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Factors affecting CO oxidation over nanosized Fe₂O₃

K.S. Abdel Halim^{a,*}, M.H. Khedr^b, M.I. Nasr^a, A.M. El-Mansy^b

^a Central Metallurgical Research & Development Institute (CMRDI), P.O. Box 87, Helwan, Cairo, Egypt ^b Materials Chemistry Department, Faculty of Science, Beni Suef University, Egypt

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Abstract

Nanocrystallite iron oxide powders with different crystallite sizes were prepared by co-precipitation route. The prepared powders with crystallite size 75, 100 and 150 nm together with commercial iron oxide (250 nm) were tested for the catalytic oxidation of CO to CO₂. The influence of different factors as crystallite size, catalytic temperature and weight of catalyst on the rate of catalytic reaction was investigated using advanced quadrupole mass gas analyzer system. It can be reported that the rate of conversion of CO to CO₂ increased by increasing catalytic temperature and decreasing crystallite size of the prepared powders. The experimental results show that nanocrystallite iron oxide powders with crystallite size 75 nm can be recommended as a promising catalyst for CO oxidation at 500 °C where 98% of CO is converted to CO₂. The mechanism of the catalytic oxidation reaction was investigated by comparing the CO catalytic oxidation data in the absence and presence of oxygen. The reaction which was found to be first order with respect to CO is probably proceeded by adsorption mechanism where the reactants are adsorbed on the surface of the catalyst with breaking O–O bonds, then CO pick up the dissociated O atom forming CO₂. (© 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

CO is a very harmful gas where it strongly binds to the iron atom in blood hemoglobin and so the hemoglobin becomes incapable of releasing oxygen. A sufficient exposure to carbon monoxide can reduce the amount of oxygen taken up by the brain to the point that the victim becomes unconscious, and can suffer brain damage or even death from anoxia. Catalytic oxidation of CO to CO_2 is a good solution to solve such serious environmental problem since CO_2 is much less harmful compared to carbon monoxide.

Currently, the oxidation of CO to CO_2 is catalyzed over noble metals as platinum and gold. The cost of noble metals does not make it economically feasible to be used in the catalytic oxidation of CO. This had lead to searching for other catalysts which are cheaper and more abundant. Nanosized materials are characterized by unique, essential and important applications especially in the field of catalysis. An important class of the materials that are rich in oxygen and yet contain O atoms with no O–O bonds are the metal oxide such as iron oxide, Fe_2O_3 [1–3].

The catalytic oxidation of CO over nanoparticle materials was recently investigated [4–11]. Li et al. [4], studied the removal of CO by iron oxide nanoparticles where Fe_2O_3 nanoparticles were characterized both as a carbon monoxide

^{*} Corresponding author. Tel.: +20 2 5010642; fax: +20 2 5010639. *E-mail address:* khaledsaad@cmrdi.sci.eg (K.S. Abdel Halim).

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catalyst and as a carbon monoxide oxidant. It was found that the small particle size and the FeOOH content presented in Fe₂O₃ contribute to its high performance as a CO catalyst, which was indicated by a reaction rate of 19 s⁻¹ m⁻² at 300 °C. The effect of catalytic activity of Au/Fe₂O₃ at low temperatures on a CO oxidation reaction was investigated by Tripathi et al. [6]. Adsorption and changes in enthalpy were determined for the interaction of CO, O₂ or CO + O₂ (2:1) pulses over Au/Fe₂O₃, Fe₂O₃ and polycrystalline gold catalysts between 28 and 179 °C. The results demonstrate that the oxidation of CO on both Fe₂O₃ and Au/Fe₂O₃ occurs by means of similar redox mechanisms involving the removal and replenishment of lattice oxygen, where the presence of gold promotes these processes.

In the present study, catalytic oxidation of CO over nanocrystallite Fe_2O_3 was investigated. The influence of different factors as crystallite size, catalytic temperature and mass of catalyst on the rate of catalytic reaction was investigated using advanced quadrupole mass gas analyzer system. Furthermore, the experimental data were used to study the mechanism of the catalytic oxidation reaction.

