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Tertiary Butylation of Aniline Over Nanosized Zeolite Beta Catalyst

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In the current paper, we report nanosized zeolite beta to be a robust and potent catalyst for tertbutylation of aniline. Nanocrystals of beta zeolite having spherical morphology were prepared via a one-pot strategy that is based on vacuum-concentration coupled hydrothermal method. The catalyst could be used in the as-synthesized form, without any further modifications. In the presence of the as-prepared catalyst, liquid-phase tert-butylation of aniline using tert-butanol as alkylating agent proceeded successfully. Reaction parameters like duration of reaction, temperature, mole ratio of substrates and quantity of catalyst were optimized. Time-dependent data obtained was subjected to kinetic studies. Detailed studies on product selectivity were conducted. The catalyst could selectively direct the formation of C–C bonds and no N-alkylated products were detected. It also demonstrated good selectivity towards mono-substitution. The catalyst could be recovered by a simple work-up plan and could then be re-used. No appreciable loss in activity was detected in consecutive runs. Thus, the nanosized beta mediated route to introduce tert-butyl group on aniline ring can be an environment-friendly alternative to the use of homogeneous catalysts.

Keywords: Heterogeneous Catalysis, Nanosized Beta, Aniline, Zeolite, Tert-Butylation, Re-Usable Catalyst.

1. INTRODUCTION

Aniline is a highly versatile starting material for the manufacture of several compounds of profound use to the society. In particular, tert-butylated anilines are useful precursors in agrochemical, pharmaceutical and polymer production.¹⁻³ These can be obtained from aniline through electrophilic aromatic substitution of amine aromatic ring by tert-butyl group, in the presence of a suitable catalyst. Besides electrophilic substitution, rearrangement is also a plausible synthetic route to procure C-alkylated amines. Along these lines, o-allyarylamines have been synthesized by amino-Claisen rearrangement of aromatic N-allylamines.⁴⁻⁶ Ring-alkylated aryl amines were also obtained as side products in N-alkylation reactions. As a matter of fact, compared to such N-alkylation reactions, there have been fewer reports on selective C-alkylation of amines.

To bring about electrophilic substitution on aromatic nucleus, Friedel Crafts catalysts are primarily used. But, despite the presence of strongly activating -NH₂ group, the usual aluminium halide Friedel Crafts catalysts fail to accomplish aromatic amine alkylation effectively. This is because this class of catalysts forms a deactivating complex by binding with -NH₂ group of aromatic amines. Thereby, aluminium halides are prevented from acting in a catalytic fashion in amine alkylation. Other catalysts like Al-AlCl₃ mixture, BF₃ or aluminium anilides⁷⁻⁹ are usually employed to prepare tert-butylated anilines from aniline and isobutylene. However, the use of these homogeneous catalysts is laden with difficulties like high capital cost, corrosion of equipment, disposal of aggressive waste materials, tedious product work-up and non-recovery of the catalyst. A surge in awareness of these drawbacks coupled with a drive towards enforcement of rigorous laws regarding the disposal of industrial effluents has spurred extensive research on re-usable heterogeneous catalysts.

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Heterogeneous catalysts like iron oxide, montmorillonite clay, heteropolyacids supported on clay and microporous molecular sieves like aluminophosphates have been successfully used to C-alkylate aromatic amine nucleus directly and selectively.¹⁰⁻¹⁴ The reaction conditions maintained in these works indicate that C-alkylation is preferred over N-alkylation at high temperatures, in the absence of excess water and over catalysts with strong acid sites.

Zeolite is an important class of heterogeneous catalysts that can be an attractive alternative to homogeneous catalysts. Among the zeolites, commercial zeolite Y, ZSM-5, mordenite and faujasite have been used to C-alkylate aromatic amines and diamines using alkenes and alcohols as alkylating agents.¹⁵⁻²⁴ Zeolite beta is a synthetic zeolite which offers great promise in the field of heterogeneous catalysis. Its structure manifests a 3-dimensional 12-ring channel system, a feature highly conducive to outstanding catalytic properties.²⁵⁻²⁷ It also possesses high thermal stability. Yet, despite its favorable properties, zeolite beta has not yet been explored for selective C-alkylation reactions of aniline. In the present work, we study the novel applicability of zeolite beta in tert-butylation of aniline, a reaction that is industrially significant, but cumbersome by homogeneous catalysis. There have been many reports in the recent past that have decisively pointed out that as compared to commercially available bulk zeolites; nanozeolites have potentially augmented catalytic abilities. This has been attributed to the presence of greater fraction of active sites on the nano-catalyst surface and higher diffusion mobility of molecules to and fro the active sites in nanozeolites.²⁸⁻³¹ Specifically, nanomorphic zeolite beta has been shown to be exceptionally better than its bulk counterpart in the test reaction, benzylation of benzene.32 Hence, it deem fit to choose and prepare nano forms of zeolite beta over the commercial bulk samples. Along these lines, nanoparticles of beta were prepared by adopting a relatively quick vacuum-concentration coupled hydrothermal method. The efficiency of this nano catalyst was then tested and compared with commercial beta in selective C-alkylation of aniline with tert-butanol. Preliminary kinetic studies were done to determine the apparent activation energy. To the best of our knowledge, this is the first report on the applicability of a nanozeolite in tertbutylation of aniline.

