

Deactivation and regeneration of the B_2O_3/TiO_2-ZrO_2 catalyst in the vapor phase Beckmann rearrangement of cyclohexanone oxime

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Abstract

The deactivation and regeneration of B_2O_3/TiO_2-ZrO_2 catalyst for the vapor phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam were studied. The fresh, deactivated and regenerated catalysts were characterized by using adsorption of nitrogen, X-ray diffraction (XRD), thermogravimetry (TG) and NH_3 -temperature-programmed desorption (NH_3 -TPD) techniques. The crystal structure and pore size distribution of the catalyst were retained after reaction, but the number of acid sites decreased significantly. There was a relationship between the amount of coke deposited on the catalyst and the decline in catalytic activity. These results suggest that the coke deposition on the surface of catalyst is mainly responsible for the catalyst deactivation. The catalytic activity can be recovered completely after calcining the deactivated catalyst in air flow at 600 °C for 8 h.

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1. Introduction

The Beckmann rearrangement of cyclohexanone oxime is an important process to synthesize ϵ -caprolactam as an intermediate for the production of nylon-6 fibers and plastics. The current industrial production of caprolactam is carried out using fuming sulfuric acid as the catalyst in the liquid phase. However, this conventional method has several problems economically and environmentally due to the use of a strong sulfuric acid catalyst, although the process yields caprolactam with very high selectivity. For instance, a large amount of low value ammonium sulfate (>1.7 pounds per pound caprolactam) is produced as a by-product in the neutralization of sulfuric acid by large quantities of ammonia. Furthermore, operational problems, such as equipment corrosion, safety hazards and waste water disposal are considered as major shortcomings. A preferable alternative is to perform the Beck-

mann rearrangement reaction in the vapor phase using solid acid instead of sulfuric acid as a catalyst. In the past two decades, a large number of solid acid catalysts have been studied such as boria supported on various carriers [1–8], silica-supported tantalum oxide and tungsten oxide [9,10], alumina pillared montmorillonite [11], tantalum pillared ilerite and magadiite [12–14], boron hydrotalcite-like compounds [15], SiMCM-41-supported phosphotungstic acid [16], anionic clays [17] and a wide variety of zeolites, such as USY [18], ZSM-5 [19–25], ZSM-11 [26], SAPO-11 [27], Beta [28,29], LTL [30], ferrierite [31] and MCM-22 [32], and mesoporous molecular sieves such as MCM-41, MCM-48, FSM-16 and SBA-15 [33–39].

It can be noted that most of the published papers as mentioned above emphasized the preparation and evaluation of catalyst. The studies on deactivation and regeneration of catalyst are still very few, although catalyst deactivation as a function of operation time is perhaps the most serious limitation of this vapor phase approach to the production of caprolactam from cyclohexanone oxime, and is a common problem with all catalyst types studied to date. Aucejo et al.

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[40] elucidated the cause of the deactivation of HNaY zeolite in the vapor phase Beckmann rearrangement reaction. They found that the catalyst decay was due to poisoning of the acid sites by the basic products, such as hydroxylamine, aniline and methylpyridine. Similarly, Takahashi et al. [41] reported that the deactivation of the ZSM-5 type zeolite was mainly due to the adsorption of volatile material on the acid sites. In another paper [42], the same authors did not observe any improvement of activity when the deactivated catalyst was maintained at the reaction temperature for 24 h in the hydrogen stream. However, when the deactivated catalyst was treated in an oxygen atmosphere at the reaction temperature for 5 h, its original activity was restored. Based on these results, they concluded that deactivation of the boron modified HZSM-5 catalyst proceeded by the deposition of coke on the catalyst. Besides coking and base adsorption, which have been suggested as the main reason for deactivation of zeolite catalysts, some other deactivation mechanisms were also proposed for supported B_2O_3 catalysts. For example, Ushikubo and Wada [9] attributed the quick deactivation of B_2O_3/Al_2O_3 catalyst to the loss of B_2O_3 , which decreased drastically from 26.5 wt.% for the fresh catalyst to 19.8 wt.% after 10 h reaction. In addition, the melting and agglomeration of B_2O_3 has been proposed as a deactivation mechanism for silica supported catalyst [5]. These results mentioned above strongly imply that the main reason for deactivation of different catalysts may be quite different.

