Pyrolysis Treatment of Chromite Ore Processing Residue by Biomass: Cellulose Pyrolysis and Cr(VI) Reduction Behavior

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S Supporting Information

ABSTRACT: The pyrolysis treatment with biomass is a promising technology for the remediation of chromite-ore-processing residue (COPR). However, the mechanism of this process is still unclear. In this study, the behavior of pyrolysis reduction of Cr(VI) by cellulose, the main component of biomass, was elucidated. The results showed that the volatile fraction (VF) of cellulose, i.e. gas and tar, was responsible for Cr(VI) reduction. All organic compounds, as well as CO and H₂ in VF, potentially reduced Cr(VI). X-ray absorption near-edge structure (XANES) spectroscopy and extended X-ray absorption fine-structure (EXAFS) spectroscopy confirmed the reduction of Cr(VI) to Cr(III) and the formation of amorphous Cr₂O₃. The remnant Cr(VI) content in COPR can be reduced below the detection limit (2 mg/kg) by the reduction of COPR particle and extension of reaction time between VF and COPR. This study provided a deep insight on the co-pyrolysis of cellulose with Cr(VI) in COPR and an ideal approach by which to characterize and optimize the pyrolysis treatment for COPR by other organics.

INTRODUCTION

Chromite-ore-processing residue (COPR) is a byproduct of the chromite-ore high-temperature lime-based roasting process to isolate and extract Cr(VI). In this process, chromite ore is roasted at 1200 °C, oxidizing Cr(III) to Cr(VI), and then the Cr(VI) chemically combines with the soda ash to form sodium chromate. During the roasting process, lime acts as a mechanical separator, allowing oxygen to react with the chromite and sodium carbonate.¹ Due to the fact that the COPR contains a large amount of toxic Cr(VI), nonlime-based process had substituted the lime-based process in the developed countries, such as the United States, U.K. and Germany, etc.² However, lots of abandoned COPR deposit sites need to be remediated.^{1,3–6} In addition, compared to the nonlime process, the lime-based process also has advantages in the chromium recovery efficiency,¹ especially from chromite ore with high Al and Si content. Hence, the lime-based process, which is still used in Russia, China, India, Pakistan, etc.,² could not be totally abandoned worldwide and may exist for a long time. As a result, more attention should be paid to the remediation of the COPR.

For the treatment of COPR, reduction of the Cr(VI) to nontoxic Cr(III) is generally considered satisfactory.^{7,8} It is practicable that Cr(VI) was extracted from COPR into aqueous solution and reduced into Cr(III) by reductants, such as Fe (II), sulfide, and calcium polysulfide.^{9,10} However, in this

process, the ineffective release of Cr(VI) into the solution from the solid subsequently delays the reduction.^{11,12} In addition, the oxidation of the reductants by air caused the ineffectiveness in Cr(VI) reduction due to the hyperalkaline condition caused by COPR.¹³ Thus, the process usually requires a long curing time (up to a few months).¹⁴

In previous research, a new technology for treatment of COPR was investigated.^{15,16} In this process, COPR was initially mixed with rice straw and subsequently pyrolyzed at low temperatures. The Cr(VI) in COPR could be reduced into Cr(III) in less than 10 min of reaction time combined with low energy consumption of 43 kg of standard coal per ton of COPR.¹⁶ The pilot-scale experiment with 20 t of COPR per day (shown in Note S1 of the Supporting Information) indicated that the treatment cost is less than 30 USD per ton of COPR. In addition, the dry process reduced the volume of the treated material, and the pyrolysis product of the biomass (i.e., the char) is environmentally friendly. The treated COPR could be reused as construction material due to its cementitious characteristics by this process.

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Although the process is promising for the remediation of COPR, the mechanism of this process should be further elucidated. The rice straw is a kind of biomass that consists of cellulose, hemicellulose, and lignin. Each component plays a different role in Cr(VI) reduction during co-pyrolysis with COPR. In the present study, the Cr(VI) reduction behavior with the co-pyrolysis of cellulose was investigated. The influence of pyrolysis variables, including temperature and reaction time, on the distribution of pyrolysis products of cellulose in terms of char, tar, and gas (as well as Cr(VI) reduction percentage) was investigated. The interaction between the volatile fraction (VF) of cellulose and Cr(VI) reduction was elucidated. In addition, X-ray absorption near-edge structure (XANES) spectroscopy and extended X-ray absorption fine-structure (EXAFS) spectroscopy were used to determine Cr speciation.

