JOURNAL OF CATALYSIS 142, 172–181 (1993)

Deactivation and Regeneration of Alumina Catalysts for the Rearrangement of Cyclohexanone Oxime into Caprolactam

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Received November 23, 1992; revised February 3, 1993

Modified alumina catalysts have been studied for the Beckmann rearrangement of cyclohexanone oxime to caprolactam in the temperature range 250–350°C. Boron oxide supported on alumina was the most successful catalyst preparation used. Good initial activities and high selectivities to the lactam were observed. Other products observed included cyclohexanone, 5-cyanopent-1-ene and aniline. Coke formation was noted from the commencement of reaction which eventually led to loss in activity, followed by a lessening in selectivity to caprolactam and a lowering of surface areas. The loss in activity was related to the cumulative amount of cyclohexanone oxime converted in the reactor, and selectivity to caprolactam diminished as the oxime partial pressure increased. There was a direct relationship also between the amount of coke which formed on the catalysts and the decline in catalytic activity. Coke formed readily on the more basic catalysts. It is postulated that two reactions which occur on surface basic sites are responsible for coke formation. The first of these is polymerization of caprolactam. The second is the formation of aniline: this by-product can condense with cyclohexanone to form a Schiff base and further condensation of this base with cyclohexanone, via the Mannich reaction, represents a possible starting point for coke formation. Evidence is presented that surface acidic sites were responsible for caprolactam formation. Treating the deactivated alumina supported boron oxide catalysts in air at 500°C did not regenerate the original catalytic activity, although the surface area was fully regenerated. X-ray diffraction, infrared, and X-ray photoelectron spectroscopies as well as chemical analysis indicated that a proportion of the boron had entered into the alumina carrier to form an amorphous phase during the deactivation process, and temperature-programmed desorption of ammonia indicated that this process was accompanied by an irreversible decline in the surface concentration of acidic sites.

INTRODUCTION

The vapour-phase Beckmann rearrangement of cyclohexanone oxime to caprolactam has been studied for a wide range of solid acid types (*1–11*). Lowering of catalytic activity with time on stream is a common problem associated with all reported catalyst types, and the literature would suggest that zeolites with very high Si : Al ratios (*6, 12*) are more resistant to this effect. Two main reasons have been suggested to account for the loss in activity: coke formation (*5, 8, 10*) and/or irreversible adsorption of basic reaction by-products (*7, 13, 14*). The adsorption of basic products is reported to be common with zeolites, while the reason reported for decay in catalytic activity for boria-impregnated alumina catalysts is coke deposition (*8, 10*). These two mechanisms of loss of catalytic activity are classified as catalyst poisoning, since they involve a physical blocking of the active site(s). This will be distinguished here from deactivation, which will be defined as loss of catalytic activity due to restructuring of the catalyst.

Very little is reported in the literature in terms of catalyst regeneration. A brief examination carried out by Sato *et al.* (*8*) on the regeneration of a B_2O_3/Al_2O_3 catalyst by

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0021-9517/93 $5.00

combustion of the coke in air at 500°C for 3 h confirmed that the oxime conversion was completely recovered but lactam selectivity remained at the level observed prior to regeneration. No reason was given for this observation. Regeneration of a boria on alumina catalyst for the disproportionation of toluene (*15*) was accomplished by burning off the coke in air, giving back the original activity. However, no details on catalyst life or selectivity to products were mentioned.

Here we present details of a study of the loss of catalytic activity observed on a series of modified alumina catalysts, with particular emphasis on B_2O_3/Al_2O_3. These catalysts certainly lose their activity more rapidly than the corresponding zeolite catalysts with high Si : Al ratios, but they nevertheless represent a suitable system for study since the phenomenon can be characterized over a shorter time.

In preceeding publications (*16–18*), we have shown that there is a general relationship between the selectivity of these catalysts for caprolactam formation from cyclohexanone oxime and the surface concentration of acidic sites of intermediate acid strength; selectivity to caprolactam is highest over those catalysts which feature the highest concentration of intermediate strength acid sites, and the boria-modified alumina featured the highest concentration of these sites. In addition, it was shown that the absence of basic sites, determined by carbon dioxide adsorption, was a key feature of catalysts which exhibited high selectivities to caprolactam. Conversely, catalysts with the largest numbers of basic sites exhibited the lowest selectivities to caprolactam (*17, 18*).

