THE EVALUATION OF SOME CATALYSTS FOR THE OXIDATION OF O-XYLENE

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Summary

The oxidation of o-xylene to phthalic anhydride over vanadium pentoxide catalysts was studied.

Possible reaction mechanisms were put forward and compared with the literature. Various methods of catalyst preparation were investigated.

In the experimental work, ten kinds of vanadium pentoxide catalysts were prepared; seven catalysts were supported with TiO_2, one with Al_2O_3 and two were commercial. The selectivities and the yields of products were determined under various conditions of temperature and flow rate using a small diamter tubular reactor. The influences of the catalyst composition and the method of preparation on the activity were investigated. Based on these results, the most promising catalyst was chosen. Rate equations for each catalyst were deduced.

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1. Introduction

Vanadium pentoxide was found to be a good catalyst for making phthalic anhydride from naphthalene by Wohl (115) and Gibbs and Conover (116) in 1916. Following this, the fixed-bed air oxidation of naphthalene on vanadium pentoxide catalyst became a process that had considerable commercial importance. o-Xylene has now largely replaced naphthalene as feed stock (69, 70), because of its several commercial advantages, which are (1) the heat evolution of the reaction is less, (2) the purity of the product is higher, (3) the theoretical amount of air for o-xylene oxidation is less that for naphthalene and (4) carbon combustion products are produced in lower yields (8).

There is much work concerned with o-xylene oxidation. The main contents concern mechanisms of the reaction, reaction rate equations, catalyst evaluation (63) and methods of preparation, factors affecting catalytic activity, surface phenomena and design and model analysis of the catalytic reactor (16, 25, 104, 105). However, data on the reaction kinetics of the catalytic oxidation of o-xylene to phthalic anhydride are few with no firm agreement on the intermediates found and reaction mechanisms involved (6, 8, 106, 107).

Loftus and Satterfield (11) studied the homogeneous partial oxidation of 1 mol % of o-xylene in air at 1atm in a flow reactor in the temperature range 455°C to 525°C. They employed gas chromatography,

infrared spectroscopy and nuclear magnetic resonance spectroscopy for identification of the products. A mechanism of the reaction was presented.

In another report (3), the partial oxidation of o-xylene was produced by bubbling the reactants through a melt of 39wt % vanadium pentoxide-potassium sulfate eutectic in the temperature range 528 to 598°C. The principal product was o-tolualdehyde, some benzene and traces of phthalide being formed but no organic acids. These products are similar to those found in the absence of acid products but are far different from the product distribution found from the former experiment.

Wright (12) investigated the kinetics of the slow combustion of the three xylene isomers in a quartz vessel under static conditions at subatmospheric pressure over the temperature range 410 to 550°C, employing 1:1 to 1:20, hydrocarbon:oxygen mixtures. It was shown that W (the maximum rate) = kP^n (the total initial pressure), where n=1.9 for o-xylene. Although W is affected by changes in mixture composition and temperature, the value of n is independent of these parameters.

Wright also studied the gas phase oxidation of o-xylene at a higher temperature of 650°C. The presence of 38 oxidation products was detected and variations in the yields of two thirds of these studied as a function of mixture composition and reaction time. Apart from CO, CO_2, CH_4, H_2 and water, 1-methyl-2-vinylbenzene and toluene were the most abundant by-products found.

The oxidation of mixed xylenes using many different catalysts was studied by Parks and Allard (94). The catalysts were compounds of molybdenum, vanadium, iron, chromium, tin, zirconium, magnesium, potasium, tungsten, titanium and aluminium. The effect of temperature, time of contact and air/xylene ratio upon the type and amount of products was studied. With a tin vanadate catalyst at 320°C, a time of contact of 0.002 minute and an air/xylene ratio[(grams of air per hour)/(grams of xylene per hour)] of 34/1, a yield of 8% phthalic anhydride was obtained. With a vanadium pentoxide catalyst supported on Alfrax at 530°C and an air/xylene ratio of 34/1, 18% phthalic anhydride was obtained. This catalyst gave yields varying from 45 to 85% phthalic anhydride on the basis of the amount of xylene oxidized per pass.

Much work concerned with the oxidation of p-xylene has been reported. Most recently, experimental studies were carried out in a packed bed employing V_2O_5-MoO_3 catalyst by Izawa and Inoue (103). The effects of temperature, initial p-xylene concentration and initial oxygen concentration on the product distribution were investigated.

A kinetic model for the reaction was proposed by considering that p-xylene reacts with adsorbed molecular oxygen on characteristic sites of the catalyst to tolualdehyde and terephthalaldehyde, and p-xylene and intermediates react with adsorbed oxygen atoms to carbon dioxide. Some investigators' results of studies of the oxidation of aromatic hydrocarbons employing V_2O_5 catalyst were also compared.

The mechanism of chain initiation over the initial period of oxidation of o-xylene was proposed by Denisova and Denisov (13). It was found that free radicals are formed by a bimolecular reaction at a rate of $W=k[RH][O_2]$.

Froment (5) proposed a simple model that has two routes for the reaction and gave reaction rate equations and the rate constants. Abo et al (26) investigated the oxidation of o-xylene with vanadium catalyst using a fluidized bed.

The literature on the selectivity of the oxidation of o-xylene to phthalic anhydride is very small. Froment (5) showed that catalyst selectivity to phthalic anhydride is seriously decreased by the presence of a temperature "hot spot" in the fixed bed reactor. A preliminary study of the oxidation of o-xylene was conducted over a number of common oxidation catalysts (20 catalysts) by Bhattacharyya and Gulati (8). The selectivities and conversions were found under several reaction conditions. Spielman (4) studied the selectivity theoretically.

Studies of the oxidation of other hydrocarbons over vanadium pentoxide catalyst are reported for toluene by Downie, Shelstad and Graydon (2) and for naphthalene by Ordrin, Korneichuk and Roev (21), Fabuss (22) and Ioffe et al (31). Wojtowcz et al (23) employed a fluidized bed, and Mars and van Krevelen (15) also investigated the oxidation of some aromatic hydrocarbons by conventional methods. Vrbaški and Mathews (7) studied the reactions producing phthalic anhydride from o-methylbenzyl alcohol and o-tolualdehyde (9) over fused vanadium pentoxide catalyst. These reactions consist of four parallel routes. Both the reaction orders and activation energies for the formation of phthalic anhydride from o-methylbenzyl alcohol and o-tolualdehyde were also determined. Schaefer (18) investigated the activity of vanadium pentoxide catalyst for the oxidation of benzene and of maleic anhydride.

Clark and Berets (20) studied the electrical properties of vanadium pentoxide. Vol'fson et al (17) established that the active components of vanadium oxide catalyst for the oxidation of naphthalene to phthalic anhydride are the oxides V_2O_5 and V_6O_{13} by a comparison of the catalytic activity and phase composition of various oxides of vanadium. Simard et al (6) investigated the transformation of V_2O_5 to $V_2O_{4.34}$, which was found during the oxidation of o-xylene. The properties of these oxides are believed to determine the catalytic mechanism.

2. The Catalytic Behaviour of Vanadium Oxides

In the vanadium pentoxide lattice, two kinds of oxygen ions may be distinguished. The greater part of the oxygen ions are present in approximately the same plane as the vanadium ions. Two fifths of the ions, however, are arranged in planes parallel to and alternating with the first (71). Mars and Van Krevelen (15) suppose the latter oxygen ions to interact with aromatic molecules at the surface. Then, the rate of oxidation will depend on the concentration of these oxygen ions (or the degree of coverage by the oxygen), and on the number of aromatic molecules absorbed on (or striking) the surface from the gaseous phase.

The two step reaction model is thus,

Aromatic compounds + Oxidised catalyst

$$\longrightarrow \text{Oxidation products} + \text{Reduced catalyst} \quad [1]$$

$$\text{Reduced catalyst} + \text{Oxygen} \longrightarrow \text{Oxidized catalyst} \quad [2]$$

The second reaction [2] is the slow step. It may be written as follows.

$$2\,e^{-}(\text{catalyst}) + \tfrac{1}{2}\,O_2\,(\text{gas}) \longrightarrow O^{-2}\,(\text{catalyst surface})$$

Therefore, the rate of oxidation is proportional to the square root of the oxygen pressure (20). This has also been shown by Krichevskaya for o-xylene oxidation (72).

Homolytic oxygen exchange on platinum and silver was investigated by Margolis (77). The formation and breaking of chemical bonds during isotopic exchange occurs with unpairing of electrons. There was no homolitic exchange on V_2O_5 and MnO_2, and on platinum and silver at low temperatures. Consequently, it was suggested that higher temperature may bring about oxygen exchange on semiconducting oxides (V_2O_5 and MnO_2).

Cameron et al (100) also studied the exchange of isotopic oxygen atoms in the systems V_2O_5-oxygen, V_2O_5-water and V_2O_5-water-oxygen in the temperature range 400-500°C. The oxygen in the alundum support was not exchanged in the catalysts of alundum supported V_2O_5, assuming the equilibrium constant for the exchange between V_2O_5 and molecular oxygen was unity. This reaction proceeded with surface reaction controlled mechanism as well as the oxygen exchange reaction between gaseous oxygen and fresh amorphous V_2O_5 microspheres. The rate of oxygen exchange in the system V_2O_5-O_2 was the rate controlling reaction.

From Roiter's experiments (76), however, at a temperature of 450°C, a vanadia catalyst which has O^{18} in the lattice did not exchange O^{18} with gaseous oxygen. But the reaction between naphthalene andair over the catalyst occurs in the temperature range 320-390°C(20). From the above experimental results and considerations, it was concluded that oxygen in the lattice does not contribute to the oxidation reaction of organic compounds with gaseous oxygen.

Vainstein and Turovskii (108) found the same result in their experiments. There was no exchange of oxygen on MnO_2 and CuO with the reaction products in the oxidation of CO using O^{18}.

Simard and his co-workers (6) postulated catalytic behaviour from their consideration of the arrangement of vanadium oxide molecules in catalysts. It is thought that a molecule of oxygen which strikes the surface of the catalyst dissociates, then ionizes and becomes incorporated into the vanadium oxide structure. If the catalyst acts as a transfer medium for oxygen, the changes in structure between the oxides $V_2O_{4.34}$ and V_2O_5 should occur readily to accommodate the addition or removal of oxygen ions.

Vol'fson (17) investigated the catalytic activity and phase composition of various oxides of vanadium for the oxidation of naphthalene to phthalic anhydride using X-ray diffraction. The presence of V_2O_5 did not contribute to high catalytic activity of the vanadium oxide catalyst with respect to the oxidation of naphthalene. V_2O_4 was the most active; V_2O_5 served only as the starting material for the formation of V_2O_4 and V_6O_{13}. Amorphous V_2O_4 showed the highest selectivity.

According to the experimental results of Scheffer (18), on the oxidation of benzene to maleic anhydride over various (vanadium oxide) catalysts $VO_{1.99}$ (V_2O_4) showed the maximum activity and the rate constant of the reaction was 3×10^4 cm/sec, while V_2O_3 and V_2O_5 were inactive and V_6O_{13} was slightly active.

Andreikov (64) investigated the oxidation of o-xylene at 340-420°C in the presence of vanadium oxide catalysts in a pulsed micro-catalytic system. He found that V_3O_7 and V_2O_5 were significantly more active than V_6O_{13}, V_2O_4 and V_2O_3 under identical conditions. The selectivity to phthalic anhydride and $HCOC_6H_4COOH$ differed for each oxide, indicating that they were formed at different active centers.

Simard et al (6) concluded that (1) the vanadium states of an unpromoted vanadium oxide catalyst during catalytic oxidation of o-xylene are V^{+5}, (2) these vanadium ions assume three crystalline forms with oxygen — V_2O_4, $V_2O_{4.34}$ (called $V_{12}O_{26}$) and V_2O_5, (3) the relative proportions of these oxides are dependent on the hydrocarbon concentration in the feed air, (4) V_2O_4 and V_2O_3 are not catalytically active for the production of phthalic anhydride or inter-mediates. This result is contrary to Vol'fson's finding.

3. Catalyst Supports

Vanadia catalysts are frequently used in conjunction with supports or carriers.

In choosing suitable support materials the following considerations among others are important (62, 109),

1) Good dispersion of the catalyst throughout the support.

2) Relatively high thermal conductivity.

3) Pore structure such that diffusional resistance is relatively low.

4) Good resistance to attrition.

5) Resistance to sintering at high temperatures.

Supports may be non-porous material with low surface area (under $3m^2/g$) or porous heat resistant material with high surface area ($100-1500m^2/g$). Metallic oxides such as Al_2O_3, $SiO_2-Al_2O_3$, TiO_2 and MgO are widely used support materials for vanadium oxide catalysts.

The ratio of active phase to support phase and the deposition mode of catalytic substances will be important to the catalyst activity. Other features such as the defect structure of the support and the area of individual crystallites will be important to catalyst activity. The common supports such as alumina, themselves have catalytic activity.

Hindin and Weller (81) found that the catalytic activity of dehydrated γ-alumina as a hydrogenation catalyst increases as drying time and temperature are increased. The activation energy for hydrogenation decreases from about 14kcal/mole after drying at 450°C, to 6kcal/mole after drying at 650°C. Water added to dried alumina has a marked inhibiting effect on activity. The magnitude of the decrease in activity depends on the amount of water added and the temperature at which it is added. About 0.15 wt % water is sufficient for complete deactivation; this corresponds to a coverage of about 2% of the total alumina surface.

Eischens and Plinskin studied the effect of support on the IR spectrum of chemisorbed CO(83). They showed that the nature of the support can influence the structure of CO adsorbed on dispersed metals, compared CO chemisorbed on silica supported platinum and on γ-alumina supported platinum.

Hightower (84) compared different supported catalysts. The relative rate of hydrogen exchange between p-xylene and deuterium varied as the support was changed from γ-alumina to α-alumina or to silica. In his experiments, strongly adsorbed water may also play a role in the exchange.

Supports such as solid acids and bases show dual functionality (80). This is the effect whereby one reaction takes place on the metal to yield an intermediate which further reacts on the support. In assessing catalyst activity it is therefore important to consider the contribution of the support.

4. The Desired Performance of Catalysts

The important factors for selecting industrial catalysts are many, as shown in Table 4 (60).

The most important factors are activity, selectivity and life time. The life time of the catalyst may be dependent on several factors such as its resistance to withstand high temperatures, its ability to resist poisoning or coking and its mechanical strength.

Ideally, it is desired to maintain high activity, high selectivity and high space velocity. However, these are related to other factors such as reaction temperature, pressure drop, possible recycle of reactant, cooling requirements, collection of products, life time and costs of installation and power. For these reasons, the best conversion and selectivity have to be decided economically.

Gas-solid catalytic reactions comprise several sequential and simultaneous rate processes:-

1) Diffusion of reactants across the external boundary layer to the external surface of the pellet.

2) Diffusion of reactants through the pore structure to the active sites.

3) Adsorption of reactants at the active sites.

4) Reaction at the surface.

5) Desorption of products from the active sites.

6) Diffusion of products through the internal pore structure towards the external surface.

7) Diffusion of products across the external boundary layer into the bulk phase.

Steps (2) - (6) occur simultaneously. Steps (1) and (7) occur simultaneously but in sequence with steps (2) - (6).

The overall rate of reaction is in general a function of the rates of the seven steps. If the number of adsorption and active sites on the catalyst surface is rate controlling, the reaction rate is proportional to the surface area.

The outer surface area of the catalyst is often very small compared with the internal (pore) surface area. The reaction rate for a porous catalyst is a function not only of the chemical process but also of physical transfer processes such as in-pore diffusion of reactant and product, so that it is influenced by surface area, pore size and volume, porosity and the structure of the internal surface of the catalyst. Activated charcoal and molecular sieve pellets have a bi-disperse pore structure which consists of both macro pore (0.1-10μ) and micro pore (5-20 Å) in the crystal. Other industrial supports such as alumina gel and aluminium silicate usually have intermediate pore sizes (15-1000Å).

If the pore size is too small and diffusion resistance is large, only the outer surface of the catalyst is used and the effectiveness of the catalyst is seriously reduced. In the case of slow reactions

Table 4. The Desired Performance and Important Physical and Chemical Properties of the Catalyst

Desired Performance

1) High activity
2) High selectivity
3) Long life time
4) Good mechanical performance (shape and diameter of pellet, distribution of pore size, density)
5) Cheap method of manufacture

Important Physical and Chemical Properties

1) Acid and base (kind, pH)
2) Components (main active materials, support)
3) Electron state (combination k valence)
4) Crystal structure (defects)
5) Surface condition (surface area, surface energy, surface potential, surface dipole)
6) Internal pore structure (pore volume, pore size and its distribution)
7) Adsorption (heat of adsorption and wetting)
8) Specific gravity, specific heat, thermal conductivity
9) Electric and magnetic characteristics
10) Shape or form

(e.g. oxichlorination of ethylene over copper chloride-alumina catalyst), a catalyst which has a small pore size and large surface area is desirable in order to promote increased collisions on the surface. However, in the case of a rapid reaction involving larger reactant and product molecules (e.g. polymerization of ethylene), the overall reaction is diffusion controlled, so that the form of the catalyst and the pore structure are important. Consequently it is necessary to optimise surface area, pore size and volume. The kind of support and the condition of preparation become very important.

The type of pore structure is particularly important in determining selectivity. Frequently, unstable intermediates react to give undesired products through over exposure with the catalyst. The desired products themselves may react further. Careful control of the pore structure is required, if possible, to improve the diffusion of products out of the pores.

Voge et al (61) explained the effect of particle size of Shell 205-Fe system catalyst on selectivity for butene dehydration by means of the resistance of material diffusion in the particle. The activity and selectivity are complicated functions of several factors, as mentioned above. Generally speaking, they are closely related to the electron structure of the catalyst metal, macro and micro pore structures and the lattice defect of the support and conditions of reaction such temperature, concentration of reactants and contact time.

The influence of catalyst particle size upon the reaction rate was studied [by Fulton and Crosser (24)] for the hydrogenation of ethylene with nickel supported on alumina in a packed bedflow reactor. j-Factor correlations were used to calculate the catalyst surface temperature and concentration.

Kayser and Hoelscher (112) studied mass transfer effects over a palladium-alumina catalyst. Mass transfer through the fluid film surrounding the catalyst particles controlled the rate of production. Yang and Hougen (113) showed some useful graphs on the effects of mass transfer on concentration gradients in gas films and in catalyst pellets.

5. The Mechanisms of the Catalytic Oxidation of o-Xylene over Vanadium Oxide

There have been some fundamental studies on the kinetics and the mechanism of the catalytic oxidation of o-xylene over vanadium oxide (94). Margolis (99) has widely studied the mechanisms of hydrocarbon oxidation, but not including the oxidation of o-xylene. Dixon and Longfield (93) have summarized the literature up to 1956.

Loftus and Satterfield (11) suggested that the xylyl radical is formed as the first step of the reaction by hydrogen abstraction from o-xylene by the oxygen molecule, the hydroxide radical, or the peroxide radical. The collision of two xylyl radicals or a xylyl radical with o-xylene results in the formation of 2.2'-dimethyldibenzyl [1]. The initial oxygenation predominantly forms the xylyl peroxide radical [2].

$$CH_3C_6H_4\dot{C}H_2 + CH_3C_6H_4CH_3 \longrightarrow (CH_3C_6H_4CH_2)_2 + H\cdot \qquad [1]$$

$$CH_3C_6H_4\dot{C}H_2 + O_2 \longrightarrow CH_3C_6H_4CH_2OO\cdot \qquad [2]$$

Then, by hydrogen abstraction, xylyl hydroperoxide may be formed [3].

$$CH_3C_6H_4CH_2OO\cdot \xrightarrow{\cdot H} CH_3C_6H_4CH_2OOH \qquad [3]$$

In the papers by Falconer and Knox (85) and Satterfield and Wilson (86), the peroxy radical was supposed to be decomposed faster than hydrogen was abstracted to form the hydroperoxide.

Wright (14) postulated the ensuing reactions involving simultaneous decomposition of the peroxide to the alcohol and the aldehyde.

$$CH_3C_6H_4CH_2OO\cdot \xrightarrow{\cdot H} CH_3C_6H_4CH_2OOH \xrightarrow{\cdot H} CH_3C_6H_4CH_2OH + \cdot OH \qquad [4]$$

$$CH_3C_6H_4CH_2OO\cdot \rightarrow CH_3C_6H_4CHO + \cdot OH \qquad [5]$$

The following equations show a reaction mechanism for the initial stages of the homogeneous oxidation of o-xylene. Equation [6] is α-hydrogen isomerization and equation [7] is β-isomerization.

[6]

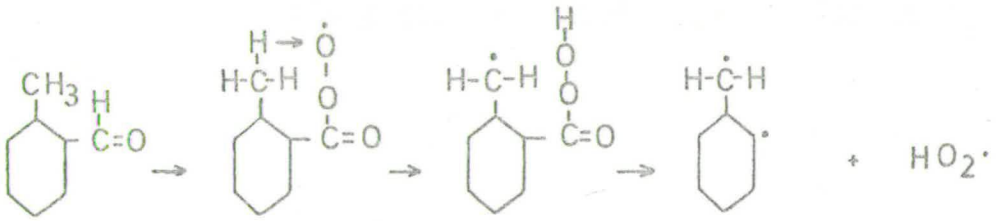
α-isomerization

[7]

β-isomerization

Subsequent cleavage of the weak O-O bond would lead to the formation of o-xylene oxide if preceded by reaction [7] and to the formation of o-tolualdehyde is preceded by reaction [6]. Finally Loftus and Satterfield (11) suggested the reaction mechanism as shown in Figure 2.

It was mentioned by Wright (87) that the oxidation of o-xylene is easier than that of m- or p-xylene and this phenomenon was explained in terms of a branching reaction involving o-tolualdehyde as an intermediate. o-Tolualdehyde is oxidized to make a reactive diradical as below, which on further reaction would give two free radicals.



In the case of m- and p-xylene, however, this reaction would be much more difficult.

o-Xylene oxidation also produces such by-products as 1-methyl-2-ethylbenzene, 1-methyl-2-vinylbenzene, naphthalene, anthracene, p- and m-xylene, benzene and toluene. Loftus and Satterfield (11) found other products such as benzaldehyde, benzofuran, phenylacetaldehyde, o-tolualdehyde, o-xylene oxide, phthalide, phthaldialdehyde ($C_6H_4(CHO)_2$), 2-2'-dimethyldibenzyl ($(CH_3C_6H_4CH_2)_2$).

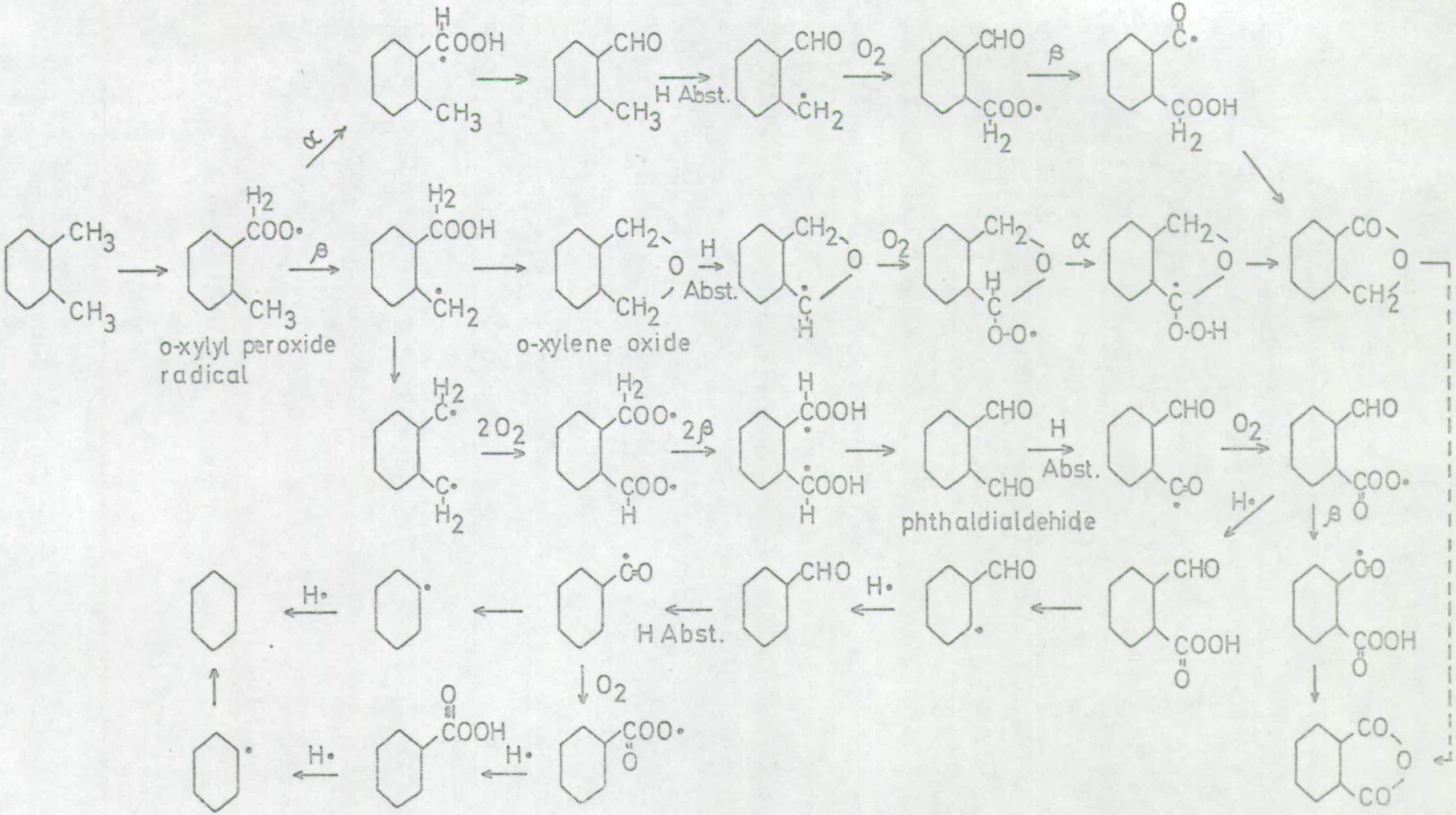
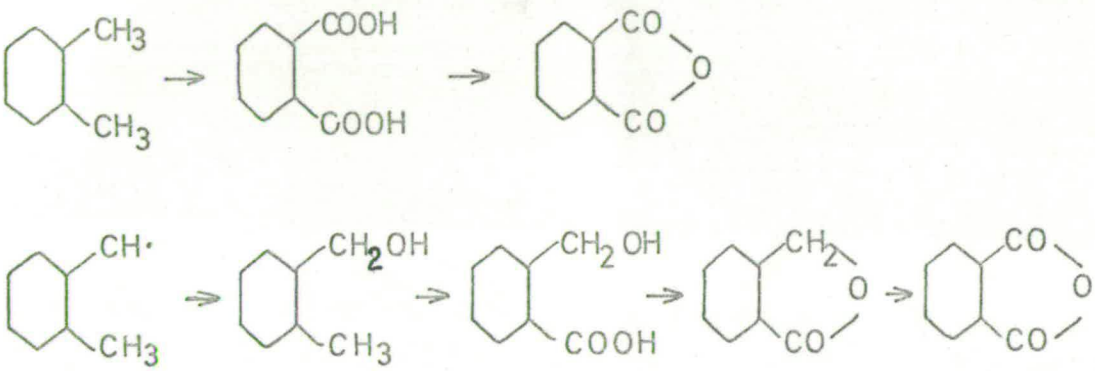


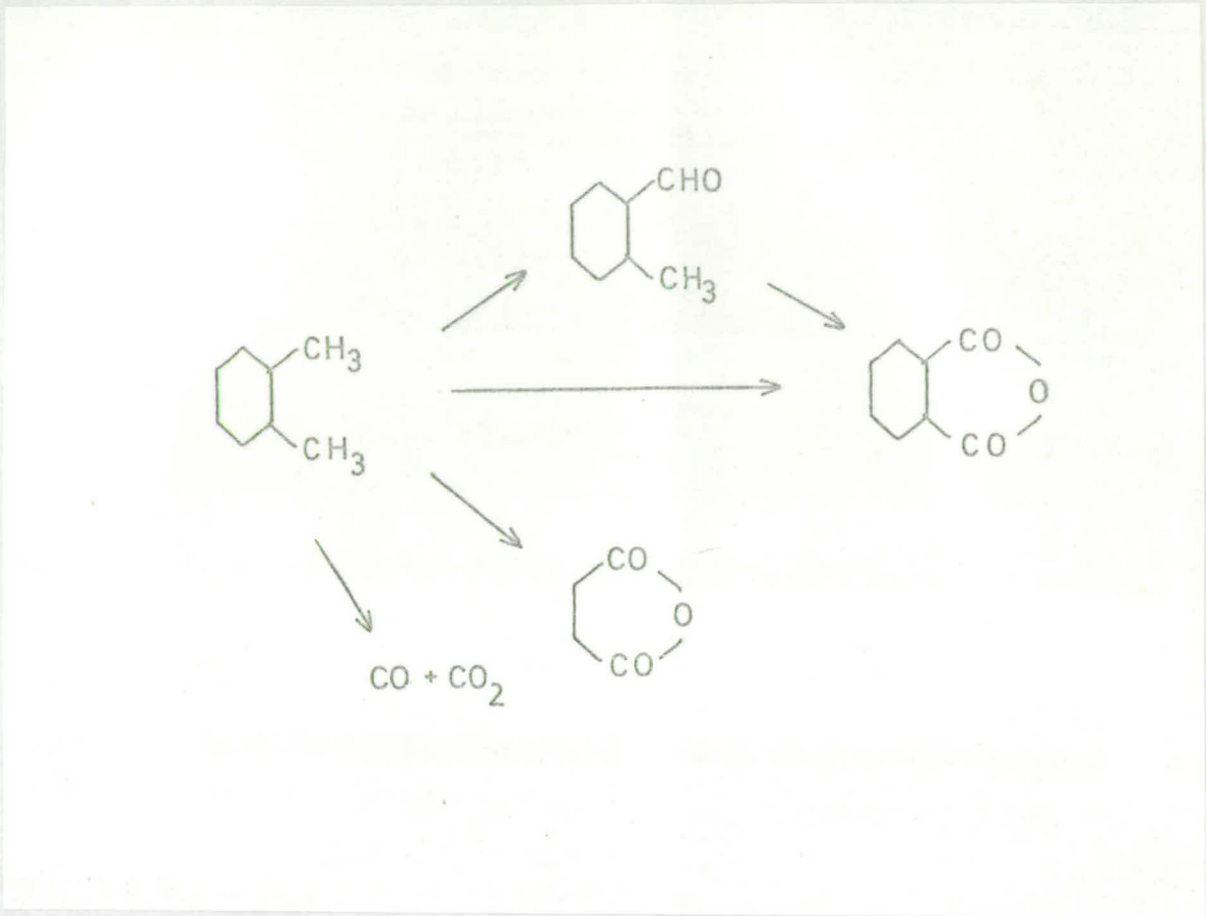
Fig. 2. o-Xylene reaction mechanism by Loftus and Satterfield

Levine (89) assumed two hypothetical reaction mechanisms, as below.