MATERIALS AND METHODS

Materials. The COPR was collected from the deposition site of a chromate production plant located in Jinan, Shandong Province, China. The raw materials for chromate production were chromite, dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), and Na_2CO_3 . The sample was sieved to 40 mesh and dried at 105°C before used. The contents of total chromium and Cr(VI) in the sample were $27\,600\text{ mg kg}^{-1}$ and 6750 mg kg^{-1} , respectively, with CaO (31.3%), MgO (25.4%), Al_2O_3 (6.1%), SiO_2 (6.3%), and Fe_2O_3 (11.9%). XRD pattern of COPR (shown in Figure S3) indicated that this COPR consisted largely of calcite (CaCO_3) and brownmillerite ($\text{Ca}_2\text{FeAlO}_5$) with minor amounts of portlandite [$\text{Ca}(\text{OH})_2$], magnesiochromite [$(\text{Mg,Fe})(\text{Cr,Al})_2\text{O}_4$], hydrogarnet [$\text{Ca}_3\text{Al}_2(\text{H}_4\text{O}_4)_3$], and periclase (MgO). The minerals in COPR are similar to those of COPR used in previous studies.^{2,17} Cellulose with the particle size between 150 and $350\text{ }\mu\text{m}$ was purchased from Sigma-Aldrich. The element contents of C, H, and O were 42.6%, 6.4%, and 50.8%, respectively. The volatile fraction, fixed carbon, and ash of the cellulose are 89.6%, 9.7%, and 0.6%, respectively.

Experimental Design. Cellulose Pyrolysis Behavior. The pyrolysis was carried out under a condition filled with N_2 (99.99%) in a fixed-bed tube furnace with an $800\text{ mm (L)} \times 30\text{ mm (I.D.)}$ quartz tube, shown in Figure S4. For the cellulose pyrolysis, 1 g of cellulose was put into a $50\text{ mm} \times 10\text{ mm}$ porcelain boat and then placed at the remote side of the tube furnace. The quartz tube was first filled with N_2 by the flow rate of 20 mL min^{-1} . The ceramic boat was then quickly moved to the center of the furnace after the reactor had stabilized at the desired temperature. Fast pyrolysis was conducted and kept for about 10 min to ensure complete conversion. The pyrolyzed volatiles were then cooled in a sequential ice bath, where the tar was condensed. The noncondensable gases were collected in a gas bag and analyzed by gas chromatography (GC). The char was recovered after it cooled in room temperature under N_2 atmosphere. The yields of char, tar, gas and VF from pyrolysis of cellulose were calculated as follows:

$$\text{yield}_{\text{char}} = \frac{m_{\text{char}}}{m_{\text{feedstock}}} \times 100\% \quad (1)$$

$$\text{yield}_{\text{tar}} = \frac{m_{\text{tar}}}{m_{\text{feedstock}}} \times 100\% \quad (2)$$

$$\text{yield}_{\text{gas}} = 100\% - \text{yield}_{\text{char}} - \text{yield}_{\text{tar}} \quad (3)$$

$$\text{yield}_{\text{volatile fraction}} = \text{yield}_{\text{gas}} + \text{yield}_{\text{tar}} \quad (4)$$

Batch Cr(VI) Reduction Study. The setup of the lab-scale experiment was based on the pilot-scale experiment as introduced in Note 1 of the Supporting Information. The specific cellulose/COPR ratios (Cel/COPR) were achieved by keeping a constant mass of COPR (3 g) and varying the mass of cellulose. The mixture was then put into the ceramic boat. After the reactor had stabilized at the desired temperature, the boat was moved quickly to the center of the furnace with the N_2 filled with the reactor. The N_2 flow was also kept at 20 mL min^{-1} . At the end, the boat was moved quickly to the cold end of the tube and allowed to cool with the flow of N_2 . The Cr(VI) reduction percentage (CRP) was calculated as follow:

$$\text{CRP} = \frac{C_0 \cdot M_0 - C \cdot M}{C_0 \cdot M_0} \quad (5)$$

where C_0 and C are the Cr(VI) content in COPR before and after pyrolysis, respectively. M_0 and M are the mass of initial and final COPR. All the experiments were carried out in triplicates, and the results were expressed as means.

Control Cr(VI) Reduction Study. Batch Study. In the study, the main compounds of VF, including tars, chars, gases, formic acid, and formaldehyde, were pyrolyzed with COPR separately. In addition, naphthalene, as a comparatively stable organic, was examined to reduce Cr(VI). Gases, tars, and chars were produced through the pyrolysis of cellulose at corresponding temperature, respectively. Tars were collected in the ice bath and chars were the solid residues after cellulose pyrolysis. The gas was pyrolyzed with COPR in the following procedure: a preset amount of cellulose was pyrolyzed at a certain temperature in one pyrolyzed reactor (reactor A). The VF generated was first driven by N_2 flow (20 mL min^{-1}) to the cool system to remove the tar and then to another pyrolyzed reactor (B), where about 3 g of COPR was laid at a preset temperature. The weights of reductants were varied as shown in Table S3. Tars and chars were pyrolyzed with COPR in the procedure the same as that of batch Cr(VI) reduction study. The reaction times were all kept as 10 min.

