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

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**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 700–25 $cm^{-1}$). 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 °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 °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 µm) 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 850–1000 °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 80–200 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 Ordinance[7] 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 700–25 $cm^{-1}$, 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 20–30 mg were heated at a rate of 10 °C/min from 30 °C to 800/1000/1200 °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
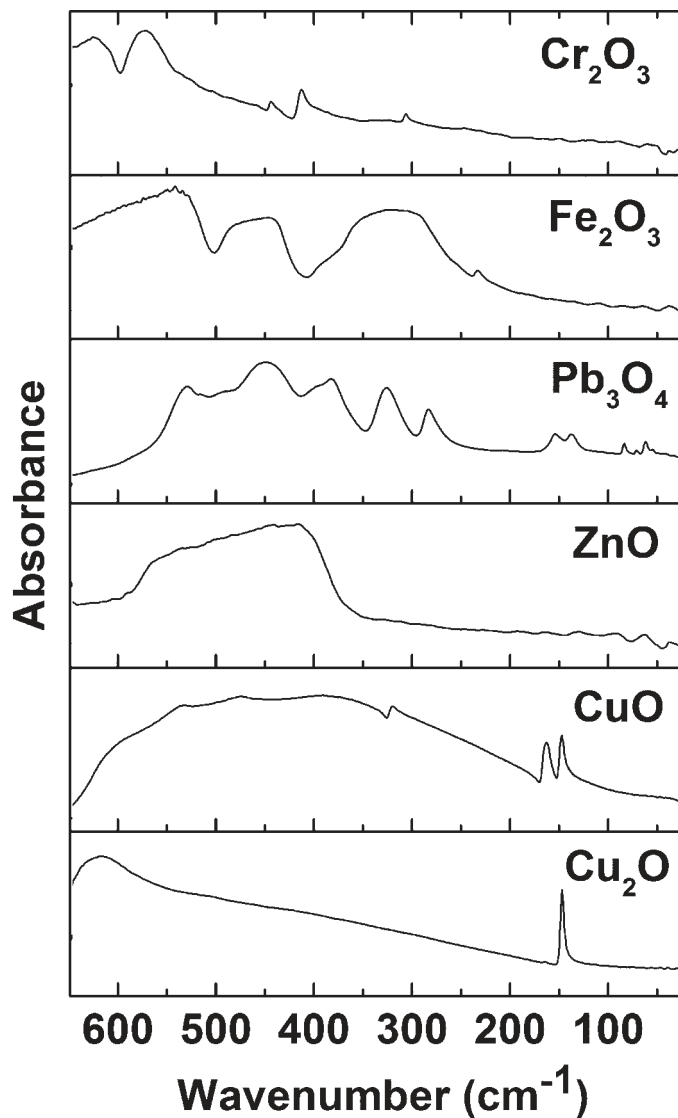
FIG. 1. Far-IR spectra of various metal oxides.



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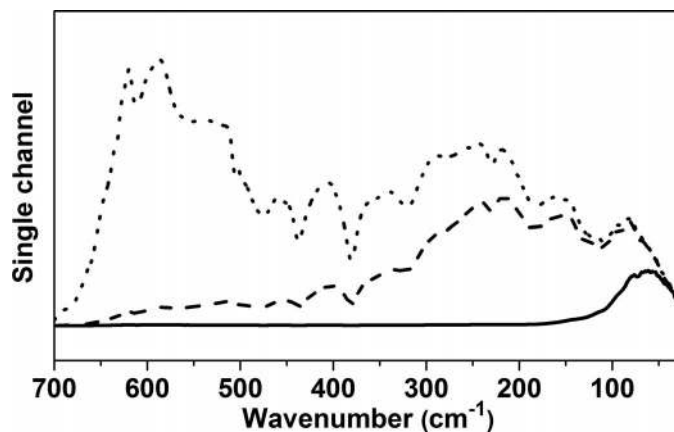
Germany), and potassium carbonate ($K_2CO_3$, J.T. Baker, Deventer, The Netherlands).

