

CATALYTIC OXIDATION OF PROPYLENE ON MOLYBDENUM-MANGANESE OXIDE CATALYST ON CARRIER

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Three molybdenum-manganese oxide catalysts with atomic ratios Mo : Mn = 7 : 1, 5 : 1 and 3 : 1 were brought on an Aerosil carrier, and their catalytic activity for propylene oxidation in gas phase has been studied. Effect of the carrier type on the activity of the catalyst with atomic ratio Mo : Mn = 5 : 1 has been followed with the carriers Aerosil, Alon and silicasol. The same catalyst has been used also for investigation of the dependence between catalytic activity and amount of the active phase brought on Aerosil.

Our previous report¹ dealt with physical characteristics and catalytic properties of pure Mo-Mn-O catalysts. The present paper deals with effect of carrier, its type and amount on the properties of Mo-Mn-O catalysts in gas phase oxidation of propylene. The catalysts with atomic ratios Mo : Mn = 7 : 1, 5 : 1 and 3 : 1 were chosen for this study.

EXPERIMENTAL

Preparation of Catalysts. The catalysts were prepared by precipitation from two stock solutions. Solution A: 300 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ was dissolved in 600 ml 15% NH_4OH . The molybdenum content was checked by oxine method. Solution B: 350 g $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was dissolved in 450 ml distilled water. The manganese content was checked manganometrically. For each sample 50 g Aerosil (high-dispersed SiO_2 , Degussa GFR) was mixed with 350 ml distilled water and 60 ml 5N- HNO_3 . Then solution B was added to make the final manganese content 2.51 g, 3.41 g and 5.30 g for the catalyst I (Mo : Mn = 7 : 1), II (Mo : Mn = 5 : 1) and III (Mo : Mn = 3 : 1), respectively. Then with continuous stirring solution A was added to make the final content 30.60 g Mo, 29.74 g Mo and 27.74 g Mo for the catalyst I, II and III, respectively. During precipitation the temperature 60°C was maintained in all three cases. pH of the suspensions was adjusted at 5.5 to 6.0 by addition of ammonia water, and 2 g graphite was added to each suspension. Then the suspensions were evaporated to paste consistency with continuous stirring. The paste was dried at 120°C 12 hours, ground to powder and calcinated at 250–300°C 2 hours and at 350–400°C 6 hours. Then the catalysts were tabletted and the tablets obtained (0.8 cm in diameter, 0.3 to 0.4 cm in height) were annealed at 480–520°C 24 hours and at 585–620°C again 24 hours. Then the tablets were ground, and fractions 0.40–0.64 mm and 0.25–0.40 mm were separated. Weight ratio carrier : sum of the metals was 1.5 in all cases. Effect of the carrier type on the catalytic activity of the Mo-Mn-O catalyst was studied with the catalyst II (Mo : Mn =

= 5 : 1) brought on silicasol (sol, 28.7% SiO_2) and Alon (high-dispersed Al_2O_3 , Cabot Corp., U.S.A.) denoted as II (silicasol) and II (Alon), respectively. The catalysts were prepared in the same way and with the same ratio carrier : active phase (1:5). Effect of the amount of active phase and carrier was studied with the atomic ratio Mo : Mn = 5 : 1 combined with various amounts of Aerosil. The used weight ratios carrier : active phase (*i.e.* sum of the metals) was in the individual samples: 1.5, 2.26, 3.52 and 6.03, the respective samples being denoted as II (1.50), II (2.26), II (3.52) and II (6.03). The preparation procedure was the same as above, the Aerosil amount was 50 g in each case.

Specific surfaces of the catalysts were determined by the BET method: adsorption of krypton at the temperature of liquid nitrogen. Effective surface of krypton atom was taken as 21 \AA^2 . The found values were: catalyst I (Mo : Mn = 7 : 1) — $63 \text{ m}^2/\text{g}$; II (Mo : Mn = 5 : 1) — $56 \text{ m}^2/\text{g}$; III (Mo : Mn = 3 : 1) — $67 \text{ m}^2/\text{g}$; II (silicasol) — $24 \text{ m}^2/\text{g}$; II (Alon) — $15 \text{ m}^2/\text{g}$.

