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# Influence of Grain Morphology of $V_2O_5$ on Its Reducibility and Selectivity for Methanol Oxidation

In many studies on the mechanism of partial oxidation reactions on vanadium oxides, the active sites were considered to be the $V^{5+}{=}O$ species (*1–6*). Following Bystrom *et al.* (*7*) the V=O bonds are on the (010) face of $V_2O_5$. Recently, Gasior and Machej (*6*) investigated the influence of the grain morphology of $V_2O_5$ on its activity and selectivity for the oxidation of *o*-xylene to phthalic anhydride. They found that the selectivity to phthalic anhydride was correlated with the relative contribution of the (010) planes and hence to the amount of V=O bonds at the external surface. The authors concluded that the sites responsible for selective oxidation of *o*-xylene to phthalic anhydride are on the (010) planes of $V_2O_5$ and those for total oxidation on the planes perpendicular to it.

In the present work we have investigated the influence of the grain morphology of $V_2O_5$ on its reducibility, and its activity and selectivity for the oxidation of methanol to formaldehyde.

Two vanadium pentoxide samples of different grain morphology were used in the experimental study. Scanning electron micrographs of the two samples are shown in Fig. 1. Sample $V_2O_5$(A) consisted of well-developed plate-like grains with the large faces corresponding to (010) planes (*7*). Sample $V_2O_5$(B) contained poorly defined agglomerates of needle-type grains. Sample A was obtained from ammonia metavanadate which was heated for 2 h at 700°C and subsequently allowed to cool in the oven. Sample B was commercially available $V_2O_5$ supplied by Fluka AG., Switzerland. The BET surface areas of the samples as measured by krypton adsorption at 77 K were: sample A, $0.32 \pm 0.02$ m²/g; sample B, $1.54 \pm 0.05$ m²/g. Calculations were based on a cross-sectional area of 19.5 Å² for a krypton atom. Figure 1 indicates that the large (010) faces (sample A) show some surface roughness. However, the contribution of this roughness to the surface area was not significant. Assuming no surface roughness, we estimated an average $V_2O_5$ plate thickness of about 2 $\mu$m from the measured BET surface area; this plate thickness agreed fairly well with the plate thickness observed by electron microscopy.

X-Ray diffraction patterns were obtained using a Philips diffractometer and Cu$K\alpha$ radiation. The plate-like grains (sample A) oriented themselves in the X-ray sample holder, resulting in a considerable change in intensity, in particular, of the reflections characteristic of perpendicular planes, i.e. (010), (101), and (400), as compared with the intensity values of the nonoriented sample B. The largest changes have been observed for the reflections (010) and (101) which are compared for the two samples in Fig. 2. The morphological factor $f = I_{101}/I_{010}$, introduced by Ziółkowski and Janas (*8*) represents a semiquantitative measure of the contribution of the two planes to the external surface of the grains. "$I$" in the above relation designates the intensity of the X-ray reflections for the respective planes given by the index, measured for oriented samples prepared by standard smoothing in a sample holder. For the well-developed plate-like $V_2O_5$ (sample A) a factor $f = 0.28$ was calculated; for the needle-type grains (sample B) $f$ was 0.95, which is in good agreement with $I_{101}/I_{010} = 0.90$ calculated for a monocrystal (*9*) and observed for nonoriented samples.

