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The Nature of Adsorbed Sites on Catalysts

I. Active Sites and Reaction Mechanism for Diphenylamine Synthesis over HCl–Al_2O_3 Catalyst

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The experiments for diphenylamine (DPA) synthesis over HCl–Al_2O_3 carried out combining a FID gas chromatography and a temperature programmed desorption (TPD) technique which was adopted by Amenomiya and Cvetanovic.

The desorption components from the catalyst surface are plotted against the desorption temperature which was raised linearly with time. The curves thus obtained are expediently called "TPD analytical curves."

From the curves, it was found that two different kinds of the sites for DPA formation were present on the Al_2O_3 and HCl–Al_2O_3 catalysts; one was found to be active in the range of 100–300°C, and the other was active at above 400°C. While the former was found unstable under the reaction conditions, the latter was stable and active under the same conditions. Therefore, it has been concluded that the latter is relevant to the active sites of the actual process.

From the kinetic studies on the previous work and the present data, the reaction mechanism included a Rideal mechanism has been induced for the DPA synthesis over HCl–Al_2O_3 catalyst.

INTRODUCTION

The behavior and reactivity of adsorbed sites on catalyst have been extensively discussed so far. The studies have been performed by the characteristic experimental means (*1–4*). Above all, Amenomiya *et al.* (*2*) have recently obtained valuable data on the active sites on the alumina catalyst using a temperature programmed desorption (TPD) technique.

The present work has been undertaken to obtain information of a similar problem on a catalyst, by combining a TPD technique and a FID gas chromatography as an analytical means. Another feature of this study is that the desorption experiments are carried out introducing a low partial pressure of a reactant to a catalyst bed.

In the present report, the diphenylamine (DPA) synthesis over HCl–Al_2O_3 catalyst which was studied kinetically previously (6) and then the reaction mechanism for the process will be revealed by the technique.

EXPERIMENTAL

Materials

Alumina was obtained from Sumitomo Kagaku Co., having a BET area of 310 m^2/g. 7.3 wt % HCl-treated alumina catalysts were prepared according to the previous report (*5,6*). The aniline used was purified by distillation with zinc dust.

Apparatus and Procedure

Some modifications of the TPD technique of Amenomiya *et al.* (*2*) were made

in order to analyze directly the desorption components from the catalyst surface. Since a FID gas chromatograph was used as an analytical means, smaller amounts of catalysts could be used for the desorption experiments under atmospheric pressure.

A schematic diagram of the apparatus is shown in Fig. 1. Part A is a TPD system, and part B is an analytical system by a FID gas chromatography.

The catalyst (50–500 mg) was placed in the U-type glass tube of 8 mm i.d. Sometimes, by passing the carrier gas into the aniline reservoir, the effect of the presence of aniline vapor on the desorption experiments could be examined. S_1 is an injection point of a desired vapor such as a reactant or product and S_2 is a sampling point of desorbed components.

TPD curves after the method of Amenomiya *et al.* (*2*) can be obtained by leading the exit gas, including desorption components, to a FID glc analytical system directly, where a glass breaker K is broken down.

Prior to the experiments, the catalysts were activated at 550°C for 2 hr in flow of air and then evacuated at the same temperature for 2 hr. The catalysts were cooled down to room temperature, carrier gas N_2 was admitted to the TPD system, and then liquid aniline was added into the catalyst bed through a capillary tube J in the absence of air.

The pretreated catalysts were allowed to stand overnight at room temperature. Excess aniline was removed from the catalyst bed by evacuating at 100°C for 2 hr.

The catalysts treated in this way were subjected to desorption experiments.

The temperature of catalyst bed was raised linearly in flow of the carrier gas at a rate of 5°C/min.

The TPD experiments were mostly carried out in the presence of aniline vapor where the carrier gas was passed through the aniline reservoir. 2 ml of exit gas including desorption components was sampled at every few minutes and analyzed. Therefore, it is desirable to select the column so as to perform the analysis within the intervals, because the desorption components are successively obtained at increasing temperatures.

