

RESEARCH PAPER

## A Systematic Study on the Effect of Desilication of Clinoptilolite Zeolite on its Deep-Desulfurization Characteristics

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### ABSTRACT

Natural clinoptilolite zeolite (CLP) in its original or metal ion-exchanged form (Ni<sup>2+</sup>) is a weak adsorbent for relatively large thiophene derivative molecules like benzothiophene (BT) and di-benzothiophene (DBT), due to its rather restricted micro-channel structure. A novelty of this work is that upon desilication treatments, it is possible to enhance the adsorption behavior of Ni<sup>2+</sup>-exchanged CLP for such large sulfur-containing molecules. A natural CLP zeolite has been desilicated using NaOH solutions in a concentration range of 0.2-2.0 M. The resulting powders have been subjected to XRF, XRD, FTIR, nitrogen adsorption/desorption, TEM and TGA analyses. The adsorption isotherms for the removal of thiophene (TP), BT, DBT and iso-propyl mercaptan (IPM) have been obtained experimentally at 20 °C from simulated liquid fuels using iso-octane as solvent. The sample treated with 1.5 M NaOH solution showed the most significant enhancement in adsorptive properties. The selectivity order is IPM > TP > BT > DBT. Regenerability tests show a quasi constant adsorption capacity after the first cycle. The observed phenomena have been thoroughly discussed based on the physico-chemical analyses of the samples.

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### INTRODUCTION

Adsorptive deep desulfurization of transportation fuels has strongly drawn an ever-increasing interest of researchers over the last decade. It is actually a post-treatment process implying to produce ultra-low sulfur or even zero-content sulfur liquid hydrocarbon fuels [1]. Propensities towards the use of fuel cells as electrical energy generators in the future supplied with zero-sulfur hydrogen fuel and adhering to the new environmental regulations regarding the production of hydrocarbon fuels with minimal sulfur content (under 10 ppm) have been the main motivations for the emergence of developing new adsorbents.

Ion-exchanged Y zeolites [2,3], especially Cu(I)-Y and metal halides supported on activated

carbon, especially PdCl<sub>2</sub> on activated carbon [4] have been reported to act as highly effective deep desulfurization adsorbents for treating liquid fuels. It is well accepted that introduction of d-block metal cations like Ni<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>+</sup>, etc. may enhance sulfur removal through  $\pi$ -complexation reactions. Considering zeolitic adsorbents, latest developments include the enhancement of the adsorptive characteristics of Y zeolite through co-ion-exchange. These include Cu(I)Ce-Y zeolite [1] and AgCe-Y zeolite [5], where the co-exchanged zeolites showed a more favorable isotherm with respect to Cu(I)-Y and Ag-Y zeolites, respectively. Our group has recently reported outstanding adsorptive behavior of Ag-X zeolite with a saturation capacity approximately more than 9 times of that

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of Ni-X or co-exchanged NiAg-X zeolites [6]. However, Ag-X zeolite is a relatively expensive catalyst which undergoes a gradual continuous decrease of sulfur removal capacity upon multiple regenerations, as preliminary experiments indicate.

Parallel to the selection of the most appropriate d-block metal (s) combination for achieving desired adsorptive characteristics for a special zeolite, it is possible to suitably change the micropore morphology and Si/Al molar ratio of the zeolite framework pursuing the same task. To be more specific, it is possible to create efficient hierarchical zeolites [7]. Hierarchical zeolites may be formed through dealumination, desilication or a combination of both. Such post-synthesis strategies may result in drastic changes in the catalytic [8-11] and adsorptive characteristics of zeolites [12-14]. A hierarchical factor has also been proposed by Perez-Ramirez *et al.* [15] for such disordered microporous/ mesoporous structures; however we will not consider it in the present study.

The literature related to the production of hierarchical zeolites aiming at improving sulfur removal characteristics is rather scarce. Tian *et al.* [16] desilicated a beta-zeolite through alkaline treatment, improving the desulfurization performance of the Ce form of the zeolite for thiophene (TP), benzothiophene (BT), di-benzothiophene (DBT) and 3-methyl thiophene (3-MTP). Tian *et al.* [17] extended the idea to enhance the desulfurization capacity of Ce-Y zeolite for the same sulfur compounds through sequential dealumination-desilication treatments. The final 'hierarchical' zeolite was reported to exhibit substantially improved desulfurization characteristics.

