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Preparation and Spectral Analysis of Nickel-containing Aluminophosphate Molecular Sieves of Type-5

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Abstract

Diffuse reflectance spectroscopy was used to study nickel ion positions in the aluminophosphate molecular sieves of the AlPO-5 type. Nickel ions were introduced into the reactant mixture of the aluminophosphate and the synthesis carried out hydrothermally through various methods of gel, clear solution and diluted suspension. The visible absorption spectra obtained of the dried, hydrated and calcined materials were studied. A distinct and well-defined triplet absorption band observed at about 625, 580 and 540 nm was assigned to tetrahedral framework-substituted nickel(II) ions. A relatively strong band at about 400 nm and two broad bands with similar intensity at 730 and 660 nm were assigned to octahedral nickel species. These 730 and 660 nm bands are observable only in the sample where nickel cations were incorporated merely in the octahedral extra-framework sites by ion-exchange treatment of SAPO-5. According to the synthesis procedure used, the amount of tetrahedral framework-substituted nickel ions in comparison with octahedral ones can be evaluated from the intensities of the characteristic bands of the 4- and 6-coordinated nickel ions. There is much more octahedral nickel compared with the tetrahedral ones estimated in the light of the intensity data taking into account the absorptivities of nickel (II) symmetries. This work showed that using our synthesis procedure of a diluted suspension will result in preparing NiAPO-5 molecular sieve with more nickel cations incorporated in the framework sites of the aluminophosphate. A very small quantity of these cations remain in their sites at temperatures as high as 550 °C.

Introduction

Modification of the microporous aluminophosphates or silico-aluminophosphates, a new type of molecular sieves, by isomorphous substitution of framework atoms by transition metal ions or by incorporation of such ions into extra-framework positions is of potential significance for specific catalytic reactions [1, 2]. The catalytic activities of such materials depend on the type, oxidation state, location and dispersion of the transition metal ion and the properties of the supporting molecular sieves. The incorporation and location of many elements into the aluminophosphate framework have recently been reviewed [3]. Transition metal ions may be incorporated into aluminophosphates by the isomorphous substitution method. In this method molecular sieves are usually synthesized by hydrothermal crystallization of reactive aluminophosphate gels containing transition metal salts and an organic template. The synthesis of transition metal-incorporated aluminophosphate from homogeneous clear solution was also developed to create a product with more incorporated transition metal ions [4-6]. Information on cation location or the incorporation of transition metal ions into aluminophsphates is typically hard to obtain since the metal concentration is low.

The catalytic importance of nickel-modified molecular sieves requires a comprehensive study of the state of nickel in these materials [7–19]. The problem with nickel is that to date there is not enough evidence for incorporation of nickel into the aluminophosphate framework or its precise state [3]. In fact nickel(II) forms a large number of compounds encompassing coordination numbers of 4, 5 and 6 and all the main structural types such as octahedral, trigonal bipyramidal, square-pyramidal, tetrahedral and square planar [20]. This property of nickel(II) ions makes a decisive conclusion rather difficult especially when a spectroscopic method is used for structural analysis. Electron spin echo modulation (ESEM) spectroscopy and electron spin resonance (ESR) have been used to study the environment of nickel ions in the aluminophosphates with different structure types [7–12]. But these methods suffer from a lack of ESR signal from the Ni(II) species. Therefore, samples should first be reduced to convert Ni(II) to Ni(I) which is ESR sensitive. This process, depending on the reduction conditions such as the temperature, may cause changes in the location of the nickel ions in the structure. The mobility of nickel cations in zeolite molecular sieves has been reported [21–24]. Particular care is also needed to establish suitable conditions of temperature, hydrogen pressure and reduction time to generate appropriate concentration of nickel(I) species and to prevent formation of metallic nickel in addition to nickel(I).

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Furthermore, the ESR studies of Ni(I) in the aluminophosphates requires special care since Ni(I) is readily oxidized by water or oxygen. Other methods such as EXAFS and XANES [16] and single-crystal crystallography [17] were also used to study the positions of nickel in some types of aluminophosphate and/or silicoaluminophosphate molecular sieves.

