

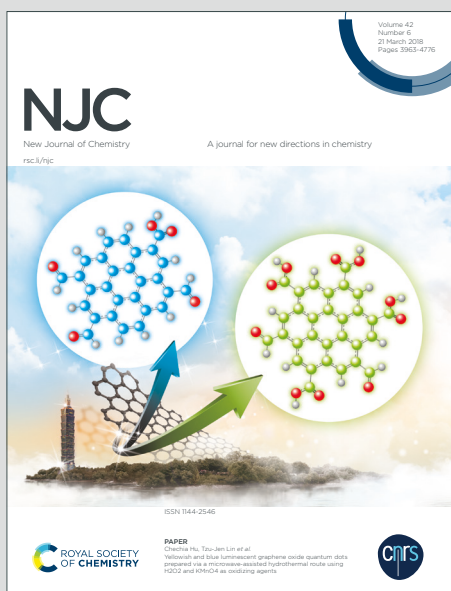
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An efficient one-pot synthesis of industrially valuable primary organic carbamates and N-substituted ureas by reusable Merrifield anchored iron(II)-anthra catalyst [Fe^{II}(Anthra-Merf)] using urea as a sustainable carbonylation source

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Abstract

An efficient synthesis of primary carbamates and N-substituted ureas are explored with a newly developed heterogeneous polymer supported iron catalyst in the presence of a sustainable carbonylation source. The Merrifield anchored iron(II)-anthra catalyst [Fe^{II}(Anthra-Merf)] was synthesized by functionalization of Merrifield polymer followed by grafting of iron metal. The catalyst [Fe^{II}(Anthra-Merf)] was characterized by several techniques like SEM, EDAX, TGA, PXRD, XPS, FTIR, CHN, AAS and UV-Vis analysis. The designed polymer embedded [Fe^{II}(Anthra-Merf)] complex is a remarkably successful catalyst for the synthesis of primary organic carbamates and N-substituted ureas by using safe carbonylation agent urea with different derivatives of alcohols and amines respectively. The reported catalyst is a potential candidate towards contributing a satisfactory yield of isolated products under suitable reaction conditions. The catalyst is recyclable and almost non-leaching in nature after six runs with an insignificant drop in catalytic activity. Thus we found an economical and viable catalyst [Fe^{II}(Anthra-Merf)] for primary carbamates and N-substituted ureas synthesis under moderate reaction conditions.

Introduction

Designing of new catalytic pathways for the production of fine chemicals under industrial approach is very urgent due to the high production cost of the classical methods.¹⁻⁵ The traditional catalysts are not much suitable to utilize in the industrial field due to their hazardous nature, production of unnecessary bi-products and non-reusability in further reaction cycle.^{6,7} Taking into consideration these points, new viable, inexpensive and cost-effective green catalysts have been applied in place of available traditional catalysts which are harsh in nature. Transition metal complex catalysts are extensively used in many organic syntheses as well as in industry for bulk production of organic products. A lot of them are hazardous for environment due to their toxic nature. So, their uses are restricted in the present decade. But transition metals are very important and highly demanding for catalyst preparation because they have empty 'd' orbital. In this regard it is to be mentioned that iron complexes binding with a solid support are widely acceptable in heterogeneous catalysis for their stability, non-toxicity, low capital cost and easy synthetic routes^{8,9} than the other transition metals. In addition to that iron salts are capable of binding with several polymeric systems easily and have proved their effectiveness in the scope of catalysis. The polymeric matrix present within the iron catalysts makes them highly reusable and thermally stable.⁹

Among the different fine chemicals, organic carbamates are very important due to their uses during the synthesis of insecticides like carbofuran and carbaryl. Iodopropynyl butylcarbamate is widely

used as paint and wood preservatives as well as in the production of cosmetics.¹⁰ Different nerve agents like EA-3990, polyurethanes, preservatives, stabilizing agent, etc. are manufactured from carbamates.¹¹⁻¹⁶ Additionally, versatile utilization of carbamates are reported in human pharmacotherapy like anxiolytic designing, rivastigmine and muscle relaxant drugs.^{17,18} Besides this carbamates are also present in many biologically active natural products. In synthetic chemistry, carbamates are frequently applied for the protection of -NH₂ groups throughout different organic transformation reactions.¹⁹ The enzymes belongs to plant with lysine residue can directly fix CO₂ in Calvin cycle in the presence of Mg²⁺ ion producing lysine carbamate which is very important for the growth of the plants.

Mainly organic carbamates are synthesized by fixation of CO₂ using different organic substrates like primary/secondary amines, alcohols, alkyl halide and by carbonylation reaction of nitro compounds. Previously a number of methodologies are revealed for primary carbamate synthesis using acid chloride, carbon monoxide involving isocyanate intermediates by different research groups.²⁰⁻²⁵ Several research groups have synthesized primary carbamates using alcohol and cyanate salts in solvent free conditions.^{26,27} An earlier work explored that a Lewis acid catalyst Zn(OAc)₂·2H₂O effectively synthesized carbamates using renewable 4-propylcatechol carbonate as a C1 reactant.²⁸ Another works from different groups reported simplistic synthesis of methyl carbamates (MC) from a combination of urea and methanol in presence of specific metal based fluorapatite catalyst.²⁹ Zhang et. al explored a straightforward synthesis of carbamates from amine, silicate ester, and carbon dioxide in presence of alkali metal salt K₂CO₃ as a Lewis acid catalyst. This method applied the high pressure CO₂ and high temperature during synthesis of carbamates and the used catalyst

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could not be recycled.³⁰ In some case the utilization of CO₂ fixation was helpful in the production of organic carbamates from the coupling reaction of different amines and alkyl halide.³¹ But all the reported strategies are much difficult to employ in the practical scenario because most of them lead to the formation of poisonous and hazardous byproducts and involvement of homogeneous catalyst or high CO₂ pressure. In order to eliminate these boundaries, an innovative green catalytic pathway is necessary for primary carbamates production. Recently Beller et al. studied an eco-friendly Lewis-acidic and homogeneous FeBr₂ catalyzed carbamoylation reaction of urea with alcohols bear for the synthesis of N-unsubstituted (primary) carbamates. The mono and di-substituted ureas were also synthesized via selective transamidation reaction by using amines as nucleophile.³² But here utilization of homogeneous catalyst leads to the recyclability and reusability problems. Motivated from the above report we have designed a heterogeneous polymer supported [Fe^{II}(Antra-Merf)] catalyst which can produced primary carbamates through carbamoylation reaction of urea with alcohols under mild conditions.

In accordance with the enormous demands of primary carbamates, the derivatives of N-substituted urea are consistently very important because of their versatile uses in numerous fields viz. the development of sensors,³³ pesticides, herbicides,³⁴ ionic liquids,³⁵ metal-organic frameworks,³⁶ etc. In recent times the researchers are continuously providing their endeavor to explore green methodologies for synthesizing biologically active urea derivatives. N-substituted ureas are one such group of urea which can be produced by nucleophilic substitution reactions of urea with an amine. The process is associated under high activation energy and consequently, a lucid, suitable specific catalytic system is essential to synthesize these derivatives. Different ionic liquid like CsOH/BMI⁺Cl⁻ and homogeneous catalysts, for example, TBD are developed by some research groups like Roberto Ballini et al.,³⁸ for this purpose but the industrial scopes are limited since their excessive production cost and non-reusability of the catalytic material. The development of economic, recyclable and thermally stable heterogeneous catalytic system is esteemed for the synthesis of different substituted urea derivatives.

In organic synthesis, urea is often used as a source of carbonyl in primary carbamate as well as in a variety of N-substituted urea derivatives.³⁹ Preference of urea rather than using molecular CO₂ is attributed to the fact of several problems regarding activating molecular CO₂, requirement of high CO₂ pressure and even less solubility⁴⁰ in the reaction medium.

In the present report we have described a straightforward route of Merrifield supported heterogeneous iron(II) catalyzed substitution reaction in which urea reacts with hydroxy- and amino- based nucleophiles for primary carbamates and unsymmetrical ureas synthesis. Previously reported metal-based catalysts require the application of high reaction temperature and also long reaction time with a low yield of isolated products. In this prospect, we have addressed a heterogeneous polymer supported iron catalyst to resolve the issues. The advantages of this report are the proposed reaction pathway is simple, benign and less harmful with regard to the generation of non-toxic byproducts during the course of the reaction. Moreover the catalyst is recyclable and almost non-leaching in nature after six runs with an insignificant drop in catalytic activity.

Experimental

Materials and reagents

Chloromethylated polystyrene (5.5 % crosslinked) was purchased from Sigma-Aldrich. 4-hydroxy benzaldehyde, anthranilic acid, ferrous chloride, 1,4-dioxane, dimethyl formamide (DMF) and various amine derivatives were purchased from Merck. Urea, ethyl acetate and all the derivatives of alcohols and amines were acquired from Alfa-aesar and used without any further processing.

Physical and spectroscopic instrument

FTIR spectra of Merrifield supported ligand and also its catalyst was recorded by placing KBr disc in a Perkin Elmer FTIR 783 spectrophotometer. The Shimadzu UV-2401PC doubled beam spectrophotometer associated with an integrating sphere counterpart was used for monitoring the UV-Vis spectra of solid [Fe^{II}(Antra-Merf)] catalyst. The TGA-DTA study of the ligand and its corresponding complex (catalyst) was performed with the help of a Mettler Toledo TGA/DSC 2 STARE instrument. ZEISS EVO40, England is a scanning electron microscope instrument which facilitates to observe the surface morphology with EDAX facility for ligand and catalyst. Percentage of iron content in the iron loaded catalyst was confirmed by using atomic absorption spectrophotometer, Varian AA240. X-ray photoelectron spectroscopy was executed by using an Omicron Nanotechnology GmbH XPS machine.