Our group has recently begun a vast study on the effect of dealumination and desilication of clinoptilolite (CLP) zeolite (ion-exchanged with Ni<sup>2+</sup>) on the deep-desulfurization behavior of the natural zeolite. Clinoptilolite zeolite is per se a rather weak adsorbent, especially for thiophene derivatives like BT and DBT which suffer from steric limitations for diffusing through the CLP channel system. Dealumination of CLP resulted in astonishingly improved sulfur removal capacity for thiophene (TP), BT and DBT [18]. It should be reminded that clinoptilolite is an abundant and cheap natural zeolite with inherent mechanical strength due to the presence of inorganic binders in its agglomerates. In the present work, we have attempted to investigate the effect of desilication on the deep-desulfurization characteristics of the CLP-Ni of CLP zeolite. Desilication has been performed by treatment of the

zeolite with NaOH solutions of different molarities. The desilicated samples have been characterized through nitrogen adsorption/desorption, XRF, TEM, FTIR, XRD and TGA analyses. The adsorption isotherms for TP, BT, DBT and iso-propyl mercaptan (IPM) have been obtained experimentally using simulated model fuels containing iso-octane solvent. The regenerability property has been studied in detail and the results have been explained based on the characterization analyses.

## EXPERIMENTAL

The clinoptilolite zeolite used in this study is an Iranian commercial product of Afrand Tuska Co. Its purity is *ca.* 90 wt.% and the Si/Al molar ratio is 5.65. The agglomerates have been sized to an average size of 180  $\mu\text{m}$  for the desilication and ion-exchange chemical treatments. Any dust or soluble salts were separated through washing of the raw material with plenty of distilled water followed by filtering and overnight drying at 110 °C.

Thiophene (TP), benzothiophene (BT), di-benzothiophene (DBT) and iso-propyl-mercaptan (IPM) were purchased from Merck. Model liquid fuels were prepared by dissolving predetermined amount of the sulfur compounds in iso-octane (Merck).

Desilication was performed by putting 1 g zeolite powder in contact with 15 g NaOH solution of predetermined molarity for 3 h at 75 °C under agitation provided by a magnetic stirrer. In continuation, the mixture was filtered, washed with plenty of distilled water and finally dried overnight at 110 °C.

Ion-exchange was performed always after the desilication treatment. To do so, 500 cm<sup>3</sup> of a 0.1 M Ni(NO<sub>3</sub>)<sub>2</sub> (Merck) solution was contacted with 7.5 g zeolite sample for 3 h at a temperature of 50 °C under sufficient agitation. Again, the final mixture was filtered, washed with distilled water and dried overnight at 110 °C.

Iso-octane was used as the liquid fuel model. Desulfurization experiments were performed as follows: 1-The powder sample was heated at 300 °C for 2 h 2-Afterwards the powder was introduced into a 50 cm<sup>3</sup> glass bottle avoiding contact with air and cooled to 20 °C 3-Some 10 cm<sup>3</sup> of the desired sulfur containing model liquid fuel was injected into the glass bottles 4-The glass bottle was gently shaken for 1.5 h at 20 °C 5-The sulfur content of the final sample was determined using a TS-100, Total Sulfur Analyzer instrument. Maximum error of the sulfur analysis experiments was 0.5-1.0 ppm over the whole range under study.

The regenerability of the optimum zeolite sample was assessed by contacting 0.7 mg of the dry powder with 10 cm<sup>3</sup> of a model solution with a concentration of 166 mg s l<sup>-1</sup> of DBT at 20 °C for 1.5 h. Desorption was performed by heating the sample for 2 h at 300 °C in air. This cycle has been repeated up to 5 times.

XRF analysis was performed using a PW1480 (Philips) instrument. XRD analysis was carried out using a PW1800 (Philips) instrument with Cu<sub>K $\alpha$</sub>  radiation. Nitrogen adsorption/desorption analysis was performed using a NOVA 200 (Quantachrome) apparatus. TEM analysis was carried out using EM 10C (Zeiss) instrument. FTIR analysis was performed using a VECTOR 22 (Bruker) instrument. Thermogravimetry analysis (TGA) was performed using a TGA931 (TA Instruments) instrument (heating rate 10 °C min<sup>-1</sup>).

