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Short Communication

Clay encapsulated ZnO nanoparticles as efficient catalysts for N-benzylation of amines

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1. Introduction

Zinc oxide is a direct wide band gap wurtzite-type semiconductor with a band gap energy of 3.37 eV and free excitation energy of 60 meV at room temperature [1]. Its high specific surface area makes it a potential candidate for a wide range of applications [2,3] with properties that are not present in solution or gas phase. Zinc oxide is non-toxic and compatible with skin, making it a suitable additive for textiles and surfaces that come in to contact with humans. It also has other wide ranging applications as sensors [4], in solar cells [5], cell labelling [6], etc. It is a well-known catalytic material in a large number of industrial processes. As a heterogeneous catalyst, it has a high catalytic activity, is non-toxic, insoluble in polar as well as non-polar solvents and also cheap. On the other hand, mixed-ZnO and its metals (i.e. zinc ferrite) have been used as photocatalysts, readily decompose halogen compounds and the photocatalytic activity increases as the size of ZnO particles is reduced to nanometer levels [7-10]. ZnO catalyses wide range of organic reactions efficiently. Reactions such as Friedel-Craft's acylation [11], dehydration of aldoximes into nitriles [12], nucleophilic ring opening of epoxides by amines to synthesise β -aminoalcohols [13], microwave assisted preparation of cyclic ureas [14], N-formylation of amines [15] and other organic transformations [16] are efficiently catalysed by ZnO. The specific chemical, surface and nanostructured properties of zinc oxide make it a suitable candidate for catalysis and gas sensing applications [17,18]. When used as a catalyst, the activity of nano ZnO is expected to be enhanced with respect reference to the commercial

ABSTRACT

ZnO nanoparticles encapsulated in K10-clay (K10–ZnO) are synthesised and characterised by UV-DRS, Emission spectra, powder XRD, SEM and HRTEM analyses. The constrained space and also the polar active sites in the clay support stabilise zinc oxide nanoparticles by preventing that aggregation and consequently no extracapping agent is required. The synthesised ZnO nanoparticles are used for the efficient N-benzylation of anilines and the reusability of the catalyst is also studied. A suitable mechanism is proposed for this transformation.

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compound, not only because of its increased surface area, but also due to the changes in surface properties such as surface defects [19].

A general problem of metal oxide nanoparticles is their tendency to undergo agglomeration, which increases their particle size and therefore, dramatically reduces their catalytic activity [20,21]. Two general strategies have been developed to stabilise the particle size of metal oxide nanoparticles by using either suitable solid surfaces or appropriate ligands [22]. New possibilities for zinc oxide catalysis can be developed when the ZnO nanoparticles can be stabilised by encapsulating them inside the clay interlayer to combine the unique catalytic properties of ZnO nanoparticles with shape-selectivity. This prompted us to develop ZnO nanoparticles encapsulated in K10-montmorillonite clay. N-benzylation of amines with alkyl halides is an important synthetic method to obtain mono- and di-N-benzylated products. However, this reaction in the presence of a base requires longer reaction time, higher temperature and affords lower yields of desired product [23]. Inorganic bases like NaHCO₃, [24] K₂CO₃, [25] etc., have also been employed in N-benzylation of amines.

In the present study, we report catalytic activity of nano ZnO–K10clay in benzylation of aromatic amines and the salient features are presented below. It is relevant to note that unlike other heterogeneous metal oxide catalysts, nano ZnO does not generate any poisonous waste end-products after the reaction is completed.

2. Experimental

2.1. Preparation of Zn²⁺-exchanged K10-montmorillonite clay

A sample of 1 g of the appropriate clay was stirred with 25 mL of 1 M zinc nitrate solution for three days. The solution was filtered

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Fig. 1. (a) UV-DRS spectra of (i) bulk ZnO, (ii) nano-ZnO powder and (iii) nano-ZnO encapsulated K10-montmorillonite clay (b) emission spectra of nano-ZnO encapsulated K10-montmorillonite clay.

and washed repeatedly with water to remove excess of zinc nitrate. It was then dried overnight in a hot air oven at 90°C.

2.2. Preparation of ZnO nanoparticles entrapped in K10-montmorillonite clay

Zn²⁺-supported on K10-clay (500 mg) is suspended in 5 mL of 1 M sodium hydroxide solution and the mixture is stirred at room temperature for 30 min, filtered, washed continuously with distilled water until the mother liquor was neutral. The solid was then dried and calcined at 250 °C for 3 h and then stored. It is characterised by UV-DRS spectra recorded by using JASCO-UV–Vis Spectrophotometer (V-550), the reflectance spheres are barium sulphate coated. Fluorescence measurements were made on a Fluoromax-4 Spectrofluorometer (HORIBA JOBIN YVON) with the excitation slit set at 2.0 nm band pass and emission at 4.0 nm band pass in 1 cm×1 cm quartz cell, powder XRD (JOEL Model JDX 8030 X-ray diffractometer using Cu K α radiation), scanning electron microscopy attached with an energy dispersive X-ray spectrometer (SEM-EDS Hitachi, S-3400 N), high resolution TEM (HRTEM, Philips CM12).

