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SPECIATION OF CHROMIUM COMPOUNDS FROM ZSM-5 INTO AN IONIC LIQUID

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The speciation of extracted chromium from ZSM-5 into an ionic liquid (IL) was studied using X-ray absorption near-edge structure (XANES) spectroscopy. The main adsorbed chromium species in ZSM-5 were Cr(VI)-HA (Cr(VI) chelated with humic acids (HAs)) (57%), $Cr(VI)_{ads}$ *(Cr(VI) adsorbed on ZSM-5) (33%), and Cr(III)-HA (Cr(III) chelated with HA) (10%). In this work, 1-butyl-3-methylimidazolium chloride (*$[C_4mim]Cl$*), was used as the IL to extract the chromium compounds from ZSM-5. Experimentally, approximately 75% of the chromium compounds were extracted within 30 min at 343 K. Combining the chromium extraction efficiency and component fitting results of the XANES spectra, almost all of Cr(VI)-HA was extracted into* $[C_4mim]Cl$*. Following extraction, 34.5% of the Cr(VI) compounds were reduced to form Cr(III)-HA and Cr(III) ions. The Cr-O bond distance of Cr compounds was 1.69 Å in* $[C_4mim]Cl$ *as shown by X-ray absorption fine structure (EXAFS) spectroscopy.* ^1H *nuclear magnetic resonance (NMR) showed that the reduction and extraction of Cr(VI) compounds were affected by* $[C_4mim]^+$*. The non-extractable chromium species in ZSM-5 were* $Cr(VI)_{ads}$ *(9%), Cr(III)-HA (10.8%), and* $Cr(III)_{ads}$ *(5.2%). The fraction of Cr(VI) was decreased greatly because of the use of* $[C_4mim]Cl$ *as the extractant.*

Keywords: *chromium, ZSM-5, ionic liquid, X-ray absorption fine structure, X-ray absorption near-edge structure.*

ВЫДЕЛЕНИЕ СОЕДИНЕНИЙ ХРОМА ИЗ ZSM-5 В ИОННУЮ ЖИДКОСТЬ

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С помощью рентгеновской абсорбционной спектроскопии XANES изучен вид хрома, извлеченного из ZSM-5 в ионную жидкость (ИЖ). Основные виды адсорбированного хрома в ZSM-5: Cr(VI)-HA(Cr(VI), хелатированный гуминовыми кислотами (HAs) 57%, $Cr(VI)_{ads}$ *(Cr(VI), адсорбированный из ZSM-5) 33% и Cr(III)-HA (Cr(III), хелатированный HA) 10%. Хлорид 1-бутил-3-метилимидазолия (*$[C_4mim]Cl$*) использован в качестве ИЖ для извлечения соединений хрома из ZSM-5. Экспериментальным путем извлечены ~75% соединений хрома в течение 30 мин при 343 K. Комбинированием эффективности извлечения хрома и результатов подгонки компонентов спектров XANES Cr(VI)-HA получен в* $[C_4mim]Cl$*. После экстракции 34.5% соединений Cr(VI) восстанавливаются с образованием ионов Cr(III)-HA и Cr(III). Согласно данным EXAFS, длина связи Cr-O в соединениях Cr 1.69 Å в* $[C_4mim]Cl$*. Результаты* ^1H *ЯМР-спектроскопии показывают, что на восстановление и экстракцию соединений Cr(VI) влияет* $[C_4mim]^+$*.* $Cr(VI)_{ads}$*(9%), Cr(III)-HA (10.8%) и* $Cr(III)_{ads}$ *(5.2%) являются неэкстрагируемыми частицами хрома в ZSM-5. При использовании* $[C_4mim]Cl$ *в качестве экстрагента доля Cr(VI) значительно снижается.*

Ключевые слова: *хром, ZSM-5, ионная жидкость, EXAFS, XANES.*

Introduction. Chromium-containing wastewater is produced and discharged from human activities such as metallurgy, electroplating, leather tanning, and wood preserving [1–3]. Therefore, chromium compounds may be released into the environment and cause pollution. A stable oxidation state of chromium in the natural environment is hexavalent chromium Cr(VI), which is genetically toxic to cells [4–6]. It has been verified that Cr(VI) compounds may be harmful to the respiratory system, immune system, liver, and kidneys [7]. Moreover, the risk of cancers that are induced in bone, the prostate, and the stomach are also increased by exposure to Cr(VI) compounds [7].