Similar to studies on catalyst deactivation, very little has been reported in the literature with respect to catalyst regeneration. Sato et al. [2] examined the regeneration of B_2O_3/Al_2O_3 catalyst by burning off the coke in air at 500 °C for 3 h and found that the oxime conversion was completely recovered but the caprolactam selectivity remained at the level prior to regeneration. They proposed that the possible reason for the latter was that the coke could not be completely removed under the regeneration conditions. Additionally, they emphasized that the regeneration temperature should be below 600 °C; otherwise about 20% of boria would be lost through vaporization. On the other hand, Hölderich and co-workers [43] investigated the long-term regeneration stability of B-MFI zeolite in a 20-day regeneration experiment. The catalyst was regenerated in air at 550 °C for 16 h after 6 h time-on-stream in the Beckmann rearrangement reaction, with the result that caprolactam selectivity and the drop in oxime conversion after 6 h time-on-stream were essentially the same as those for the first experiment. These results imply that an optimum regeneration condition for a specific catalyst should be explored carefully.

In previous publications [44–46], we have reported that the performance of boria catalyst supported on TiO_2-ZrO_2 mixed oxide in the vapor phase Beckmann rearrangement reaction was much better than that of other boria catalysts supported on TiO_2 , ZrO_2 and other binary oxides based on SiO_2 , Al_2O_3 , TiO_2 and ZrO_2 . However, its high initial activity also decreased at a relatively rapid rate with reaction time. For this reason, it is very important to study the catalyst deactivation

and regeneration. In the present paper, the deactivated and regenerated B_2O_3/TiO_2-ZrO_2 catalysts were characterized and investigated in the Beckmann rearrangement reaction in order to find the possible reasons that caused the catalyst deactivation and the suitable regeneration methods.

2. Experimental

2.1. Catalyst preparation

The 12 wt.% B_2O_3/TiO_2-ZrO_2 catalyst was prepared by impregnating the support with an aqueous solution of boric acid using the incipient wetness technique, as described previously [44–46]. The TiO_2-ZrO_2 support with a molar ratio of 1:1 was prepared by a co-precipitation method using aqueous ammonia as precipitation reagent and calcined for 6 h at 500 °C. The impregnated catalyst was dried at 110 °C for 12 h and then calcined at 600 °C for 12 h in air.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-1400 (Japan) instrument, equipped with a graphite monochromator, operated at 40 kV and 40 mA and using nickel-filtered $Cu K\alpha$ radiation ($\lambda = 0.1542$ nm).

The surface areas, pore volumes and pore size distributions of the B_2O_3/TiO_2-ZrO_2 catalysts were analyzed by the multipoint N_2 adsorption/desorption method at liquid- N_2 temperature (−196 °C) with a Micromeritics TriStar 3000 (USA) surface area analyzer. Samples were outgassed under vacuum ($<6.7 \times 10^{-2}$ Pa) and at 100 °C for 16 h to evacuate the physisorbed moisture immediately prior to analysis.

The acidities and acid strength distributions of the fresh, deactivated and regenerated catalysts were measured using ammonia temperature-programmed desorption (NH_3 -TPD). The apparatus and procedure were the same as those described in our previous reports [44–46].

The coke content of the catalyst after reaction test was determined by combustion in a thermogravimetric analyzer (Dupont, TA-4000, USA). Samples were first heated from room temperature to 150 °C in a flow of 30 ml min^{-1} of nitrogen until no more weight loss occurred. Then a stream of 50 ml min^{-1} of air was passed through the samples and the temperature was raised to 700 °C at a rate of 10 °C min^{-1} . The weight loss between 350 and 700 °C was attributed to coke [46].

2.3. Catalytic activity test

The catalytic reactions were carried out at atmospheric pressure in a down flow fixed-bed type reactor. The reactor assembly and the procedure were the same as those described in our previous papers [44–46]. A mixture of cyclohexanone oxime (5 wt.%) and benzene was injected using a high precision feed pump (Gilson, Model 05C, France) to

the evaporator at a constant flow rate. The vaporized mixture diluted with nitrogen (30 ml min^{-1}) was fed to the reactor. The weight hourly space velocity (WHSV) was 0.33 h^{-1} in terms of cyclohexanone oxime and the reaction temperature was 300°C . The effluent in outlet of the reactor was collected in a receiver after cooling with ice cold water and analyzed using a gas chromatograph (HP 4890 D fitted with an HP-1 capillary column and an FID as detector, the carrier gas being nitrogen). The conversion of cyclohexanone oxime and selectivity to caprolactam was calculated as follows:

$$\begin{aligned} &[\text{Conversion of oxime}] \\ &= \frac{([\text{Oxime}]_{\text{in}} - [\text{Oxime}]_{\text{out}})}{[\text{Oxime}]_{\text{in}}} \times 100\% \end{aligned}$$

$$\begin{aligned} &[\text{Selectivity to lactam}] \\ &= \frac{[\text{Lactam}]_{\text{out}}}{([\text{Oxime}]_{\text{in}} - [\text{Oxime}]_{\text{out}})} \times 100\%. \end{aligned}$$

