

# CATALYTIC ACTIVITY TEST OF Mo-V-Te-Nb-OXIDE IN AMMOXIDATION OF PROPANE TO ACRYLONITRILE

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## ABSTRAK

**Widi, R. K.** 2014. Catalytic activity test of Mo-V-Te-Nb-Oxide in ammoxidation of propane to acrylonitrile

The ammoxidation of propane has been investigated at a multicomponent oxidic, MoVTeNb catalyst in the temperature of 673 K. The catalyst was prepared by sol-gel method, and dried by spray dried method. The activity test of the catalyst has been carried out using micro reactor and showed that it was active for ammoxidation of propane to acrylonitrile.

**Kata kunci : ammoxidation, propane, mixed metal oxide catalyst, acrylonitrile**

## ABSTRACT

**Widi, R. K.** 2014. Uji aktivitas katalisis Mo-V-Te-Nb-Oxide pada ammoksidasi propana menjadi akrilonitril

The ammoxidation of propane has been investigated at a multicomponent oxidic, MoVTeNb catalyst in the temperature of 673 K. The catalyst was prepared by sol-gel method, and dried by spray dried method. The activity test of the catalyst has been carried out using micro reactor and showed that it was active for ammoxidation of propane to acrylonitrile.

**Keywords : ammoxidation, propane, mixed metal oxide catalyst, acrylonitrile**

## INTRODUCTION

Selective catalytic oxidation and ammoxidation processes of hydrocarbons comprise approximately one quarter of the value produced by all catalytic processes world wide. They contribute hence significantly to the gross national product of industrial countries and afford future opportunities for developing countries. These processes are not only important from a commercial standpoint and their contribution to the well-being of modern mankind, but they also present the opportunity for significant fundamental research. Such research aims at the molecular level understanding of catalytic behaviour, forming a basis for rational design of catalyst improvement of existing processes and the discovery of totally new catalysts and processes (Betahar et al., 1996).

The selective oxidation of lower alkanes to various functionalized molecules has attracted much interest in recent years. Propane partial oxidation to acrylic acid over vanadium pyrophosphate (VPO) catalysts has been reported. Propane oxidation to acrylic acid with heteropolyacids or with their corresponding salts has also been reported. In propane ammoxidation to acrylonitrile, V-Sb oxide catalysts were studied by several researchers and Mo-V-Te-Nb-

oxide catalysts were studied by Ushikubo et al. (Manhua et al., 2000).

This paper limits itself to the activity test of diluted Mo-V-Te-Nb-oxide catalyst for propane ammoxidation processes.

## MATERIALS AND METHODS

### *Catalyst preparation*

#### **Preparation of solution 1 (Mo-V-Te)**

Eleven point two and seven grams of AHM was dissolved in 100 ml of water. This solution was heated up to 353 K. A clear solution was obtained from AHM. This solution was stirred at a speed of 700 rpm. After complete dissolution of the solid, 2.24 g of AMV was added, and 3.37 g of Telluric acid was added after the AMV had dissolved completely.

#### **Preparation of solution 2 (Nb)**

Three point five and four grams of Niobium ammonium oxalate was dissolved in 29 ml of water. This solution was stirred until all solids had dissolved without heating. Solution 1 was heated up to a

temperature of 353 K, and then cooled down to ~313 K. 14.36 g of Aerosil300 was added slowly to the solution. Then Solution 2 was mixed with Solution 1. The mixture yielded an orange gel which was stirred for 10 minute before the product was transferred into a spray dryer. 20.8 g of the orange fine product was collected.

### Activation

The dried material was precalcined from room temperature to 598 K at a rate of 10 K/min in air (100 ml/min) for 1 h and then calcined from room temperature to 923 K at a rate of 2 K/min in helium (100 ml/min) for 2 h.

### Catalytic activity test

Approximately 10 g of catalyst was packed in an 12 mm ID stainless steel tubular reactor and tested at 673 K at a propane/O<sub>2</sub>/He/NH<sub>3</sub> mole ratio of 1/3/18/3, a space velocity of 1200 h<sup>-1</sup> and a pressure of 1 atm. The product streams were analyzed by gas chromatography (GC) by means Agilent.

## RESULT AND DISCUSSION

Acrylonitrile (ACN) is an important intermediates in petrochemistry and exhibit excellent annual growth; the main application includes synthetic fibers and resins. For decades, the ammoxidation of propylene to acrylonitrile is the most important process whereby more than 5 billion kg/year of acrylonitrile (with growth rate of 4% per year) are produced worldwide via the SOHIO/BP process. The said process is very efficient, fully converting propylene at the same time giving > 80% acrylonitrile yield on commercial scale.

