Catal Lett (2008) 125:110–115
DOI 10.1007/s10562-008-9522-5

Behavior of a Deactivating HZSM-5 with Varying Al^{3+} Content in Vapor Phase Aminocyclization

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Received: 15 April 2008 / Accepted: 14 May 2008 / Published online: 28 May 2008
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Abstract Aminocyclization of aldehydes to synthesize pyridine bases is an interesting reaction with HZSM-5 catalyst undergoing rapid deactivation. The catalyst characterization studies like NH_3-TPD, XRD, TGA/DTA, Pore size distribution, SEM, CHNS, IR for the fresh and deactivated catalyst at various Si/Al ratio content as evidenced by the striking difference in the behavior of HZSM-5 catalyst in terms of its physicochemical characteristics, coke formation tendencies and higher selectivity to pyridine formation.

Keywords Aminocyclization · Pyridine synthesis · NH_3-TPD · XRD · TGA/DTA · Pore size distribution · SEM · CHNS · IR

1 Introduction

Pyridine bases are formed under a series-parallel reaction mechanism in catalytic vapor phase aminocyclization. The earlier investigations [1–4] established the distinct selectivity advantages of medium acidity pentasil type of zeolite viz., HZSM-5 and silicates for this reaction since their pore diameter is almost same as pyridine molecular diameter. Pyridine synthesis is accompanied by the formation of several co-products and heavy coking of catalyst. The HZSM-5 catalyst is able to reduce the high boilers to less than 10% on account of its shape selectivity. The reactants are reported [1] to be adsorbed on acidic sites of the catalyst and the formation of imines precedes cyclization. The coke formation is reported to occur through a consecutive mechanism leading to the blockage of narrow pore openings.

The catalyst acidity has been reported [1–5] to have significant influence on product distribution as evidenced by (a) presence of both Lewis and Bronsted acid sites existing in a thermodynamic equilibrium with the latter promoting carbonium ion formation (b) high catalyst acidity retarding pyridine synthesis due to predominance of unreactive adsorbed ammonium ions and enhanced catalyst coking ability (c) The need for an optimum level of catalyst acidity and (d) Pentasil structure of HZSM-5 and silicalite catalysts promoting selective formation of pyridine under medium acidity.

The concentration of Al^{3+} ions in catalyst as represented by silica–alumina ratio (hereafter refered to as Si/Al) provides a strong basis for catalyst activity optimization. In the present work, Si/Al is varied in a fairly wide range viz., 40–240 to get a clearer understanding of its influence on physicochemical behavior of the catalyst, aldehyde conversion and selectivity towards pyridine formation.

2 Experimental

The vapor phase pyridine synthesis is carried out in a continuous tubular downflow Pyrex reactor (20 mm i.d) at

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atmospheric pressure. The catalyst bed temperature is measured with a thermocouple placed at the center of reactor cross section. The aldehyde mixture is fed from the top of the reactor using a syringe pump (Be Braun, USA) and ammonia is fed from a pressurized cylinder. Prior to this, 4 g of the catalyst is loaded into the reactor. All the experiments conducted at T = 375 °C, F = 2 mL/h, W = 4 g wt of Catalyst, $CH_3CHO/HCHO/NH_3$ mole ratio 1:1:4 with different Si/Al ratio of HZSM-5.

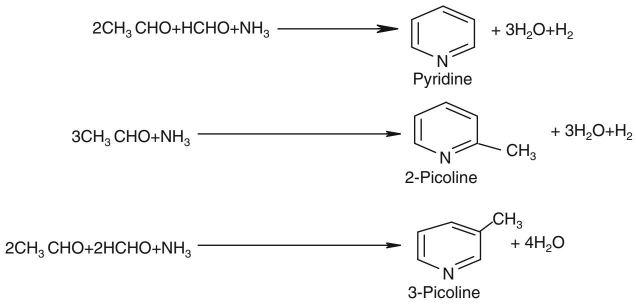
The reaction products are analyzed by GC (shimadzu-14B) using a chromosorb-102 column (6′ length, $\phi = 1/8''$, 80/100 mesh). Nitrogen is used as the carrier gas and the column, injector and detector are maintained at 200, 280 and 290 °C, respectively.

