108
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Ex-situ and In-situ Analysis of MoVTeNb Oxide by Aberration-Corrected Scanning Transmission Electron Microscopy

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Short chain olefins, especially ethylene and propylene are very important industrial raw materials and are of increasing demand worldwide. The abundance of C2-C3 light alkanes in shale gas makes production of these olefins from oxidative dehydrogenation (ODH) one of the most attractive alternatives to industrial processes [1]. Among all the catalysts for C2-C3 light alkane ODH reactions, the two-phase MoVTeNb oxide system has shown great promise [1]. Much attention has been devoted to the analysis of the crystallography structure of catalytic active M1 phase. However, the nature of the surfaces where the reactions take place and their roles in catalysis have not been resolved. Additionally, it has been reported that surfaces of the M1 phase undergo changes during ODH reactions, which would affect the catalytic activity of the system [2]. Therefore, it is also very important to perform the *in situ* experimental observations under relatively realistic conditions for a fundamental understanding of the outstanding catalytic performance of this material.

Here, we report an identification of the nature of crystalline termination of the M1 phase at atomic scale using an aberration-corrected scanning transmission electron microscope (STEM). Figure 1 shows a typical M1 phase particle viewed in the crystal growth direction (the [001] orientation). Based on the analysis of over 50 particles, it is shown that the lateral surfaces of these rods are faceted and the most preferential lateral facets have been determined. The configuration of these facets means it is possible to quantify amount of ODH active sites exposed per area on each facet. Moreover, statistical analysis of the proposed active sites exposure in the M1 phase particles with different morphologies agrees very well with experimental data, showing a ~30% higher activity of the small rounded M1 phase rods compared to the large flattened ones. These results demonstrate that morphology has a large impact on catalytic activity of the MoVTeNb oxide system. Simulations are underway to determine the energies of those surface facets with slightly different configurations, which is essential for fundamental understanding of termination mechanism of material of such complex structures.

Direct imaging of structural changes in the M1 phase was performed under an oxidative atmosphere by in-situ TEM technique using a Protochip heating holder in an environmental TEM. An M1 phase particles was heated to 350 °C in 10 mbar oxygen/argon (23%/77%) showed that tellurium units disappeared from hexagonal channels while the crystal framework remained unaffected. Control experiments with sample heated to the same temperature without oxygen showed no such effects. The crystalline structure was damaged within seconds. These results indicate that oxygen stabilizes the MoVTeNb oxide structure at elevated temperature. Further in-situ experiments using a gas stage holder which allows much higher partial pressure (above 1 bar) are underway to investigate the gas pressure effects [3].

References:
[1] F. Cavani *et al*., Catalysis Today **127** (2007), 113-131.
[2] M. Hävecker *et al*., Journal of Catalysis **285** (2012) 48–60
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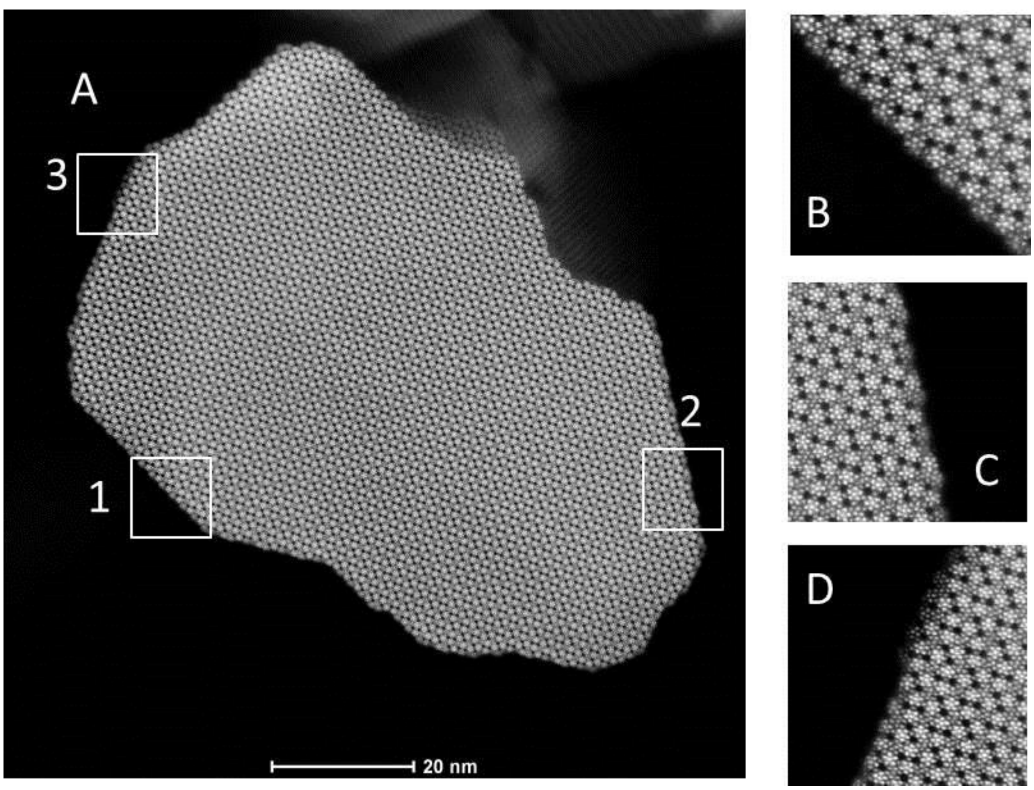

Figure 1. (A) Unprocessed STEM image showing nicely crystalline and faceted surface of M1 phase. (B-D) Magnified view of rectangular areas 1-3 in (A) respectively, showing different facets configurations.

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