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Preface:
Welcome from Chairman of 2nd ISFACHE 2014

It is our great pleasure to have you at the 2nd International Seminar on Fundamental and Application of Chemical Engineering 2014 in Bali Island, Indonesia in conjunction with the 2nd joint symposium ITS-NTUST 2014. The international seminar on Chemical Engineering has become an important annual forum for academicians, researchers and professionals from both public and private organizations in the South East Asia and the Asia-Pacific regions. It is organized to serve as venue to exchange knowledge and information of relevance to the chemical engineering.

The conference covered all aspects in chemical engineering including biochemical engineering, catalysis and reaction engineering, clean energy systems and the environment, conventional and renewable energy, nanomaterials and nanotechnologies, polymer engineering and material processing, process system engineering, thermodynamics and transport phenomena. It was a good opportunity to discuss the recent progress in chemical engineering. We hoped the conference would provide the young scientists to gather together and form a network in the South East Asia and in the Asia-Pacific for the future collaboration.

Thank you very much for your participation and contribution for the conference.

Surabaya, 15 July 2015

Prof. Renanto Handogo
Organizing Committee Chair
Department of Chemical Engineering
Institut Teknologi Sepuluh Nopember

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Reproducibility Performance Test of Multi Metal Oxide Catalyst in Selective Oxidation of Propane using Combinatorial Technology

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Abstract

The concept of rapid catalyst screening using combinatorial technology was applied in the development of selective oxidation catalyst. In this paper, the design, Design of Experiment (DOE) and catalytic results are discussed to demonstrate the importance and versatility of such technology. The instrument is implaced in COMBICAT (Universiti Malaya) to rapidly support parallel testing of catalytic material using continuous fixed bed reactor technology programme. 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 configuration of the 'nanoflow' is shown to be suitable to screen catalytic performance, and its operating conditions were mimicked closely to conventional laboratory as well as to industrial conditions. The results obtained gave very good reproducibility.

Keywords: combinatorial technology, catalyst, reactor, catalytic activity, selective oxidation of propane

1. Introduction

The application of high-throughput experimentation including combinatorial methods for the discovery of new heterogeneous catalysts is a fast developing area, which has attracted worldwide attention. Different high-throughput techniques for the preparation and the assessment of the catalytic performance of a large number of materials have been developed; this process is still continuing for meeting the different needs in catalyst research [1].

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.

2. Experimental

Reproducibility test was carried out in a Nanoflow catalytic reactor with 12 fixed bed quartz tubular reactors (i.d., 4 mm; length 225 mm), working at atmospheric pressure. Catalyst samples (0.24 – 0.45 mm particle size) were introduced into each reactor tube. The catalysts are Mo (molybdenum), catalyst556 (unsupported $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$ dried using rota evaporator), catalyst 422 (unsupported

$Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O$ dried using spray drier). Undiluted $Mo_1V_{0.30}Te_{0.23}Nb_{0.125}O_x$ has been prepared according to the method described in the patent literature [3, 4-6]. In addition to standard Mo-V-Te-Nb-O_x catalysts, diluted samples have been prepared. These preparations and the catalysts characterizations have been described in more detail before [4].

The feed flow rate to each reactor was fixed at gas hourly space velocity (GHSV of 1200h^{-1} at STP) with standard catalytic bed volume of 0.5 ml. The standard feed composition was propane/oxygen/nitrogen/steam (1/2-2.2/18-17.8/9). The reaction was carried out at 653, 663, 673 and 683 K. the analytic of the COMBICAT Nanoflow reactor is equipped with a dual gas chromatographic system for a fast and complete qualitative and quantitative analyses of the effluent gas using a combination of two fast GC (HP6890N, Agilent Technologies) with column traps (on-line system).

The set-up consists of two cubic ceramic banks with 6 reactors to each bank. Quartz tubes (i.d. = 4 mm, h = 220 mm), which are used as fixed-bed reactors, are concentrically arranged with respect to the axis of the bank. The catalyst bed is situated in the central part of the bank within the isothermal zone of the heating system. The ends of all twelve-reactor channels are enclosed in a stainless steel cylinder sealed with chemical-resistant O-rings to avoid any gas leakage. The banks can be heated up to 873 K. The pipes and switching elements are all mounted in a thermobox to avoid condensation, polymerization or thermal decomposition of products. The output liner to gas chromatography is also wrapped with heating tape to avoid deterioration of gas products.

