

The Nature of Adsorbed Sites on Catalysts

II. Behavior of Basic Compounds on Silica-Alumina Catalyst at Elevated Temperatures

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The behavior of *n*-butylamine and pyridine adsorbed on the silica-alumina catalysts at elevated temperatures was investigated by a thermal desorption method. The results showed that there are two kinds of adsorption sites on the surface except for a physical adsorption; one is an adsorption site for amine and the other is an acidic site on which the amine decomposes to lower olefins at temperatures above 300°C. The amount of the former is about five times larger than the latter. The decomposed products of the amine were a mixture of *n*-butene and propylene. Total lower olefins were equivalent to about 0.1 mmole/g of the precursor. On the other hand, desorption of pyridine from the catalyst surface showed that only one peak was observed in the desorption curve, and the minute amount of pyridine was desorbed without decomposition even at temperatures above 400°C. From this fact, it follows that the stronger acid sites on the silica-alumina are distributed in the different acid strengths. The acid sites were inhibited rather nonselectively by the alkali poisoning in comparison with such a basic compound as *n*-butylamine or pyridine. The formation of *n*-butene from *n*-butylamine on the stronger acid sites was more suppressed than that of propylene by the alkali poisoning.

INTRODUCTION

Many studies have been made to elucidate an acidity on solid acid catalysts. Concerning a strength of an acidity, however, it has been known that silica-alumina catalyst has a stronger acidity than $pK_a - 8.2$. The properties and reactivities of these solid acids have not been made clear.

The main measurements of the acid sites have been classified into the three methods; (i) titration method (1), (ii) ir method (2), and (iii) adsorption method of basic substances (3). The first two methods give some informations about solid acidities of the catalyst at room temperatures, while the last one has the advantages of providing informations about acidities under the re-

action conditions. The present study was undertaken to obtain some clue to the above subjects under the reaction conditions by a thermal desorption technique (4) using an FID gas chromatograph similarly to the previous work (5).

EXPERIMENTAL

Apparatus and Procedure

Some modifications were made to the apparatus employed in the previous study in order to prevent from dissolution of reagents into grease.

About 50 mg of catalyst in each run was activated at 580°C for 1 hr in flow of air and then the system was kept in vacuum ($\sim 10^{-4}$ Torr) at the same temperature. The catalysts were cooled down to room

temperature, and the given amount of *n*-butylamine (*n*-BA) or pyridine was adsorbed on the catalyst in vapor phase. The preadsorbed catalysts of basic substances were kept to stand overnight at room temperature, and used for the thermal desorption experiments. The excess basic compounds were recovered from the catalyst system by liquid nitrogen trap, and the recovered amounts were measured. The adsorbed amount of the basic compounds were obtained from the difference in volume between the two measurements. Subsequently, the temperature of catalyst bed was raised linearly with time in flow of the carrier gas (N₂) at a rate of about 5°C/min.

At every few minutes, about 1 ml of effluent gas from the catalyst system was analyzed by an FID gas chromatograph.

Materials

Silica-alumina catalysts were obtained from Nikki Kagaku Co. Ltd.: (i) code No. N-631-L (Al₂O₃ content: 13%) size 50–80 mesh, BET area 394 m²/g; and (ii) N-631-H (Al₂O₃ content: 25%) size 50–80 mesh, BET area 374 m²/g. The former catalyst is designated as SA-L and the latter as SA-H in the present study. Alkali poisoned catalysts were prepared by impregnation of the catalyst into the given concentration of Na₂CO₃ solution.

Chemical grade SiO₂ (supplied from Wako Pure Chemical Industry Ltd.) has a BET area 591 m²/g and size 50–80 mesh.

The *n*-BA and pyridine were purified by distillation with potassium hydroxide.

