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The relationship between acidity of aluminas and their selectivity in the conversion of cyclohexanone oxime into caprolactam

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A range of aluminas modified by addition of sodium, phosphate, sulphate, chloride and boria have been tested for the Beckmann rearrangement of cyclohexanone oxime to caprolactam in the temperature range 300–350°C. A relationship was observed between the selectivity to caprolactam and the surface concentration of acidic sites of intermediate strength.

Keywords: Acidity; alumina; cyclohexanone oxime; caprolactam; selectivity

1. Introduction

A number of processes are practiced commercially for the production of caprolactam [1], but each feature the oleum catalyzed Beckmann rearrangement of cyclohexanone oxime to yield caprolactam as the final step. A drawback associated with this step is the co-production of large amounts of ammonium sulphate. Hence, there is an interest in the development of an alternative and the use of solid acids is one possibility.

The vapour phase Beckmann rearrangement of cyclohexanone oxime to caprolactam over solid catalysts has been studied over a range of solid acid catalysts. Initially the solid catalysts most used for caprolactam production were silica gel and alumina [2] but these showed low activity and low caprolactam selectivity. Supported boria catalysts such as boria on alumina [3,4], have long been known as favourable catalysts for the Beckmann rearrangement. Other supported boria catalysts include boria supported on thoria [5], and on hydroxyapatite [6]. Zeolites such as ZSM-5 and H-Y have also been studied [7,8]. All catalysts studied to date show a tendency towards coke formation and eventual deactivation. Generally the rate of the deactivation increases as the selectivity to caprolactam decreases. Catalyst preparation method, reaction temperature and

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surface acidity have all been shown to influence oxime conversion and lactam selectivity [9–12].

Previous studies have sought correlation between acid site strength and catalyst performance. Sato et al. [7] have demonstrated the usefulness of ZSM-5 for this reaction, provided that the Si/Al ratio in the zeolite was greater than ≈ 1000. Temperature programmed desorption of ammonia indicated that when the Si/Al ratio exceeded 1000, strongly acidic sites were no longer present in the zeolite, so that the selectivity to caprolactam increased and coke formation decreased, leading also to a greater catalyst lifetime. Aucejo et al. [8] have reported that the rate of caprolactam formation on HNaY zeolite was directly proportional to the concentration of acid sites of $pKa < 1.5$.

The situation is less clear for non-zeolite solid acids. Izumi et al. [6] have emphasised the need to respect a balance between acidic and basic surface sites each of the appropriate quantity and strength. The quantities required were not quantified. Sato et al. [9–11] have also addressed this problem for boria/alumina and boria/silica catalysts prepared by a variety of methods.

This report is the result of an attempt to establish for a range of modified aluminas the relationship between the surface concentration of acidic sites of various strengths and the selectivity in caprolactam formation from cyclohexanone oxime.

2. Experimental

Catalyst preparation: Gamma alumina supplied by Rhone-Poulenc Recherche (surface area 95 $m^2\ g^{-1}$, pore volume 0.95 $cm^3\ g^{-1}$), and modified by addition of Na_2CO_3 (BDH general purpose grade), NH_4Cl (BDH general purpose), H_2SO_4 (May and Baker Ltd.), and H_3BO_3 (BDH general purpose grade), respectively. After stirring for 2 h the excess water was slowly removed by boiling until a slurry formed, which was dried overnight at 100°C. Each prepared catalyst was sieved to remove fines and excess modifier, keeping the particle diameter between 0.5 and 1 mm. All catalysts were calcined at 550°C for 5 h before use except in the case of the boric acid modified alumina which was calcined at 350°C for 3 h. Chemical analysis indicated that the sodium content of the Na_2CO_3 modified alumina was 2 wt%. B_2O_3 contents of the boron oxide modified aluminas were in the range 2–20 wt%. BET surface areas of all the aluminas used in this work are presented in table 1.

The vapour phase Beckmann rearrangement reaction was carried out using a continuous flow system operated at ambient pressure. Helium at 30 ml min^{-1} was used to entrain the cyclohexanone oxime (Aldrich general purpose grade) into the vapour phase from a saturator. This consisted of a stainless steel tube filled with cyclohexanone oxime supported on molecular sieve. The vapour pressure of the oxime was controlled by adjusting the saturator temperature. In

Table 1
Surface areas of the modified alumina catalysts

wt% boria		S_{BET} ($m^2 g^{-1}$)
modifier	measured	
none	Al_2O_3	95
boron	$2B/Al_2O_3$ [a]	89
boron	$4B/Al_2O_3$	82
boron	$7B/Al_2O_3$	70
boron	$10B/Al_2O_3$	63
boron	$14B/Al_2O_3$	51
boron	$20B/Al_2O_3$	46
sodium	Na/Al_2O_3	68
sulphate	SO_4/Al_2O_3	10
chloride	Cl/Al_2O_3	77

[a] 2 wt% boron oxide.

normal operation, the partial pressure of cyclohexanone oxime in the gas phase was 2.2 Torr, the catalyst charge was 100 mg and the reaction temperature was 300 or 350°C. Reaction products were collected at the exit of the reactor and analysed by gas chromatography.