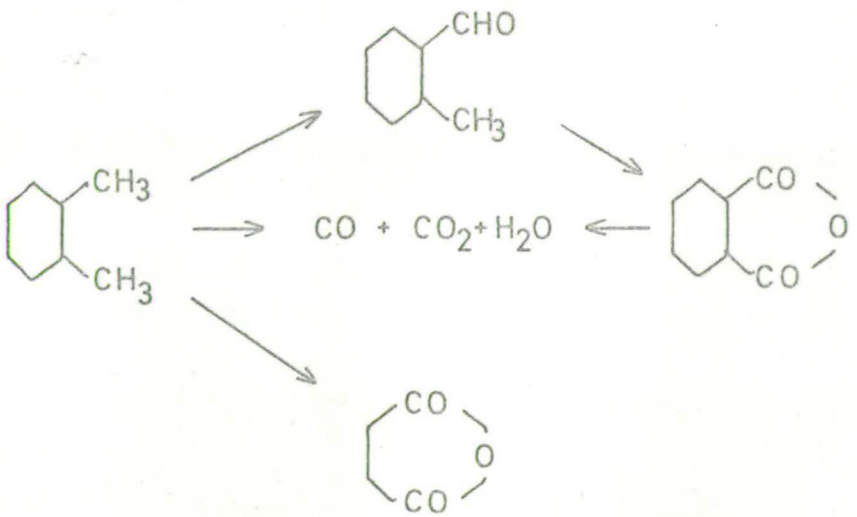
The second reaction mechanism includes alcohol compounds as intermediates, but no parallel reactions and also no maleic anhydride which has often been found by other investigators.

Simard postulated the following mechanism. His catalyst was vanadium on SiC.



The reaction order with respect to phthalic anhydride was unity.

A different scheme was postulated by E. Costa Novella et al (30) using a catalyst of V_2O_5-K_2SO_4-SiO_2 (10%, 33%, 57%, respectively).



The difference from Simard's scheme is no direct conversion of o-xylene to phthalic anhydride, and additional routes to combustion products. Rate constants for each step of the reaction were determined and the yield of phthalic anhydride was 0.52 (mole of PA/mole of o-xylene in feed) at 310°C. These are relatively simple schemes. Bernardini and Ramacci (28) proposed a more complex scheme for the oxidation of o-xylene on a silicon carbide-supported V_2O_5 catalyst as shown in Figure 3.

They found that phthalide, o-tolualdehyde, o-toluic acid and o-ethylbenzyl alcohol were oxidized to form phthalic anhydride. The vanadium oxide catalyst showed high selectivity of phthalide to phthalic anhydride and of o-toluic acid to phthalide, of o-methylbenzyl alcohol to o-tolualdehyde and of o-xylene to o-methylbenzyl alcohol.

According to the scheme, the first product of the oxidation is o-methyl-benzyl-alcohol. This alcohol is then rapidly oxidized in turn to o-tolualdehyde. The former reaction is the same as that of Wright's, mentioned previously. However, Wright assumed the production of o-tolualdehyde also occurred in parallel with the reaction of o-methyl-benzyl-alcohol. The o-toluadehyde is then converted to o-toluic acid and to the final product, phthalic anhydride. Maleic anhydride is produced from phthalic anhydride, from o-toluic acid by side reaction, and by direct conversion of o-xylene. This final route is in agreement with Blanchard's experimental result which used C^{14} labelled o-xylene (102).

The "carbon 14-labelled" o-xylene in Blanchard's work was formed by the series of reactions:-

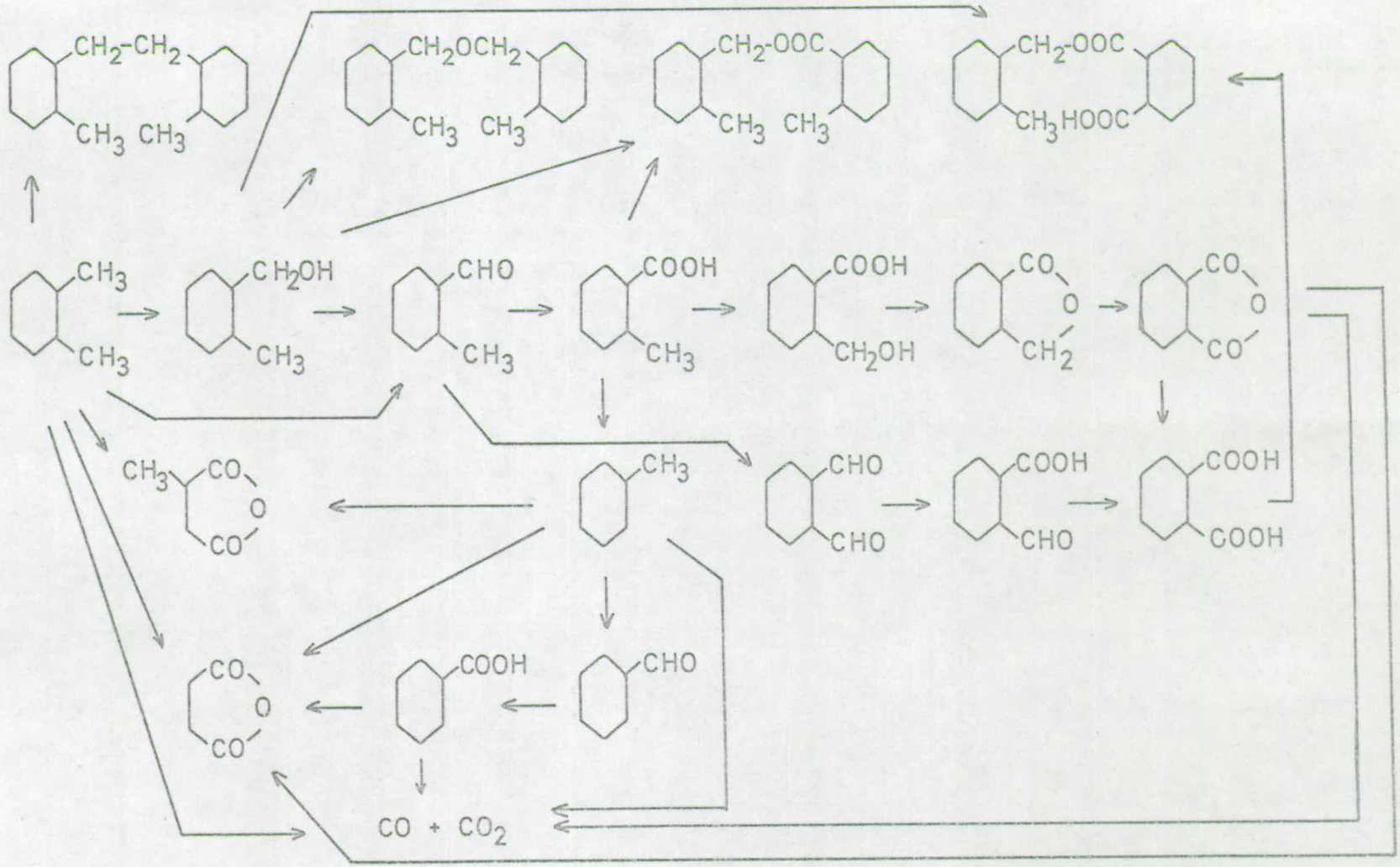
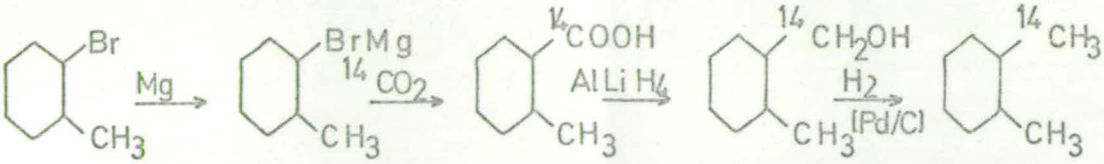
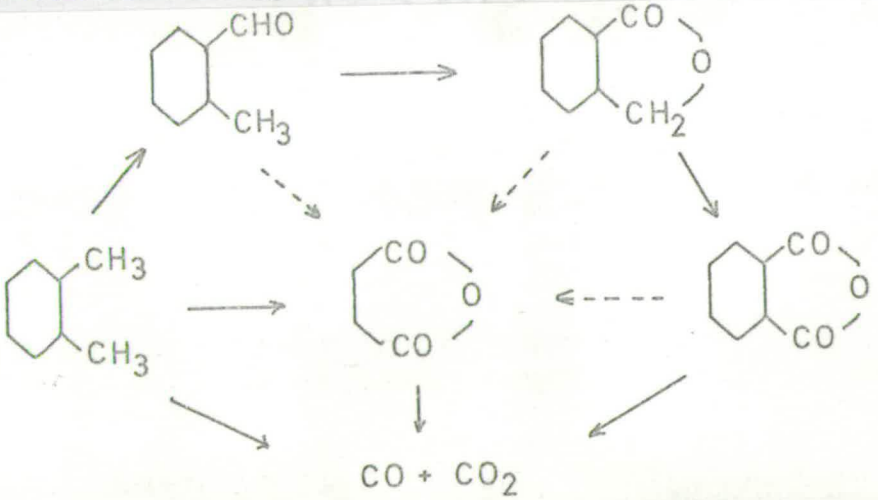


Fig. 3. o-Xylene reaction mechanism by Bernardini and Ramacci



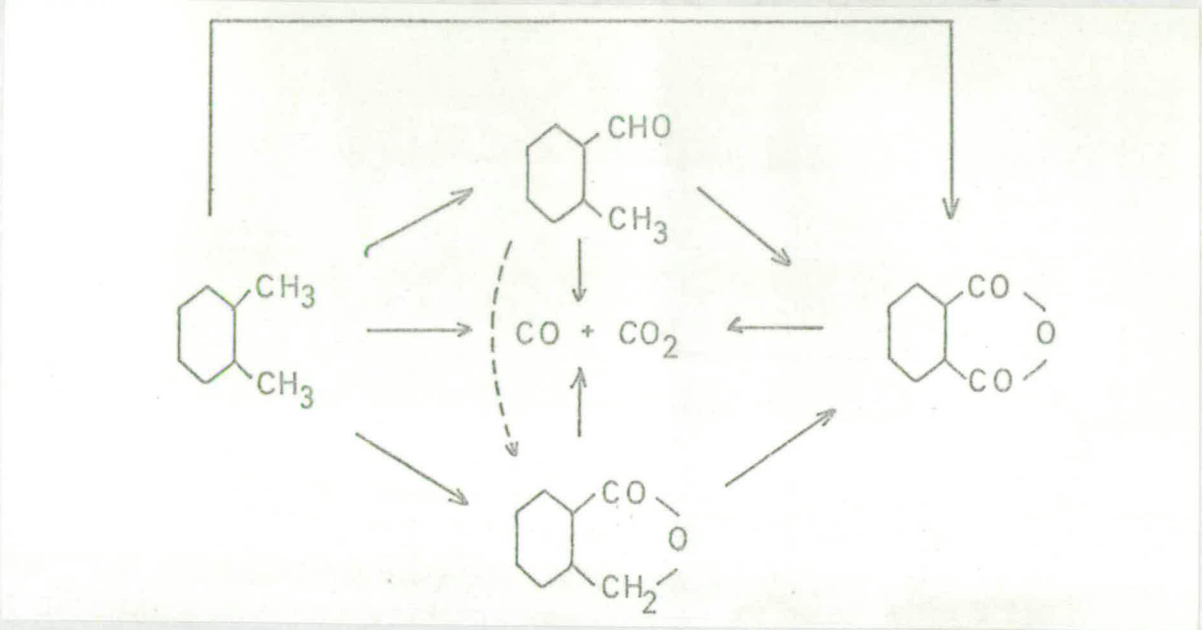
This o-xylene was then oxidised by air to minor products such as maleic anhydride at 420°C in the presence of vanadium pentoxide catalyst. The minor products did not contain C^{14}. In the case of oxidation of phthalic anhydride to CO from the labelled o-xylene at 470°C, the result was the same; i.e. - the CO included no radioactive carbon.

The results suggest that maleic anhydride is formed by degradation of the aromatic ring. If the formation of maleic anhydride occurs from phthalic anhydride, it can occur by both degradation of the aromatic ring and a remaining part of the anhydride. Since no C^{14} was found in maleic anhydride then it is plausible that maleic anhydride is <u>not</u> formed by oxidation of phthalic anhydride. The reaction scheme suggested is given below.



This result is similar to German and Langier's work on the oxidation of toluene over V_2O_5, MoO_3 and V_2O_5-MoO_3 catalysts at 400-450°C (90).

Herten and Froment (29) postulated a simple oxidation scheme, based upon product distribution curves, which includes products such as phthalic anhydride, tolualdehyde, phthalide, CO and CO_2.



They claim that the conversion of tolualdehyde into phthalide is not important. Since the conversion to maleic anhydride did not exceed 3% even when the o-xylene conversion was as high as 99.8%, maleic anhydride is not included in the scheme.

This review of the literature highlights the considerable uncertainty still surrounding the detailed structure of the o-xylene oxidation scheme. Part of this uncertainty may be attributed to differences in catalyst formulations, but much of it is due to inaccurate and insufficient data and a failure to properly interpret the data by statistical methods.

6. Methods of Preparation of the Catalysts*

Catalytic activity and selectivity are very sensitive to the method of preparation of the catalyst. Such details as the concentration of solution, contact time in solution, the procedure of washing and the drying temperature must all be optimised if the best results are to be obtained (78, 79, 80).

The distribution of pore size is one of the important factors which should be considered when preparing the catalyst. This, especially, strongly influences the selectivity. The ion-exchange method is better than the impregnation method for producing catalyst in which the distribution of pore size is narrow (91).

Recently, there is a tendency among manufacturers to reduce the quantity of metal in the catalyst because of higher costs and to improve the distribution of the metal throughout the support (80).

The relationship between the several factors involved in the manufacturing stage mentioned above are not established quantitatively at present. Finding a good catalyst is as much an art as a science.

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*References numbers : 33-58

Experience plays a large part in reducing the rather lengthy trial and error process. This might explain why such a wide variety of reaction mechanisms have been put forward.

Commercial catalysts are produced on a large scale and typical ones are easily obtained. However, details of the manufacturing process are not generally available. The patent literature is helpful with regard to the more recent catalyst formulations.

Commercial methods of preparation of the catalyst include precipitation, gel formation and impregnation. Other important procedures are ion-exchange, thermal fusion of the reactants, thermal decomposition of special compounds and acid or alkali leaching of special alloys or natural clays.

(1) Precipitation

In this method, it is desirable to make fine flock-shaped products, which have the greatest degree of homogeneous mixing and good performance for filtration, washing, drying and forming.

This method is mainly used for preparing catalysts comprising hydrous oxides, sulfides and carbonates. One starts with aqueous solutions of the desired constituents and mixes them together.

(2) Gel Formation

This is frequently used for hydrous oxides as major components. The method is quite similar to the precipitation method. There are advantages, which are (1) higher surface area of the final catalyst, (2) improved control of the density and porosity of the finished catalyst, (3) more rapid washing of impurities from the gelled material, and (4) ease of filtration of the product (92).

(3) Impregnation

The most important method is impregnation. The desired catalyst component is applied to the support either in aqueous solution or in the vapour phase. The porous support is generally in powder form initially and may be subsequently pelleted for ease of transport and depending upon the application, e.g. - packed bed or fluidized bed.

Methods of Preparation

The several methods of manufacturing the vanadia catalysts in practice are mentioned in the following. These are cited from recent patent literature. The active constituent of the catalyst mentioned in these was restricted to vanadium pentoxide. These catalysts are summarised in Table 5.

The catalyst support was mainly titanium oxide. The others were aluminium oxide, silica gel and natural ores. Therefore, the methods were divided into three groups for convenience, according to the kind of support:-

1) titanium oxide.

2) silica gel, alumina, magnesium silicate.

3) miscellaneous natural ores.

I. Titanium Oxide

1) NH_4SCN (400 parts) is melted at 130°C and treated with 200 parts vanadyl oxalate, then, at 55°C with 50 parts CH_3COCH_3. The diluted melt (500 parts) is added to 670 parts TiO_2 (0.2-0.5 mm spheres), heated to 200°C, placed in an oven into which air is passed, and heated for 2 hrs. at 400°C.

2) Granulated TiO_2 (863 parts) with a specific surface area of 9.8 m^2/g and 0.2-0.6mm diameter is mixed with 140 parts of a ground mixture of 15% V_2O_5 and 85% $K_2S_2O_7$ prepared by fusion at 400°C. After impregnation by heating for 3 hrs. at 600°C the catalyst is sieved.

3) NH_4VO_3(35.3g) is dissolved in 2ℓ water at 80°C, added to 70g TiO_2, evaporated until a skin began to form, treated with 3.6g orthotelluric acid in 10ml water, evaporated to dryness, heated for 16 hrs. at 540°C and sieved to 14-36 mesh. A gas comprising o-xylene 1, air 50, and N 49vol % is passed at 250-550°C (contact time : 9 sec) over 1 vol of catalyst diluted with 2 volumes of glass particles. Optimum yield occurred at 336°C when 92% of the o-xylene is consumed.

4) NH_4VO_3 (35g) is dissolved in 250ml HCl and 6ml C_2H_5OH, added to 63.6g of TiO_2 evaporated to dryness, and calcined in air for 16 hrs at 450°C.

5) 24 parts vanadyl oxalate and 48 parts thiourea is slowly melted. Vigorous frothing sets in at 180°C, and this temperature is maintained until gas evolution has practically ceased. After cooling to 60°C, the melt is diluted with 100 parts CH_3OH and 70 parts $(CH_2)_2CO$. 258 parts TiO_2 spheres (diameter 0.1-0.3mm) are immersed in the solution with slight stirring. The solution is fully absorbed and the product is dried at 100°C and then heated at 350°C until brown.

6) A mixture of 8.8 parts vanadyl sulfate and 23 parts K pyrosulfate in 25 parts H_2O is used to impregnate 73 parts TiO_2 of particle size 44-250μ. The paste is dried at 105°C and activated at 400°C.

7) $VOSO_4$ is added to aq. $K_2S_2O_7$ to give a blue solution, which is sprayed onto a solid TiO_2-SbO_3 mixture. The product is dried for 16 hrs. at 110°C and calcined for 6 hrs. at 400°C. Air containing o-xylene and 1% SO_2 is passed through a bed of 2.5 cm diameter and 0.6m high of the catalyst (40-50μ particle size) at 340-65°C and 9.2 sec residence time.

8) The catalyst consisted of a TiO_2 carrier with other catalytic components corresponding to (1) V_2O_5, 1-9% of the total; (2) one of the following: Sb_2O_5, Nb_2O_5, VO_2, SnO_2, PbO_2, MnO_2, GeO_2, TaO_2 : 0.1-9 moles per moleof V_2O_5, (3) K_2O, 0.4-4.0 moles per mole of Sb_2O_3, (4) SO_3, 0.5-3.0 moles per mole of K_2O. The TiO_2 is precipitated from acid solution and when washed, dried and calcined to have a grain size of 20-600μ and an internal surface of 5-200m^2/g. The other components can be added either as solids or in a solution. Thus TiO_2 having a surface of ~20m^2/g is mixed dry with enough Sb_2O_3 to give 6% of the final catalyst and then with a solution containing enough $K_2S_2O_7$ and $VOSO_4$ to give a final content of 2% K_2O, 2% SO_3 and 6% V_2O_5. The mixture is dried at 110°C compressed into tablets of 4mm x 4mm and calcined for 24 hrs at 400°C. The o-xylene vapor with SO_2 corresponding to 0.7 wt% of o-xylene, is passed through a 244cm depth of catalyst (the first 91.5cm of which is mixed to 50% with inert sand) at 0.066 kg/hr together with air at 2.345 kg/hr. The temperature is 346°C.

9) The catalyst applicable to solid fluidized beds, contains V_2O_5 2.8-2.9, Sb_2O_3 3.9-4.0, $K_2S_2O_7$ as K_2O 6.2-6.8, SO_3 9.8-12.0, Cr_2O_3 promoter 0-0.4% and TiO_2 support and is highly selective (> 70%). A mixture of TiO_2 of mesh width 0.044-0.149mm and Sb_2O_3 is impregnated with aq. V, Cr and K sulfate solutions and calcined for 5hrs at 500°C to give a catalyst containing V_2O_5 2.9, Sb_2O_3 4.0, K_2O 6.8, SO_3 12.0 and Cr_2O_3 0.4% with surface area 7m^3/g and particle size 50μ.

10) The catalyst comprises 1-20% by wt V_2O_5, 0.1-9 moles Sb_2O_3 per mole V_2O_5, K sulfate or pyrosulfate and TiO_2 support in the proportion 30-95% of the catalyst. The catalyst has a K_2O content of 0.4-4 moles per mole SbO_3, and a SO_3 content of 0.5-3 moles per mole of K_2O. Calcined TiO_2 is screened to -60 to +325 mesh screen size, (surface area 20 m^2/g and water pore volume 0.3 cm^3/g). It is dry-mixed with Sb_2O_3 and K pyrosulfate H_2O is sprayed onto a rotating bed of this mixture. The mixture is dried at 110°C and formed into 4 x 4mm pellets which are calcined at 400°C for 24 hrs.

11) TiO_2 powder (anatase type, $\leq$ 10μ diameter) 100 sulphur powder ($\leq$ 0.2μ) 50 parts, and some H_2O were mixed well, shaped into 3mm diameter x 3-4mm length pellets, dried at 80°C for 10 hrs. and fired at 900°C for 4 hrs. to give the catalyst support. The support is immersed in a vanadyl sulfate-K_2SO_4 solution (V/K mole ratio 2) for 1 hr, dried at 70°C and fired at 45°C in an air flow.

12) TiO_2 and Sb_2O_3 of 53-177 and 44μ particles size, respectively are homogeneous and impregnated with an aq. solution of $VO(SO_4)$, $K_2S_2O_7$ and Cs_2SO_4 in H_2SO_4, dried at 110°C and calcined for 5 hrs. at 450°C.

13) A mixture of 80g V_2O_5 and 20g KNO_3 are heated at 600°C, fragmented and ground, a mixture of 48g of the product and 752g TiO_2 are heated for 2hrs at 600°C.

II. Silica gel, Magnesium Silicate, Alumina

1) A mixture of 3390g $K_2S_2O_7$ and 1466g $NaHSO_4$ in H_2O is heated for 1 hr. at 350°C, 907g V_2O_5, 210g $H_2MoO_4.H_2O$, 33g $(NH_4)_2HPO_4$, and 11.1g Ag_2O added, and the mixture kept for 1 hr at 370°C, cooled and ground to give particles of size < 150μ. A mixture of 4800g particles

and 4610g silica gel (grain size 60-200μ) is agitated for 4 hrs at 350°C, kept for 4 hrs at 350°C, cooled and passed through a sieve (300μ openings).

2) A silica gel carrier of 195m^2/g surface area, 0.80 cc/g pore volume, and particle size 76-500μ is used. The carrier (250g) is impregnated with a solution of 20g K_2SO_4, 178g vanadyl oxalate (containing V_2O_5 of 12.7%), 30g H_2O and 9g H_2SO_4. The silica gel is dried for 16 hrs at 120°C and then impregnated again as above and redried. The material (294g) is then heated to 100°C and 41g H_3BO_3 in 150g H_2O is added. The mixture is dried at 120°C and calcined at 350°C for 16 hrs. yielding 300g of catalyst.

3) The particle size is 0.05-0.5mm and the carrier is rutile (obtained by calcination of anatase), argile or spherules of silica gel. 90g SiO_2 is impregnated with 86g $TiCl_4$ in 20ml CH_3OH and 60ml H_2O dried at 150°C, heated for 4 hrs. at 500°C and then treated with 22g of vanadium oxalate in 44g molten NH_4NCS being reheated for 3 hrs. at 250°C and 2 hrs. at 450°C.

4) Mg silicate balls (6mm diameter, 2500g) are coated with 400g aq. suspension of formamide 42.5, oxalic acid 18.7, V_2O_5 8.5, TiO_2 (anatase) 133, and Li acetate 0.3g at 300°C. 103g catalytic material is retained by the support. The dry catalyst is further heated to 450°C in a stream of air for 1 hr.

5) An aq. suspension of 42.5g $HCONH_2$, 18.7 oxalic acid, 8.5 V_2O_5 133 anatase, and 1 ammonium acid phosphate is added to 2500 mg silicate pellets (6mm diameter) at 300°C. The coated pellets are heated at 450°C for 1 hr. in a current of air.