The different feed gases streams are controlled by mass-flow controllers (Brooks Instrument). The liquid (water) feed is evaporated with a vaporiser set at 453 K. The mixing of steam and gases occurs in a gas-mixing chamber after the vaporiser to ensure the mixture is homogenous. The vaporizer, feeding lines and the mixer are installed inside the heated box to avoid condensation.

Product analysis

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 [7]. For selectivity frequently only the main products of interest are quantified [8]. Common analysis techniques, such as gas chromatography (GC) or mass spectrometry (MS), which are often applied for product detection in the oxidative dehydrogenation or selective oxidation of light alkanes, show some drawbacks if applied in high-throughput experimentation. Gas chromatography allows a selective and sensible detection off all products; however, the time for separation of all compounds ranging from 10-15 minutes for one analysis is generally considered to be too long. Complete analysis by MS is often restricted due to superposition of fragment signals [9].

To minimize the effect of these problems, for the selective oxidation of light alkanes using COMBICAT nanoflow catalytic reactor, a fast and complete qualitative and quantitative analysis of the effluent gas of each reactor channel was accomplished by a combination of two fast GC (HP6890N, Agilent Technologies) with columns traps.Columns connected to front TCD for permanent gases (and CO, methane) analysis. Haysep Q 80/100 traps hydrocarbon components, and permanent gases come into mole sieve column. After all hydrocarbon components come into mole sieve column, carrier gas will carry all components inside mole sieve to TCD, and all components inside Haysep Q 80/100 to vent. Columns connected to back TCD for hydrocarbon (C_1-C_3) analysis. Only hydrocarbon (C_1-C_3) come into HP-Plot Q then to TCD, the rest will be trapped into Haysep Q 80/100 then to vent.

Using this method, COMBICAT nanoflow catalytic reactor can do a fast and complete qualitative and quantitative analysis of the effluent gas of each reactor channel. The analysis time can be reduced up to 7 minutes.

3. 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:

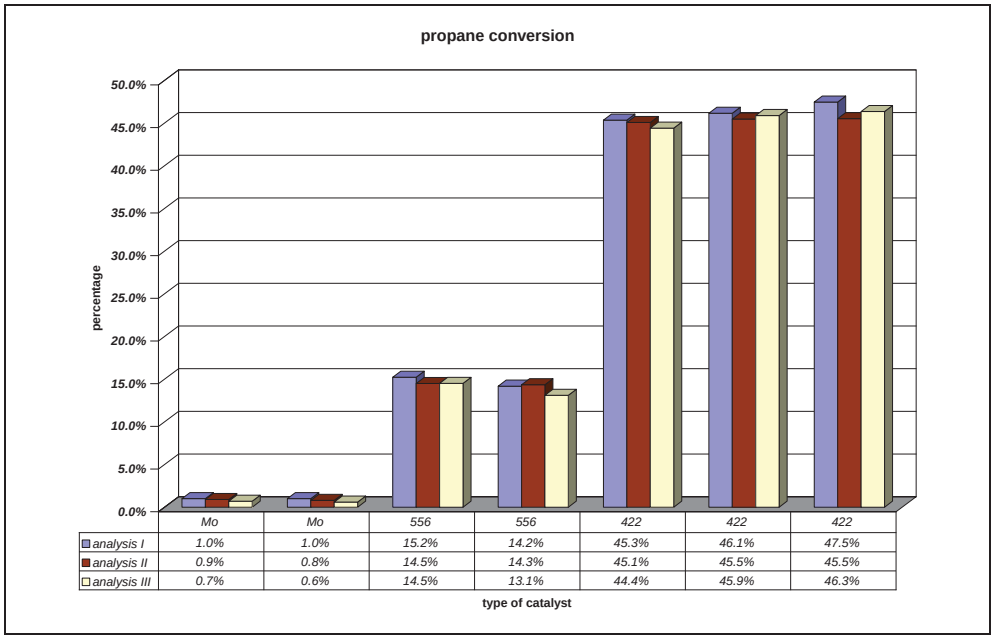
$$C_3H_8 + 2\ O_2 \rightarrow C_3H_2COOH + 2\ H_2O \quad (1)$$

$$C_3H_8 + 3.5\ O_2 \rightarrow 3\ CO + 4\ H_2O \quad (2)$$

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

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

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, catalyst 422 was loaded to three reactor tubes, catalyst 556 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 figure 1,2. 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