Even though isobutylene is generally the most common tert-butylating agent, there are difficulties associated with its availability in high degrees of purity. It is usually contaminated with other C_4 isomers such as 1-butene or 2-butene.^{13, 33} Also, it is a highly explosive and flammable gas. Alternatively, isobutylene can be generated *in situ* from tert-butanol or methyl tert-butyl ether (MTBE). However, the use of MTBE has been restricted in many parts of the world as it is known to contaminate ground water reserves.³⁴ For these reasons, in this study, tert-butanol was chosen as the alkylating agent over isobutylene or MTBE.

2. EXPERIMENTAL DETAILS

2.1. Chemicals

Commercial samples (Merck) of Aluminium iso-propoxide (AIP), tetraethoxysilane (TEOS), tetraethylammonium hydroxide (TEAOH, 25% aq.), tert-butanol and aniline were used without further purification.

2.2. Synthesis of Catalyst

In a typical procedure to prepare nanosized zeolite beta (Si/Al = 50), a three-step strategy was adopted. In the first step, a clear solution was obtained by magnetically stirring a mixture of AlP, TEAOH (25% aqueous), deionized water and TEOS, for 2 h. The clear solution ensured that TEOS has been hydrolyzed completely. The pH of this solution was 11.0. In the next step, the clear sol was concentrated to a viscous sol in a rotary evaporator at 80 °C, as mentioned in the literature.³⁵ The concentrated sol was then aged at 90 °C for 3 days. In the final step, the aged sample was treated hydrothermally in an autoclave at the crystallization temperature of 175 °C for 6 h. The sample was then centrifuged and dried. The dried sample was then calcined at 600 °C for 3 h.

2.3. Characterization of the Catalyst

Powder X-ray diffraction patterns were recorded using a Rigaku 2000 diffractometer equipped with a Cu-K α radiation (1.5418 Å) from 2.5° to 60° at a scan rate of 2°/min using a step size of 0.04°. Morphology of the zeolite nanocrystals was studied with SEM (JEOL JSM-6500f).

2.4. Catalytic Studies

The test reaction, tert-butylation of aniline in the presence of beta zeolite was carried out in a 100 ml stainless steel Parr autoclave under autogenous pressure in the temperature range 140 °C-170 °C for 6 h. A predetermined quantity of reactants and catalyst were charged into the autoclave and the temperature was raised to the desired value. A typical experiment consisted of a reaction mixture of 0.01 mol aniline, 0.05 mol tert-butanol and 0.20 g of beta catalyst at 140 °C for 6 h. The products were analyzed by gas chromatographic analysis (Hewlett Packard 5890, OV-101 column) using flame ionization detector (FID). Product identification was done by gas chromatography-mass spectrometry (GC-MS). The products were determined to be 2-tert-butylaniline (2-TBA), 4-tert-butylaniline (4-TBA) and 2,4-di-tert-butylaniline (2,4-DTBA) (Scheme 1).

The extent of reaction is expressed in terms of the percentage of aniline converted into alkylated products. The influence of reaction parameters such as reaction time, catalyst quantity, aniline to tert-butanol mole ratio and reaction temperature was studied. Kinetic data was analyzed to determine the apparent activation energy for the reaction. Also, a mechanistic route is suggested for the reaction.

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Scheme 1. Product distribution in tert-butylation of aniline over nanosized zeolite beta.

3. RESULTS AND DISCUSSION

3.1. Characterizations of the Catalyst

XRD pattern of the synthesized catalyst is shown in Figure 1. Good crystallinity is indicated as the diffractograms show the characteristic peaks at $2\theta = 6.98^{\circ}-8.31^{\circ}$ and $22.46^{\circ}-23.86^{\circ}$, which are characteristic of zeolite beta of BEA* framework.^{36,37} The broad peak at low angle region (6.98–8.31°) is due to the overlap of four peaks at $2\theta = 6.98^{\circ}$ ((100) plane, polymorph A), 7.74° ((101) plane, polymorph A), 7.34° ((110) plane, polymorph B) and 8.31° ((111) plane, polymorph B). The broad peak at $2\theta = 22.46^{\circ}$ ((311) plane, polymorph A), 22.64° ((422) plane, polymorph B), 22.65° ((240) plane, polymorph B), 23.03° ((222) plane, polymorph B) and 23.86° ((113) plane, polymorph B). Thus, the crystals obtained can be rationalized to contain both polymorphs A and B.

