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V_2O_5–K_2SO_4–Silica System

2. Correlation with Toluene Oxidation Activity

In a previous paper of this series (*1*) we have described the preparation, characterization, and testing of silica-supported V_2O_5–K_2SO_4 catalysts for oxidation of methanol to formaldehyde. The activity of V_2O_5–K_2SO_4–SiO_2 for the oxidation of toluene to benzaldehyde is presented in this note.

Although there has been some interest in the patent literature on the preparation of V_2O_5–K_2SO_4–SiO_2 catalyst for toluene oxidation (*2*), the work reported so far on the vapor phase oxidation of toluene over supported V_2O_5–K_2SO_4 is mainly that of Downie *et al.* (*3*). Their kinetic studies were, however, limited to a commercial catalyst. There is no prior study to correlate the physicochemical properties of a supported V_2O_5–K_2SO_4 catalyst system with the catalytic activity for toluene oxidation.

The present work was carried out (a) to determine the effects of operating variables such as catalyst composition and reaction temperature and (b) to study the similarities in the role of active components for the oxidation reaction of toluene with those of methanol. Studies of this type are expected to lead to a better understanding of the nature of the catalysts in relation to activity.

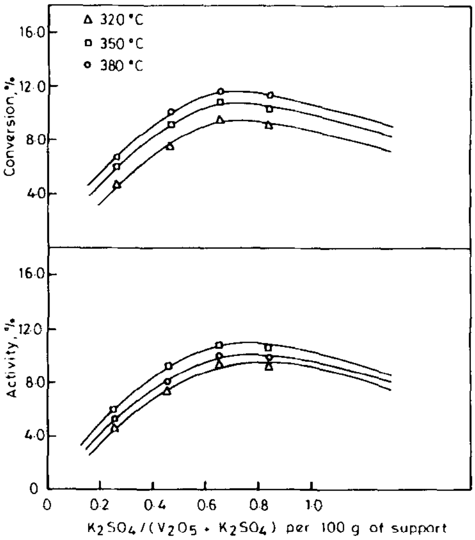

FIG. 1. Effect of promoter concentration on the activity and conversion.

EXPERIMENTAL

Experimental apparatus, procedures, and catalysts were the same as in (*1*). K_2SO_4 content in all the four samples ranged from 5 to 20%. Spent catalyst, used for about 10 runs, was analyzed by X-ray and electron microscopic techniques.

Reference will be made to the various samples as indicated previously (*1*): thus, V-20-K-15 indicates a sample of V_2O_5–K_2SO_4 supported on silica having 20% of the active elements as V_2O_5, 15% of the promoter as K_2SO_4, and the balance as silica. Extensive use of various techniques has lead to considerable insight into the structure of the V_2O_5–K_2SO_4–silica system, as discussed in Ref. (*1*).

The activity of the catalyst was studied using air oxidation of toluene in the temper-

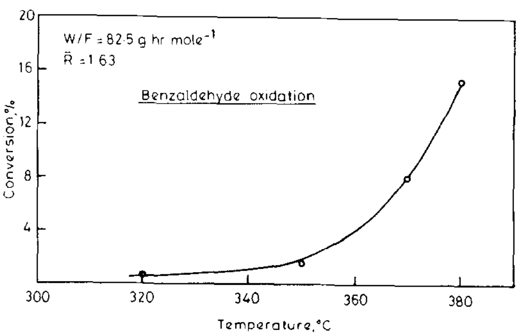

FIG. 2. Effect of temperature on benzaldehyde oxidation.

