Thermal Treatment of Chromium(III) Oxide with Carbonates Analyzed by Far-Infrared Spectroscopy

Christian Vogel,^{a,*} Jan Stemmann,^{a,b}
Karsten Holldack,^c Ryo Sekine,^d
Ewelina Lipiec,^e Christian Adam^a

^a BAM Federal Institute for Materials Research and Testing, Division 4.4 Thermochemical Residues Treatment and Resource Recovery, Unter den Eichen 87, D-12205 Berlin, Germany

^b Institute for Ecopreneurship, University of Applied Sciences Northwestern Switzerland, Gründenstrasse 40, 4132 Muttenz, Switzerland

^c Helmholtz Zentrum Berlin, Institute Methods and Instrumentation for Synchrotron Radiation Research, 12489 Berlin, Germany

^d Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, 5095 SA Adelaide, Australia

^e The Henryk Niewodniczanski Institute of Nuclear Physics, Polish Academy of Sciences E. Radzikowskiego 152, 31-342 Kraków, Poland

The chemical state of thermochemically treated chromium(III) oxide (Cr_2O_3) with various carbonates was analyzed by far-infrared (far-IR) spectroscopy (spectral region $700\text{--}25\text{ cm}^{-1}$). Non-toxic Cr_2O_3 was oxidized with potassium, sodium, and calcium carbonate, respectively, to toxic Cr(VI) and Cr(V) compounds during thermal treatment at $1000\text{ }^\circ\text{C}$. In reverse, thermochemical treatment of Cr_2O_3 with magnesium carbonate lead to the formation of the Cr(III) compound MgCr_2O_4 . Higher temperatures ($>1200\text{ }^\circ\text{C}$) or reducing atmospheric conditions prevent the formation of Cr(VI)/Cr(V) compounds, too. Additionally, it was found that polyethylene powder with a low particle size ($<70\text{ }\mu\text{m}$) is favorable for the collection of good far-IR spectra of inorganic powders.

Index Headings: **Far-infrared spectroscopy; Far-IR spectroscopy; Chromium; Carbonate; Chromate; Thermal treatment.**

INTRODUCTION

Phosphorus (P) is an essential element for all forms of life. For this reason, P in the form of phosphate is applied as fertilizer in the agricultural industry. Because P is a limited mineral resource, new alternatives for the production of phosphate fertilizers must be found. An

important source of secondary phosphates is sewage sludge ash (SSA).^{1,2}

Phosphates in SSA have a low plant availability.¹ Furthermore, SSAs are polluted with heavy metals.^{1,2} To overcome these drawbacks, over the last several years, wet chemical and thermochemical processes were developed to separate pollutants from the SSA and to increase the plant availability of phosphorus.^{2–4} One important and promising process is the thermochemical treatment of SSA with sodium carbonate (Na_2CO_3) at $850\text{--}1000\text{ }^\circ\text{C}$ that increases the plant availability of the phosphate phases in the fertilizer due to the formation of Na–Ca phosphates.

Sewage sludge ashes and SSA-based fertilizers contain approximately $80\text{--}200\text{ mg/kg}$ of total Cr with variable spread of oxidation states. Previously, we have reported that, under certain conditions, some chromium (III) in the SSA is oxidized to chromium(VI) during the thermochemical process.⁵ Chromium in the hexavalent state (Cr(VI)) is very toxic. In contrast, Cr in trivalent form (Cr(III)) is less mobile in the environment and therefore markedly less toxic.⁶ The German Fertilizer Ordinance⁷ mandates that the total Cr of fertilizers must be labeled above a content of 300 mg/kg . Furthermore, the Cr(VI) mass fraction is limited to 2 mg/kg irrespective of the overall amount of Cr present in the fertilizer.

Thus, in order to meet the strict Cr(VI) limit in the German Fertilizer Ordinance, we analyzed the behavior of Cr during thermochemical treatment of pure chromium(III) oxide (Cr_2O_3) with various carbonates under varied oxygen atmospheres by far-infrared (far-IR) spectroscopy. Far-IR spectroscopy is an appropriate method because most of the infrared absorption bands of metal oxides occur in the spectral region $700\text{--}25\text{ cm}^{-1}$, as shown for several examples of heavy metal oxides in Fig. 1. Thus, changes of the chemical state of Cr during thermal treatment can be studied by far-IR spectroscopy to understand the state of Cr in the SSA fertilizer. An overview about the oxidation state of different chromium compounds is shown in Table I.