2.3. Procedure for N-benzylation of amines

To a solution of amines (0.5 mmol) in 3 mL of water/acetonitrile (1:1), benzyl chloride (0.5 mmol) is added followed by clay entrapped ZnO nanoparticles (50 mg). This heterogeneous mixture is heated with stirring for about 12 h at 70 °C and then cooled. The

cooled solution is extracted with dichloromethane (10 mL), filtered, dried with anhydrous sodium sulphate and the solvent is removed to give the product.

The reaction mixture, after completion, is analysed by GC and the products are characterised by GC–MS. GC analysis is performed using a Shimadzu 17A model gas chromatography with capillary column (ZB-5, 30 m × 0.25 mm inside diameter (i. d.), 0.25 μ m film thickness), FID detector, high purity nitrogen as carrier gas, in the temperature range of 100–250°C (10°C/min). 0.5 μ L sample was injected for the analysis from the reaction mixture after workup procedure.

3. Results and discussion

3.1. Morphological analysis of the materials

The obtained nano ZnO–K10-montmorillonite clay composite is characterised by powder XRD, UV-diffuse reflectance and emission spectra, SEM and EDX. Particle size is determined by HRTEM analysis. The UV–Vis, spectra for ZnO–K10-montmorillonite nanohybrid is given in Fig. 1a. The freshly prepared ZnO-montmorillonite clay exhibits a new band at around 355 nm which is an indication of the formation of zinc oxide nanoparticles. Also, the samples exhibit a similar behaviour in absorption on storage, suggesting a stable zinc electronic configuration due to the partial electrostatic interaction between the guest ZnO and the host montmorillonite clay. In the fluorescence spectra, an emission peak appears at 429 nm (λ_{exc} = 365 nm), which is attributed to the



Fig. 2. Powder XRD patterns of a) pure K10-montmorillonite clay b) nano ZnO encapsulated K10-montmorillonite clay.



Fig. 3. SEM images of ZnO encapsulated montmorillonite at different magnifications.

as prepared ZnO-montmorillonite nanohybrids (Fig. 1b) and this clearly confirms the presence of the ZnO nanoparticles.

ZnO encapsulated on K10-montmorillonite clay is subjected to powder XRD analysis to reveal the crystalline nature of support as well as to examine the presence of ZnO. Zincite appears to be the predominant ZnO species [JCPDS data file (36–1451)], which has main diffraction peaks with maximum intensities at 35.2 (101), 46.7 (102) and 51.5 (110). Also, the lower intensity of the peaks (marked as *) in nano ZnO (Fig. 2) may be attributed to the deeper penetration of ZnO onto the lamellar structures of clay.

SEM analysis of ZnO nanocomposites encapsulated in montmorillonite shows the surface morphology of the clay which is found to be present in the form of granules (Fig. 3). The ZnO content of these clayentrapped nanoparticles is found to be 3.65 wt.%, using Energy Dispersive X-ray Analysis (EDX, a technique used in conjunction with SEM).

HRTEM images of ZnO encapsulated montmorillonite clay at different magnifications clearly show that the ZnO particles are in the range of 12 nm (Fig. 4) and most of the particles are embedded in the layered sheets of the clay.

3.2. Benzylation of amines

In the present study, ZnO nanoparticles encapsulated on montmorillonite are used as catalysts in benzylation of aniline and its derivatives (Scheme 1). Since the oxyanions of ZnO are mildly basic and the Zn cation on the polar surface is mildly acidic, this combination will result in an acid-base bifunctional catalytic system. In addition, the layered structure of montmorillonite, acting as a polar support, is expected to provide closer proximity between the reagents. It is pertinent to note here that, in a recent study [26] using adsorption isotherm and XRD pattern, aniline was found to adsorbed readily into the montmorillonite interlayer being perpendicularly oriented to silicate sheet (with an increase in d_{001} spacing from 1.26 nm to 1.48 nm, corresponding to on amount of aniline ~11.7 mmol g⁻¹). This increase in basal spacing will not only facilitate addition of benzyl chloride, but also ensure closer proximity between the two layers.

