

Improved Yields to Acrolein by Modified Scheelite-Type Multi Metal Oxides

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Introduction

The lower price and the global abundance of propane compared to propylene are still the main driving forces behind the search for an efficient catalyst that could be used in an appropriate selective oxidation process [1]. Due to the lower reactivity of propane compared with the target products acrolein or acrylic acid, which especially at higher temperatures tend to undergo an undesired further oxidation to carbon oxides, and due to the simultaneous necessity to avoid C-C-bond breaking, the development of such a catalyst is not an easy task. Today, mainly three catalyst systems are considered of potential interest: (I) metal phosphates, (II) heteropoly acids and salts, and (III) multi-component mixed metal oxides [2].

The present study aims at the development of a highly productive catalyst for the direct selective oxidation of propane to acrolein and/or acrylic acid. Modified vanadium phosphates (VPO) and vanadium-molybdenum-based heteropoly acids (HPA) are compared with modified scheelite-type bismuth-vanadium molybdenum oxides (BiVMo). Special attention was given to the preparation of multi-metal-oxide catalysts that were mixed with relatively large amounts of alumina. They could perhaps be regarded as a novel member in group III of the catalysts.

For this reason, numerous samples of each of the three catalyst systems mentioned above were prepared and tested, varying in preparation method, catalyst composition and addition of promoters (Nb, Sb, W, Te, Fe, Co, Ni, Li, K, Cs, Ag, Cu, Ce, Ti, Zr, and Sn). Intensive efforts were made to establish definitely reproducible preparation methods, especially for the mixed multi-metal oxides. Particular emphasis was placed on the systematic investigation of the influence of the reaction conditions on the catalyst performance. Selected samples were physicochemically characterised by XRD-, BET-, DTA/TG-, SEM-, and XPS-analysis before and after catalytic testing. Finally, isotopic labelling was applied to verify the reaction pathway of the selective oxidation of propane.

Results and Discussion

The mechanistic investigations with labelled propane over BiVMo catalysts reveal that propylene is the necessary intermediate for the formation of acrolein. This result confirms analogous observations over VPO catalysts made by other authors [3].

Concerning the catalytic behaviour of the various samples, it has been found that at comparable degrees of conversion (15-20%), the total selectivity to acrolein and acrylic acid reaches similar values (up to about 60-70%) for both the VPO and the HPA catalysts, depending on the promoter compound. The best results for the VPO

system are obtained for catalysts that were modified with zirconia or telluria: 64 and 73% selectivity to the desired oxygenates at 15% conversion. These findings are in agreement with data published elsewhere [2, 3]. Combining VPO and HPA samples by mechanical mixing improves the total yields (22%) at only slightly diminished levels of selectivity (57%). Relatively high selectivities of about 75% acrolein are seen for an alumina-supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst but at significantly lower degrees of conversion (9-10%).

As to the BiVMo catalysts, their catalytic performance strongly depends on their composition, e.g. maximum yields to acrolein are found for a molar V/Mo-ratio of 1. Such a sample was taken as a reference in order to prove the effect of various promoters on the catalytic properties. Selected examples at comparably low conversions are illustrated in Figure 1. Besides the known positive effect of Ag or Te (not shown here), the addition of Ce appears to be purposeful, whereas other promoters have no or a detrimental effect. Figure 2 demonstrates the successive development of a scheelite-type BiVMo catalyst, resulting in the formation of a considerably more selective Bi-V-Mo-Co-Sb-K-O material. DTA/TG-and XRD measurements showed that the scheelite structure of the bulk material remains stable under catalytic exploitation. However, XPS-analysis evidenced that the structure of the catalyst surface differs markedly from that of the bulk. Further improvement of the catalytic activity and selectivity is achieved by replacing potassia with relatively large amounts of alumina (cf. Fig. 2). Hence, the yield to oxygenates increases to about 25%. Unlike the various modified scheelite-type BiVMo catalysts, an alumina-containing multi-metal-oxide catalyst does not lose its catalytic performance if steam is added to the feed gas. In this case, such a catalyst is capable of additionally forming acrylic acid during selective oxidation of propane. A similar effect of water has been reported for VPO catalysts [4].

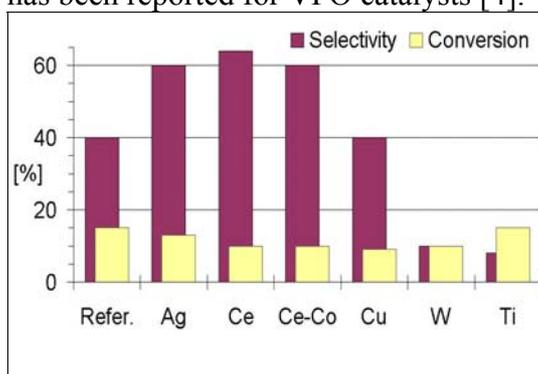


Fig.1. Promoted BiVMo-oxides tested at 500°C (SV=3000 h⁻¹, C₃H₈:O₂=1:1.5)

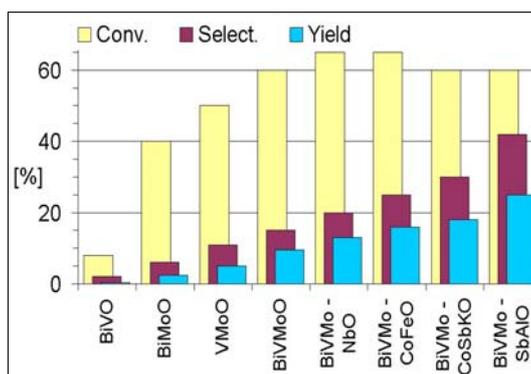


Fig.2. Various BiVMo-catalysts tested at 500°C (SV=600 h⁻¹, C₃H₈:O₂=1:1.5)

References

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