MATERIALS AND INSTRUMENTATION

Thermogravimetry–differential thermal analysis (TG–DTA) experiments were carried out on Netzsch STA 449 F3 Jupiter (Selb, Germany). Samples of $20\text{--}30\text{ mg}$ were heated at a rate of $10\text{ }^\circ\text{C/min}$ from $30\text{ }^\circ\text{C}$ to $800/1000/1200\text{ }^\circ\text{C}$ after which, the temperature was kept constant for 30 min . The gas flow (air, nitrogen–air mixture, or argon + 2% hydrogen) was 50 mL/min . The thermal experiments were done with chromium(III) oxide (Cr_2O_3 , p.a., Merck, Darmstadt, Germany), calcium carbonate (CaCO_3 , p.a., Sigma-Aldrich, Steinheim, Germany), magnesium carbonate (MgCO_3 , p.a., Merck, Darmstadt, Germany), Na_2CO_3 ($>99\%$, Carl Roth GmbH, Karlsruhe

Received 15 January 2015; accepted 5 March 2015.

* Author to whom correspondence should be sent. E-mail: cv.vogel@yahoo.de.

DOI: 10.1366/15-07878

FIG. 1. Far-IR spectra of various metal oxides.

Germany), and potassium carbonate (K_2CO_3 , J.T. Baker, Deventer, The Netherlands).

Calcium chromate ($CaCrO_4$) and chromium sulfide (Cr_2S_3 ; both ABCR, Karlsruhe, Germany), sodium chromate (Na_2CrO_4 , 98+%, ACROS Organics, Geel, Belgium), potassium chromate (K_2CrO_4 , p.a., AppliChem, Karlsruhe, Germany), iron(III) oxide (Fe_2O_3) and zinc oxide (ZnO ; Sigma-Aldrich, Steinheim, Germany), lead oxide (Pb_3O_4 , Fisher Scientific, Leicestershire, UK), copper(II) oxide (CuO , Carl Roth GmbH, Karlsruhe, Germany), and copper(I) oxide (Cu_2O , 99%, Alfa-Aesar, Karlsruhe,

TABLE I. Oxidation states of various chromium compounds.

Oxidation state	Compounds
Cr(III)	Cr_2O_3 , $Cr(OH)_3$, $CrCl_3$, $CaCr_2O_4$, $MgCr_2O_4$, $FeCr_2O_4$, Cr_2S_3
Cr(IV)/(V)	$Ca_5Cr_3O_{12}$
Cr(V)	$Ca_3Cr_2O_8$
Cr(VI)	$CaCrO_4$, $MgCrO_4$, Na_2CrO_4 , K_2CrO_4

FIG. 2. Single channel spectra of various PE powders (Micro Powders (average particle size 4.5 μm , dotted line), Vestolen (average particle size 60 μm , dashed line), ABCR (average particle size >150 μm , solid line).

Germany) were used for the spectroscopic experiments (standards reference spectra). Chromium hydroxide ($Cr(OH)_3$) was precipitated from an aqueous solution of chromium(III) chloride ($CrCl_3$, p.a., Sigma-Aldrich, Australia) with ammonia. Calcium chromite ($CaCr_2O_4$), magnesium chromite ($MgCr_2O_4$), and chromite ($FeCr_2O_4$) were prepared from 1.00 g Cr_2O_3 (p.a., Merck, Darmstadt, Germany) with 0.66 g $CaCO_3$ (p.a., Sigma-Aldrich, Steinheim, Germany), 0.66 g $MgCO_3$ (p.a., Merck, Darmstadt, Germany), and 0.51 g iron(II,III) oxide (Fe_3O_4 , 95%, ABCR, Karlsruhe, Germany) at 1250, 1000, and 1500 $^{\circ}C$, respectively, in platinum crucibles by thermal treatment (6–16 h) in a muffle furnace (Nabertherm LH 15/14, Lillenthal, Germany).⁸ $Ca_3Cr_2O_8$ and $Ca_5Cr_3O_{12}$ were prepared from Cr_2O_3 (p.a., Merck, Darmstadt, Germany) and $CaCO_3$ (p.a., Sigma-Aldrich, Steinheim, Germany) at 1000 and 1200 $^{\circ}C$, respectively, after Arcon et al.⁹ in platinum crucibles by thermal treatment in a muffle furnace.

