

STUDIES ON THE CATALYTIC OXIDATION OF PROPYLENE ON FERRIC MOLYBDATE

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Ferric molybdate is less selective in the partial oxidation of propylene than bismuth molybdate. Its catalytic behavior is similar to that observed on other transition metal molybdates. The intrafacial nature of the reaction is established through kinetic and adsorption measurements.

В отличие от молибдата висмута, молибдат трехвалентного железа менее селективен в реакции парциального окисления пропилена. Механически его поведение похоже на поведение молибдатов других металлов. Межфазная природа реакции была установлена в процессе кинетических и адсорбционных измерений.

INTRODUCTION

The search for a selective catalyst for the partial oxidation of light hydrocarbons has led to a number of catalysts, as e. g. cuprous oxide /1/, bismuth molybdate /2/ and uranium and tin antimonates /1/. Among the various molybdates, ferric molybdate has proved to be an efficient catalyst for the partial oxidation of methanol /2/. Ternary combinations containing Bi, Fe and Mo /3/ and trivalent molybdates /4/ have been used as catalysts in the selective oxidation of propylene, while studies with ferric molybdate itself are meagre. The purpose of this paper is to present results of a systematic study on the oxidation of propylene on ferric molybdate. These studies can be useful for identifying the difference in the nature of active sites responsible for the oxidation of methanol as well as that of propylene.

EXPERIMENTAL

Ferric molybdate was obtained from a solution of ferric nitrate and ammonium molybdate by precipitation with aqueous ammonia. The precipitate after washing and drying was calcined in air at 500 °C for 12 h. The catalyst was characterized by X-ray, IR and magnetic measurements. The kinetic runs were carried out in a differential microreactor with on-line analysis. Details of the experimental procedure are given elsewhere /5/.

RESULTS AND DISCUSSION

i) Kinetic studies: The variation of percentage conversion at various partial pressures of propylene shows that the reaction is first order with respect to the hydrocarbon, while conversion is independent of the oxygen partial pressure indicating a zero order dependence on oxygen pressure. The product distribution with the variation of propylene or oxygen partial pressure determined at 300 °C at a total flow rate of 100 ml/min with either oxygen or propylene flow rate equal to 40 ml/min (given in Table 1) showed that a) acrolein and carbon-dioxide are formed and selectivity with respect to acrolein increases with the increase in the partial pressure of propylene, b) with the increase of the partial pressure of oxygen, there is no appreciable change in any of these factors.

The Arrhenius parameters evaluated from the initial rate data with respect to total conversion, or with respect to acrolein or CO₂ formed are given in Table 2. ii) Effect of substrates: A series of experiments were carried out by mixing the inlet stream with different amounts of water vapor, hydrogen or CO₂ at various temperatures. It was observed (Table 3) that the presence of water vapor or carbon dioxide does not affect the activity with respect to partial or total oxidation, while hydrogen affects both activities.

Kinetic studies carried out in the absence of gas phase oxygen in the range of 300-340 °C at different flow rates of propylene and nitrogen showed that total

Table 1

Product distribution with the variation of propylene or oxygen flow; temperature: 300 °C; total flow: 100 ml/min; Oxygen or propylene flow: 40 ml/min

Propylene/ Oxygen flow (ml/min)	Conversion %	Acrolein %	CO ₂ %	Selectivity to acrolein
10	6.1	0.5	5.5	8.2
20	7.9	1.0	6.7	12.6
25	8.9	1.3	7.5	14.6
30	9.5	1.4	7.9	14.7
40	12.4	1.8	10.3	14.5
10	12.7	2.3	10.2	18.1
20	12.2	2.3	10.3	18.0
30	12.3	1.9	10.3	15.4
40	12.4	1.9	10.5	15.3

Table 2

Arrhenius parameters for the oxidation of propylene on ferric molybdate

Reaction	Energy of activation (kJ/mol)	Frequency factor (min ⁻¹ m ⁻²)	Rate constant at 330 °C (min ⁻¹ m ⁻²)	Energy of activation in the absence of gas phase oxygen (kJ/mol)
Oxidation reaction	128.5	1.0 × 10 ¹⁴	8.2 × 10 ²	59.2
Acrolein formation	115.0	1.0 × 10 ¹²	1.2 × 10 ²	66.3
Carbon dioxide formation	115.0	5.9 × 10 ¹²	6.9 × 10 ²	59.6

