Catal Lett (2007) 118:300–305
DOI 10.1007/s10562-007-9201-y

Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime Over Rare Earth Pyrophosphates

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Received: 15 December 2006 / Accepted: 30 June 2007 / Published online: 25 July 2007

Abstract A new application of rare earth pyrophosphates in vapor phase Beckmann rearrangement of cyclohexanone oxime was investigated. The rare earth phosphates were characterized by means of XRD, FT-IR, NH_3-TPD and water contact angle measurement. It was found that the weak surface acidity and appropriate surface hydrophobicity should be two key factors in the excellent performance of these catalysts.

Keywords Rearrangement · Rare earth · Pyrophosphates · Hydrophobicity · Cyclohexanone oxime

1 Introduction

In recent years, the investigations of the synthesis and characterization of rare earth phosphates have been gained much attention for their practical or potential applications in optical materials (including laser, phosphors, anti-UV materials), sensors, ceramic materials and heat-resistant materials, etc [1–8]. The application of rare earth phosphates is also very attractive in heterogeneous catalysis [9–15]. Takita et al. [9] found that some rare earth phosphates showed strong acid sites in the oxidative dehydrogenation of iso-butane, it suggested that it was possible to be a acid catalyst for rare earth phosphates. Rare earth phosphates enable to show versatile compositions and structures by using the diversity of preparation methods, which makes the surface acidity of rare earth phosphates can be modified. However, despite of these very promising properties, the applications of rare earth phosphates in acid catalysis are still very limited. This is because the acid strength of rare earth phosphates is generally lower than other solid acids.

The Beckmann rearrangement is a typical acid catalysis reaction in which oximes are transformed to the corresponding amides. The most important industrial application of Beckmann rearrangement is the conversion of cyclohexanone oxime to caprolactam, a raw material of Nylon 6. However, the current liquid phase industrial process still exist many problems such as large amount of undesirable byproduct of ammonium sulfate and the corrosion of the reaction vessel due to using concentrated sulfuric acid or oleum as catalyst. To overcome these problems, many solid acids have been tested in the vapor phase Beckmann rearrangement of cyclohexanone oxime, including silica-alumina, supported B_2O_3, Ta_2O_5/SiO_2, molecular sieve materials like Y, ZSM-5, TS-1, SAPO-11, FSM-16 and ilerate etc. Dahlhoff et al. has surveyed the heterogeneously process of Beckmann rearrangement over solid acids [16]. The conclusion on solid acids was: these solid acid could eliminate or resolved the problems from the liquid acid, but it brought about other problems such as the rapid catalysts deactivation and the low selectivity to caprolactam. Very recently, Beckmann rearrangement in the vapor-phase over a high silica MFI zeolite catalyst has been tested in industrial scale by Sumitomo Chemical Co. Ltd [17].

In present study, a new application of rare earth (Ce(III), La(III), Eu(III), Nd(III), Sm(III), Y(III)) phosphates especially Ce(III), La(III) pyrophosphates in the vapor phase Beckmann rearrangement of cyclohexanone oxime has

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been investigated systematically. And the possible reasons for better catalytic performance have also been discussed.

2 Experimental

Rare earth (Ce(III), La(III), Eu(III), Nd(III), Sm(III), Y(III)) pyrophosphates ($Re_4(P_2O_7)_3$) were synthesized by precipitation method and the typical preparation process as following: 0.00673 mol $Na_4P_2O_7 \cdot 10H_2O$ and 0.00897 mol rare earth nitrate were dissolved separately in 100 mL H_2O. Then the sodium pyrophosphate solution was droped to the rare earth nitrate solution to precipitate with stirring and kept stirring for an additional 18 h. The precipitate was recovered by filtering off, washing, and dried at 110 °C for 12 h. After calcined at 400–600 °C for 3 h, the samples were crushed and sieved to 20–40 mesh. The pH value in precipitation process can be adjusted by a small quantity of HNO_3 to promote the performance of catalysts. The alkali modified catalyst was obtained by impregnating a certain of calcined catalyst with an aqueous solution of KOH, then dried and finally calcined at ~500 °C for 3 h. For comparation, cerium (III) phosphate ($CePO_4$) and cerium (III) tripolyphosphate ($Ce_5(P_3O_{10})_3$) were also prepared by same precipitation method, in which the kind and the amount of precipitant were changed according to their chemical formula.

