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Vapor Phase Beckmann Rearrangement over Silica-Supported Tantalum Oxide Catalysts

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Silica-supported tantalum oxide catalysts (Ta oxide/SiO_2 (ALK)), prepared by chemical reaction between tantalum alkoxide and surface hydroxyl groups of SiO_2, exhibited high catalytic efficiency for the vapor phase Beckmann rearrangement of cyclohexanone oxime to caprolactam. The oxime conversion reached 96.5%, and the selectivity for caprolactam was 97.5% at 573 K. The effects of precursors of tantalum oxide, physical properties of catalyst carriers, and preparation conditions were studied, and the factors in catalytic efficiency were discussed. SiO_2 was the best carrier for the reaction among SiO_2, Al_2O_3, TiO_2, MgO, and SiO_2–Al_2O_3. The pore structure of silica carriers, especially the high ratio (>90%) of the pore volume for fine pores with diameters from 4 to 200 nm to total pore volume was effective. Ta_2O_5/SiO_2 (IMP) catalyst, prepared by impregnation of silica with an aqueous $TaCl_5$ solution and hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$) were less active and less selective. A large number of acid sites of intermediate strength, measured by NH_3-TPD method, existed on Ta_2O_5/SiO_2 (ALK) and were effective for the Beckmann rearrangement. On the contrary, strong acid sites appeared on Ta_2O_5/SiO_2 (IMP). The difference in the acid property and catalytic performance between Ta_2O_5/SiO_2 (ALK) and Ta_2O_5/SiO_2 (IMP) was assumed to be related to the difference in morphology of tantalum oxide that was observed by SEM and EPMA. Good initial activity and high selectivity for caprolactam were observed over boron oxide supported on alumina catalyst. However, the oxime conversion declined significantly. Although the NH_3-TPD profile of B_2O_3/Al_2O_3 catalyst was similar to that of Ta_2O_5/SiO_2 (ALK), tantalum oxide of Ta_2O_5/SiO_2 (ALK) was more stable than boron oxide of B_2O_3/Al_2O_3 in the course of reaction. The reaction between tantalum alkoxide vapor and the surface hydroxyl groups of SiO_2 was observed by FTIR diffuse reflectance spectrometer. A new hydroxyl group appeared on Ta_2O_5/SiO_2 (ALK) catalyst. The unique acid property and catalytic performance of Ta_2O_5/SiO_2 (ALK) were discussed in connection with the new hydroxyl group. © 1994 Academic Press, Inc.

INTRODUCTION

ε-Caprolactam is a key intermediate for nylon-6. Generally, ε-caprolactam is industrially synthesized by a liquid-phase Beckmann rearrangement reaction of cyclohexanone oxime using a strong acid such as concentrated sulfuric acid or fuming sulfuric acid. In this method, it is inevitable to neutralize sulfuric acid with ammonia in order to separate the lactam. One problem is the substantial amount of ammonium sulfate produced as a by-product.

Various studies have been made on the Beckmann rearrangement reaction without sulfuric acid, especially, in a gas phase in the presence of a solid acid catalyst. Silica–alumina (1), metal phosphate (2), boria–thoria (3), alumina-supported boria catalyst prepared by vapor decomposition method (4), and highly silicious zeolite, especially ZSM-5 (5) have been proposed as solid acid catalysts. However, when the Beckmann rearrangement is conducted with such solid acid catalysts in the gas phase, side reactions, such as thermal decomposition and polymerization, are likely to take place, and the yield of ε-caprolactam is insufficient. Furthermore, the deterioration of the catalytic activities with time is substantial.

We found previously that the hydrated tantalum oxide showed strong acid properties in its amorphous form (6) and catalyzed the Beckmann rearrangement (7), but the yield of ε-caprolactam and catalyst life was insufficient. In order to control acidic and catalytic properties of the hydrated tantalum oxide, we prepared the silica-supported tantalum oxide by the reaction between tantalum alkoxide and surface hydroxyl groups of silica (8). The physicochemical properties of the silica-supported tantalum oxide layer catalyst were different from those of hydrated tantalum oxide and Ta oxide/SiO_2(IMP), prepared by impregnating acidic aqueous $TaCl_5$ solution on SiO_2. For example, the tantalum oxide thin film did not crystallize at high temperature of about 1500 K, and the acid strength was moderate. The silica-supported tantalum oxide showed high catalytic efficiency and selectivity for the vapor phase decomposition of methyl *tert*-butyl ether.

In this paper we report that silica-supported tantalum oxide layer catalysts exhibited high catalytic efficiency for the vapor phase Beckmann rearrangement of cyclohexanone oxime, and the catalytic activity did not substantially decline during 10 h. The effects of acid properties, pore structure, and preparation conditions of the

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silica-supported tantalum oxide catalysts on the activities for the vapor phase Beckmann rearrangement were studied.

EXPERIMENTAL

Preparation of Silica-Supported Tantalum Oxide Layer Catalysts (Ta oxide/SiO$_2$ (ALK)) by the Reaction between Tantalum penta-n-butoxide and the Surface Hydroxyl Groups of Silica in the Liquid Phase

Four kinds of reference silica of the Catalysis Society of Japan and two kinds of commercial silica, supplied by Nikki Kagaku Co., were used as catalyst carriers. Specific surface area (BET method, Carlo Elba Sorptomatic 1900 apparatus) and pore size distribution (mercury injection method, Micromeritics Autopore 9200; surface tension of mercury = 480 dyn · cm^{-1}, contact angle between mercury and silica = 140°) of the silica carriers are shown in Table 1. The silica carrier was pulverized and sieved to obtain a carrier of size 0.59–0.9 mm, then evacuated at 373 K for 2 h. The silica was added to a hexane solution containing tantalum alkoxide ($Ta(OC_2H_5)_5$ or $Ta(On\text{-}C_4H_9)_5$, supplied by High Purity Chemicals Co.), and the mixture was left to stand at room temperature for 15 h. Then the mixture was subjected to filtration, and the residue was washed with hexane and dried under reduced pressure at 363 K for 5 h. The product was heat treated under the mixture of steam and nitrogen (H_2O/N_2 = 1/1 in volume) at 573 K for 2 h and heat treated in a dried air stream at the same temperature for 2 h.

