Synthesis of Nucleic Acid Bases by Metal Ferrite Nanoparticles from a Single Carbon Atom Precursor Molecule: Formamide

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Abstract

The synthesis of prebiotic molecules from simple precursors is believed to be a crucial scheme in order to study the origin of life processes. The present study describes the one-pot synthesis of purine and pyrimidine nucleic acid bases in the presence of pre-biologically significant binary metal oxide nanoparticles, metal ferrites, namely $NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$ and $MnFe_2O_4$. The products identified are cytosine, isocytosine, 4(3H)-pyrimidinone, adenine, hypoxanthine and purine. The ability of isocytosine (a constitutional isomer of cytosine) to recognize cytosine and guanine through normal and reversed Watson-Crick pairing respectively, demonstrates an important storyline for the genesis of ancient nucleic acids. The relevance of other synthesized nucleic acid bases with respect to the origin of life is also discussed. The divalent metal ions in iron oxide make it an appropriate catalytic system because it demonstrates excellent catalytic performance for the nucleic acid bases synthesis with significantly high yield, as compared to pure iron oxide and some other minerals like silica, alumina, manganese oxides and double metal cyanide complexes.

Introduction

The exact route for the evolution of life on this planet remains a matter of great debate, as current extant life exhibits highly complex pathways, cycles and hypercycles. However, the

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most logical scenario required the synthesis of polymers, especially information carrying molecules such as RNA and DNA as well as proteins (Walde 2005). Chemical precursors of these molecules, such as hydrogen cyanide (HCN), formamide (HCONH$_2$), cyanoacetylene (C$_3$HN), formic acid (HCOOH) and formaldehyde (HCHO) are thought to have been among the major reactants in prebiotic organic synthesis (Jheeta et al. 2013; Gordon and Sharov 2017). Among these chemical precursors, the roles of HCN and HCONH$_2$ may have been particularly important (Orgel 2004; Delaye and Lazcano 2005; Saladino et al. 2012a). HCONH$_2$ is the simplest amide molecule and can be found in young stellar objects like W33A, the interstellar medium, as well as on comets and the moons of planets such as Saturn's moon, Titan and Jupiter's moon, Europa (Schutte et al. 1999; Bockelée-Morvan et al. 2000; Levy et al. 2000; Borucki et al. 2002; Crovisier 2004; Parnell et al. 2006). Apart from the prebiotic availability, some of the key properties of the HCONH$_2$ molecule such as comparative stability, multifaceted reactivity and low volatility make it a good choice of potential substrate for the synthesis of nucleic bases and analogous compounds. (Barks et al. 2010). In addition, the role of the simple triatomic molecule, HCN, in the synthesis of nitrogenous heterocyclic compounds (such as adenine) on primitive Earth has been the subject of extensive research for several decades. (Miller 1955; Abelson 1966). It was Oro and co-workers who first instigated the synthesis of adenine nucleic acid bases from HCN, thus adding an important contribution to the relevance of HCN's chemistry (Oró 1960; Oró and Kimball 1961; Oró and Kamat 1961). The narrow panel of nucleic bases limited only to purines as well as the thermodynamic instability of HCN were major drawbacks in HCN's chemistry. In view of this, the option of HCONH$_2$ as a more effective selection of precursors for the synthesis of nucleic acid bases when compared to HCN has been established and is reflected in the research work done by Bredereck et al. 1959; Yamada and Okamoto 1972; Yamada et al. 1978a, b. Metal oxides and minerals may be considered relevant in prebiotic chemistry in the sense that they could mediate the chemistry of HCONH$_2$ by forming a number of prebiotic nitrogenous heterocyclic compounds and thus the scenario could possibly be regarded as a model for the primitive Earth's environment.

It is generally accepted that the conceptual foundations of the research field of prebiotic chemistry were laid by Oparin and Haldane in the 1920s and subsequently Bernal and (among others) Cairns-Smith (Bernal 1951; Cairns-Smith 1992). Saladino et al. (2001) further developed experimentation through the analysis of the simple catalytic effect of minerals in the thermal condensation process of HCONH$_2$. These minerals or oxides act typically as a heterogeneous catalyst in HCONH$_2$ condensation reactions. Their ability resides in the fact that they can protect the freshly synthesized biologically relevant molecules from both chemical and photochemical damage. (Scappini et al. 2004; Gallori et al. 2006). Moreover, the degradation kinetics of HCONH$_2$ compared to other compounds of prebiotic importance is believed to be controlled by mineral surfaces (Saladino et al. 2008). A large panel of nucleic acid bases, both purine and pyrimidine and their analogous compounds, along with the HCONH$_2$ degradation products upon the condensation of HCONH$_2$ molecule was reported in the presence of catalysts such as silica, alumina, zeolites, zirconium oxide as well as boron, phosphate, iron-sulphur minerals and finally, clays and interstellar dust particles by Saladino and co-workers (2012b). The Earth's crust contains metal oxides as an essential component, so the possibility of these compounds acting as a catalyst in respect of HCONH$_2$ chemistry cannot be ruled out. Oxides of iron and manganese have also recently been used in HCONH$_2$ condensation reactions (Shanker et al. 2011; Bhushan et al. 2016a).

