

# V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub> Catalysts Preparation and Performance Testing on the Oxidation of Benzene to Maleic Anhydride in a Fixed Bed Reactor

Uraz, Canan<sup>\*†</sup>; Atalay, Süheyda

Department of Chemical Engineering, Faculty of Engineering, Ege University, 35100 Bornova-Izmir, TURKEY

**ABSTRACT:** In this research, the selective oxidation of benzene to maleic anhydride (MAN) in a fixed-bed reactor was studied. The gas phase catalytic oxidation of benzene was carried out in a laboratory scale fixed bed reactor on the catalysts, which were prepared having two different compositions on silica gel. The effects of temperature, flow rates of benzene and air, and catalyst type on the reaction selectivity were investigated at normal atmospheric pressure. The experiments were performed at the temperature range of 300°C to 375 °C, the space-time (W/F<sub>BO</sub>) range was from 1\*10<sup>6</sup> to 2.5\*10<sup>6</sup> g.sec/mole, and the air/ benzene weight ratio changes were between 16-51. Experimental results show that the maximum conversion is obtained at 375 °C, at the space-time 1.33\*10<sup>6</sup> g.s/mol and at the benzene/air mol ratio 41.36 by using first catalyst. According to the experimental results, a difference between catalyst 1 and 2, it could not be seen. MAN conversion was observed for both catalysts and both catalysts are suitable for oxidation of benzene to MAN in a fixed bed reactor.

**KEY WORDS:** Gas-phase oxidation, Benzene, Maleic anhydride, Fixed-bed reactor.

## INTRODUCTION

Oxidation of organic compounds such as benzene in the vapour phase is an industrially important reaction since the products such as maleic anhydride, phthalic anhydride are very valuable intermediates [1, 2]. The production of maleic anhydride by the air oxidation of benzene is recently studied using a vanadium pentoxide catalyst and some new type of catalysts [3, 4, 5]. MAN is produced industrially by oxidation of suitable hydrocarbons in the gas phase. Benzene is used as the predominant starting material but in recent years oxidation of C<sub>4</sub> hydrocarbons has become increasingly important. In the oxidation of C<sub>4</sub> hydrocarbon processes, there are

three types of processes that have been developed or are in the development stage: Fixed-bed process, Fluidised-bed process, and Transport-bed process [6, 7]. The most widely used catalysts in the production of MAN include vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>), molybdenum trioxide (MoO<sub>3</sub>), and sodium oxide (Na<sub>2</sub>O). It was also found that the catalysts supported by silica gel and superacidic catalysts can also be used in the oxidation processes [8, 9]. The preparation methods and conditions are the critical factors for the catalytic performances and the structure of supported vanadium oxide, where, impregnation, flash hydrolysis, chemical vapor deposition, grafting and

<sup>\*</sup> To whom correspondence should be addressed.

<sup>†</sup> E-mail: canan.uraz@ege.edu.tr

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chemical liquid deposition are the preparation methods used [10]. Overbeek [11] developed a preparation procedure, which was cheaper and much more controllable than the preparation procedures of the VPO catalyst.

The aim of this study is to prepare catalysts by following the recommended knowledge in literature, to characterize and to test them to investigate the influences of the parameters such as catalyst type, temperature, space time and benzene/air mol ratio, on the oxidation of benzene in a laboratory scale fixed bed reactor.

## EXPERIMENTAL SECTION

### Catalyst Preparation

In a previous study [12] carried out in a fluidized-bed reactor, six different types of catalysts were investigated. This study was catalyst screening study and according to the results, the catalysts supported by silica gel were found to be the most suitable catalysts for a benzene oxidation reaction to MAN in a fluidized-bed reactor. Since these catalysts are hopeful catalysts for this reaction in a fluidized-bed reactor, it was decided to investigate these catalysts in a fixed-bed reactor for the same reaction [12]. In this study, two types of catalysts were prepared to investigate the oxidation of benzene to MAN. Compositions of the catalysts are given in Table 1. Catalyst 1 was prepared by following the procedure in the patent by *R.Marg* [13]. Catalyst 2 was prepared in the same way, as catalyst 1. But, catalyst 2 had higher vanadium content. After both of the catalysts were prepared, a sieve analysis was performed in order to achieve uniform size distribution of 150 $\mu$ . After that, the catalyst was pelletized and placed into the reactor.