The coordination of Ni(II) ions in zeolites has been extensively studied by several methods including diffuse reflectance spectroscopy (DRS). Lepetit and Che have discussed in detail the application of DRS to nickel-containing faujasite-type zeolites and they have suggested reliable DRS absorption bands of Ni(II) cations in different symmetries in faujasite [25]. Zanjanchi and Rashidi have shown diffuse reflectance spectroscopy can be used in aluminophosphate molecular sieves to obtain some structural information [26]. The aim of this contribution is to apply diffuse reflectance spectroscopy to study nickel positions in aluminophosphate molecular sieves of the AlPO-5 type, synthesized via different procedures. We will show that by our improved method of preparing NiAPO-5, more nickel cations will be incorporated in the framework of the aluminophosphate. We will claim this from distinctive data obtained for nickel environments in our samples studied by DRS.

Table 1. Method of sample preparation according to the source of aluminum and crystallization procedure

Sample	Designation	Al source[a]	Method
1	NiAPO-5(1)	AlPr	gel
2	NiAPO-5(2)	AlO(OH)	gel
3	NiAPO-5(3)	$Al(OH)_3$	clear solution
4	NiAPO-5(4)	$Al(OH)_3$	suspension
5	AlPO-5	$Al(OH)_3$	suspension
6	SAPO-5	AlPr	gel
7	Ni-SAPO-5	–	ion-exchange

[a] AlPr stands for aluminum isopropoxide and AlO(OH) stands for boehmite.

Table 2. Initial molar composition of the reactant mixtures

Sample	Al_2O_3	P_2O_5	NiO	TEA[a]	H_2O	HF	Si
NiAPO-5(1)	1.0	1.0	0.05	2.0	50	–	–
NiAPO-5(2)	1.0	1.0	0.05	2.0	60	–	–
NiAPO-5(3)	1.0	1.0	0.05	2.0	50	0.7	–
NiAPO-5(4)	1.0	1.0	0.05	2.0	50	–	–
AlPO-5	1.0	1.0	–	2.0	50	–	–
SAPO-5	1.0	1.0	–	2.0	50	–	0.05

[a] TEA stands for triethylamine, used as template.

Experimental

Sample preparation

NiAPO-5, AlPO-5 and SAPO-5 samples were prepared by the hydrothermal synthesis method with some modification in the procedures described in the literature [6, 27]. Phosphoric acid (85%, Merck) was used as the source of phosphorus in all the syntheses. Aluminum isopropoxide (Fluka, No. 06251), aluminum hydroxide (of the gibbsite structure type, Merck, No. 1091) and aluminum oxide hydroxide (of the boehmite structure type, prepared from aluminum hydroxide) were the sources of aluminum in the synthesis composition. Triethylamine (Fluka, No. 90337) was used as the template. Nickel acetate (Merck, No.6743) was used as the source of Ni^{2+} in all syntheses. Three different crystallization procedures: gel method, clear solution and diluted suspension method, were used to obtain the materials. Table 1 shows the synthesis methods used according to the source of aluminum. The initial composition of the reactant mixtures are shown in Table 2. Crystallization was performed by heating the mixtures in a Teflon vessel inside a stainless-steel autoclave under a static condition. The materials were heated at 190 °C for 13–15 hours.

Employing diluted suspension is a new feature used in our synthesis procedure. A typical procedure of preparation of the suspension for synthesis is as follow. 5.7 g of phosphoric acid was diluted in 20 mL de-ionized water. 3.9 g of aluminum hydroxide was added to the above acid solution gradually. The mixture was placed in a thermostated water bath at 60 °C for two hours while stirring. Then it was filtered, the solid residue (unreacted aluminum hydroxide) was discarded and the filtrate, aluminum phosphate solution, was transferred to a plastic beaker. Dropwise addition of 7 mL triethylamine to this vigorously stirred solution was followed by addition of 0.3 g nickel acetate dissolved in 2.5 mL de-ionized water. The stirring was continued for one and a half hours and the slurry converted to a diluted suspension, which was then transferred to the autoclave for heating. The crystallization was performed by heating the suspension in a 125 mL PTFE vessel inside a stainless-steel autoclave under a static condition. After 15 hours synthesis time, the autoclave was cooled and the crystalline product was separated from the mother liquor by centrifugation. The resultant material was washed with copious amounts of hot water and dried at 110 °C for two hours in air. AlPO-5 and SAPO-5 were also prepared as reference samples. No nickel acetate was added to the reaction mixture to prepare AlPO-5 (sample 5). SAPO-5 was obtained by the gel method using aluminum isopropoxide as the source of aluminum. At the final stage of the gel preparation, fumed silica (Aerosil-Degusa, Switzerland) was added to the mixture. The molar composition of the reactant gel is shown in Table 2.