Preparation of catalyst, [Fe^{II}(Antra-Merf)]

Chloromethylated polystyrene supported iron(II)-antra catalyst was prepared by following the pathway and was schematically represented below (Scheme 1).

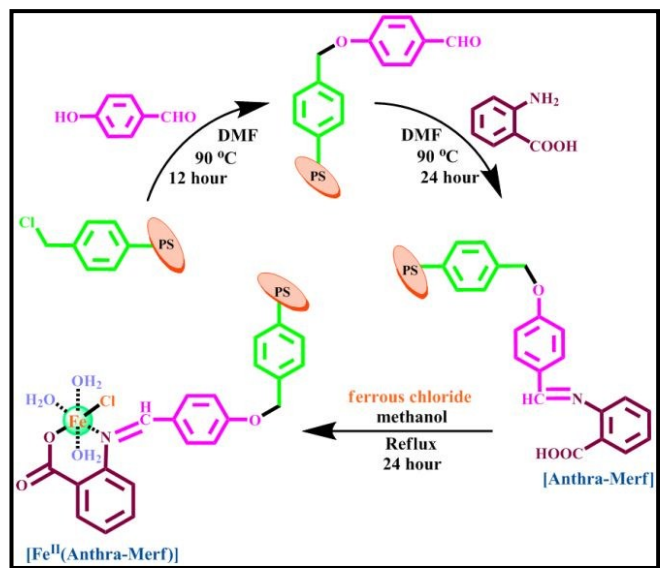
Chloromethylated polystyrene (500 mg) was stirred with 10 mL of DMF under 300 rpm followed by drop-wise addition of 4-hydroxybenzaldehyde (2 mmol) in 5 mL of DMF. Then the rb was kept for constant stirring by maintaining the same rpm up to 12 hours at 90 °C. After the specific time, the product was collected through filtration, then washed several times with methanol and dried out under vacuum condition. Subsequent preparation of chloromethylated polystyrene supported anthranilic acid ligand was synthesized by taking 700 mg of previously prepared product in a 250 mL rb and then gently stirred with DMF (20 mL). To that mixture, 500 mg of anthranilic acid was added after 5 min and the reaction bath was fixed at 90 °C temperature. The desired product was collected after 1 day through a simple filtration process and washed for 3-4 times with methanol. Later, the prepared material was used for [Fe^{II}(Antra-Merf)] catalyst preparation after drying it under vacuum.

The catalyst was prepared by taking the freshly generated ligand (500 mg) in a 100 mL rb and mixed up thoroughly with 10 mL of methanol under 500 rpm stirring condition. After 5 min, 50 mg of FeCl₂ was added to the continuously stirred solution and the temperature was set up at 90 °C under N₂ atmosphere. After 24 hours, the product was collected and methanol is used for washing exclusively. The catalyst was completely dried under vacuum so that any undesired volatile substance may not interrupt in the reaction medium.

General procedure for the synthesis of primary carbamates using iron (II) catalyst [Fe^{II}(Antra-Merf)]

In a 50 mL rb, 3.5 mL 1,4-dioxane was taken and mixed thoroughly with 2 mmol (0.12 g) of urea and 3 mmol of alcohol in presence of 0.02 g Fe^{II}(Antra-Merf) catalyst. After that, the rb was fixed with a condenser and 120 °C temperature was maintained by a oil bath

with constant stirring. After covering 6.5 h the reaction mixture was placed for cooling. Then the fresh organic portion was collected through subsequent workup with ethyl acetate (3×20 mL) and water, after centrifugation to remove the catalyst. Then the organic part poured into a sodium sulphate containing conical flask and swirled continuously to remove the residual water. Later the filtrate part was taken through filtration and concentrated under vacuum. The product was analyzed by ¹HNMR spectroscopy and FTIR spectroscopy (supporting information) after purification by column chromatography.



Scheme 1 Synthesis of Merrifield anchored iron(II)-anthra catalyst [Fe^{II}(Anthra-Merf)].

General procedure for the synthesis of N-substituted ureas from various substituted amines using [Fe^{II}(Anthra-Merf)] catalyst

Substituted unsymmetrical ureas were synthesized by following the described process. 2 mmol (0.12 g) of urea was stirred with 3 mL of dioxane which contains 2 mmol of amines in a 50 mL rb. Then stirring was sustained for 8 h in the presence of 0.025 g of Fe^{II}(Anthra-Merf) catalyst at 100 °C in an oil bath. After settled down into room temperature the mixture was separated from catalyst through a centrifugation process. The filtrate part was worked up with ethyl acetate and water for 3 times to remove the undesired substances. After completion, the remaining water was removed by passing through a sodium sulphate layer. Product was concentrated, purified by column chromatography and confirmed by ¹HNMR and FTIR spectroscopy (supporting information).

Results and discussion

Merrifield anchored iron(II)-anthra catalyst [Fe^{II}(Anthra-Merf)] was synthesized through three step procedure. In first step chloromethylated polystyrene was modified by 4-hydroxybenzaldehyde and then the material was Schiff based with anthranilic acid and finally FeCl₂ solution was used for complexation in order to form our designed catalyst.

Characterization of catalyst

The synthesized Merrifield anchored anthranilic acid ligand [Anthra-Merf] and its corresponding iron catalyst [Fe^{II}(Anthra-Merf)] has few restrictions to explore and characterize their physicochemical

properties due to insoluble nature of the materials in most of the common solvents. The prepared polymeric materials were finely characterized through SEM, EDAX, TGA-DTA, PXRD, XPS, FTIR, UV-Vis spectral analysis. The structure of ligand and catalyst was predicted through C,H,N analysis and the loading amount of Fe metal into the ligand was determined by atomic absorption spectroscopy (AAS).

Scanning electron micrographs (FE-SEM) analysis of [Anthra-Merf] ligand and [Fe^{II}(Anthra-Merf)] catalyst

Scanning electron microscopic analysis is conducted to study the external morphology of heterogeneous catalyst in the range of nm to μm scale by capturing a 2D surface image of the material. At first the sample was spread flimsily over a conductive carbon adhesive tape and then gold coating of the material was done which is important to prevent charging of the material. It also amplifies the number of secondary electrons to get a clear image. Scanning electron microscopic analysis (SEM) was detected for both [Anthra-Merf] ligand and [Fe^{II}(Anthra-Merf)] catalyst and represented in Fig. 1(A) and 1(B) respectively. The SEM analysis accounts for the morphological change at the surface of the [Anthra-Merf] ligand, when a metal (Fe) is incorporated onto free ligand. The attachment of iron on the polymeric ligand [Anthra-Merf] has converted the polymeric surface roughening to some extent.

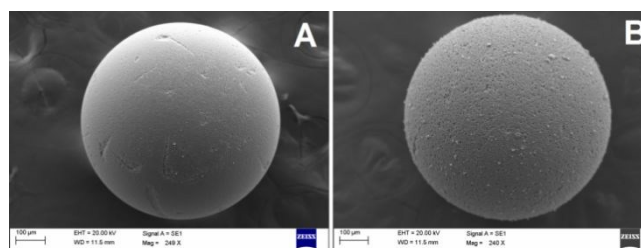


Fig. 1 SEM images of (A) [Anthra-Merf] ligand (B) [Fe^{II}(Anthra-Merf)] catalyst.

Energy dispersive X-ray analyses (EDAX) of [Anthra-Merf] ligand and [Fe^{II}(Anthra-Merf)] catalyst

The EDAX analysis (Fig. 2) is the optimal process to explore the elements present in ligand and along with the evidence of metal attached on the periphery of the ligand. EDAX facility is mounted with the SEM instrument and the sample preparation procedure is same as performed during SEM analysis. The rising of secondary electrons occurs after collision with the incident X-ray which has a fingerprint of each particular element that is present in the analyzed material. This fingerprint depends on the atomic number. EDAX facility has the authority to detect the individual fingerprint rays. By this way the different elements which are truly present are analyzed. Incorporation of metal iron with the Merrifield anchored anthranilic acid ligand transformed the structure from flat to irregular surface probably due to the interaction of the metal with the ligand (Fig. 1). The presence of Fe, Cl, O, and C elements are confirmed through EDAX analysis providing the presence of Fe metal content in the catalyst [Fe^{II}(Anthra-Merf)].

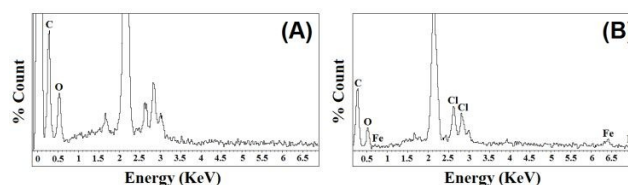


Fig. 2 EDAX spectrum of (A) Merrifield anchored anthranilic acid ligand [Anthra-Merf] and (B) Merrifield anchored iron(II)-antra catalyst [Fe^{II}(Anthra-Merf)].

