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Vapor-Phase Beckmann Rearrangement over Silica-Supported Boria Catalyst Prepared by Vapor Decomposition Method

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The present work introduced a new method of catalyst preparation which involved the vapor decomposition of $B(OEt)_3$ onto silica gel to produce a silica-supported boria (B_2O_3/SiO_2). A B_2O_3/SiO_2 catalyst prepared by this method (B_2O_3 content 34 wt%) showed high catalytic efficiency for the vapor-phase Beckmann rearrangement of cyclohexanone oxime (oxime conversion: 98%, ε-caprolactam selectivity: 96 mol%, at 250°C). The vapor decomposition B_2O_3/SiO_2 was more active and selective at any B_2O_3 content than the B_2O_3/SiO_2 obtained by the ordinary impregnation method using H_3BO_3. The amounts of the acid sites whose acid strengths exceeded 80 kJ/mol in terms of the differential heat of adsorption of ammonia (DHA) were 0.7 and 0.4 mmol/g for the most active vapor decomposition B_2O_3/SiO_2 and the most active impregnation B_2O_3/SiO_2, respectively. The vapor decomposition effected uniform deposition of B_2O_3 on SiO_2, and produced a solid acid with relatively uniform distribution of acid strength. It is suggested that the acid strength (H_0) of an effective catalyst pertinent to the vapor-phase Beckmann rearrangement should be less than -5.6 which approximately corresponds to a DHA value of more than 80 kJ/mol.

I. INTRODUCTION

The vapor decomposition of metal alkoxides or halides onto several inorganic materials has recently been applied to catalyst preparation as well as to modification of catalytic property of zeolites. Murakami *et al.* have reported that the size of the entry pore of mordenite can be narrowed by depositing SiO_2 by means of vapor decomposition using $Si(OCH_3)_4$ or $SiCl_4$. This modified mordenite showed higher selectivity of light hydrocarbons (C_1–C_3) when applied as a methanol conversion catalyst (*1*, *2*). The authors have recently attempted to prepare several solid acids by means of vapor decomposition, expecting that such a method of catalyst preparation may produce more active and selective solid acids with high uniformity in acid property. In fact, according to our preliminary studies (*3*, *4*), the supported boria catalysts prepared through the vapor decomposition of a boron ester onto silica gel and γ-alumina (B_2O_3/SiO_2 and B_2O_3/Al_2O_3) showed higher activities for the vapor-phase Beckmann rearrangement of cyclohexanone oxime, compared with those obtained through the conventional impregnation method using boric acid.

In the present study, the silica-supported boria catalysts prepared by the vapor decomposition method using $B(OEt)_3$ will be characterized in detail with respect to the acid property and the catalytic efficiency for the vapor-phase Beckmann rearrangement of cyclohexanone oxime, in comparison with the boria catalysts obtained by the ordinary impregnation method. The reason for selecting the Beckmann rearrangement as a test reaction is that supported boria catalysts such as boria–alumina (*5*–*8*) have long been known as favorable catalysts for this reaction but there is still plenty of room for improvement, particularly in the selectivity to ε-caprolactam as well as in catalyst life in view of practical application.

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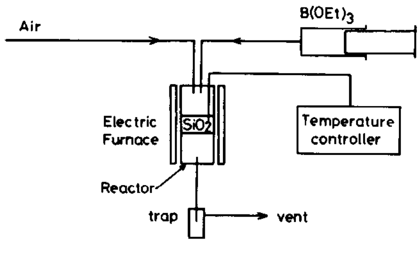

FIG. 1. An apparatus for the catalyst preparation through vapor decomposition.

II. EXPERIMENTAL

Catalyst

1. Vapor decomposition B_2O_3/SiO_2. An apparatus for the catalyst preparation through vapor decomposition technique is shown in Fig. 1. A specific silica support having a surface area of 281 m^2/g and a pore volume of 1.35 ml/g (Fuji Davison Chemical, ID type) was employed in all experiments, except for a case of the examination on the effects of physical property of silica support. Silica gel (0.5–1.0 g, 24–60 mesh granules) was placed in a Pyrex glass reactor, and $B(OEt)_3$ vapor was brought into contact with SiO_2 at 250–400°C for 0.1–6.0 h in a stream of air. The flow rates of $B(OEt)_3$ and air were 3.5 mmol/h and 115 ml/min, respectively. There was observed no carbon left on the resulting catalysts. The B_2O_3 content of catalyst was determined from the weight increase of SiO_2 after the vapor decomposition treatment; the data obtained by this method agreed closely with those by the alkalimetric titration of the H_3BO_3 extracted from catalyst with hot water.