In a similar vein, spinel ferrite minerals (having a general formula of $A^{II}B_2^{III}O_4$; where A may be Zn, Ni, Co, Cu, Mn, etc., and B = Fe.) are present almost everywhere that ancient sediments occur. These spinels are common non-silicate oxides found in the Earth's crust and upper mantle (Clarke and Washington 1924; Reichmann and Jacobsen 2006). Mineral phases such as trevorite ($NiFe_2O_4$) and cuprospinel ($CuFe_2O_4$) along with magnesioferrite ($MgFe_2O_4$) and chromite ($FeCr_2O_4$) were discovered in the Baransky (Iturup Island) and Mutnovskii (southern Kamchatka) hydrothermal systems (Rychagov et al. 1996). Jacobsite mineral ($MnFe_2O_4$) was found on manganese-rich rocks from the Ossa–Morena zone (Millan and Velilla 1998), from the Hutter Mine, Pittsylvania County, USA (Beard and Tracy 2002) and from the Central Alps, Switzerland (Brugger and Meisser 2006). In addition, jacobsite rich spinels along with galaxite have been found together in the metamorphosed manganese deposits near Bald Knob, North Carolina, USA (Essene and Peacor 1983). Hydrothermal meta-sedimentary rocks contain jacobsite as reported by Stalder and Rozendaal 2005. A significant amount of ferromanganese nodules ($MnFe_2O_4$) has been identified from the Christmas Island region of the Indian Ocean (Exon et al. 2002) and about 2–3 mm sized nodules of the same mineral have also been found on the west coast of the Pacific Ocean (Timofeeva et al. 2014). Cuprospinel has also been found in an ore dump at Baie-Verte, Newfoundland (Nickel 1973). Finally, spinels have been found in several meteorites; for instance, trevorite ($NiFe_2O_4$) a spinel ferrite mineral found in the Orgueil Soltmany and Khatyrka meteorites (Hoover 2007; Karwowski 2012; Bindi et al. 2015). Ji et al. (2008) reported a prebiotic chemistry experiment under hydrothermal conditions to synthesize hydrocarbons from CO_2 as a starting material on the surface of cobalt ferrite ($CoFe_2O_4$). The formation of $CoFe_2O_4$ along with other ferrites occurred by the incorporation of transition metals in magnetite minerals which is formed by the serpentinization of peridotites at mid-ocean ridges (Gülaçar and Delaloye 1976; Mével 2003).

With the intention of further evaluating the effect of minerals on the prebiotic chemistry of $HCONH_2$, we focussed our attention on spinel ferrite minerals. These are basically binary oxide minerals such as $MnFe_2O_4$, franklinite ($ZnFe_2O_4$), $NiFe_2O_4$, $CuFe_2O_4$, magnetite ($FeFe_2O_4$), ulvospinel ($TiFe_2O_4$), as well as $CoFe_2O_4$. Beside the prebiotic significance of this spinel group of minerals, we chose them because they can be regarded as metal oxide combined with iron oxide and the structural characteristics of spinel ferrite allows us to compare its catalytic activity with respect to pure iron oxide, as well as some previously studied $HCONH_2$ condensation reactions. The principal goal of this article is to address the following question:

Does the presence of divalent metal ions in iron oxide minerals improve the synthesis of nucleic acid bases from $HCONH_2$?

Keeping this in mind, a series of spinel ferrite nanoparticles ($NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$ and $MnFe_2O_4$) was synthesized from corresponding metal nitrate salts at high-temperature conditions compatible with a volcanic scenario on primitive Earth and $HCONH_2$ based condensation experiments were performed. The experimental findings reported here, in relation with the latest use of spinel ferrite for the entrapment of ribonucleotides and condensation of amino acids on its surface, shed further light on the role of spinel ferrites in prebiotic chemistry (Iqubal et. al 2015; 2016, 2017).

Experimental Section

Materials and Methods

Nickel (II) nitrate (Ni(NO$_3$)$_2$.6H$_2$O), Cobalt (II) nitrate (Co(NO$_3$)$_2$.6H$_2$O), Copper (II) nitrate (Cu(NO$_3$)$_2$.3H$_2$O), Citric acid (C$_6$H$_8$O$_7$.H$_2$O), and Ethylene glycol (C$_2$H$_6$O$_2$) were provided by E. Merck. Iron (III) nitrate (Fe(NO$_3$)$_3$.9H$_2$O), Manganese (II) nitrate (Mn(NO$_3$)$_2$.4H$_2$O), formamide (> 99.5%) and authentic standard of nucleic acid bases were purchased from Sigma-Aldrich. The reagents were used without further purification. Millipore water was used throughout the studies.

Preparation of Metal Ferrites

The nanosized metal ferrite, AFe$_2$O$_4$, where A = Ni, Cu, Co, and Mn was prepared according to a previously reported procedure (Sharma et al. 2015). In a typical synthesis of nickel ferrite, stoichiometric amounts of Ni(NO$_3$)$_2$.6H$_2$O (0.02 mol, 5.8 g) and Fe(NO$_3$)$_3$.9H$_2$O (0.04 mol, 16.1 g) were prepared separately and then mixed together with constant stirring at 80–90 °C. After complete mixing of the metal salts, citric acid (0.06 mol, 12.6 g) was added, followed by 10 ml of ethylene glycol to the solution. The solution was stirred until gel formation. The obtained gel was subjected to thermal treatment at 400 °C for 2 h in a muffle furnace. The same procedure was also used to synthesize the other ferrites. The synthesized material was characterized by several techniques such as XRD, FE-SEM, TEM, etc. Details of the characterization were found to be the same as reported earlier (Iqubal et. al 2016).