Thermogravimetric analysis

The thermogravimetric study (TGA-DTA) was accomplished to explore the extent of catalyst stability for both [Anthra-Merf] ligand and [Fe^{II}(Anthra-Merf)] catalyst (Fig. 3). This analysis was performed for Merrifield anchored anthranilic acid ligand and its corresponding iron(II)-antra catalyst under N₂ atmosphere at 10 °C/minute heating rate within 50-800 °C temperature range. The loss of weight for the ligand [Anthra-Merf] appeared at 338-455 °C temperature range whereas the range 358-466 °C indicated the reduction of weight for the iron-loaded complex [Fe^{II}(Anthra-Merf)]. For both cases, the loss of weight implies the breakdown of elements in the polymeric support. So, it is manifested from the thermogravimetric analysis that our prepared catalyst is stable up to 358 °C temperature i.e. its catalytic activity persists without any disintegration. Elevated thermal stability of metal incorporated ligand [Fe^{II}(Anthra-Merf)] implies that metal was loaded in the ligand surface.

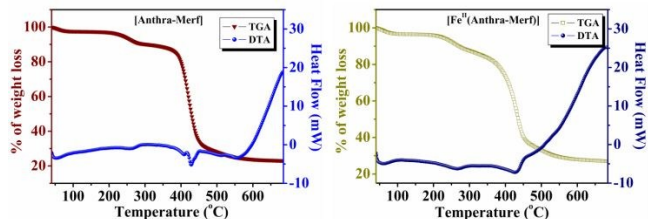


Fig. 3 TGA-DTA plot of [Anthra-Merf] ligand and [Fe^{II}(Anthra-Merf)] catalyst.

PXRD of [Fe^{II}(Anthra-Merf)] catalyst

XRD analysis was done with a scan rate of 2°/minute with a step size 2θ = 0.02°. CuK_α radiation of wavelength (λ) 0.15418 nm was used under an accelerating voltage with a current of 30 kV and 30 mA. The powder XRD pattern of Fe^{II}(Anthra-Merf) catalyst represented in Fig. 4. Figure specified the structural characterization of the designed polymer embedded catalyst. Amorphous nature of catalyst was indicated from the appearance of broadband at 2θ value near 19.32 (in degree).⁴¹ Thus no evidence was found in support of the constitution of any nano-crystalline material of iron in the Fe^{II}(Anthra-Merf) catalyst. Hence, the material is non-crystalline and amorphous in nature.

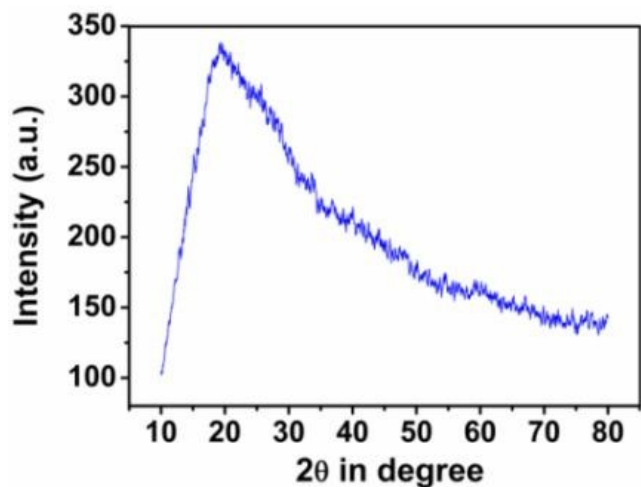


Fig. 4 Powered XRD pattern of [Fe^{II}(Anthra-Merf)] catalyst.

XPS analysis of [Fe^{II}(Anthra-Merf)] catalyst

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Finely powdered sample was firstly sonicated in methanol medium for an hour and it was drop cast on a glass bead. Then it was dried under vacuum for overnight and surface cleaning was done by Ar⁺ etching before the XPS analysis. Determination of oxidation state and major elements in our synthesized [Fe^{II}(Anthra-Merf)] catalyst is most fundamental for the determination of the accurate structure of the same. So, XPS (X-ray photoelectron spectroscopy) analysis was accomplished and data are represented in Table 1 for [Fe^{II}(Anthra-Merf)] catalyst. Fig. 5 a-d represent the narrow-range XPS spectra of iron, carbon, nitrogen, and oxygen respectively whereas Fig. 6 mention the full-range XPS spectrum of [Fe^{II}(Anthra-Merf)] catalyst. In the XPS spectrum of iron mainly two main peaks are observed at 722.4 and 709.2 eV for Fe(II) 2P_{1/2} and Fe(II) 2P_{3/2} respectively. The spin-orbit coupling, actually the j-j coupling is responsible for the appearance of the major prominent peak of Fe(II) 2P_{3/2} compared to Fe(II) 2P_{1/2}. These XPS data are reported in many Fe(II) compounds so far.⁴²⁻⁴⁵ Besides these two major peaks, two more satellite peaks were observed at the base of 728.7 and 714.4 eV and easily distinguishable from their large major peaks. This XPS analysis substantiates that iron is present in +2 oxidation state in our synthesized [Fe^{II}(Anthra-Merf)] catalyst. The difference between ΔE[Satellite - Fe(II) 2P_{3/2}] assists us to predict the proper iron oxidation state.⁴⁶ From this XPS spectra, it can also be assigned that the designed catalyst is a high spin complex of Fe(II) on account of the existence of satellite peaks and large splitting between 2P_{1/2} peak and 2P_{3/2} peak. Besides this, the full XPS scan of synthesized [Fe^{II}(Anthra-Merf)] catalyst was performed and represented in Fig. 6. The peaks for Fe(II) 2P_{1/2}, Fe(II) 2P_{3/2}, C 1s, N 1s, and O 1s are assigned successfully in the full-range XPS spectrum.

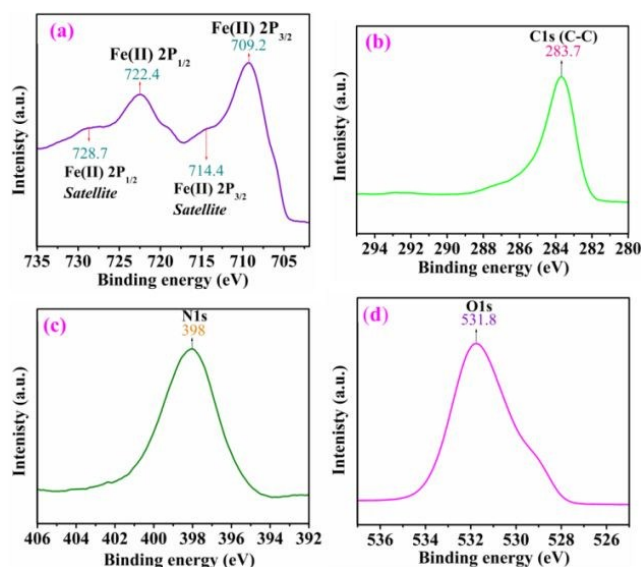


Fig. 5 Narrow-range X-ray photoelectron spectroscopy of [Fe^{II}(Anthra-Merf)] consisting (a) Fe(II) 2P_{1/2}, Fe(II) 2P_{3/2}, (b) C 1s, (c) N 1s, (d) O 1s elements.

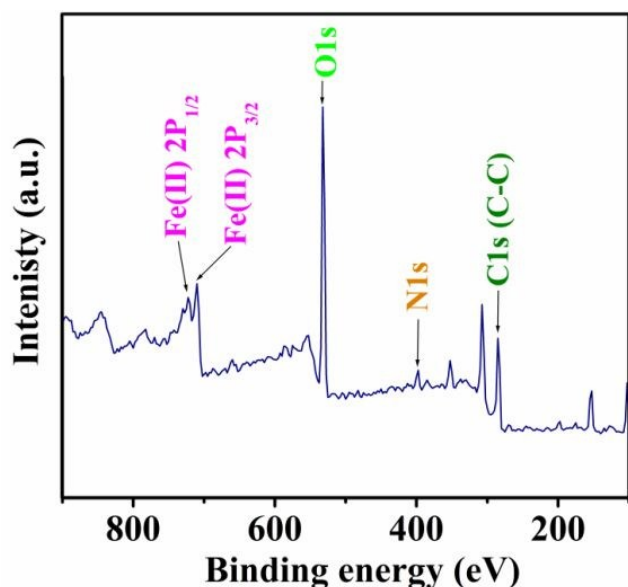


Fig. 6 Full range X-ray photoelectron spectroscopy of $[\text{Fe}^{\text{II}}(\text{Anthra-Merf})]$ catalyst.

Table 1 XPS data of $[\text{Fe}^{\text{II}}(\text{Anthra-Merf})]$ catalyst

Sample Name	Fe(II) $2\text{P}_{1/2}$ Peak position (eV)			Fe(II) $2\text{P}_{3/2}$ Peak position (eV)		
	Major Peak	Satellite Peak	$\Delta E(\text{Satellite} - 2\text{P}_{1/2})$	Major Peak	Satellite Peak	$\Delta E(\text{Satellite} - 2\text{P}_{3/2})$
$\text{Fe}^{\text{II}}(\text{Anthra-Merf})$	722.4	728.7	6.3	709.2	714.4	5.2

UV-Vis spectroscopy

The ultraviolet-visible spectroscopy of the solid samples was performed by placing a thin layer of the powder sample by diffuse reflectance spectrum mode in the provided integrating sphere. The background spectrum of BaSO_4 was taken before measuring the spectra of the powder samples. With the help of ultraviolet-visible spectroscopy, the electronic spectra of Merrifield anchored anthranilic acid ligand [Anthra-Merf] (Fig. 7A) and Merrifield anchored iron(II)-anthra catalyst $[\text{Fe}^{\text{II}}(\text{Anthra-Merf})]$ was recorded (Fig. 7B). These two spectra are useful to determine the geometrical structure of ligand and metal encapsulated catalyst. Merrifield anchored anthranilic acid ligand clearly shows the absorption near 214-235 nm range which indicates the $\pi \rightarrow \pi^*$ transition for benzenoid ring. The peak observed at 234-370 nm wavelength confirmed $n \rightarrow \pi^*$ transition for the presence of C=N moiety in the polymeric ligand. This wavelength shifted to 260-417 nm range when iron was introduced in the ligand. When N and O form a bond with iron metal almost equivalent type of spectra appeared. Due to the occurrence of ligand to metal charge transfer there minor difference in absorption band and wavelength (nm) crop up in between ligand and metal incorporated catalyst. It explains the fact that there are some changes observed for electronic configuration after metal encapsulation onto ligand.

