



On the formation and decomposition of active phases in $\text{Mo}_9\text{V}_3\text{W}_{12}\text{O}_x$ catalysts during operation in the acrolein oxidation to acrylic acid.

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The activation process of $\text{Mo}_9\text{V}_3\text{W}_{12}\text{O}_x$ mixed oxide catalysts in the reaction of acrolein oxidation to acrylic acid was investigated for various reaction conditions. Changes induced in the catalytic performance by these different activation procedures could be correlated with structural changes of the MoVW mixed oxide catalyst, as proven by XRD and electron microscopies (SEM, TEM, and EDX).

After preparation and calcination at 673 K (this material will be referred to as the initial material), mainly nanocrystalline Mo_5O_{14} -like oxide was observed by XRD with nanocrystalline MoO_3 -type oxide as the minority species [1, 2].

The rate of acrolein oxidation over the initial material increased many times during the first hours of operation in acrolein oxidation. Considerable changes in the average element distributions of Mo, V and W could not be detected post mortem by SEM-EDX for this catalyst (573-603 K).

The catalyst activation was accompanied by a reduction of the MoVW mixed oxide and the formation of crystalline Mo_5O_{14} -type oxide phases as detected post mortem by XRD, SEM and TEM after the first hours of operation in the reaction of acrolein oxidation at 573-603 K. Hence, the crystalline Mo_5O_{14} -type oxide appeared approximately on the same time scale, for a given temperature, as the considerable increase in catalytic activity.

The total degree of crystallization increased with time of operation in the reaction mixture and with the reaction temperature. The Mo_5O_{14} -type mixed oxide was found to be the main crystalline phase in samples activated in the reaction mixture. This result compares well with those described earlier after inert gas activation.

SEM-EDX analysis revealed a slight increased heterogeneity in the elemental distribution. For the initial material, the Mo content varied from 63 to 67 at.%. The V content varied between 20 to 27 at.% and that of W between 10 to 13 at.%. The activation in the reaction mixture between 573-603 K during 2 - 4 hours led to a



minor increase of the heterogeneity in the V and Mo distribution. Thus, the V content varied from 19 to 29 at.%, that of Mo between 60 to 69 at.%. W, on the other side showed an unchanged distribution. SEM characterization of the mixed oxide activated in the reaction mixture revealed the formation of crystalline particles with different morphologies having different elemental compositions. At least 2 different types of needle-shaped particles, two different platelet-like particles, cubic particles as well as spherical particles were detected within the catalyst material after activation.

Therefore, a quantitative correlation between the catalyst structure and its performance is not possible because of this heterogeneity. In addition, it cannot be ruled out that nanocrystalline material remains within the specimen after activation in the reaction mixture. Further, single crystal XRD data are yet not available for the (MoVW)₅O₁₄-type oxide in the literature. Attempts are in progress to synthesize such material.

Catalyst operation in the reaction at 673 K, on the other hand, decreased both catalyst activity and selectivity to acrylic acid. This catalyst deactivation resulted in an increase of the heterogeneity of the elemental distributions. The deactivated mixed oxide showed a varying V content between 4 and 26 at.%, an Mo variation between 92 to 60 at.%, and an altering W concentration between 4 to 14 at.%). Additionally, a smaller amount of the Mo₄O₁₅-type phase was detected thereafter and the formation of MoO₃-type crystals was observed. Accordingly, the catalytic activity of this catalyst was lower despite of the higher reaction temperature. The correlation between catalytic performance in the partial oxidation of acrolein and the formation of the Mo₅O₁₄-type oxide indicates the important role of this phase for the partial oxidation of acrolein.

1. G. Mestl, Ch. Linsmeier, R. Gottschall, M. Dieterle, J. Find, D. Herein, J. Jäger, Y. Uchida and R. Schlögl, *Appl. Catal. A*, in print.
2. M. Dieterle, G. Mestl, J. Jäger, Y. Uchida, H. Hübner, and R. Schlögl submitted to *Appl. Catal. A*.

