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Facile synthesis of mesoporous aluminosilicate nanoparticles for the selective production of *N*-benzylidenaniline in a solvent-free reaction of aniline with benzyl alcohol†

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Herein we report a simple method for the synthesis of mesoporous aluminosilicate nanoparticles (~20 nm) 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 N₂ adsorption-desorption studies. The materials exhibited novel catalytic properties towards solvent-free *N*-alkylation of aniline with benzyl alcohol for the selective production of *N*-benzylidenaniline (100% selectivity) under mild reaction conditions (100 °C and atmospheric pressure), thus providing economical and environmentally benign processes for the synthesis and reaction applications of the AlSi nano-materials.

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1. Introduction

Nano-materials have an immense impact on basic as well as industrial research areas related to the chemical, pharmaceutical, agrochemical, environmental protection and energy sectors. By virtue of their properties such as high surface area, porosity, accessibility and the dispersed nature of the active sites, these materials are capable of facilitating a variety of chemical transformations in the areas of catalysis, electrocatalysis and photocatalysis. The synthesis of nano-materials with tailored properties for conducting effective molecular transformations is a challenging subject in catalysis.^{1–4}

Mesoporous silica is one of the most promising materials for catalysis, adsorption and biomedicine, particularly as a multifunctional carrier in drug delivery.⁵ The synthesis of morphology controlled mesoporous materials such as monoliths, films and nanoparticles (NPs) has received great interest due to their applications.⁶ Mesoporous silica nanoparticles (MSNPs), which combine the unique properties of both mesoporous and nano-material substances, are particularly applied in gas adsorption, catalysis, sensing and drug delivery due to their pores and fast molecular diffusion. By virtue of their inherent large surface areas, pore volumes, the ability to functionalize their outer and/or inner surfaces and the tunability of their pore geometry, MSNPs are emerging as a potential source for catalytic applications.⁷ However, most investigations are focused on the synthesis of pure silica NPs and very few have attempted the

introduction of heteroatoms, 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} Amorós 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 nanoparticles by a two-step process.^{10a} A microwave-hydrothermal route to nanoscale mesoporous aluminosilicates has also been reported.^{10b} Zhai *et al.* have carried out pioneering work in the synthesis of nano-sized 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 a simple physical mixing method for the facile synthesis of AlPO₄ and heteroatom-containing AlPO₄ (ZnAlPO₄) materials.¹¹ In the present study we would like to explore this method for the synthesis of mesoporous aluminosilicate nanoparticles as potential materials for catalytic applications.

N-Alkylation of amines is of fundamental importance in organic synthesis because the consequential higher amines and imines are widely used as synthetic intermediates for pharmaceuticals, fine chemicals, agrochemicals, surfactant dyes and functionalized materials.¹² The most regularly used method for the preparation of *N*-alkyl amines is the coupling of amines with alkyl halides¹³ in the presence of small amounts of inorganic bases. However, this route is associated with environmental problems due to the toxic nature of alkyl halides and the related alkylating agents involved in the reaction. Moreover, the reaction produces large amounts of (in)organic salts and the selectivity towards the desired secondary amines is generally low. Reductive amination of carbonyl compounds with amines is

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another route for the synthesis 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 heterogeneous catalysts such as ruthenium hydroxyapatite, Pt-Sn/Al₂O₃, sulfated tungstate, metal oxides on gold and nanosized zeolite beta have been successfully applied to this reaction.¹⁵

In most of these studies amines are the main products accompanied by the corresponding imines as by-products. However, achieving higher selectivities for *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 amounts of oxidants such as iodosylbenzene, quinone or dioxygen, and produce huge amounts of by-products.¹⁷ One-pot synthesis of imines from alcohols and amines has also been reported.¹⁸ However most of these reactions use noble metal-containing catalysts in the presence of additional organic/inorganic base, UV irradiation, a Hg lamp, solvents, nitrogen/oxygen gas, high temperatures, and they require longer reaction times (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 properties for the production of *N*-benzylidenaniline (imine), with 100% selectivity, at more than 40% conversion levels in the direct alkylation of aniline using benzyl alcohol as the alkylating agent under solvent-free reaction conditions. This is the first study to synthesize mesoporous aluminosilicate nanoparticles by a simple physical mixing method and investigate their catalytic applications for 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(OⁱPr)₃], tetraethyl orthosilicate (TEOS), tetramethyl ammonium hydroxide pentahydrate (TMAOH·5H₂O), tetra propyl ammonium bromide (TPABr) and sodium hydroxide (NaOH).

