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Synthesis of substituted guanidines using Zn–Al hydrotalcite catalyst

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Abstract. Substituted guanidines were synthesized by the guanylation of amines with carbodiimides using Zn–Al hydrotalcite (Zn-Al HT) catalyst. Zn–Al HT was prepared by co-precipitation method and characterized by X-ray powder diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Raman and Thermogravimetric-Differential Thermal Analysis (TG-DTA). The heterogeneous catalyst afforded moderate to good yields (∼50–60 %) of substituted guanidines in toluene at 110°C in 12 h. The catalyst was recovered quantitatively by simple filtration and reused for three cycles with consistent activity. The XRD and FTIR studies of the used catalyst shows no variation in the structure of the catalyst even after three recycles.

Keywords. Guanylation; primary amine; carbodiimides; hydrotalcites.

1. Introduction

Guanidines form an important class of heteroatom-containing organic compounds, found in natural products and constitute an important unit/building block in biological, agrochemical and pharmaceutically active compounds.[1] They act as ancillary ligands for stabilizing various metal complexes, including main group, transition and lanthanide metals and also as base catalysts.[2,3]

Many synthetic strategies have been explored for the synthesis of substituted guanidines. Monosubstituted guanidines are obtained by mild guanylation of amines under mild conditions that inhibits the formation of highly functionalized guanidines.[4] Linton *et al.* explained a protocol that allowed the formation of 1, 3 multisubstituted guanidines from two separate amines with carbamoyl isothiocyanates.[5] Traditionally, guanidines have been prepared by the treatment of amines with cynamide or *S*-alkylisothiouronium salts[6] and also by direct conversion of bromoalkane to protected guanidines using N^1, N^2-bis(*tert*-butyloxycarbonyl)guanidine,[7] di(imidazole-1-yl)methanamine and di(imidazole-1-yl)cyanomethanimine as guanylating agents.[8] The uncatalysed guanylation of amines with carbodiimides is not a feasible process even under harsh reaction conditions.[9] Thus, the development of an active catalyst for such transformations has become an active area. Polymer-bound carbodiimides or amines or guanylating agents were also employed for the synthesis of guanidines, but it limits the diversity of the products.[10] Various metals, metal salts and metal complexes of main group,[11] transition and late transition[12] elements have been reported. In 2003, Richeson *et al.* reported transition metal-catalysed guanylation of aromatic amines with carbodiimides as first example.[13] Lanthanide metal complexes and half-sandwich lanthanide alkyl complexes have also been utilized for the synthesis of guanidines that have proved to be efficient catalysts.[14–18] Hou and coworkers achieved catalytic addition of both primary and secondary amines to carbodiimides through nucleophilic addition mechanism of a metal–nitrogen single bond to a carbodiimide by lanthanide metal catalysts.[19,20] However, most of these catalytic systems are air sensitive, their synthetic methods are very tedious; and further they are all homogeneous catalysts. Hence, there is an increasing demand to develop simple, convenient and environmentally benign recyclable approaches. Recently, our group has developed a protocol for the guanylation of amines with carbodimmides using heterogeneous nanocrystalline zinc oxide catalyst.[21]

Hydrotalcites (HT) are anionic clays, also known as layered double hydroxides (LDHs), with alternating cationic $M(II)_{(1-X)}M(III)_x(OH)_2^{x+}$ and anionic $A^{n-}.zH_2O$ layers that exhibit good catalytic applications for many organic transformations.[22–24] As a part of our research programme aimed at developing the synthetic utility

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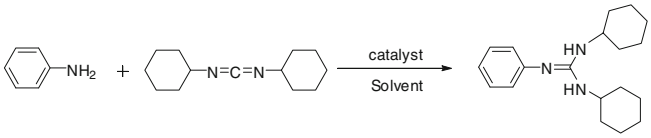


Scheme 1. Addition of aniline to dicyclohexylcarbodiimide.

of solid catalysts in fine chemical synthesis, herein we report Zn-Al hydrotalcite (Zn-Al HT) catalysed guanylation of amines with carbodiimides to afford the substituted guanidines in moderate to good yields (scheme 1).

