Gas-phase Catalytic Beckmann Rearrangement over Crystalline BPO_4 of Dehydration Ability

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The crystalline BPO_4 with a P/B ratio around 1.5 prepared by dehydration of boric and phosphoric acid was found to be an effective heterogeneous catalyst for the gas-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.

Based on the concern about chemical processes with waste-minimization, the gas-phase Beckmann rearrangement (GBR) has long been studied with a wide variety of solid acid catalysts such as single and mixed metal oxides, and zeolites.[1] Recent studies of the catalysts used in the commercial GBR process for ε-caprolactam production emphasized that the silanol nests with weak acid strength or even the neutral silanol sites presented on the external surface of highly siliceous zeolites with a MFI structure are effective for this rearrangement.[2] The argument for the effective sites seems to be settled, whereas catalysts for the GBR can still undergo improvement. In contrast with a lot of study focusing on the acidity of the catalyst surface, little attention has been paid to chemical properties of the active sites other than acidity. During the course of a study on homogeneous BR, we have become interested in the oxides of the late 3rd period elements ($T = Si$, P, and S) possessing strong dehydration ability as a catalyst for the GBR. It is known that phosphorus pentoxide is an effective acid anhydride for BR in the liquid-phase, though this does not act as a catalyst according to an interaction with amide product in a homogeneous system. Several efforts to achieve the catalytic cycle of P_2O_5 for the Beckmann rearrangement have been rewarded with a success in the liquid phase using DMF and an ionic liquid as the solvent.[3] In this study, we focused on a mixed-acid anhydride (polyacid without a proton) of boric and phosphoric acids instead of P_2O_5 which sublimes and melts at a high temperature. Here we show that the crystalline BPO_4 with an excess P is an effective heterogeneous catalyst for the GBR of cyclohexanone oxime (OXM) to ε-caprolactam (CL).

BPO_4 with different P/B ratios was prepared from an aqueous solution of boric acid and 85% phosphoric acid (P 0.12 mol).[4] Twelve gram of oxalic acid was added to the solution to facilitate dehydration and crystallization of BPO_4 during the later heating processes. After concentration of the solution and drying at 120 °C in air, about 3 g of the sieved sample was heated in air and then in an N_2 stream at 500 °C for 1 h to obtain the dehydrated forms. All the prepared BPO_4 samples within P/B ratios 1–2 showed the XRD pattern of tetragonal BPO_4 with cristobalite structure (JCPDS 34-0132, see: Supporting Information). Since small amounts of boric and phosphoric acid were sublimed during the calcination at 500 °C in an N_2 stream, the P/B ratio of the dehydrated samples was determined by ICP. The P/B ratios of the samples after the heating slightly deviated from those of the original. The GBR of OXM was conducted under atmospheric pressure using a continuous flow reactor with a quartz tube (i.d. 6 mmϕ) in an electric furnace. The BPO_4 dehydrated at 500 °C was loaded into the tube in a dry atmosphere to prevent hydration by water in ambient air. The reactor effluent collected at prescribed time intervals was analyzed using a GC.

Table 1 lists our results of the catalytic performance of BPO_4 for the GBR of OXM after 160 min time on stream. With P/B ratios greater than 1, BPO_4 exhibited higher activity and selectivity whereas the surface area remarkably decreased by raising the P/B ratio. The highest CL selectivity more than 90% at 98% conversion was obtained over the BPO_4 with a P/B ratio around 1.5 for the GBR using anhydrous benzene as a diluent at 300 °C. The inferior performance of the catalyst with P/B ratio above 1.8 to that around 1.5 would be due to the excessive decrease in surface area. The dependence on the P/B ratio similar to the catalytic performance for the GBR was obtained in the examination of dehydration ability for a reaction of *p*-toluenesulfonic acid to *p*-toluenesulfonic acid anhydride (see: Supporting Information). The results indicate that the number of the effective ≡P–O–P≡ sites of ability to dehydrate *p*-toluenesulfonic acid increases as P/B ratio increases and that such acid anhydride sites are also responsible for the high catalytic performance in the GBR.[5]

With anhydrous benzene as a diluent, the BPO_4 (P/B =

Table 1. The gas-phase Beckmann rearrangement of cyclohexanone oxime over BPO_4 catalysts[a]

Catalyst (P/B)[b]	S_{BET} /$m^2 \cdot g^{-1}$	Diluent	Conv./%	Selectivity[b]/%					Yield of CL/%
				CL	CHAN	CHEN	HXNs	Others	
BPO_4 (1.07)	19	Benzene	47.0	51.1	5.3	3.3	1.3	39.1	24.0
BPO_4 (1.32)	6	Benzene	97.5	84.3	2.5	3.1	1.1	9.0	82.2
BPO_4 (1.55)	2	Benzene	97.3	92.9	1.9	1.2	1.2	2.7	90.4
BPO_4 (1.84)	1	Benzene	83.1	85.7	0.9	1.6	2.0	9.8	71.2
Silicalite-1[d]	10.4[e]	Benzene	65.0	83.2	3.6	4.4	3.4	5.3	54.1
BPO_4 (1.55)		Ethanol	66.7	47.1	18.2	1.5	6.4	26.6	31.4
Silicalite-1		Ethanol	77.8	91.3	1.0	1.5	1.9	4.3	71.0