In soil, Cr(VI) compounds are mobile and do not adsorb well in soil [8, 9]. However, Cr(VI) can chelate with humic acid (Cr(VI)-HA) [10], which allows it to be adsorbed by soil and biochars. The biochar can remove Cr(VI) ions from water in acidic conditions but the lowest desorption of Cr(VI) from biochars was obtained by concentrated HCl and HNO_3 [11]. Therefore, technologies can be developed to use these characteristics for soil remediation, such as removing chromium pollutants from soil. Soil contains natural zeolites that are hydrated aluminosilicate minerals. At neutral pH, CrO_4^{2-} can adsorb on the zeolite because the size of the molecule matches the pore size of the zeolite [12]. ZSM-5, a microporous zeolite comprising SiO_4 and AlO_4, forms a three-dimensional structure with a 0.55-nm pore opening. ZSM-5 has high thermal and hydrothermal stabilities, uniform pore size, and Brönsted acidity properties. In this study, Cr(VI) ionic species adsorbed in the micropores of soil are simulated by adsorbed humic acid (HA) on ZSM-5.

Because of special physical and chemical properties, ionic liquids (ILs) can be applied in electrochemistry, separations, and catalysis because of their low vapor pressure, high thermal stability, non-flammability, and high viscosity [13, 14]. Here, HA is extracted with ILs, and an interaction between the IL and HA is also observed. Hydrophilic and hydrophobic ILs allow selective extraction of metal ions in aqueous solutions [15, 16]. Moreover, metals in pores, which simulate contaminated soil, can also be extracted with ILs [10, 17, 18]. In previous work, we found that the extraction efficiency of Cr(VI) chelated with HA was higher than that of Cr(III) chelated with HA by the IL [10]. Therefore, ILs are used here as the extracting solution for the separation process.

The distance between a center atom and its ligand(s) and the coordination number can be determined by the EXAFS (extended X-ray absorption fine structure) spectrum and the XANES (X-ray absorption near edge structure) spectrum reflects the state of electron orbitals in the center atom. Furthermore, X-ray absorption data reveal the speciation of contaminants. Thus, the main objective of this work is to study the speciation of chromium adsorbed on ZSM-5 and extracted into 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) using EXAFS and XANES spectroscopies.

Experimental. The simulated soil mixture contained 2 g of ZSM-5, 1.5 g of HA (humic acid sodium salt, Sigma-Aldrich), and 50 mL of deionized water. The mixture was then stirred for 24 h and dried at 343 K to remove the H_2O. The created solid will be referred to as HA-ZSM-5. The simulated chromium-contaminated soil, Cr(VI) adsorbed on HA-ZSM-5, was prepared by mixing 30 mL of 0.03 M $K_2Cr_2O_7$ (99%, Showa) and 3.5 g of HA-ZSM-5 at 298 K for 1.5 h. The slurry was then filtered with 10-μm filter paper. The solid sample was dried at 343 K. The Cr(III)-HA samples for X-ray absorption spectroscopic (XAS) studies were also similarly prepared, with $CrCl_3 \cdot 6H_2O$ (93%, Showa) being used as the Cr(III) species.

A detailed procedure for the preparation of the IL ([C_4mim]Cl) has been described previously [18]. Approximately 0.4 g of Cr(VI)/HA-ZSM-5 was extracted using 1.5 g of [C_4mim]Cl in a 10-mL glass bottle stirred at 343 K for 30 min. After extraction, the solid was leached with H_2O to remove the [C_4mim]Cl. The solids were then digested to determine the extraction efficiency of chromium from ZSM-5 to [C_4mim]Cl. The concentrations of chromium in the digested solutions were measured using an atomic absorption spectrometer (Hitachi Z-5000). After extraction, the leached [C_4mim]Cl with H_2O was dried at 373 K to remove the H_2O.

