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Chemoselective *anti*-Markovnikov hydroamination of α,β-ethylenic compounds with amines using montmorillonite clay

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Abstract

The catalytic activity of montmorillonite clays as a catalyst for the hydroamination of α,β-ethylenic compounds with amines was tested. Aniline and substituted anilines reacted with α,β-ethylenic compounds in the presence of catalytic amount of commercially available clay to afford exclusively *anti*-Markovnikov adduct in excellent yields. Aniline reacted with ethyl acrylate to yield only *anti*-Markovnikov adduct *N*-[2-(ethoxycarbonyl)ethyl]aniline (mono-addition product). No Markovnikov adduct (*N*-[1-(ethoxycarbonyl)ethyl]aniline and double addition product *N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline were formed under selected reaction conditions. For a better exploitation of the catalytic activity in terms of increased activity and improved selectivity for the mono-addition product, the reaction parameters were optimized in terms of temperature, solvent, reactant mole ratio. Under optimized reaction conditions, montmorillonite clay K-10 showed a superior catalytic performance in the hydroamination of ethyl acrylate with aniline with a conversion of aniline to mono-addition product (almost 100% chemoselectivity) with a high rate constant 0.3414 min^{-1} compared to the reported protocols. The dependence of conversion of aniline over different types of montmorillonite clays (K-10, K-20, K-30, Al-Pillared clay and untreated clay) has also been discussed. The activities of clay for the hydroamination of different aromatic and aliphatic amines have also been investigated. Under harsh reaction conditions (increased temperature and long reaction time) small amounts of di-addition products were observed. The kinetics data has been interpreted using the initial rate approach model.

Keywords: Hydroamination; K-10 montmorillonite clay; α,β-Ethylenic compounds; Amines; Chemo-selective; *Anti*-Markovnikov addition product

1. Introduction

Catalysis is one of the fundamental pillars of green chemistry. The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances has lead to the design and application of catalysts and catalytic systems to achieve the dual goals of environmental protection and economic benefit [1]. The design of a general and efficient process for the hydroamination (hereafter indicated as HA) of alkenes would be a very important (economic) endeavor in both academia and industry for the production of amines.

Clays are hydrous silicates of aluminum, magnesium, potassium and iron. It has attracted extensive research interest in recent years as environmentally benign heterogeneous acid catalyst and support for a number of organic transformations [2–4]. The interesting properties of clays are their acidity, originating from the interlayer cations; (protons or polarizing cations, e.g. Al^{3+}), giving rise to strong acidity [5]. The surface acidity of natural clays (with Na^+ and $NH_4{}^+$ as cations) ranges from +1.5 to −3 (in Hammet scale). Acid treatment of the clay with mineral acid brings down Hammet to −6 to −8, which is between the value for concentrated HNO_3 (−5) and for concentrated H_2SO_4 (−12). Our interest in environmentally benign reaction conditions and in exploring the utility and development of clay as an inexpensive and readily available heterogeneous catalysts for hydroamination reactions [6], prompted us to explore different HA reactions using clay.

The addition of nitrogen compounds across carbon-carbon multiple bonds is an unsolved synthetically important problem [7] for both basic research and for the chemical industry. Hydroamination (C–N bond forming reaction) is of consider-

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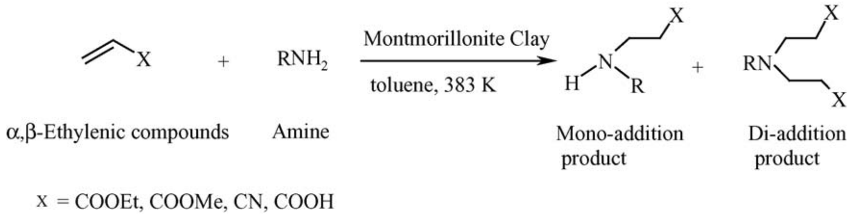


Scheme 1. Hydroamination of α,β-ethylenic compounds with amines.

able interest in organic synthesis as it utilizes readily available inexpensive starting materials and is 100% atom efficient. It is a very straightforward approach for the synthesis of substituted amines and their derivatives without any byproduct formation [8].

Although considerable progress has been made using metal complex catalysts under homogeneous conditions [9], an efficient heterogeneous and highly selective catalytic route is yet to be achieved. Recent advances have been made using lanthanide [10,11], early [12,13], and late transition metal catalysts for the hydroamination of alkynes and allenes; however, a general catalyst for the addition of amines to alkenes is still an unsolved problem. However, this transformation remains challenging, as only one process, the synthesis of t-butylamine from ammonia and isobutene, has so far been commercialized [14]. Our previous finding prompted us to investigate the further use of clays for HA reactions [15–17]. Despite some progress, the direct addition of N–H bonds on unsaturated CC bonds, an apparently simple reaction, still remains a challenging fundamental and economic task in the coming century.

