

PREPARATION, CHARACTERIZATION AND H₂S ADSORPTIVE REMOVAL OF ION-EXCHANGED ZEOLITE X

Nguyen Quang Long¹, Ho Thi Vuong¹, Huynh Ky Phuong Ha¹,
Winarto Kuniawan², Hirofumi Hinode², and Toshihide Baba³

¹Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, Ho Chi Minh City, Vietnam, e-mail: nqlong@hcmut.edu.vn

²Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Japan

³Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, Tokyo, Japan

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Abstract

This research focuses on the adsorptive removal of polluted H₂S at ambient temperature by modified zeolite X adsorbents. The zeolite X has been synthesized by hydrothermal method and ion-exchanged with six different divalent metal ions including Co²⁺, Mn²⁺, Ni²⁺, Cu²⁺, Ca²⁺, and Zn²⁺. The H₂S adsorption activity of the material was determined by a continuous fixed-bed adsorption system and expressed by the adsorption capacity performance until the H₂S output concentration reach a specified breakthrough point of 10 ppm. The materials have been subjected to X-ray diffraction (XRD) for structural analysis, low-temperature N₂ adsorption was used for specific surface area of the material (BET method), scanning electron microscopy (SEM) for morphology analysis and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for metal content analysis. The faujasite structure of zeolite was detected for the materials except the Cu²⁺-exchanged sample. Comparing to the as-synthesized zeolite X, the Zn²⁺-exchanged zeolite X has increased the H₂S adsorption capacity more than 24 times. Moreover, the Zn content in the zeolite was confirmed to be an essential factor contributed to the H₂S adsorption activity.

Keywords: Ambient temperature adsorption, H₂S removal, Ion-exchange, Modified zeolite X

Introduction

Hydrogen sulfide is a highly toxic gas for human-being and the environment [1]. Hydrogen sulfide is also well-known poison for metallic catalysts, and its concentration in feedstock such as natural gas for steam reforming reaction or H₂ for anode reaction in fuel cell should be decreased to part per million (ppm) levels before their use. To accomplish this task, ZnO-based sorbents have been successfully employed for decades in different domains of the chemical industry. These commercial sorbents however are only effective at high temperature working condition, usually higher than 400°C [2]. Modifications of ZnO materials for lowering the working temperatures have been studied. Zinc ferrite [3], zinc titanate [4], and copper-based [5] solid adsorbents still required temperatures above 300°C. Baird et al. have studied Co-Zn-Al-O mixed metal oxides as H₂S adsorbents at 28°C, where it was shown that aluminum ions in the mixed oxide matrix gave rise to an increased surface area (m²/g) but not to H₂S uptake [6]. Mixed metal oxides have been developed for efficient low-temperature. Efstathiou et. al. researched on Fe-Mn-Zn-Ti-O materials for H₂S removal at 25°C – 50°C and found that there was an optimal structural composition and properties for maximizing the H₂S uptake [7]. Samokhvalov et. al [8] studied copper-promoted ZnO/SiO₂ sorbents for the room temperature removal of H₂S

from reformat gas streams. The Cu dopant significantly enhances desulfurization capacity of ZnO/SiO₂ sorbent at room temperature (up to 92% utilization of ZnO). This research group also reported the Fe–Mn–ZnO/SiO₂ sorbents for room temperature removal of H₂S [9].

Zeolites are widely used as adsorbents for removing different chemicals in a variety of processes, as shape-selective catalysts or supports for active metals in petrochemical industry and as ion exchangers [10]. Clinoptilolite, a natural zeolite, has been studied for H₂S removal by pressure swing adsorption (PSA) process at pressure 7 atm and 25°C. This material exhibited twice the H₂S adsorption capacity of two synthetic molecular sieves [11]. Most of studies on synthetic zeolite adsorbents for H₂S removal focused on ZSM-5, A and Y zeolites [12-14]. In this paper, which is different from other reports, ion-exchanged zeolite X samples have been synthesized, characterized and tested for the H₂S removal by adsorption at ambient temperature and pressure. The adsorptive properties of the zeolites have been explained by taking into account their structure and chemical properties as determined by several analysis methods.

