

## Impact of feed composition on the reactivity of M1 catalyst

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### Introduction

The employment of catalytic membrane- and multistage reactors are reported to be more efficient compared to conventional fixed bed reactors in oxidation catalysis [1,2]. This study addresses the effect of staged addition of oxidizing and reducing gases on propane oxidation to acrylic acid over phase pure M1 MoVTenbO<sub>x</sub> catalyst.

### Experimental

The MoVTenbO<sub>x</sub> catalyst has been prepared by spray drying, which lead to an M1+M2 phase mixture [3]. After calcination, the M2 phase was removed by treatment with H<sub>2</sub>O<sub>2</sub>. Heat treatment at 873K lead to M1 phase with elemental composition of Mo<sub>1,00</sub>V<sub>0,26</sub>Te<sub>0,09</sub>Nb<sub>0,17</sub>O<sub>4,00</sub> as determined by ICP-OES analysis. The catalytic reaction has been performed in a reactor system consisting of two serially connected reactor tubes. A valve system permitted gas sampling from the first reactor only (single-tube reactor mode, designated as STR) and from the outlet of the second reactor (two-stage reactor mode, designated as TSR). The addition of different gases (O<sub>2</sub>, N<sub>2</sub>O, C<sub>3</sub>H<sub>6</sub>, CO and CO<sub>2</sub>) was performed via a T-junction installed between the reactors. In the TSR operation mode the feed composition at the inlet of the first reactor was C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub>=3/6/40/51vol%. The concentration of the added gases was varied, while the temperature of both reactors was set to 400°C. GC-MS has been used for on-line analysis of the gas leaving the second reactor tube. *In situ* XRD measurements, where the oxygen content was varied, have also been carried out.

### Results/Discussion

The maximum selectivity to acrylic acid in the STR operation mode corresponds to a space velocity of 4500 h<sup>-1</sup> and a feed composition of C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub>=3/6/40/51vol%. The various O<sub>2</sub> contents employed in the STR experiments at this space velocity covered reducing (4 vol%), stoichiometric (6 vol%) and oxidizing (8, 10 and 12 and 15 vol%) conditions, respectively. As Figure 1 demonstrates, propane conversion (X<sub>C<sub>3</sub>H<sub>8</sub></sub>) and acrylic acid selectivity (S<sub>AA</sub>) is independent on whether the initial O<sub>2</sub> concentration is introduced in stoichiometric ratio or in five-fold excess. Under reducing conditions, both X<sub>C<sub>3</sub>H<sub>8</sub></sub> and S<sub>AA</sub> are inferior to those determined under stoichiometric and oxidizing conditions. *In situ* XRD measurement under various O<sub>2</sub> concentrations revealed no phase change and no significant change in lattice

parameters. Varying the O<sub>2</sub> content in the TSR operation mode revealed that at 12 vol% overall O<sub>2</sub> concentration, the X<sub>C<sub>3</sub>H<sub>8</sub></sub> was increased by 1,1%, the S<sub>AA</sub> increased by 4,7% (absolute increase). Therefore the yield increased with 5,3% compared to the measurement with 6 vol% overall O<sub>2</sub> content.

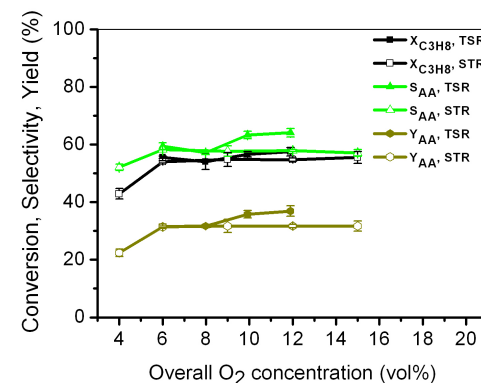


Figure 1. The effect of oxygen concentration in STR and TSR operation mode.

Addition of N<sub>2</sub>O instead of O<sub>2</sub> in the TSR did not influence the catalytic properties. Moreover, the concentration of N<sub>2</sub>O in the effluent gas was found to be identical to that in the inlet stream, regardless of concentration. This led to the conclusion that N<sub>2</sub>O is an inert gas in propane oxidation over the phase pure M1 catalyst, although it has been reported a more efficient oxidant than O<sub>2</sub> in C<sub>3</sub>H<sub>8</sub> oxidative dehydrogenation reaction [4]. The inability of the catalyst to split N<sub>2</sub>O suggests a low abundance of electrophilic species under working conditions.

The entire added amount of propylene was converted to acrylic acid, acetic acid, CO and CO<sub>2</sub>.

CO<sub>2</sub> and CO addition had no effect on the product distribution. A separate experiment on CO oxidation in STR mode showed very poor activity (X<sub>CO</sub><1,5% at 400°C, GHSV=3000 h<sup>-1</sup>), suggesting low abundance of electrophilic oxygen species on the catalyst surface [5].

### References.

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