In another experiment, the desorption components were led directly to the FID cell, as done by Amenomiya *et al.*

Desorption experiments and analysis were carried out under atmospheric pressure.

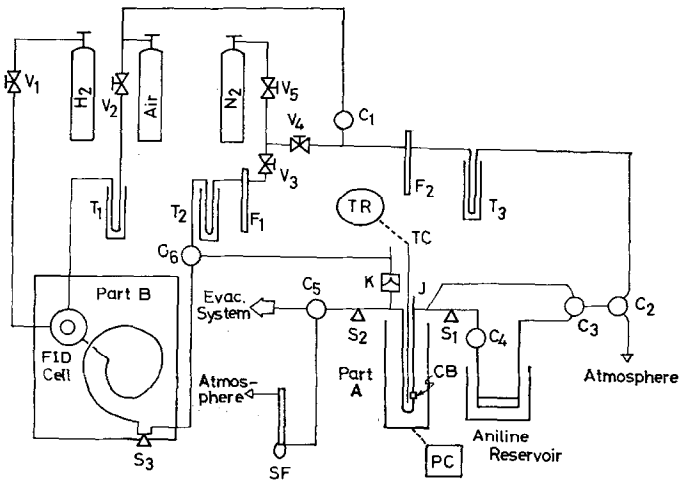

FIG. 1. Schematic diagram of apparatus. C_{1-6}, stopcocks; CB, catalyst bed; F_{1-2}, flow meters; J, capillary tube; K, glass breaker; PC, temperature programmed controller; T_{1-3}, traps; TC, thermocouple; TR, temperature recorder; S_1, injection point; S_2, sampling point; S_3, injection point in FID gas chromatograph; SF, soap film meter; V_{1-5}, valves.

Analysis

FID gas chromatography was used. The column was a 1 m, stainless-steel tube, Silicon gum SE-50 Neo Sorb NF (20/80 mesh); temperature was 160°C; carrier gas was N_2, 40 ml/min.

In most cases, the ordinates on the TPD analytical diagrams are arbitrary units for response (height or area) of the desorption components.

Results and Discussion

Alumina Catalyst

At first, TPD curves in the absence of aniline vapor were obtained in accordance with the method of Amenomiya *et al.* (*2*) and are shown in Fig. 2 for various pretreatment temperatures of adsorbed aniline.

It was found that considerable amounts of aniline strongly adsorbed on the catalyst at a higher temperature than the boiling point of aniline. Since the boiling point of aniline is 184°C, the peak at 150°C may be equivalent to physical adsorption of aniline. Correspondingly, this peak disappeared at the pretreatment temperature above 110°C. Other peaks are found at about 220°C and 400°C, and may be related to chemisorption of aniline. The adsorbed state of aniline on Al_2O_3 and HCl–Al_2O_3 catalysts was investigated by ir technique in a previous report (*7*). It was found that aniline strongly adsorbed by the interaction of surface Lewis acid sites with the free electron of aniline, and that the Lewis acidity was strengthened by HCl treatment of the catalyst.

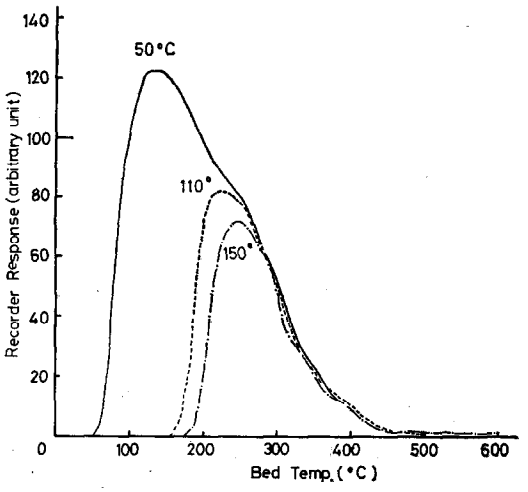

Fig. 2. TPD curves of aniline on Al_2O_3 catalyst. Temperature, preevacuation temperature of the aniline-adsorbed catalyst; catalyst wt, 50 mg.