## RESULTS AND DISCUSSION

Table 1 summarizes the nomenclature of the different samples based on their preparation procedure to be used throughout the following

text. Fig. 1 shows the Si/Al molar ratio of the CLP treated samples as a function of the molarity of the NaOH solution used. It should be mentioned that except the parent zeolite sample, all the treated samples are subjected to ion-exchange with Ni<sup>2+</sup>. It is observed that the Si/Al ratio of the CLP-Ni samples undergoes an abrupt reduction from 5.89 to 4.37 using the most dilute NaOH solution (0.2 M). Increasing the solution molarity from 0.2 to 1.5, results in a gradual decrease of Si/Al ratio down to 4.05. Increasing the NaOH molarity from 1.5 to 2.0 results in a relatively significant decrease of the ratio from 4.05 to 3.26. This trend is quite rational; the more is the alkalinity of the basic solution, the stronger is the chemical attack (hydrolysis) of the hydroxyl groups to the zeolitic framework leading to the extraction and dissolution of the silicon oxide building blocks.

Fig. 2 illustrates the XRD patterns of the different samples. It may be stated that crystallinity remains approximately unchanged up to a NaOH solution concentration of 1.0 M. The crystallinity is calculated by the following formula: (area of

Table 1. Nomenclature of the Different Samples Based on their Preparation Procedure and their Chemical Analysis. Metal and Metal Oxides Concentrations are Expressed as wt.%

Sample	NaOH solution molarity	Treatment time (min)	Si/Al molar ratio	Ni	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	TiO <sub>2</sub>	MnO	Crystallinity (%) <sup>a</sup>
CLP	-	-	5.65	0.00	1.10	3.25	2.26	0.33	0.157	0.066	100
CLP-Ni	-	-	5.89	1.25	1.17	2.45	2.09	0.36	0.155	0.086	90
D02	0.2	180	4.37	2.11	1.19	2.48	2.61	0.54	0.154	0.113	90
D05	0.5	180	4.25	1.95	1.33	2.86	2.69	0.49	0.175	0.147	90
D1.0	1.0	180	4.30	2.54	1.43	2.74	2.56	0.58	0.173	0.177	90
D1.5	1.5	180	4.05	5.02	1.9	1.95	2.2	0.66	0.184	0.203	85
D2.0	2.0	180	3.26	7.11	2.04	1.49	2.09	0.76	0.231	0.224	77

<sup>a</sup>The crystallinity has been calculated on an initial binder free basis. Recall that the raw zeolite is 90% pure. The initial binder comprehends amorphous and crystalline phases (like cristobalite).

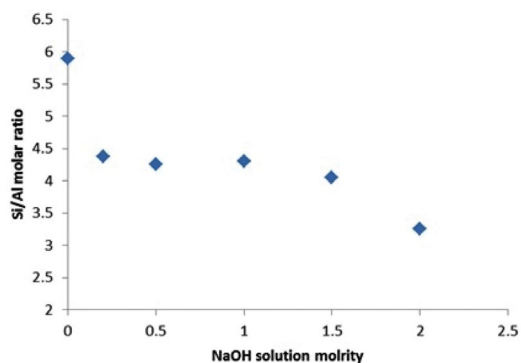


Fig. 1. Si/Al molar ratio of the CLP treated samples as a function of the molarity of the NaOH solution.

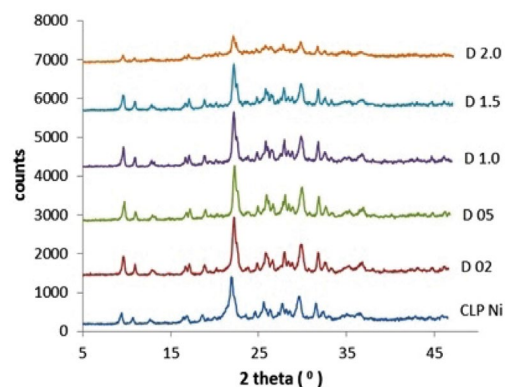


Fig. 2. XRD patterns of the raw and treated samples.

the peaks in the range of 2 theta between 5 and 40°-amorphous background area between 2 theta 5° and 40°)/(total peak area between 2 theta between 5 and 40°). Increasing the concentration to 1.5 M results in 15% decrease in crystallinity. Using higher concentrations definitely has a detrimental effect on the integrity of the zeolite framework and is accompanied with substantial amorphization.

