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Carbon Monoxide Oxidation on Vanadium Pentoxides of Different Grain Morphology: Structure Sensitivity of the Reaction

A. BAIKER,[1] P. DOLLENMEIER, R. HE, AND A. WOKAUN[2]

Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology (ETH), CH 8092 Zürich, Switzerland

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The oxidation of carbon monoxide over unsupported vanadium pentoxide of different grain morphology has been investigated in a continuous fixed-bed microreactor in the range 400–600°C and at CO partial pressures between 0.2 and 1 kPa. CO oxidation rates were first order in CO and depended strongly on the grain morphology. In the temperature range 500–600°C well-developed thin plates of V_2O_5 with a large contribution of the (010) face to the surface area exhibited an activity more than an order of magnitude higher than agglomerates of prismatic V_2O_5. The higher activity of the plates is attributed to a higher surface concentration of the active V=O species on this sample. Scaly aggregates of V_2O_5 obtained by decomposition of NH_4VO_3 exhibited activities which were lower than those of the plates. The activation energy for this sample at 400–500°C was considerably lower, indicating the predominance of a different type of active sites, probably lattice defects. At 500–600°C there was annealing of the defects and an increase of the activation energy.

INTRODUCTION

In many studies of oxidation reactions on vanadium pentoxide, the active sites were considered to be the $V^{5+}=O$ species (*1*) located on the (010) face. However, the role of these species in CO oxidation is still a subject of controversy. Kera (*2*) pointed out the high activity of the (010) face for CO oxidation. In contrast, Mori *et al.* (*3*) suggested that surface defects such as steps, kinks, or vacancies exhibit a much higher activity for CO oxidation than the surface V=O species located on the (010) face. Their conclusion was based on a comparison of turnover rates which involved the determination of the surface V=O species by using the rectangular pulse technique (*4*).

Here we report another kinetic investigation to assign the role of the sites located on the (010) face of V_2O_5 for CO oxidation. Our approach, which has been reported in a preliminary communication (*5*), is based on the comparative measurement of surface reaction rates on V_2O_5 samples with different grain morphology. Well-developed thin plates with a large contribution of the (010) face to the surface area are compared with V_2O_5 samples with relatively little contribution of this face. The aim of this investigation is to gain information about the structure sensitivity of this reaction and the nature of the active sites.

EXPERIMENTAL

Catalysts. Vanadium pentoxide samples of different grain morphology, i.e., with different contributions of the (010) planes to the surface area, were used. Sample A consisted of thin, well-developed plates with the large faces corresponding to (010) planes; sample B consisted of agglomerated prismatic crystallites, and sample C of scaly agglomerates. Scanning electron micrographs showing the morphologies of these samples are presented in Fig. 1. Sample A (plates) was obtained from the commercially available sample B (supplier,

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[1] To whom correspondence should be addressed.

[2] Present address: Institute of Physical Chemistry, University of Bayreuth, D 8580 Bayreuth, FRG.