3. Results and discussion

In Fig. 1, the conversion of cyclohexanone oxime and the selectivity to caprolactam over the $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ catalyst are plotted against time-on-stream. It can be seen that, starting with 100% activity, the oxime conversion began to decline after 4 h time-on-stream and decreased markedly to 75.4% after 8 h time-on-stream. This result indicates that the stability of the $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ catalyst is relatively poor. Unlike oxime conversion, the selectivity to caprolactam remained practically unchanged (ca. 97%) during the same time, suggesting that the catalyst deactivation proceeds via the indiscriminate poisoning of all active sites. Compared with the highly siliceous zeolite which has been used in the vapor phase Beckmann process for the industrial production of caprolactam [47], the quick deactivation of the $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$

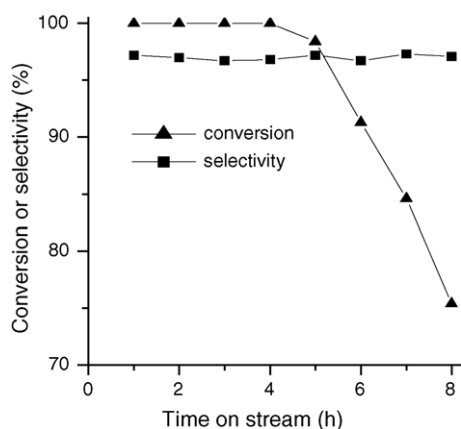


Fig. 1. Change in conversion of cyclohexanone oxime and selectivity to caprolactam with time-on-stream over the $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ catalyst. Reaction conditions: $T = 300^\circ\text{C}$; $P = 0.1 \text{ MPa}$; $\text{WHSV} = 0.33 \text{ h}^{-1}$; solvent: benzene; carrier gas: N_2 ; N_2 flow rate = 30 ml min^{-1} .

ZrO_2 catalyst at the low WHSV reveals that its activity is much lower and consequently is less suitable for industrial use. Even so, considering that supported boria catalyst is a very important and extensively studied catalyst for the vapor-phase rearrangement of cyclohexanone oxime, we think that the study of deactivation and regeneration of the $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ catalyst is significant and interesting.

3.1. Reason for catalyst deactivation

In previous papers [44–46,48,49], we have shown that the catalytic activity of the $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ catalyst in the vapor phase Beckmann rearrangement of cyclohexanone oxime is related to the acidity and the pore size of the catalyst. Catalysts with small pores need a longer time for the produced caprolactam diffusing from the stronger acid sites of catalyst, which may cause undesirable catalytic side reactions, such as polymerization and decomposition of the produced caprolactam, and consequently the catalysts deactivate rapidly. If the pore sizes of catalysts are large enough, the effect of pore size is very small and can be ignored. Then the catalytic behavior is mainly determined by acidity: the conversion of cyclohexanone oxime is closely correlated with the number of acid sites of medium strength, which are characterized by desorption of adsorbed ammonia between 200 and 350°C [44]. It should be emphasized here that the acidity requirement for the vapor-phase rearrangement reaction on zeolites and supported catalysts, such as B_2O_3 [3,8], Ta_2O_5 [9] and WO_3 [10] is quite different. For these supported catalysts, it has been well demonstrated that the acid sites of intermediate strength are responsible for selective formation of caprolactam [3,8,9,37]. However, for zeolite catalysts, a majority of previous reports have suggested that the very weak [50,51] or almost neutral hydroxyl groups [52–55] of zeolites are favorable for the Beckmann rearrangement reaction. On the other hand, Ichihashi et al. [47,56] proved that the acidity on highly siliceous ZSM-5 zeolite that can be evaluated by ammonia TPD measurements is not responsible for the vapor phase Beckmann rearrangement.

