islands on the surface of the sample.

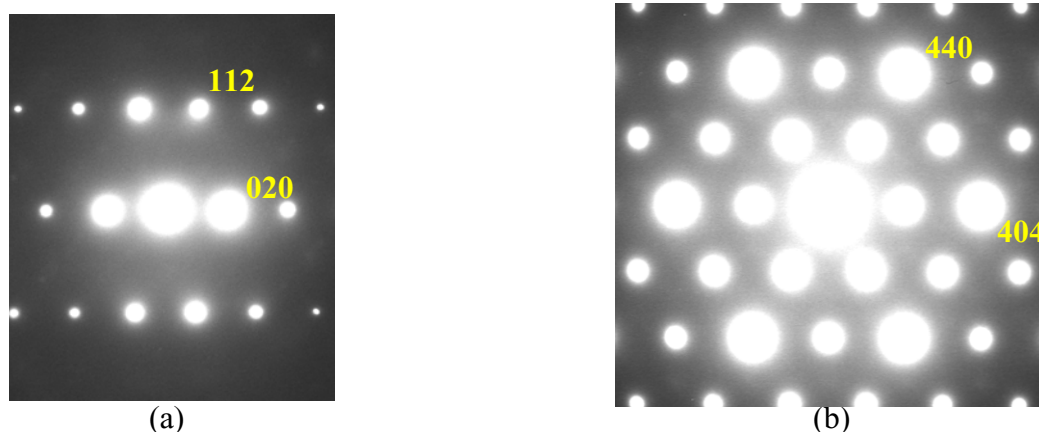


Figure 2: Transmission electron diffraction patterns of (a) $[20-1]$ $\text{Mg}_3(\text{VO}_4)_2$ zone axis (before reduction) and (b) $[111]$ $\text{Mg}_3\text{V}_2\text{O}_6$ zone axis (after reduction).