EXPERIMENTAL

Catalyst Preparation and Testing

Full details of catalyst preparation by impregnation has been presented elsewhere (*16–18*). Briefly, alumina was modified by the addition of sulphate, phosphate, sodium, chloride, and boria. Testing was in a fixed bed flow microreactor; 100 mg of catalyst was used in each test, the cyclohexanone oxime pressure was 2.2 Torr unless otherwise stated. The total gas flowrate was 30 ml min^{-1}. Catalysts were tested in the temperature range 250–350°C.

Fourier Transform Infrared Spectroscopy (FTIR)

The boria on alumina catalysts were characterised at room temperature and atmospheric pressure using a Nicolet 20 SXB FTIR spectrophotometer with a spectral resolution of 2 cm^{-1}. KBr disks were prepared by pressing a 1 wt% catalyst/KBr mixture at 30 tons using a 1-inch die, resulting in a clean disk, approximately 0.2 mm thick.

X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed on each catalyst at room temperature with an SSX-100 Model 206 Surface Science Instrument (SSI) photoelectron spectrometer, interfaced to a Hewlett–Packard 9000/310 computer. Before transferring them to the spectrometer, the powered samples were mounted on Scotch tape inside Teflon holders. The residual pressure in the spectrometer was in the range of 1.3 to 6.5 $\times$ 10^{-7} Pa. A monochromated Al anode (energy of the AlK_α line 1486.6 eV), powered at 10 eV and 20 mA, was used for X-ray production. The binding energy scale of the spectrometer was calibrated with the Au $4f_{7/2}$ line (binding energy 83.98 eV). The analyser energy and spot size were 50 eV and 1.4 mm^2, respectively. These conditions give a full width at half maximum (FWHM) on Au $4f_{7/2}$ of 1 eV. The positive charge, developed on the samples due to the photoejection process, was compensated by a charge neutraliser (a flood gun) whose energy was adjusted to 6 eV (50 mA). The binding energies were calculated with respect to the C 1*s* peak (C–C, C–H) set at 284.6 eV. The intensities were estimated by calculating the integral of each peak after subtraction of the "S-shaped" background (*19*). The transmission function of the spectrometer was assumed to be inde-

pendent of the kinetic energy (E_k) and electron mean free paths (IMFP) were taken to be proportional to $(E_k)^{0.7}$. Atomic concentration ratios were calculated by correcting the intensity ratios with the theoretical sensitivity factors based on Scoffield cross sections (*20*):

$$\frac{C_A}{C_B} = \frac{I_A F_B}{F_A I_B}$$

where

C_A, C_B: atomic concentrations of the elements A and B, respectively;
F_A, F_B: sensitivity factors for elements A and B;
I_A, I_B: measured intensities of the peaks.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were carried out on a Stanton Redcroft TG770 thermobalance. Approximately 5 mg of catalyst was heated at a rate of 10°C min^{-1} in oxygen (10 ml min^{-1}) from 20 to 900°C. In these conditions combustion of coke occurred in the temperature range 300–700°C.

Temperature Programmed Desorption of Ammonia (TPD)

The TPD apparatus consisted of a gas delivery system, a reactor, and a thermal conductivity detector. Helium was used as the carrier gas. Pulses (0.2 ml) of ammonia were introduced into the helium stream via an injector valve and passed over the sample to be tested, at room temperature, until saturation. The reactor was a straight vertical quartz tube with internal diameter of 6 mm, which was loaded with 150 mg of catalyst. TPD measurements were carried out at a heating rate of 10°C min^{-1} from room temperature to 550°C under helium.

Chemical Analysis for Boron and Surface Area Measurement

Each catalyst was analysed for boria content according to the carminic acid spectrophotometric method (*21*), using a Varian DMS 100s UV–Visible spectrophotometer. BET surface areas were measured using a standard volumetric adsorption apparatus, with nitrogen at 77 K as the adsorbate.