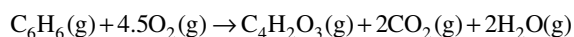
### Apparatus

The parts of the experimental set up are explained in the following: Air Stream, Nitrogen Stream, Benzene Stream, Preheater, Reactor (Fig. 1), Cooling and Collection.

## EVALUATION OF THE EXPERIMENTS

The conversion of benzene is calculated by considering two possible main reactions taking place in the reactor.

Partial oxidation (reaction 1):



Total oxidation (reaction 2):

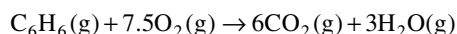


Table 1: Compositions of the Catalysts.

Type of the carrier and % by weight		Catalyst 1	Catalyst 2
		Silica Gel (72)	Silica Gel (64)
Compositions of active ingredient, wt%	V <sub>2</sub> O <sub>5</sub>	53.6	75
	MoO <sub>3</sub>	35.7	24
	Ni <sub>2</sub> O <sub>3</sub>	10.7	1

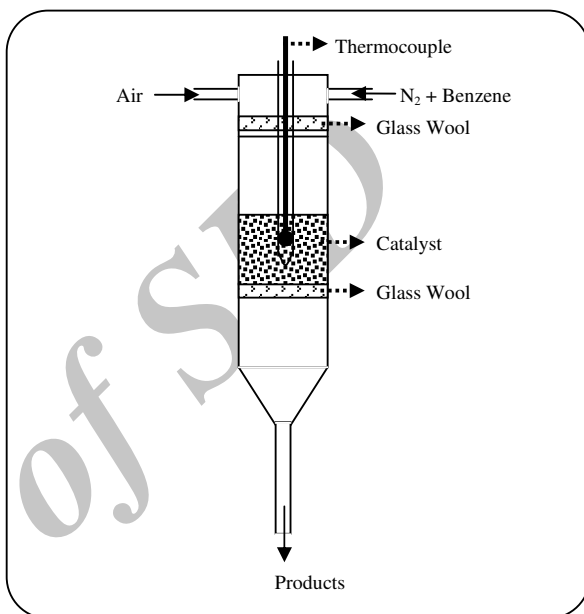


Fig. 1: Schematic representation of the reactor.

Condensed and collected components are analyzed by GC. The weight percentage of MAN is calculated with the help of the GC analysis. At the end of each experiment the collected products in the traps are weighed. The produced mol number of MAN and total benzene fed to the reactor are calculated. Then conversion of benzene for reaction 1 ( $x_1$ ) is calculated by using the following equation:

$$x_1 = \left[ \frac{\text{consumed benzene in reaction1}}{\text{Benzene Fed}} \right] \quad (1)$$

Since total flow rate of the exit gas and CO<sub>2</sub> % are measured during the experiments, the mole number of the CO<sub>2</sub> is calculated. So conversion of benzene for reaction 2 is calculated by using the following equation:

$$x_2 = \left[ \frac{\text{consumed benzene in reaction2}}{\text{Benzene Fed}} \right] \quad (2)$$

**Table 2: Operating conditions in the experiments, Pressure: 1 atm.**

Parameter	Range
Reactor Temperature, $T_R$ ( $^{\circ}C$ )	325-375
Space time ( $W/F_{B0}$ ), (g.s/mol)	$1 \cdot 10^6$ - $2.5 \cdot 10^6$
Catalyst amount, (g)	2
Air / Benzene ratio, (w/w)	16-51
Catalyst/Benzene ratio, (w/w)	1.97-3.79

Total conversion of benzene ( $x_T$ ) is calculated by using the following equation:

$$x_T = \left[ \frac{\text{Total consumed benzene}}{\text{Benzene Fed}} \right] \quad (3)$$

Partial selectivity is defined as the ratio of benzene conversion for reaction 1 and 2. Also total selectivity is defined as the ratio of benzene conversion for reaction 1 and total conversion. Their equations are:

