

PREPARATION OF A MOLYBDENUM-MANGANESE CATALYST AND ITS CATALYTIC ACTIVITY DURING OXIDATION OF PROPYLENE

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Fifteen Mo-Mn oxide catalysts of different atomic ratios were prepared and tested on a flow apparatus containing an integral reactor with respect to their catalytic activity for oxidation of propylene in the gaseous phase. Formaldehyde, acrolein, traces of organic acids, CO₂ and H₂O were found among oxidation products. MnMoO₄ was determined in the samples by the X-ray phase analysis.

Mann and Hahn^{1,2} has described preparation and use of an Mn-Mo-O catalyst for oxidation of methanol to formaldehyde with molecular oxygen. They have found out that this catalyst is highly selective for the given reaction (to 100%) at a relatively high conversion of approximately 83%. Trifiro and coworkers³ have used this catalyst successfully also for oxidation of butene to maleinanthride.

These good experiences with the Mo-Mn-O catalyst at selective oxidations had induced us to a complex study of these contacts for oxidation of propylene in the gaseous phase. In this communication we aimed our efforts at preparation of Mo-Mn oxide catalysts, determination of their physical characteristics and investigation of their catalytic properties for oxidation of propylene. Catalytic properties of Mo-Mn-O catalysts deposited on different carriers and kinetics of oxidation of propylene will be investigated in next communications.

EXPERIMENTAL AND RESULTS

Preparation of catalysts: a series of 15 Mo-Mn-O catalysts of different atomic Mo : Mn ratios was prepared from two basic solutions of (NH₄)₆Mo₇O₂₄ · 4 H₂O(A) and Mn(NO₃)₂ · 6 H₂O(B). Both solutions were heated to 60°C. Solution A was added to solution B during continuous agitation so that the agitator might be able to homogenize the arising precipitate. With the help of aqueous ammonia, pH of the solution was adjusted to 5.5-6. The solution was evaporated dry during continuous agitation at 90°C. The resulting paste was dried for 12 h at 100-120°C, powdered and annealed for 2 h at 250-300°C and calcinated for 6 h at 350-400°C. The catalysts were then pelletized to the diameter of 0.8 cm and height 0.3-0.4 cm. In the case of difficult pelletization, 2 wt. % graphite were added. The pellets were annealed again for 24 h at 480-530°C. They were then crashed and separated to mesh fractions of 0.25-0.40 and 0.40 to 0.64 mm. The actual Mo : Mn ratio in individual catalyst as determined by chemical analysis

is in Table I. Molybdenum was determined by the oxine method and manganese by permanganate titration.

TABLE I
Specific Surface of Mo-Mn-O Catalysts

| Catalyst (at. ratio) | True at. ratio | Sp. surface m ² /g | Catalyst (at. ratio) | True at. ratio | Sp. surface m ² /g |
|-------------------------|-------------------|----------------------------------|-------------------------|-------------------|----------------------------------|
| A (9 : 1) | 9.05 : 1 | 2.60 | I (1 : 2) | 1 : 1.92 | 6.81 |
| B (7 : 1) | 6.92 : 1 | 1.12 | J (1 : 3) | 1 : 3.03 | 7.02 |
| C (6 : 1) | 5.87 : 1 | 1.91 | K (1 : 4) | 1 : 4.10 | 11.70 |
| D (5 : 1) | 4.98 : 1 | 1.83 | L (1 : 5) | 1 : 5.10 | 9.68 |
| E (4 : 1) | 3.99 : 1 | 1.35 | M (1 : 6) | 1 : 5.98 | 11.99 |
| F (3 : 1) | 2.84 : 1 | 1.20 | N (1 : 7) | 1 : 6.93 | 3.88 |
| G (2 : 1) | 1.96 : 1 | 2.11 | O (1 : 9) | 1 : 8.91 | 8.08 |
| H (1 : 1) | 0.98 : 1 | 4.78 | — | — | — |