RESULTS AND DISCUSSION

Figure 1A shows the cyclohexanone oxime conversion and caprolactam selectivity for a reaction time of 30 h over a B_2O_3/Al_2O_3 catalyst featuring 13 wt% B_2O_3. Initially conversion was close to 100%, but declined to close to zero after 30 h on stream. Selectivity to caprolactam increased initially, remained steady for approximately 10 h on stream, and declined significantly thereafter. After 30 h on stream, selectivity to caprolactam was close to zero. Other products observed in this study included cyclohexanone, 5-cyanopent-1-ene, and aniline, and generally selectivities to these products remained constant for the first 10 h on stream in spite of the declining conversion. The amounts of these products observed over the range of modified aluminas tested in this study are presented in Table 1 in the form of measured selectivities during the period of operation in which selectivity remained constant.

Coke deposited on the B_2O_3/Al_2O_3 catalyst, over 30 h on stream, as measured by thermogravimetry, is shown in Fig. 1B. As reaction time proceeded, there was an increase in coke deposited and correspondingly there was a reduction in the level of oxime converted. Therefore, a correlation seems to exist between the mass of deposited coke and the fall in oxime conversion. Coke build-up was also accompanied by a loss of surface area as is shown also in Fig. 1B.

The relationship between loss of catalytic activity and the cumulative amount of oxime converted in the reactor is shown in Fig. 2A and the corresponding relationship for selectivity to caprolactam is shown in Fig. 2B. Clearly loss in catalytic activity, namely, percentage conversion of the oxime, is somewhat dependent on the partial

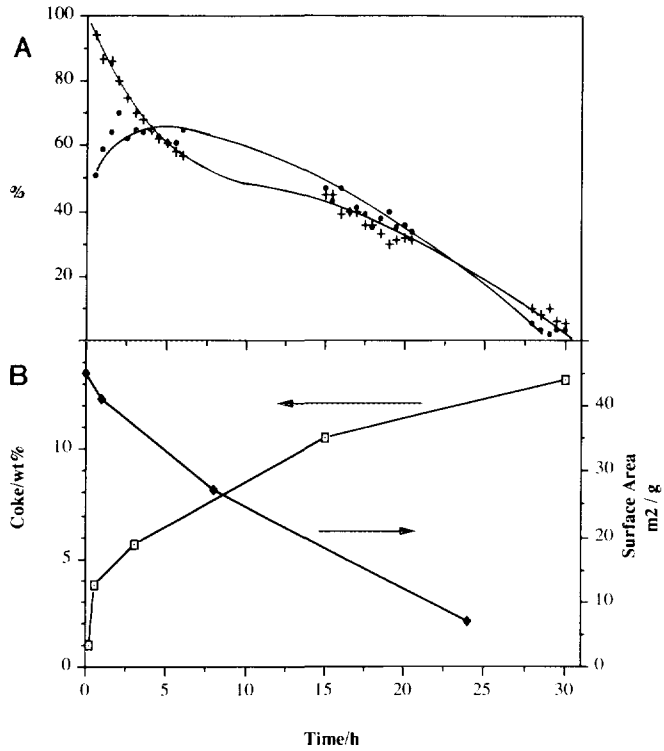


FIG. 1. (A) Oxime conversion (+) and caprolactam selectivity (●); (B) wt% coke deposited and surface area of the B_2O_3/Al_2O_3 catalyst for 30 h of use.

pressure of oxime in the feed, and the loss in activity was greatest at the highest oxime partial pressure tested. For selectivity two effects were observed: (i) greater selectivity to caprolactam was observed at lower oxime partial pressures, and (ii) selectivity was maintained at a steady-state level for larger oxime throughputs at low pressures. These data are consistent with a role for dimerization and polymerization reactions in the mechanism of coke formation, since these reactions should be more prevelent at higher reactant partial pressures.