Nucleic Acid Bases Synthesis Protocol from Formamide

In our present work the typical synthesis was as follows: 5.0 ml of neat formamide was taken in a 50 ml round bottom flask, followed by adding 50 mg of a solid metal ferrite catalyst, either nickel ferrite (NiFe$_2$O$_4$), cobalt ferrite (CoFe$_2$O$_4$), copper ferrite (CuFe$_2$O$_4$) zinc ferrite (ZnFe$_2$O$_4$) or manganese ferrite (MnFe$_2$O$_4$). The contents of the flasks were heated at a constant temperature of about 160 °C in an oil bath connected with a condenser apparatus for the duration of between 6 and 48 h. A blank reaction (without adding catalyst) was also performed. The reaction mixture was pipetted out using a micropipette at different time durations between 6 and 48 h, then centrifuged and followed by filtration through a 0.25 μm syringe filter and further progress was monitored by high-performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry analysis (LC-MS).

High-Performance Liquid Chromatography Analysis

HPLC analysis of the crude reaction mixture was performed using Waters 2489, binary system with UV detection at 260 nm using a Purosphere® RP-18 column (250X4.6 mm, 5 μm). Reaction products were eluted with 0.1 M KH$_2$PO$_4$ buffer solution which is acidified with H$_3$PO$_4$ having pH ~4.05. The mobile phase flow for the HPLC analysis was maintained at 0.50 ml/min in isocratic mode.

Liquid Chromatography-Mass Spectrometry Analysis

LC-MS analyses were performed using a Shimadzu LC–MS-8030 (Shimadzu Corporation, Kyoto, Japan), equipped with reversed-phase Shimadzu VP-ODS C18 column (250 × 4.6 mm i.d. 5 μm). The column temperature was set at 35 °C for all analyses. Ionization of analytes was carried out in ESI mode maintaining the condition as: nebulizer gas flow 10 psi, dry gas 10 L min^{-1}, capillary voltage 4000 V, fragmentor voltage 100 V, vaporizer temperature 250 °C. Separation was performed using a gradient solvent system. The mobile phase contains 0.1% acetic acid–water (eluent A) and ACN (eluent B). The gradient was set as follows: 1% B for 0–20 min, and then B was increased to 80% after 20 min and was held for 40 min.

Results

Synthesis of nucleic acid bases from $HCONH_2$ needs heat at a constant temperature in the presence of a suitable catalyst. The temperature up to which $HCONH_2$ can be heated without decomposition is 180 °C and it was taken as a standard upper-temperature limit in view of the boiling point (211 °C) of $HCONH_2$. Thus, an assemblage of conditions for $HCONH_2$ condensation reaction is an appreciable local concentration of $HCONH_2$, a suitable catalytic surface, and temperature levels between 100 and 180 °C (Saladino et al. 2001). We studied the condensation of $HCONH_2$ in the presence of metal ferrite nanoparticles. In the absence of any catalyst (that is, performing a blank reaction) only purine was detected, whilst in the presence of a series of metal ferrites catalysts, $HCONH_2$ afforded various nucleic bases in appreciable yields, namely, cytosine, isocytosine, 4(3H)-pyrimidinone, adenine, hypoxanthine and purine (Table 1). We have used HPLC and LC-MS techniques to identify and quantify the products obtained in our reaction mixture.

High-Performance Liquid Chromatography Analysis

The HPLC chromatogram given in Fig. 1 showed several peaks indicating the detection of various nucleic bases in the reaction mixture. Nucleic bases identified by HPLC were cytosine, isocytosine, 4(3H)-pyrimidinone, adenine, hypoxanthine and purine. The confirmation of the reaction products was achieved with the help of retention time and co-injection methods. Each of the standard compounds having a different set of concentrations was taken in order to generate a standard curve. The detector response was calculated and found to be linear. The peak area comparison of products to that of standards gave the yield of reaction products. The

Table 1 Yield of the products formed from the condensation of formamide at 160 °C in the presence of metal ferrite

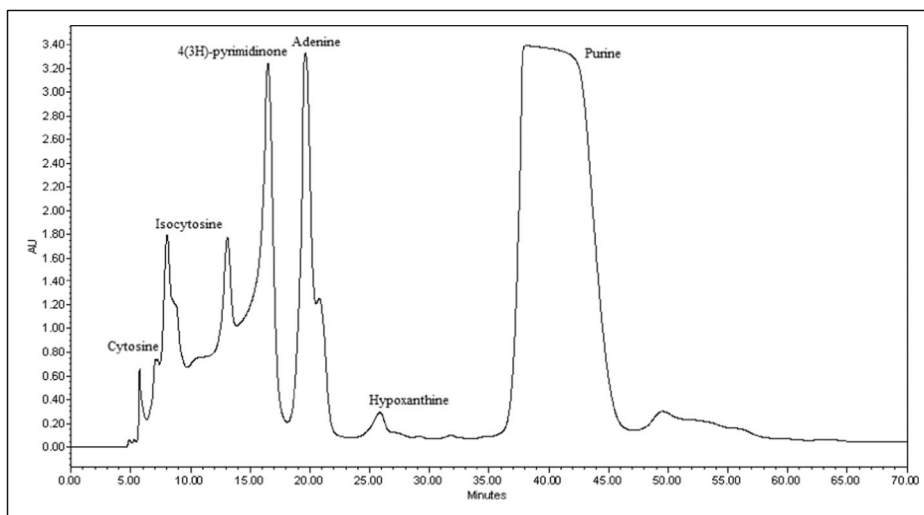| Compound	BET surface area (m^2/g)
$NiFe_2O_4$	80.64
$CoFe_2O_4$	53.66
$CuFe_2O_4$	34.67
$ZnFe_2O_4$	28.54
$MnFe_2O_4$	22.97