In order to reveal the reason for deactivation of the $\text{B}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ catalyst in the vapor phase Beckmann rearrangement of cyclohexanone oxime, the pore sizes and the acidity strength distributions of the fresh and deactivated catalysts were characterized by adsorption of nitrogen and temperature-programmed desorption of ammonia, respectively. As shown in Fig. 2, the pore size distribution of the deactivated catalyst is quite similar to that of the fresh catalyst, indicating the retention of pore structure after reaction. However, a comparison of the NH_3 -TPD profiles of the fresh and the deactivated catalysts reveals significant variation in their acidities (Fig. 3). The deactivated catalyst showed a marked decrease in the intensity of the ammonia desorption peak, indicating that the total number of acid sites was decreased noticeably after reaction. The acid strength distributions obtained by analyzing the TPD profiles, following the procedure proposed by Berteau and Delmon [57] and

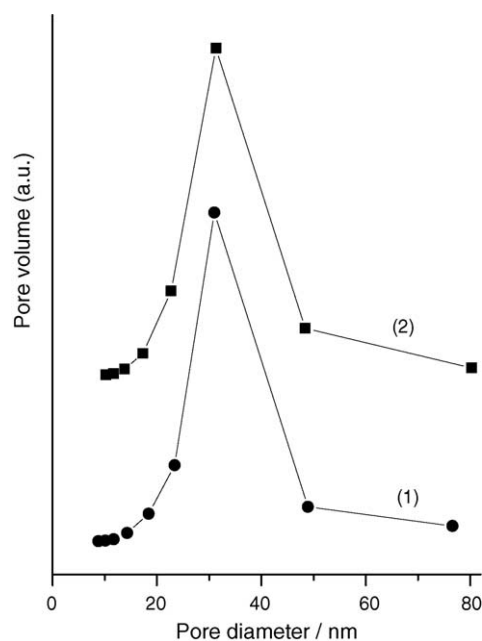


Fig. 2. Pore size distributions of the B_2O_3/TiO_2-ZrO_2 catalysts: (1) fresh and (2) deactivated.

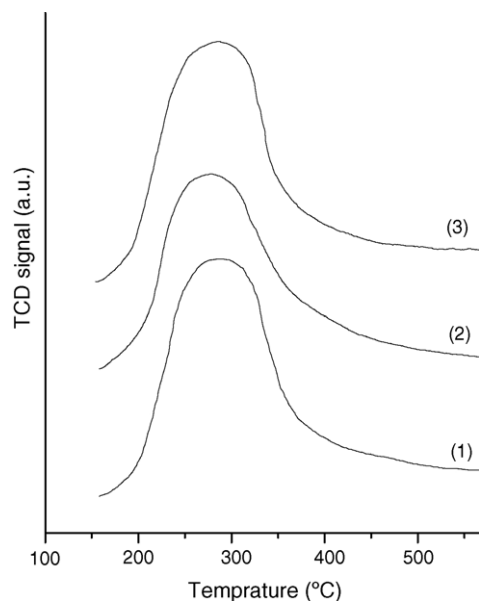


Fig. 3. NH_3 -TPD profiles of the B_2O_3/TiO_2-ZrO_2 catalysts: (1) fresh, (2) deactivated and (3) regenerated.

widely adopted by Curtin et al. [3] and Xu et al. [8], are summarized in Table 1. The sites of weak, medium and strong acid strength were characterized by desorption of adsorbed ammonia $<200\text{ }^\circ\text{C}$, $200\sim 300\text{ }^\circ\text{C}$ and $>350\text{ }^\circ\text{C}$, respectively. The data in Table 1 show that although the percentage of the number of acid sites of medium strength to the total number of acid sites remained practically unchanged, the number of acid sites of medium strength decreased. The above result demonstrated again our earlier conclusion that the oxime conversion and caprolactam selectivity are closely correlated with the number of acid sites of medium strength and its percentage to the total number of acid sites, respectively [44]. According to the above results, we conclude that the deactivation of the B_2O_3/TiO_2-ZrO_2 catalyst was due to the decline in the number of acid sites, but not due to the change of pore structure.

As mentioned in the Section 1, there are mainly four possible factors responsible for the decrease in the number of acid sites of supported B_2O_3 catalysts in the rearrangement reaction of oxime. The first one is the coke deposited on the surface of catalyst leading to the coverage of the acid sites [2,3,42]. The second one is the irreversible adsorption of basic reaction by-products resulting in the poisoning of the acid sites [40,41]. The third one is the loss of B_2O_3 [9,52]; and the last one is the melting and agglomeration of B_2O_3 [5].