2. Impregnation B_2O_3/SiO_2. The impregnation catalyst was prepared by impregnating the same silica support with aqueous H_3BO_3 followed by calcination at 350°C for 3 h.

Beckmann Rearrangement

The vapor-phase Beckmann rearrangement of cyclohexanone oxime was carried out using a fixed-bed continuous flow apparatus under atmospheric pressure. The reaction temperature, which was measured by a thermocouple placed in the catalyst bed, was maintained at 250°C. A mixture of the oxime, benzene as a diluent, and N_2 was passed in a mole ratio of 1 : 13 : 16 through the catalyst bed (0.2 g) packed in a 15-mm-i.d. Pyrex glass reactor at a WHSV of 0.81 h^{-1} in terms of the oxime. The reactor effluent was collected in a trap and analyzed by GLC using a PEG 20M column (1 m). The major by-products included cyclohexanone and hex-5-enenitrile.

Analysis

The desorption spectra of pyridine on B_2O_3/SiO_2 catalysts were measured by use of a conventional TPD apparatus. A catalyst sample (30 mg) was preheated in a TPD cell at 400°C for 1 h in a stream of He (115 ml/min). Pyridine (10 μl) was injected at 300°C, and the cell was cooled rapidly to 25°C. The TPD measurement was started from 25°C at a heating rate of 10°C/min.

The differential heat of adsorption of ammonia was measured by use of a multipurpose calorimeter (Tokyo RIKO, Model MPC-11). The sample was preheated at 400°C for 1 h.

The scanning electron microscopy for the examination of catalyst surface was performed using a JEOL JSM-T20 instrument.

III. RESULTS

Figure 2 shows the change in catalytic activity for the Beckmann rearrangement with the time on stream at 300 and 250°C. When the reaction was performed at 300°C, the catalytic activity of impregnation B_2O_3/SiO_2 gradually decreased with the time on stream owing to coking, but little change in activity was observed with vapor decomposition B_2O_3/SiO_2 up to 5 h of the run. In the present study, however, the reaction data were taken at 250°C in order to compare the catalytic efficiency of vapor decomposition B_2O_3/SiO_2 with that of impregnation B_2O_3/SiO_2, because the oxime conversion at 300°C were too high to discuss the difference in catalytic efficiency between those two

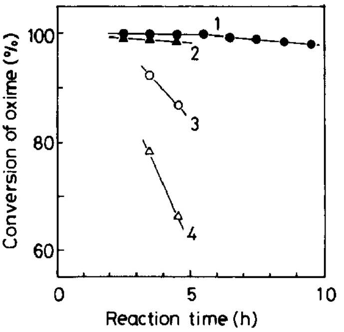

FIG. 2. The change in catalytic activity of B_2O_3/SiO_2 with the time on stream. (1) Vapor decomposition B_2O_3/SiO_2 (B_2O_3, 32 wt%), (2) impregnation B_2O_3/SiO_2 (B_2O_3, 26 wt%), reaction temperature 300°C, (3) vapor decomposition B_2O_3/SiO_2 (B_2O_3, 25 wt%), (4) impregnation B_2O_3/SiO_2 (B_2O_3, 19 wt%), reaction temperature 250°C.

catalysts in detail. At 250°C, however, the oxime conversion decreased more rapidly with the time on stream than at 300°C owing to faster coke formation which was caused probably by slower desorption of high boiling point products. Hence, the average oxime conversion and lactam selectivity obtained between 3 and 4 h after the reactant feed were taken as the standard data; mass balance was not completed during initial 3 h of each run at this reaction temperature.

Effects of Vapor Decomposition Conditions

Figure 3 shows the influence of vapor decomposition temperature on the catalytic activity of the resulting B_2O_3/SiO_2. The rate of B_2O_3 deposition on SiO_2 surface was greatly influenced by vapor decomposition temperature. The B_2O_3 content increased with increasing temperature, and the maximum B_2O_3 content was attained at 350°C. The oxime conversion was correlated well to the B_2O_3 content, but the lactam selectivity decreased markedly at above 350°C.

Figure 4 gives the influence of the duration of $B(OEt)_3$ feed at a constant rate. The B_2O_3 content increased monotonously until 3 h of $B(OEt)_3$ feed and then leveled off. The oxime conversion depended on the B_2O_3 content, but when the duration of $B(OEt)_3$ feed exceeded 3 h, the lactam selectivity decreased rapidly. Thus the B_2O_3 content could be adjusted by changing either vapor decomposition temperature or the duration of $B(OEt)_3$ feed. The best B_2O_3/SiO_2 catalyst containing 34 wt% of B_2O_3 was obtained under the condition of 350°C for 3 h at a $B(OEt)_3$ feed rate of 3.5 mmol/h. This catalyst showed an oxime conversion of 98% with a lactam selectivity of 96% at a reaction temperature of 250°C.