Continuous Study. The furnace was initially heated to preset temperature. The ceramic boat containing 3 g of COPR was then moved quickly to the center of the furnace under the continuous flow of the reducing gases. The gases, with a flow rate of 40 mL min^{-1} , were H_2/N_2 ($v/v = 25:75$), CO/N_2 ($v/v = 25:75$), $\text{alcohol}/\text{N}_2$ ($v/v = 25:75$), and $\text{pentanal}/\text{N}_2$ ($v/v = 25:75$), respectively. After the required reaction time, the boat was moved quickly to the cold end of the tube and allowed to cool with the flow of nitrogen. Alcohol and pentanal gases were produced through vaporization of the two liquids into the N_2 with a flow rate of 30 mL min^{-1} by a thermostated saturator.

Analytical Methods. The Cr(VI), extracted from 200 mesh of COPR, was measured by an alkaline digestion (United States Environmental Protection Agency, Method 3060a). The gas products were analyzed by a GC with a thermal conductivity detector (20B, Shimadzu). The tar was determined by a gas chromatography–mass spectrometry (5975C, Agilent).

The Cr K-edge X-ray absorption spectra (XAS) study was performed at Beijing Synchrotron Radiation Facility (BSRF), Institute of High-Energy Physics, Chinese Academy of Sciences. Samples were ground to fine powder and packed to a uniform thickness and sealed with transparent adhesive tape. XAS spectra were collected from the samples at beamline 4W1B in a storage ring of 2.2 GeV with an average ring current

of 90 mA. The spectroscopic data from standard samples, i.e. $K_2Cr_2O_4$ and Cr_2O_3 , were collected in transmission mode using pure N_2 gas-filled ionization chambers as gas detectors, and the other data were in fluorescence mode. Energy calibration was simultaneously performed for each measurement using a reference Cr foil placed in front of the third ion chamber and assigning the first inflection point to 5989 eV. K_2CrO_4 was used as the references of Cr(VI), and Cr_2O_3 and $CrCl_3$ were both used as the Cr(III) reference. The EXAFS data were analyzed with the software Winxas 3.1.¹⁸ The spectra were processed by removing the pre-edge background, normalizing the post-edge, and extracting the EXAFS signals from the spectra. The coordination numbers (CN) and interatomic distances (R) in the Cr local atomic environment were then determined using EXAFS shell-by-shell fitting.

RESULTS AND DISCUSSION

Cellulose Pyrolysis Behavior. The distributions of char, tar, and gas during the pyrolysis of cellulose are shown in Figure 1. It was shown that there was a sharp decrease of char

Figure 1. Cellulose pyrolysis behavior and the products distribution.

at pyrolysis temperature from 250 to 400 °C. The tar generated at around 300 °C (16.4%) and reached the maximum (70.4%) at 400 to 500 °C. The tar occurred a secondary pyrolysis to generate small molecule gases over 500 °C, leading to the increasing of gas. The characteristics of tar at 500 °C are listed in Table S1. The results showed that the compounds composed of various macromolecular organics, which could be grouped as acids, aldehydes, furans, ketones, etc.

When the temperature was lower than 350 °C, minor gas yielded indicating that the VF was mainly consisting of macromolecule compounds. The gas yield increased with the increasing of the temperature and reached the maximum of 49.8% at 800 °C. The incondensable gases from pyrolysis of cellulose were mainly CO_2 , CO , CH_4 , H_2 , C_2H_4 , and C_2H_6 . The portions as a function of temperature, shown in Table S2, indicated that the main compositions were CO_2 (52.6–69.8%) and CO (30.3–36.9%). The two compounds were mainly caused by the cracking and reforming of $C=O$ and $C-O-C$.¹⁹ The other compounds took off with the increasing of temperature. This tendency was obvious for H_2 , which was similar to the result from Shi and Wang.²⁰ Gas components, such as CO , H_2 , CH_4 , C_2H_4 , and C_2H_6 , have been proven to have the potential of reducing Cr(VI) to Cr(III) in a gas–solid reaction.^{21,22}

Cr(VI) Reduction as a Function of Pyrolysis Variables. The CRP of the COPR at different temperatures is shown in

Figure 2a. It can be seen that the Cr(VI) reduction was not significant at temperatures below 250 °C. Only 15.5% of

Figure 2. CRP of the COPR as a function of temperature (a), Cel/COPR (b), and reaction time (c).

Cr(VI) was reduced at 250 °C, with over 90% reduction at 400 °C. The CRP varied slowly from 94.9% to 96.0% with the temperature increasing from 400 to 500 °C. The conversion significantly increased to 99% at 550 °C. The mixture turned black after pyrolysis (shown in Figure S5) as a result of the carbonaceous residue deposited on the surface of COPR. Carbonaceous residue deposition is a common phenomenon during the pyrolysis of organics.^{23,24} The pH value of the raw COPR was 12.8, lower than that of the pyrolyzed one with the pH value of 12.9 to 13.8. The increased pH was probably ascribed to the decomposition of carbonate minerals, such as $CaCO_3$.