Preparation of the Other Catalysts

(a) *Ta oxide/SiO$_2$ (IMP) catalyst* was prepared by the impregnation of silica (Silica carrier A of Table 1) with a 1 *M* aqueous hydrochloric acid solution containing 1 wt% $TaCl_5$.

(b) *Effects of the catalyst carriers.* Al_2O_3 (JRC-ALO-1: Reference alumina of the Catalysis Society of Japan), TiO_2 (JRC-TIO-5), MgO (JRC-MGO-1), and SiO_2–Al_2O_3 (N631H (SiO_2 65 wt% and Al_2O_3 35 wt%), supplied by Nikki Kagaku Co.), also were used as carriers. The preparation procedure was the same as in the case of Ta oxide/SiO$_2$ (ALK).

(c) *B_2O_3 supported on Al_2O_3 catalyst* was prepared by the decomposition of a vapor of triethyl borate, supplied by Tokyo Chemical Industry Co., on the Al_2O_3, as in the literature (4).

Furthermore, the catalytic activities of H-mordenite (JRC-Z-HM15: Reference zeolite of the Catalysis Society of Japan), hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$) and hydrated niobium oxide ($Nb_2O_5 \cdot nH_2O$) were tested for comparison. These hydrated oxides were prepared as in the literature (6).

Beckmann rearrangement. The vapor phase Beckmann rearrangement of cyclohexanone oxime was carried out at atmospheric pressure in an ordinary flow-type reactor. A reaction gas containing oxime, which was a GR reagent of the Tokyo Chemical Industry, benzene as a diluent, and nitrogen was introduced to the reactor. The reaction conditions were as follows: GHSV = 4800 h^{-1}; catalyst amount = 0.5 cm^3; temperature = 573 K; feed gas ratio, oxime/benzene/N$_2$ = 4/42/54 mol%. The reaction products including ε-caprolactam were collected into cooled ethanol and analyzed by gas chromatography.

Characterization of the catalysts. The amount of tantalum supported on the catalyst carrier was determined by ICP method after the sample was dissolved in an aqueous hydrofluoric acid solution.

Morphologies of the tantalum oxide catalysts and the silica were characterized by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). SEM investigations were performed on a Hitachi S-900. EPMA measurements were carried out using JEOL JXA-8600M.

Temperature programmed desorption (TPD) of ammonia on the sample was measured by use of a conventional

TABLE 1

Physical Properties of Silica Carriers of Tantalum Oxide

Silica carrier	Total pore volume (A)[a] (cm^3 · g^{-1})	Pore volume of fine pores (B)[b] (cm^3 · g^{-1})	(B)/(A) × 100 (%)	Peak of pore diameter (nm)	Specific surface area (m^2 · g^{-1})
A	0.847	0.833	98.4	15.4	240
B	1.032	1.022	99.0	34.0	111
C	1.072	1.059	98.8	54.0	93
D	0.767	0.718	93.6	No distinct peak	330
E	0.833	0.254	30.5	No distinct peak	25
F	0.241	0.170	70.5	5.0	173

[a] Total pore volumes of pores with pore diameters of 4 to 15,000 nm.

[b] Pore volume of pores with pore diameters of 4 to 200 nm.

flow-type TPD apparatus. A catalyst sample (50 mg) was pretreated in a TPD cell at 673 K for 1 h in a stream of helium. A pulse of ammonia was introduced at 373 K, and then the cell was kept at 373 K for 1 h in a stream of helium. The TPD measurement was started from 373 K at a heating rate of 10 K · min^{-1} using helium as a carrier gas (100 ml · min^{-1}).

Observation of the preparation processes by FTIR diffuse reflectance spectrometer. An FTIR spectrometer was equipped with a diffuse reflectance spectrometer (DRS) environmental chamber (Spectratech Model 0030-102). The preparation processes, such as heating the silica (JRC-SIO-5) at 773 K in a stream of helium, introducing tantalum penta-*n*-butoxide vapor to the silica at 373 K, treating with steam, and heating at higher temperature, were observed. We focussed our observation mainly on the change in wavenumber related to hydroxyl groups of the surface species.

RESULTS AND DISCUSSION

Table 2 shows the catalytic activities of the silica-supported tantalum oxide catalysts for the vapor-phase Beckmann rearrangement, together with those of the other solid acid catalysts. The oxime conversion over the catalysts except the $\mathrm{Ta_2O_5}$ 4.3 wt%/$\mathrm{SiO_2}$ (ALK) declined significantly during the reaction. The main by-products were cyclohexanone and 5-cyanopentane. After the reaction, the color of the $\mathrm{Ta_2O_5}$ 4.3 wt%/$\mathrm{SiO_2}$ (ALK) catalyst remained unchanged, while the color of the other catalysts changed to dark gray or black due to coke deposition on the surface of the catalysts. The $\mathrm{Ta_2O_5}$ 4.3 wt%/$\mathrm{SiO_2}$ (ALK) was the most active and selective for caprolactam. $\mathrm{Ta_2O_5}$ 4.9 wt%/$\mathrm{SiO_2}$ (IMP) was inferior to the $\mathrm{Ta_2O_5/SiO_2}$ (ALK) in both activity and selectivity, although the difference in the supported amount of tantalum oxide between both catalysts was quite small. The activities of $\mathrm{Ta_2O_5/SiO_2}$ (IMP), $\mathrm{Ta_2O_5 \cdot \mathit{n}H_2O}$, and H-mordenite were almost the same, and $\mathrm{Nb_2O_5 \cdot \mathit{n}H_2O}$ was less active.

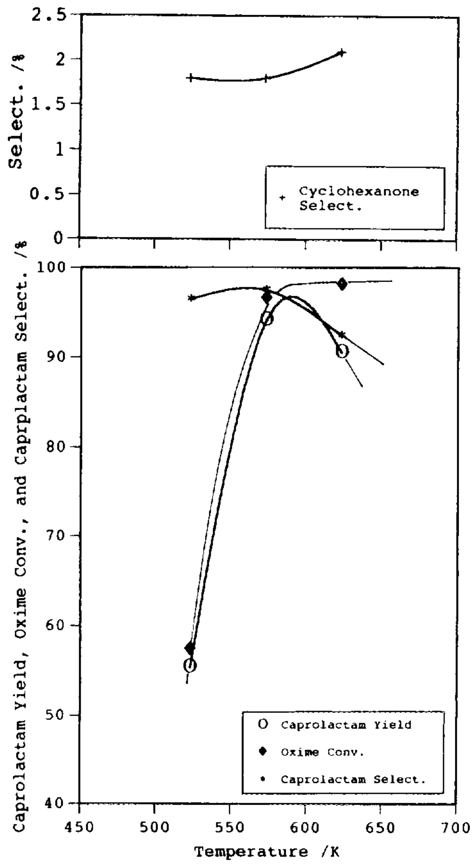


FIG. 1. Effect of the reaction temperature on the conversion of oxime and the selectivities for caprolactam and cyclohexanone over the $\mathrm{Ta_2O_5}$ 4.3 wt%/$\mathrm{SiO_2}$ (ALK) catalyst.

