

High temperature calcination for a highly efficient and regenerable B_2O_3/ZrO_2 catalyst for the synthesis of ϵ -caprolactam

Bo-Qing Xu,^{*a} Shi-Biao Cheng,^b Xin Zhang,^a Shuang-Feng Ying^a and Qi-Ming Zhu^a

^a State Key Lab of C_1 Chemical Technology and Department of Chemistry, Tsinghua University, Beijing 100084, China. E-mail: bqxu@mailtsinghua.edu.cn

^b Research Institute of Petroleum Processing, SINOPEC, Beijing 100083 China

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High temperature calcination of boria-supported zirconia leads to highly selective and regenerable B_2O_3/ZrO_2 catalysts for the synthesis of ϵ -caprolactam by Beckmann rearrangement of cyclohexanone oxime.

The Beckmann rearrangement of cyclohexanone oxime is an important industrial reaction for the production of ϵ -caprolactam. The conventional technology makes use of fuming sulfuric acid as the catalyst in the liquid phase.¹ This technique is not environmentally friendly and is considered to be one of the most inefficient chemical processes, since it produces 2–5 equivalents of valueless by-product (ammonium sulfate) for every unit of the desired lactam product. It has long been hoped that this process could be replaced with one based on a solid acid catalyst.² However, the development of such a specific solid catalyst has proven to be a big challenge in heterogeneous catalysis. Borias supported on oxide supports are reported to be efficient catalysts for the Beckmann reaction.^{3–7} The main obstacle to the practical use of these catalysts comes from the rapid deactivation and poor regeneration properties of these catalysts.^{8,9} Since supported boria was believed to be volatile above 400 °C, the preparation of supported boria catalysts in the literature was deliberately developed in order to avoid using high calcination temperatures to activate the impregnated boria catalysts. Thus, calcination at 350 °C has become a ‘standard’ activation procedure for preparing supported boria catalysts.^{3–7} Following the ‘standard’ preparation, we reported recently that boria supported on zirconia, B_2O_3/ZrO_2 , was highly active and selective for lactam synthesis; the average lactam yield during a 6 h reaction over properly prepared B_2O_3/ZrO_2 catalyst was greater than 90%.^{10,11} ‘Pure’ zirconia containing no boria showed very poor selectivity for the lactam synthesis.¹¹ Here, we show that activation of boria-loaded zirconia with high temperature (600–700 °C) calcinations produces highly selective (96–98%) catalysts for the Beckmann reaction. Although the loading of boria affects the catalyst activity and selectivity, deactivated catalysts can be regenerated, regardless of the boria loading, to their initial activity and selectivity by calcination at 600 °C.

Samples of B_2O_3/ZrO_2 were prepared by impregnation of the zirconia support with an aqueous solution of boric acid.^{10,11} The boria loading in the catalyst was determined by ICP-MS analysis, and is expressed as a weight percentage of the catalyst sample. Zirconyl hydroxide, which was obtained by hydrolysis of $ZrOCl_2 \cdot 8H_2O$ with an aqueous solution of ammonia (25–28 wt% NH_3), was used as the precursor for the support. Before introduction of the boria, this support precursor was precalcined in air at various temperatures. After the support had been loaded with boria, the catalyst sample was activated by a further calcination at elevated temperatures in air. Both the calcination of the support and of the catalyst was carried out for 10 h. The Beckmann rearrangement reaction was performed on a down-flow fixed bed reactor at 300 °C with 10wt% cyclohexanone oxime in benzene (solvent), and with N_2 as the carrier gas. The weight hourly space velocity (WHSV) of the oxime reactant was 0.32 h^{-1} . Experimental details for the catalyst preparation

and the gas-phase Beckmann reaction have been described elsewhere.^{10,11} Regeneration of the deactivated catalyst was performed by calcination in air at 600 °C for 8 h.