Fig. 1 A typical HPLC chromatogram of products formation when formamide was heated at 160 °C for 24 h in the presence of $NiFe_2O_4$

yield of the products is reported in terms of milligrams per gram of $HCONH_2$, in view of the unpredictability of the participation of the number of reactant molecules during the synthesis. It was observed that product formation started within 6 h of the reaction and gradually became constant after 24 h of the reaction (Fig. 2). Our main attention was concentrated on the synthesis and detection of purine and pyrimidine nucleic bases under the experimental conditions, where appreciable yield was noted. All the metal ferrites used here afforded the same purine and pyrimidine nucleic acid bases with different % yields. The blank experiment (without the presence of a catalyst) afforded 40.83 mg/g of purine and, compared to blank reaction results, the formation of purine was found to be the highest (92.78 mg/g) for nickel ferrite, whereas it nearly matched the blank value for manganese ferrite nanoparticles (43.00 mg/g). In addition to purine, an appreciable quantity of 4(3H)-pyrimidinone and adenine was also detected on all the metal ferrite catalysts except $CoFe_2O_4$ nanoparticles, where relatively low levels of products were observed when compared to the other catalysts. The other nucleic acid bases namely cytosine, isocytosine, and hypoxanthine were found in the range of 0.06–5.6 mg/g, which is relatively low when compared to the levels of purine, adenine and 4(3H)-pyrimidinone found, which ranged from 2.9 to 92.9 mg/g.

HPLC was done exclusively for quantification purposes. As discussed above, with the help of the standard compounds and co-injection methods we clearly obtained the existence of the mentioned compounds. However, in order to further prove the existence of the synthesized compounds, mass spectra were used for the identification of the ions (compounds) as a confirmatory technique.

Liquid Chromatography-Mass Spectrometry Analysis

The reaction mixture obtained after the condensation of $HCONH_2$ on a metal ferrite surface was then subjected to LC-MS analysis to determine the mass of each of the compounds detected by HPLC. The nucleic bases were separated in an LC-MS and from the mass ion
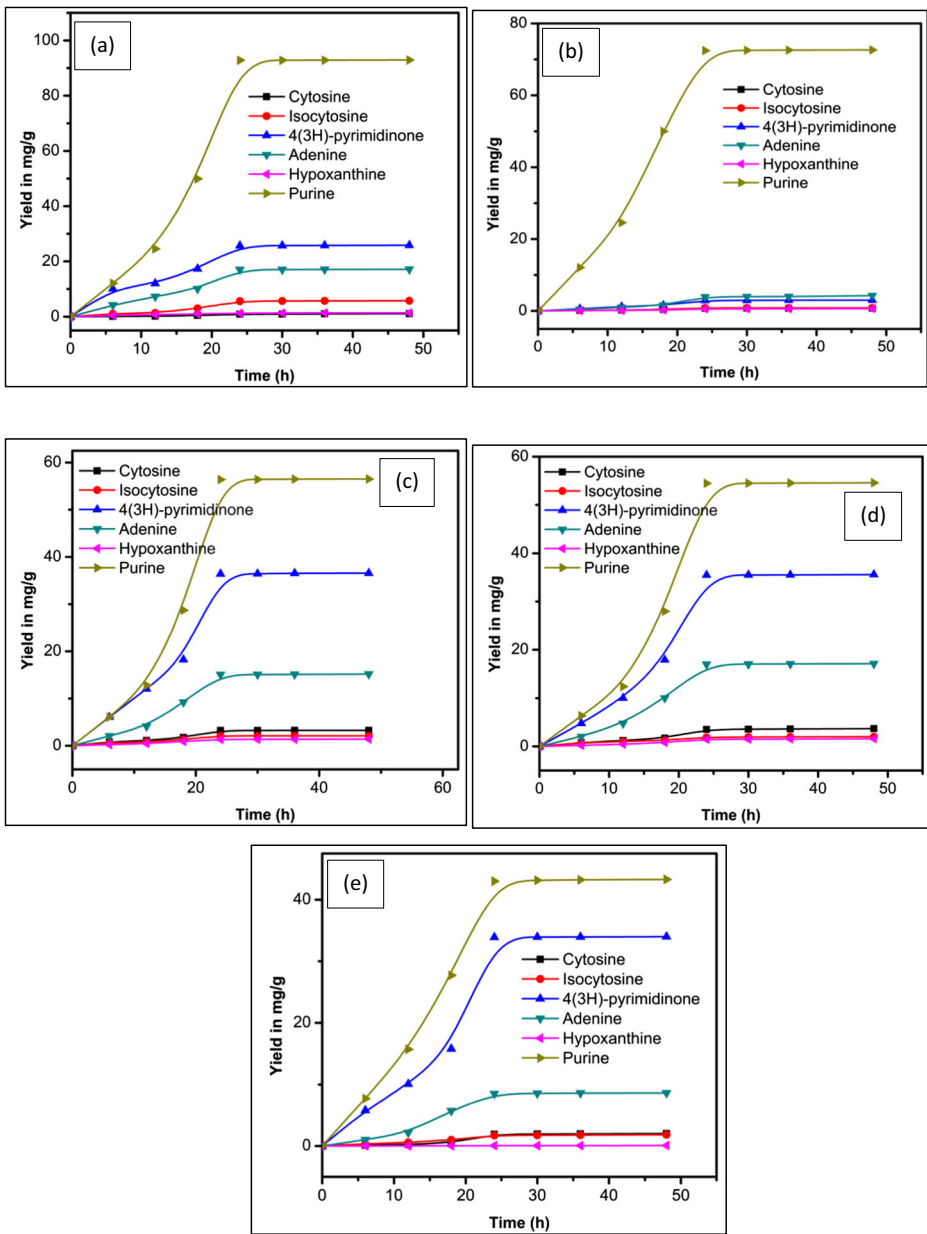
Fig. 2 Time dependent analysis of product formation at 160 °C by (**a**) NiFe$_2$O$_4$, (**b**) CoFe$_2$O$_4$, (**c**) CuFe$_2$O$_4$, (**d**) ZnFe$_2$O$_4$ and (**e**) MnFe$_2$O$_4$