The temperature programmed desorption (TPD) of ammonia has been adopted to assess the nature and magnitude of catalyst acidity by employing Autochem 2910 Micromeritics (USA) system. Oven-dried catalyst sample (250 mg at 650 K for overnight) is taken in a U-shaped quartz sample tube for pretreatment at 473 K for 1 h by passing 99.999% pure helium (50 mL/min). It is then adsorbed with anhydrous ammonia from a 10% NH_3–He mixture at 353 K flowing at 75 mL/min and subsequently flushed at 378 K for 2 h to remove physically adsorbed gas. The TPD studies are carried out from ambient temperature to 1,173 K at 10 K/min heating rate. The amount of NH_3 desorbed is calculated using GRAMS-32 software.

The C, H, N and S content of the catalyst samples have been evaluated by ELEMETAR-VARIO-EL analyser. The X-ray diffraction (XRD) studies are conducted with Siemens d-5000 Diffractometer using nickel filtered Cu Kα radiation with beam current 30 mA and beam voltage 40 KV. Thermogravimetric and differential thermal analyses have been conducted employing TGA/SDTA Mettler Toledo 851^e instrument. BET surface area measurements have been done by using multi-point Gemini 2360 analyser (Micromeritics, USA).

The surface area and pore size distribution of the catalyst have been measured from their adsorption isotherms using ASAP-2010 v.5 software support. The FT-IR spectra of various samples reported in this study are recorded on a Nicolet 740 FTIR spectrometer and some of them on Bio-Rad 175c instrument at ambient conditions using KBr as the diluent. Textural properties of the sample have been evaluated through nitrogen adsorption/ desorption using a micrometrics ASAP 2010 unit. Samples are degassed at 393 K for 24 h. The SEM analysis was done with HITACHI S-3000N instrument.

HZSM-5 zeolite (4 g) was used in the catalytic activity studies, which were carried out in a fixed bed, down flow reactor, the reaction setup [6] and product analysis [7] are reported by same authors. All the experiments are conducted at optimum conditions reported [6]. Ex situ all the spent catalysts were characterized and compared with fresh catalysts (Scheme 1).



Scheme 1

3 Results and Discussion

The typical physical characteristics of HZSM-5 (30) catalyst reported in literature [8] to achieve good performance are particle size 0.55 nm, BET Surface area 360 m^2/g, with less than 2% of external surface area, pore volume of 0.18 cm^3/g, consisting greater than 90% of micro pore volume and a crystal size of 3 μm. The results of the present investigations demonstrate the impact of Al^{3+} content of catalyst on these and other characteristics.

3.1 Influence of Si/Al ratio on Physical Characteristics of Catalyst

3.1.1 Surface Area

The measured surface area of HZSM-5 catalyst is the sum of microporous and external surface area components. It has been reported [9] that pyridine formation occurs mainly inside the pores where as its alkyl derivatives are formed on the external surface area of the catalyst. In the case of HZSM-5 catalyst, the microporous surface area constitutes more than 95% and accordingly its influence will be predominant. The BET surface area of freshly prepared and used catalysts has been evaluated for Si/Al in the range of 40–240. The details presented Fig. 1 clearly indicates the marginal negative influence (<10%) of increasing Si/Al on surface area in freshly prepared catalyst. Its magnitude and level of variations are in tune with the findings of Benito et al. [8]. The more dramatic reduction (>80%) in surface area is however observed for coked HZSM-5 catalyst with Si/Al in the range of 40–150. On the other hand, at Si/Al = 240, the surface area loss is minimum at 20%.