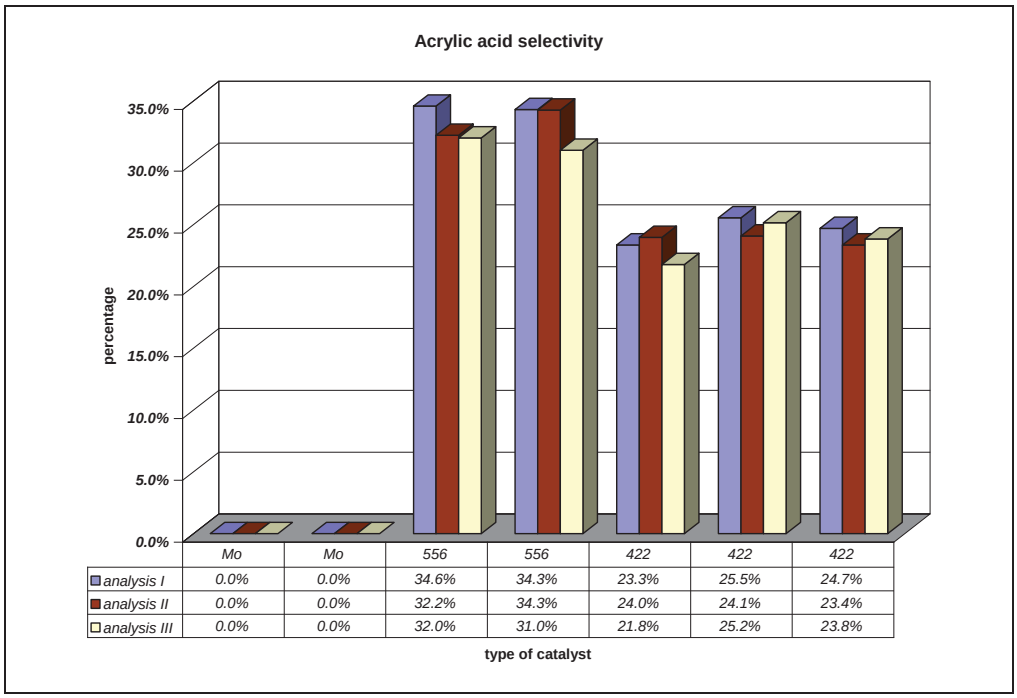


	Mo	Mo	556	556	422	422	422
analysis I	1.0%	1.0%	15.2%	14.2%	45.3%	46.1%	47.5%
analysis II	0.9%	0.8%	14.5%	14.3%	45.1%	45.5%	45.5%
analysis III	0.7%	0.6%	14.5%	13.1%	44.4%	45.9%	46.3%

Figure 1: Propane conversion from reproducibility testing of some catalytic materials for selective oxidation of propane to acrylic acid

Figure 1 shows that the propane conversions for all reactor tubes have a very similar value. For example, catalyst 556, 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 (catalyst556). The same trend is also shown by catalyst 422 from

three different reactor tubes (propane conversion are about 45%). Even from catalyst Mo shows that all the analysis data from two different reactor tubes have exactly the same value of propane conversion.



	Mo	Mo	556	556	422	422	422
analysis I	0.0%	0.0%	34.6%	34.3%	23.3%	25.5%	24.7%
analysis II	0.0%	0.0%	32.2%	34.3%	24.0%	24.1%	23.4%
analysis III	0.0%	0.0%	32.0%	31.0%	21.8%	25.2%	23.8%

Figure 2: Acrylic acid selectivity from reproducibility testing of some catalytic materials for selective oxidation of propane to acrylic acid.

Figure 2 shows the selectivity to acrylic acid during reproducibility testing of catalytic materials for selective oxidation of propane. This figure shows the selectivity trend to acrylic acid for some catalytic materials in different reactor tubes. This figure describes that catalyst 556 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, second and third analysis. The same catalytic materials in different reactor tube also have the similar value of selectivity to acrylic acid. For example, catalyst 422 in three different reactor tubes have very similar values of selectivity to acrylic acid of about 22-25%. This figure very clearly describes that the 'nanoflow' system give very good reproducibility of product, especially the main product, acrylic acid.

4. Conclusion

An interesting observation made during these experiments was that the results showed very good reproducibility in terms of both the propane conversion and acrylic acid selectivity when we repeat the experiments under the same condition. This means the high-throughput experimentation (using nanoflow catalytic reactor) is very powerful to substitute totally or at least partially the time-consuming and man power-consuming conventional experimentation without change the reproducibility.

Acknowledgment
This research has been carried out in the COMBICAT Laboratory, University of Malaya Kuala Lumpur, Malaysia.

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