The formation mechanism and thermal stability of CaCrO$_4$

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Abstract. The Cr(VI)-containing phase CaCrO$_4$ is a typical hexavalent chromium compounds, a huge harm to human and environment. Therefore it is very important to investigate formation mechanism and thermal stability. This paper studies the effect of temperature and atmosphere on the CaCrO$_4$ form, and high temperature stability is studied using XRD and TG-DSC. And CaCrO$_4$ just forms in air atmosphere below 1000 °C. When pure CaCrO$_4$ is heat to 1100 °C, it decomposes to CaCr$_2$O$_4$.

Key words: CaCrO$_4$; Leaching; Cr(VI); Quench

1. Introduction

The increasing contamination urban and industrial wastewaters which contain toxic metal ions cause significant environmental pollution. All over the world, chromium is abundantly available in nature. Chromium is known as a life activity indispensable element which contributes to glucose metabolism and control of serum cholesterol. Unfortunately, hexavalent chromium is hazardous to humans through inhalation, skin contact, and ingestion. Cr(VI) is known to be highly soluble in water, mobile, and easily contaminates soil farmland and groundwater. Cr(VI) compounds have been classified as group A inhalation carcinogens by the US Environmental Protection Agency [1] is ranked as the second most important oxidate (after arsenic) on the CERCLA 2011 Priority List of Hazardous Substances [2]. In nature chromium mainly exists as complex spinel (Fe, Mg)*(Cr, Fe, Al)$_2$O$_4$, in which chromium is present as Cr(III) [3]. But it was reported that some stainless steel dust, cement and refractory which contained chromium, when it’s been heated Cr(III) convert to Cr(VI). Reaction1, the oxidation of Cr(III) to Cr(VI) in the presence of ambient air does not occur as the thermodynamic calculations [4]. And Paoletti hypothesized Cr(III) is oxidized to Cr(VI) in the presence of O$_2$ and CaO [5]. Other researchers pointed out that in the presence of alkali and alkaline earth metals, the oxidation of Cr(III) to Cr(VI) by oxygen was made possible [6-10]. Fig .1 is stability diagram for the formation of Cr(VI)-containing process from Cr$_2$O$_3$ and oxygen it can be seen that the Gibbs free energy change for this reaction in the presence of alkali and alkaline earth metal-oxides Na$_2$O, K$_2$O and CaO is less than zero at temperatures below 792 °C and P$_{O_2}$=0.21atm. CaO was widely used in modern industry. And CaCrO$_4$ was reported exists in the metallurgical [11, 12], refractory [13], chemical [14] and cement industries [15]. Lee and Nassaralla found that chromium in the chromite could be oxidized to CaCrO$_4$ between slag and magnesite-chrome refractory. Mao and Gao reported that CaO can promoted Cr(III) oxidation in the fly ash because Cr(III) reacted with CaO to form a leachable CaCrO$_4$ product.
\[2\text{Cr}_2\text{O}_3 + 3\text{O}_2 \rightarrow 4\text{Cr}_2\text{O}_3\] (1)

The formation and control of CaCrO₄ were reported by many researchers. Bray reported that Cr₂O₃ was oxidized to CaCrO₄ in the presence of lime at temperatures in the vicinity of 800 °C in air [16] and pointed out that CaCrO₄ is unstable in the vicinity of 1100 °C in air which will convert to CaCr₂O₄. Chen and Mao investigated some acid oxide such as SiO₂ and TiO₂ could trigger Cr(VI) to be reduced, and this ability is related to their acidity [17].

Although some researchers have mentioned that CaO facilitates Cr(III) oxidation, the knowledge on the reaction CaO with Cr₂O₃ in the different atmosphere and temperature sintering is insufficient. Hu et al reported thermal treatment of fly ash under atmosphere lack of oxygen like N₂ can well prevent the oxidation of Cr₂O₃[18]. But it didn’t explain the mechanism of this phenomenon. This study investigated the transformation mechanisms of Cr(III) to Cr(VI) in a mixture of CaO and Cr₂O₃ in the air, CO₂ and N₂, respectively. At the same time it’s to investigate the thermal stability of pure CaCrO₄ in the air atmosphere.

