

CHAPTER 4

ZEOLITE DEACTIVATION IN ANILINE ALKYLATION

4.1 Introduction

Deactivation of catalysts on account of accumulation of carbonaceous deposits ("coke") on the surface is a phenomenon of considerable importance in industrial practice, and has been the subject of numerous investigations over the years (1). Zeolites are an important class of industrial catalysts (2) which as pointed out in chapter 1, owe their success to their high thermal stability, greater activity and peculiar shape-selective properties. But a major limitation in the use of zeolite catalysts is that they tend to age rather quickly. This is because in the processes wherein they are used as catalysts, heavy by-products are usually formed during the course of the reaction, and these either clog the pores or get deposited on the surface leading to zeolite deactivation (3). Coke deposition can lower the catalytic activity by site coverage(poisoning) and/or by pore blocking, which prevents the access of the reactants to the active sites (4).

Techniques ranging from catalytic activity measurements and/or separation of the coke from the zeolite and its analysis by gas chromatography to

^1H NMR and mass spectrometry have been applied to study the modes of coking and of deactivation of zeolites (5). Zeolites having perfectly defined pore structure are ideal solids for studying pore blockage and, in particular, for

establishing relationships between the characteristics of the pore structure and the deactivating effect of coke molecules (6). Coking and deactivation depend on the zeolite pore structure as well as the operating conditions such as time, temperature (7-17), pressure and nature of the reactants (18-22). Rollmann and Walsh (23,24) were the first to show that coke formation is a "shape-selective reaction", that is, the coking tendency is an intrinsic property of the zeolite pore structure. Thus the smaller the pore size, the lower is the coke yield in the cracking of a hydrocarbon mixture. The low coking rate found on ZSM-5 was related to its smaller pore structure and lower density of its acid sites (25). Guisnet *et al* (5) proposed that in zeolites coke formation occurs probably through the same steps (Fig. 4.1) as are involved in the cracking of *n*-heptane, namely oligomerization of the olefinic cracking products, cyclization of the oligomers, transformation through hydrogen transfer into monoaromatics, alkylation of these monoaromatics, then cyclization and hydrogen transfer to give biaromatics, triaromatics, etc.

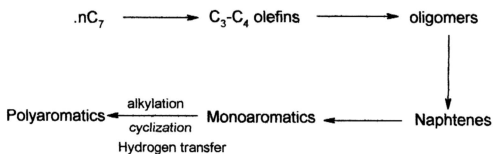


Fig. 4.1 Mode of coke formation during *n*-heptane (nC_7) cracking (Ref.5).

Schultz *et al* (26) have reported that carbonaceous species build up on the exterior of ZSM-5 crystal until they obstruct access to the interior via encapsulation. The pore structure of ZSM-5 restrict polycondensation, hydride transfer, and cyclization reactions that lead to coke formation. Coke formation and consequent deactivation of zeolite H-Y and Pt-H mordenite catalysts during hydrogenation of benzene has been reported (25). It was shown that the coke molecules were retained in the zeolite pores because of their low volatility.

Coking and regeneration of H-Y zeolite catalyst in a fixed bed reactor during cumene cracking was investigated (27). It was shown that in the cracking reactions over the zeolite catalyst, most of the coke originates from the cumene feed at low temperatures, while at higher temperatures the majority of coke is formed from propene, a product of the reaction.

Pradhan and Rao (28) studied the deactivation of faujasite and mordenite during the isopropylation of benzene. They reported that deactivation of faujasite was due to blocking (poisoning) of active sites while deactivation of mordenite was caused by pore blocking. Mori *et al* (29) studied the deactivation of H-type zeolites (H-mordenite, H-Y and HZSM-5) in *n*-hexane cracking. Their study revealed that deactivation of zeolites by coke does not occur through site poisoning but through limitation or blockage of the access of the reactant to the active sites. Excellent reports have been made correlating coking and deactivation with acidic, structural and other properties of the zeolites (30- 32). However to the best of our knowledge, there has been no

report to-date on the deactivation zeolite catalysts used in the alkylation of aniline. The purpose of the present study is to determine the longevity and possible causes of deactivation of zeolites of different activity used in the vapour phase isopropylation of aniline at atmospheric pressure.

