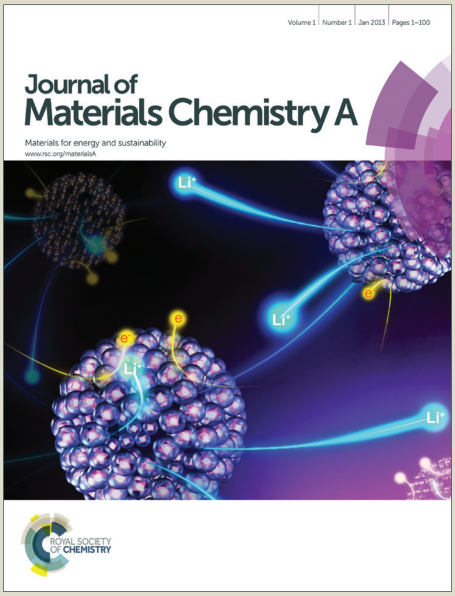
Journal of Materials Chemistry A

Accepted Manuscript



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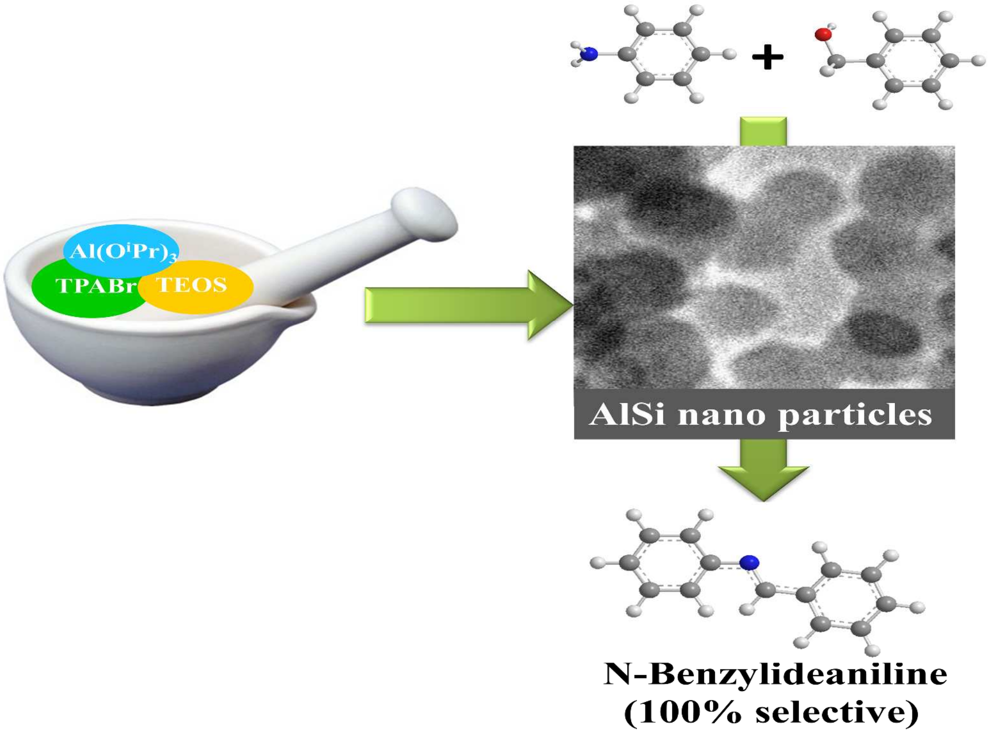
Facile synthesis of mesoporous aluminosilicate nano particles for selective production of N-Benzylidenaniline in solvent-free reaction of aniline with benzyl alcohol

Peta sreenivasulu, Nagabhatla Viswanadham* and Sandeep K Saxena

Here we report a simple method for the synthesis of mesoporous aluminosilcate nano particles (~20nm) by adopting a novel concept of using TPABr as a precursor for the structure directing agent through solvent-free physical mixing method, where the materials exhibiting different properties such as surface area and porosity were obtained by varying the thermal and hydrothermal treatment of the initial synthesis mixture. The properties of the samples are characterization by SEM, TEM, XRD, FT-IR and N_2 adsorption–desorption studies. The materials exhibited novel catalytic property towards solvent-free N-alkylation of aniline with benzyl alcohol for selective production of N-Benzylidenaniline (100% selectivity) at mild reaction conditions (100 °C and atmospheric pressure)



Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Facile synthesis of mesoporous aluminosilicate nano particles for selective production of N-Benzylidenaniline in solvent-free reaction of aniline with benzyl alcohol†

Peta sreenivasulu, Nagabhatla Viswanadham* and Sandeep K Saxena

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Here we report a simple method for the synthesis of mesoporous aluminosilcate nano particles (~20nm) by adopting a novel solvent-free physical mixing method, using TPABr as a precursor for the structure directing agent. The samples are characterized by SEM, TEM, XRD, FT-IR and N_2 adsorption–desorption studies. The materials exhibited novel catalytic property towards solvent-free N-alkylation of aniline with benzyl alcohol for selective production of N-Benzylidenaniline (100% selectivity) at mild reaction conditions (100 °C and atmospheric pressure), thus provides economical and environmentally benign processes for the synthesis and reaction applications of the AlSi nano materials.

1.Introduction

Nano materials are making immense impact on basic as well as industrial research areas related to chemical, pharmaceutical, agro, environmental-protection and energy. By virtue of their properties such as high surface, porosity, accessibility and dispersing nature of active sites, these materials are capable of facilitating variety of chemical transformations in catalysis, electrocatalysis and photocatalysis areas. Synthesis of nano materials with tailored properties for conducting effective molecular transformations is challenging subject in catalysis.[1-4]

Mesoporous silica is one of the promising materials for catalysis, adsorption and biomedicine, particularly as multifunctional carrier in drug delivery.[5] Synthesis of morphology controlled mesoporous materials such as monoliths, films, nano particles (NP) has received great interest due to their application. [6] Mesoporous silica nanoparticles (MSNP), which combine unique properties of both mesopores and nanomaterial substances, are particularly applied in gas adsorption, catalysis, sensing and drug delivery due to their pore convenience and fast molecular diffusion. By virtue of their inherent large surface area, pore volume, the ability to functionalize their outer and/or inner surfaces and the tunability of their pore geometry the MSNP are emerging as potential source for the catalytic applications.[7] However, most of the investigations are focused on the synthesis of pure silica NP and very little is attempted for the induction of heteroatom, such as Al which is important for catalytic applications. This may be associated with the difficult-to-handle conditions for the synthesis of heteroatom-modified nanosized mesoporous silica.[8-10] Amor´os and co-workers reported the synthesis of various metal-incorporated nanosized mesoporous silica catalysts using an atrane complexing method.[8, 9] Lin and co-workers synthesized mesoporous aluminosilicate nanoparicles by a two-step process.[10a] A microwave-hydrothermal route to nanoscale mesoporous aluminosilicates has also been reported.[10b] Zhai et al. have done pioneering work in the synthesis of nano-size mesoporous aluminosilicates by a binary surfactant system like CTAB and PEG-4000 that exhibited excellent catalytic cracking activity. [10c-f] Our earlier studies indicated the suitability of simple physical mixing method for the facile synthesis of $AlPO_4$ and hetero atom containing $AlPO_4$ ($ZnAlPO_4$) materials.[11] In the present study we would like to explore this method for the synthesis of mesoporous aluminosilicate nano particles as potential materials for catalytic applications.

N-Alkylation of amines is of basic importance in organic synthesis because the consequential higher amines and imines have widely been used as synthetic intermediates for pharmaceuticals, fine chemicals, agrochemicals, surfactants dyes and functionalized materials. [12] The most regularly used method for the preparation of N-alkyl amines is the coupling of amines with alkyl halides [13] in the presence of small amount of inorganic bases. But this route is associated with environmental problems due to the toxic nature of alkyl halides and related alkylating agents involved in reaction. Moreover, the reaction produces large amount of (in)organic salts and the selectivity to the desired secondary amines is generally low. Reductive amination of carbonyl compounds with amines is another route for the making of amines, which requires the use of hydrogen gas or strong reducing agents.[14] An alternative environmentally-benign route is N-alkylation of amines with alcohols as alkylating agents, where heterogenous catalysts such as ruthenium hydroxyapatite, Pt-Sn/Al_2O_3, sufated tungstate , metaloxides on gold and nanosized zeolite beta have been successfully applied for this reaction. [15]