chromatogram, we have established the mass of various nucleic acid bases. Mass spectra of the reaction mixture were analyzed in terms of $[M + nH]^+$ ions and gave the ratio results: cytosine m/z 112.0500; 4(3H)-pyrimidinone m/z 97.1000; adenine m/z 136.0500; hypoxanthine m/z 137.1000; and purine m/z 121.1000. Figure 3 shows the corresponding mass spectra of the nucleic acid bases.
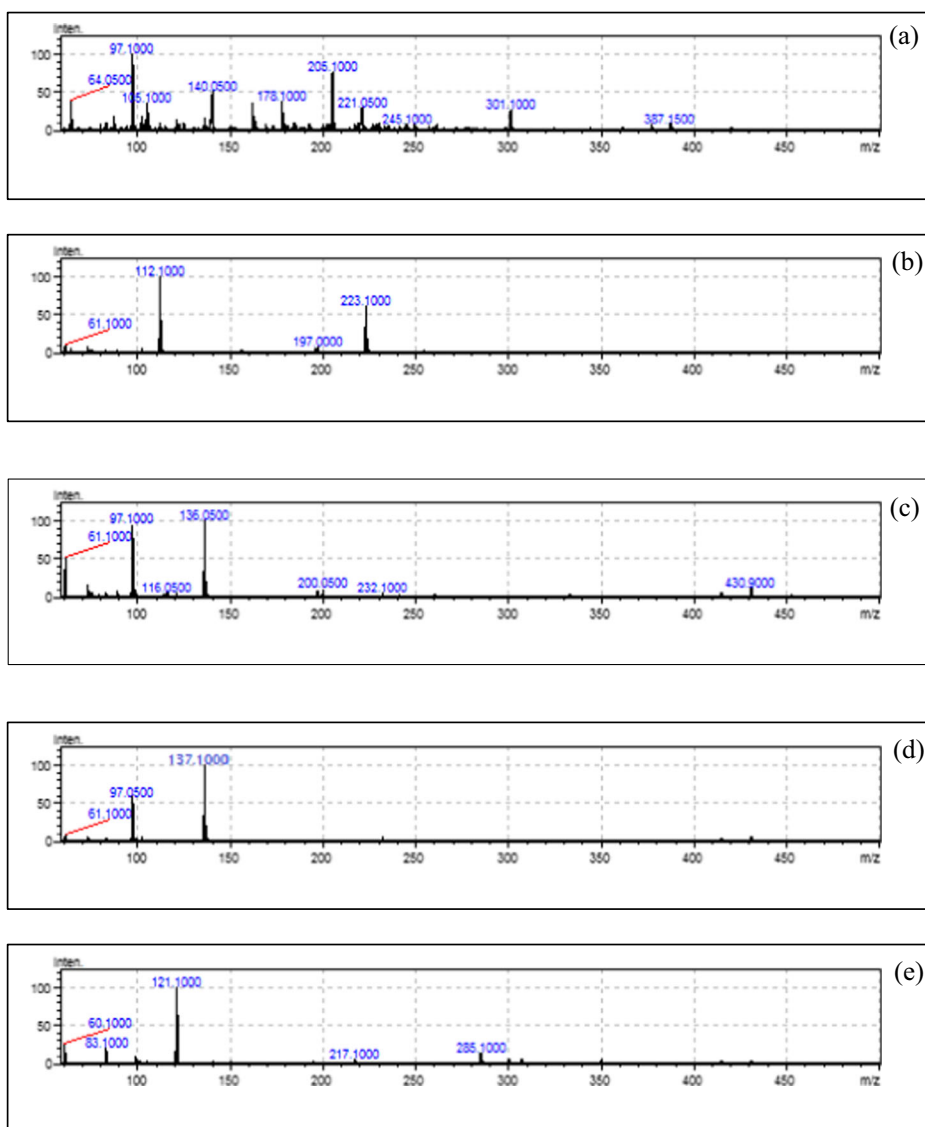
Fig. 3 A typical ESI-MS spectra of (**a**) 4(3H)-pyrimidinone, (**b**) Cytosine, (**c**) Adenine, (**d**) Hypoxanthine and (**e**) Purine when formamide was heated at 160^0 C for 24 h in the presence of $NiFe_2O_4$

Discussion

Several nucleic bases have been made from $HCONH_2$ in the presence of spinel ferrite minerals. The nucleic bases syntheses in the presence of each of the spinel ferrite minerals tested occur under moderate and relatively fast conditions. We chose $NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$ and $MnFe_2O_4$ as representative spinel ferrite compounds. Special emphasis has been given to the ferrites having metals Ni, Co, Cu, Zn and Mn. The possible role of these trace elements in chemical evolution has been increasingly considered important, due to their

