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Morphological Aspects in the Oxidation of *o*-Xylene on V_2O_5 Catalysts

Vanadium pentoxide is a well-known catalyst for the mild oxidation of *o*-xylene into phthalic anhydride. Higher activities and selectivities in this reaction can be obtained in the presence of titanium(IV) oxide (*1–3*). The mechanism of the modifying action of titania has not been adequately explained so far. Some authors ascribe this action to selective exposure of the (010) face of V_2O_5 at the surface of V_2O_5/TiO_2 catalysts (*4–6*). According to Bystrom *et al.* (*7*), there are $V^{5+}{=}O$ bonds on the (010) face of V_2O_5. The promoting effect of a TiO_2 support on the oxidation of *o*-xylene on V_2O_5 has been ascribed to an increase of the number of surface V=O bonds on the V_2O_5/TiO_2 catalysts (*8*) and weakening of these bonds (*9*). In many studies concerning the mechanism of the catalytic reactions on vanadium oxide, the V=O species have been considered to play a significant role as the active sites for the reactions (*10–14*).

In the present work the correlation between the number of surface V=O bonds on the pure V_2O_5 surface and the activity and selectivity in oxidation of *o*-xylene has been studied.

A series of samples of different grain morphology was prepared. Electron micrographs of two samples taken with a JXA-50A JEOL scanning microscope are shown in Fig. 1. The first sample (Fig. 1a) contains well-developed plate-like grains [the large face corresponds to a (010) plane (*7*)], while the second sample is an agglomerate of small grains of poorly defined shape. Differentiation of the grain shape was obtained by calcining vanadia samples in a stream of air at different temperatures (Table 1). The starting materials were ammonium metavanadate NH_4VO_3 or $(NH_4)_2V_6O_{16}$ (Preparation 2). In the case of Preparation 1 ammonium metavanadate was placed directly into an oven kept at 773 K and calcined at this temperature for 20 h, while in the case of the other preparations the temperature was raised gradually from 298 K to the appropriate annealing temperature.

The plate-like grains orientate themselves in the X-ray sample holder. This is

TABLE 1

Characteristics of V_2O_5 Preparations

Sample No.	Starting materials	Calcination conditions, Temp (K)/time (h)	BET[a,b] surface area (m^2/g)	Redn.[c] degree (% V_2O_4)	Morphological[a] factor, *f*
1	NH_4VO_3	773/20	4.7	10.2	0.58 ± 0.07
2	$(NH_4)_2V_6O_{16}$	643/20	7.3	9.7	0.34 ± 0.05
3	Sample 1	958/20	1.5	9.2	0.07 ± 0.03
4	Sample 2	958/20	1.6	9.5	0.14 ± 0.04
5	NH_4VO_3	773/20	4.2	10.8	0.44 ± 0.06

[a] The data refer to fresh catalysts. There were no measurable changes after use.

[b] Determined by Kr adsorption at 77 K.

[c] Determined for used catalysts.