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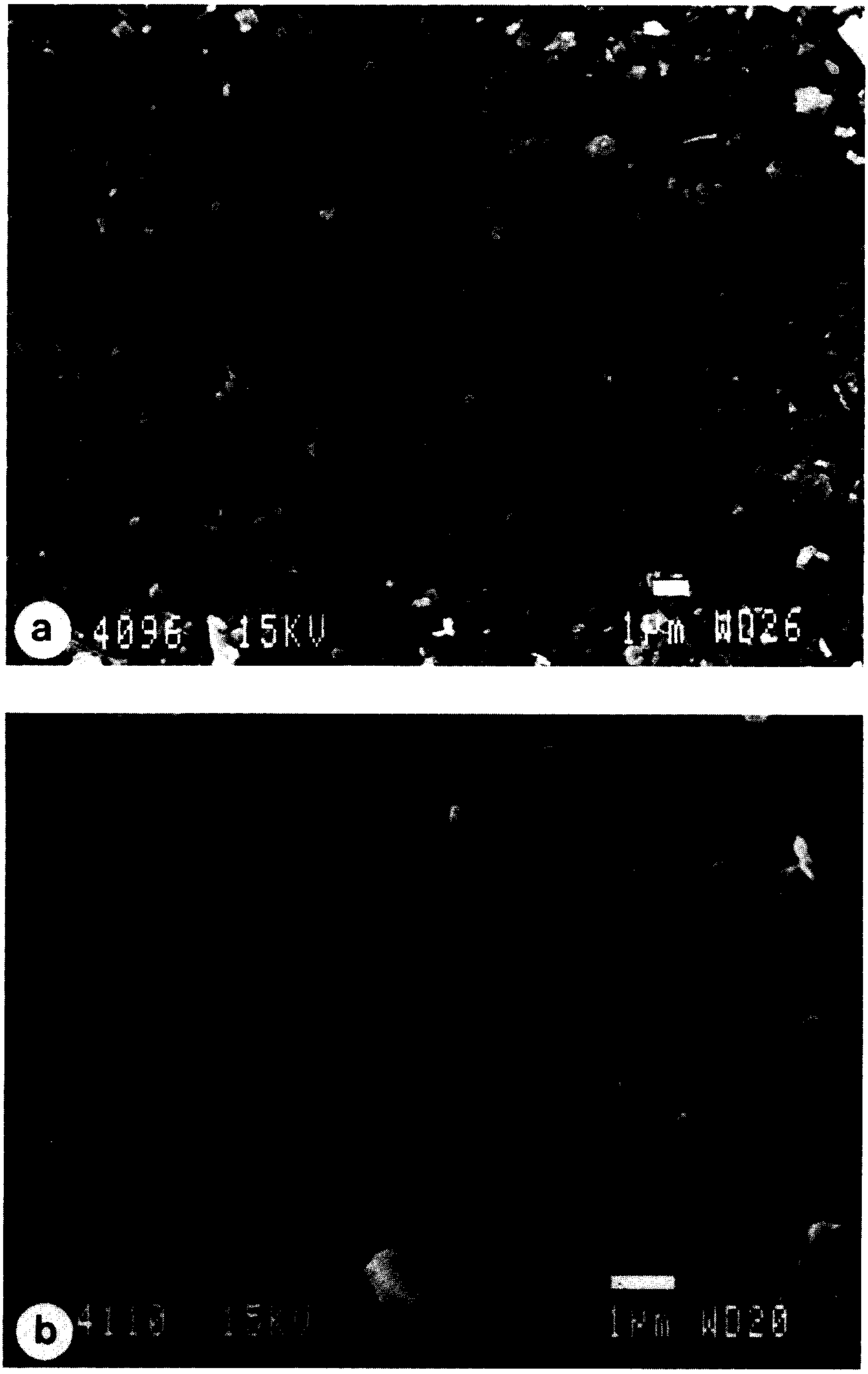

FIG. 1. Scanning electron micrographs showing the surface morphology of the V_2O_5 samples. (a) Sample A before pretreatment, (b) sample A after pretreatment at 600°C, (c) sample B after pretreatment at 600°C, (d) sample C after pretreatment at 600°C.

