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Stable room temperature magnetic ordering and excellent catalytic activity of mechanically activated high surface area nanosized Ni$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$


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Mechanosynthesized nanometric Ni$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ exhibit stable magnetic ordering at room temperature, excellent catalytic property and memory effect in dc magnetization profile.
Stable room temperature magnetic ordering and excellent catalytic activity of mechanically activated high surface area nanosized Ni$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$

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Abstract

Herein we report the structural, microstructural, dc magnetic and hyperfine properties along with catalytic activity of mechanosynthesized nanosized Ni$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ (~ 12 nm). The Rietveld refinement of the powder x-ray diffraction data, high resolution transmission electron microscopy and the infield Mössbauer study suggest that the sample is nanosized pure single phase cubic spinel of $Fd\bar{3}m$ symmetry with good crystallinity and it possesses equilibrium cation distribution ((Fe$^{3+}_{0.45}Zn^{2+}_{0.55})_A[Fe^{3+}_{1.55}Ni^{2+}_{0.45}]_B$O$_4$). The sample exhibits ferrimagnetic ordering with high saturation magnetization ($M_{SAT}$ = 53, 72 and 76 emu g$^{-1}$ at 300, 100 and 10 K, respectively), coercivity ($H_C$ = 280, 1200 and 2800 Oe at 300, 100 and 10 K, respectively), collective magnetic excitations, spin canting and memory effect in dc magnetization. The infield Mössbauer study suggests that the interior region of the particles is perfectly ferrimagnetic in
nature, while the spins at the surface region are ferrimagnetically coupled but noncollinearly aligned. Despite its nanometric size, the sample does not show superparamagnetic behavior rather retains stable magnetic order at room temperature due to enhancement of stress and surface anisotropy energy caused by high energy ball milling. We have shown that the presence of collective magnetic state along with surface spin disorder are the underlying reason for having slow dynamics and memory effect in the sample. Further, the BET (Brunauer–Emmett–Teller) surface area and the pore volume of the sample are $233 \text{ m}^2\text{g}^{-1}$ and $0.475 \text{ ccg}^{-1}$, respectively. The temperature programmed desorption (TPD) of ammonia suggests that the surface of this porous material is highly acidic ($1.516 \text{ mmol g}^{-1}$). Because of its high surface acidity and BET surface area the material acts as an efficient heterogeneous catalyst in the one pot synthesis of 3,4-dihydropyrimidine-2(1H)-ones (DHPMs) by Biginelli condensation reaction. This sample can be used in magnetic data storage devices, coding, storing and retrieving of binary number through magnetic field change and also as a very efficient heterogeneous, magnetically separable and recyclable catalyst.

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Introduction

Among all the currently studied magnetic nanomaterials, nanometric ferrites are the most popular ones not only for technological reasons but also due to their importance in understanding the fundamentals of nanomagnetism. The unique physical properties of nanometric ferrites have been the focus of extensive research in the recent years. The nanometric ferrites exhibit interesting structural property and rich crystal chemistry. They are also regarded as an exemplary model system for understanding the underlying mechanism of superparamagnetism, spin glass like behavior, spin canting effect and ferrimagnetism. The interest in the study on magnetic properties of nanostructured ferrites is fueled by their applications in high density data storage devices, magnetic resonance imaging (as contrast agent), magnetically guided drug delivery, hyperthermia treatment. However, with decreasing particle size the magnetic anisotropy energy liable to clutch the magnetization along certain orientation becomes comparable to the thermal energy and due to this the magnetic moment flips randomly with time. When this happens, particles lose their magnetic order and become superparamagnetic. The stability of magnetic order can be accomplished by the enhancement of the anisotropy energy. In recent times, the mechanically activated ferrites have come out as the potential candidates in the perspective of overcoming the direct clash between need for miniaturization and inherent superparamagnetic character of magnetic nanoparticles.

It is noteworthy that the stress anisotropy induced by ball milling acts as an extra source of anisotropy energy and it helps in retaining the stable magnetic order of the nanosized Ni-Zn ferrite at room temperature. A lot of investigations have been performed on nanometric Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ ferrites because of their high saturation magnetization, chemical stability and biodegradability. The Néel temperature ($T_N$) of mechanically milled Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ increases
significantly ($T_N \sim 592$ K) compared to its bulk counterpart ($T_N \sim 538$ K) due to cation redistribution. The strengthening of intersublattice $J_{AB}$ interaction promoted by the migration of Fe$^{3+}$ ions from (A) to [B] site leads to the enhancement of magnetization ($M_{SAT} \sim 51.3$ and 113.4 emu g$^{-1}$ at 300 and 10 K, respectively), coercivity ($H_C \sim 500$ and 1000 Oe at 300 and 10 K, respectively) and anisotropy energy of the mechanically milled nanosized ($\sim 25$ nm) Ni$_{0.35}$Zn$_{0.65}$Fe$_2$O$_4$. The cation redistribution, chemical inhomogeneity and large microstrain result in enhancement of magnetic order, magnetic ordering temperature ($T_B \sim 240$ K), saturation magnetization ($M_{SAT} \sim 42$ and 64 emu g$^{-1}$ at 300 and 10 K, respectively) and coercivity ($H_C \sim 1000$ Oe at 10 K) along with subsequent reduction of superparamagnetic relaxation in mechanically alloyed Ni$_{0.35}$Zn$_{0.65}$Fe$_2$O$_4$ ($\sim 27$ nm). Reduction of magnetization and magnetic ordering temperature of nanosized ferrites caused by surface spin canting and superparamagnetic relaxation are well established phenomena but despite some attempts the origin of counterintuitive enhancement of magnetization and magnetic ordering temperature in mechanically activated nanometric ferrites is yet not been understood properly.

