

Original Research Article

Synthesis and FT-IR, SEM, EDS studies of heterogeneous catalyst- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ supported on rice husk: A highly efficient and economical catalyst for N-formylation of amines at room temperature

ABSTRACT

A heterogeneous catalyst, rice husk supported calcium chloride dihydrate ($\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$), has been developed and characterized using energy dispersive spectroscopy (EDS), fourier transform infra-red (FT-IR) spectroscopy and scanning electron microscopy (SEM). $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$ offers simple, efficient and economical solid support synthetic protocol for the synthesis of formamides under solventless condition at room temperature to afford the formamide derivatives. The ability of $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$ to enhance the reaction rate is described in terms of preorganizing effect. This method provides green approach for N-formylation and easy isolation process. The method is superior over the existing methods as it utilizes methanolic acid in lesser amount and works well at room temperature.

Keywords: Rice husk, $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$, solid support, formamides, preorganizing effect, green approach.

1. INTRODUCTION

In recent years, the development of environmentally benign synthetic methodologies has received much attention. Presently, there is a quest for synthetic chemist to develop environment friendly, suitable and active catalysts in the field of organic synthesis and commercial process. Amines formylation is one of the most vital processes in synthetic and pharmaceutical chemistry. For the synthesis of medicinally significant compounds such as substituted aryl imidazoles [1], 1, 2 dihydroquinolines [2], oxazolidinones [3] and cancer chemo-therapeutic compounds [4]; formamides are utilized as intermediates. They have been used as chief antecedent in the synthesis of fungicides and herbicides [1]. Amides act as Lewis bases which are known to catalyze allylation [5] and hydrosilylation [6] of carbonyl compounds. Vilsmeier formylation also uses amides as reagents [7]. Formamides are very useful reagents for formamides [8] and isocyanide [9-11] synthesis. In addition, formylation is also used to protect amino groups in peptide synthesis [12].

Various catalysts have been known to catalyze formamide synthesis such as ammonium formate [13], ionic liquids [14], ZnCl_2 [15], thiamine hydrochloride [16], iridium [17], sodium formate [18], sulfated titanium oxide [19] and sulfated tungstate [20]. Mostly N-formylation procedures have drawbacks such as application of expensive, thermally unstable and toxic catalyst, increased reaction time, extreme reaction environment and difficulty in purification of products. Thus, a simple, mild and economical protocol using green catalyst would be desirable.

In continuation of our interest in the development of green synthetic procedures and catalyst [21-22] we herein report, green and economical method for the synthesis of formamides using rice husk supported calcium chloride dihydrate as a catalyst under solventless condition.

2. EXPERIMENTAL DETAILS

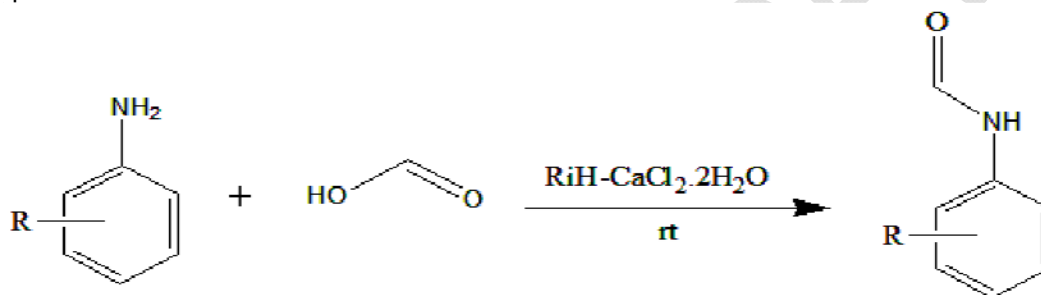
2.1. Preparation of heterogeneous catalyst- Rice husk supported $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (RiH- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)

Rice sample was collected from Crop Research Centre in Pantnagar, Uttarakhand and further processed in local mill to obtain husk. In order to remove any sticky particles on rice husk, it was washed number of times using deionised water and dried at room temperature for 24 h. The dried rice husk was grinded using electronic grinder.