Figure 1 shows the effect of reaction temperature on the conversion and selectivities for caprolactam and

TABLE 2

Activities of the Silica-Supported Tantalum Oxides for the Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime Compared with the Other Solid Acid Catalysts[a]

Catalyst	Oxime conversion (%)	Caprolactam selectivity (%)	Cyclohexanone selectivity (%)	Caprolactam yield (%)
$\mathrm{Ta_2O_5}$ 4.3 wt%/$\mathrm{SiO_2}$[b] (ALK)	96.5	97.5	1.8	94.1
$\mathrm{Ta_2O_5}$ 4.9 wt%/$\mathrm{SiO_2}$[b] (IMP)	40.8	70.5	5.3	28.8
$\mathrm{B_2O_3}$ 26.5 wt%/$\mathrm{Al_2O_3}$	93.4	92.1	2.0	86.0
H-Mordenite	42.5	63.4	4.5	26.9
$\mathrm{Ta_2O_5 \cdot \mathit{n}H_2O}$	42.6	69.9	4.8	29.8
$\mathrm{Nb_2O_5 \cdot \mathit{n}H_2O}$	21.2	67.5	3.8	14.3

[a] The reaction conditions are described under Experimental. Catalyst amount: 0.5 cm^3; 202 mg ($\mathrm{Ta_2O_5}$ 4.3 wt%/$\mathrm{SiO_2}$ (ALK)), 208 mg ($\mathrm{Ta_2O_5}$ 4.9 wt%/$\mathrm{SiO_2}$ (IMP)), 350 mg ($\mathrm{B_2O_3}$ 26.5 wt%/$\mathrm{Al_2O_3}$), 195 mg (H-Mordenite), 650 mg ($\mathrm{Ta_2O_5 \cdot \mathit{n}H_2O}$), 515 mg ($\mathrm{Nb_2O_5 \cdot \mathit{n}H_2O}$). Running time was 1 h.

[b] The catalyst carrier was Carrier A in Table 1.

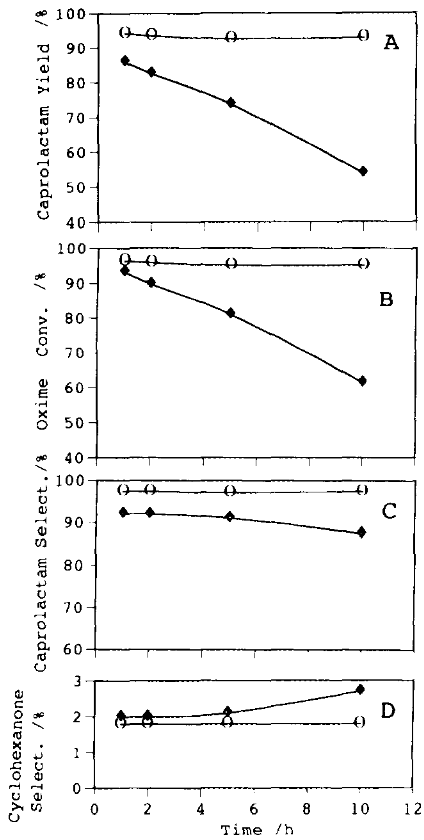


FIG. 2. (A) Caprolactam yield, (B) oxime conversion, (C) caprolactam selectivity, and (D) cyclohexanone selectivity of the Ta_2O_5 4.3 wt%/SiO_2 (ALK) catalyst (○), compared with those of B_2O_3 26.5 wt%/Al_2O_3 catalyst (◆).

cyclohexanone over the Ta_2O_5 4.3 wt%/SiO_2 (ALK) catalyst. The reaction rate increased drastically with increasing temperature from 523 to 573 K. The maximum caprolactam yield was attained at 573 K. The caprolactam selectivity decreased at the higher temperature. One suggested reason for this was an increase in side reactions. At the high temperatures, e.g., 623 K, the color of the products solution was yellow, and unknown products appeared in the gas chromatogram.

Initial activity and selectivity for caprolactam of the B_2O_3 26.5 wt%/Al_2O_3 catalyst were as high as for the Ta_2O_5/SiO_2 (ALK) catalyst, as shown in Table 2. However, the catalytic activity of the B_2O_3/Al_2O_3 declined significantly during 10 h, as shown in Fig. 2. On the other hand, in the case of the Ta_2O_5/SiO_2 (ALK) catalyst, the conversion and selectivity for caprolactam remained unchanged over the same period. The amount of cyclohexanone increased slightly at the expense of caprolactam. The amount of boron oxide of the B_2O_3/Al_2O_3 catalyst decreased drastically (26.5 → 19.8 wt%) in the course of reaction, although the amount of tantalum oxide of the Ta_2O_5/SiO_2 (ALK) catalyst remained unchanged. It is assumed that in the case of the B_2O_3/Al_2O_3 catalyst, not only did the number of active sites decrease, but also the chemical properties of the surface changed during the reaction.

