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B_2O_3/ZrO_2 for Beckmann rearrangement of cyclohexanone oxime: optimizing of the catalyst and reaction atmosphere

Bo-Qing Xu [a,*], Shi-Biao Cheng [b], Xin Zhang [a], Qi-Ming Zhu [a]

[a] *State Key Lab of C_1 Chemistry and Department of Chemistry, Tsinghua University, Beijing 100084, China*
[b] *Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China*

Abstract

Optimization of zirconia-supported boria catalyst for the Beckmann rearrangement of cyclohexanone oxime was studied with the control of three preparation parameters: the temperature of support pre-calcination (PCT: 110–700°C), the calcination temperature for the catalyst activation (CAT: 250–600°C), and the load level of boria. When the CAT is limited no higher than 500°C, the lactam yield increases with the PCT and shows maximum numbers with PCT = 350–500°C. This effect of PCT seems not important for the catalyst preparation when the late catalyst activation is done with CAT as high as 600°C. Catalyst preparations with CAT = 600°C agrees with the model that the optimized catalyst has, on the average, about two surface overlayers of boria on the support. Another part of this work focused on effects of the reaction solvents and carrier gases. A remarkable benefit for the lactam synthesis is observed with proper combination of the solvents and carrier gases.
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Keywords: Pre-calcination temperature; Catalyst preparation; B_2O_3/ZrO_2; Beckmann rearrangement; Cyclohexanone oxime

1. Introduction

Owing to its economic importance, the synthesis of ε-caprolactam by the Beckmann rearrangement of cyclohexanone oxime over solid acid catalysts has attracted much attention [1,2]. Supported boria and zeolites or zeotype materials constitute the main two groups of catalysts that have been frequently studied for this purpose [2–11]. Catalyst deactivation due to coke formation is the main obstacle for industrial application of these catalysts [12,13]. Recently, we found that boria supported on zirconia (B_2O_3/ZrO_2) shows, among many modified zirconia catalysts, the best catalysis for the synthesis of ε-caprolactam [14]. With a zirconia support that was arbitrarily calcined at 500°C before the impregnation of boria, the optimum boria load was at ca. 10% (10% B_2O_3/ZrO_2). This catalyst showed superior catalysis for the lactam production at 300°C than boria catalysts supported on Al_2O_3, TiO_2, SiO_2, MgO, and HZSM-5 [15]. During a 6 h on-stream time, the average lactam yield remained as high as 95%. Acid sites of intermediate strength are shown to be crucial for the desired catalysis.

Catalysts supported by zirconia often produce superior catalysis to the ones supported by other oxides for a number of reactions [16–19]. The property of zirconia-supported catalyst is subject to the preparation methods. Temperature (calcination) histories of the support and the supported catalyst could be decisive for catalyst–support interaction [19]. For example, the acidity of sulfated zirconia is known to be affected greatly by the temperature history of the catalyst preparation both before and after the sulfate loading. Loading of the sulfate groups onto the zirconium hydroxide precursor produced the best catalyst with very

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* Corresponding author. Fax: +86-10-6277-0304.
E-mail address: bqxu@mail.tsinghua.edu.cn (B.-Q. Xu).

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strong acid sites; sulfate loading onto zirconia that had a high-temperature calcination history usually produced less strong acidity [19,20]. High-temperature calcination was also shown to be important for better acid catalysis of the WO_3/ZrO_2 catalyst [21].

In the present study, we report some key factors of catalyst preparation that affect the catalysis efficiency of B_2O_3/ZrO_2 catalyst for the Beckmann rearrangement of cyclohexanone oxime. Besides, attempts have been made to optimize the reaction atmosphere for improving the lactam selectivity and for minimizing the catalyst deactivation by selections of the solvents and carrier gases.