In the present study, we observed that the B_2O_3/TiO_2-ZrO_2 catalyst changed to black after reaction from original white, suggesting that the catalyst was completely covered by coke. Consequently, the content of coke deposited on the B_2O_3/TiO_2-ZrO_2 catalyst after different time-on-stream was measured by thermogravimetric (TG) analysis. It was observed that, after TG analysis, the white color of the catalyst was restored as a result of coke combustion. The relationship between loss of catalytic activity and the amount of coke deposited on catalyst surface is depicted in Fig. 4. It can be seen that when the process time was short (no longer than 4 h), the oxime conversion remained practically unchanged, although there was an increase in the amount of coke deposited as reaction time proceeded. This result suggests that the content of coke deposited in the stage is not large enough to decrease the activity. When the process time was longer than 4 h, however, there was a decrease in the level of oxime converted corresponding to the increase in the amount of coke deposited on the catalyst. Therefore, a correlation seems to exist between the mass of coke deposited on the catalyst surface and the drop in oxime conversion. In

Table 1

Surface areas, pore volumes and acid strength distributions of the different B_2O_3/TiO_2-ZrO_2 catalysts

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	Strength distributions of acid sites		
			$<200\text{ }^\circ\text{C}$	$200\sim 350\text{ }^\circ\text{C}$	$>350\text{ }^\circ\text{C}$
Fresh	20.08	0.109	27 ^a (4.2 ^b)	584 ^a (91.4 ^b)	28 ^a (4.4 ^b)
Deactivated	19.21	0.114	23 (4.4)	481 (91.0)	24 (4.6)
Regenerated ^c	21.42	0.100	28 (4.5)	579 (91.2)	27 (4.3)

^a The number of acid sites with special strength (arbitrary units).

^b The percentage of the number of acid sites with special strength to the total number of acid sites.

^c Regeneration conditions: $T = 600\text{ }^\circ\text{C}$; $t = 8\text{ h}$; air flow rate = 50 ml min^{-1} .

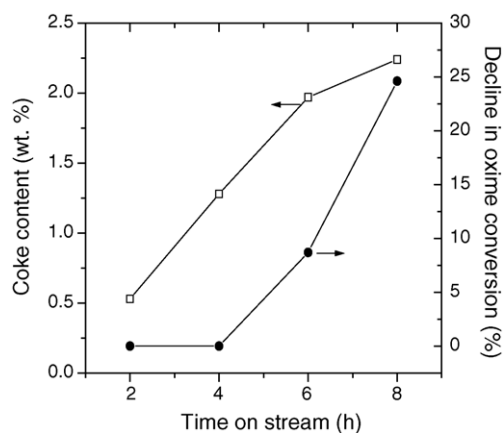


Fig. 4. Plots of the amount of coke and decline in oxime conversion vs. reaction time.

addition, when the catalyst was regenerated in the presence of air at 600 °C for 8 h, the original activity was completely restored (see below). Based on the above results, it is concluded that the coke formation may be the main reason for catalyst deactivation.

On the other hand, when the catalyst was regenerated by heating at 500 °C for 24 h in a nitrogen stream, the activity was not totally recovered. This result suggests that base adsorption cannot be the main reason for deactivation of the present B_2O_3/TiO_2-ZrO_2 catalyst.

Furthermore, if the adsorption of basic products was the main cause of catalyst deactivation, deactivation would be retarded by replacing the nitrogen carrier gas by a carbon dioxide stream, since it is suggested that the addition of acidic CO_2 promotes the desorption of basic products from the acidic sites [24,52,58,59]. However, this is not the case for the B_2O_3/TiO_2-ZrO_2 catalyst. As a matter of fact, compared to nitrogen carrier gas, the use of CO_2 led to a slightly faster deactivation rate [46]. A very similar result was also reported recently by Forni et al. [4] on the B_2O_3/Al_2O_3 catalyst prepared by a non-conventional sol-gel method. As they explained, carbon dioxide has electrophilic properties and might interact with electron-rich sites thus modifying the global catalyst acidity. The number of acid sites is then reduced and the catalyst is susceptible to deactivation by coke deposition.

