

Ferric molybdate—A catalyst for the oxidation of toluene

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MS received 17 September 1980 ; revised 5 August 1981

Abstract. Production of benzaldehyde has been carried out by vapour phase oxidation of toluene over silica supported ferric molybdate catalyst, at different support/catalyst ratio. The temperature, concentration of the catalyst and space-velocities were varied over a wide range with each catalyst. The best results were obtained with ferric molybdate (60%) supported on SiO_2 at a temperature of 450°C , space velocity 10373 ± 20 litre hour⁻¹ litre⁻¹, air/toluene ratio 610 and volume of the catalyst 20 cc. The yield of benzaldehyde on the basis of toluene reacted is 70.2% per pass, total conversion 34.9% and conversion to benzaldehyde is 24.5%, surface area and pore size structure of the catalyst was determined by gravimetric method using quartz fibre spring technique.

Keywords. Ferric molybdate ; catalytic oxidation of toluene ; surface area ; pore size distribution.

1. Introduction

Most of the catalysts system used to date for the oxidation of toluene are covered by the patent literature. Volynkin (1968, 1971) studied the oxidation of toluene to benzaldehyde over a number of solids and partially reduced catalysts and in presence of catalysts occurring in molten metals and alloys.

Recently Sharma and Bhattacharyya (1976) have reported the oxidation of toluene over molten oxides. The authors have already reported the use of Cobalt molybdate (Srivastava and Madhok 1980 b) and bismuth molybdate (Srivastava and Madhok 1980 a) as catalysts for the oxidation of toluene. The present paper describes our studies on the adsorption at 45°C and catalytic oxidation of toluene on ferric molybdate.

2. Experimental methods

All the chemicals used were either BDH 'AnalaR' quality or E. Merck G.R. reagent. Toluene was distilled before it was used. The catalyst ferric molybdate was prepared by coprecipitation of FeCl_3 and ammonium molybdate at pH 2 and was subsequently dried in air at 420°C for 4 hr. The composition of the catalyst

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was (by wt. %), Fe_2O_3 as $\text{Fe}_2(\text{MoO}_4)_3$ 17.5, MoO_3 as $\text{Fe}_2(\text{MoO}_4)_3$ 47.3 and MoO_3 excess 35.2. The calculated amount of $\text{Fe}_2(\text{MoO}_4)_3$ was added to the required amount of silica gel in water and dried to get the supported catalyst. The catalyst was used in the form of pallets.

The reactor was made of a pyrex glass tube of internal diameter 3 cm and 70 cm long and provided with a thermocouple. The reactor was connected to another glass tube which functions as preheater zone (P.H.) and mixer (M). The catalyst was packed between two plugs of purified glass wool in the reactor. The reactor and preheater zones were heated by two separate tabular heaters controlled by variable transformers. The temperature of the catalyst bed was measured with a calibrated chromel alumel thermocouple. After each experiment the proper packing of the catalyst zone was checked. The catalyst was charged in the reactor. Purified air was bubbled through a toluene bubbler after passing through a flow meter. The air toluene mixture thus required was heated to 400°C before it was introduced in the reactor. The additional air required was supplied as secondary air. The secondary air was blown through the apparatus before each run was started and up to the rise of catalyst temperature and after the primary air was turned off at the end of each run, was continued until the catalyst temperature had dropped to the normal temperature. The reaction products were collected in an air condenser, water condenser and finally through an ice cold condenser. To prevent benzaldehyde vapours from escaping along with the air stream, the effluent gases were passed through a bubbler containing 2,4-dinitro phenylhydrazine solution. Carbon dioxide produced in the reaction was absorbed by 250 ml of a standard solution of potassium hydroxide (5%), kept in three bubblers. The oxidation product obtained was a mixture of benzaldehyde, benzoic acid and maleic acid with unreacted toluene. Toluene was distilled out and the remaining portion (A) was extracted with 500 cc of dry ether (sodium dry). The ethereal layer was shaken well with a saturated solution of sodium bicarbonate. Benzoic acid and maleic acid separated out in the bicarbonate layer (B) and the benzaldehyde remained in the ether layer (C). The products were analysed quantitatively as reported earlier (Srivastava and Madhok 1980b).

