



Studies on the solid-state ion exchange of nickel ions into zeolites using DRS technique

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Abstract

The coordination of Ni^{2+} ions in the dehydrated nickel-exchanged zeolites was investigated from the analysis of diffuse reflectance spectra. Solid-state ion exchange method was used to prepare nickel-containing mordenite, Y, L and mazzite zeolites. In the dehydrated mordenite and zeolite Y, nickel cations are presented in both forms of tetrahedral and distorted tetrahedral symmetries. The relative amount of tetrahedral and distorted tetrahedral nickel species are related to the heating temperature and heating time used for calcinations. In the dehydrated zeolite L and mazzite, Ni^{2+} ions are mainly in the distorted octahedral symmetries.

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1. Introduction

Post-synthesis modification of the zeolites is used for the preparation of tailored catalysts and/or further control of catalyst activity and shape selectivity of a specific microporous material. One of the most important processes for modification is ion exchange to replace some or all of their exchangeable cations with those of transition metals. The accessibility, distribution and nature of the new sites are important for the catalysis. Ion exchange in zeolites is commonly done in the conventional way, i.e. employing aqueous salt solution [1]. However, due to the increase in the effective size of the cations in aqueous solution resulting from hydration, incomplete exchange or exchange only at positions close to the pore opening may occur [2]. The circumstances is significantly different in solid-state ion exchange (SSIE) where a high degree of exchange can be achieved in only one step in addition to the fact that those restrictions can be overcome [3]. The SSIE is a new technique where systematic work on this system was begun in mid-1980s [4,5]. A very comprehensive recent review on SSIE in microporous and mesoporous materials written by Karge and Beyer [6] describes in full detail the concept,

experimental procedures and the systems investigated which is the best updated source of information in this field.

Although, the successful incorporation of the many metal cations has been studied, but analyzing of the local structure of some of the ions has been described in less detail. Nickel is among those transition metal cations that requires more consideration because of the lack of enough definite data on its position in the structure of microporous materials. The coordination and location of nickel in the structure of Ni-exchanged zeolites prepared by ion exchange in the aqueous solution have been widely studied in the last three decades. Either of two main approach of single crystal or powder X-ray diffraction (XRD) [7–12] or diffuse reflectance spectroscopy (DRS) [13–16] have been employed to study location of nickel in Ni-exchanged zeolite samples. After calcinations of the zeolite samples, the nickel cations are distributed among the zeolite sites in the places that they could be stabilized by appropriate coordination to the lattice oxygen atoms. But often the results calculated from the XRD data was not in good accord with the absorption band assignments based on the spectroscopic data. This problem was puzzled out by Lepetit and Che [17] when they suggested that the main DRS absorption bands for the calcined Ni-exchanged Y zeolite should be reassigned to distorted tetrahedral sites. They claimed that the absorption bands previously assigned to nickel cations in an octahedral or distorted octahedral symmetry lie out of the range

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expected for these symmetries. The origin of their reassignment was the work of Dooryhee et al. [18] who studied the hydrated and dehydrated Ni-exchanged Y zeolite by simultaneous X-ray absorption spectroscopy (EXAFS) and powder XRD.

The structural studies for the nickel incorporated into zeolites by SSIE are more recent. Various techniques such as EXAFS [19], neutron diffraction [20], ESR [21–23] and XPS [24,25] have been used to obtain structural information about nickel positions in the microporous materials prepared by SSIE methods. The aim of this contribution is to study coordination of nickel cations introduced by SSIE into some zeolites by DRS. The coordination of Ni^{2+} cations in dehydrated and partially hydrated mordenite, zeolite Y, zeolite L and mazzite will be investigated. Our DRS data will provide further conformity and extension for the reassignment proposed by Lepetit and Che [17], while showing our evidences for the presence of some nickel ions in tetrahedral symmetry in addition to the distorted tetrahedral ones found by them in the completely dehydrated Y zeolite.

2. Experimental

2.1. Sample preparation and treatments

Zeolite Y was obtained from Union Carbide and has a Si/Al ratio of ≈ 2.5 . Mordenite was prepared by hydrothermal synthesis method described in Ref. [26]. Sodium silicate solution (27% SiO_2 , 8% Na_2O , 65% H_2O , Merck 5621) and aluminum sulfate (Fluka 06421) were used as sources of silicon and aluminum of the synthesis gel, respectively. Zeolite L was synthesized with some modification in the described procedure [27]. Aluminum hydroxide (hydragillite Merck 1091) and fumed silica (Aerosil, Degusa-AG, Switzerland) were sources of aluminum and silicon, respectively. Zeolite mazzite was synthesized in the presence of tetramethylammonium hydroxide (Merck 8123) as a structure directing template according to the procedure reported previously [28,29]. To remove occluded template molecules out of the channels of mazzite, the sample was heated in a muffle furnace at 550 °C for 5 h.