presence in current biological systems. According to Oskar Baudisch (1943), the transition metal ions present in primeval seas as well as in the Earth's crust undoubtedly entered into the life cycle ancestrally and thus become a mandatory part of living cells. The precursors of metal enzymes might have played an important role by acting as catalysts for the synthesis of macromolecules of prebiotic significance. Sulfido, carbonyl etc., ligand-bound transition metals such as Fe, Ni, Co etc., can potentially act as catalysts in macromolecule synthesis (Wächtershäuser 1990). Fe, Zn and molybdenum (Mo) are considered to be key elements in all living organisms, whereas Ni, Co, Cu and Mn are essential elements for higher animals' chemistry only. The elements having multiple oxidation states, such as Fe, Cu, Mo, are of special relevance as they participate in electron transfer catalytic reactions in redox enzymes, whilst elements like Zn and Mn catalyze enzymatic reactions by behaving as Lewis acids (Kobayashi and Ponnamperuma 1985). These metal ions are present in the active sites of several enzymes. For example, Fe, Ni, Co, Cu, Zn and Mn are present as active site metals in the metalloenzymes: ferredoxin, urease, transcarboxylase, cytochrome oxidase, carboxypeptidase A and pyruvate carboxylase respectively (Vallee and Wacker 1976). Metal ferrites can easily be synthesized from the reaction of corresponding metal nitrate salts at high-temperature conditions compatible with the volcanic geological conditions on the early Earth.

$$A(NO_3)_2 + FE(NO_3)_3 \xrightarrow[\text{high temperature}]{\text{citric acid+ethylene glycol}} AFe_2O_4 + CO_2 + N_2 + H_2O$$
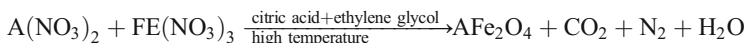
where $A = Ni^{2+}$, Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}

Spinel ferrite minerals can be treated as divalent metal oxides combined with iron (III) oxides of the type $AO.Fe_2O_3$. These particular minerals have the general formula AB_2O_4 where A = a divalent metal ion eg Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+} and B = Fe^{III} cation. In the spinel-type structure, there are T_d (tetrahedral) and O_h (octahedral) sites that are denoted by A and B while O represents the anionic sites. The unit cell of the spinel ferrite is categorized as a cubic structure containing 8 units of $AOFe_2O_3$ and 32 of O^{2-} anions. The partial packing of Fe^{III} and A^{II} cations among the $64T_d$ and 32 O_h sites complete the close face-centred cubic (FCC) skeleton of spinel ferrites (Mehdiye et al. 2008). They have the same crystallographic structure as mineral spinel (e.g. $MgAl_2O_4$) and that is the reason they are known as spinel ferrite minerals.

In the $HCONH_2$ condensation reactions, the role of the catalyst is pivotal. Catalysts provide their surfaces for concentrating the $HCONH_2$ molecules, reducing the necessary energy of activation of product formation and further preserving the product from degradation through the surface binding phenomenon. Basically, the $HCONH_2$ guest molecule is positioned on the surface of the catalyst in an ordered structure through the non-covalent interaction taking place between the host (catalyst) and the guest ($HCONH_2$). The well-arranged layout of the guest molecule on the surface of the host along with the non-covalent interactions taking place between them can activate the overall condensation processes. In respect of the present study, the catalytic effect of spinel ferrite minerals in $HCONH_2$ condensation is probably due to the presence of transition metal atoms in their corresponding structures. Demonstrating which parts of the minerals are acting as a catalyst in the reaction system is beyond the scope of this study. However, in accordance with the previous study regarding $HCONH_2$ condensation (Kumar et al. 2014) and in analyzing the catalytic role of spinel ferrite minerals in several heterogeneous catalytic reactions (Viswanathan et al. 1979; Ramankutty and Sugunan 2001; Wang et al. 2012; Kooti and Afshari 2012; Kharisov et al. 2014; Agrawal and Singh 2016), we

propose a probable surface interaction scenario involving $HCONH_2$ and the metal ions present in the framework of spinel ferrite nano-particles as given in Fig. 4. The surface distribution of the divalent and trivalent cations in the T_d and O_h sites of the spinel ferrite structure primarily direct the catalytic activity of the metal ferrites. It is well established that the octahedral sites of the spinel structure are almost exclusively exposed towards the interacting molecules and that is why octahedral cations in the spinel structure are mainly responsible for showing the catalytic activities towards a heterogeneous catalytic reaction (Jacobs et al. 1994). Moreover, metal ions can interact freely with the reactant molecules because octahedral sites are placed at larger distances. As shown in Fig. 4, in the normal spinel structure, divalent metal ions are completely located in tetrahedral sites where octahedral sites are populated by trivalent iron. On the other hand, in the case of an inverse spinel structure, divalent metal ions are arranged in tetrahedral sites whereas trivalent iron is equally distributed between tetrahedral and octahedral sites. The structure of the spinel is well described by the parameter λ, defined as the fraction of B ions present in tetrahedral sites. The value of λ ranges from 0 for normal spinels to 0.5 for inverse spinels. According to literature (Huheey et al. 2006), all of the spinel minerals tested in the present study are of the inverse type - except zinc ferrite which is a normal spinel. An electrostatic interaction may take place between electropositive metal ions present in the spinel ferrite catalyst and $HCONH_2$ bearing electronegative oxygen atoms. As in the inverse structure, octahedral sites are occupied by divalent metal ions and trivalent iron, so it is likely that these two ions will participate in the interaction with $HCONH_2$ molecule, whereas in normal spinels the octahedral sites are completely occupied by trivalent iron, so here a contribution of divalent metal ion in the interaction process may be treated as negligible.

