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# Oxidation of *o*-Xylene on Some Olefin Oxidation Catalysts

Oxidation of *o*-xylene has been studied in recent years in connection with the production of phthalic anhydride. The active catalyst for this process contain, as a rule, vanadium pentoxide, often in mixture with other oxides, among which titanium dioxide has been recently reported in several papers (*1–5*). In addition to the main product, viz., phthalic anhydride, oxidation of *o*-xylene on catalysts of this type yields small amounts of phthalide, maleic anyhydride, toluic acid, and tolualdehyde, the formation of this last compound being generally considered as the first step of the reaction. The partial oxidation is accompanied by total combustion to $CO_2$, the yield of which in the case of the most selective catalysts amounts to 15–20% (*1–5*).

Little is known about the catalytic properties of other oxide systems in this reaction. The scarce data on this subject are concerned with single oxides of transition metals (*6, 7*) and they show low activities for these systems, the yields of phthalic anhydride and tolualdehyde not exceeding 1–3%.

In the present work oxidation of *o*-xylene has been studied on molybdate catalysts, already known as active in allylic oxidation of olefins, with the view of seeking analogies between the behavior of these systems in olefin oxidation and that in oxidation of *o*-xylene. For this purpose we selected the catalysts active in the first stage of allylic oxidation, i.e., formation of an unsaturated aldehyde or a diene [bismuth molybdates or tin–antimony oxide catalysts (*8, 8a*)], and those capable also of carrying through the next step of oxidation, namely, that to unsaturated acid [cobalt–molybdenum and nickel–molybdenum oxide catalysts (*9*)].

For comparison, magnesium molybdate ($MgMoO_4$), inactive in selective oxidation of propylene (*10*), and Mg–Mo–O catalyst with a Mg/Mo ratio of $\frac{1}{3}$, which shows activity in this reaction (*11*), have been examined in *o*-xylene oxidation.

Bismuth molybdates, $Bi_2MoO_6$ and $Bi_2Mo_2O_9$, were the same preparations as those used in the previous studies on oxidation of propylene and butene-1 (*12*) and were obtained by precipitation at pH 2 and calcination at 500°C. Cobalt and nickel molybdates were prepared by precipitation at 60°C and pH 5.5 and calcination at 500°C; the details of the preparation were given elsewhere (*13*). These contained some $MoO_3$, as shown by X-ray analysis. Mg–Mo–O samples were obtained by recrystallization from the filtrate after solubilization of MgO and $MoO_3$ in boiling water and calcination at 600°C; they were the same samples as those used in Refs. (*10*) and (*11*). Tin–antimony oxide catalysts with an Sn/Sb ratio equal to $\frac{1}{4}$ were prepared from tin and antimony chlorides by the method described in Ref. (*14*); they were calcined at 540°C. Molybdenum trioxide was obtained by thermal decomposition of ammonium paramolybdate at 500°C.

Oxidation of *o*-xylene was studied in a fixed-bed reactor in the temperature range

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370–510°C, analysis of all the products was performed using gas chromatography. The details of the experimental setup and conditions of analysis have been described in Ref. (*4*). Samples 4-mm in size diluted with quartz beads (1:1) were used; the concentration of *o*-xylene in air was 38 g/nm$^3$ and the GHSV value was 2.000 sec$^{-1}$.

Table 1 shows the total activity in the oxidation of *o*-xylene expressed as the temperature of 50% conversion for the catalysts under study, giving at the same time the values of the maximum yields of the main products of partial oxidation, namely, tolualdehyde and phthalic anhydride. In Table 2 the values of selectivities to various products at selected temperatures are given. For comparison the respective data for vanadia–titania catalysts (*4*) are also included in the tables.

As seen from the tables, besides considerable combustion, the catalysts studied are active in partial oxidation of *o*-xylene, yielding tolualdehyde, phthalic anhydride, phthalide, and maleic anhydride, i.e., products typical for the oxidation of *o*-xylene on vanadium oxide catalysts, accompanied also by small amounts of dealkylation products (benzene and toluene). The distribution of these products depends, however, on the type of catalyst. Two groups of catalysts may be distinguished: One group comprising cobalt and nickel molybdates shows relatively high selectivities to phthalic anhydride, whereas, at similar conversion values, bismuth molybdates, magnesium molybdate, and tin–antimony oxide catalysts permit only the first step of *o*-xylene oxidation, i.e., formation of tolualdehyde. Molybdenum trioxide yields tolualdehyde as the main product whereas the Mg–Mo–O catalyst produces both the aldehyde and the anhydride. Among other products of partial oxidation, phthalide, maleic anhydride, and dealkylation products are observed on the molybdate catalysts and are not produced on the Sn–Sb–O catalyst. On all catalysts small amounts (1–3%) of toluic acid are also observed. The amount of phthalide