The acidic forms of the zeolites were prepared by NH_4^+ ion exchange followed by thermal treatments. Ammonium exchanged forms of the mordenite, zeolite L and mazzite were prepared by treating them with 1 M solution of NH_4NO_3 under reflux at 80 °C for 10 h separately. The ammonium exchange treatment for zeolite Y was performed three times at 25 °C with a 0.4 M solution of NH_4Cl . A filtration and washing process was done for all the samples. To convert the ammonium form of the zeolites to acidic ones, they were heated in a muffle furnace at a rate of 10 °C/min and holding at 500 °C for at least 7 h.

The SSIE reaction was performed by grinding the zeolite together with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and then loading it into a special

cell. This cell was elaborated in our laboratory and includes a flat quartz window to permit recording of the spectra. The stoichiometry of the nickel salt to zeolite was for a 100% ion exchange. The samples were heated in a helium atmosphere at a rate of 5 °C/min up to 300–500 °C and kept at this temperature for 3–6 h. The completeness of the reaction was monitored by employing an acid indicator paper at the outlet of the helium purge cell. Also, samples were tested for excess of unreacted nickel chloride, at the end of the spectroscopic studies. The solid samples were washed with deionized hot water several times and the filtrate was checked for nickel by the addition of dimethylglyoxime. None of the samples studied contained soluble nickel chloride.

2.2. Characterization

XRD measurement was performed on a Philips PW1840 diffractometer with $\text{Cu K}\alpha$ radiation at room temperature. All the samples were analyzed before and after SSIE to check their crystallinity.

Diffuse reflectance spectra were recorded by a UV-2100 Shimadzu spectrophotometer equipped with an integrated sphere assembly. The spectra were recorded at room temperature against barium sulfate and plotted in terms of absorption.

The silicon and aluminum content of the zeolite samples was measured by energy dispersive X-ray emission (EDX) joint to a Philips XL30 scanning electron microscope. Water content of the zeolites were determined by gravimetric method.

3. Results and discussion

The type and unit cell composition of the zeolite samples are shown in Table 1. Their crystallinity and structural purity was checked with our X-ray diffractometer at first and at the end of each experiment. For the samples reported here a good accordance with the reference XRD data was a basis [30]. The unit cell formula of the zeolites were calculated from the EDX data.

The DR spectra for the SSIE of Ni^{2+} into mordenite are shown in Fig. 1. Depending on the exchange temperature and exchange time, samples are designated and referred. For instance, NiHMOR-500-6 stands for a mixture of nickel chloride and acidic mordenite heated at 500 °C for 6 h.

Table 1
Type and unit cell composition of the as-received or as-synthesized zeolites

Sample	Structure code	Unit cell formula
Mordenite	MOR	$\text{Na}_{6.7}[\text{Al}_{6.7}\text{Si}_{41.3}\text{O}_{96}]23.5 \text{ H}_2\text{O}$
Zeolite Y	FAU	$\text{H}_1\text{Na}_{52.5}[\text{Al}_{53.5}\text{Si}_{138.5}\text{O}_{384}]265 \text{ H}_2\text{O}$
Zeolite L	LTL	$\text{K}_{8.7}[\text{Al}_{8.7}\text{Si}_{27.3}\text{O}_{72}]23 \text{ H}_2\text{O}$
Mazzite	MAZ	$\text{Na}_{3.2}\text{TMA}_{1.9}[\text{Al}_{5.1}\text{Si}_{30.9}\text{O}_{72}]26.5 \text{ H}_2\text{O}$