Concerning the prebiotic significance of $HCONH_2$ products, we are mainly interested in the synthesis and characterization of purine and pyrimidine derivatives. Amongst the nucleic bases that were synthesized, adenine and cytosine are the natural nucleic bases. Although isocytosine is not a natural nucleic base, it still has considerable prebiotic significance; isocytosine, a constitutional isomer of cytosine is capable of identifying cytosine via Normal Watson-Crick (NWC) pairing and it recognizes guanine via Reversed Watson-Crick (RWC) interactions (Zhanpeisov and Leszczynski 1999; Oyelere et al. 2002). The ability of isocytosine to identify cytosine via NWC hydrogen bonding akin to that of cytosine/guanine couple could perhaps imitate guanine as a substitute ancient genetic alphabet. It is noteworthy that recognition of guanine by cytosine through RWC interactions increases the feasibility of hydrogen bonding
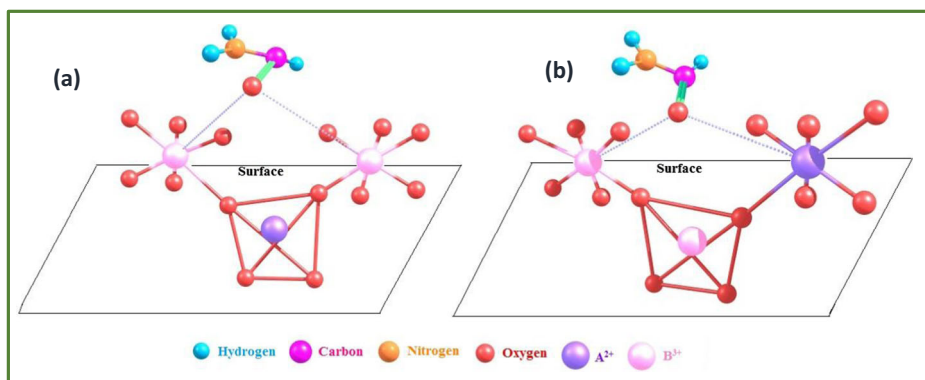

Fig. 4 Schematic structural arrangement of (a) normal spinel ferrite and (b) inverse spinel ferrite and their possible interaction scheme with formamide molecule

interactions in substitute pre-ribonucleic acid molecules. (Gupta et al. 2004). Moreover, simple hydrolysis of cytosine to give uracil makes it a potential choice of substrate for the synthesis of uracil. Cytosine can also pair up with adenine analogs through GC/AT transitions in the following replication (Hirao et al. 2002). A considerable amount of pyrimidine nucleic base 4-(3H)-pyrimidinone was obtained in the presence of all of the spinel ferrite minerals. This pyrimidine nucleic base is of significant prebiotic importance, as it is found to be abundant in the Murchison meteorite (Stoks and Schwartz 1982; Botta and Bada 2002). The possible prebiotic role of nucleic bases has been investigated in recent times by researchers. Gounaris and co-workers (Gounaris et al. 2014) shed light on the prebiotic synthesis of the amino acid, alanine, demonstrating that cytosine can reductively aminate the α-keto acid pyruvate into amino acid alanine. The biological importance of hypoxanthine lies in the fact that it is mutagenic by inducing A/T → G/C transitions at the DNA damaged site (Karran and Lindahl 1980; Hill-Perkins et al. 1986). Inherent uniform hydrogen bond patterns in hypoxanthine between the keto and enol forms may make it a substitutive choice of nucleic base for the ancestor of the A-T(U) and G-C base pairs because it can pair up with both T(U) and C by means of simple tautomerism (Shugar and Kierdaszuk 1985). In addition, hypoxanthine is believed to be an important intermediate in the synthesis and degradation of purine nucleotides (Martins et al. 2008).

A comparative study of the mineral in relation to $HCONH_2$ condensation reactions is difficult because the trend in the product formation may depend on several properties of the mineral such as surface area, method of preparation, particle size, structural shape, surface acidity, oxidation state, number of products formed etc. However, a few previous studies have been discussed that can allow us to compare the experimental results reported here. Iron (III) oxide minerals, namely hematite, goethite and akaganeite have been used for the $HCONH_2$ condensation reactions and gave purine, adenine, cytosine, 9-(hydroxyacetyl) purine and 4(3H)-pyrimidinone whilst in the presence of a series of manganese oxides, namely manganosite (MnO), bixbyite (Mn_2O_3), hausmannite (Mn_3O_4) and pyrolusite (MnO_2), $HCONH_2$ gave the same set of products along with thymine. The dissimilar structural characteristics of iron oxide minerals played an important role during the synthesis of nucleic bases where akaganeite, having a body-centered-cubic arrangement, was found less catalytically active when compared to hexagonally-close-packed structures bearing goethite and hematite. Among the employed manganese oxides in $HCONH_2$ condensation, the lower oxides of manganese were proved to be efficient catalysts that support the catalytic activity of these oxides in early Earth's reducing atmosphere (Shanker et al. 2011; Bhushan et al. 2016a, b). Surface acidity of montmorillonite clay was portrayed as a key parameter towards the efficient synthesis of nucleic base and their analogous compounds as reported by Saladino et al. 2004. Among the metal ferrites, nickel ferrite (having the largest surface area of 80.64 m^2/g) gave the highest yield of nucleic acid bases in the case of adenine, and isocytosine only; manganese ferrite having the lowest surface area (22.97 m^2/g), yielded higher levels of cytosine nucleic acid bases compared to nickel ferrite under identical conditions. The surface area of the ferrites is given in Table 2. The yield of the product was in accordance with surface area with respect to purine only, but as we compare this to the yield of other nucleic acid bases, the trend is not followed at all. For instance, the surface area of manganese ferrite (22.97 m^2/g) is nearly 2.5 times smaller than the surface area of cobalt ferrite (53.66 m^2/g) but the yield of the nucleic acid base 4(3H)-pyrimidinone was found to be almost 11 times higher in the case of the former compound. Yields of other nucleic acid bases such as adenine, cytosine, isocytosine, and 4(3H)-pyrimidinone were also high in the case of manganese ferrite when

