Combinatorial methods for selective oxidation of propane to acrylic acid on Mo-V-Te-Nb oxides

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Introduction

One of the important parts of the petrochemical industry is the upgrading of cheaper feedstocks to more valuable products. Along these lines, selective oxidation reactions appear to be a feasible alternative to upgrade and utilize light alkanes (C_2-C_4), in substitution of more expensive olefins, to produce highly demanded oxygenated compounds. Catalytic selective oxidation of low molecular weight alkane is motivated by both the potential economic and environmental advantages.

Until recently the main way of better utilization of light alkanes was their transformation into the corresponding olefins. Thus, acrolein, acrylonitrile and acrylic acid are produced from propane in two step process via propylene. However, in the present economic circumstances, the high cost of propylene production prompted the development of researches on the direct transformation of propane into oxygenates through selective oxidation.

When considering the selective catalytic oxidation of propane into oxygenates, two main difficulties arise. The first one is, as for the partial oxidation of other light alkanes, the lower reactivity of the reactant as compared to that of the formed products. Activation of the reactant needs operating conditions (temperature as high as 450°C) which are detrimental to the stability of the products. Therefore, the considered reaction requires catalysts with specific properties: activation of propane partial oxidation and decrease or inhibition of the product oxidation. The second difficulty is to design suitable catalysts because of not much information available about the involved reaction mechanisms [1-3].

The selective oxidation of light alkanes to oxygen containing products is a very attractive method for utilization of natural gas. Partial oxidation of propane is one of such methods. Especially, one-step direct transformation of propane to acrylic acid is of great interest. Presently, acrylic acid is produced by two-steps reaction, propene to acrolein and then acrolein to acrylic acid.

Materials and Methods

The most promising catalyst for the direct oxidation of propane to acrylic acid is Mo-V-Te-Nb oxide, developed by Mitsubishi Chemicals. By similar preparation procedure reported in the literature [4-6], we prepared the catalyst for our experiments. Mo-V-Te-Nb oxide catalysts have been prepared by slurry method with different chemical compounds and have been tested with high throughput screening method in the selective oxidation of propane to acrylic acid. We have prepared the new Mo-V-Te-Nb oxide based catalysts with diverse chemical treatment. 32-multi-channel reactor was used for high-throughput screening of the catalysts. The product streams were analyzed with GC and mass spectroscopy to determine the values of propane conversion, acrylic acid yield and the distribution of other products. The catalysts were characterized by XRD, SEM and Raman Spectroscopy.

Results and Discussion

The experimental results led to the conclusion that catalyst preparation methods and parameters greatly affected the bulk as well as surface structure of complex metal oxide catalyst, which, in turn, affect their catalytic performance in the selective oxidation of propane to acrylic acid (Fig. 1). The results in table 1 show the variation of the activity in the reaction for the catalyst prepared by some favorable treatment materials like I_2, NH_4OH, HIO_3. By the interpretation of Raman spectrums and the XRD recognized the influences of preparation methods and parameters like shifts of the peaks. It was found that an effective Mo-V-Te-Nb oxide catalyst for propane selective oxidation to acrylic acid can be obtained with a combination of proper metal compositions and proper preparation methods. Finally based on oxides of pure phase M1 and exclusively enriched phase M2, our results have enabled the identification of distinct SEM characteristics and also revealed the actual catalytic function of the two critical crystal phases (phases M1 and M2) in effective Mo-V-Te-Nb complex oxides catalysts. In conclusion, phase M1 is active in propane activation but are relatively unselective for acrylic acid formation, and that phase M2 is reasonably active for propane activation while also fairly selective for acrylic acid formation.

Table 1. Selective oxidation of propane on $MoV_{0.33}Te_{0.22}Nb_{0.11}$ oxide catalyst

Treated by	C_3H_8 Conversion (%)	Acrylic Acid Selectivity (%)	Acrylic Acid Yield (%)
I_2 0.0052 mol	27.78	67.43	18.72
NH_4OH (pH6)	22.38	72.22	16.17
HIO_3 (pH3.06)	47.28	47.18	22.31

Significance

Combinatorial synthesis and screening technique have been applied to investigate the catalytic activity and selectivity of quaternary mixed-metal oxide catalysts for the selective oxidation of propane. The 32-channel sequential/parallel fixed bed reactor system was developed with all the operations were computer-controlled.

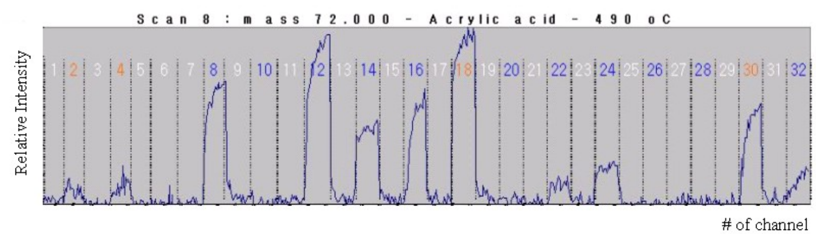

Figure 1. Intensity (in case of acrylic acid, m/z=72) of mass spectroscopy for selective oxidation of propane in high-throughput screening experimental. The catalyst prepared by the different methods was loaded at each of the 32-channels

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