Figure 2b shows the Cr(VI) reduction percentage profile with a specific ratio of cellulose and COPR. The increase of

cellulose caused the CRP increasing until a certain Cel/COPR was attained (for example, 0.2 for 300 °C and 0.05 for 400 and 500 °C). A further increase of Cel/COPR had little influence on the Cr(VI) reduction.

As shown in Figure 2c, the CRP increased sharply at reaction time from 1 to 5 min, following a minor increase. For example, at 500 °C, there was only a slight rise from 97.4% to 98.5% with the reaction time of 5 to and 10 min.

XAS Study. XAS study was used to identify the speciation of reduced Cr(VI). The treated sample was the pyrolyzed COPR at 550 °C with a Cel/COPR ratio of 0.1 and a reaction time of 10 min. The XANES spectra of the samples are shown in Figure 3. The XANES spectra of treated COPR were similar to

Figure 3. Cr K-edge XAS spectra of the treated and untreated materials CRP.

that of Cr_2O_3 at around 5993 eV. This indicated that the Cr(VI) was completely reduced to Cr(III), which corresponded to the high CRP of over 99%. However, the XANES result was based on the Cr(III) reference of Cr_2O_3 rather than CrCl_3 . As shown in Figure S6, the normalized absorbance of CrCl_3 was lower than those of Cr_2O_3 and treated COPR. Hence, the XANES data alone could not verify the high CRP value. EXAFS was used to further analyze the Cr speciation. The Fourier transforms of EXAFS spectras for standard Cr_2O_3 , treated COPR, and the treated model are shown in Figure 4. There

Figure 4. Fourier transforms of EXAFS spectra for the standard Cr_2O_3 and the treated model.

were two major shells in both materials, the Cr–O shell and the Cr–Cr shell. Based on the EXAFS spectra, the bond distances and coordination numbers were calculated in Table 1. It was

Table 1. Fitted Cr K-edge EXAFS Parameters for Cr_2O_3 and Treated Model

sample	shell	CN ^a	R (Å) ^b	σ^2 (Å ²) ^c
Cr_2O_3	Cr–O	6.0	2.00	0.004
treated COPR	Cr–O	2.9	2.00	0.002
	Cr–Cr	3.2	2.95	0.008
treated Model	Cr–O	3.3	2.00	0.005
	Cr–Cr	4.9	2.97	0.007

^aCN: coordination number. ^bR: bond distance. ^c σ^2 : Debye–Waller factor

shown that Cr–O distance and coordination number of standard Cr_2O_3 were 2.00 and 6.0, respectively, which was corresponding to the previous research.²⁵ The Cr–O distance of treated COPR was 2.00 Å, in line with that of Cr_2O_3 . Previous research showed that the bond distances for Cr(VI)–O and Cr(III)–O were 1.62–1.66 Å and 1.97–2.01 Å, respectively.^{25,26} This result further indicated that the Cr(VI) in COPR was truly reduced to Cr(III). Cr_2O_3 was a suitable Cr(III) reference for XANES detection.

Considering the complicated Cr-containing minerals in COPR, the model COPR was used to better understand the speciation of the reduced Cr(VI). The model was prepared through calcining the diatomite at 800 °C to remove the reductants and then spiking K_2CrO_4 to the calcined diatomite to produce the model with Cr(VI) content of 6500 mg kg^{−1}. The model COPR was mixed with the cellulose with Cel/COPR of 0.1 and then pyrolyzed at 550 °C for 10 min, which was donated as the treated model. The XANES spectrum of treated model is shown in Figure 3. Its pre-edge peak, around 5993 eV, was agreed with that of Cr_2O_3 . As shown in Table 1, the Cr–O and Cr–Cr distances in the treated model were 2.00 and 2.97 Å, respectively. Generally, K_2CrO_4 should be reduced to Cr_2O_3 . However, the coordination numbers of Cr–O of the treated model was different from that of crystal Cr_2O_3 . Hence, the reduced Cr(III) probably was in the form of amorphous Cr_2O_3 , which was also found in previous study on the reduction of K_2CrO_4 by H_2 .²⁷ As mentioned in Note 2 of the Supporting Information, through the thermogravimetric (TG) analysis, it was found that H_2 , CO, and CH_4 could all reduce the K_2CrO_4 into Cr_2O_3 .

Control Batch Cr(VI) Reduction. As shown in Table S3, at a lower temperature (500 °C), the CRP with tar was the highest compared with the results from gas and char. The additions of gas and char facilitated the Cr(VI) reduction. However, the CRP for char was lower than 10%. The char was in solid state during the pyrolysis and could not fluidized to effectively contact Cr(VI) in the matrix. At 800 °C, it was shown that gas played a major role in Cr(VI) reduction. This was ascribed to the increase of gas yield and reduction of tar yield at higher temperature, as shown in Figure 1. Formic acid, formaldehyde, and naphthalene, which could all evaporate at over 500 °C, were found to effectively reduce Cr(VI). Previous studies also showed that naphthalene and tar could even reduce Fe(III) to Fe(II)/Fe(0).^{28,29} Naphthalene was a relatively inactive reductant with a stable C–H bond compared with the alkyl group. Thus, the organics with C–H bond from VF could potentially reduce Cr(VI). It also indicated that derivatives such

as the carbonyl group and carboxyl group could reduce Cr(VI) from Table S3. The volatile fraction of cellulose comprised the mentioned three groups. Thus, it could presume that all the organic compounds in the VF as well as CO and H₂ potentially reduced Cr(VI).