Rice husk supported $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (RiH- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was developed by sorption of aqueous solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.05 mmol) in 1 ml distilled water on rice husk (RiH) (0.25 g). The catalyst was then put in oven at 110°C for 4 h to give RiH- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

2.2. General procedure for N-formylation of amine

To the 100 ml round bottom flask, add substituted aniline (1 mmol), methanolic acid (2 mmol) and RiH- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.05 mmol $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ supported on 0.25g rice husk) and put it at constant stirring at room temperature (Scheme 1). Reaction progress was monitored by thin layer chromatography (TLC). After reaction completion, synthesized formamide was extracted using separating funnel using ethyl acetate followed by washing with 5% aqueous hydrochloric acid, 5% aqueous sodium carbonate and distilled water. Organic layer obtained after extraction was dried over anhydrous sodium sulfate to afford final product.



Scheme 1. General procedure for N-formylation of substituted aniline

2.3. Instrumental studies for characterization

Bruker Avance II 300 MHz NMR spectrophotometer was used to obtain ^1H NMR spectra of synthesized formamides using CDCl_3 at ambient temperature. FT-IR spectra were recorded on Thermo Nicolet 380 FT-IR Spectrophotometer utilizing KBr pellets. The morphological analysis of rice husk and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ supported on rice husk (RiH- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was done by SEM-JEOL (JSM-6610 LV) Scanning Electron Microscope using a primary beam voltage of 5 KV fitted with an EDS which detect and gave weight percentage of elements present in adsorbent.

2.4. Statistical Analysis

Percent yield presented in table 1, 2 and 3 are mean of three replicates ($n=3$) with \pm standard deviation.

3. RESULTS AND DISCUSSION

Initial probing was done using o-chloroaniline as a prototype to investigate the efficiency of heterogeneous catalyst RiH- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. We started with reaction using amine: methanolic acid ratio (1:1) and 0.2 mmol $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ impregnated on 0.25 g rice husk under constant stirring at room temperature. We found that reaction completed within 2 h (Table 1, entry 2). Most of the methods reported in literature

used higher temperature. Encouraged by the results we optimized the conditions at room temperature and the best suited reaction conditions were established. The results are given in Table 1.

Table 1. Optimization of reaction conditions for N-formylation of o-chloroaniline with methanolic acid in presence of RiH-CaCl₂.2H₂O at room temperature

Entry	Reaction Conditions				Time	Yield (%)*
	Amine (mmol)	HCOOH (mmol)	Catalyst			
			CaCl ₂ ·2H ₂ O (mmol)	Rice Husk (RiH)		
1	1	1	0	0	5 h	63 ± 1.24
2	1	1	0.2	0.25 g	2 h	87 ± 0.94
3	1	2	0.2	0.25 g	1 h	95 ± 0.88
4	1	2	0.1	0.25 g	1 h	95 ± 1.24
5	1	2	0.05	0.25 g	1 h	95 ± 0.58
6	1	2	0.05	0.50 g	50 min	90 ± 1.52
7	1	2	0.05	0.10 g	1.5 h	88 ± 0.90
8	1	2	0.05	0.40 g	1 h	94 ± 1.16
9	1	3	0.05	0.25 g	1 h	93 ± 1.64
10	1	4	0.05	0.25 g	1 h	93 ± 1.20

*% Yield is mean of three replicates (n=3) with ± standard deviation.

Firstly, perusal of table 1 clearly reveals that 1 mmol o-chloroaniline and 2 mmol methanolic acid in presence of 0.05 mmol of CaCl₂.2H₂O impregnated on 0.25 g rice husk afforded product giving highest quantitative yield i.e. 95% (Table1, entry 5) in 1 h. Increased amount of catalyst didn't contribute to enhance the corresponding yield (Table1, entry 4, 6, 7 and 8). Also, the ratio (1:2) of amines and methanolic acid was found optimum and it was observed that further increase in the amount of methanolic acid did not contribute to increase the yield (Table1, entries 9 and 10). Secondly, we screened different catalyst such as anhydrous CaCl₂, CaCl₂.2H₂O, rice husk (RiH) to find out the efficiency of CaCl₂.2H₂O supported on Rice husk (RiH-CaCl₂.2H₂O) as a catalyst on the progress of reaction. The results are given in Table 2. It is clear that RiH-CaCl₂.2H₂O gave much better results. Also, the water molecules associated with calcium chloride dihydrate was found to be ideal additive as with anhydrous CaCl₂ low yield product formation with longer reaction time was observed (Table 2, entry 1).