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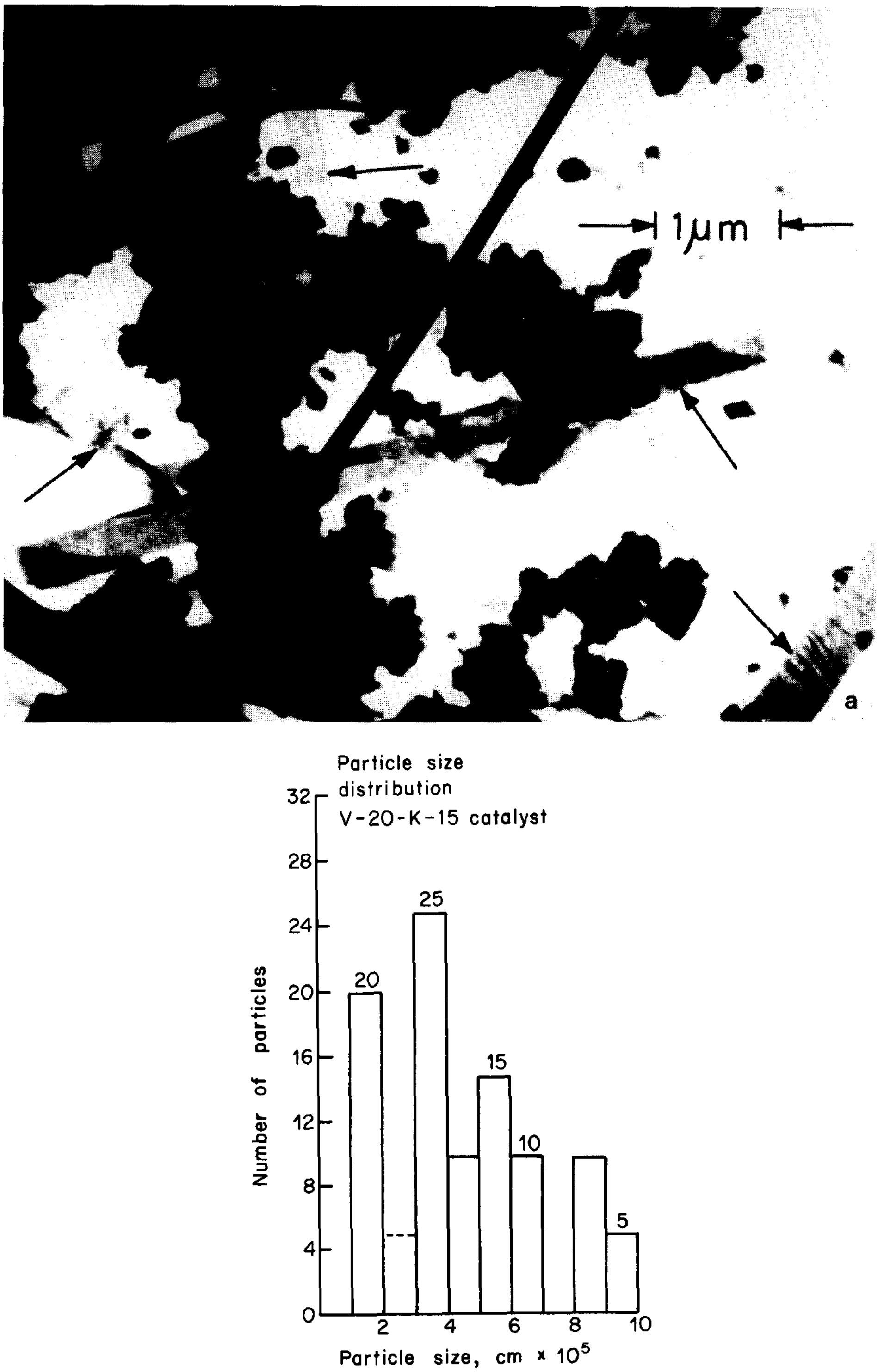

FIG. 3. Electron micrograph from (a) fresh and (b) spent catalyst with corresponding particle size distribution curves.