Beside the issues related with magnetism, the ferrite nanoparticles have enormous potential for wide variety of catalytic applications. Recently, the nanosized ferrites have emerged as easily recyclable and recoverable catalysts for various organic reactions by discarding the hazardous process of separation and recycling of catalyst using conventional methods. This has immense importance in the field of green chemistry. For example, the nanometric CuFe$_2$O$_4$ acts as a competent reusable initiator in the synthesis of $\beta$, $\gamma$-unsaturated ketones from different allyl halides and acid chlorides, the catalyst-oxidant combination of NiFe$_2$O$_4$ and H$_2$O$_2$ has been used in the oxidation of thiols to disulfides and sulfides to sulfoxides, ZnFe$_2$O$_4$ nano powders have been successfully utilized as a catalyst for the one pot
three component synthesis of 4H-pyrans in water\textsuperscript{14} while the Ni-Co ferrite nanoparticles are efficient candidate for the reduction of nitro aromatic compounds and photo-oxidative degradation of toxic dyes.\textsuperscript{27}

It has been reported that the mechanically activated nonosized Ni- Zn ferrites are magnetically superior compared to its counterparts synthesized by chemical routes\textsuperscript{3,9,16,21} As most of the applications rely on the stability of magnetic order of the nanoparticles with time and high magnetization at room temperature therefore the mechanically activated nanosized Ni-Zn ferrites of different compositions deserve much more attention. To the best of our knowledge, there is no report on the structural, magnetic, hyperfine properties and catalytic activity of mechanically activated nanosized Ni\textsubscript{0.45}Zn\textsubscript{0.55}Fe\textsubscript{2}O\textsubscript{4} In this background, we have synthesized the nanosized Ni\textsubscript{0.45}Zn\textsubscript{0.55}Fe\textsubscript{2}O\textsubscript{4} by high energy ball milling, rigorously characterized it by using powder x--ray diffraction (PXRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive x--ray spectroscopy (EDS), and Mössbauer spectroscopic techniques and thoroughly examined the magnetic and hyperfine properties of the sample in order to reveal the role of microstrain, cation redistribution and stress anisotropy induced by ball milling in determining the magnetic and hyperfine properties of the sample. Moreover, we have evaluated the catalytic activity of the sample through the synthesis of 3,4-dihydropyridin-2-1H-(ones) (DHPMs) by solvent-free one-pot Biginelli condensation reaction.

In this context, it is pertinent to mention that the functionalized 3,4-dihydropyrimidine-2(1H)-ones (DHPMs) can be used for a variety of biological and pharmacological activities which include antibacterial, antifungal and antihypertensive as well as anticarcinogenic applications. They can act as alpha/a-adrenergic antagonists, neuropeptide mitotic kinesine inhibitors and HIV gp-120-CD\textsubscript{4} inhibitors\textsuperscript{30,31} The synthetic route of such DHPMs follows a
one-pot multi-component condensation reaction (Biginelli condensation) between an aldehyde, a \( \beta \)-keto ester and urea. The reaction can be catalyzed by various Lewis and Brønsted acids as well as bases. The drawbacks associated with homogeneous catalysts are catalyst separation, product isolation, low yield and stringent reaction condition. So an easily removable solid acid catalyst giving high yield of products is desirable.\(^{32,33}\) Herein we have studied the role of mechanically activated nanosized \( \text{Ni}_{0.45}\text{Zn}_{0.55}\text{Fe}_2\text{O}_4 \) as a magnetically removable catalyst for the synthesis of DHPMs for the first time.

**Experimental Section**

**Materials**

We have used powder oxides of \( \alpha\text{-Fe}_2\text{O}_3 \), NiO and ZnO. All the oxides are of 99.99\% purity and have been procured from Sigma Aldrich.

**Synthesis**

Bulk \( \text{Ni}_{0.45}\text{Zn}_{0.55}\text{Fe}_2\text{O}_4 \) has been prepared by standard ceramic method. At first all the oxides were mixed together in stoichiometric ratio and then manually grounded in an agate mortar for few hours. After that, the mixture was pelletized at a pressure of 20 tons/cm\(^2\). The pellets were sintered at 900 °C for 12 h and cooled down to room temperature at a rate of 3 °C/min. The pellets were grounded again and then passed through the same process of sintering at temperature 950 °C. Finally, the sample was annealed at 700 °C for 12 h and slowly cooled down to the room temperature.

The nanosized \( \text{Ni}_{0.45}\text{Zn}_{0.55}\text{Fe}_2\text{O}_4 \) was synthesized by grinding course powders of extremely pure \( \text{Ni}_{0.45}\text{Zn}_{0.55}\text{Fe}_2\text{O}_4 \) prepared by standard ceramic method at ambient temperature using Fritsch Planetary Mono Mill Pulverisette 6. The speed of the grinder was set at 330 rpm.
Grinding was carried out for 50 hours with ball to mass ratio of 20:1 using Tungsten Carbide vials and balls.

**Experimental**

The PXRD pattern of the sample was recorded by Bruker D8 Advanced Diffractometer using Cu Kα (λ=1.54184 Å) radiation by setting the generator at 40 kV and 40 mA. The data was collected at room temperature (21 °C) over the range of 2θ = 15-80° with step size and counting time of 0.0199° and 5 s/step, respectively. The high resolution transmission electron (HRTEM) micrographs of the sample were recorded by JEOL 2100 HRTEM. The FESEM (FEI, INSPECT F50) was used for the morphological and microstructural characterizations. The presence of constituent elements in the sample was probed by BRUKER EDS system attached with the FESEM equipment. The Fourier transform infrared (FTIR) spectrum of the sample was recorded by Perkin Elmer spectrometer (Spectrum Two) equipped with attenuated total reflectance (ATR) attachment in the wave number range of 400-4000 cm\(^{-1}\).

The dc magnetization (M) as a function of temperature (T) and external magnetic field (H) was measured using superconducting quantum interference device magnetometer (Quantm Design, SVSM, USA). The Mössbauer spectra of the sample were recorded in transmission geometry using constant acceleration drive (CMTE-250) with a 25 mCi \(^{57}\)Co source. The Mössbauer spectrum of the sample at 10 K in an external magnetic field of 5 T applied parallel to the γ-ray direction was recorded using superconducting magnet (JANIS SuperOptiMag). The natural iron sample is used as standard. The Mössbauer spectra of the sample were fitted by Recoil program.\(^{34}\) In all the spectra the solid lines indicate the simulated curves and the solid circles represent experimental data points.
The N$_2$ adsorption/desorption isotherm of the sample was recorded in a Quantachrome Instrument Autosorb 1C at 77 K. The sample was degassed at 453 K for 3 h under high vacuum before the analysis. Non local density functional theory was employed for the determination of the pore size distribution from the N$_2$ adsorption/desorption isotherm. The temperature programmed desorption (TPD) profile of ammonia over nanosized Ni$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ nanomaterial has been analyzed by using a thermal conductivity detector (TCD) in a Micromeritics Chemisorb 2720 instrument. For this experiment, the sample (372 mg) was first degassed in flow of He (flow rate 30 CC) for 2 hour at 100 °C. Then the sample was saturated with 10 % NH$_3$ in He at room temperature for 30 minutes. The excess NH$_3$ was removed by flow of He (flow rate 30 CC) for 45 minutes and after that the temperature programmed desorption of ammonia (carrier gas He) was studied by heating the sample from room temperature to 700 °C at a temperature ramp of 10 °C/ min.