Table 3
Effect of substrates on the oxidation of propylene
on ferric molybdate at 300 °C

Substrate (A)	Ratios $C_3H_6:O_2:N_2:A$	Conversion %	Acrolein %	CO ₂ %	Selectivity to acrolein
Water	15:30:30:0	9.7	1.5	8.1	15.5
	15:30:24:6	9.5	1.4	7.9	14.7
	15:30:17:13	9.1	1.3	7.6	14.3
	15:30:11:19	8.8	1.2	7.5	13.6
Hydrogen	15:30:25:5	7.8	0.5	7.2	6.4
	15:30:15:15	6.1	0.4	5.7	6.6
	15:30:5:25	4.7	0.2	4.5	4.3
Carbondioxide	15:30:25:5	9.4	1.5	7.9	15.9
	15:30:15:15	9.4	1.4	7.8	14.9
	15:30:5:25	9.2	1.4	7.7	15.2
	10:0:40:0	8.4	2.6	5.6	30.7
	20:0:80:0	6.7	1.6	5.0	23.6
	25:0:100:0	4.5	0.9	3.4	20.5

conversion, as well as carbondioxide formation decreased, while the amount of acrolein formed slightly increased indicating that acrolein formation proceeds through the participation of lattice oxygen, and carbondioxide formation could have occurred via a consecutive reaction path. iii) Adsorption studies: A series of adsorption measurements was carried out on ferric molybdate in the following order:

a) adsorption of propylene on the fresh catalyst in the temperature range of 135-235 °C; b) readsorption of propylene at any given temperature after evacuation of the reversibly adsorbed propylene; c) adsorption of oxygen on the fresh

Table 4
Heats of adsorption for various substrates in kJ/mol

	From the Clapeyron equation	From P_0 values* according to Matsuura's analysis
Propylene adsorption (I) on fresh surface	18.0-9.7 (0.05-0.65)	9.7
Propylene adsorption (II)	8.7-9.15 (0.05-0.45)	8.8
Oxygen adsorption (I)	18.0-21.0 (0.05-0.25)	..
Oxygen adsorption (II)	23.9-22.7 (0.05-0.25)	..
Strong propylene adsorption		24.0

Figures in brackets refer to the limits of the volume adsorbed in ml NTP within which the variation in heat of adsorption is calculated

*I. Matsuura, G.C.A. Schuit: *J. Catal.*, 20, 19 (1971)

catalyst; d) adsorption of oxygen on the adsorbent evacuated at 400 °C after propylene adsorption, e) adsorption of oxygen on the surface after evacuation of adsorbed propylene at the temperature of adsorption.

The heats of adsorption deduced from these isotherms are given in Table 4. These adsorption measurements show that: a) the catalyst takes up more oxygen after pretreatment with propylene than on the bare surface; b) oxygen taken up could be utilized for reoxidation of the catalyst or for direct reaction with adsorbed propylene; c) there seems to be only one type of reactive adsorbed form of propylene which yields partial or complete oxidation products depending on the experimental conditions.

Thus this study showed that ferric molybdate behaved exactly in a similar manner as other transition metal molybdates in the oxidation of propylene.

REFERENCES

1. G.W. Keulks, L.D. Krenzke, T.M. Notermann: *Adv. In Catalysis*, 27, 183 (1978).
2. P. Jiru, B. Wichterlova, J. Tichy: *Proc. 3rd, Intern. Congr. Catalysis, Amsterdam* 1, 199 (1965).
3. C. Daniel, G.W. Keulks: *J. Catal.*, 24, 529 (1972).
4. M.M. Agaguseinova, K.Yu. Adzhamov, T.G. Alkhazov: *Kinet. Katal.*, 17, 1335 (1976).
5. B. Viswanathan, C.V. Bhuvana, M.V.C. Sastri: *Ind. J. Chem.*, (in press).