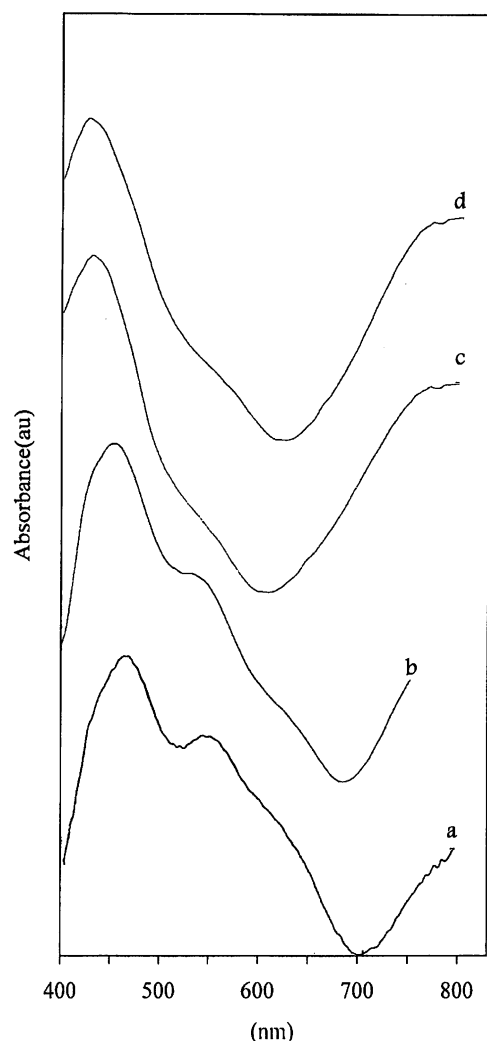


Fig. 1. Diffuse reflectance spectra of solid-state nickel-exchanged mordenite zeolites: (a) NiHMOR-500-3; (b) NiHMOR-400-3; (c) NiHMOR-300-3; and (d) NiHMOR-500-3 exposed to the air.

Fig. 1a shows the DR spectrum of NiHMOR-500-3 sample. This spectrum was recorded after removing the sample cell from the helium purge system and cooling it to room temperature. The sample was purple at this stage. The exposure of the sample to the air of our lab showed a color change to yellow (Fig. 1d). We repeated the experiment at temperatures 400 and 300 °C and the spectra are shown in Fig. 1b and c, respectively. The spectrum of NiHMOR-300-3 resembles that of NiHMOR-500-3 after its exposure to the lab atmosphere (Fig. 1d). Influence of the ion exchange time can be observed in Fig. 2. In this figure, the spectra of NiHMOR-500-6 sample (6 h heating time) just following the solid-state reaction and after exposure to the air are shown. The intensity of the two 620 and 560 nm bands are comparable to that of 475 nm in NiHMOR-500-6 (spectrum a). Whereas, they have lower intensities compared to that of 475 nm band in NiHMOR-500-3 (spectrum b). The other features of the two spectra are the same.

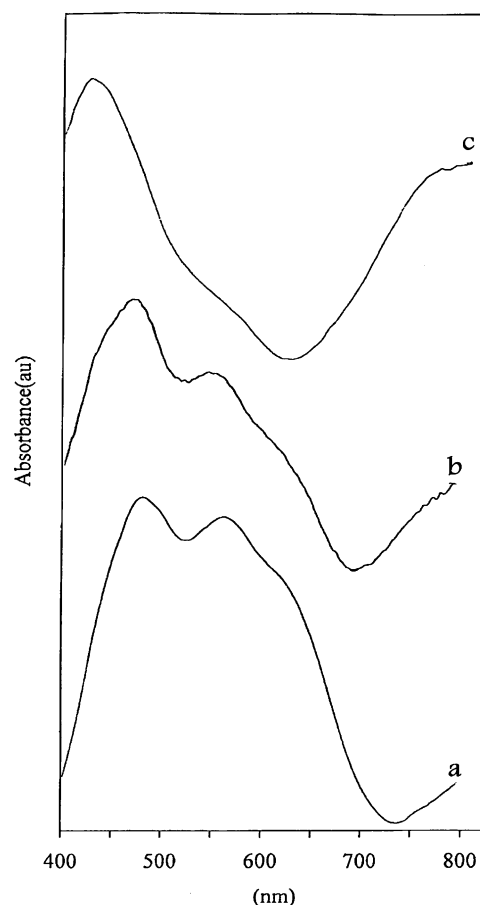


Fig. 2. Diffuse reflectance spectra of solid-state nickel-exchanged mordenite zeolites: (a) NiHMOR-500-6; (b) NiHMOR-500-3; and (c) NiHMOR-500-6 exposed to the air.

The NiHMOR-500-6 sample also turned to yellow when exposed to the air (Fig. 2c).