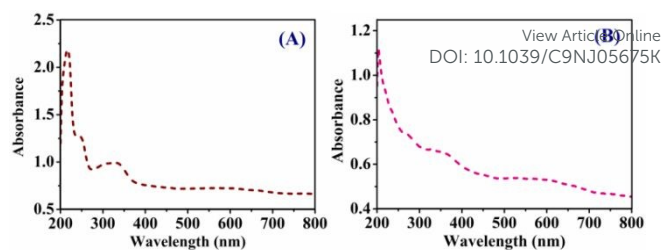


Fig. 7 UV-Vis spectra of (A) Anthra-Merf and (B) $[\text{Fe}^{\text{II}}(\text{Anthra-Merf})]$ catalyst.

FTIR spectroscopy

FTIR analysis was done by taking a small quantity of sample, which firstly mixed with KBr and a thin pellet was made using a hydraulic press. Merrifield anchored anthranilic acid ligand [Anthra-Merf] and its complex $[\text{Fe}^{\text{II}}(\text{Anthra-Merf})]$ contain many functional groups with their corresponding stretching vibrations are useful to assign the structure of ligand and catalyst. FT-IR spectroscopic analysis corroborates the structure, under the observation of stretching frequencies present in polymeric ligand and metal incorporated polymeric ligand (Fig. 8).

The ligand [Anthra-Merf] shows its corresponding stretching frequency at 1511 cm^{-1} indicating the C=C stretching for aromatic region present in it.⁴⁷⁻⁴⁹ In the ligand for aromatic C-H, the wave number appears at 3028 cm^{-1} .⁹ Condensation of chloromethylated polystyrene with anthranilic acid gives rise to the formation of C=N bond as indicated from the stretching vibrations at 1616 cm^{-1} . The wavenumber for -OH group in -COOH moiety was assigned at 3374 cm^{-1} . The peak exhibits at 1708 and 1216 cm^{-1} corresponding to the C=O and C-O group of Merrifield anchored anthranilic acid ligand [Anthra-Merf] respectively.

In Merrifield anchored iron(II)-anthra catalyst the frequency was shifted to 1667 and 1223 cm^{-1} for C=O and C-O stretching respectively. Stretching vibration at 3414 cm^{-1} indicates the appearance of water molecule coordinated to the metal iron in the catalyst. The relative lowering of bond stretching for C=N at 1602 cm^{-1} is due to the attachment of iron through nitrogen donor center.⁵⁰ The $\nu_{(\text{C-H})}$ and $\nu_{(\text{C=C})}$ aromatic stretching were shifted to 3015 and 1504 cm^{-1} in the $[\text{Fe}^{\text{II}}(\text{Anthra-Merf})]$ catalyst respectively. Appearance of two new peaks at 687 and 582 cm^{-1} are signifying the Fe-N and Fe-O stretching frequencies respectively. This could be ascribed to the interaction of iron metal with the ligand present in the Merrifield supported iron(II)-anthra catalyst.⁵¹⁻⁵³ The FTIR spectral analysis provided the small shifting of frequency values for both $\nu_{(\text{C=N})}$ and $\nu_{(\text{C=O})}$ stretching and is in accordance with the formation of Merrifield anchored iron(II)-anthra catalyst where Fe(II) is bonded with the nitrogen and oxygen atom.

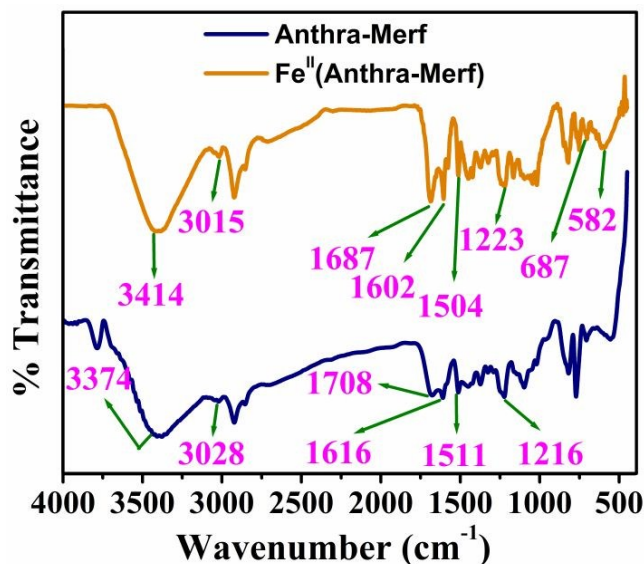


Fig. 8 FT-IR spectra of Merrifield anchored anthranilic acid ligand [Anthra-Merf] and Merrifield anchored iron(II)-antra catalyst [Fe^{II}(Anthra-Merf)].

Chemical analysis

AAS instrument was used to measure the incorporation of metal quantitatively in the [Anthra-Merf] ligand and could afford an idea to analyze the structure of Merrifield anchored iron(II)-antra catalyst. Here, the quantity of iron was precisely measured from metal integrated ligand complex in the liquid phase with the help of AAS instrument. The AAS analysis shows that 5.27% of Fe loaded on the polymer matrix Fe^{II}(Anthra-Merf). It is also true that the elemental composition of Fe^{II}(Anthra-Merf) catalyst confirmed the formation of the complex. Table 2 represents the elemental analysis of Anthra-Merf ligand and Fe^{II}(Anthra-Merf) catalyst which offers validation of complex formation as proposed here.

The data of C, H, N elemental analysis corresponding to the ligand (Anthra-Merf) and catalyst [Fe^{II}(Anthra-Merf)] are correlated with the composition of ligand and catalyst respectively as their proposed structure.

Table 2 Elemental analysis (in % weight) of the Merrifield anchored anthranilic acid ligand and Merrifield anchored iron(II)-antra catalyst

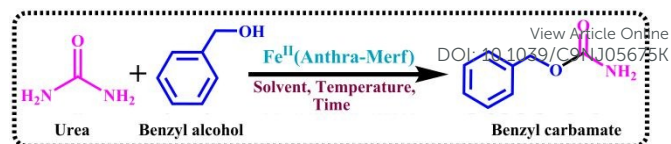
Compound	C ^a	H ^a	N ^a	Fe ^b
Anthra-Merf	81.26	5.16	4.34	-
Fe ^{II} (Anthra-Merf)	73.41	6.14	4.12	5.27

^adetermined by CHN analysis; ^bdetermined by AAS analysis.

Catalytic Activities

Activity of Fe^{II}(Anthra-Merf) catalyst for carbamate synthesis

The extent of activity of the newly synthesized Merrifield anchored anthranilic acid catalyst [Fe^{II}(Anthra-Merf)] over the model reaction (benzyl carbamate synthesis; Scheme 2) was observed with respect to various parameters like temperature, time, solvent, etc.



Scheme 2 Benzyl carbamate synthesis using urea and benzyl alcohol in the presence of Fe^{II}(Anthra-Merf) catalyst.

The reaction of urea and benzyl alcohol was performed using Fe^{II}(Anthra-Merf) catalyst in accordance with the development of benzyl carbamate was investigated with different solvents in the course of reaction (Table 3). After a series of solvent analysis it was observed that indeed DMSO and acetonitrile are polar in character, but water offers a trace amount of product yield probably because of its high polarity factor. When an excess benzyl alcohol was used as substrate at the same time as solvent, trace yield of product was observed. On the other hand some comparatively less polar solvents like dioxane, benzene, *o*-xylene provided a significant yield than the above mentioned solvents. Surprisingly dioxane as a solvent contributes to deliver better yield of 97% (Table 3, entry 5). So, dioxane is considered as an appropriate solvent for carbamates synthesis from urea and benzyl alcohol with Fe^{II}(Anthra-Merf) catalyst.

Table 3 Effect of solvent on catalytic benzyl carbamate synthesis^a

Entry	Solvent	Yield (%) ^b
1.	Water	trace
2.	Acetonitrile	30
3.	Benzene	76
4.	<i>O</i> -xylene	78
5.	Dioxane	97
6.	Dimethyl sulphoxide	36
7 ^c .	Benzyl alcohol	trace

^aReaction conditions: urea (2 mmol), benzyl alcohol (3 mmol), solvent (3.5 mL), Fe^{II}(Anthra-Merf) catalyst (0.02 g), temperature (120 °C), time (6.5 h); ^bIsolated yield; ^cBenzyl alcohol (substrate) used in excess as solvent.

The newly synthesized catalyst Fe^{II}(Anthra-Merf) plays a vital role in benzyl carbamate synthesis and the role of amount of catalyst on the reaction is also a requirement for discussion. When the Fe^{II}(Anthra-Merf) catalyst amount was increased the percentage yield of the product was continuously raised till the highest yield (97%) of the desired product from urea and benzyl alcohol was achieved. Only 0.02 g of catalyst was perfectly sufficient for yielding the maximum quantity of benzyl carbamate product (Fig. 9).

