

Structural changes of vanadium–molybdenum–tungsten mixed oxide catalysts during the selective oxidation of acrolein to acrylic acid

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Abstract

The catalytic performance of vanadium–molybdenum–tungsten mixed oxides with the basic composition $V_2Mo_8W_xO_y$ with $0 \leq x \leq 5$ and their structural changes were examined by TPR and XRD. The variation of the tungsten content in the vanadium–molybdenum oxide matrix allowed the study of structural and catalytic performances under laboratory conditions in a downscaled version of the complex industrial catalyst.

Focussing the influence of morphology and tungsten doping on the redox properties and the oxygen dynamics, TPR experiments revealed a strong impact of the preparation method on the catalytic activity. A higher selectivity towards acrylic acid with increasing tungsten content was detected. Parallel to this, a shift of the selectivity maximum to higher temperatures was found. For the spray-dried samples, an increasing yield of acrylic acid was observed while the yield of the crystallized samples remained constant. The conversion of acrolein changed to the total oxidation products at above 450 °C. Additional cyclic temperature programmed experiments were carried out to examine the start-up behavior of the calcined catalysts under transient conditions. These experiments give also an indication of the catalysts' stability.

The structural changes of the samples were examined by Rietveld refinements of X-ray data. For the solid-state prepared samples only thermodynamically stable phases like orthorhombic MoO_3 or V_2MoO_8 were detected. $Mo_{0.6}W_{0.4}O_3$ and $Mo_{0.29}W_{0.71}O_3$ were observed at increasing tungsten content. The wet chemically prepared samples showed thermodynamically metastable phase compositions like hexagonal $(V,Mo)O_3$ and triclinic $(V,Mo)_2O_5$. Amorphous to nanocrystalline diffraction pattern are characteristic for the spray-dried samples with a tungsten content $x > 1$. A complete switch of the phase system after reduction was observed for lower tungsten contents. Only binary oxides like MoO_2 or VO_2 were measured. A destruction of the phase systems depending on the gas phase composition was observed from 450 °C on by *in situ* X-ray diffraction. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The production of acrylic acid increased from only 400.000 tons per year in 1980 [1] to more than 2 million tons in 2004 [2]. (Poly)acrylic acid is mainly used for superabsorbing materials, disposable diapers and low-phosphorous detergents. Vanadium–molybdenum mixed oxide catalysts are applied in the industrial production. Different elements (e.g. Mn, Fe, Cu, W) are added as promoters in order to improve the selectivity

of the oxidation reaction of acrolein to acrylic acid [1] and the long-term stability of the catalyst. Some of them, e.g. copper [3] and tungsten [4] modify the acid-base properties of the surface and consequently the heat of adsorption [5,6].

The detailed mechanism, the structure and structural modifications of the catalyst have extensively been studied in the past. The main results obtained by EPR, IR, XPS, XRD, catalytic and sorption experiments were published in two review articles [5,6]. Bulk oxide material as well as supported catalysts on high-surface-area SiO_2 [5] were examined for their phase composition, active centers and catalytic activity [5,6]. A major influence of the support was experimentally excluded [7], the active phases and centers should be identical for bulk oxides and supported catalysts. In material with a V_2O_4 content up to

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3 mol.% the compound $\text{VMo}_3\text{O}_{11+x}$ was identified as the most active phase whereas for higher V_2O_4 contents other phases as $\text{VMo}_2\text{O}_{8+x}$, $\text{V}_6\text{Mo}_4\text{O}_{25}$ or V_2MoO_8 were formed. These materials exhibit lower selectivity than $\text{VMo}_3\text{O}_{11+x}$ for acrylic acid in this order which decreased parallel to an increase of the V(V) content and parallel to a considerable shift to total oxidation products [5].

The reaction of acrolein to acrylic acid is accompanied by a fast deactivation of the material under technical conditions for bulk vanadium–molybdenum mixed oxides. This operation mode results in thermodynamically stable phases like orthorhombic MoO_3 and monoclinic V_2MoO_8 which are inactive towards the formation of acrylic acid as shown by solid-state prepared samples [8].

In the copper-modified vanadium–molybdenum oxide catalysts the active phase was reported as $\text{VMo}_3\text{O}_{11+x}$ and $\text{VMo}_2\text{O}_{8+x}$ where vanadium is partially substituted by variable amounts of copper [3]. For catalysts with tungsten as promoter, Mo_5O_{14} is suggested as active phase with variable but minor contents of vanadium and tungsten [4].

