Rational high throughput experimentation: Novel catalysts for the production of acrylic acid

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Introduction

Evaluation of the performance of catalysts under industrial process conditions can be performed in a rapid way by applying rational high throughput experimentation. The use of experimental design and modeling tools creates enhanced insight into catalyst performance as a function of catalyst synthesis and process conditions. Rational high throughput experimentation allows finding new active and selective catalysts for commercially existing chemical processes or new alternative routes such as the production of acrylic acid from propane.

Acrylic acid is commonly produced via the catalytic reaction of propylene with oxygen at a high temperature in the vapor phase. However, in view of the considerable price difference between propane and propylene, there is a growing interest in methods for the production of acrylic acid in one step from propane, by a vapor phase catalytic oxidation. The main hurdle to this route is defining highly active and selective catalyst.

Oxide catalysts comprising molybdenum (Mo), vanadium (V), tellurium (Te) and niobium (Nb) are commonly applied for the catalytic oxidation of propane in the gaseous phase [1-2]. Such oxides are prepared by mixing a niobium-containing aqueous solution with aqueous mixtures containing Mo, V, Te to form a compound mixture, which is then dried and calcined. However, the exact selection of the catalyst starting material and preparation procedure appear decisive for obtaining highly selective catalysts [3].

The present work relates to exploring new methods for the preparation of a Mo-V-Te-Nb catalyst using rational design and high throughput experimentation. The study comprises a wide variety of catalyst preparation parameters, catalyst compositions, and process conditions.

Materials and Methods

A large number of synthesis and composition parameters for the preparation of a Mo-V-Te-Nb oxide catalyst were evaluated to identify main synthesis and composition parameters. The method chosen for the preparation of Mo-V-Te-Nb catalyst comprises the following steps: preparing a slurry consisting of ionic species of Mo, V, Te and Nb and an inert carrier, drying of the slurry to obtain a dried particulate product, precalcining the dried particulate product at a temperature of 150-350 °C in an oxygen-containing atmosphere and calcining the precalcined dried particulate product at a temperature of 350-750 °C in an inert atmosphere.

The catalytic tests were performed in Avantium's parallel fixed bed Nanoflow reactor system, at a temperature range of 340 - 410 °C and at atmospheric pressure. Both unsupported and supported catalysts were exposed to the reaction mixture typically consisting of 3.3% C_3H_8, 10% O_2, 40% N_2 and 46.7% H_2O. GHSV was varied from 400 to 2400 h^{-1}.

Results and Discussion

The preparation of the acrylic acid is typically performed in a conventional fluidized bed or moving-bed reactor. The catalysts that were developed in this work performed particularly well in a fixed bed reactor. The catalytic tests were also successfully run under realistic conditions.

Our work indicated that using the carrier in the form of a dry powder resulted in a catalyst with improved activity in comparison to the catalyst obtained using a sol. When the catalyst was supported on Aerosil 300 and dried in rota-evaporation mode, the selectivity to acrylic acid increased from 45% to 77% (Table 1). Furthermore, the results indicated that with respect to the catalytic activity, it is preferred to combine the ceramic inert carrier with one solution comprising all the Mo, V, Te and Nb ionic species instead of sequential addition of solutions of one ionic specie.

Table 1. Catalyst test results ($Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$) obtained during the oxidation of propane to acrylic acid at 410 °C

Catalyst	Drying method	Support	Content metals [%]	Propane conversion [%]	Acrylic acid selectivity [%]
No.1	Spray-drying	None	67.8	30	64
No.2	Rota-evaporation	None	67.8	55	45
No.3	Spray-drying	Aerosil 300	33.9	40	75
No.4	Rota-evaporation	Aerosil 300	33.9	38	77

The drying and calcination conditions were found to be of a crucial importance for achieving a high selectivity of acrylic acid. The effect of drying method, i.e. spray-drying and rota-evaporation, on the catalytic performance is shown Table 1.

Furthermore, the catalytic tests of 96 catalysts with the same composition but which were prepared by using variable recipe parameters were performed for the conversion of propane to acrylic acid at several process conditions. From the results, which varied from very low to very high acrylic acid selectivities, it is clear that the selectivity of the catalyst is not only determined by the right composition of the catalyst but also by choosing the right conditions for its preparation.

A new class of catalysts for the selective oxidation of propane to acrylic acid was identified after screening approximately 1000 catalysts. Higher propane conversions and higher selectivities to acrylic acid were obtained compared to a reference catalyst. Optimized catalyst synthesis was successfully scaled up resulting in a catalyst with an identical performance.

Significance

Rational high throughput experimentation is an excellent way for rapidly finding and developing new active and selective catalysts together with the identification of the right process conditions for the best catalytic performance.

References

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