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Applied Catalysis A: General 111 (1994) 133–142

applied  
catalysis A

# Vapour phase aniline alkylation activity and selectivity over H-ZSM-5<sup>†</sup>

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(Received 19 July 1993, revised manuscript received 10 December 1993)

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## Abstract

Vapour phase alkylation of aniline with ethanol is studied over a series of H-ZSM-5 zeolites containing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 30, 50, 70, 150 and 280. The influence of feed rate, temperature and pressure on activity and selectivity of the products, namely *N*-ethylaniline and *N,N'*-diethylaniline are investigated. The effect of acidity and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of H-ZSM-5 on alkylation activity is discussed. H-ZSM-5 with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 70 seems to have the acid sites required for optimum aniline alkylation activity and selectivity of the products.

*Key words:* acidity; alkylation; ammonia TPD; aniline; H-ZSM-5; zeolites

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## 1. Introduction

Alkylation of aniline is industrially important, as the major products of this reaction form the basic raw materials for synthesis of organic chemicals and intermediates in dye stuffs, pharmaceuticals and agrochemical industries. The traditional route [1,2] of liquid-phase alkylation of aniline under pressure using acids and Friedel–Crafts catalysts suffer from the disadvantages of high capital cost, reactor corrosion and the formation of by-products that cannot be recycled. The vapour-phase alkylation process involving the use of solids acids as catalysts is free of such problems and the used catalysts are easily disposable. Several types of catalysts [1–9] based on oxides, supported oxides and zeolites have been tested for aniline alkylation. More work is still to be carried out to demonstrate the continuous alkylation process involving aniline and lower alcohols over heterogeneous catalysts. The authors who studied [3,5–7] the vapour-phase alkylation of aniline with methanol and dimethyl ether have found alumina to be the best catalyst among the various catalysts

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<sup>†</sup>IICT Communication No.: 3149.

studied. A low temperature normally favours *N*-alkylation. A high temperature favours ring alkylation by rearrangement of methyl groups. The other possibility is that the methanol is dehydrated to dimethyl ether or alkenes which then methylate the ring. There are enough examples [10–15] in the literature to show the formation of *N*- and *C*-methylanilines depending on the reaction conditions and catalytic systems. Prasad and Rao [16] have studied the simultaneous alkylation of aniline with methanol and the reaction of *N,N'*-dimethylaniline over  $\text{AlPO}_4\text{-5}$  to demonstrate that the isomerization reaction takes place by a carbo-cation mechanism. *N*-methylaniline appears to be favoured at low temperature, which is subsequently converted to *N,N'*-dimethylaniline. This undergoes further isomerization to give *N*-methyltoluidines at high temperatures.

As a part of our continued effort [17–25] to selectively synthesize chemicals and chemical intermediates using alkylation, we have chosen the alkylation of aniline in the present investigation. H-ZSM-5 is used as a catalyst. This work is different from that of Chen et al. [12] who have studied aniline alkylation with methanol using Na-ZSM-5 and modified ZSM-5. A systematic investigation of the effect of temperature and pressure on ethylation of aniline over H-ZSM-5 zeolites of different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios is reported. The total acidity of the zeolite is measured by the temperature-programmed desorption (TPD) of ammonia. An attempt has also been made to study the effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and acidity on aniline alkylation activity and selectivity.

## 2. Experimental

Commercially available H-ZSM-5 zeolites with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (30–280) were used. The surface area measured by (BET) nitrogen adsorption at 77 K for all H-ZSM-5 zeolites is around  $400 \text{ m}^2 \text{ g}^{-1}$ .

Atmospheric alkylation of aniline with ethanol was carried out in a glass tubular reactor (25 mm × 300 mm) and pressure reaction was carried out in a stainless steel tubular reactor (12 mm × 300 mm) in the region of 10–30 bar. Ca. 0.5–1 g of the zeolite powder was pelletized, crushed and sieved to 1600–1800  $\mu\text{m}$ . These particles were diluted with ceramic beads of the same dimension before loading in the reactor. At the start of the experiment the catalyst was activated at 773 K in nitrogen flow. The temperature of the reactor was measured by a moving Cr–Al thermocouple that was placed in the catalyst bed. A premixed aniline–ethanol feed (aniline to ethanol molar ratio = 1:5) was pumped at different feed rates (WHSV = 0.97 to  $14.6 \text{ h}^{-1}$ ). Nitrogen was used as carrier gas and the flow was maintained at 3–6  $\text{h}^{-1}$ . Liquid product collected in the ice trap at every hour during a 5 h run was analysed on a Chemito 3865 gas chromatograph using 8 ft. 10% Apiezon L + 2% KOH on chromosorb 80/100 A W. The products were mainly *N*-ethyl and *N,N'*-diethylanilines. The percentage composition reported is based on ethanol free aniline feed.

