Steam Influence and Effect of Oxidant Amount on Propane Oxidation over Multi Metal Oxide Catalyst Using High-Throughput Experiment

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ABSTRACT

The high-throughput experimentation technique was used to verify the testing conditions due to the effects of catalyst structure modifications and/or due to reaction parameter variation in parallel. In this paper, the design of experiment and catalytic results are discussed in the development of selective oxidation catalyst, to demonstrate the importance and versatility of such technology. It is used for the automated parallel testing of selective oxidation of propane to acrylic acid over some types of multi metal oxide catalysts. The catalysts used for performance test were Mo (molybdenum), cat-1 (unsupported $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$), and cat-2 (supported $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$). All catalysts were dried using spray drier. The effect of some reaction parameters, such as the amount of oxidant, presence of steam and reaction temperature was also investigated during the test. The configuration of the 'nanoflow' is shown to be suitable to screen catalytic performance. The results obtained gave very good reproducibility.

ABSTRAK

High throughput merupakan metode penentuan hasil percobaan yang dilakukan secara paralel dan dalam waktu cepat. Metode ini seringkali digunakan untuk menguji hasil reaksi katalitik yang disebabkan oleh modifikasi struktur katalis dan/atau disebabkan oleh variasi parameter kondisi reaksi. Dalam artikel ini, dipaparkan desain percobaan dan hasil reaksi katalitik untuk reaksi katalitik oksidasi selektif untuk menunjukkan pentingnya pemanfaatan metode percobaan ini. Metode ini digunakan untuk reaksi secara parallel dan otomatis pada oksidasi propana menjadi asam akrilat menggunakan katalis Mo (molybdenum), cat-1 (unsupported $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$), and cat-2 (supported $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$. Semua katalis dikeringkan mengunakan pengering semburan. Pengaruh parameter reaksi seperti jumlah oksidan, keberadaan uap air dan temperatur reaksi juga dipelajari selama uji reaksi. Kondisi reaksi dan peralatan uji yang disebut 'nanoflow' menunjukkan kemampuan yang baik dalam proses uji reaksi. Hasil reaksi juga memberikan keterulangan hasil yang sangat baik.

INTRODUCTION

Combinatorial Technology is a new interdisciplinary field joining computer-assisted with automated parallel synthesis of chemical libraries followed by automated screening. The main purpose of computer assisted combinatorial chemistry is to generate thousands structurally diverse compounds as libraries, maximizing their diversity, which are then considered in an experimental parallel automated synthesis and screening on the basis of their properties [1].

The application of high-throughput experimentation including combinatorial methods for the discovery of new heterogeneous catalysts is a fast developing area. The combinatorial approach requires at least three basic technologies. The first one is the parallel synthesis of many hopeful candidates. The second one is their evaluation in a short time. The third one is the optimization of hopeful candidate and planning an improved library. Although the problems depend on each catalytic system for the application of the combinatorial method, the development of a rapid screening would be the key technology in many catalytic systems [2]. The high-throughput experimentation should be able to substitute totally or at least partially the time-consuming and man power-consuming conventional experimentation. In this paper, the design, Design of Experiment (DOE) and catalytic

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results are discussed to demonstrate the importance and versatility of such technology.

One of the catalytic process which studied by researchers is selective oxidation of propane to acrylic acid over multi metal oxide catalyst. This process has been developed for the recent past. The investigation more focused on the study the alternative pathway to acrylic acid from propane, since 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. The development of this alternative process is driven by the expected price increase and shortage of propene in the future [3]. The multi metal oxide catalyst that used for this process including MoVTeNb catalyst [4-9] and MoVW catalyst [10-13]. This paper deals with performance test of Mo (molybdenum), supported and unsupported $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$ catalyst using high-throughput experimentation. This article also focus on the effect of some reaction parameters, such as the amount of oxidant, presence of steam and reaction temperature on the catalyst activity for propane conversion and its selectivity to acrylic acid.

