Preparation of Nickel Nanoparticles by Intramolecular Reaction of Nickel(II) Hydrazine Complex in the Solid State at Room Temperature

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$[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$ complex was prepared according to literature report. The reaction between aforementioned complex *via* sodium alkoxides as a reactants, were carried out in the solid state. The $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8]$ $(SO_4)(H_2O)_{10}$ undergoes an intramolecular two electrons oxidation-reduction reaction at room temperature and metallic nickel nanoparticles (Ni1-Ni5) was produced. The aforesaid complex contains nickel(II) as an oxidizing agent and also hydrazine ligand as a reducing agent. Its redox reaction leads to the formation of other products, sodium azide and ammonia gas and alcohols. In such a solid state reaction, not only the intramolecular redox reaction is important but also it is a novel method in the synthesis of nanoparticles. The nickel metal nanoparticles were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) analysis. The synthesized nickel nanoparticles have similar morphologies however the particle size distributions are different. The nickel nanoparticles have particle size distributions ranging from 10-75 nm. This work presents a novel approach in the intramolecular redox reactions in the solid state, and provides insight into the synthesis of metal nanoparticles *via* metal hydrazine complexes at room temperature.

Keywords: Intramolecular reaction, Chemical reduction, Mechanochemical reaction, Nickel nanoparticle

INTRODUCTION

Among the ferromagnetic elements Ni nanoparticles have a wide range of application in chemical catalysis, optoelectronics and magnetic recording media and rechargeable batteries [1]. Many interesting properties were observed when magnetic metal particles prepared in nanoscale. As particle size decreases, the surface-to-volume ratio increases, and properties depend on this ratio changes. Thus, nanoparticles show many unusual chemical and physical properties relative to bulk [2]. Various methods have been developed for the synthesis of metal nanoparticles including vapor, liquid, solid state processing routes [3-5]. In literature, the top down, and the bottom up approaches are used to synthesize nanoparticles [6]. The mechanochemical synthesis is an interdisciplinary new area

between the top down and bottom up approaches [7]. The idea of performing reactions directly between solids, excluding the dissolving stage, is attractive to chemists [8]. Because reactions in aqueous solution undergo side reactions. Therefore solid state reaction method has the advantage of avoiding some of the side reactions associated with the aqueous route. Mechanochemistry refers to reactions that are induced by mechanical processing usually milling or grinding. The synthesis of nanocrystalline materials by mechanical milling, mechanical alloying and mechanochemical processing has been studied [9]. On the other hand the studies of coordination mechanochemical redox reactions are in their infancy [10]. The chemistry of coordination compounds is a wide range of inorganic chemistry and an enormous number of reactions are known to occur in this area [11]. When mechanical stress is exerted on molecular crystalline solids of coordination compounds, not only crystalline lattice but also the constituent molecules

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are subjected to distortion. The numerous types of reactions including ligand exchange, isomerization, redox and coordinated ligands reactions have been reported [12-13]. On the other hand, a great number of coordination compounds have been prepared by the oxidation or reduction of a metal compound in the presence of a ligand [14]. In most of the transition metal complexes the electronic interaction between metal and ligands play an important role in intramolecular reactions [15]. Consequently, intramolecular electron transfer involving metal and ligands take place between coupled redox centers. In many cases, ligand to metal charge transfer excitation is associated with the reduction of the metal and oxidation of the ligand [16]. But in some cases, ligands serve as the source of the reducing agent. Hydrazine is such a compound, and preparation of many complexes is based on it [17]. The extensive coordination chemistry of hydrazine is evidence for this type of reaction. Transition metal complexes have several unique features. The most important one is the pattern of electron transfer [18]. So far, no reports has been published about the mechanochemical reduction of nickel(II) complexes into metallic nickel nanoparticles in any literatures. In this work $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$ complex is used for preparation of nickel nanoparticles in the solid state. In this case it is quite clear that the electron is transferred from the ligand to metal and intramolecular oxidation reduction reaction has been occurred.

