

Studies on Physico-Chemical Changes in Zeolite Beta in Mononitration of Toluene¹

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Abstract—In the present work, the stability and regenerability of H-Beta zeolite in toluene mononitration is studied. Nitration of toluene is carried out in batch mode under reflux conditions using various molar ratios of toluene and nitric acid. Semi batch experiments under reflux are also conducted where nitric acid is dosed at predetermined rates to the reaction mixture containing toluene and the catalyst. The catalyst used in semi batch experiments is found to exhibit consistent performance upto three cycles. The possible cause of consistent activity of the catalyst with respect to *para*-selectivity has been explored. The physico-chemical changes, if any, in the catalyst is examined for structural stability and presence of pore blockages using sophisticated analytical tools like XRD, EDX, FTIR and ²⁷Al MAS-NMR. These studies indicate the commercial potential of cleaner option of replacing sulfuric acid with zeolites in toluene nitration.

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INTRODUCTION

The nitration of toluene is one of the most important ways to obtain substituted aromatics for the production of chemical intermediates viz., nitro and dinitrotoluenes for the synthesis of various compounds, mainly after reduction of the nitro group, and the *para*-substituted products as desired. In the conventional industrial nitration, however, the production of the *ortho*-isomer exceeds that of the *para*-isomer. To overcome this limitation, various nitration systems using solid acids as catalysts were investigated.

It has been reviewed by G.A. Olah et al. [1] that aromatic nitration could be carried out using nitronium salts like nitronium tetrafluoroborate under anhydrous conditions with yields of 80–100%; with alkyl nitrates/acetone cyanohydrin nitrate in the presence of BF_3 with yields of 75–80%; with silver nitrate in the presence of Lewis acids under heterogeneous conditions with yields of around 60%; with solid superacid catalysts like polystyrene sulfonic acid, perfluorinated sulfonic acid (Nafion H) with HNO_3 or its metal salts, mixed anhydrides or nitrate esters catalyzed by H_2SO_4 and transfer nitrations under essentially neutral conditions using N-nitropyridinium, N-nitroquinolium salts, nitro and nitrite onium salts to enhance the reactivity of the nitrating agent.

Smith and Fry [2] reported *para*-selective mononitration of alkylbenzenes under mild conditions using benzoyl nitrate in the presence of aluminium or proton

exchanged large pore mordenite. A maximum *para*-selectivity of 64% was achieved employing tetrachloromethane as solvent. It was also reported that other catalysts like silica, alumina, K10 clay couldn't give high *para*-selectivity. Choudary et al. [3] reported to have achieved higher *para*-selectivities (upto *para/ortho* ratio of 2) and space time yields in aromatic nitration employing various solid acid catalysts like Fe^{3+} montmorillonite, K10 montmorillonite, Zeolite beta, ZSM-5, mordenite, HY and TS-1 with 60–90% nitric acid and with azeotropic water removal.

Kogelbauer et al. [4] have demonstrated that sulfuric acid supported on preshaped silica to be a good recyclable catalyst for the nitration of toluene to dinitrotoluene using 65 wt % nitric acid. Dagade et al. [5] reported vapor phase nitration of toluene at 120°C using dilute nitric acid (20%) and beta zeolite and achieved maximum conversion of 55%, *para*-selectivity of 70% and catalyst life of 75 h. It was also observed by them that the beta zeolite is highly stable and that the shape selective nitration of toluene takes place inside the pores. The production of dinitrotoluene by nitrating toluene and nitrotoluene in vapor phase mode and in liquid phase with simultaneous distillation were reported by Vassena et al. [6]. They found that zeolite beta exhibited high stability and gave high *para*-selectivity compared with other zeolites like ZSM-5, ZSM-12 and mordenite though its activity was slightly low. It was also observed that liquid phase reaction with simultaneous distillation was preferable to vapor phase reaction for the formation of dinitrotoluene. Nitration of