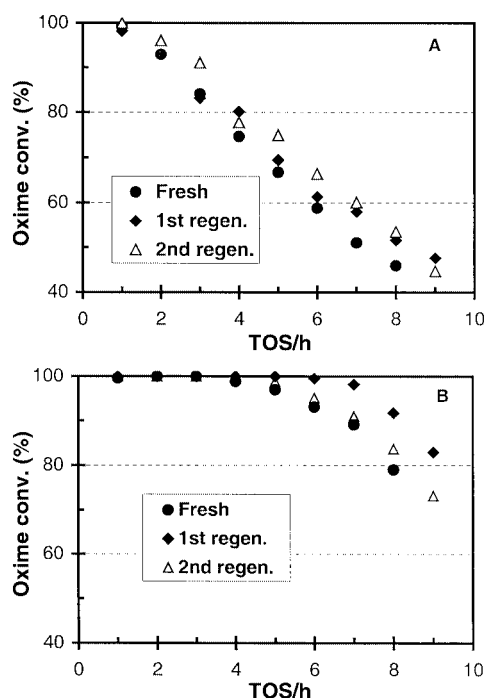
The precalcination temperature (PCT) of the support precursor [$ZrO(OH)_2 \cdot xH_2O$] before loading with boria, the loading of boria, and the catalyst activation (calcination) temperature (CAT) after the loading are important parameters for catalyst preparation.^{12,13} When the CAT is fixed for the preparation, the catalyst activity and selectivity at a fixed loading of boria can be significantly modified by changing the PCT. When the temperature for the catalyst activation is kept at or below 500 °C (CAT \leq 500 °C), support precalcination at 300 °C (*i.e.* PCT = 300 °C) leads to the highest oxime conversion activities among 10% B_2O_3/ZrO_2 samples with various PCT histories.¹³ Catalysts with PCT \geq 300 °C also effectively reduce the formation of undesirable by-products when compared with samples prepared using lower PCTs.¹³ In this work, the PCT is fixed at 300 °C for the catalyst samples to examine the effect of varying the CAT on the Beckmann reaction. A catalyst loaded with 9.5% B_2O_3 has been used for this purpose. This loading of boria is close to the optimum load with the ‘standard’ preparation (CAT = 350 °C) on a zirconia support precalcined at 500 °C (PCT = 500 °C).¹¹ Table 1 shows that oxime conversion and the selectivity and yield of the lactam are little affected over the entire period on an 8 h reaction time on stream (TOS) when the CAT is increased from the ‘standard’ activation temperature (350 °C) to 500 °C over this 9.5% B_2O_3/ZrO_2 catalyst. However, a further increase in the CAT to 600 °C results in dramatically improved selectivity and yield of the desired lactam; the selectivity increases from 70–80% to values greater than 95%, and the average lactam yield increases from *ca.* 70% to 92%. The last group of data at the bottom of the Table 1 gives the results of the reaction over a ‘pure’ zirconia support that was activated at 600 °C. Except at the very beginning of the reaction, the desired lactam product is basically not produced. This observation agrees with our conclusions from earlier work that the active catalytic sites for the Beckmann reaction are connected with boria in the sample.¹³ ICP-MS analysis showed that the B_2O_3 loading in the three samples with CAT = 350, 500 and 600 °C are in the range 9.0–9.7%, which indicates that no significant loss of boron occurs during catalyst activation (calcination) with CAT > 400 °C. It is, therefore, clear that high temperature activation (calcination) is essential for the preparation of highly efficient B_2O_3/ZrO_2 catalysts. The ability of B_2O_3 to withstand the high temperature calcinations suggests a strong interaction between B_2O_3 and the support surface.