Characterization was by temperature programmed desorption (TPD) of ammonia following adsorption at ambient temperature.

3. Results and discussion

Fig. 1 demonstrated typical variations in oxime conversion with time on stream for three of the catalysts studied. 20 wt% B_2O_3/Al_2O_3 gave the greatest

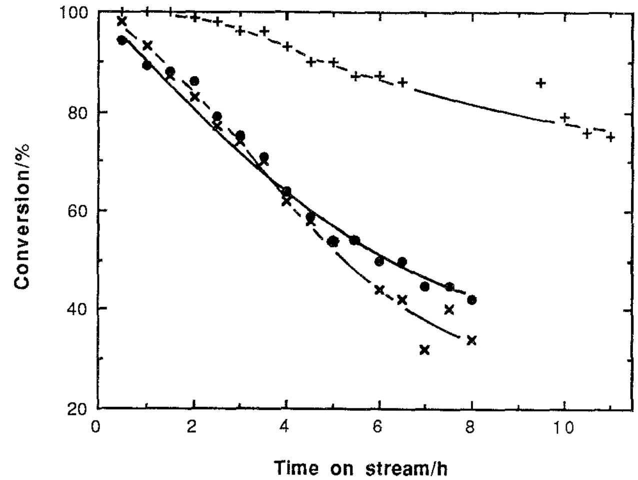

Fig. 1. Conversion of cyclohexanone oxime over 20 wt% B_2O_3/Al_2O_3 (+), SO_4-Al_2O_3 (●) and Na-Al_2O_3 (×).

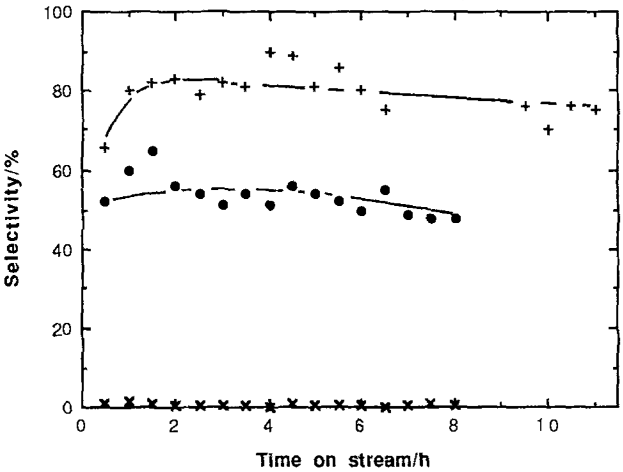

Fig. 2. Selectivity to caprolactam over 20 wt% B_2O_3/Al_2O_3 (+), SO_4–Al_2O_3 (●) and Na–Al_2O_3 (×).

sustained conversion of those catalysts presented in fig. 1, but nevertheless conversion declined to less than 80% after 8 h on stream. During this time selectivity of caprolactam remained constant at about 80% (fig. 2). By contrast, conversion over Na–Al_2O_3 declined very rapidly and selectivity to caprolactam was essentially zero throughout the test. In this case the principal volatile product observed was cyclohexanone. 5-cyanopent-1-ene was also observed as a reaction product as well as small quantities of aniline. Conversion over the sulphate modified alumina also declined rapidly during testing, but selectivity to caprolactam remained constant at about 50% through the test. For all catalysts studied mass balance was always less than 100% and this was associated with coke formation.

For all catalysts studied coke formation was the primary cause of deactivation. Apart from the first hour on stream, where some increase in selectivity to caprolactam was observed, coke formation seems to proceed via the indiscriminate poisoning of all surface sites, as indicated by the lowering in conversion without any appreciable influence on selectivity to caprolactam.