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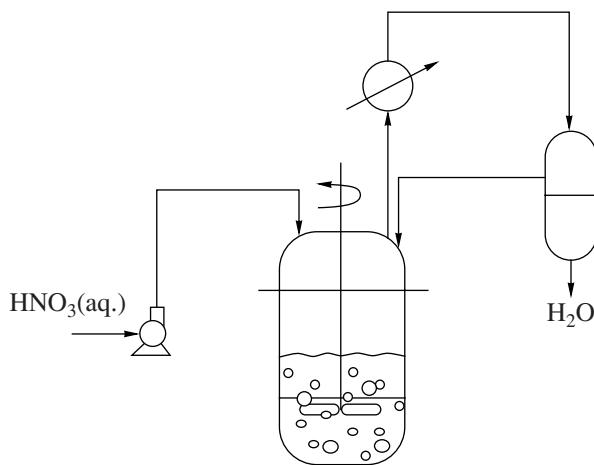


Fig. 1. Experimental set-up for batch and semi-batch modes of toluene nitration.

toluene and 2-nitrotoluene has been performed by Bernasconi et al. [7] using acetyl nitrate and zeolite BEA of different Si/Al ratios and different sizes of crystallite and observed that the number of Brønsted acid sites and diffusion play a major role in determining the performance of BEA. It was found that zeolite BEA gave maximum *para*-selectivity in the nitration of toluene and even in the nitration of 2-nitrotoluene due to the fact that heterogeneously catalyzed reaction compete successfully with the homogeneous nitration in the liquid phase.

In the present investigations, catalytic nitration of toluene has been conducted in batch and semi batch modes using zeolite H-beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 22$) and the physicochemical changes in the catalyst have been examined with various investigative tools like XRD, ^{27}Al MAS-NMR, FT-IR and EDX to study the suitability and stability of the catalyst in toluene mononitration and the possible cause for the consistent *para*-selectivity of the catalyst.

EXPERIMENTAL

Materials and Methods

Toluene (99%, commercial grade) and nitric acid (70 wt %, Merck) are used as received. The zeolite catalyst H-beta ($\text{SiO}_2/\text{Al}_2\text{O}_3$ or S/A = 22) is procured from Sud-Chemie India Ltd. The catalyst in powder form is calcined at 450°C for 6 h before using in the nitration reactions.

Experimental Set-Up

The experimental set-up consists of a four necked Borosil-glass reactor of 1-l capacity (108 mm dia and height, 178 mm height) fitted with a glass stirrer with teflon blade, reflux condenser and decanter leg to remove water as and when formed. For semi batch

experiments, a syringe pump is used to dose nitric acid at specified rates. The experiments in the glass reactor are performed under batch and semi batch modes with azeotropic water removal as shown in Fig. 1 under reflux conditions (120°C) at atmospheric pressure.

Analytical

The product samples from the organic phase are taken using a sampling syringe and immediately quenched in an ice bath to arrest any further reaction. They are then filtered and thoroughly washed with water till neutralization before analyzing them employing gas chromatograph (GC 17A Shimadzu). The catalyst after reaction is filtered, washed with water and acetone and dried. It is then examined for physicochemical changes using the investigative tools of XRD, FTIR, MAS-NMR and EDX. Powder X-ray diffraction is done on SIEMENS/D5000 X-ray diffractometer using Ni-filtered CuK_α radiation ($\lambda = 1.506 \text{ \AA}$). The operating parameters are 40 kV and 30 mA. The scanning electron microscopic analysis of the catalyst samples for changes in Si/Al ratio is done using Hitachi S-520 instrument. The EDX is done on LINK ISIS 300 (Oxford, UK). FTIR spectrometer of Nexus 670 model (USA) has been used in this work in the frequency range of 400–4000 cm^{-1} to determine the changes in overall and Brønsted acidity levels. The solid state MAS-NMR analysis has been done by employing Varian (PALO ALTO, CA (USA); UNITY INOVA model) with a frequency of 400 MHz. $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ is used as a standard for ^{27}Al .