2. Experimental

2.1. Experimental procedure

High purity chemicals were employed as raw materials (Sigma-Aldrich, Germany). CaO, powders were pre-treated before using by calcining them at 1000 °C for 8 h in a muffle furnace in order to decompose any hydroxide and carbonate phases present therein. Cr₂O₃ powder was heat-treated at 110 °C for 8 h in order to remove any moisture. The CaO and Cr₂O₃ were mixed with the mole ratio of 2:1. The oxides were weighed in appropriate proportions and thoroughly mixed in a tungsten carbide mill and agate mortar. A part of this fine powder is given for high temperature XRD and TG-DSC. Then others were pressed into pellets, 15mm in diameter. These pellets were subsequently reacted in a MoSi₂-heated tube furnace in air, CO₂ and N₂ atmosphere. Each sample was placed on platinum crucible in the centre of the furnace where the temperature variation was less than ±1 °C. The samples were sintered at 850 °C for 2 h in air, CO₂ and N₂ atmosphere, and afterward allowed to cool in furnace. In order to determine the chromium phase at different temperature, the sample was sintered by placing it in a MoSi₂-heated tube furnace and heated from room temperature to the target temperature (between 400 °C and 1200 °C), then maintaining this temperature for 2h. After the sintering process had been performed, the samples were removed and quenched by Helium gas blowing.

In order to study thermal stability of CaCrO₄, pure hexavalent chromium compounds of CaCrO₄ was synthesized by mixing high purity CaO and Cr₂O₃ (molar ratio of 2:1), pressed the mixture into a pellet, and sintering at 850 °C for 8 h in air. The samples were ground into powder, re-pelletized and sintered again. This process was repeated for two times more.

2.2. Analysis

The thermal behavior of pure CaO and Cr₂O₃ mixture in air was characterized and the change of solid mass on heating determined by TG-DSC (STA449C instrument; Netzsch, Germany) with a linear heating rate of 5 °C/min, 10 °C/min and 20 °C/min from room temperature to 1200 °C. The phase transformation of different compositions sample was monitored by XRD using a Bruker X'Pert Pro powder diffractometer with X'Celerator detector and with Cu Kα X-radiation, with 20 scans collected from 10° to 90°. Phase identification was done using PANalytical X'Pert Highscore plus software.

The leachability of Cr(VI) was determined according to the TRGS 613 standard method (Technische Regeln für Gefahrstoffe-TRGS 613-October 2002). Samples of 2.00 g were weighed into bottles and suspended in 40 ml of distilled water, vigorously stirred for 15 minutes with a magnetic stirrer (stirrer bar 40 mm, 300 rpm) and then filtered through 0.45 µm membrane filters. The Cr(VI) content in the leachate was determined with 1,5-diphenycarbazide method.
3. Results and Discussion

3.1. Effect of temperature on the formation of CaCrO$_4$

X-ray diffraction patterns of quenched samples (CaO and Cr$_2$O$_3$) were shown in Fig. 1. At 400 °C, 600 °C and 800 °C, large amount of Cr(VI)-containing phase CaCrO$_4$ formed. And it was clear that when it was heated to 1000 °C, CaCrO$_4$ decomposed to form Ca$_3$(CrO$_4$)$_2$ in which the valence of chromium is +5 and CaCr$_2$O$_4$ (Eq. 2). According to Eq. 2, 50% of chromium was transformed into CaCr$_2$O$_4$ in the decomposition of CaCrO$_4$. When the temperature further increased to 1200 °C, the peak for new chromium compound (Ca$_3$Cr$_2$O$_7$)$_2$ was observed in which the valence of chromium is +4 and +5. The characteristic peak intensity of CaCrO$_4$ increases with the rise of room temperature to 800 °C, while intensity of CaCrO$_4$ decreases from 800 °C to 1200 °C.

$$4\text{CaCrO}_4 \rightarrow \text{Ca}_3(\text{CrO}_4)_2 + \text{CaCr}_2\text{O}_4 + 2\text{O}_2 \quad (2)$$