3.1.2 Pore Size Distribution

The pore size distribution plays an important role in catalytic activity, product distribution and deactivation phenomenon in aminocyclization reactions. The pore size distribution pattern of freshly prepared and coked HZSM-5 catalyst as a function of Si/Al ratio is shown in Fig. 2. No

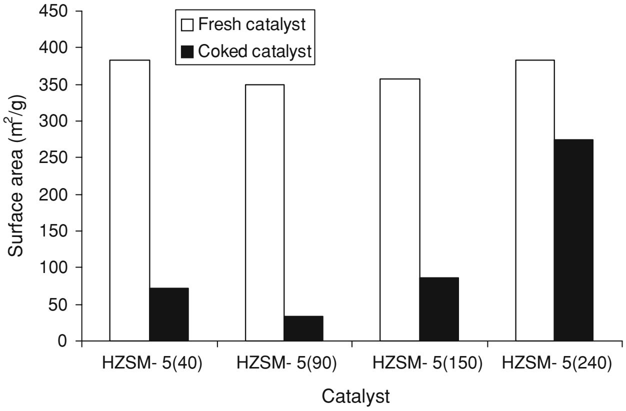


Fig. 1 Surface area of fresh and coked catalyst

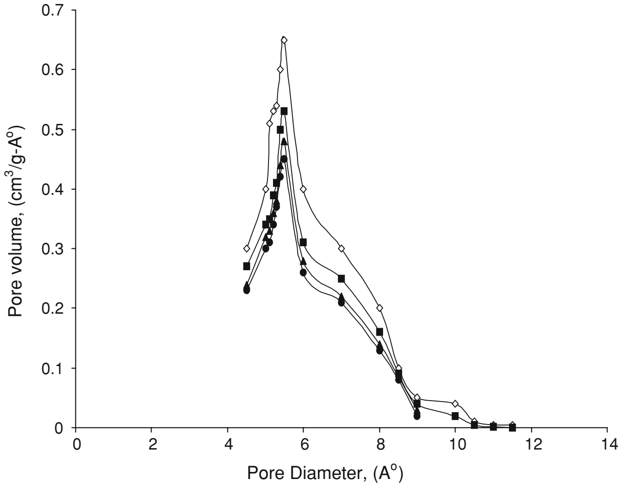


Fig. 2 Pore size distribution of HZSM-5 fresh (◇), Coked HZSM-5 (240) (■), Coked HZSM-5 (150) (▲), Coked HZSM-5 (40) (●)

Table 1 Pore volume (PV) variations in freshly prepared and coked catalyst

Pore diameter (Å)	PV (cm^3/g-Å)	% Drop in PV in coked catalyst	
	HZSM-5	HZSM-5 (40)	HZSM-5 (240)
6	0.65	30.0	15.0
7	0.34	40.0	20.0
8	0.20	30.0	17.5
10	0.04	NA	25.0

T = 375 °C, F = 2 mL/h, W = 4 g wt of Catalyst, $CH_3CHO/HCHO/NH_3$ mole ratio 1:1:4

significant variation has been observed in pore size distribution pattern for freshly prepared and coked catalysts when Si/Al = 240. In other cases, a narrower distribution pattern has been observed for coked catalyst. The deactivation of catalysts with coke deposition in generally accompanied [8] by a decrease in pore volume. Table 1 shows that pore volume drop is minimal in the case of coked catalyst with Si/Al = 240 and relatively large when Si/Al = 40.

3.1.3 *Coke Structure*

XRD has been employed to assess the structure of the coke formed during pyridine synthesis. We reported [6] the XRD patterns of freshly prepared and coked HZSM-5 catalyst with Si/Al in the range of 40–240. The XRD patterns of fresh and coked catalysts have displayed reflections at $2\theta = 7.93$, 8.90, 23.19, 23.84, and 45.33 at all Si/Al values suggesting amorphous nature of coke formed. However, a slight shift in its intensity in case of coked catalyst has been noticed probably due to pore volume reduction [10].