The TPD of ammonia from the zeolite was carried out in a flow type glass reactor. Ca. 0.25 g of the sample was packed between quartz wool plugs and pretreated in situ at 773 K for 5 h in helium (Matheson pure) flow. After the pretreatment the zeolite was saturated with ammonia at a slow flow-rate for 1 h at 353 K. Physically adsorbed ammonia was flushed with a flow of helium ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) for a period of 15 h. The ammonia chemisorbed at 353 K was desorbed with a flow of helium ( $10 \text{ cm}^3 \text{ min}^{-1}$ ) and by stepwise

heating of the sample from 353 to 823 K. The desorbed ammonia in each step was measured quantitatively by absorbing it in a known volume ( $25 \text{ cm}^3$ ) of  $0.1 \text{ M}$  HCl solution in three glass bubblers arranged in series. The unreacted acid was titrated against a base to determine the ammonia desorbed from the sample.

### 3. Results and discussion

#### 3.1. Effect of feed rate

Aniline alkylation reaction with ethanol was carried out at 623 K and 1 bar with different feed rates of the reaction mixtures (WHSV of aniline  $0.97\text{--}14.6 \text{ h}^{-1}$ ) on H-ZSM-5 of  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$  (Fig. 1). Both aniline conversion and selectivity for  $N,N'$ -diethylaniline decreased with WHSV and reached a rather steady state at higher feed rates. On the other hand,  $N$ -ethylaniline increased with WHSV and reached a steady value at higher feed rates. For a detailed investigation of temperature and pressure effects, a WHSV of  $2.2 \text{ h}^{-1}$  was used.

#### 3.2. Effect of temperature

The results of alkylation of aniline in the temperature range 573–723 K and at 1 bar on H-ZSM-5 with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio varying from 30 to 280 are shown in Table 1. It is clearly

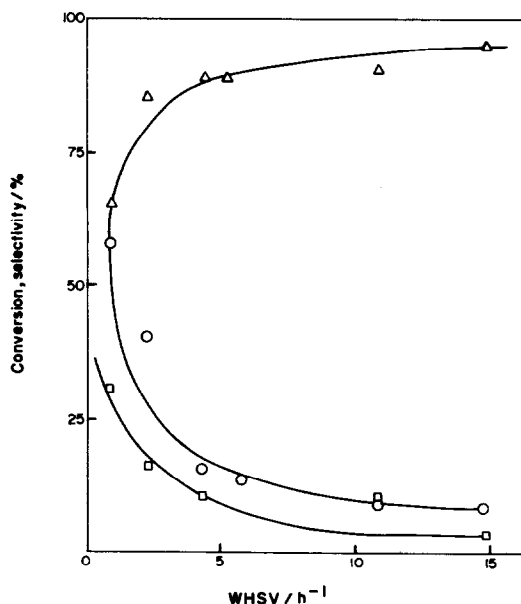


Fig. 1. Effect of feed rate on aniline alkylation over H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ ) at 623 K and 1 bar: (○) aniline; (Δ) NEA; (□)  $N,N'$ -DEA.

Table 1  
Aniline alkylation activity over H-ZSM-5 zeolites in the temperature range 573–723 K

Reaction temp. (K)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio				
	30	50	70	150	280
573	10	6	26	7	1
623	12	5	47	20	1
673	12	5	65	32	2
723	17	7	50	40	3

seen from the table that there is a small increase in aniline conversion with increase in temperature on H-ZSM-5 zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios 30, 50 and 280. Whereas on H-ZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios 70 and 150, the increase in aniline alkylation activity with increase in temperature is considerable. The general trend for the alkylation reaction is that conversion usually increases with increase in temperature, levelling off at elevated temperatures [20,22,26]. More or less the same trend is maintained on H-ZSM-5 zeolites used in the present investigation except on H-ZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio 70 where the conversion was maximum at 673 K and it decreased with further increase in temperature.