The powder X-ray diffraction (XRD) data were obtained by using an X-ray diffractometer (D/MAXIIB, Rigahu), operating at 40 kV and 10 mA, using Cu Kα radiation combined with Nickel filter. FT-IR spectra were taken on the instrument BRUKER Vertex 70 FTIR by using KBr wafers with the resolution of 1 cm^{-1}. The specific surface area was measured by using Mircomeritics ASAP 2010. NH_3-TPD spectra were performed on a homemade apparatus equipped with TCD as a detector. After treated at 550 °C for 1 h and cooled to 100 °C in the same atmosphere, the samples were exposed to 20 mL/min NH_3 for 30 min, and then swept with helium at a rate of 20 mL/min, finally the sample was heated at a rate of 10 °C/min in helium. Contact angles were measured on a Drop Shape Analyzer (DSA10, KRÜSS GmbH, Hamburg 2001) at ambient temperature. Water droplets (about 2 μL) were dropped carefully onto well-pressed PAN samples surface. The average contact angle value was obtained by measuring at three different positions of the same sample.

The Beckmann rearrangement of cyclohexanone oxime was carried out in a fixed bed glass reactor with an internal diameter of 8 mm. Before the reaction, the catalyst was heated at 350 °C in N_2 stream for 1 h. Then a mixture of 10 wt.% cyclohexanone oxime in benzene was inject to the reactor by a syringe pump at WHSV of 0.43 h^{-1} under N_2 flow at 350 °C. The reactor effluent was collected in a liquid nitrogen-trap and analyzed by GC using a SE-60 capillary column. Here, chlorobenzene was chosen as the internal standard, which was added into product after reaction.

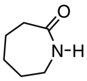
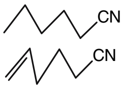
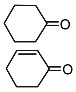
3 Results and Discussion

Table 1 gives the results of the rearrangement reaction over some rare earth pyrophosphates at the same reaction condition. All catalysts were prepared by same precipitation method and calcined at 550 °C. From Table 1, it was found that the conversion of cyclohexanone oxime over rare earth pyrophosphates all reaches to ~99% except La and Y. It shows that most rare earth pyrophosphates were active for the conversion of cyclohexanone oxime. However, the selectivity of rare earth pyrophosphates was not so good as the results of high siliceous ZSM-5 or supported B_2O_3 (both ~95%). It seems that the formation of polymers and cokes affects the performance of these catalysts at this high reaction temperature. Anyway, the high activity and relative good selectivity of these catalysts suggests they are of the prospective catalysts for this reaction.

Table 2 gives the result of cerium (III) pyrophosphate compared with cerium (III) phosphate, cerium (III) tripolyphosphate and lanthanum (III) pyrophosphate. From Table 2, all rare earth phosphates show the better performance except cerium phosphate. Cerium (III) phosphate shows poor activity for Beckmann rearrangement, in which the conversion is only 1.6% after 2 h. The conversions of oxime over cerium (III) pyrophosphate, cerium (III) tripolyphosphate and lanthanum (III) pyrophosphate were also slowly decreased with the time on stream gradually. The decrease in the conversion for these three catalysts was in the order: cerium (III) tripolyphosphate > lanthanum (III) pyrophosphate > cerium (III) pyrophosphate. The selectivities of the three catalysts were very similar at initial time, but the selectivities of cerium (III) pyrophosphate and lanthanum (III) pyrophosphate exhibited a little increase with the time on stream, whereas the cerium (III) tripolyphosphate suffered a quick decrease within the time on stream. The specific surface areas of three types of cerium phosphates were also listed in Table 2. From Table 2, the specific surface area of cerium (III) phosphate is 53.1 m^2/g, which is much greater than that of cerium (III) pyrophosphate (13.8 m^2/g), but the former showed very poor activity. This can be ascribed to the surface acidity of the phosphates.

Figure 1a–f showed the NH_3-TPD profile of the four samples, which is to illuminate the action of polyphosphate anions. From Fig. 1a, the surface acidity of cerium (III) phosphate is very weak when compared with cerium (III) pyrophosphate, cerium (III) tripolyphosphate and

Table 1 Vapor phase Beckmann rearrangement of cyclohexanone oxime on rare earth catalysts[a]

Catalyst	Conversion (%)	Selectivity (%)			other[b]
					