The catalytic reactions were carried out in an Anton Paar microwave reactor Monowave 300. In a typical reaction β-keto ester (8 mmol), aldehyde (8 mmol), urea (12 mmol) and our sample as catalyst (30 mg) were mixed thoroughly and irradiated in the reactor for 10 minutes at 120 °C under solvent-free condition. After completion of the reaction, the reaction mixture was cooled to room temperature and 10 ml ethanol was added to it and the catalyst was removed magnetically. The mixture was evaporated to dryness and the resultant solid product was stirred in water and filtered. The product was washed with hexane and recrystallized from hot ethanol to obtain in pure form. The products were characterized by $^1$H and $^{13}$C NMR and compared with reported values. This procedure was followed to prepare all the dihydropyrimidones.
Result and discussion

Structural studies

It is well known that the cation redistribution is a common feature of nanosized ferrites. So, to determine the crystal structure of nanosized ferrite unambiguously the information about the cation migration is required. Therefore, we have recorded the infield Mössbauer spectrum of the sample at 10 K in the presence of 5 T external magnetic field. The infield Mössbauer spectrum exhibits two clear subpatterns (Fig.1(a)). The non-zero intensity of the 2nd and 5th line in the infield Mössbauer pattern indicates the presence of spin canting, which is mainly regarded as a surface phenomena. Moreover, many uncommon magnetic features of ferrite nanoparticles have been explained by core-shell model, where it is assumed that the spins in the interior region (core) of the particle are perfectly aligned while the spins at the surface (shell) region are noncollinear in nature. To account for the effect of diverse structural and magnetic character of the surface and core of the sample together we have fitted the infield spectrum with two pairs of sextets by assuming that the sample is composed of ferrimagnetically aligned core (interior region) surrounded by magnetically disordered shell (surface region). Further, to verify the validity of this assumption, the without field Mössbauer spectrum at 10 K has been fitted by four Lorentzian sextets maintaining the relative occupancies of the Fe ions among the (A) and [B] sites same as those obtained from fitting of the infield pattern. The simulated and the experimentally observed patterns are presented in Fig. 1 and the values of hyperfine parameters are listed in Table 1. Following the standard practice, the pair of sextet with high canting angle and low hyperfine field (HMF) is assigned to the shell region of the particles, whereas the pair with high HMF and very small canting is ascribed to the ferrimagnetically ordered core. In each pair the sextet with higher hyperfine field (HMF) and lower isomeric shift (IS) accounts for
the (A) site \( \text{Fe}^{3+} \) ions, while the other sextet with lower HMF and higher IS takes care of the [B] site \( \text{Fe}^{3+} \) ions.\(^3\)\(^9\) The resultant curves obtained by simulation matches well with the experimentally observed Mössbauer patterns (Fig.1) and the values of hyperfine parameters obtained by fitting the infield and without field Mössbauer spectra are in good agreement with each other (Table 1). From the calculated values of the canting angles (Table 1) it may be inferred that the spins at the surface region of the particle is highly disordered, while the core behaves like almost perfect ferrimagnetically ordered systems. This endorses the fact that the basic assumption adopted for the fitting of infield Mössbauer spectrum at 10 K is correct and further confirms that the particles of the sample are composed of ferrimagnetically ordered core surrounded by a ferrimagnetic shell with disordered spin structure. The results of infield and without field Mössbauer studies together with suggest that only \( \text{Fe}^{3+} \) ions are present in the sample.\(^3\) The ratio of \( \text{Fe}^{3+}_{\text{A}}/ \text{Fe}^{3+}_{\text{B}} \) has been calculated from the relative area of the sextets.\(^3\) The values of \( \text{Fe}^{3+}_{\text{A}}/ \text{Fe}^{3+}_{\text{B}} \) at core region and at the surface are 0.291 and 0.298, respectively. These are nearly equal. The average value of \( \text{Fe}^{3+}_{\text{A}}/ \text{Fe}^{3+}_{\text{B}} \) is 0.2945 and it is used during structural refinement for providing the initial occupancies of \( \text{Fe}^{3+} \) ions at (A) and [B] site.\(^9\)

The indexing of the PXRD pattern, initial structural and microstructural characterization together with phase analysis were carried out by using NTREOR90 of EXPO2009 package, DICVOL06 and TREOR90 of Fullprof.2k package, FINDSPACE of EXPO2009 package and Rietveld based software package MAUD2.33.\(^{36-40}\) The Details of the methodology adopted for structural, microstructural and phase analysis was reported by our group earlier.\(^9,21,41,42\) The Rietveld refinement plot obtained by using MAUD2.33 is presented in Fig.S1. The refinement converges with negligible difference between the experimental and simulated data and
satisfactory values of reliability parameters. The relevant structural, microstructural and reliability parameters are listed in Table 2.

To determine the crystal structure, bond length and bond angle of the sample more precisely we performed the Rietveld refinement of the PXRD data using GSAS program with EXPGUI interface (Fig. 2). The occupancies of the iron ions at the (A) and [B] sites were provided according to the value of the ratio of Fe$^{3+}_A$ / Fe$^{3+}_B$ (0.2945) as obtained from the infield Mössbauer study as initial input. The details of the methodology followed here is available in our earlier reports. The results suggest that the sample is a single phase spinel ferrite and it has crystallized in space group $Fd\bar{3}m$ of f.c.c. lattice with structural formula (Zn$^{2+}_{0.55}$Fe$^{3+}_{0.45}$)$_A$ [Ni$^{2+}_{0.45}$Fe$^{3+}_{1.55}$]$B$O$_4$. It is noteworthy that the cation distribution in the sample is almost equal to the ideal equilibrium value of bulk Ni$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$. The Miller indices and the space group obtained by the Rietveld structure refinement method are in good agreement with JCPDS database (JCPDS No.08-0234). Fig.3 depicts the asymmetric unit, surroundings of metal and oxygen ions, bond angle and bond length and the values of structural and microstructural parameters and fractional coordinates along with the occupancy of different ions are listed in Table 2 and Table 3.