Previous studies showed that Cr(VI) can be reduced by CO and H₂ in the following way:^{21,22}

The volatile organics, such as hydrocarbon, aromatic, and aliphatic, might reduce Cr(VI) through direct reduction and indirect reduction. For direct reduction, the C–H bonds in the organics could easily react with Cr(VI) and subsequently reduce it.^{30,31} The carbonyl products were formed after C–H bonds reacted with Cr(VI).^{32,33} In the indirect reduction, the secondary cracking of the volatile organics could form new products, which could react with Cr(VI). For instance, H₂ and CO could form through the dehydrogenation of hydrocarbon^{33,34} and the cracking of carbonyl products,^{35,36} respectively. The CO and H₂ can react with Cr(VI) as in eqs 6 and 7. The Cr₂O₃, chromite, and calcite in the COPR minerals were all good catalysts for the dehydrogenation and cracking of the macromolecular organics.³⁷ Thus, in the ideal condition, the organic compounds could finally be converted to CO₂ and H₂O by Cr(VI). To better understand the stoichiometric ratio of reductant/oxidant, we proposed MCRA/C. MCRA is the maximum Cr(VI) reduction amount of the VF in cellulose, and C is the Cr(VI) amount in COPR. The calculation of MCRA/C was shown in Note 2 of the Supporting Information. Based on the calculation, the result from Figure 2b was converted to the Cr(VI) reduction as a function of MCRA/C, which was shown in Figure S9.

Figure S8 clearly showed that the Cr(VI) reduction was highly related with MCRA/C at the three temperatures. The increase of MCRA/C resulted in the CRP increasing until MCRA/C of about 17 was attained. There obviously was adequate volatile reducing compounds for Cr(VI) reduction. However, even when MCRA/C exceeded 100, the remnant Cr(VI) content in the pyrolyzed products was still high (>100 mg/kg). The reason will be explained in the next section.

Control Continuous Cr(VI) Reduction. Figure S9 introduced the VF generation as a function of reaction time. The figure showed there was also a sharp increase of VF generation at reaction time from 1 to 5 min, followed a minor increase. For example, the VF increased only from 74.7% to 85.3% with the reaction time from 5 to 10 min at 500 °C. The VF shortage probably caused the slight rise of CRP at the reaction time from 5 to 10 min.

To better understand the Cr(VI) reduction behavior, we studied the continuous Cr(VI) reduction with the flows of H₂, CO, alcohol, and pentanal. As shown in Figure 5, the CRP decreased along with the increase of reaction time. For all of the reducing gases, the final Cr(VI) contents at 10 min were below 22 mg kg^{−1}, lower than that from batch Cr(VI) study. It confirmed that remnant Cr(VI) could be further reduced when continuously contacted with reducing gas. From Figure 5, H₂ performed the highest reduction rate with the final Cr(VI) content of 3.1 ± 0.5 mg kg^{−1}, and the final Cr(VI) content of copyrolyzed with pypentanal was 20 ± 1.5 mg kg^{−1}. It was obviously seen that gas products (H₂ and CO) performed better than the tar products (alcohol and pentanal). With light

Figure 5. Isothermal Cr(VI) reduction under various reducing gas ((a): CRP, (b): Cr(VI) content, and (c): model stimulation).

molecules, low kinetic diameters (or collision diameters), and viscosity, the gas products easily penetrated the matrix of COPR and reduced Cr(VI).^{29,38,39}

A 3D phase-boundary model ($1-(1-\text{CRP})^{1/3} = Kt$)³⁹ was used to stimulate the Cr(VI) reduction kinetics. The initial 2 min reaction time was excluded due to the impact of heating process on the Cr(VI) reduction. From Figure 5c, it was found there were linear relationships between $1-(1-\text{CRP})^{1/3}$ and reaction time in the initial stage with CRP below 99%. The trend gradually became flat in the later stage due to the probable domination of intraparticle diffusion. Previous results showed that the reductions of Fe₂O₃ to Fe(II)/Fe(0) by H₂ and CO were initially controlled by phase boundary reaction and followed by intraparticle diffusion.^{29,40,41} It required over 30 min to achieve 90% conversion of Fe(III) to Fe(II)/Fe(0), and it required less than 10 min to achieve an over 99% conversion of Cr(VI) to Cr(III). Generally, Cr(VI) was distributed on the surface and diffuse in the COPR due to the fact that Cr(VI) was physically and chemically adsorbed by

the minerals of COPR during the lixiviation of water to recover Cr(VI).^{12,42}

As shown in Figure 6a, the particle size of COPR was reduced to below 200 mesh to achieve a better performance.