The SEM micrograph of the synthesized zeolite is shown in Figure 2. The particles show spherical



morphology. The formation of spherical particles can be traced to Ostwald ripening effect.³⁸ The particle size is approximately 30 nm. This shows the success of the synthesis protocol in directing the formation of small-scale zeolite nanoparticles. The use of TEAOH as the organic structure-directing agent (SDA) and the incorporation of concentration and aging steps lead to nanomorphic zeolite beta. Because of the addition of vacuum concentration step and low-temperature aging prior to the hydrothermal crystallization, more number of viable nuclei could be created which subsequently developed into small crystals. These steps thus boosted the rate of nucleation over crystallization in a relatively short period of time.

3.2. Catalytic Activity

Systematic investigation was conducted to test the efficiency of the synthesized nanosized zeolite beta in tertbutylation of aniline with tert-butanol, under autogenous autoclave pressure. The effects of various parameters like reaction time, catalyst quantity, reactant mole ratio and temperature were studied. The optimized conditions that have been so arrived at are set forth in following sub-sections.



Figure 2. SEM image of nano sized zeolite beta.

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Figure 3. Effect of reaction time on aniline percent conversion in tertbutylation of aniline (catalyst, 0.20 g nanosized zeolite beta; aniline, 0.01 mol; tert-butanol, 0.05 mol; aniline:*tert*-butanol, 1:5; temperature, 150 °C; pressure, autogenous pressure in 100 ml autoclave).

3.2.1. Effect of Reaction Time

In order to investigate the effect of reaction time, series of experiments under a specified set of conditions were conducted and reactant conversions were tracked at regular intervals. With increase in the duration of reaction, the change in extent of reaction becomes progressively less pronounced (Fig. 3).

This is because as time passes and reactants get coned by sumed in the reaction, the rate of adsorption of the reactant molecules on the catalyst surface decreases. Also with time, more and more product molecules get accumulated in the reactant mixture and there is a decrease in their rate of desorption from the catalyst sites. In fact, most of the aniline conversion was obtained in the first 6 h (Fig. 3). Accordingly, further conditions were monitored by allowing the reaction to occur for 6 h.

3.2.2. Effect of Catalyst Quantity

The influence of the amount of catalyst on percent conversion of aniline after a fixed reaction time (6 h) was examined. Sets of experiment were conducted by varying the catalyst amount in the range 0.05 g to 0.25 g in a reaction mixture containing 0.01 mol of aniline and 0.05 mol of tert-butanol. The temperature was kept constant at 140 °C. GC-MS studies confirmed that no product formation took place in the absence of the catalyst. Thus the nanosized zeolite beta plays a pivotal role in driving the reaction by providing a surface and active sites to the reactants to undergo a series of bond-breakings and bond-makings. With an increase in the catalyst amount, initially, the percent conversion of aniline increased (Fig. 4(a)). This is due to a concomitant increase in the number of active sites. But beyond 0.20 g, the increase in percent conversion is only marginal. This trend towards a plateau suggests that

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Figure 4. Effect of the amount of catalyst on (a), aniline percent conversion (b), product selectivity in tert-butylation of aniline (catalyst, nanosized zeolite beta; aniline, 0.01 mol; tert-butanol, 0.05 mol; reaction time, 6 h; aniline:tert-butanol mole ratio, 1:5; temperature, 140 °C; pressure, autogenous pressure in 100 ml autoclave).

the catalyst mass is nearing the superfluous value. Catalyst quantity of 0.20 g seems to provide enough active sites to well-accommodate most of the reactant molecules available at the chosen concentration of reactants. Besides, when catalyst quantity is increased to 0.25 g, less selectivity is displayed and di-substituted product is also produced (3%) (Fig. 4(b)). This is in tandem with a decrease in the yield of 2-*tert*-butylaniline. It is thus implicit that as the number of active sites becomes progressively more, they tend to become less discriminatory and catalyze disubstitutions alongside mono-substitutions. Hence, taking into the account the selectivity and economic factors, further studies were conducted using 0.20 g of the catalyst.

