Nanostructured Phase-Pure MoV-based Oxides in Selective Oxidation of Propane to Acrylic Acid

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Introduction

The activation of the inert C-H bonds in propane and its selective oxidation to valuable oxygenates, such as acrolein or acrylic acid, are effectively catalyzed by multi-metal oxides with a high degree of structural and chemical complexity. The best performance has been reported for MoVTeNb oxides. Generally, this catalyst is consisted of two or more crystalline phases, wherein the most relevant in C-H activation of propane being the so-called M1 phase [1]. M1 is generated by corner-sharing of MO_6 (M=Mo, V, Nb) octahedrons forming pentagonal, hexagonal, and heptagonal channels in [001] direction of the orthorhombic crystal structure. Nb occupies the pentagonal channels, whereas the hexagonal, and heptagonal channels are partially filled by Te. Typically, the M1 crystals are characterized by a cylindric shape with (001) planes termination at the basal surface and (hkl) planes termination at the lateral surface. The active sites have been suggested to be exclusively located on the (001) plane [2]. However, a recent study indicated activity of the entire surface in oxidation of propane to acrylic acid [3]. To approach the fundamental understanding of the catalytic behavior of M1, a series of phase-pure powdered M1 catalysts with various particles morphologies has been prepared applying different synthesis methods, keeping the chemical composition of M1 nearly constant. Powder X-ray and neutron diffraction, electron microscopy, chemical analysis, and adsorption of N_2 and C_3H_8 have been used to characterize the title catalysts.

Materials and Methods

Highly crystalline M1 has been synthesized by hydrothermal treatment of a suspension generated by mixing aqueous solutions of metal salt precursors at 150°C for 48 h (sample **HT-M1**). M1 of different morphology has been prepared from phase mixtures that have been washed with H_2O_2 solution to dissolve unwanted phases (samples **W-M1**). Nanostructured M1 has been obtained by spray-drying of homogeneous aqueous solutions of the metal salt precursors followed by gentle calcination of the product at 275°C and subsequent treatment in superheated water vapor at 500°C for 2 h (sample **SH-M1**). Finally, all catalysts have been activated *via* thermal treatment at 600°C for 2 h in Ar flow. Propane oxidation has been performed in a fixed bed reactor at 360-400°C, varying feed composition and space velocity.

Results and Discussion

With respect to the metals, all synthesized materials are composed of 64 at% Mo, 16 at% V, 6 at% Te, and 14 at% Nb. The elements are homogeneously distributed within the M1 particles, as established by STEM-EDS. Further characteristics and catalytic properties of the differently prepared M1 catalysts are summarized in Table 1. Nitrogen adsorption reveals an increase in the surface area S_{BET} in the order **HT-M1** < **W-M1** < **SH-M1**. This trend is reflected in decreasing domain size measured by XRD. Particle size distributions of all phase-pure M1 catalysts have been obtained by analysis of SEM data. Based on the mean length and width of the rod-like crystals, specific surface areas S of the total, lateral, and basal (001) surface have been calculated assuming ideal cylindrical particle geometry and the crystallographic density of 4.4 g/cm^3. The trend in the calculated total surface area S_{total} is almost consistent with the measured S_{BET} surface area. The growth is mainly due to an increasing fraction of lateral surface area. The activity in propane oxidation at 400°C passes through a maximum. **W-M1-b** with intermediate total surface area shows the highest conversion. Similar selectivity to acrylic acid of about 60% is observed at a propane conversion of approximate 50% for the catalysts **HT-M1** and **W-M1-b** that differ significantly in the $S_{(001)}/S_{total}$ ratio. On the other hand, the selectivity is one order of magnitude lower for the catalyst **SH-M1** that exposes proportionally less basal (001) surface.

Table 1. Characteristics and properties of the M1 catalysts in propane oxidation

Catalyst	ID	D_{XRD} [nm]	S_{BET} [m²/g]	S_{total} [m²/g]	$S_{(001)}$ [m²/g]	$S_{lateral}$ [m²/g]	$S_{(001)}/S_{total}$	X_{C3H8} [%][#]	S_{C3H4O2} [%][#]
HT-M1	5511	63.9	5.9	5.4	1.1	4.3	0.20	52	58
W-M1-a	5591	57.7	7.4	12.3	2.3	10.0	0.19	68	34
W-M1-b	6059	55.6	8.8	10.5	2.4	8.1	0.29	72 47[*]	40 62[*]
SH-M1	5737	46.7	13.3	17.2	2.3	14.9	0.13	56	5

reaction conditions:
[#] T = 400°C, $C_3H_8/O_2/H_2O/N_2$ = 3/6/40/51 vol%, GHSV=1200 h^{-1}
[*] T = 400°C, $C_3H_8/O_2/H_2O/N_2$ = 3/6/40/51 vol%, GHSV=5000 h^{-1}

Significance

The present study demonstrates that the crystal habit of M1 has a significant impact on the catalytic performance. A linear correlation between the abundance of terminating lattice planes and activity or selectivity to acrylic acid in propane oxidation has not been observed. The results clearly illustrate the complexity of M1 catalysts. It has been shown that the presence of Te is not sufficient for high selectivity to acrylic acid. Nanostructuring of M1 leads to a drastic decrease in the selectivity. Other solid state and surface properties that are related to particle size and shape, such as oxidation state of the metals, redox properties, surface composition, surface topography, bulk and surface conductivity are currently under investigation.

References

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