The quartz fibre spring technique was employed in the present investigations for surface area determination. The adsorbent was evacuated for 2-3 hr in an adsorption apparatus before starting a sorption-desorption cycle. The adsorption apparatus was kept inside an air thermostat of the type constructed by Vernon (1931). The temperature of the thermostat was kept at $45^\circ \pm 0.1^\circ\text{C}$ by means of a toluene regulator in conjunction with an electronic relay. Springs of sensitivities ranging from 18.72 to 24.04 cm/g load were used. Pressure of 10^{-2} mm was used. The manometer tube had a bore diameter of 1.2 cm. A cathatometer reading correct to within 10^{-2} mm was employed for measuring the stretch of the spring. By exposing the evacuated adsorbent to toluene at the saturation pressure of toluene, at 45°C , the extent of sorption was measured.

2.1. Parameters studied

Runs were carried out with the above catalysts at the following conditions:

- (i) Reaction temperature : 350 to 550°C
- (ii) Space velocity : 5191 to 12961 litre hr^{-1} litre $^{-1}$.

2.2. Definitions

During the consideration of the results and discussion the various terms used are defined as follows:

Air/toluene ratio	:	$\frac{\text{Volume of the air in the reaction mixture}}{\text{Volume of the toluene passed}}$
Space velocity	:	Volume of gas mixture (dry air and toluene vapour) at N.T.P. passing per hour per volume of the catalyst. (litre hour ⁻¹ litre ⁻¹)
Conversion per cent to a particular product	:	$\frac{\text{Grams toluene converted to a particular product}}{\text{Grams toluene passed}} \times 100.$
Yield of specific product	:	$\frac{\text{Toluene converted to a particular product}}{\text{Toluene converted to particular partial and complete oxygenated products}} \times 100.$

3. Results and discussions

3.1. Catalytic oxidation of toluene

The discussion herewith describes the results obtained with catalyst $\text{Fe}_2(\text{MoO}_4)_3$: SiO_2 in the following manner.

3.1a. *Effect of catalyst composition* : The variation of the benzaldehyde obtained by the oxidation of toluene on varying $\text{Fe}_2(\text{MoO}_4)_3$: SiO_2 ratio is shown in figure 1. While studying the effect of ferric molybdate concentration on the oxidation of toluene, it has been observed that the lowest conversion to benzaldehyde was 10.9% which increased to 24.5% on increasing concentration of ferric molybdate from 10% to 60%. It is evident from figure 1 that the optimum $\text{Fe}_2(\text{MoO}_4)_3$: SiO_2 ratio is 60:40. On further increasing the ferric molybdate ratio to 90%, the percentage conversion to benzaldehyde falls rapidly to 21%. It seems probable that the composition $\text{Fe}_2(\text{MoO}_4)_3$: SiO_2 (60:40) corresponds to the maximum electron work function, a similar observation was made by Margolis *et al* (1963) in the case of oxidation of propene to acrolein using bismuth oxide, molybdenum oxide catalysts.

3.1b. *Effect of temperature* : The optimum reaction temperature of the catalyst in the oxidation of toluene to benzaldehyde has been determined to be 450°C. Figure 2 shows the effect of temperature on the % conversion of benzaldehyde per pass of toluene, at different space velocities. It is observed that maximum conversion is obtained at 450°C, at space velocity 10373, maximum conversion 24.5%, after which there is a rapid fall in the activity of the catalyst upto 550°C, the maximum conversion being 22.4%.

3.3c. *Effect of space velocity* : Figure 3 contains the data representing the effect of space velocity on the activity of ferric molybdate catalyst supported on SiO_2 .