While the conversion of oxime seems to depend on the supported amount of Ta_2O_5, the selectivities for caprolactam and cyclohexanone seem to be affected by porosity of the silica carrier, as shown in Table 3. The selectivity for caprolactam exceeded 90% over the Ta_2O_5 supported on silica carriers A–D. In these cases, the pore volume for pores with diameters from 4 to 200 nm is more than 90% of the total pore volume for pores with diameters from 4 to 15,000 nm. The silica carriers A–C have one peak of the pore size distribution within 10 to 60 nm in diameter. The total pore volume, the pore volume of fine pores, the pore size distribution, and the specific surface area remain unchanged not only in the course of preparation of Ta_2O_5/SiO_2 (ALK), but also during the Beckmann rearrangement, as shown in Table 4 and Fig. 3a. On the other hand, the tantalum oxide catalysts supported on the silica carriers E and F were less active and less selective

TABLE 3

Effect of Silica Carriers of Tantalum Oxide for the Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime[a]

Silica carrier	Supported amount of Ta_2O_5 (wt%)	Oxime conversion (%)	Caprolactam selectivity (%)	Cyclohexanone selectivity (%)	Caprolactam yield (%)
A	4.3	96.5	97.5	1.8	94.1
B	3.5	88.4	95.5	1.9	84.4
C	2.8	81.0	95.5	1.9	81.8
D	6.2	88.7	92.2	2.6	81.8
E	3.4	72.8	72.5	5.6	52.8
F	6.7	53.6	72.5	7.5	38.9

[a] The reaction conditions are described under Experimental. Catalyst amount: 0.5 cm^3; 202 mg (Ta_2O_5/Silica carrier A), 197 mg (Ta_2O_5/Silica carrier B), 194 mg (Ta_4O_5/Silica carrier C), 215 mg (Ta_2O_5/Silica carrier D), 200 mg (Ta_2O_5/Silica carrier E), 240 mg (Ta_2O_5/Silica carrier F). Running time was 1 h.

TABLE 4

Pore Volume and Surface Area of Silica-Supported Tantalum Oxide Catalysts

Catalyst		Total pore volume (A)[a] ($cm^3 \cdot g^{-1}$)	Pore volume of fine pores (B)[b] ($cm^3 \cdot g^{-1}$)	(B)/(A) × 100 (%)	Peak of pore diameter (nm)	Specific surface area ($m^2 \cdot g^{-1}$)
Ta_2O_5 4.3 wt%/Carrier A (ALK)	Fresh	0.805	0.782	97.1	14.8	225
	Used[c]	0.781	0.754	96.5	14.8	219
Ta_2O_5 3.5 wt%/Carrier B (ALK)	Fresh	0.980	0.935	95.1	32.5	104
	Used	0.931	0.916	98.4	32.5	100
Ta_2O_5 2.8 wt%/Carrier C (ALK)	Fresh	1.018	0.975	95.8	52.6	88
	Used	0.967	0.936	96.8	52.6	86
Ta_2O_5 6.2 wt%/Carrier D (ALK)	Fresh	0.706	0.644	91.2	No distinct peak	312
	Used	0.642	0.594	92.5	No distinct peak	306
Ta_2O_5 3.4 wt%/Carrier E (ALK)	Fresh	0.750	0.243	32.4	No distinct peak	21
	Used	0.562	0.205	36.5	No distinct peak	16
Ta_2O_5 6.7 wt%/Carrier F (ALK)	Fresh	0.145	0.088	60.9	5.0	118
	Used	0.091	0.051	56.0	5.0	74
Ta_2O_5 4.9 wt%/Carrier A (IMP)	Fresh	0.720	0.662	92.0	15.4	194
	Used	0.468	0.446	95.3	15.4	142

[a] Total pore volumes of pores with pore diameters of 4 to 15,000 nm.

[b] Pore volume of pores with pore diameters of 4 to 200 nm.

[c] Reaction time was 10 h.

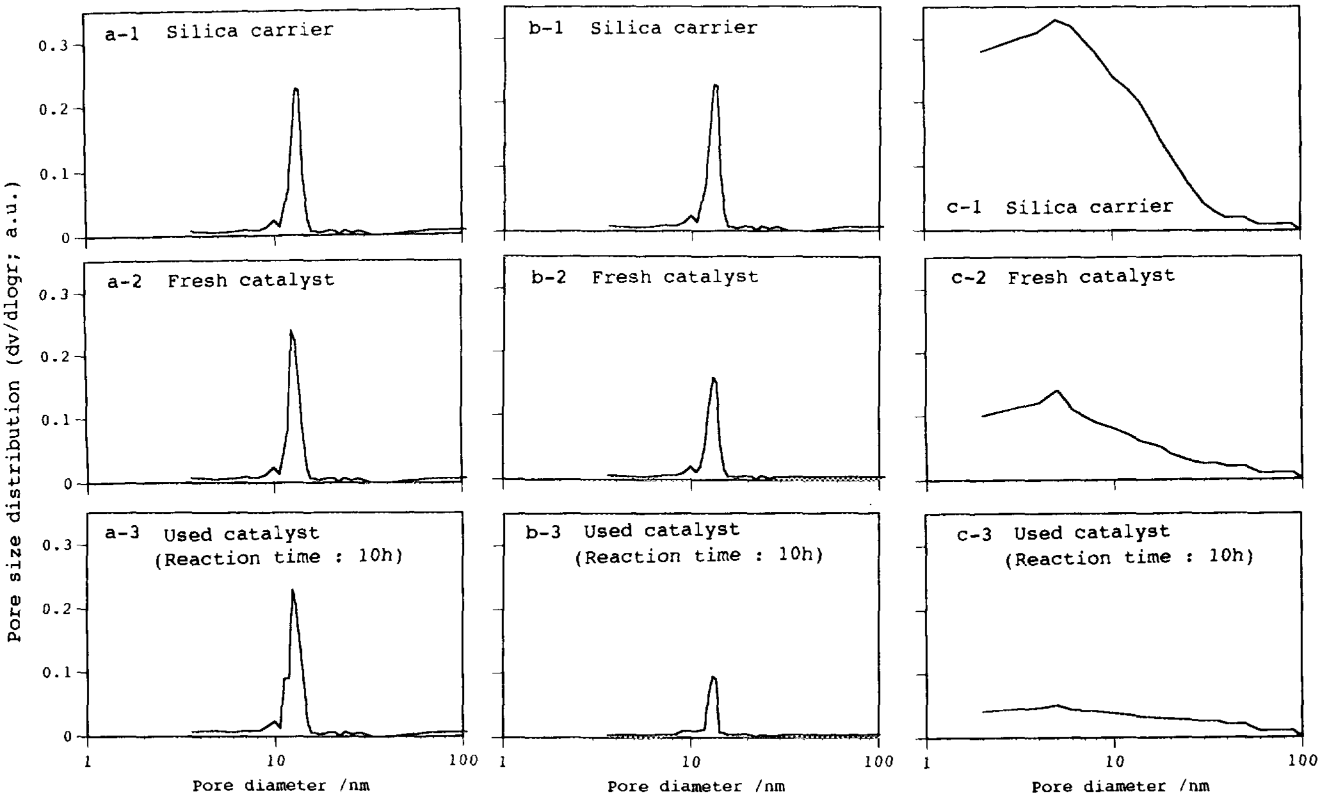


FIG. 3. Pore size distribution curves of (a) Ta_2O_5 4.3 wt%/SiO_2 (Carrier A; ALK), (b) Ta_2O_5 4.9 wt%/SiO_2 (Carrier A; IMP), and (c) Ta_2O_5 6.7 wt%/SiO_2 (Carrier F; ALK).