Analysis

Hydrogen flame ionization detector (FID) gas chromatograph was used as an analytical means. Analytical columns: (i) Apiezon grease L (on Neopak 1A) 2 m or Armeen SD (on Celite 545) with glass tube 20 cm for separation of *n*-BA, pyridine, and lower hydrocarbons, and (ii) alumina with tailing reducer 80 cm or Dioctyl

sebacate (on Neopak 1A) 1 m for lower hydrocarbons.

RESULTS

(i) Effect of Pretreatment Temperature on Desorption Curves

The catalysts adsorbed *n*-BA were pretreated in vacuum ($\sim 10^{-4}$ Torr) to remove the excess amine from the catalyst surface either at room temperature (r.t.-pretreatment which is the standard procedure) or boiling point of *n*-BA (b.p.-pretreatment), and then the thermal desorption measurements were made.

The analytical results of effluent gases are plotted against the desorption temperatures. The desorption curves are illustrated in Fig. 1. The ordinate is a concentration of the components in 1 ml of the effluent gas, as shown in a previous report (6).

The solid line shows the desorption curve in r.t.-pretreatment, and the dotted line shows the one in b.p.-pretreatment. From the diagram, it is found that there are two peaks in each run; one exists in the temperature range of 50–200°C, and the other does in the range of 300–500°C. The small adsorption amount of *n*-BA is also detected in the temperature range of 200–300°C. In both experiments, the peaks above 300°C are almost superimposed. From the analysis of the desorbed components, the one obtained at temperatures less than 300°C was found to be *n*-BA and those above 300°C were a mixture of *n*-butene and propylene. No dibutylamine was detected.

These facts mean that there are two kinds of adsorbed sites of *n*-BA on the catalyst surface; one is the adsorption sites of *n*-BA, and the other is the decomposition sites for the amine. The former is likely to be an adsorption sites relating to both physical and chemisorption site, and the latter is a rather strong acid site on the SiO₂-Al₂O₃ catalyst, as discussed later. In the diagrams of Figs. 1–3, however, the total olefins are shown in the higher temperature range, to

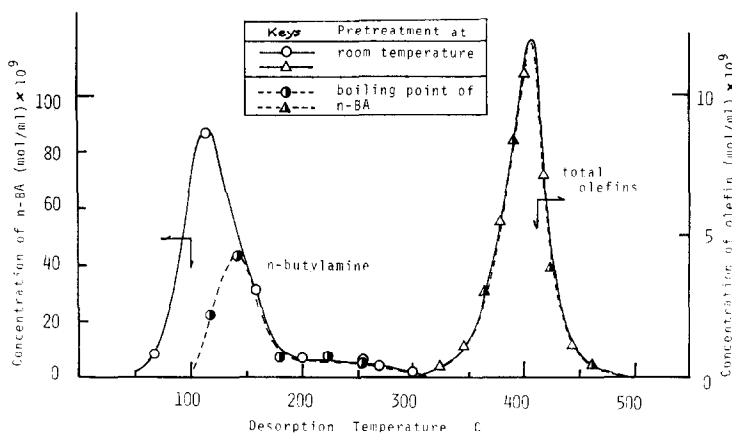


Fig. 1. Thermal desorption curves of *n*-butylamine on silica-alumina (SA-L).

avoid complicated diagrams. The formation of both olefins is dealt with separately in a later section. It should be noted that physically adsorbed amines are involved in the lower temperature range in the diagrams, because of the boiling point of *n*-BA being 77.8°C.

In order to examine the physical adsorption of amines on the catalyst surface, the catalysts preadsorbed amines were evacuated at 78°C for an hour, followed by the desorption experiments. The results are shown with dotted line in Fig. 1. The graph indicates that the amount of the amine in the lower temperature range (shown by the dotted line) decreases to about half of the solid line as the pretreatment temperature

increases. On the other hand, the peak in the higher temperature range is superimposed on the solid line. The desorption curves obtained from the regenerated catalysts are almost the same as the results shown in Fig. 1. It should be pointed out that considerable amount of the amine is adsorbed strongly on the catalyst without decomposition even at a temperature above the boiling point of *n*-BA. These sites are considered to be the stronger adsorbed ones different from the acidic sites in the higher temperature range. The acidic property of the catalyst is also discussed later.