As shown in Table 1 the effect of solvents and temperature are studied in the reaction of aniline as a model compound with benzyl chloride under various reaction conditions. The reaction is also studied with various conventional catalysts such as zinc powder, ZnO bulk and ZnO nano. With nano ZnO-clay composite (entries 3-10), the percentage conversion is high in acetonitrile-water mixture. Increasing the temperature (70 °C for 12 h) results in a higher yield of di-N-benzylated products. In pure methanol, only 52% conversion is noticed. However, in methanol-water mixture, a very significant increase in percentage conversion is obtained. Similarly, in solid state reactions also, the conversion is good, but both mono- and dibenzylated products are formed in equal amounts. The yield is very low, when only water is used as the solvent. In the absence of a catalyst, the reaction is slow at room temperature (entry 1). The effect of various forms of Zn as catalyst using bulk ZnO, ZnO nano and zinc powder are also studied (entries 13–17). The observed results clearly indicate that mono-N-benzylated product is the major product at room temperature while on the other hand yield of di-N-benzylated product increases at higher temperature.

Monosubstituted product is obtained when methanol:water is used as a solvent in 2:1 ratio and 1:2 ratio for 12 h (Table 2, entry 6) and 8 h (entry 16) respectively. When the reaction is carried out in aqueous medium, only monosubstituted product is obtained when the reaction time is 6 h (entry 18) and 12 h (entry 20). If the reaction time is 8 h (entry 19), the selectivity is reduced to 76%.



Fig. 4. (a-b) HRTEM images of highly dispersed ZnO nanoparticles embedded in clay matrix. (c) HRTEM image of a selected portion of ZnO nanoparticles on clay matrix.



Scheme 1. Benzylation of amines.

Benzylation studies are also extended to other aromatic amines and the observed results are given in Table 3, which shows that di-N-benzylated product predominates in aniline as well as in p-toluidine. In a similar manner, benzylamine also gives di-Nbenzylated product as the major one than its mono benzylated product. Another interesting feature of this protocol is the absence of ring benzylated products. m-Chloroaniline, on the other hand, yields mono N-benzylated product as the predominant product. Aliphatic amine such as N-butylamine yields exclusively the di-Nbenzylated product. N-Methylaniline reacts in a facile manner to afford the corresponding tertiary amine in very good yield. Aromatic secondary amines like indole, 1,2,3,4-tetrahydrocarbazole and imidazole fail to give the corresponding N-benzylated products at room temperature as well as at 70 °C.

The reusability of the clay entrapped ZnO nanoparticles is also studied for the benzylation of N-methylaniline. After the reaction, the solution is filtered, washed with dichloromethane and dried at 60 °C. The catalyst is reused directly without further purification and is used for two consecutive runs with only a marginal decrease in percentage yield. The reusability of the clay entrapped ZnO catalyst was also tested for the benzylation of aniline up to five successive runs, with only marginal decrease in catalytic activity (Table 4).

3.3. Mechanism of benzylation of amines

To account for these observations, the following mechanism may be visualised (Scheme 2). Oxygen atom of clay encapsulated ZnO nanoparticles [ZnO (0001^{-}) –O polar surface] polarises C–Cl bond in benzyl chloride which is then attacked by aniline [brought in close proximity as it is attracted by the zinc cations of ZnO (0001)–

sively the di-iv-	18ª	H_2O	6 h	70	
le manner to af-	19	2	8 h	80	
yield. Aromatic	20 ^a		12 h	RT	
rbazole and im- ted products at	Substrate (0.5 mmol), benzyl chloride (0 centage conversion is determined by GC. ^a Only monobenzylation is observed.				

Zn polar surface] to facilitate the formation of benzylated products. It is also likely that ZnCl₂, generated *in situ* by the reaction of ZnO with HCl, may also catalyse the reaction.

4. Conclusions

K10-montmorillonite clay nano ZnO is synthesised and characterised by spectroscopic and microscopic techniques. They are used in the N-benzylation of anilines to give mono- and di-benzylated products in good yield. Secondary amine is also converted to the corresponding N-benzylated product in a facile manner, indicating clearly that it is a new protocol for the synthesis of secondary and tertiary amines over conventional catalysts. Other significant advantages of the present study include stabilisation of nano ZnO in clay layers

Table 1

Optimization of the reaction conditions for the N-benzylation of aniline using clay entrapped ZnO nanoparticles as catalyst.