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) | $CaCrO_4$, $MgCrO_4$, $Na_2CrO_4$, $K_2CrO_4$ |

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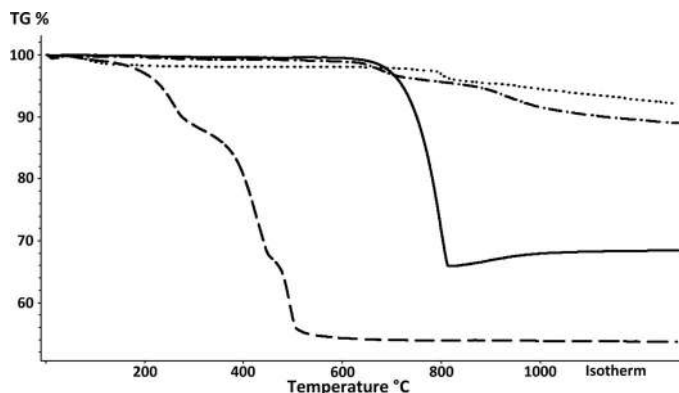
FIG. 3. Thermogravimetry (TG) curves of thermochemical treatment of $Cr_2O_3$ with $MgCO_3$ (dashed line), $CaCO_3$ (solid line), $Na_2CO_3$ (dashed-dotted line), and $K_2CO_3$ (dotted line; atmosphere: air; heating rate: 10 K/min; isotherm segment: 30 min).

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 transparence in the 700–25 $cm^{-1}$ region was found for the PE powder with the lowest average particle size (Micro powders, 4.5 $\mu m$). 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 °C. In contrast, the reactions of $Cr_2O_3$ with $CaCO_3$, $Na_2CO_3$, and $K_2CO_3$ start at approximately 750 °C. Figure 4 shows the far-IR spectra of the reaction products of these thermal
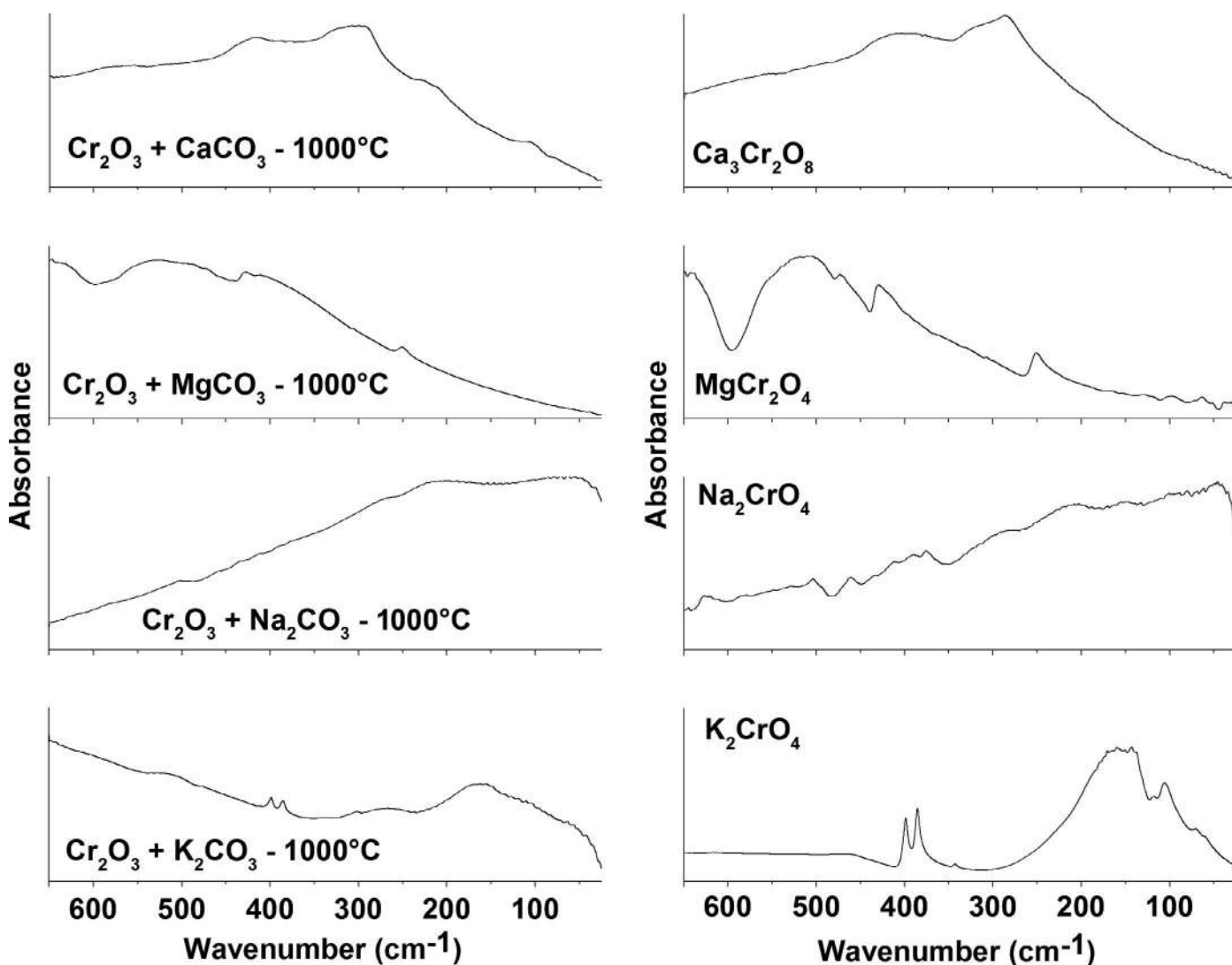