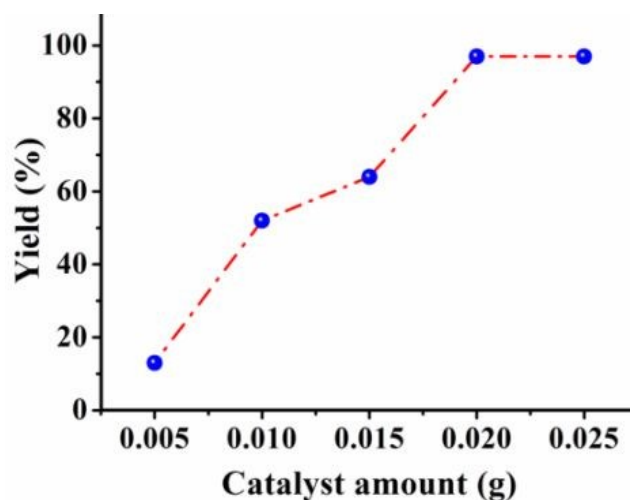


Fig. 9 Effect of amount of Fe^{II}(Antra-Merf) on benzyl carbamate synthesis. Reaction conditions: urea (2 mmol), benzyl alcohol (3 mmol), 1,4-dioxane (3.5 mL), temperature (120 °C), Fe^{II}(Antra-Merf) catalyst, time (6.5 h).

For further increase of catalyst amount up to 0.025 g there was no salient change of yield observed.

For carbamate synthesis, the reaction temperature and reaction time conveys an important message with respect to the yield of product. As the temperature is near about room temperature (40 °C) very slight yield of benzyl carbamate formation was noticed after 8 h of reaction (Table 4, entry 1). Keeping the reaction time fixed (at 8 h), the gradual increase in temperature from 40 to 70 °C increases the yield of benzyl carbamate in a regular manner (Table 4, entry 2). If the time was reduced to 6.5 hours from 8 hours the yield of product was decreased at same temperature (Table 4, entry 3). After several optimizations of reaction time and temperature, the suitable optimized temperature and time were found to be 120 °C and 6.5 h respectively by which the maximum yield of isolated product (benzyl carbamate) was observed (Table 4, entry 6). Further elevation of reaction time could not influence the yield of the reaction product. Maintaining all other reaction conditions constant, the rising of temperature up to 130 °C, no remarkable change of the product yield was obtained (Table 4, entry 11).

Table 4 Effect of temperature and time on catalytic benzyl carbamate synthesis^a

Entry	Temperature (°C)	Time (h)	Yield (%) ^b
1.	40	8	18
2.	70	8	51
3.	70	6.5	40
4.	90	6.5	61
5.	110	6.5	86
6.	120	6.5	97
7.	120	7	97
8.	120	10	97
9.	120	6	90
10.	120	5	62
11.	130	6.5	97

^aReaction conditions: urea (2 mmol), benzyl alcohol (3 mmol), 1,4-dioxane (3.5 mL), temperature, time, Fe^{II}(Antra-Merf) catalyst (0.02 g, 0.0188 mmol based on Fe active centre); ^bIsolated yield.

Different Lewis acid catalysts were tested for benzyl carbamate synthesis and their results are tabulated in Table 5. The iron-anthranilic acid complex without chloromethylated polystyrene support (Table 5, entry 5) was tested for benzyl carbamate synthesis and it was observed better yield of isolated product was obtained compared to other Lewis acid catalyst but lower than the Fe^{II}(Antra-Merf) catalyst (Table 5, entry 6).

Table 5 Performance of different commercially available Lewis acid catalysts for benzyl carbamate synthesis^a







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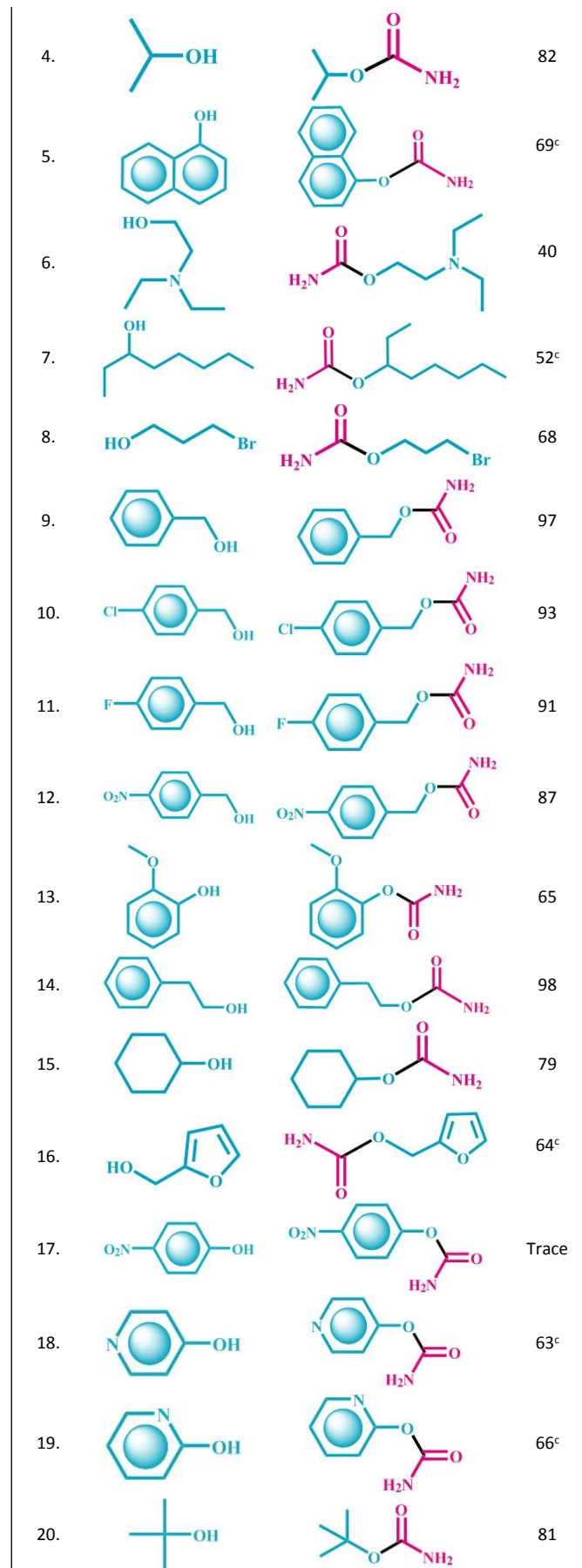
Entry	Catalyst	Yield (%) ^b
1.	CoCl ₂	75
2.	NiCl ₂	69
3.	CuCl ₂	76
4.	ZnCl ₂	64
5.	Iron(II)-antra	82
6.	Fe ^{II} (Antra-Merf)	97

^aReaction conditions: urea (2 mmol), benzyl alcohol (3 mmol), 1,4-dioxane (3.5 mL), catalyst (0.02 g), temperature (120 °C), time (6.5 h); ^bIsolated yield.

After performing several optimization conditions, the various nature containing alkyl and aromatic alcohols were used towards the catalytic carbamates synthesis reaction under optimum conditions. A variety of aromatic, aliphatic, and heterocyclic alcohols were encountered with urea using 0.02 g of Fe^{II}(Antra-Merf) catalyst (Table 6). Phenethyl carbamate, benzyl carbamate, and decyl carbamate obtained as maximum amount of isolated yield through this reaction (Table 6, entries 1,9,14). When urea was treated with a heterocyclic alcohols like furfuryl alcohol, 2-hydroxy pyridine, 4-hydroxy pyridine in the presence of Fe^{II}(Antra-Merf) catalyst the corresponding carbamate yields were obtained in moderate range (63-66 %) at 130 °C temperature (Table 6, entries 16, 18, 19). Alternatively, among aromatic alcohols, 2-methoxyphenol for its steric hindrance delivers the corresponding carbamate comparatively in a lower yield (Table 6, entry 13). An interesting observation was made that 4-nitrobenzyl alcohol (Table 6, entry 12) performs well during carbamate synthesis but 4-nitrophenol (Table 6, entry 17) just failed in this said reaction. Tertiary butyl alcohol (Table 6, entry 20) when subjected for carbamate synthesis it was observed that the yield of isolated product is 81 % which is slightly stumpy compared to other aliphatic alcohols.

Table 6 Synthesis of different carbamate derivatives from alcohols and urea using Fe^{II}(Antra-Merf) catalyst^a

Entry	Alcohol	Product	Yield (%) ^b
1.			97
2.			95
3.			94

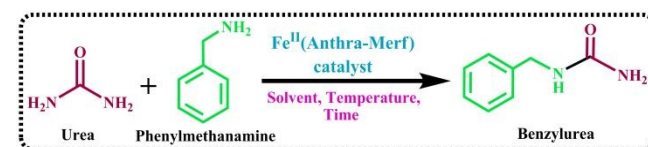


^aReaction conditions: urea (2 mmol), alcohol (3 mmol), 1,4-dioxane (3.5 mL), Fe^{II}(Antra-Merf) catalyst (0.02 g, 0.0188 mmol based on Fe active centre), temperature (120 °C), time (6.5 h); ^bIsolated yield; ^cReaction done at temperature 130 °C.

