Characterization and Catalytic Behaviour of Nanostructured Iron Oxide Powder from Waste Pickle Liquor of Steel Industry

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Abstract

Nanostructured iron oxide powder that has been recovered from waste pickling liquor unit of steel industry was studied for oxidation catalytic applications. In this research, the powder was characterized by X-ray diffraction (XRD) and transition electron microscopy (TEM) for determination of phase structure, morphology and particle size. Furthermore, the specific surface area of the powder was achieved by BET method. Results show that the powder consists of α-Fe_2O_3 particles with wide range distribution particle sizes between 50-300 nm. Specific surface area of the powder is about $4.33 m^2g^{-1}$. Moreover, catalytic behaviour of the iron oxide powder was investigated. A quartz tubular furnace was applied as a reactor for measuring catalytic activity. Conversion test results show that CO to CO_2 conversion reaction was initiated at about 300°C (light-off temperature) and was completed at about 600°C. Also, the CO to CO_2 conversion ratio was almost constant during long-term stability test.

Keywords: Iron oxide powder, characterization, Oxidation catalyst, CO removal

1. Introduction

Exhaust gas that exits from the automobile engine and some furnace stack contains poisonous components, such as carbon monoxide and hydrocarbon volatile gasses. Oxidation catalytic materials could convert these harmful components to inert gases e.g. carbon dioxide and water. Nowadays Pt, Pd, and other platinum group metals (PGM), as an active catalytic sites are used for the removal of poisonous gasses. However, due to the rising cost of PGM, many researchers have been searching for alternative materials as the active catalytic phase. Use of nanostructure and nanoparticle transient metallic oxides for catalytic applications was studied in the last decade [1-5]. These compounds are promising materials as an oxidation catalyst due to low cost, stability in high temperature and high sintering temperature.

Hematite (Fe_2O_3) is one of transient metal oxides that is well-known with an unusual magnetic behavior. It is used for different applications such as pigment for paints, biomedical application, magnetic component fabrication, removal of heavy metals from aqueous solutions, and catalysts for petrochemical industries [6-10]. Fe_2O_3 nano-powder is acknowledged as a suitable material for oxidation catalytic systems. Various methods such as sol-gel, chemical precipitation, and high-energy ball milling have been used to produce

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nanostructure and nano-particles iron oxide [9-12].

Li et al. have investigated catalytic behavior of Fe_2O_3 with 3 nm particle sizes (NANOCAT) for the removal CO from pollution gases. Experimental results show CO to CO2 conversion reaction was completed at 350 °C. Also, the conversion reaction kinetics was first-order with respect to CO [3]. Similar results were reported for this powder by Kwon et al. [2]. Halim et al. have studied the catalytic behavior of different sizes of nano-crystalline and nano-particles of iron oxide powders that are prepared by sol-gel method [4-5].

In this research, iron oxide powder that has been achieved from waste pickling liquor unit of steel industry was examined for oxidation catalytic behavior. For this purpose, XRD, TEM and BET methods were used to characterize this material.

2. Materials and method

The powder structure was characterized by X-ray Diffraction (XRD, Philips Expert, Germany) with Cu Kα (λ = 1.5406Å) radiation in 2θ range from 5 to 80°. Transition Electron Microscopy (TEM, Philips CM200 FEG, Germany) was used for the investigation of morphology and size of the powder. The specific surface area of the catalyst powder was obtained by Brunauer- Emmett-Teller method (BET, Bel-Belsorp mini, Japan).

For measuring catalytic activity, a quartz tubular furnace was used. Glassy wool was impregnated by catalyst materials and then, was inserted in the furnace. An amount of 500mg Fe_2O_3 powder was used as an oxidation catalyst material. Furnace temperature increases gradually by rate of 3°C/s. A mixed gas that consists of $1\%O_2$-$0.5\%CO$-$98.5\%N_2$ was passed

through the furnace, and CO concentration in the outlet flow gas was detected by gas analyzer instrument (Testo 327-1, Germany). CO to CO_2 Conversion ratio was calculated as follow:

$$\text{CO to } CO_2 \text{ Conversion Ratio } = \frac{\%CO_{int} - \%CO_{ext}}{\%CO_{int}} \quad (1)$$

Also, long-period conversion test was performed to investigate the conversion reaction stability. The stability test was carried out for several temperatures as long as 450 minutes.