for caprolactam formation. These silica carriers have fewer pores ranging from 4 to 200 nm in diameter compared with the silica carriers A–D. Furthermore, the tantalum oxide supported on the silica carrier F, which had many small pores around 5 nm, showed the highest selectivity for cyclohexanone. In these cases, especially for silica carrier F (Fig. 3b), the total pore volume and pore volume of fine pores decreased considerably due to coke formation. These results suggest that the pore structure was important for the catalytic activity and selectivity. The diffusion rates of oxime and caprolactam could depend on the pore structure, and the fine pores seem to fill the effective role of diffusion.

The pore volume and the pore size distribution changed drastically in the course of preparation of the Ta_2O_5/SiO_2 (IMP) (Fig. 3c). Tantalum pentachloride seems to form easily the agglomerated tantalum oxide species inside the pores of the silica carrier. On the other hand, in the case of the Ta_2O_5/SiO_2 (ALK), tantalum alkoxide, e.g., $Ta(On\text{-}C_4H_9)_5$, reacted with the surface hydroxyl groups of SiO_2, and tantalum oxide thin film formed on the surface without substantial change of the pore structure.

For a detailed morphological characterization, the catalyst samples were examined by SEM and EPMA. Figure 4a shows a SEM photograph of the silica carrier. Only small amorphous particles are contaminated with agglomerated species with diameters of smaller than 2×10^3 nm. In Fig. 4b, showing the Ta_2O_5 4.3 wt%/SiO_2 (ALK), the deposited tantalum oxide layer was not visible in the SEM photograph nor in the corresponding EPMA image. This result implies that well-dispersed tantalum oxide species formed on the surface of silica. On the contrary, agglomerated tantalum oxide species with diameters of 1×10^3 to 4×10^3 nm existed on the surface in the Ta_2O_5 4.9 wt%/SiO_2 (IMP) (Fig. 4c). It is evident that the morphologies of tantalum oxide were quite different from each other between the Ta_2O_5 4.3 wt%/SiO_2 (ALK) and the Ta_2O_5 4.9 wt%/SiO_2 (IMP), although the silica carriers used were the same, and the contents of the tantalum oxide were almost the same in both samples. From these results, the morphologies of tantalum oxide seem to be affected by the precursors of Ta_2O_5 and seem to have a great influence on the catalytic performance for Beckmann rearrangement.

Figure 5 shows the NH_3-TPD profiles of the Ta_2O_5/SiO_2 (ALK), Ta_2O_5/SiO_2 (IMP), B_2O_3/Al_2O_3, and hydrated tantalum oxide. The acid strengths of Ta_2O_5/SiO_2 (ALK) and the B_2O_3/Al_2O_3 were moderate compared with hydrated tantalum oxide and the Ta_2O_5/SiO_2 (IMP). Curtin *et al.* investigated the effect of the amount of intermediate strength acid sites on the activity and the selectivity of the Beckmann rearrangement using the supported boron oxide catalysts (9). They also reported that B_2O_3/Al_2O_3 catalyst presented excellent selectivity for caprolactam at the largest concentration of intermediate strength acid sites, but suffered serious catalyst deactivation. Although the NH_3-TPD profiles of the Ta_2O_5/SiO_2 (ALK) and the B_2O_3/Al_2O_3 were almost the same, their catalytic performances for the Beckmann rearrangement were remarkably different. These results imply that there are some factors other than the surface concentration of intermediate strength acid sites which determine the catalytic performance. Curtin *et al.* suggested that the supported boron oxide catalysts were deactivated by coke deposition and/or basic by-product adsorption. They suggested also that the conversion of water soluble crystal boron oxide to amorphous water insoluble boron species was responsible for the catalyst deactivation (10). They assumed that the water soluble crystal boron oxide was the active species in the Beckmann rearrangement. Furthermore, the supported boron oxide catalyst deactivated drastically by addition of steam to the reactant, which causes vaporization of the hydrated boron oxide. On the contrary, the structure of Ta_2O_5/SiO_2 (ALK) did not change during the reaction. Highly dispersed amorphous tantalum oxide species may not only be active for the vapor phase Beckmann rearrangement but may also offer resistance to the deactivation by steam. For example, the Ta_2O_5/SiO_2 (ALK) showed the resistance for the deactivation by steam also in the vapor phase decomposition of methyl *tert*-butyl ether (8). In the case of the Ta_2O_5/SiO_2 (IMP) catalyst, the selectivity for caprolactam was quite low because there were substantial amounts of strong acid sites on the surface. The acidic property of the Ta_2O_5/SiO_2 (IMP) was almost the same as the hydrated tantalum oxide, which was determined by the measurement of NH_3-TPD. Oxime and/or caprolactam seem to adsorb tightly on such strong acid sites, and the Beckmann rearrangement was prevented from proceeding. The acid properties of tantalum oxide on the surface seem to be affected by the precursors and the morphologies.