Each catalyst studied also exhibited a characteristic TPD profile, representative samples of which are presented in fig. 3. These profiles were divided into three parts, so that ammonia desorbed below 200°C was considered to have been physisorbed or to have been desorbed from weakly acidic sites; ammonia desorbed between 200 and 350°C was considered to derive from acidic sites of intermediate strength and ammonia desorbed at higher temperatures was associated with strongly acidic sites. Using this technique the concentration of weak, intermediate and strong acid sites could be calculated for each catalyst used in a similar manner to that outlined by Berteau and Delmon [13]. Ultimately the concentration of acid sites in each grouping was calculated per unit of surface

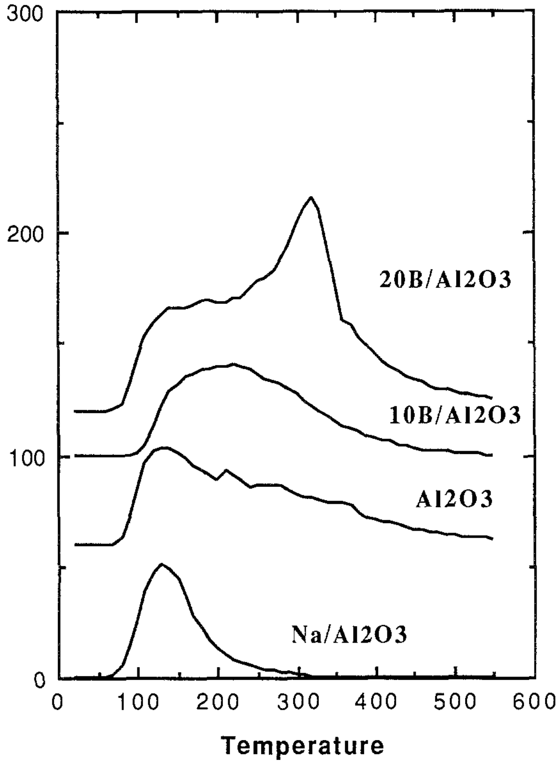

Fig. 3. Temperature programmed desorption of ammonia from the modified aluminas indicated.

area and correlations sought between these surface concentrations and the observed catalytic performance.

Fig. 4 presents the relationship between selectivity to caprolactam (measured at close to 100% conversion after 1–2 h on stream) over the full range of modified aluminas studied and the surface concentration of surface acidic sites of intermediate acidity. Considering the range of materials studied a very clear relationship emerged; as the surface concentration of acid sites of intermediate strength increased the selectivity to caprolactam also increased, initially in an almost linear fashion. The least acidic of the catalysts, namely Na–Al_2O_3 showed the lowest selectivity, although it did feature a large number of weakly acidic sites, i.e. a large amount of ammonia desorbed below 200°C. Selectivity to caprolactam increases in an almost linear fashion with surface concentration for intermediate strength acidic sites up to values of ≈ 3 μmol m^{-2}. Thereafter, a further increase in selectivity was observed up to the maximum intermediate strength acid sites.

Correlations were not observed between selectivity and the concentration of weak or strong acid sites.

Reports of additional aspects of the role of surface acidity in selectivity and in catalyst deactivation are in preparation.

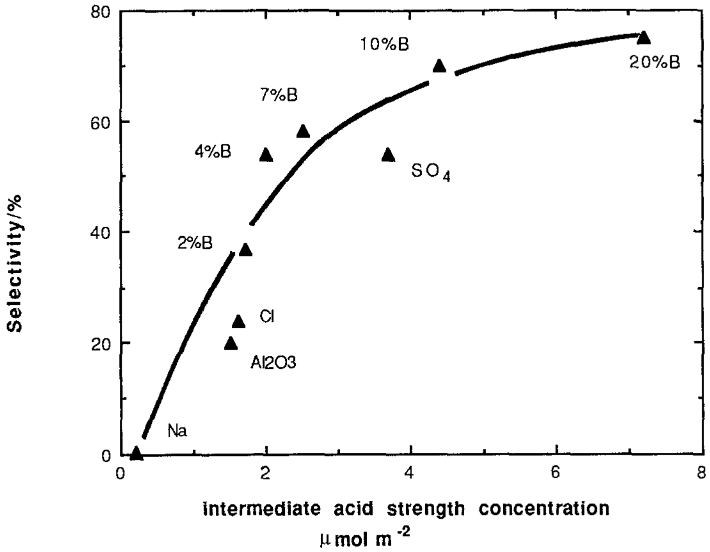

Fig. 4. Relationship between selectivity to caprolactam over the solid acids indicated and the surface concentration of intermediate strength acid sites, as determined by TPD of ammonia.

In conclusion, this work shows that there is a clear relationship between the surface concentration of sites of intermediate acid strength and the selectivity of modified aluminas for caprolactam formation from cyclohexanone oxime.

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