Entry	Medium	Time (h)	T °C	Catalyst	Percentage conversion ^a	Mono	Di	Ratio mono:di
1	CH ₃ CN	10	RT	-	14.0	11.0	03.0	3.6:1
2	CH₃OH	24	RT	K10-clay	-	-	-	-
3 ^b	H ₂ O	12	RT	K10-nanoZnO	37.1	37.1	-	-
4 ^b	H ₂ O	24	RT	K10-nanoZnO	43.0	43.0	-	-
5	CH₃OH	10	RT	K10-nanoZnO	52.0	47.0	05.0	9.4:1
6	CH ₃ OH	12	RT	K10-nanoZnO	95.0	42.1	52.9	0.8:1
7	CH ₃ OH	24	RT	K10-clay	-	-	-	-
8	CH ₃ OH:H ₂ O ^c	10	RT	K10-nanoZnO	88.0	73.0	15.0	408:1
9	CH ₃ CN:H ₂ O ^c	24	RT	K10-nanoZnO	76.0	47.0	29.0	1.62:1
10	CH ₃ CN:H ₂ O ^c	12	70	K10-nanoZnO	89.0	39.0	50.0	0.78:1
11	CH ₃ OH:H ₂ O ^d	6	70	K10-nanoZnO	72.5	57.0	15.5	3.68:1
12	CH ₃ OH:H ₂ O ^e	6	70	K10-nanoZnO	69.5	28.2	37.9	1:1.34
13	CH ₃ OH:H ₂ O ^c	8	80	Bulk ZnO	65.6	51.6	14.0	3.67:1
14	CH ₃ OH:H ₂ O	6	80	Nano ZnO	98.6	71.6	27.0	2.65:1
15 ^b	CH ₃ OH:H ₂ O ^c	5	80	Powder Zn powder	30.8	30.8	-	-
16	CH ₃ CNH ₂ O ^c	8	80	Bulk ZnO (Bulk)	54.1	50.6	03.5	14.4:1
17	CH ₃ CN:H ₂ O ^c	5	80	Powder Zn	40.1	35.9	04.2	8.54:1

50 mg of catalyst was used for all reactions.

^a Determined by GC.

^b Only monobenzylation is observed.

^c Solvent ratio is 1:1.

^d Ratio of aniline:benzyl chloride is 2:1.

^e Ratio of aniline:benzyl chloride is 1:2.

 Table 2

 Effect of medium and temperature on mono/di; selectivity in N-benzylation of aniline.

Entry	Medium	Time (h)	T °C	Percentage conversion	Mono	Di	Ratio of mono:di
1	CH ₃ OH	6 h	70	100.0	57.5	42.5	1.34:1
2		8 h	80	100.0	48.4	51.6	0.93:1
3		12 h	RT	95.2	42.3	52.9	0.80:1
4	CH ₃ OH:H ₂ O	6 h	70	93.7	50.2	43.5	1.10:1
5	(2:1)	8 h	80	96.5	53.1	43.4	1.20:1
6 ^a		12 h	RT	49.2	49.2	-	-
7	$CH_3OH:H_2O$	6 h	70	84.5	34.8	49.7	0.70:1
8	(1:1)	8 h	80	71.0	39.0	32.0	1.21:1
9		2 h	RT	93.4	50.0	43.4	1.15:1
10		4 h	RT	96.8	53.1	43.7	1.20:1
11		6 h	RT	98.2	54.6	43.6	1.25:1
12		8 h	RT	100.0	52.3	47.7	1.10:1
13		10 h	RT	55.2	42.1	13.1	3.21:1
14		12 h	RT	88.3	82.5	05.8	14.20:1
15	$CH_3OH:H_2O$	6 h	70	78.0	65.5	12.5	5.20:1
16 ^a	(1:2)	8 h	80	53.0	53.0	-	-
17		12 h	RT	74.7	70.2	04.5	15.60:1
18 ^a	H ₂ O	6 h	70	61.6	61.6	-	-
19		8 h	80	85.6	77.7	07.9	9.80:1
20 ^a		12 h	RT	37.1	37.1	-	-

Substrate (0.5 mmol), benzyl chloride (0.5 mmol), ZnO nano-K10-clay (50 mg); percentage conversion is determined by GC.

Table 3

N-benzylation of substituted anilines with ZnO nanoparticles encapsulated in clay matrix.



Substrate (0.5 mmol), benzyl chloride (0.5 mmol), ZnO nano-K10-clay (50 mg), water: acetonitrile (1.5:1.5 mL), 12 h, 70 $^\circ\text{C}.$

^a Determined by GC.

^b Yield after second recycle.

and the ability of clay interlayer to bring the reactants in close proximity thus favouring the reaction. Another advantage is using clays as support, through their basic sites, clays act as scavengers for HCl released during the reaction.

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Table 4

Reusability of N-benzylation of aniline using clay entrapped ZnO nanoparticles as catalyst.

Run	First	Second	Third	Fourth	Fifth
Yield (%)	89	87	85	83	82

Aniline (0.5 mmol), benzyl chloride (0.5 mmol), ZnO nano-K1O clay (50 mg), water: acetonitrile (1.5:1.5 mL), 12 h, 70 °C. After completion of the reaction, catalyst is filtered and washed thrice with dichloromethane, air dried and reused for successive runs percentage conversion is determined by GC.



Scheme 2. Plausible mechanism for N-benzylation of aniline catalysed by nano $\mbox{ZnO}/\ \mbox{clay composite.}$

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