Table 5 shows the effects of the kind of alkoxy group of tantalum alkoxide, concentration of tantalum *n*-butoxide in the hexane solution, and temperature of impregnating silica in the hexane solution used to prepare the Ta_2O_5/SiO_2 (ALK) catalysts on the activities and selectivities for the vapor phase Beckmann rearrangement. Previously, we reported that the preparation conditions, such as the kind of alkoxy group and concentration of tantalum alkoxide, were important for the formation of highly dispersed tantalum oxide species on the surface (8). The amount of supported Ta_2O_5 of the Ta_2O_5/SiO_2 (ALK) prepared from $Ta(On\text{-}C_4H_9)_5$ was less than that of the Ta_2O_5/SiO_2 (ALK) prepared from $Ta(OC_2H_5)_5$. Nevertheless, the former catalyst was more active and selective for caprolactam. Furthermore, when the concentration of $Ta(On\text{-}C_4H_9)_5$ was higher in the preparation, the caprolactam yield decreased. These results imply that morpholog-

TABLE 5

Effect of the Preparation Conditions of Silica-Supported Tantalum Oxide (ALK) for the Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime[a]

(1) Kind of alkoxy group of alkoxide[a]

Alkoxy group	Supported amount of Ta_2O_5 (wt%)	Catalyst weight (mg)	Oxime conversion (%)	Caprolactam selectivity (%)	Cyclohexanone selectivity (%)	Caprolactam yield (%)
$-OC_2H_5$	7.2	228	93.5	92.0	1.9	86.0
$-On-C_4H_9$	4.3	202	96.5	97.5	1.8	94.1

(2) Concentration of $Ta(On-C_4H_9)_5$ in the hexane solution[b]

Concentration of $Ta(On-C_4H_9)_5$ (wt%)	Supported amount of Ta_2O_5 (wt%)	Catalyst weight (mg)	Oxime conversion (%)	Caprolactam selectivity (%)	Cyclohexanone selectivity (%)	Caprolactam yield (%)
1	4.3	202	96.5	97.5	1.8	94.1
2	5.0	218	96.6	94.3	1.8	91.1
5	6.8	226	97.8	94.4	1.8	92.3

(3) Temperature of impregnating silica in the hexane solution containing 1 wt% of $Ta(On-C_4H_9)_5$

Impregnating temperature (K)	Supported amount of Ta_2O_5 (wt%)	Catalyst weight (mg)	Oxime conversion (%)	Caprolactam selectivity (%)	Cyclohexanone selectivity (%)	Caprolactam yield (%)
293	4.3	202	96.5	97.5	1.8	94.1
323	5.2	209	96.6	97.1	1.8	93.8

[a] Concentration of the tantalum alkoxide in hexane solution was 1 wt%. Silica carrier A was impregnated into the hexane solution containing tantalum alkoxide at 293 K.

[b] Silica carrier A was impregnated into the hexane solution containing $Ta(On-C_4H_9)_5$ at 293 K.

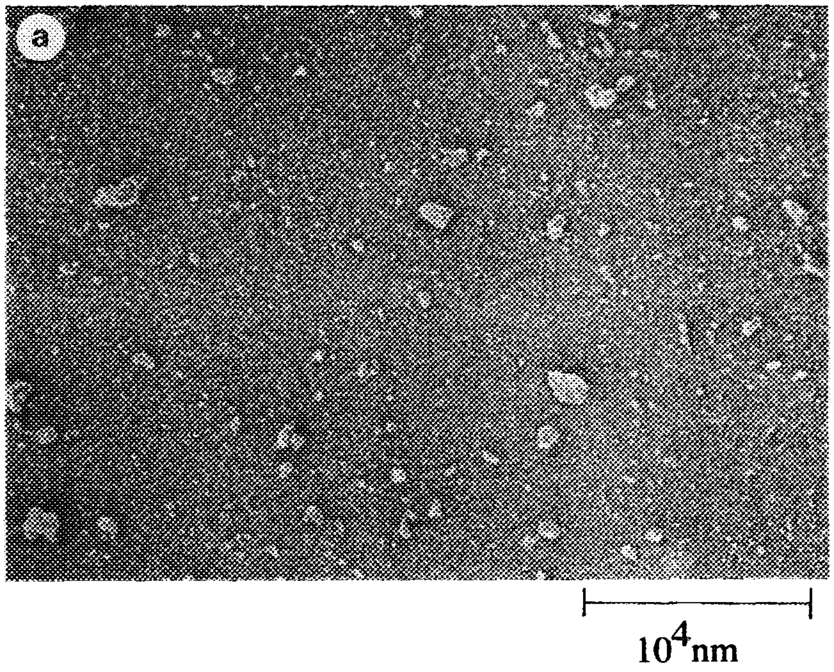
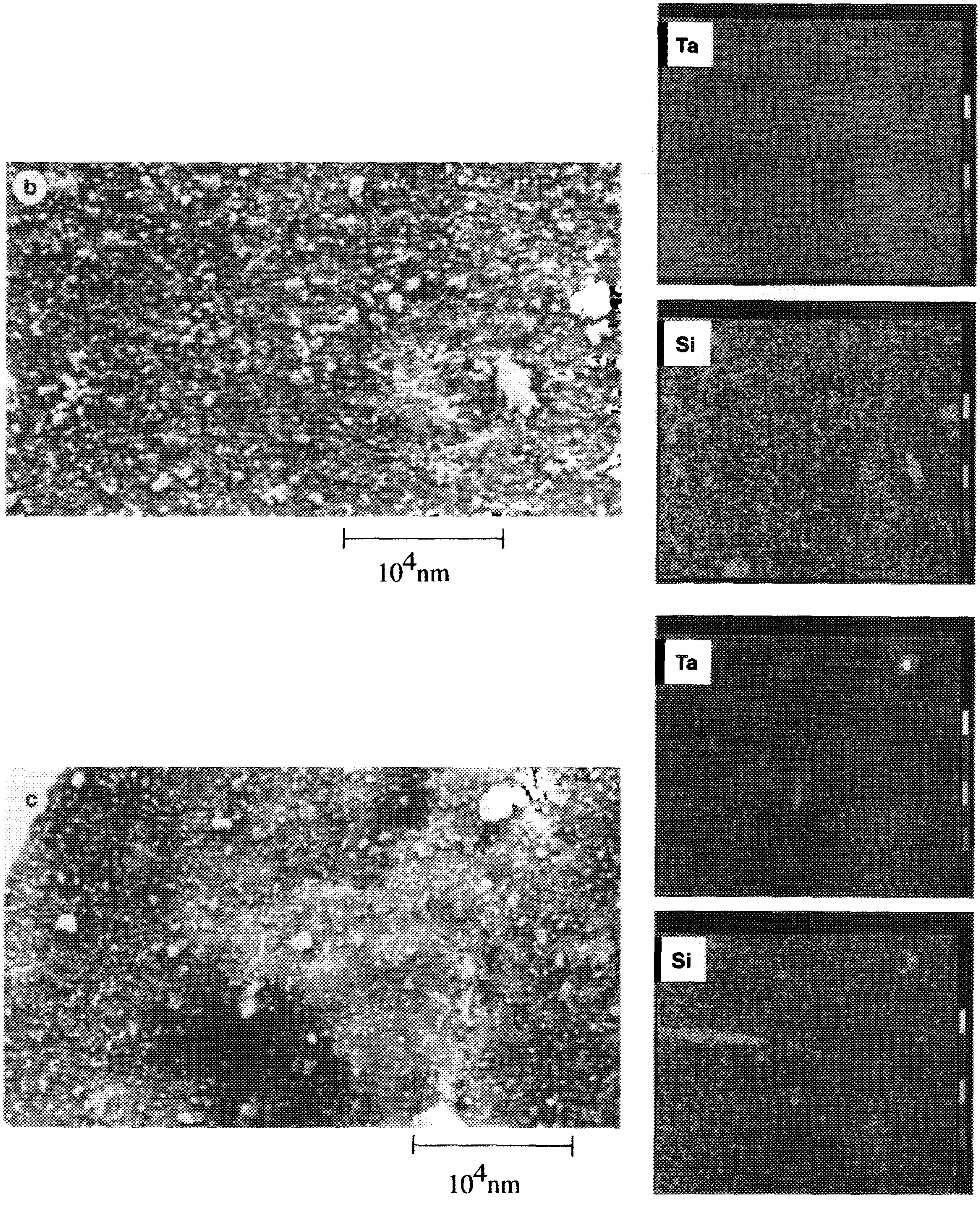