Figure 6. Isothermal Cr(VI) reduction as a function of particle size (a) and temperature (b) (Cr(VI) content below detection limit was assigned to be 1 mg/kg).

Under the continuous flow of H₂, the Cr(VI) was below the detection limit (2 mg/kg) after 4 min. It required 9 min to achieve the same content for pentanal. Figure 6b shows the isothermal Cr(VI) reduction as a function of temperature. It indicated that high temperature obviously helped the Cr(VI) reduction for higher temperature and could help Cr(VI) reduction in the generation of low-molecule-reducing gases, as shown in Figure 1.

Environmental Significance. Effective reaction time between VF and Cr(VI) was important for Cr(VI) reduction during the pyrolysis. However, in the present pilot-scale pyrolysis system, as shown in Figure S2, the inert hot gas, generated from the incomplete combustion of fuel (excess air ratio: 0.95), can take away the VF generated from biomass pyrolysis. Hence, it could reduce the effective reaction time between VF and Cr(VI). It seemed rational to generate VF from cellulose-containing biomass in one pyrolysis reactor initially. The VF was then flown to internal heat rotary kiln where COPR motioned in a reverse direction to achieve a longer effective contact time between VF and COPR. The temperature in the reactor for biomass pyrolysis could be higher to generate more reducing gas for a better Cr(VI) reduction performance. Other available organic wastes, such as

plastics and sewage sludge, can also be used as reductants because they may generate the volatile organics as well as CO and H₂ during pyrolysis.

It was verified in this study that Cr₂O₃ was a suitable Cr(III) standard reference through the XANES coupled with EXAFS method. However, Cr₂O₃ had a higher absorbance value at 5993 eV than other standard Cr(III) references such as CrCl₃ or Cr(NO₃)₃, which were usually used as standard Cr(III) reference in many previous reported researches on Cr(VI) detection by XANES alone method.^{2,14,43,44} Hence, EXAFS study was required to be performed on the rationality of the Cr(III) standard sample in these studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05707.

Additional details on Pilot scale experiment of the pyrolysis treatment of COPR, thermogravimetric of Cr(VI) reduction under the reducing gases, and calculation of MCRA/C. Tables showing components identification of tars obtained at 500 °C, gas compositions as a function of temperature, batch control Cr(VI) reduction study, elemental contents of organic fractions in the char, and calculated element contents of volatile fraction from the cellulose and its corresponding maximum Cr(VI) reduction capacity. Figure showing the pilot-scale experiment equipment, a schematic diagram of the pilot-scale experiment apparatus, XRD pattern of Chinese COPR, schematic diagram of apparatus for pyrolysis, images of mixture of COPR plus cellulose before and after pyrolysis, Cr K-edge XAS spectra of the treated and untreated materials, TG study of K₂CrO₄ in the different reducing gas, Cr(VI) reduction as a function of MCRA/C, and VF yield as a function of reaction time. (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Kanchinadham, S. B. K.; Loganathan, V. D.; Kalyanaraman, C. A preliminary study on leachability of chromium from a contaminated site. *Environ. Prog. Sustainable Energy* **2013**, 32 (4), 1096–1100.
- (2) Dermatas, D.; Moon, D. H.; Chrysoschoou, M.; Grubb, D. G.; Wazne, M.; Christodoulatos, C. Ettringite-Induced heave in chromite ore processing residue (COPR) upon ferrous sulfate treatment. *Environ. Sci. Technol.* **2006**, 40, 5786–5792.
- (3) Földi, C.; Dohrmann, R.; Mansfeldt, T.; Matern, K. Characterization of chromium-containing wastes and soils affected by the production of chromium tanning agents. *J. Soils Sediments* **2013**, 13 (7), 1170–1179.

