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# Hg<sup>0</sup> removal from flue gas over different zeolites modified by FeCl<sub>3</sub>

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## ABSTRACT

The elemental mercury removal abilities of three different zeolites (NaA, NaX, HZSM-5) impregnated with iron(III) chloride were studied on a lab-scale fixed-bed reactor. X-ray diffraction, nitrogen adsorption porosimetry, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and temperature programmed desorption (TPD) analyses were used to investigate the physicochemical properties. Results indicated that the pore structure and active chloride species on the surface of the samples are the key factors for physisorption and oxidation of Hg<sup>0</sup>, respectively. Relatively high surface area and micropore volume are beneficial to efficient mercury adsorption. The active Cl species generated on the surface of the samples were effective oxidants able to convert elemental mercury (Hg<sup>0</sup>) into oxidized mercury (Hg<sup>2+</sup>). The crystallization of NaCl due to the ion exchange effect during the impregnation of NaA and NaX reduced the number of active Cl species on the surface, and restricted the physisorption of Hgº. Therefore, the Hgº removal efficiencies of the samples were inhibited. The TPD analysis revealed that the species of mercury on the surface of FeCl<sub>3</sub>-HZSM-5 was mainly in the form of mercuric chloride (HgCl<sub>2</sub>), while on FeCl<sub>3</sub>-NaX and FeCl<sub>3</sub>-NaA it was mainly mercuric oxide (HgO).

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#### Introduction

Mercury is one of the most toxic heavy metal elements in the environment. It is a priority toxic pollutant because of its high volatility, long persistence, and strong bioaccumulative properties (Presto and Granite, 2006; Brown et al., 1999; Dastoor and Laroque, 2004).

According to reports by US Environmental Protection Agency (EPA), coal combustion is one of the major anthropogenic mercury emission sources. Thus, researchers have explored various technologies for the control of mercury emissions from coal combustion flue gas (Reddy et al., 2012).

Elemental mercury  $(Hg^0)$ , oxidized mercury  $(Hg^{2+})$ , and particulate-bound mercury (Hg<sub>p</sub>) are the main forms of mercury in coal combustion flue gas (Reddy et al., 2012).  ${\rm Hg}^{2+}{\rm is}$  soluble in water, so it can be removed by wet flue gas desulfurization systems. Most Hg<sub>p</sub> can be removed by electrostatic precipitators or fabric filters. However, the majority of Hg<sup>0</sup> cannot be removed by existing pollution control devices because of its low solubility in water and high volatility. Thus, the removal of Hg<sup>0</sup> is the most important and difficult work in flue gas mercury control (Granite et al., 2006; Wang et al., 2010; Cao et al., 2008; Pavlish et al., 2003).

Among the technologies under investigation, activated carbon (AC) injection has been employed in coal-fired power plants as the most feasible technology so far. Nevertheless, the application of this technology is limited due to its high operation cost. In addition, the high carbon/mercury weight ratio may restrict the utilization of fly ash (Feeley et al., 2004). Therefore,

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new technologies that are efficient and cost-effective still need more exploration.

Noncarbon materials or mineral oxides modified with various active additives would be economically viable alternatives for removal of mercury from flue gas, as they do not impact fly ash recycling (Lee et al., 2006). Among these materials, zeolites are widely used as drying agents and adsorbents in adsorption and separation processes, because of their adsorption ability and ion-exchange properties (Kesraouiouki et al., 1994). It has been proved that zeolites have distinctive framework structures. As a result, they show high selectivity in adsorption and catalytic processes. As shown in previous works, natural zeolites treated by different methods show considerable  $Hg^0$  adsorption performance with simulated flue gas (Morency et al., 2000; Morency, 2002; Eswaran et al., 2007). Silver-modified zeolite NaA can be used to remove the residual mercury from natural gases, and is regenerable and stable for long term operation (Yan, 1994). Zeolite HZSM-5, with higher mechanical strength and chemical and thermal stability, was modified by CeO<sub>2</sub> and CuO to efficiently oxidize and remove  $\mathrm{Hg}^{\mathrm{0}}$  from simulated coal-fired flue gas (Fan et al., 2012a, b). In this study, zeolites NaA, NaX and HZSM-5 were chosen and compared as parent materials.

