nated or their environments radically changed. At the same time, the population of silanol groups is markedly increased particularly with the higher calcination temperatures. When pyridine was reacted with sample (c) a sharp band was observed near 3680 cm^{-1} and the structureless absorption between 3670 and 3600 cm^{-1} was eliminated. Pyridinium ions, indicative of proton acidity, were detected on all the samples studied, thus indicating the presence of some acidic hydroxyl groups.

The locations of the newly formed hydroxyl groups are not clear at this time. The poorer resolution obtained in the spectra suggests that the hydroxyl groups are less specifically localized than in hydrogen Y zeolite. The band near 3660–3670 cm^{-1} could possibly represent AlOH groups due to $Al(OH)_3$, $Al(OH)_2^+$, or $Al(OH)^{2+}$ as suggested by Kerr (*1*). The nature and assignment of the lower frequency bands is uncertain.

The results show that stabilized zeolites prepared by several different methods contain silanol and other structural hydroxyl groups, which are different from those of hydrogen and magnesium hydrogen Y zeolites, even after calcination at temperatures as high as 815°C. Spectra of hydroxyl groups can be used to distinguish the different decomposition products of ammonium Y zeolites.

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The Effective Surface Area of the Promoted Vanadium Pentoxide Catalyst Supported on Silica Gel

Many authors have investigated the oxidation of sulfur dioxide on the promoted vanadium pentoxide catalyst, and have shown that the active component of the catalyst is the compound of vanadium pentoxide, potassium oxide, and sulfur trioxide (*1–3*). We have studied the rate of the oxidation of sulfur dioxide on the promoted vanadium pentoxide catalyst supported on silica gel with large surface area, and found that there is an optimum amount of the active component supported on the carrier. This result is interpreted by the concept of the effective surface area, and the rate determining step of the reaction is discussed.

The catalysts with various amount of the active component were prepared by impregnating the silica granules (0.5 ~ 1.0 mm) with a desired amount of aqueous solution of vanadyl sulfate and potassium bisulfate. The specific surface area of the silica gel was 249 m^2/g. The molar ratio of the catalyst ingredients, $V_2O_5:K_2O:SO_3$

was 1:3:4, throughout this study. The reaction rate was measured by an ordinary flow type reactor at 380 ~ 440°C. In most of these experiments the partial pressures of sulfur dioxide and oxygen were 0.10 and 0.15 atm, respectively, and the remainder was nitrogen. The catalyst was treated with reaction gases at 500°C for a few hours before the kinetic measurement. The concentration of the reactant was analyzed continuously by a thermal conductivity detector.

The rate of the reaction was well expressed by the first order with respect to oxygen and the Arrhenius plots obtained were linear. These results were similar to those obtained by Mars and Massen (*4*) in their low temperature experiments.

In Fig. 1, the logarithm of the first order rate constant, *k*, are plotted versus the logarithm of the amount of the supported active component, V_a, or logarithm of the amount of the supported vanadium pentoxide, V_t. As shown in Fig. 1, the rate constant increases in proportion to $(V_t)^m$ to the maximum at 0.07 g of the vanadium pentoxide and then decreases in proportion to $(V_t)^n$. From the slopes of the straight lines the values of *m* and *n* are found to be 2 and —2, respectively.

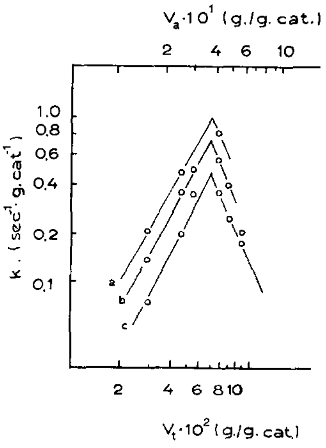

FIG. 1. Dependence of the rate constant, *k*, on the amount of the active component: V_a, Supported amount of the active component; V_t, Supported amount of the V_2O_5; (a) 440°C; (b) 420°C; (c) 400°C.

