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Combinatorial design and preparation of transition metal doped MoVTe catalysts for oxidation of propane to acrylic acid

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ABSTRACT

In this study Mo–V–Te–Nb based multi-component catalysts were designed and tested using combinatorial and high-throughput methods. Based on the composition of the M1 matrix phase new compositions were designed containing additional promoters Mn, Ni, W and In. The following promoters were tested too in preliminary experiments and disregarded because of the detrimental effect on acrylic acid yields: Cu, Sb, Fe, Sm, Sn, Bi, Co, and Cr. In addition, citric acid in different ratios was used in the synthesis as a structure-directing agent. An optimization variable has been defined as the molar ratio of a given component to Mo in the synthesis mixture. Consequently, the experimental space had eight variables. The discrete levels of variables are established in such a way that the size of the multi-dimensional experimental space was in the range of 200 000 theoretical experiments. Five generations were designed using an optimization platform consisting of artificial neural networks and holographic optimization algorithm. Altogether 215 catalysts were prepared and tested. The elite list in each generation was created according to the yield of acrylic acid (AA). The yield of AA over the best catalyst after five generations was 59%. On the basis of holographic maps correlations between the composition of the synthesis mixture and yield of AA were visualized. Two catalysts families amongst the good performing catalysts have been distinguished that differ from each other in their low and high V content as referenced to molybdenum.

1. Introduction

The classical acrylic acid, also known as propenoic acid, technology by oxidizing propene in a two-stage process was developed by companies like BASF, Mitsubishi Chemical Company, BP, Celanese, Nippon Shokubai, Rohm & Haas, and more recently Shanghai Huayi Group and LG Chem. This classical two stage process has been brought to an unprecedented performance level for oxidation reactions with selectivities of about 90% during the past six decades of constant research and improvement [1,2]. Acrylic acid (AA) and its esters belong to the most important monomers for a variety of polymers which are used in surface coatings, sealants, adhesives, polymer additives, textiles, inks as well as in paper treatment and electronic manufacturing processes. An important fraction of the acrylic acid produced is upgraded into glacial acrylic acid which then is polymerized into polyacrylic acid, the so-called super absorber that has a strongly growing market. The global acrylic acid demand in 2009 was about 4 million tons and it is expected that it will rise to about 5 million tons per year by 2014.

Today all acrylic acid plants operate exploiting this two stage process for which the two oxidation steps, from propene to acrolein, and from acrolein to acrylic acid, have been and can independently be further optimized. The catalysts used for this process are based on Mo multimetal oxides with several promoters for optimum selectivity. About 3550 patents and about 1800 scientific publications focus on the acrylic acid process and related catalysts thus reflecting its high commercial importance [3].

More recently several new routes to acrylic acid have been developed, like Cargill's sugar fermentation to hydroxyl propionic acid [4], and its dehydration to acrylic acid. Arkema too has developed a new route to acrylic acid starting from glycerol [5].

Another alternative pathway to acrylic acid starts from propane which is oxidized in a one-step reaction to acrylic acid. The development of this alternative process is driven by the expected price increase and shortage of propene in the future [6]. Propene is mainly used for the production of polypropylene which accounts for nearly two thirds of the global consumption, and it is fed too into the bigger market of acrylonitrile production. Furthermore, it is assumed that propane will be increasingly available in the future

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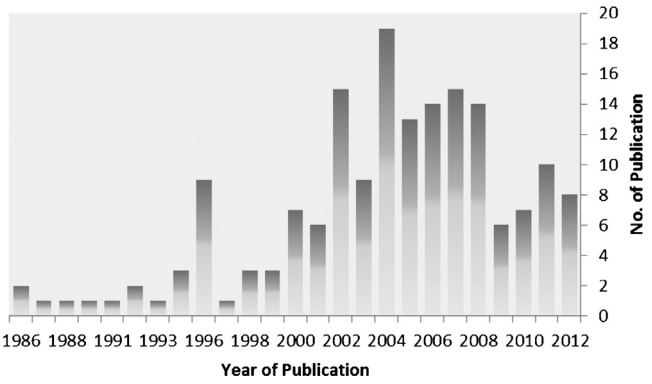

Fig. 1. Number of publications per year on the propane based acrylic acid process.

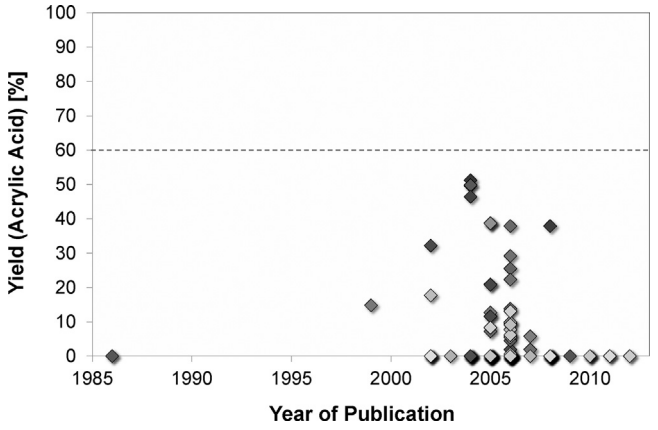

Fig. 2. Reported acrylic acid yield vs. year of publication.

from shale gas exploitation, and it is expected that direct propane to acrylic acid plants will be first build close to such shale gas fields.