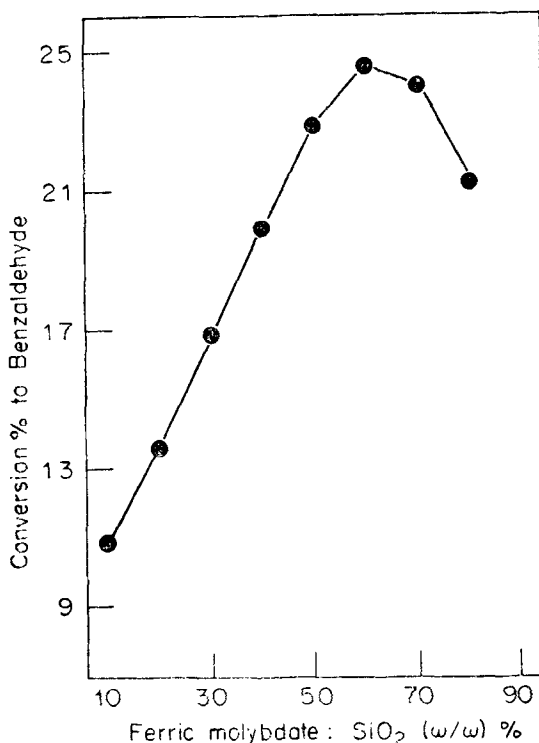


Figure 1. Effect of ferric molybdate concentration on the per cent conversion of toluene to benzaldehyde. ($T = 450^{\circ}\text{C}$; Sp. Vel. 10373 ± 20 litre hour⁻¹ litre⁻¹).

With the increase in space velocity, the conversion to benzaldehyde is increased till an optimum value is reached. The maximum conversion to benzaldehyde 24.5% is obtained at 10373 litre hour⁻¹ litre⁻¹, at a temperature of 450°C . If the space velocity is increased beyond the optimum value, up to 12961 litre hour⁻¹ litre⁻¹, the per cent conversion to benzaldehyde declined considerably, from 25% to 22%.

3.1d. *Role of the catalyst*: Trifiro *et al* (1971) studied the active component in Fe_2O_3 - MoO_3 catalysts at high temperature in the oxidation of methanol, 1-butene and epoxidation of cyclohexene. From their physical studies, they concluded that bulk reduction of the catalyst takes place around 400°C resulting in the high formation of CO in the oxidation of methanol, whereas the decrease in the isomerization of 1-butene occurs at about 450 - 500°C , which they attributed to the complete oxidation of Fe^{+2} to Fe^{+3} , at 600°C . Finally decrease of surface area occurs decreasing the catalytic activity. In the case of ferric molybdate catalyst supported on silica, it has been observed that maximum activity is at 450°C when the ratio of ferric molybdate:silica is 60:40. Beyond 500°C , activity of the catalyst falls rapidly. From these results it seems that like pure ferric molybdate catalysts studied by Trifiro *et al* in these supported catalysts also complete oxidation of Fe^{+2} to Fe^{+3} and decrease in surface area occurs beyond 500°C . Volynkin (1968) also supported the increased activity of mixtures of metallic

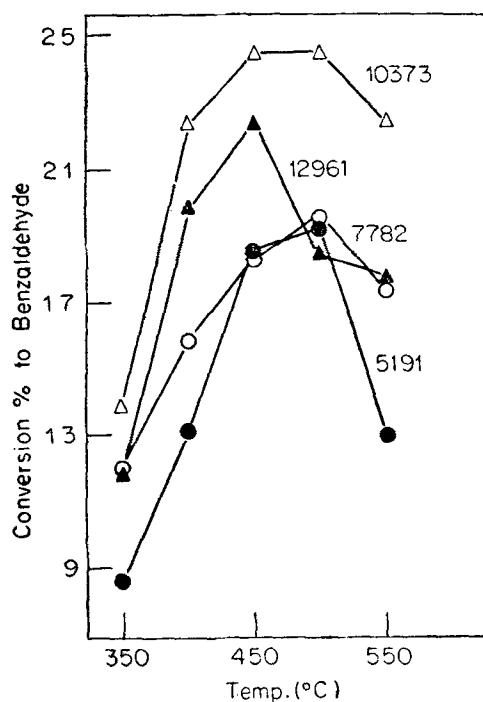


Figure 2. Effect of temperature on the oxidation of toluene for different space velocities (litre hour⁻¹ litre⁻¹).