The solid acid mediated HA of acrylates with amines (Scheme 1) is a simplistic approach towards the synthesis of amino acid derivatives that can be used in peptide analogues or as precursors to optically active amino alcohols, diamines and lactums. In the absence of the catalysts such reactions require very high temperatures and longer reaction times. The addition of various aliphatic amines with acrylates has been reported with different homogeneous and heterogeneous catalytic system [18–22]. Some of them have expressed the inability of aromatic amines to undergo hydroamination under their reaction conditions. To our surprise only Sugi and co-workers have reported the HA of acrylates with aromatic amines using zeolites as catalysts [23] recently. Even though the literature shows a broad spectrum of the reactions performed on the addition of α,β-ethylenic compounds to aliphatic amines, to the best of our knowledge the report on the selective HA (chemoselective, *anti*-Markovnikov addition) of aromatic amines with α,β-ethylenic compounds to mono-addition products using inexpensive heterogeneous catalysts is not available in the open literature.

Herein is presented, to the best of my knowledge, the first the chemo-selective HA of a series of aromatic and aliphatic amines with α,β-ethylenic compounds on commercially available clays as catalysts to afford only mono-addition *anti*-Markovnikov product (linear addition product).

2. Experimental

2.1. Materials

Montmorillonite clays were purchased from Fluka AG, Switzerland. Ethyl acrylate was purchased from Lancaster Chemicals, U.K. Methyl acrylate, acrylonitrile and acrylic acid were procured from Loba Chemicals, Mumbai. All the amines and toluene were purchased from S.D. Fine Chem. Ltd., Mumbai. All the chemicals were used as received. Toluene used in the reaction was distilled over sodium wire before use.

2.2. Characterization methods

The FT-IR spectra of the clays were recorded on a Shimadzu (model 8201 PC) spectro-photometer in the DRIFT (diffusive reflectance IR Fourier transform) mode in a frequency range 1750–1300 cm^{-1} using pyridine as a probe for acidity measurement. The sample was saturated with pyridine at room temperature and then heated to a temperature of 473 K for a period of 1 h. Nitrogen adsorption and desorption isotherms were measured at 77 K on a Quantachrome Autosorb 1 sorption analyzer. The samples were outgassed for 3 h at 473 K under vacuum in the degas port of the adsorption analyzer. Specific surface area was calculated using the BET model. The chemical composition of the samples was measured by atomic absorption spectrometer (AAS-Hitachi Model Z-8000). The composition of the clay catalysts was obtained by chemical analysis. About 0.5 g of the sample was weighed into a platinum crucible of known weight and heated to red-hot intensity using an electrical Bunsen burner for 3 h to remove moisture and volatile matter. The sample was then cooled and weighed. The sample was then treated with a mixture of 1 ml concentrated H_2SO_4 and 10 ml HF (40% solution) and evaporated to dryness. The treatment was repeated thrice. The residue was then dissolved in a 1:1 mixture of concentrated HCl and HNO_3 and diluted with 250 ml of water. The solution was analyzed for the different contents using AAS. Table 2 depicts the chemical analysis data of all the clays used in this study. The ^1H NMR and ^{13}C NMR spectrum of the isolated product was recorded after dissolution of the sample in $CDCl_3$ with TMS as reference (200 MHz).

2.3. Hydroamination

Anhydrous A.R. grade chemicals were used without further purification. The liquid phase HA of α,β-ethylenic com-

Table 1
Surface area and pore volume characteristics of clay catalysts

Catalyst	Surface area BET ($m^2\ g^{-1}$)	Pore volume ($cm^2\ g^{-1}$)	*I*(B)	*I*(L)	B/L ratio (*I*(B)/*I*(L))
K-10	240	0.93	0.14	0.20	0.70
K-20	240	1.05	0.14	0.23	0.61
K-30	330	1.23	0.13	0.05	2.60
Al-Pillared clay	250	–	0.07	0.29	0.24
Untreated clay	179	–	0.08	0.23	0.35