TABLE 1

Total Activity in the Oxidation of *o*-Xylene and Maximum Yields of Phthalic Anhydride and Tolualdehyde for Olefin Oxidation Catalysts

| Preparation | Sp. surface area, (m$^2$/g) | Temperature of 50% conversion, °C | Phthalic anhydride | | Tolualdehyde | |
|---|---|---|---|---|---|---|
| | | | (%)[a] | Temperature[b] (°C) | (%)[a] | Temperature[b] (°C) |
| $Bi_2Mo_2O_9$ | 1.51 | 470 | — | | 14.9 | 490 |
| $Bi_2MoO_6$ | 3.47 | 420 | 1.8 | 510 | 20.0 | 510 |
| Sn-Sb-O[c] | 34.70 | 500 | — | | 10.1 | 490 |
| $CoMoO_4$ | 12.50 | 400 | 34.2 | 450 | 3.6 | 390 |
| $NiMoO_4$ | 11.09 | 380 | 27.0 | 410 | 2.7 | 370 |
| $MgMoO_4$ | 3.00 | —[d] | — | | 5.3 | 510 |
| Mg–Mo-O[e] | 3.60 | 440 | 18.1 | 490 | 10.9 | 470 |
| $MoO_3$ | 1.24 | 520 | 1.5 | 510 | 21.9 | 510 |
| $V_2O_5$–$TiO_2$[f] | 9.00 | 360 | 65.0 | 390 | 4.6 | 370 |

[a] Maximum yield.

[b] Temperature of maximum yield.

[c] Sn/Sb = $\frac{1}{4}$.

[d] Low activity, maximum conversion approx. 20% at 510°C.

[e] Mg/Mo = $\frac{1}{3}$.

[f] V/Ti = $\frac{1}{2}$.

TABLE 2

Oxidation of *o*-Xylene on Olefin Oxidation Catalysts[a]

| Preparation (1) | Temperature (°C) (2) | Conversion (%) (3) | Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | TA (4) | PA (5) | PD (6) | MA (7) | DA (8) | $CO_2$ (9) |
| $Bi_2Mo_2O_9$ | 370 | 5.5 | 45.4 | — | — | — | — | 52.8 |
| | 430 | 35.0 | 33.7 | — | 6.3 | 1.0 | trace | 54.3 |
| | 470 | 49.5 | 29.9 | — | 5.3 | 2.0 | 2.0 | 52.9 |
| $Bi_2MoO_6$ | 370 | 18.5 | 45.5 | — | 3.2 | — | — | 45.9 |
| | 430 | 52.5 | 34.7 | — | 4.0 | — | 2.6 | 54.5 |
| | 470 | 71.7 | 25.6 | trace | 3.8 | trace | 6.7 | 58.0 |
| Sn-Sb-O[b] | 390 | 7.5 | 45.3 | — | — | — | — | 49.3 |
| | 450 | 21.0 | 34.8 | — | — | — | — | 54.8 |
| | 490 | 42.0 | 24.0 | — | — | — | — | 70.2 |
| $CoMoO_4$ | 390 | 30.0 | 12.0 | 10.6 | 9.3 | — | — | 60.0 |
| | 410 | 56.0 | 5.2 | 26.4 | 3.2 | 1.8 | 1.0 | 57.0 |
| | 450 | 94.0 | trace | 36.4 | trace | 3.5 | 4.8 | 48.0 |
| | 470 | 98.0 | trace | 31.2 | trace | 5.5 | 6.1 | 48.0 |
| $NiMoO_4$ | 370 | 40.0 | 6.8 | 13.0 | 7.0 | trace | 1.0 | 62.8 |
| | 390 | 76.0 | 2.5 | 19.5 | 3.2 | 1.0 | 1.3 | 71.0 |
| | 410 | 93.0 | 1.0 | 29.0 | trace | 3.0 | 3.8 | 62.4 |
| | 450 | 99.0 | trace | 25.2 | trace | 3.9 | 7.0 | 56.0 |
| $MgMoO_4$ | 470 | 9.0 | 33.3 | — | — | — | — | 56.6 |
| | 510 | 17.0 | 31.1 | — | 1.0 | — | — | 62.4 |
| Mg-Mo-O[c] | 410 | 18.0 | 25.0 | 3.3 | 3.8 | — | 1.0 | 63.8 |
| | 450 | 55.0 | 19.3 | 21.3 | 4.0 | trace | 1.0 | 47.4 |
| | 490 | 69.0 | 14.5 | 26.3 | 3.1 | 2.8 | 1.0 | 49.3 |
| $MoO_3$ | 450 | 15.0 | 50.0 | 3.3 | 3.3 | — | — | 32.7 |
| | 490 | 30.5 | 51.1 | 2.3 | 7.5 | — | — | 30.8 |
| $V_2O_5$-$TiO_2$[d] | 350 | 29.0 | 14.5 | 34.8 | 17.9 | — | — | 32.4 |
| | 370 | 65.0 | 7.1 | 49.2 | 13.8 | 1.5 | — | 21.4 |
| | 390 | 99.0 | — | 64.5 | — | 6.4 | — | 27.6 |

[a] TA, Tolualdehyde; PA, phthalic anhydride; PD, phthalide; MA, maleic anhydride; DA, dealkylation products (benzene + toluene).