Referring to the well established assignment made by Schoonheydt et al. [16] and Briend-Faure et al. [15], these 620 and 560 nm bands belong to Ni^{2+} in a tetrahedral symmetry in the zeolite. These two bands in the visible region belongs to ν_3 (one out of the three spin-allowed electronic transitions) to be referred as ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$. Due to spin-orbit coupling, the ${}^3\text{T}_1(\text{P})$ state splits into three components as observed by the later authors. But, the former workers observed a doublet band. In our nickel-exchanged mordenite prepared by SSIE method, we found a doublet at about the same band position reported by Schoonheydt et al. Occurrence of this triplet band for tetrahedral nickel is not rare and has been reported by Zanjanchi and Abdollahi [31] and Rajic et al. [32] in the as-synthesized aluminophosphate molecular sieves. At this stage, according to the DR spectra indicated in Figs. 1a and 2a and despite our limitation in not covering the entire wavelength range corresponding to all electronic transitions of tetrahedral nickel, we can say that part of our Ni^{2+} are in a tetrahedral environment.

An intense and well defined absorption band at about 475 nm and a peak on its shoulder at ≈ 445 are another

Table 2

DRS absorption bands observed for Ni^{2+} ions in dehydrated mordenite, Y and X zeolites

Zeolite	Wavelength in the visible range				Assigned symmetry	Ref.
NiHMOR	620	560	475	445	T + DT	This work
NiHY	625	585	480	455	T + DT	This work
NiY	616		494	467	DT	[17]
NiLaX	621	571			T	[16]

T, tetrahedral; DT, distorted tetrahedral.

features of the spectra recorded for NiHMOR-500-3 and NiHMOR-500-6 samples. These two bands are very similar to what was observed by Lepetit and Che in their NiY sample heated at 400 °C and assigned by them to Ni^{2+} in a distorted tetrahedral position. Their results are compared with our data in Table 2. The ≈ 20 nm shifts in wavelengths between their results and our data is attributed to the structural differences. Various parameters such as nickel–oxygen distances, crystallographic positions of the cations in the structure and origin and nature of surrounding may give a different wavelength and intensity. Lepetit and Che assignment solved a problem that existed for some years because of poor justification of the interpreted spectroscopic data (see Ref. [17]). Our data shows that some of the Ni^{2+} ions in mordenite are in the tetrahedral sites and some others are in a distorted tetrahedral positions. Comparing the spectra of NiHMOR-500-3 and NiHMOR-500-6 in Figs. 1a and 2a, respectively, indicate that the amount of tetrahedral nickel is higher in NiHMOR-500-6 which is heated for a longer time. Also comparing the spectra of NiHMOR-500-3 with that of NiHMOR-400-3 (Fig. 1a and b) shows that there is higher amount of tetrahedral nickel in the sample heated at a higher temperature.

Fröster and Hatje [19] have studied SSIE of Ni^{2+} ions in zeolite Y by EXAFS method. They have assumed several configurations for nickel and oxygen atoms. Two Ni^{2+} ions on neighboring cation sites and formation of Ni–O–Ni species connected to zeolite lattice oxygen is one of the possible configuration. Dalconi et al. [33] have located Ni^{2+} coordinated to four lattice oxygens in dehydrated nickel-exchanged ferrierite zeolite from their synchrotron X-ray powder diffraction analysis. They have prepared their sample by aqueous ion exchange method and have stated that their nickel ions are poorly coordinated to the framework but they are extremely accessible to the reactant molecules. In a first approach, our DRS data obtained for NiHMOR samples are related to the forms of the Ni^{2+} coordinated to the lattice oxygens. We assume favorable formation of tetrahedral nickel in the samples heated at higher temperature and/or longer heating time, according to the increase of the intensity of the two 620 and 560 nm bands at those specified conditions (Figs. 1 and 2). The tetrahedral environment of the nickel ions may be constituted entirely by three lattice oxygens and one extra-lattice oxygen [16] or by a combination of three lattice