$Ce_4(P_2O_7)_3$	97.6	74.2	5.0	6.5	14.3
$La_4(P_2O_7)_3$	90.7	70.6	3.7	5.5	20.2
$Eu_4(P_2O_7)_3$	99.3	66.5	9.3	9.3	16.1
$Nd_4(P_2O_7)$	99.1	68.9	5.5	7.2	18.4
$Sm_4(P_2O_7)_3$	99.5	60.3	8.7	9.3	21.7
$Y_4(P_2O_7)$	94.4	50.4	10.3	16.8	22.5

[a] Reaction Conditions: P = 0.1 Mpa, T = 350 °C, WHSV = 0.43 h^{-1}, Catalyst charge = 0.60 g, cyclohexanone oxime: benzene = 1:9, N_2 = 80 ml/min. time on stream = 2 h

[b] Mostly coke and polymer

Table 2 Vapor phase Beckmann rearrangement of cyclohexanone oxime on Re(III) phosphates[a]

Catalyst	t/h	Conversion of oxime (%)	Selectivity of caprolactam (%)	BET surface area (m^2/g)
$CePO_4$	2	1.6	44.1	53.1
$Ce_4(P_2O_7)_3$	2	97.6	74.2	13.8
	8	75.9	78.6	
$Ce_5(P_3O_{10})_3$	2	66.3	76.1	8.8
	8	36.6	56.7	
$La_4(P_2O_7)_3$	2	90.7	70.6	
	8	61.3	72.8	
$Ce_4(P_2O_7)_3^b$	2	98.1	81.8	
	8	83.9	78.6	
$Ce_4(P_2O_7)_3^c$	2	32.4	49.0	

[a] Reaction Conditions: P = 0.1 Mpa, T = 350 °C, WHSV = 0.43 h^{-1}, Catalyst charge = 0.6 g, cyclohexanone oxime: benzene = 1:9, N_2 = 80 ml/min

[b] 3.2 wt.% KOH modified $Ce_4(P_2O_7)_3$

[c] 6.3 wt.% KOH modified $Ce_4(P_2O_7)_3$

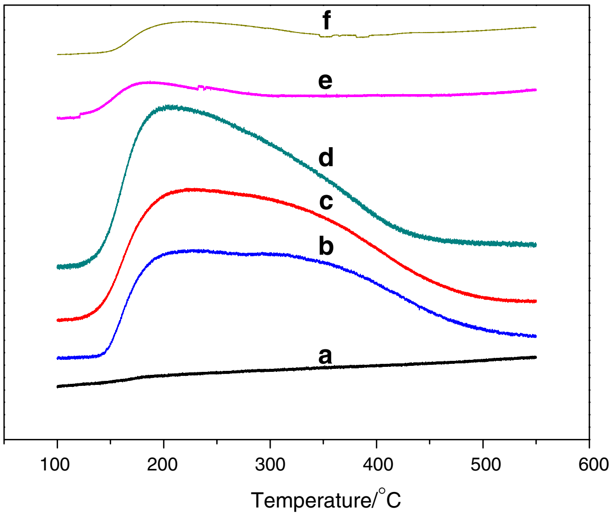


Fig. 1 NH_3-TPD profile of (**a**) cerium (III) phosphate (**b**) cerium (III) pyrophosphate (**c**) cerium (III) tripolyphosphate; (**d**) 3.2 wt.% KOH modified $Ce_4(P_2O_7)_3$ (**e**) 6.3 wt.% KOH modified $Ce_4(P_2O_7)_3$ (**f**) lanthanum (III) pyrophosphate

lanthanum (III) pyrophosphate. There are obviously two NH_3 desorption peaks at about 200 °C and 320 °C for cerium (III) pyrophosphate (Fig. 1b) and cerium (III) tripolyphosphate (Fig. 1c). But there is only one weak peak at 200 °C for lanthanum (III) pyrophosphate (Fig. 1f). This means that the weak acidic site is active center in Beckmann rearrangement.

$CePO_4$ possesses the higher specific surface area than $Ce_4(P_2O_7)_3$ and $Ce_5(P_3O_{10})_3$, but it's surface acidity is much weaker than the other two samples. It suggests that polyphosphate anions might be a key factor for the formation of surface acidity, which is playing an important role in the reaction of Beckmann rearrangement. Similarly, the activity of $CePO_4$ is much lower than $Ce_4(P_2O_7)_3$ and $Ce_5(P_3O_{10})_3$, this inferior performance of the $CePO_4$ catalyst might be ascribed to its insufficient amount of surface acid sites compared to the other two samples. The better performance of $La_4(P_2O_7)_3$ further proved the importance of polyphosphate anions for the surface acidity and activity.