All the samples contain the trapped triethylamine templating agent, and this could be removed by heating in air at a rate of 2 °C min^{-1} up to 550 °C keeping at this temperature for 5 hours. The as-synthesized dried sample was kept in a desiccator over P_2O_5. For hydration, the samples were left in a desiccator containing saturated ammonium nitrate solution for at least 48 hours.

The calcined SAPO-5 sample was treated in 0.1 M nickel acetate solution. This is done to convert SAPO-5 to Ni-SAPO-5 by an ion-exchange reaction. 5 g of the dried and calcined SAPO-5 was stirred in 250 mL of nickel acetate solution at room temperature for 12 hours. The solid product was separated by centrifugation, washed with hot water several times and finally dried at 110 °C.

Characterization

X-ray diffraction measurements were performed on a Philips PW1840 diffractometer with Cu-K_α radiation at room temperature. XRD patterns were recorded using an automatic divergence slit system.

Diffuse reflectance spectra were recorded using a UV-2100 Shimadzu spectrophotometer equipped with an integrating sphere assembly. All the spectra were recorded against barium sulfate in the visible region at room temperature and plotted in absorbance.

Quantitative analysis of the materials was done by energy dispersive X-ray analysis (EDX) coupled to a Philips XL30 scanning electron microscope.

Results and discussion

The method of sample preparation according to the source of aluminum and crystallization procedure is shown in Table 1. At first, we started with the gel method employing two highly recommended reactive aluminum sources: aluminum isopropoxide and aluminum oxide hydroxide for the preparation of aluminophosphate molecular sieves [27–29]. The products obtained NiAPO-5(1) and NiAPO-5(2) showed good crystallinity and phase purity belonging to the AFI crystallographic designation for type-5 aluminophosphate [30]. NiAPO-5(2) showed traces of an impurity phase which is unreacted AlO(OH). Examination of the spectra of these samples revealed that a considerable amount of nickel ions are octahedral as extra-framework species, even if a characteristic triplet absorption band of tetrahedral Ni(II) could also be detected (Figures 2a, b). Taking into consideration that the absorptivity of tetrahedral nickel(II) is considerably greater than that of octahedral Ni(II) (by at least an order of magnitude) [20, 31], nickel incorporation in the framework sites should be regarded as negligible. Alternative methods to improve framework substitution are needed. We tried in the next step a method of a clear solution in the presence of HF to evaluate it for possible incorporation of Ni(II) in the framework of AlPO-5. The advantages of using hydrofluoric acid in aluminophosphate molecular sieves synthesis compared to the classical gel method has been reported [5, 6, 32, 33]. It seems likely that fluoride anions assist in the solubility of aluminum and metal species, thus synthesis in the presence of HF may lead to more metal incorporation in the framework. However uncontrolled addition of HF to the reaction mixture will cause incomplete transfer of the aluminum and metal species to the molecular sieve phase, probably because of the stability of the soluble fluoride complexes. The presence of fluoride ions also leads to a slower rate of crystal growth and therefore favors formation of large crystals which is not desirable in catalyst preparation.

The crystallinity of the synthesized NiAPO-5(3) sample, prepared by a clear solution method, is good as evidenced by the XRD shown in Figure 1(c). The observed small changes in the intensity of some reflections in the XRD pattern is due to the presence of HF in the synthesis media. Inspecting the recorded spectrum for NiAPO-5(3) showed the amount of nickel incorporated in the framework sites was still negligible and no significant improvement was attained.

