



The catalytic effect of iron oxides on the formation of nano-carbon by the Boudouard reaction in refractories



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ABSTRACT

The catalytic decomposition of carbon monoxide via the Boudouard reaction in the presence of iron has been a subject of numerous studies. This reaction produces a solid carbon deposit in which CO is a reactant and results in deleterious effects on refractory materials. Only a few studies have used a gas mixture primarily composed of CO + H₂, which is generated in new energy applications. We investigated the effect of the degree of oxidation and the grain size of the Fe_xO_y catalyst particles on the amount of carbon, in CO + H₂, using thermogravimetric analysis and Raman-spectroscopy as well as scanning and transmission electron microscopy. All of the Fe_xO_y resulted in similar carbon formation. The effect of the grain size and specific surface particles was demonstrated, in particular due to the large decrease in the catalyst particle size. This study could be helpful for the future development of new refractories materials in reducing conditions.

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1. Introduction

The mechanism of iron catalysis of carbon monoxide (CO) decomposition, which results in the deposition of solid carbon, called the Boudouard reaction ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}_{(\text{solid})}$), has been studied for long time [1]. Refractory materials are very affected by this reaction because of the presence of iron particles in raw materials. This leads to a drastic damaging of high alumina refractories. The CO resistance is usually improved by the selection of raw materials with low content of iron particles and by the increase of refractory sintering temperature. However, these solutions are not quite effective for new applications in which refractories are subjected to CO and H₂ gas mixture which are generated in biomass and coal gasification applications. The mechanisms of iron catalysis with this type of mixture are not really demonstrated and understood. In this study, the mixture consists of the following gas composition: 71% CO, 3% CO₂, 11% H₂ and 15% N₂, very closed to that used in industrial processes.

Catalytic decomposition of CO into CO₂ and solid carbon (C) was first described in the early part of the 20th century by Boudouard [1]. This reaction produces solid carbon deposition in

many industrial processes, which eventually leads to the destruction of building stone and industrial materials. This reaction is associated with small amounts of iron oxides that are localised in the cracks and grains boundary of materials as well as in the pores. As early as 1903, Schenk et al. demonstrated that the formation of solid carbon from carbon monoxide was catalysed by the presence of metallic iron and to lesser extent by iron oxides. The carbon deposition in 100% CO appears to be completely controlled by the Boudouard reaction, and the rate of carbon deposition is proportional to the amount of iron catalyst present in the system. Numerous studies of carbon deposition in 100% CO were reported (e.g. Ref. [2]), however no recent study of this phenomenon using a gas mixture with hydrogen are available in the literature. The introduction of H₂ to the CO gas significantly increased the reaction. For example, Walker et al. [3] reported the deposition of 10 grams of solid carbon after ≈350 min over 0.10 g of carbonyl iron in a 9%-H₂-91% CO gas mixture at 602 °C. Fig. 1 illustrates this phenomenon where a few grams of Fe₂O₃ result in a large amount of solid carbon, which is similar to “popcorn” formation, when it is subjected to a gas mixture consisting of 71% CO, 3% CO₂, 11% H₂ and 15% N₂, for 5 h at 600 °C under atmospheric pressure.

The rate of carbon formation using an iron catalyst in a CO–H₂ mixture from the Boudouard reaction is significant in a temperature range of 400 to 750 °C, and the maximum rate occurs at 500–600 °C [3]. However, the addition of H₂ to the CO gas favours the production of solid carbon [4], and the maximum rate occurs at 500–600 °C for a gas mixture composed of 25% H₂ and 75% CO [5]. During this

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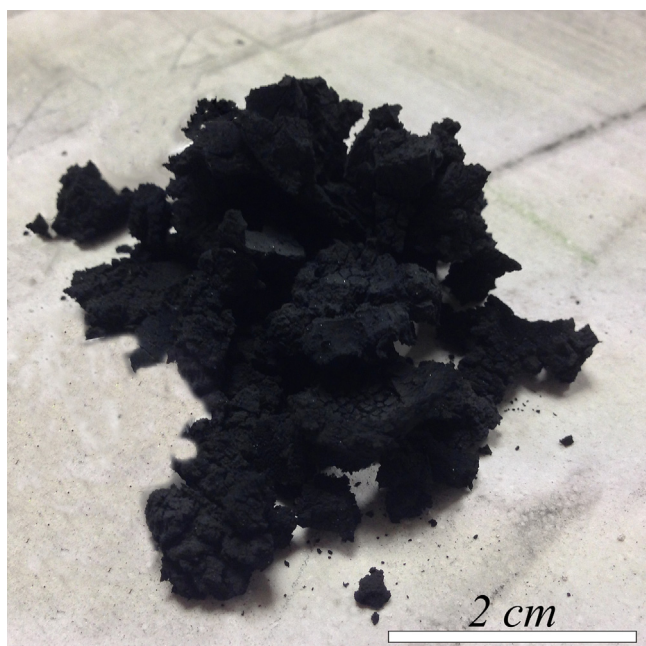
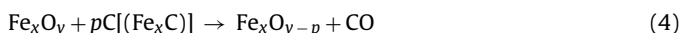
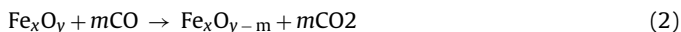


Fig. 1. Carbon deposition on a Fe₂O₃ sample after exposure to a gas mixture consisting of 71% CO, 3% CO₂, 11% H₂ and 15% N₂ for 5 h at 600 °C under atmospheric pressure.

reaction, the iron particles appear to transform into different iron carbides, such as Fe₃C (cementite) and Fe₇C₃ [4] and references therein. When the entire catalyst was converted to iron carbide, no further carbon deposition occurred [4]. Despite the complexity of these mechanisms, the main reaction can be summarised by the following equations [5]:



It is important to note that Reactions (1), (2) and (4) would lead to a weight loss, and reaction (3) results in a large increase in the solid carbon weight.