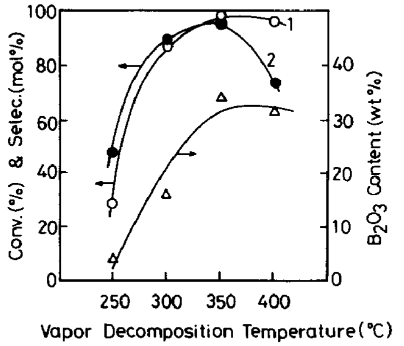

FIG. 3. The effect of vapor decomposition temperature. (1) Oxime conversion, (2) lactam selectivity; vapor decomposition condition, $B(OEt)_3$ feed 3.5 mmol/h for 3 h; reaction condition, 250°C.

Figure 5 illustrates the change in catalytic performance with B_2O_3 content, comparing vapor decomposition B_2O_3/SiO_2 with im-

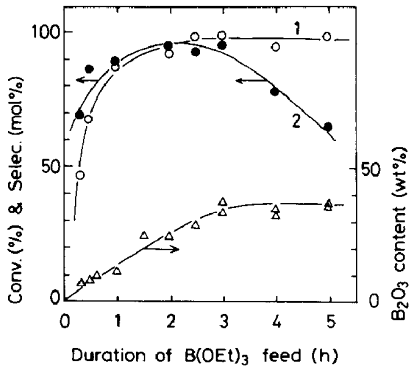

FIG. 4. The effect of the duration of $B(OEt)_3$ feed. (1) Oxime conversion, (2) lactam selectivity; vapor decomposition condition, 350°C, $B(OEt)_3$ feed 3.5 mmol/h for 3 h; reaction condition, 250°C.

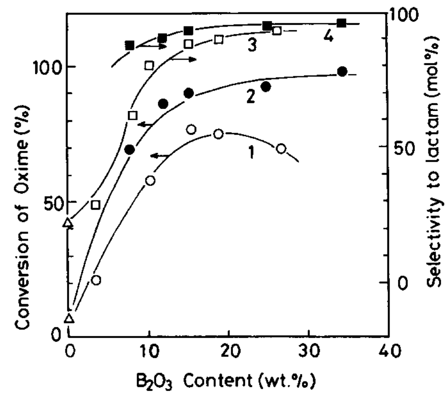

FIG. 5. The effect of B_2O_3 content. (1) Oxime conversion of impregnation B_2O_3/SiO_2, (2) oxime conversion of vapor decomposition B_2O_3/SiO_2, (3) lactam selectivity of impregnation B_2O_3/SiO_2, (4) lactam selectivity of vapor decomposition B_2O_3/SiO_2; reaction condition, 250°C.

pregnation B_2O_3/SiO_2. Both the oxime conversion and the lactam selectivity increased with the B_2O_3 content, but the oxime conversion over impregnation B_2O_3/SiO_2 began to decrease at a B_2O_3 content above 20 wt%. It is obvious that vapor decomposition B_2O_3/SiO_2 excelled impregnation B_2O_3/SiO_2 in the catalytic efficiency for the Beckmann rearrangement.

When N_2 was employed as a carrier gas in place of air in the vapor decomposition operation, only a little deposition of B_2O_3 (0.8 wt%) was attained under the condition of 350°C for 3 h at a $B(OEt)_3$ feed rate of 3.5 mmol/h. The resulting B_2O_3/SiO_2 was as inactive as SiO_2 support itself for the Beckmann rearrangement. On the other hand, when steam was used in place of air in the vapor decomposition operation, a B_2O_3/SiO_2 having a B_2O_3 content of 29 wt% was obtained. But in this case B_2O_3 was deposited exclusively on the upper side of the SiO_2 bed packed in the reactor for vapor decomposition, because $B(OEt)_3$ had already changed into B_2O_3 or H_3BO_3 through hydrolysis in the gas phase before the borate reached the surface of SiO_2 particles. The B_2O_3/SiO_2 prepared by the vapor decomposition using H_2O showed lower catalytic activity (oxime conversion; 82%; lactam selectivity, 93 mol%, at 250°C) than the B_2O_3/SiO_2 prepared by use of air. It is, therefore, necessary for uniform B_2O_3 deposition to decompose $B(OEt)_3$ with O_2 not with H_2O.