Various additives, such as sulfur, sulfide, transition metal oxides and halides, have been added to adsorbents to enhance their mercury removal ability in previous works (Xu et al., 2013). Among the transition metal halides, FeCl<sub>3</sub> has been applied to modify various kinds of noncarbon materials, resulting in high Hg removal efficiencies close to those of CuCl<sub>2</sub> and CuBr<sub>2</sub>. Impregnated Cl as an active element can greatly strengthen the Hg oxidation ability (Shen et al., 2010; Tao et al., 2012), especially when HCl is absent from the flue gases. In addition, FeCl<sub>3</sub> is cheap and easy to obtain, reducing the cost of materials.

In this study, we chose FeCl<sub>3</sub> as the additive to modify three different zeolites (NaA, NaX and HZSM-5). The  $Hg^0$  removal efficiencies of modified zeolites from simulated flue gas were evaluated in a lab-scale fixed-bed device. XRD, nitrogen adsorption porosimetry, FT-IR, XPS, and TPD analyses were used to investigate the physicochemical properties. On the basis of the characterization results, the reasons for the differences in  $Hg^0$  removal efficiencies were discussed.

#### 1. Materials and methods

#### 1.1. Sample preparation

Commercially available Na-A, Na-X (purchased from Sinopharm Chemical Reagent Co., LTD.) and HZSM-5 (with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 150, purchased from Nanjing Jcnano Tech Co., Ltd., China) zeolites were modified with iron chloride aqueous solution by a method of impregnation, in proportions corresponding to different loading values ( $\rho$ , where  $\rho$  is the mass ratio of Fe/zeolite). After stirring for 3 hr at room temperature, the mixtures were placed into a rotary evaporator to be dried quickly, and then dried at 120°C for 12 hr. The derived samples were crushed and sieved to 60–80 mesh particles for Hg<sup>0</sup> removal testing.

#### 1.2. Removal efficiency measurement

As shown in the diagrammatic sketch in Fig. 1, the experimental device consisted of a simulated flue gas system, a fixed bed system, and an  $Hg^0$  analyzer system. A constant quantity of  $Hg^0$  vapor was supplied into the gas-mixing tank by passing a branch of  $N_2$  flow (300 mL/min) through a  $Hg^0$  permeation tube, which was immersed in a water bath maintained at 50°C.  $N_2$  was used as a balance gas to control the total gas flow at 1 L/min in each experiment, corresponding to a space velocity of about 700,000 hr<sup>-1</sup>. Other gas components could be introduced into the gas stream when necessary. The initial  $Hg^0$  concentration in this system was kept at 40.7 ± 0.3 µg/m<sup>3</sup>. A separate branch of  $N_2$  gas was used as purge flow to pretreat the samples at the experimental temperature for 1 hr. The outlet  $N_2$  was introduced into the Hg<sup>0</sup> analyzer to confirm and adjust the baseline. Two four-way valves were used to switch between different branches of gas flows, which were introduced into the reactor or the Hg<sup>0</sup> analyzer.

A quartz tube (custom made, Beijing, China) with an inner diameter of 4 mm was used as a fixed-bed reactor. 50 mg of the samples was supported on a quartz fiber filter at the center of the tube. The reactor was heated by a temperature-controlled tubular furnace (Tianjin Weiye Science apparatus Limited Co., Tianjin, China) and maintained at 120°C in each experiment, with a thermocouple placed beside the external wall of the quartz tube. The Hg<sup>0</sup> concentrations at inlet and outlet of the fixed-bed reactor were measured in real time with an Hg<sup>0</sup> analyzer (RA-915M, Lumex, Russia). The Hg<sup>0</sup> removal efficiency  $\eta$  (%) was defined by the following equation:

$$\eta = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \times 100\% \tag{1}$$

where,  $C_{\text{inlet}}$  (µg/m<sup>3</sup>) and  $C_{\text{outlet}}$  (µg/m<sup>3</sup>) represent Hg<sup>0</sup> concentrations at the inlet and outlet of the reactor, correspondingly.