This propane based process too has seen quite some scientific interest in the recent past, as reflected in about 80 patents and 90 publications (Fig. 1). The reported AA yields are plotted according to the publication year in Fig. 2. The black dashed horizontal line indicates the commercialization criterion, i.e. the minimum AA yield which at least has to be reached by a novel propane-based process in order to be competitive with the current two-stage process. A Mo-based multimetal oxide containing vanadium, niobium and tellurium as well as silicon is generally accepted to be the most active and selective catalyst if crystallized in the so-called M1 structure [7].

Arkema has developed a fluidized bed process based on M1 type catalyst which operates in the temperature regime between 350 and 440 °C and with residence times from 0.1 to 30 s [8].

BASF has recently followed another route from propane to acrylic acid, on which propane is dehydrogenated, at least partially in a first step to propene, and on which the resulting mixture of propene and propane is fed to the classical 2-stage reactor setup [9].

According to patent literature and open scientific work on the propane route, maximum acrylic acid yields currently do not exceed 50–52%. Accordingly, there is a continuous interest to further develop improved catalyst systems which potentially might allow the realization of less temperature-demanding process conditions. We have focused our research on the optimization of the well described MoVNbTe M1 type oxide catalyst by addition of a series of promoters. Previously, a few studies have already focused on the promotion of the M1 phase with the aim to improve the AA yields [10–12]. For example, Hibst et al. [11] reported no increase in activity when substituting Mo and V for Ta, Nb, Bi or W, whereas Shiju and Guliants [12] observed no increase in activity when exchanging Nb for Fe. Deniau et al. [10] reported on the exchange with Ti, Sn, Ge and W and found that W did not affect catalyst activity while Ti and Sn decreased it. A positive effect was observed for Ge addition but Ge was not incorporated into the M1 structure. In this approach we used an advantageous, combinatorial and high-throughput research concept. The so-called holographic research strategy (HRS) and its combination with artificial neural networks (ANNs) were applied in catalyst library design [13–15].

2. Methods

2.1. Holographic mapping (HM) and holographic research strategy (HRS)

Holographic mapping is described in detail in our previous studies [13,16]. It is used for two-dimensional visualization of multidimensional experimental spaces. Variables are arranged along the orthogonal *X*- and *Y*-axes (see e.g. Fig. 6 later). Lines of different lengths substitute the discrete levels of the different variables. A given line represents one level of a variable and the length of a line is proportional to the number of data points displayed along the line. The visualization is based on a wavelike arrangement of levels of independent variables along the *X*- and *Y*-axes. The level of each component increases gradually until it reaches its maximum then it decreases gradually again generating the wave-like appearance. Accordingly, when moving along any axis from one experimental point to the next one only one level of a single variable is changed. This arrangement results in a 2D matrix where the adjacent points are neighbors in the original multidimensional space as well.

In the present study a variable is considered to be molar ratio of a component of the synthesis mixture and Mo. Accordingly, there are 8 variables to be visualized, an 8-dimensional experimental space has to be transformed to a 2D matrix. It has to be emphasized that full permutations of 8 variables along the *X*- and *Y*-axes leads to a total number of possible images being equal to 8-factorial. The transformation resulting in other images is called variable position change, which is generally used in holographic maps [13–16] for better visualization of effects. Nevertheless, from the point of view of information content, the different 2D images are identical to each other.

It is usually advisable to arrange the variables in such a way that the ones having the most pronounced effect should change their levels with the lowest frequency, while all indifferent variables can be represented by high frequencies.

HRS optimization is strongly based on this two-dimensional representation of experimental points in HMs. The details of the HRS optimization are described elsewhere [14,17]. In HRS optimization, the initial experimental points (first catalyst generation) have been created with maximum diversity in the given experimental space. The forthcoming generations have been created by rectangular-shaped experimental regions 5×5, 4×4 and 2×2 in size around the best three hits of the preceding generations.

2.2. Data analysis by means of partial least square (PLS) regression

PLS has been used for the classification of catalytic data and analysis of relationships between the variables of the multidimensional experimental space.

Detailed description and tutorial on PLS can be found elsewhere [18]. Multidimensional and multivariate data sets, i.e. consisting of multiple independent (**X** block) and dependent (**Y** block) variables can be processed by means of PLS. In order to find correlations between **X** and **Y** blocks the axes of the original multidimensional