RESULTS AND DISCUSSION

Catalyst Stability and Regenerability Catalyst Stability

XRD investigations have been done prior to and after nitration reaction to study the structural changes experienced by H-Beta catalyst. In our present studies, batch nitration of toluene in the presence of catalyst has been conducted using various mole ratios of toluene and nitric acid. It has been established that the structural integrity of the catalyst is maintained in all cases. To demonstrate the longevity of the catalyst, batch nitration of toluene has been conducted for 24 h under high (0.9) and low (0.42) volume fractions of toluene in the reaction mixture. The basic objective of these studies is to assess the structural and performance stability of H-Beta catalyst employed in this work after exposing it to specific process conditions for longer duration viz., 24 h. The XRD profiles show that the structural integrity of the catalyst is maintained even after long exposure time at high volume fractions of toluene. This observation reinforces the stability of zeolite H-Beta in highly acidic dispersed phase conditions. The crystalline nature of the catalyst is found to be very little affected by the volume fraction of toluene. The FT-IR profiles (Fig. 2) demonstrate that the bands at about 3600 and 1600 cm^{-1} (ascribed to hydroxyl groups

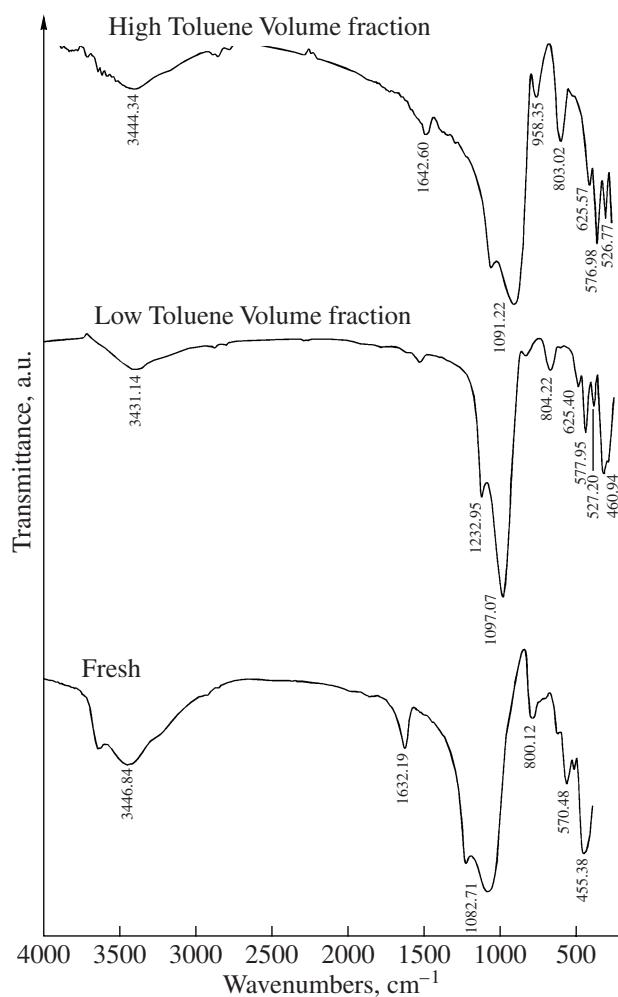


Fig. 2. FTIR plot after batch toluene nitration continued for 24 h under low and high toluene volume fraction.

attached to lattice aluminium and Brønsted acidity respectively) got significantly reduced under the conditions prevailing at low volume fraction of toluene. This indicates the reduction in total and Brønsted acidity under high concentrations of the acid as continuous phase. Hence nitric acid dispersed in toluene is preferable to toluene dispersed in nitric acid as far as catalyst stability is concerned.

Catalyst Regenerability

With reference to the regenerability and reuse of H-Beta zeolite catalyst for toluene nitration, there are no reports to confirm its behavior when recycled. An attempt has, therefore, been made in this work to assess the catalyst characteristics during and after three regenerations and recycles. The catalyst after the reaction has been filtered and thoroughly washed with water and acetone till the filtrate is neutralized. It is then dried in

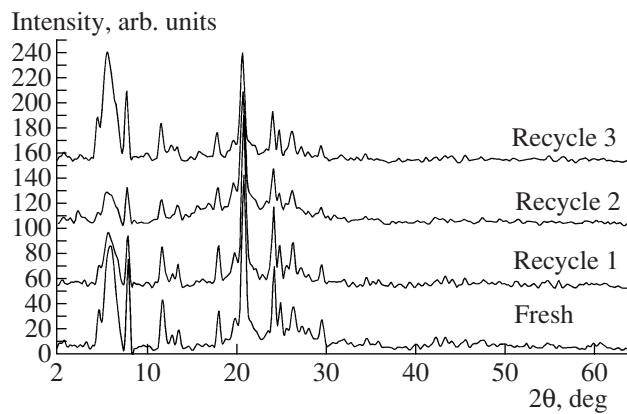


Fig. 3. XRD patterns of H-Beta catalyst in semi-batch nitration with nitric acid dosing rate 30 ml/h upto 3 recycles.

an oven to remove the moisture for about 2 h and then calcined at a temperature of 450°C for 6–8 h.