Both adsorbed amount of *n*-BA and desorbed amount of components from the catalyst surface are shown in Table 1.

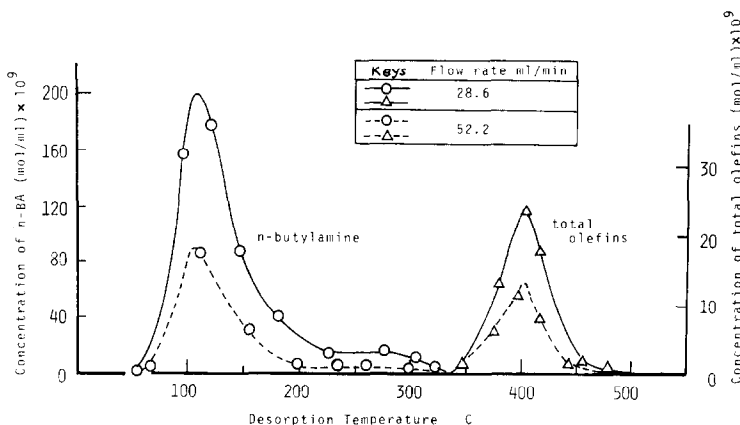


Fig. 2. Effect of flow rates on the desorption curves (SA-L).

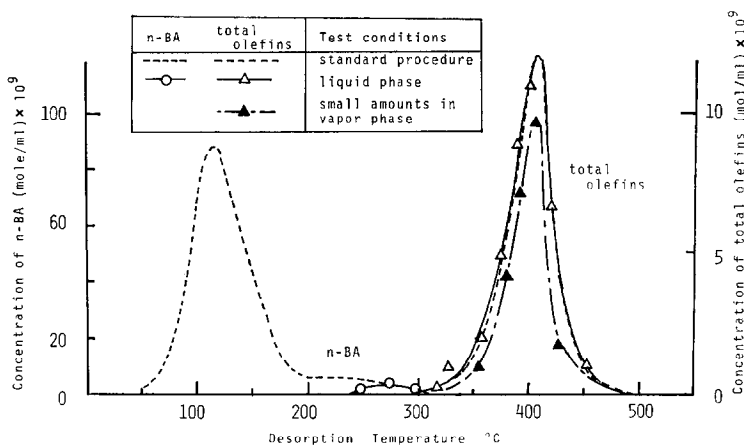


Fig. 3. Comparison of desorption curves of *n*-BA in vapor and liquid phase (*n*-BA).

The table shows that the total amounts of lower olefins are about 0.1 mmole/g. Since each product is formed by decomposition of the amine, the amount is equivalent to the adsorbed amount of the precursor on the catalyst surface.

(ii) *Change in Flow Rates*

Effects of the flow rates on the desorption curves are examined and the results are illustrated in Fig. 2. It is found that the peak maxima in lower and higher tempera-

TABLE 1
Distribution of Thermal Desorption Components on Various Catalysts

Catalyst (adsorption substance)	Adsorption amounts (mmole/g)	Desorption amounts (mmole/g)				Butene Propylene ratio	Remarks
		<i>n</i> -BA	<i>n</i> -Butene	Pro- pylene	Total		
SA-L (<i>n</i> -BA)	1.15	0.937	0.079	0.046	1.06	1.70	r.t.-pretreatment
	0.60	0.455	0.079	0.046	0.58	1.70	b.p.-pretreatment
	1.20	1.10		0.115	1.22	—	Flow rate: 28.6 ml/min
	1.18	0.98		0.120	1.10	—	52.2 ml/min
	0.079	0.00		0.088	0.088	—	Pentane solution stand. for 1 day
		0.05		0.120	0.17	—	Stand. for 2 days
			0.048	0.026	0.074	1.81	Adsorption of small amounts (vap. phase)
SA-H (<i>n</i> -BA)	1.00	0.90	0.117	0.032	1.05	3.68	r.t.-pretreatment
SA-L (pyridine)	0.90				0.82		r.t.-pretreatment
	0.19				0.17		b.p.-pretreatment
SiO ₂ (<i>n</i> -BA)	1.54	1.50	ca. 0.01		1.51		r.t.-pretreatment
	0.495	0.50			0.50		b.p.-pretreatment