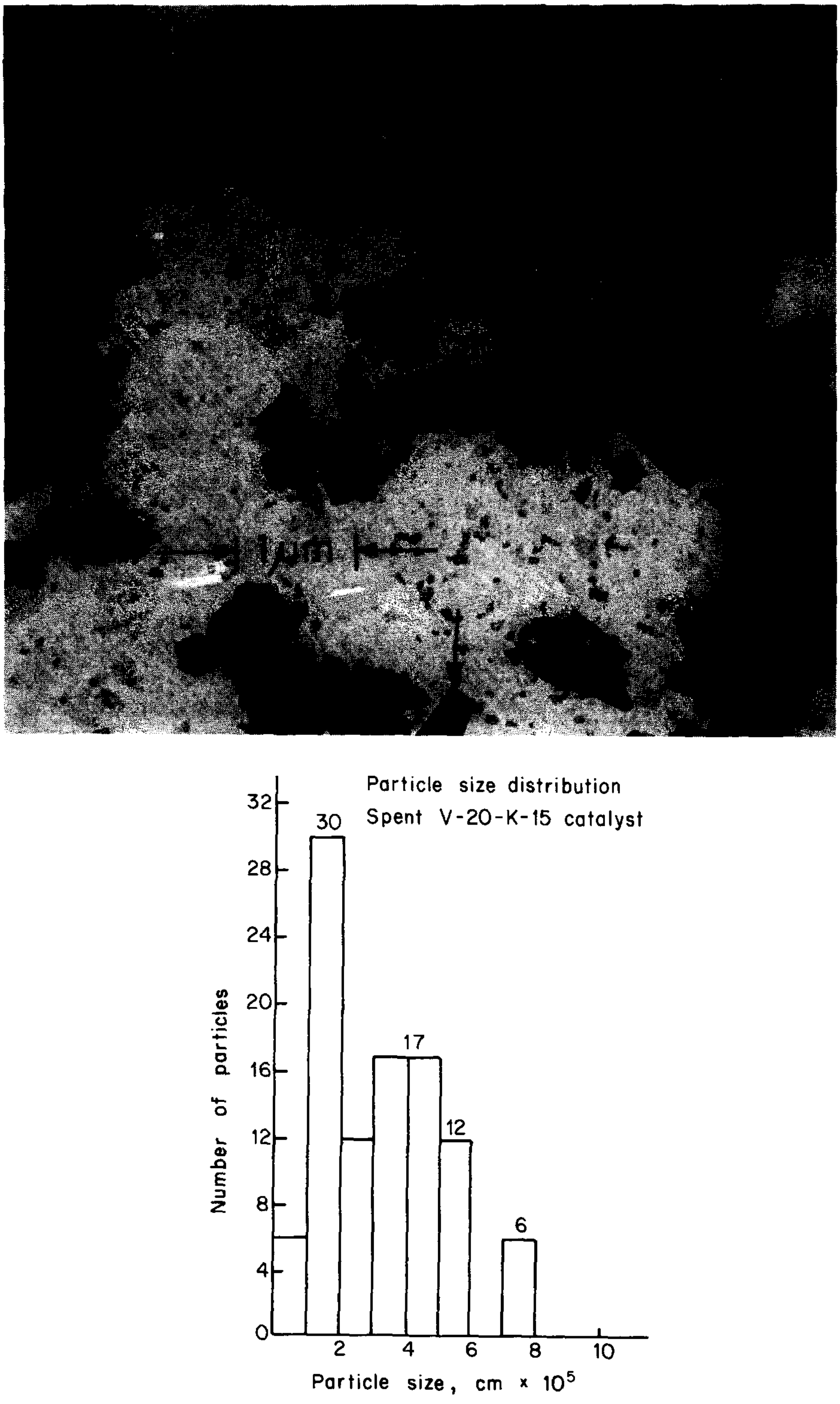

FIG. 3.—*Continued.*

TABLE 1

Product Distribution at Different Temperatures[a]

Catalyst: V-20-K-15

Temperature (°C)	Toluene	Oxygen	Benzaldehyde	Water	Carbon-dioxide
320	6.53	92.10	0.67	0.68	0.02
350	6.44	91.99	0.76	0.78	0.03
370	6.39	91.64	0.77	0.92	0.28
380	6.38	91.07	0.72	1.12	0.71

[a] All the concentrations are reported in mole% (nitrogen-free basis).

ature range 320–380°C. Product samples were analyzed in a chromatographic column, containing 10% SE-30 on Chromosorb W and analyzed by flame ionization detection.

RESULTS AND DISCUSSION

The activity of a series of supported V_2O_5–K_2SO_4 catalysts for toluene oxidation was investigated at the temperatures of 320, 350, and 380°C with toluene to air mole ratio, $\bar{R}$ = 1.63% and W/F = 82.5 g · hr/mole. The catalytic activity was defined as the number of moles of benzaldehyde formed per mole of toluene fed. The product analyses indicated the presence of benzaldehyde and unreacted toluene. Carbon oxides were detected significantly with the runs conducted at 380°C.