The features shown in Fig. 1 for B_2O_3/Al_2O_3 were observed generally for all the modified aluminas tested. All the catalysts were originally white but after reaction had turned either black, brown, or grey. A thermogravimetric analysis was carried out on each catalyst after 8 h on stream. After TG analysis, the white colour was restored as a result of either coke combustion or base desorption.

There was a simple relationship between the amounts of coke deposited after 8 h on stream and the loss of catalytic activity over the same period of time. For the full series of aluminas tested in this study, high levels of coke deposition correlated with strong decreases in oxime conversion over 8 h. This trend is shown in Fig. 3, which plots the decline in oxime conversion over 8 h on stream against the wt% coke deposited. Alumina and boria on alumina maintained a relatively high oxime conversion up to 8 h and simultaneously resulted in low levels of coke deposition. By contrast, sodium, the least acidic and most basic of the modified aluminas (*17*), and the chloride treated alumina had almost completely deactivated after 8 h on stream. More generally, 14–15 wt% coke resulted in total

TABLE 1

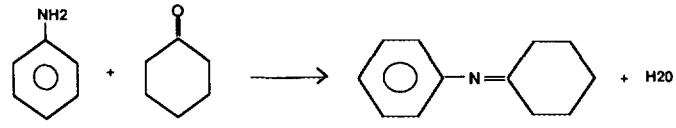
Selectivity to the Indicated Products after 2 h on Stream at 300 or 350°C

Solid acid	Caprolactam	Cyclohexanone	5-Cyanopent-1-ene	Aniline
Na/Al_2O_3 (350°C)	1	30	0	3
Cl/Al_2O_3 (300°C)	22	5	1	0.5
Cl/Al_2O_3 (350°C)	20	1	nd	2
PO_4/Al_2O_3 (300°C)	20	23	nd	0.5
PO_4/Al_2O_3 (350°C)	43	1	nd	0.8
SO_4/Al_2O_3 (300°C)	26	24	6	0
SO_4/Al_2O_3 (350°C)	65	15	nd	nd
Al_2O_3 (300°C)	20	9	4.5	0
B_2O_3/Al_2O_3 (300°C)	60	20	0	0

Note. nd: not determined

loss of catalytic activity for all the catalysts studied.

A feature of interest in the data presented in Table 1 may now be referred to, namely, that decay in catalytic activity was most pronounced over those catalysts which produced the largest amounts of aniline, i.e., Na/Al_2O_3 and Cl/Al_2O_3 (Fig. 3), and that cyclohexanone was a reaction product to varying degrees over all the catalysts studied. Aniline can readily condense with cyclohexanone to form a Schiff base (*22*):



The product of this reaction can in turn react with cyclohexanone, for example, via the Mannich reaction (*22*), with the eventual formation of carbonaceous deposits. An alternative source of coke formation arises from the polymerization of caprolactam, which is base catalysed (*23*). Since coke formation is most prevalent over the most strongly basic catalyst, namely, the sodium-treated alumina, these data would seem to indicate that basic sites aid in the polymerization of caprolactam, or are responsible for the dehydrogenation sites which must be present on the catalysts over which aniline was produced from the starting oxime.

Figure 4 shows the infrared spectra of alumina, the fresh boria on alumina catalyst, and the same catalyst after 30 min and 15 h on stream. The three strong bands at 3220, 1454, and 1196 cm^{-1} can be assigned to three infrared active in-plane vibrations (*24*). Of these, the 3220 and 1193 cm^{-1} bands can be assigned to OH stretching (νOH) and in-plane B–O–H angle deformation (δOH) vibrations, respectively. The 1454 cm^{-1} was shifted to a lower wavelength by comparison with pure boria (1470 cm^{-1}), but was assigned to the νBO (BO stretching vibrations) type. The 881 and 639 cm^{-1} bands corresponded to coupled γBO (out-of-plane BO deformation) and γOH (out-of-plane OH deformation) vibrations, respectively.