Fig. 3 shows the Ni<sup>2+</sup> content of the zeolite agglomerate as a function the NaOH solution molarity. It is observed that there exists a clear linear relationship between the NaOH solution concentration and the nickel content in the concentration range of 1.0-2.0 M of the alkaline solution. While the CLP-Ni parent zeolite contains *ca.* 1.25 wt.% Ni<sup>2+</sup>, the samples treated with 1.0 M (D1.0) and 2.0 M (D2.0) NaOH solutions contain 2.54 and 7.11 wt.% Ni<sup>2+</sup>, respectively. It is noteworthy that decreasing the Si/Al ratio keeping the crystallinity relatively high is accompanied with the increase of the Ni<sup>2+</sup> cation exchange capacity due to the increase of the Al content of the zeolite framework. This increased Ni content obviously should have a direct effect on the improvement of the desulfurization capacity of the Ni-exchanged zeolite. However, this is only plausible if the filling of the pores with Ni<sup>2+</sup> cations do not result in the narrowing of the pore windows, preventing sulfur compounds to enter the pores and proceed further. It is well known that the increase of the Ni content of Y zeolites may result in the decrease of the desulfurization capacity due to the decrease of the steric limitation imposed by the pore narrowing due to the extra Ni<sup>2+</sup> cations introduced in the pore windows [19]. Considering as typical example the D1.5 sample, it is observed that the decrease of the Si/Al ratio with respect to the CLP-Ni sample is 31% corresponding to a theoretical increase

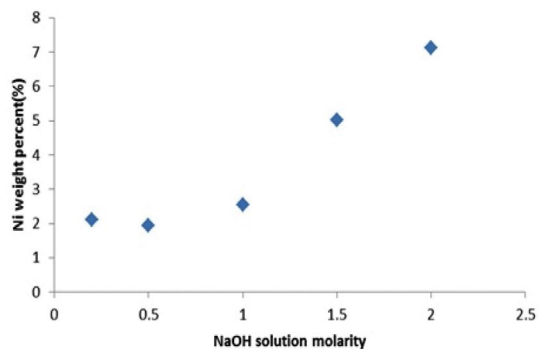


Fig. 3. Ni<sup>2+</sup> content of the product zeolite agglomerates as a function of the NaOH solution molarity.

of Ni<sup>2+</sup> weight percent of 62%. Interestingly, the experimental increase of Ni<sup>2+</sup> content is calculated to be 64%, in a fair agreement with theory. Deviations should exist as we ignored any changes in the microporous structure of the zeolite as a function of desilication. The relative high content of Ni leads to consequences in the adsorption/desorption of the zeolite which will be addressed later. A more detailed chemical analysis of the different samples concerning to the subject of this study is in Table 1.

Fig. 4 shows the FTIR spectra of the CLP, CLP-Ni, D05, D1.5 and D2.0 samples. The broad peak with its maximum located at 1062 or 1058 cm<sup>-1</sup> in the CLP and CLP-Ni samples is attributed to T-O stretching vibrations of TO<sub>4</sub> tetrahedra, where T is a Al or Si atom. Treatment with 0.5, 1.5 and 2.0 M NaOH solutions shifts this peak to lower wave numbers (*ca.* 1053 cm<sup>-1</sup>). This is the opposite phenomenon observed in case of dealumination, where the peak is shifted towards larger wave numbers [20]. The peak at 791 cm<sup>-1</sup> present in the spectrum of the CLP and CLP-Ni samples tends to vanish upon alkaline treatment. This peak is attributed to O-T-O groups stretching vibrations [21]. Desilication extracts T = Si atoms out of the framework. Accordingly, the attenuation of this peak upon alkaline treatment is another proof for the desilication process to take place. The parent CLP zeolite shows a peak *ca.* 3640 cm<sup>-1</sup> which is attributed to free bridging hydroxyls or Broensted acid sites. These types of sites have already been reported for natural CLP in the past and are the main cause of their intrinsic catalytic activity for reactions like methanol dehydration [22]. It is observed that the latter peak attenuates upon nickel exchange in the CLP-Ni, D05, D1.5 and D2.0 samples. This seems quite rational as the protons are likely substituted with Ni atoms, thus

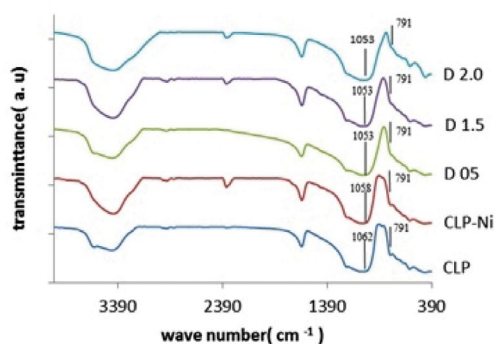


Fig. 4. FTIR spectra of the CLP, CLP-Ni, D05, D1.5 and D2.0 samples.

attenuating the acidic character of the zeolite.