Quantitative measurements of boria contents in the B_2O_3/TiO_2-ZrO_2 samples revealed that no significant loss of boria occurred during the reaction. Forni et al. [4] also reported no leaching of B_2O_3 from the B_2O_3/Al_2O_3 catalyst in the reaction process as not any boron compound was found in the condensed product solution. Since boria is volatile above 400 °C [60], no loss of B_2O_3 during the rearrangement reaction can be envisaged considering that the reaction temperature was normally not higher than 350 °C for the supported B_2O_3 catalyst [1–5,8]. On the other hand, the melting and agglomeration of B_2O_3 is not thought to be the reason for deactivation in the present case since the XRD result on the used catalyst did not show any evidence of the presence

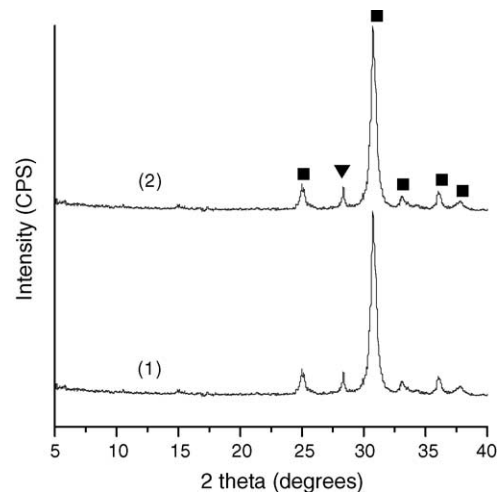


Fig. 5. XRD patterns of the B_2O_3/TiO_2-ZrO_2 catalysts: (1) fresh, (2) deactivated. (■) $ZrTiO_4$; (▼) B_2O_3 .

of larger amount of crystalline B_2O_3 . As shown in Fig. 5, the XRD patterns of the deactivated catalyst were almost the same as those of the fresh catalyst, indicating the retention of crystal structure after reaction. This result can be ascribed to the higher melting temperature of B_2O_3 (450 °C) [61] than the reaction temperature (300 °C). In short, the above results indicate that base adsorption, loss, melting and agglomeration of B_2O_3 cannot be the main reason for catalyst deactivation, which further supports our conclusion obtained above that coke deposition is the main cause of deactivation of the B_2O_3/TiO_2-ZrO_2 catalyst.

3.2. Catalyst regeneration

From the above results, we conclude that the main reason for deactivation of the B_2O_3/TiO_2-ZrO_2 catalyst is the coke deposition. The regeneration of the catalyst deactivated by coking is usually carried out by a thermal treatment in air at an elevated temperature. For example, the spent B-MFI zeolite can be regenerated in the presence of air at 500 °C for 16 h. In contrast, the catalyst was not regenerated at 300 °C for 16 h [43].

In order to completely remove the carbonaceous materials deposited on catalyst the regeneration conditions should be optimized. Thus, the spent B_2O_3/TiO_2-ZrO_2 catalyst was regenerated in air at different temperatures and for different times. The results of Table 2 show that when regeneration was undertaken at a lower temperature or for a shorter time, the oxime conversion obtained was much lower compared to those of both the fresh catalyst and the catalyst regenerated at a higher temperature and for a sufficient time. It can be seen that the regeneration conducted at 600 °C for 8 h restores totally the activity.

As mentioned above, the used catalyst showed a marked decrease in the number of acid sites (Fig. 3). Comparing the NH_3 -TPD profile of the regenerated catalyst to that of the fresh catalyst, we can find that all of the acid sites were

Table 2
Oxime conversion and caprolactam selectivity of the B₂O₃/TiO₂-ZrO₂ catalyst

Catalyst	Oxime conversion (%)	Lactam selectivity (%)
Fresh	91.3	97.0
Regenerated at 500 °C for 16 h	82.5	97.1
Regenerated at 600 °C for 4 h	79.6	96.8
Regenerated at 600 °C for 8 h	95.0	97.0

Reaction conditions: $T = 300\text{ }^{\circ}\text{C}$; $P = 0.1\text{ MPa}$; $\text{WHSV} = 0.33\text{ h}^{-1}$; solvent: benzene; carrier gas: N₂; N₂ flow rate = 30 ml min^{-1} ; time-on-stream = 6 h.

restored. This result indicated that when the catalyst was regenerated in the presence of air at 600 °C for 8 h, the coke deposited over acid sites was completely burnt off and that the shielded acid sites were again exposed to interact with the reactant molecules; accordingly the activity was totally recovered.