Table 2. N-formylation of o-chloroaniline with methanolic acid (1:2) at room temperature using various catalysts

Entry	Catalyst	Time (h)	Yield (%)*
1	Anhydrous CaCl ₂ (0.2 mmol)	6	46 ± 1.05
2	CaCl ₂ .2H ₂ O (0.2 mmol)	4	86 ± 1.02
3	Rice husk (RiH) (0.25 g)	No reaction	-
4	RiH-CaCl ₂ .2H ₂ O (0.2 mmol CaCl ₂ .2H ₂ O supported on 0.25 g RiH)	1	95 ± 0.08

*% Yield is mean of three replicates (n=3) with ± standard deviation.

In order to achieve efficacy and scope of the method, we utilize various substituted aromatic primary amines. In every case, N-formylation gives yield ranging from good to excellent depending on substrate. Table 3 represents the summarized results. Secondary amines were found difficult to be N-formylated (Table 3, entries 9 and 10). Also, to illustrate the promineny of RiH-CaCl₂.2H₂O, table 3 compares our results with some of those reported in the literature. Comparative experimental data reveal that among the other catalysts viz. ammonium formate [13], ZnCl₂ [15], thiamine hydrochloride [16], sodium formate [18] and sulfated titanium oxide [19], RiH-CaCl₂.2H₂O was found to be the most efficient in respect of time, temperature and mole ratio of amine and methanolic acid.

In the present method, we found that the reaction afforded good yield with the mole ratio 1:2 (amine: methanolic acid), except for compounds N-(p-nitrophenyl)-formamide and N-(o-hydroxyphenyl)-formamide (Table 3, entries 2 and 4) while with catalysts reported in literature the ratio is either 1:3 or 1:4. In most of the reported methods N-formylation of amines takes place at high temperature or at reflux (Table 3, entries 1, 2, 4, 5 and 8) while our method is carried out conveniently at room temperature.

Table 3. Synthesized formamides in presence of heterogeneous catalyst- $\text{RiH}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$

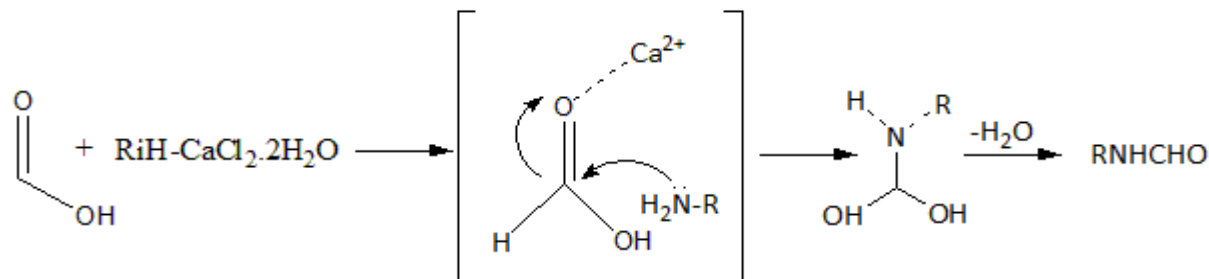
Entry	Products	Reaction time (min)	Time(min)/ Temperature ^a	Amine: Methanolic acid		%Yield ^c	%Yield ^d	Ref ^e
				Ratio	Ratio ^b			
1		45	660/ reflux	1:2	-	93±1.09	96	13
2		20	40/ 80°C	1:4	1:4	92±0.09	94	16
3		60	180/ rt	1:2	1:4	95±1.11	95	18
4		240	30/ 80°C	1:4	1:4	91±0.84	88	16
5		240	30/ 70°C	1:2	1:3	78±0.76	98	15
6		120	420/ rt	1:2	1:3	89±0.58	90	19
7		180	90/ 70°C	1:2	1:3	67±1.09	85	15
8		240	-	-	-	- ^f	-	-
9		320	-	-	-	- ^f	-	-

^{a, b, d, e} Reported in the literature

^c Isolated (%) yield is mean of three replicates (n=3) with ± standard deviation.