EXPERIMENTAL SECTION

Materials

The chemicals that used were Ammonium heptamolybdate tetrahydrate (Merck), Ammonium metavanadate (Riedel-de Haën), Telluric acid (Aldrich), Niobium ammonium oxalate (Aldrich), Steam (demineralized water), Nitrogen (99.9%, MOX-Malaysian Oxygen Bhd), Propane (98.9%, MOX-Malaysian Oxygen Bhd), and Oxygen (99.9%, MOX-Malaysian Oxygen Bhd).

Instrumentation

The set-up consists of two cubic ceramic modules with 12 channels. The glass tube with quartz in the middle of tube (i.d. = 4 mm, h = 220 mm) used as fixed-bed reactors, which are concentrically arranged with respect to the axis of the module. The catalyst bed is situated in the central module. All twelve channels are enclosed in a stainless steel cylinder sealed (the glass tube also sealed) with O-rings to avoid any gas leakage. For sampling the reactor channel effluent the outlets are connected individually to a set of multi-port valves (1x18 port valves, breakable, Valco Instruments). This allows fast switching between the different reactors channels for sequential analysis of the reaction products without interruption of the gas flow. The output piping and the multi-port valves are installed inside a heated box to

avoid condensation, polymerization or thermal decomposition of products.

The different feed gases and one liquid are supplied by mass-flow controllers (Brooks). The liquid (water) feed is evaporated in the vaporizer (180 °C). The mixing of steam and gases occurs after the vaporizer to ensure the mixture is homogenous mixture. All the vaporizer, feeding lines and the mixer are install inside the heated box to avoid condensation. Often in high-throughput screening of catalyst libraries only the activity for a specific reaction by means of the degree of conversion or the heat reaction released is determined [9]. For selectivity frequently only the main products of interest are quantified [14-15]. The compositions of all products were confirmed by two on-line gas chromatograph systems (HP6890N, Agilent Technologies).

Procedure

Synthesis of catalyst

The preparation of Diluted $Mo_1V_{0.30}Te_{0.23}Nb_{0.125}O_x$ and its characterization have been described in more detail before [4].

Reproducibility test and reaction study

The reaction study has been carried using which its process flow diagram has been illustrated before [6]. The reproducibility of testing catalytic materials in the 12-channel reactor set-up is illustrated for the selective oxidation of propane. The catalysts are Mo (molybdenum), cat-1 (unsupported $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$), and cat-2 (supported $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$). All catalysts were dried using spray drier. These preparations and the catalysts characterizations have been described in more detail before [4]. Each catalytic materials or support materials (0.24–0.45 mm particle size) was loaded into quartz tube reactor (i.d. = 4 mm, h = 220 mm) until volume of catalytic bed of 0.5 mL. The gas hourly space velocity (GHSV) was 1237 h^{-1}, and reaction temperature was 400 °C. The effluents from the reactor were analyzed by two on-line gas chromatographers.
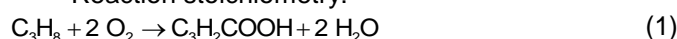
The catalyst screening and reaction study were carried out in a twelve-fixed bed quartz tubular reactor (i.d. = 4 mm; l = 225 mm, Nanoflow catalytic reactor at COMBICAT Malaysia), working at atmospheric pressure. Catalyst samples (0.24–0.45 mm particle size) were introduced into each reactor tube until volume catalyst bed of 0.5 mL. The feed flow rate of each reactor was 10 mL N/min in order to achieve gas hourly space velocity (GHSV) of 1200 h^{-1} (at STP). The standard feed composition is propane/oxygen/nitrogen/steam (1/2/18/9).

The compositions of all products were confirmed by two on-line gas chromatograph systems. Molecular sieve columns and Porapak columns with a thermal conductivity detector in first gas chromatographer were utilized for the analysis of inorganic gases and hydrocarbons (C_1-C_3). Capillary column (HP-FFAP) with a flame ionization detector in second gas chromatographer was utilized for the analysis of oxygenates hydrocarbons. Some results from catalytic tests have also been reported before [5-8].