Far-IR spectroscopic measurements of the thermochemically treated samples were carried out at the Terahertz Beamline at Helmholtz-Zentrum Berlin (Bruker IFS 125, far-IR DTGS-detector with black PE-window, multilayer beam splitter (Bruker T222)). Reference substances were measured at the Terahertz Beamline at Helmholtz-Zentrum Berlin and Far-Infrared and High-Resolution FT-IR Beamline at the Australian Synchrotron (Bruker IFS 125, He-cooled Si-bolometer, multilayer beam splitter). Spectra were collected with a spectral resolution of 2 cm^{-1} (100 scans were co-added per spectrum) in transmission. For comparison of the data, some samples were measured on both instruments. For the analysis of the far-IR transparency of polyethylene (PE) powders, the following high-density PE powders were used: Micro Powders Inc. MPP-620XXF (average particle size 4.5 μm ; Tarrytown, NY), Vestolen A6016 (average particle size 60 μm ; Hüls, Germany) and ABCR PE UHMW (average particle size >150 μm ; Karlsruhe, Germany). For the collection of far-IR spectra of the metal oxides, 3 mg of sample were ground with a pestle and mortar and afterwards mixed with 47 mg PE powder (Vestolen). The sample/PE

FIG. 3. Thermogravimetry (TG) curves of thermochemical treatment of Cr_2O_3 with MgCO_3 (dashed line), CaCO_3 (solid line), Na_2CO_3 (dashed-dotted line), and K_2CO_3 (dotted line); atmosphere: air; heating rate: 10 K/min; isotherm segment: 30 min).

mixture was pressed without heating in a pellet press (13 mm diameter) for 1 min with a pressure of 5 tons. The pellet thickness after pressing was approximately 0.5 mm.

RESULTS AND DISCUSSION

Far-IR transparency of the used PE powder is a critical issue for the collection of far-IR absorption spectra with a high spectral quality. Figure 2 shows the single channel spectra of three different PE powders. The highest infrared radiation transparency in the $700\text{--}25\text{ cm}^{-1}$ region was found for the PE powder with the lowest average particle size (Micro powders, $4.5\text{ }\mu\text{m}$). With an increasing average particle size of the PE powder, a decreasing infrared radiation transparency was detected, with the high energy cutoff wavenumber almost reciprocal to the grain size of the PE powder.¹⁰ Thus, higher grain sizes of the PE powder result in stronger scattering of the infrared radiation whereby more IR radiation is lost.

Figure 3 shows the TG curves of thermal treatment of Cr_2O_3 with CaCO_3 , MgCO_3 , Na_2CO_3 , and K_2CO_3 , respectively. The reaction of Cr_2O_3 with MgCO_3 starts already at low temperatures of approximately $300\text{ }^\circ\text{C}$. In contrast, the reactions of Cr_2O_3 with CaCO_3 , Na_2CO_3 , and K_2CO_3 start at approximately $750\text{ }^\circ\text{C}$. Figure 4 shows the far-IR spectra of the reaction products of these thermal

FIG. 4. Far-IR spectra of thermochemically treated Cr_2O_3 with CaCO_3 , MgCO_3 , Na_2CO_3 , and K_2CO_3 ($1000\text{ }^\circ\text{C}$, 30 min isotherm, air atmosphere; left column) and corresponding reference substances (right column).