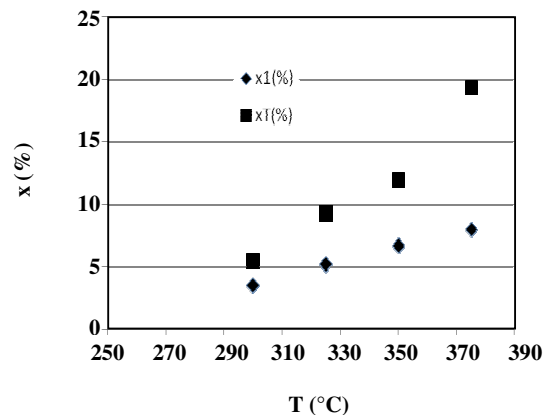
$$\text{Partial Selectivity} = \left[ \frac{x_1}{x_2} \right] \quad (4)$$

$$\text{Total Selectivity} = \left[ \frac{x_1}{x_T} \right] \quad (5)$$

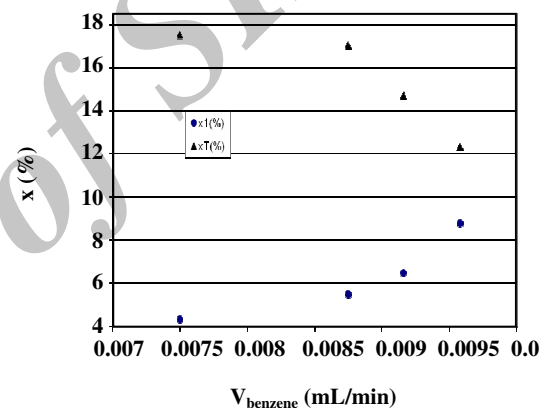
## RESULTS AND DISCUSSION

Operating conditions are given in Table 2.

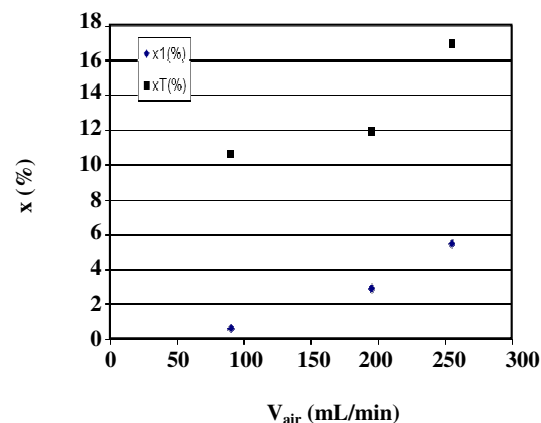
Some of the results obtained on the first catalyst are plotted in Figs. 2, 3, and 4. It can be seen from Fig. 2 that both total conversion of benzene ( $x_T$ ) and conversion of benzene to MAN ( $x_1$ ) increased with increasing temperature. Although this increase in total conversion is very sharp, it is not very significant in the conversion of benzene to MAN ( $x_1$ ). As it can be seen from Fig. 3, although the total conversion of benzene decreased, conversion of benzene to MAN increased with the increasing benzene flow rate. So it can be said that; when the benzene flow rate is increased, the reaction tends to the direction of MAN production. The decrease in total conversion is an expected behavior due to the decrease in space time. Fig. 4 is plotted to see the effect of the flow rate of air on the conversion. It can be followed that conversion of benzene both through MAN and through  $CO_2$ , increased generally with increasing air flow rate. But low conversion values were obtained in reaction 1.



**Fig. 2: Conversion vs. Temperature at constant space time= $1.33 \cdot 10^6$  g.s/mol and at constant benzene/air mole ratio= $41.36$ .**



**Fig. 3: Conversion vs. flow rate of benzene at constant temperature= $350^{\circ}C$  and at constant flow rate of air= $255$  mL/min.**



**Fig. 4: Conversion vs. flow rate of air at constant temperature= $350^{\circ}C$  and at constant space time= $1.33 \cdot 10^6$  g.s/mol.**

As the flow rate of air is increasing, it can be pass the region at which the external mass transfer effect can be neglected. The results presented in the figure show that the reaction is still under the mass transfer effect.

The results obtained by the second catalyst are plotted in Figs. 5, 6, and 7. It can be seen from Fig. 5 that the conversion of benzene through MAN increased with increasing temperature. The drastic decrease in total conversion beyond 350°C can be explained by the possible controlling of the reaction by mass transfer rather than the reaction kinetics. Fig. 6 is plotted to see the influence of the flow rate of benzene on the conversion. Although an increase in the flow rate positively affects, the benzene conversion to MAN, total conversion first increases then decreases. This trajectory can be explained by the suppressing in total oxidation to CO<sub>2</sub> due to the decrease in space time. Fig. 7 was prepared to see the influences of the flow rate of air on the conversion. It can be followed that the conversion of benzene through MAN and to total oxidation increased with the increasing air flow rate. As the flow rate of air is increasing, it can pass the region at which external mass transfer effect can be neglected. The results presented in the figure show that the reaction is controlled by reaction kinetic.