2.2. Synthesis of mesoporous aluminosilicate nanoparticles

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 wet. The wet mixture was converted to a dry mixture upon 10 min of grinding. However, further grinding of the mixture resulted in the formation of a wet gel. The resultant wet gel was divided into two equal parts and treated using two different methods. The first method involved a hydrothermal (HT) treatment in an autoclave (closed system) at 140 °C for 48 h, while the second one involved a simple thermal (T) treatment

(open vessel) at 140 °C for 48 h. At the end of the treatment, the compounds were washed, filtered and calcined at 500 °C for 5 h. The as-synthesized Na-forms of the samples were treated with ammonium nitrate solution followed by calcination at 500 °C for 5 h to obtain the corresponding protonated forms. Based on the treatment method the samples are denoted as AlSi-HT and AlSi-T representing the hydrothermal and thermal methods respectively.

2.3. Characterization

Powder X-ray diffraction patterns of the samples were recorded using a D8 advance instrument, Bruker, Germany, equipped with a rotating anode and Cu K α radiation. FE-SEM images were recorded using a Quanta 200f instrument, Netherlands, to obtain particle morphologies. FT-IR spectra of the samples were recorded using a Thermo Nicolet 8700 instrument, Thermo-scientific Corporation, USA. TEM images were recorded using a Tecnai-12 model, FEI, Netherlands and analysis was carried by GC equipped with a DB wax column and FID detector.

2.4. *N*-Alkylation of aniline with benzyl alcohol

N-Alkylation of aniline with benzyl alcohol was carried out in a round bottomed flask under constant stirring and reflux with a continuous flow of cold water in a condenser attached to the reaction pot. In a typical reaction study, 0.25 g catalyst, 1 mole aniline and 5 moles benzyl alcohol were mixed thoroughly in a round bottomed flask and the reaction mixture was allowed to stir at 100 °C in an open (air) atmosphere for 4 h. The product obtained at the end of the run was filtered and analyzed by GC-Mass for product identification, while the product quantification was conducted using GC equipped with a 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 confirmed by studying the elemental composition of both synthesized samples by EDX analysis (ESI Fig. S1†). The morphologies of both of the samples (AlSi-HT and AlSi-T) were thoroughly investigated using FE-SEM (Fig. 1A and B). It is unexpected that both of the samples would exhibit identical macro-structures without an apparent impact of the synthesis treatment (thermal/hydrothermal), but both of the materials exhibited comparable morphologies and particle sizes. This was further supported by TEM (Fig. 1C and D) of the samples, where both of the samples exhibited a narrow grain size of ~20 nm irrespective of the nature of the treatment. The homogeneous distribution of elements in these two samples was identified using 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 of the samples was the amorphous nature of the materials, confirmed

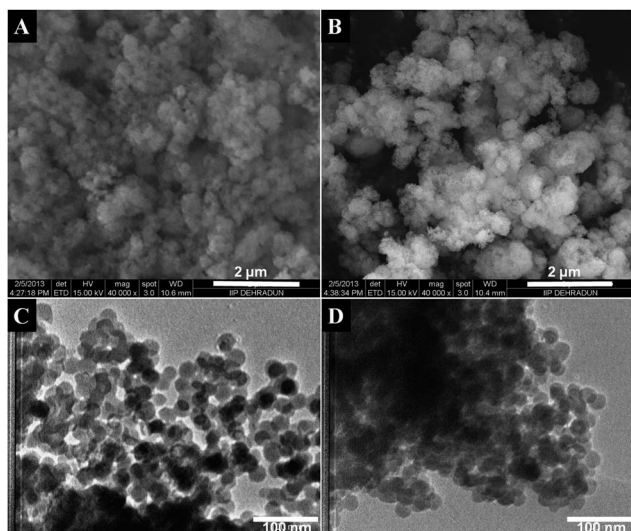


Fig. 1 (A and B) are SEM images and (C and D) are TEM images of the AlSi-T and AlSi-HT samples respectively.