Fig. 5. Far-IR spectra of calcium carbonate and various chromium compounds.

treatments at 1000 °C (left side). Thermal treatment of Cr_2O_3 with Na_2CO_3 and K_2CO_3 developed the Cr(VI) compounds Na_2CrO_4 and K_2CrO_4 , respectively (see corresponding spectra of reference substances on the right side). K_2CrO_4 has characteristic sharp absorption bands at 399, 385, and 155 cm^{-1} . In reverse, in the spectrum of Na_2CrO_4 , only a broad band at lower wavenumbers is detectable. During the treatment with MgCO_3 , the Cr(III) compound MgCr_2O_4 is formed. It was previously determined that magnesium chromate (MgCrO_4) is thermally stable only up to approximately 700 °C.⁸ At higher temperatures, it decomposes to the trivalent chromite MgCr_2O_4 . However, Na_2CrO_4 and K_2CrO_4 are stable until temperatures >1000 °C.⁸

Fig. 6. Far-IR spectra of thermochemically treated Cr_2O_3 with CaCO_3 at 800, 1000, and 1200 °C (30 min isotherm, air atmosphere; first three from top to bottom) and thermochemically treated Cr_2O_3 with CaCO_3 at 1000 °C under 5 vol% oxygen and reducing conditions (2% H_2 in Ar).

The major product of the thermal treatment of Cr_2O_3 with CaCO_3 at 1000 °C is the Cr(V) compound $\text{Ca}_3\text{Cr}_2\text{O}_8$ ($=\text{Ca}_3(\text{CrO}_4)_2$). In the spectrum, some unreacted CaCO_3 is also detectable at its bands at 315, 228, and 110 cm^{-1} (see also Fig. 5, top). Figure 6 also shows the far-IR spectra of the products from the thermal treatment of Cr_2O_3 with CaCO_3 at 800 and 1200 °C, respectively. Similar to the 1000 °C treatment, the product of the treatment at 800 °C shows $\text{Ca}_3\text{Cr}_2\text{O}_8$ as a major mineral phase formed. Furthermore, some bands of the Cr(VI) compound CaCrO_4 at 256 and 178 cm^{-1} are detectable. For comparison, far-IR spectra of other chromium reference compounds are shown in Fig. 6. Holder and Schwarz¹¹ showed that $\text{Ca}_3\text{Cr}_2\text{O}_8$ is developed by thermal treatment of CaCrO_4 with calcium oxide (CaO). Thus, primarily CaCrO_4 will be formed, which reacts during the thermal treatment with developing CaO , from the combustion of CaCO_3 , to the Cr(V) compound

Ca₃Cr₂O₈. Equations 1 and 2 show the reactions of Cr₂O₃ with small and large amounts of CaCO₃, respectively.

The thermal treatment at 1200 °C results in a predominant formation of the Cr(V)/Cr(IV) compound Ca₅Cr₃O₁₂ (=Ca₅(CrO₄)₃) and some Ca₃Cr₂O₈. Previously, it was mentioned that, at temperatures >1000 °C, a decomposition of Cr(VI) to Cr(III) takes place.^{8,12} However, the presented results show that the thermally initiated reduction of Cr(VI) to Cr(III) does not take place in one step, but runs through the chemical states Cr(V) and Cr(IV).

With a reduced oxygen concentration in the atmosphere (5 vol% instead of 20 vol%), bands at 420 and 288 cm⁻¹ indicate that Ca₃Cr₂O₈ was again formed during thermochemical treatment of Cr₂O₃ with CaCO₃ at 1000 °C (see Fig. 6). In this spectrum, again, some CaCO₃ is detectable at its bands at 315, 228, and 110 cm⁻¹. Only reducing atmospheric conditions (a mixture of 2% hydrogen in argon was used) prevent an oxidation of Cr(III) to toxic Cr(VI)/Cr(V) compounds (Fig. 6, bottom). No reaction between Cr₂O₃ and CaCO₃ was detectable under reducing conditions. The spectrum shows a mixture of pure Cr₂O₃ (weak absorption bands at 626 and 572 cm⁻¹) and pure CaCO₃ (315, 228, and 110 cm⁻¹) bands. In the literature,⁸ it is also mentioned that Cr₂O₃ is not reduced by hydrogen even at high temperatures which can be confirmed by our results.