2. Experimental

Samples of the catalyst were prepared by incipient wetness impregnation with aqueous solution of boric acid. Zirconyl hydroxide, which was obtained by hydrolysis of $ZrOCl_2\cdot 8H_2O$ with ammonia water, was used as precursor of the support. Details of the catalyst preparation were described earlier [14,15]. Three preparation parameters were controlled for optimizing the B_2O_3/ZrO_2 catalyst: these are the pre-calcination temperature (PCT) (110–700°C) of the hydroxide precursor (before loading of the boria), the catalyst activation (calcination) temperature (250–600°C, after loading of the boria), and the boria load (up to 25 wt.%). The support pre-calcination as well as the catalyst activation were done in static air for 10 h with a muffle. Nitrogen adsorption was conducted to measure the surface area, pore volume and pore-size distribution; some results of the measurement are given in Table 1. The crystal phases of the support and the supported catalyst were characterized with XRD technique. Unless otherwise specified the boria load, measured by ICP-MS, was 9.3–10% in exploring the temperature effects of the support pre-calcination and of the catalyst activation.

The Beckmann rearrangement of cyclohexanone oxime was conducted at 300°C under atmospheric pressure in a flow Pyrex reactor (i.d. 8 mm) with 1.0 g catalyst. A mixture of the oxime, solvent and carrier gas at molar ratio of 1:13:28 was passed into the reactor at WHSV $= 0.32\,h^{-1}$ in terms of the oxime. The oxime was dissolved in the solvent (10 wt.%) and was fed into the reactor with a micro-pump. Before run of the reaction, the catalyst was pretreated at 350°C for 1.5 h in flow of dry nitrogen (60 ml/min). Without further specification benzene is used as the solvent and N_2 as the carrier gas. Other solvents are methanol, ethanol, hexan-1-ol, acetone and cyclohexane. CO_2, He, and H_2 are used as the other carrier gases. Usually, the initial 30 min of the reaction was deducted from the reaction time-on-stream (TOS) since material balance in this initial period was poor. After this 30 min of reaction, products from the reactor were collected each hour in an ice/water trap and were analyzed on a GC equipped with a 20% PEG 20M (2 m) column and an FID detector.

Table 1
Effect of support PCT on the sample texture by BJH analysis of nitrogen adsorption

PCT	ZrO_2 support			10% B_2O_3/ZrO_2-PCT-350		
	S (m^2/g)[a]	V (cm^3/g)[b]	D (nm)[c]	S (m^2/g)[a]	V (cm^3/g)[b]	D (nm)[c]
110	296	0.288	2.0	200	0.197	<2.0
210	328	0.362	2.4	219	0.232	2.3
300	294	0.355	3.2	211	0.250	2.9
350	124	0.282	13.2	102	0.229	11.5
400	99	0.224	14.8	77	0.181	12.5
500	62	0.208	21.9	42	0.154	19.0
700	24	0.125	118.0	12	0.074	114.0

[a] Cumulative specific surface area.
[b] Cumulative pore volume.
[c] Most probable pore diameter.

3. Results

We will name the catalyst samples by B_2O_3/ZrO_2-PCT-CAT. Here, PCT indicates the pre-calcination temperature of the support before it is loaded with boria, while CAT is the catalyst activation temperature after the boria loading. In some cases, boria load in the sample is indicated as the weight percentage of the catalysts. For example, 10% B_2O_3/ZrO_2-500-350 refers to the sample that was prepared by loading with 10% boria to the support obtained by pre-calcination at 500°C of the zirconyl hydroxide; the calcination after the boria loading was done at 350°C to “activate” the catalyst.

An earlier publication investigated the effect of reaction temperature on the Beckmann reaction with 10% B_2O_3/ZrO_2-500-350 catalyst by the present nomination; the optimum reaction temperature was

Table 2
Effect of support PCT on activity and selectivity of 10% B_2O_3/ZrO_2-PCT-350 catalysts[a]

PCT	Conversion (%)	Product selectivity (wt.%)							
		Lactam	c-Hexanone	c-Hexenone	Aniline	5-Cyanopent-1-ene	Phenol	TH-carbazide[b]	OH-phenazine[c]
110	84.7	43.5	20.9	16.4	0.8	0.7	1.3	5.6	3.7
210	93.8	63.4	16.7	12.2	0.7	0.5	0.6	4.3	2.6
300	96.3	76.5	0.6	1.0	0.2	0.5	0.5	8.3	11.9
350	90.6	94.1	4.1	0.7	0.5	0.5	–	–	–
400	85.7	95.2	3.2	0.3	0.4	0.6	–	–	–
500	88.2	96.7	2	0.3	0.3	0.4	–	–	–
700	62.9	97.5	1.5	0.2	0.5	0.1	–	–	–

[a] The data are averaged for TOS = 8 h.
[b] Tetrahydrocarbazide.
[c] Octahydrophenazine.

shown to be 300–320°C [15]. In this present work, all the reaction tests are conducted at 300°C to examine effects of the support pre-calcination and the catalyst activation. Unless otherwise specified, the reaction data for every catalyst represent the averages during 8 h TOS.