It should be noted that components thus obtained were desorbed from the "reversibly adsorbed species" on the catalyst at various desorption temperatures.

No diphenylamine formed in this experiment.

HCl-treated Al_2O_3

The previous study has indicated that HCl-treated alumina is more effective than alumina for DPA synthesis. In order to investigate an effect of the HCl treatment of the catalyst on TPD analytical curves, the desorption experiments were performed in the absence of aniline vapor. The results obtained are shown in Fig. 3.

The desorption curve for aniline on HCl–Al_2O_3 resembles that on Al_2O_3 catalyst. From the comparison of both curves under the same conditions, it was found that the amounts of aniline desorbed from HCl–Al_2O_3 were comparable to those of Al_2O_3. This fact indicates that the number of adsorbed sites of aniline on the catalyst may not be increased by the HCl treatment. The desorbed amounts of aniline (100–600°C) in Fig. 3 came to about 0.46 mmole/g. Nevertheless, DPA was observed on HCl–Al_2O_3 as shown by broken line in Fig. 3, while no DPA formed on Al_2O_3.

There are two regions for the DPA formation: (i) a peak at 100–300°C, and (ii) minute amounts at above 300°C.

It is of interest to note that DPA formation is observed even at 250°C unlike the flow system experiments in the previous study (*6*).

It was observed, however, that the active sites of the DPA formation at low temperature (100–300°C) were remarkably varied on regeneration of the catalysts.

To investigate these effects on regeneration, desorption amounts of aniline and DPA in low temperature region were measured for regeneration times of the

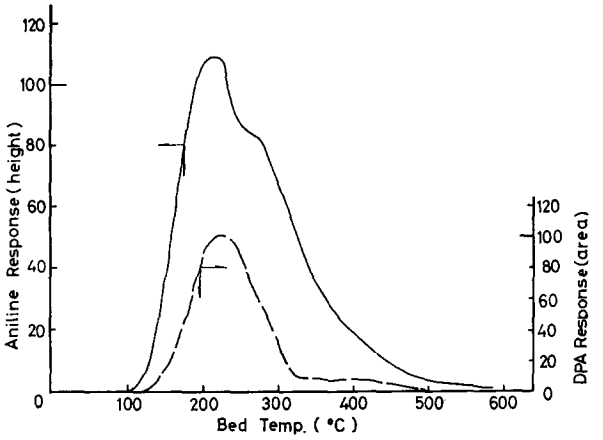

FIG. 3. TPD analytical curves of desorbed components on $HCl-Al_2O_3$ in the absence of aniline vapor. Ordinate, arbitrary unit; catalyst wt, 400 mg.

catalysts. The results are shown in Fig. 4.

Amounts of both aniline and DPA in this figure are illustrated by an area of each component on the TPD analytical curves. While the desorption amounts of aniline are almost constant, the amounts of DPA formation shows little reproducibility on the regeneration of the catalyst. From these observations, it can be concluded that the active sites for DPA formation in the low temperature region are unstable.

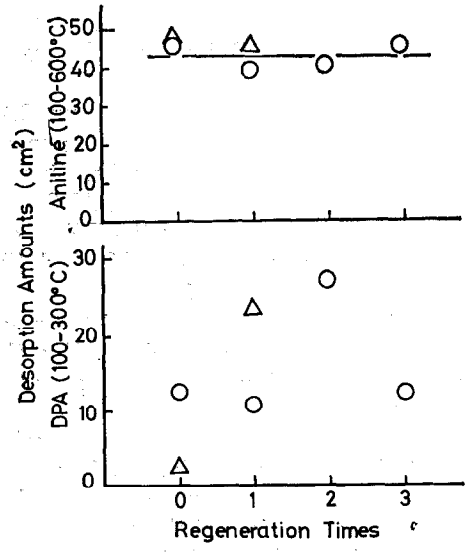

FIG. 4. Reproducibility of desorption amounts on regeneration of the catalyst ($HCl-Al_2O_3$). Ordinate, arbitrary unit; catalyst wt, 450 mg; ○, catalyst 1; △, catalyst 2.