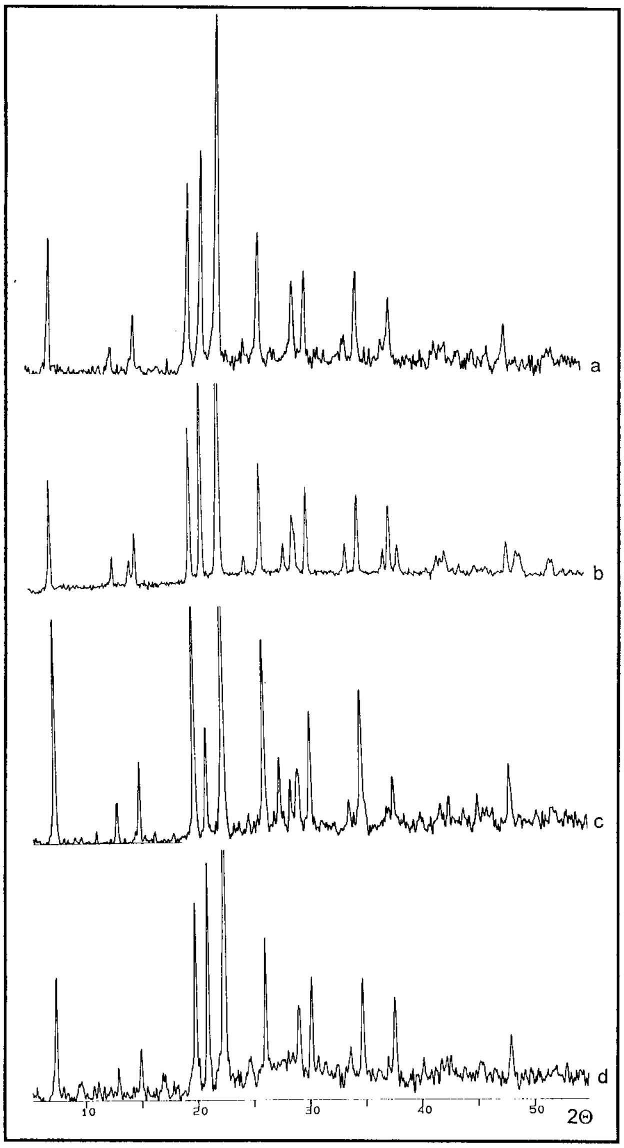

Figure 1. X-ray diffraction patterns of as-synthesized: (a) NiAPO-5(1), (b) NiAPO-5(2), (c) NiAPO-5(3), (d) NiAPO-5(4).

In most of the synthesis procedures, a reactive aluminum source such as AlPr or AlO(OH) is directly added to the reactant mixture as described above. Since these reactants are thermodynamically stable, it takes some time for aluminum to enter the molecular sieve phase. We purposed using a reactive aluminophosphate reactant mixture called a diluted suspension to facilitate framework substitution. In this system, both aluminum and phosphorus exist mainly as active polymerized ions in solution prior to addition of nickel acetate and the template. HF was not added to the suspension to make a clear solution. This is a new feature in our synthesis method. The absence of HF will enhance the rate of crystal growth while formation of stable soluble

Table 3. Chemical composition of the as-synthesized samples determined by EDX/SEM[a]

Sample	Al	P	Ni
NiAPO-5(1)	44.4	48.4	7.2
NiAPO-5(2)	46.0	48.6	5.4
NiAPO-5(3)	42.2	50.9	6.9
NiAPO-5(4)	45.7	48.5	5.8
AlPO-5	48.7	51.3	–

[a] Results are in atomic percent.

flouride complexes is prevented. We will show later that employing this method will produce a significant modification in the extent of nickel incorporation in the framework site of the aluminophosphate. The XRD pattern of NiAPO-5(4) is shown in Figure 1(d). The slightly raised background observed for this sample suggests that there is a small amount of amorphous material in NiAPO-5(4). An explanation for the formation of this may be connected with addition of triethylamine to the aluminophosphate solution. TEA is basic and will increase the pH of the synthesis mixture favoring possible formation of aluminum hydroxide species. Another alternative explanation is the source of aluminum and also the Al/P ratio in the reactant mixture. Either aluminum hydroxide used for preparation of NiAPO-5(4) and/or the low Al/P ratio could favor formation of dense byproducts [34, 35].