pounds with amines was carried out in a 50 mL two necked flask equipped with a nitrogen inlet for maintaining an inert atmosphere and an additional port with a septum for sample withdrawal. The temperature of the reaction vessel was maintained by placing the above assembly in thermostated oil bath. The reaction was carried out at selected reaction conditions, i.e. at 368 K with ethyl acrylate hereafter indicated as EA, to aniline molar ratio of 1 and with 10 wt.% (total reaction mixture) of catalyst. The catalysts were activated at 373 K in air for 15 h and cooled to room temperature prior to their use in the reaction. To the reaction mixture 1 ml toluene was added. The reaction mixture was magnetically stirred and heated to the required temperature under atmospheric pressure. Samples were withdrawn at regular intervals and analyzed using a gas chromatograph (Shimadzu 14B) equipped with a cross linked 5% diphenyl–95% dimethylpolysiloxane capillary column (30 m) and a flame ionization detector and the identity of the product was confirmed by GCMS (Shimadzu GCMS QP 5000) equipped with an identical column and a mass selective detector. Conversion was calculated based on amine.

The reaction mixture was then cooled and filtered to remove the catalyst and volatiles were removed by distillation. The product was separated by column chromatography using neutral alumina as stationary phase and (petroleum ether/ethyl acetate 95:5) as eluent. The single product was characterized by NMR, GC-MS, and FT-IR analysis which confirmed the product to be *N*-[2-(ethoxycarbonyl)ethyl]aniline.

Yield: 90%, ^{1}H NMR (200 MHz, $CDCl_3$): 7.21–7.06(m, 2H), 6.68–6.53(m, 3H), 5.21(s, 1H), 4.13–4.01(m, $J = 3.72$ Hz, 2H), 3.41–3.34(t, $J = 6.45$ Hz, 2H), 2.57–2.47(q, $J = 6.32$ Hz, 2H), 1.22–1.14(t, $J = 7.07$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 200 MHz,): $\delta = 147.73$ (C), 129.52 (CH), 129.34 (CH), 117.72 (CH), 113.10 (CH), 112.70 (CH), 60.64 (CH_2), 39.51(CH_2), 34.02 (CH_2), 14.24 (CH_3); FT-IR (neat): υ 3409, 2985, 1731, 1604, 1504, 1373, 1319, 1249, 1176, 1099, 1029, 1864, 748, 694. GCMS: *m*/*z* (relative intensity): 193 (11.83), 118 (2.55), 106 (100), 93 (2.46), 77 (11.26), 65 (6.57), 51 (7.79).

3. Results and discussion

3.1. Characterization of the catalysts

The properties of various grades of acid-treated clays of the K series (K-10, K-20, K-30) catalysts and Al-pillared clay used in this work are listed in Tables 1 and 2 The Lewis and Brönsted acidity of clays have been determined using pyridine as a probe molecule by monitoring the bands in the range of 1350–1600 cm^{-1} arising from its ring vibration modes [24,25]. The characteristic absorption band for Brönsted acidity appeared at 1540 cm^{-1} and that due to Lewis acidity appeared at 1450 cm^{-1}. However, in the case of solid acids, as important as the number and type of acid sites is their acid strength since this will be responsible for the extent to which a given bond in the reactant molecule will be polarized and, consequently, will determine the type of reaction that the solid acid will be able to catalyze.

The surface area, pore volume, intensity of Brönsted acidity and Lewis acidity peaks and B/L ratio determined using pyridine is given in the Table 1. Pore volume and BET surface area increased in the order untreated clay < K-10 < K-20 < Al-Pillared clay < K-30. Taking into account the surface area, the total amount acid sites per unit surface area decreased in the order K-10 ∼ K-20 > K-30.

3.2. Catalytic activity

The liquid phase HA of acrylates with amines was carried out using clay as catalysts and the reaction follows as shown in Scheme 1. The data on the catalytic performances of various aromatic amines with EA using clay (K-10) along with reaction conditions and the data on the catalytic activity are presented in Table 3. The HA of EA with various aromatic amines mainly gave excellent chemoselectivity for mono-addition product. All reactions were exclusively regioselective giving the product of *anti*-Markovnikov addition of amine to CC double bonds. The

Table 2
Chemical analysis of clay catalysts

Catalyst	Chemical analysis (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Loss on ignition	Total
K-10	73.0	14.0	2.7	0.2	1.1	0.6	1.9	6.0	99.5
K-20	75.0	12.5	2.4	0.3	1.2	0.3	1.5	6.3	99.5
K-30	80.0	10.0	1.8	0.2	1.0	0.3	0.5	6.0	99.8
Al-Pillared clay	69.8	24.5	1.8	0.2	2.5	0.3	0.9	–	100
Untreated clay		15.1	3.2	–	2.1	–	–	–	–

Table 3
Effect of the presence substituents on benzene ring of aniline in the HA reaction with EA over K-10 at a reaction temperature of 383 K