In order to investigate the long-term regeneration stability of the B₂O₃/TiO₂-ZrO₂ catalyst, repeated deactivation–regeneration cycle experiments were carried out according to the procedure proposed by Hölderich and co-workers [43]. Firstly, the reaction was carried out at 300 °C. After 6 h time-on-stream the catalyst was regenerated at an elevated temperature of 600 °C in an air stream of 50 ml min^{-1} for 8 h. It is evident from Table 3 that the catalyst does not lose any activity for the Beckmann rearrangement of cyclohexanone oxime, even after three repeated deactivation–regeneration cycles. Oxime conversion, caprolactam selectivity and decline in oxime conversion within 6 h time-on-stream over the regenerated and fresh catalysts remained almost the same. These results clearly suggest that the B₂O₃/TiO₂-ZrO₂ catalyst has excellent regeneration ability. This may be very important, since complete restoration of catalyst activity and selectivity could prove attractive for industrial application.

According to Sato et al. [2] the regeneration of B₂O₃/Al₂O₃ catalyst at 500 °C for 3 h in air led to the complete recovery of activity but the selectivity to caprolac-

Table 3
Oxime conversion and lactam selectivity of the B₂O₃/TiO₂-ZrO₂ catalyst after regeneration

Deactivation–regeneration cycle	Time-on-stream (h)	Oxime conversion (%)	Lactam selectivity (%)
0	1	100	96.8
	6	91.3	97.0
1	1	100	97.2
	6	95.0	97.0
2	1	100	96.5
	6	92.3	96.8
3	1	100	96.8
	6	94.3	97.1

Reaction conditions: $T = 300\text{ }^{\circ}\text{C}$; $P = 0.1\text{ MPa}$; $\text{WHSV} = 0.33\text{ h}^{-1}$; solvent: benzene; carrier gas: N₂; N₂ flow rate = 30 ml min^{-1} . Regeneration conditions: $T = 600\text{ }^{\circ}\text{C}$; $t = 8\text{ h}$; air flow rate = 50 ml min^{-1} .

tam remained at the level prior to regeneration presumably because the coke was not totally removed. Furthermore, they reported that if the regeneration temperature was raised to higher than 600 °C, about 20% of boron was lost through vaporization. Forni et al. [4] also observed a loss of 37.5 wt.% of the total boron content in the B₂O₃/Al₂O₃ catalyst when it was regenerated in air at 500 °C for 15 h. Consequently, the regenerated catalyst was more rapidly deactivated in terms of the oxime conversion and caprolactam selectivity than the fresh catalyst. On the other hand, Curtin et al. [62,63] found that although the total boron amount of the regenerated B₂O₃/Al₂O₃ catalyst was still high (11.1%) compared with the fresh catalyst (12.7%), a large part of boron was converted to an amorphous water-insoluble non-selective boron species. Almost 100% of the total boron present in the fresh catalyst was in a water-soluble form, but only 70% of the boron was of this form in the regenerated catalyst. Coupled with the loss of water-soluble boron, there was a corresponding irreversible loss of acid sites of intermediate strength. Accordingly, caprolactam selectivity of the regenerated catalyst rapidly deactivated, even though a slightly higher oxime conversion was attained. Contrary to the above-mentioned observations, quantitative measurements of boron in the B₂O₃/TiO₂-ZrO₂ samples revealed that no noticeable loss of boron occurred during the regeneration process. Similarly, Xu et al. [60] also reported that the difference in boron loadings between the fresh and regenerated B₂O₃/ZrO₂ samples was less than 6% of the loading in the fresh sample. Furthermore, they found that when the boron was supported on zirconia with a high surface area, the loss of boron was even less than 1% [64]. Hence, the B₂O₃/ZrO₂ catalyst did not lose any activity and selectivity after three repeated deactivation–regeneration cycles. Moreover, Colorio et al. [61] did not observe any loss of B₂O₃ even after four times of successive cycles of hydration–dehydration on the B₂O₃/Al₂O₃ catalyst. It is very important to note that the calcination temperature for the preparation of the supported B₂O₃ catalysts in which loss or structural modification of B₂O₃ occurred in the regeneration process was relatively low, i.e. 350 °C [2,3,10,62,63] or 500 °C [4]. Nevertheless, those boron catalysts in which no loss or structural modification of B₂O₃ occurred during the regeneration process were all prepared by calcining at a high temperature, i.e. 600 °C [8,58,61,64]. These facts clearly suggest that high calcination temperature is favorable for the preparation of regenerable supported B₂O₃ catalyst.