2. Experimental

Iron oxide samples with different crystallite sizes were prepared by wet technique using highly purified FeCl₃ and NH₄OH solution. The precipitate was dried at 120 °C for 24 h. The produced powders were fired in a muffle furnace fitted with an on/off temperature controller. The temperature sensor was 13% Pt/Pt–Rh thermocouple. The maximum deviation of the thermocouple reading from the set point was 20 at 1300 °C. Samples were placed in high alumina refractory holders then introduced in the hottest zone of the furnace. After proper soaking for a period of 3 h at 600 °C, the powder was left to cool gradually to room temperature to avoid cracking due to thermal shocks. The samples were thoroughly mixed in a ball mill at different times 24, 2 and 0 h to control the crystallite size at 75, 100 and 150 nm, respectively.

Phase identification and crystallite size of the products were determined at room temperature by X-ray diffraction (XRD, Bruker axs D8, Germany) with Cu K α ($\lambda = 1.5406$ Å) radiation and secondary monochromator in the range 2θ from 10° to 80°. Crystallite size is automatically calculated from X-ray diffraction data using the diffraction peaks and a computer software TOPAS 2 which applied Scherer's formula [12].

The experimental apparatus of CO catalytic oxidation used pure CO gas obtained by passing CO₂ over coal in a tube furnace at 1100 °C. The produced CO is purified by soda lime to absorb any traces of CO₂ then passed over silica gel to remove moisture. Certain weight (0.3, 1, 2 and 3 g) of the prepared iron oxide samples were held between two pieces of quartz wool in a tubular horizontal flow reactor (length 120 cm, i.d. 1.5 cm). The reactor was heated in a tube furnace up to the required catalytic oxidation temperature. The sample was kept at that temperature for about 30 min before the onset of the experiment to refresh the catalyst. CO/O₂/N₂ gas mixture was passed over the catalyst at a constant rate. The starting composition of the gas mixture is 24% CO, 38% O₂ and 38% N₂. Monitoring of the individual gas concentration in the gases mixture during measuring the catalytic activity of the samples is performed using gas analyzer (QMS sample analysis HPR 20, Hiden-analytical, Warrington, UK).

3. Results and discussion

3.1. Crystal structure

Three types of nanocrystallite iron oxide powders were prepared in different crystal size values, namely 75, 100 and 150 nm for ball milling for 24, 2 and 0 h, respectively. A commercial iron oxide powder (ADWIC, 97%) with crystal size 250 nm is used in the present study to test the catalytic behavior of the commercial samples. X-ray diffraction patterns of the prepared powders are summarized in Fig. 1. The most abundant phase identified in all prepared samples was Fe_2O_3 . The narrow and high intensity peaks of samples show that the prepared powders are highly crystallized.

Fig. 2 shows photomicrographs of Fe_2O_3 powders with different crystallite size indicating two types of aggregates with different grain sizes. One type of grains consists of dense matrix (light gray) constituting the majority of the sample. The second type consists of smaller grains (dark gray), which is more likely to be maghamite and also in nanosize range but more agglomerated.

TEM images for Fe_2O_3 samples with crystal size 75 and 100 nm are shown in Fig. 3. It was observed that iron oxide powder was most probably formed in agglomerated and separated iron oxide nanosize.



Fig. 1. XRD patterns of nanocrystallite iron oxide powders with different crystal sizes: (a) 75 nm, (b) 100 nm and (c) 150 nm.