Semi batch mode of nitration is employed for regeneration and recycle studies. Two nitric acid dosing rates viz., 30 and 60 ml/h at high toluene volume fraction have been employed to assess the catalyst behavior at two levels of *para*-selectivity. The results are presented in Table 1 for 3 catalyst recycles. They clearly establish that the toluene conversions and *para*-selectivity are practically unaffected by the catalyst regeneration and recycle.

The XRD patterns (Fig. 3) showed that they remained unchanged after the reaction even after three cycles except for the marginal decrease in the relative peak intensities. This indicates that the catalyst crystalline structure remained intact after the reaction. This also confirms the efficacy of simple thermal treatment for catalyst regeneration. XRD profiles also demonstrated that HNO₃ dosing rate has a marginal influence on the structural integrity of the catalyst even in highly acidic environment. Similar observation was made by Dagade et al. [5] in vapor phase nitration of toluene, Breck et al. [8] for hydration and He and co-workers [9] for methylation reaction. The FTIR spectra presented in Fig. 4 show that with an increase in acid dosing rate, there is a reduction in the total and Brønsted acidity. This observation again reinforces our selection of lower dosing rate for achieving higher conversions and *para*-selectivity.

Effect of HNO₃ Concentration

Dealumination of alumino silicate catalysts has been reported in literature. The extent of dealumination depends on the aluminium content of the precursor and the free acid concentration of reaction environment. A sufficiently high acid concentration can effectively remove non structural Al species. Bertia et al. [10] studied the dealumination of mordenite on leaching with 1 N HCl. They found that the extent of dealumination

Table 1. Influence of catalyst regeneration and recycle on toluene conversion and *para*-selectivity

Nitric acid dosing rate, ml/h	Cycle no.	Dosing time, h	Tol conversion (%)	ONT	MNT	PNT	Others	<i>para/ortho</i>
30	I	1	18.5	8.97	0.7	8.3	0.5	0.93
		2	23.2	9.3	0.8	11.7	1.4	1.25
		4.5	33.0	11.8	1.2	17.6	2.4	1.50
30	II	1	16.5	8.17	0.5	7.5	0.3	0.92
		2	21.7	8.8	0.5	11.2	1.2	1.27
		4.5	31.5	11.3	0.9	17.1	2.2	1.51
30	III	1	16	7.92	0.5	7.25	0.3	0.92
		2	21.5	8.8	0.5	11.4	1.2	1.30
		4.5	31	11	0.9	16.9	2.2	1.54
60	I	1	22.5	11.7	0.6	9.7	0.5	0.83
		2	40.7	20.1	1.8	17.7	1.1	0.88
		4.5	55.0	27.4	2.3	23.9	1.4	0.87
60	II	1	21.0	11.2	0.3	9.2	0.3	0.82
		2	39.5	19.6	1.7	17.2	1.0	0.88
		4.5	53.0	26.6	2.1	23.0	1.3	0.86
60	III	1	20.5	11.0	0.2	9.0	0.3	0.82
		2	39.2	19.4	1.6	17.2	1.0	0.89
		4.5	52.5	26.4	2.0	22.9	1.2	0.87

Note: Toluene = 2.2 mol; catalyst (H Beta S/A, 22) = 10 g; agitation speed = 200 rpm; temperature = 130°C.

increases with acid concentration. They also established that the higher the alumina content in the mordenite sample, more of it can be removed by ther-

mal and acid treatments at a suitable temperature. Sufficiently high acid concentration can remove the non structural Al species which are formed during thermal treatment.

The dealumination phenomenon in aromatic nitration in the presence of zeolite catalysts has not received much attention. In the present work, an attempt is, therefore, made to study this phenomenon at low and high toluene volume fractions with the objective of assessing the catalyst performance under these conditions. Both batch and semi batch modes of operation have been employed.