6) V_2O_5 (210g) is dissolved in conc. HCl (1000g) containing NH_4Cl (134g) and the solution heated to 85-90°C, then mixed with MoO_3 (90g), cooled to 50°C and mixed with NaCl (15.8g) dissolved in distilled water (50ml). To the resulting solution P_2O_5 (2g) in distilled water (50ml) is added and the mixture is left for 12-20 hrs. and mixed with $AgNO_3$ (23.45g) solution in distilled water (50ml) and C_2H_5OH (160ml). The final mixture is spread on 2kg of α-Al_2O_3, dried at 90°C and the resulting catalyst maintained at 250°C for 4-6 hrs.

III. Miscellaneous Natural Ores

1) Steatite spheres (diameter 5.5mm, 469g) are moistened with 10cc of a solution prepared from 2.5g molybdic acid 4cc ethanolamine, 1cc H_2O, 5g urea and $HCONH_2$, dried at 200°C and heated for 15 min. at 830°C. The carrier is coated in a drum with a slurry of 270g anatase and 40g vanadyl oxalate in 100cc $HCONH_2$ and 75cc H_2O, dried at 200°C and calcined for 5 hrs. at 400°C.

2) A water solution (500cc) containing 12.5g NH_4 metavanadate and 8.1g NH_4 chromate is sprayed on granular silicon carbide (4-6 mesh) which is packed in a tube (inner diameter 20mm) and treated for 3 hrs at 450°C with preheated air (120 l/hr). The treated catalyst is taken out and kept for 30 min. at 700°C then cooled and used.

3) Oxalic acid (534g) and 15.4 NaCl are dissolved in 2400ml H_2O, then 620g NH_4VO_3 and 180g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ are added. An aq. solution of 7.2g H_3PO_4 and 5.6g H_3BO_4 is added, and an aq. solution of 25.2g $AgNO_3$ dropped in, 2600g carborundum granules added, the mixture gradually evaporated, and the residue heated for 8 hrs. at 400°C.

4) Ammonium metavanadate (20g) and ammonium chromate are dissolved in 800 ml hot H_2O, a solution of 0.45g GeO_2 in 20ml 20% NH_4OH added, the mixture stirred with 125g SiC of 8-10 mesh and evaporated, and the residue burned at 400°C for 3 hrs. and then at 700°C for 1.5 hr.

5) Vanadyl oxalate (790g) is dissolved in 1670g formamide and mixed with 10650g H_2O and 5900g of finely divided anatase. The mixture is sprayed on 75kg steatite balls of 6mm diameter, which are heated in a drum to 350°C. The sprayed balls contained 6.14% active component of which 0.48 is V_2O_5. Dropping this catalyst from a height of 3m caused only a 0.25% loss of activity, as compared with 12% loss for a catalyst prepared by the wet mixing and drying technique.

6) Porcelain pellets (6mm diameter) are heated at 350°C in a pill-coating drum and sprayed with a slurry of TiO_2, vanadyl oxalate, and $HCONH_2$ in H_2O. The coated pellets are heated for 4 hrs. at 400°C.

7) Talc spheres (6mm diameter) are heated to 300°C and coated with a 4% mixture containing 6% V_2O_5 and 94% anatase TiO_2.

8) H_3PO_4 (336g), and 140g kieselguhr are calcined at 1000°C for 3 hrs. and crushed. The carrier (70g) formed is mixed with aq. vanadyl oxalate (30g as V_2O_5) and 5.0g Ag_2SO_4, 7.5g thallium oxide and stirred at 70-90°C to make a paste. The paste is dried at 100-20°C for 1 hr and calcined at 500°C for 3 hrs.

9) H_3PO_4 (335g) and 140g diatomaceous earth are fired for 3 hrs at 1000°C and the solid pulverized. An aq. suspension of 70g of the powdered carrier, 9g V_2O_5, 21g equivalent V_2O_5 of aq. vanadyl oxalate, 5.1g Ag_2SO_4 and 1.6g $CsNO_3$ are stirred at 80°C to a paste, which is packed onto a stainless perforated plate, dried for 1 hr at 100-20° and fired for 3 hrs at 500°C.

10) Steatite granuls heated to 300°C are sprayed with an aq. suspension containing ZrO_3, anatase, vanadyl oxalate and formamide.

11) H_2O (270kg), oxalic acid (150kg) and V_2O_5 (60kg) under CO_2 are stirred at 70°C, $NH_4H_2PO_4$ (10kg) anatase (846 kg) $HCONH_2$ (270 kg) and H_2O (1050kg) added, and the mixture sprayed onto 100kg steatite balls at 300°C.

Table 5. Catalysts of Vanadium Oxides for the Oxidation of o-xylene to Phthalic Anhydride

Support	V_2O_5	Components in addition to V_2O_5	Yield: Phthalic Anhydride [mol %]	Yield: Maleic Anhydride [mol %]	Reference	Method
TiO_2 (0.2-0.5mm sphere)	11.5	NH_4SCN	...	...	117	I-1
Silica gel (60-200μ)	8.15	$K_2S_2O_7$, $NaHSO_4.H_2O$ H_2MoO_4, $(NH_4)_2HPO_4$, Ag_2O	63.8	...	118	II-1
TiO_2	15	$K_2S_2O_7$	71.0	6.6	119	I-2
Silica gel	4	K_2O, SO_3	...	...	120	
TiO_2, SnO_2 and ZrO_2	10-70	$NaVO_3$	88.4?	...	121	
TiO_2 and SnO_2	33.3	$NaVO_3$			121	
TiO_2 and ZrO_2	33.3	$NaVO_3$			121	
TiO_2	30	NH_4VO_3, TeO_2	71	...	122	I-3
Steatite (5.5mm)	0.35	Molybdic acid, Ethanol amine, Urea, $HCONH_2$ anatase	30.7	6.1	123	III-1
TiO_2	30.1	...	73	10	124	I-4

? : The units are unknown.

TiO_2	20.0	...	74	11	124	I-4
TiO_2	...	Thiourea	67.6	4.6	125	I-5
Silicon carbide (4-6 mesh)	...	NH_4metavandate, NH_4chromate	85.5?	12.9?	126	III-2
Silica gel (76-500μ)	12.7	K_2SO_4,H_3BO_3	...	...	127	II-2
Al_2O_3(3-5mm)	72.5	WO_3,PoO_5,Na_2O	71.1	8.1	128	
Pumice (3mm)	62.5	TiO_2, K_2SO_4	97?	0.07?	129	
Carborundum	46.5-81.3	MoO_3,P_2O_5,Na_2O,Ag_2O	76.8	8.6	130	III-3
Silicon carbide	9.5	CrO_3	...	...	131	
TiO_2 (44-250μ)	...	K pyrosulfate	70.2	...	132	I-6
Silica gel	...	NH_4NCS	73.5	4.8	133	II-3
Silicon carbide	55.5	Cr_2O_3,GeO_2	87.7?	...	134	III-4
TiO_2	1-4	K pyrosulfate, Sb_2O_3 (TeO_2)	70-80 (Selectivity)	...	135	
Mg silicate (6mm)	1-40	TiO_2,Al, Li, Zr oxides	79.5	...	136	II-4
Steatite (6mm)	< 15	TiO_2	...	...	137	III-5
TiO_2	3	Sb_2O_3,$K_2S_2O_7$	...	...	138	I-7

Porcelain pellet (6mm)	25	TiO_2,$HCONH_2$	77.1	4.6	139	III-6
Talc sphere	0.24	TiO_2(Anatase)	...	...	140	III-7
Silicate pellet (6mm)	4.2	$HCONH_2$, Oxalic acid Anatase	77.5	4.1	141	II-5
TiO_2	6	Sb_2O_5,Nb_2O_5 or SnO_2 etc.	87.2 (Selectivity)	...	142	I-8
α-Al_2O_3	...	MoO_3+Na,Li,Ca or Sr Oxides + or Phosphoric acid + or Ag oxide with Co or Fe oxides	...	...	143	II-6
TiO_2(50μ)	2.8-2.9	Sb_2O_3,K_2O, SO_3,Cr_2O_3	76.0 (Selectivity)	...	144	I-9
Mg silicate (7.5mm)	6	P_2O_5, Anatase	78.1	...	145	
Kieselghr	30.0-26.8	H_3PO_4 or + Ag_2SO_4, Thallium	...	...	146	III-8
Alundum	16.1-76.3	$TiCl_4$,K_2SO_4	> 10	...	147	
Mg silicate	6	P_2O_5, Anatase	77.4	...	148	
TiO_2(4mm)	1-20	Sb_2O_3, K_2O,SO_3	87.2 (Selectivity)	...	149	I-10

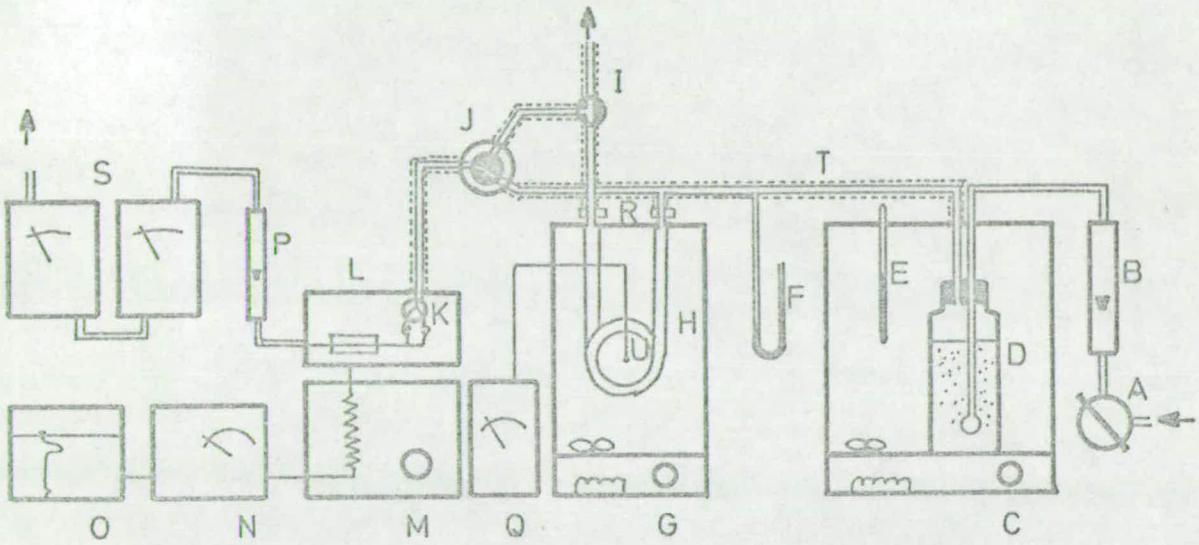
Phosphoric acid	28.1	Ag_2SO_4,Cs salt	83?	...	149	I-10
Alundum or Silicon carbide	...	Tartaric acid	90.2?	4.0	150	
Alundum	...	TiO_2 or Zr oxalate	76.6-69.5	...	151	
Alundum, Carborundum	...	TiO_2,K_2SO_4	73.8	...	152	
Alundum	...	TiO_2,K_2SO_4	68.1	...	152	
Alundum, Carborundum	...	K_2SO_4	58.0	...	152	
Alundum, Carborundum	...	TiO_2	53.8	...	152	
Steatite	4.1	ZrO_3,$HCONH_2$	...	...	153	
Steatite	6	ZrO_3,TiO_2	...	...	154	III-10
Steatite	6	P_2O_5	77.4	...	155	III-11
TiO_2	6-9	Phosphate	79.5	...	156	
TiO_2	6	ZrO_2	79.5	...	157	
TiO_2	...	Sulphur powder	71.6	...	158	I-11
TiO_2	2.7	Sb_2O_3,$Cs_2S_2O_7$,$K_2S_2O_7$	71.9	6.3	159	I-12

7. Experimental Procedure

Apparatus

Figure 1 shows the experimental flow sheet and apparatus. The compressed air flow rate was controlled by a regulator (A) and was bubbled through o-xylene before entering a tube reactor (H). The reactor has connections (R) at both ends for convenience of re-packing the catalyst into the tube. o-Xylene and the gaseous products were analysed by a Perkin-Elmer flame ionization detector (L) and gas chromatograph (M). The peak areas were integrated by a Kent Chromalog integrator (N). The sample valve (K) had dual sample loops. The carrier gas was nitrogen at a pressure of 2.0 kg/cm^2. Both CO and CO_2 contents were analysed (CO_2 was measured by Grubb Parsons Infrared Gas Analyzer). The calibration curves were obtained by standard gas samples and checked occasionally.

The tube from the o-xylene bubbler to the gas chromatograph was heated with thermocord and lagged with asbestos tape (T) in order to prevent deposition of phthalic anhydride or other higher melting point products inside the tube. The temperature of the line was controlled to minimise any reactions which may occur. It was periodically washed with acetone once a week to remove deposits and prevent choking.



A. Regulator for compressed air
B. Rotameter
C. Thermostat
D. o-Xylene bubbler
E. Thermometer
F. Manometer
G. Thermostat for a reactor
H. Tube reactor
I. Valve
J. Valve for inlet and outlet gas analyses
K. Sample valve
L. Flame ionization
M. Gas chromatogragh
N. Integrator
O. Recorder
P. Rotameter
Q. Electric thermometer
R. Connections
S. CO and CO_2 Gas analyzers
T. Thermocord and asbestos tape
U. Thermocouple

Fig. 1. Experimental flow sheet

The reactor tube was contained in a thermostat (G) which could be set to any desired temperature. A thermocouple (U) was inserted in the thermostat and positioned at the center of the coiled tube reactor (as shown). The tube reactor is made of aluminium and its length is 90cm, inner diameter 7mm.

o-Xylene liquid in a bubbler was held at a constant temperature of 30°C throughout the experiment by a thermostat. Its vapor pressure, therefore, was always constant. A laboratory reagent grade (BDH Chemical Ltd.) was employed.

Catalysts

Ten kinds of catalysts were employed with V_2O_5 as active component. Six catalysts were supported with TiO_2, one with Al_2O_3, one with corundum and the other two were commercial. The composition of the catalysts employed is shown in Table 1 together with the conditions of preparation.

The method of preparing V_2O_5-TiO_2 catalysts (B2, B5, B7, C1, C2 and C3) was as follows:- V_2O_5 powder (laboratory reagent grade, BDH Chemicals Ltd.) was heated in a porcelain crucible in an electric furnace for forty minutes at 800°C and completely melted. Then half of the required amount of TiO_2 powder was added and stirred. Because of the increase in viscosity, it was heated further. Forty minutes later, the remaining TiO_2 powder was added and the temperature raised to 900°C. The mixture was stirred every hour to promote homogeneity. After heating for several hours (the time depending on the catalyst as shown in the table) and cooling, the lumps were crushed and the product was sieved. The diameter of catalyst employed in each experiment was between 3-5mms.

For V_2O_5-Al_2O_3 and V_2O_5 - corundum catalysts (B3 and B4), V_2O_5 powder was mixed together with Al_2O_3 spheres in a crucible. During heating for one and a half hours, the mixture was stirred twice and the support was coated with the melted V_2O_5 uniformly and showed a black gloss appearance. After heating, the surface became brown and dry, indicating that V_2O_5 had penetrated into the support. Cylindrical V_2O_5 - corundum catalyst was prepared by the same method.

The characteristics of TiO_2 employed B7 and C1 are shown in Table 2.

Calculation of Selectivity

The tendency of a catalyst to produce a particular product may be expressed in many ways. Selectivity, however, is a convenient measure of this tendency.

The selectivity for production of desired component may be defined as,

$$\text{Selectivity} = \frac{[P]}{[R]}$$

where [P] is the quantity of product P when [R] of reactant R is consumed. The selectivity in this report refers to phthalic anhydride, phthalide and o-tolualdehyde, so [P] is the quantity of these products analysed by the gas chromatograph. [R] is the quantity of o-xylene reaching, which is found by subtraction of inlet and outlet values to and from the reactor. Correction factors are necessary to calculate the selectivity and carbon balance from the data of the gas chromatograph, because the integrated peak area of the gas chromatograph for each mole of product and reactant are not the same.

The correction factors are shown in Table 3. Each factor is given by the integrated peak area for phthalic anhydride (e.g. 1mole %) divided by the integrated peak area of the same molar concentration of the corresponding substance (1mole %). These factors are determined by the following procedure.

Pure material (e.g. o-xylene) was placed in a bubler in a thermostat and held at a constant set temperature. Air at a constant flow rate was passed through the bubbler to a gas chromatograph. The integrated peak area corresponding to the concentration of the material in the air stream was measured. The latter may be determined from the vapor pressure of material in the bubbler and the temperature. By changing these conditions, the factor at all other concentrations may be found. By this means, it was confirmed that the integrated peak area of each material varies linearly with the concentration.

Table 1. Conditions of Preparation and Selectivities of Catalysts Employed

Catalyst	Support	Preparation			Performance	
		V_2O_5 [wt %]	Temperature of Furnace [°C]	Heating Period [hr]	Best Selectivity [%]	Corresponding Conversion [%]
B1	SiC (3-6 mesh)	9.0	...	...	71	95
B2	TiO_2	61.0	900	5	74	98
B3	Al_2O_3 (4mm sphere)	23.4	850	4	74	> 54
B4	Corundum (4mm cylinder)	18.0	800	5	62	> 30
B5	TiO_2	60.0	900	4.5	75	> 95
B6	Silica gel (5mm cylinder)	...	...	...	68	> 30
B7	TiO_2 (Rutile)	46.6	900	6	69	> 20
C1	TiO_2 (Rutile)	37.5	900	6	76	> 70
C2	TiO_2	56.4	900	5	74	99
C3	TiO_2	69.9	900	3	45	98

Table 2. Specifications of TiO_2 employed in Catalysts B7 and C1

Material	rutile 98.9 %	rutile 99.9%
Impurities	SiO_2, Al_2O_3 less than 0.1%	...
Primary crystal size	greater than 0.5μ	...
BET surface area	2 m^2/g	1 m^2/g
Sample No.	CLD 746/2	CLD 746/5

Made by British Titan Products

Table 3. Correction Factors for Integrated Peak Areas in Gas Chromatograph

Material	Factor
o-xylene	0.75
Phthalic anhydride	1.00
Maleic anhydride	1.25
o-Tolualdehyde	0.86
Phthalide	0.75

8. Results and Discussion

Conversion and Selectivity

Experimental conditions and results are shown in Table 6. Selectivities are shown in Figure 4. Mean selectivities to 8C products (phthalic anhydride, phthalide and o-tolualdehyde) for all catalysts are listed in Table 1.

In all cases studied, the concentration of o-xylene in air was 1.1mole % and all runs were made at the same contact time, so that the conversion of o-xylene increased with increase of temperature. The variation of products composition and yields with the conversion might be some what different than if studies were made at constant temperature but with varying flow rates.

Several catalysts show a maximum selectivity near to 400°C. If the temperature is too high, the conversion becomes near complete but the selectivity begins to fall.

Catalyst C3(V_2O_5-TiO_2) showed the lowest selectivity in Table 1, compared with the other vanadium pentoxide catalysts (4 to 5 hours). If this is so the selectivity can be improved by extending the heating period.

Brookes et al (114) showed an influence of the calcination temperatures on the selectivity. When V_2O_5-TiO_2 catalyst (Bib III; V_2O_5, 10.5 mole %; TiO_2, 89.5%) was calcined at a temperature of 720°C from 500°C the selectivity was improved, i.e. - a selectivity of 55% at 500°C, 60% at 720°C (a gas flow rate of 0.25 ℓ/min, a conversion of 60%). However, when the calcination temperature was 1000°C, the activity of the catalyst was reduced.

Although the highest amount of V_2O_5 (69.9 wt%) was present in catalyst C3, the selectivity was the lowest. Bhattacharyya and Gulati (8) found that the selectivity of V_2O_5-kieselguhr catalyst become independent of V_2O_5 concentration above 31%. It is apparent from this and Tables 1 and 6 that increasing the amount of V_2O_5 in the catalyst does not always increase the value of selectivity.

The kind of catalysts supported with TiO_2 (e.g. B7 and C2) investigated contains nearly 50wt % of V_2O_5 and other catalysts more than 60wt % except C1.

It is very difficult to obtain fused catalyst with less than 50 wt % V_2O_5 by the present method of manufacture. This seems to be a disadvantage.

Figure 4 shows the trend selectivity with changing reactor temperature, and Figure 6 also shows selectivity and conversion based on the former figures. As can be seen from these figures, the highest selectivity is obtained when the conversion is nearly 100%. All catalysts except C3 have selectivities to phthalic anhydride of above 50% and to BC products of approximately 75%.

Catalysts B2 and C2 show selectivities of 74%. These are supported with the same TiO_2, and were prepared at the same temperature of 900°C and 5 hours heating in the furnace. However, the composition of the catalysts as regards V_2O_5 is slightly different, that is, 61 wt % in B2, 56.4 wt% in C2. Therefore, these catalysts are very similar. The mean contact time was 0.58 sec in the both cases. Catalyst B2 shows a constant selectivity of 74% over 410°C, as shown in Figure 4. However, C2 shows a maximum value at 390°C, and a slightly decreasing selectivity over 390°C.

Catalyst B5 which was prepared under similar conditions, showed a relatively high selectivity of 75%.

Abo et al (26) investigated the oxidation of o-xylene over vanadium oxide-potassium catalyst supported with titanium oxide in the temperature range between 370 and 410°C using a 2 inch inner diameter fluidized bed reactor. They obtained a maximum selectivity of 71.6% to phthalic anhydride at an o-xylene conversion 99.5%, which is almost the same value as this data.

In Figure 5, the yield curve shows that catalyst B2 produces relatively small amount of side products in relation to phthalic anhydride at large o-xylene conversions. At 99.7% conversion, the only side product (apart from combustion products) is maleic anhydride (3.5%). At 50% conversion, yield of o-tolualdehyde is nearly 9%, phthalid is 7%.

Catalyst B3 which consists of 4mm Al_2O_3 spheres as support requires a higher temperature compared with catalyst B4 to achieve complete conversion of o-xylene. This might be due to the presence of internal diffusion limiting the reaction rates. Inspection of the catalyst indicated that V_2O_5 had penetrated to the centre of the

spherical support.

The yield of o-tolualdehyde at 50% conversion is about 10% the same as for catalysts B2 and C2.

Bernardini and Ramacci (28) obtained a yield of 53.7% of phthalic anhydride from o-xylene oxidation in their work using vanadium pentoxide catalyst supported with corundum, kaolin and silica as promoter. At 500°C and a contact time of 0.07sec, o-xylene conversion was 62.7% and other yields were maleic anhydride, 1.00%; phthalide, 1.00; o-tolualdehyde, 1.45% and benzoic acid, 0.30%. The value of o-tolualdehyde, 1.45% is much lower than for catalyst B4.

Catalyst B4 supported on corundum shows a low yield of phthalic anhydride, approximately 40% only in this experiment. Since this catalyst and that of Bernadini and Ramacci showed only moderate selectivity, in spite of the use of promoters in the latter work, it is probably necessary to look for another way of making the catalyst when using corundum as support.

"Alumina supported" vanadium pentoxide catalyst (alumina 85%, V_2O_5 15%) showed a 44% maximum yield of phthalic anhydride and 10% of maleic anhydride at 330°C in the work of Costa Novella et al. (30). They also investigated three other catalysts supported with alumina of slightly different composition. However, they all showed lower yields of phthalic anhydride. Two silica-supported catalysts (silica 57% and 55%, V_2O_5 10%) were also tested by Costa Novella et al. with yields of phthalic anhydride of 52% and maleic anhydride of 15% at 310°C.

These results are similar to the present work in the case of catalyst B4 which is supported with alumina. This catalyst shows 49% yield of phthalic anhydride but a lower yield of maleic anhydride (2%) compared with their data, and it requires a higher temperature of 490°C. Below 400°C, the conversion of o-xylene was less than 8%.

Blanchard and Vanhove (102) studied the oxidation of o-xylene employing V_2O_5-TiO_2 catalysts. They used various amounts of TiO_2 to V_2O_5 in the catalysts from 0 to 100% to study the influence on the selectivity, and obtained interesting results. The selectivity depended on the amount of TiO_2 in the catalyst, that is, TiO_2 of 35% showed a selectivity of 60% and TiO_2 of 25 to 50% and 100% showed the lowest selectivity. Good selectivity of 74% was obtained at 12.5% TiO_2 and the highest of 75.5% at 90% TiO_2.

TiO_2 supported catalysts such as B2, B5, B7, C1 and C2 were compared with their results. However, there are some differences in methods of preparation and experimental conditions between this and their experiments. Their results showed selectivities of 68% at 41% TiO_2 and 71.5% at 54.5%, but catalysts B2, B5 and C2 show selectivities of 74, 75 and 74% at 39, 40 and 43.6% TiO_2 respectively, and C2 shows 76% at 62.5%. These values are higher than their values by about 5%. In the case of catalyst B7, the selectivity is 69% at 53.4% TiO_2, which is good coincidence with their results.

Two kinds of commercial catalysts (American and German) have also been investigated. The American catalyst B1 (Catalyst and Chemicals Inc.) has a relatively high selectivity of 71% at 99% conversion and over 410°C. This value is the same as in Brookes'

report (114). The yield of phthalide at this conversion is 8.1%. In the case of the German catalyst B6 (Kontakt Wo), the selectivity is 68% at a conversion of o-xylene of 24 to 87%.

Bhattacharyya and Gulati (8), who studied vanadium pentoxide catalyst supported with silica gel (V_2O_5-silica gel, 20 : 100) similar to the German catalyst (B6), found a relatively poor selectivity for oxidation to phthalic anhydride of 42.9% at a contact time of 0.58 sec and 52.2% at 0.84 sec. In the case of V_2O_5-kieselguhr catalyst (kieselguhr contains silica), vanadium pentoxide concentrations above 31% do not lead to any improvement in phthalic anhydride yield.

Both catalysts B7 and C1 employed similar rutile supports (TiO_2: British Titan Products) as shown in Table 2. Catalyst C1 showed the highest selectivity of 76% of all the catalysts in this experiments, but catalyst B7 showed a lower value of 69% selectivity.

Parks and Allard (94) found that a fused vanadium pentoxide catalyst was less active for oxidizing mixed (o-, m- and p-) xylenes than the Alfrax-supported vanadium pentoxide catalyst. Bhattacharyya and Gulati (8) reported that while various vanadates, as well as molybdic oxide and phosphomolybdic acid, were poor catalysts, the activity of vanadium pentoxide-kieselguhr was appreciable. This catalyst gave a maximum yield of 42.7% to phthalic anhydride and 11.3% to maleic anhydride at 400°C. The fused vanadium pentoxide catalysts, in general, give considerably improved conversion and selectivity. Herten and Froment (29) obtained a high selectivity of 76% at 325°C and only 3% maleic anhydride yield. However, the precise composition of the catalyst was not given.

Addition of some modifiers to a catalyst may improve the selectivity. In the patent survey in Chapter 6, there are a number of kinds of modifiers reported. Brookes et al (114) obtained a high selectivity of 84% using catalyst Bib. I. (V_2O_5:2.9, TiO_2: 91.3, Sb_2O_3:1.8, K_2O_5:1.8, SO_3:2.2mole %, from W.R. Grace and Co. Patent (149)).

The surface areas of the catalysts used here were not measured, but it may be one of the factors influencing the conversion. Bhattacharyya and Gulati (8), however, showed that comparison of surface areas with data on efficiency of o-xylene oxidation to phthalic anhydride did not show any correlation. One example showed that while unfused vanadium pentoxide-kiselguhr catalyst had a surface area of 22.19m^2/g, fused unsupported vanadium pentoxide catalyst, which exhibited the highest activity had the lowest surface area of 0.4578m^2/g.

We must now consider the effect of diffusion on heterogeneous catalytic reactions. First, the problem of diffusion mass transfer to the external surface of the catalyst, and second the problem of in-pore diffusion in the catalyst.

The absence of mass and heat transfer effect at the external film was established experimentally . Experimental runs were made a a constant contact time but with differing gas feed rates and catalyst volumes. Typical results from some runs are shown in Figure 7. Where the gas flow rate is over 11cm^3/sec, mass and heat transfer appear to be unimportant.