**HRTEM, FESEM and FTIR study**

The transmission electron microscopy and selected area electron diffraction (SAED) technique were employed for comprehensive structural and microstructural (particle size, shape and crystallinity) characterization of the sample. The TEM micrographs at low and high magnification along with SAED pattern are shown in Fig.4. The individual size of the particles in the sample is in the range of 8-20 nm, the particles in the sample are of assorted size and irregular shape (Fig. 4 (a), (b) and (c)). The particle size distribution histogram is fitted with a
log-normal function and the fitting suggests that the average particle size is ~ 12 nm, which corroborates the crystallite size obtained from the PXRD study. The good polycrystalline nature of the sample is confirmed by the gleaming lattice fringes in the HRTEM image (Fig. 4(c)) and prominent Deby Scherrer rings in the SAED pattern (Fig. 4(d)).\textsuperscript{16} The crystallographic “d” values calculated from the radius of the rings corresponding to the different lattice spacing are in consonance with the values obtained from the PXRD study.

The energy dispersive x-ray spectrum of the sample has been shown in Fig. S2. The well-resolved peaks originating from the constituent atoms have been found in the energy range from 0 to 8 keV. The peak attributed to Au Lα appears as the sample was coated with gold prior to EDS study. In addition, elemental mapping (Fig. S3) also indicates the presence of all the constituent elements (Fe, Ni, Zn and O). The FTIR spectrum of the sample is shown in Fig. S4. The absorption bands at about 427 and 538 cm\textsuperscript{-1} are attributed to the stretching vibrations of the octahedral and tetrahedral site metal-oxygen bonds, respectively.\textsuperscript{45} Thus the FTIR study supports the results of PXRD study.

\textbf{N\textsubscript{2} adsorption/desorption analysis}

The N\textsubscript{2} adsorption/desorption isotherm for the sample is shown in Fig. 5. This isotherm has the characteristic features of both type I (at low P/P\textsubscript{0} region) and type IV (at high P/P\textsubscript{0} region) isotherms. Further, this isotherm also shows a mild hysteresis loop in the pressure region 0.5-0.9 P/P\textsubscript{0} of N\textsubscript{2}, indicating the presence of large mesopores.\textsuperscript{46} The BET (Brunauer–Emmett–Teller) surface area and a pore volume of the porous sample are 233 m\textsuperscript{2}g\textsuperscript{-1} and 0.475 ccg\textsuperscript{-1}, respectively. The nonlocal density functional theory (NLDFT) is used to determine the pore size distribution of the sample (inset of Fig. 6), where two types of pores: micropore with pore width
of 0.94 nm and mesopore of 6.4 nm are observed. The interparticle porosity of ca. 6.4 nm could be attributed to the observed mild hysteresis.

Magnetic nanoparticles have an inherent tendency to form agglomerates. It may be noted that we have adopted a special technique for TEM sample preparation to prevent the inherent tendency of agglomerate formation. In spite of that agglomerates are observed in the HRTEM image (Fig. 4) due to very high magnetization of the sample. The HRTEM images (Fig. 4) give no evidences in favor of the presence of intragranular pores in the sample. It may therefore be inferred that the intergranular pores have been formed in between the boundaries of the particles. The HRTEM study suggests that the particles in the sample are of irregular shape and assorted size. The variation in pore size can be attributed to the irregular shape and assorted size of the particles.

**TPD profile of ammonia**

The NH$_3$-TPD profile of the porous sample is presented in Fig. 6 which shows two peaks at temperatures 348 and 558 K. The low temperature peak represents weak acidic site and is comparatively smaller than the other one. It corresponds to a surface acidity of 0.416 mmol g$^{-1}$. Whereas, the high temperature peak indicates the presence of strong acidic sites corresponding to 1.1 mmol g$^{-1}$. Thus the total acidity of the material is 1.516 mmol g$^{-1}$. The Lewis acidity of the transition metals present at the surface of this porous material could be responsible for such high surface acidity.

**Magnetic and hyperfine property**

The ZFC-FC magnetization curves of the sample at an external magnetic field of 500 Oe are shown in Fig. 7. The ZFC magnetization remains almost independent of temperature between 300 and 120 K ($T_d$) and tumbles rapidly on further cooling. The FC magnetization increases
leisurely on cooling and gets almost saturated below 10 K. The nature of the ZFC-FC curves is far and away different from those obtained in purely superparamagnetic system.\textsuperscript{9} No signature of superparamagnetic blocking has been observed up to 300 K. Similar type of behavior in ZFC-FC magnetization curves has been earlier observed for mechanosynthesized Ni\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4},\textsuperscript{9} Co\textsubscript{0.2}Zn\textsubscript{0.8}Fe\textsubscript{2}O\textsubscript{4}\textsuperscript{47,48} and ZnFe\textsubscript{2}O\textsubscript{4}\textsuperscript{49} nanoparticle systems and explained in the paradigm of collective magnetic state and spin glass like behavior.

The sample exhibits clear hysteresis loop at room temperature (H\textsubscript{C}=280 Oe), which indicates that the sample is in magnetically well ordered state at this temperature (Fig. 8). The high value of coercive field has been observed in the M-H curves (inset of Fig. 8) recorded at lower temperatures (H\textsubscript{C} = 1200 and 2800 Oe at 100 and 10 K, respectively). The saturation magnetization (M\textsubscript{SAT}) of the sample has been calculated from the M vs. 1/H plot using the law of approach to saturation. The values of M\textsubscript{SAT} at 300, 100 and 10 K are 53, 72 and 76 emu g\textsuperscript{-1}, respectively. Moreover, the nonsaturated nature of the magnetization curve up to 5 T external magnetic field may be ascribed to the presence of spin canting in the sample.\textsuperscript{21}