#### 1.3. Analytical methods

The nitrogen adsorption-desorption isotherms were determined at -196°C on an automatic porosity analyzer (Autosorb-iQ, Quantachrome, USA). The specific area was calculated with the BET method, and the pore size distribution was calculated on the basis of the N<sub>2</sub> adsorption isotherm using the NLDFT method. X-ray diffraction (XRD) measurement was carried out on an X-ray diffractometer (X'Pert PRO MPD, PANalytical, Netherlands) with Cu K $\alpha$  ( $\lambda$  = 0.15406 nm) radiation to determine the crystal structures of the samples. Fourier transform infrared spectroscopy (FT-IR) was obtained using the KBr pellet method on a Fourier transform instrument (Nicolet 6700, Thermo, USA). Samples were prepared by compressing a well-mixed sample powder with potassium bromide (KBr). And the scan range was 400-4000 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was carried out on an X-ray photoelectron spectrometer (ESCALab 250Xi, Thermo, USA) using Al K $\alpha$  radiation (hv = 1486.8 eV). Binding energy was calibrated using adventitious carbon (284.8 eV). Before the temperature programmed desorption tests, the samples were first exposed to the simulated gas with 40.7  $\pm$  0.3  $\mu\text{g/m}^3$  Hg^0 for 8 hr at 120°C, and then purged with nitrogen at a flow rate of 1 L/min at 120°C until the Hg<sup>0</sup> concentration at the outlet of the reactor decreased to zero. For each test, the sample was heated from 120 to 720°C at a rate of 5°C/ min under a nitrogen atmosphere with a flow rate of 1 L/min. The outlet  $\mathrm{Hg}^{\mathrm{0}}$  concentrations were measured online by the  $\mathrm{Hg}^{\mathrm{0}}$ analyzer (RA-915M, Lumex, Russia) during the test.

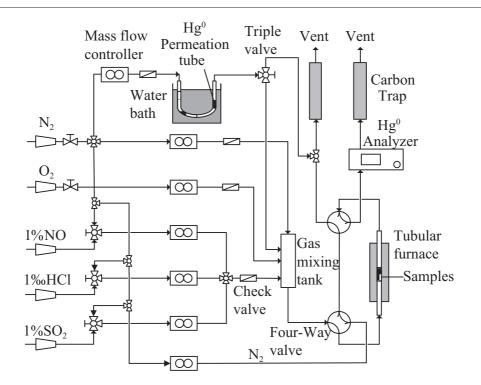


Fig. 1 - Diagrammatic sketch of the experimental devices.

# 2. Results and discussion

# 2.1. Removal of Hg<sup>0</sup> by modified zeolites

The  $Hg^0$  removal efficiencies of different samples were measured online under a nitrogen atmosphere at 120°C. As shown in Fig. 2, the 5% FeCl<sub>3</sub>-NaA sample exhibited a  $Hg^0$  removal

efficiency of only about 3%, which was close to zero considering the systematic error of the experimental devices. 5% FeCl<sub>3</sub>–NaX showed an initial efficiency of about 65%, and the efficiency decreased to 45% in 180 min. The efficiency of 5% FeCl<sub>3</sub>–HZSM-5 was initially over 98%, and still remained over 95% after 180 min. These three types of zeolites showed significantly different Hg<sup>0</sup> removal efficiencies after modification under the same conditions.

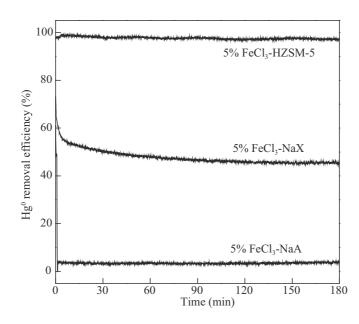


Fig. 2 –  $Hg^0$  removal efficiency of 5% FeCl<sub>3</sub> modified zeolites (NaA, NaX, HZSM-5). 5% FeCl<sub>3</sub> modified NaA, NaX, HZSM-5 are respectively defined as 5% FeCl<sub>3</sub>- NaA, 5% FeCl<sub>3</sub>- NaX and 5% FeCl<sub>3</sub>- HZSM-5 in all the figures in this article. Reaction conditions temperature of 120°C, sample mass of 50 mg, total flow rate of 1 L/min,  $Hg^0$  concentration of 40.7 ± 0.3  $\mu$ g/m<sup>3</sup>, N<sub>2</sub> as balance.

