

# Molybdenum, Phosphorous and Antimony Doping Effect on Titania-supported Vanadium Catalysts in Propane Ammoxidation Reaction

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## Introduction

An influence of molybdenum, antimony and phosphorous doping on titania-supported vanadia catalysts was investigated for propane ammoxidation to acrylonitrile (ACN). Vanadium (V) is responsible for activation of alkanes, i.e. for dehydrogenation of propane [1], while propylene is an intermediate in acrylonitrile production [2]. Antimonates with rutile structure were commonly investigated for ACN production. The nature of the active site in ACN formation is probably related to the redox cycle between dispersed V (V) and lattice reduced V sites species [3], which is consistent with the very high structural flexibility of the rutile type phase [4]. Use of a support enhances the population of surface V (V) species, which leads to increase of ammoxidation activity; such scenario was observed in supported SbVO<sub>4</sub> [3]. Doping elements may result in the formation of phases which facilitate the vanadium redox cycles by interaction between vanadium reduced ion in the corresponding phases and the dispersed fully oxidized vanadium species [3]

Molybdenum, antimony and phosphorous were used as dopants for titania-supported vanadium catalyst. The objective was to observe differences caused by the presence of the dopants and to determine the strength of its influence.

## Experimental

Molybdenum, antimony and phosphorous doped titania-supported vanadia catalysts were synthesized by "spray impregnation" method with a total coverage of vanadium of 8 atoms/nm<sup>2</sup> of titania support and addition of molybdenum, Mo-V/TiO<sub>2</sub>; molybdenum and antimony, MoSb-V/TiO<sub>2</sub>; or molybdenum, antimony and phosphorus, MoSbP-V/TiO<sub>2</sub> (0.4 at/nm<sup>2</sup> of each). The catalysts were calcined at 450 °C/6 h, characterized by Raman spectroscopy, XRD, BET, XRF and TPR and tested in propane ammoxidation reaction.

## Results/Discussion

TiO<sub>2</sub> anatase Raman bands dominate below 900 cm<sup>-1</sup>. The spectra of fresh catalysts exhibit vibrations at 996 and 280 cm<sup>-1</sup> characteristic of crystalline V<sub>2</sub>O<sub>5</sub>, which are no longer observed after use in catalysis.

At 5% propane conversion the selectivity to ACN is similar for all investigated catalysts and reach ca. 0,6%. At higher conversions (10 and 15%) PSbMo-V/TiO<sub>2</sub> is the most selective to ACN with the difference of more than 10% in comparison to Mo-V/TiO<sub>2</sub> and SbMo-V/TiO<sub>2</sub> at 15% of propane conversion. Doping has an influence for the activity and selectivity of the catalysts, Mo-V/TiO<sub>2</sub> is the most selective catalyst to propylene (Mo might promote dehydrogenation of propane), the highest selectivity to acetonitrile was reached for SbMo-V/TiO<sub>2</sub>, while the PSbMo-V/TiO<sub>2</sub> in comparison to Mo-V/TiO<sub>2</sub> and SbMo-V/TiO<sub>2</sub> shows the highest selectivity to acrylic acid at low propane conversion (5%) and to ACN at higher propane conversion (of 10 and 15%).

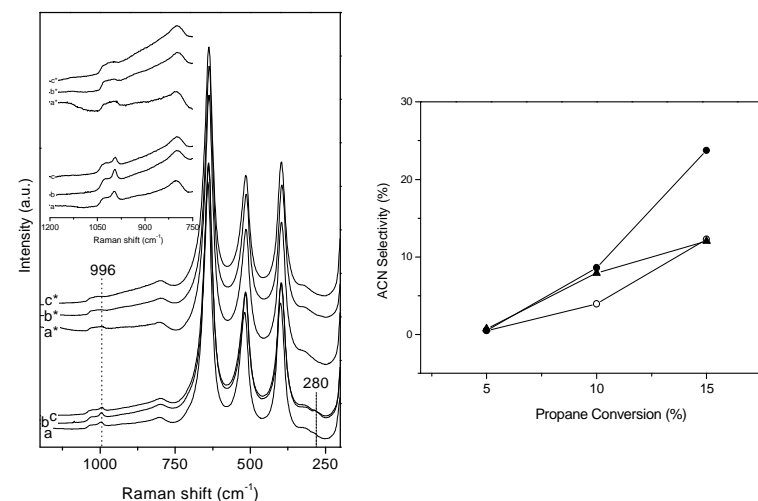


Figure 1. Raman spectra of fresh (a: Mo-V/TiO<sub>2</sub>; b: SbMo-V/TiO<sub>2</sub>; c: PSbMo-V/TiO<sub>2</sub>) and used catalysts (a\*: Mo-V/TiO<sub>2</sub>; b\*: SbMo-V/TiO<sub>2</sub>; c\*: PSbMo-V/TiO<sub>2</sub>) and selectivity to ACN at 5, 10 and 15% of propane conversion (○-Mo-V/TiO<sub>2</sub>; ▲-SbMo-V/TiO<sub>2</sub>; ●-PSbMo-V/TiO<sub>2</sub>).

## References

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