Experimental

The ion-exchanged zeolite X samples in this study were synthesized via two steps. First, NaX was prepared by hydrothermal method from sodium silicate solution, which contained 30 wt.% SiO₂, and aluminum hydroxide, sodium hydroxide. These chemicals were purchased from Tan-Binh chemical company, Vietnam. SiO₂ sol was produced when the sodium silicate was dissolved in sodium hydroxide solution. Aluminum hydroxide was slowly dissolved in sodium hydroxide solution, followed by filtration in order to remove the insoluble residue. After that, these solutions were mixed together. The mixture was aged at room temperature for 24 hours and crystallized at 100°C for 36 hours in an autoclave by hydrothermal process. The obtained solid were then washed with distilled water until the pH value reached 8.0, and dried overnight at 100°C. In the second step, the modified zeolites were prepared by ion-exchange method. Metallic chloride salts was used for preparation of Me²⁺ solution, except the Cu²⁺ solution which prepared from the sulfate precursor. Typically, each 5.0 gram of the NaX was poured in 100ml Me²⁺ aqueous solutions at 70°C. The solution then was stirred for 4 hours. After that, the ion-exchanged zeolite was obtained by filtering, and dried at 100°C overnight. Without other note, the Me²⁺ concentration was kept at 0.5mol/L. The samples were denoted as ZnX, CuX, MnX, NaX, CaX, NiX and CoX for the Zn²⁺, Cu²⁺, Mn²⁺, Na²⁺, Ca²⁺, Ni²⁺ and Co²⁺ ion-exchange solution, respectively.

Crystalline structure of the adsorbents were analyzed by X-ray diffraction (XRD) technique using Rigaku Multiflex diffractometer operating at 40 kV, 20 mA and CuK α radiation. Low temperature N₂ adsorption isotherms were used for the determination of specific surface area of the material (BET method) using Autosorb-1 (Quanta-Chrome) equipped with an analysis software. Scanning electron microscopy (SEM) analysis was carried out by using a Keyence VE8800 apparatus. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was also applied using an SPS7800 (Seiko Instrument Corp.) for metal content analysis in the adsorbents.

Adsorption experiments were performed at room temperature and normal pressure. Figure 1 shows the scheme of the experimental set-up for the adsorption test. A mass of 0.5 gram of the adsorbent was packed in the pyrex reactor. Prior to adsorption test, the

adsorbent was pretreated with nitrogen stream at a flow rate of 3.0 L/hour under ambient pressure at 200°C by a controllable furnace for 2 hours. After that, the system was fed with a H₂S/N₂ mixture with 100 ppm H₂S. During the adsorption test, the flowrate of the H₂S/N₂ was also kept constant at 3.0 L/hour. H₂S concentrations were measured continuously by a H₂S sensor system purchased from Alphasense sensor technology company (United Kingdom). The H₂S concentration was measured until the H₂S concentration of the outlet stream reach a specified breakthrough point of 10 ppm. The H₂S removal capacity was calculated by the following equation:

$$C_s = 10^{-3} \times \frac{M_s}{m} \frac{FP}{RT} \int_0^{t_b} (C_{S_{in}} - C_{S_{out}}) dt$$

Where: C_s - H₂S adsorption capacity (mgS/g); M_s - molecular weight of S (= 32); m - mass of the adsorbent; $C_{S_{in}}$ - H₂S concentration of the input stream; $C_{S_{out}}$ - H₂S concentration of the output stream; F - total gas flow rate; t - time; t_b - time of the adsorption until the concentration of the output stream higher than the breakthrough point (breakthrough time).