Though high conversions of toluene could be achieved in laboratory nitration at its low volume fractions, the stability of the catalyst need to be investigated since nitric acid, in high concentrations, has been reported to remove extra framework aluminium species from the zeolite catalysts.

Due to practical difficulty in handling toluene nitration under very high HNO_3 concentration, the catalyst performance was evaluated in our earlier studies at two volume fractions viz., 0.42 and 0.9 (Fig. 5) at which the

Table 2. Dealumination of catalyst

Element	Fresh catalyst	Toluene volume fraction 0.9	Toluene volume fraction 0.42
O	61.43	64.14	62.13
Al	2.86	2.80	1.15
Si	35.72	33.06	36.72
Total	100.00	100.00	100.00
		99.2%*	92.8%*

Note: Semi batch experiments under reflux; toluene = 1.2 mol; nitric acid dosing rate = 30 ml/h, temperature = 120°C; catalyst (H-Beta zeolite S/A, 22) = 10 g; *relative percent crystallinity.

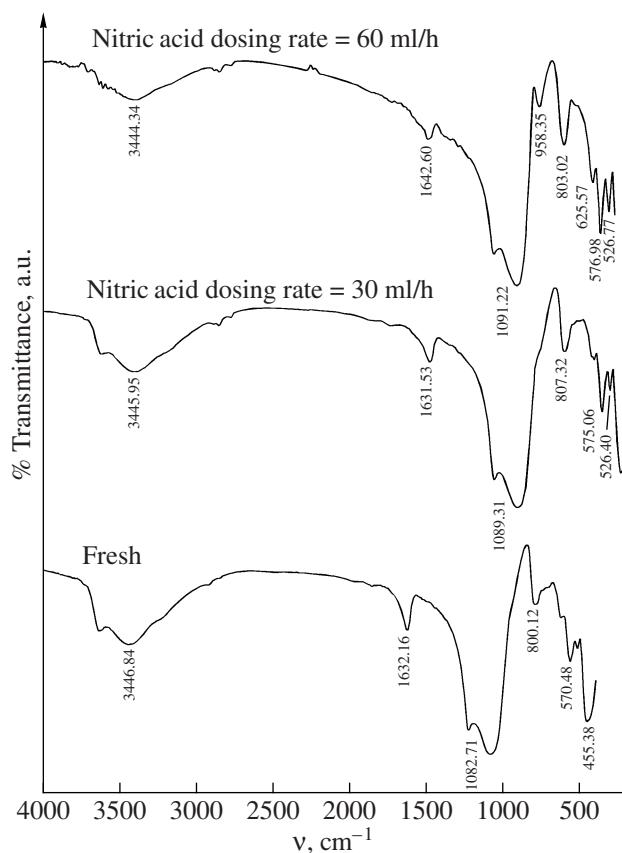


Fig. 4. FTIR plot after 3 cycles of semi batch nitration with nitric acid dosing rate of 30 and 60 ml/h.

conversions are found to be nearly equal in the dispersion morphological studies [11]. From the elemental analysis of the catalyst, it is interesting to note from Table 2 that H-Beta catalyst employed in this work, has undergone significant dealumination within 4 h of reaction at lower toluene volume fraction of 0.42. On the other hand, no appreciable dealumination has been noted at higher toluene volume fraction of 0.9. In order to establish the effect of catalyst dealumination on *para*-selectivity, semi batch nitration is carried out in a laboratory reactor employing a nitric acid dosing rate of 30 ml/h for a specific duration maintaining toluene vol-

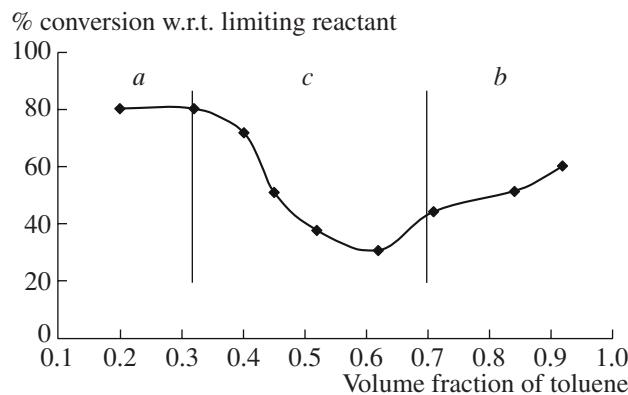


Fig. 5. Effect of phase inversion of toluene nitric acid dispersion. Batch experiments with azeotropic water removal; catalyst (H-Beta S/A, 22) = 10 g; temperature = 120°C; agitation speed = 200 rpm; a—toluene dispersed in nitric acid; b—nitric acid dispersed in toluene; c—ambivalent region.

