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A Study on Solid Acid Catalyst Selection and Characterization

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Abstract – The nitration of toluene is most important route to obtain substituted aromatic intermediates viz., nitrotoluenes and dinitrotoluenes for the production of speciality chemicals mainly after reduction of the nitro group. In the conventional nitration, however, the production of the ortho isomer exceeds that of the para isomer. To overcome this limitation, nitrations using solid acids as catalysts are receiving increased attention. Solid super acid catalysts like polystyrene sulfonic acid, perfluorinated sulfonic acid (Nafion H) with HNO3 or its metal salts, mixed anhydrides or nitrate esters catalyzed by H2SO4 and nitrations under essentially neutral conditions using N-nitropyridinium, N-nitroquinolium salts, nitro and nitrite onium salts have been reported to enhance the reactivity of the nitrating agent.

Keywords:- Nitration, Aromatic, Sulfonic Acid, Nitropyridinium, Solid Acid etc.

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INTRODUCTION

The activity of H-Beta and ZSM-5 type zeolites is ascribed to their Bronsted acidity whereas the improved *para*-selectivity to their pore size and shape selectivity. Haouas et al., ascribed the higher *para*-selectivity of H-Beta to the lattice aluminium transformations during the reaction. In the present work, H-Beta and H-ZSM-5 catalysts are employed for liquid phase nitration in view of their stated advantages in conversion levels and selectivity. The lower *para*-selectivity of HZSM-5 may be due to its hydrophobic pores that resist the diffusion of aqueous nitric acid resulting in fewer acidic sites available to generate required nitronium ions. The reported molecular modeling studies revealed that *para*-nitrotoluene encountered least resistance for vapor diffusion in H-Beta catalyst and diffusivities decrease in the order *para*> *ortho*> *meta* nitrotoluenes. The role of SiO_2 / Al_2O_3 ratio (hereinafter called S/A) of catalyst on the product distribution is experimentally investigated in the present work. Fig. 4.1 shows the conversion and *para*-selectivity achieved by using four catalyst samples with different S/A ratios in the batch nitration experiments conducted under reflux. It shows H-Beta zeolite with S/A of 22 has provided better conversions and *para*-selectivity. It is interesting to note that the same catalyst was reported to be highly *para*-selective in liquid phase nitration with acetyl nitrate Smith et al. and in vapor phase nitration of toluene and fluoro benzene and reactive distillation of toluene Our experimental results and these reported advantages have reinforced our decision to select H-Beta catalyst. H-Beta has also superior structural characteristics as shown in The other advantages are its regenerability through a simple thermal treatment and its facilitated separation from the reaction products. Its limitations viz., the necessity to maintain higher concentration of acid sites for sustaining its activity and the need to remove the water formed during nitration effectively from its acid sites have been given due consideration in this work. After examining the various options of water removal viz., separation as vapor at high temperature, chemical trapping and azeotropic distillation,the latter was favored in the present work in view of its advantages of integrating it with the reaction system in making efficient use of available reaction enthalpy and enabling excellent control of the reaction temperature.

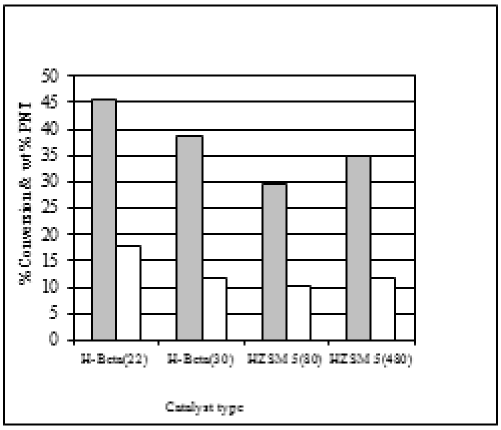

Fig. 1 Effect of catalyst on toluene conversion (■) and wt.% para-nitrotoluene formation (□). Toluene: nitric acid (molar ratio) = 2.2 : 1.4; catalyst= 10 g; temperature= 110 °C; time= 3 h; agitation speed= 200 rpm; S/A ratio in parenthesis