4.2 Experimental

Na and Ce forms of Y-type zeolites were prepared by the ion-exchange method as described in Chapter 2. Aniline and isopropanol were purified by distillation. Experiments were carried out in a fixed bed reactor. The reaction was carried out over 15 hours. The products were passed through a water-cooled condenser and collected in an ice-cooled receiver. The liquid products obtained were analysed by gas chromatography by using 5 m×0.22mm i.d. methylsilicone column, the oven temperature was programmed from 30-220°C at the rate of 10°/min using nitrogen as carrier gas. The amount of coke present in the catalyst was estimated by volumetric analysis as described in Chapter 2.

4.3 Results

4.3.1 Study on the stability of Na-Y zeolite

The results on the isopropylation of aniline over a fixed bed of Na-Y zeolite are listed in Table 4.1. The reaction was performed at 400°C and at a flow rate of 5mL/hr of the reagents. Continuous monitoring of the reaction was carried out

for 15 hours, with sampling done at the end of each hour. As seen from the table, the rate of conversion of aniline remained almost constant at 33 mole% for the first six hours. Thereafter, the conversion rate slowly declined registering a value of 8 mole % by the 15th hour. However, it was noticed that the selectivity of N-isopropylaniline over C-alkylated aniline products increased by over 20% with ageing of the catalyst over the 15 hours. At the end of this period, the deactivated catalyst was regenerated by heating at 500°C in a stream of air for 8 hours followed by passing nitrogen for 15 minutes. The aniline conversion rate obtained with the regenerated catalyst was found to be 29.7 mole %.

4.3.2 Study on stability of Ce-Y zeolite

The results of a time-on-stream study of the same reaction over Ce-Y zeolite catalyst bed again performed continuously for 15 hours (Table 4.2). The product samples were collected hourly for analysis. The conversion of aniline decreased as the time progressed. Initially the conversion of aniline decreased as the time progressed. Initially the conversion of aniline was 57.3mole %, and this fell to 12.1% at the end of 15th hour. As with the case of Na-Y zeolite, increased N-isopropylaniline formation was noted with the ageing of the catalyst. After the 15th hour, the catalyst was regenerated by heating in a current of air at 500°C for 8 hours. The aniline conversion rate obtained with the regenerated catalyst was 51.4 mole %.

4.4 Discussion

The results of the reaction of aniline with isopropanol over Na-Y and Ce-Y zeolites showed that the percentage conversion of aniline was almost constant for the first 6 hours and then slowly decreased with time. Deactivation, as reflected in the declining aniline conversion values (Tables 4.1 and 4.2) was more pronounced for the Ce-Y zeolite than for the Na-Y zeolite after 11 hours. The amount of carbonaceous compounds ("coke") present in the deactivated catalyst after 15 hours was estimated by volumetric analysis (Table 4.3) as well as indirectly by thermogravimetric analysis (Table 4.4). Greater coke deposition was observed in the Ce-Y zeolite than in the Na-Y zeolite. The greater deactivation effect found on Ce-Y zeolite than in the Na-Y zeolite may be attributed, in part, to the relatively stronger acidic sites available on this catalyst. Previous studies on large pore zeolites such as USHY, which has a heterogeneous distribution of acidic sites, have shown that the strongest acidic sites are the sites of preferential coke formation (29). Since the strongest acidic sites are also the most active sites favouring catalysis, it follows that the deactivating effect of coke will be more pronounced on Ce-Y than on Na-Y. After the catalyst is essentially deactivated the coke continues to migrate over the catalyst surface. Another possible cause of catalyst deactivation that cannot be excluded is loss of surface area with time. For the case at hand, it is seen that both Ce-Y and Na-Y suffer a decrease in surface area of about 20% after 15 hours in use (Table 4.4).

