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Investigation of the Crystallographic (001) Plane of the M1-Phase in the Selective Oxidation of Propane to Acrylic Acid

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1. Introduction

Direct synthesis of acrylic acid from propane is an alternative, challenging approach in view of displacing the current industrial two-stage oxidation process starting from propylene, reducing thus the price of the feedstock and the complexity of the process. Among the catalysts proposed to date for the selective oxidation of propane, mixed metal oxides of Mo, V, Te, and Nb, containing mainly two phases, designated as M1 and M2 phase [1], have shown the most promising catalytic properties [2]. Propane activation and high selectivities towards acrylic acid are generally attributed to the presence of the orthorhombic M1 phase [3, 4]. It has been suggested that the (001) planes of the M1 phase (cross-section of the needle-like M1 crystals) contain the active and selective surface sites for this reaction [5, 6]. Thus, increased activity after grinding of M1 needles has been attributed to the generation of additional (001) surface area [5, 7]. Even though an increased specific surface area is observed [7], the downside of the grinding process is the well known impact of mechanical treatment on the nature and concentration of defects on the overall surface of transition metal oxides [8]. In the present study the role of the (001) plane of the M1 phase in the propane oxidation is addressed by providing a M1 model catalyst that exposes preferentially this plane.

2. Results and discussion

A batch of crystalline, phase-pure M1 prepared by hydrothermal synthesis was divided into two parts. One part was fully coated with silica. The complete coverage of the mixed metal oxide surface by SiO₂ was verified by HS-LEIS. Both, the coated material and the non-coated reference M1, were pressed into pellets, crushed and sieved in order to prepare sieve fractions, which were then loaded into a micro-reactor and studied in the partial oxidation of propane to acrylic acid. The preparation of the sieve fraction represents a gentle mechanical treatment that generates new M1 surface, which has been quantified by LEIS for the silica-coated catalyst. The surface fractions of the elements can be quantified using the reference spectra. It is found that the sum of the surface fractions of V₂O₅, Nb₂O₅, MoO₃ and TeO₃ in the treated silylated sample amounts to 30% of that in treated non-silylated sample. The 30% thus represents the new surface generated by the mechanical treatment.

Special attention has been paid to a comprehensive microstructural characterization of the model catalysts before and after the propane oxidation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that complete coverage of M1 followed by breakage of the SiO₂-covered needles generates a model catalyst that predominantly exposes (001) planes. In case of the treated non-silylated materials, 20% of the total surface area belongs to the (001) plane whereas in case of the treated silylated material is the 50%. The rates per exposed MoVTenNbO_x

surface area observed are quite similar for both catalysts, meaning that the intrinsic catalytic properties of the entire M1 surface are similar to the catalytic behaviour of a surface composed of 50% (001) planes. This finding casts some doubts on the uniqueness of the basal plane of M1.

3. Conclusions

The model studies presented here suggest that a distinguished lattice plane of the M1 crystal structure, the (001) plane, is not solely responsible for its outstanding catalytic activity and selectivity in the partial oxidation of propane to acrylic acid. Similar intrinsic reactivity irrespective of the terminating lattice plane implies that related active ensembles of metal-oxo clusters are exposed to the reactants on the entire surface of the M1 needles. The lateral surface of the needles accounts for the main part of the surface area of M1 (80%). The stepped morphology of the latter surface may generate similar metal-oxo arrangements as on the surface of the basal plane of the needles.

References

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