REVIEW OF LITERATURE

Various scientists were reported different methods for the synthesis of ceria. They also studied characterization as well as catalytic activity of ceria catalyst over various reactions. Among these, B. Subramanian et al. were synthesized ceria nanoparticles via precipitation route. The structural and textural properties of ceria nanoparticles were studied by using XRD, TEM, BET surface area, Raman, SEMEDS and AFM analysis techniques. They reported that ceria nanoparticles gave good absorption of UV light as well as transparency in visible region. Therefore, ceria catalyst exhibits an application as UV blockers.

Furthermore, Bondioli (2006) et al., were synthesized nanocrystalline ceria powder under microwave hydrothermal route. They used cerium ammonium nitrate and NaOH as precursors for the catalyst preparation.

During synthesis, (2009) authors investigated the influence of various reaction parameters, such as concentration of starting solutions, reaction time and pressure on powder properties.

Guo et al. (1999) were prepared thermally triangular CeO2 microplates using cerium nitrate as precursor, aqueous carbamide as carbon source and cetyltrimethylammonium bromide as a surfactant. These researchers reported the multifunctionalized role of ceria in various fields such as catalysts, hydrogen storage devices and electronic function.

Zhou et al. (2008) were studied CO oxidation reaction over hydrothermally synthesized crystalline CeO2 nanorods. They reported that these nanorods could exhibit better catalytic performance than CeO2 nanoparticles. One of the most Jie Xu and co-workers were synthesized and characterized mesoporous ceria materials through a soft-templating method using cerium nitrate as a precursor and bromide as a template reagent.

FOCUS AND SCOPE OF PRESENT INVESTIGATIONS

The main focus of present investigations is on the solid acid catalyze Selection And Characterization oluene nitration which has tremendous potential for commercial exploitation. The literature survey has shown that it has not been well studied from reaction engineering point of view. The kinetic and mass transfer effects have not received much attention. It is therefore the objective of the present study to cover following:

- Providing a new perspective to solid catalyzed aromatic nitrations by investigating the precise role of acid – aromatic hydrocarbon dispersion morphology on the product distribution and process / catalyst stability.
- Examining the micro reaction environment around the catalyst particle and its influence on heightening the para- selectivity.
- Process standardization with particular reference to catalyst characteristics, mode of operation, temperature, agitation speed, catalyst to toluene ratio, nitric acid to toluene ratio, nitric acid dosing rate, boil-up rate and dispersion morphology to achieve high conversion and high *para* selectivity.
- The study of multiphase mass transfer characteristics of liquid-liquid-solid reaction system as applicable to toluene nitration.

LIMITATIONS OF RESEARCH STUDY

The following are the limitations of the research study

- Evaluation of the contribution of non catalytic reaction in the catalytic toluene nitration is found to be difficult with the available experimental tools.
- The mass transfer resistance offered by the liquid-liquid-solid system in toluene nitration is treated as sequential resistances offered by liquid-liquid and liquid-solid systems.
- The kinetic parameters for toluene nitration could not be evaluated in a batch reactor since the process is very fast to obtain measurable time-conversion data. In the present studies, semi-batch experiments are instead conducted for kinetic studies.
- Evaluation of catalyst performance in toluene dispersed in HNO_3 as continuous phase is found to be difficult with the available experimental tools.

RESULTS & DISCUSSION

Our experimental results and these reported advantages have reinforced our decision to select H-Beta catalyst. H-Beta has also superior structural characteristics as shown in Table 4.2. The other advantages are its regenerability through a simple thermal treatment and its facilitated separation from the reaction products. Its limitations viz., the necessity to maintain higher concentration of acid sites for sustaining its activity and the need to remove the water formed during nitration effectively from its acid sites have been given due consideration in this work. After examining the various options of water removal viz., separation as vapor at high temperature, chemical trapping and azeotropic distillation,the latter was favored in the present work in view of its advantages of integrating it with the reaction system in making efficient use of available reaction enthalpy and enabling excellent control of the reaction temperature. Batch and semi-batch nitrations have accordingly been conducted with a reflux bridge with Dean- stark separation leg attached to it. This has enabled the evaporated water-nitric acid –toluene mixture to be condensed in the reflux condenser and collected in the Dean-stark leg for separation of aqueous and organic phases. Titration of the collected aqueous phase is carried out to determine the nitric acid content.