Table 4.1. Study on the stability of Na-Y zeolite used in alkylation of aniline with isopropanol^a

Time-on-stream(hr)	Mole % conv. of aniline	% Selectivity of products ^{b,c}		
		(1)	(2)	(3)
1	33.3	73.1	20.6	6.3
2	33.2	73.2	20.4	6.4
3	33.6	72.8	20.1	7.1
4	33.1	73.0	20.3	7.7
5	33.2	73.1	19.1	8.8
6	33.0	73.4	18.0	8.6
7	32.1	74.0	16.7	9.3
8	31.0	75.1	16.2	8.7
9	29.2	76.3	15.3	8.4
10	27.0	77.2	14.8	8.0
11	26.0	81.2	10.9	7.9
12	24.0	83.1	10.7	6.2
13	20.3	86.2	9.0	4.8
14	11.8	88.0	8.3	3.7
15	8.0	90.0	7.7	1.3
Regenerated catalyst	29.7	75.3	21.6	3.1

^a aniline/isopropanol mole ratio : 1/3; wt. catalyst = 7g; temperature: 400^oC; flow rate : 5mL/hr

^b selectivity of products = [mole% yield of products/ mole% conversion of aniline] × 100

^c (1) = N-isopropylaniline (2) = o-isopropylaniline (3) = p-isopropylaniline

Table 4.2 Study on the stability of Ce-Y zeolite used in alkylation of aniline with isopropanol^a

Time-on-stream (hr)	Mole% conv. of aniline	% Selectivity of products ^{b,c}			
		(1)	(2)	(3)	(4)
1	57.3	62.7	24.3	8.7	4.3
2	57.4	62.4	24.2	9.2	4.2
3	57.2	62.8	24.0	9.2	4.0
4	56.9	64.7	21.7	9.7	3.9
5	57.1	66.2	22.2	9.5	2.1
6	55.7	70.5	19.0	8.5	2.0
7	53.3	71.3	19.1	7.7	1.9
8	48.0	73.2	18.2	7.1	1.5
9	42.7	76.3	16.6	6.0	1.1
10	31.5	78.6	16.1	4.0	1.3
11	24.3	82.0	13.5	4.5	-
12	19.2	83.0	13.1	3.9	-
13	17.1	84.3	12.7	3.0	-
14	13.2	85.2	11.8	3.0	-
15	12.1	85.3	12.0	2.7	-
Regenerated catalyst	51.4	63.0	21.2	11.8	4.0

^a aniline/isopropanol mole ratio: 1/3; wt. of catalyst = 7g; temperature : 400°C; flow rate : 5mL/hr.

^b selectivity = [mole% yield of product/mole% conversion of aniline] × 100.

^c (1) = N-isopropylaniline (2) = o-isopropylaniline
(3) = p-isopropylaniline (4) = dialkylated products

Table 4.3 Determination of coke by volumetric analysis after 15 hours.

catalyst ^a	wt.of carbon	% carbon
Na-Y	0.126	18.1
Ce-Y	0.162	23.2

^awt. of catalyst = 7g.

Table 4.4 Surface area and weight loss measurements by TGA on Na-Y and Ce-Y zeolite catalysts

Catalyst	Surface area m ² /g	Activity	% wt. loss(TGA) ^a
Na-Y fresh	332 ^b	33.3	18.7
Na-Y used	265 ^c	9.8	20.3
Na-Y regenerated	309 ^d	29.7	18.7
Ce-Y fresh	351 ^b	56.3	22.8
Ce-Y used	276 ^c	13.2	24.6
Ce-Y regenerated	334 ^d	51.3	22.8

^a 30°C to 800°C : heating range.

^b measured prior to activation at 500°C for 4 hours , i.e. before weight loss.