3.1. Effects of the support pre-calcination and the catalyst activation

Table 2 shows the reactivity and product selectivity of cyclohexanone oxime over a series of 10% B_2O_3/ZrO_2-PCT-350. The activation temperature of these catalysts is 350°C, which was the most frequently used activation temperature in many works for supported boria catalysts [4–7,12]. The conversion of cyclohexanone oxime is clearly seen to increase with increasing PCT up to 300°C, further increase in PCT results in lowering the oxime conversion. On the other hand, the increase in PCT results steadily in increase of the selectivity for the desired lactam. While the lactam selectivity is less than 50% when the catalyst is prepared directly with the zirconyl hydroxide dried at 110°C (PCT = 110°C), it is improved to more than 90% when the PCT is $\geq$350°C. When the catalyst is made with a PCT = 700°C, the lactam selectivity can be as high as 98%.

The undesirable products are dominated by cyclohexanone and cyclohexenone. Other byproducts of significance are tetrahydrocarbazide and octahydrophenazine. Aniline, 5-cyanopent-1-ene and phenol are formed only in trace amount. All these byproducts are reduced rapidly with the increase in PCT up to 300°C. Formations of phenol, tetrahydrocarbazide and octahydrophenazine become undetectable over the catalysts with higher PCTs.

Table 3 compares the PCT effects on the Beckmann reaction over the catalysts that are calcined with CAT = 250, 500, and 600°C, respectively. The boria load in these catalysts are kept at the level of 9.3–10 wt.%. These data indicate that the effects of PCT observed with the 10% B_2O_3/ZrO_2-PCT-350 catalysts are held when the CAT is no higher than 500°C. It is remarkable, however, that catalyst activation at 600°C results, irrespective of the pre-calcinations, in very high selectivity for the desired lactam (96–97%). Catalysts prepared with this CAT produce little cyclohexanone (1–3%), and trace amounts of cyclohexenone, 5-cyanopent-1-ene and aniline (<0.5%) as the byproducts.

Fig. 1 summarizes the effects of CAT and PCT on the lactam synthesis. It is clear that the PCT is determinative for the catalysis when the CAT is limited no higher than 500°C. With this limitation, maximum lactam yields are obtained with PCT = 350–500°C. This effect of PCT disappears when the late catalyst activation is done with CAT = 600°C.

3.2. Effect of the boria load

Two samples of the support pre-calcined at 300 and 500°C, respectively, are used for optimizing of the boria load. After the impregnation with different load levels of boria ($\leq$25%), the two series of catalyst samples obtained are activated by calcination at 600 and 350°C, respectively, and, they are

Table 3
Effect of CAT on activity and selectivity of 10% B_2O_3/ZrO_2-110, 300 and 500-CAT catalysts[a]

CAT (°C)	Conversion (%)	Product selectivity (wt.%)							
		Lactam	c-Hexanone	c-Hexenone	Aniline	5-Cyanopent-1-ene	Phenol	TH-carbazide[b]	OH-phenazine[c]
PCT = 110°C									
250	80.4	43.9	18.5	16.2	1.3	0.9	1.5	7.5	3.7
500	74.3	63.6	13.5	10.6	1.5	0.2	0.6	6.3	3.7
600	92.6	97.7	1.7	0.1	0.1	0.3	–	–	–
PCT = 300°C									
250	97.5	75.7	12.2	8.3	0.6	0.5	0.2	1.5	1.0
500	96.0	72.2	12.8	8.8	0.7	0.5	0.4	2.6	2.2
600	96.0	96.5	2.5	0.4	0.1	0.5	–	–	–
PCT = 500°C									
250	87.6	96.7	2.2	0.2	0.2	0.4	–	–	–
500	90.3	96.9	2.2	0.2	0.3	0.4	–	–	–
600	91.8	97.1	2.1	0.1	0.2	0.4	–	–	–

[a] The data are averaged for TOS = 8 h.