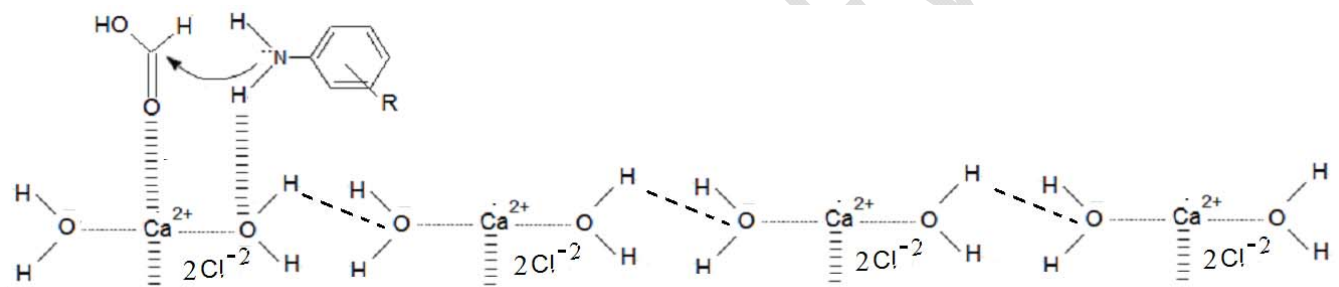
^f No reaction

The probable mechanism of the N-formylation of amines involves activation of carbonyl carbon of methanolic acid by the calcium ion and then nucleophilic attack of amine which results in amide formation (Scheme 2).



Scheme 2. Mechanism of $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$ catalyzed N-formylation of o-chloroaniline with methanolic acid.

It is suggested that the reactants undergo preorganizing effect due to the presence of water molecules associated with calcium ion. It involves the interaction of catalyst and substrate resulting in decreasing the entropy of transition state and consequently in decreasing the energy of activation. Water molecules present in calcium chloride dihydrate impregnated on rice husk have strong electrostatic interaction with hydrogen of the amino group (Scheme 3). Same preorganizing effect has been reported in Diels-Alder reaction in which cyclodextrin acts as preorganizing additive [23-24].



Scheme 3. Pre organizing effect shown by $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$ with amine

3.1. Characterization of heterogeneous catalyst- $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$

3.1.1. IR analysis

The FTIR spectra of the RiH and $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$ are reflected in figure 1. Stretching vibration of silanol O-H bond gave the broad band in the range of $3430\text{--}3480\text{ cm}^{-1}$ (figure 1a). C-H stretching of saturated aliphatic compounds is observed at about 2900 cm^{-1} [25]. C=O stretching of hemicelluloses and lignin attained maximum at $1600\text{--}1750\text{ cm}^{-1}$ and C-C stretching of aromatic carbon attained peak at $1400\text{--}1600\text{ cm}^{-1}$ [26]. The structural siloxane bond, Si-O-Si showed strong peaks between 1025 and 1100 cm^{-1} . The intense peak at $1600\text{--}1650\text{ cm}^{-1}$ in $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$ spectra is due to calcium chloride dihydrate and broad peak at 3200 to 3600 cm^{-1} corresponds to intermolecular association of OH groups of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ on rice husk (Figure 1b) [27].

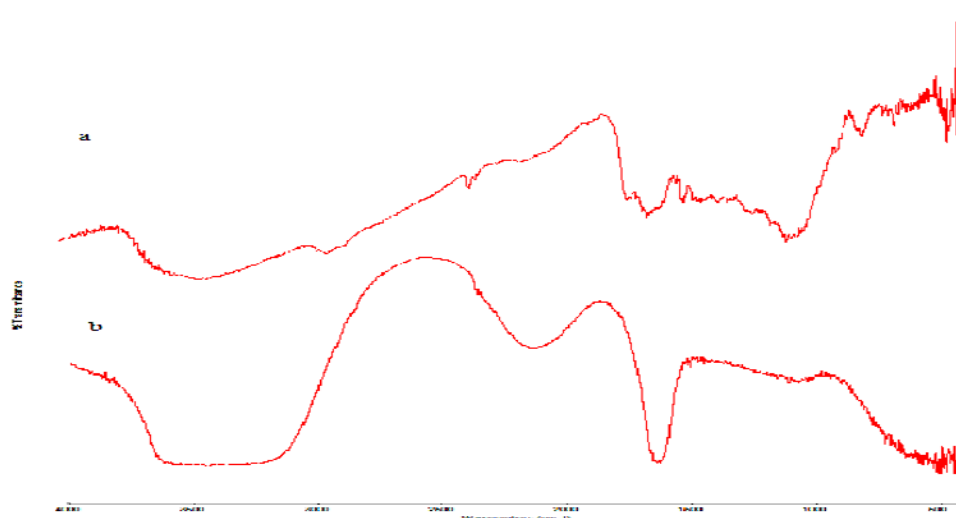


Figure 1. The infrared spectra of (a) RiH and (b) RiH- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