It seems very informative to allude to the results of nitrogen adsorption/desorption at this stage. Table 2 lists specific surface area and the average pore diameter and pore volume calculated based on the BJH theory from the experimental adsorption and desorption branches of the different samples. The pore size distribution (based on the desorption branch) of the CLP-Ni and D1.5 samples is illustrated in Fig. 5. Generally speaking, the average mesopore diameter remains approximately intact upon treatment with NaOH solutions. However, the pore volume undergoes a clear increase due to desilication (almost 2.2 fold). The mesopore size distribution is generally tri-modal, with major peaks centering around 2.0, 3.6 and 16.0 nm for both samples. However, the intensity of the peaks (especially those corresponding to 3.6 and 16.0 nm) increases substantially after desilication. This is while the specific area increases only *ca.* 53% after desilication with 1.5 M NaOH solution. Usually dealumination of clinoptilolite results in more than 3 times, increase in surface area [11,18], while the mesopore volume is reduced [18]. Based on the chemical analysis, XRD results and FTIR spectra just explained, it is clear that alkaline treatment

results in zeolite desilication. Desilication removes Si atoms out of the framework structure and should result in some microporosity development. Based on the nitrogen adsorption experiments, the micropore volume of the CLP-Ni and D1.5 samples has been calculated as 0.011 and 0.014 cm<sup>3</sup> g<sup>-1</sup>, respectively. Therefore, it goes without saying that desilication is accompanied with an increase of the microporosity. In the case of the D1.5 sample, microporosity increase amounts to *ca.* 30%.

Figs. 6a and b show the TEM pictures of the CLP-Ni parent sample and the sample treated with 1.5 M NaOH solution (D1.5), respectively. It is clearly observed that the external surface of the zeolite particles undergoes a strong chemical attack upon treatment with the basic solution. It looks as if the external surface is bitten. As indicated in Fig. 6b, desilication may create meso-pores with diameters less than 30 nm within the zeolite crystals, beginning from the outer surface. Creation of such mesopores may result in the increase of the BJH pore volume, and this is in accordance with the experimental results. Such a phenomenon has been reported for MFI zeolites with a framework Si/Al ratio less than 15 after desilication with NaOH solutions [7].

Table 2. Specific Surface Area, Average Pore Diameter and Pore Volume Calculated Based on the BJH Theory from the Experimental Adsorption and Desorption Branches of Samples CLP-Ni, D05 and D1.5

Sample	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Adsorption branch average pore diameter (nm)	Adsorption branch mesopore volume (cm <sup>3</sup> g <sup>-1</sup> )	Desorption branch average pore diameter (nm)	Desorption branch mesopore volume (cm <sup>3</sup> g <sup>-1</sup> )
LP-Ni	37.34	3.07	0.169	3.58	0.171
D05	39.71	3.06	0.291	3.65	0.291
D1.5	57.47	2.73	0.376	3.60	0.381

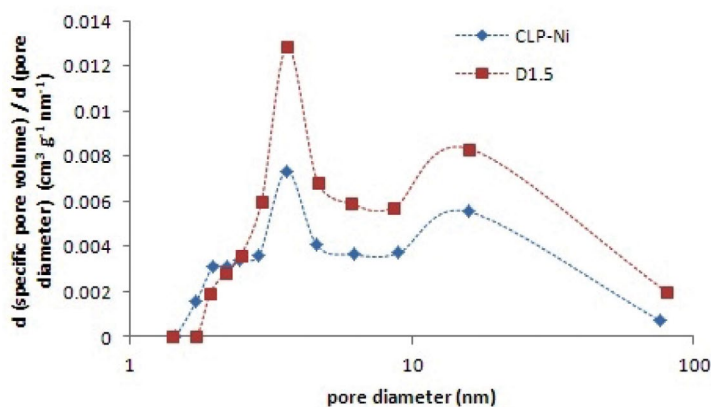


Fig. 5. Pore size distribution of the CLP-Ni and D1.5 samples (based on the isotherm desorption branch).