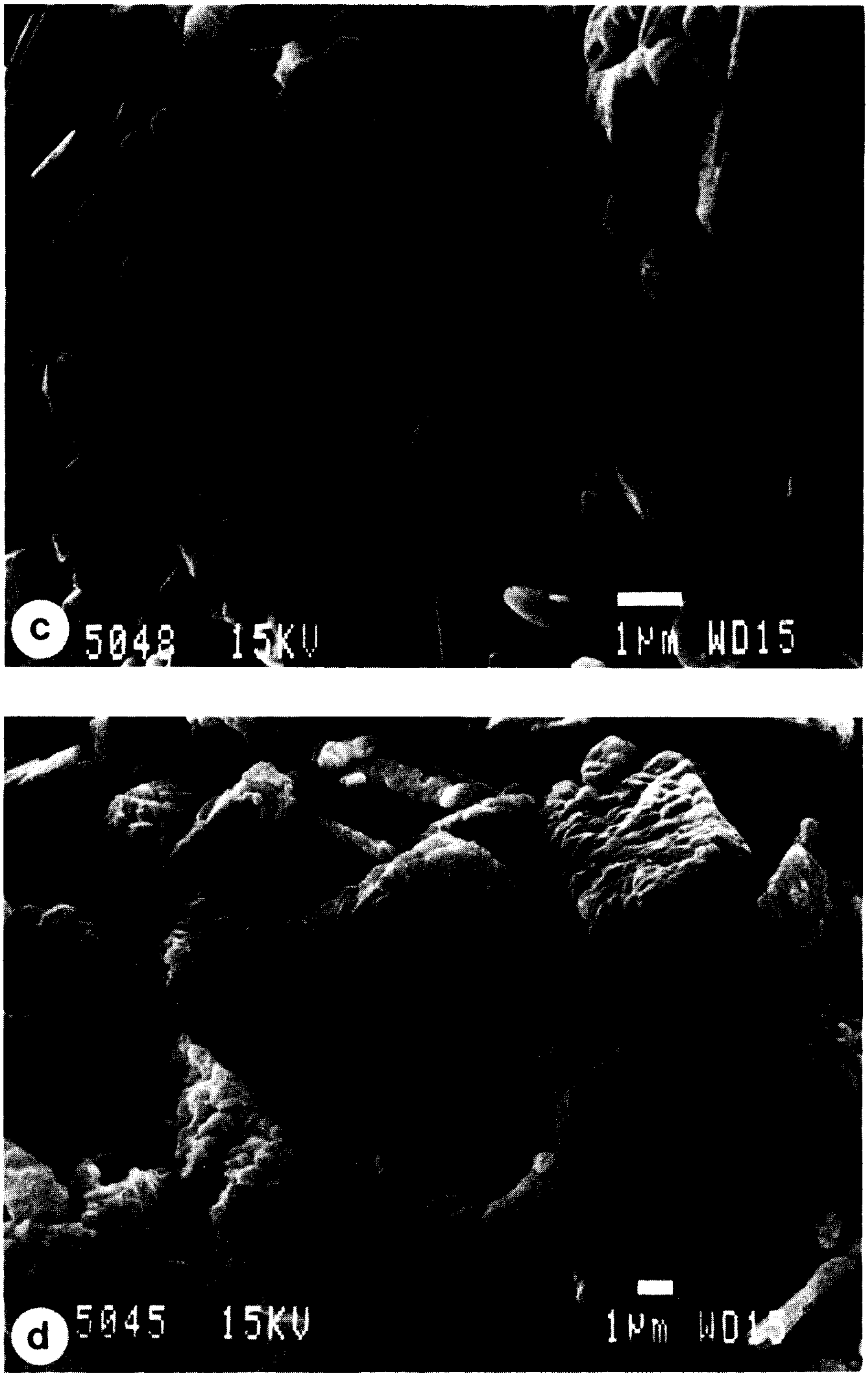

FIG. 1—*Continued.*

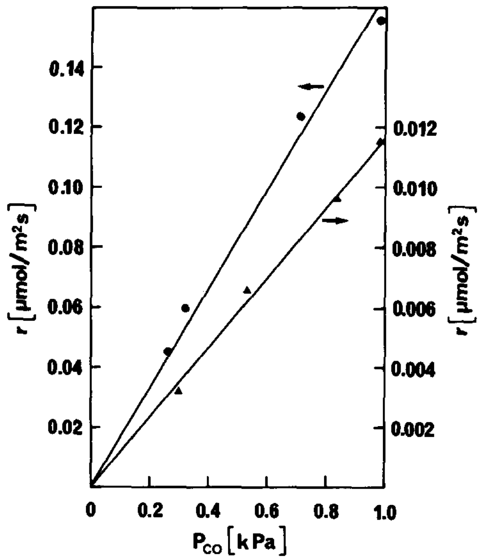

FIG. 2. Dependence of the CO oxidation rates of samples A (circles) and B (triangles) on the CO partial pressure.

Fluka, AG, Switzerland) by melting at 700°C and subsequent slow cooling under atmospheric conditions. Sample C was prepared by thermal decomposition of ammonium metavanadate, NH_4VO_3, at 773 K in flowing O_2, as reported by Mori *et al.* (*3*) (sample V_2O_5-U). BET-surface areas of the fresh samples as measured by krypton adsorption were: sample A, 0.285 ± 0.04 m²/g; sample B, 1.54 ± 0.05 m²/g; sample C, 3.05 ± 0.06 m²/g. An average V_2O_5 plate thickness of 2–5 µm was estimated from the electron micrographs.

