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Review

Isothermal reduction process and kinetic of nanomaterials in reducing atmosphere: A review

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ABSTRACT

The Isothermal reduction processes of nanomaterials received considerable attention because the reduction reaction considers one of the most important routes in the production of nanoally and magnetic nanomaterials. In view of this; thermal reduction processes of nano-size metal oxide or metal ferrite in reducing atmosphere has been reviewed. The rate and way of reduction reaction depend mainly on various parameters such as reduction temperature, flow rate and composition of reducing gas, preparation conditions, crystal size, morphology and composition of the reduced materials…etc. In all reduction process, the reduction rate increase with increasing reduction temperature, but a complete reduction process (100%) was limited and controlled. The literatures showed that; the reduction process can follow either by weight loss or conductivity techniques.

The kinetic and activation energy of reduction process was also discussed in details. The reduction processes were controlled by various mechanisms and it was obtained that; single reduction process can proceed through more than one mechanism. The type of controlled mechanism depends on the values of apparent activation energy (Ea), these values were found to be affected by different parameters such as preparation and reduction temperature. The validity of controlling mechanism deduced from activation energy values was confirmed via different mathematical models.

1. Introduction

1.1. Nano-metal ferrites and their important

The term ferrite is used to describe a class of ceramic sintered compounds that have combined electric and magnetic properties. Ferrites consist of two components, iron oxide as an essential part and one or more metal oxides to give the required characteristic properties of the prepared materials. In addition to that; ferrites consider semiconductor magnetic materials with great technological importance due to their interesting electrical and magnetic properties. The feasible utilize of ferrite and its study of structural, electrical and magnetic properties has started in the year 1930, then ferrites are extensively studied by many researchers [1].

Ferrites have continued to receive considerable attention over the years due to their unique characteristic properties and a wide range of applications in numerous areas [2]. They are approximately inexpensive, high-quality filters, stable and have a wide range of technological applications in transformer core, high-frequency circuits and operating devices [2–4]. Moreover, ferrite shows high electrical resistivity, high saturation magnetization, high permeability, moderate permittivity, low eddy current and dielectric losses. In addition to their permanent magnet applications, ferrites have greater heat corrosion resistance [5]. Due to the magnetic and semiconducting properties of ferrites they can be used in various applications such as; antenna rods, magneto-optical devices, memory chips, high-density magnetic recording media, transducers, activators, and microwave devices [6,7]. In addition to that; the ferrites materials represent potential activity in the area of water treatment for environmental applications [8,9]. Ferrite materials are recognized as more important and essential for the further development of electronics than before; hence the production of ferrites will increase year by year as their applications become more diverse. Reviewing ferrite history and accurately analyzing its present situation will do great to further development in the future [1–8].

The practical applications of ferrites have been expanded by completely utilizing these advantages properties. The properties of metal ferrites were found to be strongly affected by material composition, crystal structure [10], sintering conditions [11], preparation methods, the amount of constituent metal oxide and various additives [12,13].

Nano-size metal ferrites or iron oxides materials have gained more considerable interest due to the new, unique and amazing size dependent properties, and high surface area due to small particle size. Hence they represent more potential applications in new fields like magnetic resonance imaging (MRI), magnetically guided drug delivery and

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hydrocarbon gases removal and decomposition [14–16].

2. Reduction of nano-size metal oxides and metals ferrite

According to the previously mentioned importance of nano-size metals oxides and metals ferrites it is significant to focus on their reduction way as potentials technique for the development of nano-size magnetic alloy for potential applications. [17–19].

The reduction of ferrites is a significant step in metallurgical processes as applied to M–Fe–O systems and also in the production of alloys in steel production [20]. The reduction results of iron ores and/or metal ferrites depend mainly on the mass transfer techniques used in a blast furnace, direct reduction, and melting reduction processes [21]. In the case of iron oxides doped metal oxides, their reduction process includes many complicated reactions and takes place in a stepwise manner via formation of a series of metal ferrites and intermediate oxides. The reduction process has been extensively studied using H_2, CO, H_2/CO, CO/CO_2 gas mixtures and even with solid carbon under isothermal or non-isothermal conditions [22–31].

The way and kinetic of reduction process were followed up via two different techniques; thermo-gravimetric and electrical conductivity [6,22–30]. In thermo-gravimetric technique; during reducing gas exposure, oxygen from the surface as well as from the bulk was removed as H_2O or CO_2 molecules, this removed or weight loss oxygen is measured directly with a digital balance. The reduction extent was calculated from the following relation:

% reduction = ([weight loss Of O_2 at a given time]/[mass of O_2 in the sample]) × 100.