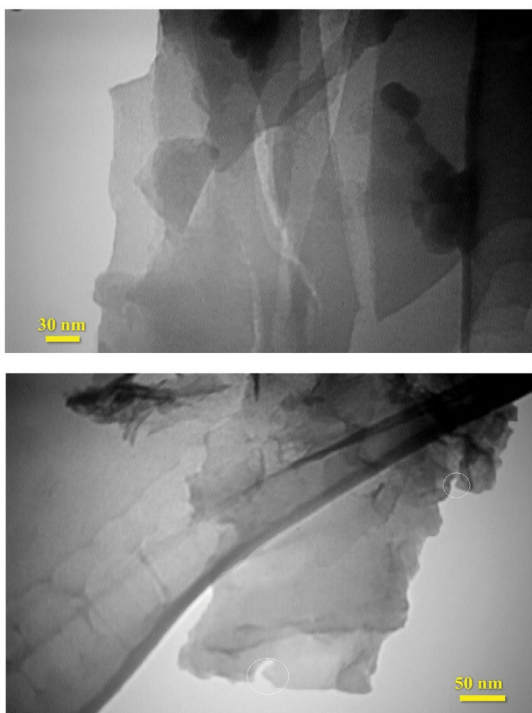


Fig. 6. TEM pictures of the a) CLP-Ni and b) D1.5 sample (external mesopores due to desilication procedure are indicated by circles).

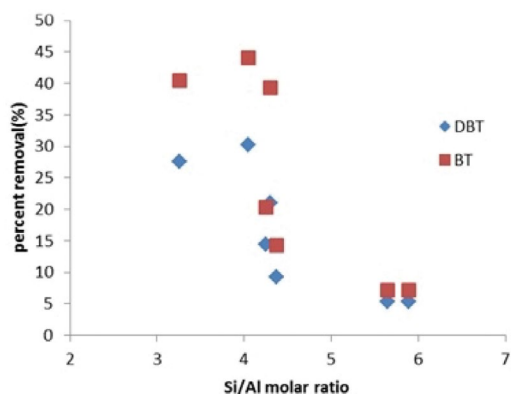


Fig. 7. The extent of sulfur removal as a function of Si/Al ratio for BT and DBT sulfur compounds

Fig. 7 shows the extent of sulfur removal as a function of Si/Al ratio of BT and DBT using an initial sulfur concentration of 84 and 76 mg s l<sup>-1</sup> for BT and DBT, respectively. There is a clear trend irrespective of the type of sulfur compound employed. The CLP-Ni parent zeolite shows the lowest adsorption capacity. The adsorption capacity undergoes a sharp increase as the Si/Al ratio decreases from 4.37 to 4.05. Further decrease in the Si/Al ratio is accompanied with loss in the adsorption capacity. Accordingly, maximum sulfur

removal occurs for a Si/Al molar ratio equal to 4.05, corresponding to the D1.5 sample. The results are quite rational, as treatment with more concentrated alkaline solutions results in the collapse of the zeolitic framework. The adsorption extent of BT is always larger than DBT and this will be explained in the next paragraph.

As a corollary, sample D1.5 was chosen for sulfur adsorption isotherms experiments. Fig. 8 shows the isotherms of the Ni-exchanged un-treated zeolite (CLP-Ni) for TP, BT, DBT and IPM sulfur compounds obtained at 20 °C. The corresponding isotherms for the D1.5 sample are shown in Fig. 9. Comparing Figs. 8 and 9, it is clearly observed that upon alkaline treatment, the adsorption capacity for all types of the sulfur compounds under investigation is enhanced. For both cases, the order of selectivity is as follows:

IPM > TP > BT > DBT

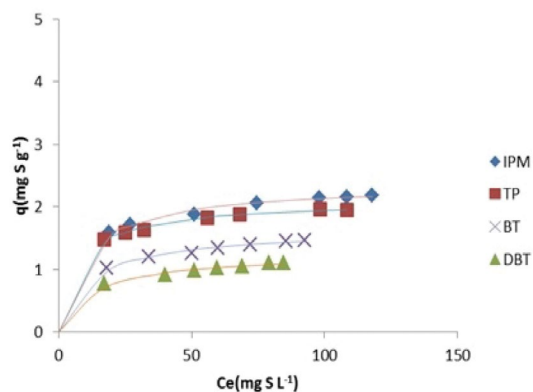


Fig. 8. The isotherms obtained at 20 °C for TP, BT, DBT and IPM sulfur containing molecules using the CLP-Ni sample. Dashed lines show the simulated curves based on the Langmuir-type correlation.