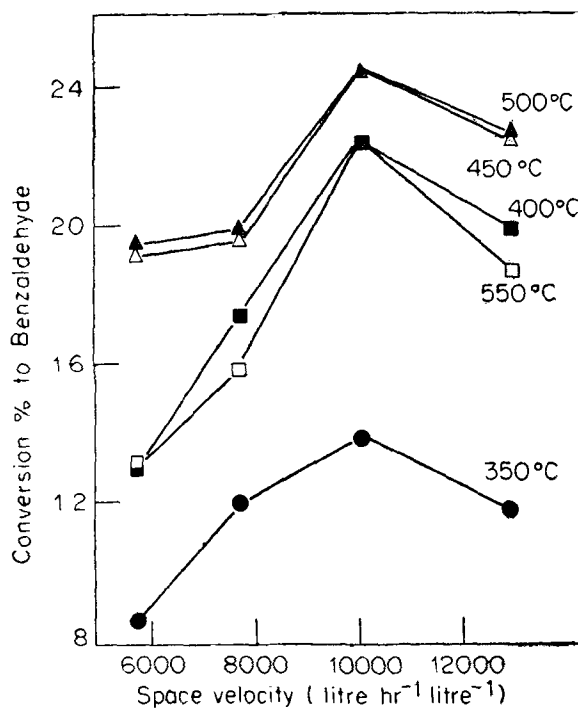


Figure 3. Effect of space velocity on the oxidation of toluene.

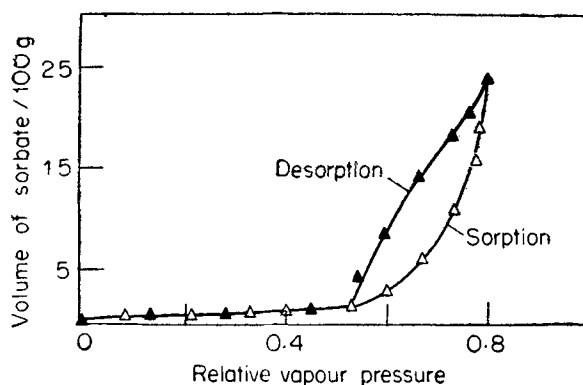


Figure 4. Sorption and desorption of toluene at 45° C on ferric molybdate activated at 450° C.

oxides due to structural changes occurring in the crystal lattice (Saznov *et al* (1968).

4. Surface area and pore size distribution

A series of sorption-desorption studies at 45° C, of toluene vapours have been carried out on ferric molybdate catalyst, activated at 350, 450, 500 and 550° C, employing the quartz fibre spring technique. A permanent and reproducible hysteresis loops (up to 4th cycle of sorption and desorption) are obtained with the four samples. The isotherms are presented by plotting the volume of sorbate taken per 100 g of ferric molybdate against the relative vapour pressure. The amount of toluene taken up by ferric molybdate, activated at 350, 450, 500 and 550° C, at saturation pressure of toluene, in the first cycle are 22.5 cc, 24.9 cc, 23.0 cc and 22.8 cc respectively. The isotherms of toluene have clearly defined 'knees' (figure 4). The hysteresis can be explained in the light of 'ink bottle' or 'cavity theory' (Mc Bain 1935). The cavity theory postulates that sorption-desorption hysteresis is due to the entrapping of liquid sorbate by cavities with constricted necks.

4.1. Application of BET equation

According to BET theory (Brunaur *et al* 1938) the 'knee' signifies the transition from monomolecular to multimolecular sorption. The BET equation has been applied to the isotherm of toluene by plotting $P/x(P_s - P)$ against P/P_s and the BET plots are straight lines. From the slope and intercept of the lines the monolayer capacity, X_m and hence the total number (N_0) of toluene molecules contained in a monolayer on the surface of 1 g of catalyst have been calculated.

4.1a. *Specific surface* : From the monolayer capacity, the specific area of the surface (S) of the sorbent (activated at 350, 450, 500 and 550° C) is calculated by the equation (Gregg and Sing 1967)

$$S = \frac{X_m}{M} N A_m 10^{-20}$$

Table 1. Monolayer capacities, X_m in g per g of sorption, number of toluene molecules (N_0) contained in the monolayer on the surface of 1 g of ferric molybdate. The corresponding relative vapour pressure and specific surface in m^2/g of ferric molybdate.

Ferric molybdate	X_m	N_0 $\times 10^{22}$	P/P_0	Specific surface m^2/g
Activated at 350° C	0.0096	6.28	0.52	227.00
Activated at 45° C	0.0120	7.85	0.53	283.80
Activated at 500° C	0.0117	7.69	0.53	278.00
Activated at 550° C	0.0111	7.26	0.50	262.56

where A_m is the molecular cross-section of sorbate. The molecular diameter $D_{\text{spherical}}$ (6.01 Å) is assumed for calculating the molecular cross-section. The molecular diameter $D_{\text{spherical}}$ is given by the equation (Moelwyn Hughes 1947)

$$D = 1.33 \times 10^{-8} \times V_m^{1/3}$$

where V_m is the molecular volume. The specific surface areas of ferric molybdate activated at different temperatures are shown in table 1.