- (4) Brose, D. A.; James, B. R. Hexavalent chromium reduction in solution and in chromite ore processing residue-enriched soil by tartaric acid with isopropyl alcohol and divalent manganese as co-reductants. *J. Environ. Qual.* **2013**, *42* (3), 766–773.
- (5) Bewley, R. J. F.; Jeffries, R.; Watson, S.; Granger, D. An overview of chromium contamination issues in the south-east of Glasgow and potential for remediation. *Environ. Geochem. Health* **2001**, *23*, 267–271.
- (6) Meegoda, J. N. Remediation of chromium-contaminated soils: Bench-scale investigation. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management* **1999**, *3* (3), 124–131.
- (7) Tokunaga, T. K.; Wan, J.; Lanzirrotti, A.; Sutton, S.; Newville, M.; Rao, W. Long-term stability of organic carbon-stimulated chromate reduction in contaminated soils and its relation to manganese redox status. *Environ. Sci. Technol.* **2007**, *41* (12), 4326–4331.
- (8) Kožuh, N.; Štupar, J.; Gorenc, B. Reduction and oxidation processes of chromium in soils. *Environ. Sci. Technol.* **2000**, *34* (1), 112–119.
- (9) Sun, T.; Chen, J.; Lei, X.; Zhou, C. Detoxification and immobilization of chromite ore processing residue with metakaolin-based geopolymer. *J. Environ. Chem. Eng.* **2014**, *2* (1), 304–309.
- (10) Du, J.; Lu, J.; Wu, Q.; Jing, C. Reduction and immobilization of chromate in chromite ore processing residue with nanoscale zero-valent iron. *J. Hazard. Mater.* **2012**, *215–216*, 152–158.
- (11) Hillier, S.; Lumsdon, D. G.; Brydson, R.; Paterson, E. Hydrogarnet: A host phase for Cr(VI) in chromite ore processing residue (COPR) and other high pH wastes. *Environ. Sci. Technol.* **2007**, *41* (6), 1921–1927.
- (12) Chrysoschoou, M.; Fakra, S. C.; Marcus, M. A.; Moon, D. H.; Dermatas, D. Microstructural analyses of Cr(VI) speciation in chromite ore processing residue (COPR). *Environ. Sci. Technol.* **2009**, *43* (14), 5461–5466.
- (13) He, Y. T.; Chen, C. C.; Traina, S. J. Inhibited Cr(VI) reduction by aqueous Fe(II) under hyperalkaline conditions. *Environ. Sci. Technol.* **2004**, *38* (21), 5535–5539.
- (14) Moon, D. H.; Wazne, M.; Jagupilla, S. C.; Christodoulatos, C.; Kim, M. G.; Koutsospyros, A. Particle size and pH effects on remediation of chromite ore processing residue using calcium polysulfide (CaSS). *Sci. Total Environ.* **2008**, *399* (1–3), 2–10.
- (15) Zhang, D.; He, S.; Kong, H.; Dai, L.; Hu, X.; Wu, D.; Peng, K.; Bu, G.; Pang, H. Treatment of Chromite Ore Processing Residue by pyrolysis with rice straw. *Chemosphere* **2009**, *77* (8), 1143–1145.
- (16) Zhang, D.; He, S.; Kong, H.; Dai, L.; Xie, Y.; Wu, D.; Bu, G.; Peng, K. Impact of pyrolysis process on the chromium behavior of COPR. *J. Hazard. Mater.* **2009**, *172* (2–3), 1597–1601.
- (17) Kamolpornwijit, W.; Meegoda, J. N.; Hu, Z. Characterization of chromite ore processing residue. *Pract. Period. Hazard., Toxic, Radioact. Waste Manage.* **2007**, *11* (4), 234–239.
- (18) Ressler, T. WinXAS: A program for X-ray absorption spectroscopy data analysis under MS-Windows. *J. Synchrotron Radiat.* **1998**, *5* (2), 118–122.
- (19) Patwardhan, P. R.; Dalluge, D. L.; Shanks, B. H.; Brown, R. C. Distinguishing primary and secondary reactions of cellulose pyrolysis. *Bioresour. Technol.* **2011**, *102* (8), 5265–5269.
- (20) Shi, X.; Wang, J. A comparative investigation into the formation behaviors of char, liquids and gases during pyrolysis of pinewood and lignocellulosic components. *Bioresour. Technol.* **2014**, *170*, 262–269.
- (21) Józwiak, W. K.; Ignaczak, W.; Dominiak, D.; Maniecki, T. P. Thermal stability of bulk and silica supported chromium trioxide. *Appl. Catal., A* **2004**, *258* (1), 33–45.
- (22) Lillehaug, S.; Jensen, V. R.; Børve, K. J. Catalytic dehydrogenation of ethane over mononuclear Cr(III)-silica surface sites. Part 2: C–H activation by oxidative addition. *J. Phys. Org. Chem.* **2006**, *19* (1), 25–33.
- (23) Airaksinen, S. M. K.; Bañares, M. A.; Krause, A. O. I. In situ characterization of carbon-containing species formed on chromia/alumina during propane dehydrogenation. *J. Catal.* **2005**, *230* (2), 507–513.
- (24) Korhonen, S. T.; Airaksinen, S. M. K.; Krause, A. O. I. In situ characterization of carbonaceous deposits formed on chromia/zirconia during isobutane dehydrogenation. *Catal. Today* **2006**, *112* (1–4), 37–39.