Figure 5 shows the TPD analytical curves obtained by the catalyst used in the DPA synthesis.

Though the experiment was carried out in a vapor pressure flow of aniline, it was of interest to note that no active site for DPA formation was observed in the low temperature region.

According to the previous report (*5*), DPA synthesis on HCl-treated alumina has been well performed at a temperature greater than 400°C.

Therefore, it seemed likely that the active sites for DPA formation in the low temperature region were deactivated and consequently not effective in the actual synthetic reaction.

Attention must be paid to the above facts in an experiment using a microreactor, because such unstable sites may be effective under the reaction condition of a microreactor which requires only a small amount of a reactant.

Effect of Aniline Vapor ($HCl-Al_2O_3$ Catalyst)

Since the amounts of adsorbed component decreased as the temperature raised, the experiments were carried out in the presence of aniline vapor to increase the adsorbed amounts of aniline.

The results using 7 wt % $HCl-Al_2O_3$ are shown in Fig. 6. The horizontal broken line

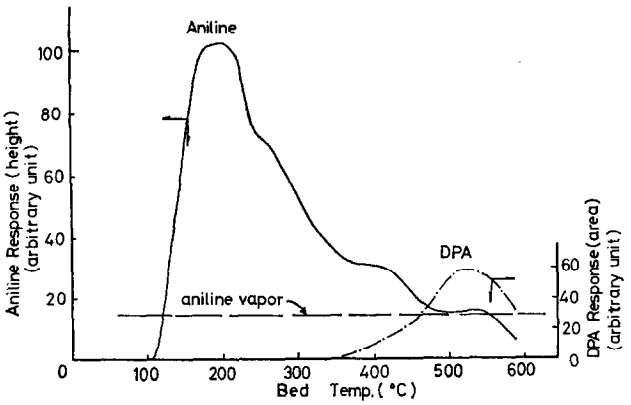

FIG. 5. TPD analytical curves of the catalyst used in flow reaction. Vapor pressure of aniline, 0.4 mm Hg; catalyst wt, 450 mg.

shows the amounts of aniline vapor introduced.

The fact that the desorption amounts of aniline above 550°C are lower than the vapor pressure of aniline introduced suggests that decomposition of aniline occurs at this temperature. The desorbed aniline is almost constant regardless of the presence of aniline vapor, if a correction for the vapor is made. On the other hand, DPA formation in higher temperature region is greatly affected by the presence of aniline vapor.

These DPA formation sites at higher temperature were stable on regeneration of the catalyst unlike the sites at low temperature.

Diphenylamine formation was also observed on Al_2O_3 in the presence of aniline vapor unlike the case in the absence of the vapor. The amounts of DPA on Al_2O_3, however, was smaller than those on HCl–Al_2O_3 and the maximum temperature for DPA formation was 50°C higher than peak maximum on HCl–Al_2O_3.

The results obtained on Al_2O_3 and HCl–Al_2O_3 are summarized in Table 1.

The effects of aniline vapor on DPA formation in the higher temperature region were investigated using 7 wt % HCl–Al_2O_3 catalyst. In these experiments, the carrier gas was saturated with aniline vapor through an aniline reservoir kept at 12°, 20°, and 46°C, respectively.