Fig. 2 shows the aniline alkylation activity and selectivity over H-ZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio 70 in the temperature range 523–723 K. Conversion of aniline was maximum at 673 K and it decreased with further increase in temperature. The selectivity of *N*-ethylaniline was high at 523 K and with increase in temperature further alkylation of *N*-

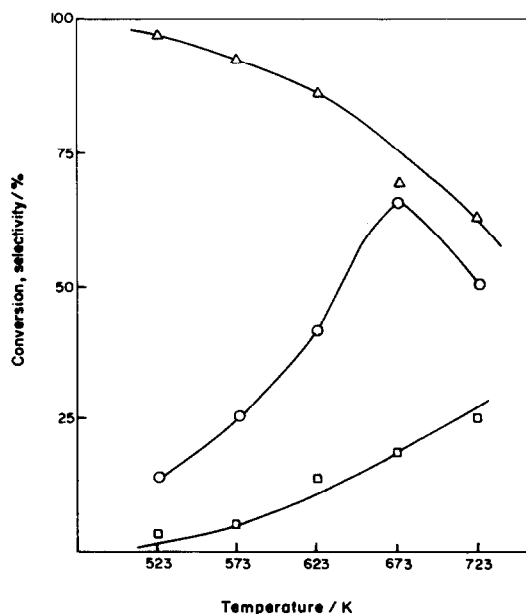


Fig. 2. Effect of temperature on aniline alkylation over H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 70) at 1 bar: (○) aniline; (△) NEA; (□) *N,N'*-DEA.

ethylaniline formed *N,N'*-diethylaniline and above 673 K *C*-alkylated anilines were formed which accounted for 10–15% of the total selectivity. The decrease in aniline alkylation activity above 673 K may be due to ethanol side reactions forming alkenes and aromatics [27]. Alkenes formed are likely to be coke precursors [28]. The coke formed is deposited on acidic sites of the zeolites, leading to a decrease in the number of available sites by site coverage or by blocking of pores. Thus the activity of the main reaction may decrease.

### 3.3. Effect of pressure

The results of the alkylation of aniline at three different temperatures (623, 673 and 723 K) in the pressure range 1–30 bar over H-ZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  70 are shown in Figs. 3 and 4. The effect of the temperature on the alkylation reaction—conversion increase with increase in temperature—is clearly observed at 10, 20 and 30 bar (Fig. 3). It is interesting to note the pressure effect on the reaction at the three different temperatures studied. At 623 K aniline alkylation decreased with an increase in pressure. This may be seen as the slow desorption of the products under pressure when the temperature of the reaction is low. At optimum temperature of activity, that is at 673 K, aniline alkylation activity is almost maintained at the same level over the entire pressure range studied, indicating that pressure has no effect on activity at this temperature as the rate of adsorption of reactants is equal to the rate of desorption of products. In contrast, aniline alkylation activity increased at 723 K with increase in pressure. Under pressure the side reactions of ethanol are minimized, making the alcohol available for alkylation. Thus the activity of H-ZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio 70 is retained at 723 K under pressure.

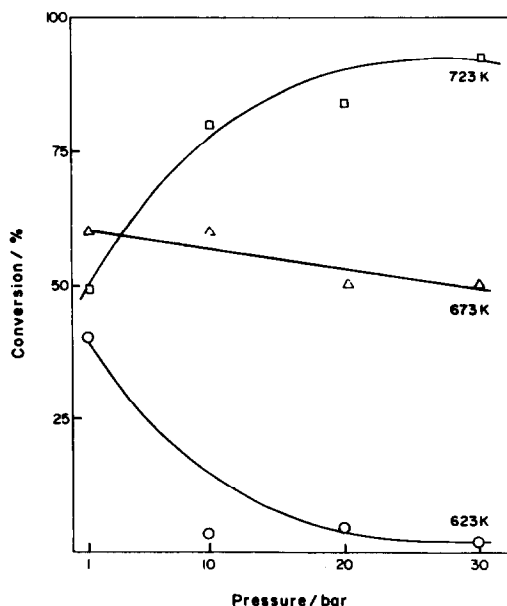


Fig. 3. Effect of pressure on aniline alkylation over H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ ): (○) at 623 K; (△) at 673 K; (□) at 723 K.

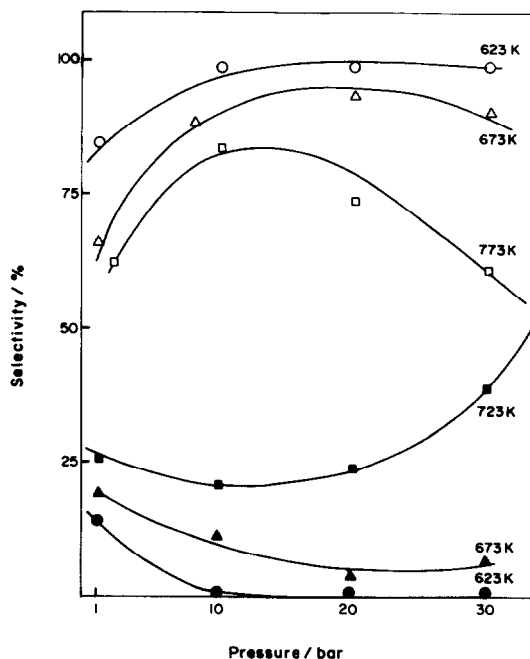


Fig. 4. Effect of pressure on NEA and  $N,N'$ -DEA selectivity over H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ ) at 623 K, 673 K and 723 K. Open symbols:  $N$ -ethyl-aniline and filled symbols:  $N,N'$ -diethyl-aniline.