Alternatively, the formation of CaCr$_2$O$_4$ might occur through direct interaction between CaO and Cr$_2$O$_3$. From TG-DSC curves (Fig.2) shows that around 850 °C it has one exothermic peak and means have a combination reaction occurred around this temperature which was in good agreement with the theoretical prediction according to the reaction CaO+0.5Cr$_2$O$_3$+0.75O$_2$→CaCrO$_4$ reported by Kirk et al. It is also found that the reaction started at about 600 °C and the reaction becomes more rapid at temperature of 850 °C. And around 1080 °C, it has one endothermic peak that means decomposition reaction occurred. The concentration of Cr(VI) after leaching is shown in Fig.3. The amount of Cr(VI) increases when the heating temperature was less than 1000 °C. But with temperature increasing, Cr(VI) concentration decreased. From leaching and phase diagram most Cr(VI) formed at 800 °C. And the XRD analysis and DSC consistent to the leaching results.

Figure 1. XRD patterns of the different temperature quenched samples
3.2. Effect of atmosphere on CaCrO₄ formation

The XRD patterns of samples reacted in different atmosphere are shown respectively in Fig. 4. The main phase that formed in air is CaCrO₄ and still had some Cr₂O₃. But in N₂ and CO₂ the peak of CaCrO₄ wasn’t detected. And the Cr(III) compound CaCr₂O₄ also didn’t detected because . The peak of Ca(OH)₂ maybe CaO reacted with H₂O in air, because it took a long time to wait for XRD analysis, and the powders of samples were not kept in a desiccator. Leaching and XRD present similar phenomenon that Cr(III) can be oxidized to Cr(VI) only in air when the mixture been heated to 850 °C. The concentration of Cr(VI) in leach liquor from different thermal treated sample, namely thermal treated samples in air, CO₂ and N₂, is shown in Fig. 5. It was found that large amount of Cr(VI) was leached out when the mixture heated in air, but almost no Cr(VI) was leached out when samples were thermal treated in N₂ or CO₂ atmosphere.
3.3. Thermal stability of CaCrO$_4$

In order to better understand the thermal stability of CaCrO$_4$, pure CaCrO$_4$ was successfully synthesized. The XRD analysis confirmed it (Fig. 6).

Then the pure CaCrO$_4$ was ground into fine powder and pressed slice, soaked for 1 h at 1000 °C, 1100 °C, 1200 °C, and 1300 °C, respectively, quenched by Helium gas blowing. The colors of the samples after quenched are shown in Fig. 7. It is well known that Cr(III) oxides are dark green, Cr(VI) oxides are yellow. So it can therefore be deduced that the Cr(VI) compound formed at 1000 °C and the Cr(III) compound formed at 1100 °C, 1200 °C, and 1300 °C.

The XRD patterns of quenched samples were shown in Fig. 8. It can see that CaCrO$_4$ is stable below 1100 °C. When it was heated further, it decomposed to β-CaCrO$_4$ and δ-CaCrO$_4$ from 1100 to 1300 °C. The δ-CaCrO$_4$ decreased with the temperature increasing, while the β-CaCrO$_4$ increased with the temperature increasing. CaCr$_2$O$_4$ crystals are crystallographically divided into the high-temperature (α), low-temperature β form and metastable (δ) forms.
Figure 8. XRD pattern of the quenched pure CaCrO$_4$ heated in air.

Peaks and troughs on the TG-DSC represent endothermic/exothermic changes during heating (Fig. 9). At 1059.88 °C, peak (1) implies some reaction occurred of CaCrO$_4$ which converted to CaCr$_2$O$_4$ according to Eq (1). The mass loss ratio of peak (1) is 4.97%. Peak (2) maybe it has a liquid phase. It was consistent to the XRD analysis.

Figure 9. TG and DSC curves of pure CaCrO$_4$ heated in air.

4. Conclusion
1. The large amount CaCrO$_4$ formed below 800 °C, and there are some Cr(V) and Cr(IV) formed from 800 °C to 1200 °C.
2. CaCrO$_4$ just formed in air atmosphere, and I can not form in N$_2$ and CO$_2$ atmosphere.
3. The pure CaCrO$_4$ was stable below 1000 °C, when it was heat more than 1100 °C, it will decomposed to CaCrO$_4$. Its crystals structure are divided into three forms with different temperature, the high-temperature ($\alpha$), low-temperature $\beta$ form and metastable ($\delta$) forms.

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