The Cr *K*-edge XAS spectra of chromium samples before and after extraction with [C_4mim]Cl were recorded on the Wiggler beam line (16A1) at the Taiwan National Synchrotron Radiation Research Center. The electron storage ring was operated at an energy of 1.5 GeV and a current of 300 mA. A chromium foil absorption edge at 5989 eV was used to calibrate the photon energy. The fluorescence mode with a Lytle detector was used to measure the Cr K-edge absorption spectra. The XANES spectra of chromium model compounds such as $CrCl_3 \cdot 6H_2O$, K_2CrO_7, $Cr(NO_3)_3$, $Cr(OH)_3$, Na_2CrO_4, Cr_2O_3, CrO_3, Cr(VI)-HA, Cr(III)-HA, $Cr(VI)_{ads}$ (by impregnation of K_2CrO_7 (3 wt%) on ZSM-5), $Cr(VI)_{ads}$ (by impregnation of $CrCl_3 \cdot 6H_2O$ (3 wt%) on ZSM-5), Cr(VI) ion (prepared by dissolution of 0.5 g K_2CrO_7 in 50 mL H_2O), Cr(III) ion (prepared by dissolution of 0.5 g $CrCl_3 \cdot 6H_2O$ in 50 mL H_2O) and Cr foil were also measured.

The EXAFS data were analyzed using UWXAFS 3.0 and FEFF 8.0 simulation programs [19–22]. The normalization of edge jump of isolated EXAFS data was processed and then the data was converted to a wavenumber scale. To diminish the residual and Debye–Waller factors of analysis, a Fourier transform was performed on k^3-weighted EXAFS oscillations in the range of 25±5 to 120±5 nm^{-1}.

^{1}H NMR shifts of the IL samples were determined on a Bruker Advance 300 spectrometer with tetramethyl silane (TSM) as an internal standard (acquisition time is 1.373 s, actual pulse repetition time is 2 s, number of scans is 32, and excitation pulse angle is 30°).

Results and discussion. The chromium species in ZSM-5 prior to and after extraction was obtained by XANES and EXAFS. The chemical changes of chromium compounds during extraction were also revealed at the molecular scale. In the pre-edge of XANES spectra, the intensity of 3*d*-elements with T_d symmetry is larger than those with O_h symmetry (Fig. 1). Because of the p component in *d*-*p* hybridized orbital, the intense pre-edge peaks for tetrahedral compounds of 3*d*-transition metals appear. The height of the pre-edge peak depends on the number of *d*-electrons in tetrahedral compounds [23, 24]. The pre-edge peak at 5993.5 eV in the XANES spectra demonstrates the existence of Cr(VI), Cr(V) or Cr(IV) in the ZSM-5 and [C$_4$mim]Cl (Fig. 1). The Cr(VI) compound is a stable species found in the environment. Therefore, the chromium compound in ZSM-5 and [C$_4$mim]Cl may likely be a Cr(VI) species. The pre-edge peak is barely observed in the octahedral structure of Cr(III) [24].