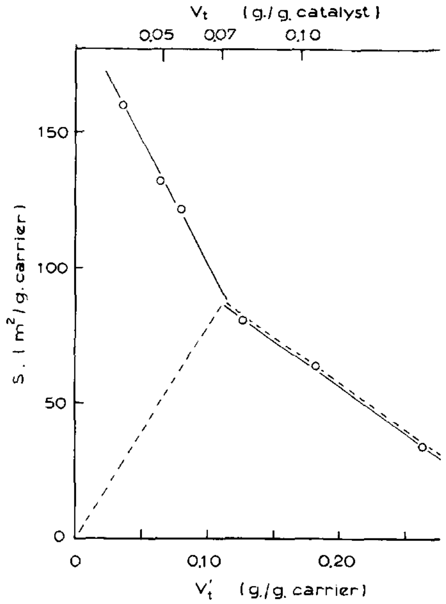

FIG. 2. Dependence of the surface area on the amount of V_2O_5: (---) estimated effective surface area; (—) observed surface area.

Figure 2, shows the change of the surface area of the catalyst with the amount of vanadium pentoxide supported on the carrier. The surface area of the catalyst after each run was obtained by the BET method of nitrogen adsorption at —196°C. The surface area decreased linearly with the increasing amount of the active component, and at 0.07 g of the vanadium pentoxide per gram of the catalyst the straight line changes the slope abruptly into another straight line of the different slope.

From Figs. 1 and 2, no reasonable relation between the catalytic activity and the specific surface area of the catalyst is observed. This shows that the whole surface of the catalyst is not effective in catalysis. The amount of the vanadium pentoxide at the break point in Fig. 2, and the optimum amount of the active component in Fig. 1 lies close together. Under the conditions of the reaction, the active component is in molten state (*1–3*) and is considered to spread to fill the micro pores of the carrier. When the amount of the active component is not enough to cover the whole surface of the carrier, the observed surface area of the catalyst consists of the effective surface of the active component and the uneffective surface of the exposed carrier. Assuming that the effective surface area is proportional to the amount of the active component supported on the carrier, it should increase linearly up to the break point and the whole surface area inversely, as shown in Fig. 2. When the amount of the active component is enough to cover the carrier completely, the measured surface area is identical with the effective surface area, and it decreases with the increasing amount of the active component. The effective surface area passes through the maximum at the break point, where the active component has just covered the carrier, as shown by broken line in Fig. 2. This change of the effective surface area and the change of the catalytic activity with the amount of the active component are in close similarity. Both the effective surface area and the catalytic activity reaches the maximum at the same amount of the active component.

As previously described, the rate of the oxidation of sulfur dioxide, r, was expressed by

$$r = k \cdot P_{O_2}, \qquad (1)$$

where k is the rate constant and P_{O_2} is the partial pressure of oxygen. For values of V_t below 0.07, the results in Fig. 1 show Eq. (1) has the form:

$$r = k'(V_t)^2 \cdot P_{O_2} \qquad (2)$$

where this latter equation holds, the amount of active component may be correlated with the number of the active sites on the surface of the catalyst. Assuming that the number of active sites is proportional to the amount of the active component and that the coverage with oxygen is low, Eq. (2) represents the rate of the adsorption of oxygen accompanied by the dissociation on the active site. The rate constant per active site, k'', is given by Eq. (3).

$$k'' = k' \ (V_t/\text{effective surface area})^2 = k/(\text{effective surface area})^2. \qquad (3)$$

TABLE 1
RATE CONSTANT AT DIFFERENT TEMP AND V_t

$V_t \cdot 10^2$ (g/g of cat)	$k'' \cdot 10^3$ (g of cat sec^{-1} m^{-4}) Temp (°C): 400	420	440
2.88	1.40	2.52	3.92
4.71	1.48	2.45	4.33
5.49	2.09	2.61	3.41
7.80	1.42	2.16	3.62

The values of k'', calculated according to Eq. (3) are tabulated in Table 1. As is obvious from Table 1, the values of k'' are practically constant over the wide range of the supported active component. Therefore, the value of the effective surface area estimated in Fig. 2 seems a reasonable one.

From these results it must be concluded that the rate determining step of the reaction is the chemisorption of oxygen accompanied by the dissociation. The dependence of the rate constant on the amount of the supported active component has been successfully interpreted by the concept of the effective surface area.

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