The reduction percentage was calculated as a function of exposure time to reducing gas, hence a set of dynamic curves is obtained. Approximately, the reduction curves may be divided into initial and final stages. Generally, the initial stage represents a high reduction percentage with time (jump stage from 0 to 65%) while the final stage shows a slow reduction rate (saturation step 65 to 85) as deduced in Fig. 1 [6,22–30].

On the other hand, for conductivity dynamics technique, each removal of oxygen atom liberates at least two electrons without molecular orbitals to accommodate them. The two free electrons are transferred into the conduction band, resulting in modifies and increase the electronic conductivity of the reduced materials. Losing of oxygen and hence formation of oxygen vacancies control the conductivity way of reduced materials. Conductivity transients at various temperatures were calculated as a function of reduction time as illustrated in Fig. 2a,b [6,26]. Despite that; follow up reduction way and kinetic via electrical conductivity technique was not extensively used. A complete reduction process is deduced by minimum resistant, while conductivity change with time is an indication of the reduction rate.

2.1. Factors affecting the reduction rate

2.1.1. Nature of the solid reactant and product

The rate of chemical reaction was found to be affected and controlled by various parameters. A. P. Prosser had concluded that; the surface orientation, crystal structure and the presence of dislocations show great influence on the rate of chemical reaction. In addition to that; the impurities in solid solution and the non- stoichiometry of solid phase represent the clear effect on the rate of chemical reaction [32].

Naturally occurring ores, which have many impurities such as silica and oxides of various metals such as Ca, Al and Mg, have been used in studies on the reduction kinetics [33–38]. Many investigators have used reagent grade materials either to eliminate the influence of impurities present in natural ores or to determine the effect of these impurities by making appropriate additions [39–48]. It is essential however to have a complete description of the thermal history, the origin of the particles and the impurities levels of the reactant solid material. The structure of the solid product is important in all heterogeneous gas–solid reactions since the transport of the reacting gas to the reactant interface must occur across this layer [49]. The structures and properties of this layer are, therefore, important in kinetic studies. The porosity and surface morphology of the product phase is often different from those of the starting material and consequently, the effective diffusion coefficient will be affected by the structural changes during reduction.

2.1.2. Reduction temperature

From basic principles of chemical thermodynamics, kinetics, and the fundamental laws of diffusion, it was predicted that the rate of reduction should increase with increasing the reduction temperature [50–52].

Bahgat et al; have investigated the influence of temperature and gas composition on the reduction way of pure wustite samples and those from iron ore sinter in 1173–1373 K. The reduction process was done in reducing atmosphere of different ratios of CO/CO_2/N_2 which closely represent the coke gases in the blast furnace [53]. The reduction way was followed up using the thermogravimetric technique. It was found that; the rate of reduction of pure wustite was increased by increasing the reduction temperature for all percentages of reducing gases. Moreover, the rate of reduction was highest in the early stages and decreased as the reduction proceeded until the end of the reduction process. The sample of wustite from iron ore sinter represents

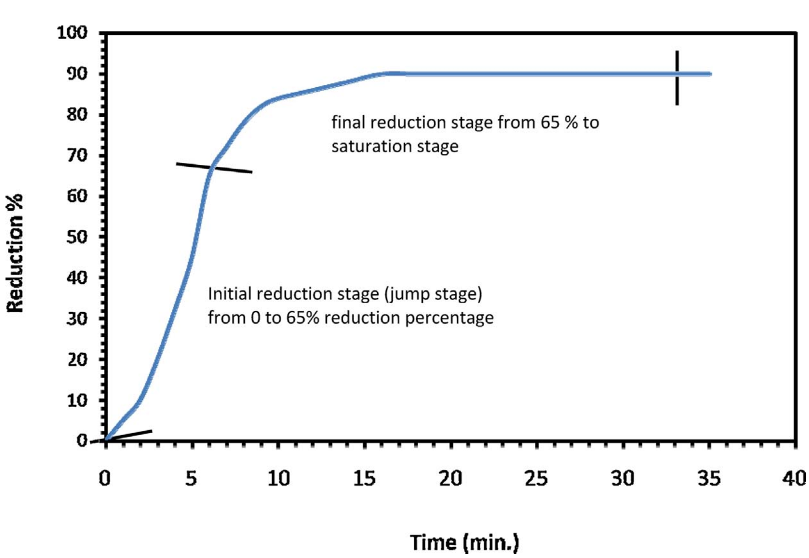

Fig. 1. reduction curve represent reduction stages by thermo-gravimetric technique.