3.2.3. Effect of Mole Ratio

The effect of aniline to *tert*-butanol mole ratio was studied by keeping the total volume of the reactant mixture constant. An increase in the amount of alkylating agent augmented the reactant conversion, but diminished the product selectivity (Fig. 5(a)). Beyond aniline: tert-butanol mole



Figure 5. Effect of mole ratio of reactants on (a), aniline percent conversion (b), product selectivity in tert-butylation of aniline (catalyst, 0.20 g nanosized zeolite beta; reaction time, 6 h; temperature, 140 °C; pressure, autogenous pressure in 100 ml autoclave).

ratio of 1:5, there is not much increase in the percent conversion of aniline. At aniline to tert-butanol ratio 1:10, the aniline amount has approached the limiting value. Moreover, higher concentrations of alkylating agent are promoting di-substitution at the cost of 2-*tert*-butylaniline yield. This is detrimental for the selectivity towards the monosubstituted product (Fig. 5(b)). Hence, it can be concluded that for the reaction under study, optimum aniline to *tert*-butanol mole ratio is 1:5.

3.2.4. Effect of Temperature

The reaction was conducted by varying the temperature in the range of 140 °C to 170 °C, in steps of 10 °C. All other reaction parameters were kept constant. Data collected indicates that temperature affected the rate of conversion markedly, particularly in the lower ranges (Fig. 6(a)). Temperature also had an influence on the product selectivity ((Fig. 6(b)). Apparently, percentage yield of 2,4-DTBA increased, at the cost of reduction of selectivity towards mono-alkylated products, with an increase in reaction temperature. This takes place despite the fact that high temperature conditions can cause faster desorption of mono-substituted products from catalyst sites, thereby preventing their further alkylations. It can thus be elucidated that at high temperatures, the fraction of molecules having energy equal to or greater than the



Figure 6. Effect of temperature on (a), aniline percent conversion (b), product selectivity in tert-butylation of aniline (catalyst, 0.20 g nanosized zeolite beta; aniline, 0.01 mol; tert-butanol, 0.05 mol; reaction time, 6 h; aniline:*tert*-butanol mole ratio, 1:5; pressure, autogenous pressure in 100 ml autoclave).

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Figure 7. Comparison of efficiency of nano-beta with commercial beta in tert-butylation of aniline (catalyst amount, 0.20 g; aniline, 0.01 mol; tert-butanol, 0.05 mol; aniline:*tert*-butanol mole ratio, 1:5; reaction time, 6 h; temperature, 140 °C; pressure, autogenous pressure in 100 ml autoclave).

activation energy for di-substitutions must have increased and this factor outweighs the desorption effects. Significantly, at 140 °C (413 K), there is an exclusive production of mono-alkylated products. Our findings also reveal that 2-*tert*-butylaniline is more prone to di-substitution than the corresponding para isomer. The increase in percent conversion to 2,4-DTBA was accompanied by a conspicuous d decrease in the selectivity of 2-TBA. The effect on selectivity towards 4-TBA was less evident. This trend was the same for all reaction parameters studied (Figs. 4–6).



Figure 8. Reusability of nanosized zeolite beta in tert-butylation of aniline (reaction conditions: Catalyst, 0.20 g nanosized zeolite beta; aniline, 0.01 mol; tert-butanol, 0.05 mol; aniline:*tert*-butanol mole ratio, 1:5; reaction time, 6 h; temperature, 140 °C; pressure, autogenous pressure in 100 ml autoclave).

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Figure 9. SEM image of nanosized zeolite beta after the fourth catalytic run.

3.2.5. Comparison with Bulk Beta Catalyst

A comparative study was done to assess the efficiency and product selectivity that can be achieved in the presence of nanosized zeolite beta relative to commercial bulk beta in tert-butylation of aniline, under identical reaction

 Table I.
 Percent conversion of aniline in tert-butylation of aniline at different temperatures.
 09:25

Scientific Pu	ıblishers	Temperature (K)		
Time (h)	413	423	433	443
0	0	0	0	0
2	40.3	43.5	56.9	75.2
4	52.1	72.1	82.1	91.0
6	74.3	85.8	93.0	96.7

Notes: Reaction condition: Catalyst, 0.20 g nanosized zeolite beta; aniline, 0.01 mol; tert-butanol, 0.05 mol; *tert*-butanol:aniline mole ratio, 5:1; pressure, autogenous pressure in 100 ml autoclave.



Figure 10. Kinetic plot for tert-butylation of aniline.