In most of these studies amines are main products accompanied with corresponding imines as bi-products. However, achieving higher selectivity to N-alkylated imines is challenging and important for the production of pharmaceuticals and agricultural chemicals in the chemical industry.[16] Proposed methods for the production of imines mainly adopt catalytic dehydrogenation of secondary amines and nearly all of them require stoichiometric amount of oxidants such as iodosylbenzene, quinone or dioxygen and produces huge amount of byproducts.[17] The one-pot

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**Catalysis and Conversion Processes Division, CSIR-Indian Institute of Petroleum, Dehradun-248005, India, Fax: 91-135-2525702, Tel: 91-135-2525856, E-mail: nvish@iip.res.in*

†Electronic supplementary information (ESI) available: Experimental details, wide angle XRD, EDX, IR spectra, GC data etc

synthesis of imines from alcohols and amines are also reported.[18] However most of these reactions use noble metal containing catalysts in presence of additional organic/inorganic base, UV irradiation, Hg lamp, solvent, presence of nitrogen/oxygen gas, high temperature and requires higher reaction time(ESI-Table S1).

In an attempt to develop a novel catalyst system, we have synthesized mesoporous aluminosilicate nanoparticle materials by a simple solvent-free physical mixing method. The materials exhibited excellent catalytic property for the production of 100% selectivity to N-benzylidenaniline (imine) at more than 40% conversion levels in the direct alkylation of aniline using benzyl alcohol as alkylating agent in solvent free reaction conditions. This is first of its kind to synthesize the mesoporous aluminosilicate nano particles by a simple physical mixing method and their catalytic applications to the N-alkylation of aniline for the selective production of N-benzylidenaniline (imine).

2. Experimental section

2.1. Materials

The reagents used in this work were aluminum tri-isopropoxide [$Al(O^iPr)_3$], tetraethyl orthosilicate(TEOS)**,** tetramethyl ammonium hydroxide pentahydrate ($TMAOH.5H_2O$), tetra proplyl ammonium bromide (TPABr) and sodium hydroxide (NaOH)

2.2. Synthesis of mesoporous aluminosilicate nanoparticle

The typical synthesis method involves the admixing of 0.3 g of aluminum iso-propoxide, 4.8 g of tetraethyl orthosilicate, 4 g of tetramethyl ammonium hydroxide pentahydrate (25 wt%) in methanol (TMAHP), 4 g of tetra propyl ammonium bromide (TPABr) and 0.16 g of sodium hydroxide. Initially the mixture was in wet form. The wet mixture got converted to dry mixture upon 10 min grinding. However, further grinding of the mixture resulted in the formation of a wet gel. The resultant wet gel is divided into two equal parts and treated by two different methods. The first method involves the hydrothermal (HT) treatment in an autoclave (closed system) at 140 °C for 48 h while the second one involves the simple thermal (T) treatment (open vessel) at 140° C for 48 h. At the end of the treatment, the compounds are washed, filtered and calcined at 500 °C for 5 h. The as-synthesized Na-form of samples are treated with ammonium nitrate solution followed by calcination at 500 °C for 5 h to obtain the corresponding proton form. Based on the treatment method the samples are designated as AlSi-HT and AlSi-T representing hydrothermal and thermal methods respectively.

2.3. Characterization

Powder X-ray diffraction patterns of the samples were recorded on D8 advance instrument, Bruker, Germany equipped with rotating anode and CuKα radiations.FE-SEM images were recorded on Quanta 200f instrument, Netherland, for obtaining particle morphology. The FT-IR spectra of the samples were recorded on Thermonicolate 8700 instrument, Thermoscientific Corporation, USA. TEM images were recorded on Tecnai-12 model, FEI, Netherland and GC equipped with the DB wax column and FID detector.