EXPERIMENTAL

All chemical reagents used were pure grade and used without further purification. Nickel sulfate heptahydrate, hydrazine monohydrate solution, metallic sodium, methanol, ethanol, n-propanol, iso-propanol and n-butanol were purchased from Merck. The water used throughout this work was doubly distilled water. The preparation of $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$ has been carried out in aqueous solution under atmospheric conditions. Sodium alkoxides, (sodium methoxide, sodium ethoxide, sodium n-propoxide, sodium iso-propoxide and sodium n-butoxide) were prepared by reacting sodium metal with respective alcohol [19]. The nickel nanoparticles (Ni1-Ni5) were prepared in the solid state at room temperature in
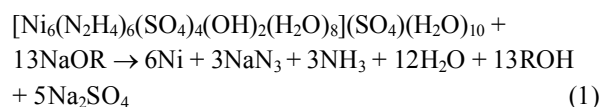
the form of powder.

Synthesis of Polynuclear Nickel(II) Complex $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$

A total of 2.5150 g of $NiSO_4.7H_2O$ (8.95×10^{-3} mol) was dissolved in 20 ml of deionized water. A total of 0.50 ml (1.03×10^{-2} mol) of hydrazine monohydrate was added to the solution under intensive stirring. A small amount of a precipitate was formed immediately. The mixture was stirred for another 10 min, followed by filtration. The solution was then gently heated on a hotplate up to 40 °C for 5 h and was then left at room temperature to cool. Blue crystals formed in the solutions within 48 h. The crystals were filtered and washed with a small amount of cold distilled water and methanol [20].

Mechanochemical Preparation of Metallic Nickel Nanoparticles

In a typical solid state reaction to produce nickel nanoparticle, a mixture 0.692 g (0.5 mmol) of $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$ complex and 0.351 g (6.5 mmol) sodium methoxide were loaded into a mortar pestle of 50 ml capacity. The molar ratio of the nickel(II) hydrazine complexes to sodium methoxide was varied from 1 to 13, and grinding was carried out for 4 h. For the purification, the product was transferred to a beaker and washed. The product (Ni1) was washed with methanol, filtered, and dried in a vacuum oven at room temperature for a period of at least 24 h. In a similar reaction of aforementioned complex and alkoxides, the nickel nanoparticles (Ni2-Ni5) in the solid phase were produced. The mole ratio for preparation of (Ni2-Ni5) were similar to Ni1, however the time of reaction are 8, 5, 6 and 12 h respectively. In the solid phase intramolecular chemical oxidation reduction between ligand and central atom is occurred and metallic nickel is generated (Eq. (1)) at room temperature.

$$[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10} + 13NaOR \rightarrow 6Ni + 3NaN_3 + 3NH_3 + 12H_2O + 13ROH + 5Na_2SO_4 \qquad (1)$$

$(NaOR = NaOCH_3, NaOCH_2CH_3, NaOCH_2CH_2CH_3, NaOCH(CH_3)_2$ and $NaOCH_2CH_2CH_2CH_3)$

During the milling of reactants in the redox reactions ammonia gas released, and NaN_3 was produceed. Ammonia combines with hydrochloric acid and forms ammonium chloride. Colorimetric testing is used to detect NaN_3 [21]. A drop of the filtered solution is placed in the depression of a spot plate and treated with 1 or 2 drops of dilute hydrochloric acid. A drop of ferric chloride solution is added and the spot plate gently is heated. A red color indicates hydrazoic acid and the presence of sodium azide in the solution, as well.

Characterization of Materials

The nickel complex and nickel powders were characterized by X-ray powder diffraction (XRD). XRD measurements were performed using a Philips X'pert pero MPD diffractometer with Cu Kα radiation in the range 2θ from 10-80 at room temperature. IR spectra were obtained as KBr pellets in the range 4000-400 cm^{-1} using a Shimadzu FTIR spectrometer. Scanning electron microscopy (Philips XL30ESEM) was used to characterize nickel nanoparticles. A vibrating sample magnetometer (VSM, Maghnetis Daghigh Kavir Co) was used to evaluate the magnetic parameters.