TABLE II
Infrared Spectra of the Catalysts Studied

| Catalyst (at. ratio) | Absorption band, cm ⁻¹ | | | | | |
|-------------------------|-----------------------------------|-------|-------|-------------|-------|-------|
| MoO ₃ | 990 s | — | — | c 880 s,v b | 818 w | — |
| A (9 : 1) | 990 s | — | — | c 880 s,v b | 816 w | — |
| B (7 : 1) | 988 s | — | — | c 880 s,v b | 820 w | — |
| C (6 : 1) | 991 s | 952 w | 932 w | 880 s,b | 821 w | — |
| D (5 : 1) | 991 s | 953 w | 931 w | 880 s,b | 824 w | 800 w |
| E (4 : 1) | 987 m | 951 w | 932 w | 880 s | 819 w | 802 w |
| F (3 : 1) | 993 m | 955 w | 930 w | 876 s | — | 800 w |
| G (2 : 1) | 990 w | 954 w | 931 w | 877 m | — | 800 s |
| H (1 : 1) | — | 955 w | 930 w | 871 s | — | 800 s |
| I (1 : 2) | — | 950 w | 929 w | 869 s | — | 800 s |
| J (1 : 3) | — | 953 w | 931 w | 868 s | — | 800 s |
| K (1 : 4) | — | 954 w | 929 w | 867 m | — | 800 m |
| L (1 : 5) | — | 950 w | 930 w | 869 m | — | 800 m |
| M (1 : 6) | — | 950 w | 929 w | 868 m | — | 800 m |
| N (1 : 7) | — | 952 w | 931 w | 869 m | — | 800 w |
| O (1 : 9) | — | 950 w | 928 w | 867 m | — | 800 w |

s Strong, m medium, w weak, b broad, v very.

Specific surfaces of the catalysts are in Table I and they were determined by the method of low-temperature desorption of nitrogen. The gaseous mixture contained 20% N_2 and 80 vol. % He and the flow rate was 1.44 l/h. Before the actual measurements of the surfaces, the catalysts were heated in flowing nitrogen for 2 h at 120°C.

The X-ray phase analysis was performed on a URS-50IM diffractograph with a copper anticathode, Ni filter and at 32 kV and 10 mA. The diagram of diffraction lines of individual catalysts is on Fig. 1. Diffraction lines of free MoO_3 , which had been described by Westman⁴ and Magneli⁵, were found in all the catalysts. Their intensity and number decrease sharply with increasing content of manganese from the atomic ratio $Mo : Mn = 1 : 1$. Only one line corresponding to MoO_3 ($d = 3.466 \text{ \AA}$) was identified in sample N (1 : 7). It follows from Fig. 1 that $MnMoO_4$ diffraction lines described by Carlston⁶ were found for all samples except for N (1 : 7). However, only one of them ($d = 2.866 \text{ \AA}$) was observed in samples with a higher excess of manganese, *i.e.* L (1 : 5) and M (1 : 6). By comparing the intensities it was found that maximal amounts of free $MnMoO_4$ are in samples G, H, I of the atomic ratios $Mo : Mn = 2 : 1, 1 : 1$ and 1 : 2. Free Mn_2O_3 was not observed in samples with the atomic ratio $Mo : Mn$ higher than 1 : 2; taking into account its low crystallinity, relatively few diffraction lines were found for samples I (1 : 2) to N (1 : 7). Sample O (1 : 9) was entirely amorphous and its phase composition could not be determined.

Infrared absorption spectra were measured on a UR-10 apparatus in a Nujol suspension of catalysts. A NaCl cuvette was used for the measurements and the spectrum of Nujol was measured

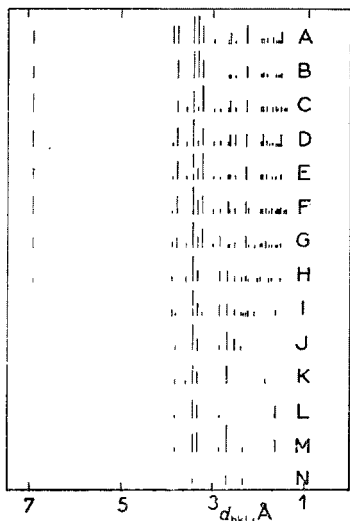


FIG. 1

Diagram of the Diffraction Lines of the Mo-Mn Oxide Catalysts

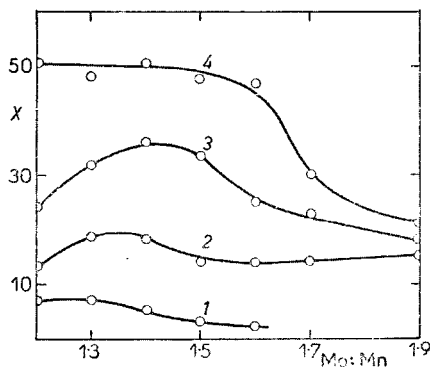


FIG. 2

Dependence of the Propylene Conversion (X , %) on Composition of Catalysts with the Atomic Ratio $Mo : Mn < 1$ at Constant Temperature

1 220°C; 2 260°C; 3 300°C; 4 340°C.