Effects of Physical Property of SiO_2 Support

Table 1 summarizes the influences of physical property of SiO_2 support on the efficiency of vapor decomposition catalyst. The amount of the B_2O_3 deposited on SiO_2 depended neither on the surface area nor on the average pore diameter, but depended on the pore volume. The larger the pore volume of support was, the more B_2O_3 could be deposited to give more active catalysts.

Table 2 represents the effect of pretreatment of SiO_2 support on the catalytic activity of the resulting B_2O_3/SiO_2. When the calcination temperature was below 600°C, no appreciable influences were observed both on the B_2O_3 content and on the catalytic activity. However, when SiO_2 support was treated at 800°C, the catalyst obtained became less active because of the decrease in surface area, although its B_2O_3 content was as much as 30 wt%. Probably, when

TABLE 1

The Effect of Physical Property of SiO_2 Support

Physical property of SiO_2[a]			Vapor decomposition B_2O_3/SiO_2		
SA (m^2/g)	PD (A)	PV (ml/g)	B_2O_3[b] content (wt%)	Oxime[c] conversion (%)	Lactam selectivity (mol%)
281	192	1.35	34	98.6	96.4
70	583	1.02	32	66.3	94.0
585	51	0.86	15	69.6	91.0
115	223	0.64	29	47.1	95.0
347	93	0.81	41	37.7	97.1
649	36	0.59	7.2	22.3	58.5
166	140	0.58	2.0	11.1	35.6

[a] SA, specific surface area; PD, average pore diameter; PV, pore volume. These values were given by the suppliers.

[b] Vapor decomposition, 350°C, 3 h; $B(OEt)_3$, 3.7 mmol/h; air, 115 ml/min.

[c] Average conversion of 3–4 h at 250°C.

TABLE 2

The Effect of Calcination of SiO_2 Support

Calcination temperature of SiO_2[a] (°C)	Vapor decomposition B_2O_3/SiO_2 catalyst			
	B_2O_3[c] content (wt%)	BET surface area (m^2/g)	Oxime conversion (%)	Lactam selectivity (mol%)
350[b]	34	135	98.6	96.4
450	30	—	94.9	95.4
600	28	—	95.8	97.0
800	30	85.4	72.4	96.8

[a] Calcination 3 h.

[b] Calcination 1 h.

[c] Vapor decomposition, 350°C, 3 h; $B(OEt)_3$, 3.7 mmol/h; air, 115 ml/min.

calcined at 800°C, the surface hydroxy groups of SiO_2 were irreversibly dehydrated to reduce its surface area (*9*).

The pore size distribution of vapor decomposition B_2O_3/SiO_2 was measured to study the process of B_2O_3 deposition on the internal surface of SiO_2 (Fig. 6). SiO_2 support had a sharp peak at about 66 Å in addition to a broad peak at between 200 and 500 Å in the pore size distribution. When the B_2O_3 content increased, the broad peak in a larger pore size region got smaller and the sharp peak at 66 Å shifted to a larger size of about 100 Å. At the same time, the pore volume was changed from 1.25 to 0.68 ml/g. Similar tendency of the change in pore size distribution was observed with the impregnation B_2O_3/SiO_2.

Characterization of Vapor Decomposition B_2O_3/SiO_2

Figure 7 shows the change in BET surface area of B_2O_3/SiO_2 catalyst with B_2O_3 content. The surface area decreased with increasing B_2O_3 content with respect to both vapor decomposition and impregnation catalysts. The surface area of impregnation B_2O_3/SiO_2 was larger than that of vapor decomposition B_2O_3/SiO_2 at any B_2O_3 content. This result implies that there remained more parts of the SiO_2 surface free from B_2O_3 deposition in the case of impregnation catalyst.

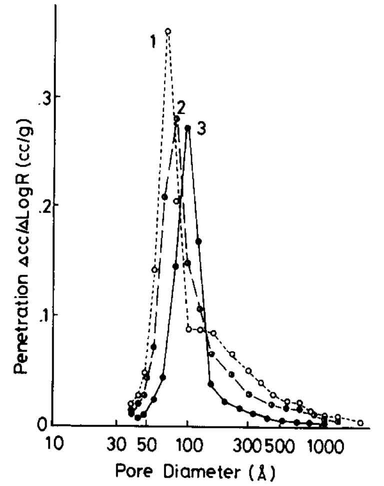

FIG. 6. The pore size distribution of vapor decomposition B_2O_3/SiO_2. (1) SiO_2 support, (2) B_2O_3/SiO_2 (B_2O_3, 15 wt%), (3) $B_2O_3SiO_2$ (B_2O_3, 34 wt%).