RESULTS AND DISCUSSION

Water is a common solvent of most chemical reactions. The hydrolysis reaction happens when a substance reacts chemically with water, which can influence the composition and properties of the final products. In the solid state $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$ undergoes an intramolecular two electron oxidation reduction reaction. These reactions under sodium alkoxide conditions $(NaOCH_3, NaOCH_2CH_3, NaOCH_2CH_2CH_3, NaOCH(CH_3)_2, NaOCH_2CH_2CH_2CH_3)$ lead to formation of metallic nickel, azide and ammonia. In solution, depending on the oxidizing agent, pH, and temperature, hydrazine reacts in different pathways. In aqueous solution, hydrazine reacts as one, two, or four electron oxidation paths, and is converted to a mixture of dinitrogen and ammonia, azide and ammonia and/or only dinitrogen, respectively. During the solid state redox reactions, besides metallic nickel the ammonia gas and NaN_3 are produced. Intramolecular redox reactions of nickel complexes have several unique features, the most

important of them being the patterns of electron transfer from ligand to metal. On the other hand, these mechanochemical reactions occurred at room temperature, and the final product is metallic nickel nanoparticles. Moreover, the average particle size of nickel powders can be controlled from 10 to 75 nm by adjusting the reaction conditions. In this work, the nickel nanoparticles are prepared with spherical shapes by using a mechanochemical route. However, when the nickel complex as a reactant was used in aqueous solution, nickel nanoparticles with different morphologies were formed [22-23]. The metallic nickel nanoparticles were characterized using XRD, IR, VSM and SEM analysis.