Comparing the spectra of the used catalysts with spectra of fresh boria on alumina, it was noted that with increased time on stream the band at 3220 cm^{-1}, assigned to B–O–H stretching, diminished in intensity and shifted to 3230 cm^{-1}. This indi-

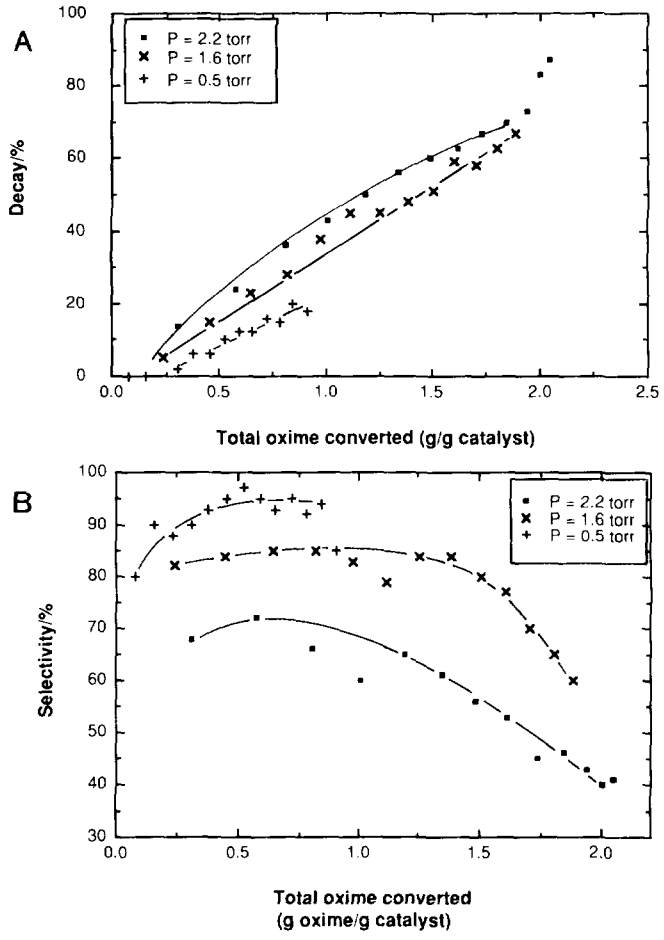


FIG. 2. (A) Relationship between decline in conversion and the total amount of oxime converted over a B_2O_3/Al_2O_3 catalyst for the oxime partial pressures indicated. (B) Relationship between selectvity to caprolactam and the total amount of oxime converted over B_2O_3/Al_2O_3 for the oxime partial pressures indicated.

cated a change in the structure of the boria, perhaps due to additional interaction with alumina. Two small bands appeared at 2930 and 2880 cm^{-1} during reaction. These two corresponded to C–H stretching and confirmed the presence of coke. The absorbance at 1196 cm^{-1}, due to in-plane B–O–H angle deformation, also diminished in size as the coke level increased. Therefore, the bonds most affected by coke deposition were those corresponding to the bands at 3230 and 1196 cm^{-1} which were assigned to νOH and δOH vibrations, respectively. This reduction was accompanied by a decline in oxime conversion, to about 50% of the original activity. Selectivity was also much lower after 15 h (see Fig. 1). This seems to indicate that the active sites were associated with these bands, and once these sites were poisoned, by coke or otherwise, the activity of the catalyst diminished.

Catalyst Regeneration

Thermogravimetric analysis indicated that coke could be removed at 500°C in

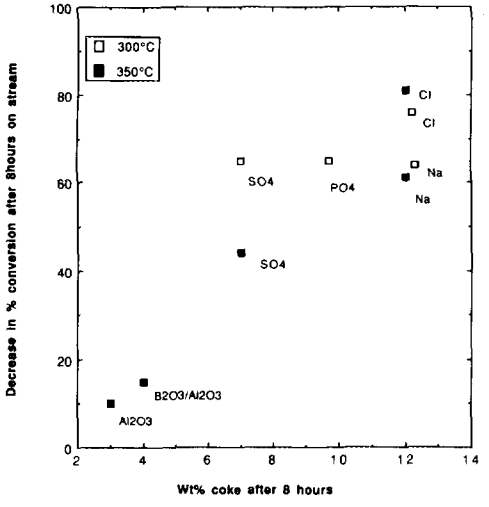


FIG. 3. Relationship between loss in oxime conversion and wt% coke deposition for the catalysts indicated.

flowing air. Hence, the regeneration procedure involved placing the used catalyst in an oven, at 500°C for 48 h in air. After this time, the catalyst regained its original white appearance, and the surface area was fully recovered.