[b] Tetrahydrocarbazide.

[c] Octahydrophenazine.

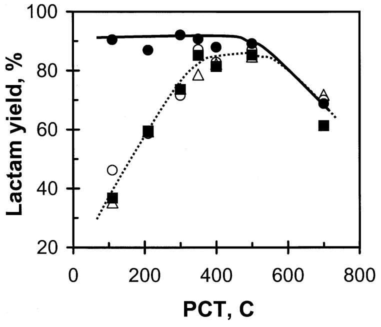

Fig. 1. Dependencies of the lactam yield on PCT and CAT of the 10% B_2O_3/ZrO_2 catalysts. CAT: 250°C (△), 350°C (■), 500°C (○), 600°C (●).

called B_2O_3/ZrO_2-300-600 and B_2O_3/ZrO_2-500-350 catalysts. As it appears in Fig. 2, the change of boria load shows different effects on the activity and selectivity of the Beckmann rearrangement. A maximum oxime conversion appears on the catalyst with 10% B_2O_3 for the B_2O_3/ZrO_2-500-350 sample series (Fig. 2a), it is ca. 12% (between 10 and 13.6% B_2O_3) for the B_2O_3/ZrO_2-300-600 (Fig. 2b) ones. Surprisingly, the lactam selectivity increases also with the boria load up to these optimum load levels for the maximum catalyst activities. Beyond these levels of boria load the lactam selectivity becomes hardly affected.

In Fig. 3, variations of the lactam yield in relation to TOS are compared for the two series of catalyst sam-

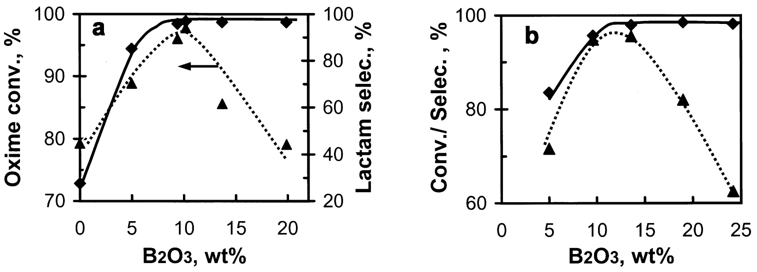

Fig. 2. Effects of boria load on the oxime conversion (▲) and lactam selectivity (◆) with B_2O_3/ZrO_2-500-350 (a) and B_2O_3/ZrO_2-300-600 (b) catalysts.

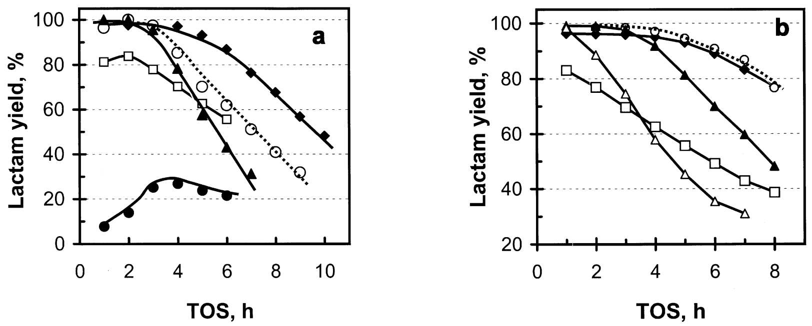

Fig. 3. Effects of boria load on the time course of the lactam yield. (a) B_2O_3/ZrO_2-500-350: (●) ZrO_2-500; (□) 5.0%; (◆) 11%; (○) 14%; (▲) 20% B_2O_3. (b) B_2O_3/ZrO_2-300-600: (□) 5.0%; (◆) 9.5%; (○)13.5%; (▲) 19%; (△) 24% B_2O_3.

ples. Interestingly, the catalysts with optimized levels of the boria load show also the slowest deactivation during the reaction. Except with low levels of the boria load, e.g. 5%, the catalyst deactivation is always seen to induce a slow increase in the formation of the byproducts (not shown in the figure), especially cyclohexanone, though the overall change in the lactam selectivity does not exceed 8% [15].