According to the XRD patterns which have been reported in literature $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)$ $(H_2O)_{10}$ crystallizes in the triclinic system [20]. During solid state reactions the nickel(II) complex is converted to metallic nickel thus, all diffraction peaks of complex patterns disappeared. In accordance with the diffraction pattern analysis, it could be concluded that the nanoparticles prepared in this work was pure nickel with an fcc crystal structure, and JCPDS file number of nickel nanoparticles is (87-0712) (Fig. 1). The mechanochemical reaction of nickel(II) complex to metallic nickel is accompanied by a change in the crystal structure. All the diffraction peaks can be well indexed to fcc phase nickel, with lattice constants of a = 3.5299 Å. The crystallite size are estimated from the full-width at half maximum (FWHM) of the diffraction peaks by the Scherrer formula (Table 1). Crystallite sizes in Ni1 and Ni2, show that the both crystals are grown in (111) face direction. On the other hand, a crystal growth in the Ni3 is observed in the (220) face direction. Although crystallite sizes in Ni4 and Ni5, show a different growth in (200) and (111) face direction respectively (Table 2). The results show that nickel complex under alkoxide conditions has a fundamental effect on nucleation and morphologies of metallic nickel. The shape of the crystal depends on the shape of the unit cell, but it is not necessarily the same as that of the unit cell. The general rule relating to the growth velocity is that the fast-growing faces disappeared whereas the slow-growing faces remain. Growth velocities are obtained by measuring the diameter of the crystal in different directions.
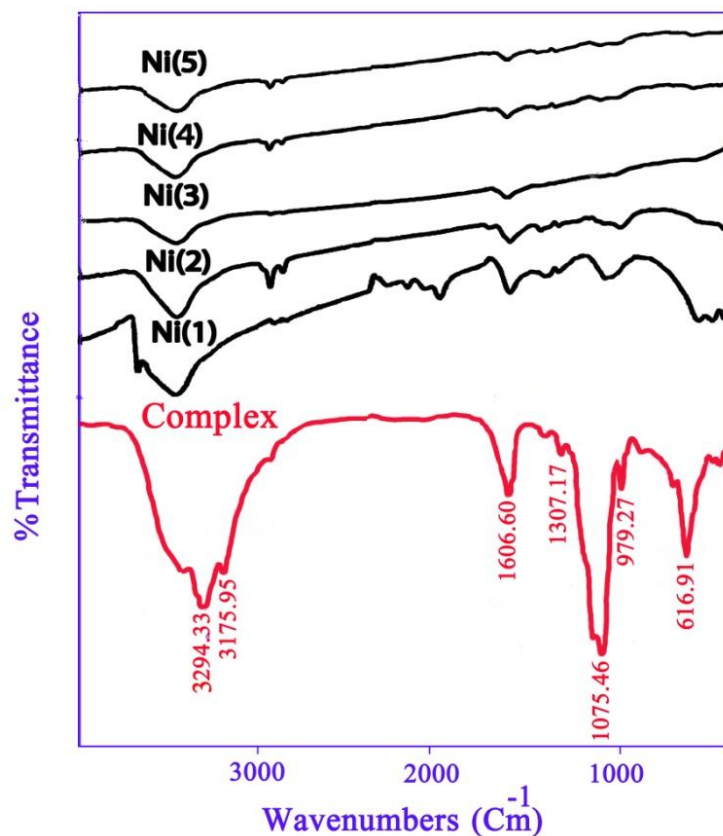
Vibration spectra of $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8]$
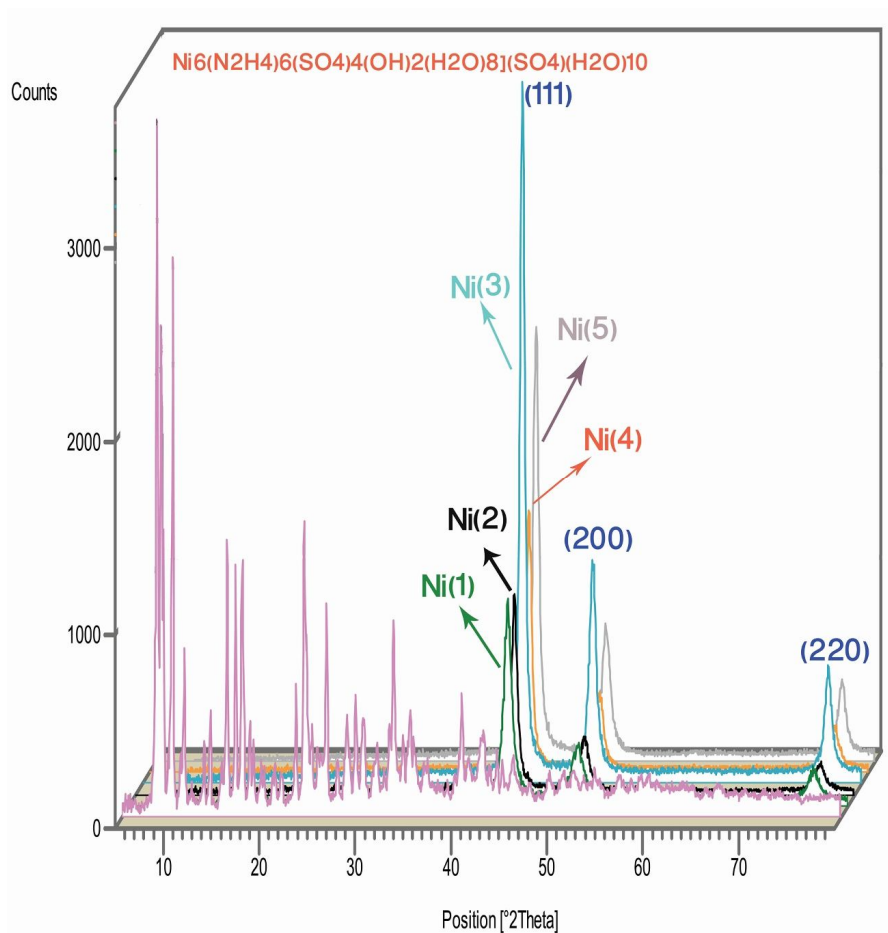
Fig. 1. X-ray diffraction patterns of the$[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$ as a precursor, with triclinic system and their products nickel metal nanoparticles (Ni1-Ni5) in fcc lattice.

Table 1. Crystallite Size and Particle Size Distribution in Nickel Metal Nanoparticle Samples

Nickel metal nanoparticles	Crystallite size of nickel	FWH	hkl	Particle size distribution in SEM
Ni1	20.77 nm	0.4133	111	10-55 nm
Ni2	20.77 nm	0.4133	111	15-65 nm
Ni3	18.17 nm	0.4723	111	15-65 nm
Ni4	14.59 nm	0.5904	111	20-70 nm
Ni5	16.15 nm	0.5314	111	15-65 nm

Fig. 2. IR spectra of Complex $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$ in the region 1650-500 and 3500-3000 cm^{-1} that show the ligands vibrations, finally after the reaction the nickel nanoparticles (Ni1-Ni5) is produced and the absorption bands disappear.