Figure 5 shows a plot of oxime conversion, caprolactam selectivity and yield, over a fresh sample of boria on alumina and a regenerated sample. The regenerated catalyst was previously on stream for 30 h and then heated in air at 500°C for 48 h. This process did not cause a large improvement in lactam selectivity. However, the fact that higher overall conversions were attained meant that the lactam yield recovered somewhat.

In the case of the regenerated catalyst, improved lactam yields (compared to that of the deactivated catalyst) were sustained for much shorter operating times compared to the performance of the fresh catalyst, presumably because not all of the sites on which caprolactam formed selectively were regenerated. There is ample evidence both from the present and other work (*8*, *14*) that coking and readsorption of basic reaction by-products play a part in catalyst poisoning.

An FTIR comparison of a typical fresh, used and regenerated B_2O_3 catalyst (Fig. 4 (a) and (e)) shows that coke combustion at 500°C did not alter the intensity of the absorbance band at 3230 cm^{-1}, which remained at a much lower intensity than that observed for the fresh catalyst. The band at 1196 cm^{-1}, however, did regain some intensity and the two C–H stretching bands at 2930 and 2880 cm^{-1} were eliminated. Regeneration, therefore, conclusively removed the deposited coke. However, the surface structure did not recover to its original form, i.e., the bands at 3230 and 1196 cm^{-1} did not recover their original intensities.

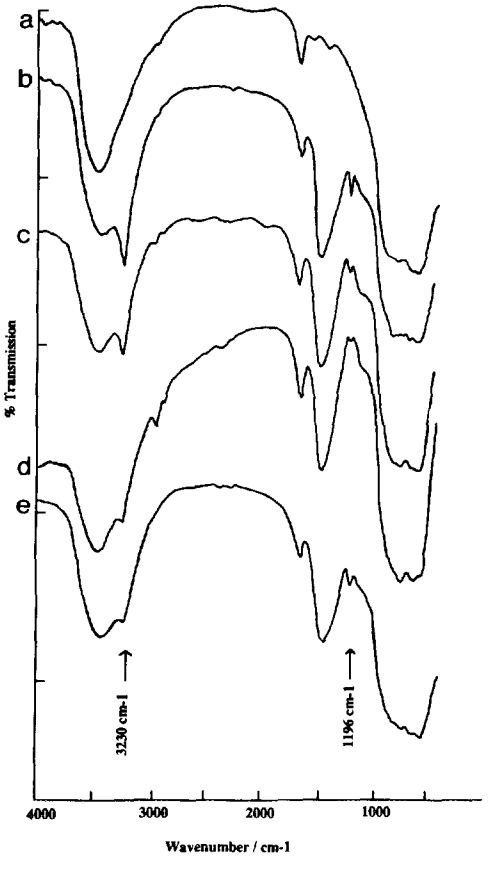


FIG. 4. FTIR spectra of (a) Al_2O_3, (b) B_2O_3/Al_2O_3, and (c) B_2O_3/Al_2O_3 after 30 min; (d) after 15 h on stream and (e) following regeneration.