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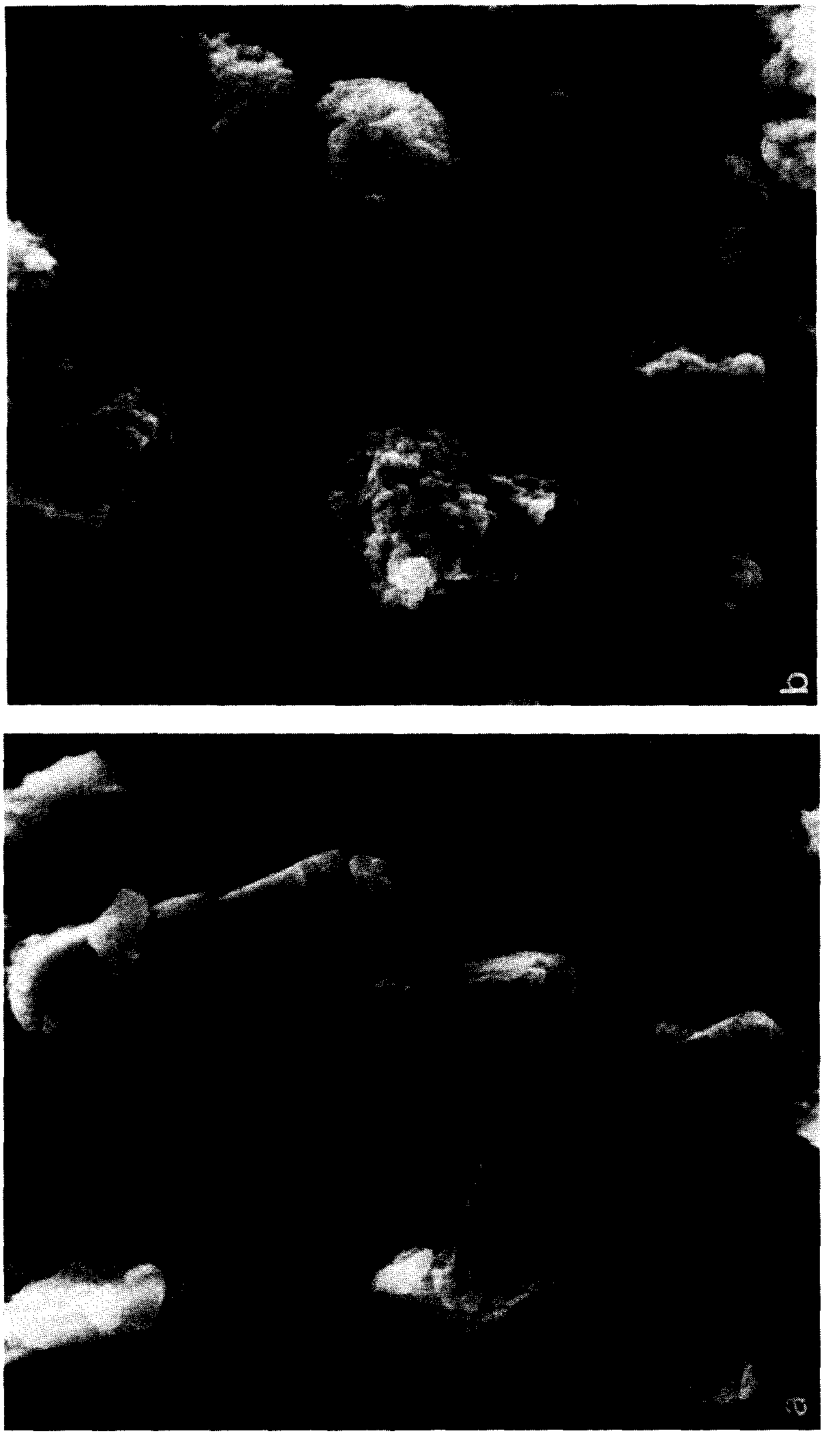

FIG. 1. Scanning electron micrograph of V_2O_5. (a) Sample 4, ×3000. (b) Sample 1, ×3000.

manifested by a considerable change in intensity of some X-ray reflections as compared with the intensity values calculated or measured in a spectrum recorded with a special technique ensuring an entirely unoriented sample layer (*15*). The largest changes have been observed for the reflections characteristic of perpendicular planes, i.e. (010), (101), and (400). A morphological factor, *f*, introduced by Ziółkowski and Janas (*16*) and defined as:

$$f = \frac{I_{101}}{I_{010}}$$

was taken as a semi-quantitative measure of the contribution of the two planes to the external surface of the grains. The character of the changes of the I_{400}/I_{010} ratio is similar but their extent is much smaller. I in the above ratio designates the intensity of the X-ray lines for the respective planes given by the index, measured for oriented samples prepared by standard smoothing in a sample holder. X-Ray spectra were registered in a DRON 2 LOMO (USSR) apparatus using Cu$K\alpha$ radiation.

The value of the I_{101}/I_{010} ratio calculated for a monocrystal is 0.90 (*17*), which is in good agreement with experimental values obtained for nonoriented samples. For the oriented samples the values of f (Table 1) vary over a wide range depending on the calcination temperature and the type of the starting material. As can be seen from Table 1, increase in the calcination temperature causes the contribution of the (010) plane to the external surface of the grains to rise (decrease in f) and thus the number of V=O bonds which are exposed on this plane increases on the V_2O_5 surface. The nature of the starting material used is also of substantial importance as seen from the example of sample 2. The crystal habit of V_2O_5 was determined in the stage of preparation of $(NH_4)_2V_6O_{16}$ [slow crystallization from the NH_4VO_3 solution at pH < 2.2 (*18*)].