The difference in the stability for the regeneration of supported B₂O₃ catalysts calcined at different temperatures may be related to the different interaction between boron and the support which can be reflected by the different states of boron on the surface of catalysts. In this context, infrared spectroscopy was used to ascertain the nature of the B₂O₃ structure existing on the B₂O₃/TiO₂-ZrO₂ catalysts calcined at 500 and 600 °C. As shown in Fig. 6, the sample calcined at 500 °C showed two bands at around 1390 and 1190 cm⁻¹, respectively. Increasing the calcination temper-

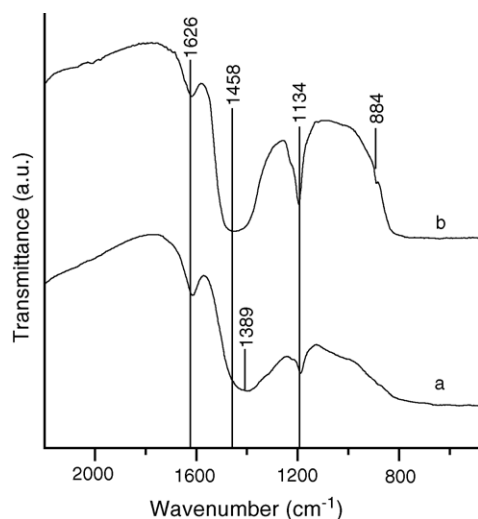


Fig. 6. IR spectra of the B_2O_3/TiO_2-ZrO_2 catalysts calcined at different temperatures: (a) 500 °C and (b) 600 °C.

ature to 600 °C, the intensities of both bands increased and the position of the band at 1390 cm^{-1} was shifted to high frequency, i.e. from 1389 to 1458 cm^{-1} . Meanwhile, a new band was clearly observed at about 880 cm^{-1} . On the other hand, the band near 1630 cm^{-1} was not present in the spectra recorded on pressed disks of the pure powders (without KBr) after evacuation at temperatures above 200 °C. This suggests that this band is due to the scissoring-mode of water molecules, probably involved in H-bonding, as proposed by Delmastro et al. [65].

It is well known that, in borates, boron is present in two structure units (i.e. tetrahedral BO_4 and trigonal BO_3) [4,8,65]. Information on the structure of the borate species present on B_2O_3/TiO_2-ZrO_2 catalyst can be obtained from the above spectra, taking into account the characteristic spectra of the different boron-oxygen compounds. By comparison with the spectra of boric acid (only BO_3 units) and borax (both

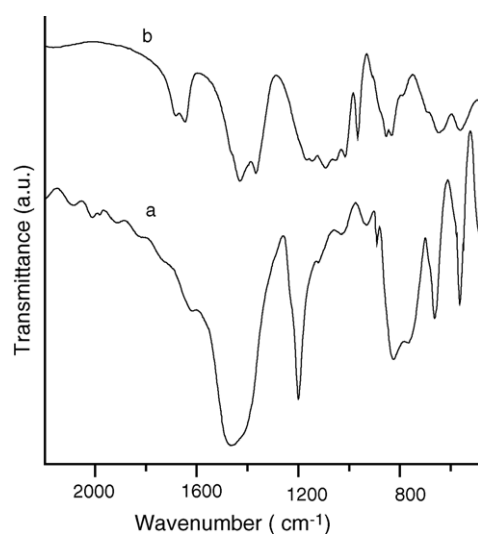


Fig. 7. IR spectra of boric acid (a) and borax (b).

BO_3 and BO_4 units) (Fig. 7), it is concluded that the bands at 1460, 1190 and 880 cm^{-1} represent the formation of BO_3 units, while the bands at 1300–1400 and 1050–1150 cm^{-1} represent the formation of BO_4 units [5]. The spectra of B_2O_3/TiO_2-ZrO_2 samples calcined at different temperatures showed that both tetrahedral and trigonal boron species exist on their surface, and the amount of BO_3 units increased with increasing calcination temperature. The difference in the structure of borica on the surface of catalysts calcined at different temperatures reveals the different interactions between borica and the support, which may lead to the difference in stability in regeneration of deactivated catalysts.

4. Conclusions

In summary, the deactivation of the B_2O_3/TiO_2-ZrO_2 catalyst in the vapor phase Beckmann rearrangement of cyclohexanone oxime may be caused by several factors, but the main one is deposition of coke on the catalyst surface which covers the active sites. After the deactivated catalyst was regenerated by calcining in air at 600 °C for 8 h, the coke deposited over the catalyst surface was completely burnt off, the shielded active sites were again exposed to interact with the reactant molecules, and accordingly the activity was totally recovered. Furthermore, high calcination temperature is beneficial to the preparation of highly regenerable supported borica catalyst.

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