2. Experimental

Zn-Al hydrotalcite was prepared by using chloride salts of zinc and aluminum, by co-precipitation method with NaOH solution. All amines and carbodiimides were purchased from Sigma Aldrich, Fluka and SRL, India, and were used without further purification. All the solvents were of analytical grade and used as received. The products were purified by column chromatography using mixture of ethyl acetate and hexane as eluent and neutral-alumina of 100–200 mesh as stationary phase. The products are well-characterized by Proton and 13C Nuclear Magnetic Resonance (^{1}H , ^{13}C NMR) and mass spectroscopy. Samples were scanned on AVANCE 300 MHz and INNOVA 500 MHz, using Trimethylsilane (TMS) as internal standard, and $CDCl_3$ and Dimethyl sulphoxide (DMSO) as solvents. High-resolution mass spectrometry was performed on QSTARXL (Applied Biosystems/MDSSCiex Foster City, USA). Low resolution mass spectrometry was performed using LCQ ion-trap mass spectrometer (Thermo Fisher, San Jose, CA, USA) equipped with an electron spray ionization (ESI) source. Elemental analysis of catalyst was carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo Electron ICP-OES model IRIS intrepid II XDL. Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer as KBr pellets. X-ray powder diffraction (XRD) data were collected on Siemens/D-5000 diffractometer using Cu–Kα radiation with a scan speed of $2\theta = 0.045/0.5$ s in the range of 2–65° at room temperature. TG-DTA analysis was recorded on a Mettler-Toledo TGA/SDTA 821 instrument in the temperature range of 25–1000°C with a heating rate of 10°C/min in nitrogen atmosphere. Raman spectra of the samples were measured on a HORIBA Jobin Yvon Raman Spectrometer, equipped with an excitation source of He–Ne laser (632.8 nm), Charge Coupled Device (CCD) camera and a scan resolution held at 2 cm^{-1}. Temperature-programmed desorption of ammonia (NH_3–TPD) was performed in laboratory-built equipment containing a programmable temperature controller and a gas chromatograph equipped with thermal conductivity detector (TCD). About 100 mg of catalyst was taken and pretreated at 300°C for 1 h in He flow (60 mL/min). Then the catalyst was exposed to 10% NH_3 balance He gas for 1 h at 100°C. The physisorbed NH_3 was removed under He flow (60 mL/min) for 50 min at the same temperature. Then the temperature of sample was raised up to 800°C at a heating rate of 10°C/min. The desorbed NH_3 gas was monitored with a gas chromatograph by using TCD.

2.1 *Preparation of catalyst*

The Zn-Al HT (Zn/Al 2:1) was synthesized by co-precipitation method (see supporting information) as reported in the literature.[25] The catalyst was characterized by XRD, FT-IR, Raman, ICP-AES, energy dispersive X-ray (EDX) and TG-DTA.

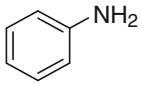
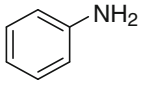
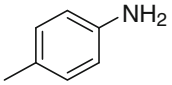
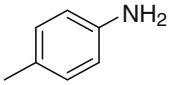
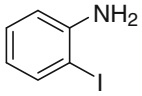
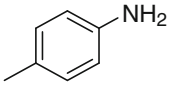
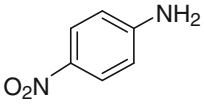
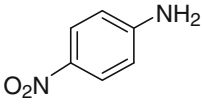
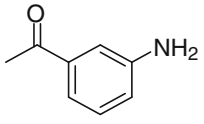
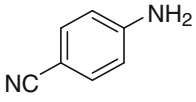
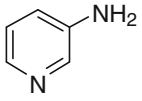
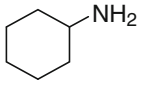
2.2 *General procedure for synthesis of substituted guanidines*

In a typical procedure, Zn-Al HT (0.05 g, 20 mol%), aromatic amine (1 mmol) and carbodiimide (1 mmol) were stirred in a 15 mL reaction vessel sealed with a Teflon screw cap using 2 mL toluene at 110°C for 12 h. After cooling to room temperature, the reaction mixture was filtered and washed with ethyl acetate (EtOAc). The organic solvent was concentrated under reduced pressure, column chromatography on neutral alumina using hexane/EtOAc (3:2) as eluent to afford the pure product. The products were characterized by ^{1}H, ^{13}C-NMR and high resolution mass spectrometry.