Table 2. Relative Crystals Growth of Various Faces Formed on Nickel Metal Nanoparticles

| Nickel metal crystallite size (nm)	(111)	(200)	(220)
Ni1	20.77	9.35	8.77
Ni2	20.77	13.60	14.04
Ni3	18.17	18.70	20.06
Ni4	14.59	30.00	15.62
Ni5	16.15	12.47	14.04

$(SO_4)(H_2O)_{10}$ shows N_2H_4, sulfate, lattice water, aqua water and hydroxide vibration frequencies (Fig. 2). Hydrazine coordinates to a Ni(II) as a bridging bidentate ligand showing (N-N) band near 970 cm^{-1} [24]. Sulfate ion shows a strong absorption bands due to antisymmetric stretching at 1050-1150 and also antisymmetric bending at 615-620 cm^{-1} in the infrared spectrum. When SO_4^{2-} coordinates to nickel(II), its symmetry became lower and changes in the spectrum are expected. Vibrations split in the spectrum are appeared at 1050-1150 and 615-620 cm^{-1} absorption bands (Fig. 2). Therefore Sulfate ions can be considered as a tridentate ligand. Here lattice and aqua water stretching absorption bands occur at 3550-3200 cm^{-1} and also HOH bending at 1630-1600 cm^{-1} was observed [25]. In the chemical reaction the nickel complex is converted to metallic nickel nanoparticles (Ni1-Ni5) thus, the absorption bands belong to ligand groups in complex are disappeared and the nickel metal has no absorption bands in medium IR. Nickel metal has been known to be one of the most important magnetic materials. The magnetic susceptibility reveals antiferromagnetic interaction between nickel(II) ions in the polynuclear complex. The conversion of nickel(II) complex to metallic nickel can be accompanied by a change in magnetization. This molecular antiferromagnetic complex is changed into ferromagnetic nickel metal nanoparticles (Fig. 3). The saturation magnetization (M_S) values of Ni1-Ni5 are 32.70, 41.17, 48.57, 45.97 and 46.36 emu g^{-1}, respectively (Table 3). Here the nickel nanoparticles have a saturation magnetization less than that of the bulk nickel. The M_S value of the bulk nickel was about 55 emu g^{-1} at 300 K. It is reported in the literature that in magnetic nanoparticles, the magnetization is often smaller than that of the bulk solid [26].

Figure 4 shows an SEM image of a typical nickel particle prepared *via* intramolecular chemical reduction, for which all products have similar morphology. Morphologies of the nickel nanoparticles depend on the complex structure as reactant. The synthetic nickel nanoparticles and their frequencies as a function of particle size in Ni1-Ni5 were measured (Fig. 4). The SEM of Ni1 shows aggregated spherical structure and normal particle size distribution ranging from 10-55 nm with a maximum distribution at 30 nm. A partial aggregated spherical and normal distribution of nanoparticles ranging from 15-65 nm with a maximum at

33 nm was observed in Ni2. Ni3, Ni4 and Ni5 nanoparticles have nonaggregated spherical and bimodal particle size distributions ranging from 15-65 nm, 20-70 nm, 15-75 nm, and two maximum distributions at 33 and 47 nm, 45-60 nm and 40-60 nm, respectively. The Ni3 nanoparticles has nonaggregated spherical and a bimodal particle size distribution ranging from 15-65 nm and with two maximum distributions at 33 and 47 nm. The Ni4 nanoparticles has nonaggregated spherical and a bimodal particle size distribution ranging from 20-70 nm and with two maximum distributions at 45 and 60 nm. The Ni5 nanoparticles has nonaggregated spherical and a bimodal particle size distribution ranging from 15-75 nm and with two maximum distributions at 40 and 60 nm. The results show that when the $NaOCH_3$ and $NaOCH_2CH_3$ are used in reaction the complex will be changed to aggregated and monodisperse nickel nanoparticles (Ni1 and Ni2). Whenever other alkoxides such as $NaOCH_2CH_2CH_3$, $NaOCH(CH_3)_2$ and $NaOCH_2CH_2CH_2CH_3$ are used in such reactions, the complex will be converted to a nonaggregated and polydisprese nickel powder Ni3, Ni4 and Ni5, respectively. In the new solid state method an intramolecular chemical reduction of nickel complex causes the formation of particle in the range of nanoscale.