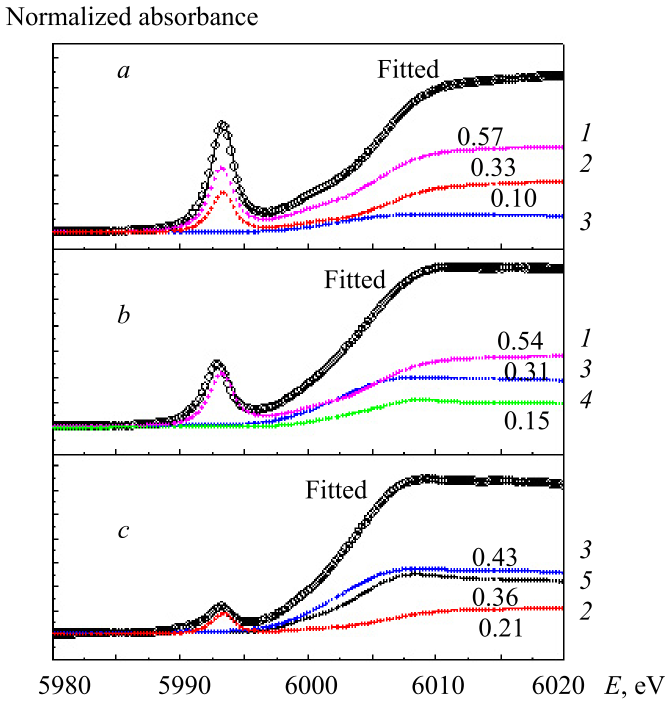

Fig. 1. The least-squares fitted XANES spectra of chromium compounds (Cr(VI)-HA (1), Cr(VI)$_{ads}$ (2), Cr(III)-HA (3), Cr(III) ion (4), Cr(III)$_{ads}$ (5)): (a) adsorbed in ZSM-5, (b) extracted in [C$_4$mim]Cl, and (c) remains in ZSM-5 (not extractable).

Figure 1a shows that Cr(VI) compounds can migrate into the channels of ZSM-5 and then be adsorbed onto ZSM-5. Moreover, the reduction of Cr(VI) by HA to form Cr(III)-HA was found. Figure 1a shows that the main species in ZSM-5 were Cr(VI)-HA (57%), Cr(VI)$_{ads}$ (33%), and Cr(III)-HA (10%). This demonstrates that Cr(VI) compounds can be adsorbed on ZSM-5.

Approximately 75% of the chromium compounds from the sorbent (ZSM-5) were extracted into [C$_4$mim]Cl at 343 K within 30 min. After extraction, the main species in [C$_4$mim]Cl were Cr(VI)-HA (54%), Cr(III)-HA (31%), and Cr(III) ions (15%) (Fig. 1b). Experimentally, the extraction efficiency of the Cr(III)-HA and Cr(III) ions into [C$_4$mim]Cl was less than 1%. Therefore, the Cr(VI) compounds were the main extracts from ZSM-5 into [C$_4$mim]Cl. To obtain the interaction of the extracted compounds and [C$_4$mim]Cl, the ^{1}H NMR spectra of [C$_4$mim]$^{+}$ were determined prior to and after extraction, as shown in Fig. 2. The ^{1}H NMR features of [C$_4$mim]$^{+}$ at 0.81, 1.17, 1.72, 3.89, 8.02, and 9.86 ppm were broadened, which suggests interactions between the chromium compounds and the imidazole ring of [C$_4$mim]$^{+}$ during extraction.

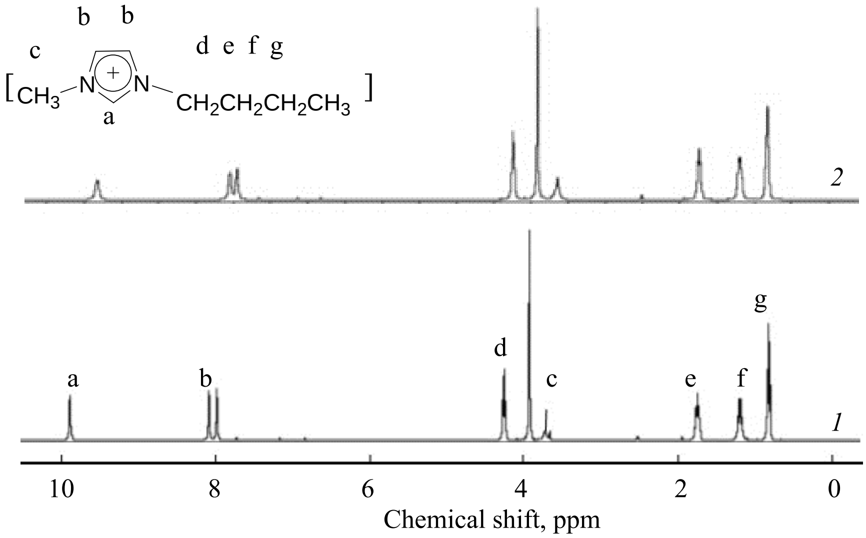

Fig. 2. ^{1}H NMR spectra of the IL ([C_4mim]Cl) prior to (1) and after (2) extraction.