2.3 *Selected spectral data*

2.3a *1,3-Dicyclohexyl-2-phenylguanidine (table 1, entry 1)*: Colourless solid, ^{1}H NMR ($CDCl_3$) : δ 7.19 (t, $J = 7.55$ Hz, 2H), 6.86 (t, $J = 7.36$ Hz, 1H), 6.76 (d, $J = 7.36$ Hz, 2H), 3.55 (br, 4H), 3.38 (m, 2H), 2.02–1.02 (m, 20H). ^{13}C NMR ($CDCl_3$): 154.44, 138.67, 129.40, 124.94, 122.15, 52.56, 32.84, 24.93, 24.84. IR (KBr) υ in cm^{-1}: 3677, 3265, 3067, 2932, 2854, 1637, 1618, 1384, 1327, 892. ESI-MS: $(M+H)^+$ 300, high resolution mass spectrometry (HRMS) calculated (300.2439 amu), found (300.2432 amu).

Table 1. Zn-Al HT catalysed guanylation[a].

Entry	Amine	R,R′	Yield(%)[b]
1		Cy	56, 63[c], 64[d],64[e]
2		iPr	54
3		Cy	57
4		iPr	56
5		Cy	59
6		iPr	57
7		Cy	54[f]
8		iPr	52[f]
9		Cy	53[f]
10		Cy	52[f]
11		Cy	57
12		Cy	52

[a] Reaction conditions: Amine (1 mmol), carbodiimides (1 mmol), Zn-Al HT (0.05 g), toluene (2 mL), 110 °C, 12 h
[b] Isolated yields
[c] Amine: carbodiimide 1: 2 mmol
[d] Amine: carbodiimide 1: 3 mmol
[e] Amine: carbodiimide ratio 1: 4 mmol
[f] Reaction time 14 h, Cy = Cyclohexyl, iPr = Isopropyl

2.3b *1,3-Diisopropyl-2-(4-nitrophenyl)guanidine (table 1, entry 8)*: Yellow solid, ^{1}H NMR ($CDCl_3$): δ 8.15 (d, J = 8.87 Hz, 2H), 7.11 (d, J = 8.30 Hz, 2H), 5.67 (br, 2H), 3.70–3.56 (m, 2H), 1.23 (d, J = 6.42 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 153.39, 152.01, 141.72, 125.43, 121.40, 44.43, 22.93, 22.54. IR (KBr) υ in cm^{-1}: 3492, 3370, 3085, 2976, 2641, 2397, 1934, 1574, 1268, 1113, 1067, 862, 739. ESI-MS: $(M+H)^+$ 265, HRMS calculated (265.1664 amu), found (265.1677 amu).

3. Results and discussion

3.1 *Characterization of catalyst*

Elemental analysis of the catalyst was carried out by ICP-AES that gives Zn: Al ratio as 2.15:1, which is in close agreement with metal ratios originally charged. EDX studies reveal the presence of Zn, Al, Cl and O in relative amounts of 41.43% of atomic zinc, 7.99% of atomic aluminum, 8.92% of atomic chlorine and 41.66% of atomic oxygen. Powder XRD pattern of the (Zn-Al-Cl) HT is shown in figure 1a, and is in good agreement with literature,[26] with unit cell parameters a = 3.06 Å and c = 23.074 Å.

FTIR spectra of Zn-Al HT (figure 2a) shows the characteristic vibrational spectrum of Zn-Al HT with a broad band of around 3400–3600 cm^{-1}, which is the characteristic hydroxyl (–OH) stretching vibration of water; whereas the deformation mode of –OH appeared around 1630 cm^{-1}, which corresponds to the interlayer or physically adsorbed water. A band at 1383 cm^{-1} indicates the presence of traces of carbonate in solid material. Strong absorption bands that appear in the low frequency region correspond to the lattice vibration modes and can be attributed to M–O (782 and 617 cm^{-1}) and O–M–O (427 cm^{-1}) vibrations.[26,27] Raman spectrum of the Zn-Al HT is shown in figure 3a. Band in the range of 100 to 200 cm^{-1} is assigned to OMO bending modes, band at 217 cm^{-1} is associated with hydrogen bonding