CONCLUSIONS

Fine nickel powders with a similar morphology were prepared from nickel(II) hydrazine complex by intramolecular redox reaction in the solid state. Here depending on the interaction between the metal ion and ligands, the special nickel(II) complex is suitable for intramolecular redox reaction. Therefore, the coordination sphere of complex has a profound effect on the intramolecular redox reaction. The results show that when alkoxides are changed from $NaOCH_3$ to $NaOCH_2CH_3$, $NaOCH_2CH_2CH_3$, $NaOCH(CH_3)_2$ and $NaOCH_2CH_2CH_2CH_3$ the crystallite size and morphologies of metallic nickel nanoparticles will not change significantly. However, the nickel metals are produced from $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2 (H_2O)_8](SO_4)(H_2O)_{10}$ complex, have different particle size distributions. The advantages of this work for preparing the metallic powders lie in narrow size distribution and similar morphology, the high yield, and the solid state reaction
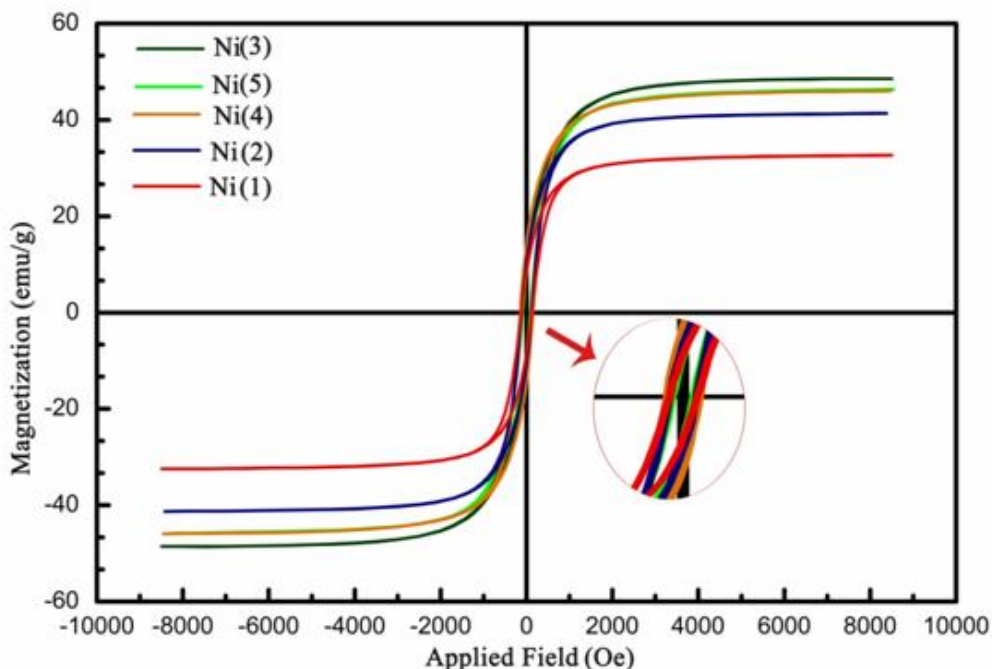
Fig. 3. Show hysteresis loop and the saturation magnetizations of nickel nanoparticles (Ni1 = 32.70, Ni2 = 41.17, Ni3 = 48.57, Ni4 = 45.97 and Ni5 = 46.36 emu g^{-1}), respectively.

Table 3. Magnetic Parameters in Nickel Metal Nanoparticles

Sample	H_C (Oe)	M_R (emu g^{-1})	M_S (emu g^{-1})
Ni1	123.50	8.60	32.70
Ni2	146.22	10.64	41.17
Ni3	138.09	11.43	48.57
Ni4	152.00	14.42	45.97
Ni5	93.45	13.16	46.36

conditions. In comparison with the method of preparing nickel powders from nickel(II) salts in aqueous solution, the intramolecular redox reaction of nickel(II) hydrazine complex shows a high purity of metal nickel. Therefore, intramolecular redox reaction is attractive and offers a new method in preparation of metallic nickel nanoparticle.

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