FIG. 4. Far-IR spectra of thermochemically treated $Cr_2O_3$ with $CaCO_3$, $MgCO_3$, $Na_2CO_3$, and $K_2CO_3$ (1000 °C, 30 min isotherm, air atmosphere; left column) and corresponding reference substances (right column).
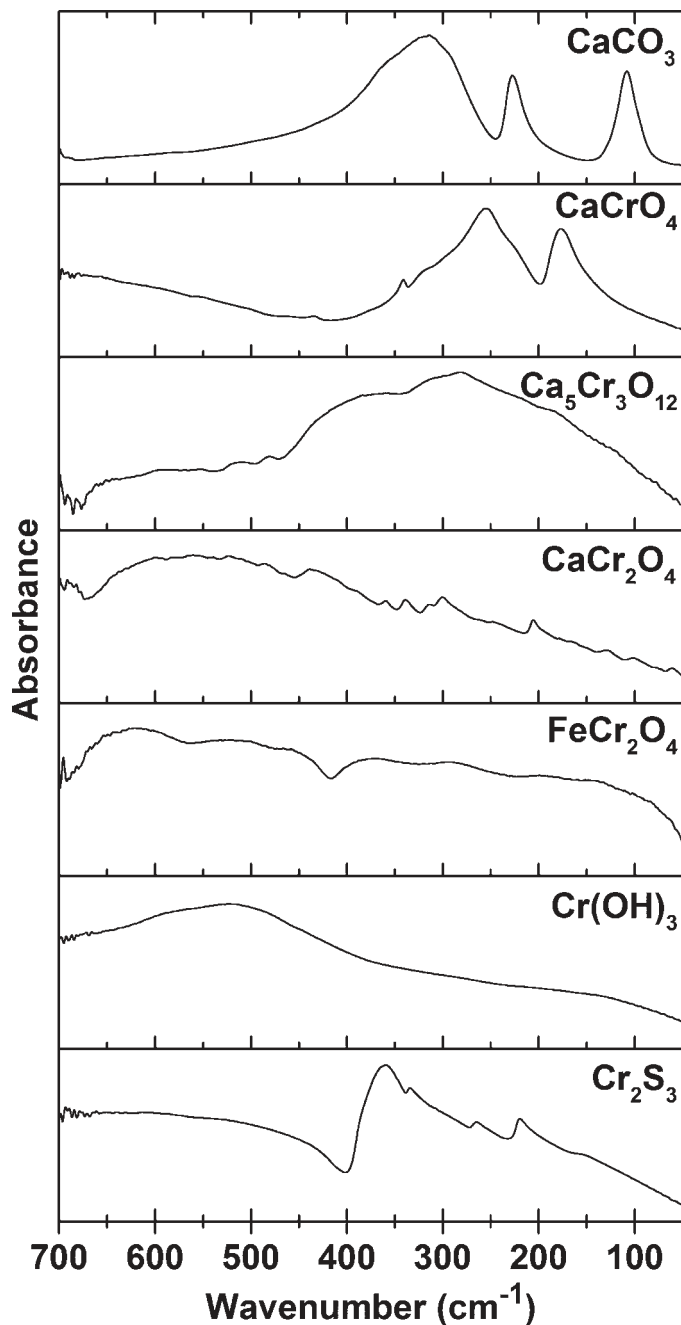
FIG. 5. Far-IR spectra of calcium carbonate and various chromium compounds.