ture range at the two flow rates are almost the same, although the flow rate changed twofold. Since the concentrations of desorption components are low at a higher flow rate, the apparent concentrations of components at the flow rate are less than those at a lower flow rate. The desorption amount at higher temperatures is about 0.1 mmole/g at both flow rates, as shown in Table 1.

(iii) Decomposition Sites for *n*-BA

As described above, it is found that there are three kinds of adsorption sites of *n*-BA on $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst.

In order to obtain the informations about the adsorption process of *n*-BA onto these sites in a solution, thermal desorption experiments were carried out using the $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst (SA-L) treated with a low concentration of *n*-BA in pentane solution (0.01 *N*). The pentane was used as a solvent, because of its low boiling point. The catalysts were allowed to stand for 1 or 2 days in this solution at room temperature, and evacuated to remove the solvent and excess *n*-BA. Then, desorption experiments were carried out under the standard procedure. The desorption curves of *n*-BA obtained from the catalyst dipped for 2 days in the solution are shown in Fig. 3, compared with those (dotted line) of Fig. 1. In the diagram, the peaks in the higher temperature range are superimposed.

The adsorption of *n*-BA onto the catalyst in the solution occurred preferably on the acidic sites, because the desorption curve shows only one peak in the higher temperature range. Almost same results were also obtained in the benzene solution. The results of the catalyst dipped 1 day in the solution are also presented in Table 1. The desorbed amount of olefins from this catalyst is somewhat smaller than that of the catalyst dipped for 2 days. In order to examine the adsorption process of *n*-BA in vapor phase, the desorption experiments using a small adsorption amount of the

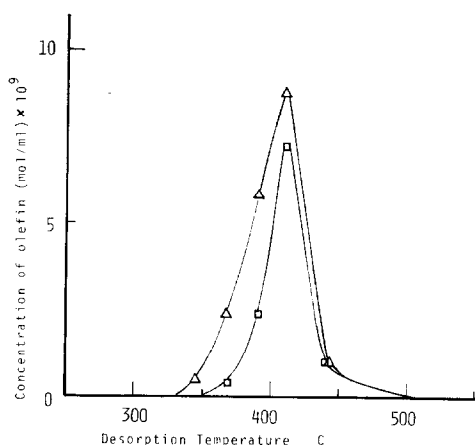


FIG. 4. Analysis of desorption components in the higher temperature range (SA-L); — Δ —, *n*-butene; — \square —, propylene.

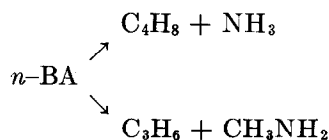
amine were carried out. As shown in Fig. 3, there exists only one peak in the higher temperature range and the amine is not observed in the low temperature range.

Concerning the adsorption process of *n*-BA irrespective of in vapor or liquid phase, it is of interest to note that the basic substances are adsorbed on the catalyst surface from the strong acidic sites to weak sites, in turn.

(iv) Active Sites in Higher Temperature Range

The gaseous components from the decomposition sites of *n*-BA were analyzed more exactly, and confirmed to be a mixture of propylene and *n*-butene. Both lower olefins are desorbed in the same temperature range as shown in Fig. 4, although the propylene is formed at rather higher temperature. The molar ratio of *n*-butene/propylene is about 1.7 for SA-L and the value for SA-H is more higher (3.7).