With CAT = 600 °C for the catalyst preparation, samples of B_2O_3/ZrO_2 catalysts were prepared with various loadings of boria. Fig. 1 presents the time course of the oxime conversion over two B_2O_3/ZrO_2 samples with 5 and 13.5% B_2O_3 by weight, respectively. While the oxime conversion decreases more or less with reaction time, no significant change (<2%) in the lactam selectivity is observed over both catalysts; the lactam selectivity is 81–83% with the 5% B_2O_3/ZrO_2 sample and 96–97% with the 13.5% B_2O_3/ZrO_2 sample (not shown in the figure). Experiments were undertaken in order to ascertain the

Table 1 Effect of catalyst activation/calcination temperature (CAT) on the Beckmann rearrangement of cyclohexanone oxime^a

Sample	TOS/h								Average
	1	2	3	4	5	6	7	8	
CAT = 350 °C									
Oxime conv. (%)	98.2	100	100	100	100	98.9	85.3	88.0	96.3
Lactam selec. (%)	76.5	73.6	70.9	74.5	75.7	74.4	81.6	80.0	76.5
Lactam yield (%)	75.1	73.6	70.9	74.5	75.7	73.6	69.6	70.4	73.7
CAT = 500 °C									
Oxime conv. (%)	100	100	100	100	100	97.4	89.6	80.9	96.0
Lactam selec. (%)	71.4	68.7	69.0	69.0	69.4	69.3	74.7	79.3	71.4
Lactam yield (%)	71.4	68.7	69.0	69.0	69.4	67.5	66.9	64.2	68.5
CAT = 600 °C									
Oxime conv. (%)	100	100	100	100	100	96.1	89.9	81.8	96.0
Lactam selec. (%)	96.7	96.1	96.3	96.2	96.0	95.8	95.7	95.0	96.0
Lactam yield (%)	96.7	96.1	96.3	96.2	96.0	92.1	86.0	77.7	92.1
ZrO ₂ -600 ^b									
Oxime conv. (%)	73.5	—	16.9	—	0.2	—	0.1	0	18.2
Lactam selec. (%)	4.2	—	0	—	0	—	0	0	0.9
Lactam yield (%)	3.1	—	0	—	0	—	0	0	0.6

^a Catalyst: 9.5% B₂O₃/ZrO₂; reaction temperature: 300 °C; WHSV: 0.32 h⁻¹; solvent/carrier: benzene/N₂. ^b Zirconia support calcined at 600 °C.

**Fig. 1** Time course of cyclohexanone oxime conversion over fresh and regenerated 5% B₂O₃/ZrO₂ (A) and 13.5% B₂O₃/ZrO₂ (B) catalysts.

reusability of the deactivated catalyst when regenerated by calcination in air at 600 °C for 8 h. Quantitative measurement of boron in the samples revealed that the difference in boria loading between the fresh and corresponding regenerated samples is less than 6% of the loading in the fresh sample.

It is evident from Fig. 1 that these two catalysts do not lose any activity for the Beckmann reaction, even after two repeated deactivation–regeneration cycles. Also, no meaningful change in the lactam selectivity was detected over these two catalysts in the deactivation–regeneration cycles. Very similar behavior was also observed with samples containing higher boria loadings, e.g. 20% B₂O₃. These observations may be very important, since complete restoration of catalyst activity and selectivity could prove attractive for industrial application. The effect of boria loading on the catalytic performance of ‘fresh’ B₂O₃/ZrO₂ catalysts has been a focus of discussion in other publications.^{11,13}

For the 10% B₂O₃/ZrO₂ catalysts prepared with CAT = 600 °C, it has been shown that the precalcination temperature (PCT = 110–500 °C) of the support precursor has little effect on the catalytic efficiency for the lactam synthesis.¹³ Attempts were therefore made to impregnate boric acid directly onto zirconyl hydroxide that had been dried at 110 °C, but with an even higher temperature (700 °C) used for the catalyst activation. This preparation produced even more efficient B₂O₃/ZrO₂ catalysts (boria loading 8–15%) that are able to yield 98% ε-caprolactam for longer than 10 h TOS, which further demonstrates that high temperature catalyst activation/calcination is beneficial for the production of highly efficient and regenerable solid acid catalysts based on supported boria. This conclusion could be important for the development of a practical boria catalyst for industrial application. Additionally, the discovery that zirconia-supported boria catalysts are able to withstand high temperature (600–700 °C) calcination seems of interest for fundamental research. Further study is required to understand the chemistry of the interaction between boria and the surface of the zirconia support.

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