FIG. 4. Scanning electron micrographs and EPMA images of silica-supported tantalum oxide samples. (a) Silica carrier, (b) Ta_2O_5 4.3 wt%/SiO_2 (ALK), and (c) Ta_2O_5 4.9 wt%/SiO_2 (IMP). The color change, from blue to white, of EPMA images corresponds to the concentrations of elements (Ta and Si) on the surface of the samples.


b
Ta
Si
10⁴nm
c
Ta
Si
10⁴nm

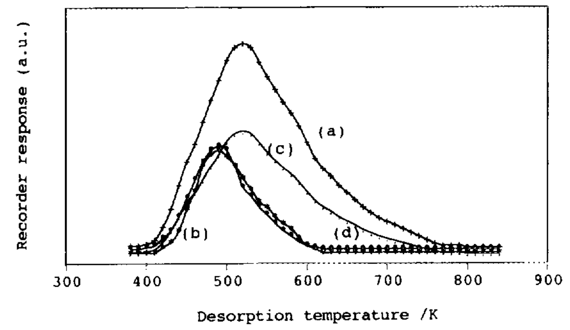


FIG. 5. TPD profiles of the adsorbed ammonia on (a) hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$), (b) Ta_2O_5 4.3 wt%/SiO_2 (ALK), (c) Ta_2O_5 4.9 wt%/SiO_2 (IMP), and (d) B_2O_3 26.5 wt%/Al_2O_3.

ies of tantalum oxide were changed by the preparation conditions, and the morphology of the Ta_2O_5/SiO_2 (ALK) was more important for the catalytic efficiency than the amount of Ta_2O_5 supported. The impregnation temperature did not affect substantially the catalytic performance.

In order to clarify the difference of the active sites between the silica-supported tantalum oxide layer catalyst and hydrated tantalum oxide, the preparation steps for the Ta_2O_5/SiO_2 (ALK) were investigated by FTIR diffuse reflectance spectrometer. The results are shown in Fig. 6. The broad band at 3500–3600 cm^{-1} and the small band at 3730 cm^{-1} appeared when the silica carrier was heat treated at 773 K in a stream of helium. The broad band at 3500–3600 cm^{-1} was weakened by introducing $Ta(On\text{-}C_4H_9)_5$ vapor to the silica at 373 K. At the same time, the band at 2900–3000 cm^{-1}, assigned to the stretching of CH_2, appeared. When the silica was exposed to $Ta(On\text{-}C_4H_9)_5$ vapor at 373 K for 5 h, the broad band at 3500–3600 cm^{-1} disappeared. However, the small band at 3730 cm^{-1} did not change substantially. The small band at 3730 cm^{-1} of silica, assigned to the free silanol of amorphous silica (11), seems to be inactive for the reaction with $Ta(On\text{-}C_4H_9)_5$ vapor. After degassing at 773 K in a stream of helium, the catalyst sample was treated with steam. At that time the band at 2900–3000 cm^{-1} disappeared. This shows that *n*-butoxy groups were hydrolyzed to form *n*-butanol by treatment with steam and the *n*-butanol was removed. The band at 3680 cm^{-1} began to appear when the catalyst sample was heat treated at 773 K in a stream of helium. The wavenumber due to the hydroxyl group of Ta_2O_5/SiO_2 (ALK) was different from the wavenumbers of hydroxyl groups of $Ta_2O_5 \cdot nH_2O$ and SiO_2. These results imply that the structure of the acid sites of Ta_2O_5/SiO_2 (ALK) was different from that of the hydrated tantalum oxide. In other words, the unique acid property and catalytic performance of Ta_2O_5/SiO_2 (ALK) seem to be related to the new hydroxyl group, which was formed by well-controlled reaction between tantalum alkoxide and surface hydroxyl groups of silica. The preparation processes for the silica-supported tantalum oxide is shown in Fig. 7.

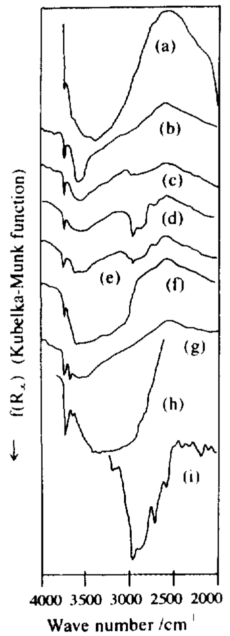


FIG. 6. FTIR diffuse reflectance spectra of the preparation processes for tantalum oxide supported on SiO_2. The spectra are (a) SiO_2 at 293 K, (b) SiO_2 at 773 K, (c) SiO_2 after introducing $Ta(On\text{-}C_4H_9)_5$ vapor at 373 K for 1 h, (d) the same procedure as (c) for 5 h, (e) SiO_2 degassed at 773 K, (f) SiO_2 treated with steam at 573 K, (g) SiO_2 degrassed at 773 K, (h) hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$), and (i) $Ta(On\text{-}C_4H_9)_5$ vapor.