The chemical composition of the samples as determined by EDX/SEM is given in Table 3. EDX analysis was made upon several crystalline parts of the samples observable by a scanning electron microscope, the mean of the separate analysis was taken. According to the mechanism suggested by Flanigen *et al.*, metal cations mainly substitute aluminum in aluminophosphate molecular sieves [1]. EDX results show this mechanism applied to our samples, because the sum of the Ni + Al concentration in the samples are approximately equal to that of P. Also, EDX data show the nickel loading in NiAPO-5(1) and NiAPO-5(3) is a little higher than the 5% used in the initial synthesis composition. This may arise from heterogeneous nickel distribution resulting from a very fast nickel consumption in the early nucleation and crystallization stages. This kind of heterogeneity has also been observed for cobalt distribution in CoAPO-5 type material studied comprehensively by EDX/SEM [36]. In view of the product composition it may also be concluded that samples are not completely pure since the (Al + Ni)/P ratio is not equal to one. In our case part of the aluminum and/or nickel may be present as extra-framework species. EDX analysis cannot tell whether both aluminum and nickel or only one of these elements forms non-framework species. The quantitative monitoring of nickel and aluminum in the framework remains a requirement to be assessed using the MAS NMR technique. However, clarification of nickel positions in the structure of AlPO-5 could reliably be studied by diffuse reflectance spectroscopy as described later.

Heating the samples at a temperature of 550 °C in air is sufficient to burn off and remove the template from the pores of our prepared NiAPO-5 aluminophosphates. The calcined samples preserve their crystallinity upon heating at this temperature.

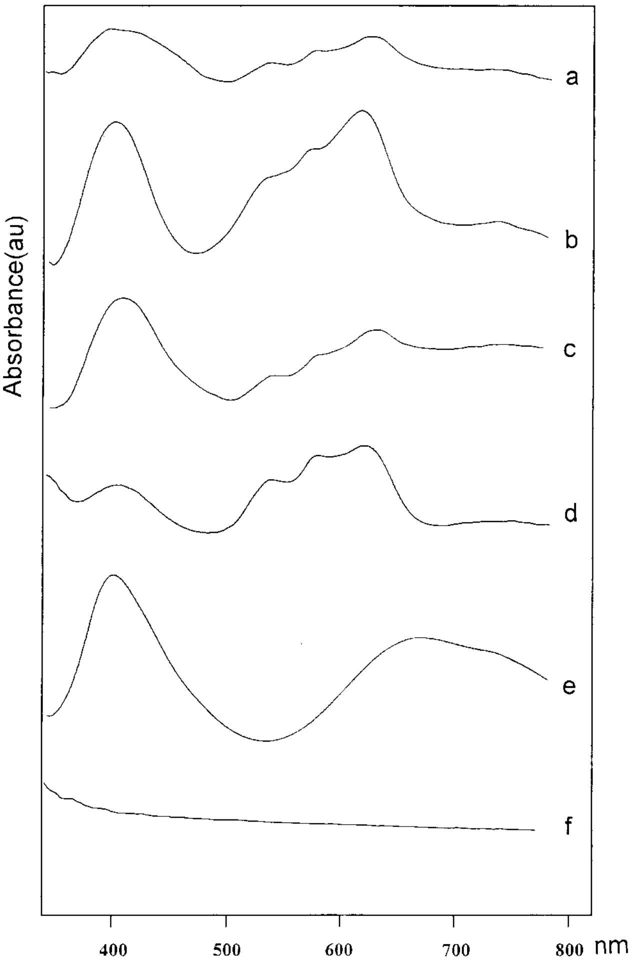

Figure 2. Diffuse reflectance spectra of as-synthesized hydrated samples (a) NiAPO-5(1), (b) NiAPO-5(2), (c) NiAPO-5(3), (d) NiAPO-5(4), (e) Ni-SAPO-5 and (f) AlPO-5.

Diffuse reflectance spectra of as-synthesized hydrated samples are shown in Figure 2. All NiAPO-5 samples show four absorption bands observed at about 625, 580, 540 and 400 nm. But the relative intensity of the 400 nm band in comparison with the other three bands is different among the samples giving samples of different colors. NiAPO-5(4) is a pale violet color whereas NiAPO-5(3) is green and NiAPO-5(2) is pale blue. AlPO-5 as a reference sample lacking nickel cations is white and shows no absorption band in the visible region (Figure 2f). We will present enough evidence to prove that at least some of the nickel cations in some samples are substituted in the framework. For this let us look at the d-d transitions of 4-coordinate nickel. There are three spin-allowed electronic transitions referred to as ν_1, ν_2 and ν_3 and assigned as follows:

$$\nu_1 : {}^3T_1(F) \longrightarrow {}^3T_2(F)$$

$$\nu_2 : {}^3T_1(F) \longrightarrow {}^3A_2(F)$$

$$\nu_3 : {}^3T_1(F) \longrightarrow {}^3T_1(P)$$

Table 4. Typical diffuse reflectance absorption bands for nickel(II) cations in tetrahedral symmetry[a]

Sample	λ_1	λ_2	λ'_3	λ''_3	λ'''_3	Reference
NiLaX	2660	1220	620	570	–	37
NiLaX	2500	1210	615	570	524	38
NiAPO-5	*	*	625	580	540	This work
$NiCr_2O_4$	2000	1120	637	555	–	39

[a] Absorption bands are given in the order of decreasing λ in nm.