[b] Sn/Sb = $\frac{1}{4}$.

[c] Mg/Mo = $\frac{1}{3}$.

[d] V/Ti = $\frac{1}{2}$.

in the case of cobalt and nickel molybdates decreases with increase in the reaction temperature, similar to the case of active vanadia catalysts (*4*), whereas in the case of bismuth and magnesium molybdates, the amount of phthalide practically does not change with temperature.

The results described above show distinct analogies between the behaviors of different catalysts in the oxidations of olefins and *o*-xylene: the catalysts active in the formation of unsaturated aldehyde from propylene give tolualdehyde as the main product in the partial oxidation of *o*-xylene, whereas those capable of sustaining further stages of propylene oxidation toward acrylic acid are also active in the formation of phthalic acid anhydride. The low overall activity of magnesium molybdate in the oxidation of *o*-xylene compares well with its low activity in propylene oxidation (*10*). the fact of consecutive formation of phthalic anhydride from tolualdehyde has been generally recognized (*15, 16*): also the formation of acrylic acid most probably takes place by a consecutive path involving acrolein (*17*).

In terms of the "rake mechanism" of complex reactions (*18*), the formal difference in behavior of these two types of catalysts must lie either in easier desorption of the aldehyde-like intermediate in the case of Bi–Mo–O and Sn–Sb–O catalysts as compared with $CoMoO_4$ and $NiMoO_4$, and/or in a low rate constant of the surface reaction of the aldehyde–acid step in the oxidation on the former catalysts.

In terms of the "center mechanism" of olefin oxidation (*19*), the same facts could be described as being due to the absence of the additional type of centers on Bi–Mo–O or Sn–Sb–O catalysts capable of reacting aldehyde in acid, whereas such centers exist on cobalt and nickel molybdates. The first step of the reaction, namely, the hydrocarbon activation, can occur in both olefin and *o*-xylene oxidation on the same types of sites consisting probably of the activation of a C–H bond in a methyl group of both types of hydrocarbons (*20*).

The nature of the centers active in the aldehyde–acid step of oxidation remains a matter of speculation, although perhaps the fact that the side reactions usually considered as acid-type processes, such as dealkylation and formation of maleic anhydride, occur more distinctly on catalysts active in phthalic anhydride formation could argue for their acidic character.

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## REFERENCES

*1.* Vanhove, D., and Blanchard, M., *Bull. Soc. Chim. Fr.* 3291, 4134 (1971).

*2.* Badische Anilin and Soda Fabrik, British Patent 1,140,264, 1969.

*3.* Grabowski, R., Grzybowska, B., Haber, J., and Słoczyński, J., *React. Kinet. Catal. Lett.* 2, 81 (1975).

*4.* "Annual Report of Research Laboratories of Catalysis and Surface Chemistry." Polish Academy of Sciences, 1976.

*5.* Boreskov, G. K., Ivanov, A. A., Ilynich, O. M., and Panomareva, V. G., *React. Kinet. Catal. Lett.* **3**, 1 (1975).

*6.* Skorbilina, T. G., Pyatnicki, Yu. I., and Golodets, G. I., *Kinet. Katal.* **5**, 1207 (1975).

*7.* Popova, I. I., and Kabakova, B. V., *Kinet. Katal.* **6**, 499 (1965).

*8.* Voge, H. H., and Adams, C. R., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 17, p. 151. Academic Press, New York, 1967.

*8a.* British Patents 864,666; 876,446; 902,952; Trifiro, F., Lambri, C., and Pasquon, I., *Chim. Ind.* **53**, 339 (1971).

*9.* American Patent 3,240,806; French Patents 1566,924 and 1541,629; Polish Patent 88,583.

*10.* Grzybowska, B., German, K., Haber, J., and Słoczyński, J., "Materials of All-Union Conference on Mechanism of Heterogeneous Catalytic Reactions, Moscow, 1974," Paper 105.

*11.* German, K., and Haber, J., unpublished data.

*12.* Grzybowska, B., *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* 22, 519, 525 (1974).

*13.* Grzybowska, B., German, K., Haber, J., Kowalski, T., and Mazurkiewicz, A., "Materials of Symposium on Mechanisms of Hydrocarbon Reactions, Siofok, 1973," p. 265. Akadémiai Kiado, Budapest, 1975.

*14.* Trifirò, F., and Pasquon, I., *Chim. Ind.* **52**, 228 (1970).

*15.* Novella, E. C., and Benlloch, A. E., *An. Real Soc. Espan. Fis. Quim. Ser. B* **58**, 783 (1962).

16. Boag, I. F., Bacon, D. W., and Downie, J., *J. Catal.* **38**, 375 (1975).
17. Grzybowska, B., and Mazurkiewicz, A., unpublished data.
18. Germain, J. E., "Catalytic Conversion of Hydrocarbons," p. 259. Academic Press, London, 1969.
19. Haber, J., *Z. Chem.* **13**, 241 (1973).
20. Weiss, F., Marion, J., and Cognon, J. M., *Kinet. Katal.* **14**, 45 (1973).

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