3.3. Effect of the reaction atmosphere: solvents and carrier gases

One of the optimized catalysts, 10% B_2O_3/ZrO_2-500-350, was used to study the effects of the reaction solvents and carrier gases. Fig. 4 shows the effect of solvents on the averaged oxime conversion and lactam selectivity of Beckmann reaction during 6 h TOS. The averaged oxime conversion and lactam selectivity levels are at 85–90 and 95–97%, respectively, when the non-polar solvent, such as benzene, cyclohexane, or acetone is used for dissolving the oxime reactant. In contrast, the selectivity to the desired lactam becomes almost totally lost when the non-polar solvent is replaced by polar alcohol, like methanol and ethanol, though the oxime conversion can be kept fairly high. A decrease of the polarity by the use of hexan-1-ol for the solvent produces 60% selectivity for the lactam in the first hour. This lactam selectivity is reduced to 20% at TOS = 3 h and is totally diminished at longer TOS. Also, the use of hexan-1-ol for the solvent induces much faster deactivation of the catalyst.

The effect of changing the reaction carrier gas is shown in Fig. 5. Apparently, nitrogen and weakly acidic CO_2 are the most favorable carrier gases. On

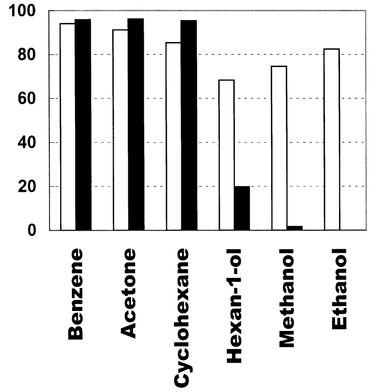

Fig. 4. Effects of solvents on the oxime conversion (open bar) and lactam selectivity (filled bar) with 10% B_2O_3/ZrO_2-500-350 catalyst.

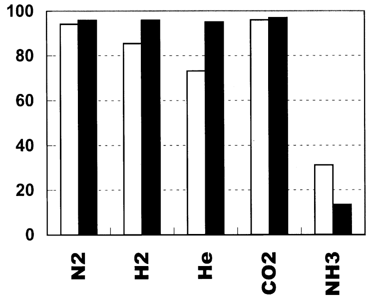

Fig. 5. Effects of carrier gases on the oxime conversion (open bar) and lactam selectivity (filled bar) with 10% B_2O_3/ZrO_2-500-350 catalyst.

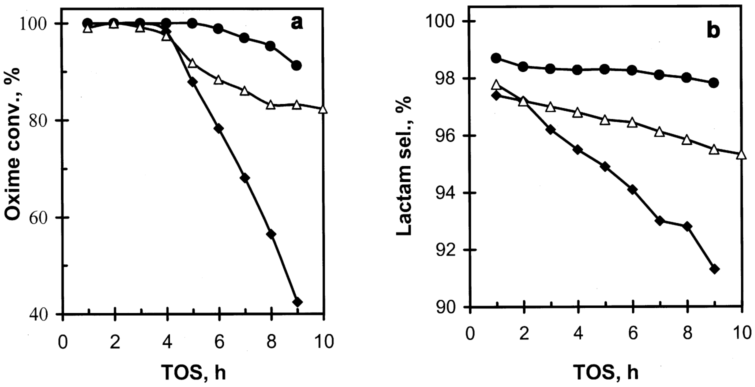

Fig. 6. Effects of the solvent and carrier gas combinations on the oxime conversion (a) and lactam selectivity (b) with 10% B_2O_3/ZrO_2-500-350 catalyst. (◆) Benzene/N_2; (△) benzene/CO_2; (●) acetone/CO_2.

the other hand, the use of basic ammonia for the carrier gas causes to lose the catalyst activity as well as the selectivity to the desired lactam.