separately. The measurements encompassed the region of $400-1100\text{ cm}^{-1}$; the results are in Table II. Absorption bands at 990 , 875 and 815 cm^{-1} correspond to MoO_3 and they have been described by Barraclough⁷. A weak absorption band at 950 cm^{-1} appears starting from the atomic ratio $\text{Mo} : \text{Mn} = 6 : 1$ and its magnitude does not change with increasing content of manganese. According to Trifiro⁸, this band corresponds to MnMoO_4 . A weak band at 800 cm^{-1} appears from sample D ($5 : 1$) and its maximal intensity is reached at the atomic ratios $\text{Mo} : \text{Mn} = 2 : 1$, $1 : 1$, $1 : 2$, $1 : 3$. We assume that this band also belongs to MnMoO_4 .

Apparatus for the measurement of the catalytic activity. The testing was being performed on a common flow apparatus with an integral reactor and connected to a gas chromatograph. Precise composition of the reaction mixture was achieved through capillary flowmeters filled with silicone oil. Reaction gases — C_3H_6 (purity 97% and the rest mainly C_3H_8), O_2 and N_2 were taken from pressure vessels. Steam was dosed by saturation of flowing nitrogen in two saturators thermostated to required temperatures of presaturation and saturation with the accuracy of $\pm 0.1^\circ\text{C}$. The dosing part was all-glass. The flow apparatus itself was placed in a thermally insulated metal sheet box and thermostated to $110-120^\circ\text{C}$ during the testing. Chromatographic analysis of the reaction mixture at the reactor inlet and outlet was performed with the help of three dosing six-way teflon cocks inserted in metal cases (system Perkin-Elmer). The integral reactor made of quartz glass including its sintered part was connected to the flow apparatus outside the box; the diameter of the reaction space was 2 cm and height 5 cm. Through the centre of the reactor bed passed a tube which served for fixing a chromel-alumel thermocouple. Liquid products from the oxidation of propylene — aldehydes and acids — were absorbed in a glass countercurrent aqueous absorber of the diameter of 2 cm and height 50 cm. Uniform flow rate of water through the absorber was controlled by Mariotte's bottle.

Analysis: The gases, *i.e.* C_3H_6 , O_2 , CO_2 and CO were analyzed gas-chromatographically. A 200 cm-long glass column of the I.D. 0.4 cm was filled with Porapak N. The working temperature in the column was 130°C . CO was determined only qualitatively from -5 to -10°C . Carbonyl compounds were identified by descending paper chromatography with 2,4-dinitrophenylhydrazine in 2M-HCl. A 1 : 1 mixture of N,N-dimethylformamide and acetone was used as the stationary phase, cyclohexane as the mobile phase. The total content of aldehydes was determined by the oxime method according to Smith and Mitchell⁹. Acrolein was determined polarographically by Moshier¹⁰ (the half-wave potential of acrolein is -1.34 V , neither formaldehyde nor acetaldehyde interferes) and also gas-chromatographically. A glass 180 cm-long column of the I. D. 0.4 cm was filled with Carbowax 1500 (4 wt. %) deposited on Chromosorb G. The working temperature in the column was 38°C . Acrolein was burned in a furnace on CuO and Co_3O_4 packings at 680°C to CO_2 and H_2O , which was subsequently converted to hydrogen on Fe filings at 520°C . CO_2 was being removed by a molecular sieve. The acids were determined by titration with sodium methanolate.

Testing conditions. The prepared catalysts were tested on the flow apparatus with the integral reactor at the following conditions: amount of the catalyst 10 g; grain size 0.40–0.64 mm, composition of the reaction mixture: C_3H_6 7.5, O_2 7.5, H_2O 20, N_2 65 vol. %. The total feed of the reaction mixture 51 (NTP)/h; height of the reactor bed 2.5 cm; temperature gradient of the bed 20°C . The actual measurements of the catalytic activity were performed after a 5 h treatment of the catalyst at the given conditions, *i.e.* after a steady-state had been reached. The activity of each catalyst was measured at four temperatures. By paper chromatography it was established that aldehydes found on the A (9 : 1) to H (1 : 1) catalysts are mixtures of formaldehyde and acrolein. The qualitative composition of resulting organic acids was not determined. Results of the tests for the A (9 : 1) to H (1 : 1) catalysts are in Table III. On catalysts with atomic ratio $\text{Mo} : \text{Mn} < 1$, *i.e.* on samples I (1 : 2) to O (1 : 9), only CO_2 and H_2O were observed as products

of the catalytic oxidation of propylene. On samples I (1 : 2), K (1 : 4) and especially, O (1 : 9), also CO was found. The dependence of the propylene conversion on composition of catalysts with the atomic ratio Mo : Mn < 1 at different temperatures is on Fig. 2.