oxygens and one remaining water molecule. Our NiHMOR-500-3 and NiHMOR-500-6 samples were heated at 500 °C and at these temperatures, coordination of a water molecule to the Ni^{2+} is very unlikely. Therefore, we should think of other possibilities. We might have Ni^{2+} at such positions to form a Ni–O–Ni species where each nickel ion is connected to three lattice oxygens. We also consider that in our sample prepared by SSIE method, Ni^{2+} may be coordinated to three lattice oxygens and one Cl^- ion in tetrahedral or distorted tetrahedral symmetry. Our inspection of EDX data always revealed traces of chloride in the solid samples analyzed by EDX method. Finding chlorides in the Ni-exchanged zeolite samples prepared by SSIE technique using NiCl_2 has been reported. Haniffa and Seff [20] in their neutron diffraction study of the dehydrated NiY zeolite prepared by SSIE method, found the $[\text{Ni}_3\text{Cl}_2]^{4+}$ cluster. They declared that the exchange was not completed and some NiCl_2 were imbibed by the zeolite during SSIE process.

In the DR spectra of NiHMOR samples, exposed to the air, no signal of tetrahedral or distorted tetrahedral was observed. Instead, two bands at 745 and ≈ 425 belonging to Ni^{2+} in octahedral coordination were observed (Figs. 1d and 2c). Evidently, adsorption of water molecules by those nickel cations in the tetrahedral or distorted tetrahedral symmetries will convert them to the new symmetry. The color of the samples is yellow at the beginning of this stage. However, upon keeping the samples for a very long time (i.e. 2 weeks) in the humidity condition, their color gradually changes to green and they show the absorption band very similar to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ [34]. This supports the EXAFS studies that in this state nickel present as fully hydrated hexaaqua cations in electrostatic interaction with zeolite framework [18].

The dehydrated NiHY-500-3 is purplish-blue and its DR spectrum is shown in Fig. 3. The spectrum is similar to the ones observed for dehydrated NiHMOR samples except that the doublet band assigned to tetrahedral nickel is observed at 625 and 585 nm. The DR spectrum for NiHY-500-6 also shows these bands. However, it is not clear for us why the doublet is more resolved in NiHY-500-3 compared to that of NiHY-500-6. The spectrum of NiHY-500-3 also indicates emergence of 480 and 455 nm bands which are related to the presence of nickel ions in distorted tetrahedral environment in the structure of nickel-exchanged zeolite Y. Our inspection of the DR spectra reveals that there is no signal of the regular or distorted octahedral nickel ions in the dehydrated NiHY samples. In another words there is no nickel cations in SI sites. The typical DRS absorption bands reported for Ni^{2+} in octahedral [17] or distorted octahedral symmetries [35–37] are not observed in our dehydrated sample. There is a major difference between our results obtained for dehydrated Ni-exchanged zeolite Y prepared by SSIE method and that of Lepetit and Che [17] reported for dehydrated NiY prepared by aqueous ion exchange. We found nickel cations with both tetrahedral and distorted

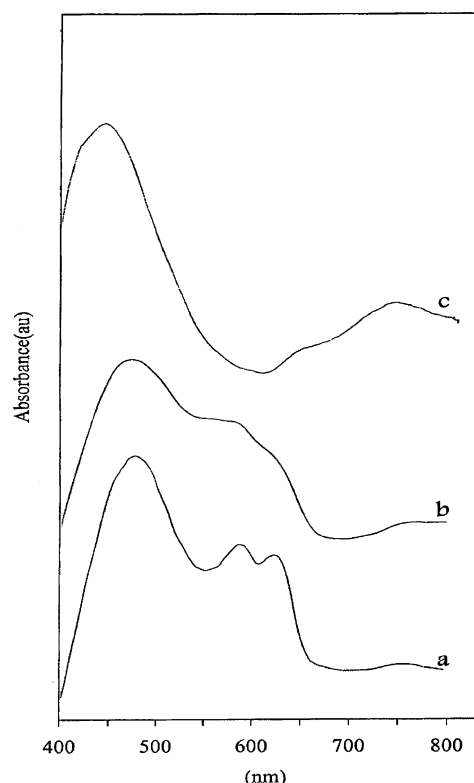


Fig. 3. Diffuse reflectance spectra of solid-state nickel-exchanged Y zeolites: (a) NiHY-500-3; (b) NiHY-500-6; and (c) NiHY-500-3 exposed to the air.

tetrahedral symmetries in our sample, whereas, they found Ni^{2+} ions only in distorted tetrahedral environment. Probably, presence of chloride ions in the SSIE system is responsible for establishment of tetrahedral symmetry in addition to the fact that our course of dehydration procedure was different from them. But the criticism for the Ni ions location in SI sites (center of hexagonal prism) still remains unresolved. More works should be done to find out which of the possibilities brought up by Lepetit and Che should be considered. They argued that the DRS absorption bands of Ni^{2+} ions positioned in SI sites are either hidden by the more intense bands arising from low-symmetry Ni^{2+} species or they are not DRS-sensitive. We believe that we should not expect high occupation of SI sites in zeolite Y due to higher Si/Al ratio in this zeolite compared to that of zeolite X. Therefore, a low concentration of nickel ions in this site may be responsible for disappearance of this band. Haniffa and Seff [20] found only four, out of 30 nickel cations, in SI sites in their dehydrated NiY sample.