Activity measurements were also performed with samples A and B after subjecting them to a reduction–reoxidation treatment. Mori *et al.* (3) have argued that such a pretreatment of a solid with an annealed surface (platelets) tends to increase the number of surface defects. The redox pretreatment consisted of reduction in flowing hydrogen for 1 h at 400°C and subsequent reoxidation in air for 1 h at the same temperature. This redox cycle was repeated five times previous to the activity measurements.

Catalytic activity measurements. Kinetic measurements were performed in an all-glass continuous flow microreactor. The reactor temperature was stabilized to within ±1°C. Comparative activity tests were carried out under the following conditions: temperatures, 500–600°C (samples A, B, C), and 400–500°C (sample C*); partial pressures: CO, 1 kPa; O_2, 1.2 kPa; total pressure, 100 kPa; balance gas, N_2; total flow rate, 1.83 cm³/s; catalyst load, 1 g; particle size, 120–250 µm. Under these conditions, conversion of CO never exceeded 5%. The concentrations of CO and CO_2 were measured by IR analyzers at the reactor inlet and outlet, respectively. Reactant gas mixtures were dosed from premixed pressure gas cylinders. Before all activity measurements the V_2O_5 samples were heated to the highest reaction temperature (600°C, samples A, B, and C; 500°C, sample C*) for 1 h under a continuous flow of air. Reported reaction rates are steady-state values.

Catalyst characterization. Physical and chemical properties of the V_2O_5 samples were characterized by surface area measurements, X-ray analysis, scanning electron microscopy, and thermoanalytical measurements (TG, DTG, DTA). BET-surface areas were measured by krypton adsorption at 77 K, using a cross-sectional area of 19.5 Å² for the krypton atom. X-Ray analysis was carried out on a Guinier IV-camera FR 552 with a Johansson monochromator (Nonius, Delft) using $\mathrm{Cu}K\alpha_1$ radiation. Thermoanalytical measurements were performed on a Mettler 2000C thermoanalyzer.

RESULTS

CO oxidation rates, *r*, are defined as

$$r = -\frac{1}{S}\frac{dn_{\mathrm{CO}}}{dt} \quad (\mathrm{moles/m^2\ s}) \qquad (1)$$

where dn_{CO} corresponds to moles CO converted to CO_2, and S is the surface area of the catalyst.

Figure 2 depicts the dependence of the reaction rate on the partial pressure of CO at 600°C. Note that with both types of samples [plates (A) and agglomerates (B)] the reaction rate is first order with respect to CO in the partial pressure range $P_{CO} \leq 1$ kPa. Hence, under the conditions used (excess of oxygen) the reaction rate is described by

$$r = kP_{CO} \qquad (2)$$

where $k = k_0\, e^{-E/RT}$. With the legitimate assumption that the volume change caused by the reaction can be neglected (diluted system), we may set up the following equations to describe the CO balance over a differential section [from position z to $(z + dz)$] of the isothermal catalyst bed:

$$n^*_{CO}(z) - n^*_{CO}(z + dz) = kP_{CO}\, dS \qquad (3)$$

$$\frac{V^*_0}{RT_0} P_{CO} - \frac{V^*_0}{RT_0}(P_{CO} + dP_{CO}) = kP_{CO}\, dS \qquad (4)$$

which after integration and rearrangement gives

$$k = -\frac{V^*_0}{RT_0S}\ln(1 - X), \qquad (5)$$

where

$$X = \frac{n^*_{CO,in} - n^*_{CO,out}}{n^*_{CO,in}}. \qquad (6)$$

In these equations, $n^*_{CO,in}$ and $n^*_{CO,out}$ are the molar flow rates of CO at the reactor inlet and outlet, respectively; V^*_0 is the volumetric flow rate of CO under standard conditions (273 K, 1 atm), T_0 is the standard temperature (273 K), S is the catalyst surface area, and X is the conversion of CO.

Equation (5) was used to evaluate the experimental kinetic data. The Arrhenius plots of the rate constants obtained with the four different V_2O_5 samples are compared in Fig. 3. The following results emerge from these comparative kinetic measurements.