Experiments to investigate the effect of total active phase concentration on the activity indicated that activity increases upto about 55 g (V_2O_5 + K_2SO_4) per 100 g support and then decreases. The corresponding catalyst composition was V-20-K-15.

The results of the experiments conducted on the catalysts with different K_2SO_4 to total active phase weight ratios are given in Fig. 1. Reaction conditions were the same as indicated above. The figure shows that the activity is maximum at about 65% concentration in the active phase. This corresponds to the catalyst composition V-20-K-15.

From these plots it is also evident that the activity increases upto 350°C. At a temperature of 380°C, the activity clearly declines. The conversion of toluene, however, rises steadily with temperature. This can be explained on the basis of the direct oxidation of benzaldehyde to carbon oxides since significant amounts of carbon oxides were found present in the exit stream at 380°C.

In order to clarify this point further, oxidation of toluene was carried out at the temperatures of 320, 350, 370, and 380°C over a catalyst V-20-K-15. Table 1 shows the distribution of reaction products at different temperatures. The oxidation of benzaldehyde was negligible at 350°C, however, at 380°C, the conversion of benzaldehyde was approximately 14%. A separate oxidation experiment with benzaldehyde in the absence of toluene showed (Fig. 2) that carbon oxides were produced significantly at the temperatures of 370°C and above, with a conversion of approximately 15% at 380°C. The decrease in activity from 350 to 380°C is really caused by the oxidation of benzaldehyde.

A close link between electron microscope observation to the activity of the catalysts was established for the oxidation of methanol where the maximum activity also corresponded to V-20-K-15 composition (*1*). It was found that the proportion of the needle type of V_2O_5 was different in all the catalyst samples (depending on K_2SO_4 concentration), the highest being for the catalyst composition V-20-K-15 (*1*). This

TABLE 2

Physical Characteristics of V_2O_5–K_2SO_4–Silica

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Porosity ($cm^3/100\ cm^3$)	Average pore radius (Å)
V-20-K-5	8.20	0.4186	49.6	1020.9
V-20-K-10	2.80	0.3588	45.1	2562.8
V-20-K-15	5.20	0.3030	41.7	1165.3
V-20-K-20	18.00	0.2821	39.7	313.4

again indicates that the catalyst with the greater tendency to exhibit these needle structures has the higher activity. The BET results as presented in Table 2 indicate that with the increase in K_2SO_4 concentration, pore volume and porosity decrease but the surface area passes through a minimum. Also, average pore radius first increases and then decreases. There is an optimum value of K_2SO_4 concentration at which both the surface area and the pore radius are optimum. This corresponded to V-20-K-15 where the maximum activity was obtained.

The spent catalyst was studied by X-ray diffraction and by transmission electron microscopy, with the aim of getting a better insight into the physicochemical changes that may take place during the catalytic reaction, and their possible relationship with the catalytic properties. The activity for such a spent catalyst was about 6% less than that for a fresh catalyst. The X-ray diffraction analysis showed that no new phases are formed and V_2O_5 and K_2SO_4 do not undergo any structural transformation during the reaction. Electron microscopy has, however, indicated some modifications in the microstructure of the catalyst. The electron micrographs from a fresh and a spent catalyst of the same composition are shown in Figs. 3a and b. The corresponding particle size distributions are included in these figures. The proportion of the needle-type V_2O_5 crystals in the spent catalyst seems to be smaller as compared to that in the fresh catalyst. A similar observation was made in the studies of the activity for methanol oxidation (*1*). The electron diffraction studies have however shown that the long needles and other large particles are disintegrated leading to an extended structure of small grains. The average particle size was also found to decrease from 0.40 to 0.25 μm.

Correlation of results of catalytic oxidation of toluene over supported V_2O_5–K_2SO_4 catalyst with studies in solid-state properties has permitted us to confirm the role of needle-type V_2O_5 crystals in such oxidation reactions.

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