Aromatic amine	Time (h)	Conversion (%)[*]	*Anti*-Markovnikov product selectivity (%)[#]		Rate constant, k_1 ($\times 10^{-4}$ min^{-1})
			Mono-addition	Di-addition	
Aniline	6	85	97	2.8	52.60
	12	94.5	95.1[1a]	4.8[1b]	40.18
4-Bromoaniline	6	60	100	0	25.42
	12	82	96.5[2a]	3.5[2b]	23.72
p-Anisidine	6	79	98.6	1.39	43.35
	12	94.6	94.3[3a]	5.6[3b]	40.53
2,4-Xylidene	6	60.9	96.7	3.28	26.08
	12	82.3	96.8[4a]	3.1[4b]	23.97
o-Nitroaniline	12	Nil	Nil	Nil	Nil
p-Isopropylaniline	6	61.5	98.2	1.6	26.43
	12	74.5	96.9[5a]	2.8[5b]	18.92
o-Chloroaniline	6	26	99.7	0.3	6.93
	12	40	99.2[6a]	0.79[6b]	
o-Toluidene	6	39.5	99.8	0.2	13.95
	12	60	98[7a]	2[7b]	12.72
p-Ethylaniline	6	70	97	2.8	33.43
	12	90	96[8a]	4[8b]	31.97
N-Methylaniline	6	59	99.2	0.8	24.77
	12	80	97[9a]	3[9b]	22.35
1-Naphthylamine	6	16	100	0	8.52
	12	32	99.5[10a]	0.5[10b]	5.35
2,4,6-Trimethylaniline	6	10	100	0	3.00
	12	15	100[11a]	0[11b]	2.25

Amine to EA ratio = 1; amount of catalyst = 0.3 g (10 wt.% of total reaction mixture).

[1a] *N*-[2-(ethoxycarbonyl)ethyl]aniline (mono-addition product).

[2a] 4-bromo-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[3a] 4-methoxy-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[4a] 2,4-dimethyl-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[5a] 4-isopropyl-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[6a] 2-chloro-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[7a] 2-methyl-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[8a] 4-ethyl-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[9a] *N*-methyl-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[10a] *N*-[2-(ethoxycarbonyl)ethyl]-1-naphthyl amine.

[11a] 2,4,6-trimethyl-*N*-[2-(ethoxycarbonyl)ethyl]aniline.

[1b] *N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[2b] 4-bromo-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[3b] 4-methoxy-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[4b] 2,4-dimethyl-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[5b] 4-isopropyl-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[6b] 2-chloro-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[7b] 2-methyl-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[8b] 4-ethyl-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[9b] *N*-methyl-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[10b] *N*,*N*-bis[2-(ethoxycarbonyl)ethyl]-1-naphthyl amine.

[11b] 2,4,6-trimethyl-*N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.

[*] Conversion determined by GC analysis with respect to aniline.

[#] Selectivity was determined by GC analysis.

high chemo selectivity in the HA reaction could be used for the synthesis of precursors for amino acids. The results indicate that the aniline derivatives that have electron-donating groups at the *ortho* and *para* positions reacted smoothly with EA to give corresponding HA products (Table 3). Strongly electron-donating substituents having methoxy group gave slightly higher conversion as compared to methyl groups in the same positions (Table 3). In contrast, the reaction of amines with electron withdrawing substituents like nitro group did not undergo HA reaction. However, 1-Naphthylamine reacted sluggishly with EA to give the HA product (32%) which could be because of the bulky nature of amine. On the other hand, in the course of

Table 4
HA of aliphatic amines with EA over K-10 at room temperature

Aliphatic Amine	Conversion (%)[a]	*Anti*-Markovnikov product selectivity (%)[b]	
		Mono-addition	Di-addition
Morpholine	97	100	0
Piperidne	97	100	0
di-Propylamine	96	100	0
n-Propylamine	96	92.16	7.8
Benzylamine	95	99.9	0.1

Reaction conditions: amine to EA ratio = 1; amount of catalyst = 0.1 g (5 wt.% of total reaction mixture).

[a] Conversion determined by GC analysis with respect to aniline.

[b] Selectivity was determined by GC analysis, temperature = 298 K, time = 1 h.

investigations we found that EA reacted with *N*-methylaniline to yield 80% mono-addition product, which demonstrates the feasibility of secondary amines to undergo this reaction. However, sterically hindered amines like 2,4,6-trimethyl aniline gave less yield for corresponding HA product indicating that bulkier groups around NH_2 affect the activity of amines (Table 3).