The other substituted benzyl alcohols with electron withdrawing group contribute enhanced percentage of transformation to their corresponding products with excellent yield (Table 6, entries 10-12). Nevertheless, along with aromatic alcohols, the aliphatic alcohols are more concerned towards the synthesis of desired carbamates in high yield. When alkyl alcohol reacts with urea under the influence of Fe^{II}(Antra-Merf) catalyst the desired primary carbamates have been obtained in higher yield (Table 6, entries 1-4). As the chain length of alcohol increase in a continuous manner, the +I effect also boost the nucleophilic character over alcohol moiety and increases the yield of the reaction. But it is surprising that the aliphatic alcohols containing steric hindrance e.g. 2-ethylhexanol, 2-diethyl amino ethanol produces their corresponding carbamates with lower yield 52% and 40% respectively (Table 6, entries 6,7). Conversely, among the synthesized alkyl carbamates, the 3-bromopropyl carbamate was isolated in 68% yield (Table 6, entry 8).

Activity of Fe^{II}(Antra-Merf) catalyst for N-substituted urea synthesis

The catalytic activity of Fe^{II}(Antra-Merf) catalyst was also tested in synthesis of unsymmetrical urea using amine in place of alcohol and the resulting outcome was described after optimizing temperature, time and amount of catalyst, urea, amine, etc. The reaction optimization was carried out by taking urea and benzylamine as model substrate for the synthesis of benzylurea in presence of the Fe^{II}(Antra-Merf) catalyst (Scheme 3).



Scheme 3 Synthesis of benzylurea using urea and benzylamine in the presence of Fe^{II}(Antra-Merf) catalyst.

During the conversion of urea to N-substituted urea (in this protocol), temperature and time have a significant role in obtaining a very good amount of product yield (Table 7). Increasing the temperature gradually by maintaining 10 hours reaction time it was observed that the yield of product increases in the same manner (Table 7, entries 1-3). But unfortunately, the yield of benzylurea decreased slightly with lowering of reaction time (Table 7, entries 4,5). Varying temperature and time continuously, the highest 96% isolated product yield was achieved at 100 °C temperature after 8 h of reaction in presence of Fe^{II}(Antra-Merf) catalyst (Table 7, entry 7). Interestingly, after achievement of maximum yield, an increase of reaction time no effect was observed on the yield (Table 7, entry 9).

Table 7 Effect of temperature and time on benzylurea synthesis catalysed by Fe^{II}(Antra-Merf)^a

Entry	Temperature (°C)	Time (h)	Yield (%) ^b
1.	40	10	17
2.	70	10	42

3.	80	10	67
4.	80	8	58
5.	80	7	51
6.	90	7	63
7.	100	8	96
8.	100	7	81
9.	100	9	96

^aReaction conditions: urea (2 mmol), benzylamine (2 mmol), 1,4-dioxane (3 mL), Fe^{II}(Antra-Merf) catalyst (0.025 g, 0.0235 mmol based on Fe active centre), temperature, time; ^bIsolated yield.

Effect of catalyst amount on benzylurea synthesis

Fe^{II}(Antra-Merf) catalyst amount is a leading factor for the synthesis of benzylurea and other derivatives of mono substituted urea. The optimization of catalyst amount for better and maximum yield was described in Fig. 10. It is clear from the graph that when catalyst amount (in g) was gradually increased, the transformation of urea to unsymmetrical N-substituted urea with respect to yield also increased. Eventually, it was confirmed that 0.025 g of Fe^{II}(Antra-Merf) catalyst is enough for maximum conversion of substrate and affording 96% (i.e. highest) yield of benzylurea. Afterward, when the amount of Fe^{II}(Antra-Merf) was increased to 0.03 g there was not any alteration of the product yield observed.

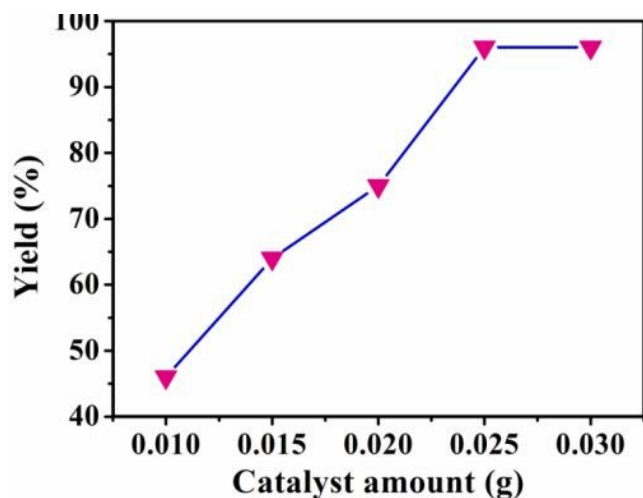


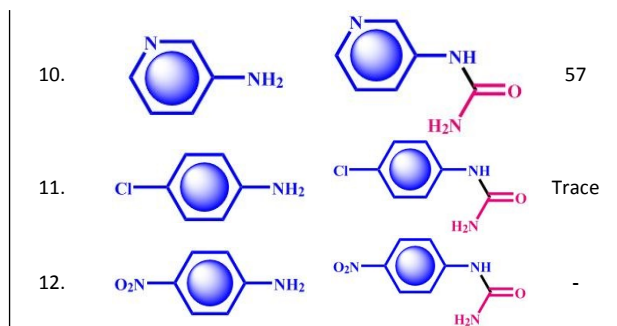
Fig. 10 Effect of Fe^{II}(Antra-Merf) catalyst amount for synthesis of benzylurea. Reaction conditions: urea (2 mmol), benzylamine (2 mmol), 1,4-dioxane (3 mL), temperature (100 °C), time (8 h), Fe^{II}(Antra-Merf) catalyst.

After examining all reaction parameters, we choose other substituted amines to go through this reaction with urea in presence Fe^{II}(Antra-Merf) catalyst and the results are given in Table 8. Under optimized reaction condition several substituted amines (2 mmol) were reacted with urea (2 mmol) in 3 mL of dioxane at 100 °C temperature for 8 h reaction time. Various aromatic, as well as aliphatic amines, were subjected to the reaction mixture to explore the effect of different substrates on the yield of different N-substituted urea. The mono substituted unsymmetrical product benzylurea was formed with an excellent

96% yield when benzylamine reacts with urea (Table 8, entry 5). Remarkably, the substrate 1-(4-methoxyphenyl) amine furnished the highest percentage of yield (98%) (Table 8, entry 6). In connection to this discussion, aniline-urea reaction did not provide the product up to the desired yield (Table 8, entry 1). The reaction of nucleophilic aliphatic amines shows a reluctance for the corresponding urea synthesis, as the percentage yield is lower than other N-substituted urea products (Table 8, entries 2-4). When secondary amines were subjected to N-substituted urea synthesis it was observed that morpholine (Table 8, entry 7) which is an aliphatic secondary amine provided good yield of isolated product. On the other hand N-methyl aniline (Table 8, entry 8) provided only slight amount of product may be due to steric hindrance of methyl group. Beside this heterocyclic aromatic primary amines were also tested for this reaction. 3-amino pyridine (Table 8, entry 10) offered better yield compared to 2-amino pyridine (Table 8, entry 9). When electron withdrawing groups (Table 8, entry 11, 12) were introduced in aniline, they almost failed in the reaction compared to the electron donating groups present in aniline i.e. electron withdrawing substituents are almost reluctant to undergo this reaction. Thus, we have explored the mono substituted urea with the maximum amount of yield value under the supervision of Fe^{II}(Antra-Merf) catalyst.

Table 8 Synthesis of N-substituted urea from urea and amines catalysed by [Fe^{II}(Antra-Merf)]^a

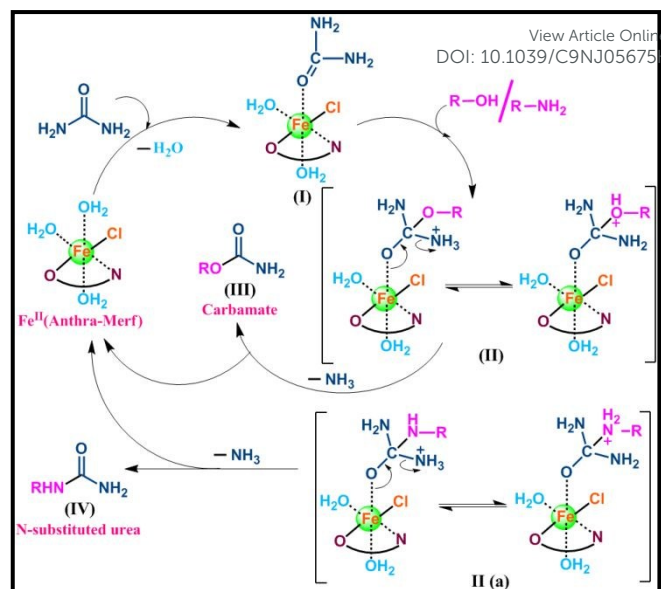
$\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2 + \text{R}_1-\text{N}(\text{H})-\text{R}_2 \xrightarrow[\text{Dioxane (solvent) (3 mL)}]{\text{Fe}^{\text{II}}(\text{Antra-Merf}) (0.025 \text{ g}), 100^\circ\text{C}, 8 \text{ hour}}$ $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{N}(\text{R}_1)(\text{R}_2)$			
Entry	Amines	Products	Yield (%) ^b
1.			68
2.			87
3.			77
4.			80
5.			96
6.			98
7.			79
8.			27
9.			42



^aReaction conditions: urea (2 mmol), amine (2 mmol), 1,4-dioxane (3 mL), Fe^{II}(Anthra-Merf) catalyst (0.025 g, 0.0235 mmol based on Fe active centre), temperature (100 °C), time (8 h); ^bIsolated yield.