3.1.2. SEM analysis

The morphological modification of RiH before and after $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatment was investigated using SEM. The inner surface of lemma visible to be smoother than the outer one (Figure 2b,d) which is profoundly stiffed and these stiffed structure have a linear profile (Figure 2a). Due to the presence of systematically spaced conical protrusions the external surface of the rice husk appeared highly rippled which is demonstrated at higher magnification (Figure 2c) [28-29]. The results of scanning electron microscopy confirmed that $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ treatments results in the morphological changes of RiH. The rupture of conical protrusions of the external surface is prompted by $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and an uneven irregular surface greatly appeared (Figure 3a). The topological changes such as ruptures and roughness are elevated in the inner surface (Figure 3b).

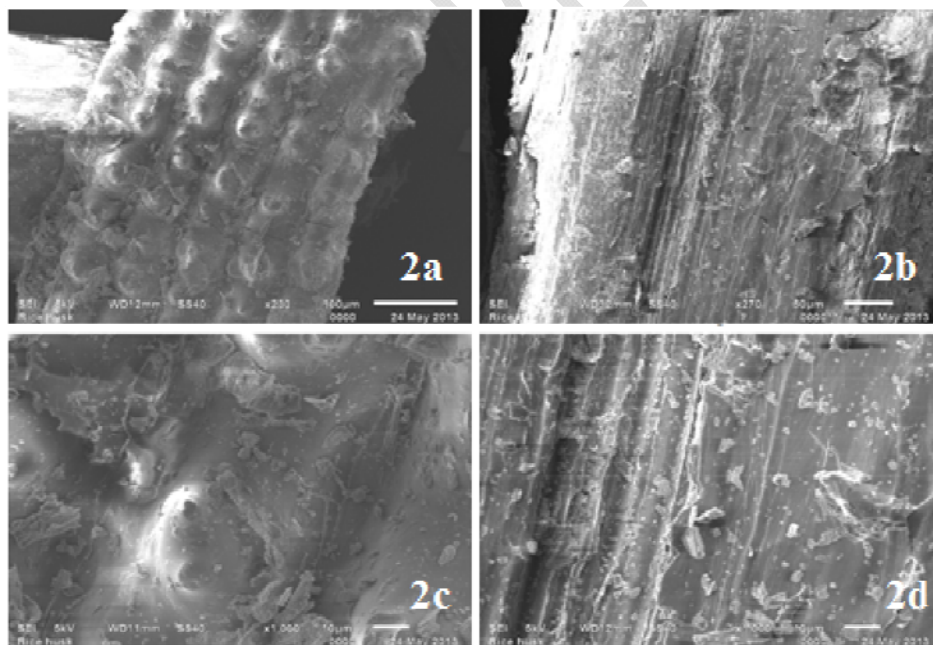


Figure 2. SEM micrograph of untreated rice husk (RiH)

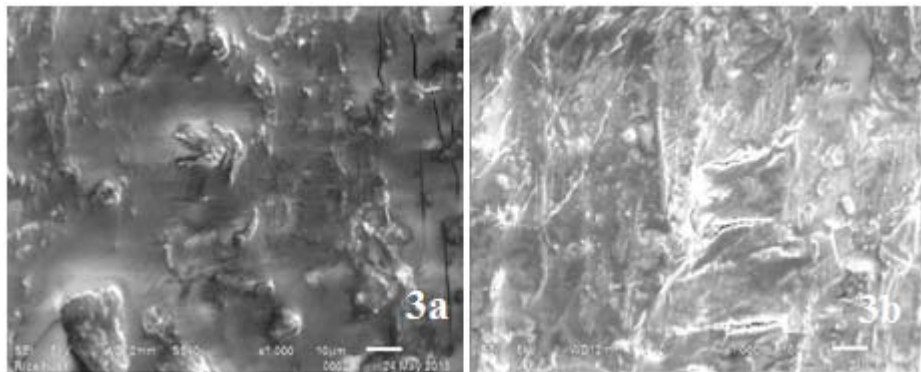


Figure 3. SEM micrograph of RiH-CaCl₂.2H₂O

3.1.3. EDS analysis

Energy dispersive spectroscopy (EDS) has been taken for evaluating the elemental constitution of the surface of rice husk (RiH) and CaCl₂.2H₂O adsorbed rice husk (RiH). EDS spectra (Figure 4 and 5) and elemental data (Table 4) showed that RiH-CaCl₂.2H₂O has Ca and Cl present with element percent ratio 4.7Ca: 11Cl, whereas, there was no traces of Ca and Cl in RiH. The results confirmed the development of CaCl₂.2H₂O adsorbed rice husk (RiH-CaCl₂.2H₂O) heterogeneous catalyst.