The chemical equation of the SOHIO/BP process as extracted from literature (Olga et al., 2004) is given as follow:-



Catalyst: (K,CS)<sub>0.1-0.2</sub>, Ni,Co,Mn,Mg)<sub>7.5-9.5</sub>, (Fe,Cr)<sub>2.3-2.5</sub>, Bi<sub>0.5-1.0</sub>, Mo<sub>12</sub>O<sub>x</sub>/SiO<sub>2</sub> (MCM)

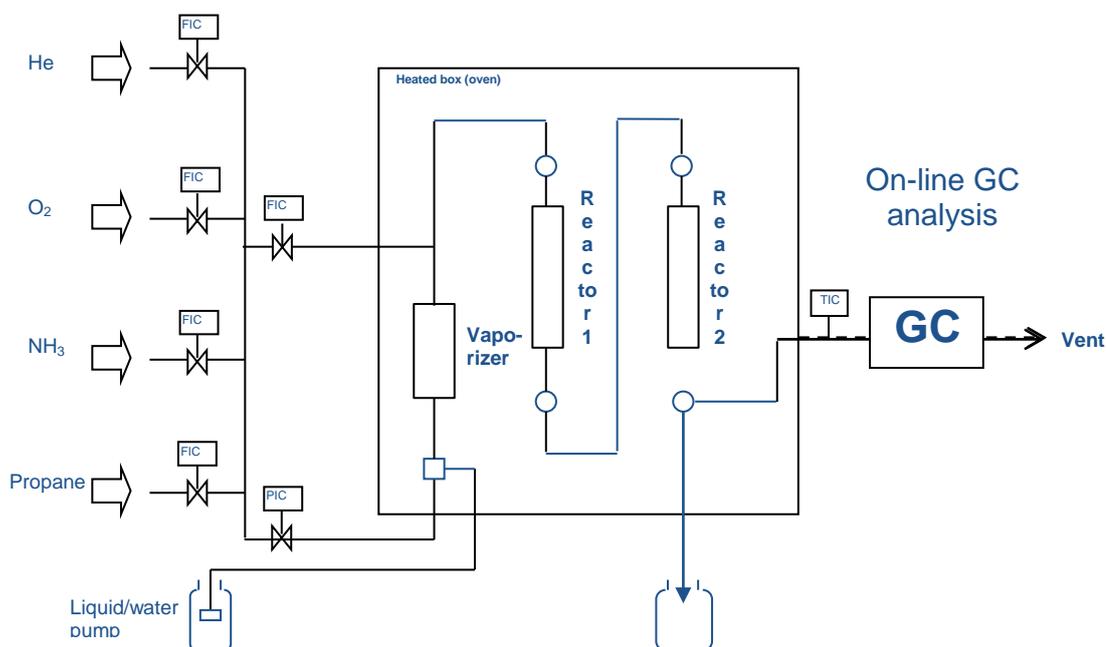
Despite the efficiency of the process, the price of propylene has seen attention being drawn to develop a method for producing acrylonitrile by ammoxidation reaction whereby lower alkane such as propane is used as a starting material *i.e.* propane catalytically reacted with ammonia and oxygen in a gaseous phase in the presence of a catalyst. Beside the economical factor of propane being a cheaper and more abundant feed, ammoxidation of propane is also a less energy intensive process. As such, promising acrylonitrile yield above 58% have already been obtained from propane using a patented Mo-V-Nb-Te-O<sub>x</sub> catalyst developed by Mistsubishi Chemical Company (Olga et al., 2004).

Future Process utilizing propane as starting material:-



Mo-V-Te-Nb mixed oxides is an interesting developing catalyst in the transformation of short-chain alkanes, *i.e.* C1-C4. It has been known that acrylonitrile (ACN) and acrylic acid (AA) can *selectively* be obtained in the ammoxidation and the oxidation of propane. Observation made based on the previous work of Olga et al. (2004) found that the best catalysts (V-Sb-Al) for ammoxidation are those exhibited the lowest yield in the oxidation process to acrylic acid and vice versa. The fact that Mo-V-Te-Nb-oxides could be used in both ammoxidation and/or oxidation underlines the advantage of this new multi-mixed oxide catalyst as compared to conventional catalysts such as Sb-containing material (V-Sb-Al, Mo-V-Sb-O<sub>x</sub>, etc.) (Hinago & Komada, 2000).

