

Mixed Metal Oxide Catalyst Development for Selective Oxidation and Ammoxidation of Light Hydrocarbons

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Selective oxidation catalysis is used in production of roughly 25% of all important organic chemicals and intermediates used for making consumer and industrial products [1]. The abundance of natural gas from shale resources makes efficient catalytic oxidation of light hydrocarbons to more valuable intermediates particularly desirable. Complex mixed metal oxides (MMO) based on molybdenum-vanadium oxide bronzes offer particular promise for C2 and C3 conversions. Mo-V-O bronzes are both active and selective for oxidative dehydrogenation (ODH) of ethane to ethylene. Since high temperature thermal conversion of ethane to ethylene is one of the most energy consuming chemical processes employed today, replacement of this process by catalytic ODH is highly desirable. More complex Mo-V-Nb-(Te,Sb)-O variants show promise for selective oxidation of propane to acrylic acid and ammoxidation to acrylonitrile. Several different periodic structures exist in these multimetallic suboxide systems, and sometimes these can form intergrowth structures, complicating the preparation. In the case of propane (amm)oxidation, the most effective catalyst seems to require a blend of two crystalline forms, commonly known as M1 and M2. These catalysts may replace existing technology involving multicomponent bismuth molybdate catalysts that require more costly propylene as the feed. Careful structural and compositional characterization of these newer catalytic MMO bronze materials is needed to quantitatively assess phase content. Evaluation of mixed site occupancies and mixed valences from combining Rietveld analysis of diffraction data with direct space studies provides insights into catalytic mechanisms [2]. Recent studies indicating unusual lattice dynamics in the active site at elevated temperatures suggest that dynamics may also play an important mechanistic role [3]. Challenges remain that impede commercialization, particularly with issues of scale up and with control of crystallite size and habit. Observation of the self-assembly process during crystallization [4] suggests that there are some parallels with the growth of zeolites in that they do not exhibit simple nucleation and growth. The M1 phase and some other related forms initially require formation of M_6O_{21} pentagonal subunits that connect with linking octahedra to form periodic frameworks with nanochannels [5]. These nanochannels permit intercalation of species that can modify valence states in the framework and can participate in the catalysis. Advancing our understanding of how to synthetically direct the self-assembly process will be needed to fully realize the potential of these materials.

References

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