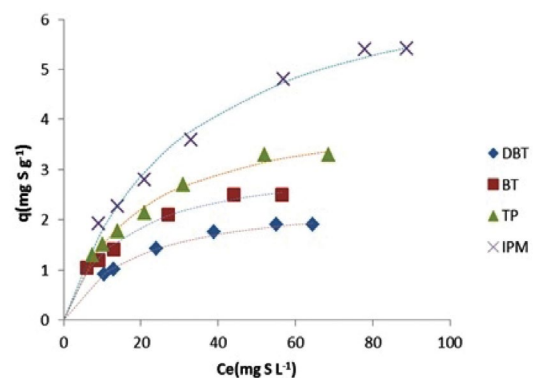


Fig. 9. The isotherms obtained at 20 °C for TP, BT, DBT and IPM sulfur containing molecules using the D1.5 sample. Dashed lines show the simulated curves based on the Langmuir-type correlation.

Table 3. The Corresponding Langmuir Parameters of the Adsorption Isotherm of the D1.5 Sample for Different Sulfur Compounds

Sulfur compound	$q_m$ (mg s g <sup>-1</sup> )	B (l mg <sup>-1</sup> s <sup>-1</sup> )	R <sup>2</sup>
TP	4.29	0.053	0.993
BT	3.20	0.069	0.992
DBT	2.47	0.056	0.996
IPM	7.34	0.032	0.990

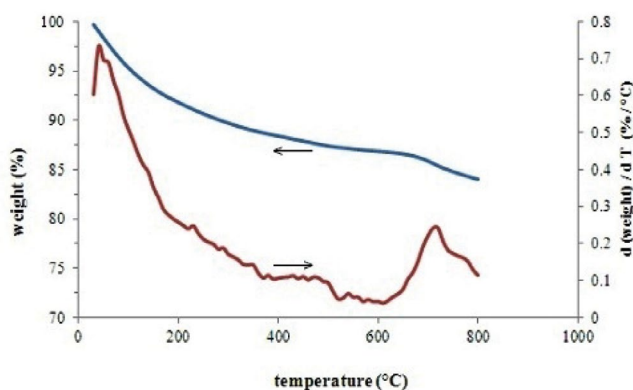


Fig. 10. TGA diagrams of the D1.5 sample initially saturated with DBT.

Excluding IPM, the observed order for the thiophenic compounds is exactly opposite of that reported by Wang *et al.* [3] using Cu(I)-Y as adsorbent. They supported their experimental finding by molecular orbital calculations which showed the following order for the strength of the  $\pi$ -complexation bond:

DBT > BT > TP

This contradiction may be attributed to the different channel structure of CLP with respect to Y zeolite. Y zeolite has 12-ring channels with an average diameter of 7.4 Å. CLP has three channels: an 8-ring  $2.6 \times 4.7$  Å<sup>2</sup>, an 8-ring  $3.3 \times 4.6$  Å<sup>2</sup> and one 10-ring  $3.0 \times 7.6$  Å<sup>2</sup>. The smaller sizes in our case pose steric hindrance to the incoming sulfur compound. Accordingly, the selectivity order follows the size order of the molecules, *i.e.*, TP > BT > DBT. With the same reasoning, the linear character of IPM results in better adsorption with respect to the thiophenic compounds.

The adsorption isotherms do follow a Langmuir-type correlation which is demonstrated in Fig. 9 as dashed lines, where the following relationship is assessed:

$$q = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

where  $q_m$  is the maximal adsorption capacity

(mg s g<sup>-1</sup>),  $b$  is a constant (l (mg s<sup>-1</sup>)),  $C_e$  is the equilibrium liquid phase sulfur concentration (mg s l<sup>-1</sup>) and  $q$  is the adsorption capacity (mg s g<sup>-1</sup>).

Table 3 shows the corresponding Langmuir parameters of the D1.5 sample for different sulfur compounds. It is observed that the saturation adsorption capacity ( $q_m$ ) is increased to *ca.* 80% (with respect to the CLP-Ni sample) upon desilication.