2.4. N-Akylation of aniline with benzyl alcohol

N-Akylation reaction of aniline with benzyl alcohol was carried out in a round bottom flask at constant stirring and reflux condition with continuous cold water flow in a condenser attached to the reaction pot. In a typical reaction study, 0.25g catalyst, 1 mole aniline and 5 moles benzyl alcohol were mixed thoroughly in a round bottom flask and the reaction mixture was allowed to stir at 100°C in an open (air) atmosphere for 4 h and the product obtained at the end of the run was filtered and analyzed by GC-Mass for product identification, while the product quantification is conducted by using GC equipped with the DB wax column and FID detector.

3. Results and discussion

3.1. Properties of the mesoporous aluminosilicate nanoparticles

The presence of Al, Si and O atoms in the material was identified by elemental composition of both the synthesized samples by EDX analysis (ESI Fig.S1). Morphologies of both the samples (AlSi-HT and AlSi-T) were thoroughly investigated by FE-SEM (Fig. 1A and B). It is unexpected that both the samples exhibit identical macro-structures without an apparent impact of synthesis treatment (thermal/hydrothermal), but both the materials exhibited comparable morphology and particle size. This was further supported by the TEM (Fig.1 C and D) of the samples, where both the samples exhibited a narrow grain size of ~20 nm irrespective to the nature of treatment. The homogeneous distribution of elements in these two samples is identified from SEM EDX elemental mapping (ESI Fig. S2). In FT-IR spectra, a maximum transmittance at 3400 cm^{-1} related to the stretching vibration of O–H and a transmittance at 1050 cm^{-1} related to the stretching vibration of Si–O–Al (Fig. 2) were observed.[19] Another commonality observed in both the samples was the amorphous nature of the materials confirmed by wide-angle XRD (ESI Fig. S3). Overall, the SEM, TEM and IR results indicate the formation of nano size aluminosilicate materials.

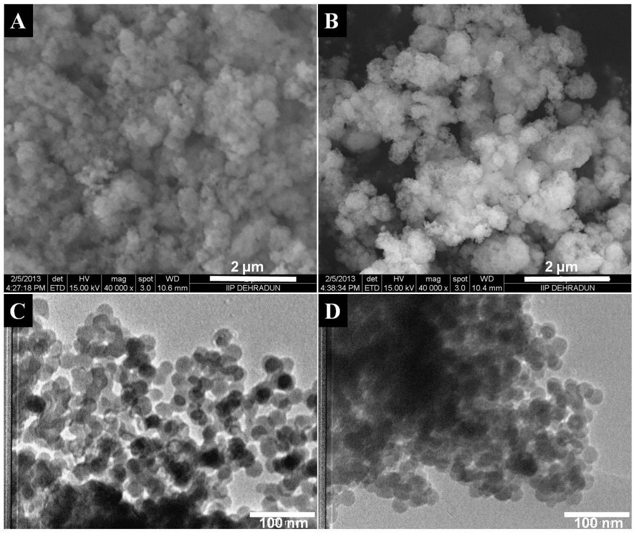


Fig. 1. A and B are SEM images, C and D are TEM images of AlSi-T and AlSi-HT samples respectively.