* Not observed because of our spectrophotometer's wavelength limits.

With our spectrophotometer we can only inspect the visible region of the spectrum and the ν_3 transition is within this range. Due to spin-orbit coupling the ^{3}T1(P) state splits into three components. Therefore the 625, 580 and 540 nm absorption bands are clearly the triplet of the ν_3 transition corresponding to tetrahedral Ni^{2+}. Schoonheydt *et al.* have studied the coordination of Ni^{2+} to lattice oxygens of zeolites X and Y [37]. They have detected tetrahedral nickel in the spectra of NiLaX dehydrated at 500 °C. But they have argued that the ν_3 transition is observed as a doublet band at 620 and 570 nm and not a triplet as reported by Briend-Faure *et al.* [38]. However our results for the assignment of the three bands at 625, 580 and 540 nm to the ν_3 transition of tetrahedral Ni^{2+} in NiAPO-5 samples is very close to the data reported by Briend-Faure *et al.* They observed three bands at 615, 570 and 525 nm in the reflectance spectra of NiLaX zeolites heated up to 300°C. They explained their finding is related to the nickel ions in tetrahedral position with three lattice oxygens and one extra-lattice oxygen of zeolite. Their DRS results for 4-coordinated nickel ions are compared with other reported data in Table 4.

An absorption band at about 400 nm which is strong in NiAPO-5(3) and weaker in NiAPO-5(4) is attributed to octahedral nickel ion. This is very close to the main absorption band of $Ni[(H_2O)_6]^{2+}$ [20, 31]. This band is also similar to that of octahedral nickel reported for hydrated NiY zeolite samples [24, 25]. It should be noted here that there are three spin-allowed transitions expected for octahedral Ni^{2+} where two of these characteristic bands are within the visible range [20, 25, 31, 39]. Therefore we must observe another band at about 600–750 nm in the reflectance spectra of the samples. This band cannot be distinguished in the spectra. To clarify the matter properly and make an evaluation of the extent of the tetrahedral and octahedral nickel cations based on the intensities of the spectra, we also prepared a SAPO-5 sample. We used its calcined form for an ion-exchange treatment in the nickel acetate solution. According to the mechanism of Flanigen *et al.*, silicon substitutes for phosphorus which will result in an anionic framework similar to the zeolite molecular sieves giving the ability to exchange cations [1]. The framework negative charge is normally balanced by protonated amine in the as-synthesized form and by H^+ ions in the calcined form. The HSAPO-5 in the nickel acetate solution will take up Ni(II) cations where all of those will be located in the octahedral extra-framework sites. This sample is designated as Ni-SAPO-5. Ni-SAPO-5 is green, a color usually ascribed to 6-coordinate Ni(II) cations. The spectrum of Ni-SAPO-5 is shown in Figure 2(e). The expected absorption bands for octahedral nickel in the visible region are clearly observed at about 400 and 660–730 nm in this sample. Careful inspection of the spectrum reveals the presence of the two 660 and 730 nm bands. This result is in exact conformity with the spectral data reported by Lepetit and Che for hydrated nickel-containing Y zeolites [25]. They have observed three bands at 729, 665 and 393 nm in the visible region and have attributed these to the presence of octahedral $[Ni(H_2O)_6]^{2+}$ complexes located in the supercages and in electrostatic interaction with the zeolite framework. The presence of the spin-forbidden transition, 665 nm, has been ascribed to the influence of the spin-orbit coupling in "mixing" a spin singlet (^1E_g) with the ^{3}T1g(F) spin triplet, which are very close in energy of the $\Delta_\circ$ value given by $6H_2O$, thereby allowing the spin forbidden transition to gain intensity from the spin-allowed transition. The absorption bands at 730 and 660 nm cannot be observed in NiAPO-5 samples because they are hidden by the tetrahedral nickel bands.