TABLE III
Catalytic Oxidation of Propylene on Mo-Mn-O Catalysts with the Atomic Ratio Mo : Mn \geq 1
Feed rate of propylene $1.673 \cdot 10^{-2}$ mol/h.

| Catalyst (at. ratio) | Temp. °C | Conversion, % | | Yield, mol/h 10^{-4} | | |
|-------------------------|-------------|-------------------------------|----------------|---------------------------------|-------------------|------------|
| | | C ₃ H ₆ | O ₂ | C ₃ H ₄ O | CH ₂ O | org. acids |
| A (9 : 1) | 496 | 9.9 | 47.7 | 2.10 | 4.04 | 0.94 |
| | 517 | 11.5 | 50.1 | 3.92 | 3.23 | 0.97 |
| | 556 | 12.8 | 52.4 | 5.26 | 3.01 | 1.01 |
| | 585 | 16.9 | 81.2 | 6.21 | 4.22 | 0.92 |
| B (7 : 1) | 479 | 3.5 | 15.4 | 4.57 | 2.22 | 0.98 |
| | 510 | 9.8 | 38.6 | 5.61 | 4.61 | 1.57 |
| | 545 | 15.1 | 51.5 | 7.79 | 5.55 | 1.68 |
| | 586 | 25.2 | 72.1 | 9.45 | 7.31 | 1.82 |
| C (6 : 1) | 469 | 2.5 | 11.2 | 1.86 | 2.18 | 0.63 |
| | 514 | 6.2 | 26.2 | 3.40 | 3.49 | 1.10 |
| | 552 | 8.1 | 38.8 | 4.20 | 3.23 | 0.60 |
| | 578 | 16.3 | 71.9 | 5.98 | 3.08 | 0.38 |
| D (5 : 1) | 500 | 7.0 | 10.1 | 4.43 | 1.30 | 0.95 |
| | 519 | 8.1 | 13.4 | 5.33 | 1.42 | 1.15 |
| | 545 | 11.7 | 23.4 | 4.63 | 1.52 | 0.71 |
| | 577 | 16.4 | 53.1 | 4.54 | 4.40 | 0.61 |
| E (4 : 1) | 487 | 1.8 | 12.3 | 2.74 | 2.04 | 0.27 |
| | 510 | 9.0 | 34.3 | 3.72 | 2.21 | 0.78 |
| | 550 | 16.3 | 48.4 | 4.29 | 3.77 | 0.87 |
| | 569 | 23.0 | 62.1 | 4.69 | 3.10 | 0.89 |
| F (3 : 1) | 427 | 0.5 | 1.5 | 0.27 | 0.18 | — |
| | 459 | 0.9 | 4.5 | 1.47 | 0.44 | 0.18 |
| | 528 | 5.1 | 25.3 | 4.51 | 3.47 | 0.26 |
| | 559 | 9.9 | 55.0 | 5.54 | 3.58 | 0.56 |
| G (2 : 1) | 443 | 4.2 | 17.3 | 3.25 | 2.68 | 0.39 |
| | 493 | 10.2 | 39.9 | 5.84 | 3.39 | 0.41 |
| | 529 | 11.7 | 53.2 | 7.89 | 4.77 | 0.67 |
| | 550 | 14.6 | 56.1 | 7.91 | 5.74 | 1.07 |
| H (1 : 1) | 417 | 6.4 | 16.3 | 0.35 | 1.65 | — |
| | 429 | 8.3 | 20.8 | 0.55 | 1.98 | — |
| | 467 | 12.3 | 25.2 | 1.02 | 1.30 | — |
| | 516 | 17.6 | 39.9 | 1.24 | 1.15 | — |

