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

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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 up to three cycles. The possible cause of consistent activity of the catalyst with respect to \textit{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 \textsuperscript{27}Al MAS-NMR. These studies indicate the commercial potential of cleaner option of replacing sulfuric acid with zeolites in toluene nitrination.

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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 \textit{para}-substituted products as desired. In the conventional industrial nitration, however, the production of the \textit{ortho}-isomer exceeds that of the \textit{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. \cite{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\textsubscript{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 (Nafton H) with HNO\textsubscript{3} or its metal salts, mixed anhydrides or nitrate esters catalyzed by H\textsubscript{2}SO\textsubscript{4} and transfer nitrations under essentially neutral conditions using N-nitropyridinium, N-nitroquinolinium salts, nitro and nitrite onium salts to enhance the reactivity of the nitrating agent.

Smith and Fry \cite{2} reported \textit{para}-selective mononitrination of alkylbenzenes under mild conditions using benzyol nitrate in the presence of aluminium or proton exchanged large pore mordenite. A maximum \textit{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 \textit{para}-selectivity. Choudary et al. \cite{3} reported to have achieved higher \textit{para}-selectivities (upto \textit{para}/\textit{ortho} ratio of 2) and space time yields in aromatic nitrations employing various solid acid catalysts like Fe\textsuperscript{3+} montmorillonite, K10 montmorillonite, Zeolite beta, ZSM-5, mordenite, HY and TS-1 with 60–90% nitric acid and with azotropic water removal.

Kogelbauer et al. \cite{4} have demonstrated that sulfuric acid supported on preshaped silica to be a good recyclable catalyst for the nitrination of toluene to dinitrotoluene using 65 wt \% nitric acid. Dagade et al. \cite{5} reported vapor phase nitration of toluene at 120°C using dilute nitric acid (20\%) and beta zeolite and achieved maximum conversion of 55\%, \textit{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. \cite{6}. They found that zeolite beta exhibited high stability and gave high \textit{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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tolluene 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 (SiO$_2$/Al$_2$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 (SiO$_2$/Al$_2$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 SIEEMENS/D5000 X-ray diffractometer using Ni-filtered Cu$_K\alpha$ radiation ($\lambda = 1.506$ Å). 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. Al$_2$(SO$_4$)$_3$·6H$_2$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