In order to check for the possibility of diffusion resistance in the pores of the catalyst, there is a useful criterion (110).

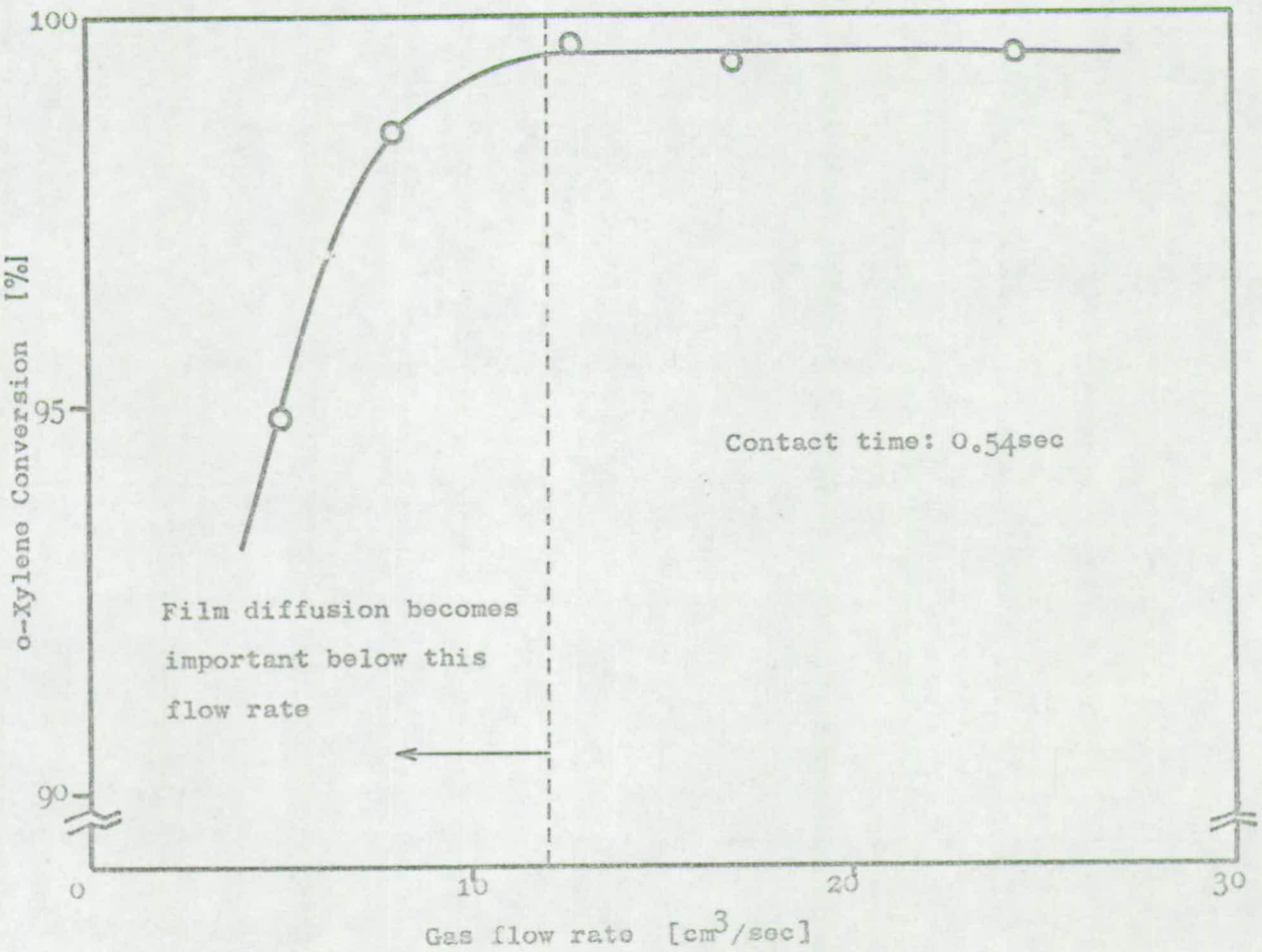


Fig. 7. Determination of the Influence of Mass and Heat Transfer on Reaction

For the isothermal case, a criterion for negligible resistance to in-pore diffusions is the following,

$$h = \frac{R}{3}\sqrt{\frac{k}{D}} \ll 1$$

where R is the radius of the spherical catalyst pellet, k is the rate constant per unit volume, and D is the effective diffusivity in the pellet. The following values were assumed for the estimation; R=0.20cm, k=0.674/sec (from Juusola, Mann and Downie (1)) and D=1cm^2/sec.

$$h = 0.055$$

From this, the ratio of the rate of in-pore diffusion to the rate of oxidation in the present experiments may well be negligible.

Rate Constant and the Activation Energy

The Arrhenius plots from the data with each catalyst are shown in Figure 8. In the higher range of the temperatures (the minimum temperatures depended on the catalysts), rate studies lead to a pseudo-first order kinetic law for o-xylene consumption and overall activation energies were calculated there from as shown in Table 7.

Catalyst B2 has the maximum activation energy of 37kcal/g-mole and catalyst B5 has the minimum value of 15kcal/g-mole.

Satterfield and Loftus (68) reported that the reaction rate was first order respect to o-xylene and had an activation energy of

20kcal/mole. Wright (12) found that the values of the activation energy in the temperature range 410 to 550°C were 38,39 and 40kcal/mole for o-, m- and p-xylene respectively. It was shown that the order of relative ease of oxidation is ortho>meta>para. The kinetics of inhibitor consumption in o-xylene was studied by Denisova and Denisov (13). They showed that chain initiation in o-xylene proceeds by a bimolecular reaction: $W_o=k[RH][O_2]$. The activation energy of chain initiation was $E=31\pm1$ kcal/mole, thus, the rate equation is $k=2.0\times10^{8}\exp(-31000/RT)$. The temperature range was between 110°C and 150°C. Therefore, it cannot be compared with the present data directly.

Juusola, Mann and Downie (1) studied the kinetics of o-xylene oxidation using a catalyst of "potassium sulfate-promoted" vanadium oxide on silica carrier, and found that the rate constant was 6.74×10^{-4} ℓ/g-catalyst.sec (310°C) and well correlated in the temperature range 290°C and 310°C by the Arrhenius relationship.

$$k_r = 16.8 \times e^{-28000/RT}$$

The activation energy 28kcal/mole is coincident with catalyst B7 in the present work in spite of the difference in supports.

Abo et al (26) found the overall oxidation rate of o-xylene was proportional to the concentration of o-xylene. The apparent activation energy was 10kcal/mole for a catalyst particle size of 0.8mm, which is a smaller value than the present data and indeed any other literature values. There are some catalysts for which the slopes on Arrhenius plots are changed at a particular temperature.

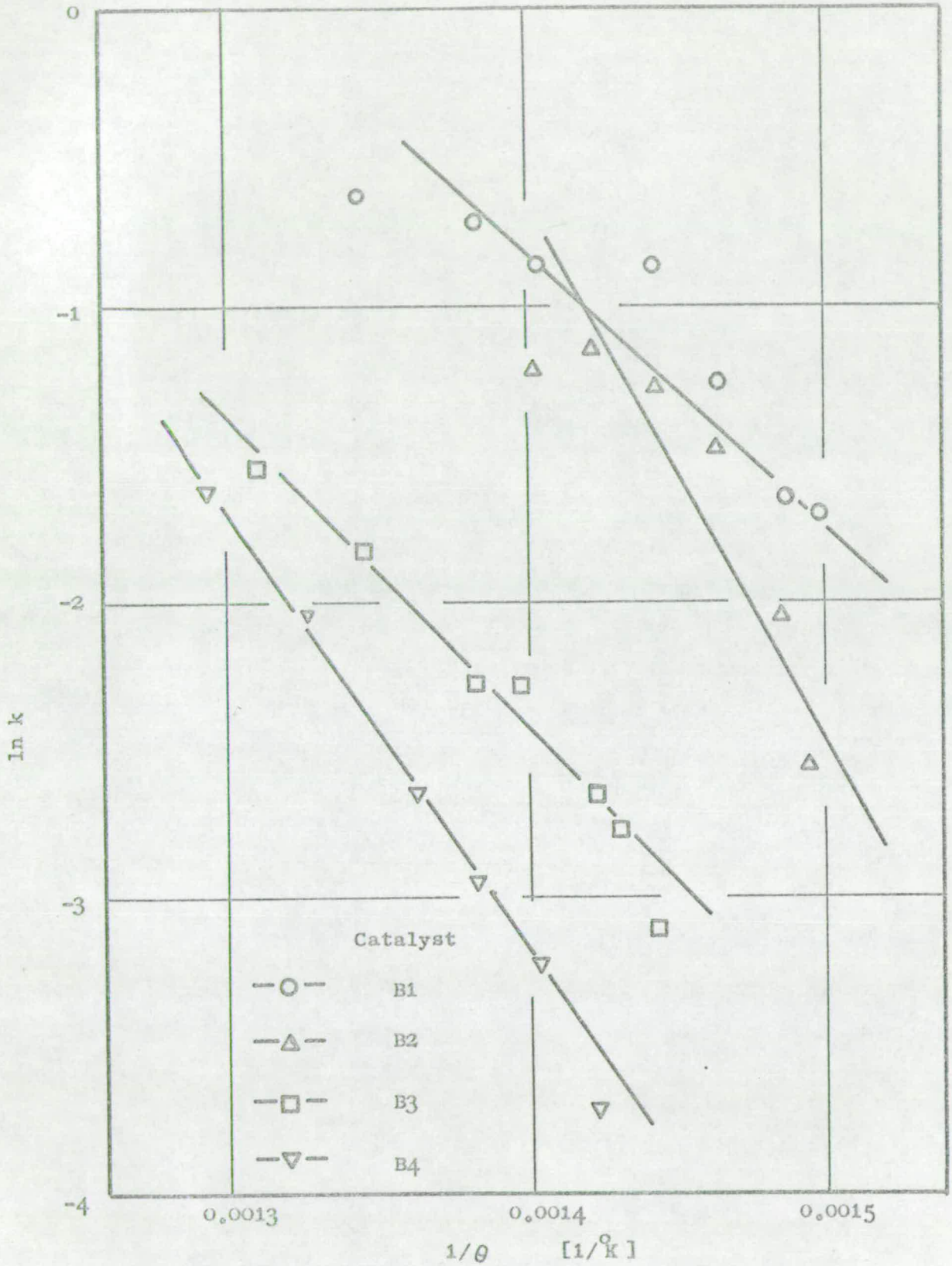


Fig. 8-1. Arrhenius plots of vanadium pentoxide catalysts

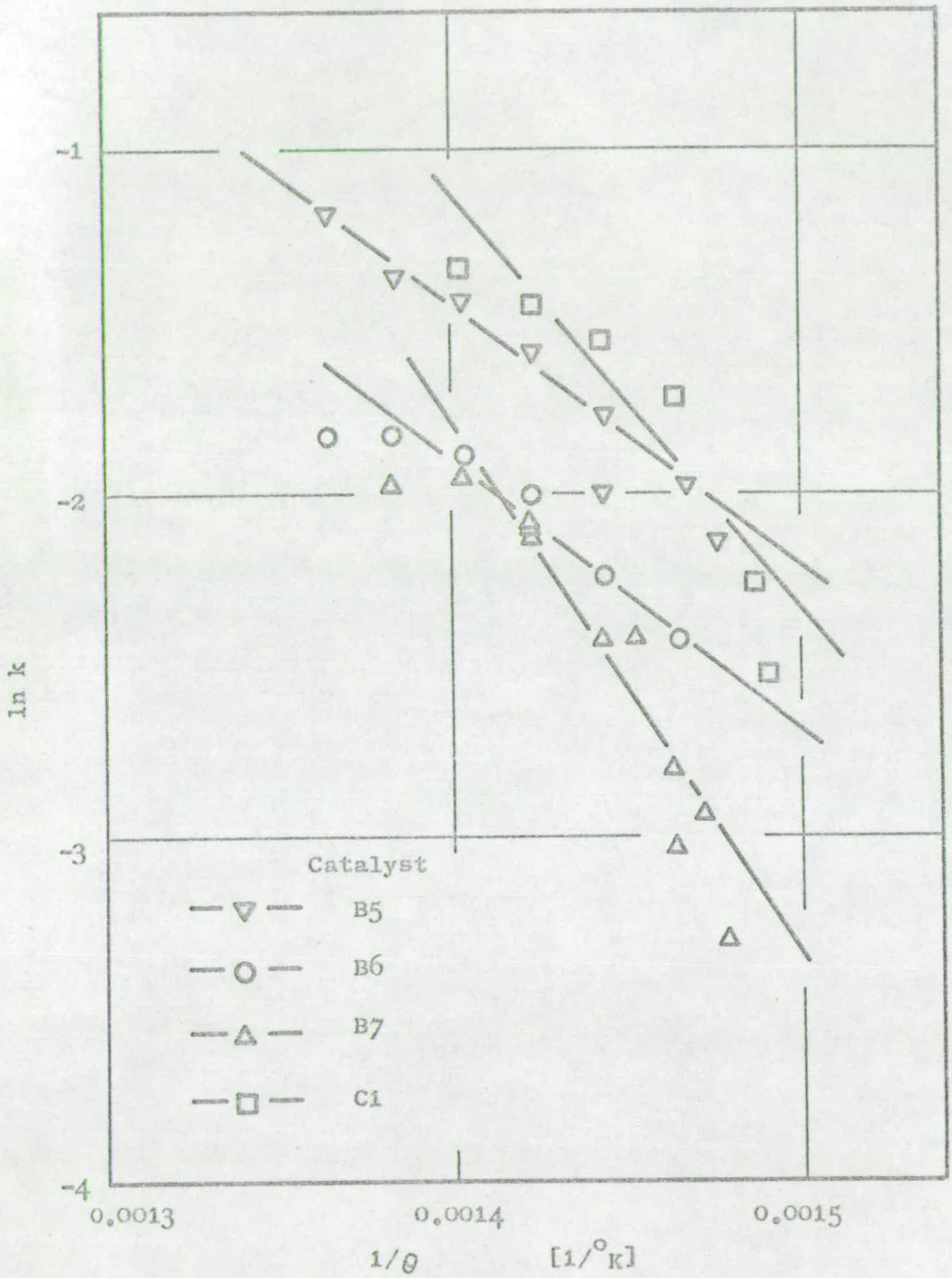


Fig. 8-2. Arrhenius plots of vanadium pentoxide catalysts

Table 7. The Rate Equations

Catalyst	
B1	$k = 1.33 \times 10^{5}\ e^{-17900/RT}$*
B2	$k = 1.95 \times 10^{11}\ e^{-37700/RT}$
B3	$k = 4.68 \times 10^{5}\ e^{-20200/RT}$
B4	$k = 5.35 \times 10^{7}\ e^{-29800/RT}$
B5	$k = 9.77 \times 10^{3}\ e^{-15100/RT}$
B6	$k = 1.09 \times 10^{4}\ e^{-15900/RT}$
B7	$k = 4.88 \times 10^{7}\ e^{-27800/RT}$
C1	$k = 8.59 \times 10^{6}\ e^{-24200/RT}$

---

*k = The first order rate constant [g-mole/g-Catalyst.hr.atm]

R = 1.986 [cal/mole.^{o}K]

In Figure 9, the slope of the curve changes from 50kcal/mole at a high temperature to 20kcal/mole at a low temperature. The reason could be a change in the oxidation mechanism in the catalyst. This phenomenon is remarkable in the case of the larger size supports such as catalysts B3 and B4 which are 4mm alumina spheres and corundum cylinders respectively. Because of the comparative large cross-sectional area of such a catalyst particle and the long distance from the center to the surface, there could be a considerable distribution of temperature inside the catalyst and also some difficulty in product diffusion from the pores.

The result can also be explained in terms of internal diffusion. If the Thiele modulus is large, the observed reaction rate depends on the square root of the true reaction rate constant. The observed activation energy for fast reactions in small pores is only one half of the true value in large pores where diffusion does not influence the rate (111).

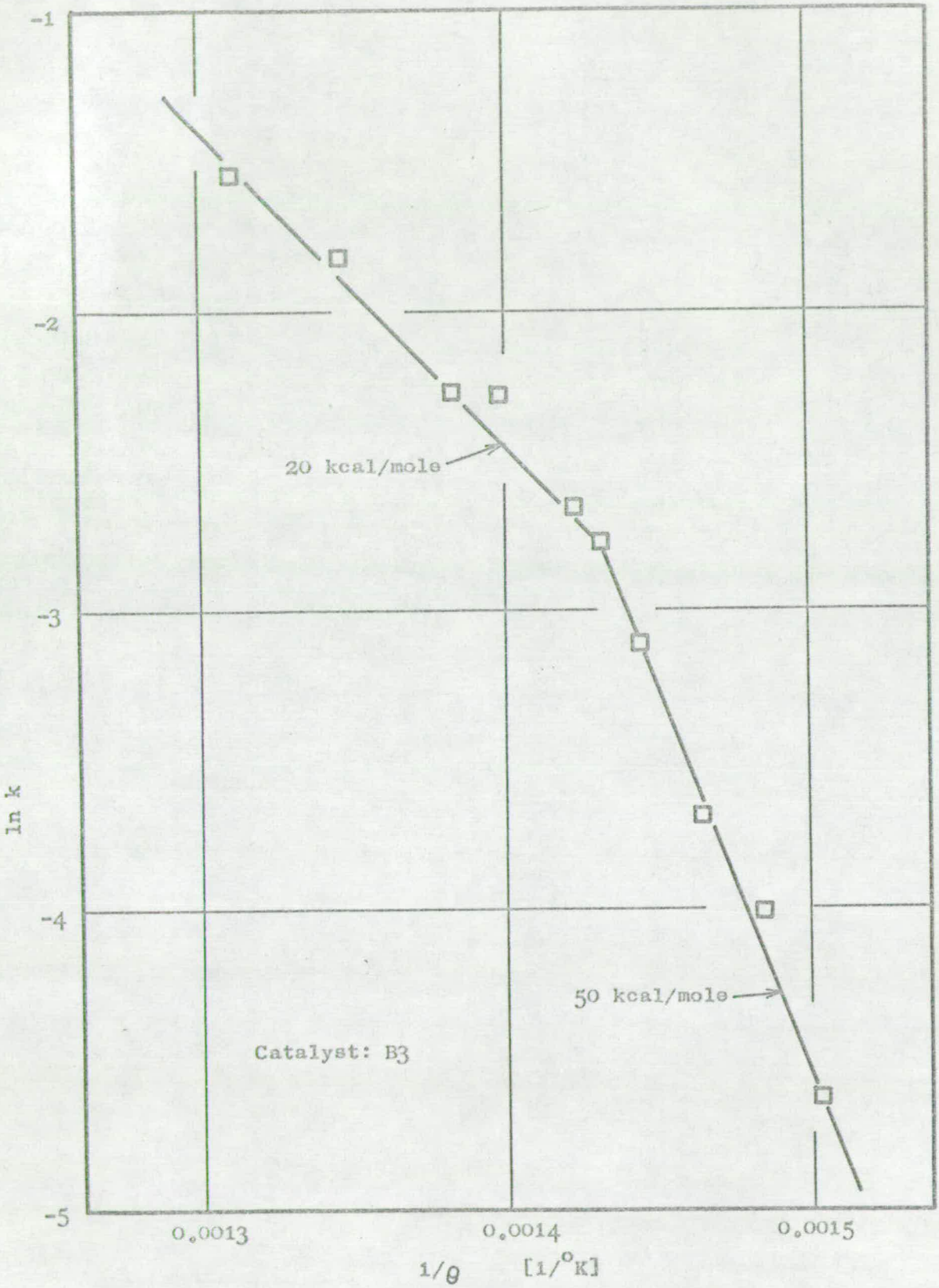


Fig.9. The effect of temperature on Arrhenius plot

9. Conclusions

Ten kinds of catalyst for the oxidation of o-xylene to phthalic anhydride were employed. These were vanadium pentoxide catalysts supported on titanium dioxide, alumina and corundum, and included two commercial ones. The activities on each catalyst were studied under several conditions.

Catalyst C1 showed the maximum 8c selectivity of 76 mole % at a conversion of o-xylene of 70 to 99% in the temperature range between 400 and 440°C. Catalyst B5, which was supported on titanium dioxide and contained 60% vanadium pentoxide, had a higher selectivity.

The effect of method of preparation on the catalyst activity was considered. In the case of the catalyst which comprised vanadium pentoxide, and titanium dioxide as support, the highest activity was found using a heating period of 6 hours at 900°C in the preparation.

Rate equations for o-xylene disappearance were determined for each catalyst.

The mechanisms of o-xylene oxidation were discussed and the practical methods of preparation of the catalysts were cited from the recent literature.

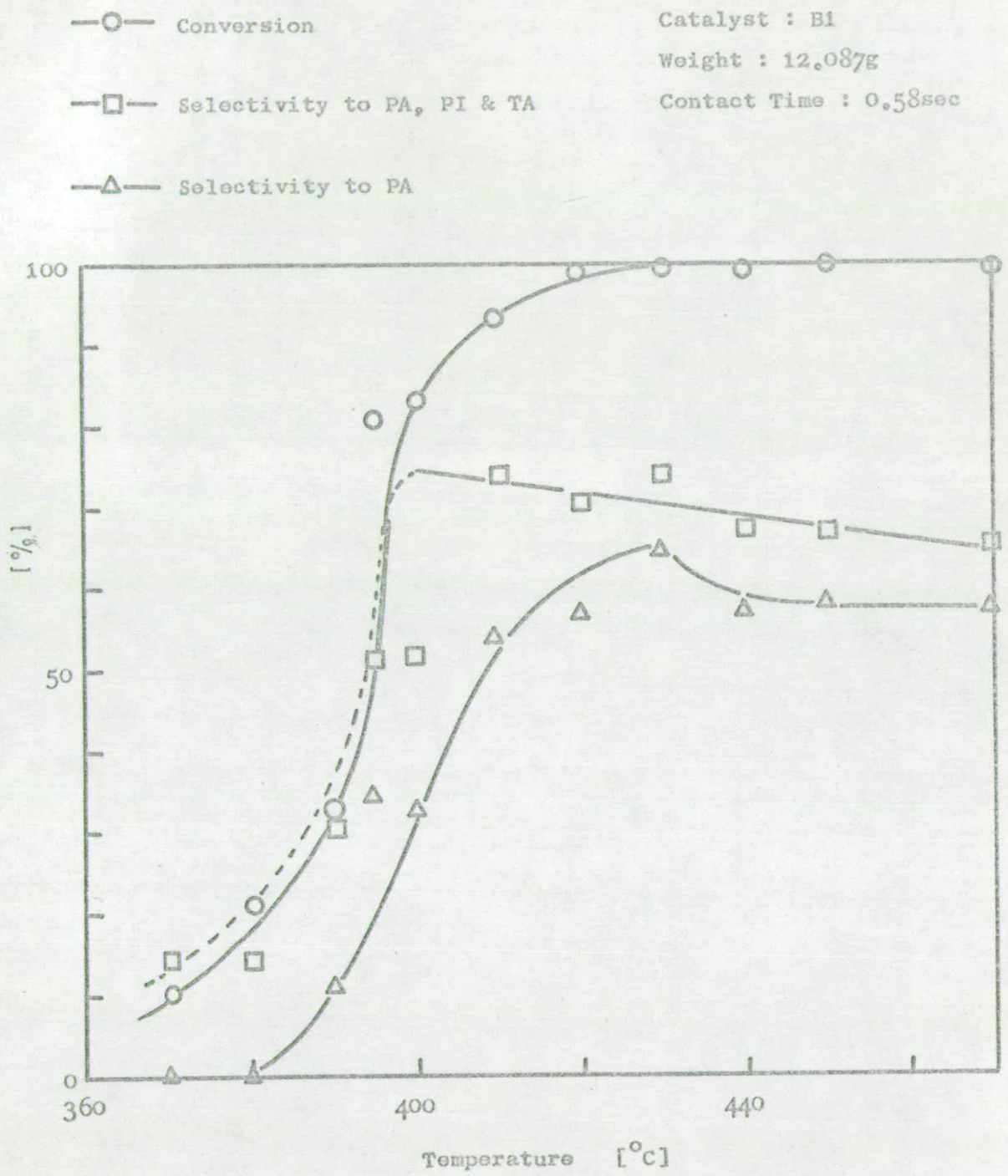


Fig. 4-1. Selectivity and conversion of o-xylene under various temperatures

Catalyst: B2

Weight: 13.240g

Contact Time: 0.58sec

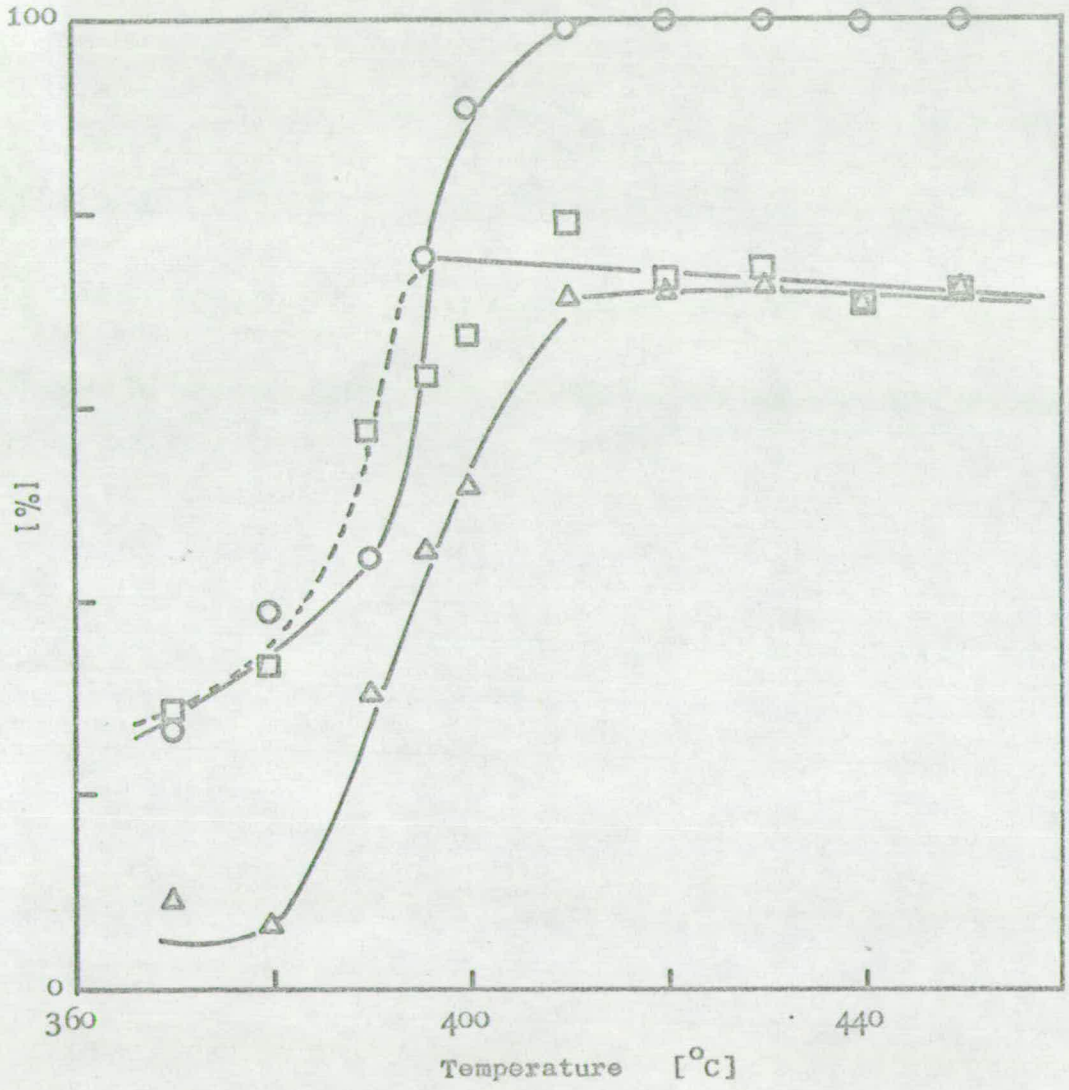


Fig. 4-2.