Both oxides, Mo_4O_{11} and Mo_5O_{14} with partial substitution of vanadium and tungsten for molybdenum, build layer structures which, by integration or removal of oxygen, may form shear structures.

In order to deepen the knowledge of the active sites and oxygen transfer in these catalytic systems, mixed oxides were prepared differently and examined by nitrogen adsorption (BET model), X-ray diffraction (XRD) and temperature programmed reduction with acrolein (TPR).

2. Experimental

2.1. Preparation

The preparation of catalysts with the formal composition $\text{V}_2\text{Mo}_8\text{W}_x\text{O}_y$ ($0 \leq x \leq 5$) was performed via two different ways

(Table 1). The first oxide series I was prepared by melting and calcination of the binary oxides MoO_3 , V_2O_5 and WO_3 in the desired stoichiometry to obtain oxides with thermodynamically stable phases. Therefore, the oxides were homogenized in an agate mortar and melted in a sealed vacuum quartz tube. Then the powder was pressed into pellets and was annealed in a muffle furnace for seven days at 600°C . After the calcination procedure the pellets were quenched in liquid nitrogen to stabilize the formed crystalline phases.

The second method of preparation is based on aqueous solutions of the ammonium salts acidified with nitric acid. To prepare the oxides, the precursor solutions were dried via crystallization (IIa) and spray-drying (IIb). The obtained powder was treated in a special furnace with an annealing program up to 400°C as temperature maximum. The details of preparation (I) can be found in Adams et al. [8] and the preparation of the oxides through aqueous solutions (IIa and IIb) in Kunert et al. [9].

2.2. Temperature programmed reduction

The performance of the catalysts was characterized by TPR in a micro reactor with acrolein as reducing agent. The design of the TPR equipment was published by Boehling et al. [10]. The reaction products were analyzed by a quadrupole mass spectrometer (Balzers, QMG 511). A continuous analysis of acrolein, acrylic acid, carbon dioxide, carbon monoxide and water was achieved through online monitoring.

Two hundred fifty milligrams of a probe was pre-treated at 400°C for 60 min with 10 vol.% oxygen (Messer Griesheim) in inert gas with a flow rate of 1.2 l/h and subsequently cooled down to room temperature in inert gas. An inert gas mixture, argon with 5 vol.% helium (Messer Griesheim) as internal standard for the MS analysis was applied. The reduction was carried out with 5 vol.% acrolein (BASF) in the standard inert gas mixture Ar/He. The temperature was raised with a constant heating rate of $10^\circ\text{C min}^{-1}$ to a maximum of 480°C and cooled down to

Table 1
Observed structure types for the samples of preparation methods I, IIa and IIb before and after TPR

Structure types	Preparation method		I	IIa		IIb	
	SG	Reference		Before	After	Before	After
VO_2	<i>P 2₁/c</i>	[21]		X ^a			
VO_2	<i>C 2/m</i>	[25]			X		X
$(\text{V},\text{Mo})\text{O}_3$	<i>P 6₃</i>	[18]		X		X	
$(\text{V},\text{Mo})_2\text{O}_5$	<i>P 1</i>	[19]		X		X	
V_2MoO_8	<i>C2/m</i>	[15]	X				
MoO_2	<i>P 2₁</i>	[24]			X		X
MoO_3	<i>Pnma</i>	[14]	X				
MoO_3	<i>Pbnm</i>	[26,28]			X	X ^b	X ^c
MoO_3	<i>P 2₁/c</i>	[27]			X		
Mo_5O_{14}	<i>P 2₁/a</i>	[22]		X ^a	X ^a		
Mo_5O_{14}	<i>P 4/mbm</i>	[29]				X ^b	X ^c
$\text{Mo}_{0.6}\text{W}_{0.4}\text{O}_3$	<i>Cmc2₁</i>	[16]	X				
$\text{Mo}_{0.29}\text{W}_{0.71}\text{O}_3$	<i>P2₁/n</i>	[16]	X				
WO_3	<i>P6/mmm</i>	[20]		X ^a	X		X

^a Only $x = 3$.

^b $x > 1$ nanocrystalline/amorphous.

^c $x > 2$ nanocrystalline/amorphous.

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