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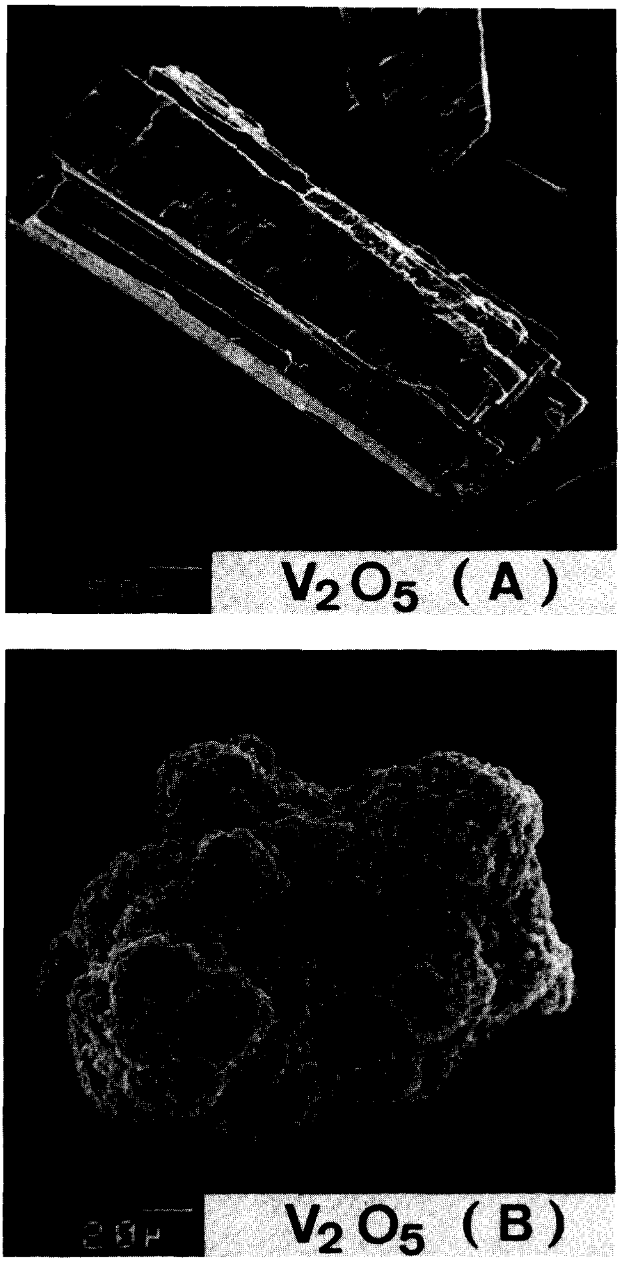

FIG. 1. Scanning electron micrographs of samples $V_2O_5$(A) and $V_2O_5$(B) showing the particle shape.

Temperature-programmed reduction (TPR) measurements of the samples were performed using an apparatus described elsewhere (*10*). The TPR profiles of the two $V_2O_5$ samples which are presented in Fig. 3 indicate that their reducibility depended on the grain morphology. The reduction profile of sample $V_2O_5$(A) which has a large contribution of the (010) planes to the surface area is shifted to higher temperatures as compared to sample $V_2O_5$(B) which has a low contribution of the (010) planes.

The most significant change is observed for the high-temperature peak. The hydro-

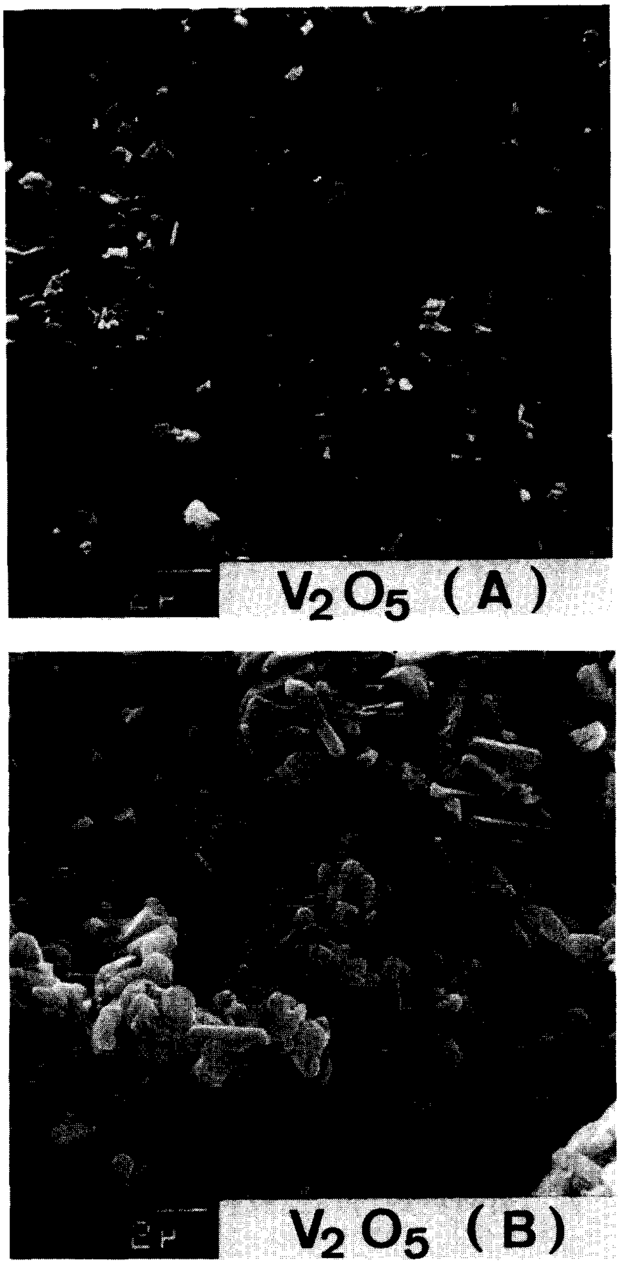

FIG. 1—*Continued.* Scanning electron micrographs showing the corresponding surface morphologies.