It is well known that the magnetic ordering of the iron containing materials can be easily investigated with the help of \textsuperscript{57}Fe Mössbauer spectroscopic technique.\textsuperscript{3,9,16,21,50-55} The Mössbauer spectrum at 300 K (Fig. 9) has been fitted by Lorentzian site analysis method of the Recoil program. The Mössbauer spectrum at 300 K consists of a relaxed sextet (76.2\%) and a superparamagnetic doublet (23.8\%), which suggest that the blocking temperature (T\textsubscript{B}) of the system is higher than room temperature, most of the particles (72.2\%) in the sample exhibit the phenomenon of collective magnetic excitation and the rest are in superparamagnetic state.\textsuperscript{21} The magnetization vector of the particles in collective magnetic state fluctuates very slowly but remains close to easy axis while the magnetization vector of particles in superparamagnetic state
flip randomly with faster rate.\textsuperscript{3} Moreover, it is well known that for system exhibiting superparamagnetic relaxation and collective magnetic excitation, the outcome of an experiment depends upon the window time of the measurement technique adopted.\textsuperscript{3} Due to the lower window time of Mössbauer spectroscopy ($\sim 10^{-7}$-$10^{-9}$ s) compared to dc magnetic measurement ($\sim 100$ s), it succeeded in probing the presence of superparamagnetic state in the sample, the signature of which has not been found in the dc magnetization measurements.\textsuperscript{16} It may be noted that the room temperature Mössbauer spectrum has been recorded without applied magnetic field while the ZFC magnetization has been recorded in presence of 500 Oe field. The results of ZFC-FC magnetization together with the Mössbauer spectroscopic study suggests that 500 Oe field is enough to align the magnetization vectors of the particles in collective magnetic state.\textsuperscript{3} As most of the particles in the sample are in collective magnetic state (72.2\%) and dc magnetic measurement provides the information regarding the magnetic character of a sample as a whole, so the contribution coming from few superparamagnetic particles has been masked in the ZFC-FC magnetizations and M-H measurement. Because of this, the ZFC magnetization remains constant in the temperature range 120-300 K and the M-H loop at room temperature has displayed hysteresis.\textsuperscript{9}

The abrupt and rapid fall of ZFC magnetization below 120 K reveals that the magnetic moments of the particles in the sample get frozen randomly below this temperature.\textsuperscript{9} Under such a situation, the local magnetic order persists and Mössbauer spectroscopy, being a sensitive local tool for probing hyperfine character, can easily provide the information about such local magnetic order.\textsuperscript{3,9} In fact the Mössbauer spectrum at 10 K exhibits a clear sextet and gives evidence in favor of the existence of local magnetic order in the sample (Fig. 1(b)).\textsuperscript{9} This result suggests that the thermal fluctuation induced relaxation has been completely wiped out in low
temperature and the system is either in magnetically ordered state as a whole or there are certain
regions in the sample which are magnetically ordered. The abrupt fall of ZFC magnetization
below 120 K discards the possibility of existence of magnetically well ordered state below this
temperature. The low temperature M-H and Mössbauer spectroscopic studies indicate the
presence of spin canting. Thus by keeping in mind the outcomes of dc magnetic and Mössbauer
study at low temperature, it may be inferred that the sharp drop of the magnetic moment below
$T_f$ in the ZFC magnetization curve is caused by the random freezing of the canted surface spins
and the cooperative freezing of magnetic moments exhibiting collective magnetic excitation. In
collective state, the particles in the system behave like an assembly rather than an individual one
and the anisotropy energy of such an assembly shows multiminima in phase space. This type of
system can display spin glass like freezing behavior below a certain temperature ($T_f$) due to
cooperative freezing of the magnetic moments. Therefore we propose that the magnetic moment
of the sample drops sharply below 120 K ($T_f$) as the core region of the particles in the sample
undergoes magnetic phase transition from collective magnetic state to spin glass like state
through cooperative freezing of spins at the core region and the random freezing of the spins at
the surface due to spin canting effect. Further, it is true that in spin glass like state the
magnetization falls rapidly but the coercive field remains unaffected and due to this the sample
displays hysteresis below 120 K.

Now a days, the industrial applications of ferrite nanoparticles demand stable magnetic
order and high magnetization at room temperature. However, in most of the cases the unstable
spontaneous magnetization at higher temperature in consequence of superparamagnetism and
reduction of magnetization caused by spin canting severely limit their application possibilities.
The dc magnetic study together with infield and without field Mössbauer spectroscopic study
reveal that the sample under investigation is magnetically well ordered at 300 K along with it displays substantial amount of coercive field \( (H_C = 280 \text{ Oe}) \) and this has been noticed only in very few nanometric ferrites.\(^3\)\(^9\) It may be noted that the high energy ball milling has induced large microstrain among the lattice planes, ample amount of grain boundary defect together with shape and size irregularity which collectively enhance the stress and surface anisotropy of the system.\(^9\) Thus the total anisotropy energy of the system gets enhanced. The extra anisotropy contribution due to high energy ball milling has positive contribution in maintaining stable magnetic order at room temperature and promoting high coercivity.\(^9\)

Moreover, the \( M_{SAT} \) at 300 K (53 emu g\(^{-1}\)) has been found to be the highest among all the reported values of \( M_{SAT} \)s of mechanochemically synthesized Ni-Zn ferrite nanoparticles at the same temperature.\(^9\) It is well known that the magnetization of nanometric ferrites depends upon the relative distribution of magnetic cations between tetrahedral (A) and octahedral [B] sites of spinel lattice and the canting angle between [B] site moments. In most of the nanometric ferrites magnetization reduces due to unfavorable migration of magnetic cations between [B] to (A) site and surface spin disorder or both.\(^3\)\(^,\)\(^47\)\(^,\)\(^48\) In our earlier work on nanosized \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \), we have proposed that the inherent tendency of the reduction of magnetization of nanometric ferrites due to surface spin canting can be countered by maintaining equilibrium cation distribution.\(^9\) Even though the present sample exhibits high surface spin canting, it maintains the equilibrium cation distribution which helps in retaining high magnetization in the sample.

**Magnetic coding experiment**

We have performed the memory experiment (Fig. 10) on the sample by adopting the following steps: (i) at first, an external magnetic field of 100 Oe was switched on and the sample was cooled down below 300 K and the magnetization was recorded, (ii) after reaching at 70 K,
the 100 Oe field was switched off and the system was detained in the same state for 1 h and then the 100 Oe field was restored and the sample was cooled down to 50 K, (iii) at 50 K, the field was switched on to 200 Oe and the system was arrested at this state for 1 h and then 100 Oe field was restored and the system was cooled down to 25 K, (iv) at 25 K, the 100 Oe field was switched off and the system was maintained in that state for 1 h, after that the 100 Oe field was restored and the system was cooled down to 10 K, (v) at 10 K, 200 Oe field was switched on and the system was arrested at this state for 1 h, then the 100 Oe field was restored and the system was cooled down to 3 K and (vi) finally the system was heated back from 3 K in the presence of 100 Oe magnetic field and the magnetization was recorded. The cooling and heating rate was kept constant at 2 K/min during the entire measurement period. The recorded magnetization profile has been shown in Fig. 13 which suggests that the heating curve exhibits wiggles at all the points where the field was switched off and on during cooling cycle. The memory experiment has revealed that the sample can remember the temporal and spatial variation of magnetic field and successfully recollect its past history on recovering the same temperature. This type of memory effect is emblematic manifestation of the fact that the sample exhibits spin glass like slow dynamics at low temperature.9,56-59 The presence of collective magnetic state along with frustrated magnetic interaction at the surface region are the underlying reason for having slow dynamics and memory behavior in the sample. It may be noted that for samples exhibiting collective magnetic excitation no unique ground state of anisotropy energy exists but rather the anisotropy energy of the system shows multiple minima in phase space. For such configuration of anisotropy energy, the system can approach toward equilibrium but cannot be able to reach it and this leads to spin glass like slow dynamics in the system.60 By tagging the “H drop” as 0 and “H rise” as 1 we can easily store binary number in the sample and same can be recovered back
by warming the sample in a constant magnetic field. Thus the sample can be used for sensing the spatial and temporal variation of magnetic field and coding, storing and retrieving of binary number through magnetic field change.