The effect of pressure on the selectivities of  $N$ -ethyl-aniline and  $N,N'$ -diethyl-aniline at 623, 673 and 723 K are shown in Fig. 4. For a given pressure the selectivity pattern for  $N$ -ethyl-aniline follows the order 623 K > 673 K > 723 K, whereas the selectivity for  $N,N'$ -diethyl-aniline follows the reverse order. It appears that more than the pressure, temperature has got a greater role in aniline alkylation activity and selectivity.

#### 3.4. Effect of acidity on alkylation activity

The acidity dependence of the aniline alkylation activity over oxides and supported vanadia oxides have been dealt with [23–25]. The effect of acidity and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on aniline alkylation over H-ZSM-5 zeolite has been attempted in this paper.

The variation in the aniline alkylation activity with respect to temperature is correlated with the total acidity of H-ZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$  in Fig. 5. Acidity is measured as the amount of ammonia desorbed from the zeolite at a given temperature. The cumulative acidity increases with desorption temperature from 473 K to 823 K. Aniline alkylation goes through a maximum around 673 K and falls. It is observed that upto 673 K there is a direct relationship between the acidity increase and alkylation activity. The drop in activity beyond 673 K, in spite of the increase in the total acidity may be explained as follows: (1) At temperatures higher than 673 K ethanol enters into side reactions and is not available for alkylation. (2) The acidity measured beyond 673 K may represent strong acid sites. It might also suggest that strong acid sites are not required for aniline alkylation and weak to moderate acid sites are responsible for the reaction.

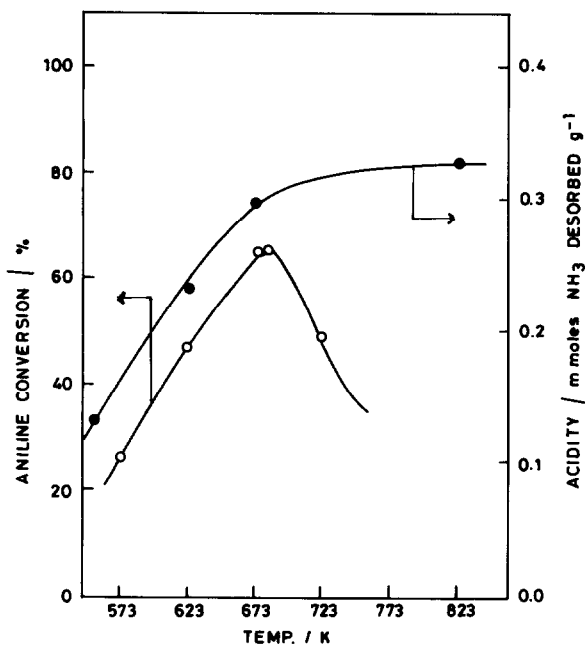


Fig. 5. Effect of acidity measured by TPD of ammonia on aniline alkylation activity in the temperature range 573–823 K over H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ ).

### 3.5. Effect of silica alumina ratio and acidity on alkylation activity

It is generally believed that on increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio the strength of acid sites increases in zeolites [29]. The number of active acid sites in H-ZSM-5 is found to decrease almost linearly with the Si/Al ratio. On the other hand the number of active acid sites per aluminium atom of the zeolite increases with Si/Al ratio upto the Si/Al ratio of 31.1 and levels off there after [30]. Choudhary and Nayak [31] have shown by stepwise thermal desorption of ammonia that the number of total acid sites and strong acid sites in H-ZSM-5 zeolite decreases with the increase in Si/Al ratio. It has also been found that the number and strength of acid sites increase with an increase in aluminium content in H-ZSM-5 zeolites. The extra lattice species of aluminium which increase with increasing aluminium concentration may form super acid sites by interacting with acidic OH groups [29].

