Generating functionality in metal oxide catalysts for selective oxidation of light alkanes

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Transition metal oxides are the active component of most important heterogeneous catalysts for the selective oxidation of ethane to ethylene and methane to methanol. These materials face multiple challenges regarding net activity at mild temperatures and avoidance of total combustion reactions. Unlike other heterogeneous catalysts, there is a limited structural understanding of the active species and little control of the properties of the final materials. Gaining knowledge on the chemical processes involved in the formation of active sites will enable ways to design synthesis protocols and new strategies to improve the catalytic performance of metal oxide catalysts.

In the first part, it will be discussed different strategies to enhance the formation of active sites in complex Mo and V mixed oxides. Control of the synthesis parameters and understanding of the crystallization kinetics – in particular the assembly of polyoxometalate precursors – is necessary to direct synthesis methods towards active morphologies of the metal oxide. We have recently developed a new synthesis method for Mo-V-Te-Nb oxides with unusually high intrinsic activity in oxidative dehydrogenation (ODH) of ethane for ethylene production. Analysis of HAADF-STEM images with atomic resolution revealed that the superior catalytic performance of the new material is linked to its crystal morphology (see Figure). The crystallization process has been directed towards formation of particles exposing a large proportion of active facets [1]. Another strategy is related to the dynamic response of the catalyst under reaction conditions. Environmental TEM studies allowed observation of mobility of Te ions in the lattice. This phenomenon is linked to the promoting effect of Te by formation of additional active sites under reaction conditions.

In the second part it will be explored the activity of Cu-exchanged zeolites in the selective oxidation of methane to methanol. Mordenite (MOR) was earlier identified as the most suitable framework to stabilize active Cu-oxo nanoclusters [2,3]. It has been recently found that other frameworks are also very effective in the stabilization of active Cu-oxo clusters. Cu cations undergo a series of thermally driven steps during activation that precede the formation of active oxidizing species. Zeolite properties and the mobility of Cu ions upon thermal treatment has been revealed to be central in the formation active species. In this study, we investigate the elementary steps involved in the formation of Cu-oxo active sites and discuss the role of geometry and constrains of zeolite frameworks.

On the left HAADF-STEM image of a MoVTeNb oxide particle with modified crystal termination exposing active sites. On the right a comparison of ethane ODH rates for MoVTeNb oxide samples crystallized at low and high temperatures.


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