The XRD experiment results show that the intensity of all the XRD peaks of the four samples are very weak (Fig. 2), which indicates that $CePO_4$, $Ce_4(P_2O_7)_3$, $Ce_5(P_3O_{10})_3$ and $La_4(P_2O_7)_3$ possess the poorly ordered structure under the calcination conditions in this work. From FT-IR spectra (Fig. 3), the bands at 770 cm^{-1} and 1267 cm^{-1} appeared in $Ce_4(P_2O_7)_3$, $Ce_5(P_3O_{10})_3$ and $La_4(P_2O_7)_3$, which are attributed to $P_2O_7^{4-}$ and $P_4O_{12}^{4-}$ [18], which do not appeared in $CePO_4$. Combining the activities and FT-IR spectra of these four catalysts, it can be concluded that $P_2O_7^{4-}$ structure (polyphosphate anions) in $Ce_4(P_2O_7)_3$, $Ce_5(P_3O_{10})_3$ and $La_4(P_2O_7)_3$ playing an important role in vapor phase Beckmann rearrangement.

As we know, the hydrophilicity/hydrophobicity of the catalyst surface is also playing a role in the desorption of the products. Dai et al. [19, 20] have reported that an appropriate hydrophobic environment is very important for vapor Beckmann rearrangement. Komatsu et al. [21] also consider the hydrophilicity/hydrophobicity of solvent is very important for the desorption of caprolactam with silicate-1 as catalyst. Hydrophobic surface will favor to the desorption of the polar products. Here, caprolactam is the more polar, so the stronger hydrophobicity of the catalyst surface should be expected in this reaction. The surface hydrophilicity/hydrophobicity of various cerium (III) salts is determined by means of the contact angles for water, the shapes of water on the catalyst films were shown in Fig. 4. The contact angles for water are ~0°, ~12.4° and ~28.6° over cerium phosphate, cerium pyrophosphate and cerium tripolyphosphate, respectively. These results show that pyrophosphate and tripolyphosphate are inheriting a certain degree of surface hydrophobicity, which should affect the activity and selectivity in the Beckmann rearrangement.

It could be found that cerium (III) phosphate is fully hydrophilic, whereas both the cerium (III) pyrophosphate

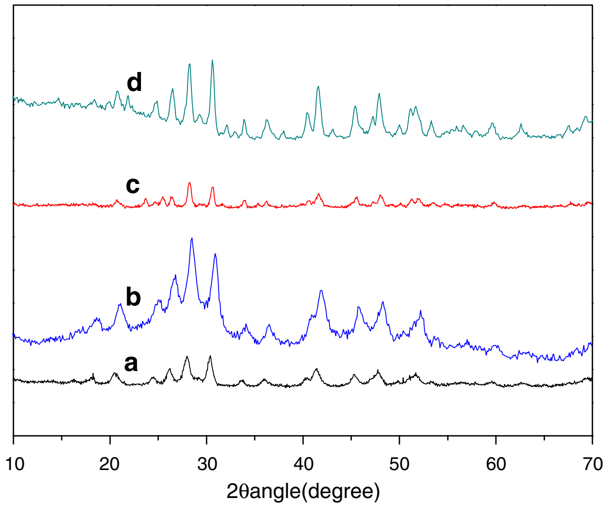


Fig. 2 Powder XRD pattern of (**a**) $CePO_4$, (**b**) $Ce_4(P_2O_7)_3$, (**c**) $Ce_5(P_3O_{10})_3$ and (**d**) $La_4(P_2O_7)_3$

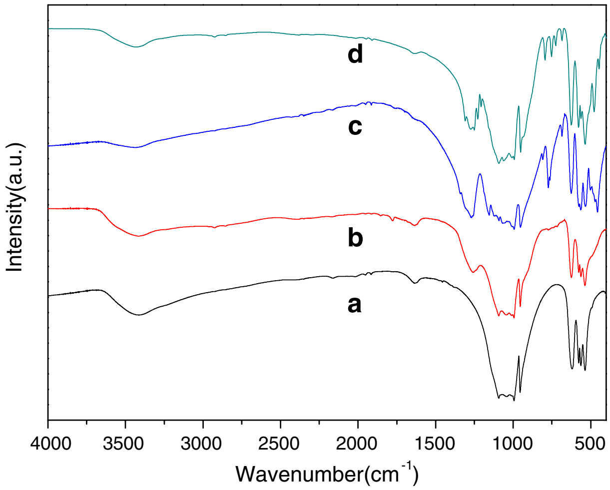


Fig. 3 FT-IR spectra of (**a**) $CePO_4$, (**b**) $Ce_4(P_2O_7)_3$, (**c**)$Ce_5(P_3O_{10})_3$ and (**d**) $La_4(P_2O_7)_3$