(i) In the temperature ranges investigated, sample A (plates) exhibits an activity more than an order of magnitude higher than sample B (agglomerates), and three to six times higher than samples C, C*.

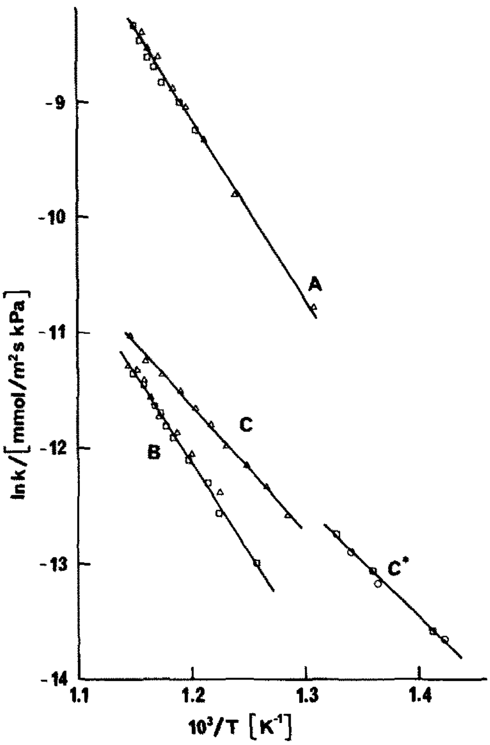

FIG. 3. Arrhenius plots of the CO oxidation rates for samples A, B, C, and C*.

(ii) The higher activity of sample A is attributed to its larger preexponential factor.

(iii) The activation energies estimated for samples A and B are not significantly different statistically, i.e., the 95% confidence limits are overlapping. Samples C and C*, however, have a significantly lower activation energy than samples A and B.

Table 1 summarizes estimated kinetic parameters and important characteristic properties of the V_2O_5 samples. Calculated reaction rates are given for two temperatures (743 and 823 K) and compared to literature data. Reported reaction rates are steady-state values; i.e., they were recorded after conversion had reached a constant value. Generally, initial reaction rates were higher, and steady-state conversion was obtained after about 1 h on stream. Surface area measurements of the samples after pretreatment in air for 1 h at 600°C indicated a decrease in surface area due to sin-

TABLE 1

Estimated Kinetic Parameters and Catalyst Properties

Author	Sample	E_a (kJ/mol)	ln k_0 (nmol m^{-2} s^{-1} kPa^{-1})	Temperature range (K)	BET surface area (m^2/g)		r^a (nmol m^{-2} s^{-1})	
					Fresh	After pretreatment	743 K	823 K
This work	A	129 ± 10	22.9 ± 1.5	773–873	0.285	0.080	7.5	57.3
This work	B	122 ± 7	19.3 ± 1.1	773–873	1.540	1.510	0.6	4.3
This work	C	91 ± 2.5	15.4 ± 2.5	773–873	3.05	1.82	2.0	8.2
This work	C*	79 ± 1	13.6 ± 1.5	673–773	3.05	2.93	2.2	7.8
Roozeboom *et al.* (*7*)	Freshly prepared	79.5	13.35	600–800	9.5	—	1.6	5.7
Roozeboom *et al.* (*7*)	Annealed	107.6	16.5	600–800	8.2	—	0.4	2.2
Mori *et al.* (*3*)	V_2O_5-U	90 ± 6	—	613–743	5.4	—	2000[b]	—
Mori *et al.* (*3*)	V_2O_5-F	90 ± 6	—	613–743	0.8	—	100[b]	—

[a] Measured at p_{O_2} = 1.2 kPa.
[b] Measured at p_{O_2} = 76 kPa.

tering. Note that the decrease of the surface area was substantial with the plates (A) and agglomerates (C) only. The disappearance of fine dust particles, which contribute to the surface area of the fresh plates after annealing, is seen by a comparison of Figs. 1a and b. Sample B and sample C* (used in the lower temperature range, i.e., pretreated at 500°C) did not exhibit significant sintering.

Reduction–reoxidation pretreatment performed at 400°C had no significant influence on the surface area. Confirmation for this behavior emerged from a scanning electron microscopy study, which showed that the grain morphologies did not change significantly during the redox cycles (*6*).