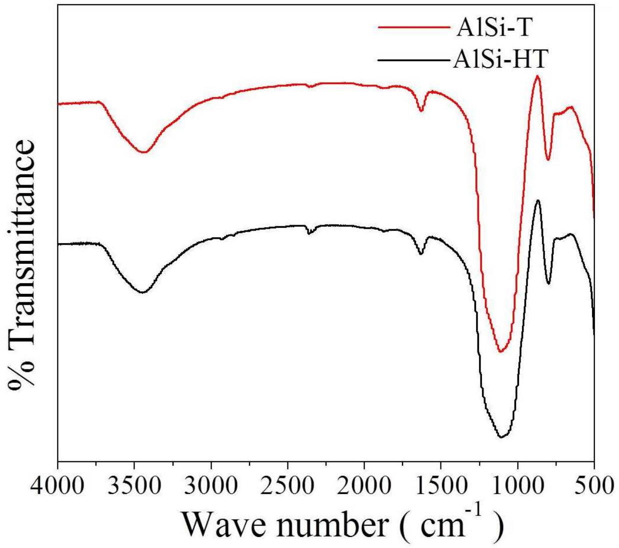


Fig. 2. FT-IR Spectra of AlSi nano materials

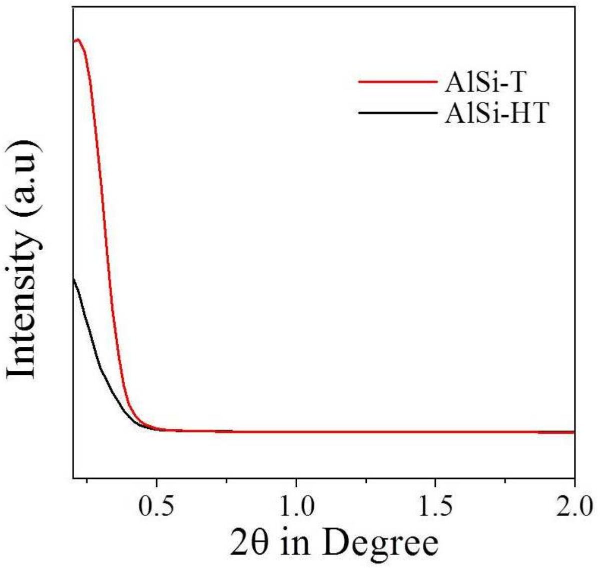


Fig. 3. Low angle XRD of AlSi nano materials

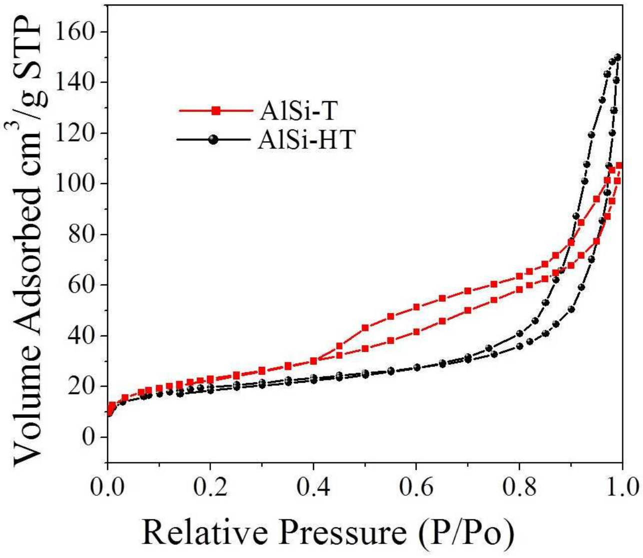


Fig. 4. N_2 adorption- desoption isotherm of AlSi nano material

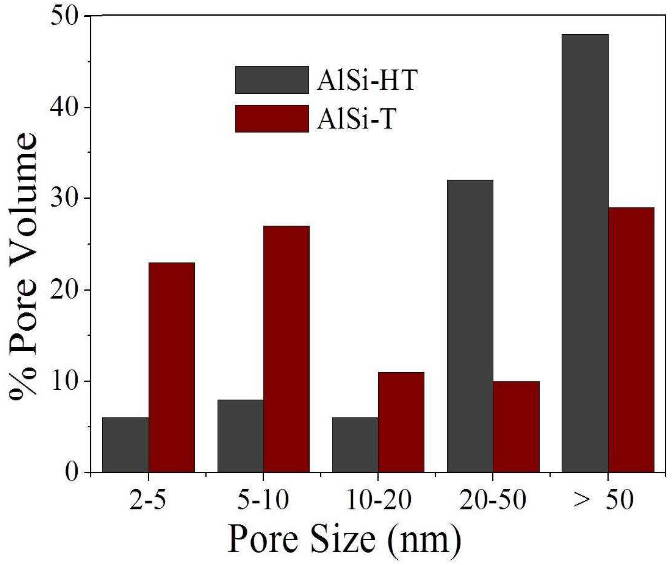


Fig. 5. Porosity distribution of AlSi nano materials

The low-angle XRD patterns (Fig. 3) of the samples (below 0.5 2θ) indicate the presence of mesopores in these materials, [20] which is further confirmed from the N_2 adsorption–desorption isotherms (Fig. 4). The adsorption-desorption isotherm represents the presence of mixed type of isotherms (combination of type I, II and IV) indicating the presence of mesopores and macropores. However, there is a difference in the loop configuration of the samples, where the sample AlSi-T represents relatively broad range of pore size distribution with N_2 uptake ranging from P/P0 of 0.4–1.0, when compared to that of the AlSi-HT representing the relatively narrow range N_2-uptake above P/Po of > 0.8. The pore size distribution patterns (measured by BJH method) of the samples compared in Fig. 5 reflects the clear cut difference in the distribution, where the AlSi-T possesses most of the pores in the lower mesopore region of 2-5 nm and 5-10 nm, while the AlSi-HT exhibits lesser population of pores in this region. Majority of mesopores in AlSi-HT falls in higher mesopore range of 20-50 nm. But, both the samples exhibited the presence of mesopores ranging from 2-50 nm along with considerable amount of macropores (> 50 nm). The presence of larger mesopores in AlSi-HT resulted in relatively lower surface area but higher pore volume of this sample (Table 1). Since, the particle size of the materials is measured to be of ~20nm range in TEM (Fig. 1), the formation of relatively larger pores (>20nm) observed in the samples suggests the contribution of inter-particle voids to the meso/macroporosity. The pore size data given in Table 1 indicates the comparable mesopore volume in both the samples, while the macropores are more in case of AlSi-HT sample. This condition indicates the relatively loose packing of the nano particles in the AlSi-HT sample that is responsible for formation of relatively larger inter-crystalline voids measured in the range

Table.1: Textual properties of AlSi nano materials

Samples	BET Surface area (m^2/g)	Total Pore Volume (cm^3/g)	Meso Pore Volume (cm^3/g)	Macro Pore Volume (cm^3/g)
AlSi-T	84.25	0.171	0.121	0.05
AlSi-HT	69.30	0.225	0.117	0.10

