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Reduction kinetics of cobalt oxide powder by methane in a fluidized bed reactor

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ABSTRACT

In the present work, cobalt oxide in powder form with an average particle size of 100 μm has been reduced by methane used as a reducing agent in a batch fluidized bed reactor. The reaction was carried out in the temperature range of 800–950 °C with mole fractions of methane at the values of 0.15, 0.3 and 0.5. Argon was used as a fluidizing gas with a velocity of 1.3 times the minimum fluidization velocity. Approximately 4 g of cobalt oxide powder has been used in a laboratory scale fluidized bed reactor with 18-mm inner diameter and 1.1 m length. The ratio of the bed height to the bed diameter, after fluidization, was approximated near unity. The chemical reaction kinetics has been found as the rate limiting step under the experimental conditions used. The activation energy and the order of reaction have been calculated as 120 kJ/mol and 0.9, respectively, on the basis of the shrinking unreacted core model.

1. Introduction

Cobalt is an important metal with diverse industrial and military applications. Its largest usage is in super-alloys, which are used primarily to make parts for aircraft gas turbine engines [1]. Cobalt is also an important component of steel when high strength is required, as it increases the tempering resistance of steel. High-strength steels are used in the aerospace, machine tool and marine equipment industry. Cobalt is also used to make magnets, corrosion- and wear-resistant alloys, high-speed steels, hard-metal and cobalt–diamond tools, cobalt discs and other cutting and grinding tools, catalysts for the petroleum and chemical industries, pigments, battery electrodes, airbags in automobiles and magnetic recording media [1]. The cemented carbides are materials in which metallic carbides are bound together or cemented by a soft and ductile metal binder, usually cobalt or nickel. One of the most important applications of cobalt powder is use as a binder for producing hard metals. The mechanical properties of hard alloys are optimized mainly by controlling the grain size and the uniformity of distribution of the components in the solid-phase mixture [2].

Cobalt is recovered from concentrates and occasionally directly from the ore itself by hydrometallurgical, pyrometallurgical and electrometallurgical processes. Cobalt powder can be produced by a number of methods, but those of industrial importance involve the reduction of oxides, the pyrolysis of carboxylates, and the reduction of cobalt ions in aqueous solution with hydrogen under pressure [1]. Use of methane instead of carbon as a reducing agent can help decrease the operating temperature and diminish the emission of greenhouse gases and other pollutants such as heavy metals, sulfur dioxide and fly ash in extractive metallurgy [3–5]. Reduction with methane is applied for metal and metal carbide production from oxide compounds. The advantages of this method include shorter times and lower temperatures for cobalt formation than other methods [6]. The raw materials are inexpensive and do not need any post-treatment for separation and refinement, in comparison with other cobalt production methods. A major disadvantage of using methane is related to carbon deposition arising from cracking of methane. Carbon deposition has a deleterious effect on the reduction reactions because of blocking of the interior porous structure of the solid causing decrease in the overall reaction rate [3,4].

Methane has been reported as an effective reducing agent by Ghosh et al. [7] for iron oxide, Khoshandam et al. for chromium oxide [8], manganese oxide [9] and cobalt oxide [10], by Anacleto and Ostrovski for chromium oxide [11], Ale-Ebrahim and Jamshidi [12] for zinc oxide, Alizadeh et al. [13] for nickel oxide, Takeuchi et al. [14] for wustite and Ostrovski and Zhang for iron ore and manganese, chromium and titanium oxides [15].

According to Khoshandam et al. [10] studies, the cobalt oxide powder, Co_3O_4, was reduced to CoO, at first, without any reducing agent and then to metallic cobalt with methane. Tucakovic et al. studied the kinetics of cobalt oxide reduction with hydrogen [16]. They used three different particle sizes of 9, 17 and 31 nm which gave rise to different reaction orders and therefore different activation energies.

A relatively low reaction temperature and a small initial precursor particle size are preferred for the production of nano-structured

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powders. In this respect, a fluidized-bed reactor can be an attractive alternative [17]. Fluidized bed reactors have widespread applications in the chemical and metallurgical industries [18,19]. There are several advantages of fluidized bed reactors: non agglomeration of the particles, excellent mass and heat transfer, temperature uniformity through the bed, excellent thermal efficiency and low investment costs [20,21].

Evans et al. [22] studied the kinetics of nickel oxide reduction in a batch fluidized bed laboratory reactor for measuring the rates of gas solid reactions. On the laboratory scale, Srinivasan and Sheasby [23] have studied the hydrogen reduction of hematite to magnetite in a fluidized bed. Srinivasan and Steffansson [24] studied the iron ore reduction by gases containing CO and H_2 in a fluidized bed reactor, from a theoretical point of view. They developed a kinetic model for the reduction process. Doherty et al. [25] have studied the hematite reduction to wustite by considering different mixtures of $CO–CO_2$, $H_2–H_2O$, and $CO–CO_2–H_2–H_2O$ in a small fluidized bed which has been operated under bubbling bed conditions. Maroufi et al. [26] presented a mathematical modeling based on the grain model for non-catalytic gas–solid reactions in fluidized bed reactors. Gomez-Barea et al. [27] presented a simplified model for non-catalytic gas–solid reactions in fluidized bed reactors. However their model that is defined based on catalytic gas–solid reaction models, can be used for different types of non-catalytic gas–solid reactions. Morales et al. [17] studied the kinetics of reduction of Fe_2MoO_4 with hydrogen in a laboratory fluidized bed reactor. They reported that using fluidized bed reactor operating at a lower temperature and just above the minimum fluidization velocity has been found to be acceptable in obtaining nano scale-sized particles of Fe_2Mo. Ahmed et al. [28] studied the kinetics of $NiO–WO_3$ precursors with hydrogen in a fluidized bed reactor operating at just above the minimum fluidization velocity. They suggested that the process conditions would have impact on the particle size of the product.