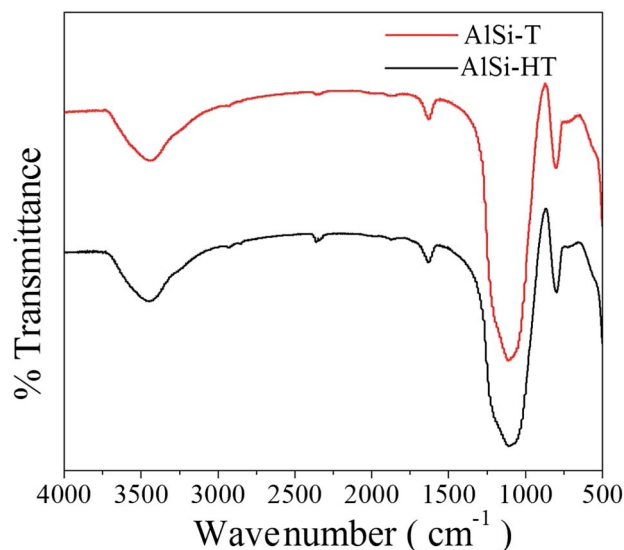


Fig. 2 FT-IR spectra of the AlSi nano-materials.

by wide-angle XRD (ESI, Fig. S3†). Overall, the SEM, TEM and IR results indicate the formation of nano-sized aluminosilicate materials.

The low-angle XRD patterns (Fig. 3) of the samples (below $0.5\ 2\theta$) indicate the presence of mesopores in these materials,²⁰ which is further confirmed by N_2 adsorption-desorption isotherms (Fig. 4). The adsorption-desorption isotherms contain a mixture of different types of isotherm (a combination of type I, II and IV) indicating the presence of mesopores and macropores. However, there is a difference in the loop configurations of the samples, where sample AlSi-T has a relatively broad pore size distribution with N_2 uptake ranging from a P/P_0 value of 0.4–1.0, compared to that of AlSi-HT which has a relatively narrow range and a N_2 -uptake above a P/P_0 value of >0.8 . The pore size distribution patterns (measured using the BJH

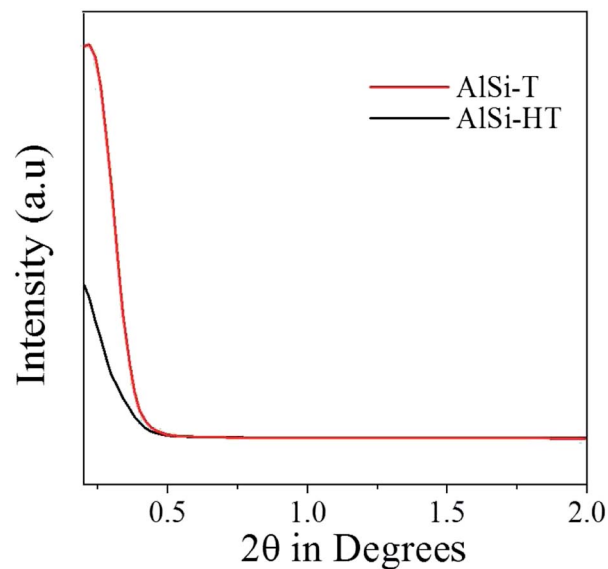


Fig. 3 Low angle XRD of the AlSi nano-materials.

method) of the samples compared in Fig. 5 reflect the clear cut difference in the distributions, where the AlSi-T possesses pores which are mostly in the lower mesopore size ranges of 2–5 nm and 5–10 nm, while the AlSi-HT exhibits a lesser population of pores in these ranges. The majority of mesopores in AlSi-HT fall in a higher mesopore size range of 20–50 nm. But, both of the samples exhibited the presence of mesopores ranging from 2–50 nm along with considerable amounts of macropores (>50 nm). The presence of larger mesopores in AlSi-HT resulted in a relatively lower surface area but a higher pore volume of this sample (Table 1). Since the particle size of the materials was measured to be in the range of ~ 20 nm by TEM (Fig. 1), the formation of relatively large pores (>20 nm) observed in the