RESULT AND DISCUSSION

The conversion was defined as the fraction of consumed hydrocarbon of the moles of hydrocarbon fed to the reaction. Selectivities are the fractions of consumed hydrocarbon converted for each product.

Reaction stoichiometry:

$$C_3H_8 + 2\,O_2 \rightarrow C_3H_2COOH + 2\,H_2O \qquad (1)$$

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO + 4\,H_2O \qquad (2)$$

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \qquad (3)$$

$$C_3H_8 + 0.5\,O_2 \rightarrow C_3H_6 + H_2O \qquad (4)$$

This testing has been done to observe the reproducibility of 'nanoflow' system during selective oxidation of propane to acrylic acid. One of the reactor tubes (channels) was left empty, and the same catalytic materials were charged to two or three of the reactor tubes, i.e., the inert material (Aerosil300) was loaded to two reactor tubes, cat-2 was loaded to two reactor tubes, cat-1 was loaded to two reactor tubes, and catalyst Mo was loaded to two reactor tubes. To ensure that the data acquisition from gas chromatography was stable, the analysis was repeated up to three times. The results are shown in Table 1. The material balance (based on carbon balance) for all the reaction analysis always about 90% and above, which indicates that no material loss during the reaction.

Table 1 shows that the propane conversions for all reactor tubes have a very similar value. For example, catalyst cat-1, the first, the second and the third analysis give almost the same values of propane conversion. In addition, this value (propane conversion) is reproduced

from different reactor tubes, which is contains the same catalytic material (cat-1). The same trend is also shown by cat-2 from three different reactor tubes. The results show that the propane conversion are about 32%. Even from catalyst Mo shows that all the analysis data from two different reactor tubes have exactly the same value of propane conversion.

Table 1 also shows the selectivity to acrylic acid during reproducibility testing of catalytic materials for selective oxidation of propane. The result demonstrate the selectivity trend to acrylic acid for some catalytic materials in different reactor tubes. It describes that catalyst cat-2 is the most selective catalyst to acrylic acid compare to the others; on the other hand catalyst Mo is the less selective catalyst to acrylic acid. In addition, all the reactor tubes have the similar values of selectivity to acrylic acid for first and second analysis. The same catalytic materials in different reactor tube also have the similar value of selectivity to acrylic acid. For example, catalyst cat-1 and cat-2 in two different reactor tubes have very similar values of selectivity to acrylic acid of about 18% and 65%. This data very clearly describes that the 'nanoflow' system in combinatorial technology created very good reproducibility of product, especially the main product, acrylic acid.

In the previous report [4], we described that supported catalyst has M1 phase in higher proportion compare to that of unsupported catalyst. The M1 and M2 refer to single-crystalline phase of the MoVTeNb oxide catalyst. The catalytic behavior of MoVTeNb catalysts in the oxidation of propane to acrylic acid could also be explained by the presence of three moieties: (i) a V-Nb-O phase as paraffin activator; (ii) a Te-Mo-O phase to oxidize olefins to aldehyde; and (iii) a V-Mo-O phase to convert the aldehyde to corresponding acid. Lin [16] reported that Ushikubo and co-workers further suggested that phase M1 is effective for propane activation and that phase M2 is less active for propane conversion but very selective for the subsequent step of propylene ammoxidation. From the explanation above, it can be suggested that the active component, which plays a very important role

Table 1. Propane conversion and acrylic acid selectivity from reproducibility testing of some catalytic materials for selective oxidation of propane to acrylic acid

Catalyst	Propane Conversion (%) Analysis			Acrylic Acid Selectivity (%) Analysis		
	I	II	III	I	II	III
Mo	1.0	0.9	0.7	0.0	0.0	0.0
Mo	1.0	0.8	0.6	0.0	0.0	0.0
cat-1	39.2	38.5	40.5	18.0	18.2	19.0
cat-1	38.2	40.6	40.1	17.3	17.2	19.4
cat-2	31.3	32.1	34.4	66.3	65.0	64.8
cat-2	33.6	32.3	31.4	68.1	67.4	65.2