Table 2 Surface area of metal ferrites

Catalyst	The yield of the products formed (mg/g of formamide)					
	Purine	4(3H)-pyrimidinone	Cytosine	Isocytosine	Hypoxanthine	Adenine
No catalyst	40.8	–	–	–	–	–
$NiFe_2O_4$	92.8	25.7	0.9	5.6	1.2	17.0
$CoFe_2O_4$	72.5	2.9	0.7	0.8	0.5	3.9
$CuFe_2O_4$	56.4	36.4	3.2	2.1	1.3	15.1
$ZnFe_2O_4$	54.4	35.5	3.5	1.9	1.5	17.0
$MnFe_2O_4$	43.0	33.9	1.9	1.7	0.06	8.5

compared to cobalt ferrite. The correlation between the yield of the products and surface area of the samples suggests that surface area is not a crucial parameter during the condensation of $HCONH_2$ and this experimental observation is in accord with the zirconium oxide mineral catalyzed $HCONH_2$ condensation reaction as performed by Saladino et al. (2010). In contrast, Kumar et al. (2014) reported surface areas to be the dominating parameter in the $HCONH_2$ condensation reaction in the presence of a series of metal(II) octacyanomolybdate complexes. The different behavior in respect to the governing parameters that affects the yield of the products between a metal oxide and double metal cyanide complexes could probably be due to different mineral types. In reality, $HCONH_2$ chemistry is mainly surface chemistry and any parameter that can optimize the interaction between the surface mineral and $HCONH_2$ will optimize (in principle) the yield of the process. It is noteworthy that some minerals can be partially soluble in $HCONH_2$ (e.g. phosphate minerals; Saladino et al. (2006). In these cases, the system is expected to be more complex, forming miscellanea between homogeneous and heterogeneous catalysis. The yield of the reaction products in the presence of spinel ferrite nanoparticles was found to be appreciably higher compared to some previously studied catalytic systems comprising of silica, alumina, iron oxides, manganese oxides and metal(II) octacyanomolybdate complexes (Saladino et al. 2001; Shanker et al. 2011; Kumar et al. 2014; Bhushan et al. 2016a, b). That makes it a unique material for $HCONH_2$ condensation reactions in respect of prebiotic chemistry. It is well established that ferrites present fascinating catalytic activity in comparison to monocomponent metal oxides (Kooti and Afshari 2012). The enhanced catalytic performance of bimetallic ferrite nanoparticles in relation to single component catalytic systems could possibly be due to their unique chemical and physical properties, arising from the synergistic effect between the two metals (Toshima and Yonezawa 1998; Beletskaya and Tyurin 2010; Moghaddam et al. 2014; Roy et al. 2016). Moreover, as discussed earlier the large unit cell of metal ferrite consists of 64 T_d and 32 O_h sites. Out of these, only 16 O_h and 8 T_d sites are filled by divalent and trivalent cations (Goldman 2006). Thus, a huge portion of interstitial empty sites in the crystal structure of spinel ferrite can act as grooves and could possibly enhance the overall catalytic activity in the condensation process. Complete comparative studies with all the minerals tested for $HCONH_2$ condensation reactions seems unrealistic because a systematic comparison can only be done when very similar sets of products are obtained in each case. That is why we have not considered those previously described syntheses for comparison (Saladino et al. 2003, 2004, 2005, 2006, 2008, 2010, 2011a, b) where a large number of other competitive products were identified compared to the metal ferrite catalyzed $HCONH_2$ condensation experiment.

It is a shared opinion that minerals possessing metal in its reduced state rather than in an oxidized state might have been more efficient in the context of chemical evolution and the origin of life. (Saladino et al. 2008; Bhushan et al. 2011, 2016a, b). The current study deals with the catalytic activity of spinel ferrite minerals where iron is in an oxidized form as Fe^{3+}, along with divalent metal ions A^{2+} towards nucleic acid base synthesis from $HCONH_2$. The experimental observation revealed that divalent transition metal oxides combined with iron (III) oxides (belonging in a spinel category with oxidized iron) are important for the synthesis of purine and pyrimidine nucleic acid bases from $HCONH_2$. The capability of oxidized iron (Fe^{3+}) and divalent metal ions (M^{2+}) for nucleic acid base synthesis from $HCONH_2$ as reported in this study is in accord with Shanker et al. (2011), where they have used only pure Fe^{III} oxide. The divalent metal ion in iron oxide makes it a novel catalytic system because it demonstrates excellent catalytic performance for nucleic acid base synthesis with significantly high yields when compared to pure iron oxide and some other minerals as discussed above.

Conclusion

The synthesis of a number of purine and pyrimidine nucleic acid bases from the thermal condensation of the prebiotic molecule, $HCONH_2$ in the presence of metal ferrite nanoparticles has been demonstrated. A series of catalysts employed during these experiments produced some purine and pyrimidine nucleic acid bases in appreciable quantities. The experimental yields of the condensation studies showed that divalent metal ion present in iron oxide enhances the catalytic activity of the overall process, compared to pure iron oxide as well as some previously studied catalytic systems such as silica, alumina, manganese oxides and metal(II) octacyanomolybdate complexes. Thus, the present catalytic system may be considered as a potential prebiotic catalyst in respect of the chemical evolution and origin of life.

Compliance with Ethical Standards

Author Disclosure Statement No competing financial interests exist.

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