**Catalysis**

The high surface acidity and BET surface area together with the magnetic separation potential of the sample have motivated us to explore its activity as heterogeneous catalyst for the synthesis of 3,4-dihydropyridin-2-1H-(ones) (DHPM) via solvent-free one-pot Biginelli condensation reaction. We have carried out the reactions with a wide range of substituted aldehydes, methyl acetoacetate and urea. The products were characterized by $^1$H and $^{13}$C NMR. The results are listed in Table 4. The yield of the DHPM products as calculated from the weight ranged ca, 60-75% for different aldehydes. When the reaction was carried out in the absence of any catalyst under similar reaction conditions no desired product was obtained. This result suggests that this mechanically activated nanosized Ni/Zn-ferrite is highly reactive catalyst for this acid catalytic condensation reaction.

**Reusability of the catalyst**

After separating the used catalyst magnetically, it was washed several times with ethyl acetate and dried in the oven. Further, we have reused this catalyst for four consecutive cycles and it was found that the catalyst was reusable without any significant loss of activity. For entry 1 of Table IV, the yield decreased from 67 % to 64 % after fourth cycle and in other cases yield did not change significantly. Compared to filtration and centrifugation, the magnetic separation is a simpler and easier procedure for recovering the catalyst from the reaction mixture with minimum loss of the catalyst. Thus this magnetically separable nanosized Ni/Zn-ferrite material
has large potential to be used as heterogeneous catalyst compared to other related non-magnetic catalysts reported in the literature.

**Conclusion**

The mechano-synthesized nanometric (~12 nm) Ni$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ possesses good crystalline character and nearly equilibrium cation distribution ([(Fe$^{3+}_{0.45}$Zn$^{2+}_{0.55}$)$_A$[Fe$^{3+}_{1.55}$ Ni$^{2+}_{0.45}$]$_B$O$_4$]) and it exhibits stable magnetic order, good amount of coercive field (280 Oe) and high saturation magnetization (~53 emu g$^{-1}$) at room temperature. We have shown that the high energy ball milling induced enhancement of stress and surface anisotropy helps in retaining stable magnetic order of ferrite nanoparticles at room temperature and the reduction of magnetization due to spin canting can be counteracted by tuning the cation distribution in the sample in a favorable manner. These intriguing magnetic characters of the sample can be successfully used for the fabrication of magnetic data storage and recording devices by overcoming the impediments of miniaturization. Furthermore, the sample is able to store the memory of sudden changes in magnetic field while cooling and it can reminisce the changes during heating that can be used in coding, storing and retrieving of binary number through magnetic field change. It can also be used to detect the spatial and temporal variation of magnetic field. Further, the sample is highly porous and it contains both micropores (0.94 nm) and mesopores (6.4 nm). High catalytic efficiency together with easily recovery of the magnetic Ni$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ nanocatalyst for the synthesis of one pot synthesis of 3,4-dihydropyrimidine-2(1H)-ones (DHPMs) suggested its further utility as a heterogeneous catalyst in future.
Acknowledgments

One of the authors (SD) gratefully acknowledges the financial support of Jadavpur University for providing research fellowship. RG acknowledges CSIR, New Delhi for a senior research fellowship. The UPE program of UGC and the PURSE program of DST, Govt. of India are also acknowledged. We are thankful to UGC-DAE CSR, Indore Center for infield Mössbauer measurement. We also gratefully acknowledge Prof. R. N. Joarder (Retd.) for helpful discussion.
Notes and references


61. $^1$H and $^{13}$C NMR data of some of the condensation products reported in Table 4.

5-Methoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyridin-2 (1H)-one (entry 1). $^1$H NMR (DMSO-d$_6$, 500 MHz) : δ (ppm): 9.17 (s, 1H), 7.71 (s, 1H), 7.18-7.30 (m, 5H), 5.10 (d, $J$ = 3 Hz, 1H), 3.50 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz): δ (ppm): 166.4, 152.7, 149.2, 145.3, 129.0, 127.8, 126.7, 99.6, 54.4, 51.3, 18.4.

5-Methoxycarbonyl-4-(4-bromophenyl)-6-methyl-3,4-dihydropyridin-2(1H)-one (entry 2). $^1$H NMR (DMSO-d$_6$, 500 MHz) : δ (ppm): 9.26 (s, 1H), 7.78 (s, 1H), 7.51 (d, $J$ = 8.5 Hz, 2H), 7.17 (d, $J$ = 8.5 Hz, 2H), 5.12 (d, $J$ = 2.5 Hz, 1H), 3.52 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz): δ (ppm): 166.3, 152.5, 149.5, 144.6, 131.9, 129.0, 120.9, 99.1, 53.9, 51.4, 18.4.

5-Methoxycarbonyl-4-(4-hydroxyphenyl)-6-methyl-3,4-dihydropyridin-2(1H)-one (entry 3). $^1$H NMR (DMSO-d$_6$, 500 MHz) : δ (ppm): 9.31 (s, 1H), 9.10 (s, 1H), 7.60 (s, 1H), 7.01 (d, $J$ = 8Hz, 2H), 6.67 (d, $J$ = 8.5 Hz, 2H), 5.02 (s, 1H), 3.51 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz): δ (ppm): 166.4, 157.0, 152.7, 148.5, 135.7, 127.8, 115.5, 99.9, 53.7, 51.2, 18.3.