The value of specific surface increases at first instance from 227 m^2/g to 283 m^2/g if the temperature of activation is increased from 350° C to 450° C. Further, increase in temperature from 450° C to 550° C decreases the specific surface to 262.5 m^2/g .

4.1b. Pore size distribution : According to the cavity theory of hysteresis, the desorption curve of hysteresis loop indicates the neck radius and sorption curve the body radius of the cavity. The predominant neck and body radii of cavities are obtained from the mid point of the steep parts of desorption and sorption curves respectively. The isotherm (figure 4), activated at 450° C, has been employed. Body and neck radii have been calculated by applying the Kelvin equation (Thomson 1871).

$$D = \frac{2V_m Y}{RT \ln (P/P_0)} \cos \theta,$$

where D = diameter of the sorbate molecule ; V_m = molar volume of the adsorbate ; Y = surface tension of the adsorbate ; R = gas constant ; T = absolute temperature ; θ = angle of wetting.

The pore size distribution curve obtained with toluene adsorption on ferric molybdate activated at 450° C is shown in figure 5. The predominant neck and body radii of cavities for ferric molybdate activated at 350, 450, 500 and 550° C with toluene are shown in table 2. The results show that the values of smallest neck radius, the predominant neck radius, and the predominant body radii decreases first by increasing the activation temperature from 350° C to 450° C. A further

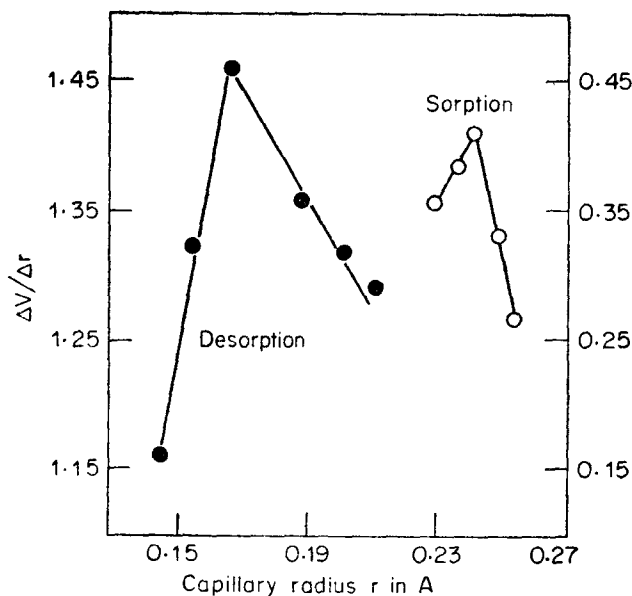


Figure 5. Isotherms showing pore size distribution in ferric molybdate activated at 450° C.

Table 2. Pore size distribution in Å and specific surface of ferric molybdate.

	Specific surface m ² /g	Smallest neck radius Å	Predominant neck radius Å	Predominant body radius Å	Average of predominant neck and body diameter Å
Ferric molybdate activated at 350°	227.00	16.2	18.4	30.3	48.7
Ferric molybdate activated at 450°	283.80	14.5	16.5	24.5	41.0
Ferric molybdate activated at 500°	278.00	15.0	17.2	32.4	49.6
Ferric molybdate activated at 550°	262.58	15.5	18.0	34.3	54.3

increase in temperature from 450 to 550° C also increases the pore radii. Thermal treatment is responsible for alteration of the pore diameter and to some extent the surface area and hence the activity of catalyst. The catalyst when calcined at 350° C, has a surface area of 227 m²/g and average pore diameter 48.7 Å, showing the maximum activity of 23.7%. On heating at 450° C the surface area increases to 283.8 m²/g and pore diameter decreases to 41 Å, conversion 34.9%. Further heating of the catalyst upto 550° C has shown a considerable decrease

in surface area $262.5 \text{ m}^2/\text{g}$ and increase in the pore size 54.3 \AA with decreased activity of 32.1%.

On calcination at higher temperatures (550°C) the porous structure of the catalyst gets transformed, larger pores are formed at the expense of micropores and there are concomitant changes in surface area. These factors affect the activity of catalyst.

Acknowledgements

The authors are thankful to CSIR, New Delhi, for financial assistance and to the Head, Chemistry Department for providing laboratory facilities.

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