JOURNAL OF CATALYSIS 30, 276–282 (1973)

Kinetics of Oxidation of 2-Methylpropene over Bismuth–Molybdate Catalyst

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Received March 1, 1973

The vapor phase air oxidation of 2-methylpropene to methacrolein over a bismuth–molybdate catalyst was investigated in an isothermal integral flow reactor at atmospheric pressure between 300 and 560°C. The effects of several variables, feed ratio of oxygen to 2-methylpropene, reaction temperature and the reciprocal of space velocity on the conversion and product distribution were determined by gas chromatography.

Though 13 different mechanisms were postulated, the rate of reaction was most satisfactorily correlated by a mechanism which assumes the rate-controlling step to be the surface reaction between charged absorbed 2-methylpropene and oxygen. The rate expression

$$r = \frac{(K_S K_H P_H)}{(1 + K_H P_H + K_M P_M)} \cdot \frac{(K_O P_O)}{(1 + K_O P_O)}$$

fitted the data best.

1. INTRODUCTION

In recent years, the controlled oxidation of olefins to useful intermediate products has attracted wide attention. The heterogeneous catalytic oxidation of propylene and 2-methylpropene to corresponding unsaturated aldehydes, are generally carried out over the same type of catalyst as the same reaction mechanism appear to be involved for both reactions. A survey of the patents and published literature pertaining to the partial oxidation of olefins indicates that though the oxidation of propylene has been carried out extensively, on copper oxide and bismuth-molybdate type catalysts, very little is reported about 2-methylpropene oxidation. According to Adams and Jennings (*1*), the reaction mechanism of catalytic oxidation of propylene over the two catalysts are the same. Nevertheless, the kinetics are quite different. Recently Mann and Yao (*2*) have investigated the kinetics of the catalytic oxidation of 2-methylproprene to methacrolein over Se_2O, SO_2 and halogen-modified copper oxide catalysts. The selectivity of the oxidation was improved considerably by employing trace amount of modifiers.

Uckijima and Oda (*3*) studied the oxidation of 2-methylpropene over bismuth–molybdate catalyst. They observed a pronounced effect of temperature on the selectivity. Maximum selectivity was noted between 450 and 550°C. Kitahara and Moriya (*4*) investigated the catalytic oxidation of 2-methylpropene, over various metal oxides and their mixtures, and found vanadium oxide–molybdenum oxide–phosphorous oxide supported on an alumina sponge to be the most effective catalyst. Brill and Finley (*5*) oxidized 2-methylpropene in a tube coated with α-alumina, and molybdenum oxide. They obtained a selectivity of 40%, for methacrolein at a conversion of 34%. Zhizneuskii *et al.* (*6*) studied the oxidation of 2-methylpropene

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over iron–molybdenum–tellurium catalyst containing Fe, Mo, and Te in a ratio of 1:0, 85:1 between 360 and 420°C.

In this paper, we report the effect of various variables, ratio of oxygen to 2-methylpropene in the feed ($\tilde{R}$), process temperature and reciprocal of space velocity, on conversion and yield. Based on experimental data the rate controlling step and the rate equation for the partial air oxidation of 2-methylpropene to methacrolein were determined.

NOMENCLATURE

F	Flow rate of feed, mole/hr
K	Thermodynamic equilibrium constant
K	Adsorption equilibrium constant (with subscripts, S, M, H and O)
P	Partial pressure
$\tilde{R}$	Oxygen to 2-methylpropene ratio in the feed
S	Selectivity, methacrolein produced, mole hr^{-1}/2-methylpropene reacted, mole hr^{-1}
T	Temperature, K
W	Weight of catalyst, g
X	Conversion, 2-methylpropene reacted, mol hr^{-1}/2-methylpropene reacted, mole hr^{-1}
Y	Yield, products formed, mole hr^{-1}/2-methylpropene fed, mole hr^{-1}

Subscripts

M	Methacrolein
H	2-methylpropene
O	Oxygen
S	Surface

2. EXPERIMENTAL

2.1. Apparatus

The partial air oxidation of 2-methylpropene was investigated in an isothermal integral flow reactor. The equipment was constructed of 316 stainless steel.