3.2. Effect of crystal size on the CO oxidation

Catalytic oxidation tests were carried out in the simulated reactor to study the effect of crystal size of the prepared iron oxide powders on the removal of CO by catalytic oxidation reaction. The oxidation tests were investigated isothermally through the oxidation of CO to CO_2 as a function of crystal size of the prepared samples in the temperature range 200–500 °C. Before the catalytic tests, iron oxide was heated for 30 min in ambient atmosphere in order to activate the catalyst by removing any adsorbed gases, then CO, O_2 and N_2 were allowed to pass over the powdered oxide at the desired temperature. The degree of conversion of CO to CO_2 is estimated from the following equation:

$$CO_{conversion} (\%) = \frac{CO_i - CO_t}{CO_i} \times 100$$



Fig. 2. Photomicrograph of iron oxide powders: (a) 75 nm and (b) 150 nm (×1000).

where CO_i is the initial CO concentration and CO_t is the CO concentration at time t. The efficiency of using Fe₂O₃ powder as a catalyst for CO oxidation can be defined by the maximum degree of CO conversion extent. Fig. 4 shows the effect of crystallite size of iron oxide powders on the maximum value of CO conversion (efficiency%). It can be noticed that crystallite size of the prepared powders plays a considerable role in the removal of CO by catalytic oxidation reactions. The maximum value of CO conversion increased with decreasing of crystallite size of the prepared samples. The complete oxidation of CO to CO₂ was observed upon using iron oxide powders with 75 nm crystallite size at 500 °C. However, the typical behavior of CO oxidation reaction as a function of time is shown in Fig. 5 for iron oxide samples tested at 300 °C. It was observed that for all test samples, as the time of oxidation reaction increases, the CO conversion extent increases till the maximum value and then remains constant. The catalytic oxidation curves are very close to each other at the early stages of reaction, till 35% conversion extent. This can be attributed to the homogeneity of the prepared samples and the presence of more active sites on the surface of the catalyst which enhance and control the catalytic activity of the samples. At moderate and final stages of oxidation reactions, the effect of crystallite size of iron oxide samples on the CO conversion becomes significant and CO conversion extent increased by lowering crystallite size of the catalyst (40-70% conversion extent). The commercial iron oxide samples with crystallite size 250 nm show very low response toward CO oxidation ($\sim 20\%$ conversion extent) which reports the effective using of nanocrystallite iron oxide samples prepared by co-precipitation method.



(a)

250 nm



250 nm

Fig. 3. TEM micrographs of iron oxide powders: (a) 75 nm and (b) 100 nm.



Fig. 4. Effect of crystal size of nanocrystallite iron oxide on the catalytic oxidation of CO.



Fig. 5. Variation of CO conversion extents with time for nanocrystallite iron oxide powders at 300 °C.

The apparent activation energy for CO oxidation was calculated using Arrhenius equation [4]:

$$\ln[-\ln(1-x)] = \ln A + \ln\left(\frac{v}{u}\right) - \left(\frac{E_{a}}{RT}\right)$$

where (x) is the carbon monoxide to carbon dioxide conversion rate, (A) the pre-exponential factor in s^{-1} , (u) the flow rate in ml s^{-1} , (v) the total volume of the catalyst in cm³, (E_a) the apparent activation energy in kJ mol⁻¹, (R) the gas constant and (T) is the absolute temperature in Kelvin.

The value of activation energy can be calculated by plotting $\ln[-\ln(1 - x)]$ versus 1/T as shown in Fig. 6 for iron oxide samples with different crystallite sizes. It can be observed that the value of activation energy decreased with increasing crystallite size which confirms again the increasing of CO conversion with decreasing of crystallite size.

3.3. Effect of temperature on the CO oxidation

The catalytic oxidation temperature is one of the most important factors that control the efficiency of catalytic reaction. Fig. 7a–c shows CO conversion extents as a function of time at the temperature range 200–500 °C for iron



Fig. 6. Arrhenius plots for CO oxidation over iron oxide nanocatalyst at 200-500 °C.