Based on only the Boudouard reaction (3), the resulting solid carbon is assumed to be structurally less organised (i.e., “black carbon”). However, the carbon material formed from iron catalysts in a H₂–CO mixture is relatively well ordered [3]. The three main families of carbon include (1) filamentous carbon, which is the most frequently encountered, (2) carbon in platelet, disk and column form and (3) flocculent carbon, which is the most typical form [6] and references therein. Krause and Pötschke [2] reported other carbon morphologies including “bucky onions” and “carbon nanotubes”. This type of carbon deposition has also been observed in metal dusting processes on a Fe or Ni base and causes catastrophic corrosion on metallic materials (e.g., Refs. [7–10]).

Although the catalytic decomposition of CO into solid carbon is well known and industrially adapted for the preservation of refractory material, the effects of the initial characteristics of the iron catalyst (e.g., size and oxidation degree) have not been investigated in CO + H₂ atmosphere. A fundamental laboratory study was initiated to investigate the effect of the iron oxide valence (i.e., oxidation degree: Fe, FeO, Fe₃O₄ and Fe₂O₃) and grain size (nanometre to millimetre size) on the carbon deposition amount in a CO + H₂ gas mixture. The behaviour of iron oxide particles was studied on the micrometre scale in the carbon deposit experiments. The evolution

Table 1

Origin and characteristics of the samples.

Material	Origin	Grain size (μm)	Specific surface (m ² /g)	Purity (%)
Fe	Sigma	2–5	2.0	> 99
FeO	Sigma	2–5	6.0	99.9
Fe ₃ O ₄	LKAB	2–5	2.0	> 99
Fe ₂ O ₃	Sigma	2–5 ^a	8.0	> 99
Fe ₂ O ₃	Sigma	0.0035 ^a	42.0	> 99
Fe ₂ O ₃	Carajas ^b	160–250	10.5	> 98
Fe ₂ O ₃	Carajas ^b	1000–2000	3.7	> 98

of the size of the catalyst particles during the experiment was investigated. The microscopic morphology of the produced carbon was determined and interpreted through the catalysis reaction. Finally, the carbon formation mechanism in a CO + H₂ gas mixture on the micrometre scale has been proposed.

2. Materials and methods

2.1. Materials

Pure iron (Fe) and iron oxides (FeO, Fe₂O₃ and Fe₃O₄) powders with different grain sizes (nm to mm scale) were used. The Fe, FeO and Fe₂O₃ particles were purchased from Sigma Aldrich Company, and Fe₃O₄ was obtained from LKAB Company with a purity of more than 99%. As reported in Table 1, the grain sizes of some of these samples were provided by the company, and the remaining samples were crushed and then separated to obtain their grain sizes. To complete the sample selection, two Fe₂O₃ samples from Carajas iron ore with a purity of approximately 98% (traces of Fe²⁺ were also observed) were used. The initial specific surface area was determined from the N₂ adsorption isotherms at 77 K in a relative pressure (P/P₀) range of 10^{−6} to 1 atm (Autosorb-1MP, Quantachrome) by applying the BET equation.

2.2. Methods

Microscopic measurements were performed using a thermobalance from NETZSCH STA 409C/CD. The prepared samples were placed in an alumina crucible, and these samples were then heated to 600 °C under a N₂ atmosphere at a rate of 5 °C/min prior to being exposed to the gas mixture (i.e., 71% CO, 3% CO₂, 11% H₂ and 15% N₂) that was similar to that used in industrial processes. For all the experiments, the gas flows were approximately 4.2 l/h over 5 h at 600 °C under atmospheric pressure. The carbon deposition was observed at approximately 600 °C in agreement with literature [1,3]. Gas composition is controlled using needle valves and manifolds, with high precision. Gases are provided by industrial specialist with a high purity (<99%). And no further purification was performed except a purge before each experiment. The reproducibility of the instrument, given by NETZSCH, is at +/- 0.1%.

After cooling, the samples were characterised using various methods. The crystalline phases were determined by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer (Cu Kα_{1,2} radiation, 40 kV, and 30 mA) equipped with a Lynx Eye detector enabling a significant decrease of the fluorescence effect. Each scan was recorded in a 2θ range from 20 to 70° with a step size of 0.016 at 10 s per step. The structural organisation of the formed carbon was determined by Raman spectroscopy using an InVia Reflex Renishaw spectrometer. A green laser beam (514.5 nm wavelength and ≈1 mW output power) was focused on the material through a 50× microscope objective. The Raman scattered light was collected by a holographic grating with 1800 grooves per mm and detected by a charge coupled device (CCD) camera. The samples were also observed with transmission electron microscopy (TEM) using a Philips CM20/STEM with a Lacey grid preparation. Finally, pol-

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