The catalytic activity in *o*-xylene oxidation was measured in a conventional flow reactor in the temperature range 623–703 K, the data being taken with decreasing temperature at 20 K intervals. Reaction products were analyzed gas-chromatographically. The apparatus and analysis conditions were described in detail elsewhere (*19*). Two-milliliter samples of catalyst of grain size 0.5–0.7 mm diluted with 4 ml of glass beads were used; the *o*-xylene concentration in air was 44 g/m^3. After reaction the samples were analyzed for the content of vanadium ions of valency lower than 5+ using the method described in Ref. (*20*).

All the samples gave high conversions of the order of 96–100% in the temperature range 643–663 K. Besides phthalic anhydride and total combustion products, small amounts of maleic anhydride. tolualdehyde, toluic acid, and phthalide were also observed in the products.

Figure 2 gives the dependence of the phthalic anhydride yields on the morphological factor *f*. As already mentioned, *f* is a measure of the relative contribution of the (010) plane and hence of the amount of the V=O bonds at the external grain surface.

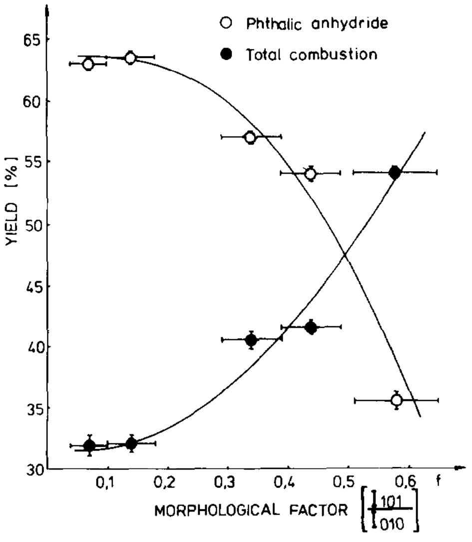

FIG. 2. Phthalic anhydride and corresponding total combustion products yield at 100% *o*-xylene conversion on V_2O_5 samples of different morphological factors. Reaction temperature: Samples 1, 3, and 4—683 K, samples 2 and 5—663 K.

As seen from Table 1, the values of the phthalic anhydride yield are not related to the values of the BET surface area but can be correlated (see Fig. 2) to the values of f: the higher the amount of V=O bonds, the higher is the phthalic anhydride yield and the lower the yield of the total combustion products. For the samples of large f, i.e., those in which the plane *perpendicular* to the (010) plane contributes predominantly to the external grain surface, the reaction proceeds mainly toward total oxidation.

It can thus be concluded that the centers responsible for the partial oxidation of *o*-xylene to phthalic anhydride and the centers active in total oxidation are situated on different planes of the V_2O_5 grains; the first centers are on the (010) plane, and the second centers on the planes perpendicular to it.

It should be noted that in the conditions of the *o*-xylene oxidation the V_2O_5 catalysts operate in the reduced state. The reduction degree of all the samples after the reaction was not high, amounting to about 10 at% V^{4+} (cf. Table 1). X-Ray analysis of the samples after the reaction did not show the presence of any phases besides V_2O_5. When vanadium pentoxide is reduced, it very readily loses oxygen from one third of the (010) planes, transforming into V_6O_{13} (*21*). It is the bridging oxygen of the (101) planes through which the whole (010) layer of oxygens can be extracted, resulting in the formation of a shear plane. It may be thus concluded that V^{4+} ions appear along the shear planes terminating on the (101) face but never on the (010) face (*21*).

Finally, we would like to draw attention to one more experimental fact. The V_2O_5 samples giving poor yield to phthalic anhydride could be "improved" by simple calcination at higher temperatures. Thus samples 3 and 4 were obtained by calcination at 958 K for 20 h of samples 1 and 2, respectively. Within the limits of the experimental errors, the same values of f and yields of phthalic anhydride and combustion were obtained in both cases.

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