Figures 8a and b show the SEM images of the external surfaces of impregnation and vapor decomposition catalysts, respectively. Large B_2O_3 crystallites (ca. 50 μm) were deposited on the surface of impregnation catalyst. On the other hand, such large B_2O_3 crystallites were hardly observed on the surface of vapor decomposition catalyst; the surface was as smooth as that of SiO_2 support itself.

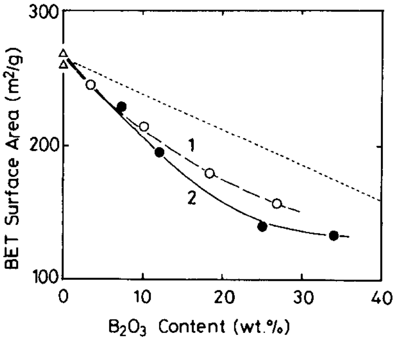

FIG. 7. The change in BET surface area. (1) Impregnation B_2O_3/SiO_2, (2) vapor decomposition B_2O_3/SiO_2. Dotted line denotes the surface area of SiO_2 alone calculated from the amount of silica support in a unit weight of catalyst.

Figure 9 illustrates the TPD profiles of

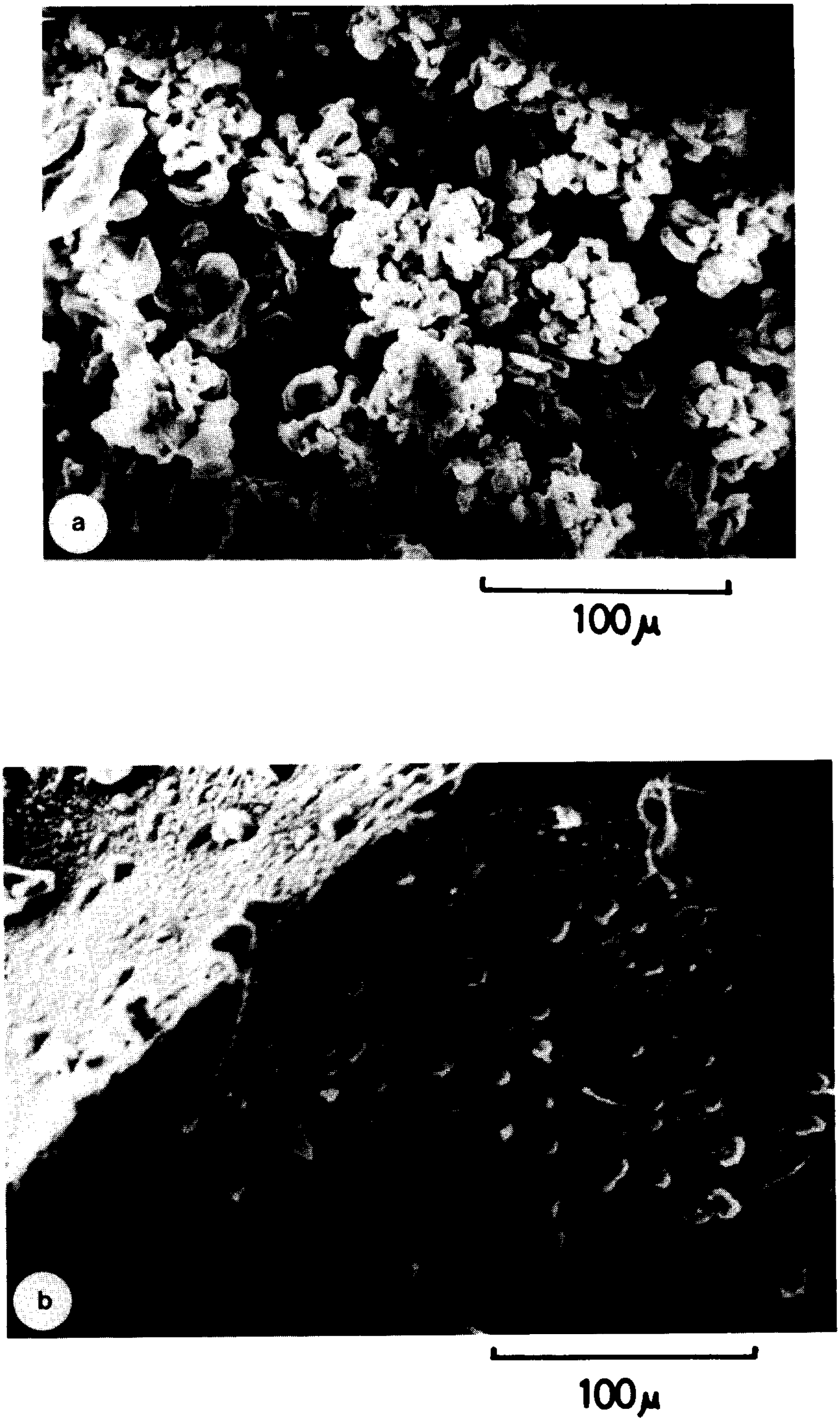

FIG. 8. The SEM images of B_2O_3/SiO_2 external surfaces. (a) Impregnation B_2O_3/SiO_2 (B_2O_3, 19 wt%), (b) vapor decomposition B_2O_3/SiO_2 (B_2O_3, 34 wt%).

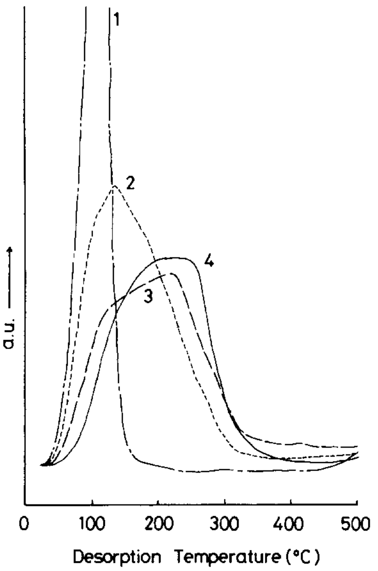

FIG. 9. The TPD profiles of the adsorbed pyridine on the vapor decomposition B_2O_3/SiO_2. (1) SiO_2 support, (2) B_2O_3/SiO_2 (B_2O_3, 10 wt%), (3) B_2O_3/SiO_2 (B_2O_3, 22 wt%), (4) B_2O_3/SiO_2 (B_2O_3, 33 wt%); all samples were treated at 400°C for 1 h prior to adsorption of pyridine.

the pyridine adsorbed on vapor decomposition B_2O_3/SiO_2 catalysts having different B_2O_3 contents. The TPD profile of SiO_2 support showed only a single sharp peak at 100°C, and all the pyridine adsorbed was removed below 150°C. In contrast, the TPD profiles of B_2O_3/SiO_2 catalysts had the desorption maxima between 150 and 250°C. The