of larger mesopores and macropores. In spite of their comparable composition, morphology and particle size, the difference in pore size distribution of the samples observed in the present study can be ascribed to the difference in chemistry involved in the synthesis of these materials by two different treatments, namely, thermal and hydrothermal. Since, the physical mixing of chemical ingredients and the synthesis temperature adopted in both the methods are similar, the difference in porosity of AlSi-T and AlSi-HT materials seem to be resulted by thermal or hydrothermal treatments. In hydrothermal treatment method the wet gel in autoclave (closed system) can produce some water or chemical vapors from the chemical ingredients and the close contact of such vapors with the reaction mixture under autogenous pressure can influence the formation and arrangement (packing) of nano particles. This may be the reason for the higher amount of larger mesopores and macropores formed in the HT sample. Different from that the thermal method involves open heating of the wet gel that is expected to loose any water are decomposed chemical vapors during the treatment, that is eventually responsible for the difference in arrangement of nano particles and their pore size distribution.

Overall, the synthesis method adopted in the present study has successfully produced the AlSi nano particles possessing hierarchical mesopores ranging from 2-50 nm along with considerable amount of macro pores created by inter-crystalline voids. The bulky reagents such as CTABr and block copolymers are used as structure directing agents (SDA) in the preparation of mesoporous aluminosilicates. Most of the SDA reagents function through micelle formation (as void fillers). Different from that, the TPABr (smaller) used in the present study releases TPA+ cations that are believed to facilitate interaction and reordering of initially formed complex silicates anions [21].

The synthesis method has the following advantages; 1) simple and convenient for the synthesis of porous materials with desired properties and involves only grinding and aging of raw material. 2) the solvent-free process significantly reduces the formation of pollutants originate from otherwise commonly used solvent-based systems that form large amount of waste liquor. 3) gives high product efficiency with high yield of porous solid material by avoiding the large space occupation that generally lead to low product yields in case of solvo-thermal processes, and 4) minimizes energy consumption as it operates under low temperature conditions. Therefore, the aluminosilicate nano materials synthesized in the present study via ‘‘physical mixing’’ method are of great importance for industrial processes and were explored here for the direct synthesis of imines from aniline and benzyl alcohol.