4.3 A plausible reaction mechanism for synthesis of carbamate and N-substituted urea

From our experimental result and with the help of previous literature support the probable mechanistic pathway was successfully established for carbamate (Scheme 4) and N-substituted urea (unsymmetrical) synthesis using Fe^{II}(Anthra-Merf) catalyst.³² With Fe^{II}(Anthra-Merf) catalyst, the catalytic pathway was continue, in which urea reacted with a nucleophile such as alcohol or amine respectively. Here urea molecule is initiated by the interaction of the iron atom of Fe^{II}(Anthra-Merf) through the oxygen atom of urea (structure I). Most probably the Fe^{II}(Anthra-Merf) enhances the electrophilic character of the carbonyl carbon through coordination with Fe(II) ion leading to the (intermediate I).⁵⁴ Then the very reactive nucleophilic alcohol attacks the electron deficient carbonyl carbon (structure I) centre of urea residue leading to the formation of an intermediate structure II.⁵⁵ This intermediate undergoes an intramolecular proton transfer from protonated aromatic/aliphatic/heterocyclic alcohol (ROH) to the amine group of urea. The transfer of proton generates an iron coordinated ammonium intermediate. The subsequent step involves the self decomposition of the ammonium species by rupturing of iron-oxygen co-ordinate bond and simultaneous removal of ammonia molecule to produce the final product carbamate (III). After achieving the finishing point of the reaction the Fe^{II}(Anthra-Merf) catalyst remains intact and unaffected which could be utilized for further reaction cycle. The formation of N-substituted urea follows a similar mechanistic approach as the production of carbamate experiences. In this path, the amines analogous to the alcohols, perform as nucleophile and attack the electronically deficient carbonyl group of the activated urea in presence of Fe^{II}(Anthra-Merf) catalyst. The process undergoes with similar type of intermediate (IIa) and provides the N-substituted urea (IV) as the final desired product by release of ammonia. The process of ammonia removal from intermediate (IIa) delivers the desired product via regenerating the catalyst Fe(II)-catalyst.⁵⁴ The XPS analysis explored the fact that the spent Fe^{II}(Anthra-Merf) catalyst is found unaffected after the formation of target product carbamate and N-substituted urea. The result suggested that in spite of being actively involved in the reaction, there were no significant changes in the catalytic structure. The XPS experimental study of the recovered [Fe^{II}(Anthra-Merf)] catalyst also assigns that the oxidation state of iron *i.e.* +2 remains unaltered after completion of reaction (Fig. 11). The catalyst can be recycled for both the reaction in the next cycle.



Scheme 4 Probable mechanistic reaction pathway for primary carbamate and N-substituted urea synthesis.

Heterogeneity test of Fe^{II}(Anthra-Merf) catalyst

Whether the catalyst Fe^{II}(Anthra-Merf) is heterogeneous or not, it was confirmed by examining the heterogeneity test during synthesis of carbamate (as shown in model reaction). The Initial reaction of urea and benzyl alcohol was performed with Fe^{II}(Anthra-Merf) catalyst for 4 hours; a lower amount of benzyl carbamate yield was observed (51%). After that, the catalyst was withdrawn from the reaction medium and the reaction was continued for the rest of the time but there is no satisfactory rise in the yield of benzyl carbamate (Fig. 12). After performing the filtration process, the filtrate was analyzed by AAS, which confirmed that there is no leaching of iron from the Fe^{II}(Anthra-Merf) catalyst. Moreover, another reaction was performed without using Fe^{II}(Anthra-Merf) catalyst and it was observed that very trace amount of corresponding product was formed. So, it is concluded that catalytic description of iron is the prime centre in Fe^{II}(Anthra-Merf) catalyst towards the synthesis of carbamate and it is heterogeneous in nature.

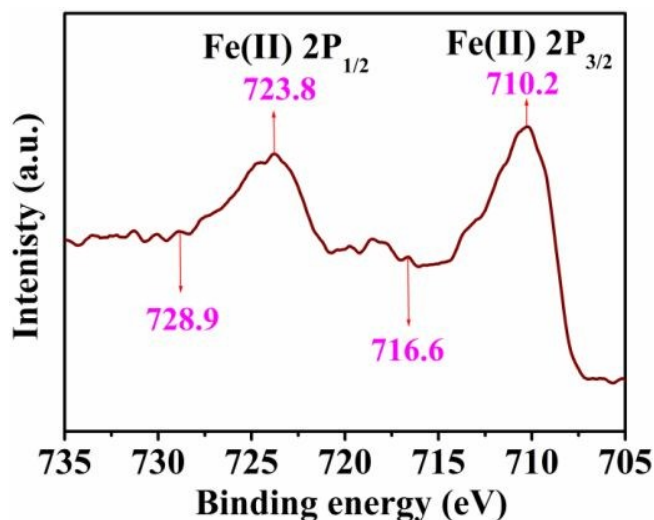


Fig. 11 X-ray photoelectron spectroscopy of reused [Fe^{II}(Anthra-Merf)] catalyst.

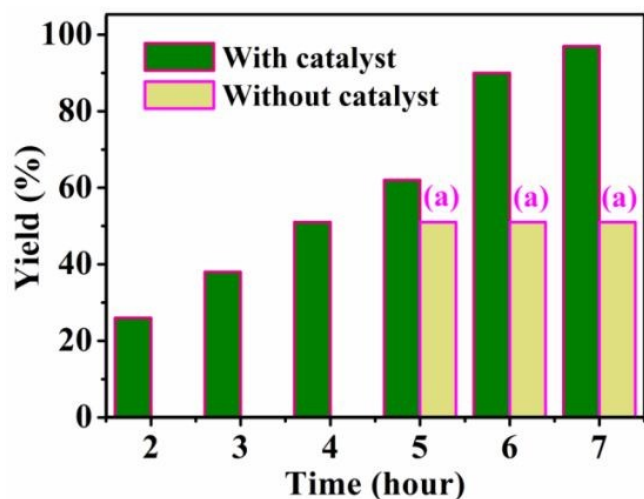


Fig. 12 Heterogeneity test of Merrifield anchored iron(II)-antra catalyst. Reaction conditions: urea (2 mmol), benzyl alcohol (3 mmol), 1,4-dioxane (3.5 mL), temperature (120 °C), Fe^{II}(Antra-Merf) catalyst (0.02 g). Where (a) represents the reaction continues without catalyst.

Recyclability and leaching studies of Fe^{II}(Antra-Merf) catalyst

Heterogeneity and recyclability both are considered as an imperative factor for improving the characteristic nature of the catalyst. Reaction with Fe^{II}(Antra-Merf) catalyst is more suitable for preparation of carbamate and N-substituted urea under safe convenient process other than any common hazardous process which upgrades iron catalyst's appearance in terms of deteriorating the leaching function of catalyst as well as rising the iron stability. The recyclability of catalyst and leaching of iron metal in each cycle is described in Fig. 13, Table 9 respectively. After carrying out the first reaction cycle, Fe^{II}(Antra-Merf) catalyst was collected and reused for several times followed by washing with methanol and drying at 50 °C. In recyclability graph, the first two runs did not alter the yield of carbamate and N-substituted urea. After that the percentage of yield decreased to some extent at about 2%, 3% in each run but not too much appreciable change. This indicated the retention of catalyst activity on both carbamate and N-substituted urea formation (under optimized condition) even after 6 times recycle. Small amount of decrease in yield percentage during recycling experiment indicates no observable change in the character of catalyst. The catalyst remains intact in nature even after 6 times recycling performance as verified by PXRD, SEM, FTIR. The powdered XRD of the recycled catalyst was supported from the manifestation of broadband at 2θ value near 20.62 (in degree), indicate there is no particular change in XRD pattern (Fig. 14). From SEM image (Fig. 15) of recycled catalyst, it is confirmed that after recycling, any appreciable change is not observed on the catalyst surface and it maintains its activity towards the reactions continuously. The FTIR spectra (Fig. 16) of the recycled Fe^{II}(Antra-Merf) catalyst shows almost the same frequency region of C=C and C-H aromatic stretching as in fresh catalyst. It is also confirmed from the stretching frequency of Fe-N and Fe-O, that the catalyst Fe^{II}(Antra-Merf) remains intact even after six times recycle.

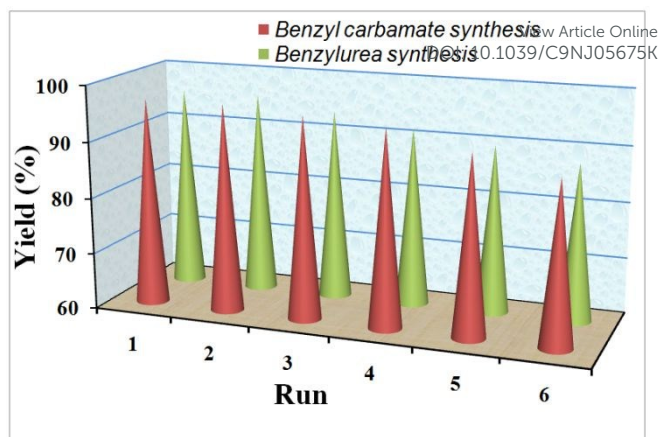


Fig. 13 Recyclability of Fe^{II}(Antra-Merf) catalyst for benzylurea and benzyl carbamate synthesis. Benzylurea synthesis: urea (2 mmol), benzylamine (2 mmol), 1,4-dioxane (3 mL), Fe^{II}(Antra-Merf) catalyst (0.025 g, 0.0235 mmol based on Fe active centre), temperature (100 °C), time (8 h); Benzyl carbamate synthesis: urea (2 mmol), benzyl alcohol (3 mmol), 1,4-dioxane (3.5 mL), Fe^{II}(Antra-Merf) catalyst (0.02 g, 0.0188 mmol based on Fe active centre), temperature (120 °C), time (6.5 h).