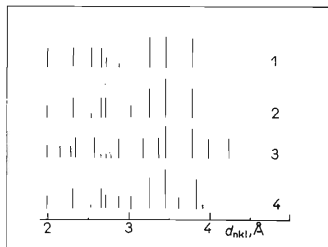
X-Ray analysis was carried out with a diffractograph type URS-50 IM with copper target; imposed voltage 32 kV, current 10 mA; Ni filter. Fig. 1 gives the diagrams of diffraction lines of the contacts II (Aerosil), II (Alon), II (silicasol) and catalyst II (Mo : Mn = 5 : 1) in pure state.

Apparatus for the catalytic activity measurements. Testing of the prepared contacts was carried out with the described¹ flow-apparatus with integral reactor and counter-current water absorber serving for absorption of liquid reaction products — aldehydes and acids. The flow-apparatus was connected with a gas chromatograph.

Analytical methods. The carbonyl compounds were identified by descending paper chromatography with 2,4-dinitrophenylhydrazine in 2M-HCl as dinitrophenylhydrazones. The paper was impregnated with N,N-dimethylformamide and acetone (1 : 1), cyclohexane being used as eluent. The total aldehyde amount was determined by oxime method according to Smith and Mitchell². Acrolein was determined polarographically according to Moshier³ and chromatographically. Glass column $0.4 \times 180 \text{ cm}$ was packed with Chromosorb G with 4% (by wt.) Carbowax 1500. Column temperature 38°C ; carrier gas nitrogen. Acrolein was combusted over $\text{CuO} + \text{Co}_3\text{O}_4$ and converted into hydrogen over Fe fillings. Carbon dioxide was removed by molecular sieve. Organic acids were determined titrimetrically with sodium methoxide. Gaseous components (C_3H_6 , O_2 and CO_2) were analyzed by gas chromatography. The glass column $0.4 \times 200 \text{ cm}$ was packed with Porapak N; the column temperature 130°C ; carrier gas nitrogen.

FIG. 1
Diffraction Pattern of the Catalyst II (Mo : Mn = 5 : 1)

Carrier: 1 Aerosil, 2 Alon, 3 Silicasol, 4 None.



Testing conditions. Catalytic activity of the contacts with Aerosil, *i.e.* I (Mo : Mn = 7 : 1), II (Mo : Mn = 5 : 1) and III (Mo : Mn = 3 : 1) was measured at five temperatures each. Catalyst weighing was 0.5 g; grain 0.40 to 0.63 mm, temperature gradient in the bed 3 to 5°C.

RESULTS AND DISCUSSION

Table I gives the results of the measurements. Comparison of the catalyst II (Mo : Mn = 5 : 1) activity with various carriers (Aerosil, Alon, silicasol) and various ratios of Aerosil was carried out at constant temperature 545°C. In every case the catalyst weighing was 1 g, grain 0.40 to 0.63 mm. Composition of the reaction mixture was the same in all cases: 7% C₃H₆, 14% O₂, 20% H₂O, 59% N₂ (by vol.). Initial feed of the reaction mixture was 5 l (NTP)/h. The proper measurement of catalytic activity was carried out always after 5 hours of "running-in" of the catalyst in the reaction mixture at the respective reaction temperature, so that steady state was reached in the catalyst. The test results of all the catalysts at 545°C are given in Table II.

TABLE I

Catalytic Oxidation of Propylene on Mo-Mn-O Catalysts with Aerosil Carrier
Propylene feed rate $15.6 \cdot 10^{-3}$ mol/h.

Catalyst (Mo : Mn)	Temperature °C	Conversion ^a C ₃ H ₆ , %	Yield, mol/h . 10 ⁻³		
			CH ₂ O	C ₃ H ₄ O	CO ₂
I (7 : 1)	514	7.3	0.55	0.51	1.30
	533	16.7	1.52	0.61	4.39
	551	32.3	1.76	0.79	10.87
	562	49.1	1.88	0.45	19.67
	576	65.2	2.03	0.28	27.58
II (5 : 1)	502	10.3	0.64	0.41	2.88
	537	14.6	0.98	0.53	4.26
	559	22.5	1.59	0.62	7.00
	572	33.7	2.21	0.71	11.39
	587	53.6	2.81	0.83	19.72
III (3 : 1)	521	8.0	0.84	0.36	1.70
	545	19.8	1.33	0.59	6.07
	563	32.6	1.25	0.53	12.37
	572	51.0	1.27	0.41	21.29
	596	77.1	1.20	0.20	34.25

^a (Mol of reacted propylene per mol of propylene in the feed) . 100.