3.1.4 *Surface Texture and Crystal Size*

The Scanning Electron Microscopy (SEM) studies of freshly prepared and coked HZSM-5 catalysts have been undertaken to observe the changes in surface texture and morphology of coke when Si/Al ratio is varied from 40 to 240. It is interesting to note from Fig. 3 that at lower Si/Al ratios, the coked crystallites are smaller in size and exist in aggregation whereas at high Si/Al ratios, the aggregation tendencies are far less and the crystallites are cuboid and octahedral in shape. The crystallite sizes vary from 200 nm to 2 μm. The larger crystal sizes of freshly prepared catalyst with Si/Al = 240, is indicative of wider pore openings to promote higher pyridine selectivity. Smaller crystallites may be attributed to the presence of more external surface sites than larger crystals. However, no measurable change in crystallite sizes is noticed when freshly prepared and coked catalysts are compared.

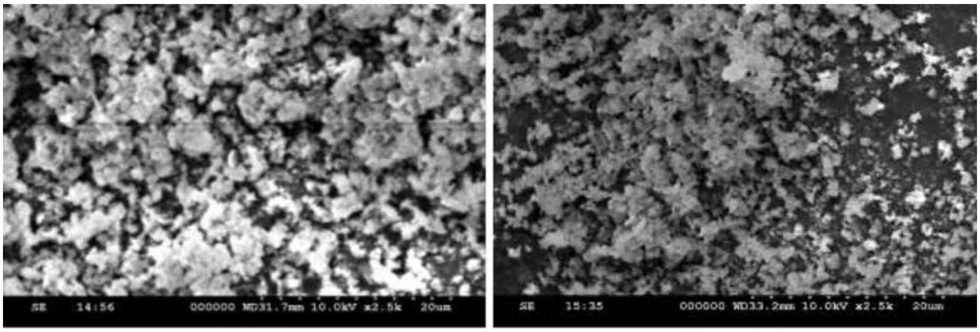
3.2 Influence on Chemical Characteristics of Coke

The acidity levels, the nature of hydroxyl groups present, C, H, N variations and oxidation characteristics of freshly prepared and coked catalysts have been measured with Si/Al as the variable parameter.

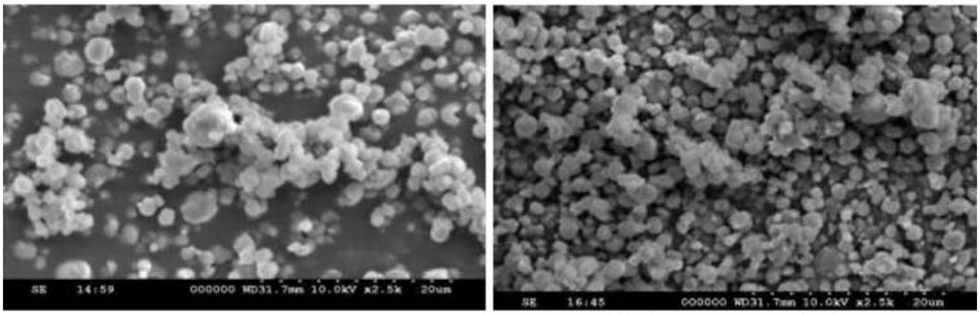
3.2.1 *Acidity Levels*

As stated earlier, aminocyclization requires [3, 4] optimum number of acidic centers on the catalyst for achieving desired product distribution and desorption of reaction products without significant decomposition. Temperature programmed desorption (TPD) of ammonia were undertaken by the authors [7] to assess the acidity levels of freshly prepared and coked HZSM-5 catalyst with Si/Al as variable parameter. They indicated that the ammonia