#### 2.2. Sample characteristics

The BET surface areas ( $S_{BET}$ ) and total volumes of parent and modified zeolites are summarized in Table 1. Among these three parent zeolites, NaX had the highest BET surface area of 632.9 m<sup>2</sup>/g and the largest total pore volume of 0.3988 cm<sup>3</sup>/g. Those of HZSM-5 were lower, 405.3 m<sup>2</sup>/g and 0.2314 cm<sup>3</sup>/g, respectively. However, they all decreased after being modified by FeCl<sub>3</sub>. The BET surface area of NaX sharply reduced to 149.8 m<sup>2</sup>/g and total pore volume of 0.2314 cm<sup>3</sup>/g after being modified. As a result, the values for 5% FeCl<sub>3</sub>–HZSM-5 were the largest among the modified zeolites, only being reduced to 358.9 m<sup>2</sup>/g and 0.2263 cm<sup>3</sup>/g. Nevertheless, those of NaA were the smallest. Its BET surface area increased from 24.45 to 44.63 m<sup>2</sup>/g after modification, but the total pore volume decreased slightly.

The pore size distribution profiles calculated using the NLDFT method are displayed in Fig. 3. It could be observed that HZSM-5 had significant pore size distribution peaks at 3.2 nm and smaller than 1 nm before and after modification. The peak at 3.2 nm decreased slightly after modification, which was consistent with the reduction in BET surface area and pore volume. The fresh NaX had an obvious micropore distribution at 1.3 nm and below 1 nm. These micropores almost disappeared after modification; however, the mesopore peaks increased. This led to the sharp decrease in the BET surface area and pore volume of NaX. As for NaA, the pore distribution peak at about 4 nm slightly increased, which resulted in the increase of its BET surface area. It can be concluded from the results that the micropores of NaX were blocked after modification with FeCl<sub>3</sub>, and the textural properties of HZSM-5 barely changed. The significant differences in the BET surface areas and pore size distribution among modified zeolites contributed to their different Hg<sup>0</sup> removal efficiencies.

The XRD analysis results of parent and modified zeolites are shown in Fig. 4. The specific peaks of each zeolite before and after modification were detected at the same positions, but their intensities decreased markedly after modification. No diffraction peaks of FeOx or FeCl<sub>3</sub> were detected for any of the three modified samples. However, peaks attributed to crystalline NaCl at the marked positions were clearly observed for the modified NaA and NaX. This indicated that NaCl crystals were formed, which was due to the ion exchange of Fe<sup>3+</sup> in the solution with Na<sup>+</sup> in the zeolite during the modification processes. This effect may cause the blocking of the internal porosity of zeolites, resulting in the sharp decrease of the BET surface area of modified NaX. As for NaA, which has a small surface area, the emergence of NaCl

Table 1 – Specific surface area and volume of the samples.							
Samples	BET surface area (m²/g)	Total pore volume (cm <sup>3</sup> /g)					
NaA	24.45	0.1218					
5% FeCl <sub>3</sub> –NaA	44.63	0.1184					
NaX	632.9	0.3988					
5% FeCl <sub>3</sub> –NaX	149.8	0.2404					
HZSM-5	405.3	0.2314					
5% FeCl <sub>3</sub> –HZSM-5	358.9	0.2263					

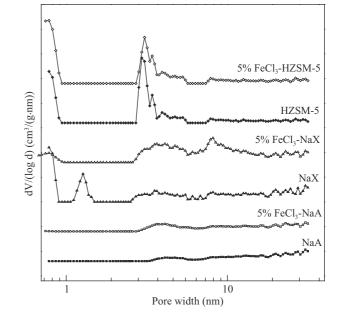
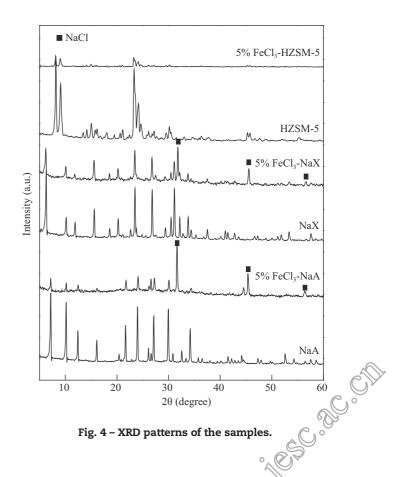


Fig. 3 – Pore size distribution of the samples calculated with NLDFT method.

crystals improved the surface area due to their small particle size. But for HZSM-5, the cation in the structure is  $H^+$ , so that no NaCl was crystallized to block the pores in the zeolite.