The decomposition of *n*-BA at the higher temperature, therefore, may be followed by two ways as follows:



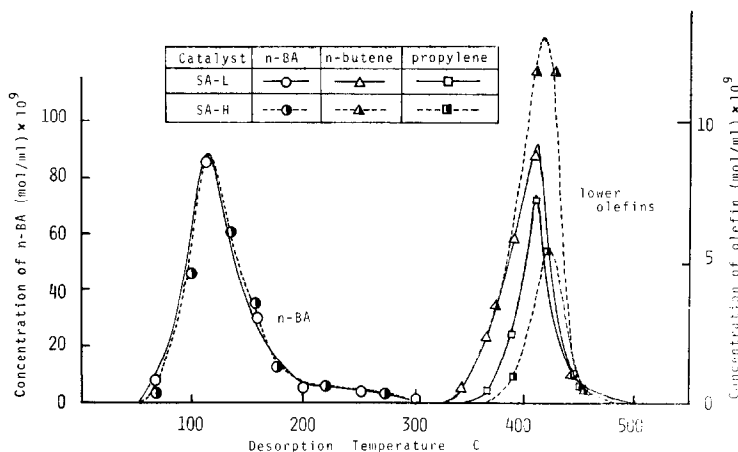


FIG. 5. Comparison of the desorption curves of *n*-BA on SA-L and SA-H.

This reaction scheme is probably affected by factors such as kinds of acidic sites, acid strengths, and adsorbed state of *n*-BA. The existence of CH_3NH_2 was detected by analysis in a mass spectrometer.

Further experimentation is necessary to explain fully this reaction scheme.

(v) Comparison of SA-L and SA-H

Two kinds of $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts have been commercially produced in different alumina contents. The catalyst (SA-L) used in the present work is equivalent to 13% Al_2O_3 content catalyst, and SA-H contains 25% Al_2O_3 .

In order to investigate the effect of the alumina content on the desorption curves, the experiments were carried out using SA-H and the results are compared with those of SA-L in Fig. 5.

The amount of the sites desorbed *n*-BA at temperatures below 300°C is almost the same in two cases. The characteristics of the results are found in the curve above 300°C (acidic sites). The formation of propylene in SA-L is larger than SA-H, whereas the total amount of *n*-BA in the higher temperature range of SA-H is comparable to that of SA-L as presented in Table 1.

(vi) Desorption of Pyridine (SA-L)

Since *n*-BA is a strong base ($\text{p}K_a = 10.60$), the weak acidic sites can be measured by using the amine. On the other hand, pyridine is a weak base ($\text{p}K_a = 5.18$) and therefore, the informations about strong acidic sites can be obtained.

The desorption experiments using pyridine were performed under the standard procedure and the results are illustrated in Fig. 6. Only one desorption curve is observed in thermal desorption chromatogram unlike the case of *n*-BA. The desorption component was confirmed as pyridine by gc analysis. Dotted line is obtained from the catalyst which was evacuated at the boiling point of pyridine for 1 hr to remove a excess pyridine. From Table 1, the adsorption amount of pyridine except for the physical adsorption is found to be comparable to that of strong sites observed at temperatures above 200°C in the thermal desorption of the amine.

It is also emphasized that the small amount of strong adsorption sites is distributed even at the temperatures above 400°C. This fact means that the stronger acid sites are distributed widely in the different acid strengths.