Attempts are made to investigate the combinatorial effects of solvents and carrier gases. Fig. 6 shows the time course of three different combinations. We use solvent/carrier-gas to define the combinations, e.g. benzene/N_2 refers to the conventional combination that has most frequently been used for the Beckmann reaction in most of this and the literature works [2–15,22–24]. Apparently, the change of the carrier gas from the conventional N_2 to the CO_2, while keeping the benzene solvent unchanged, results remarkably in preventing the catalyst deactivation and in enhancing the lactam selectivity. The most remarkable effects appear when the conventional combination (benzene/N_2) is changed to the acetone/CO_2 combination. In the latter case, the catalyst deactivation is controlled to less than 10% in 9 h TOS, and selectivity to the lactam remains as high as 98% during the whole reaction period.

4. Discussion

4.1. Optimization of the catalyst preparation

The present results indicate that the temperatures of support pre-calcination and of the catalyst activation are important preparation parameters that affecting the catalytic property of B_2O_3/ZrO_2 catalyst. The lactam yield increases with PCT and gives the maximum numbers with PCT = 350–500°C when the CAT is limited no higher than 500°C. This effect of PCT seems not important for the catalyst preparation when the late catalyst activation is set at CAT = 600°C. With CAT = 600°C, a PCT that is higher than 600°C, e.g. 700°C, causes to reduce the catalyst activity and hence the lactam yield (Fig. 1).

It should be helpful to recall the catalysis of the support alone for the Beckmann reaction before any explanation of the PCT effects is addressed. We showed earlier that a pre-calcination of the zirconyl hydroxide at 500°C produced a support (ZrO_2-500) that was not selective for the lactam synthesis at the first few hours of TOS; the dominant product was cyclohexanone (>60%) [15]. The lactam yield of this ZrO_2-500 catalyst increased to about 20% in 6 h TOS (Fig. 3a). Another support prepared with PCT = 300°C is tested in the present study, the oxime conversion over this ZrO_2-300 catalyst is comparable to those over the ZrO_2-500, but the lactam selectivity is less than 1% during the whole reaction period that lasts for longer than 8 h TOS.

Thus, one of the reasons for the lower lactam yield using the lower PCT preparations is the catalytic contribution from the bare-support surface. This is supported by the effect of boria load on the Beckmann reaction (Figs. 2 and 3). Physical characterization of the B_2O_3/ZrO_2-500-350 catalysts with varying boria loads by N_2 adsorption, FT-Raman, and XPS showed that the monolayer dispersion capacity of boria on the

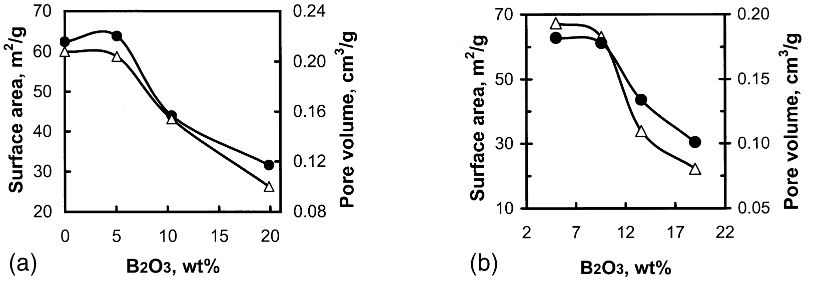

Fig. 7. Effects of boria load on the surface area (△) and pore volume (●) of B_2O_3/ZrO_2-500-350 (a), and B_2O_3/ZrO_2-300-600 (b) catalysts.

ZrO_2-500 (BET: 62 m^2/g; most probable pore diameter: 22 nm) support was ca. 5% by B_2O_3, or 12 μmol B_2O_3/m^2-ZrO_2 [15,25]. As shown in Table 1, the surface areas of the supports with PCT $<$ 350°C are more than three times higher than that of ZrO_2-500, thus the 10% boria load is not enough to form a full monolayer over those support surfaces.

A second reason for the lower lactam yield using the lower PCTs may be related to the crystal phases and texture of the 10% B_2O_3/ZrO_2 catalysts. Since no correlations between the percentage of tetragonal phase in the zirconia support and the catalysis of B_2O_3/ZrO_2 catalysts were observed [22], significant consequence of the support crystal structure on the lactam yield can thus be excluded. Detailed effects of PCT and CAT on the surface area and pore structure based on nitrogen adsorption measurements are the focus of another report [26]. One of the main conclusions is that a high percentage of the surface of supports or their supported catalysts with PCT $<$ 350°C is contributed by micropores ($<$2.0 nm), as indicated by the data in Table 1 for the 10% B_2O_3/ZrO_2-PCT-350 catalysts and their related “pure” supports. High percentage of the micropores can cause boria dispersion outside the pores and then induces, in addition to insufficient boria load (10%), in even higher percentage of the bare-support surface, which results in conversion of the oxime to the undesired byproducts. These micropores are converted to mesopores when the PCT is set higher than 350°C or when a CAT as high as 600°C is used for the catalyst activation [26].