Catalyst: B3

Weight: 14.848 g

Contact Time: 0.58 sec

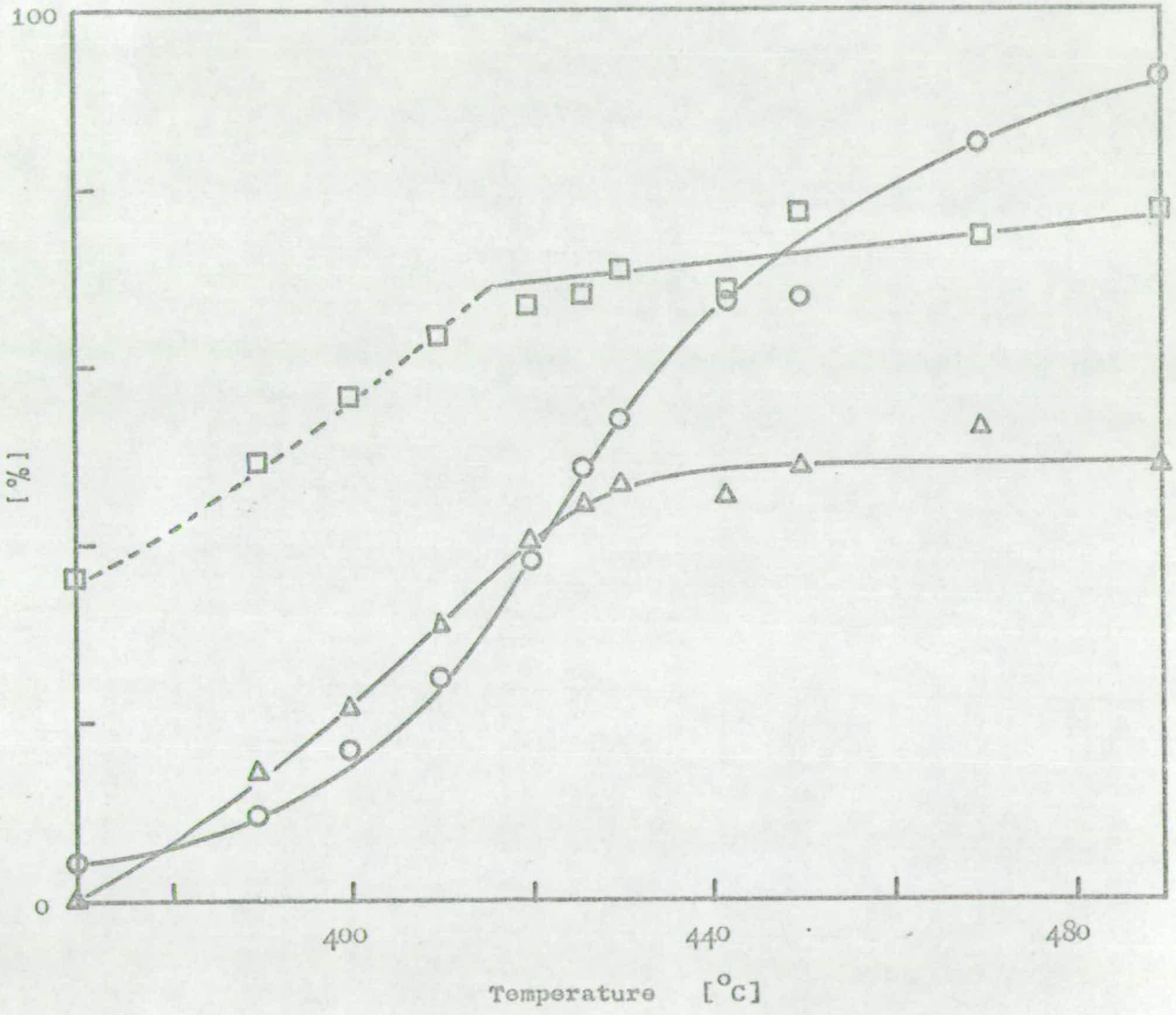


Fig. 4-3.

Catalyst: B4

Weight: 13.909g

Contact Time: 0.58sec

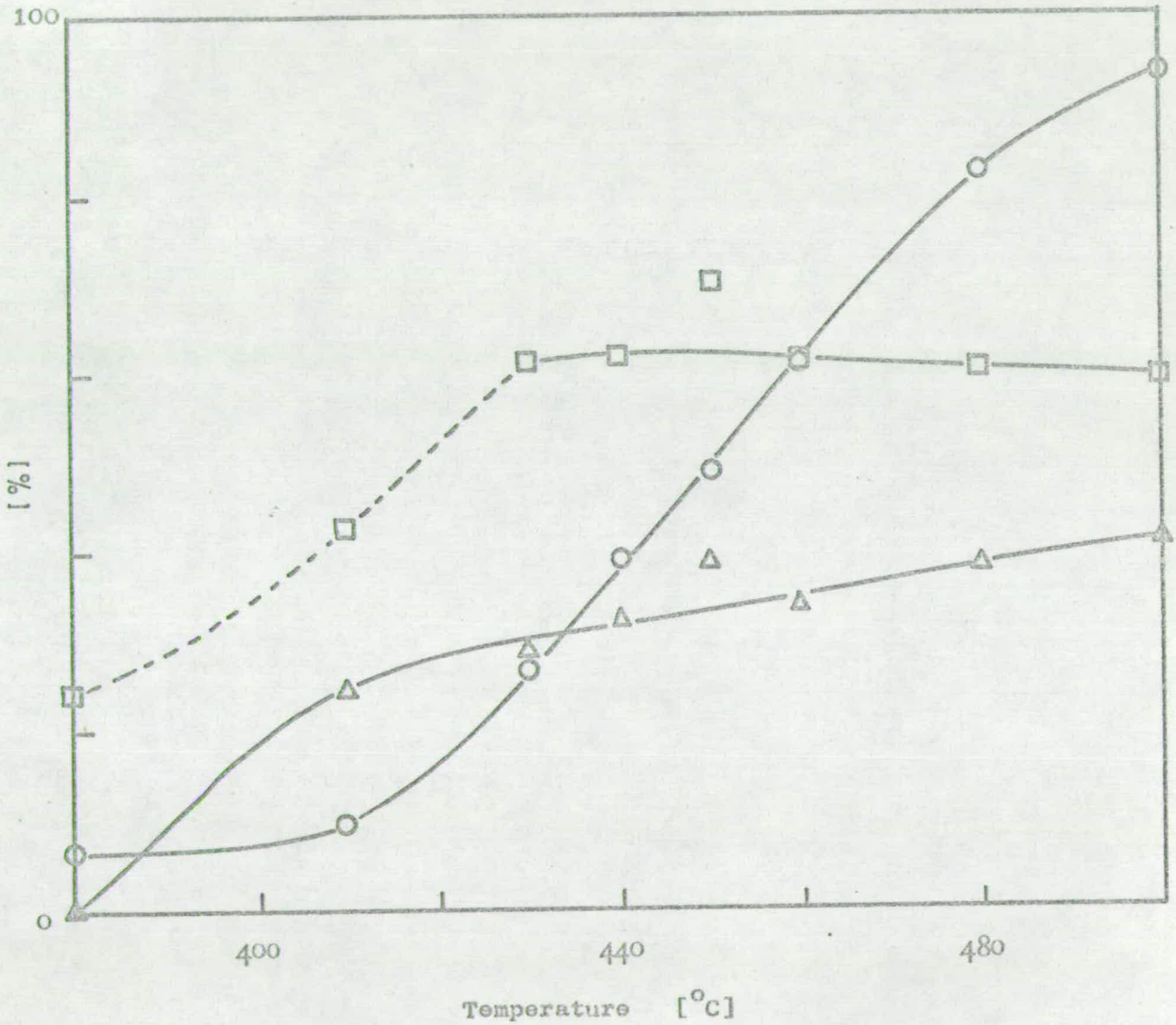


Fig. 4-4.

Catalyst: B5

Weight: 16.367g

Contact Time: 0.58sec

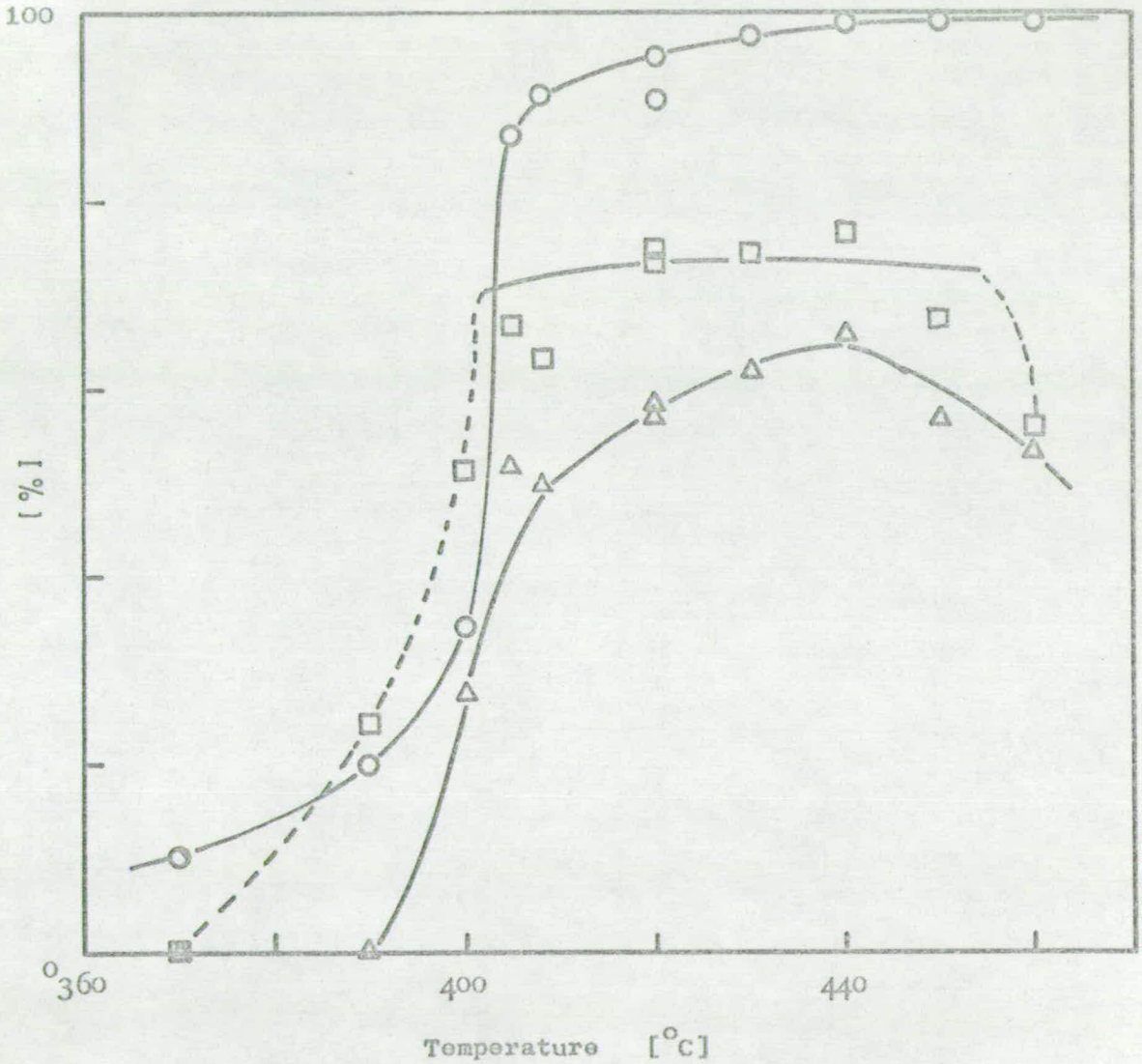


Fig. 4-5.

Catalyst: B6

Weight: 15.374g

Contact Time: 0.58sec

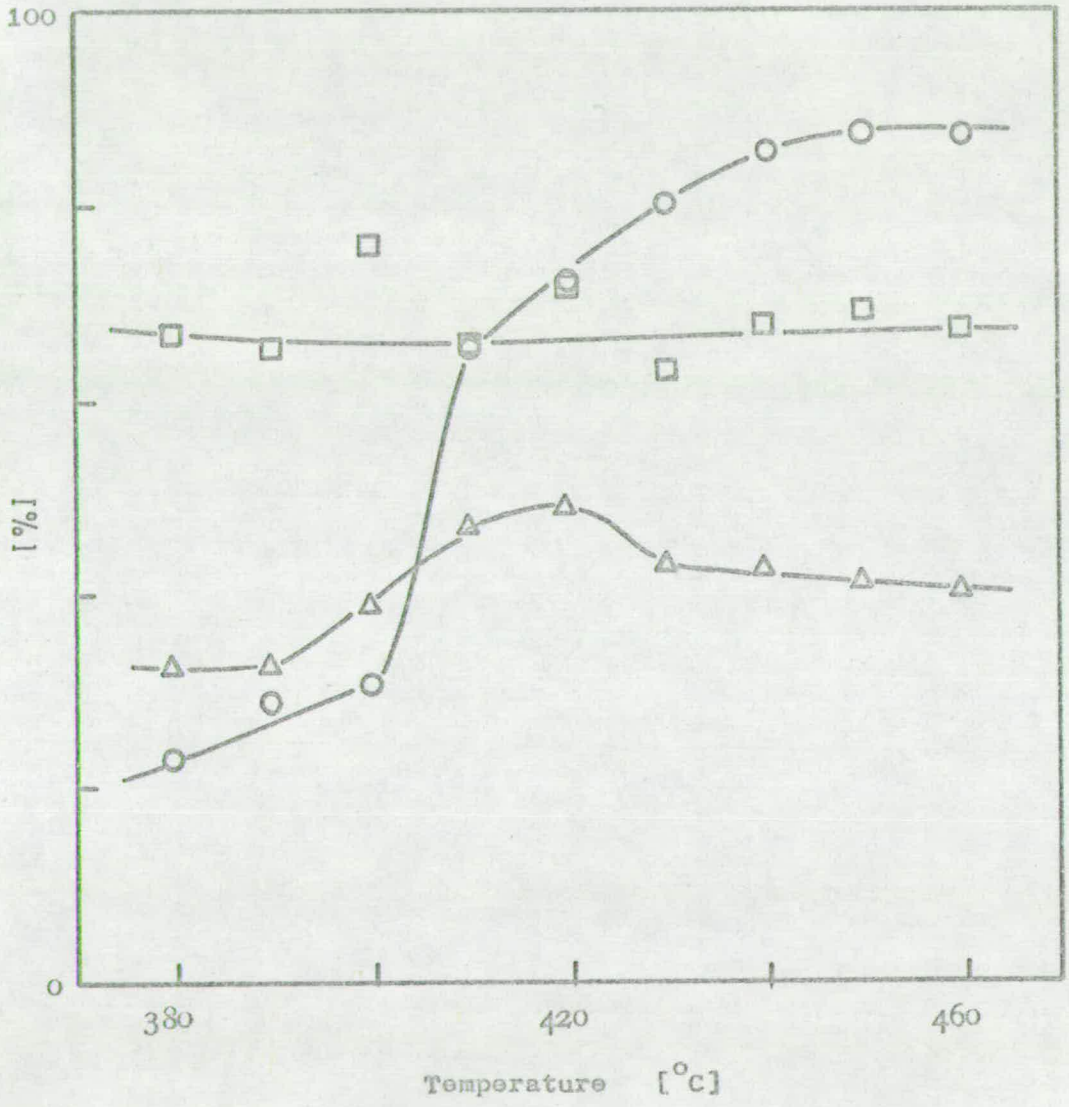


Fig. 4-6.

Catalyst: B7

Weight: 15.097g

Contact Time: 0.95sec

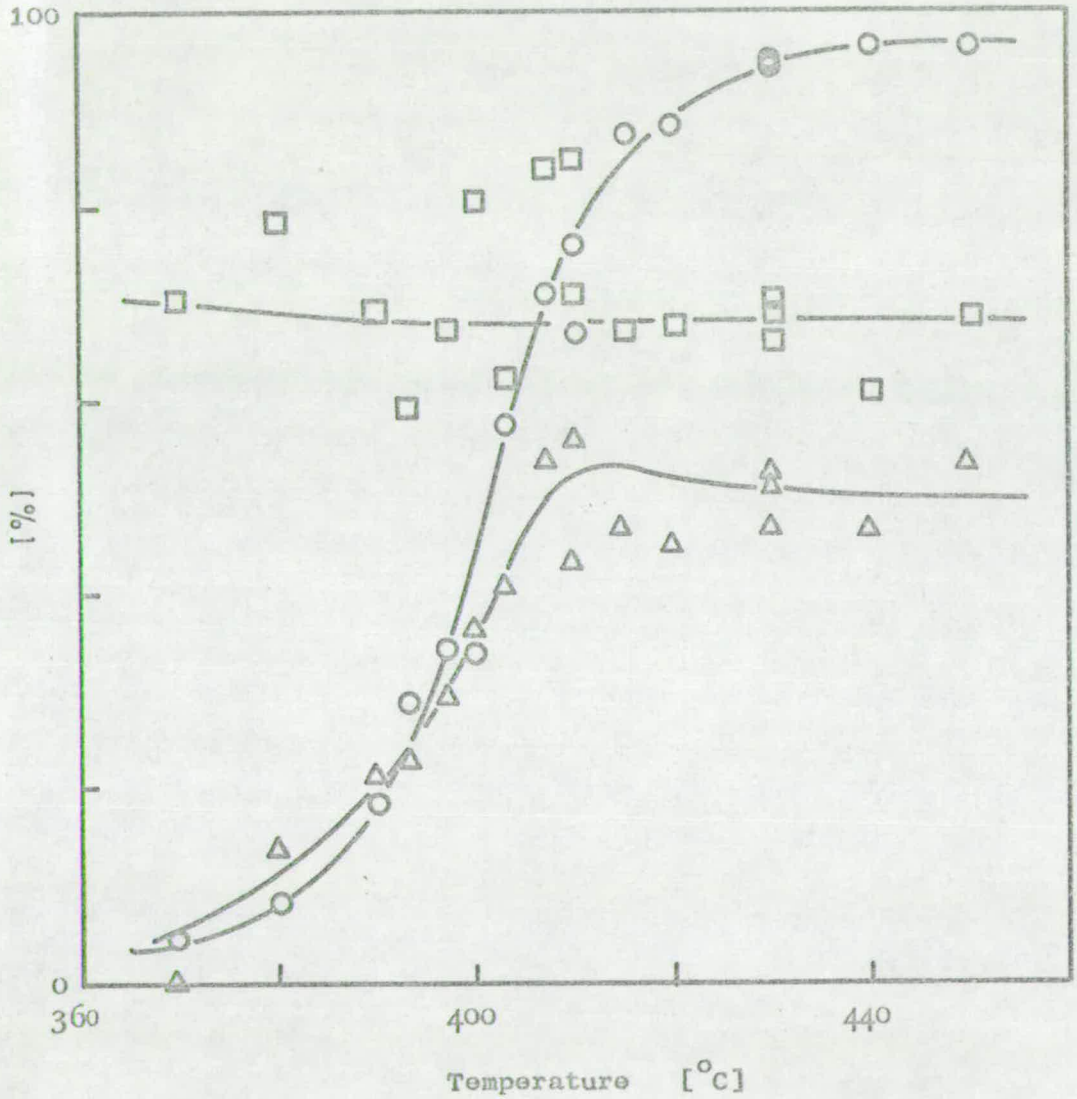


Fig. 4-7.

Catalyst: C1

Weight: 15.815g

Contact Time: 0.58sec

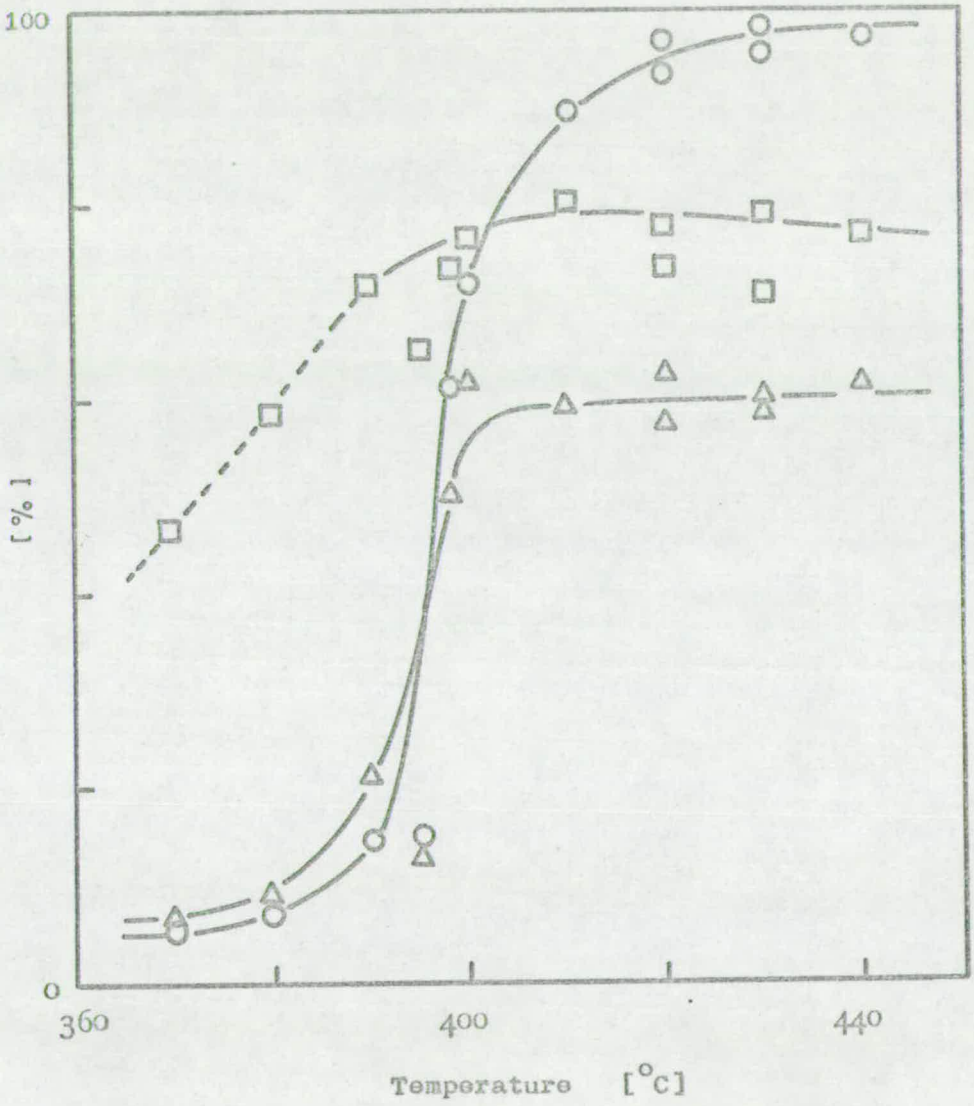


Fig. 4-8.

Catalyst: C1

Weight: 15.815g

Contact Time: 0.95sec

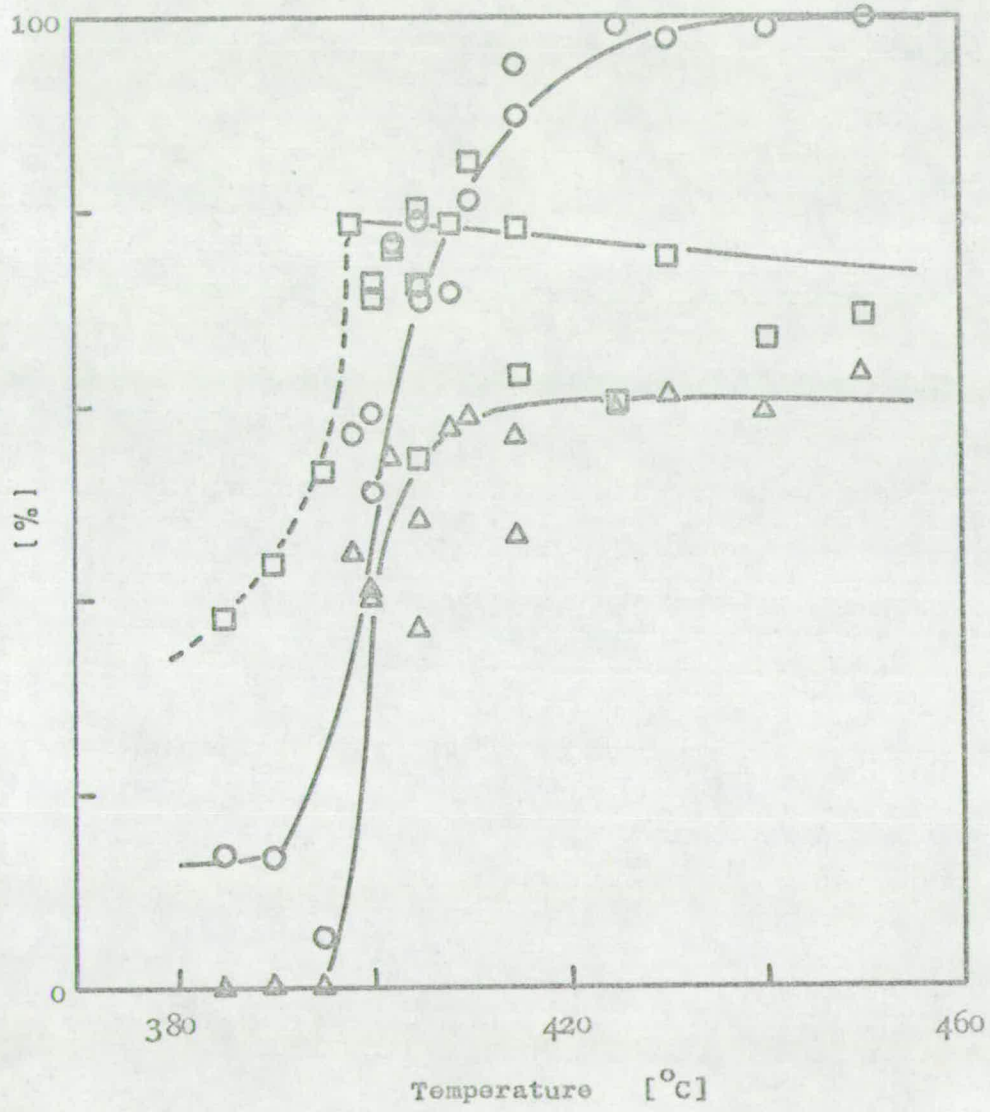


Fig. 4-9.