[a] $T = 300$ °C, $P = 0.1$ MPa, cyclohexanone oxime:diluent:N_2 = 1:10:30 (molar), WHSV of cyclohexanone oxime = 1 h^{-1}, catalyst amount = 0.20 g, time on stream = 160 min (collected from 140 min to 180 min). [b] P/B ratio determined by ICP. [c] CL = ε-caprolactam, CHAN = cyclohexanone, CHEN = cyclohexen-1-one, HXNs = hexanenitrile + 5-hexenenitrile. [d] Time on stream = 120 min (collected from 100 min to 140 min). [e] Outer surface area.

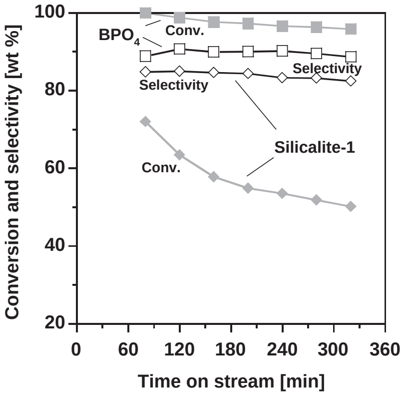

Figure 1. Change in conversion and selectivity of ε-caprolactam with time on stream in the gas-phase Beckmann rearrangement of cyclohexanone oxime using anhydrous benzene as a diluent. Reaction conditions are given in Table 1 footnote.

1.55) rivaled silicalite-1 ($Si/Al_2 = 1250$, supplied from the Catalysis Society of Japan) in the selectivity to CL. The activity normalized to the unit surface area was much higher for the BPO_4 than silicalite-1. The OXM conversion and CL selectivity with time on stream are shown in Figure 1 for the BPO_4 ($P/B = 1.56$) and silicalite-1. The conversion decreased rapidly with time for silicalite-1. High performance of the BPO_4, on the other hand, was kept after reaching a steady state level.[6] The decrease in conversion was within 5% for 6 h, while coke formation on the catalyst was visually observed after the reaction. When ethanol was used as a diluent, the performance of BPO_4, however, was significantly damaged as opposed to that of silicalite-1 for which the promotion effects using alcohol were reported (see: Table 1).[7] This indicates that the nature of the active sites is not consistent with those for the catalysts comprising Si and O. For the BPO_4 of dehydration ability, the surface alkoxide and/or hydroxyl group generated in the interaction with alcohol would lead to undesired side reactions.

With respect to the mechanism on the BPO_4 surface, we expect that the properties of the main group elements of the late 3rd period (T = Si, P, and S) could be advantageous to completion of the catalytic cycle. On the analogy of the mechanism of homogeneous BR, the BPO_4 of strong dehydration ability should initiate the rearrangement via the OXM-phosphoric acid ester intermediate (**a** in Figure 2) under anhydrous condition.[8] The bond between the main group elements of the late 3rd period (T = Si, P, and S) and O or N involves a $d\pi$–$p\pi$ orbital interaction originating from low energy level for 3*d* orbital of T and the lone pair of electrons of O and N.[9] Thereby, it is possible for the surface T sites to interact more preferably with O than N.[10,11] In addition, nucleophilic bases are more likely to attack and substitute on the T sites than to coordinate to the T sites, which is different from those for so-called Lewis acid sites consisting of early period elements. If a similar approach is applicable to the present system at 300 °C, the OXM nucleophile is possible to kinetically substitute the CL formed by BR on the T sites (CL-phosphoric acid ester, **b** in Figure 2), thus completing the catalytic cycle.

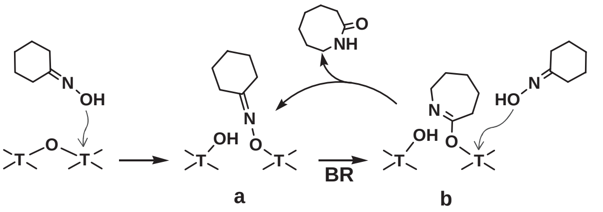

Figure 2. Possible mechanism for catalytic cycle completion over BPO_4.

In summary, we found that the BPO_4 of strong dehydration ability is an effective catalyst for the GBR. The results suggest that the acid anhydride sites play a major role for the catalytic GBR. Theoretical and spectroscopic approaches are ongoing to understand the nature of the ≡T–O–T≡ sites for the BPO_4.

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References and Notes

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6 More than 20 years ago, Haber and Szybalska concluded that BPO_4 with a P/B ratio above 1 shows no activity for the GBR on the basis of their results obtained with a pulse reactor. In the present study, material balance between the inlet and outlet of the reactor was poor for several ten minutes just after feeding the reactant. We guess that they measured the catalytic performance at an unstable state during the initial period even if they turned their attention to the dehydration of the catalysts prior to the catalytic examination: J. Haber and U. Szybalska, *Faraday Discuss.*, **72**, 263 (1981).

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