The FT-IR spectra of different samples, recorded at 25°C, are shown in Fig. 5. These spectra each agree with those



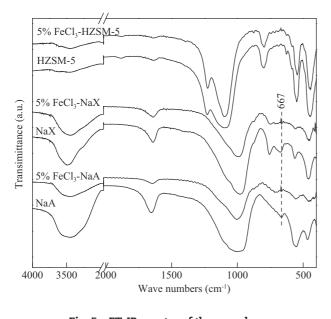


Fig. 5 - FT-IR spectra of the samples.

reported previously for the same zeolite. The broad bands in the region 3700–3000  $\rm cm^{-1}$  are due to the OH groups of zeolites (Förster, 1992; Trombetta et al., 2000), and they were barely changed after modification. These bands for HZSM-5 were much weaker than those of NaA and NaX. This indicates that the OH groups of the zeolites may be not the active sites for Hg<sup>0</sup> removal on HZSM-5. The bands in the region 1,300–400  $\text{cm}^{-1}$  are associated with the oscillation of the zeolite framework (Förster, 1992). For NaA, the characteristic bands are at 1001, 667, 555 and 462 cm<sup>-1</sup>, and for HZSM-5, they are at 1226, 1100, 624, 798, 547 and 453 cm<sup>-1</sup>. The bands in this region of NaA and NaX are clearly changed after modification, especially the band at around 667 cm<sup>-1</sup>, which almost disappeared in the spectra of these two samples after modification. This means that Fe<sup>3+</sup> interacts with the zeolite framework of NaA and NaX after modification, due to the ion exchange effect or the entrance of Fe<sup>3+</sup> into the channels of NaA and NaX. As for HZSM-5, the bands in this region are little changed. We can conclude that the interaction between  $Fe^{3+}$  and the HZSM-5 framework is relatively weaker in the modified sample compared to the other zeolites. Thus, the ion exchange reaction did not occur noticeably during the preparation of FeCl<sub>3</sub>-HZSM-5 according to the FT-IR results. This means that Fe<sup>3+</sup> is mainly distributed on the surface of the HZSM-5 crystal, so that it can more easily participate in the oxidation and capture processes of Hg<sup>0</sup>.

The  $Hg^0$  TPD results of three modified zeolites are shown in Fig. 6. According to the thermal decomposition curves of pure mercury compounds obtained in the previous studies, the mercury species in the samples can be inferred from their thermal decomposition temperature (Lopez-Anton et al., 2010). Though the thermal decomposition temperature of mercury compounds varies on different matrixes, the order of Hg desorption temperatures is always  $HgCl_2 < HgO$  (Lopez-Anton et al., 2010, 2011; Wu et al., 2011). According to the previous report (Wu et al., 2011; Uddin et al., 2009), and considering the elements existing in the samples, the mercury compounds formed on different materials in the

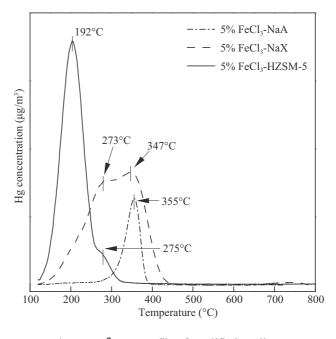


Fig. 6 – Hg<sup>0</sup>-TPD profile of modified zeolites.

presence of Cl should mainly be HgCl<sub>2</sub>. Thus, it could be concluded that the desorption peaks at 192°C in this experiment could possibly correspond to HgCl<sub>2</sub>, and the peaks at 347 and 355°C might correspond to HgO. The small peaks at 273 and 275°C possibly corresponded to the desorption peaks of HgO as well. It could be inferred that the adsorption products of Hg<sup>0</sup> on 5% FeCl<sub>3</sub>–NaA were mainly HgO. A majority of Hg compounds on 5% FeCl<sub>3</sub>–NaX were HgO, and a very small portion of HgCl<sub>2</sub> was also observed. For 5% FeCl<sub>3</sub>–HZSM-5, the mercury compounds formed on the sample were mainly HgCl<sub>2</sub>, and the remaining portion was HgO.