Encouraged by the results with aromatic amines we turned our attention to aliphatic amines and as we expected they were more reactive for addition with α,β-ethylenic compounds compared to the aromatic amines. Table 4 summarizes the results obtained by the HA of EA with aliphatic amines. Interestingly, under the selected reaction conditions using 5 wt.% of K-10, amine/acrylate molar ratio of 1 and in the absence of any solvent, all the aliphatic amines gave excellent conversion for HA product at room temperature. Morpholine and piperidine reacted with EA to yield 97% HA product over a period of 1 h. Primary aliphatic amine (*n*-propylamine) however, gave a mixture of mono and di-addition product with a selectivity of 92% for mono-addition and 8% to di-addition product over a period of 1 h. On the contrary reaction of benzylamine with EA in the presence of clay showed high conversion of amine and excellent chemo-selectivity for mono-addition product (Table 4).

A control experiment was carried out without adding any catalysts at a temperature of 368 K. There was only 2% reaction without catalyst. The activity (in terms of conversion and moreover chemoselectivity) of clay-K-10 was superior to that of Hβ. (Table 5). In addition K-10 exhibited excellent characteristic of being recyclable simply by filtration followed by washing of the catalyst with methanol. To further explore the reaction we have carried out the reaction of aniline with different α,β-ethylenic compounds like methyl acrylate, acrylonitrile, and acrylic acid with 10 wt.% K-10, at 368 K and aniline/acrylate molar ratio of 1. The conversion and product distributions for the HA of different α,β-ethylenic compounds are given in Table 5. Under the selected reaction condition ethyl acrylate with aniline gave maximum conversion of 49.5% over a period of 2 h.

The conversion of aniline in the HA with EA over different types of montmorillonite clays (K-10, K-20, K-30, untreated clay, Al-Pillared clay) at 368 K is shown in Table 5. Aniline reacted with EA to yield only *anti*-Markovnikov adduct *N*-[2-(ethoxycarbonyl)ethyl]aniline (mono-addition product) (**1a**) (Scheme 2). No Markovnikov adduct (*N*-[1-(ethoxycarbonyl)ethyl]aniline and double addition product *N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline (**1b**) were formed. For all the catalysts, the aniline conversion increased linearly with time up to a conversion of 70–95%. K-10 clay gave the highest conversion (49.5%) with respect to aniline over a period of 2 h under the selected reaction conditions (Table 5) with a rate constant of 56.90×10^{-4} min^{-1}. Under the optimized reaction condition K-10 displayed exceptionally high catalytic activity and gave the highest conversion of 85% over a period of 12 h. The apparent rate constants for the different catalyst declines in the following order: K-10 > K-20 > K-30 > untreated

Table 5
Properties of the catalysts in the hydroamination of aniline using ethyl acrylate at 368 K

Catalyst	Conversion (%)[a]	Selectivity (%)[b]		Rate constant, k_1 ($\times 10^{-4}$ min^{-1})
		(Mono-addition)[c]	(Di-addition)[d]	
No catalyst	2[e]	100	–	–
Hβ	39	100	–	–
K-10[f]	49.5	100	0	56.90
K-20[f]	37.5	99.83	0.13	39.12
K-30[f]	32.21	100	0	25.83
Al-Pillared clay[f]	26.44	99.84	0.13	25.57
Untreated clay	26.7	100	0	25.85
HA of aniline using different types of α,β-ethylenic compounds using K-10[f] at 368 K				
Ethyl acrylate	49.5	100	0	56.90
Methyl acrylate	31.1	100	0	31.00
Acrylonitrile	7.61	100	0	65.83
Acrylic acid	37	100	0	38.50

Reaction conditions: aniline:EA = 1(molar ratio).

[a] Conversion determined by GC analysis with respect to aniline.

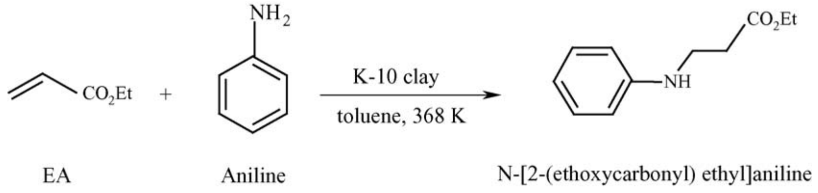
[b] Selectivity was determined by GC analysis.

[c] *N*-[2-(ethoxycarbonyl)ethyl]aniline (mono-addition product).

[d] *N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline, time = 2 h.

[e] Time = 12 h.

[f] Amount of catalyst: 0.3 g (dried at 373 K for 15 h before use).