Figure 4. EDS Spectrum of rice husk (RiH)

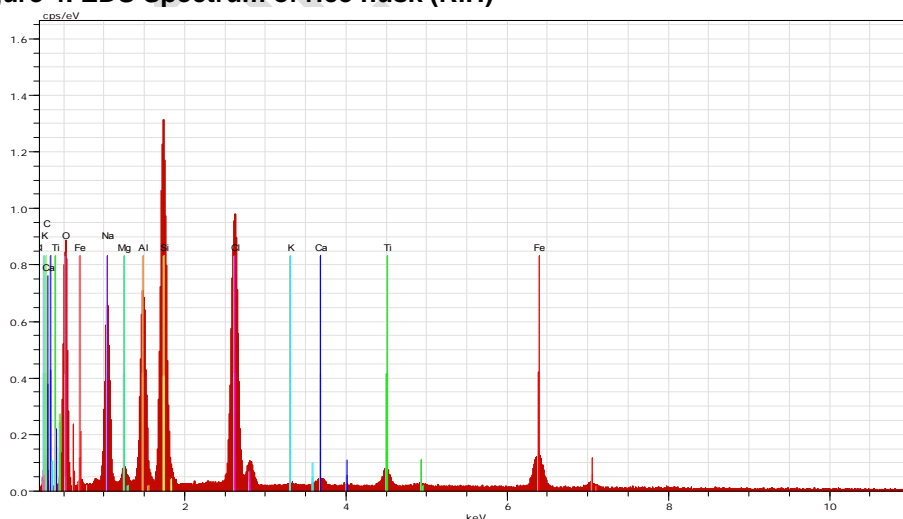


Figure 5. EDS Spectrum of CaCl₂.2H₂O adsorbed Rice husk (RiH-CaCl₂.2H₂O)

Table 4. Elemental constitution of Rice husk (RiH) and CaCl₂·2H₂O adsorbed Rice husk (RiH-CaCl₂·2H₂O) using EDS analysis

Rice husk (RiH)			CaCl ₂ ·2H ₂ O adsorbed Rice husk (RiH-CaCl ₂ ·2H ₂ O)		
Element	Atomic No.	Normalised Concentration [wt.%]	Element	Atomic No.	Normalised Concentration [wt.%]
O	8	57.74	O	8	35.79
Si	14	17.67	Si	14	14.51
Al	13	11.75	Al	13	9.90
C	6	5.38	C	6	3.05
Fe	26	4.46	Fe	26	4.87
Ti	22	1.85	Ti	22	1.75
Mg	12	0.75	Mg	12	1.05
Na	11	0.37	Na	11	13.38
K	19	0.03	K	19	0.09
Cl	17	-	Cl	17	11.02
Ca	20	-	Ca	20	4.58
Total		100	Total		100

3.2. Characterization of N-formylated compounds

The compounds gave spectral characterization data as follows:

Table 3, Entry 1: N-phenylformamide:

IR (KBr, cm⁻¹): 3301, 3114, 2904, 1685, 1365.

¹H NMR (CDCl₃, 300 MHz): δ ppm 7.2-7.5 (m, 5H, Ar), 8.4 (s, 1H, NH), 8.6 (s, 1H, CHO).

Table 3, Entry 2: N-(4-nitrophenyl)formamide:

IR (KBr, cm⁻¹): 3245, 3116, 2978, 1699, 1464, 1340.

¹H NMR (CDCl₃, 300 MHz): δ ppm 6.9-7.6 (m, 4H, Ar), 8.15 (s, 1H, NH), 8.3 (s, 1H, CHO).

Table 3, Entry 3: N-(2-chlorophenyl)formamide:

IR (KBr, cm⁻¹): 3060, 3016, 2949, 2858, 1684, 1506, 1366.

¹H NMR (CDCl₃, 300 MHz): δ ppm 7.2-8.0 (m, 4H, Ar), 8.5 (1s, 1H, NH), 8.8 (1s, 1H, CHO).

Table 3, Entry 4: N-(2-hydroxyphenyl)formamide:

IR (KBr, cm⁻¹): 3411, 2908, 2410, 1610, 1518, 1318.