gen consumption peak of $V_2O_5$(B) appearing at the lowest temperature corresponds to the reduction of $V_2O_5$ to $V_6O_{13}$ as was evidenced by X-ray analysis. On reduction, $V_2O_5$ readily loses oxygen from one-third of the (010) planes transforming into $V_6O_{13}$ (*11*). It is interesting to note that $V_6O_{13}$ is the only shear phase found in the composition range $V_2O_5$–$VO_2$ (*12*). The readiness of exchange of oxygen between the gas phase and the $V_2O_5$–$V_6O_{13}$ system is one of the important features which determine its catalytic properties in oxidation reactions (*13*). The integral hydrogen consumption

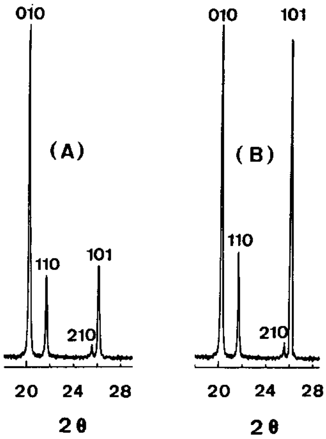

FIG. 2. Comparison of intensities of X-ray reflections (010) and (101) of samples $V_2O_5$(A) and $V_2O_5$(B).

was the same for both samples within the experimental error. This was also confirmed by titrimetric determination of the average valency of the vanadium. X-Ray analysis and titrimetric measurements (*3*) indicated that in both cases the $V_2O_5$ was reduced to $V_2O_3$.

Methanol oxidation experiments were performed in a fixed-bed reactor in the temperature range 500 to 700 K. The apparatus and analysis conditions were described in detail elsewhere (*14*). The sequence of selected reaction temperatures was random.

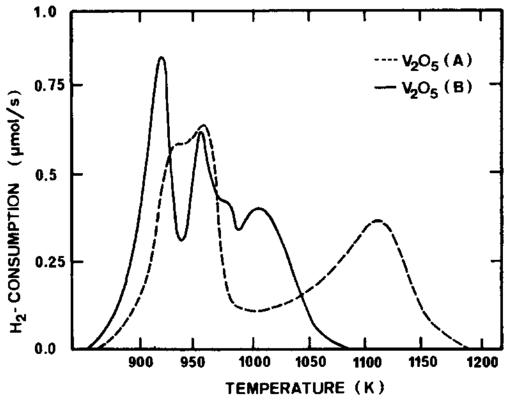

FIG. 3. Reduction profiles (TPR) measured for samples $V_2O_5$(A) and $V_2O_5$(B). Conditions: heating rate, 0.15 K/s; reducing gas mixture, 6% hydrogen in nitrogen; gas flow rate, 1.25 $cm^3$(NTP)/s; sample weight, 40.3 mg.

The experiments were started by heating the $V_2O_5$ in air (4.6 ml/s) to the desired reaction temperature. After the temperature in the fixed bed was stable, the reactants were fed to the reactor.

Figure 4 shows the conversion, selectivity, and yield measured for the methanol oxidation performed with $V_2O_5$(A) and $V_2O_5$(B). Conversion, selectivity, and yield are defined by

Conversion $X$

$$= \frac{\text{moles ME reacted per min}}{\text{moles ME fed per min}} \tag{1}$$

Selectivity $S$

$$= \frac{\text{moles FA formed per min}}{\text{moles (FA + CO + CO}_2\text{) formed per min}} \tag{2}$$

$$\text{Yield} = X \cdot S, \tag{3}$$

where ME and FA correspond to methanol and formaldehyde, respectively.