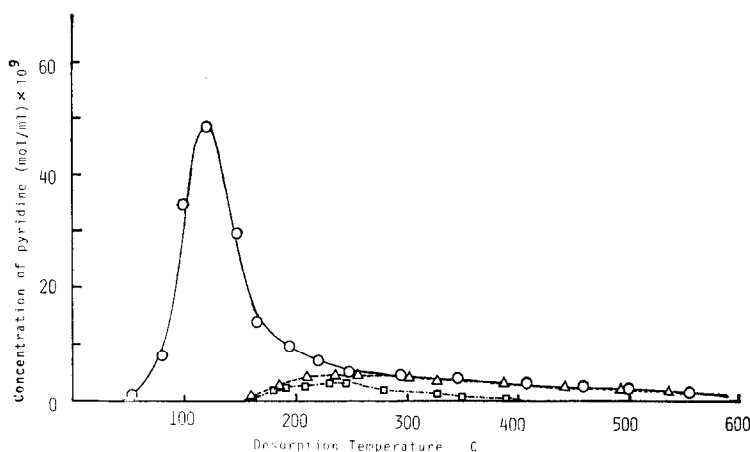


FIG. 6. Desorption curves of pyridine on SA-L; —○—, r.t.-pretreatment; ---△---, b.p.-pretreatment; ---□---, Na_2CO_3 3.5 wt% alkali poisoning, b.p.-pretreatment.

(vi) Poisoning of SA-L by Alkali Compound

One of the convenient modifications of the solid acid catalysts is to poison them by a proper alkali salt. Here, the catalysts (SA-L) were poisoned by sodium carbonate in wt% of 1.2, 3.5, and 6.2, respectively. The desorption curves of *n*-BA for the typical catalysts are shown in Fig. 7. Solid line shows the desorption curve for the unpoisoned catalyst (SA-L) to compare with the poisoned catalyst. Dotted line is the curve for the catalyst poisoned by 3.5 wt% alkali. The data for other poisoned catalysts are summarized in Table 2. There are some features in the diagram. First, the peaks in

the low temperature range are superimposed in two cases; that is, the adsorption sites in this range are not affected by the alkali poisoning, and so, the adsorption of *n*-BA on the sites is mainly attributed to physical one. However, the adsorption sites in the temperature range of 200–300°C are not merely physical ones, because *n*-BA on these sites are not desorbed at temperatures above boiling point of the amine. Second, the strong acidic sites above 300°C in the diagram are remarkably affected by a degree of the poisoning. The *n*-butene formation is more affected by the alkali poisoning than propylene formation in the same temperature range.

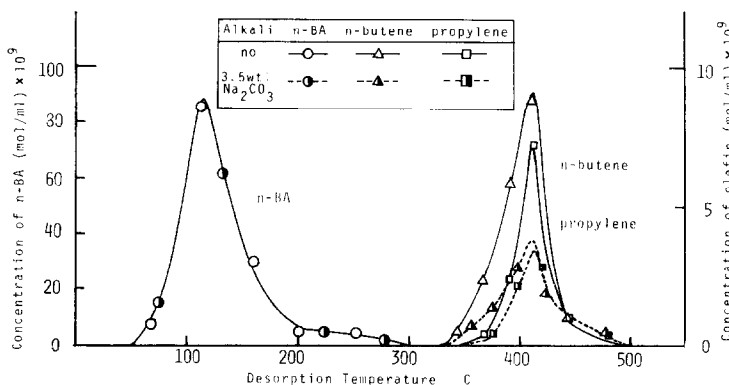


FIG. 7. Desorption curves of *n*-BA on alkali poisoned catalyst (SA-L).

TABLE 2

Distribution of Thermal Desorption Components on the Alkali-Poisoned Catalysts (SA-L)^a

Alkali poisoning Na ₂ CO ₃ (wt%)	Adsorption amounts (mmole/g)	Desorption amounts (mmole/g)				Butene Propylene ratio	Relative poisoning efficiency*
		<i>n</i> -BA	<i>n</i> -Butene	Pro- pylene	Total		
No	1.15	0.94	0.079	0.046	1.06	1.70	0.00
1.2	1.18	0.91	0.051	0.037	1.00	1.39	7.05
3.5	1.05	0.95	0.038	0.030	1.02	1.28	13.35
6.2	1.11	1.08	0.015	0.021	1.12	0.68	15.13

^a Adsorbate: *n*-BA.* Ratio of Na⁺ ion (used)/*n*-BA (eliminated).