CATALYST CHARACTERIZATION

H-Beta catalyst was characterized before and after toluene nitration for its structural, physical and chemical properties using various techniques such as XRD, FTIR, SEM, GC, DTA, TGA, MAS-NMR and others.

X-Ray Diffraction Studies (XRD)

The catalyst crystallinity determination by XRD measurements, involves the division of sum of several specific peak intensities by the respective sum found for a well crystallined sample measured under the same conditions. X-ray diffraction has been used in the present studies to investigate not only the structural stability of the catalyst used in this work but also zeolite phase characteristics.

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. Fig 4.6 shows the XRD patterns of the freshly prepared catalyst and that used under different process conditions. 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 (0.2) 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. Figures 4.7 to 4.9 provide XRD, TGA and FTIR profiles of H-Beta catalyst after long duration exposure (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 TGA profiles, however, show the vulnerability of H-Beta catalyst under low toluene volume fraction viz., nitric acid as a continuous phase and toluene as dispersed phase. The FTIR profiles demonstrate that the bands at about 3600 cm^{-1} and 1600 cm^{-1} (ascribed to hydroxyl groups attached to lattice aluminium and Bronsted acidity respectively) got significantly reduced under the conditions prevailing at low volume fraction of toluene. This indicates the reduction in total and Bronsted 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.

SCOPE OF THE STUDY

1. An attempt has been made in the present work to experimentally determine the apparent or macrokinetic rate of toluene nitration in a semi-batch mode of operation. The rate so obtained is compared with the rates of external mass transfer as applicable to agitated liquid-liquid-solid systems considering the following resistances in series

   a) Transfer of toluene from continuous phase to aqueous phase surrounding the catalyst particle.

   b) Liquid-solid mass transfer

   c) Diffusion of reactants into the catalyst particle and simultaneous nitration

2. The present work has opened up new R&D avenues in solid acid catalyzed aromatic nitrations. The notable amongst them are:

   a) The solid acid catalyzed aromatic nitration requires more extensive reactor studies to facilitate its commercial utilization on larger scale. Our investigations have established the desirability of employing reactive distillation concept for toluene nitration to achieve higher levels of conversion and *para*-selectivity with minimum catalyst dealumination since it facilitates effective removal of water from the reaction front and maintenance of desired nitric acid concentration locally. The solid acid catalyst can be conveniently packed in the distillation column and a liquid-liquid separator can be incorporated after condenser to recycle toluene after separation from water formed during the reaction. Such a configuration which facilitates effective nitration-water separation processes will have a positive effect on catalyst acidity and enhanced mass transfer as well as reaction rates. The chemical reaction and inter and intraphase diffusion steps will drive each other in a proactive fashion. Incorporation of distillation column to the reactor will ensure spatial continuity along the axial direction. Both reaction and separation will take place in all sections of the packed distillation column. Reaction engineering studies on a reactive distillation system will be more complex and there will be a definite need to evaluate kinetic and mass transfer parameters relevant to a gas-liquid-sold system. There is tremendous scope and academic challenges to model such a system to simulate the reactor operation.

b) Application of reaction calorimetry to assess intrinsic reaction rates and catalyst life through the measurement of microthermal responses will be a challenging task in standardizing the continuous process based on solid catalyzed aromatic nitrations in general and toluene nitration in particular.

c) The aromatic nitrations being highly exothermic, the accumulation of unreacted HNO_3 in high concentration can be hazardous if accompanied by a phase inversion under mass transfer controlled reaction rate. This aspect needs attention to ensure safe operation of solid catalyzed aromatic nitrations.

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