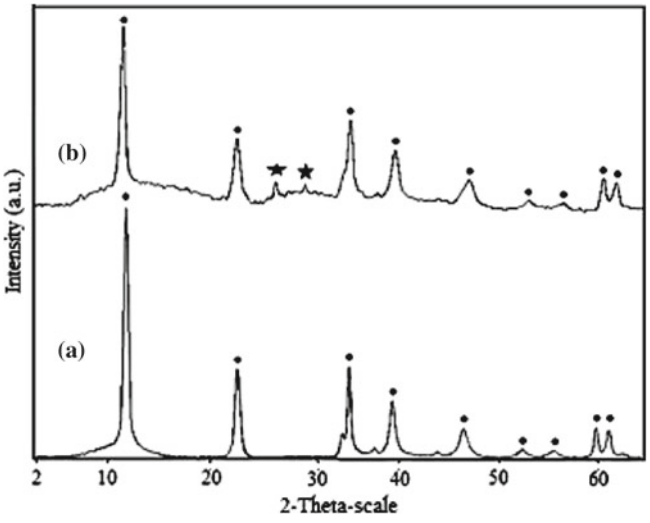


Figure 1. XRD pattern of (**a**) as prepared Zn-Al HT and (**b**) used catalyst. (●) Zn-Al HT, (★) Zn $(OH)_2$/AlOOH.

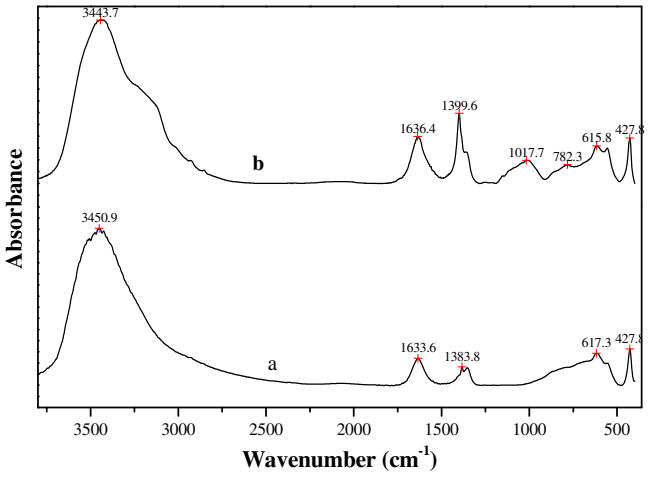


Figure 2. FTIR spectra of (**a**) as prepared Zn-Al HT and (**b**) used catalyst.

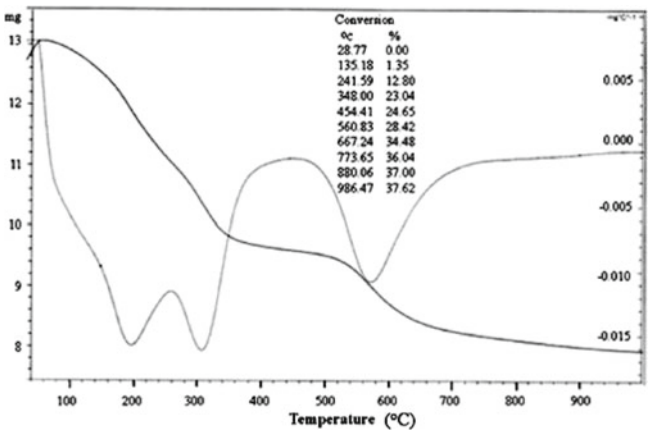


Figure 4. TG-DTA curves of as-synthesized Zn-Al HT.

of OH with interlayer anions. Band at 487 cm^{-1} occurs due to Zn–O stretching vibration in the Zn–Al HT. Band at 556 cm^{-1} is assigned to Zn–OH and Al–OH.[28,29]

The TG-DTA curves (figure 4) of this material exhibits three endotherms at 200°C, 300°C and 550–600°C similar to a typical LDH pattern corresponding to loss of interlayer water and loss of hydroxyl groups (OH^-) and anions (Cl^-), respectively.