Air and 2-methylpropene rates were measured by the rotameters and the reactants were well mixed before they entered the preheater (a 5-ft long, ⅛-in. o.d. 316 stainless steel tubing wound around the reactor). The reactor with the preheating section was immersed in a fluidized sand bath heated externally. The hot effluent from the reactor was first directly introduced into a gas chromatograph through a high-temperature sampling valve for analyzing water, acrolein, methacrolein and other aldehydes. The temperature and pressure of the sampling gas were well controlled. The exit gases from the high-temperature sampling valve which could not be separated by the first gas chromatograph were led to a condenser and ice-cooled trap. The noncondensable gases passed through another gas sampling valve leading to another gas chromatograph which could separate CO_2, O_2, N_2, C_3H_6, C_4H_8, and CO.

During the runs, though the rate of hydrocarbon charged into the reactor was maintained constant, different feed ratios (oxygen/hydrocarbon ratio) were obtained by adjusting the air flow rate, while the reciprocal of space velocity was varied by changing the amount of catalyst.

2.2. Analysis

The main features of the analytical procedure for analyzing the reaction products were the same as described earlier (7), except that aldehyde and water were directly analyzed by the vapor fractometer (Perkin–Elmer Model 154C). The gases were analyzed by Fisher Gas Partitioner, Model No. 25V, containing 2 columns joined in series. A 6-ft long 30% HMPA (hexamethyl phosphoramide) coated on celite diatomaceous silica followed by 1-ft long 30% DEHS (di-2-ethyl hexyl sebacate) coated on celite diatomaceous silica, was followed by a second column packed with 7 ft long molecular sieve.

2.3. Catalyst

Bismuth molybdate catalyst was prepared by impregnation of an inert support, zirconium oxide, with aqueous solution of bismuth and molybdenum salts of hydroxypolycarboxide acid with a very small amount of copper nitrate. Two hundred grams of bismuth citrate was dissolved in 160 g of aqueous ammonia, (28% of NH_3) and diluted to 1000 ml (Soln. A); 85.2 g of molybdic acid was dissolved in 80 g of aqueous ammonia (28% NH_3) and was

TABLE 1
PHYSICAL CHARACTERISTICS OF THE CATALYST

Particle diameter = 0.0313 in.
Particle density = 46.3 lb/cu. ft
Sphericity (average) = 0.8
Surface area = 0.6 m^2/g

diluted to 500 ml (Soln. B). Solutions A and B, in a 2:1 ratio were mixed and a small amount of copper nitrate (0.8 g per 50 g zirconium oxide) added. One hundred milliliters of the mixture of Solution A and B were added to 50 g of zirconium oxide (20–40 mesh). Water was evaporated in vacuum on a steam bath. The solid was calcined at 450°C for 6 hr in a muffle furnace. The catalyst was activated in the reactor by passing air over it for 24 hr at 450°C. The physical characteristics of the catalyst are given in Table 1.

3. RESULTS AND DISCUSSION

Experimental data were obtained by means of a quasi-isothermal fixed bed reactor (*8*). The steady state was not only realized from the operating conditions but also from the products analysis. The effect of various variables, oxygen to olefin in the feed ($\bar{R}$), reaction temperature, T, and the reciprocal of space velocity, W/F on the conversion of olefins, X, and yield of various products, carbon dioxide, water and methacrolein, Y, and the selectivity for methacrolein, S, were investigated. While the conversion (X) is defined as the moles of olefin reacted per hour to the moles of olefin, fed per hour, the yield (Y) is referred as the moles of various products formed per hour to the moles of 2-methylpropene fed per hour. The ratio of moles of methacrolein produced per hour to the moles of 2-methylpropene reacted per hour has been defined as selectivity (S).

3.1. Effect of Oxygen/2-Methylpropene Ratio in Feed

Figure 1 shows the effect of feed ratios ($\bar{R}$) on the conversion of 2-methylpropene and selectivity for the oxidation of 2-methylpropene to methacrolein over bismuth molybdate catalyst in the temperature range, 360–560°C, for a W/F ratio of 3.75. While the selectivity for methacrolein increased with increased oxygen/2-methylpropene ratios, the conversion decreased with increased feed ratios. Also while the conversion of 2-methylpropene increased steadily with temperature, the selectivity decreased at all W/F ratios.