Redox cycles were also studied by means of DTA, DTG, and X-ray diffraction. Intermediate phases detected during reduction to V_2O_3 were V_6O_{13} and VO_2 (rutile) for all samples. Dependent on the grain morphology different reduction profiles were obtained. The corresponding reoxidation profiles (DTG and DTA curves) were found to be only weakly dependent on the grain morphology of the reduced form, V_2O_3. For all three samples, the temperature where reoxidation started was significantly lower than the temperature of the onset of reduction.

DISCUSSION

Reaction orders (Fig. 2) found for CO and O_2 are in agreement with those reported by Roozeboom *et al.* (*7*), i.e., first order with respect to CO, and zero order with respect to O_2.

Table 1 shows that the plates (A) are more than an order of magnitude more active than the prismatic agglomerates (B). This higher activity is exclusively due to the higher number of active sites on the plates, which expose mainly the (010) planes on which the V=O species are located. The similarity in the activation energies of samples A and B indicates that the activities are governed by the same active sites. Since both samples are annealed for one hour at 600°C before the kinetic measurements, it can be assumed that lattice defects do not play a significant role in the investigated temperature range.

Three types of samples are characterized in Table 1 that have been prepared in a very similar manner by three different groups. These are samples C and C* of the present work, the freshly prepared V_2O_5 catalyst of Roozeboom *et al.* (*7*), and sample V_2O_5-U of Mori *et al.* (*3*). All these samples were prepared by decomposition of NH_4VO_3 in flowing oxygen or air. Note the excellent agreement in the kinetic parameters (activation energies and absolute rates) between our samples C, C* and the freshly prepared catalyst of Roozeboom *et al.* (*7*). No explanation can be found for the strikingly different activity of the V_2O_5-U sample of Mori *et al.* (*3*), which is three orders of magnitude more active. Unfortunately the method of the kinetic evaluation was not reported explicitly in their paper. It would be interesting to reexamine the data of Mori *et al.* in light of the results of Roozeboom *et al.* (*7*) and those of the present work.

The different activation energies obtained for the samples annealed at 600°C (A and B) and 500°C (C*) indicates that the V=O species are less active than lattice defects, which exhibit a lower activation energy. Nevertheless, the overall activity of sample A, which exposes mainly (010) planes, is significantly higher in the measured temperature range, due to the larger number of active sites (V=O) as compared to the other morphologies (B and C). The low activation energy of sample C is in agreement with the one found by Mori *et al.* (*3*) for V_2O_5-U, and the one found by Roozeboom *et al.* (*7*) for their freshly prepared catalyst. Summarizing, one can state that lattice defects with low activation energy are important at lower temperatures. During catalytic operation at sufficiently high temperatures, defects are thoroughly annealed, and the catalytic activity is dominated by the V=O species.

The overall activity of A is about three times higher than that of C*, which indicates that the smaller activity of the V=O species, as compared to the lattice defects, is more than compensated by the larger number of active sites (V=O) on the (010) planes. This result contrasts with that of Mori *et al.* who found that sample V_2O_5-U (prepared by decomposition of NH_4VO_3) was 20 times more active than the fused V_2O_5-F catalyst. It should however be taken into account that sample V_2O_5-F did not consist of well-developed platelets, as evidenced by a comparison of the electron micrographs. Therefore the fused sample of Mori *et al.* may not exhibit a high enough contribution of (010) planes to the surface area. Electron micrographs of our sample A, reproduced in Ref. (*8*), exhibit a predominance of the (010) planes. The surface area contribution of (010) planes in our sample A has been qualitatively established by X-ray diffraction, as reported previously (*8*). For the well-developed plates, a morphological factor (*9*) $f = I(101)/I(010) = 0.28$ was determined. For the prismatic agglomerates, sample B, a value $f = 0.95$ was found, which is in good agreement with $f = 0.90$ calculated for a monocrystal (*10*) and measured for nonoriented samples.