Likewise, the elimination of the PCT effect with CAT = 600°C can be accounted for by the micropore to mesopore change and by boria redispersion during the late activation at 600°C of the catalysts. The much lower lactam yields over the 10% B_2O_3/ZrO_2-700-CAT catalysts are determined by the much lower activity for the oxime conversion (Fig. 1), which should be a direct consequence of the small support surface (24 m^2/g) with PCT = 700°C (Table 1).The optimum boria load (10%) of the B_2O_3/ZrO_2-500-350 catalyst is connected with its highest density of intermediate strong acid sites which seem related with the dispersion structure of the boria overlayers [14,15]. On the average, about two boria overlayers are required for an optimum B_2O_3/ZrO_2 catalyst [15,25]. A higher levels of the boria load means to a higher stack thickness of the boria overlayers on the support and a lower percentage of the contribution of the loaded boria to the desired acid sites. This model seems also applicable to the present B_2O_3/ZrO_2-300-600 catalyst samples. As shown in Fig. 7, the influence of the borial load on the surface area and porosity of the B_2O_3/ZrO_2-300-600 samples is exactly the same as for the B_2O_3/ZrO_2-500-350 ones. For the B_2O_3/ZrO_2-300-600 samples, the higher optimum boria load (ca. 12%) is consistent with the higher catalyst surface of the specified preparations (Table 1). For comparison, a 10% B_2O_3/ZrO_2-500-350 catalyst shows a cumulative surface of 42 m^2/g and a most probable pore diameter of 19 nm, the numbers are 68 m^2/g and 20 nm for the 10% B_2O_3/ZrO_2-300-600 catalyst. Thus, it is clear that the preparation with lower PCT and higher CAT produces the catalyst with higher surface area and desirable pore structure for the Beckmann reaction. Consequently, an even better method for the catalyst preparation may be a direct loading of the boria to the zirconyl hydroxide (PCT = 100°C) followed by calcination with temperature as high as 600°C to activate the catalyst, this was demonstrated with our updated primary work [27].

4.2. Optimization of the reaction atmosphere

The present observation that non-polar solvents are beneficial while the polar alcohol solvents are harmful to the Beckmann reaction agrees well with the work of Landis and Venuto [3] on zeolite catalysts with rare earth or transition metal cations. It differs, however, from recent works over high-silica zeolite [10,23] and mesoporous zeotype catalysts [24]. This difference may arise from the different requirement for acidity of the active sites with zeolite [10,11,23,24] and supported boria catalysts [4–7,14,15].

The remarkable effect of CO_2 as the carrier gas in enhancing both the lactam selectivity and the catalyst stability agrees qualitatively with the literature [3,8,11]. Since basic sites proved to induce formation of byproducts and to cause catalyst deactivation [12–15], it is suggested that the CO_2 molecules function to keep the basic sites from intervening into the reaction. Alternately, the use of basic NH_3 as the carrier proves to suppress the reactivity of the oxime as well as to diminish the lactam formation (Fig. 5), which is at variance of Landis and Venuto [3] over REX catalyst. This minus effect results from a poisoning of the intermediate strong acid sites by NH_3 molecules.

The remarkable positive effects of the solvents and reaction carrier (Figs. 4 and 5) stimulate a concept to optimize the reaction atmosphere by combining together both the effects. This is well demonstrated by the combinatorial effect of using acetone as the solvent and CO_2 as the carrier gas (Fig. 5). While this concept can be explored for even better combinations and further study is required to detail the chemistry of the combinatorial effect, it gives an interesting direction for more efficient catalytic reaction (process). For the present gas-phase Beckmann reaction, the selection of the reaction atmosphere could be as important as the selection of catalyst.

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