3. Results and discussion

3.1. Powder charactrization

During hot rolling process, iron oxide layer forms on surface of steel slab. This layer must be removed by risining process after hot rooling. The acidic solution obtained in this stage is called waste pickle liqour (WPL) and is transfered to acid recycle unit. Then, WPL is sprayed into the furnace (spray roasting process) to recover acid solution. In this stage, iron chloride solution is converted to Fe_2O_3 powder in the presence of water vapor and oxygen at high temperatures according to the following reactions [13]:

$$2FeCl_2 + 2H_2O + \tfrac{1}{2}O_2 \rightarrow Fe_2O_3 + 4HCl \quad (2)$$

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl \quad (3)$$
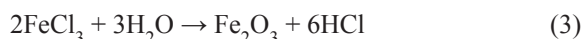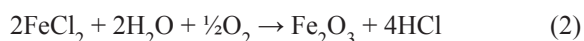
Subsequently, submicron red-brown iron oxide powder was formed. Fig. 1 shows the micrograph of the iron oxide powder. This Iron oxide powder was commercially used as a yellowocher pigment dye in paint industry [6].
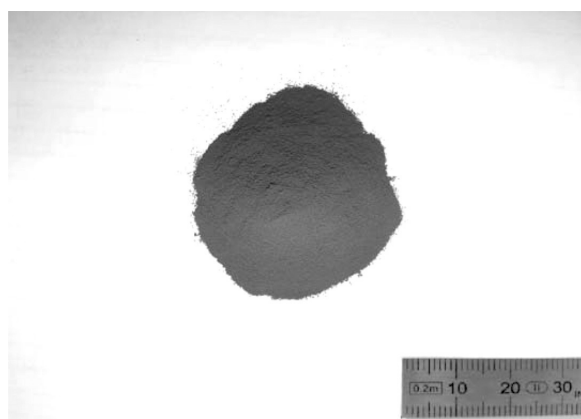

Fig. 1. Micrograph of the iron powder used in this research.

Fig. 2 shows X-ray diffraction pattern of the iron oxide particles. All of the sharp and narrow peaks in this figure are related to the α-Fe_2O_3 phase according to Joint Committee on Powder Diffraction Files (JCPDF card No. 24-0072). This result indicates the purity and highly crystalline of the Fe_2O_3 particles.

Crystallite size has been calculated by using Scherer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (4)$$

where D is the mean crystallite size of the powder, λ is the wavelength of Cu kα equal to 1.54056Å, β is the full width at half-maximum (FWHM) intensity of the (104) peak in radian that is measured by X'Pert HighScore software, θ is Bragg's diffraction angle and K is a constant usually equal to 0.9. According to this equation, averrage crystallite size is about 50 nm.
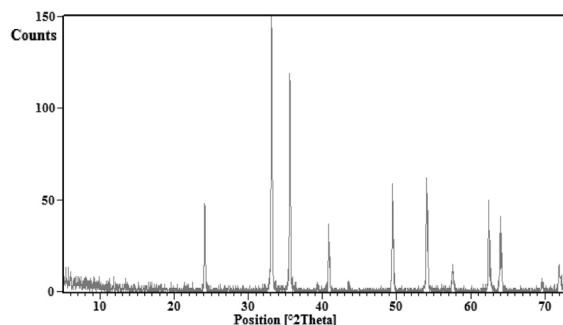

Fig. 2. X-ray diffraction pattern of iron oxide nano-particles.

Micrograph of nanoparticles iron oxide obtained by transition electron microscopy is shown in Fig. 3. It is clear that the shape of the particles is spherical and their sizes vary from 50 to 300 nm.

Because of conversion of CO to CO_2 was done on the surface of the powder, specifiec surface area is an important parameter in oxidation catalytic materials. BET test results demonstrated that the specific surface area of the powder is 4.33 m^2/g. Therfore, these particles can be used as oxidation catalyst for CO conversion to CO_2 due to relatively high specific surface area.
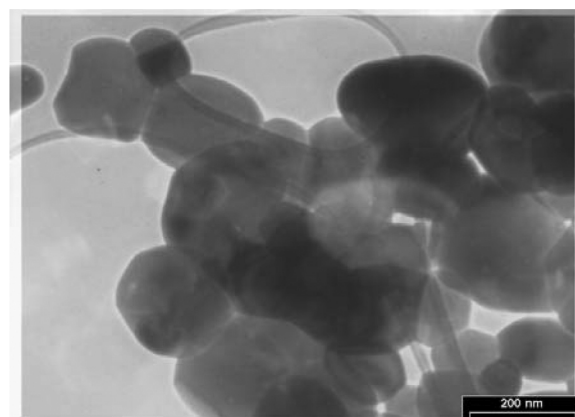

Fig. 3. Transmission electron microscopic images of the iron oxide nano-powder.

3.2. Oxidation catalytic activity

CO to CO_2 conversion ratio versus temperature of

iron oxide powder for $1\%O_2$-$0.5\%CO$-$98.5\%N_2$ gas mixture is illustrated in Fig. 4. It is obvious that catalytic activity increases with process temperature. As shown in this figure, a temperature of about 300°C is required for the initiation of oxidation reaction and no conversion reaction is detected at less than this temperature. Therefore, light-off temperature of conversion reaction is determined about 300°C.