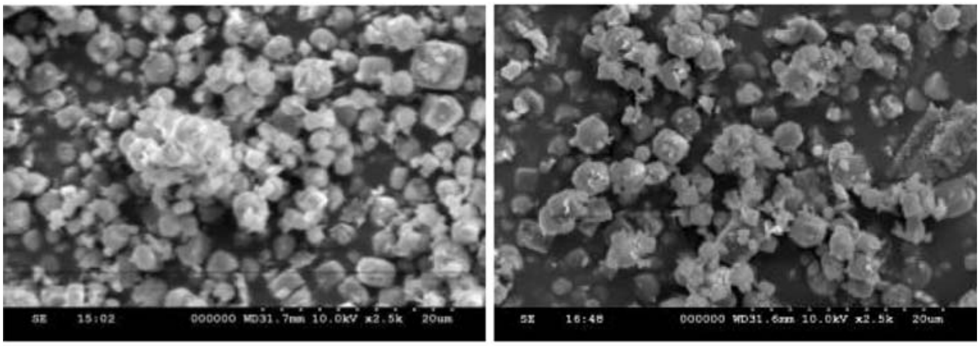
Fig. 3 SEM pictures of freshly prepared and coked catalyst at different Si/Al's of HZSM-5



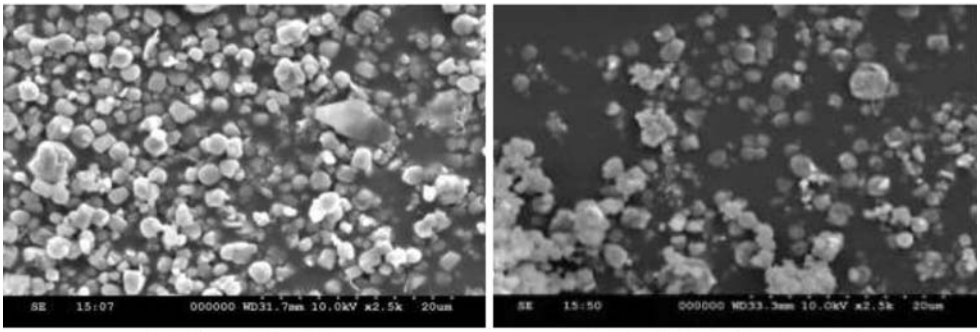
HZSM- 5 (40) HZSM- 5 (40) coked



HZSM- 5 (90) HZSM- 5 (90) coked



HZSM- 5 (150) HZSM- 5 (150) coked



HZSM- 5 (240) HZSM- 5 (240) coked

uptake is inversely proportional to Si/Al increase as evidenced by the significant drop in total acidity and very strong acid sites. They also show the unique behavior of HZSM-5 catalyst with Si/Al = 240 in terms of absence of very strong acidic sites and predominance of moderate strong acid sites.

In order to assess the impact of acidity levels of the catalysts on conversion, selectivity and coking in pyridine synthesis, vaporphase aminocyclization runs of acetaldehyde and formaldehyde mixture has been carried out in a continuous tubular downflow packed mini reactor (~4 g of catalyst loaded). The results are given in Fig. 4. While Si/