Catalyst: C2

Weight: 18.347g

Contact Time: 0.58sec

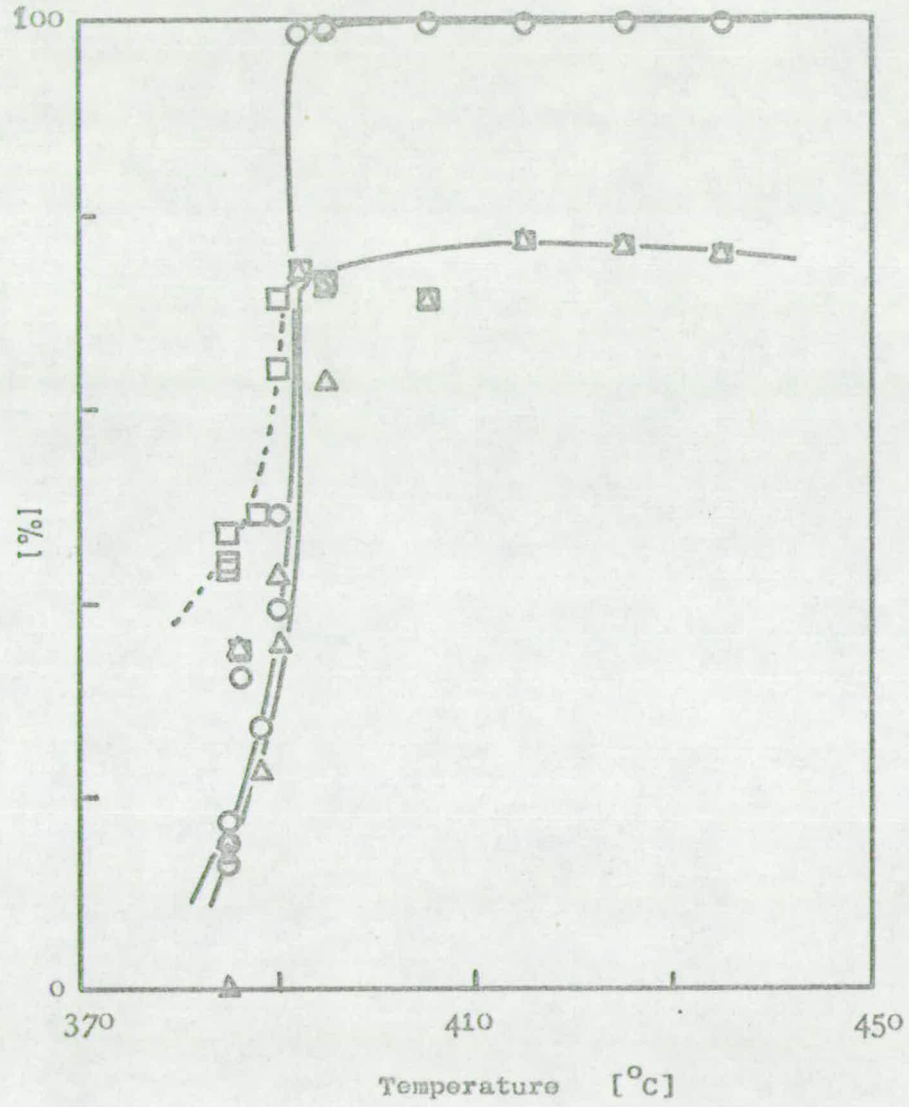


Fig. 4-10.

Catalyst: C2

Weight: 18.347g

Contact Time: 0.95sec

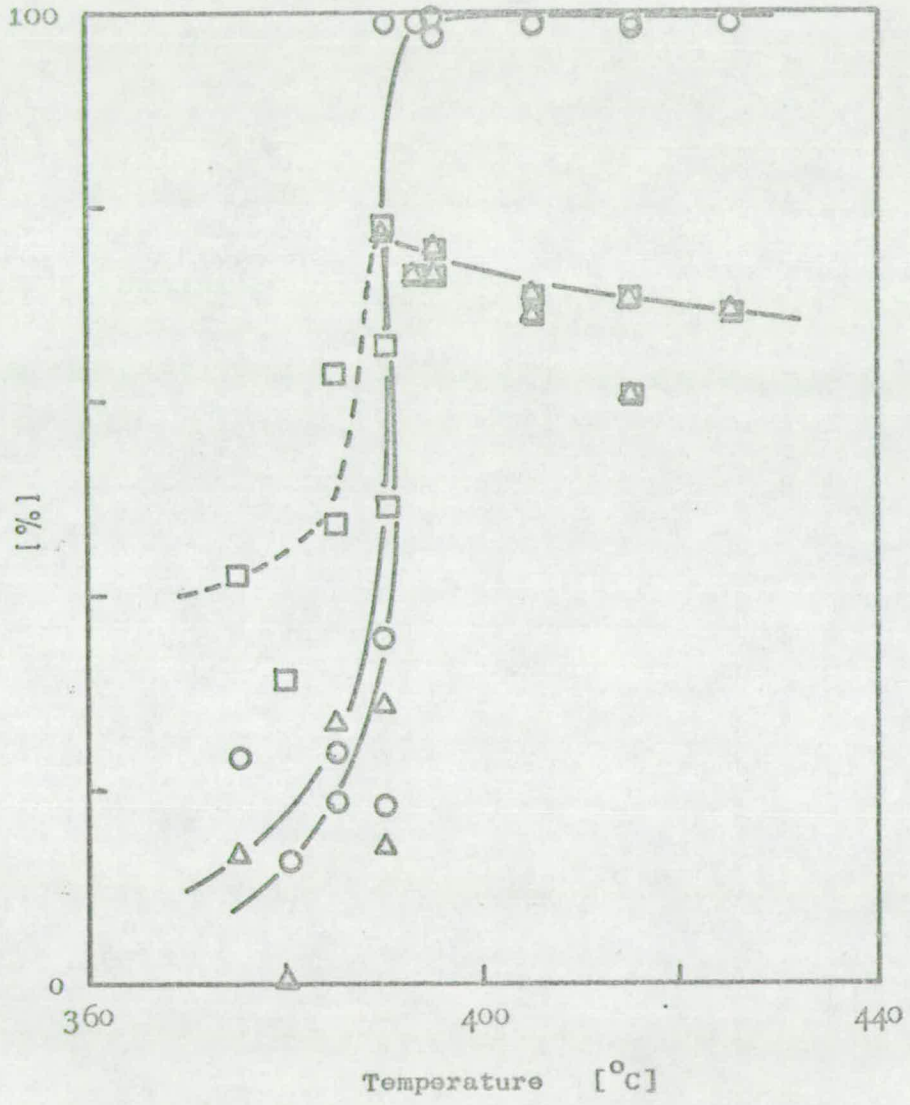


Fig. 4-11.

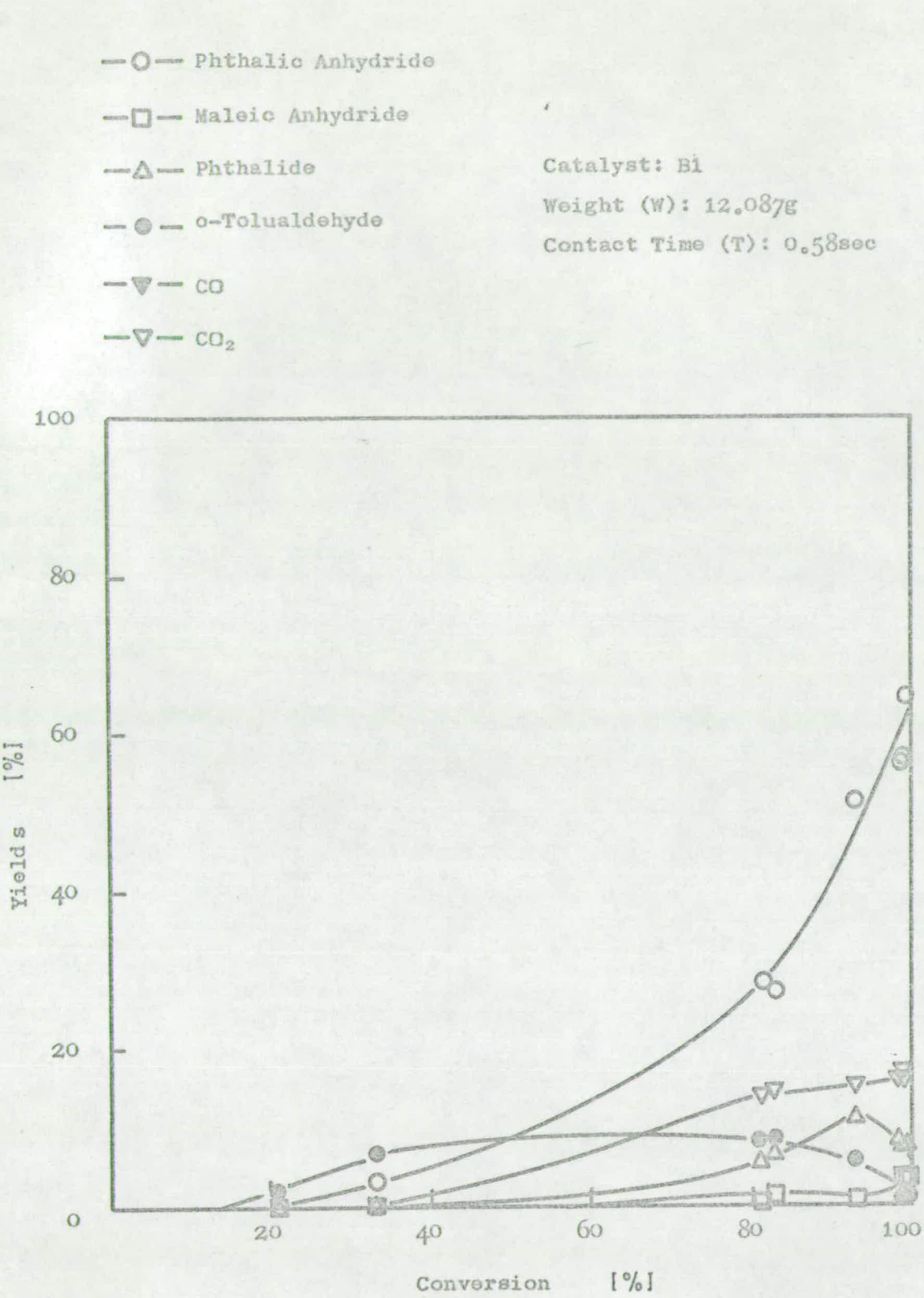


Fig. 5-1. Product yields of o-xylene oxidation over the vanadium pentoxide catalysts

B2

W: 13.240g

T: 0.58sec

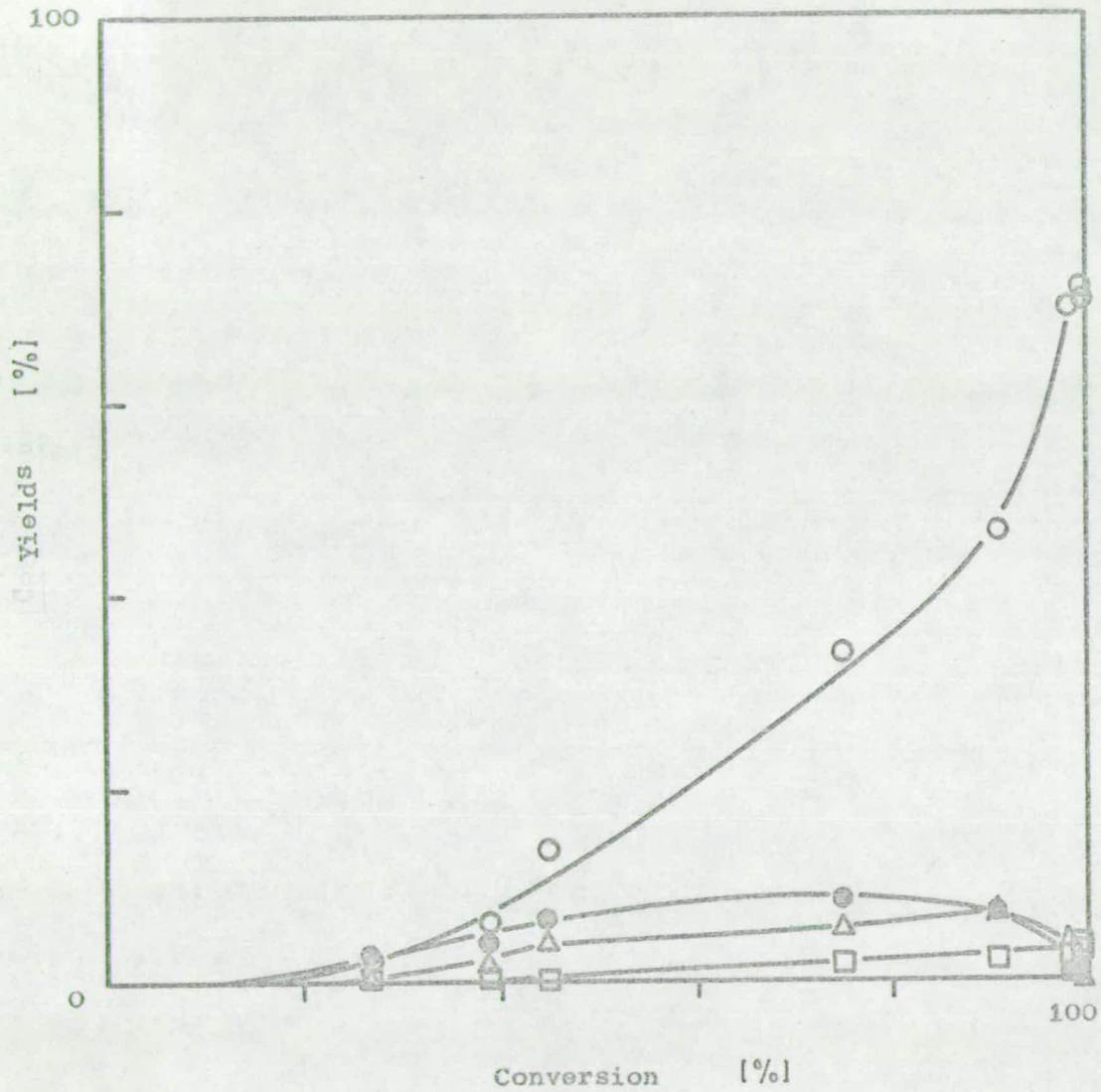


Fig. 5-2.

B3
W: 14.848g
T: 0.58sec

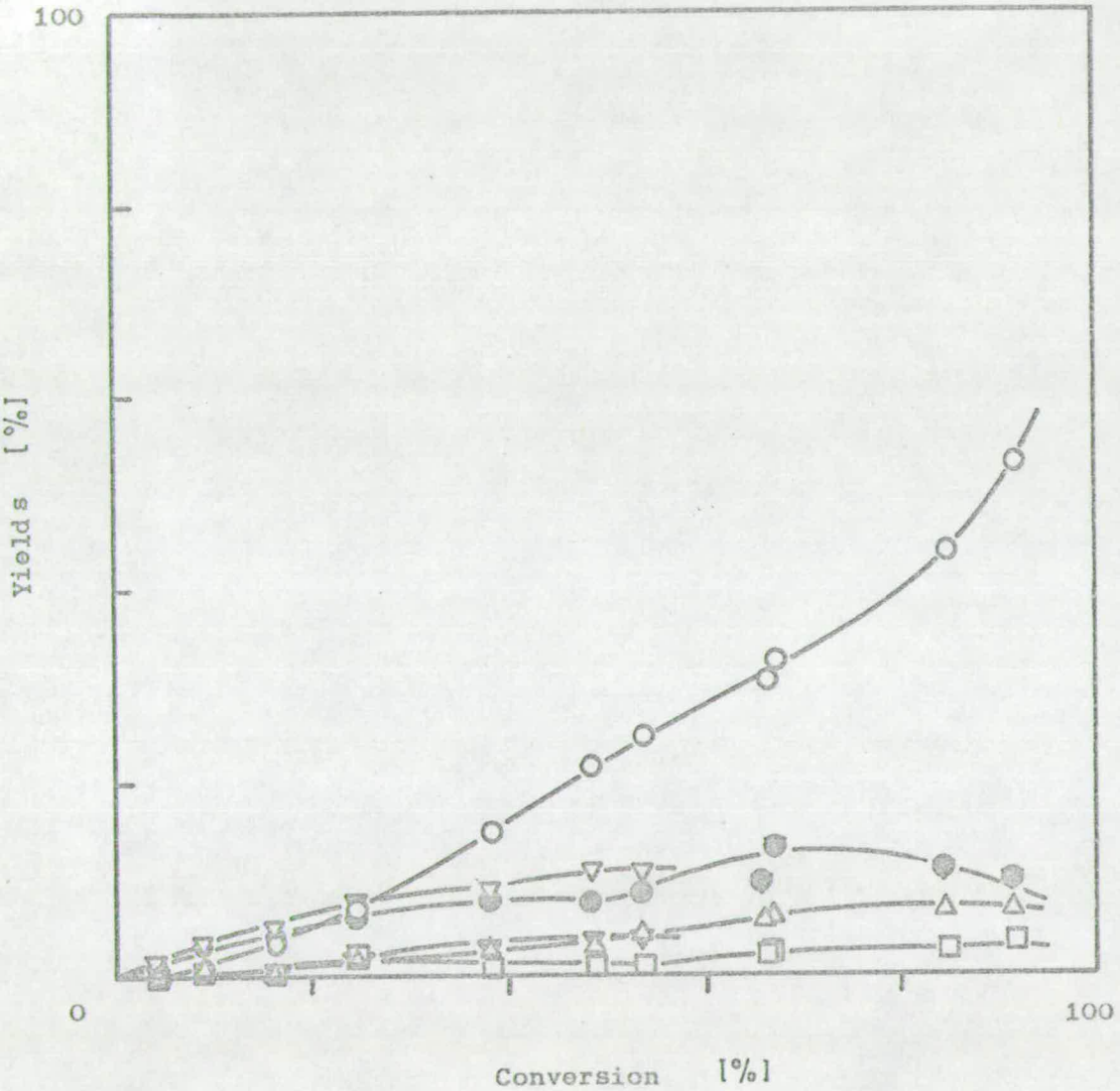


Fig. 5-3.

B4
W: 13.909g
T: 0.58sec

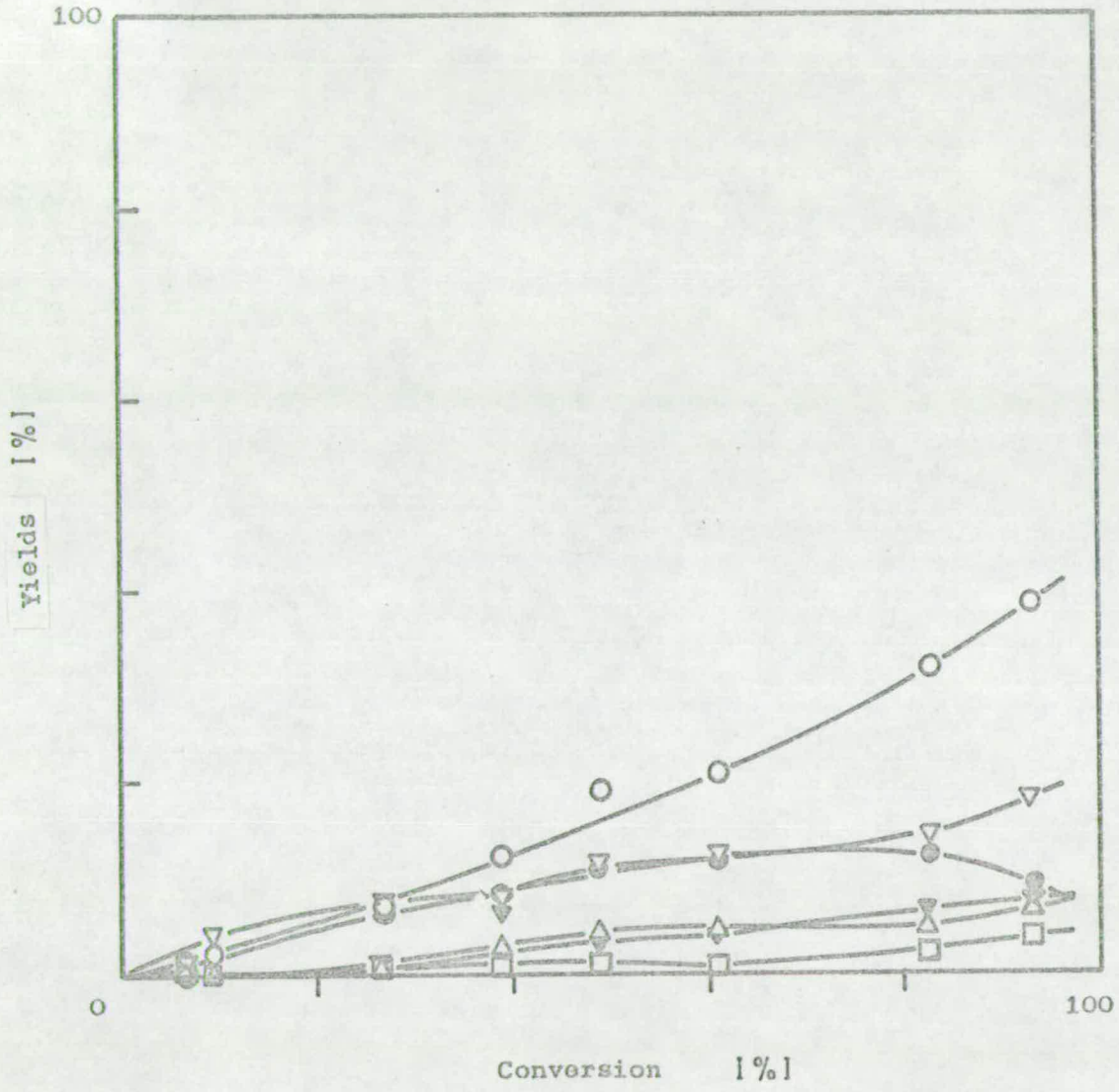


Fig. 5-4.

B5
W: 16.367g
T: 0.58sec

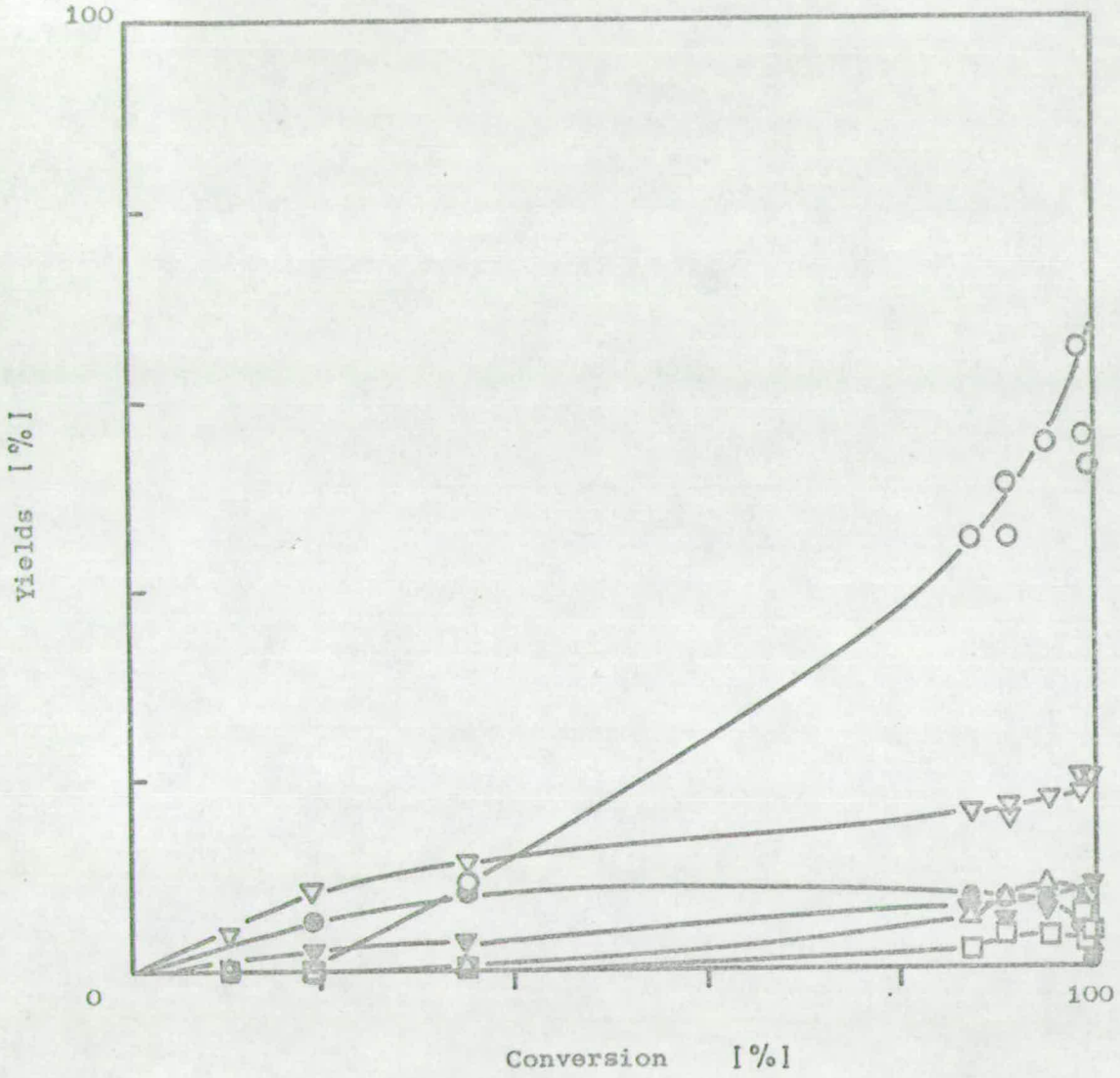


Fig. 5-5.

B6

W: 15.374g

T: 0.58sec

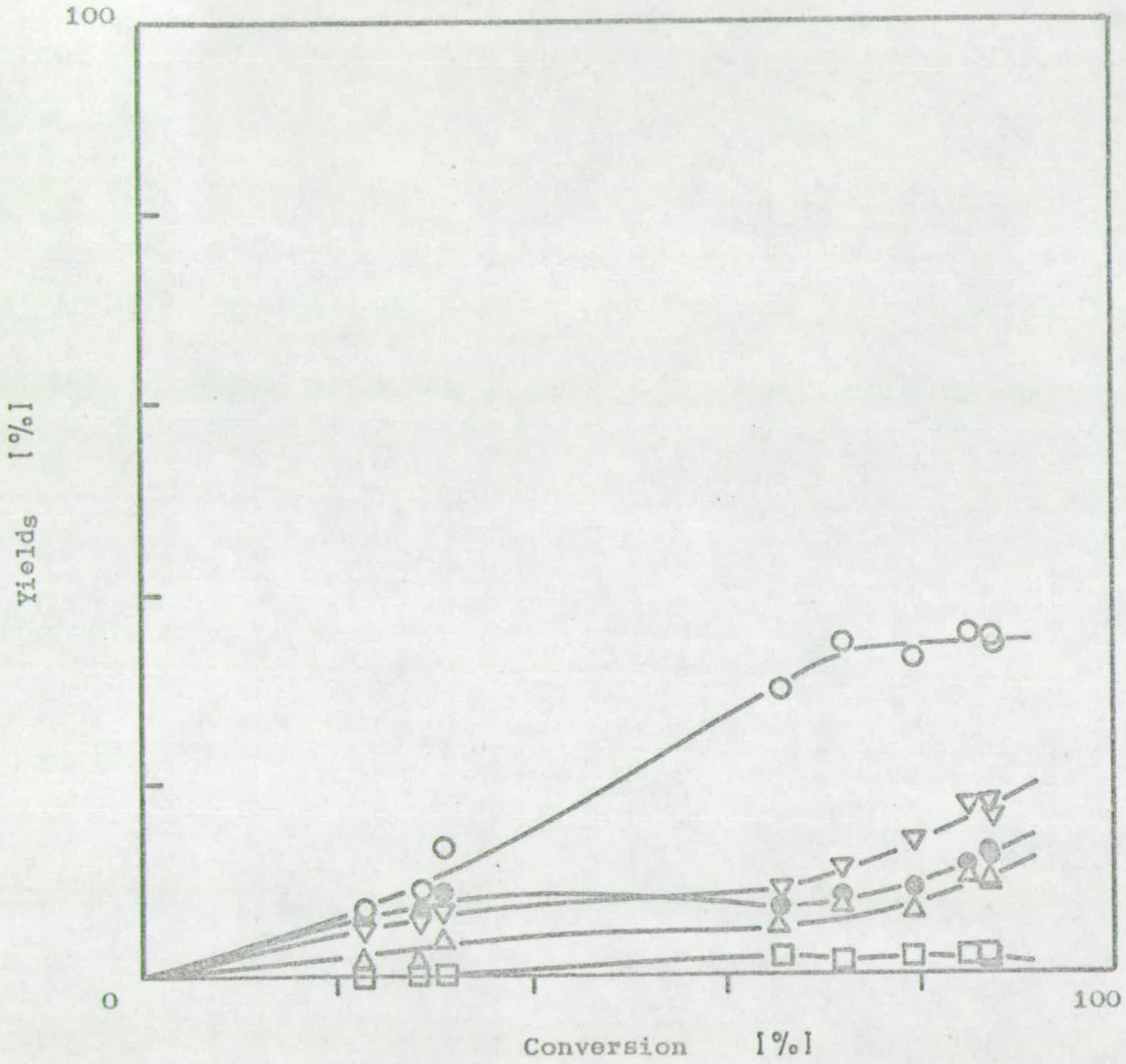


Fig. 5-6.