All the Mo-Mn-O-carrier catalysts gave traces of organic acids as oxidation products, too, their composition being not determined.

Influence of Aerosil as a carrier (compared with pure Mo-Mn-O catalysts with ratios 7 : 1, 5 : 1, 3 : 1; ref.¹) results mainly in 2 to 3 fold increase in propylene conversion and increase in formaldehyde yield. Yield of acrolein was not fundamentally affected by Aerosil. The most active Mo-Mn-O-Aerosil catalyst is the sample I (Mo : Mn = 7 : 1); 50% conversion of propylene is obtained at 565°C, whereas with the least active catalyst II (5 : 1) the respective temperature is 585°C. We suppose the higher activity to be caused by greater content of free MoO₃ in the catalyst I, which was proved by X-ray analysis¹. In the cases of samples I and III the yield of CO₂ increases steeply with temperature starting already from 515–520°C, whereas with the catalyst II only a mild increase of CO₂ yield is observed within 500 to 540°C. A marked difference in catalytic properties between the contacts I, III and II is manifested in the temperature dependence of the acrolein yield. Whereas with the contacts I and III the acrolein yield reaches maximum at 550°C and then rapidly decreases, with the catalyst II this yield steadily increases up to the last measured temperature (587°C). Similarly, also the formaldehyde yield increases with temperature if the catalyst II is used, this increase being almost linear above 550°C, whereas with the catalyst III the formaldehyde yield begins to decrease above 550°C. Selectivity with respect to acrolein and formaldehyde is greater with the catalyst II above 550°C compared to that of the remaining two catalysts, and it does not fall below

TABLE II

Comparison of Catalytic Activity (at 545°C) of the Catalyst II (Mo : Mn = 5 : 1) on Various Carriers and in Various Amounts on Aerosil

Propylene feed rate $15.6 \cdot 10^{-3}$ mol/h.

Catalyst	Conversion C ₃ H ₆ , %	Yield, mol/h · 10 ⁻³			CH ₂ O : C ₃ H ₄ O
		CH ₂ O	C ₃ H ₄ O	CO ₂	
II (Aerosil)	36.4	2.90	0.82	11.10	3.54
II (Alon)	13.3	traces	0.40	4.7	—
II (silicasol)	47.7	0.50 ^a	0.37	20.1	—
II (1.50)	36.4	2.90	0.82	11.10	3.54
II (2.26)	37.5	2.84	0.71	12.45	4.00
II (3.52)	60.0	7.35	1.16	17.02	6.33
II (6.03)	60.8	4.95	0.70	20.85	7.07

^a This value involves acetaldehyde, too. Its amount was not determined.

10% in the temperature range measured with the catalyst II (which also is not true for the other two catalysts). It was proved by X-ray analysis¹ that the sample II contains the greatest amount of MnMoO_4 , which could cause the greater resistance of the catalyst against total combustion at higher temperatures. By the same method it was found that the silicasol carrier forms a new phase with the catalyst II, its composition being not identified. The diffraction pattern shows ten new lines compared with the pure catalyst; the maximum intensity belongs to the line of $d_{hkl} = 3.786 \text{ \AA}$. However, this line was identified (as the only one) in the sample II(Aerosil), too. Hence it is possible that also Aerosil forms a new compound with the sample II, its amount, however, would not exceed 3–5% by wt. It is interesting that silicasol carrier changes qualitative composition of propylene oxidation products. The sample II(silicasol) was the only one to produce acetaldehyde among the reaction products. The Alon carrier diminishes considerably the specific surface (as compared to Aerosil), and only traces of formaldehyde are formed on II(Alon) contact. Lowering of the amount of active phase in the catalyst II on Aerosil results in increase of propylene conversion and of ratio of formaldehyde to acrolein yields. Maximum yields of formaldehyde and acrolein were obtained with the sample II(3-52), the selectivity with respect to acrolein and formaldehyde being 12% and 26%, respectively.

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