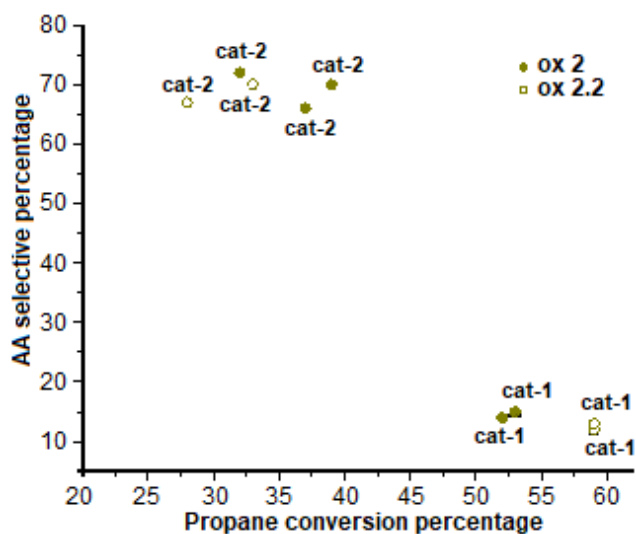**Fig 1.** The effect of oxidant amount towards selectivity to acrylic acid and propane conversion at reaction temperature of 400 °C
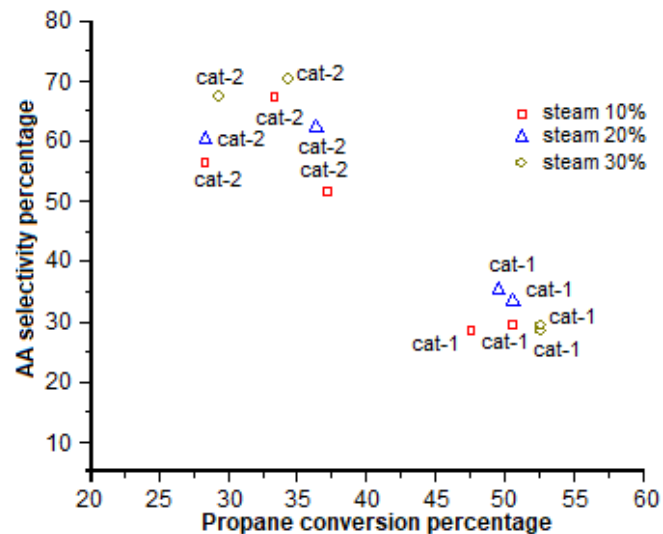

Fig 2. Steam influence towards selectivity to acrylic acid and propane conversion at reaction temperature of 400 °C

in the selective oxidation of propane to acrylic acid is the M1 phase. This is in accordance with the data in Table 1 which shows that cat-1 has selectivity to the higher product as compared to cat-2.

Fig. 1-2 illustrate the effect of oxidant amount, the effect of steam, and the effect of reaction temperature to selective oxidation of propane to acrylic acid over unsupported and supported MoVTeNb catalyst.

Fig. 1 shows that increasing of oxidant amount is followed by increasing of propane conversion and/or acrylic acid selectivity. Although the stoichiometric reaction (1) illustrate that 2 mole of oxygen is needed for 1 mole of propane to convert to acrylic acid, the result shows that more oxygen (2.2 moles for 1 mole of propane) in the reaction give a better result. This phenomenon can be explained by the assumption about how the catalyst works mentioned above, that the amount of oxygen molecule involved on the reaction is more than oxygen amount in the stoichiometric ratio. Oxygen molecule is needed during the formation of reactive intermediate and also during the formation of the desired product.