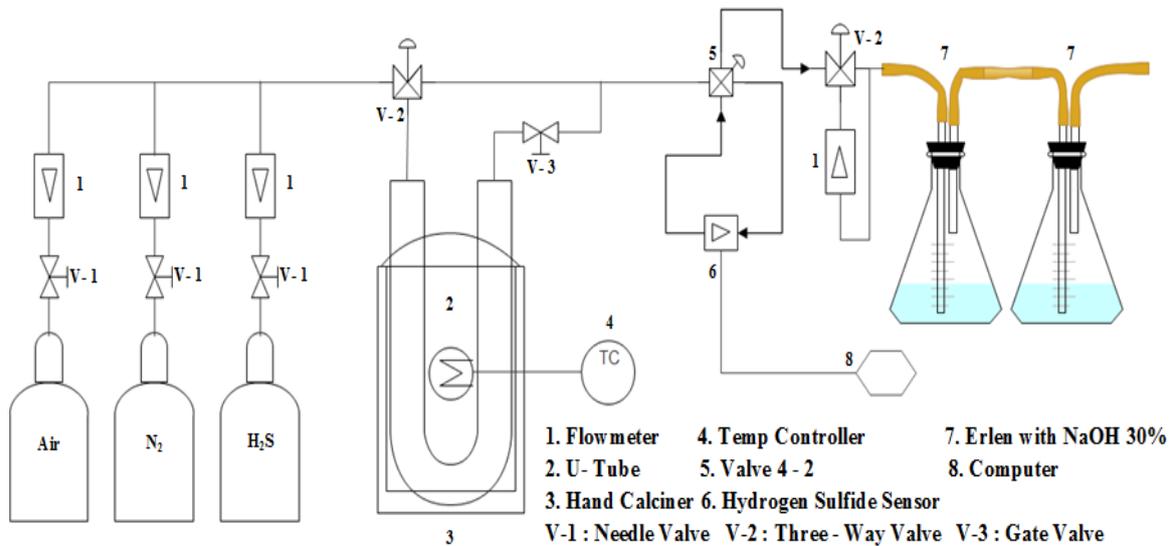


Figure 1. Scheme of experimental set-up for H₂S adsorption test

Results and Discussion

The XRD pattern corresponding to the prepared zeolite X (in sodium form – NaX) is shown in Figure 2. The result revealed typical diffraction peaks of the zeolite with the faujasite (FAU) structure (JCPDS No. 39-0218). Therefore, it can be concluded that the zeolite NaX was successfully synthesized by the hydrothermal process using the chemicals provided by local chemical companies. Morphology of the zeolite was obtained by SEM method and shown in Figure 3. It can be seen that the FAU zeolite particles gathered and generated pores leading to mass transfer improvement during the adsorption process.