As CO to CO_2 conversion reaction was completed at about 600°C, Fe_2O_3 nano-powder can catalyze oxidation of 100% carbon monoxide in the inlet gas mixture to carbon dioxide.
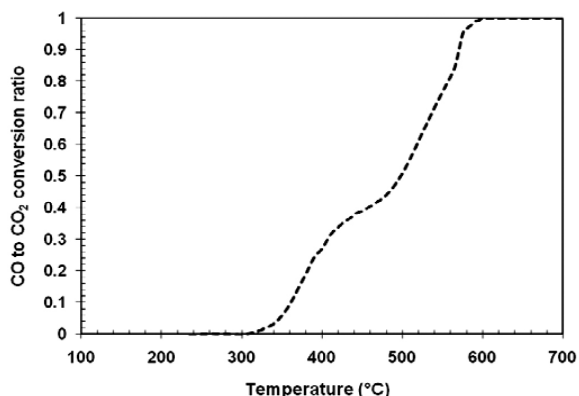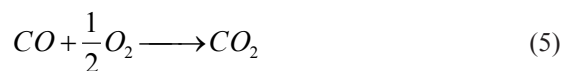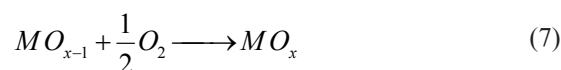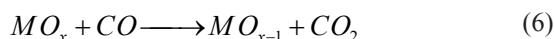

Fig. 4. Behaviour of CO to CO_2 conversion at different temperature (500mg Fe_2O_3).

Overall reaction of CO to CO_2 oxidation is:

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2 \qquad (5)$$

This reaction consists of two steps as follows [3]:

$$MO_x + CO \longrightarrow MO_{x-1} + CO_2 \qquad (6)$$

$$MO_{x-1} + \frac{1}{2}O_2 \longrightarrow MO_x \qquad (7)$$

As the above reactions show, CO molecules partially reduce metal oxide, and carbon dioxide molecule forms according to (6). In the second step, reduced metal oxide repeatedly absorbs oxygen from gas stream. Finally, catalytic material remains without change at the end of the process [3]. It is clear that the presence of oxygen in passed gas stream is essential, so this is called oxidation catalyst system.

A series of oxidation catalytic tests was performed in various CO concentrations of inlet gas mixtures. Oxygen concentration in inlet gas flow was considered constant in all tests. The effect of CO concentration on conversion ratio at 500°C was plotted in Fig. 5. As shown in this figure, by increasing CO concentration, conversion ratio linearly decreses. So, it indicates that

CO to CO_2 conversion reaction is a first-order reaction with respect to CO concentration. Similar results were reported by other researchers [3].
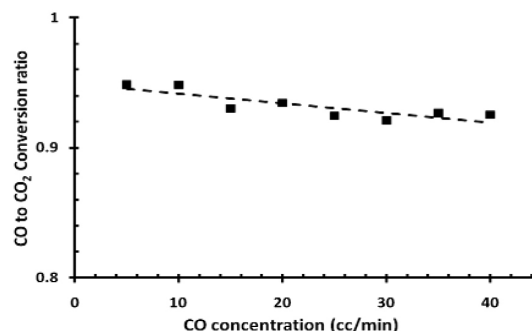

Fig. 5. The effect of CO concentration on CO to CO_2 conversion ratio at 500°C.

One of the main specifications of catalyst materials is their behavior in long-term service. In order to investigate this parameter, CO to CO_2 conversion ratio was measured at 600°C for long time (450 min). Fig. 6 indicates that CO to CO_2 conversion ratio is almost constant and it even gradually increases from 0.97 to 0.98 after 450 minutes.
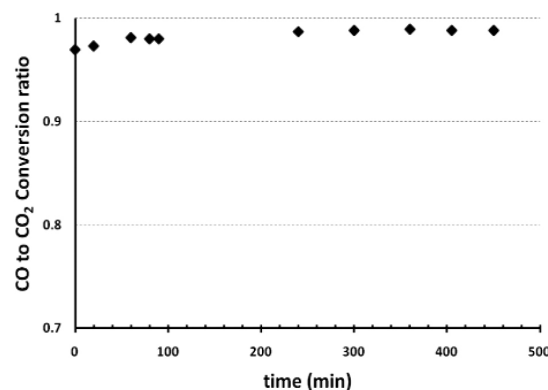

Fig. 6. Stability of CO to CO_2 conversion reaction at 600°C for 450 minutes.

4. Conclusions

Iron oxide powder that has been precipitated from waste pickling liquor unit of steel industry is a suitable material for oxidation catalytic applications. Some aspects such as stability in high temperature, relatively high specific surface area, low cost, rapid fabrication procedure and ease of availability are the advantages of these powders. CO to CO_2 conversion reaction is completed about 600°C for low concentration of CO in the gas stream. Also, the conversion reaction is stable for long-term service.

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