Novel mesostructured Mo-V-Te-Nb mixed oxide catalysts for selective oxidation of propane to acrylic acid

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Introduction

Structurally and chemically complex Mo-V-Te-Nb mixed oxides are particularly promising as catalysts for selective oxidation and ammoxidation of propane to acrylic acid and acrylonitrile, respectively [1]. The activated catalysts are crystalline materials essentially composed of two different orthorhombic phases, denominated as M1 and M2 [1], respectively, usually exhibiting specific surface areas less than 20 m^2g^{-1}. M1 corresponds to a complex three-dimensional structure assembled from MO_6 and MO_5 units (M=Mo,V,Nb) forming six- and seven-sided channels, stabilized by built-in tellurium. Although the importance of M1 for propane activation is indisputable, its precise mode of action remains a matter of ongoing discussion bearing models that consider specific metal positions on the *ab* plane of the M1 phase as active sites [2]. In different concepts, M1 is regarded as a reservoir of chemically and structurally dynamic surface species formed under reaction conditions at the M1 surface [3]. Hydrothermal synthesis enables the preparation of highly crystalline single-phase M1 catalysts without the need for further purification of the product by chemical treatments. To a certain extent, the specific surface area is adjustable by the thermal activation procedure. The resulting catalysts convert propane into acrylic acid with more than 80% selectivity whereas the activity increases with increasing specific surface area. Consequently, our efforts have been focused on nanostructuring $MoVTeNbO_x$. PEO-PPO-PEO block copolymers have been successfully applied to prepare a thermally stable mesostructured $MoVTeNbO_x$ possessing x-ray amorphous bulk structure, which shows activity in the oxidation of propane to acrylic acid.

Materials and Methods

In the present work, gels with the metal stochiometry $Mo_1V_{0.25}Te_{0.23}Nb_{0.124}$ were prepared by combining aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$, $VOSO_4 \cdot x\ H_2O$, $Te(OH)_6$, $(NH_4)_2Nb_2(C_2O_4)_5$, and optionally the triblock copolymer $EO_{20}PO_{70}EO_{20}$. Black-purple colored products were obtained after hydrothermal synthesis at 403 K for 96 h. If present, the template was removed to various degrees by extraction as verified by thermal analysis. Finally, the materials were activated in argon at 873 K.

Results and Discussion

High temperature treatment results in crystallization of pure M1, if the mixed oxide was prepared in absence of the template. In contrast, the block copolymer assisted synthesis leads to x-ray amorphous materials. The residual carbon content amounts to about 6 wt-% as shown by thermal analysis. Nitrogen adsorption-desorption measurements revealed a type IV isotherm with a sharp inflection at $p/p_0=0.7$ and a broad hysteresis loop, characteristic of capillary condensation in the channels of a mesoporous material (Fig. 1). BJH analysis evidenced a broad pore size distribution in the range of 6-12 nm (Fig. 1). The porous nature of

the material was confirmed by SEM showing pore openings ranging from 7 to 12 nm in diameter (Fig. 2). In agreement with the absence of small angle x-ray diffraction lines, TEM images confirm an irregular spatial arrangement of the pores. The surface areas of the novel materials amount 100 m^2g^{-1}, which is two orders of magnitude higher than that of the crystalline $MoVTeNbO_x$ reference (1 m^2g^{-1}). EDX assessed a similar chemical composition of amorphous and crystalline products with slightly increased vanadium content in the mesoporous material. The marked similarities in electronic structure, as shown in Figures 3-4 for, e.g., Mo and V, permits the new mesoporous material to serve as an model system to study the function of crystallinity on the reactivity of Mo-V-Te-Nb mixed oxides.

Significance

The synthesis of a stable mesoporous Mo-V-Te-Nb mixed oxide is reported for the first time. Tuning of the novel materials may result in entirely new catalytic properties.
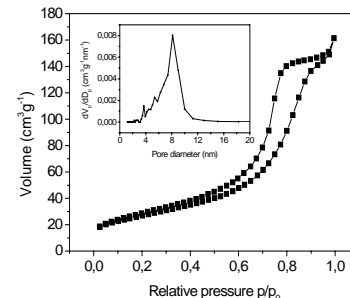

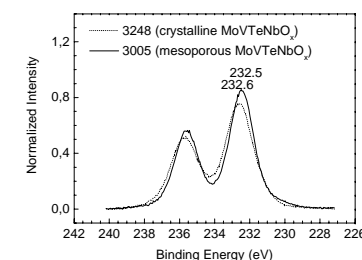**Figure 1.** N_2 adsorption on template-free $MoVTeNbO_x$ activated at 873 K.
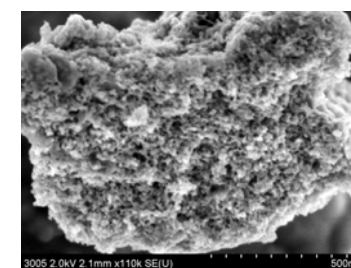

Figure 2. SEM image of mesoporous $MoVTeNbO_x$ activated at 873 K.
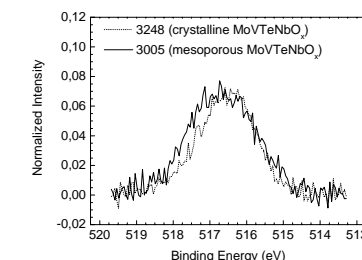

Figure 3. Mo 3d XPS spectra.

Figure 4. V $2p_{3/2}$ XPS spectra.

References

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