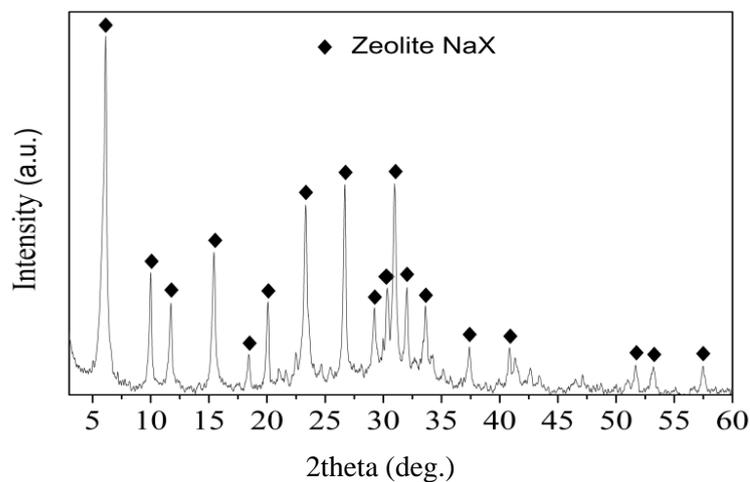


Figure 2. XRD patterns of the NaX

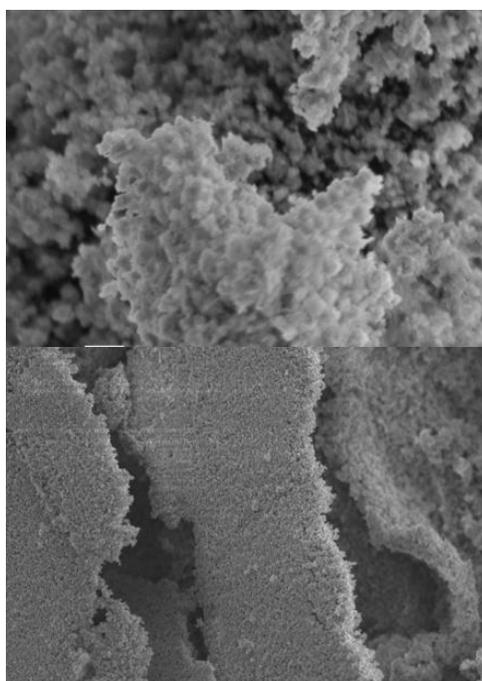


Figure 3. SEM images of the NaX

Figure 4 reports XRD patterns of the divalent-cation exchanged zeolite X samples. In this figure, XRD pattern of NaX is used as the standard for comparison. As shown in this figure, most of the characteristic peaks of the crystalline NaX were completely appeared in XRD patterns of CoX, NiX, CaX, MnX and ZnX. However, the decrease of intensity of these peaks was observed in the ion-exchanged zeolites. On the other hand, diffraction peaks of $\text{Cu}_3\text{SO}_4(\text{OH})_4$ (antlerite) appears in XRD pattern of CuX illustrate that the zeolite X structure may be collapsed or was possibly covered by antlerite layers on its surface. It is important to note that the peaks representative to the metal oxides in CoX, NiX, CaX, MnX and ZnX were not detected even though the existence of the metal in these samples have been confirmed by chemical analysis method (ICP method) as reported in Table 1. Thus, these metal ions were incorporated into the zeolite structure or oxide forms with very small particle sizes which were smaller than XRD detectable limitation.