In the present work, reduction of cobalt oxide with methane has been studied in a fluidized bed reactor and the kinetic parameters have been evaluated after measuring the gas–solid reaction rates. The activation energy and order of reaction have been calculated in this study that can be applied in reactor design contains nano-scale size particles.

2. Experimental

2.1. Materials

The cobalt oxide as Co_3O_4 powder (Merck, mean particle size 10.6 μm, 98.8% purity) has been used as the precursor material. Good fluidizing could not be achieved because of this very dusty starting powder. For increasing the size of cobalt oxide powder, the starting materials were compacted into cylindrical pellets of 3 cm and 2 cm in diameter and height, respectively. The pellets were placed on a ceramic plate and then heated to 700 °C in a batch furnace (Exciton Furnace) and kept at this temperature for 45 min. After cooling the pellets to ambient temperature, the samples crushed easily and were meshed to 100 μm. The composition of the powder prepared by this method was examined by X-ray diffraction. The XRD analysis is shown in Fig. 1 which corresponds well to Co_3O_4 phase. Methane was used as the reactant gas through the fluidized-bed reactor, while argon was employed during the heating and cooling steps (both gases: plus grade, and maximum 10 ppm impurities). In practice, a mixture of methane and argon has been used to achieve the metallic cobalt by reduction of CoO.

2.2. Apparatus

A schematic diagram of the fluidized-bed reactor used in the experiments is shown in Fig. 2. The reactor consists of a quartz tube,

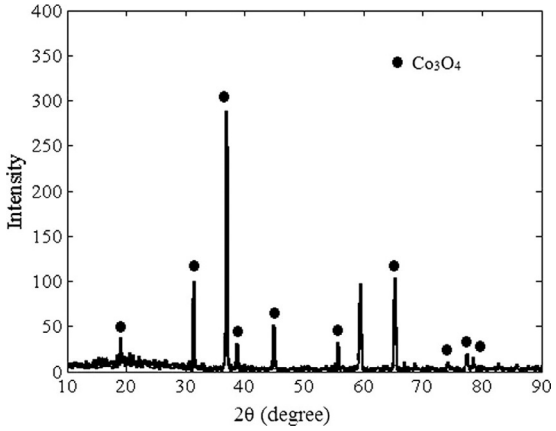

Fig. 1. XRD pattern of the initial fluidizing powders revealing Co_3O_4 phase.

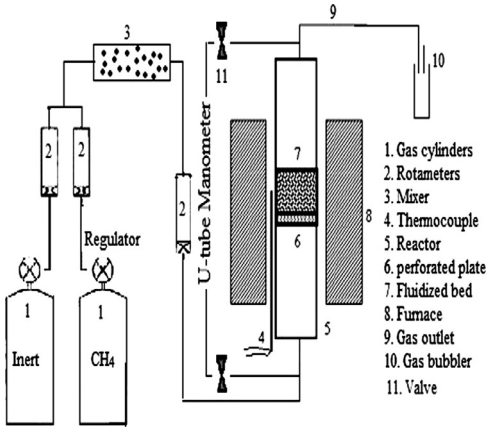

Fig. 2. A schematic diagram of the experimental setup.

18-mm i.d. and 1.1 m long, was vertically positioned in the temperature-controlled vertical tube furnace (Azar Furnaces, Iran). The gas distributor was a 3-mm-thick perforated quartz plate contains 21 perforations (average size of 1 mm–totally 6% open access). The quartz tube was placed in such a way that the distributor plate was at a level of about 3 cm below the center of the furnace temperature zone. The fluidized-bed temperature was measured by a k-type thermocouple. Rotameters suitable to the ranges of the gas flow rates which calibrated prior to the experiments were used to measure the flow rates of the gases before entering the reactor through the bottom. Also a glassy tube contains several ceramic grains was used for mixing two gases as well, before the methane containing gas enters the reactor. The flow rate of the outlet gas stream leaves the mixer was measured by another rotameter (to check the summation of methane and argon flow rates). The outlet gas stream leaves the system from the top and through a bubbler for slight oxygen presence prevention in the reactor. Also a balance system with a detection limit of 1 mg was used for measuring the samples weight at the beginning and periodic times through the course of reaction.

2.3. Procedure

To ensure a good fluidization, the minimum fluidization velocity (U_{mf}) was approximated experimentally by measuring the pressure drop through the powder bed at room temperature. The total pressure drops in the reactor with and without the powder beds were measured independently to determine the net pressure drop in the powder bed. The pressure drops across the bed were measured using a U-tube manometer at each flow rate. The difference between the two pressure drops ($P_{d\,(\text{with powder bed})} - P_{d\,(\text{empty reactor})}$) was taken as