3.2 *Application of catalyst (Zn-Al HT) in guanylation of amine*

Preliminary testing on guanylation of amine with carbodiimides is carried out by treating amine (1 mmol) with carbodiimides (1 mmol) in different solvents with Zn-Al HT (0.05 g) as catalyst (scheme 1) and the results are summarized in table 2. There is a pronounced effect of solvent in these reactions; the non-polar aromatic solvent, toluene was found to be best as it afforded good yield of desired guanidine product at 110°C in 12 h (table 2, entry 2). Interestingly, when polar solvents such as DMF and ethanol were used as solvent, no product of guanylation was observed (table 2, entries 7 and 8). Very notably, when THF (a polar, aprotic solvent) is used, it afforded moderate yield in 16 h (table 2, entry 6). From solvent screening experiments, it can be said that co-ordination ability of solvent plays a vital role in the reaction.[30] Toluene being non-polar will be unable to solvate intermediates formed during the reaction and thus facilitate a facile reaction of the unsolvated species. A control experiment was conducted in the absence of catalyst under identical conditions and no product was observed despite prolonged reaction time (table 2, entry 1). By increasing the catalyst amount from 0.05 g to 0.1 g, marginal improvement in yield was observed (table 2, entry 2). When calcined Zn-Al HT (calcined at 550°C for 6 h, rate 5°C/min) was used, low yield was observed (table 2, entry 3). Subsequently, various catalysts were screened and different supported zinc catalysts such as Zn-hydroxyapatite and Zn-fluorapatite (Zn-HAP and Zn-FAP) were prepared as per literature[31,32] and tested (table 2, entries 9 and 10) for guanylation reaction, but no effective conversions were observed. This can be explained based on the NH_3-TPD curves of Zn-Al HT, Zn-HAP and Zn-FAP (figure 5), which shows moderate acidic sites in 200–400°C temperature region in case of Zn-Al HT (figure 5a). No product formation was observed with Ni-Al HT and Mg-Al HT (table 2, entries 11 and 12), indicating that neither Ni nor Mg is capable of generating the reaction intermediates to enable a facile and clean reaction. In case of Mg-Al HT, Mg^{2+} is a hard Lewis

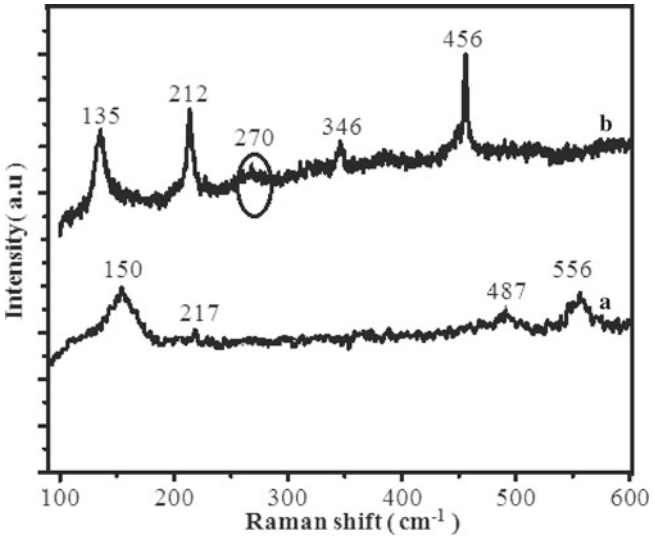


Figure 3. Raman spectra for Zn-Al HT (**a**) fresh Zn-Al-HT and (**b**) used Zn-Al HT catalyst.

Table 2. Screening of reaction parameters for guanylation[a].

Entry	Catalyst	Solvent	Temp. (°C)	Time(h)	Yield(%)[b]
1	–	Toluene	110	24	n.d
2	Zn-Al HT	Toluene	110	12	56, 58[c]
3	Calcined Zn-Al HT	Toluene	110	24	10
4	Zn-Al HT	Benzene	80	14	51
5	Zn-Al HT	Xylene	100	14	52
6	Zn-Al HT	THF	70	16	49
7	Zn-Al HT	DMF	130	24	n.d
8	Zn-Al HT	Ethanol	80	24	n.d
9	Zn-FAP	Toluene	110	24	20
10	Zn-HAP	Toluene	110	24	25
11	Ni-Al HT	Toluene	110	24	n.d
12	Mg-Al-HT	Toluene	110	24	n.d

[a] Reaction conditions: Aniline (1 mmol), dicyclohexylcarbodiimide (1 mmol), catalyst (0.05 g), solvent (2 mL)
[b] Isolated yields
[c] 0.1 g Zn-Al HT
n.d: not detected

acid and it could attack the nitrogen of anilines which is a hard Lewis base instead of weak Lewis base such as carbodiimide.[33] Among the above catalysts, only Zn-Al HT (2:1) was found to be an effective catalyst.