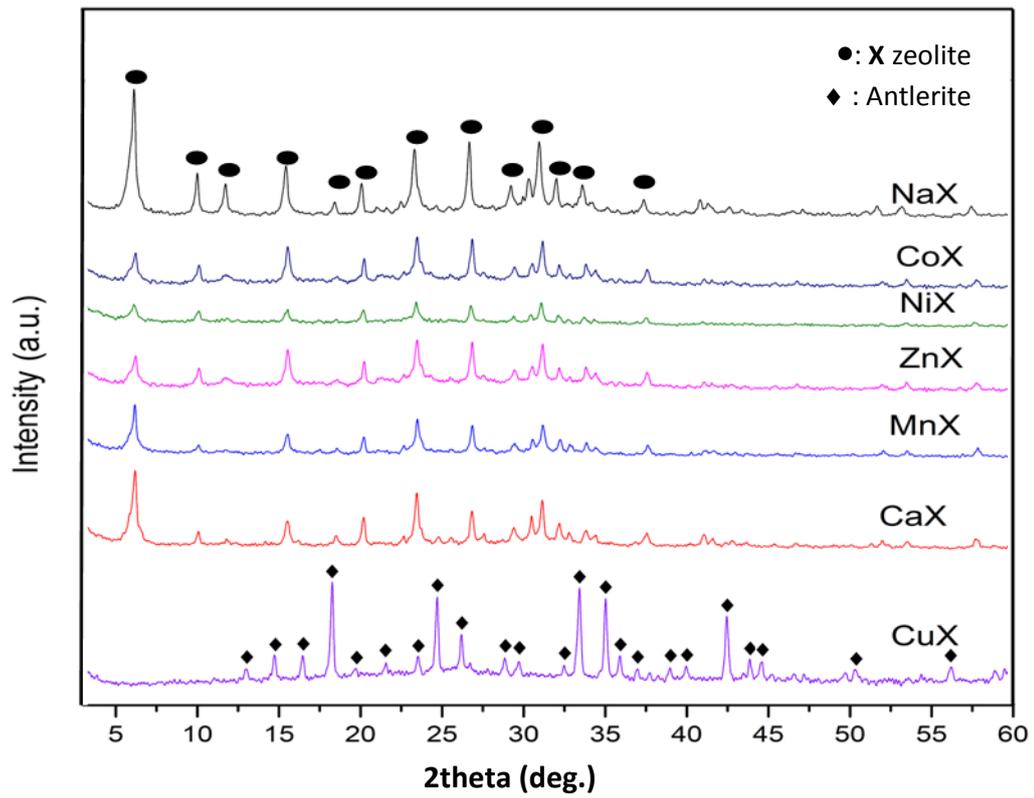


Figure 4. XRD patterns of ion-exchanged zeolite X samples

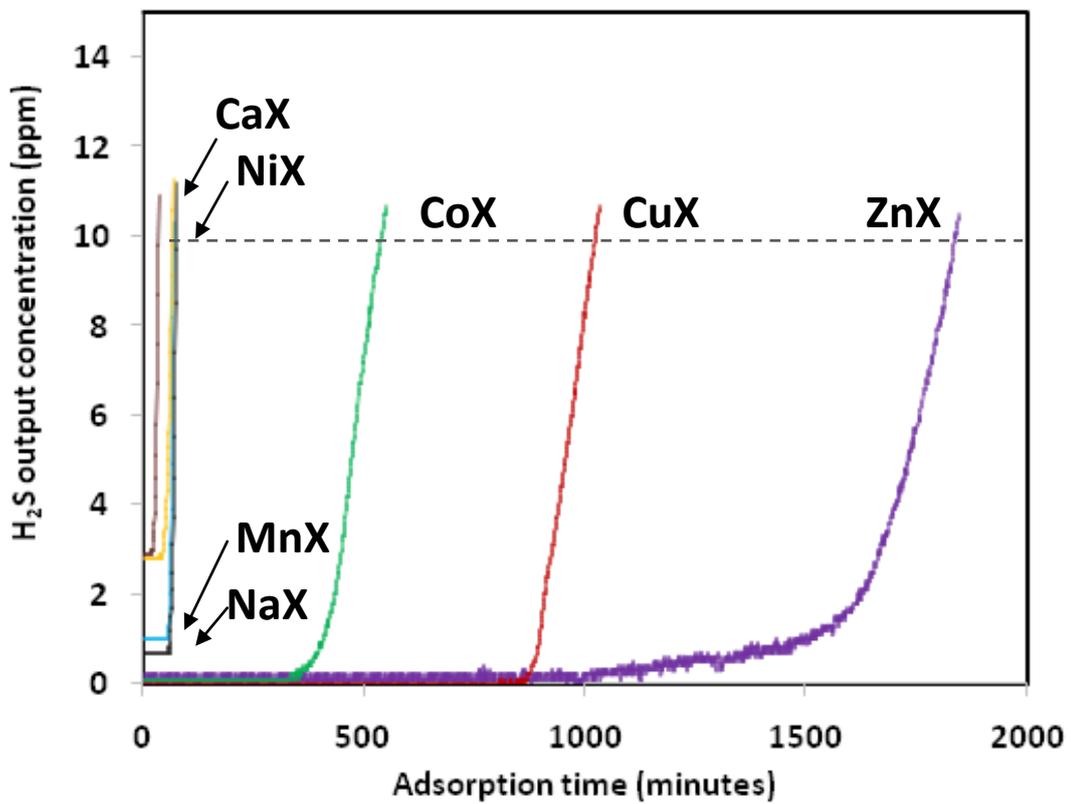


Figure 5. H₂S adsorption breakthrough curves of the zeolites at ambient temperature

Table 1. Properties and H₂S Adsorption Capacity of Ion-Exchanged X Zeolites

Sample	Me ²⁺ Conc. of the Exchange Solution (M)	Metal Content by ICP (wt.%)	BET Specific Surface Area (m ² /g)	H ₂ S Adsorption Capacity (mg S/g)
NaX	n.a	n.a	492	0.9
CuX	0.5	20	111	13.1
ZnX	0.5	14	427	23.5
CoX	0.5	3.9	n.a	6.9
MnX	0.5	3.7	n.a	0.9
NiX	0.5	5.4	n.a	0.8
CaX	0.5	n.a	n.a	0.4