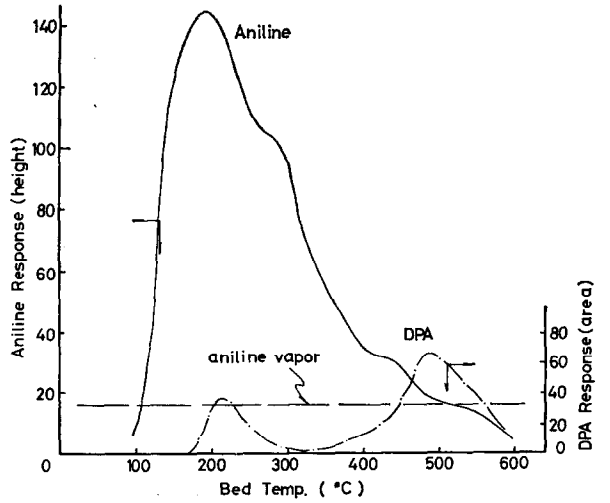

FIG. 6. TPD analytical curves of desorbed components on HCl–Al_2O_3 in the presence of aniline vapor. Vapor pressure of aniline, 0.5 mm Hg; catalyst wt, 400 mg; ordinate, arbitrary unit.

TABLE 1
PEAK TEMPERATURE ON TPD CURVES

Catalyst	Al_2O_3		$HCl-Al_2O_3$	
Aniline vapor	absent	present	absent	present
Aniline formation (°C)	220	220	220	220
			300	300
	400	400	400	400
DPA formation (°C)	—	220 (unstable)	220 (unstable)	220 (unstable)
	—	550 (stable)	—	500 (stable)

The results thus obtained are shown in Fig. 7, where the ordinate is the peak area of DPA at 400–600°C calculated from the TPD analytical curves and the abscissa is the vapor pressure of aniline. It was found that the amounts of the DPA formation at 400–600°C were almost in proportion to the saturated vapor pressure of aniline. Therefore, these facts followed that DPA formation at higher temperature depended on either adsorbed aniline or a partial pressure of anilin in gaseous phase, because both amounts increased with the increase of vapor pressure of aniline.

Isotherm of Aniline

To investigate the relationship between the adsorbed aniline and gaseous aniline at the reaction temperature, the isotherm of aniline was measured in the higher temperature range.

The experiments were carried out after Eberly's method (*8*) using a FID gas chromatography, and the results are shown in Fig. 8.

Since the decomposition of aniline occurred at the temperature above 550°C, the measurements were performed in the range of 440–490°C and aniline vapor pressure 0–2.2 Torr.

As shown in Fig. 8, the adsorbed amounts of aniline at higher temperature were almost constant in the range of vapor pressure of aniline used.

It can be concluded that the increase of the DPA formation is related to the gaseous aniline rather than the adsorbed one under the experimental conditions.

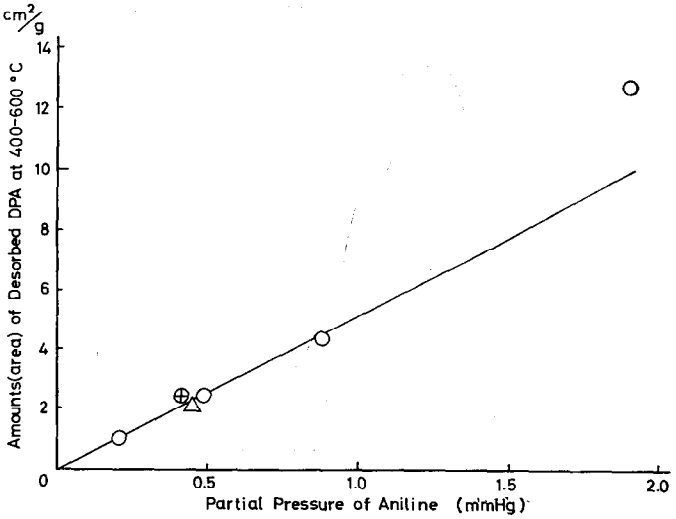

FIG. 7. Effect of aniline vapor on desorbed amounts of DPA in higher temperature region ($HCl-Al_2O_3$). ○, Fresh catalyst; △, regenerated catalyst; ⊕, catalyst used in flow reaction.