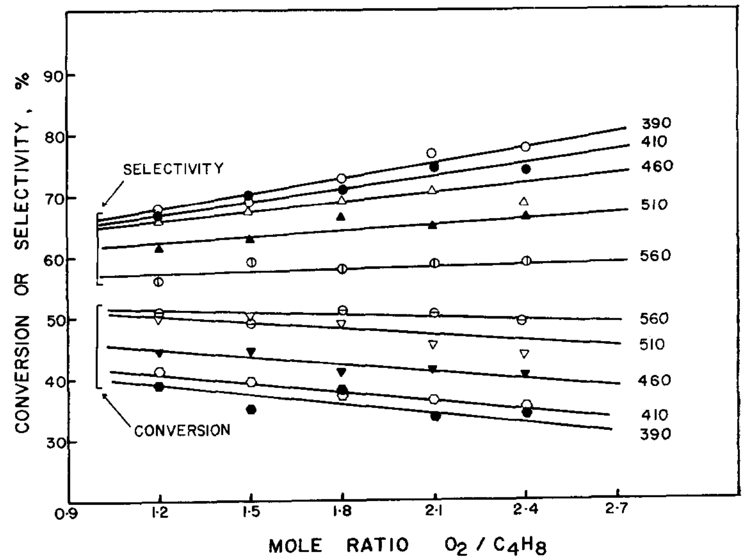

FIG. 1. Effect of feed ratio, O_2/C_4H_8 on conversion and selectivity.

3.2. Effect of W/F Ratios

Figure 2 shows the effect of the reciprocal of space velocity (W/F) on the conversion of 2-methylpropene, and the yield of methacrolein, and CO_2 at 410°C for a $\bar{R} = 1.20$. It is seen that though the fraction of 2-methylpropene consumed (% conversion) increased rapidly up to a W/F ratio of 3, the change in the conversion for W/F ratios between 3 and 5 was very small.

3.3. Kinetic Analysis of Data and Mechanism

A kinetic analysis of the experimental data was made using the approach suggested by Hougen and Watson (*9*), based on Langmuir–Hinshelwood (*10*) mechanism. In this method, various mechanisms, which might control the reaction are postulated, based on a single site (Table 1a), and two types of active site (Table 1b). The rate expressions consistent with these hypothesis are derived. The rate-controlling mechanism of the solid catalyzed gas reaction may be the mass transfer of the reactants, or products, or adsorption of the reactants or desorption of products or chemical reaction between adsorbed molecules at the catalyst surface. The rate expressions thus arrived at are fitted to the experimental data. The rate expression which gives the best fit is retained and the others are discarded.

3.4. Heat and Mass Transfer Effects

The temperature and partial pressure gradients between the flowing fluid and the exterior surface of the catalyst were evaluated by the method of Yoshida *et al.* (*11*). The highest temperature difference across the film thus calculated was of the order of about 5°C. The highest partial pressure gradient thus calculated was about 0.05 atm, which showed that the partial pressure drop across the gas film was insignificant. Hence the effect of heat and mass transfer can be considered negligible.

The effects of diffusion were kept at a minimum by using a high velocity of the gas through the catalyst. Figure 3 shows the effect of feed velocity on the conversion of 2-methylpropene. The fair constancy of conversion obtained by changing the feed ratio while keeping W/F constant suggested that the diffusion of the gases was

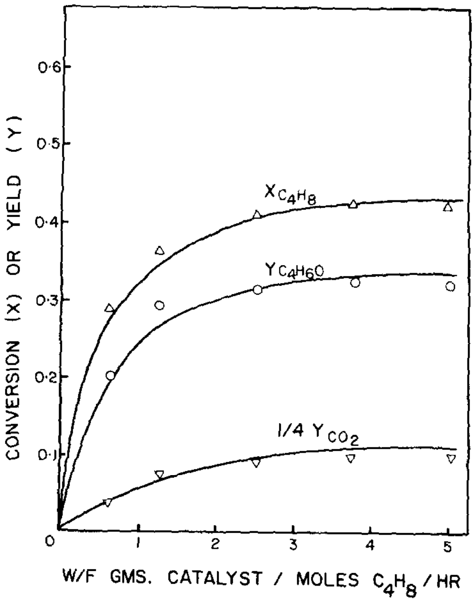

FIG. 2. Effect of the reciprocal of space velocity on conversion and yield.