- (25) Park, D.; Yun, Y. S.; Park, J. M. XAS and XPS studies on chromium-binding groups of biomaterial during Cr(VI) biosorption. *J. Colloid Interface Sci.* **2008**, *317* (1), 54–61.
- (26) Wang, S. L.; Lee, J. F. Reaction mechanism of hexavalent chromium with cellulose. *Chem. Eng. J.* **2011**, *174* (1), 289–295.
- (27) Li, P.; Xu, H. B.; Zheng, S. L.; Zhang, Y.; Li, Z.-H.; Bai, Y.-L. A green process to prepare chromic oxide green pigment. *Environ. Sci. Technol.* **2008**, *42* (19), 7231–7235.
- (28) Ma, C.; Luo, S. Y.; Bu, Q. J. Coupling of degradation of tar model compound naphthalene with direct reduction of iron ore for ironmaking (In Chinese). *Renewable Energy Resource.* **2015**, *33* (7), 1097–1102.
- (29) Luo, S.; Yi, C.; Zhou, Y. Direct reduction of mixed biomass-Fe₂O₃ briquettes using biomass-generated syngas. *Renewable Energy* **2011**, *36* (12), 3332–3336.
- (30) Botavina, M. A.; Martra, G.; Agafonov, Y. A.; Gaidai, N. A.; Nekrasov, N. V.; Trushin, D. V.; Coluccia, S.; Lapidus, A. L. Oxidative dehydrogenation of C3–C4 paraffins in the presence of CO₂ over CrOx/SiO₂ catalysts. *Appl. Catal., A* **2008**, *347* (2), 126–132.
- (31) Botavina, M. A.; Evangelisti, C.; Agafonov, Y. A.; Gaidai, N. A.; Panziera, N.; Lapidus, A. L.; Martra, G. CrOx/SiO₂ catalysts prepared by metal vapour synthesis: Physical-chemical characterisation and functional testing in oxidative dehydrogenation of propane. *Chem. Eng. J.* **2011**, *166* (3), 1132–1138.
- (32) Lau, T. C.; Wu, Z. B.; Bai, Z. L.; Mak, C.-K. Dalton communications. Lewis-acid catalysed oxidation of alkanes by chromate and permanganate. *J. Chem. Soc., Dalton Trans.* **1995**, *4*, 695–696.
- (33) Carotenuto, G.; Tesser, R.; Di Serio, M.; Santacesaria, E. Kinetic study of ethanol dehydrogenation to ethyl acetate promoted by a copper/copper-chromite based catalyst. *Catal. Today* **2013**, *203*, 202–210.
- (34) Weckhuysen, B. M.; Schoonheydt, R. A. Alkane dehydrogenation over supported chromium oxide catalysts. *Catal. Today* **1999**, *51* (2), 223–232.
- (35) Lv, G.; Wu, S.; Yang, G.; Chen, J.; Liu, Y.; Kong, F. Comparative study of pyrolysis behaviors of corn stalk and its three components. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 185–193.
- (36) Neri, G.; Pistone, A.; De Rossi, S.; Rombi, E.; Milone, C.; Galvagno, S. Ca-doped chromium oxide catalysts supported on alumina for the oxidative dehydrogenation of isobutane. *Appl. Catal., A* **2004**, *260* (1), 75–86.
- (37) Arena, U.; Di Gregorio, F. Energy generation by air gasification of two industrial plastic wastes in a pilot scale fluidized bed reactor. *Energy* **2014**, *68*, 735–743.
- (38) Li, J. R.; Kuppler, R. J.; Zhou, H. C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1477–1504.
- (39) Luo, M.; Wang, S.; Wang, L.; Lv, M. Reduction kinetics of iron-based oxygen carriers using methane for chemical-looping combustion. *J. Power Sources* **2014**, *270*, 434–440.
- (40) Kazemi, M.; Glaser, B.; Sichen, D. Study on direct reduction of hematite pellets using a new TG setup. *Steel Res. Int.* **2014**, *85* (4), 718–728.
- (41) Tiernan, M. J.; Barnes, P. A.; Parkes, G. M. B. Reduction of iron oxide catalysts: The investigation of kinetic parameters using rate perturbation and linear heating thermoanalytical techniques. *J. Phys. Chem. B* **2001**, *105* (1), 220–228.
- (42) Tinjum, J. M.; Benson, C. H.; Edil, T. B. Treatment of Cr(VI) in COPR using ferrous sulfate-sulfuric acid or cationic polysulfides. *J. Geotech. Geoenviron. Eng.* **2008**, *134* (12), 1791–1803.
- (43) Malherbe, J.; Isaure, M. P.; Séby, F.; Watson, R. P.; Rodriguez-Gonzalez, P.; Stutzman, P. E.; Davis, C. W.; Maurizio, C.; Unceta, N.; Sieber, J. R.; Long, S. T.; Donard, O. F. X. Evaluation of hexavalent chromium extraction method EPA method 3060A for soils using

XANES spectroscopy. *Environ. Sci. Technol.* **2011**, 45 (24), 10492–10500.

(44) Moon, D. H.; Wazne, M.; Koutsospyros, A.; Christodoulatos, C.; Gevgilili, H.; Malik, M.; Kalyon, D. M. Evaluation of the treatment of chromite ore processing residue by ferrous sulfate and asphalt. *J. Hazard. Mater.* **2009**, 166 (1), 27–32.