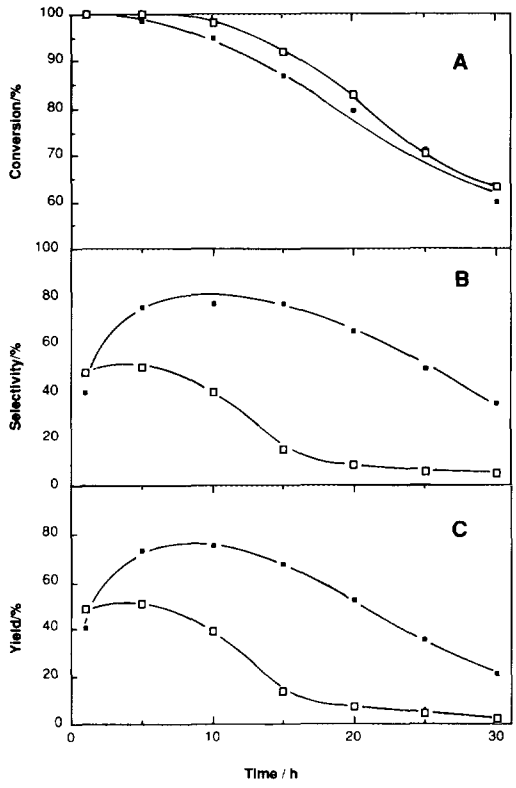


FIG. 5. (A) Oxime conversion, (B) caprolactam selectivity, and (C) caprolactam yield over (■) boria on alumina and (❑) regenerated boria on alumina at 300°C for 30 h on stream.

In an effort to selectively remove adsorbed bases, the used boria on alumina catalyst was placed in a quartz vertical tube reactor and subjected to a temperature of 500°C in a stream of helium for 1 h. This resulted in volatilisation of some adsorbed bases from the surface of the catalyst. However, removal of these bases did not result in any recovery in oxime conversion or caprolactam selectivity when re-tested, indicating that bases desorbed below 500°C were not involved in the poisoning of the boria on alumina catalyst.

The boron analyses (see Table 2) and XRD data indicated that crystalline water soluble B_2O_3 was present in the fresh catalyst but, it was significantly less in the regenerated samples, even though the total boron content (water soluble and water insoluble) was still high. Almost 100% of the total boron present in the fresh catalyst was in a water soluble form (B_2O_3). However, only 70% of the boron was of this form in the regenerated catalyst (This analysis was not attempted for the used catalyst because deposited coke might interfere with the solubility of the boron oxide). It is apparent from the present results that coking and base readsorption cannot be the only catalyst deactivation mechanisms, since, if they were, it would be expected that the regenerated catalysts would have contained the same amounts of crystalline, water-soluble B_2O_3 as did the fresh catalyst. This suggested a third deactivation mechanism, whereby the B_2O_3 present on the fresh catalyst was converted during the catalytic reaction into an amorphous water-insoluble boron species which was not selective for lactam formation. This deactivation process was not thought to be caused by a temperature effect alone, since unused catalyst samples which were prepared by calcination in air at 500°C (same conditions as for regeneration) showed lactam yields as good or better than conventional preparations (calcined at 350°C).

A summary of the XPS analyses of the different forms of B_2O_3/Al_2O_3 are presented in Table 3. The binding energy values for all elements were found to be constant (±0.2 eV) for all samples. Nitrogen was detected in all but the fresh sample. This was not surprising, since nitrogen is present in

TABLE 2

Boron Analysis of Catalyst Samples

Sample	% Boron (as B_2O_3)	
	Total boron	Water-soluble boron
Fresh B_2O_3/Al_2O_3	12.7	12.3
Regenerated catalyst[a]	11.1	7.8

[a] Regenerated in air at 500°C for 48 h.

TABLE 3

XPS Information on the B_2O_3/Al_2O_3 Catalysts Listed

Treatment	Atomic intensity ratios	
	B 1s/Al 2p	N 1s/Al 2p
Fresh	0.4123	0
Used	0.3937	0.1240
Regenerated	0.3367	0.0130
Washed[a]	0.0658	0.0055

[a] The regenerated catalyst was washed to remove water-soluble boron.

cyclohexanone oxime and some nitrogen could be incorporated into the coke which formed. Regeneration removed most of this nitrogen and washing in water removed even more.