Scheme 2. Hydroamination of ethyl acrylate with aniline.

clay > Al-Pillared clay. The apparent rate constant for HA reaction over K-10 is $56.90 \times 10^{-4}\,\mathrm{min}^{-1}$ that of K-20 is $39.12 \times 10^{-4}\,\mathrm{min}^{-1}$ while Al-Pillared clay registered an apparent rate constant of only $25.57 \times 10^{-4}\,\mathrm{min}^{-1}$.

The dependence of reaction temperature on conversion and product selectivities was studied in the range of 358–383 K as a function of time and the results are presented in Fig. 1(a–c). The results show that the performance of the catalyst increases substantially with increasing reaction temperature. Fig. 1(a–c) and Table 6 illustrates that with increase in temperature, aniline conversion increases linearly with time up to 95% (constant k_1 increased from $18.85 \times 10^{-4}\,\mathrm{min}^{-1}$ at 358 K to $92.63 \times 10^{-4}\,\mathrm{min}^{-1}$ at 383 K). The rate constants calculated at different temperatures are presented in Table 6. It is seen that k_1 increases with increase in temperature. The activation energy for HA of ethyl acrylate with aniline was calculated from the Arrhenius graph and was found to be 24.7 kcal mol^{-1}.

It is seen that at reaction temperature up to 368 K, the selectivity for product **1a** is 100% for a period of 6 h (Fig. 1(b)). After 6 h very small amount of product **1b** starts forming and its selectivity increases up to 2% over a period of 12 h (Fig. 1(c)). However, it is significant to note that on increasing the reaction temperature to 383 K product **1b** starts forming after 50 min and the selectivity for product **1b** increased and that of product **1a** decreased with time (Fig. 1(b and c)). It is noteworthy that the reaction is feasible even at 358 K and the selectivity towards linear mono addition product is significantly better at lower temperature (Fig. 1(b)).

The effect of catalyst weight percent on the conversion and product selectivity was also studied between 5–10 wt.% of the total reaction mixture over clay K-10 at a reaction temperature of 368 K and with aniline to EA molar ratio of 1. An increase in catalyst loading from 5 to 10 wt.% is associated with a decrease in reaction time from 120 to 70 min for a conversion of 50% and a decrease in selectivity for **1a** from 100% to 96% over a period of 2 h.

The effect of the stoichiometric ratios of aniline with EA on conversion and product selectivity was also studied over clay K-10 catalyst at a reaction temperature of 368 K. The molar ratio of aniline with EA was varied in the range of 1–4 and the product distribution at various aniline to EA ratios is shown in Table 7. It was found that both activity and selectivity were influenced drastically by the change of reactant molar ratio. The results show that the conversion of aniline increases from 49.5 to 67.1% on varying the molar ratio from 1 to 4 over a period of 2 h. It can also be seen from Table 6 that the selectivity for **1b** increases and