B7

W: 15.097g

T: 0.95sec

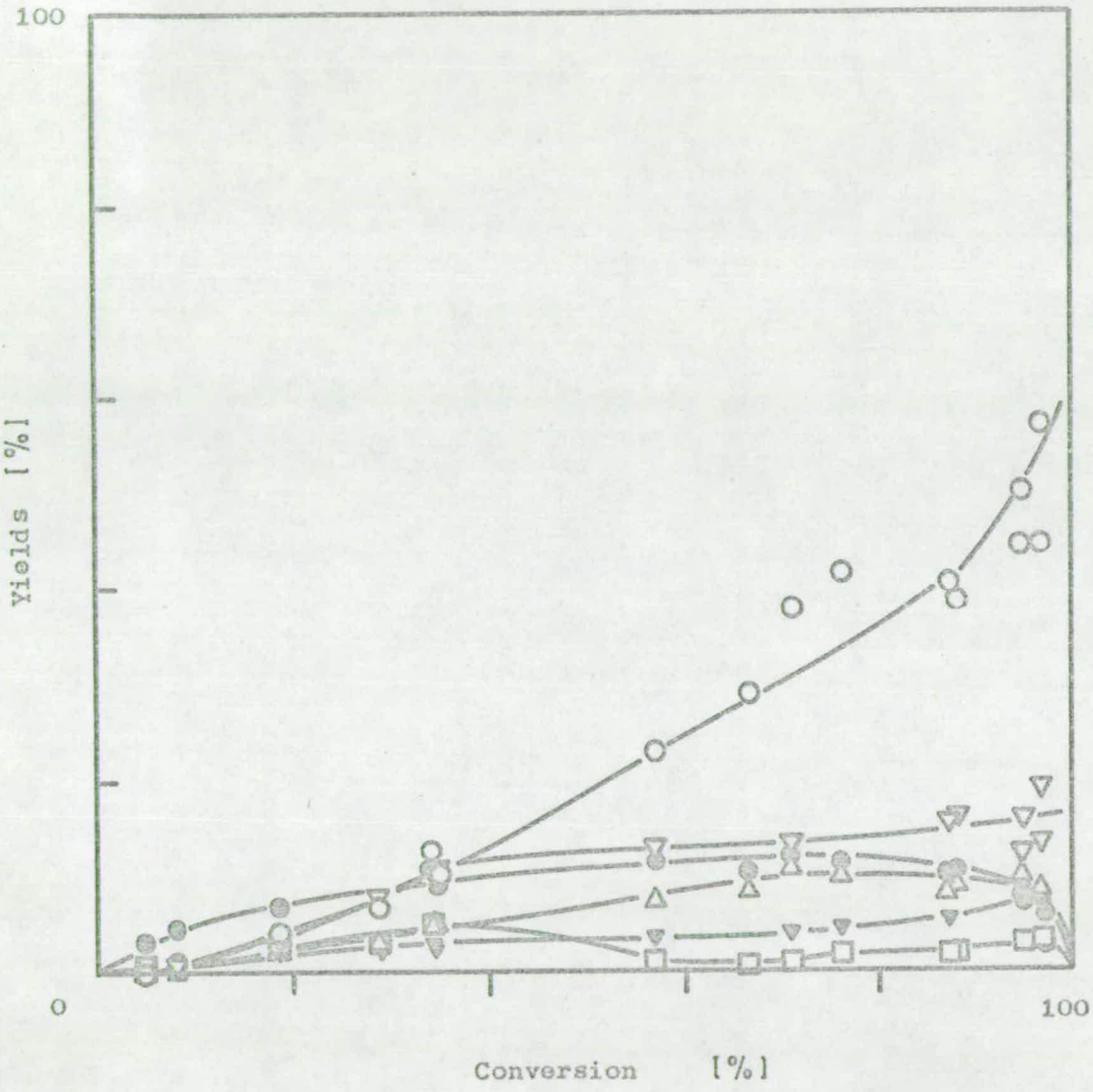


Fig. 5-7.

C1

W: 15.815g

T: 0.95sec

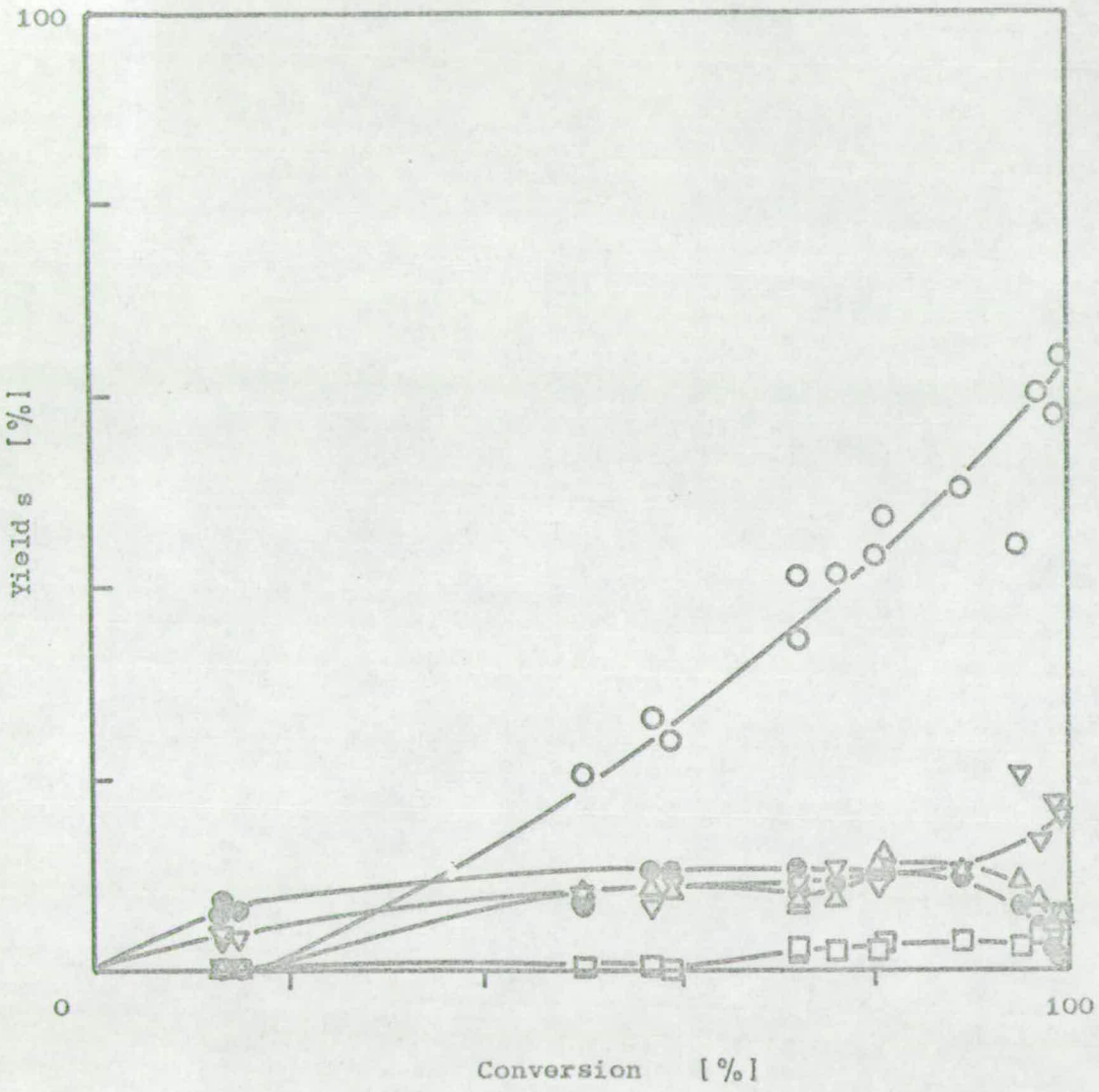
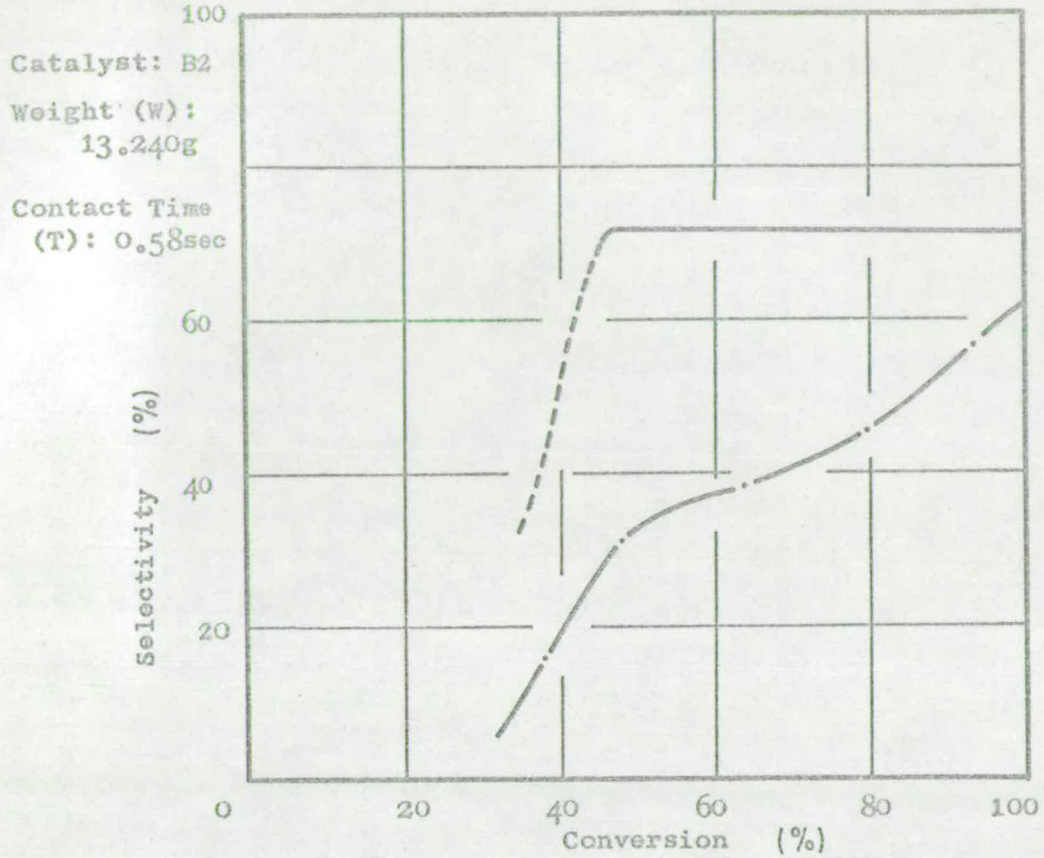


Fig. 5-8.



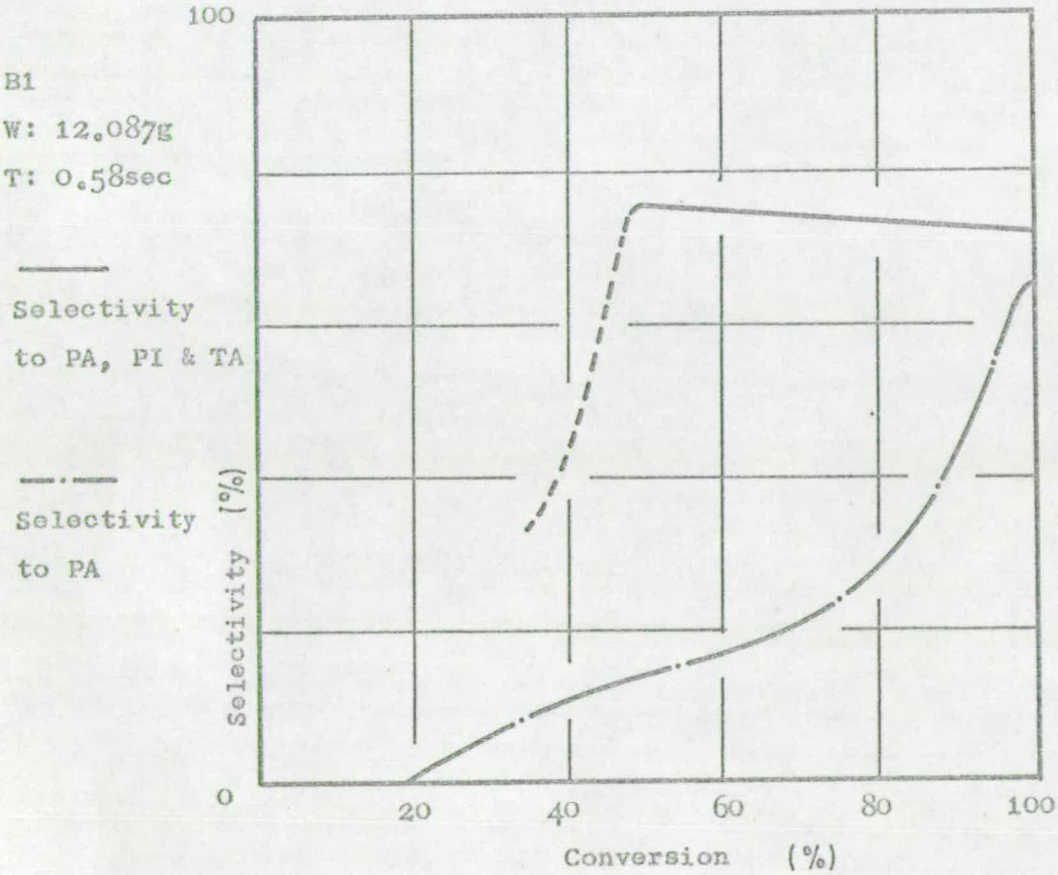
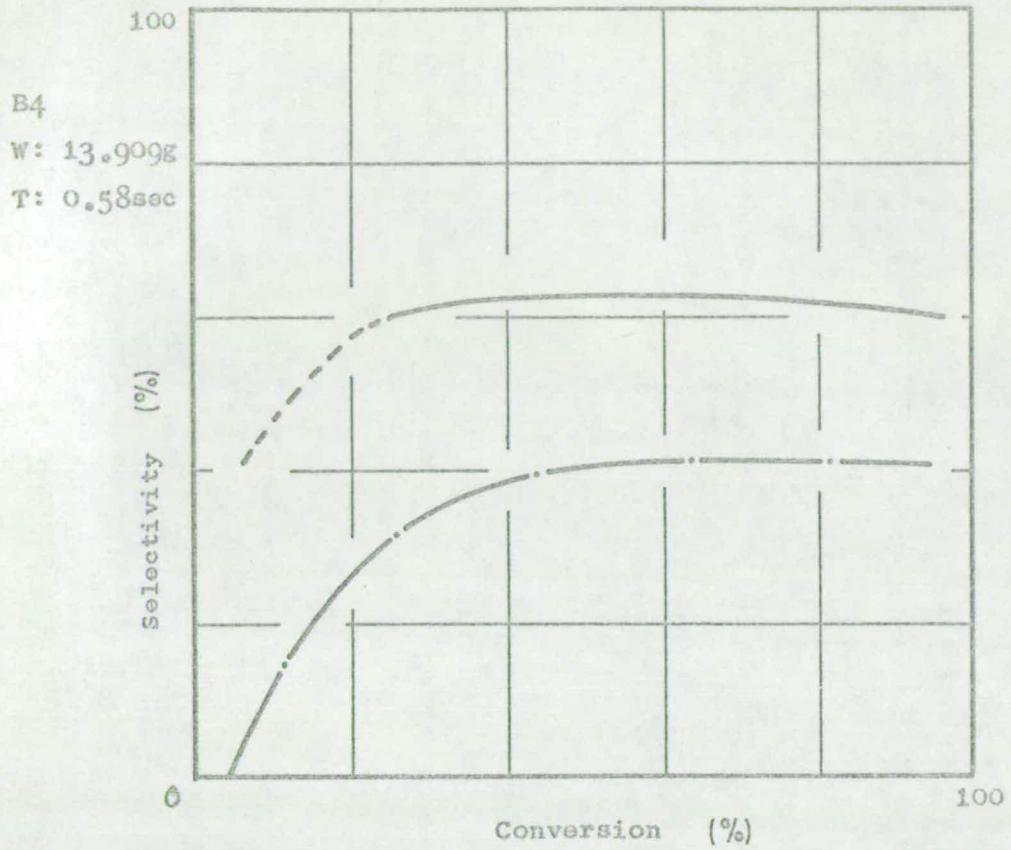


Fig. 6-1. Selectivity vs. conversion of o-xylene


B4
W: 13.909g
T: 0.58sec
100
0
100
Selectivity (%)
Conversion (%)

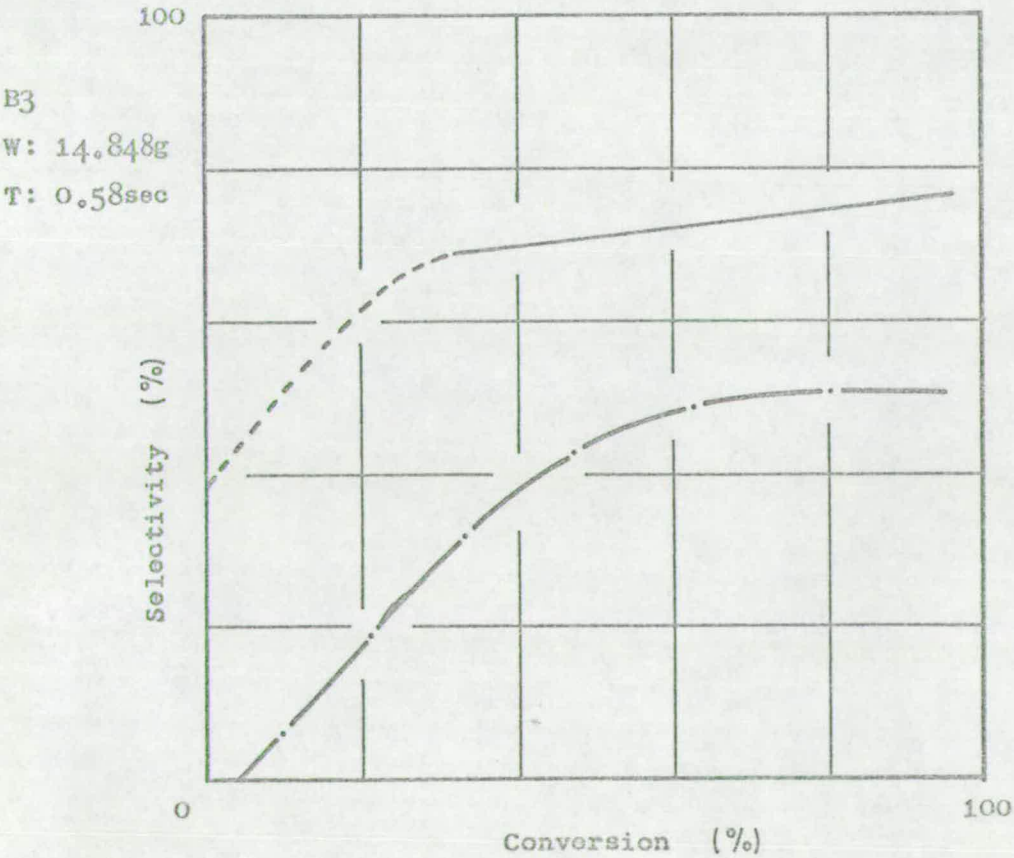
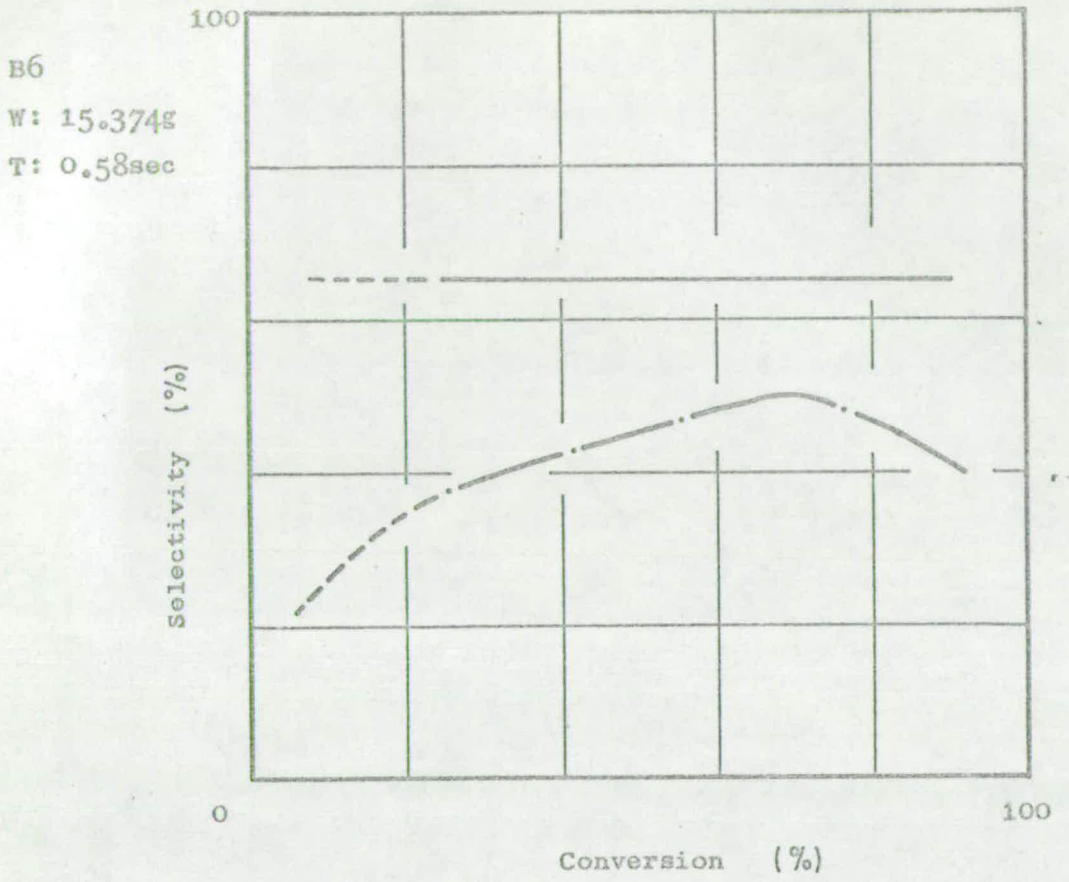

B3
W: 14.848g
T: 0.58sec
100
0
100
Selectivity (%)
Conversion (%)

Fig. 6-2.


B6
W: 15.374g
T: 0.58sec
100
Selectivity (%)
0
100
Conversion (%)

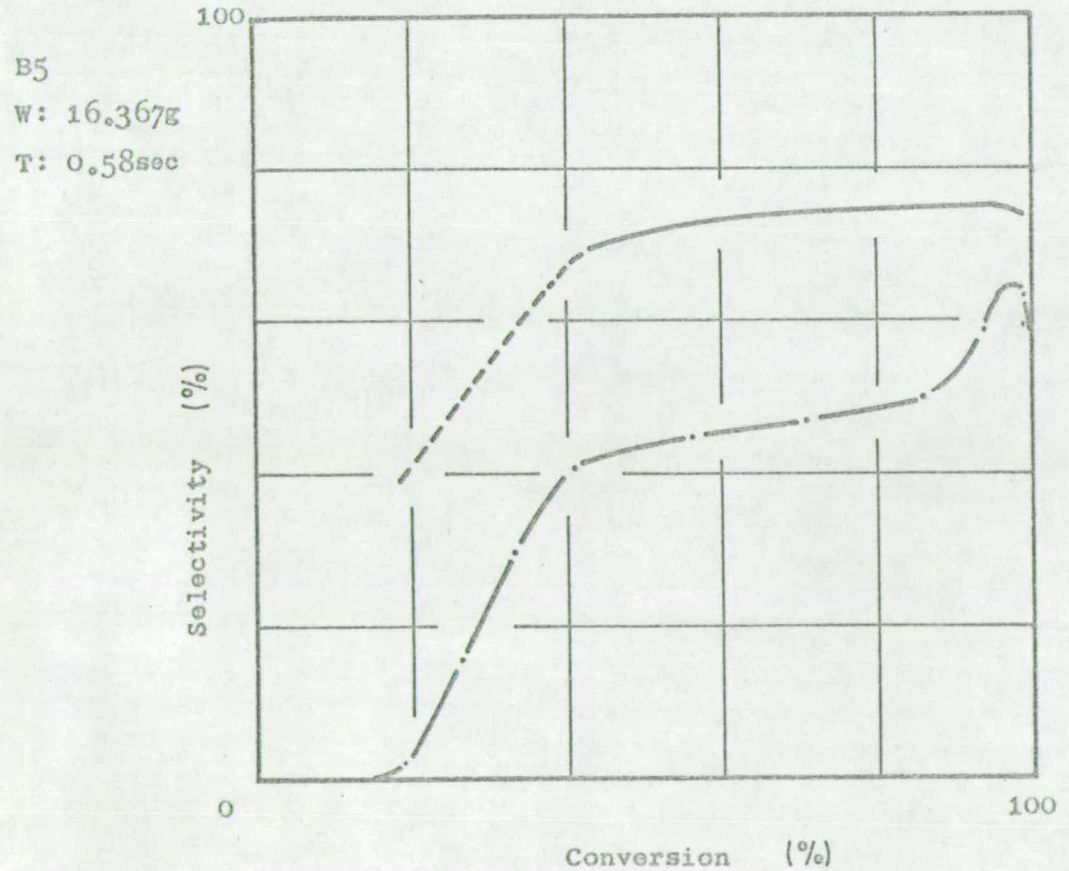
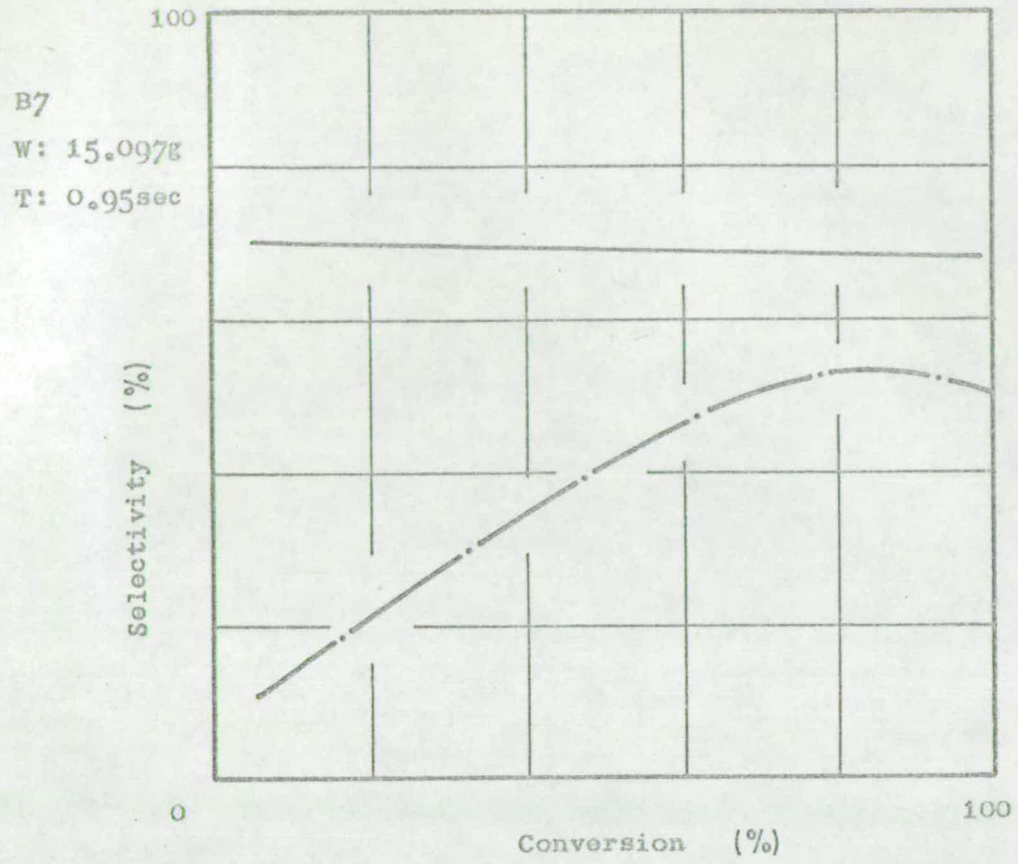

B5
W: 16.367g
T: 0.58sec
100
Selectivity (%)
0
100
Conversion (%)

Fig. 6-3.