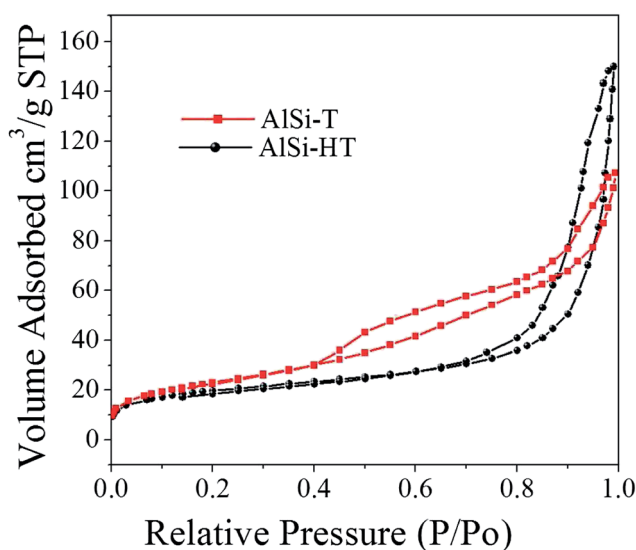


Fig. 4 N_2 adsorption-desorption isotherms of the AlSi nano-materials.

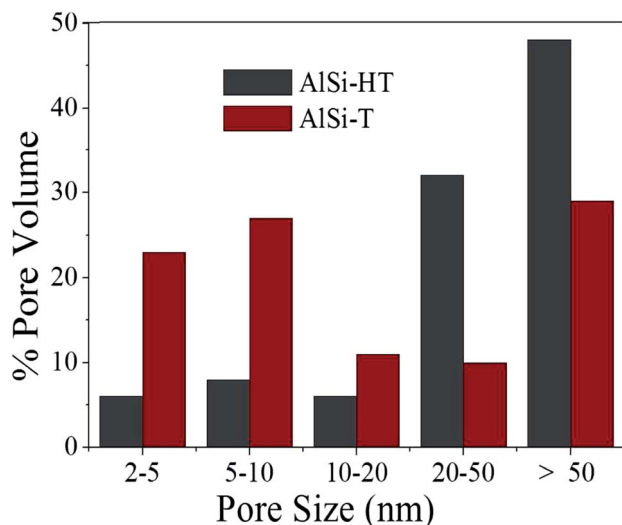


Fig. 5 Porosity distributions of the AlSi nano-materials.

samples suggests the contribution of inter-particle voids to the meso/macroporosity. The pore size data given in Table 1 indicate the comparable mesopore volumes in both of the samples, while there are more macropores in the case of the AlSi-HT sample. This indicates the relatively loose packing of the nanoparticles in the AlSi-HT sample that is responsible for the formation of relatively large inter-crystalline voids, which were measured to be in the range of larger mesopores and macropores. In spite of their comparable compositions, morphologies and particle sizes, the difference in the pore size distributions of the samples observed in the present study can be ascribed to the difference in the chemistry involved in the synthesis of these materials by two different treatments, namely, thermal and hydrothermal. Since the physical mixing of the chemical ingredients and the synthesis temperatures adopted in both of the methods are similar, the difference in the porosities of the AlSi-T and AlSi-HT materials seems to be a result of the thermal or hydrothermal treatment. In the hydrothermal treatment method the wet gel in the autoclave (closed system) can produce some water or chemical vapor 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 nanoparticles. This may be the reason for the higher amount of larger mesopores and macropores formed in the HT sample. In contrast, the thermal method involves open heating of the wet gel, which is expected to remove any water or decomposed chemical vapors during the treatment. This is eventually responsible for the difference in the arrangement of the nanoparticles and their pore size distribution.