Table 2 presents the reduced amount of *n*-BA by alkali poisoning, and molar ratio of C₄H₈/C₃H₆ using SA-L catalyst.

The effect of alkali poisoning on pyridine adsorption is also illustrated in Fig. 6. It is interesting to note that the adsorption of pyridine is rather affected in the higher temperature range by the alkali poisoning, in agreement with the results of Hirschler (1).

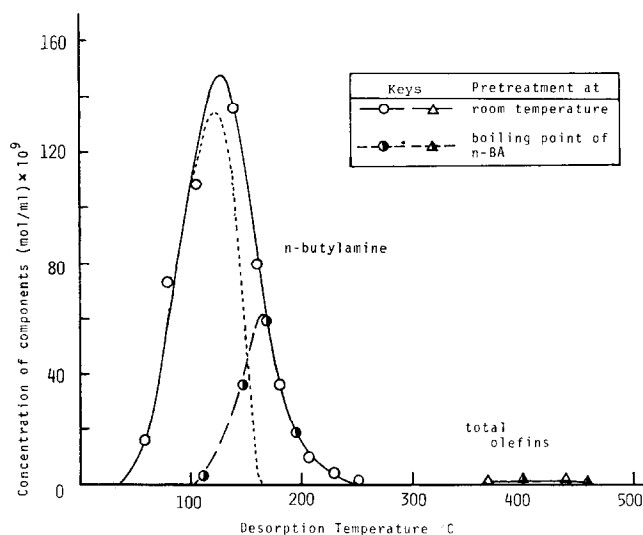
DISCUSSION

In order to confirm the properties of the adsorption sites on SiO₂-Al₂O₃, the desorption experiments were carried out using

n-BA-SiO₂ system under the same experimental conditions. The results are shown in Fig. 8.

Adsorption and desorption amounts of *n*-BA on SiO₂ in both r.t.- and b.p.-pretreatments are also presented in Table 1.

The peak at 50–150°C shown by a dotted line is based on physical adsorption, because this peak is disappeared by a recovery of the excess amine from the catalyst at the boiling point of amine. On the other hand, the small peak at 100–250°C shown by a dashed line is observed at the temperatures over the boiling point of

FIG. 8. Desorption curves of *n*-BA on SiO₂.

amine, and therefore, *n*-BA molecules are probably chemisorbed on these sites.

The amount of lower olefins on SiO₂ is almost negligible compared with that of SiO₂-Al₂O₃. The fact that the thermal desorption chromatograms are different in two cases suggests that a transport phenomena of components is not controlling factor in the desorption process. It follows, therefore, that lower olefins detected in the higher temperature range are desorbed from the acidic sites on SiO₂-Al₂O₃ catalysts.

The adsorption sites of *n*-BA on SiO₂-Al₂O₃ consist of three types of sites, as shown in Fig. 1. First sites (I) desorb *n*-BA in the temperature range of 50–150°C, and seem to be the ones for the same physical adsorption as in the case of SiO₂. The second sites (II) also desorb *n*-BA in the range of 100–300°C in the diagram. The *n*-BA on the sites cannot be eliminated by the pretreatment of the catalyst at the boiling point of amine. Since the sites are also not affected by the poisoning of alkali, these sites are considered to be strong adsorption sites rather than acidic ones. On the other hand, the third sites (III) decomposed the amine at temperatures above 300°C are exclusively affected by an addition of alkali, and the sites adsorb about 0.1 mmole/g of *n*-BA. These sites belong to the second peak in Fig. 1, and decompose the amine to propylene and *n*-butene. The sites for *n*-butene formation are preferably inhibited by alkali poisoning, as given in Table 2. The adsorption amount of *n*-BA for each site and the reduced amount of *n*-BA by alkali poisoning are also summarized in Table 2.

The adsorption amount of *n*-BA on sites (II + III) on which *n*-BA cannot be removed at the boiling point of amine is approximately equal to 0.6 mmole/g. It is of interest to note that almost the same value was obtained by an ordinary titration method, using the similar catalyst which was produced by the same company (7).