Results of the H₂S adsorption test are shown in Figure 5 and the H₂S adsorption capacities of the adsorbents have been calculated and listed in Table 1. It can be seen that modification of the zeolite by ion-exchanging with some metal ions has improved the H₂S adsorption capacity of the zeolite X. The breakthrough time of the Co²⁺, Zn²⁺, and Cu²⁺ exchanged zeolite X were obviously much longer than those of the parent NaX and the Mn²⁺, Ni²⁺, and Ca²⁺ exchanged zeolites. The adsorption capacity was increased about 7 times, 13 times and 24 times more than that of NaX when the NaX was modified by Co²⁺, Cu²⁺, and Zn²⁺, respectively. The promotive effects of Co²⁺ and Cu²⁺ on the H₂S uptake by metal oxides were consistent to results reported in [6] and [8]. It may be due to the fact that the reaction between CuO and CoO with H₂S are highly thermodynamically favorable. Moreover, this study reports for the first time the significant improvement in H₂S adsorption capacity of the Zn²⁺ - exchanged zeolite X. The parent zeolite X provided high surface area (492 m²/g) and FAU structure. The FAU structure has large pore window of 0.74 nm [10] which is large enough for the transport of H₂S molecule since the kinetic diameter of H₂S is 0.36 nm [12,15]. The Zn²⁺-exchanged zeolite X, which contained 14 wt.% of Zn (Table 1), still had high surface area (427 m²/g – Table 1) and FAU structure (Figure 4). Moreover, if all Zn²⁺ ions in the materials were reacted with H₂S, the H₂S adsorption capacity had been around 68 mg S/g. Therefore, the obtained capacity of the Zn²⁺- exchanged zeolite X (23.5 mg S/g) was only one third of the maximum capacity. This phenomenon can be explained by the short reaction time (around 0.6 seconds) in the testing condition of this study.

Table 2. Properties and H₂S Adsorption Capacity of Zn²⁺ - Exchanged Zeolite X Samples

Sample Code	Zn ²⁺ Conc. of the Exchange Solution (M)	Zn Content by ICP (wt.%)	H ₂ S Adsorption Capacity (mg S/g)
ZnX-1M	1.0	13.8	17.1
ZnX-0.5M	0.5	14.0	23.5
ZnX-0.1M	0.1	10.0	26.0
ZnX-0.05M	0.05	6.1	17.0

Having been discussed above, ZnX are the most effective adsorbent in comparison with other ion exchanged zeolites in this study. Difference in concentration of Zn²⁺ gives significant changes on adsorption ability of the zeolite. As showed in Table 1, the increase in Zn²⁺ concentration of the ion-exchange solutions gave rises of Zn contents on the solid adsorbents. However, the highest Zn containing sample (ZnX 1M) did not have the highest adsorption capacity. When Zn²⁺ concentration increases from 0.05M to 0.1M, adsorption capacity dramatically increased from 17.0 to 26.0 mgS/g. Otherwise, when Zn²⁺ concentration continually increased from 0.1M to 1M, the capacity of the zeolite samples dropped from 26.0 to 17.1 mgS/g. Therefore, the zeolite which was ion-exchanged with 0.1M Zn²⁺ solution gives the best result in comparison with other samples.

Figure 6 shows the effect of Zn²⁺ concentration on crystalline structure illustrated by XRD patterns. It can be seen that the zeolite X structure was observed clearly in all four samples. Interestingly, ZnO crystalline peaks did not appeared in all three XRD patterns which leads to the conclusion that Zn²⁺ was successfully exchanged or ZnO in the samples possibly presented in a small particle size or the amount of crystalline ZnO was lower the detectable limit of the apparatus. Moreover, Figure 7 demonstrates that the absolute shifts of diffraction peaks in 2θ-angle increase strongly with the increase of concentration of ion-exchange solutions. For instance, the deviation of 9.999° peak increased from 0.019° to 0.140° and the 15.478° peak shifted from 0.038° to 0.098°. It can be concluded that the larger amount of Zn on zeolite X gives more changes on its structure because the Zn²⁺ was successfully exchanged with Na⁺ in the zeolite structure. Morphology structure of ZnX is presented by SEM analysis in Figure 8. The Figure 8a shows the morphology of the ZnX at the magnification of 1000X and the Figure 8b shows the morphology of the ZnX at the magnification of 5000X. It is reflected from Figure 8 that the Zn ion exchange zeolite X consisted of micro particles leading to the porous structure of the adsorbent.