After optimizing reaction conditions, Zn-Al HT was chosen as catalyst for guanylation of various aromatic amines with carbodiimides under standardized conditions (scheme 2) and the results are summarized in table 1. As can be seen from table 1, the reaction of simple aniline with dicyclohexylcarbodiimide resulted in 56% of 1, 3-dicyclohexyl-2-phenylguanidine (table 1, entry 1). The yield of substituted guanidines increased to 63% when molar ratios of aniline to dicyclohexylcarbodiimide (table 1, entry 1) is increased to 1:2 in comparison to 1:1, but there is no change in yield when the ratio is changed to 1:3 and 1:4 in comparison to 1:2. When the reaction time is increased to 24 h with 1:1 ratio, no change in yield was observed. Aromatic amines with diverse functional groups such as Me, NO_2, I, COMe, CN, etc. survived the reaction conditions to afford desired products in moderate yields (table 1, entries 1–10). The reaction was not influenced by either electron-donating or electron-withdrawing substituents irrespective of their position on the aromatic ring. A variety of carbodiimides such as *N*, *N*′-dicyclohexylcarbodiimide and *N*, *N*′-diisopropylcarbodiimide also underwent guanylation reaction under optimized conditions (table 1, entries 1–8). No change in catalytic activity was observed in case of aromatic heterocyclic amine and aliphatic cyclic amine (table 1, entries 11 and 12).

Lower efficiency of catalyst in comparison to existing homogeneous catalysts could be attributed to basic character of Zn-Al HT and the aluminum in hydrotalcite is six-coordinated (octahedral) and thermally stable and therefore unable to produce a catalytically active three-coordinate Al species.[34] A salient feature of the study reported herein is the heterogeneity of the catalyst without significant drop in both yield and catalytic activity.

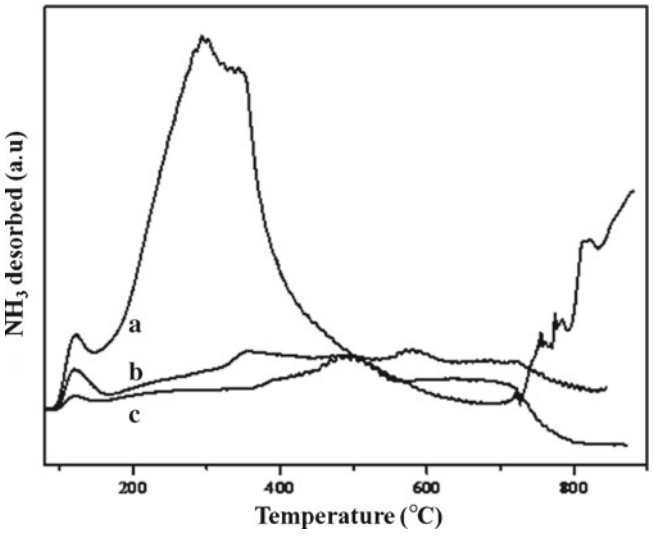
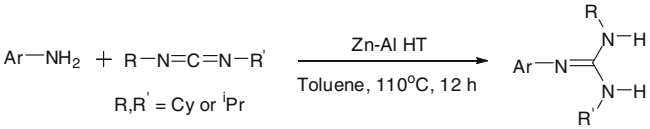


Figure 5. NH_3–TPD profiles of (**a**) Zn-Al HT, (**b**) Zn-HAP and (**c**) Zn-FAP.



Scheme 2. Guanylation of amines.

Table 3. Recyclability of catalyst for addition of aniline to dicyclohexylcarbodiimide.

Entry	No. of cycles	Yield (%)
1	1	56
2	2	55
3	3	53
4	4	50

3.3 *Reusability of catalyst*

Reusability of the Zn-Al HT was studied for guanylation of aniline by dicyclohexylcarbodiimide in toluene up to four cycles. Zn-Al HT was removed after the reaction by centrifugation; washed with ethyl acetate trice (by sonication for 5 min) to remove organic substances from the surface, later oven dried. To this recovered catalyst, fresh aliquots of reactants were added and were reused for 3 cycles with consistent activity for the selected substrate (table 3). The catalyst displayed good recyclability. A small decrease in activity is attributed to blocking of some of the sites by residual organics; endotherms at 350–450°C and at 700°C in the TG-DTA of used catalyst (figure 5) correspond to organic residue and further indicate fair stability of the catalyst under experimental conditions. Zinc content was found to be almost same in the fresh and used catalyst after the 4th cycle as shown by ICP-AES analysis. The XRD of the used catalyst shows the presence of zinc hydroxide and aluminum oxyhydroxy phases (figure 2b). The FT-IR shows the presence of metal organic molecule bonding on the catalyst at 978 cm^{-1}.