The activities and selectivities of the supported tantalum oxide catalysts prepared by the reaction between $Ta(On\text{-}C_4H_9)_5$ and surface hydroxyl groups were changed by the selection of carriers, as shown in Table 6. Silica was the best carrier for tantalum oxide. Tantalum oxide supported on the other carriers, namely, Al_2O_3, TiO_2, MgO, and SiO_2–Al_2O_3, was less active and less selective for caprolactam. The morphologies of the tantalum oxide supported on these carriers were almost same as that of the Ta_2O_5/SiO_2 (ALK), which was confirmed by SEM and EPMA. However, there were clear differences in the

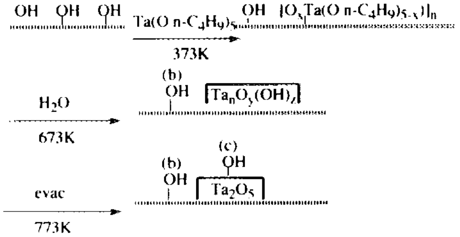


FIG. 7. Scheme of the preparation processes for the silica-supported tantalum oxide. The wavenumbers due to hydroxyl groups are (a) 3500–3600 cm^{-1}, (b) 3730 cm^{-1}, and (c) 3680 cm^{-1}.

TABLE 6

Effect of Carriers of Tantalum Oxide for the Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime[a]

Carrier	Supported amount of Ta_2O_5 (wt%)	Catalyst weight (mg)	Oxime conversion (%)	Caprolactam selectivity (%)	Cyclohexanone selectivity (%)	Caprolactam yield (%)
SiO_2	4.3	202	96.5	97.5	1.8	94.1
Al_2O_3	4.2	311	73.2	74.1	5.4	54.2
TiO_2	3.8	245	60.2	44.5	5.9	26.8
MgO	4.0	298	43.5	74.1	5.3	32.2
SiO_2–Al_2O_3	4.2	305	82.1	78.8	5.7	64.7

[a] The reaction conditions are described under Experimental. Running time was 1 h.

shapes of the Ta L_I-XANES spectra, especially peak tops among the tantalum oxide supported on these carriers (12). The electronic structure and symmetry around tantalum in supported tantalum oxides seem to be different from each other, and their effects on catalytic performance are under further investigation.

CONCLUSIONS

Silica-supported tantalum oxide catalysts (Ta oxide/SiO_2 (ALK)), prepared by chemical reaction between tantalum alkoxide and surface hydroxyl groups of SiO_2, exhibited high catalytic efficiency for the vapor-phase Beckmann rearrangement of cyclohexanone oxime to caprolactam. The oxime conversion reached 96.5%, and the selectivity for caprolactam was 97.5% at 573 K. The activity and selectivity were preserved during 10 h. The effects of precursors of tantalum oxide, physical properties of catalyst carriers for tantalum oxide, and preparation conditions on the catalytic performances were studied, and the important factors in high catalytic efficiency were discussed.

The following key points emerge from this study:

(1) The pore structure of silica carriers was important for the catalytic performance. The high ratio (>90%) of the pore volume for fine pores with diameters from 4 to 200 nm to total pore volume (4 to 15,000 nm in diameter) of silica carriers was effective. The fine pores seem to fill the effective role of diffusion of oxime and caprolactam. Tantalum oxide catalysts supported on Al_2O_3, TiO_2, MgO, and SiO_2–Al_2O_3 were less active and less selective for the Beckmann rearrangement.

(2) Ta_2O_5/SiO_2 (IMP) catalyst, prepared by impregnation of silica with an aqueous $TaCl_5$ solution, and hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$) were less active and less selective, compared with Ta_2O_5/SiO_2 (ALK) catalyst. A large number of acid sites of intermediate strength, measured by NH_3-TPD method, existed on Ta_2O_5/SiO_2 (ALK) and were effective for the Beckmann rearrangement. On the contrary, strong acid sites appeared on Ta_2O_5/SiO_2 (IMP) and hydrated tantalum oxide. Oxime and/or caprolactam seem to adsorb tightly on such strong acid sites, and the Beckmann rearrangement was prevented from proceeding. The difference in the acid property and catalytic performance between Ta_2O_5/SiO_2 (ALK) and Ta_2O_5/SiO_2 (IMP) was assumed to be related to the difference in morphology of tantalum oxide. Well-dispersed tantalum oxide species formed on the surface of Ta_2O_5/SiO_2 (ALK), which was observed by SEM and EPMA. Furthermore, the pore structure hardly changed in the course of the catalyst preparation and the Beckmann rearrangement in the case of Ta_2O_5/SiO_2 (ALK), although the pore volume decreased drastically in the case of Ta_2O_5/SiO_2 (IMP).

(3) The reaction between tantalum alkoxide vapor and the surface hydroxyl groups of SiO_2 was observed by FTIR diffuse reflectance spectrometer. The absorption band at 3680 cm^{-1} appeared on Ta_2O_5/SiO_2 (ALK), assigned to a new hydroxyl group, and the wavenumber was different from the wavenumbers of hydroxyl groups of hydrated tantalum oxide and silica. The unique acid property and catalytic performance of Ta_2O_5/SiO_2 (ALK) were discussed in connection with the new hydroxyl group.

(4) Good initial activity and high selectivity for caprolactam were observed over boron oxide supported on alumina catalyst. However, the oxime conversion declined significantly. The NH_3-TPD profile of B_2O_3/Al_2O_3 catalyst was similar to that of Ta_2O_5/SiO_2 (ALK). Although the supported amount of tantalum oxide of Ta_2O_5/SiO_2 (ALK) scarcely changed during the Beckmann rearrangement, loss in supported amount of boron xoide of B_2O_3/Al_2O_3 was substantial. Tantalum oxide of Ta_2O_5/SiO_2 (ALK) was more stable than boron oxide of B_2O_3/Al_2O_3 in the course of reaction.

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