The formation of acrylonitrile (ACN) also strongly depends on the presence of ammonia. The proportion of ammonia to be supplied for the reaction is preferably within a range of from 0.2 to 5 moles, particularly from 0.5-3 moles, per mol of propane (Ushikubo, 1995)

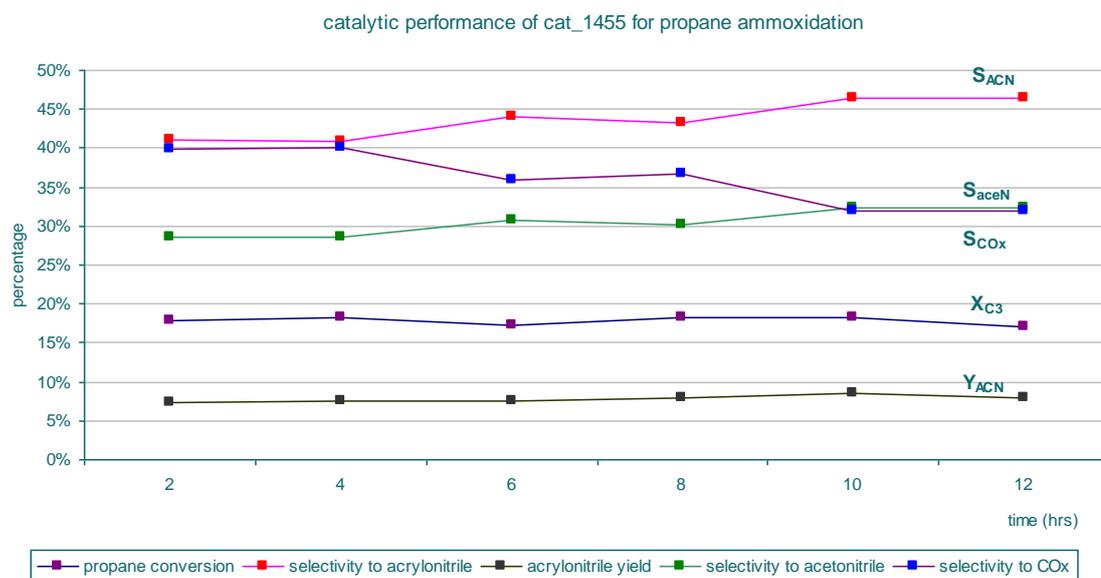


**Figure 1.** The schematic diagram of the reactor for ammoxidation of propane

In the absence of ammonia, only acrylic acid is obtained over Mo-V-Te-Nb catalyst [5]. The incorporation of ammonia using the same catalyst increases both the propane conversion and the selectivity to ACN although the catalytic results depend strongly on the  $\text{NH}_3 / \text{C}_3\text{H}_8$  ratio. Therefore, *caution* need to be taken to juggle the proportion of feeds used, i.e. propane/oxygen (air)/ ammonia. In too excess of oxygen, higher conversion of propane as a

trade off to the selectivity of nitriles may be obtained. On the other hand, the use of the right  $\text{NH}_3/\text{C}_3\text{H}_8$  ratios may be in favors to an important decrease in propane conversion and at the same time increase in the selectivity to ACN.

The activity test of Mo-V-Te-Nb-oxide catalyst from this study using the reactor (figure 1) is shown below (figure 2);



**Figure 2.** Catalytic Performance for Propane Ammoxidation Using Petrochemical Reactor

Figure 2 describes that the Mo-V-Te-Nb-oxide catalyst used for this reaction is active for ammoxidation of propane to acrylonitrile. The conversion of propane is about 18% and the selectivity to acrylonitrile is slightly increased from about 42% to 47% during the reaction. This indicates that the catalyst is active until 12 hours reaction. It might be still active even if the reaction is carried out for longer time. The potential of this catalyst for propane ammoxidation need to improve, since the product stream still contains CO<sub>x</sub> (CO<sub>2</sub> and CO) in quite high amount. There are some suggestions to improve the catalytic performance of this catalyst, i.e. improve the drying process, improve the calcinations process, or improve the reaction condition of propane ammoxidation.

## CONCLUSIONS

Based on the result, it can be concluded that Mo-V-Te-Nb-oxide catalyst is an active catalyst for ammoxidation of propane to acrylonitrile. The formation of acrylonitrile (ACN) strongly depends on the presence of ammonia..

## ACKNOWLEDGMENT

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

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