amount of pyridine desorbed above 250°C increased with B_2O_3 content. These results obviously tell that B_2O_3/SiO_2 catalyst is more acidic than SiO_2 support, and that the amount of strongly acidic sites whose acid strengths correspond to pyridine desorption temperatures above 150°C increased with B_2O_3 content.

The TPD profiles shown in Fig. 10 demonstrate the difference in acid property between vapor decomposition and impregnation B_2O_3/SiO_2 whose B_2O_3 contents are similar. Compared with the spectra of impregnation catalysts, each pyridine desorption peak on vapor decomposition catalyst slightly shifted to the higher temperature side.

Figure 11 shows the changes in the differential heat of adsorption of ammonia (DHA) on the most active vapor decomposition and impregnation catalysts, together with the data of SiO_2 support. The level of DHA corresponds to the acid strength of B_2O_3/SiO_2 and the adsorbed amount of ammonia means the number of acid sites. The initial value of DHA obtained with SiO_2 support was less than 80 kJ/mol, and the DHA decreased with increasing amount of adsorbed ammonia. The acid strength to catalyze the Beckmann rearrangement is thought to be at least 80 kJ/mol, because SiO_2 support alone had little activity for this reaction. The initial value of DHA on the impregnation catalyst was 110 kJ/mol, and the amount of adsorbed ammonia in the region where the DHA level exceeded 80 kJ/mol was 0.4 mmol/g. As to vapor decomposition catalyst, the DHA change was similar to that of impregnation catalyst up to 0.2 mmol/g of adsorbed ammonia, but