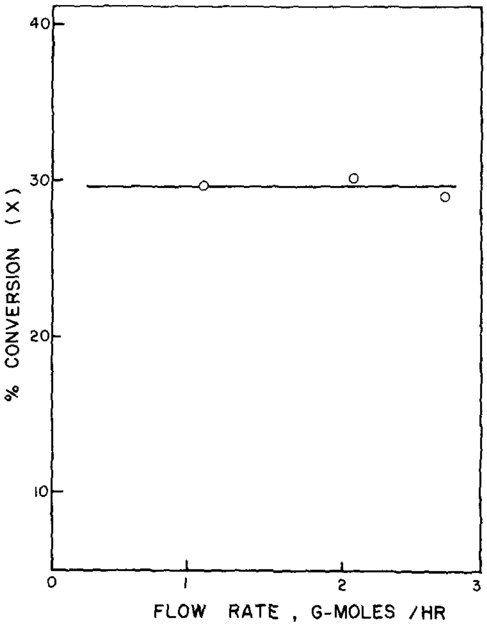

FIG. 3. Effect of feed velocity on conversion.

TABLE 2

RATE EQUATIONS DERIVED USING HOUGEN–WATSON METHOD

No.	Rate-controlling step	Mechanism	Rate equation
		(a) One Type of Active Site	
1	Adsorption of 2-methylpropene	Surface reaction between adsorbed 2-methylpropene and oxygen	$r = \dfrac{K_S P_H}{1 + K_{\mathrm{O}} P_{\mathrm{O}} + K_M P_M}$
2	Adsorption of 2-methylpropene	Surface reaction between adsorbed 2-methylpropene and O_2 in gas phase	$r = \dfrac{K_S P_H}{1 + K_M P_M}$
3	Adsorption of oxygen	Surface reaction between adsorbed 2-methylpropene and oxygen	$r = \dfrac{K_S P_{\mathrm{O}}}{1 + K_H P_H + K_M P_M}$
4	Adsorption of oxygen	Surface reaction between adsorbed oxygen and 2-methylpropene in gas phase	$r = \dfrac{K_S P_{\mathrm{O}}}{1 + K_M P_M}$
5	Desorption of methacrolein	Surface reaction between adsorbed 2-methylpropene and oxygen	$r = \dfrac{k'_d \left(\dfrac{K P_H P_{\mathrm{O}}}{P_W} - P_M\right)}{1 + K_H P_H + K_{\mathrm{O}} P_{\mathrm{O}} + K K_M \dfrac{P_M P_{\mathrm{O}}}{P_W}}$
6	Desorption of methacrolein	Surface reaction between adsorbed 2-methylpropene and oxygen in gas phase	$r = \dfrac{k'_d \left(\dfrac{K P_H P_{\mathrm{O}}}{P_W} - P_M\right)}{1 = K_H P_H + K K_M \dfrac{P_H P_{\mathrm{O}}}{P_W}}$
7	Desorption of methacrolein	Surface reaction between adsorbed oxygen and 2-methylpropene in gas phase	$r = \dfrac{k'_d \left(\dfrac{K P_H P_{\mathrm{O}}}{P_W} - P_M\right)}{1 + K_{\mathrm{O}} P_{\mathrm{O}} + K K_M \dfrac{P_H P_{\mathrm{O}}}{P_W}}$
8	Surface reaction	Surface reaction between adsorbed 2-methylpropene and adsorbed oxygen	$r = \dfrac{K_S K_H P_H K_{\mathrm{O}} P_{\mathrm{O}}}{(1 + K_H P_H + K_{\mathrm{O}} P_{\mathrm{O}} + K_M P_M)^2}$
9	Surface reaction	Surface reaction between adsorbed 2-methylpropene and oxygen in the gas phase	$r = \dfrac{K_S K_H P_H P_{\mathrm{O}}}{1 + K_H P_H + K_M P_M}$
10	Surface reaction	Surface reaction between adsorbed oxygen and 2-methylpropene in the gas phase	$r = \dfrac{K_S K_{\mathrm{O}} P_{\mathrm{O}} P_H}{1 + K_{\mathrm{O}} P_{\mathrm{O}} + K_M P_M}$
		(b) Two Types of Active Site	
11	Surface reaction	Surface reaction between charged adsorbed 2-methylpropene and oxygen	$r = \dfrac{K_S K_H P_H}{1 + K_H P_H + K_M P_M} \cdot \dfrac{K_{\mathrm{O}} P_{\mathrm{O}}}{1 + K_{\mathrm{O}} P_{\mathrm{O}}}$
12	Irreversible charged adsorption of oxygen and 2-methylpropene	Surface reaction between charged adsorbed 2-methylpropene and oxygen	$r = \dfrac{K_H P_H}{1 + \left(\dfrac{K_H}{K_{\mathrm{O}}}\right)\left(\dfrac{P_H}{P_{\mathrm{O}}}\right)}$
13	Irreversible charged adsorption of oxygen and 2-methylpropene	Surface reaction between charged adsorbed 2-methylpropene and oxygen, oxygen is dissociated	$r = \dfrac{K_H P_H}{1 + \left(\dfrac{K_H}{K_{\mathrm{O}}}\right)\left(\dfrac{P_H}{P_{\mathrm{O}}^{1/2}}\right)}$

not controlling. The use of a 20–30 mesh catalyst support reduced the internal diffusional resistance. The internal diffusional resistance in the catalyst particles was practically negligible as shown by a no measurable change in the reaction rate on varying the catalyst size between 0.3 to 0.59 mm.