It is difficult to make a comparison between catalyst 1 and 2. According to the experimental results, the difference between the catalyst 1 and 2, could not be seen. MAN conversion was observed for both catalysts. Both catalysts are suitable for oxidation of benzene to MAN in a fixed bed reactor. As a result, it can be said that both catalysts could be used for oxidation of benzene to MAN in a fixed bed reactor.

## CONCLUSIONS

V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub> and NiO<sub>3</sub> are essential active components. SiO<sub>2</sub> is a suitable support for the oxidation of benzene to MAN reaction. Conversion of benzene to MAN and to total oxidation increased with increasing temperature. When the benzene flow rate is increased, the reaction tends to the direction of MAN production. As the flow rate of air is increasing, it can pass the region at which the external mass transfer effect can be neglected. The results show that the reaction is still under the mass transfer effect. The adsorption isotherms for both catalysts may be classified as type V indicating the presence of microporosity or mesoporosity. After

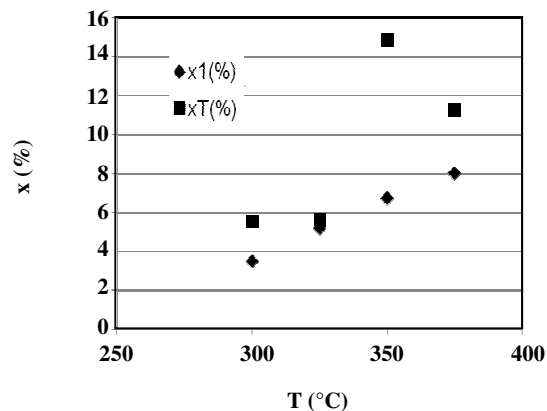


Fig. 5: Conversion vs. temperature at constant space time and at constant air/benzene mole ratio.

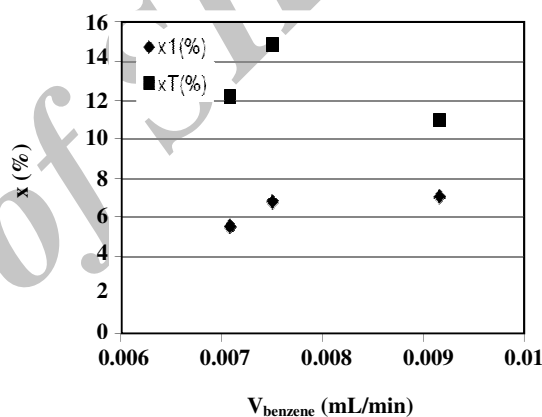


Fig. 6: Conversion vs. flow rate of benzene at constant temperature and at constant flow rate of air.

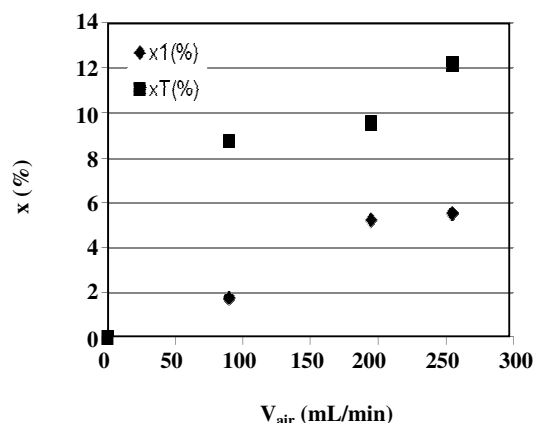


Fig. 7: Conversion vs. flow rate of air at constant temperature=350°C and at constant space time=1.33\*10<sup>6</sup> g.s/mol.

reaction, the surface and the micropore area of both catalysts decreased due to the possible plugging of the pores by metal oxide crystallites. Catalyst 2 has the highest specific surface area. However, catalyst 1 found that the particles had an amorphous structure. The catalyst may be affected by the calcinations process. Generally, a small amount of weight loss was observed and there was no significant weight loss in both fresh catalysts.

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