There appeared to be some loss of surface boron after regeneration. When boron was leached from the catalyst by mixing with warm water for 2 h some still remained (see Table 3). Here it is proposed that the B/Al ratio of 0.0658 observed in XPS is associated with the water-insoluble boron observed by leaching experiments. This is consistent with a change in the nature of the boron oxide, i.e., that about 30% of the boria is no longer water soluble following regeneration (Table 2). These results indicate that a portion of the water-insoluble boron migrated into the Al_2O_3 lattice and thus remained undetected by XPS.

A study on the acidity of the used and regenerated catalysts was carried out by comparing their ammonia TPD profiles to that of the fresh boria on alumina catalyst. This is presented in Fig. 6. The used catalyst showed a marked decrease in the intensity of the ammonia desorption peak at 320°C. Heating the used catalyst in air, at 500°C for 48 h, did not fully regenerate of this peak. So, coupled with the loss of water-soluble boron, there was a corresponding loss of sites of intermediate acidity (*17*).

In a preceeding study (*17, 18, 25*), we have demonstrated a significant relationship between selectivity to caprolactam and the concentration of intermediate strength acid sites, measured in terms of the amount of ammonia which desorbed per unit of surface area between 200 and 350°C in the temperature-programmed desorption profile. Further examination of Fig. 5 indicates that the used and regenerated catalysts have lost acid sites of intermediate strength as indicated by the reduced intensity of ammonia desorption in the temperature range 200–350°C. This supports the theory that sites of intermediate strength are responsible for caprolactam selectivity in the Beckmann rearrangement and these are the sites that are partially destroyed during reaction (*17, 18, 25*).

CONCLUSIONS

The following key points emerge from this study:

(1) There is a strong relationship between coke deposition and catalyst performance:

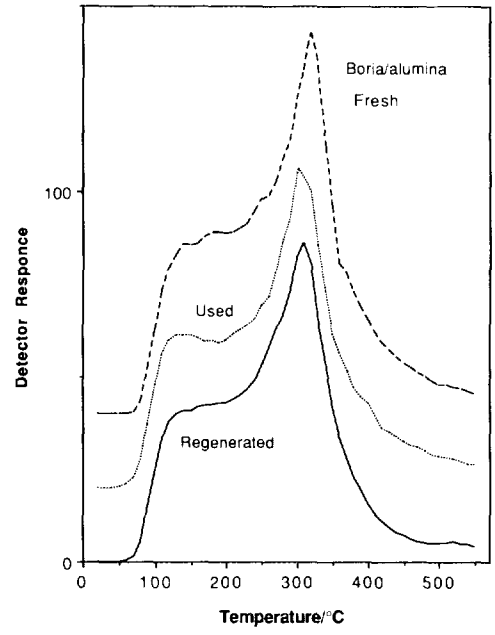


FIG. 6. Ammonia TPD profiles of fresh, used, and regenerated boria on alumina catalysts.

as coke builds up, conversion and selectivity decline, as does surface area (Figs. 1–3).

(2) Loss in catalytic activity was more prevalent at higher oxime partial pressures, and selectivity was lower even when compared in terms of total oxime converted (Fig. 2). This is consistent with a role for dimerisation and/or polymerisation reactions in coke formation.

(3) Some aspects of coke formation seem to be related to the presence of basic surface sites which catalyse caprolactam polymerisation and help in the formation of aniline, which in turn can give rise to coke formation via condensation reactions.

(4) The FTIR bands of boria at 3230 and 1196 cm^{-1}, corresponding to OH stretching and in-plane B–O–H angle deformation, respectively, are reduced in intensity during reaction (Fig. 4).

(5) The B_2O_3/Al_2O_3 catalysts cannot be regenerated by treatment in air.

(6) Part of the B_2O_3 becomes insoluble in water following reaction and regeneration. However, the original surface area was fully recovered, indicating that pore closing with trapping had not occurred.

(7) There is a lowering in the number of acid sites of intermediate strength during reaction which is not reversed during regeneration. This process is probably associated with diffusion of boron into the alumina carrier.

(8) From XPS results (Table 3), the surface boria concentration lessens during testing, presumably due to deposition of coke; a further reduction occurred during regeneration. Some boria remained on the surface after washing, consistent with migration of boron into the alumina carrier with subsequent solid solution formation.

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