CONCLUSIONS

In this paper, we demonstrated the ability of far-IR spectroscopy for the determination of the chemical state of inorganic chromium compounds. Thermochemical treatment of Cr₂O₃ with CaCO₃, Na₂CO₃, and K₂CO₃, respectively, at 1000 °C developed toxic Cr(VI) and Cr(V) compounds. Higher temperatures (>1200 °C) or reducing atmospheric conditions are required to prevent the formation of these toxic compounds. In contrast, thermochemical treatment of Cr₂O₃ with MgCO₃ led solely to

the formation of the Cr(III) compound MgCr₂O₄ because MgCrO₄ is only stable up to approximately 700 °C. Furthermore, it was demonstrated that PE powder with a low particle size (<70 µm) is necessary for the collection of far-IR spectra with a high quality.

ACKNOWLEDGMENTS

This research was undertaken on the Far-Infrared and High-Resolution FT-IR Beamline at the Australian Synchrotron, Victoria, Australia, and Terahertz Beamline at Helmholtz-Zentrum Berlin, Germany. We thank these institutions for the allocation of synchrotron radiation beamtime. Christian Vogel thanks the German Research Foundation for financial support (VO 1794/1-1 and VO 1794/2-1). We also gratefully acknowledge Anka Kohl (BAM, Division 1.4) for help with the pellet preparation and Dr. Marion Gemeinert (BAM, Division 5.5) for the analysis of the particle size.

1. O. Krüger, A. Grabner, C. Adam. "Complete Survey of German Sewage Sludge Ash". *Environ. Sci. Technol.* 2014. 48(20): 11811-11818.
2. C. Adam, B. Peplinski, M. Michaelis, G. Kley, F.-G. Simon. "Thermochemical Treatment of Sewage Sludge Ashes for Phosphorus Recovery". *Waste Manage.* 2009. 29(3): 1122-1128.
3. C. Vogel, C. Adam. "Heavy Metal Removal from Sewage Sludge Ash by Thermochemical Treatment with Gaseous Hydrochloric Acid". *Environ. Sci. Technol.* 2011. 45(17): 7445-7450.
4. S. Donatello, C.R. Cheeseman. "Recycling and Recovery Routes for Incinerated Sewage Sludge Ash (ISSA): A Review". *Waste Manage.* 2013. 33(11): 2328-2340.
5. C. Vogel, C. Adam, P. Kappen, T. Schiller, E. Lipiec, D. McNaughton. "Chemical State of Chromium in Sewage Sludge Ash Based Phosphorus-Fertilizers". *Chemosphere.* 2014. 103: 250-255.
6. A.K. Shanker, C. Cervantes, H. Loza-Tavera, S. Avudainayagam. "Chromium Toxicity in Plants". *Environ. Int.* 2005. 31(5): 739-753.
7. German Fertilizers Ordinance. Ordinance on the Circulation of Fertilizers, Soil Nutrients, Soil Substrates and Plant Protection Substances. *Bundesgesetzblatt.* 2008. Pt. I (60): 2524-2581.
8. L. Gmelin. *Handbuch der anorganischen Chemie, Chrom* [B]. Weinheim (Bergstrasse): Verlag Chemie Germany, 1962. Pp. 42-43, 55-56, 466, 468, 518, 784, 807.
9. I. Arcon, B. Mirtic, A. Kodre. "Determination of Valence States of Chromium in Calcium Chromates by Using X-Ray Absorption Near-Edge Structure (XANES) Spectroscopy". *J. Am. Ceram. Soc.* 1998. 81(1): 222-224.
10. P. Born, K. Holldack, M. Sperl. "Particle Characterization Using THz Spectroscopy". *Granular Matter.* 2014. arXiv:1407.6592.
11. R. Holder, H. Schwarz. "Zur Kenntnis der Erdalkalichromate(V)". *Zeitschrift für anorganische Chemie.* 1963. 326: 11-24.
12. F. Solymosi, I. Nagy. "On the Reactions Occurring in the CaO-Cr₂O₃-O₂ System". *Zeitschrift für anorganische Chemie.* 1970. 378(2): 217-224.