¹H NMR (CDCl₃, 300 MHz): δ ppm 7.3-8.1 (m, 4H, Ar), 4.9 (s, 1H, OH), 8.2 (s, 1H, NH), 8.9 (s, 1H, CHO).

Table 3, Entry 5: N-(4-methylphenyl)formamide:

IR (KBr, cm⁻¹): 3380, 3101, 1658, 1591, 1377.

¹H NMR (CDCl₃, 300 MHz): δ ppm 2.3 (s, 3H, CH₃), 7.0-7.5 (m, 4H, Ar), 8.3 (1s, 1H, NH), 8.8 (1s, 1H, CHO).

Table 3, Entry 6: N-(4-fluorophenyl)formamide:

IR (KBr, cm⁻¹): 3420, 2892, 2804, 1614, 1521, 1342.

¹H NMR (CDCl₃, 300 MHz): δ ppm 7.1-7.8 (m, 4H, Ar), 8.4 (1s, 1H, NH), 8.9 (1s, 1H, CHO).

Table 3, Entry 7: N-(3-acetophenyl)formamide:

IR (KBr, cm⁻¹): 3392, 2979, 1659, 1517, 1320.

¹H NMR (CDCl₃, 300 MHz): δ ppm 2.6 (1s, 3H, CH₃), 7.1-7.8 (m, 4H, Ar), 8.3 (1s, 1H, NH), 8.7 (1s, 1H, CHO).

4. CONCLUSION

In conclusion, $\text{RiH-CaCl}_2 \cdot 2\text{H}_2\text{O}$ has been proved to be an efficient and economical heterogeneous catalyst for the synthesis of formamides. This Letter describes first time the pre organizing effect of catalyst for the rate enhancement in N-formylation of amines. It offers simple, economical and environment friendly method at room temperature and need not require any special conditions and equipments.

REFERENCES

1. Chen BC, Bednarz MS, Zhao R, Sundeen JE, Chen P, Shen Z et al. A new facile method for the synthesis of 1-arylimidazole-5-carboxylates. *Tetrahedron Lett.* 2000;41:5453-5456.
2. Kobayashi K, Nagato S, Kawakita M, Morikawa O, Konishi H. Synthesis of 1-Formyl-12-dihydroquinoline Derivatives by a Lewis Acid-Catalyzed Cyclization of o-(1-Hydroxy-2-alkenyl)phenyl Isocyanides. *Chem Lett.* 1995;24:575-576.
3. Lohray BB, Baskaran S, Rao BS, Reddy BY, Rao IN. A Short Synthesis of Oxazolidinone Derivatives Linezolid and Eperezolid: A New Class of Antibacterials. *Tetrahedron Lett.* 1999;40(26):4855-4856.
4. Petit RG, Kalnins VM, Liu HMT, Thomas GE, Parent K. Notes- Potential Cancerocidal Agents (III) Formamides. *J Org Chem.* 1961;26:2563.
5. Kobayashi S, Nishio K. Facile and Highly Stereoselective synthesis of Homoallylic alcohols using organosilicon intermediates. *J Org Chem.* 1994;59:6620-6628.
6. Kobayashi S, Yasuda M, Hachiya I. Trichlorosilane-dimethylformamide (CL3SIH-DMF) as an efficient reducing agent Reduction of aldehydes and imines and reductive amination of aldehydes under mild conditions using hypervalent hydridosilicates. *Chem Lett.* 1996;25:407-408.
7. Downie IM, Earle MJ, Heaney H, Shuhaibar KF. Vilsmeier formylation and glyoxylation reactions of nucleophilic aromatic compounds using pyrophosphoryl chloride. *Tetrahedron.* 1993;49:4015-4034.
8. Han Y, Cai L. An efficient and convenient synthesis of formamidines. *Tetrahedron Lett.* 1997;38(31):5423-5426.
9. Effenberger F, Eichhorn J. Stereoselective synthesis of thienyl and furyl analogues of ephedrine. *Tetrahedron: Asym.* 1997;8:469-476.
10. Schollkopf U. Recent Applications of α -Metalated Isocyanides in Organic Synthesis. *Angew Chem Int Ed Engl.* 1977;16:339-422.
11. Humer LG, Herr F, Charest MP. Chemistry and Pharmacology of 5-methylene-4- substituted dibenzo [α , d] cycloheptenes. *J Med Chem.* 1971;14:982-985.
12. Martinez J, Laur J. Active Esters of Formic Acid as Useful Formylating Agents: Improvements in the Synthesis of Formyl-Amino Acid Esters N- α -Formyl-Met-Leu-Phe-OH and Formyl-Met-Lys-ProArg a Phagocytosis Stimulating Peptide. *Synthesis.* 1982;1982(11):979-981.
13. Reddy PG, Kumar GDK, Baskaran S. A convenient method for the N-formylation of secondary amines and anilines using ammonium formate. *Tetrahedron Lett.* 2000;41:9149-9151.
14. Akbari J, Hekmati M, Sheykhan M, Heydari A. Guanidine derived ionic liquids: catalyst free medium for N-Formylation of amines. *Arkivoc.* 2009;11:123-129.
15. Shekhar AC, Kumar AR, Sathaiah G, Paul VL, Sridhar M, Rao PS. Facile N-formylation of amines using Lewis acids as novel catalysts. *Tetrahedron Lett.* 2009;50:7099-7101.
16. Lei M, Ma L, Hua L. A convenient one-pot synthesis of formamide derivatives using thiamine hydrochloride as a novel catalyst. *Tetrahedron Lett.* 2010;51:4186-4188.
17. Saidi O, Bamford MJ, Blackerc AJ, Lynch J, Marsden SP, Plucinski P et al. Iridium-catalyzed formylation of amines with paraformaldehyde. *Tetrahedron Lett.* 2010;51:5804-5806.
18. Brahmachari G, Laskar S. A very simple and highly efficient procedure for N -formylation of primary and secondary amines at room temperature under solvent-free conditions. *Tetrahedron Lett.* 2010;51:2319-2322.
19. Krishnakumar B, Swaminathan M. A convenient method for the N-formylation of amines at room temperature using TiO_2 -P25 or sulfated titania. *J Mol Catal A: Chem.* 2011;334:98-102.