Fig. 2 depicts that generally the increasing of steam concentration and the amount of oxidant (Fig. 1) lead to increase of propane conversion and/or selectivity to acrylic acid. As a consequence, the increasing of steam concentration also forces to increase the yield of acrylic acid. Fig. 2 illustrates that most of catalysts have the same trend of propane conversion, i.e. the higher oxidant/feed ratio, the higher the propane conversion. While the selectivity to acrylic acid, the trends are slowly decreased with increasing of oxidant/feed ratio. Although not included in the pathways, water seems to play an important role in the reaction. When water was not fed to

the reaction, propylene and CO_2, CO (CO_x) were observed as the major product while an only trace amount of acrylic acid was obtained. Thus, water may enhance the further oxidation of propylene, and hence absent or present in very small quantities, most propylene produced is released to the product stream. Water may increase the concentration of hydroxyl groups on the catalyst surface and facilitate the reaction between the adsorbed acryloyl species and hydroxyl groups to form acrylic acid. Water may also enhance the desorption of acrylic acid or acetic acid from the surface of catalyst to prevent them being further oxidized to CO_x. The addition of steam favors the desorption of oxygenated hydrocarbons and enhance the selectivity towards acids. Steam also used to inhibit the formation of coke on the catalyst especially when the reactions carry out below temperature of 330 °C. Again, when water was absent or only present in very small quantities, the adsorbed acids could have stayed longer on the catalyst surface, thus increasing the chance of being further oxidized to CO_x [4-6].

Fig. 3 shows very clearly that reaction temperature is very important parameter for selective oxidation of propane to acrylic acid. Fig. 3 depicts that as increasing of reaction temperature, the conversion of propane also increases significantly. On the other hand, the selectivity to acrylic acid is decreasing a little bit while increasing of reaction temperature, especially at temperature of 410 °C. For example, Fig. 3 shows that the propane conversion for the selective oxidation of propane over catalyst cat-1 increases significantly from 38.2% at 380 °C to 50.8% at 410 °C. The cat-2 also gives similar trend, i.e. the conversion of propane
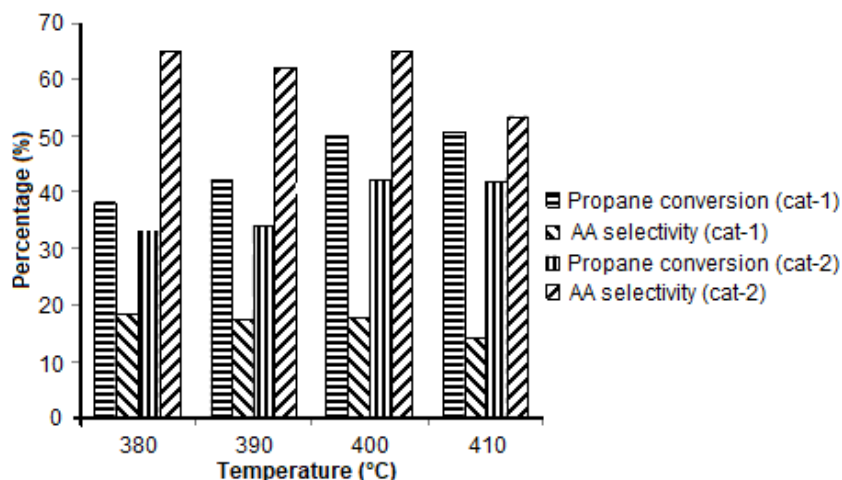
Fig 3. The effect of reaction temperature towards selectivity to acrylic acid and propane conversion

increases from 33.6% at 380 °C to 41.9% at 410 °C. However, that the acrylic acid selectivity for the selective oxidation of propane over catalyst cat-2 decreases from 65% at 380 °C to 53.4% at 410 °C. This is reflected in the trend of Fig. 3 showing a system that begins to profit from elevated reaction temperatures. The reason is the suppression of the low-temperature effective total oxidation and the beneficial effect of higher temperatures on the partial oxidation pathway.

CONCLUSION

From data observation, it is very clear that the application of combinatorial technology in experimentation is very powerful to substitute totally or at least partially the time-consuming and man power-consuming conventional experimentation without change the reproducibility. Even though, when we vary the reaction condition, it still gives the consistent result in term of the propane conversion and the acrylic acid selectivity. The reaction parameters such as ratio of reactant and reaction temperature play an important role in oxidation reaction of propane.

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