these data that bismuth oxide and bismuth molybdate crystallites probably existed as isolated clusters throughout the pores of the silica gel support.

Data on more catalysts are obviously needed to prove the validity of this technique for measuring active surface areas. Our work indicates that it would be necessary to experiment with temperature, contact time, and sample size with each catalyst to find the best conditions for detection of the transition point described. Refinements are also needed to improve the accuracy of the method.

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Investigation of Reactions in the Adsorbed Layer: Decomposition of *tert*-Butylbenzene on Silica-Alumina

The cracking of alkylbenzene on silica-alumina catalysts has been investigated by many workers (*1*). The nature of alkylbenzene adsorbed on the catalyst has been discussed indirectly on the basis of the kinetics of the reaction. If the decomposition of adsorbed alkylbenzene can be followed by direct measurements, the information on the reactivity of adsorbed species will be much improved. The present study was undertaken to present such an attempt for *tert*-butylbenzene on a silica-alumina. An investigation along this line has been already carried out by us for the decomposition of formic acid adsorbed on silver and magnesium oxide catalysts (*2*).

The *tert*-butylbenzene was obtained from the Tokyo Kasei Kogyo Co. It was purified by preparative gas chromatography. The purity as checked by gas chromatography was 99.5%. The silica-alumina catalyst containing 13% alumina was obtained from the Shokubaikasei Co. It has a BET surface area of 437 m^2/g. Prior to the experiments, the catalysts were heated in air at 450°C followed by evacuation for 24 hr at this temperature.

Investigation of the decomposition of adsorbed *tert*-butylbenzene (TBB) was carried out as follows: A constant volume apparatus was used. After the adsorption of TBB at room temperature, the desorption experiment was started by immersing a trap attached to the reaction vessel in liquid nitrogen. Analysis of the desorption products collected in the trap was carried out by gas chromatography. It was found that in addition to TBB an appreciable amount of benzene was desorbed from the catalyst, suggesting that even at room temperature the decomposition of TBB takes place. The rate of decomposition of TBB in the adsorbed layer can be given by the rate of appearance of benzene in the gas phase when the adsorption of benzene on the catalyst is negligible. As will be described later, the benzene adsorption can not be neglected at room temperature. In such case the rate of formation of benzene in the adsorbed layer can be obtained in the following manner: The rate of appearance of benzene in the gas phase R_D is given by

$$R_D = k_D\theta$$

where θ is the coverage of benzene and k_D is the rate constant of desorption. Value of θ varies according to the equation

$$d\theta/dt = R_F - R_D$$

where R_F is the rate of formation of benzene in the adsorbed layer. Considering that in the initial range of the reaction R_F is larger than R_D, with the progress of the reaction R_F will decrease while R_D increase. Thus, after a particular time of reaction the condition $R_F = R_D$ will hold. At this moment R_D is expected to show a maximum. This maximum rate should be equal to the rate of formation of benzene R_F. The remaining amount of TBB adsorbed corresponding to this maximum rate can be calculated from the value of θ during the reaction, i.e., from information on the benzene adsorption on the catalyst.

In order to obtain information on the extent of benzene adsorption during the decomposition reaction, benzene desorption experiments were carried out under similar conditions to the decomposition reaction. Details of the experiment are as follows: A mixture of 48.5 cc STP of benzene and TBB (TBB/benzene = 8.7), was introduced at 20°C onto 4.99 g of catalyst, on which 16.3 cc STP of ammonia had been adsorbed. The purpose of the ammonia adsorption is to prevent the decomposition of TBB on the catalyst, thereby making it possible to determine the amount of benzene adsorbed during the desorption experiment. After the adsorption was completed, the rates of desorption of benzene were measured at 20°C. After that, the temperature of the catalyst was raised up to 60°C, similar rate measurements being repeated. The results are shown in Table 1. It is seen that at 20°C benzene adsorption is appreciable while at 60°C the adsorption is negligible. The amount of benzene adsorbed during the desorption experiments can be estimated from data on the benzene desorption shown in Table 1.