20. Pathare SP, Sawant RV, Akamanchi KG. Sulfated tungstate catalyzed highly accelerated N-formylation. *Tetrahedron Lett.* 2012;53:3259–3263.
21. Agarwal D Dhanik J Verma A, Kasana VK. One Pot Multicomponent Reactions Using Cu²⁺ Immobilized Coconut Coir: An Efficient and Reusable Heterogeneous Catalyst for Green Synthesis of Imidazoles β -Acetamidoketones and β -Hydroxyketones. *Chem Sci Rev Lett.* 2018;7(26):556-561.
22. Agarwal D Dhanik J Verma A, Kasana VK. Synthesis of Co²⁺/ Zn²⁺ Impregnated Bentonite -Chitosan Composite Hetero- catalyst and Application of Principal Component Analysis to Evaluate its Catalytic Activity for the Synthesis of Nitrogen Containing 5 and 6 Membered Heterocyclic Compounds. *Int Res J Pure Appl Chem.* 2018;16(3):1-12.
23. Schneider HJ, Sangwan NK. Diels-Alder reactions in hydrophobic cavities: a quantitative correlation with solvophobicity and rate enhancements by macrocycles. *J Chem Soc Chem Commun.* 1986;1787-1789.
24. Sangwan NK, Schneider HJ. The kinetic effects of water and of cyclodextrins on Diels-Alder reactions Host-guest chemistry Part 18. *J Chem Soc Perkin Trans2.* 1989;1223-1227.
25. Cherian BM, Pothan LA, Nguyen-Chung T, Menning G, Kottaisamy M, Thomas SA. Novel method for the synthesis of cellulose nanofibril whiskers from banan fibres and characterization. *Agric Food Chem.* 2008;56:5617-27.
26. Chuai C, Almdal K, Poulsen L, Plackett D. Conifer fibers as reinforcing materials for polypropylene-based composites. *J Appl Polym Sci.* 2001;80:2833-2841.
27. Casadio F, Toniolo L. Polymer treatments for stone conservation: Methods for evaluating penetration depth. *J of the American Institute for Conservation.* 2004;43:03-21.
28. Park BD, Wi SG, Lee KH, Singh AP, Yoon TH, Kim YS. Characterization of anatomical features and silica distribution in rice husk using microscopic and micro-analytical techniques. *Biomass Bioenerg.* 2003;25:319-337.
29. Ciannamea EM, Stefani PM, Ruseckaite RA. Medium-density particleboards from modified rice husks and soybean protein concentrate-based adhesives. *Bioresour Technol.* 2010;101(2):818-825.