This result suggested that the active component for  $Hg^0$  oxidation and removal in 5% FeCl<sub>3</sub>–HZSM-5 was mainly chlorine. Nevertheless, chlorine in 5% FeCl<sub>3</sub>–NaA and 5% FeCl<sub>3</sub>–NaX could not promote the removal of  $Hg^0$  since it was mostly in the form of crystalline NaCl. The oxygenic functional groups such as hydroxyl at the surface of 5% FeCl<sub>3</sub>–NaA and 5% FeCl<sub>3</sub>–NaX may be the main active oxidant that oxidized  $Hg^0$  to HgO. Moreover, a small portion of Fe<sub>2</sub>O<sub>3</sub> might be generated by hydrolysis of FeCl<sub>3</sub> during preparation, which could serve as a mercury oxidant in flue gas in accordance with the literature (Bhardwaj et al., 2009; Worathanakul et al., 2008). The reactions could be hypothesized as follows:

$$Hg^0 + zeolite surface \rightarrow Hg^0(ad)$$
 (2)

$$Hg^{0}(ad) + surface-O \rightarrow surface-O-Hg$$
 (3)

$$Hg^{0}(ad) + Fe_{2}O_{3} \rightarrow 2FeO + HgO(ad)$$
 (4)

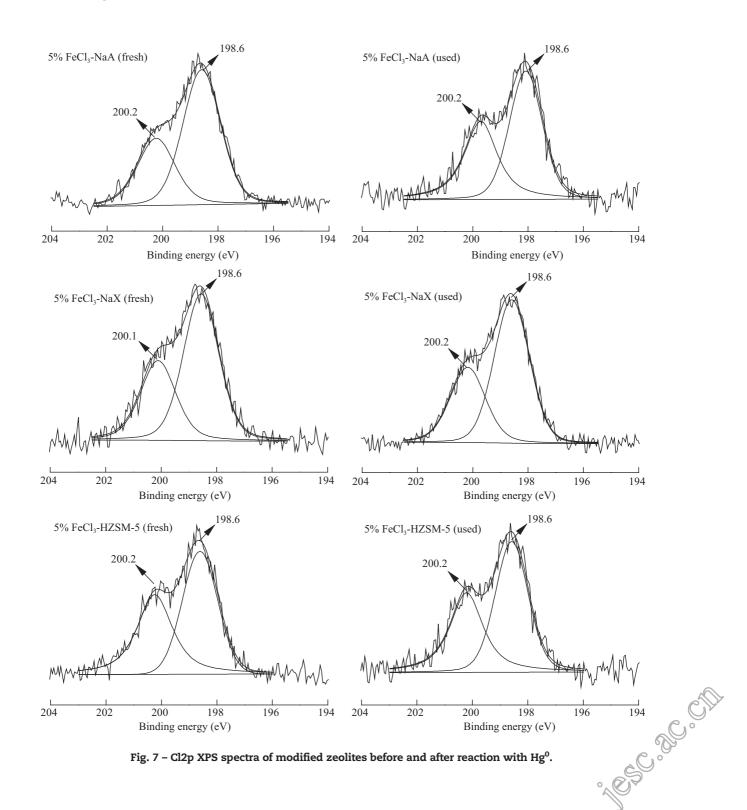
As  $Hg^{2+}$  in the gas was not analyzed in the experiment, the  $Hg^0$  desorption amount on different zeolites could not be quantitatively compared accurately.

An XPS analysis was employed to determine the surface species on the modified zeolites before and after reaction with Hg<sup>0</sup>. Fig. 7 shows the XPS spectra for the Cl 2p region on the samples. The peak at about 200.2 eV was assigned to adsorbed

active Cl species with less ionic charge, and 198.6 eV assigned to ionic Cl<sup>-</sup> moieties, respectively (Kautek and Gordon, 1990). It can be inferred that a portion of Cl in FeCl<sub>3</sub> was transformed after combining with the zeolite. The ratio of the spectral area with respect to active Cl and ionic Cl<sup>-</sup> was about 0.87 for the fresh sample of 5% FeCl<sub>3</sub>-HZSM-5, and this ratio decreased to 0.77 for the used sample of 5% FeCl<sub>3</sub>-HZSM-5 after reaction with Hg<sup>0</sup>. But this ratio for 5% FeCl<sub>3</sub>-NaA decreased slightly from 0.53 to 0.50 after reaction, and from 0.57 to 0.56 for 5% FeCl<sub>3</sub>-NaX. This phenomenon indicated that some of the active Cl species on the surface of 5% FeCl<sub>3</sub>–HZSM-5 were transformed to ionic Cl<sup>-</sup> by reacting with  $Hg^0$  in the experimental process, and possibly formed  $HgCl_2$ , which could be observed in the TPD process in Fig. 6. The oxidation reaction mechanism can be described as follows, which is based on the Mars–Maessen mechanism:

$$Hg^0 + zeolite surface \rightarrow Hg^0(ad)$$
 (2)

$$Cl^* + Hg^0(ad) \rightarrow HgCl$$
 (5)



(6)

 $HgCl + Cl^* \rightarrow HgCl_2$ 

However, this oxidation reaction of  $Hg^0$  by active Cl species was not observed for 5% FeCl<sub>3</sub>–NaA and 5% FeCl<sub>3</sub>–NaX during the  $Hg^0$  removal process, and the  $Hg^0$  was oxidized mainly by the oxygenic functional groups on the surface and Fe<sub>2</sub>O<sub>3</sub>. Thus, the difference in  $Hg^0$  oxidation abilities of the active Cl species on the surfaces of the modified zeolites was the major factor causing the different  $Hg^0$  removal efficiencies.

#### 2.3. Effect of FeCl<sub>3</sub> loading value

The effect of FeCl<sub>3</sub> loading value on the  $Hg^0$  removal efficiency of FeCl<sub>3</sub>–HZSM-5 is exhibited in Fig. 8. The  $Hg^0$  removal ability of FeCl<sub>3</sub>–HZSM-5 clearly improved when the loading value of FeCl<sub>3</sub> increased from 1% to 3%. However, when the FeCl<sub>3</sub> loading value exceeded 3%, the  $Hg^0$  removal efficiencies of the samples reached a plateau above 95% and showed little change within the testing time. Therefore, taking economic considerations into account, the proper FeCl<sub>3</sub> loading value is 3% when applied for the removal of  $Hg^0$  from industry coal combustion flue gas.

# 3. Conclusions

Different FeCl<sub>3</sub>-modified zeolites showed significant differences in their Hg<sup>0</sup> removal abilities. FeCl<sub>3</sub>–HZSM-5 showed excellent Hg<sup>0</sup> removal efficiency as a result of its relatively higher BET surface area, and the high Hg<sup>0</sup> oxidation activity of Cl species on the surface of the sample. FeCl<sub>3</sub>–NaX showed a relatively lower Hg<sup>0</sup> removal efficiency, mainly because of the ion exchange effect during the impregnation process of the sample. The exchanged Na<sup>+</sup> and aqueous Cl<sup>-</sup> crystallized into NaCl crystals when the sample was dried, which is not an effective Hg<sup>0</sup> oxidant. The NaCl crystals blocked the micropores in the structure and reduced the BET surface area of the sample, which restricted the physisorption of Hg<sup>0</sup>. The Hg<sup>0</sup> removal efficiency of FeCl<sub>3</sub>–NaA was the lowest among the three samples for reasons similar to that of FeCl<sub>3</sub>–NaX as well as its low surface area. The XPS analysis results indicated that the adsorbed active Cl species on the surface of FeCl<sub>3</sub>–HZSM-5 were consumed during the reaction with Hg<sup>0</sup>. The TPD results revealed that the oxidation products of Hg<sup>0</sup> adsorbed on the surface of FeCl<sub>3</sub>–HZSM-5 were mainly HgCl<sub>2</sub>, and those on the surface of FeCl<sub>3</sub>–NaX and FeCl<sub>3</sub>–NaA were mainly HgO.

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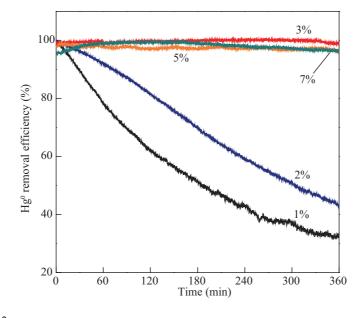


Fig. 8 – Hg<sup>0</sup> removal efficiency of modified HZSM-5 with different loading values of FeCl<sub>3</sub>.



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