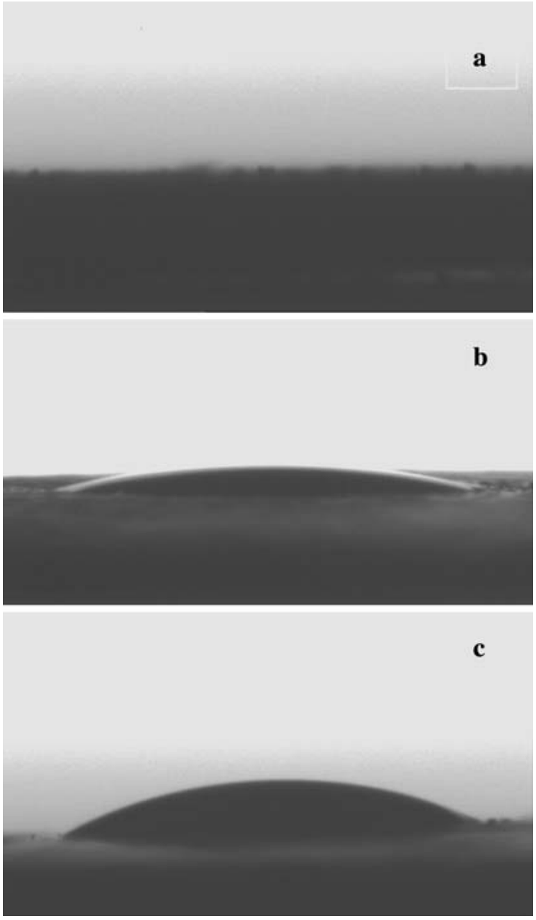


Fig. 4 Shapes of water droplet on surfaces of three samples: (**a**) cerium (III) phosphate (**b**) cerium (III) pyrophosphate (**c**) cerium (III) tripolyphosphate

and cerium (III) tripolyphosphate are some hydrophobic. So the hydrophobic solvent benzene might be difficult to contact the active sites of cerium (III) phosphate, the reactant oxime and produced caprolactam being adsorbed strongly on the surfaces undergo a series of reactions, result in the increase of the byproducts, and finally leads to the rapid deactivation of the catalyst. On the contrary, the surface of cerium (III) pyrophosphate and cerium (III) tripolyphosphate is relatively appropriate hydrophobic, which is more favored to the caprolactam formation and desorption. Cerium (III) tripolyphosphate also showed a quite high initial conversion and selectivity compared to cerium (III) pyrophosphate due to its inherent acid character. However, the conversion of oxime over this catalyst decreases much faster than cerium (III) pyrophosphate. It should be explained on the fact, that the specific surface area of this catalyst is smaller compared to cerium (III) pyrophosphate (Table 2). So the active sites on the surface are easier to be covered with coke by side reactions and it results in the rapid deactivation of Cerium (III) tripolyphosphate.

As the description in foregoing part, Fig. 1b shows that there are two desorption peaks on the NH_3-TPD profile of cerium (III) pyrophosphate, which showed that there are two kinds of acid sites on the surface of this catalyst. NH_3 desorpted peak at about 200 °C is assigned to the weak acid sites, and the desorpted peak at about 320 °C is assigned to the medium strength acid sites.

Many researchers [22, 23] suggested that intermediate acid sites of B_2O_3-loaded catalysts are active sites for the Beckmann rearrangement of cyclohexanone oxime. As for molecular sieve catalysts, strong Brønsted acid, [24] medium Brønsted acid, [25, 26] the neutral [27] or weakly acid silanol groups or silanol nests [28, 29] have ever been reported to be effective for the Beckmann rearrangement reaction. In addition, Haber et al. believed that Lewis acid sites can also been the active sites of the Beckmann rearrangement [30].