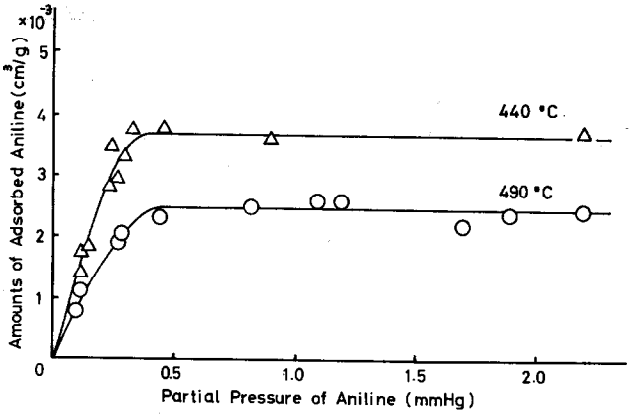

FIG. 8. Isotherm of aniline on $HCl-Al_2O_3$ catalyst.

Reaction Mechanism

In the previous report (*6*), the following reaction scheme had been deduced from the kinetic studies:

$$C_6H_5NH_2 + \sigma \rightarrow C_6H_5NH_2\cdots\sigma \quad (1)$$

$$C_6H_5NH_2\cdots\sigma + C_6H_5NH_2 \rightarrow \underset{\vdots}{C_6H_5NHC_6H_5}\ + NH_3 \quad (2)$$
$$\sigma$$

$$2\ C_6H_5NH_2\cdots\sigma \rightarrow \underset{\vdots}{C_6H_5NHC_6H_5} + NH_3 + \sigma \quad (3)$$
$$\sigma$$

$$\underset{\vdots}{C_6H_5NHC_6H_5} \rightarrow C_6H_5NHC_6H_5 + \sigma \quad (4)$$
$$\sigma$$

where σ are active sites on the catalyst.

The rate equation of the process can be exclusively derived from the case where the adsorption step of aniline (Eq. 1) controls the rate. Equation 2 shows a surface reaction between adsorbed aniline and gaseous aniline according to a Rideal mechanism. On the other hand, Eq. 3 corresponds to a surface reaction of both adsorbed anilines according to a Langmuir-Hinshelwood mechanism. Both mechanisms can not distinguish kinetically one from the other.

In the desorption experiments, the adsorption step is not necessary to take into consideration, because aniline is saturated on the surface before the experiments. Therefore, the Rideal mechanism can be distinguished from the L-H mechanism for the process.

Since the amount of adsorbed aniline is almost constant regardless of the increase of aniline vapor as shown in Fig. 8, it can be concluded that the surface reaction for the process is relevant to the Rideal mechanism rather than L-H mechanism.

Now, it should be pointed out that the rate determining step in the flow system was the adsorption step of aniline as mentioned before. The discrepancy between the mechanism in the flow system and the present mechanism could be explained as follows.

The partial pressure of aniline in the flow experiments is much higher than the aniline pressure in the present work. The higher the partial pressure of aniline, the more the reaction proceeds, and the more the vacant sites appear on the catalyst surface. Therefore, the adsorption of aniline on the vacant sites is the rate controlling step in the flow system. On the other hand, only a small number of vacant sites appeared in the present study because of the low partial pressure of aniline.

CONCLUSION

From the TPD analytical curves, it was found that two different kinds of the sites for DPA formation were present on Al_2O_3 and $HCl-Al_2O_3$ catalysts; one was found to be active in the range of 100–300°C and the other active at above 400°C.

While the former was unstable under the reaction conditions, the latter was stable

under the same conditions and relevant to the active sites of the actual process.

From the kinetic studies and the present work, the following reaction mechanism has been deduced for the DPA synthesis over HCl–Al_2O_3 catalyst.

$$C_6H_5NH_2 + \sigma \rightarrow C_6H_5NH_2\cdots\sigma \quad (5)$$

$$C_6H_5NH_2\cdots\sigma + C_6H_5NH_2 \rightarrow \begin{matrix} C_6H_5NHC_6H_5 \\ \vdots \\ \sigma \end{matrix} + NH_3 \quad (6)$$

$$C_6H_5NHC_6H_5 \rightarrow \begin{matrix} C_6H_5NHC_6H_5 \\ \vdots \\ \sigma \end{matrix} + \sigma \quad (7)$$

Acknowledgment

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