Table 9 Leaching studies of the recycled Fe^{II}(Antra-Merf) catalyst

Entry	No. of cycles	Iron leaching (ppm)	
		Carbamate synthesis	N-substituted urea synthesis
1.	1	-	-
2.	2	-	-
3.	3	0.002	0.004
4.	4	0.005	0.006
5.	5	0.009	0.013
6.	6	0.028	0.025

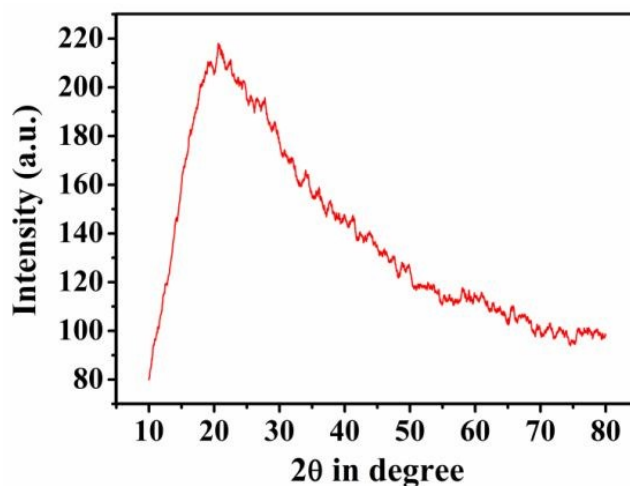


Fig. 14 PXRD of recycled Fe^{II}(Antra-Merf) catalyst.

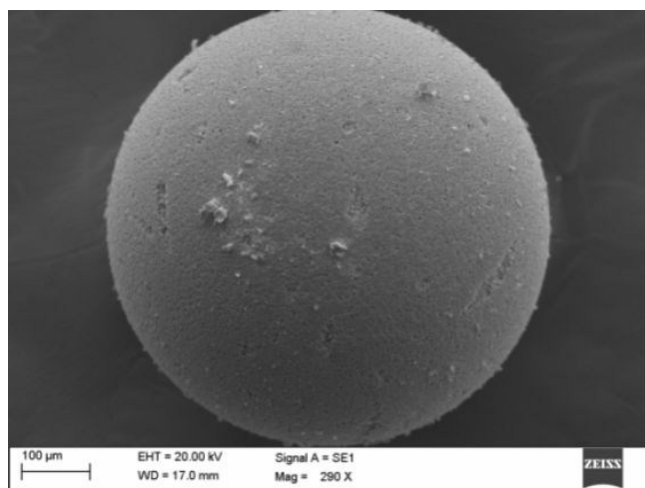


Fig. 15 SEM image of recycled Fe^{II}(Anthra-Merf) catalyst.

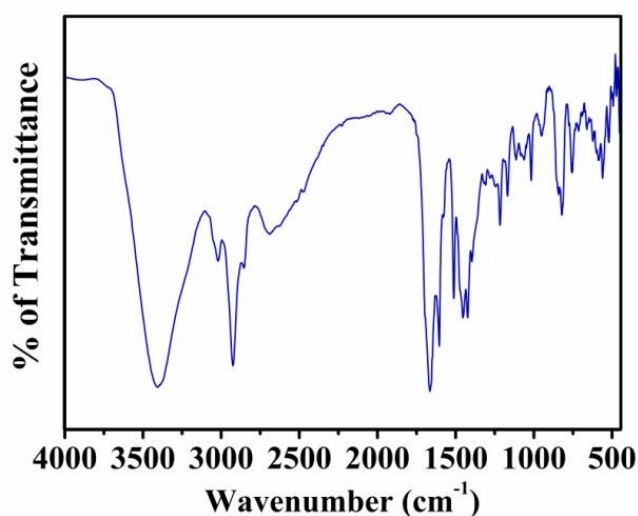


Fig. 16 FTIR spectra of recycled Fe^{II}(Anthra-Merf) catalyst.

Table 10 Control experiments for benzyl carbamate and benzylurea synthesis under optimized conditions^a

Reactions	Conditions	Yield (%)
Benzyl carbamate synthesis	Without catalyst	11
	Anthra-Merf	14
	Iron(II)-anthra	82
	Fe^{II}(Anthra-Merf)	97
Benzylurea synthesis	Without catalyst	16
	Anthra-Merf	18
	Iron(II)-anthra	77
	Fe^{II}(Anthra-Merf)	96

^aReaction conditions: benzyl carbamate synthesis: urea (2 mmol), benzyl alcohol (3 mmol), 1,4-dioxane (3.5 mL), temperature (120 °C), time (6.5 h). benzylurea synthesis: urea (2 mmol), benzylamine (2 mmol), 1,4-dioxane (3 mL), temperature (100 °C), time (8 h).

The corresponding yields without catalyst, with the solid-supported catalyst before incorporation of the iron (Anthra-Merf), and with a

homogeneous version of iron(II)-Anthra catalyst (without the solid support) for both of the reactions are recorded. The comparative table for the evaluation of the relative yields for different catalytic conditions are represented in Table 10.

Table 11 Comparison with other reported systems

Reaction	Catalyst	Reaction condition	Yield (%)	Ref.
Carbamate synthesis	FeBr ₂	FeBr ₂ (0.01 mmol), urea (0.5 mmol), benzylalcohol (0.75 mmol), 1,4-dioxane (1 mL), temperature (150 °C), time (6 h).	92	32
	MNP-Fe ₃ O ₄	Benzylalcohol (1 mmol), urea (2 mmol), [ChCl][ZnCl ₂] (3 mL), MNP-Fe ₃ O ₄ (10 mol %), temperature (130 °C), time (6 h).	90	55
	[ChCl][ZnCl ₂] ₂	Isopropylalcohol (1 mmol), N, N'-diphenylurea (2 mmol), [ChCl][ZnCl ₂] ₂ (3 cm ³), temperature (120 °C), time (18 h).	72	56
	Fe^{II}(Anthra-Merf)	Urea (2 mmol), benzylalcohol (3 mmol), Fe^{II}(Anthra-Merf) catalyst (0.020 g, 0.0188 mmol based on Fe active centre), 1,4-dioxane (3.5 mL), temperature (120 °C), time (6.5 h).	97	This work
N-substituted urea synthesis	No Catalyst	Cyclohexylamine (22 mmol), urea (10 mmol), H ₂ O (0.5 mL), temperature (170 °C), time (10 h), 4.8 MPa CO ₂ .	45	57
	B(OCH ₂ CF ₃) ₃	4-methoxybenzoic acid (1 mmol), benzylamine (1 mmol), B(OCH ₂ CF ₃) ₃ (2.0 mmol), MeCN (2 mL), temperature (80 °C), time (5h).	29	58
	MNP-Fe ₃ O ₄	Benzylamine (1 mmol), urea (2mmol), [ChCl][ZnCl ₂] (3 mL), MNP-Fe ₃ O ₄ (10 mol %), temperature (130 °C), time (6 h).	86	55
	Fe^{II}(Anthra-Merf)	Urea (2 mmol), cyclohexylamine/benzylamine (2 mmol), Fe^{II}(Anthra-Merf) catalyst (0.025 g, 0.0235 mmol based on Fe active centre), 1,4-dioxane (3 mL), temperature (100 °C), time (8	77/96	This work

		h).		
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5. Conclusions

At the end of these present discussions, it can be explored that we have developed an efficient polymer-based iron catalyst Fe^{II}(Antra-Merf) which can effectively promotes upto the satisfactory yield of primary carbamates and N-substituted ureas. The proposed catalytic pathway is inexpensive, convenient as well as industrially valuable. The synthesized Fe^{II}(Antra-Merf) catalyst is thermally stable up to 358 °C. Additionally iron being a less contaminated element, so our developed Fe^{II}(Antra-Merf) catalyst is environmentally benign and safe. Concerning with this current catalytic system, the proposed pathway is highly advantageous due to mild reaction temperature, less time consuming and high product yield having immense importance compared to the former reported system. We have used different alcohols for carbamate synthesis and it was noticed that alcohols with electron withdrawing group have more influence in carbamate synthesis as indicated from the high yield of desired products. In this connection, aliphatic alcohols are also better candidates for their corresponding carbamate synthesis. During the synthesis of N-substituted ureas by taking aniline as a substrate, surprisingly it produced an isolated product with minute yield compared to the substituted aromatic and aliphatic amines. The important part of our catalytic system is that up to six reaction cycles it can be recycled. The characterizations like XRD, FE-SEM, and FTIR instrumental analysis were executed for recycled Fe^{II}(Antra-Merf) catalyst and no special change in structure or configuration was examined compared to that of fresh catalyst. From the above discussion and to the best of our delight the developed Fe^{II}(Antra-Merf) catalyst may explore a new degree of advancement to the economic synthesis of organic primary carbamates and N-substituted ureas in industrial scale as well as in the catalysis field.

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Conflicts of interest

There are no conflicts to declare.

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An efficient one-pot synthesis of industrially valuable primary organic carbamates and N-substituted ureas by reusable Merrifield anchored iron(II)-anthra catalyst [Fe^{II}(Anthra-Merf)] using urea as a sustainable carbonylation source

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Merrifield anchored iron(II)-anthra catalyst [Fe^{II}(Anthra-Merf)] has been synthesized for the production of primary carbamates and N-substituted ureas using carbonylation source.