In order to investigate the action of these two kinds of acid sites in the rearrangement, the TPD experiment of alkali modified cerium (III) pyrophosphate was also carried out, as shown in Fig. 1d–e. The results of catalysis reactions are also listed in Table 2. From Fig. 1 and Table 2, in condition of 3.2 wt.% KOH modified cerium (III) pyrophosphate, the medium acid sites have been eliminated by KOH neutralization, but the catalyst still exhibited the better catalytic performance. At the same time, the lifetime of the catalyst and the initial selectivity was obviously improved compared with the no alkali modified one. It indicates that weak acid sites are effective for Beckmann rearrangement while the medium strength acid sites are easier leading to the formation of byproducts at this reaction temperature, in which the forming cokes and polymer accelerate the deactivation. Cerium (III) pyrophosphate modified with 6.3 wt.% KOH showed the weakest acid sites, in which the most of weak acid sites have also been eliminated by KOH neutralization, so the catalyst exhibits poor catalytic performance. This conclusion can also be confirmed further by the testing of lanthanum (III) pyrophosphate. Athough lanthanum (III) pyrophosphate is lack of medium strength acid sites, it still exhibits a high initial conversion of cyclohexanone oxime. Based on above experiment, it can be concluded that the weak acid sites over rare earth pyrophosphates are active sites for the Beckmann rearrangement. The above results also suggested that the catalytic performance of rare earth pyrophosphates could be improved by appropriate surface modification with alkali.

Figure 5 is the comparison of cerium (III) pyrophosphate, lanthanum (III) pyrophosphate and 25% B_2O_3/γ-Al_2O_3, in which cerium (III) pyrophosphate and lanthanum (III) pyrophosphate are both precipitated at the condition of pH is 3 and calcined at 550 °C. Vapor phase Beckman rearrangement of cyclohexanone oxime were carried out at same condition as in Table 1 except 25% B_2O_3/γ-Al_2O_3. B_2O_3/γ-Al_2O_3 was performed at an optimized reaction temperature of 300 °C [31]. Cerium (III) pyrophosphate, lanthanum (III) pyrophosphate and B_2O_3/γ-Al_2O_3 all exhibited high initial conversion, but B_2O_3/γ-Al_2O_3 rapidly deactivated with the time on stream and the conversion decreased from 100% to 60.7% in 8 h. The selectivity also rapidly decreased from 95% to about 80%. However, the cerium (III) pyrophosphate and lanthanum (III) pyrophosphate both caused only a little deactivation and the conversion was still 96.5% and 91.3% at 8 h of time on stream. At the same time, the selectivities of them maintained constant near 80% in all reaction time.

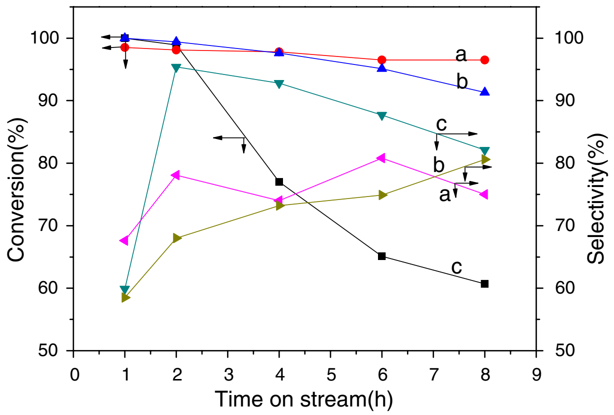


Fig. 5 Comparison of conversion & selectivity of vapor Beckmann rearrangement with time on stream. (**a**) $Ce_4P_2O_7$ (**b**) $La_4P_2O_7$ (**c**) B_2O_3/γ-Al_2O_3 25% B_2O_3/γ-Al_2O_3 was prepared by impregnation of γ-Al_2O_3 in aqueous solution of boric acid, then the catalyst was dried at 110 °C overnight and calcined at 350 °C

Rare earth pyrophosphates are a novel kind of expected catalysts applied in vapor Beckmann rearrangement besides extensively studied B_2O_3-loaded and molecular sieve materials. As detailed narrated in literatures, the lifetime of B_2O_3-loaded catalysts is always limited. The new kind of rare earth pyrophosphates can easily prolong their lifetime by optimize the condition of catalysts preparation and reaction atmosphere in Beckmann rearrangement. However, for industrial purposes selectivity higher than 97–98% should be achieved at 100% conversion. Such selectivity and conversions can be achieved by the application of highly siliceous ZSM-5 or deboronated B-ZSM-5 as catalysts. The performance of the catalysts investigated in this work were inferior to that of above mentioned molecular sieve catalysts, therefore, great improvement is still needed before it become a commercial applied catalyst.

Acknowledgement We thank the Ministry of Science and Technology of China (973 program 2003CB615805) and the National Natural Science Foundation (20573103) for the support of this research.

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