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]
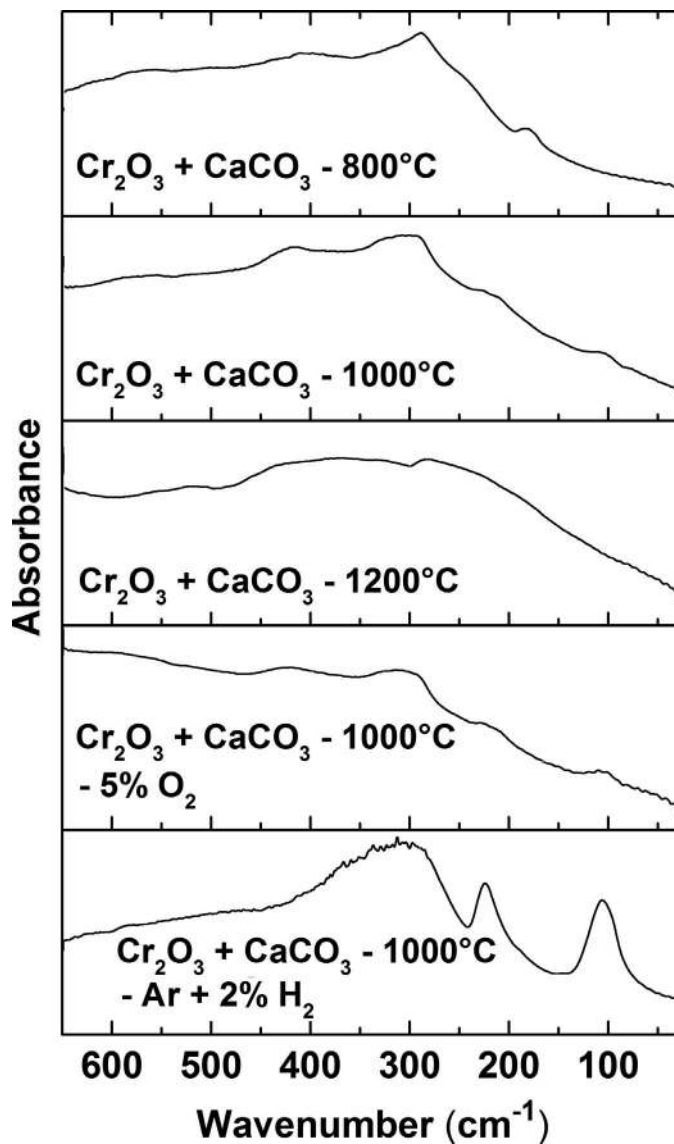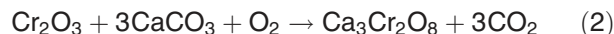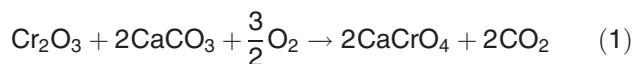


FIG. 6. Far-IR spectra of thermochemically treated $Cr_2O_3$ with $CaCO_3$ at 800, 1000, and 1200 °C (30 min isotherm, air atmosphere; first three from top to bottom) and thermochemically treated $Cr_2O_3$ with $CaCO_3$ at 1000 °C under 5 vol% oxygen and reducing conditions (2% $H_2$ in Ar).

The major product of the thermal treatment of $Cr_2O_3$ with $CaCO_3$ at 1000 °C is the Cr(V) compound $Ca_3Cr_2O_8$ ($=Ca_3(CrO_4)_2$). 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 $Ca_3Cr_2O_8$ 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 Schwarz[11] showed that $Ca_3Cr_2O_8$ 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

$Ca_3Cr_2O_8$. Equations 1 and 2 show the reactions of $Cr_2O_3$ with small and large amounts of $CaCO_3$, respectively.

$$Cr_2O_3 + 2CaCO_3 + \frac{3}{2}O_2 \rightarrow 2CaCrO_4 + 2CO_2 \qquad (1)$$

$$Cr_2O_3 + 3CaCO_3 + O_2 \rightarrow Ca_3Cr_2O_8 + 3CO_2 \qquad (2)$$

The thermal treatment at 1200 °C results in a predominant formation of the Cr(V)/Cr(IV) compound $Ca_5Cr_3O_{12}$ ($=Ca_5(CrO_4)_3$) and some $Ca_3Cr_2O_8$. 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 $Ca_3Cr_2O_8$ was again formed during thermochemical treatment of $Cr_2O_3$ with $CaCO_3$ at 1000 °C (see Fig. 6). In this spectrum, again, some $CaCO_3$ 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 $Cr_2O_3$ and $CaCO_3$ was detectable under reducing conditions. The spectrum shows a mixture of pure $Cr_2O_3$ (weak absorption bands at 626 and 572 $cm^{-1}$) and pure $CaCO_3$ (315, 228, and 110 $cm^{-1}$) bands. In the literature,[8] it is also mentioned that $Cr_2O_3$ 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 $Cr_2O_3$ with $CaCO_3$, $Na_2CO_3$, and $K_2CO_3$, 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 $Cr_2O_3$ with $MgCO_3$ led solely to the formation of the Cr(III) compound $MgCr_2O_4$ because $MgCrO_4$ 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.

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