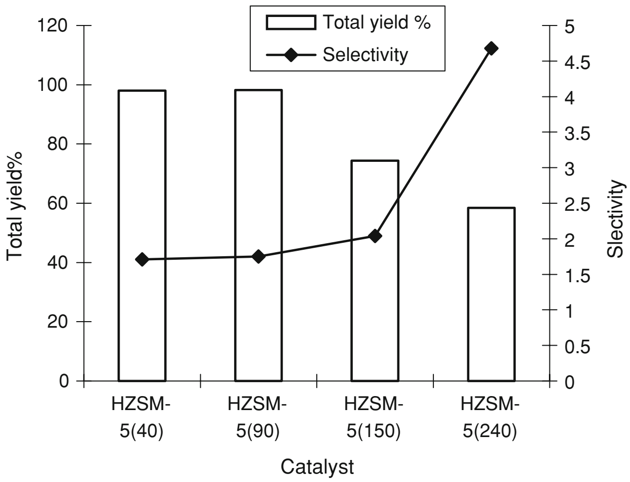


Fig. 4 Effect of Si/Al ratio on selectivity and yield

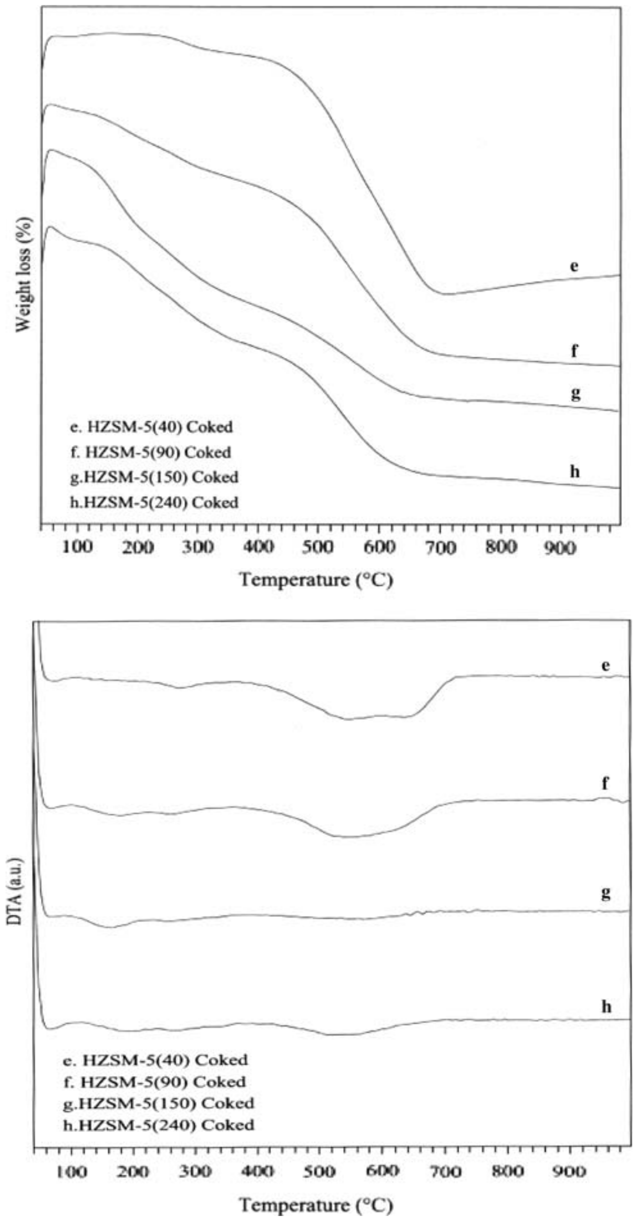


Fig. 5 TGA/DTA profiles for coked HZSM-5 catalyst at different Si/Al ratios

Al in a range of 40–90 contributed to high yield, low selectivity to pyridine formation and high coke formation, a totally different trend viz., relatively lower yield, high selectivity and low coke formation is observed for Si/Al in the range of 150–240. This indicates that modulation of catalyst acidity contributes to enhance selectivity to pyridine formation and minimum coke formation though with a significant drop in aldehyde conversion.

3.2.2 Coke Oxidation Characteristics

The extent of reaction between oxygen and coke depends on the oxygen partial pressure, composition, morphology and location of coke, its affinity with catalyst and nature of impurities present in the system. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been undertaken to study the phase transition temperatures and the weight loss of material on coke oxidation. The details are shown Fig. 5. The results show that the coke moiety is lost in HZSM-5 catalyst between 723 and 973 K with no subsequent weight loss. The DTA peak temperature and coke loss are inversely proportional to Si/Al ratio of catalyst. Variation in DTA temperatures is indicative of the change in coke characteristics with silica–alumina content of the catalyst. The lower Al^{3+} ion concentration contributed to the formation of less coke with lower DTA peak temperature. The TGA/DTA data generated in the present study is in good agreement with earlier literature [11].