Since the diffusion steps, which are physical processes, were found not to be rate controlling, the remaining steps, viz. the adsorption of the reactants, the desorption of products, and the reaction between adsorbed gases were examined in detail. The method of initial rates as suggested by Yang and Hougen (*12*) was applied to the experimental data to eliminate several of the chemical steps. The initial rate was determined by measuring the slope of tangent to x vs W/F curves at $x = 0$ for various feed compositions. A plot of initial rates against partial pressures of 2-methylpropene indicated that the desorption of products was definitely not rate controlling.

Mann and Yao (*13*) have proposed a mechanism for the oxidation of olefins using the Electron Theory of Catalysis considering the surface to consist of two types of active sites, electrons and positive holes on which oxygen and olefin are selectively adsorbed. The surface reaction can be considered to be taking place through the following steps: (i) electron transfer from or to the reactants; (ii) homogeneous reaction (formation of activated complex and rearrangement of the charged particles on the surface); (iii) electron transfer from or to the products.

Writing the stoichiometric equation for the reaction as:

$$C_4H_8 + O_2 \rightleftarrows C_4H_6 + H_2O$$

and following the usual procedure of derivations (*14*), and neglecting the term $(P_{C_4H_6O})(P_{H_2O})/K$, since K, equilibrium constant for the gas phase oxidation of 2-methylpropene, was very large, $(\ln K \gg 20)$ equation for various postulated mechanisms, relating the rate of formation of methacrolein and water were derived (Table 2a and 2b) and tested for the best fit of the data.

The data were most satisfactorily correlated by mechanism (*12*), which assumes that the rate-controlling step was the surface reaction between charged adsorbed 2-methylpropene and oxygen.

$$r = \frac{K_S K_H P_H}{(1 + K_H P_H + K_M P_M)} \cdot \frac{K_O P_O}{1 + K_O P_O}$$

where K_S, K_H and K_M are temperature dependent, and can be expressed by the following equations.

$$\ln K_{C_4H_8} = 5.18 + 17.79 \times 10^3/T$$

$$\ln K_{C_4H_6O} = 4.30 + 24.47 \times 10^3/T$$

$$\ln K_{O_2} = 0.75 + 3.64 \times 10^3/T$$

$$\ln K_S = 7.44 - 7.32 \times 10^3/T$$

Figure 2 shows the comparison between the experimental and predicted values with the rate equation for an oxygen/2-methylpropene ratio of 1.2 at 410°C. The solid lines in the figure refer to the curve predicted by substituting the values of K_S, K_H, K_M and K_O in the rate equation derived above; the circles represent the experimental data. The maximum deviation between the predicted values and the experimental ones has been found to be ±4%, except for high values of W/F. This rate equation is similar with the rate equation derived by Mann and Yao (*2*) for the oxidation of 2-methylpropene over modified copper oxide catalyst. This is in agreement with Adams and Jennings (*1*), who have suggested that the reaction mechanism of catalytic oxidation of olefins over the two catalysts should be the same.

CONCLUSIONS

The catalytic air oxidation of 2-methylpropene over bismuth molybdate catalyst has been investigated between 300 and 560°C, and the effects of several variables, feed ratio of oxygen to 2-methylpropene, reaction temperature and reciprocal of space velocity on the conversion and product distribution were determined. The highest selectivity of about 82% was obtained at over 30% conversion at 390°C for a $\bar{R} = 2.1$ and a W/F of 2.5. However at a little sacrifice in the selectivity much higher conversions were obtained. The rate equation, which satisfactorily correlated the experimental data, has been evaluated based on the mechanism which postulates the rate controlling step to be the surface reaction between charged absorbed 2-methylpropene and oxygen.

ACKNOWLEDGMENT

The authors are indebted to the National Research Council of Canada for financial support of the project (A-1125).

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