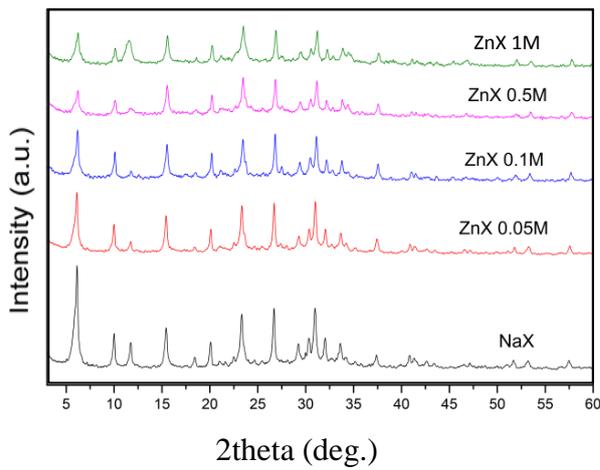


Figure 6. XRD patterns of Zn^{2+} -exchanged zeolite X

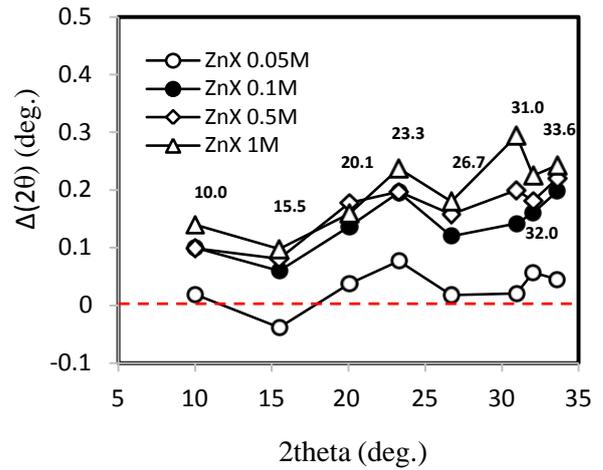


Figure 7. Angular deflection of zeolite modified with Zn^{2+} in comparison with angle diffraction of NaX