Our data show that some of the nickel is in tetrahedral positions (supporting evidence for isomorphous substitution of Ni^{2+} for Al^{3+}) and most are in octahedral positions. The octahedral nickels could have been formed by replacement of octahedral aluminum atoms or they could be present as extra-framework species. The presence of octahedral aluminum in the as-synthesized aluminophosphate molecular sieves has been observed by ^{27}Al MAS NMR techniques [40, 41]. These aluminums are formed by a secondary interaction of the framework aluminums with the occluded template or water molecules within the micropores of the aluminophosphates.

We found that the extent of nickel substitution for tetrahedral framework aluminum varies according to the synthesis method used. In sample NiAPO-5(4) the intensity of the triplet band in comparison with that of the 400 nm band is higher compared with other NiAPO-5 samples and we may conclude that in this sample more nickel ions are substituted in the framework. However, the amount of tetrahedral Ni(II) is very low compared with that of the octaheral Ni(II) in NiAPO-5(4), taking into account absorptivities. We cannot correlate the observed intensities of the tetrahedral and octahedral bands to the nickel concentration without considering the absorptivities of these two symmetries which was discussed before. Duke *et al.* claimed synthesis of NiAPO-20 crystals but they have not confirmed framework substitution of nickel in their aluminophosphate [42]. They obtained a pale green NiAPO-20 sample which clearly shows the presence of octahedral Ni^{2+} in their aluminophosphate. We think the violet color could be a rational clue for the presence of tetrahedral nickel in this type of material. Hartmann *et al.* reported a violet color for the as-synthesized NiAPSO-5 sample (a 1% Ni loading) claiming that nickel occupies a framework position [8]. We ran an experiment to demonstrate the existence of diversity among the samples and also to strengthen our opinion about the correlation between the violet color of the sample and tetrahedral nickel

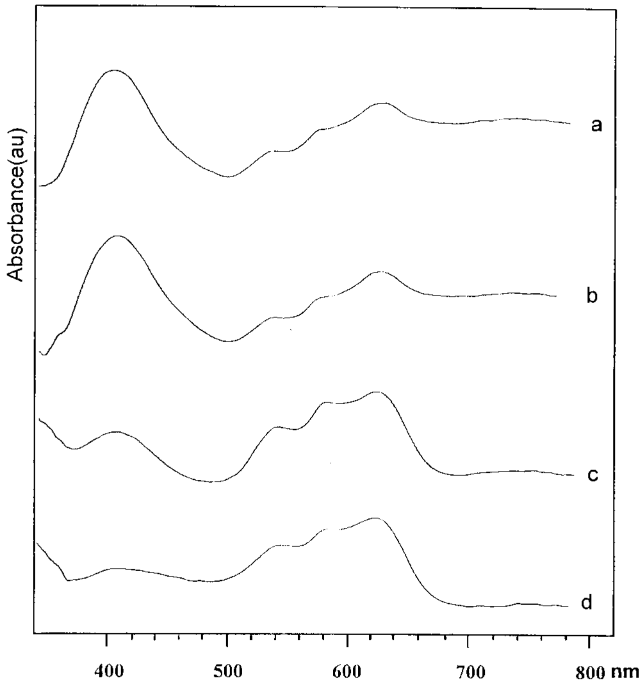

Figure 3. Diffuse reflectance spectra of as-synthesized hydrated and dried samples: (a) NiAPO-5(3) hydrated, (b) NiAPO-5(3) dried, (c) NiAPO-5(4) hydrated, (d) NiAPO-5(4) dried.

concentration in the aluminophosphate. The diversity could be magnified by looking at the spectra of dried samples. Figure 3 compares reflectance spectra of both dried and hydrated NiAPO-5(3) and NiAPO-5(4) samples. The spectra of the dry and hydrated NiAPO-5(3) are similar. This was expected because the green color of the hydrated NiAPO-5(3) sample did not change after drying. The intensity of the 400 nm band in NiAPO-5(4) decreases considerably after drying at 110 °C and the color of the sample changed to deeper violet. The decreasing intensity of the 400 nm band should be correlated to the loss of coordinated water of some of the octahedral nickel cations. The dehydration is probably accompanied by a decrease in the nickel coordination number from six to four.