ume fraction at 0.42 and other conditions as specified in Table 2. The dealuminated catalyst is regenerated and recycled two times and in each cycle, toluene conversion and selectivity are measured. It is found that the *para*-selectivity has dropped by 25% in first recycle and by 40% in second recycle. These results show that toluene dispersed in nitric acid does not provide a viable option. On the other hand nitric acid dispersed in toluene as the continuous phase is more preferred for achieving consistent catalyst activity for toluene nitration. Toluene nitration in semi batch mode has also been conducted at two different acid dosing rates of 30 and 60 ml/h upto three cycles at a toluene volume fraction of 0.42. The elemental analysis of the catalyst has been conducted to calculate the amount of Si and Al remaining at the end of each cycle and the results are shown in Tables 3. It shows the level of dealumination experienced by the catalyst on its recycle. The deterioration is faster at higher HNO₃ dosing rates.

Dealumination phenomenon has also been studied in a batch nitrator and the results corroborate the above findings.

Table 3. Effect of catalyst recycle on dealumination at lower toluene volume fractions (0.42)

Element, %	Freshly prepared catalyst	First cycle 30 ml/h	Second cycle 30 ml/h	Third cycle 30 ml/h	First cycle 60 ml/h	Second cycle 60 ml/h	Third cycle 60 ml/h
O	69.9	61.5	64.1	65.09	66.1	68.42	76.5
Al	2.4	1.8	1.51	1.27	0.84	0.72	0.6
Si	27.8	36.8	34.42	33.64	33.0	30.86	22.8

Note: Semi batch experiments under reflux; toluene = 1.2 mol; nitric acid dosing rate = 30 ml/h and 60 ml/h, temperature = 120°C; catalyst (H-Beta zeolite S/A, 22) = 10 g.

Table 4. Effect of exposure time on dealumination

Element, %	Freshly prepared catalyst	Toluene volume fraction after 24 h exposure	
		0.9*	0.42*
O	69.9	59.51	62.44
Al	2.4	1.38	0.00
Si	27.8	39.1	37.56

Note: Batch experiments under reflux, temperature = 120°C; catalyst (H-Beta zeolite S/A, 22) = 100 g; duration 24 h.

* Toluene volume fraction.

Effect of Prolonged Exposure

Batch nitration studies have been conducted under prolonged exposure (24 h) at 0.42 and 0.9 volume fractions of toluene. The results are presented in Table 4. They clearly show the drastic effect of prolonged exposure on H-Beta catalyst at a toluene volume fraction of 0.42 and somewhat moderate effect on it at a toluene volume fraction of 0.9. In the case of former, there is a need to restrict long exposure of catalyst to the acidic environment of the reaction mixture. A low residence time continuous process nitration is best suited for achieving high conversion and selectivity.

Lattice Aluminium Transformations in H-Beta Catalyst

Haouas et al. [12] found that the transformation of lattice aluminium from tetrahedral to octahedral config-

uration is mainly responsible for heightening *para*-selectivity in toluene nitration. By employing semi batch mode of nitration in the present study, we are able to confirm this phenomenon by MAS-NMR studies. The details are given in Fig. 6.

An attempt has been made in the present work to broadly assess the status of lattice aluminium transformation in freshly prepared, regenerated and recycled catalyst employed in the toluene nitration. Approximately three fold increase in octahedral coordination has been observed (Fig. 6) when freshly prepared Beta zeolite catalyst is employed for semi batch nitration with nitric acid (70 wt %) dosing rate of 30 ml/h for 3 h. Once, twice and thrice recycled catalysts have been used in semi batch nitration at a HNO_3 dosing rate of 30 ml/h and the ^{27}Al MAS-NMR spectra of the catalyst samples have been taken after each cycle and the results are presented in Fig. 7. They show that the lattice aluminium transformation continues to be present in recycled catalysts indicating their ability to maintain high *para*-selectivity.