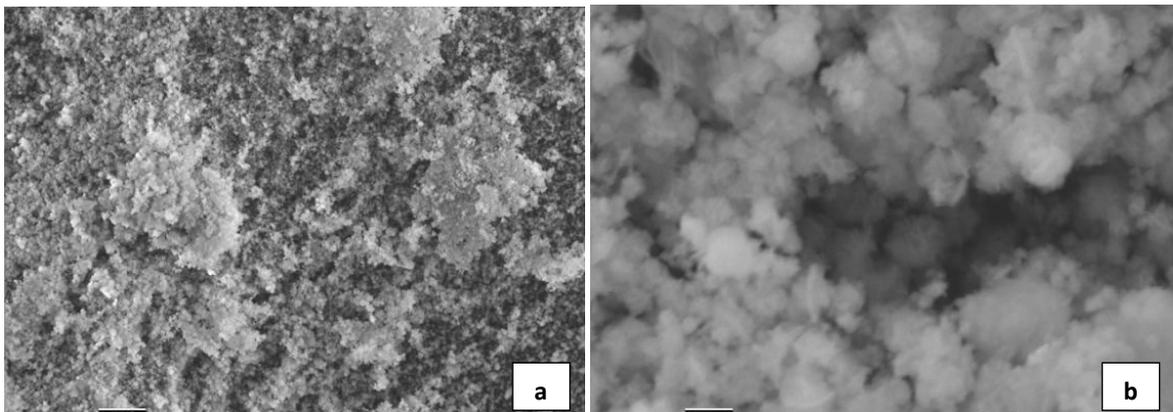


Figure 8. SEM images of the ZnX with different magnifications

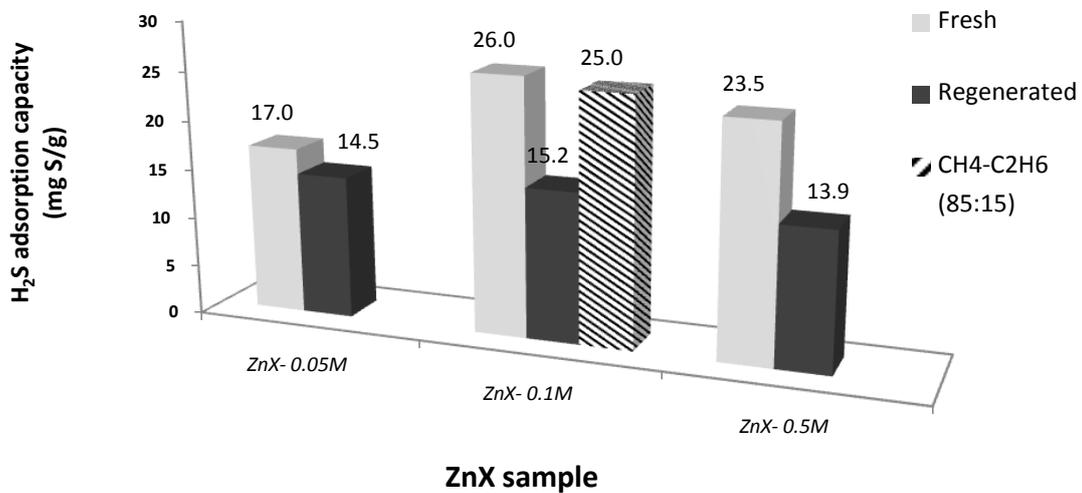


Figure 9. Comparison of H_2S adsorption capacity of ZnX samples

The adsorbent reusability is an important in economic consideration. Three ZnX samples (ZnX-0.05M, ZnX-0.1M, and ZnX-0.5M) were regenerated by a simple method in which the samples were subjected to 200°C for 2 hours under vacuum condition. The H₂S capacity of reused materials in comparison with new materials in Figure 9 demonstrates that a part of the samples can be regenerated. Basing on the obtained experimental data, the removal of H₂S by the Zn²⁺ - exchanged zeolite X possibly can occur by reactions: (1) $Zn^{2+} + H_2S = (Zn-SH_2)^{2+}_{ads.}$ and (2) $(Zn-SH_2)^{2+}_{ads.} = ZnS + 2H^+$. Reaction (1) is proposed because a coordination bond (donor – acceptor bond) can be formed between H₂S (donor) and Zn²⁺ (acceptor). The reaction (2) is suggested because the ZnX could not completely regenerated by heating in vacuum as seen in Figure 9. However, more analysis works should be conducted to completely confirm this mechanism.

In order to test for the possibility of H₂S removal from the natural gas, the utilization of methane - ethane mixture (85:15 v/v), which is almost similar to the composition of Vietnam natural gas, as balance gas replacing for N₂ was also tested for the sample ZnX -0.1M. For total flowrate of 3 L/hour and H₂S concentration of 100 ppm, the methane-ethane at flow rate of 2.7 L/hour was mixed with 1000 ppm H₂S/N₂ stream at flowrate of 0.3 L/hour. It can be seen from Figure 9 that only small decrease in the H₂S adsorption capacity was observed. This test indicated that the presence of CH₄ and C₂H₆ in the natural gas does not influence significantly the H₂S adsorption ability of the Zn²⁺ - exchanged zeolite X.

Conclusions

The preparation, characterization and H₂S adsorption activity of the ion-exchanged zeolite X have been investigated in this study. Zn²⁺, Cu²⁺ and Co²⁺ ion-exchanged zeolites enhanced the H₂S adsorption capacity of the zeolite X. In particular, ZnX shows the greatest performance in H₂S adsorption among the tested samples. The FAU structure of the materials was obviously confirmed by the XRD analysis in the all samples except the sample CuX. The content of Zn in the zeolite played an important role in promotion of the H₂S adsorption. XRD patterns of these samples indicated that higher concentrations of the cation made more changes in the FAU crystalline cell. According to adsorption result, the highest H₂S adsorption capacity was obtained on the sample ZnX which was ion-exchanged with the 0.1M Zn²⁺ solution. The results of the regeneration test indicated that a part of the adsorbent cannot be regenerated by heating in vacuum condition. Moreover, the presence of model natural gas (CH₄/C₂H₆ mixture) has not significantly influenced the H₂S adsorption activity of the Zn²⁺ - exchanged zeolite X.

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