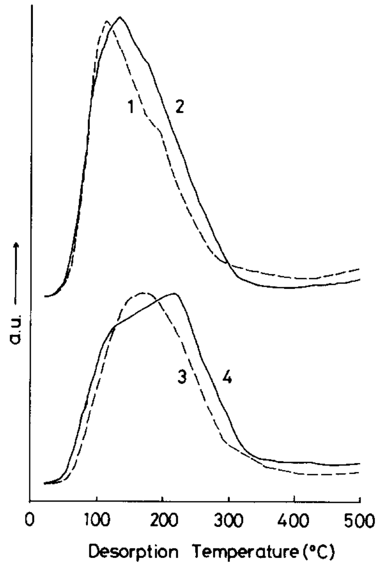

FIG. 10. Comparative TPD profiles of vapor decomposition and impregnation B_2O_3/SiO_2. (1) Impregnation B_2O_3/SiO_2 (B_2O_3, 8.0 wt%), (2) vapor decomposition B_2O_3/SiO_2 (B_2O_3, 10 wt%), (3) impregnation B_2O_3/SiO_2 (B_2O_3, 27 wt%), (4) vapor decomposition B_2O_3/SiO_2 (B_2O_3, 22 wt%); all samples were treated at 400°C for 1 h prior to adsorption of pyridine.

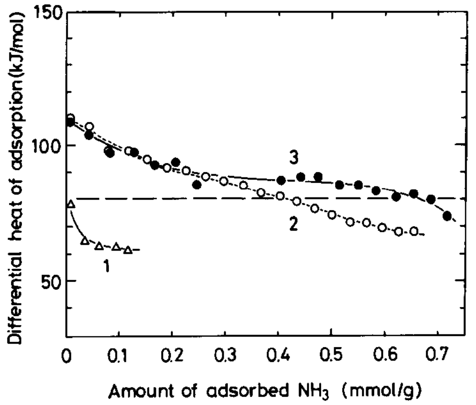

FIG. 11. The change in the differential heat of adsorption of ammonia. (1) SiO_2 support, (2) impregnation B_2O_3/SiO_2 (B_2O_3, 17 wt%), (3) vapor decomposition B_2O_3/SiO_2 (B_2O_3, 34 wt%); all samples were treated at 400°C for 1 h prior to adsorption of ammonia.

the total amount of the effective acid sites having DHA values more than 80 kJ/mol was as much as 0.7 mmol/g. Moreover, it should be noted that the DHA curve observed with the vapor decomposition catalyst became flat in the range of adsorbed ammonia from 0.3 to 0.6 mmol/g.

IV. DISCUSSION

Deposition of B_2O_3 on SiO_2 through Vapor Decomposition

On the basis of the above experimental observations, the following two schemes in which O_2 participates can be suggested to explain the deposition of B_2O_3 on SiO_2 surface in the process of vapor decomposition:

Scheme 1:

$$B(OEt)_3 \xrightarrow{O_2} B_2O_3 \xrightarrow{SiO_2} B_2O_3/SiO_2$$

Scheme 2:

$$B(OEt)_3 \xrightarrow{SiO_2} \xrightarrow{O_2} B_2O_3/SiO_2$$

According to Scheme 1, B_2O_3 is formed by the combustion of $B(OEt)_3$ in the gas phase to be directly deposited on the SiO_2 surface. In Scheme 2, first $B(OEt)_3$ reacts with the hydroxyl groups of SiO_2 surface forming Si—O—B bonds, and then the residual ethoxy groups on boron are oxidized to form surface B—OH groups; B_2O_3 can be deposited on SiO_2 surface through repetition of these surface reactions. If the vapor decomposition process proceeds via Scheme 1, a certain B_2O_3 deposition should be observed also on the internal wall of the reactor. The deposition of B_2O_3, however, was never observed on the reactor wall around the SiO_2 bed, and in contrast with the case of vapor decomposition using H_2O, no preferential B_2O_3 deposition occurred on the upper side of the SiO_2 bed. Moreover, it was confirmed that only a trace amount of B_2O_3 (0.8 wt%) was deposited by the vapor decomposition of $B(OEt)_3$ in a stream of N_2, but a certain amount of B_2O_3 (4.0 wt%) could be introduced through repetition (18 times) of a pulse procedure which involved the vapor decomposition of $B(OEt)_3$ in a stream of N_2 followed by the combustion with air. These results suggest that the vapor decomposition with O_2 in the present study proceeds substantially via Scheme 2.

When the vapor decomposition was performed at 400°C, more B_2O_3 was deposited on the upper side than on the lower side of the SiO_2 bed. This undesirable phenomenon was probably due to an increase in the rate of B_2O_3 deposition at higher temperature. In addition, the SiO_2 particles were adhered each other with B_2O_3 melt at 400°C. At higher temperatures, the reaction via Scheme 1 may be predominant.