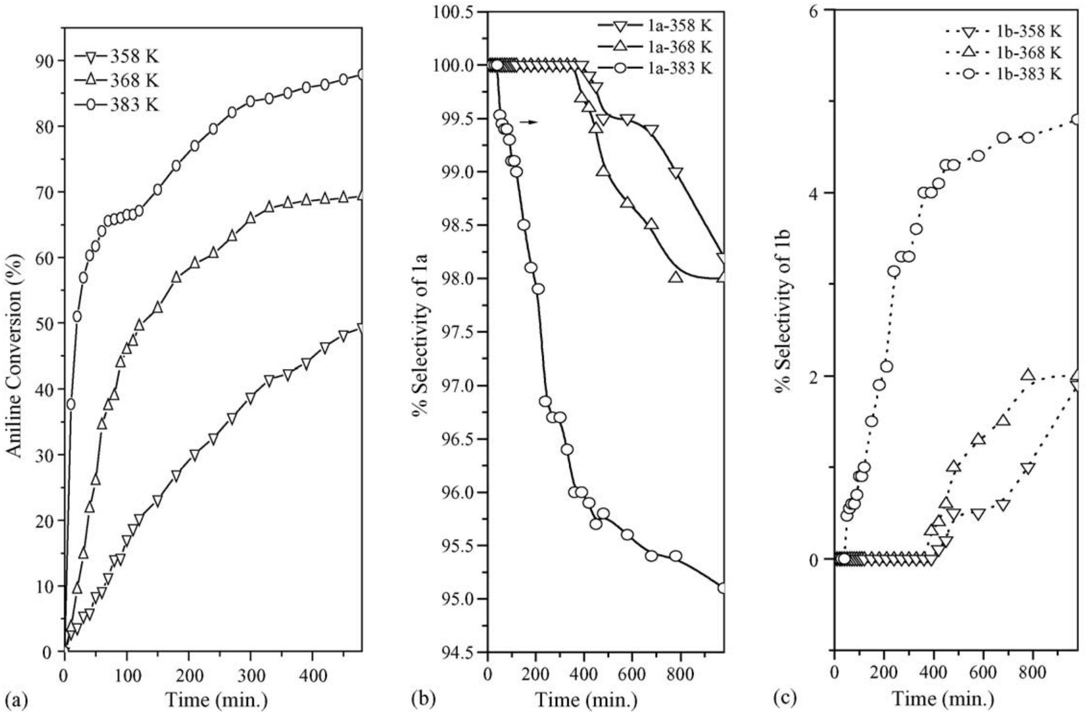


Fig. 1. Dependence of reaction temperature on the conversion of aniline and selectivity of **1a** and **1b** as a function of time in the HA with EA with reaction over clay K-10 at (▼) 358, (▲) 368, and (■) 383.

Table 6
Influence of reaction temperature on the catalytic activity of aniline in the HA with EA for HA reaction over clay K-10 catalyst

Temperature (K)	Conversion (%)[a]	Selectivity (%)[b]		Rate constant, k_1 ($\times 10^{-4}$ min^{-1})
		Mono-addition[c]	Mono-addition[d]	
358	20.26	100	0	18.85
368	49.50	100	0	56.90
378	58.40	99.5	0.5	73.28
383	67.10	99	1	92.63
Regeneration of clay K-10 HA of aniline using ethyl acrylate at 368 K				
Fresh catalyst	49.50	100	0	–
First recycle	48.4	100	0	–
Second recycle	48.9	100	0	–
Third recycle	48	100	0	–

Reaction conditions: aniline:EA = 1 (molar ratio), amount of catalyst = 0.3 g (10 wt.% of total reaction mixture).
[a] Conversion determined by GC analysis with respect to aniline.
[b] Selectivity was determined by GC analysis.
[c] *N*-[2-(ethoxycarbonyl)ethyl]aniline (mono-addition product).
[d] *N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline, Time = 2 h.

that of **1a** reduces with increasing EA concentration. Availability of excess of EA leads to the addition of another molecule of EA with **1a** to form double addition product.

Under the optimized condition, the HA of EA with aniline was carried out with K-10, 0.3 g (10 wt.% of total reaction mixture), aniline/EA molar ratio 1 at 368 K for 12 h to see the effect aniline conversion and products selectivity as a function of time (Fig. 1(a)). With increase in time, conversion of aniline increases to a maximum of 85% after 12 h with selectivity for **1a** = 98%, and **1b** = 2%.

Recycling of the clay K-10 was attempted at 368 K by separating the catalysts by filtration followed by washing with toluene and refluxing in methanol (methanol has great affinity to clay surface, hence used for regeneration of the catalyst) for 2 h to remove products remaining from the first run and drying in oven at 373 K for 15 h in air. The catalyst was used for HA of EA with aniline under selected reaction conditions. The extent of catalyst regeneration was studied for three consecutive runs by refluxing the catalysts with methanol each time followed by drying. Same procedure is repeated for second cycle and the data on the conversion of amine are presented in Table 6. From the result it is concluded that there is no appreciable loss in the catalytic activity and product selectivities in the two cycles and catalyst could be reused. As shown in the Table 6, percentage conversion for amine was maintained after recycling three times. The conversions of the amine were 48.4%, 48.9% and 48% for the first reuse after methanol wash, second reuse after methanol wash, and third reuse after methanol wash, respectively and with 100% selectivity for mono-addition product. This implies that deactivation of K-10 did not occur with repeated use of the catalyst and this mode of regeneration. From the result it is concluded that there is no appreciable loss in the catalytic activity and product selectivities in the two cycles and catalyst could be reused.

