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THE NATURE OF ACID SITES ON SILICA-ALUMINA AND ALUMINA CATALYSTS

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Acid sites of SiO_2-Al_2O_3 and Al_2O_3 were investigated by the thermal desorption of n-butylamine. SiO_2-Al_2O_3 gave n-butylamine and n-butene as desorbed components, while dibutylamine and n-butene were formed on Al_2O_3. The differences in desorption behavior could be explained by the different assembly of the sites on these catalysts.

Many studies have been carried out to elucidate an acidity on solid acid catalysts, so far. The principal measurements of the acid sites have been divided into three methods; i) titration method,1) ii) infrared method,2) and iii) adsorption method of basic substances.3) The first two methods give some informations about solid acidities at room temperature, while the last method have the advantages of providing informations about acidities under the reaction conditions. The present study has been undertaken to throw light on the same subjects under the reaction conditions, using a temperature programmed desorption method4) which was modified by combining a FID gas chromatography.5)

SiO_2-Al_2O_3 was obtained from Nikki Kagaku Co. Ltd., having a BET area of 321 m^2/g and Al_2O_3 from Sumitomo Kagaku Co. Ltd., having an area of 277 m^2/g. About 100 mg of the catalyst was used for the experiments, n-butylamine were preadsorbed on the catalysts and after evacuation of the catalysts for 1-2 hr at room temperature, the catalyst bed was heated up linearly at a rate of 4-5 °C/min in flow of the carrier gas (He: 50 ml/min). The desorbed components from the catalyst surface were successively analyzed by a FID gas chromatography at a few minutes intervals.

The analytical results were plotted against the desorption temperature and typical desorption curves for the n-butylamine adsorbed on both catalysts are shown in Fig. 1. It was found that there were two peaks on the diagram of SiO_2-Al_2O_3; one existed in the temperature range of 100-350°C and the other was at rather higher temperature. From the analysis of the desorbed components, the former was n-butylamine and the latter was n-butene. This facts mean that there are two kinds of adsorbed sites of n-butylamine on the catalyst; one is the adsorbed site of n-butylamine and the other is the site for decomposition of n-butylamine. Consequently, the former presumably corresponds to a weak acid site and the latter is relevant to a rather strong acid site in the SiO_2-Al_2O_3 catalyst. By taking into account of the relative sensitivity of n-butylamine (I) and n-butene (II), the total amounts of the adsorbed components (I)+(II) are calculated to be about 310 μmole/g and the ratio (I)/(II) is about 2.5.

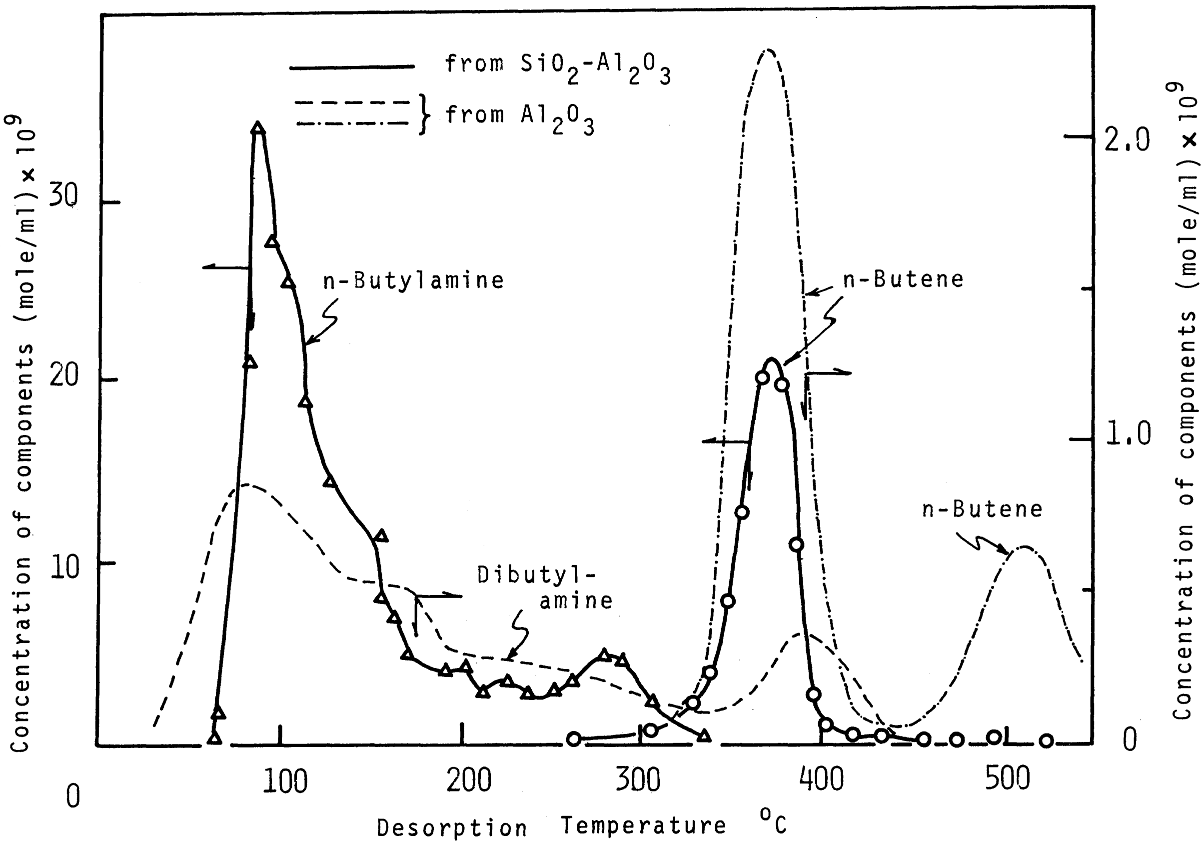

Fig. 1. Analytical curves of desorbed components from the catalysts.

On the other hand, the different results were obtained on Al_2O_3 catalyst as shown by dotted line in Fig. 1. In this case, it was found that dibutylamine was observed in the low temperature range and no n-butylamine was obtained. Moreover, the two peaks of n-butene were observed in the higher temperature range. The fact that the dibutylamine formed exclusively on Al_2O_3 catalyst means presumably that the weak acid sites on Al_2O_3 exist more closely each other, different from the case of SiO_2-Al_2O_3 catalyst.

Since one mole of dibutylamine is produced from two moles of n-butylamine, the total amounts of n-butylamine adsorbed on Al_2O_3 is equivalent to 48 μmole/g, reducing a dibutylamine to the precursor, and the ratio (I)/(II) is about 1.7.

The total amounts of amine on Al_2O_3, therefore, are found to be about one sixth of the value obtained on SiO_2-Al_2O_3 catalyst.

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