The effect of the ratio of reactants. To determine the effect of a change of the oxygen concentration in the reaction mixture on the oxidation process, catalyst B (7 : 1) had been selected and the $C_3H_6 : O_2$ ratio of 1 : 1.5 or 1 : 2 was studied. Experimental conditions: the amount of the catalyst 5 g; grain size 0.40–0.64 mm, composition of the reaction mixture C_3H_6 7.5, O_2 11.25 or 15, H_2O 20, and N_2 61.25 or 57.5 vol. %, total feed of the reaction mixture 51 (NTP)/h. By paper chromatography it was found that formaldehyde and acrolein appear at higher oxygen concentrations. The propylene conversion and the yield on the aldehydes at both $C_3H_6 : O_2$ ratios are illustrated on Fig. 3. It is obvious from this figure that the propylene conversion increases mildly at the higher oxygen concentration, especially at temperatures to 550°C. The yield on acrolein decreased to approximately one half at the higher oxygen concentration, but it increases with increasing temperature at both $C_3H_6 : O_2$ ratios. It is an interesting fact that courses of the temperature dependences of the yield on formaldehyde for both $C_3H_6 : O_2$ ratios are just opposite. The total yield of the aldehydes at $C_3H_6 : O_2 = 1 : 2$ is lower than at 1 : 1.5. However, this difference decreases at higher temperatures (above 550°C). Traces of acids were also found among the products at both $C_3H_6 : O_2$ ratios.

DISCUSSION

It has been proved by X-ray analysis that the catalysts prepared contain MoO_3 , $MnMoO_4$ and Mn_2O_3 . Catalysts A (9 : 1) to H (1 : 1) contain only MoO_3 and $MnMoO_4$, catalysts I (1 : 2) to M (1 : 6) also Mn_2O_3 . Catalyst N (1 : 7) is again a mixture of only two compounds – MoO_3 and Mn_2O_3 . According to their physical and catalytic properties, these materials may be divided into two distinct groups. The first one comprises catalysts of the atomic ratio $Mo : Mn > 1$. They contain only a negligible amorphous portion, their specific surface is relatively low and the oxidation of propylene proceeds only at temperatures about 500°C. Among the oxidation products, formaldehyde, acrolein, traces of organic acids, CO_2 and H_2O were found. Characteristically, their infrared spectra display a strong absorption band at 990 cm^{-1} .

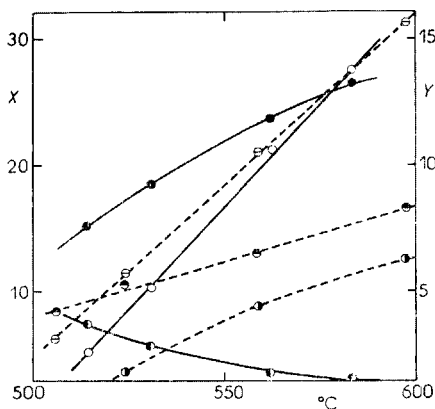


FIG. 3

Dependence of the Propylene Conversion (X , %) and the Yields on Formaldehyde and Acrolein (Y , %) on the B (7 : 1) Catalyst on Temperature

Ratio $C_3H_6 : O_2 = 1 : 1.5$ (solid line); ratio $C_3H_6 : O_2 = 1 : 2$ (dashed line); \circ , \ominus C_3H_6 conversion (%), \bullet , \ominus yield on CH_2O ($\text{mol/h } 10^{-4}$), \bullet , \bullet yield on C_3H_4O ($\text{mol/h } 10^{-4}$).

Into the latter group, catalysts of the atomic ratio $\text{Mo} : \text{Mn} \leq 1$ may be included. They contain a large amorphous portion and the 0 (1 : 9) catalyst is even entirely amorphous. Their specific surface is higher than that of catalysts from the first group and reaches as much as $12 \text{ m}^2/\text{g}$. The absorption band at 990 cm^{-1} has not been observed in their infrared spectrum. The oxidation of propylene proceeds at temperatures lower than 300°C , but the oxidation products are only CO_2 , H_2O and in some cases CO . It is interesting to note that this abrupt change in the catalytic properties occurs at the atomic ratio $\text{Mo} : \text{Mn} = 1 : 1$. The aldehydes (formaldehyde and acrolein) in the amount of $13.6 \cdot 10^{-4} \text{ mol/h}$ still appear on the G (2 : 1) catalyst at 550°C , whereas the oxidation of propylene on the I (1 : 2) catalyst proceeds already at 220°C , but yielding only the reaction products of the total oxidation of propylene. This remarkable increase in the activity and the total loss of selectivity with respect to products of the partial oxidation of propylene is probably brought about by the presence of free Mn_2O_3 in these samples. The pronounced increase in the amount of the amorphous portion and the related change in the heterogeneity of the surface of catalysts with the atomic ratio $\text{Mo} : \text{Mn} \leq 1$ will obviously also considerably affect their activity and selectivity. The concentration of activity centres for the total oxidation of propylene in the amorphous portion is considerably enhanced and the rate of diffusion of these centres from the inside of the amorphous grain to the surface is also higher than that from the lattice.

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