3.2.3 Catalyst OH Groups and Their Role in Coke Formation

It is important to study the influence of OH groups on the catalyst on coke deposition. IR spectroscopy has been used to study the freshly prepared and coked catalysts with variations in Si/Al ratios. The fresh and uncarbonized HZSM-5 catalysts show a broad infrared absorption band centered at around 3,400 cm^{-1} which is due to stretch vibrations in hydrogen bonded OH groups on the catalyst and in adsorbed water. A strong band also appeared at 1,585 cm^{-1} and is attributed to the presence of very strong acidic OH groups in the zeolite super cage. The catalyst also has strong IR absorption bands at 1,200 cm^{-1} and below which are due to Si–O and Al–O linkages. It is interesting to note that the coked catalyst shows a progressive increase of 1,585 cm^{-1} band and decrease

Table 2 CHNS analysis for coke

Catalyst	C (%)	H (%)	N (%)	H/C	N/C
HZSM-5 (40)	8.27	0.85	1.09	1.23	0.13
HZSM-5 (90)	7.51	0.80	0.82	1.29	0.11
HZSM-5 (150)	3.82	0.76	0.50	2.38	0.13
HZSM-5 (240)	3.25	0.71	0.14	2.62	0.04

T = 375 °C, F = 2 mL/h, W = 4 g wt of catalyst, $CH_3CHO/HCHO/NH_3$ mole ratio 1:1:4

of 3,400 cm^{-1} bands as Si/Al ratio is decreased from 240 to 40.

3.2.4 H/C and N/C Ratios of Coke

During aminocyclization of aldehydes over HZSM-5 catalyst, there is good scope for formation and retention of heavy side products either in the pores or on outer surface or on both. These non-desorbed products provide the coke, which is the main cause of the rapid catalyst deactivation in aminocyclization. The composition of coke depends on the acidity of the catalyst, aldehyde composition, operating conditions and chemical constituents of non-desorbed products. The elemental constituents of coke formed during aminocyclization of aldehydes have been evaluated by CHNS analysis and the details provided in Table 2. It is interesting to note the significant increase in atomic H/C ratio of the coke as Si/Al is varied from 40 to 240. This provides an indication of the decreased aromacity with an increase in Si/Al ratio.

Also, a sudden reduction in N/C ratio is observed in the case of HZSM-5 catalyst with Si/Al = 240 whereas it remained more or less same at lower Si/Al ratios. The low N/C ratio may be due to minimum nitrogen containing non-adsorbed products formed during aminocyclization.

4 Conclusions

The Al^{3+} ion concentration as represented by Si/Al ratio of HZSM-5 catalyst has very significant influence on the physico-chemical and deactivation characteristics of HZSM-5 catalyst during vapor phase aminocyclization. The studies show very distinct catalyst behavior Si/Al = 240 as compared to other Si/Al values. This is significant for improving time on stream behavior of HZSM-5 catalyst for pyridine synthesis. The results of this work can be summarized as:

1. The behavior of catalyst with Si/Al = 240 is very distinct as compared to its performance at lower Si/Al ratios with reference to variations in surface area, acidity and coke composition. Minimum Surface area, Pore size distribution and acidity variations, high aromacity and minimum N/C ratio of the coke are the major observation.
2. A slight shift in XRD patterns of coked catalyst provides a broad indication of a partial pore blockage.
3. Changes in surface texture and crystallite shape and size have been noticed as Si/Al of the catalyst freshly prepared catalyst is varied from 40 to 240.
4. The Thermal analysis of coked catalyst indicates that DTA peak temperatures and coke oxidation losses are inversely proportional to Si/Al ratio.
5. The FT-IR analysis shows that optimization of OH groups on catalyst will be a key factor for minimizing coke formation.

Acknowledgements K. Suresh Kumar Reddy is thankful to CSIR, New Delhi for the award of SRF-GATE Fellowship.

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