When the samples are exposed to higher temperature (calcination at 550 °C) the occluded template decomposes and template-free samples are produced. Our XRD results after calcination of the samples showed that the crystal structures were preserved and no impurity phase was detected. Figure 4 shows reflectance spectra of the calcined samples. As can be observed, the intensity of the triplet band decreases in nearly all of them compared with the as-synthesized ones but the extent of the decrease is not the same. It is also noticeable that the 400 nm bands in the calcined samples were shifted to about 420 nm. The color of the NiAPO-5(4) changed to very light violet after calcination. The change of color and also decreasing intensity of the triplet band in NiAPO-5(4) may suggest dislodging some of the tetrahedral nickel from their positions. But as mentioned earlier the crystallinity of the sample was preserved after calcination at 550 °C. Samples NiAPO-21 and NiAPO-12 prepared by Rajic *et al.* did not resist temperatures above 220 °C and at this temperature collapse of the structures took place [19]. They have explained this by the impossibility of Ni^{2+} to attain a stable tetrahedral geometry as a constituent of the aluminophosphate skeleton. Due to the absence of water and the ethylenediamine (used by them as template) the crystalline structure collapsed by heating at 220 °C. They considered that nickel(II) cations can only replace the hexacoordinated aluminum of the AlPO-21 framework which is octahedrally coordinated by the four oxygen atoms of the aluminophosphate lattice, water and/or template molecules. Our spectroscopic data obtained from highly crystalline materials clearly shows the triplet band remaining after calcination of the NiAPO-5(4) at 550 °C and this provides more support for the existence of tetrahedral nickel in this sample.

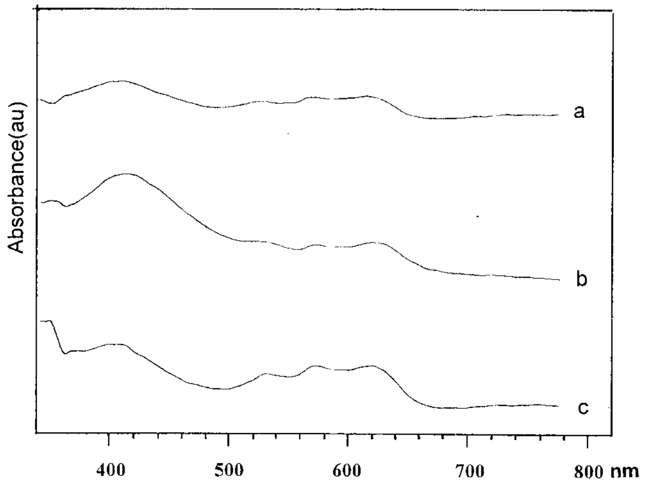

Figure 4. Diffuse reflectance spectra of samples calcined at 550 °C: (a) NiAPO-5(1), NiAPO-5(3) and (c) NiAPO-5(4).

Conclusion

Despite our limitation in not covering the entire wavelength range corresponding to all electronic transitions of tetrahedral and octahedral nickel(II) ions, it seems we were able to relate the spectral data to the positions of nickel in NiAPO-5 and Ni-SAPO-5 samples. In this work, we have shown that using our synthesis procedure of diluted suspension may change the concentration ratio of four- and six- coordinated nickel in favour of four in this type of aluminophsphate samples. A triplet band with three maxima at about 625, 580 and 540 nm was attributed to the tetrahedral framework-substituted nickel(II) cations. The absorption bands at 730, 660 and 400 nm correspond to octahedral nickel(II) cations. The two bands at 730 and 660 nm are observable only in the Ni-SAPO-5 sample where Ni(II) was incorporated in the extra-framework positions by ion-exchange treatment of SAPO-5. The octahedral nickel ions can be formed either by replacement of octahedral framework aluminum atoms or most probably they could be present as extra-framework species in NiAPO-5. The intensity of the triplet band in comparison with that of the 400 nm band, taking into account that the absorptivity for tetrahedral Ni(II) is about one order of magnitude greater than the octahedral one, shows to what extent tetrahedral framework aluminum sites are replaced by nickel(II) ions. According to this statement, Ni(II) incorporation in the tetrahedral framework positions is relatively small. The intensity of the triplet band decreases upon calcination at 550 °C, but never becomes zero. This suggests that a very small quantity of the tetrahedral nickel(II) cations are firmly bound to framework oxygen atoms of the aluminophosphates.

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