The rate of desorption of benzene during the decomposition of TBB adsorbed, R_D, was determined as follows: Two U-traps were attached to the reaction vessel. By immersing a trap in liquid nitrogen alternatively, the desorption could be continued without interruption. Thus, values of R_D were determined continuously from the analysis of the desorption products collected in the trap. It was found that R_D passed through a maximum with the progress of the reaction, as expected from the consideration described above. The amount of benzene adsorbed corresponding to such a maximum value of R_D was estimated from the data in Table 1. In the case of the initial amount of 7.8 cc STP/g of TBB introduced the maximum value of R_D was 3×10^{-3} cc/min g. The corresponding amount of benzene adsorbed was estimated as 0.1–15 cc STP/g, being much less than the remaining amount of TBB adsorbed (10% of the initial amount of which was decomposed). Consequently, the amount of TBB adsorbed was calculated by assuming that no benzene adsorption takes place on the catalyst. By varying the initial amount of TBB introduced, and measuring the maximum values of R_D, the relationship

TABLE 1

RATES OF DESORPTION OF BENZENE

Temp. (°C)	Time of desorption (min)	Rate of desorption of benzene (cc STP min^{-1}g^{-1} × 10^4)	Amount adsorbed of benzene (cc STP g^{-1} × 10^2)	Amount adsorbed of TBB (cc STP g^{-1})
20°	0	69.7	50.00	9.27
	30	59.5	32.15	9.04
	60	42.0	19.54	8.88
	90	28.9	10.87	8.75
60°	0	0.15	0.49	7.63
	30	0.03	0.39	7.19
	60	0.00	0.39	6.82

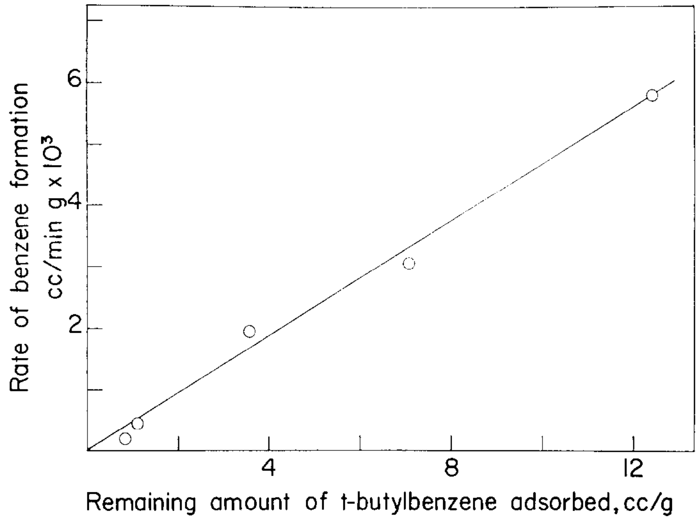

FIG. 1. Rates of decomposition of TBB adsorbed on silica-alumina.

between the amount of TBB adsorbed and the rate of decomposition of TBB was obtained. The result is shown in Fig. 1. It is seen that the rate of decomposition of TBB is proportional to the amount of TBB adsorbed. The ratio of benzene to TBB in the desorption products was calculated from the same data as shown in Fig. 1. As seen in Fig. 2, this ratio is increased markedly with decreasing amount of TBB adsorbed.