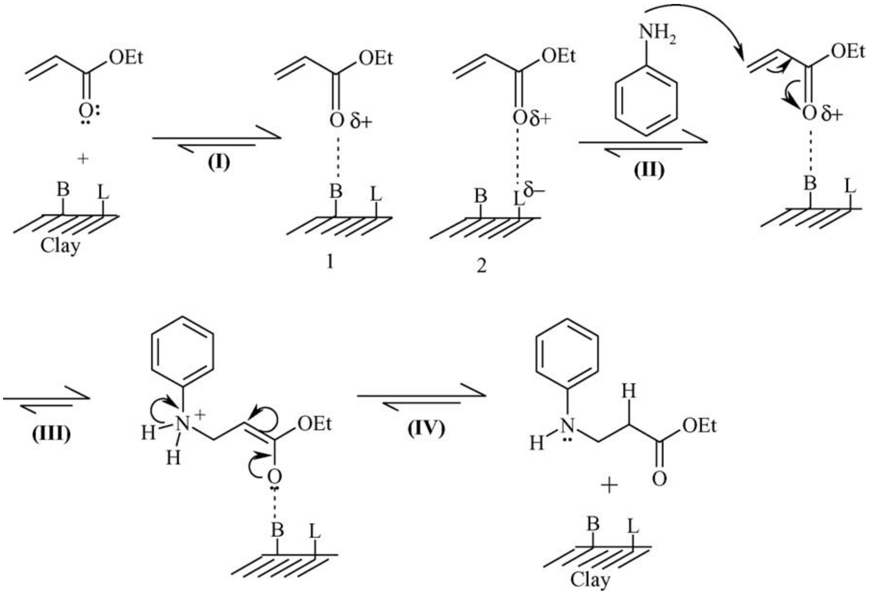
In order to check the leaching into the reaction mixture, the reaction was carried out for 2 h under selected reaction conditions using fresh K-10 clay activated at 373 K. The reaction was stopped and catalyst was separated by filtration and then the filtrate was stirred for 1 h under same reaction conditions. It was found that in the absence of the catalyst, there was no further increase in the conversion of amine, which indicated the absence of leaching of any acid into the reaction mixture. This observation confirmed that the reaction was catalyzed heterogeneously.

The kinetic investigations results revealed a first order reaction rate dependence with respect to amine concentrations. The standard equations for a first-order series reaction $C_{\mathrm{A}}/C_{\mathrm{Ao}} = \mathrm{e}_1^{-K}t$ has been used for the determination of rate constant, where C_{A} and C_{Ao} are the concentration of aniline at initial time and at time *t*, respectively. From the plot of ln(rate) versus 1000/*T*, by applying the initial rate approach model, the thermodynamic parameters were evaluated to be $E_{\mathrm{a}} = 24.7$ kcal mol^{-1}, $\Delta H^{\#} = 23.9$ kcal mol^{-1}, $\Delta S^{\#} = -12.2$ cal deg^{-1} mol^{-1} and $\Delta G^{\#} = 28.5$ kcal mol^{-1}.

Table 7
Influence of stoichiometric ratio of aniline with EA for HA reaction over clay K-10 catalyst at a reaction temperature of 368 K

Aniline to EA molar ratio	Conversion (%)[a]	Selectivity (%)[b]		Rate constant, k_1 ($\times 10^{-4}$ min^{-1})
		Mono-addition[c]	Di-addition[d]	
1:1	49.5	100	0	56.90
1:2	53.58	99.6	0.35	64.17
1:4	67.1	98.36	1.5	92.77

Reaction conditions: Amount of catalyst = 0.3 g (10 wt.% of total reaction mixture, Time = 2 h.
[a] Conversion determined by GC analysis with respect to aniline.
[b] Selectivity was determined by GC analysis.
[c] *N*-[2-(ethoxycarbonyl)ethyl]aniline (mono-addition product).
[d] *N*,*N*-bis[2-(ethoxycarbonyl)ethyl]aniline.



Scheme 3. Proposed reaction mechanism for the hydroamination of EA with aniline by clay.

3.3. *Proposed reaction mechanism*

The data obtained from the kinetic experiments and literature suggests the mechanism shown in Scheme 3 for the intermolecular hydroamination of EA with anilines using clay as catalyst. The carbonyl group of EA combines with the electron deficient centers in the acidic clay (either Brönsted or Lewis acid sites), which makes β-carbon electron deficient, which attacks the electron rich center in the amine (Scheme 3(I and II)). This is followed by 1,3-proton shift in step III with the release of *anti*-Markovnikov product in step IV to regenerate the acidic clay.

4. Conclusions

In summary a successful application of a very inexpensive, effective and recyclable catalysts for the hydroamination of different aromatic and aliphatic amines have been demonstrated. The influence of various reaction parameters such as reaction temperature, time, reactant feed ratio and catalyst amount and the effect of substituents on the activity and selectivity of K-10 have been discussed. Montmorillonite clay K-10 showed a superior catalytic performance in the HA of EA with aniline with a conversion of aniline to mono-addition product with a very high rate constant compared to the reported protocols. Interestingly, use of K-10 resulted in quantitative conversion of aniline with a high rate constant of $56.90 \times 10^{-4}\ \mathrm{min}^{-1}$ under the optimized reaction conditions.

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