Combining the chromium extraction efficiency and fitting the results from the XANES spectra, the percentages of chromium species in ZSM-5 and [C_4mim]Cl prior to and after extraction are shown in Table 1. Approximately 75% of the Cr(VI) compounds were extracted, and then, 34.5% of the Cr(VI) compounds underwent enhanced reduction to form Cr(III)-HA and Cr(III) ions. We also found that the main Cr(VI) compound was Cr(VI)$_{\text{ads}}$ in ZSM-5 after extraction. Therefore, [C_4mim]Cl has the selectivity to extract most of the Cr(VI)-HA. Furthermore, the enhanced reduction of Cr(VI) occurred in the presence of [C_4mim]Cl. After extraction, the Cr(VI)/Cr(III) ratios were 1.17 and 0.56 in [C_4mim]Cl and ZSM-5, respectively.

TABLE 1. Percentages of Chromium Compounds in ZSM-5 and [C_4mim]Cl During Extraction

Compounds	Prior to extraction	After extraction	
	in ZSM-5	in [C_4mim]Cl	in ZSM-5 (not extractable)
Cr(VI)-HA, %	57	40.5	–
Cr(VI)$_{\text{ads}}$, %	33	–	9
Cr(III)-HA, %	10	23.3	10.8
Cr(III)$_{\text{ads}}$, %	–	–	5.2
Cr(III) ion, %	–	11.2	–
Cr(VI)/Cr(III)	9	1.17	0.56

TABLE 2. Speciation Parameters of Chromium Compounds Adsorbed in ZSM-5 and Extracted in [C_4mim]Cl

Condition	First shell	Bond distance, Å	Coordination number	σ^2, Å^2
Prior to extraction	Cr-O	1.61	2.0	0.001
After extraction				
in [C_4mim]Cl	Cr-O	1.69	1.4	0.001
in ZSM-5 (not extractable)	Cr-O	1.98	3.4	0.001

Note. $\Delta\sigma^2$: Debye-Waller factors.

Table 2 shows the EXAFS data of chromium in ZSM-5 and [C_4mim]Cl. The Fourier transform converted the EXAFS spectra so that the coordination numbers (CNs) and bond distances could be determined. The Cr(VI) compounds in ZSM-5 had a Cr-O bond distance of 1.61 Å with a CN of 2.0. After extraction, Cr(VI)-HA, Cr(III)-HA, and Cr(III) ions were found in the [C_4mim]Cl. The ratio of Cr(VI)/Cr(III) was 1.17, and the Cr-O bond distance of chromium compounds was 1.69 Å. The non-extractable chromium remaining in the ZSM-5 phase had bond distance of 1.98 Å. This suggests that the fraction of Cr(III) compounds is increased in ZSM-5.

Conclusions. Using FTIR spectroscopy, chromium adsorbed on humic acid and ZSM-5. The main chromium species in ZSM-5 were Cr(VI)-HA, Cr(VI)$_{ads}$ and Cr(III)-HA. Approximately 75% of chromium compounds were extracted into [C_4mim]Cl at 343 K within 30 min. After extraction, most of the Cr(VI) compounds that were extracted were then reduced to form Cr(III)-HA and Cr(III) ions in the [C_4mim]Cl. The ^{1}H NMR spectra show that an interaction between the chromium species and [C_4mim]$^+$ occurred. The enhanced reduction of Cr(VI) compounds with HA was affected by [C_4mim]$^+$. Furthermore, the Cr(VI)/Cr(III) ratios in [C_4mim]Cl and ZSM-5 were decreased after extraction. The EXAFS spectrum showed that the Cr-O bond distance in ZSM-5 was 1.61 Å with a coordination number of 2.0. Because of the increased fraction of Cr(III) in [C_4mim]Cl and ZSM-5 after extraction, the Cr-O bond distances were 1.69 and 1.98 Å in [C_4mim]Cl and ZSM-5, respectively.

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