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Further Insight into the Formation and Oxidation of $CaCr_2O_4$ during Solid Fuel Combustion

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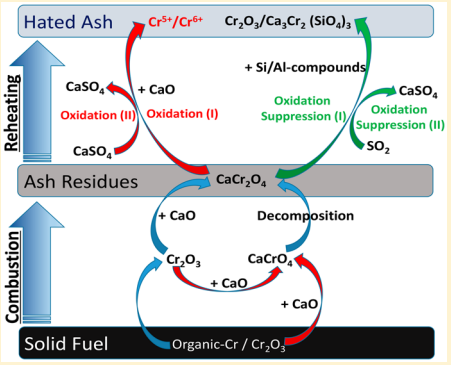
Supporting Information

ABSTRACT: The control of toxic chromate (Cr^{6+}) formation is still a significant challenge in solid fuel combustion. In particular, the mechanism of chromium transformation from Cr^{3+} to chromate or other unoxidized forms remains unclear. The present study confirms the formation of a significant unoxidized Cr-containing compound $CaCr_2O_4$(Cr^{3+}) during solid fuel combustion. Experiments were conducted, for the first time, to clarify the mechanism of $CaCr_2O_4$ oxidation, which is quite different from Cr_2O_3 oxidation. The findings demonstrate that $CaCr_2O_4$ was formed at temperatures above 1200 K, through rapid decomposition of $CaCrO_4$ or slow and direct interaction between CaO and Cr_2O_3. Compared to Cr_2O_3, $CaCr_2O_4$ could be oxidized at lower temperatures under the influence of free CaO. In the absence of free CaO, the oxidation of $CaCr_2O_4$ was minimal; however, in the presence of $CaSO_4$, calcium in the form of $CaCr_2O_4$ participated in the oxidation of $CaCr_2O_4$. Thus, chromium in the form of $CaCr_2O_4$ was more likely to be oxidized when $CaCr_2O_4$-containing fly ash was reheated. Fortunately, $CaCr_2O_4$ showed slight basicity on the surface, allowing it to react with acidic gases. Accordingly, measures were proposed to suppress the oxidation of $CaCr_2O_4$ by stimulating the reactions between $CaCr_2O_4$ and acidic substances, like SO_2 and Si/Al-compounds. These compounds competed with chromium at high temperatures to react with calcium in the fly ash and in $CaCr_2O_4$. As a result, the unoxidized chromium was transformed into highly stable Cr_2O_3 or $Ca_3Cr_2(SiO_4)_3$.



INTRODUCTION

Chromium is widely distributed in coal, municipal solid waste, sewage sludge, and other solid fuels.[1,2] In China, a large amount of chromium is released within flue gas into the atmosphere during solid fuel combustion,[3] which is a great threat to human health. Even so, most of the chromium is transferred into ash residues, predominantly as trivalent chromium (Cr^{3+}).[2] More importantly, trivalent chromium can partly oxidize to form more toxic hexavalent chromium (Cr^{6+}), which is classified as a group A inhalation carcinogen.[4] Compared with Cr^{3+}, Cr^{6+} is more easily leached from ash residues, leading to serious water and/or soil pollution.[5] Therefore, a series of stringent policies were implemented by the Chinese government for emission control of Cr^{6+}.[6]

Generally, the predominant form of chromium in solid fuels is Cr^{3+}, and it is difficult to oxidize during fuel combustion.[7,8] However, a large fraction of Cr^{6+} was found in the fly ash during the combustion of solid fuels that contained high contents of alkali and/or alkaline earth metal compounds.[1,9] Among these substances, CaO is confirmed to facilitate Cr^{3+} oxidation over a wide temperature range.[10,11] Conversely, CaO is widely used as a sorbent for the capture of acid gases, such as SO_2, and toxic trace elements, such as As_2O_3, from flue gas.[12,13] CaO is also commonly used as a conditioner for dewatering of sewage sludge.[14] Because of its prevalence and ubiquitous use, CaO is frequently introduced into solid fuels, and it is essential to understand the oxidation of Cr^{3+} in the presence of CaO.

To date, several studies have been conducted to understand the mechanisms involved in Cr^{3+} oxidation in the presence of CaO. The oxidation of Cr^{3+} was found to be a slow process, and most chromium still existed as Cr^{3+} in the ash produced in the combustion of coal and waste sludge.[8,11] Nevertheless, the unoxidized Cr^{3+} may transfer into various species,[5,15] and to our knowledge, few studies have distinguished these unoxidized species or examined their potential oxidizing capacity. When ash residues containing unoxidized Cr^{3+} are reheated at high temperature, the oxidation of unoxidized Cr^{3+} compounds likely determines the Cr^{6+} concentration in the products, such as in the case of fuel combustion in a circulating fluidized bed or in the case of ash thermal treatment for the production of building materials.

Our previous study found that $CaCr_2O_4$ was an important intermediate in chromium oxidation in the presence of CaO.[16]

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