If the *n*-BA molecules adsorb in monolayer on the catalyst surface, the area covered by the *n*-BA on sites (II + III) could be calculated assuming the sectional area of *n*-BA as 20 Å² (8). Since the total amounts of *n*-BA on the sites II and III are equivalent to 0.6 mmole/g and the surface area of SA-L is 394 m²/g, the coverage is equal to 0.18 on the assumption that the *n*-BA molecules stand perpendicularly on the catalyst surface.

From the decrease of the desorption amount of olefins by the alkali poisoning, one can estimate roughly about the poisoning effect of the alkali.

Since the adsorption sites belong to I and II are not affected by the alkali poisoning, the adsorption of *n*-BA on the site III should be taken into account for the estimation. The amount of alkali which can eliminate one adsorption site of *n*-BA could be estimated from the ratio of Na⁺ ion (used)/*n*-BA molecule (eliminated). The ratios are presented on the last column in Table 2. The values are not unity, but they are increased with an increase of the alkali contents. This fact means that the acid sites are inhibited rather nonselectively by the alkali poisoning.

The adsorption states of basic compounds on acidic solids have been studied by many investigators using ir technique. Parry (8) has already shown that both pyridinium ion (1540 cm⁻¹) and strongly coordinately bonded pyridine (1455–1459 cm⁻¹) exist on silica-alumina catalyst after evacuating the pyridine adsorbed on the catalysts at 300°C.

The pyridine has a rather lower basicity and therefore, the information of stronger acid sites on the surface can be obtained. From Fig. 6, it is found that the small amount of pyridine are strongly adsorbed at temperatures above 300°C without any decomposition.

Basila *et al.* (9) have also shown that the ratio of Lewis acidic sites to Broensted sites is about 2.9–6.0 in some kinds of silica-

alumina catalysts, after consideration of the absorption coefficients of pyridine on both sites. The ratio of *n*-butene/propylene for SA-L in the present study is about 1.70 and the value for SA-H about 3.7. The values are comparable to the ones obtained by Basila *et al.* However, the similarity of these values does not seem to have an obvious reason, because the propylene was hardly obtained from an H-Y type zeolite catalyst, as will be shown in another paper (10).

Hildebrandt *et al.* (11) have concluded that there exists only the strong protonic acidic sites on the silica-alumina catalyst, from their oxygen consumption pattern obtained from the oxidation of ammonia on the surface.

Morimoto *et al.* (12) have recently investigated the ir spectra of *n*-BA on silica-alumina at temperature below 500°C, and demonstrated that there are more than two kinds of NH₃⁺ species on the catalyst surface according as the acid site strengths. They have observed, however, that the symmetrical NH₃⁺ bending vibration is disappeared at temperature above 400°C. This result is somewhat different from the present work in respect of disappearing of amines adsorbed on the strong acidic sites above 400°C. This discrepancy is not clear, but one of the explanations may be due to the difference of the temperature measured in two cases.

From the results in Fig. 6, it should be pointed out that the stronger acid sites are distributed in the different acid strengths, and both number and strength of the sites are affected by the alkali poisoning, as suggested by Hirschler (1).

In the present study, it has demonstrated that the *n*-BA adsorbed on the stronger acidic sites are decomposed into propylene and *n*-butene in the same temperature range. The formation of propylene and *n*-butene are caused by a fission of either C-C or C-N bond in *n*-BA, respectively. Both fissions may be resulted from the

difference of the adsorption state of the amine on the catalyst surface.

If the amine stands perpendicularly on the acidic sites, it may be difficult to decompose the amine to propylene. Alternatively, so as to form propylene from *n*-BA, a configuration of the amine on the surface is probably different from the standing state mentioned above, so that the fission of C-C bond in the amine will be occurred easily with some interactions from the surface.

The reactivities of these acidic sites will be dealt with in another paper (13).

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