In the vapor decomposition procedure using a fixed-bed apparatus (Fig. 1), a gradient of $B(OEt)_3$ concentration through SiO_2 bed may cause a little difference in the rate of B_2O_3 deposition between upper and lower sides of the SiO_2 bed. In order to assure more uniform vapor decomposition of B_2O_3 onto SiO_2 throughout the support bed, it seems convenient to use a rotary reactor or a fluidized-bed reactor. The study on the vapor decomposition using a rotary reactor is now under way.

Catalytic Feature of Vapor Decomposition B_2O_3/SiO_2

It is obvious that vapor decomposition B_2O_3/SiO_2 is more active and selective than impregnation B_2O_3/SiO_2 (Fig. 5). The most active B_2O_3/SiO_2 catalyst for the Beckmann rearrangement was obtained through vapor decomposition performed at 350°C for 3 h at a $B(OEt)_3$ feed rate of 3.5 mmol/h. The lactam selectivity, however, was dropped when vapor decomposition was carried out either at 400°C for 3 h (Fig. 3) or at 350°C for more than 3 h (Fig. 4). The selectivity drop may be due to the change in acid property of catalyst through high-temperature or long-time operation of vapor decomposition which causes melting of a part of B_2O_3 crystallites. In fact, at 400°C, the SiO_2 particles were adhered to each other with glassy B_2O_3. In this context, it was confirmed experimentally that B_2O_3 alone without support was quite inactive for the rearrangement reaction (oxime conversion, 4.0%; lactam selectivity, 26.4 mol% at 300°C), and that after the reaction B_2O_3 particles changed into a glassy melt with a very small surface area. This fact suggests that melting of B_2O_3 may be also responsible for the decreases both in activity and in selectivity.

The change in BET surface area with B_2O_3 content (Fig. 7) as well as the comparative SEM images of B_2O_3/SiO_2 (Fig. 8) clearly suggest that the SiO_2 surface is uniformly covered with B_2O_3 by means of vapor decomposition. On the other hand, the present impregnation method involves a step of calcination of the supported H_3BO_3, so that H_3BO_3 is prone to aggregate into large B_2O_3 particles in the course of dehydration leaving the SiO_2 surface free from the accumulation of B_2O_3. Since SiO_2 itself is inactive for the rearrangement reaction and furthermore the exposure of SiO_2 surface is not preferable to enhancement of the lactam selectivity (Fig. 5), it is necessary for obtaining an efficient B_2O_3/SiO_2 catalyst to cover the SiO_2 surface with B_2O_3 uniformly and completely as exemplified by a vapor decomposition catalyst having a B_2O_3 content of 34 wt%. According to our preliminary study on the vapor decomposition of $B(OEt)_3$ onto γ-alumina (*4*), a B_2O_3 content between 20 and 25 wt% was enough to cover the alumina surface to give the most active rearrangement catalyst, because the surface area of the alumina was smaller (160 m^2/g) than that of the SiO_2 used in the present study (281 m^2/g).

The result of the measurement of DHA (Fig. 11) indicates that the most active vapor decomposition B_2O_3/SiO_2 possesses much more effective acid sites whose DHA values are at least 80 kJ/mol, compared with the most active impregnation B_2O_3/SiO_2. Since the maximum DHA values are almost the same for both catalysts, the average acid strength of the vapor decomposition catalyst must be greater than that of the impregnation catalyst. This reasoning is in good harmony with a result obtained in the TPD measurement that the pyridine desorption peaks observed with vapor decomposition catalysts shifted to the higher temperature side compared with those observed with impregnation catalysts (Fig. 10).

Reportedly, a DHA value of 76 kJ/mol corresponds to a pK_a value of -5.6 (*10*). According to our qualitative measurement of acid strength by use of the Hammett indicators, both vapor decomposition and impregnation B_2O_3/SiO_2 could change Benzalacetophenone ($pK_a = -5.6$) into its acidic color, but SiO_2 could change only Dimethyl Yellow ($pK_a = +3.3$). Since SiO_2 support itself (DHA < 80 kJ/mol) is inactive for the Beckmann rearrangement, it can be deduced that the acid sites of B_2O_3/SiO_2 whose acid strengths are less than -5.6 in terms of H_O should be responsible for catalyzing the rearrangement reaction. In addition, the acid strength of vapor decomposition B_2O_3/SiO_2 was found reasonably uniform, judging from the flatness of DHA curve.

In conclusion, higher catalytic activity and selectivity of vapor decomposition B_2O_3/SiO_2 for the Beckmann rearrangement in comparison with impregnation B_2O_3/SiO_2 should be attributed to a larger amount of effective acid sites in addition to more uniform acid strength. Such favorable acid property was obtained through uniform deposition of B_2O_3 by means of vapor decomposition.

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