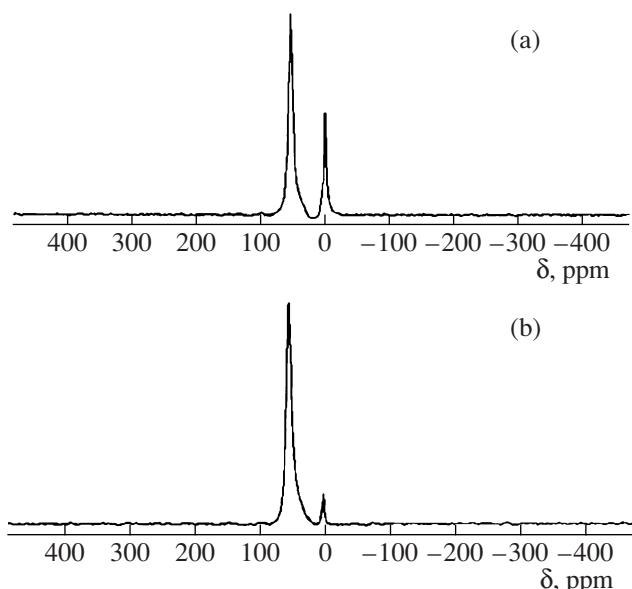


Fig. 6. Solid state ^{27}Al MAS-NMR spectra of zeolite H-Beta (a) freshly prepared zeolite (b) after semi batch nitration at 30 ml/h HNO_3 dosing rate for 3 h.

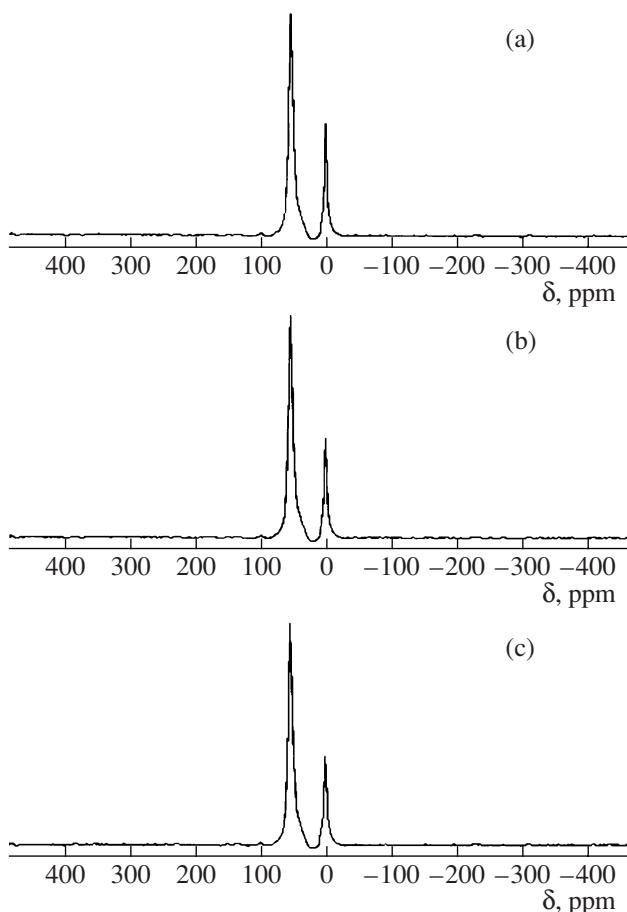


Fig. 7. Solid state ^{27}Al MAS-NMR spectra of recycled zeolite H-Beta catalyst in semibatch nitration at 30 ml/h HNO_3 dosing rate for 3 h; (a) after 1st cycle, (b) after 2nd cycle, and (c) after 3rd cycle.

CONCLUSIONS

The physico-chemical changes in zeolite H-beta catalyst have been studied in toluene nitration to establish its stability and regenerability. The effect of the microenvironment around the catalyst particle has been examined using ^{27}Al MAS-NMR spectra to explain its consistent *para*-selectivity. The possible cause for this phenomenon was found to be the consistent transformation of flexible lattice aluminium network from tetrahedral to octahedral configuration.

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