^c measured after prior activation and recovery from reactor following the experimental run at 400°C for 15 hours.

^d measured after regeneration of the used catalyst at 500°C for 8 hours.

However, the activity of the regenerated catalyst as well as its selectivity were little impaired in either case when subjected to a short time-on-stream study (1hour) (see Tables 4.1 and 4.2). Both catalysts (Ce-Y, Na-Y) showed high initial conversions (Tables 4.1& 4.2) followed by gradual deactivation. From product compositional analysis, it is noted for both catalysts that the selectivity for N-isopropylaniline increases after 6 hours, while that for the C-alkylated (*ortho* and *para*) products decreases. It is further noted that there is an apparent increase in the *ortho*- product over the *para*- product with deactivation of the Ce-Y zeolite; the trend, although erratic, is somewhat reversed for the case of Na-Y zeolite.

A plausible explanation for the observed increase in N-isopropylaniline is that secondary transalkylation reactions involving this product leading to C-alkylated products as indicated in Chapter 3 (Scheme 3.3) become less favoured with ageing and consequent loss of reactive sites of the catalyst. Alternatively, the C-alkylated products that are formed within the confines of the zeolite pores become increasingly inhibited in their release because of clogging of the pores and consequent alteration of the diffusional characteristics of the zeolite. This results in a superficially high concentration of N-isopropylaniline component in the product mixture. The unreleased C-alkylated products contribute to the coke content in the pores. As has already been pointed out in Chapter 3, C-alkylated products can also arise from aniline and isopropanol via the S_N2 pathway. Deactivation of the number of active sites on the zeolite with time will markedly reduce the formation of

C-alkylated products. The third possible pathway for the formation of C-alkylated products which involves the reaction between propene (obtained from the dehydration of isopropanol) and aniline, will also be diminished with increasing deactivation of the catalyst on account of the lesser availability of propene or the increasing tendency of the propene to polymerise to produce coke. The lower amount of *para*-isomer relative to the *ortho*- in the

C-alkylated product composition is more pronounced for the case of Ce-Y than Na-Y. This is on account of the development of greater coke content in Ce-Y with time, and the constraints thereby imposed in forming as well as releasing the larger *para*- isomer molecule relative to the smaller *ortho*.

The coke molecules deposited in the pores of the zeolites can be removed to regenerate the catalyst. During regeneration, which involves heating the catalyst to 500°C for 8 hours, the temperature inside the reactor, as monitored by a chrome-aluminium thermocouple rises. The temperature rise was observed to be higher with the Ce-Y zeolite than with the Na-Y zeolite. This is in agreement with other published reports (9) which have related temperature rises during catalyst regeneration to the levels of coke present in them.

4.5 Conclusion

Deactivation of zeolite used in aniline alkylation by isopropanol in vapour phase under atmospheric pressure was investigated. For both zeolites, the conversion and product composition was constant for the duration of -

first 6 hours, but decreased on further usage. Blockage of pores and coverage of surface of zeolite by carbonaceous materials and loss of surface area are causes of deactivation. Greater coke deposition was observed in the Ce-Y zeolite than in the Na-Y zeolite. This is attributed to the relatively stronger acidic sites available on Ce-Y than on the Na-Y zeolite. It is to be noted that while the deactivation is to the extent of 75-80% over 15 hours, the decrease in surface area is relatively small at 20-25%. This suggests that coke formation largely blocks the active sites rather than cause the plugging of the pores. Another significant observation in this study has been that as the catalyst became increasingly deactivated, the selectivity for N-alkylaniline increased, while that for the C-alkylated (*ortho* and *para*) products decreased. Regeneration of the deactivated catalyst was achieved by heating in a current of air at 500°C for 8 hours. The regenerated catalyst showed activity closely comparable to its original state. Its surface area was noted to be approximately 90% of the fresh catalyst. This may be due to the possibility of sintering because of the exothermic nature of coke combustion.