Mori *et al.* (*3*) observed a twofold increase in the activity by reduction–oxidation pretreatment of the fused sample V_2O_5-F. A similar pretreatment of samples A and B with subsequent use in the temperature range 500–600°C did not result in a significant activity increase. The lack of a change in activity by the redox cycles in our systems indicates that defects are annealed during the pretreatment at 600°C. Evidence for this fact is shown in the scanning electron micrographs (Figs. 1a and b) before and after annealing.

For kinetic measurements performed in this temperature range an accurate recording of changes in the BET surface area is a necessity. Note that the surface area of sample C used in the low-temperature region (C*) remained practically constant during pretreatment at 500°C, whereas sample C pretreated at higher temperatures exhibited a decrease in the surface area of 40%, and sample A even a decrease by 70% (cf. Fig. 1, scanning electron micrographs of sample A before and after pretreatment). Note that sample B, which consisted of prismatic needles, was virtually thermally stable even in the high temperature range.

The thermoanalytical measurements (reduction and reoxidation profiles) performed on all samples indicated that the starting temperature of reduction was considerably higher than the corresponding starting temperature of reoxidation. This is in agreement with the observations of Roozeboom *et al.* (*7*) who concluded that reoxidation of the surface may be the rate-determining step of CO oxidation on V_2O_5.

Finally it is interesting to compare a conservatively estimated turnover rate of our sample A (well-developed plates) with the one reported by Mori *et al.* (*3*) for the fused V_2O_5-F sample. Assuming that only (010) planes contribute to the surface area of sample A, and using a density of 4.872 nm^{-2} of V=O species on an (010) plane, we calculate a turnover frequency TF = 1 $(ks)^{-1}$ at 743 K. V_2O_5-F of Mori *et al.* was quoted (*3*) to have a turnover frequency TF = 15 $(ks)^{-1}$ at 673 K, whereby the surface area contribution of the (010) faces was stated (*3*) to be 50%.

CONCLUSIONS

Kinetic studies of CO oxidation performed on V_2O_5 catalysts of different morphologies indicate that the reaction is structure sensitive, and that two sites of significantly different activity are of importance. At high temperatures (600°C) vanadyl groups (V=O), which are predominantly exposed on the (010) faces of V_2O_5, contribute most to the activity of CO oxidation. At lower temperatures (400°C) the most active sites are lattice defects which exhibit a significantly lower activation energy than the V=O species. High-temperature pretreatment (600°C) anneals the defects and thereby leads to an increase in the activation energy.

REFERENCES

1. Kera, Y., and Hirota, K., *J. Phys. Chem.* **73,** 3973 (1969); Cole, D. J., Cullis, C. F., and Hucknall, D. J., *J. Chem. Soc., Faraday Trans. 1* **72,** 2185 (1976); Bond, G. C., Sárkány, A. J., and Parfitt, G. D., *J. Catal.* **57,** 176 (1979); Akimoto, M., Usami, M., and Echigoya, E., *Bull. Chem. Soc. Japan* **51,** 2195 (1978).
2. Kera, Y., *Bull. Chem. Soc. Japan* **50,** 2841 (1977).
3. Mori, K., Miyamoto, A., and Murakami, Y., *J. Phys. Chem.* **88,** 2735 (1984); Miyamoto, A., Mori, K., Miura, M., and Murakami, Y., *in* "Studies in Surface Science and Catalysis" (M. Che and G. C. Bond, Eds.), Vol. 21, p. 371. Elsevier, Amsterdam, 1985.
4. Miyamoto, A., Yamazaki, Y., Inomata, M., and Murakami, Y., *J. Phys. Chem.* **85,** 2366 (1981).
5. Baiker, A., Dollenmeier, P., and He, R., *J. Chem. Soc., Chem. Commun.,* 413 (1985).
6. Maciejewski, M., Reller, A., and Baiker, A., *Thermochim. Acta* **96,** 81 (1985).
7. Roozeboom, F., van Dillen, A. J., Geus, J. W., and Gellings, P. J., *Ind. Eng. Chem. Prod. Res. Dev.* **20,** 304 (1981).
8. Baiker A., and Monti, D., *J. Catal.* **91,** 361 (1985).
9. Ziólkowski, J., and Janas, J., *J. Catal.* **81,** 298 (1983).
10. ASTM Powder Diffraction File, 9-387, ed. Joint Committee on Powder Diffraction Standards, Pennsylvania, 1979.