Chandawar et al. [32] have studied benzene alkylation with ethanol over pure and modified (P and B) H-ZSM-5 zeolites with varying  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio versus alkylation activity shows that the suitable  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio for this reaction is 70 and above. TPD of ammonia over pure and modified H-ZSM-5 zeolites clearly indicated that the high-temperature peak decreased with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and disappeared on modification with phosphorus, enhancing the selectivity on H-ZSM-5 zeolite for this reaction. Unnikrishnan et al. [26] have studied alkylation of ethylbenzene with ethanol over H-ZSM-5, H-ZSM-11 and H-ZSM-23 with Si/Al ratio 50, 100 and 150.

In order to find the influence of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and acidity on vapour-phase aniline alkylation activity a number of commercially available H-ZSM-5 zeolites are chosen. The

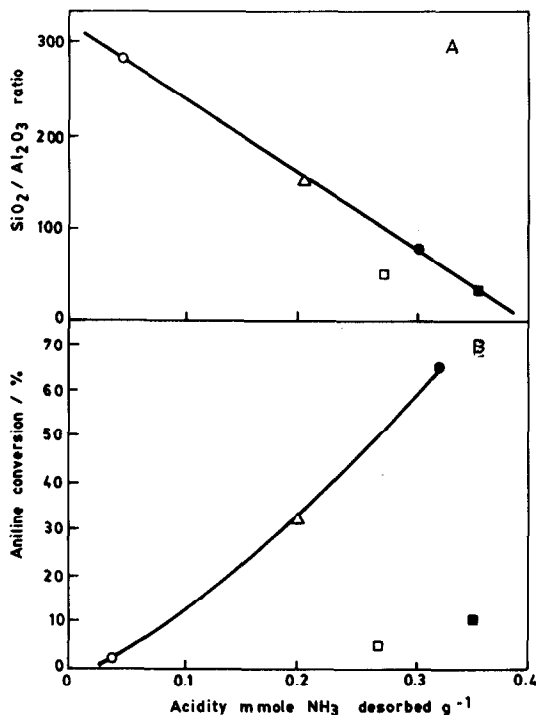


Fig. 6. (A) Relationship of acidity measured by TPD of ammonia at 673 K, with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and (B) effect of acidity on aniline alkylation activity over H-ZSM-5 zeolites. (■)  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ ; (□)  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$ ; (●)  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ ; (△)  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$ ; (○)  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 280$ .

H-zeolites are CBV-1000 series from Conteka, Netherlands containing 0.02 wt.-% of  $\text{Na}_2\text{O}$  with surface area around  $400 \text{ m}^2 \text{ g}^{-1}$ . The acidity of these zeolites is measured by TPD of ammonia and the cumulative ammonia desorbed upto 673 K is taken as an index of total acidity of the sample. The variation in the acidity with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is given in Fig. 6A. The aniline alkylation activity in terms of percent conversion is plotted against acidity in Fig. 6B. With decrease in  $\text{SiO}_2/\text{Al}_2\text{O}_3$  from 280 to 70 the acidity increases from 0.04 to 0.30 mmol  $\text{NH}_3 \text{ g}^{-1}$ . The aniline alkylation activity increases correspondingly from 2 to 65%. With further decrease in  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio we have shown an increase in acidity (Fig. 6A). However, the aniline alkylation activity values for zeolites with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio 50 and 30 are nevertheless well outside the line suggesting that sites with varying acid strength have different activity in alkylation. It may be derived from the above result that the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is an important factor deciding the aniline alkylation activity over H-ZSM-5 zeolites. Catalyst with almost the same acidity, namely  $\text{SiO}_2/\text{Al}_2\text{O}_3$  50 and 70 have completely different activity. The only factor that may be responsible for the difference in their activity is the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. Therefore, zeolites with low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio are expected to have strong acid sites due to a high aluminium content, these acid sites may not be directly responsible for alkylation. It appears that the H-ZSM-5 zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio 70 has the required acid sites responsible for aniline alkylation as reported above.



#### 4. Conclusions

Aniline alkylation under vapour-phase conditions is a stepwise reaction. *N*-ethylaniline is easily formed at low temperatures and is converted to *N,N'*-diethylaniline and *C*-alkylanilines at higher temperatures. Pressure has less influence than temperature on the reaction. A SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio 70 and a temperature of 673 K are suitable conditions for aniline alkylation over H-ZSM-5 zeolite. The activity decrease at higher temperatures may be due to coking and deactivation. The TPD studies of ammonia on H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 70) also revealed that strong acidity contributes to deactivation. A direct relationship between acidity as measured by TPD of ammonia and the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is established. However, no such relationship could be observed for the acidity and alkylation activity for the entire SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio range investigated.

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