5-Methoxycarbonyl-4-(2-nitrophenyl)-6-methyl-3,4-dihydropyridin-2(1H)-one (entry 4). $^1$H NMR (DMSO-d$_6$, 500 MHz) : δ (ppm): 9.36 (s, 1H), 8.12-8.10(m, 2H), 7.90 (s, 1H), 7.65-7.60 (m, 2H), 5.28 (d, J=3Hz, 1H), 3.52 (s, 3H), 2.26 (s, 3H).

5-Methoxycarbonyl-6-methyl-4-styryl-3,4-dihydropyrimidin-2 (1H)-one (entry 5). $^1$H NMR (DMSO-d$_6$, 500 MHz) : δ (ppm): 9.15 (s, 1H), 7.54 (1H, s), 7.23-7.40 (m, 5H), 6.36 (d, $J$ = 15 Hz, 1H), 6.21 (dd, J = 6 Hz, 16 Hz, 1H), 4.72 (d, J = 3 Hz, 1H), 3.61 (s, 3H), 2.18 (s, 3H); $^{13}$C
NMR (DMSO-d$_6$, 125 MHz) : \( \delta \text{ (ppm)}: 165.6, 152.6, 148.6, 136.2, 130.0, 128.6, 127.9, 127.5, 126.3, 97.6, 51.7, 50.8, 17.7, 14.2. \)
Figure Caption

Fig.1 Mössbauer spectra of the sample at (a) 10 K with 5 T external magnetic field and (b) 10 K fitted by the “Lorentzian site analysis” of the Recoil program.

Fig.2 The Rietveld refinement plot of the sample using GSAS, showing the difference (blue color line) between the experimental (red color symbol) and the simulated pattern (black color line).

Fig.3 Unit cell of the sample showing the tetrahedral (A) and octahedral [B] sites, along with the bond angles and lengths.

Fig.4 (a), (b) and (c) HRTEM micrograph and (d) SAED pattern of the sample.

Fig.5 N₂ adsorption/desorption isotherms of the sample at 77 K. Adsorption points are marked by filled circles and desorption points by empty circles. Pore size distributions obtained by using NLDFT method is shown in the inset.

Fig. 6 Temperature programmed desorption profile of NH₃ of the sample.

Fig. 7 ZFC-FC magnetization of the sample at 500 Oe external magnetic field.

Fig. 8 M-H (hysteresis) loops of the sample at 300, 100 and 10 K. (Inset shows the M-H loops between ±0.3 T for clarity).

Fig.9 Mössbauer spectrum of the sample at 300 K fitted by the “Lorentzian site analysis” of the Recoil program.

Fig. 10 Memory effect in the dc magnetization of the sample (green line indicates heating cycle and the solid pink circles represent the cooling cycle).
Table Caption

**Table 1** Values of zero field and infield Mössbauer parameters of the sample at 10 K determined by Lorentzian profile analysis of Recoil program.

**Table 2** Crystal Data and Refinement parameters obtained by MAUD† and GSAS* programs.

**Table 3** Fractional coordinates and occupancy of different ions obtained by GSAS program.

**Table 4** Biginelli condensation reactions over nanosized Ni/Zn-ferrite catalyst.
Table 1. Values of zero field and infield Mössbauer parameters of the sample at 10 K determined by Lorentzian profile analysis of Recoil program.

<table>
<thead>
<tr>
<th>Temperature / Field</th>
<th>Site</th>
<th>Width (mm s⁻¹)</th>
<th>IS (mm s⁻¹)</th>
<th>2ε (mm s⁻¹)</th>
<th>B&lt;sub&gt;eff&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (T)</th>
<th>B&lt;sub&gt;hf&lt;/sub&gt; (T)</th>
<th>A&lt;sub&gt;23&lt;/sub&gt; (%)</th>
<th>θ&lt;sup&gt;b&lt;/sup&gt; (Degree)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 K /5 T</td>
<td>[Fe&lt;sup&gt;3+&lt;/sup&gt;&lt;sub&gt;A&lt;/sub&gt;] s 0.25</td>
<td>0.45</td>
<td>0.00</td>
<td>57.0</td>
<td>52.3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.250</td>
<td>20.06</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Fe&lt;sup&gt;3+&lt;/sup&gt;&lt;sub&gt;B&lt;/sub&gt;] s 0.30</td>
<td>0.50</td>
<td>0.01</td>
<td>49.5</td>
<td>53.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.450</td>
<td>46.80</td>
<td>23.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Fe&lt;sup&gt;3+&lt;/sup&gt;&lt;sub&gt;A&lt;/sub&gt;] c 0.30</td>
<td>0.45</td>
<td>0.00</td>
<td>58.0</td>
<td>53.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.002</td>
<td>1.80</td>
<td>15.8</td>
<td></td>
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<tr>
<td></td>
<td>[Fe&lt;sup&gt;3+&lt;/sup&gt;&lt;sub&gt;B&lt;/sub&gt;] c 0.35</td>
<td>0.50</td>
<td>0.02</td>
<td>50.0</td>
<td>55.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.010</td>
<td>4.05</td>
<td>54.2</td>
<td></td>
</tr>
<tr>
<td>10 K /0 T</td>
<td>[Fe&lt;sup&gt;3+&lt;/sup&gt;&lt;sub&gt;A&lt;/sub&gt;] s 0.25</td>
<td>0.45</td>
<td>0.00</td>
<td>-</td>
<td>52.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Fe&lt;sup&gt;3+&lt;/sup&gt;&lt;sub&gt;B&lt;/sub&gt;] s 0.30</td>
<td>0.50</td>
<td>0.01</td>
<td>-</td>
<td>53.2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
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<td></td>
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<tr>
<td></td>
<td>[Fe&lt;sup&gt;3+&lt;/sup&gt;&lt;sub&gt;A&lt;/sub&gt;] c 0.30</td>
<td>0.45</td>
<td>0.00</td>
<td>-</td>
<td>53.1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Fe&lt;sup&gt;3+&lt;/sup&gt;&lt;sub&gt;B&lt;/sub&gt;] c 0.35</td>
<td>0.50</td>
<td>0.02</td>
<td>-</td>
<td>55.4&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>54.2</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Observed HMF (BHF) is the vector sum of the internal HMF and the external applied magnetic field.