Fig. 10 shows the thermogravimetry analysis (TGA) diagrams of the D1.5 sample initially saturated with DBT. It is observed that DBT is desorbed over a wide temperature range of 100-800 °C. Considering the weight derivative curve in the temperature range of 100-600 °C, more than three broad peaks are present which are attributed to DBT desorption. Water molecules may be present in the fresh sulfur saturated D1.5 sample due to unavoidable exposure to air. However, it is well known that water molecules of CLP-Ni are desorbed in a very smooth fashion and distinct peaks are never observable [18]. The peaks observed for temperatures less than 600 °C in Fig. 10 are assigned to  $\pi$ -complexation Ni-S interactions [6]. Two peaks are observed in the temperature range 600-800 °C, which are attributed to  $\sigma$ -bond Ni-S interactions. The multiplicity of the peaks in both temperature ranges may be attributed to the complex channel structure and the different Ni<sup>2+</sup>

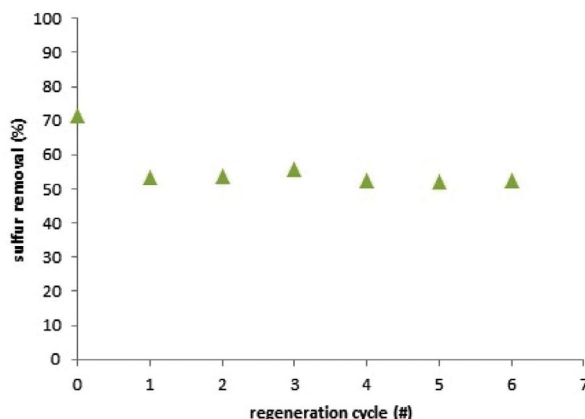


Fig. 11. Extent of sulfur removal as a function of number of regeneration cycles

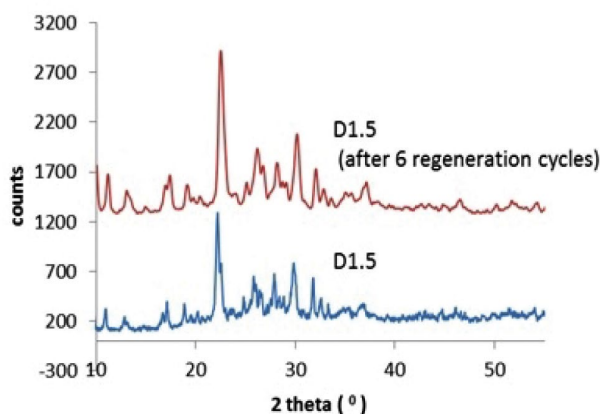


Fig. 12. The XRD spectra of the D1.5 sample before and after 6 regeneration cycles

cation locations at the intersections of the channels.

From an industrial point of view, the  $\pi$ -complexation interactions are preferred over the  $\sigma$ -bond interactions.

Desorption of  $\sigma$ -bonded sulfur compounds is usually accompanied with deactivation of the adsorption site, perhaps due to the creation of poly-carbon residues on them because of the high temperatures involved. It is difficult to quantitatively discriminate between the  $\pi$  and  $\sigma$  bonds in Fig. 10 due to the presence of eventual water molecules in the initial sample. Such quantification, however, is possible with some approximation referring to the regeneration experiments and will be addressed in the following discussion.

Fig. 11 shows the extent of sulfur removal as a function of number of regeneration cycles. Two interesting results may be drawn: 1-The adsorption capacity undergoes a 20% reduction after the first regeneration cycle and 2-The adsorption

capacity remains approximately constant after the first regeneration cycle. These findings may be explained based on the previous discussion of the TGA diagrams. As the regeneration is performed at 300 °C for 1 h, it is most probable that the  $\sigma$ -bond Ni-S interactions are not affected by the thermal treatment. Accordingly, the initial sites able to provide  $\sigma$ -bonds loose activity after the first regeneration cycle merely because they remain covalently bonded with the adsorbed sulfur compounds. The result is a loss of adsorption capacity after the first cycle.

During the next regeneration steps, the sulfur adsorbed *via*  $\pi$ -complexation sites is desorbed and the  $\sigma$ -bonded sulfur from the first regeneration step is always present. The result is an approximately constant adsorption capacity after the first cycle, as shown in Fig. 11. Based on the latter discussion, it may be stated that the  $\sigma$ -sites constitute about 20% of the total sites. Fig. 12 shows the XRD spectra of



the D1.5 sample before and after 6 regeneration cycles. It is observed that the crystallinity remains almost intact upon the severe multiple heat treatment cycles.

## CONCLUSIONS

The present work shows that upon desilication treatments, it is possible to enhance significantly the adsorption behavior of Ni<sup>2+</sup>-exchanged CLP for large sulfur-containing molecules like BT and DBT. The sample treated with 1.5 M NaOH solution showed the most significant enhancement in adsorptive properties with a selectivity order of IPM > TP > BT > DBT. Regenerability tests show a quasi constant adsorption capacity after the first cycle. The observed phenomena could be thoroughly discussed based on the physico-chemical analyses of the samples.

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