Table 1 Textual properties of the AlSi nano-materials

Samples	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Mesopore volume ($\text{cm}^3 \text{g}^{-1}$)	Macropore volume ($\text{cm}^3 \text{g}^{-1}$)
AlSi-T	84.25	0.171	0.121	0.05
AlSi-HT	69.30	0.225	0.117	0.10

Overall, the synthesis method adopted in the present study has successfully produced AlSi nanoparticles possessing hierarchical mesopores in the range 2–50 nm along with a considerable amount of macropores created by inter-crystalline voids. Bulky reagents such as CTABr and block copolymers are used as structure directing agents (SDA) in the preparation of the mesoporous aluminosilicates. Most of the SDA reagents function through micelle formation (as void fillers). In contrast, the TPABr (smaller) used in the present study releases TPA^+ cations that are believed to facilitate interactions and reordering of the initially formed complex silicate anions.²¹

The synthesis method has the following advantages: (1) it is simple and convenient for the synthesis of porous materials with desirable properties and involves only the grinding and aging of raw materials. (2) The solvent-free process significantly reduces the formation of pollutants which otherwise originate from commonly used solvent-based systems that form large amounts of waste liquor. (3) The method gives a high product efficiency with high yields of porous solid material by avoiding occupying large amounts of space that generally leads to low product yields in the case of solvo-thermal processes, and (4) it minimizes energy consumption as it operates at low temperatures. Therefore, the aluminosilicate nano-materials synthesized in the present study *via* a “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.

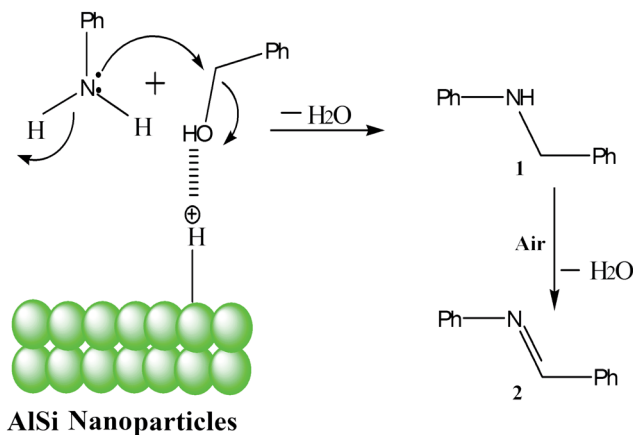
3.2. Synthesis of *N*-benzylidenaniline from reactions of aniline with benzyl alcohols

A solvent-free direct *N*-alkylation reaction of aniline with benzyl alcohol is conducted on both of the aluminosilicate nano-materials.

The results given in Table 2 indicate a selectivity of as high as 100% towards the *N*-benzylidenaniline (imine) product at >40% conversion of aniline. Generally *N*-benzylaniline (structure 1, Scheme 1) is the expected product in this reaction. In contrast, the 100% selectivity towards the corresponding imine (structure 2, Scheme 1) obtained in the present study indicates the new

Table 2 Performance of AlSi nano-materials in *N*-alkylation of aniline

Catalyst	Conversion (%)	<i>N</i> -benzylidenaniline (imine) selectivity (%)
AlSi-T	40	100
AlSi-HT	45	100
AlSi-T (3 rd cycle)	35	100
AlSi-HT (3 rd cycle)	42	100



Scheme 1 Plausible mechanism for *N*-alkylation of aniline and the formation of an imine.

application of the mesoporous aluminosilicate nano-materials for this reaction. Though there are higher aniline conversions reported in the literature, almost all of the methods use precious metals as the active components, work at much lower aniline concentrations and have longer reaction times (Table S1, 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 is 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 stage and the corresponding imine is produced with 100% selectivity. This can be explained by the oxy-dehydrogenation activity of the catalyst in the presence of oxygen available from air during the reaction.^{15c} Furthermore, the higher stability of the conjugated double bonds possessed by the imine product, when compared to that of the corresponding amine, may be responsible for the facile production of *N*-benzylideneaniline (100% selectivity) in the present study. Here, both of the catalysts exhibited excellent catalytic activity with 100% selectivity towards *N*-benzylideneaniline. The catalysts have also shown their reusability, even after three reaction cycles, to produce comparable product yields (ESI, Tables S2 and S3†).

4. Conclusion

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

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