Figure 11. Arrhenius plot.

conditions. As expected, due to shorter diffusion pathways and greater density of accessible acid sites, nano-form showed significantly much better performance than the bulk beta, both in terms of yield and selectivity (Fig. 7). As the products could desorb faster from nanosized zeolite beta, they were less available for di-substitution which consequently improved selectivity towards monoalkylated products.³⁹

3.2.6. Catalyst Reusability

The recoverability and reusability of the catalyst was tested for upto four runs. The catalyst after each use was centrifuged and was washed with ethanol. It was then dried at 120 °C for 24 h, and was reused under optimum reaction conditions. There was no appreciable decline in the percent conversion of aniline in consecutive runs after the fresh use (Fig. 8).



Scheme 2. Mechanistic pathway for tert-butylation of aniline (a) adsorption of both reactants on the catalyst surface (b) protonation from the catalyst and attack of tert-butanol on aniline (c) formation of mono-substituted products which may undergo further substitution (d) desorption of the products.

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Though insignificant, the slight decrease in the percent conversion observed in subsequent runs can be attributed to the particle agglomeration that took place, as also indicated in the SEM image of the used catalyst (Fig. 9). The spherical morphology of the nano-catalyst remains unaltered even after repetitive use (Fig. 9). It follows that the catalyst is quite sturdy to be reused. After the removal of the catalyst by centrifugation, the reaction was conducted in the supernatant for another 2 h, under the optimized reaction conditions. No further change in the product concentration was observed in this duration. This indicates the easy recoverability of the catalyst and its trueheterogeneous character.

3.3. Kinetic Studies

Depending on whether one or both reactants are adsorbed, reactions on heterogeneous catalysts may follow Eley–Rideal or Langmuir–Hinshelwood–Hougen–Watson (LHHW) mechanism. Yet, LHHW mechanism is more probable as the time-scale for a gas-surface collision is extremely short, in orders of pico-second.⁴⁰ In an attempt to obtain the apparent activation energy and frequency factor for the reaction between aniline (A) and tert-butanol, the fractional conversion of aniline as a function of time was obtained at different temperatures (Table I). The data was tried to be fitted into integrated rate equation for second-order kinetics on the surface of solid-acid catalysts, as has been previously reported.¹³

$$\ln \frac{(M - X_A)}{M(1 - X_A)} = (M - 1)k_R[A]_0 t \tag{1}$$

The data obtained (Table I) could be fitted well in Eq. (1), at all temperatures studied (Fig. 10). From the slopes of the linear plots, the values of rate constant, k_R were determined at different temperatures, which was then used to obtain the Arrhenius plot (Fig. 11). From the Arrhenius plot, the apparent activation energy and frequency factor for the net reaction were determined to be 51.3 kJ/mol and 20.3 respectively. This high value of activation energy clearly indicates that the reaction is not purely diffusion-controlled. It can thus be justified that the rate determining step in the reaction involves bond-breaking and bond-formations between the reactants and is not just governed by the diffusion of the molecules through the catalyst.

Taking into consideration the above points and to justify the product distribution, mechanistic pathway as shown in Scheme 2 is suggested. Both the reactants get adsorbed on zeolite. Following the adsorption of both reactants, tert-butanol attacks aniline through a concerted mechanism. Protonation from the catalyst causes the breaking of $C_{butanol}$ - $O_{butanol}$ bond and the concomitant formation of $C_{butanol}$ - $C_{aniline}$ bond.

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4. CONCLUSIONS

Nanosized zeolite beta was fabricated successfully by a one-pot, facile, vacuum concentration-hydrothermal-based process. The as-synthesized catalyst proved to be efficient in direct and selective tert-butylation of aniline. It could selectively direct the formation of C–C bonds, as opposed to N-alkylation. Additionally, it showed high selectivity towards mono-tert-butylated aniline relative to the di-substituted products. The effects of various reaction parameters were investigated and optimum conditions were derived. Under optimum conditions, aniline percent conversion of 74% and 100% selectivity towards mono-substituted products were recorded.

The as-synthesized catalyst also demonstrated superior performance (1.6 times more conversion under identical conditions) when compared to commercial beta sample. Thus the nano-scaling proved to be vital in enhancing the catalytic ability of zeolite. The nanocatalyst could be recovered easily and re-used without any appreciable loss of activity. This renders the whole process economically reasonable and environmentally benign. Additionally, only water was produced as the by-product, which makes the process even more eco-friendly. From the fitting of timedependent data, apparent activation energy in the presence of catalyst was determined to be 51.3 kJ/mol. The reaction is thus essentially in the kinetic regime.

In conclusion, our findings imply that nanosized zeolite beta can be an environment-friendly alternative to homogeneous catalysis in the challenging reaction, tert-butylation of aniline.

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