The DR spectra for NiHL-500-3 and NiHMAZ-500-3 samples are shown in Fig. 4. They seem alike and show the same features. The purple or purplish-blue color observed for the dehydrated NiMOR and NiHY samples, respectively, were not found for these later samples. They showed a light pink-yellow color when dehydrated at 500 °C. This color and the positions of the bands in their DR spectra (Fig. 4a and b) are similar to those observed for NiHMOR

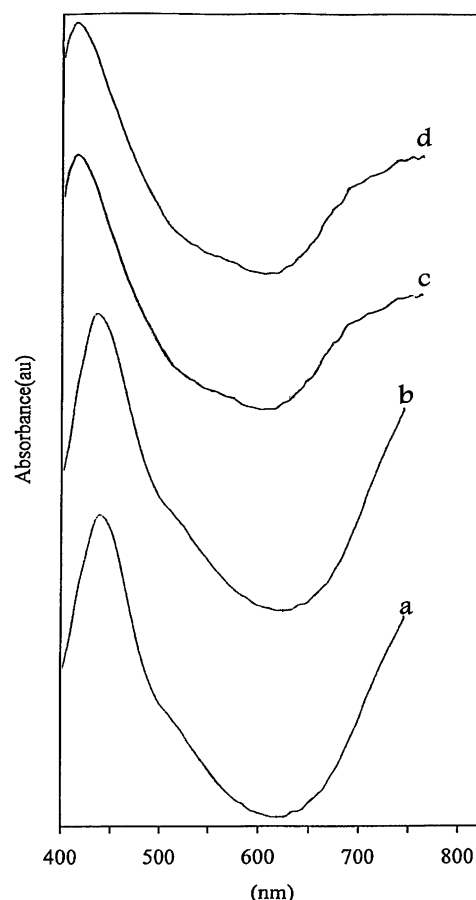


Fig. 4. Diffuse reflectance spectra of solid-state nickel-exchanged L and mazzite zeolites: (a) NiHL-500-3; (b) NiHMAZ-500-3; (c) NiHL-500-3 exposed to air; and (d) NiHMAZ-500-3 exposed to the air.

and NiHY samples exposed to the air (see for instance Figs. 1d and 3c). Upon these data, we assume that the majority of Ni^{2+} ions are in distorted octahedral symmetry in dehydrated NiHL and NiHMAZ samples. Extra-lattice oxygen(s) and/or chloride ion(s) in addition to the lattice oxygens may have contributed for the formation of nickel ions in distorted octahedral symmetry. It is not possible at this time and merely based on the spectroscopic data to define more precise configuration of the nickel ions in the structure. A neutron diffraction study will reveal the exact positions for Ni^{2+} ions.

An excellent feature of DRS is manifested here. The DR spectra of NiHL and NiHMAZ samples after exposing to the air of lab showed that the distorted octahedral nickel cations in the dehydrated samples change to octahedral symmetries. This is evident from the bands observed at about 750 and 420 nm in the DR spectra of the NiHL-500-3 and NiHMAZ-500-3 samples (Fig. 4c and d).

4. Conclusion

Despite our limitation in not covering the entire wavelength range corresponding to all electronic transitions

of Ni^{2+} ions, we were able to show various features of the nickel-containing zeolites prepared by SSIE method. In this work, we showed that both tetrahedral and distorted tetrahedral nickel cations are formed in dehydrated mordenite and Y zeolites. The amount of tetrahedral form in the structure is higher when a higher temperature (500 °C) or longer heating time (6 h) are employed. In nickel-exchanged zeolite L and mazzite prepared by SSIE method, distorted octahedral coordination was the main symmetry for the nickel species in the dehydrated samples. All of the samples showed octahedral symmetry for the nickel cations, upon exposure to the air.

Acknowledgements

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