Sample $V_2O_5$(B) consisting of the poorly defined agglomerates of needle-type grains exhibited about the same conversion-selec-

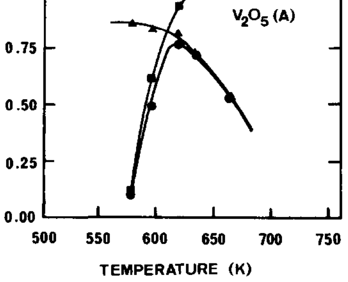

FIG. 4. Comparison of activity and selectivity of $V_2O_5$ samples for methanol oxidation. Conditions: amount of $V_2O_5$ $W = 1.478$ g; particle size range 100–200 μm; molar feed rates: methanol $F = 16.42$ μmol/s; air, 188.8 μmol/s; $W/F = 9 \times 10^4$ g s/mol; pressure, 100 kPa.

tivity behavior as the plate-like shaped $V_2O_5$(A). It should be noted that TPR and titrimetric measurements performed on the $V_2O_5$ samples after they had been used for methanol oxidation did not indicate a significant change in the degree of reduction of the $V_2O_5$. In addition, X-ray analysis of the samples after reaction did not show the presence of any other phases besides $V_2O_5$. Obviously, the $V_2O_5$ samples were not reduced significantly under the reaction conditions, at least not to a degree detectable by the analysis methods used. A similar behavior was recently observed for the ammoxidation of 3-picoline to 3-cyanopyridine on $V_2O_5$ (*15*).

Our results indicate that the V=O species on the (010) planes of $V_2O_5$ do not play a dominant role for selective oxidation of methanol to formaldehyde. $V_2O_5$ with a large contribution of the (010) planes to the external surface (well-developed plate-like grains; sample A) showed about the same selectivity behavior as $V_2O_5$ with little contribution of these planes (agglomerates of needle-type grains; sample B). The higher activity of sample B as compared to sample A can be explained by the significant higher specific surface area of sample B.

A comparison of the TPR profiles of the two samples indicates (Fig. 3) that the $V_2O_5$ plates (sample A) are less easily reduced than the needle-type agglomerates of $V_2O_5$ (sample B). It should be noted that the more weakly bound oxygen in sample B did not lead to a lower selectivity to formaldehyde.

To sum up, the experimental evidence shows that a significant change in the contribution of the (010) plane to the external surface area of $V_2O_5$ does not have a marked influence on its selectivity for the oxidation of methanol to formaldehyde. However, the selectivity was found to be strongly correlated with the conversion. Further work, in particular on well-defined single crystal surfaces, as has been performed for butene and propene oxidation (*16, 17*), will be necessary to finally assess the role for selective oxidation of the different sites located on $V_2O_5$.

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## REFERENCES

*1.* Tamara, K., Yoshida, S., Ishida, S., and Kakioka, H., *Bull. Soc. Chem. Jpn.* **41,** 2840 (1968).

*2.* Kera, Y., and Hirota, K., *J. Phys. Chem.* **73,** 3973 (1969).

*3.* Nakamura, M., Kawai, K., and Fujiwara, Y., *J. Catal.* **34,** 345 (1974).

*4.* Cole, D. J., Cullis, C. F., and Hucknall, D. J., *J. Chem. Soc. Faraday Trans. 1* **72,** 2185 (1976).

*5.* Akimoto, N., Usami, M., and Echigoya, E., *Bull. Chem. Soc. Jpn.* **51,** 2195 (1978).

*6.* Gasior, M., and Machej, T., *J. Catal.* **83,** 472 (1983).

*7.* Bystrom, A., Wilhelmi, K. A., and Brotzen, O., *Acta Chem. Scand.* **4,** 1119 (1950).

*8.* Ziółkowski, J., and Janas, J., *J. Catal.* **81,** 298 (1983).

*9.* ASTM Powder Diffraction File 9-387, Ed. Joint Committee on Powder Diffraction Standards, Pennsylvania, 1979.

*10.* Monti, D., and Baiker, A., *J. Catal.* **83,** 323 (1983).

*11.* Haber, J., *in* "Catalysis" (J. R. Anderson and M. Boudart, Eds.), Vol. 2, p. 14. Springer-Verlag, Berlin, 1981.

*12.* Dziembaj, R. J., *Solid State Chem.* **26,** 159 (1978).

*13.* Bielanski, A., and Haber, J., *Catal. Rev.* **19,** 1 (1979).

*14.* Monti, D., Reller, A., and Baiker, A., submitted for publication.

*15.* Baiker, A., and Zollinger, W., *Appl. Catal.* **10,** 231 (1984).

*16.* Colpaert, N. M., *Z. Phys. Chem.* **84,** 150 (1973).

*17.* Fiersman, L., Clauws, P., Lambrecht, W., Vandenbroucke, L., and Vennik, J., *J. Microsc. Spectrosc. Electron.* **4,** 543 (1979).

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