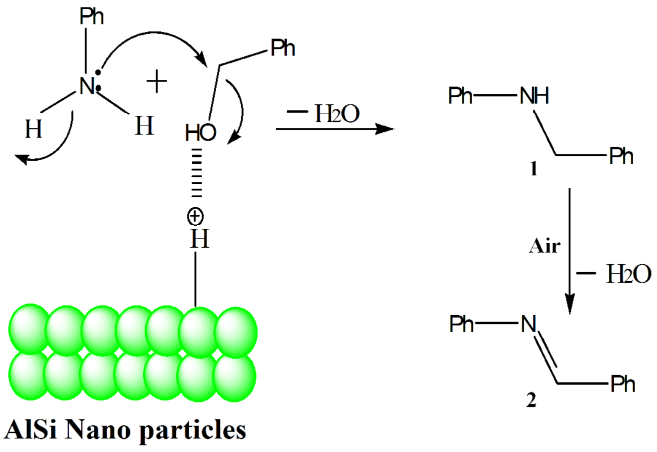
3.2. Synthesis of N-benzylidenaniline from reactions of aniline with benzyl alcohols

Solvent-free direct N-alkylation reaction of aniline with benzyl alcohol is conducted on both the alumino-silicate nano materials.

The results given in Table 2 indicate as high as 100% selectivity to N-benzylidenanline (imine) product at >40% conversion of aniline. Generally N-benzylaniline (Structure 1, Scheme 1) is the expected product in this reaction. Different from that, the 100% selectivity to corresponding imine (Structure II in Scheme 1) obtained in the present study indicates the new property of the mesoporous aluminosilicate nanomaterials for this reaction. Though the higher aniline conversions reported in the literature all most all of them use precious metals as active components and work at much lower aniline concentration and higher reaction time (Table 1 ESI). The novelty of the present catalyst system lies in its selective imine formation (100%) and a plausible reaction mechanism for the formation of this compound is given in Scheme 1. Here the activation of the benzyl alcohol will be initiated by the proton sites of the catalyst, followed by the interaction of aniline with the activated benzyl alcohol to produce the corresponding N-alkylation product (Structure 1). However, the reaction is not stopped at this level and the formation of corresponding imine is produced with 100% selectivity. This can be explained by the oxy-dehydrogenation activity of the catalyst in presence of oxygen available from the air during the reaction. [15e] Further, the higher stability of the conjugated double bonds possessed by imine product when compared to that of the corresponding amine may be responsible for the facile production

Table 2: Performance of AlSi nano matereial in N-Alkylation of aniline.

Catalyst	Conversion (%)	N-benzylidenaniline (imine) Selectivity (%)
AlSi-T	40	100
AlSi-HT	45	100
AlSi-T (3rd cycle)	35	100
AlSi-HT (3rd cycle)	42	100



Scheme-1: Plausible mechanism for N-Alkylation of aniline for formation of imine.

of N-benzylidenaniline (100% selectivity) in the present study. Here both the catalysts exhibited excellent catalytic activity with 100 % selectivity to N-benzylidenaniline. The catalysts are also shown the reusability even after three reaction cycles to produce comparable product yields (ESI-Table-2 and Table-3).

4. Conclusion

In summary, the studies provide a simple solvent-free physical mixing method using low cost template for the synthesis of mesoporous aluminosilicate nano particles. The study provides the physical mixing method as an efficient tool for the production of heteroatom containing silica nano particles which can be further expanded for the synthesis of other mixed oxide nano particles. The materials possessed excellent catalytic properties towards N-alkylation reaction, where as high as 100% selectivity to N-benzylidenaniline (imine) is obtained from aniline and benzyl alcohol under environmentally benign solvent-free, low severity reaction conditions. Here, the solvent-free conditions adopted both in the synthesis of materials and in their catalytic application makes the process simple, economic, user-friendly and environment-friendly. This is first of its kind to observe the selective production of imines (100%) on aluminosilicate materials that reports the novel property of the materials. The selective imine formation property of the materials can be exploited for other industrially important N-alkylation reactions to improve the selectivity towards the desired product.

Acknowledgment

We acknowledge the CSIR for the research funding of the project under 12th FYP. PS acknowledges CSIR, New Delhi for awarding fellowship. We are thankful to XRD, IR, SEM and GC-Mass groups at IIP for analysis.

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