B7
W: 15.097g
T: 0.95sec
100
0
100
Selectivity (%)
Conversion (%)

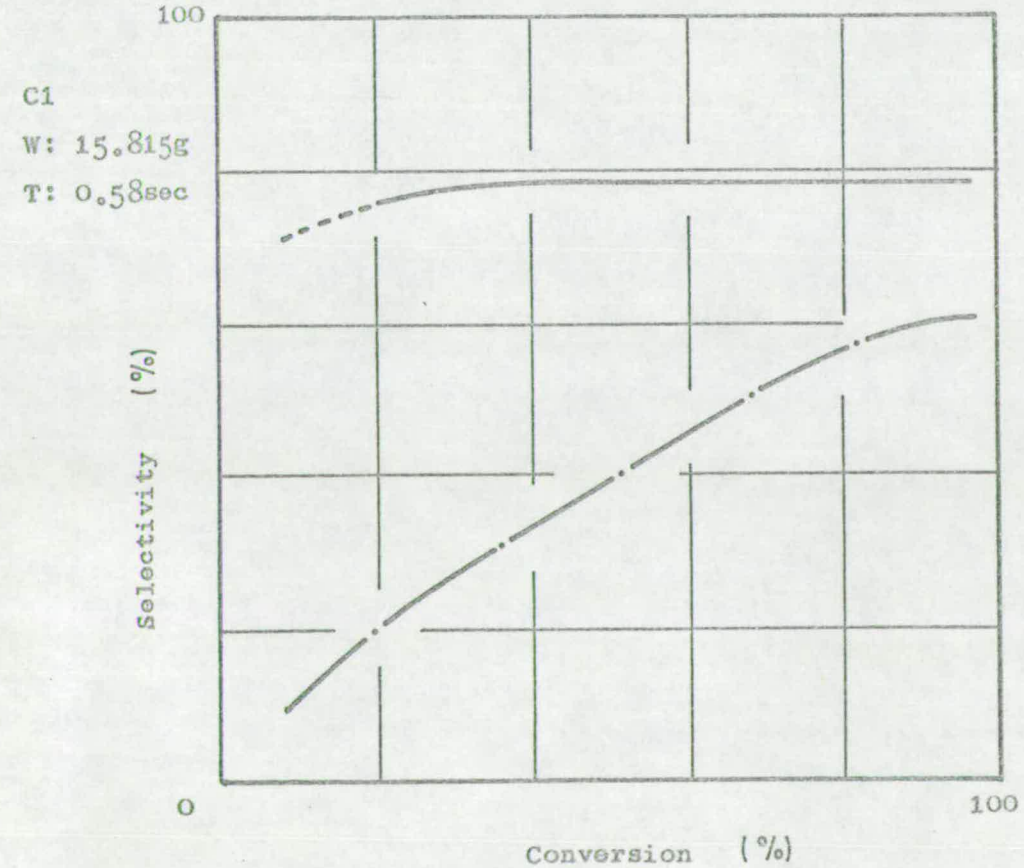
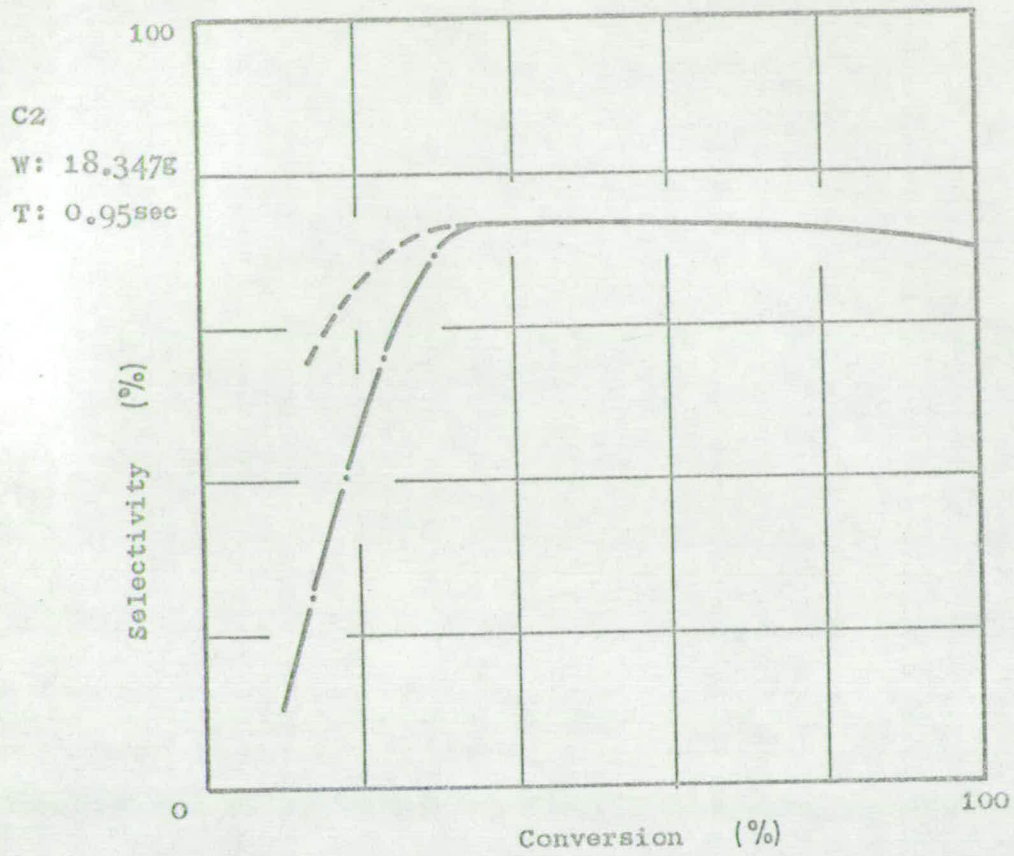

C1
W: 15.815g
T: 0.58sec
100
0
100
Selectivity (%)
Conversion (%)

Fig. 6-4.


C2
W: 18.347g
T: 0.95sec
100
0
100
Selectivity (%)
Conversion (%)

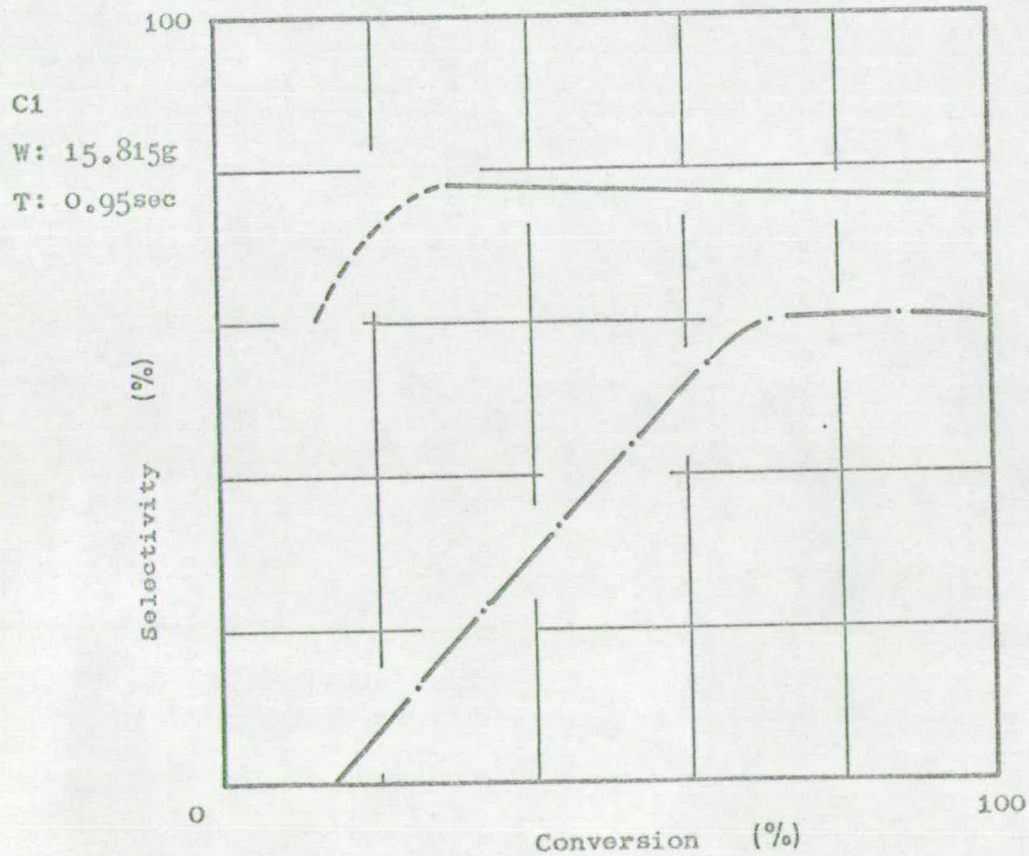

C1
W: 15.815g
T: 0.95sec
100
0
100
Selectivity (%)
Conversion (%)

Fig. 6-5.

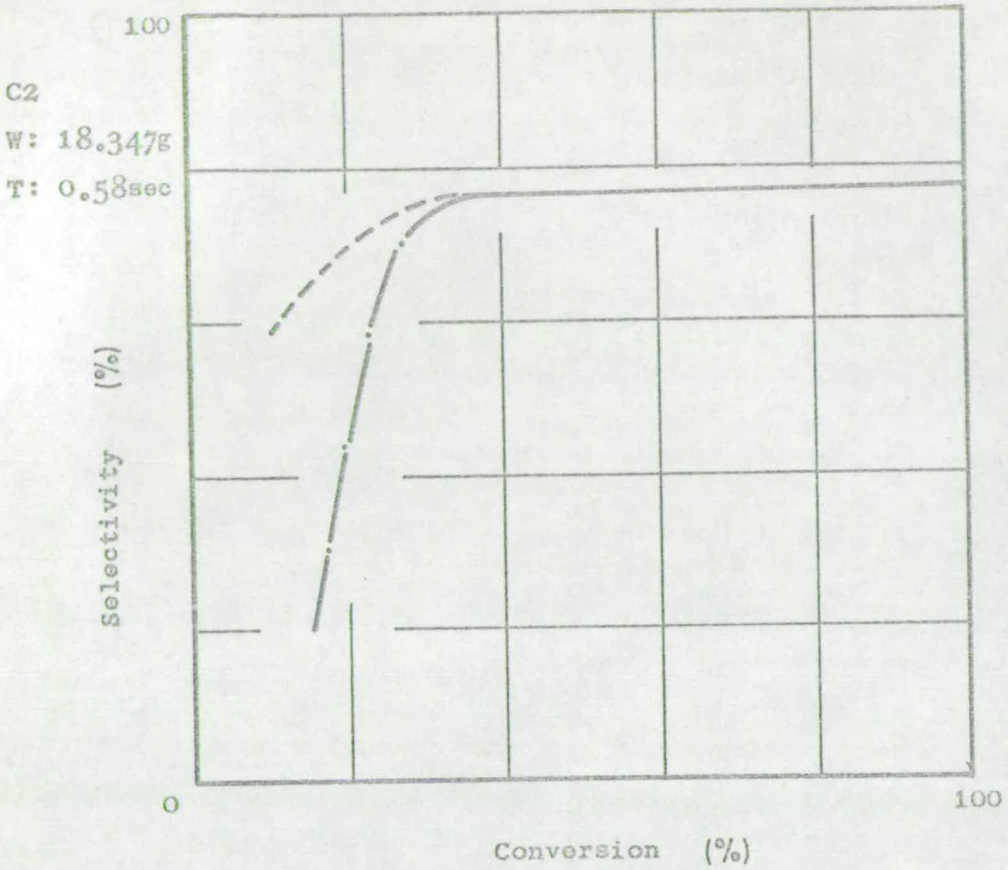


Fig. 6-6.

Table 6. Experimental Conditions and Results*

Catalyst	Catalyst Weight [g]	Apparent Volume of Catalyst packed [cm^3]	Flow Rate [cm^3/sec]	Contact Time [Sec]	Temperature of Reactor [°C]	Conversion of o-Xylene [mole %]	Yield [mole %]						Selectivity	
							PA	MA	PI	TA	CO	CO_2	to PA	to PA,PI + TA
B1	12.087	11.59	20.0	0.58	470	99.6	56.6	3.2	7.1	0.4	...	16.5	57.0	64.5
					450	99.3	57.6	3.2	6.7	2.3	...	17.1	58.1	67.3
					440	99.0	56.4	3.3	7.3	3.0	...	16.6	57.1	67.6
					430	99.6	64.5	3.7	8.1	0.5	...	16.1	64.8	73.5
					420	98.4	56.6	2.7	8.4	4.2	...	15.5	57.6	70.5
					410	93.7	51.2	2.7	11.1	6.6	...	15.5	54.6	73.5
					400	83.2	27.5	1.7	6.2	8.2	...	14.4	33.1	50.6
					395	81.4	28.3	1.7	5.2	8.3	...	14.4	34.8	51.3
					390	33.7	3.5	0.0	0.0	6.8	...	...	10.5	30.6
					380	20.8	0.0	0.0	0.0	3.5	...	...	0.0	14.7
					370	10.4	0.0	0.0	0.0	1.5	...	...	0.0	14.6

* Molar o-xylene/air ratio of inlet gas to a reactor: 0.0110 (at 30.0°C)

PA: Phthalic anhydride

MA: Maleic anhydride

PI: Phthalide

TA: o-Tolualdehyde

Catalyst	Weight	Volume	Flow Rate	Contact Time	Temperature	Conversion	Yield						Selectivity	
							PA	MA	PI	TA	CO	CO_2	to PA	
B2	13.240	6.35	11.0	0.58	450	99.7	70.8	3.5	0.0	0.5	...	...	71.1	71.5
					440	99.7	70.1	3.5	0.0	0.7	...	...	69.9	70.6
					430	99.8	72.7	3.0	0.0	1.2	...	...	72.9	74.1
					420	99.5	71.1	2.7	0.0	1.8	...	...	71.3	73.2
					410	98.4	70.4	2.6	4.1	3.1	...	...	71.5	78.9
					400	90.3	46.9	2.0	7.1	7.0	...	...	51.9	67.4
					396	75.5	34.1	1.5	4.9	8.8	...	...	45.3	63.4
					390	44.2	14.0	0.4	4.2	7.4	...	...	30.2	57.9
					380	38.7	5.7	0.2	2.1	5.0	...	...	6.7	33.1
					370	26.7	2.6	0.0	1.2	3.9	...	...	9.7	28.8

Catalyst	Weight	Volume	Flow Rate	Contact Time	Temperature	Conversion	Yield						Selectivity	
							PA	MA	PI	TA	CO	CO_2	to PA	
B3	14.848	12.71	21.9	0.58	490	92.0	53.1	3.2	7.7	9.0	...	...	48.7	77.1
					470	84.5	44.3	2.6	7.2	11.2	...	...	52.4	74.2
					450	67.6	32.9	2.0	6.1	13.1	...	...	48.7	77.1
					442	67.3	30.7	1.3	6.0	9.4	...	...	45.6	68.5
					430	53.6	24.9	1.1	4.6	8.8	3.9	10.6	46.5	71.5
					426	48.2	21.2	1.0	3.7	7.9	3.5	10.0	44.0	68.0
					420	38.0	15.2	0.6	2.7	7.4	2.9	8.9	40.0	66.6
					410	24.5	7.7	3.1	1.9	6.0	2.0	7.1	31.4	63.7
					400	16.9	3.7	0.0	1.4	4.4	1.3	5.1	21.9	56.2
					390	9.6	1.4	0.0	0.0	3.3	0.8	3.6	14.6	49.0
					370	4.4	0.0	0.0	0.0	1.6	0.4	2.2	0.0	36.4
B4	13.909	10.09	17.4	0.58	500	93.6	38.7	3.2	6.3	9.7	7.0	18.4	41.3	58.4
					480	82.9	31.9	2.4	5.4	12.6	5.9	14.7	38.5	60.2
					460	61.2	20.9	1.5	4.2	12.7	4.5	12.2	34.2	61.8
					450	49.1	19.1	1.0	4.1	11.4	3.4	11.0	39.0	70.4
					440	39.2	12.8	0.6	2.8	8.4	7.0	8.4	32.7	61.2
					430	26.8	7.8	0.3	1.9	6.8	1.9	7.0	29.1	61.6
					410	9.8	2.4	0.0	1.8	0.0	1.2	4.5	24.5	42.9
					380	6.1	0.0	0.0	0.0	1.5	0.4	2.3	0.0	24.3

Catalyst	Weight	Volume	Flow Rate	Contact Time	Temperature	Conversion	Yield						Selectivity	
							PA	MA	PI	TA	CO	CO_2	to PA	
B5	16.367	8.28	14.3	0.58	460	99.7	53.0	4.0	2.3	0.4	9.6	20.3	53.2	55.8
					450	99.1	56.5	2.9	6.4	2.4	6.9	19.5	57.0	66.9
					440	98.8	65.0	3.0	7.7	3.3	6.8	18.1	65.8	76.9
					430	97.9	60.6	2.5	7.4	4.7	6.3	17.0	61.9	74.2
					420	95.2	55.8	2.3	8.9	6.7	6.0	17.5	58.6	75.0
					420	90.8	51.4	3.8	7.8	7.4	5.7	17.0	56.6	73.4
					408	91.3	45.4	2.3	5.9	6.9	5.9	15.8	49.7	63.7
					405	87.7	45.2	2.0	6.0	7.4	5.7	17.0	51.5	66.9
					400	34.3	9.5	0.0	0.0	8.1	3.2	11.3	27.7	51.3
					390	19.9	0.0	0.0	0.0	4.9	2.2	8.3	0.0	24.4
					370	10.0	0.0	0.0	0.0	0.0	0.9	4.5	0.0	0.0
B6	15.374	11.55	20.0	0.58	460	87.4	34.9	0.8	10.0	13.8	...	18.7	39.0	67.0
					450	87.6	36.1	1.3	10.7	13.6	...	17.5	41.3	69.0
					440	84.9	36.1	2.1	10.3	11.3	...	18.7	42.5	67.9
					430	79.8	33.8	1.3	6.9	9.6	...	14.0	42.4	63.1
					420	72.1	35.3	1.3	7.6	8.8	...	11.7	48.9	71.6
					410	65.5	30.8	1.2	5.6	7.2	...	9.6	47.0	66.6
					400	30.8	13.3	0.0	3.0	9.1	1.5	6.5	38.3	77.6
					390	28.5	9.2	0.0	2.1	7.3	1.0	6.4	32.3	65.3
					380	23.5	7.6	0.0	2.0	6.3	0.7	5.3	32.3	67.7

Catalyst	Weight	Volume	Flow Rate	Contact Time	Temperature	Conversion	Yield						Selectivity to PA	
							PA	MA	PI	TA	CO	CO_2		
B7	15.097	9.43	9.95	0.95	450	96.8	56.5	2.9	6.4	3.4	6.9	19.5	53.8	68.5
					440	96.8	44.9	2.0	8.2	6.5	...	13.4	46.4	60.6
					430	94.7	50.0	3.0	8.9	7.8	...	15.8	52.8	70.5
					430	94.5	44.1	1.7	10.2	8.1	...	12.0	46.7	66.0
					430	95.1	48.1	2.2	9.6	7.5	...	15.8	50.5	68.4
					420	88.3	39.6	1.4	9.6	10.2	...	15.2	44.9	67.3
					415	87.7	41.2	1.8	7.9	10.4	5.5	15.8	46.9	67.4
					410	76.0	42.8	1.3	10.0	11.7	4.6	6.3	56.4	85.0
					410	66.7	28.8	0.5	8.3	10.4	...	...	43.2	71.2
					407	71.3	38.2	1.2	10.4	11.3	4.1	13.4	53.6	83.6
					403	57.7	23.1	0.9	7.0	11.4	3.7	12.2	40.4	72.0
					400	33.8	12.2	5.2	4.6	10.4	2.6	2.9	36.1	80.5
					397	34.4	10.1	4.5	3.9	9.1	2.2	10.0	29.4	67.2
					393	28.2	6.4	2.9	2.5	7.8	1.9	7.6	22.7	59.2
					390	18.3	4.0	2.0	1.5	7.1	1.4	3.0	21.9	68.9
					380	8.0	1.1	0.0	0.0	5.2	1.0	1.5	14.0	78.8
					370	4.9	0.0	0.0	0.0	3.5	0.6	1.3	0.0	70.6

Catalyst	Weight	Volume	Flow Rate	Contact Time	Temperature	Conversion	Yield						Selectivity	
							PA	MA	PI	TA	CO	CO_2	to PA	
C1	15.815	11.17	19.4	0.58	440	96.9	58.8	4.2	5.9	4.2	...	15.7	61.1	76.9
					430	98.1	59.2	4.2	8.9	6.4	...	12.0	59.9	70.2
					430	95.2	56.4	3.9	10.1	7.7	...	12.0	58.4	77.9
					420	93.2	53.8	2.8	10.8	8.1	...	8.5	57.7	77.9
					420	96.6	60.6	3.8	7.8	5.5	...	10.9	62.7	73.9
					410	89.7	53.2	2.6	9.9	8.7	...	8.0	59.3	80.0
					400	72.2	44.5	1.5	9.6	1.1	...	8.3	61.6	76.4
					398	61.1	30.5	1.3	3.0	11.5	...	8.9	50.0	73.8
					395	14.2	1.9	0.0	1.2	5.6	...	2.4	13.4	64.9
					390	14.7	3.1	0.0	2.0	5.5	...	2.5	21.1	72.1
					380	6.7	0.6	0.0	0.2	3.1	...	1.4	9.0	58.2
					370	5.2	0.3	0.0	0.0	2.1	...	1.1	5.8	46.2
C1	15.815	11.17	11.17	0.95	450	99.5	64.0	4.8	4.1	0.4	9.1	16.0	64.3	68.8
					440	99.2	58.3	3.7	5.6	2.1	8.9	17.6	58.8	66.5
					430	97.9	59.3	3.2	9.6	4.2	...	11.4	60.6	74.7
					425	99.7	59.3	3.4	0.0	0.6	...	29.8	59.5	60.1
					415	95.2	44.1	1.8	9.7	6.2	...	20.6	46.3	63.0

Catalyst	Weight	Volume	Flow Rate	Contact Time	Temperature	Conversion	Yield						Selectivity	
							PA	MA	PI	TA	CO	CO_2	to PA	
C1	15.815	11.17	11.7	0.95	415	89.2	50.3	2.7	10.5	9.2	...	10.5	56.4	78.5
					410	81.2	47.8	2.2	12.1	9.0	...	10.5	58.9	84.9
					408	96.9	60.3	3.5	7.1	4.3	...	13.3	62.2	74.0
					408	71.9	41.5	2.0	7.3	7.8	...	8.3	57.7	78.7
					405	79.0	43.7	1.4	10.5	9.7	...	9.1	55.3	80.9
					405	72.2	26.5	1.2	9.4	10.5	6.0	18.3	36.7	64.3
					405	71.0	34.2	1.4	7.0	10.1	...	9.8	48.2	72.3
					402	76.4	41.7	1.4	7.4	9.0	...	10.1	54.7	76.1
					400	59.1	24.2	0.0	8.3	10.3	...	9.2	40.9	72.4
					400	50.5	20.5	0.0	8.0	7.4	...	8.1	40.6	71.1
					398	57.4	26.0	0.0	9.1	10.0	...	5.8	45.3	78.6
					395	13.4	0.0	0.0	0.0	7.2	...	4.6	0.0	53.7
					390	15.8	0.0	0.0	0.0	6.9	...	3.2	0.0	43.7
					385	13.1	0.0	0.0	0.0	5.0	...	3.6	0.0	38.2
C2	18.347	8.86	9.3	0.95	425	99.7	63.3	4.1	0.0	0.0	...	16.8	69.5	69.5
					425	99.7	59.2	3.6	0.0	0.0	...	25.2	59.4	59.4
					415	99.8	59.6	5.3	0.0	0.0	...	...	59.7	59.7

Catalyst	Weight	Volume	Flow Rate	Contact Time	Temperature	Conversion	Yield						Selectivity	
							PA	MA	PI	TA	CO	CO_2	to PA	
C2	18.347	8.86	9.3	0.95	415	99.6	70.6	3.9	0.0	0.0	...	14.4	70.9	70.9
					405	99.7	70.5	4.0	0.0	0.0	...	14.5	70.6	70.6
					405	99.7	67.6	3.1	0.0	0.0	...	15.3	67.6	67.9
					395	97.8	72.1	0.6	0.0	0.0	...	12.9	73.7	73.7
					395	99.8	73.5	3.2	0.0	0.0	...	14.9	73.6	73.6
					395	99.7	74.8	3.2	0.0	0.0	...	14.2	75.1	75.1
					395	99.7	72.5	3.2	0.0	0.0	...	15.5	72.7	72.7
					393	99.7	72.6	3.4	0.0	0.0	...	15.3	72.8	72.8
					390	18.0	2.5	0.0	0.0	6.3	...	4.7	13.9	48.9
					390	34.6	9.8	0.5	4.5	8.5	...	6.9	28.4	65.7
					390	99.4	77.3	3.8	0.0	0.7	...	12.6	77.8	78.5
					385	23.8	6.5	0.0	0.0	4.7	...	7.0	27.3	47.1
					385	18.6	4.1	0.2	1.8	5.8	...	5.0	21.9	62.5
					380	12.6	0.0	0.0	0.0	3.9	...	4.2	0.0	31.0
					375	22.9	3.3	0.0	2.3	5.1	...	2.6	13.2	42.8

Catalyst	Weight	Volume	Flow Rate	Contact Time	Temperature	Conversion	Yield						Selectivity to PA	
							PA	MA	PI	TA	CO	CO_2		
C2	18.347	8.86	15.4	0.58	435	99.6	75.2	3.9	0.0	0.0	10.2	10.2	75.5	75.5
					425	99.7	76.1	3.8	0.0	0.0	9.2	10.3	76.3	76.3
					415	99.8	76.7	3.0	0.0	0.0	8.3	11.0	76.9	76.9
					405	99.8	77.3	3.2	0.0	0.4	...	11.3	70.4	70.8
					395	99.5	62.4	3.4	7.6	2.2	...	15.5	62.8	72.6
					395	99.8	73.5	3.0	0.0	0.0	...	14.4	73.6	73.6
					392	99.7	71.5	6.7	0.0	0.0	...	12.5	74.2	74.2
					390	39.2	16.8	0.0	0.0	8.3	...	6.8	42.9	64.0
					390	48.5	17.3	0.0	7.3	7.9	...	8.3	35.7	71.3
					388	27.9	6.3	0.0	0.0	7.3	...	7.5	22.6	48.7
					386	32.1	11.3	11.2	0.0	0.0	...	6.9	35.2	25.2
					385	13.8	0.0	0.0	0.0	6.0	...	6.4	0.0	43.5
					385	17.4	2.8	0.0	0.0	4.8	...	4.9	16.1	43.7
					385	15.8	2.6	0.0	1.1	3.8	...	3.9	16.4	47.5

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