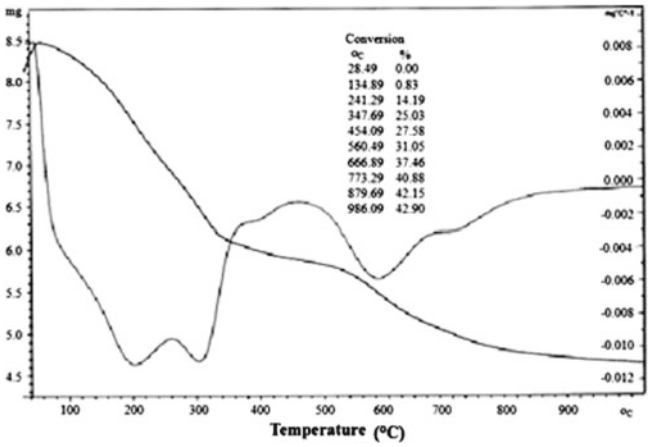
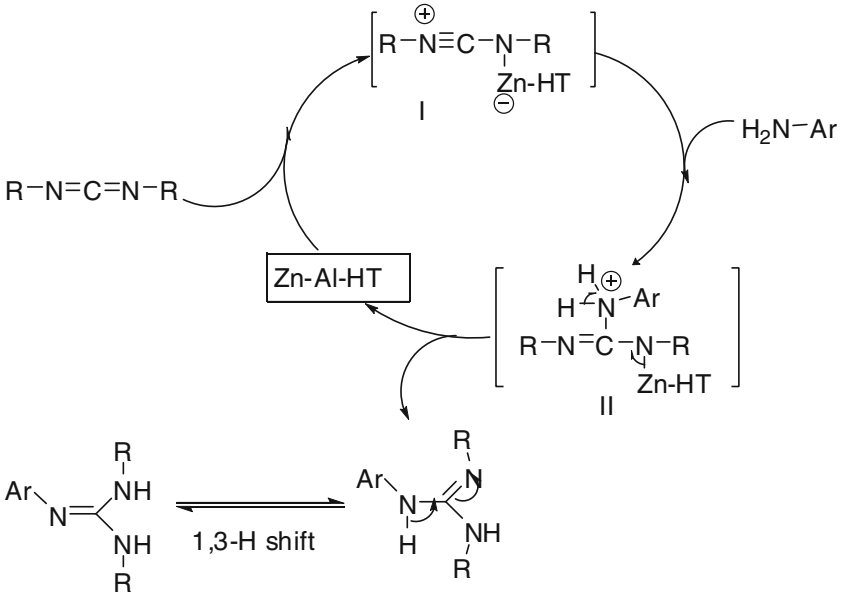


Figure 6. TG-DTA curves of used Zn-Al HT.

3.4 *Plausible mechanism*

A plausible mechanism for the guanylation of amines using Zn-Al HT as catalyst (scheme 3) was proposed.[21] Carbodiimides were activated by zinc in the catalyst to generate intermediate I, nucleophilic addition of amine to I results in the formation of intermediate II, followed by intramolecular proton transfer to regenerate Zn-Al HT and release of guanidine, thereby continuing the catalytic cycle. Formation of Zn–N bonding in the used catalyst (catalyst was filtered out after 6 h and dried in oven without washing) is evident from Raman studies (figure 3b) of the used catalyst shows an additional band at 270 cm^{-1}, which is assigned to the Zn–N bond formed.[35] Two other additional bands at 345 and 456 cm^{-1} can be attributed to disorder in the Zn–O bonding because of nitrogen incorporation into the



Scheme 3. Possible mechanism for Zn-Al-HT catalysed guanylation of primary aromatic amines.

lattice. Such modes are expected to disappear after the reaction is completed and the catalyst regains its original structure. This fact is confirmed from the XRD pattern of the used sample showing no variation from the fresh catalyst, further supports our claim that there is no variation in the structure of the catalyst because of the reaction (figure 6).

4. Conclusion

In conclusion, Zn-Al HT was used as a heterogeneous catalyst for guanylation of amines with carbodiimides to form substituted guanidines in moderate to good yields. Though the catalyst reported gives moderate yields compared to other catalysts reported earlier, it offers several advantages; such as ready availability of raw material and easy method for preparation of catalyst, and the catalyst can be readily recovered and reused without loss of activity, thus making this process more environmentally acceptable.

Supplementary information

The electronic supporting information can be seen in www.ias.ac.in/chemsci.

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