<sup>b</sup> The average canting angle estimated from the ratio of the intensities of lines 2 and 3 from each subspectra, I<sub>2</sub>/I<sub>3</sub> (A<sub>23</sub>) according to θ = arccos[(4·I<sub>2</sub>/I<sub>3</sub>) / (4+ I<sub>2</sub>/I<sub>3</sub>)<sup>1/2</sup>. Where I<sub>2</sub>/I<sub>3</sub>=A<sub>23</sub>.

<sup>c</sup> Estimated according to the relationship of B<sub>eff</sub>, B<sub>hf</sub> and applied field.
Table 2. Crystal Data and Refinement parameters obtained by MAUD\(^+\) and GSAS\(^*\) programs

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula(^{†,∗})</td>
<td>(\text{Ni}<em>{0.45}\text{Zn}</em>{0.55}\text{Fe}_2\text{O}_4)</td>
</tr>
<tr>
<td>Formula Weight(^{†,∗})</td>
<td>238.06</td>
</tr>
<tr>
<td>Crystal System(^{†,∗})</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group(^{†,∗})</td>
<td>Fd-3m</td>
</tr>
<tr>
<td>Crystallite size (nm)(^{†})</td>
<td>11.70(0.06)</td>
</tr>
<tr>
<td>Microstrain ((×10^{-4})^{†})</td>
<td>2.393(0.4)</td>
</tr>
<tr>
<td>a (Å)(^*)</td>
<td>8.4150(6)</td>
</tr>
<tr>
<td>(V \text{[Å}^3])*</td>
<td>595.885(2)</td>
</tr>
<tr>
<td>(Z^{*})</td>
<td>8</td>
</tr>
<tr>
<td>(D_{\text{cal}} / \text{gcm}^{-3})*</td>
<td>5.307</td>
</tr>
<tr>
<td>(\mu_{\text{CuK}\alpha} / \text{mm}^{-1})*</td>
<td>84.334</td>
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<tr>
<td>(R_{wp}^{†})</td>
<td>0.020</td>
</tr>
<tr>
<td>(R_{exp}^{†})</td>
<td>0.014</td>
</tr>
<tr>
<td>GOF(^{†})</td>
<td>1.43</td>
</tr>
<tr>
<td>(R_{wp}^{∗})</td>
<td>0.0118</td>
</tr>
<tr>
<td>(R_{p}^{∗})</td>
<td>0.0105</td>
</tr>
<tr>
<td>(R_{F}^{2∗})</td>
<td>0.1935</td>
</tr>
<tr>
<td>(\chi^{2∗})</td>
<td>1.727</td>
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Table 3. Fractional coordinates and occupancy of different ions obtained by GSAS program.

<table>
<thead>
<tr>
<th>Ions</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
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</thead>
<tbody>
<tr>
<td>Zn(A)</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.550</td>
</tr>
<tr>
<td>Fe(A)</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.450</td>
</tr>
<tr>
<td>Fe(B)</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.775</td>
</tr>
<tr>
<td>Ni(B)</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.225</td>
</tr>
<tr>
<td>O</td>
<td>0.2624(12)</td>
<td>0.2624(12)</td>
<td>0.2624(12)</td>
<td>1.000</td>
</tr>
</tbody>
</table>
Table 4. Biginelli condensation reactions over nanosized Ni/Zn-ferrite catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Products</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>TOF(^a) (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHO</td>
<td><img src="image1.png" alt="Product 1" /></td>
<td>10</td>
<td>67</td>
<td>708</td>
</tr>
<tr>
<td>2</td>
<td>CHO</td>
<td><img src="image2.png" alt="Product 2" /></td>
<td>10</td>
<td>73</td>
<td>771</td>
</tr>
<tr>
<td>3</td>
<td>CHO</td>
<td><img src="image3.png" alt="Product 3" /></td>
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<td>71</td>
<td>749</td>
</tr>
<tr>
<td>4</td>
<td>CHO</td>
<td><img src="image4.png" alt="Product 4" /></td>
<td>10</td>
<td>65</td>
<td>687</td>
</tr>
<tr>
<td>5</td>
<td>CHO</td>
<td><img src="image5.png" alt="Product 5" /></td>
<td>10</td>
<td>66</td>
<td>696</td>
</tr>
<tr>
<td>6</td>
<td>CHO</td>
<td><img src="image6.png" alt="Product 6" /></td>
<td>10</td>
<td>No product</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)TOF = moles converted/mole of active site/time. Total acidity 1.516 mmol g\(^{-1}\) (obtained from TPD-NH\(_3\) analysis).
Mössbauer spectra of the sample at (a) 10 K with 5 T external magnetic field and (b) 10 K fitted by the "Lorentzian site analysis" of the Recoil program.

Fig. 1
The Rietveld refinement plot of the sample using GSAS, showing the difference (blue color line) between the experimental (red color symbol) and the simulated pattern (black color line).

The peaks at 2θ (Degree) are labeled as (220), (222), (311), (422), (511), (400), (333), and (620) for the experimental data. The simulated pattern for these peaks is also shown.

Fig. 2

Intensity (a.u. x 10^4)

2θ (Degree)
Unit cell of the sample showing the tetrahedral (A) and octahedral [B] sites, along with the bond angles and lengths.

Fig. 3

1806x1290mm (72 x 72 DPI)
Fig. 4

(a), (b) and (c) HRTEM micrograph and (d) SAED pattern of the sample.

920x1010mm (72 x 72 DPI)
N2 adsorption/desorption isotherms of the sample at 77 K. Adsorption points are marked by filled circles and desorption points by empty circles. Pore size distributions obtained by using NLDFT method is shown in the inset.

Fig. 5

N2 adsorption/desorption isotherms of the sample at 77 K. Adsorption points are marked by filled circles and desorption points by empty circles. Pore size distributions obtained by using NLDFT method is shown in the inset.

1443x1255mm (72 x 72 DPI)
Temperature programmed desorption profile of NH3 of the sample.

Fig. 6

Temperature (K)

TCD signal

1.1 mmol g⁻¹

0.416 mmol g⁻¹
ZFC-FC magnetization of the sample at 500 Oe external magnetic field.

$T_f = 120\ \text{K}$

Fig. 7
Fig. 8

M-H (hysteresis) loops of the sample at 300, 100 and 10 K. (Inset shows the M-H loops between ±0.3 T for clarity).

1456x1237mm (72 x 72 DPI)
Mössbauer spectrum of the sample at 300 K fitted by the "Lorentzian site analysis" of the Recoil program.

Fig. 9
Memory effect in the dc magnetization of the sample (green line indicates heating cycle and the solid pink circles represent the cooling cycle).