DISCUSSION

The results shown in Figs. 1 and 2 suggest that the heat of adsorption of TBB is changed with the coverage (*3*) while the activation energy of its decomposition is almost constant throughout the coverage. Such behavior might be explained in terms of the concept that a small fraction of the total surface is active in the reaction, this fraction being of a homogeneous character. If the adsorption on such an active fraction were strong and the amount adsorbed on it were determined by adsorption equilibrium, the amount adsorbed on the whole surface would not be proportional to that adsorbed on the active fraction, i.e., such a linear relation shown in Fig. 1 would be unex-

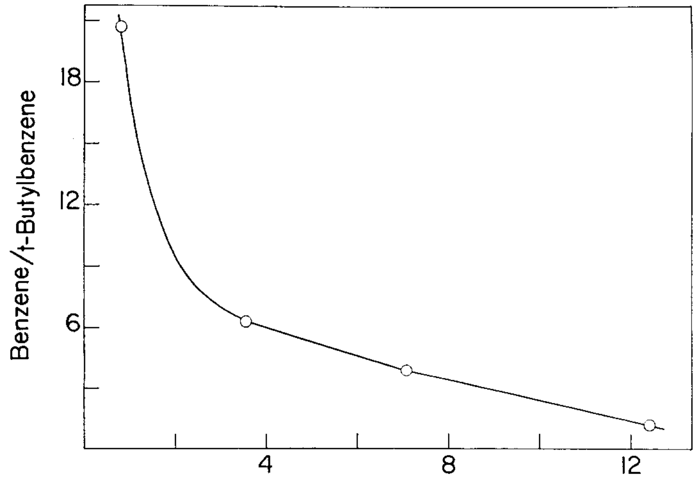

FIG. 2. Ratio of benzene to TBB in the desorption products.

pected. The results in Figs. 1 and 2 seem to be explained by a reaction scheme similar to that proposed by Johnson *et al.* (*4*).

$$\text{TBB (gas)} \rightarrow \text{TBB (adsorbed)} \quad (1)$$

$$\text{TBB (adsorbed)} + \text{H}^+\text{(catalyst)} \rightarrow \text{Protonated TBB} \quad (2)$$

$$\text{Protonated TBB} \rightarrow \text{Reaction products} + \text{H}^+\text{(catalyst)} \quad (3)$$

Step (1) represents the adsorption of TBB on the whole surface of the catalyst, not confined to the acid sites. Its heat of adsorption is changed with the amount adsorbed as described previously. Step (2) is the interaction of TBB (adsorbed) with the acid sites. If we can assume equilibrium in this step, as proposed by many workers, the strength of interaction is described as the interaction-equilibrium constant K. Step (3) is the decomposition reaction. After the reaction the acid sites are regenerated. Assuming that the rate constant k of step (3) as well as the equilibrium constant K of step (2) are independent of the adsorption of TBB, being constant irrespective of the change in the heat of adsorption of TBB, and that in addition, the interaction of TBB (adsorbed) with the acid sites is weak, the following equation results:

$$K = \frac{[\text{protonated TBB}]}{B_0[\text{TBB}_{\text{adsorbed}}]}$$

$$\text{Rate} = k[\text{protonated TBB}]$$

$$\text{Rate} = kKB_0[\text{TBB}_{\text{adsorbed}}] = k'[\text{TBB}_{\text{adsorbed}}] \quad (4)$$

where B_0 is the number of acid sites and $k' = kKB_0$. Equation (4) predicts the behavior shown in Fig. 1.

The value of k' determined from the data shown in Fig. 1 was 4.69×10^{-4} min^{-1}. Similar measurements were carried out at higher temperatures, e.g., 40°C. From comparison of k' values at different temperatures an activation energy of 16.2 kcal/mole was obtained. It should be noted that this value is the "true" activation energy of the reaction.

The considerations given above indicate that the term (TBB $_{\text{adsorbed}}$) in Eq. (4) determines the pressure dependence of the rate. It may therefore be concluded that the heat of adsorption of TBB determined from the pressure dependence of the rate, i.e., from the kinetics of the reaction, is associated with the whole surface, not confined to the special active sites. This suggests that for this system it seems unreasonable to discuss the adsorption on the active sites from the viewpoint of the kinetics of the reaction, as has been done by many workers.

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