Fig. 7. Influence of catalytic oxidation temperature on the CO conversion for nanosized Fe₂O₃: (a) 75 nm, (b) 100 nm and (c) 150 nm.

oxide samples with crystallite size 75, 100 and 150 nm, respectively. As time proceeds, CO conversion increases and the rate of conversion is high initially and slows down till the end of the reaction. At relatively lower temperature (200 °C), the maximum CO oxidation extents were almost 20–25% for all samples which reflects the low sensitivity of iron oxide as catalyst for conversion of CO to CO₂ at lower temperatures. As temperature increases to 300 °C, the maximum conversion extents jump to about 50% and iron oxide samples with lower crystallite size show good response towards oxidation of CO. At relatively high temperatures 400 and 500 °C, the conversion extents increases to



Fig. 8. Photomicrographs of nanocrystallite iron oxide powders with 100 nm: (a) pure Fe_2O_3 , (b) Fe_2O_3 after oxidation at 300 °C and (c) Fe_2O_3 at 500 °C (×1000).

90 and 98%, respectively, for samples with 75 nm (Fig. 7a). It was observed that the response of all samples toward CO oxidation at 400 °C is generally better than that obtained at 500 °C. This phenomenon could be attributed to sintering processes which occurred for iron oxide samples at relatively high temperature (500 °C). Fig. 8a–c shows photomicrographs of iron oxide powders with crystallite size of 100 nm before and after oxidation reaction. It was observed that with increasing temperature, micropores decreased and macropores increased whereas grain growth with partial coalescence takes place which decreases the number of active sites available for catalytic process.

The results of catalytic oxidation tests were used to investigate the kinetics and mechanism of CO oxidation. The order of CO oxidation was measured at 400 °C for a gas mixture containing 38% O_2 and CO content ranged from 20 to 25% which resulted in a conversion extent between 70 and 90%. The extent of CO conversion to CO_2 was calculated and the corresponding data are shown in Fig. 9, from which a straight line is obtained indicating that the catalytic CO oxidation is a first order reaction with respect to CO.

On the other hand, the conversion of CO in absence of O_2 over the nano-Fe₂O₃ catalyst (75 nm) at 200–500 °C was investigated to confirm the mechanism of the reaction. The CO oxidation reaches only a maximum value of $\approx 27\%$ at 500 °C while at lower temperature 300 and 400 °C it gives only 5 and 18%, respectively, as shown in Fig. 10.

The value of activation energy was calculated by plotting $\ln[-\ln(1 - x)]$ versus 1/T (Fig. 6). The obtained value of E_a for CO oxidation in the absence of O_2 is 34.6 kJ mol⁻¹ which is greater than E_a for CO oxidation in the presence of O_2 reported to be 26.3 kJ mol⁻¹. These values together with the low reduction extents in absence of O_2 reveal that the adsorption mechanism probably controls the oxidation of CO where the reactants are adsorbed with breaking O–O bonds, then CO pick up the dissociated O atom forming CO₂ [13].



Fig. 9. CO oxidation extent as a function of inlet CO for the calculation of the reaction order.



Fig. 10. CO conversion extent as a function of time at temperatures 200-500 °C in absence of O2.

3.4. Effect of catalyst weight

The effect of catalyst weight on the catalytic oxidation of CO was studied at different crystallite sizes and temperatures. The experimental results are summarized in Table 1. It was found that catalyst weight has a significant effect on the CO conversion.

Fig. 11 shows the effect of Fe_2O_3 weight (0.3, 1, 2 and 3 g) on the CO conversion at 200–500 °C for Fe_2O_3 with 75 nm crystallite size. At 200 °C, the change in weight is insignificant whereas at 300 °C, the change in weight from 1

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alues of activation energy at different weights of Fe ₂ O ₃ nanosized samples with maximum conversion of carbon monoxide	

Weight (g)	Crystallite size (nm)							
	75		100		150		250	
	$\frac{E_{\rm a}}{(\rm kJ\ mol^{-1})}$	Maximum conversion of CO (%)	$E_{\rm a}$ (kJ mol ⁻¹)	Maximum conversion of CO (%)	$\frac{E_{\rm a}}{\rm (kJ\ mol^{-1})}$	Maximum conversion of CO (%)	$E_{\rm a}$ (kJ mol ⁻¹)	Maximum conversion of CO (%)
0.3	13.71	82	10.48	60	12.8	65	9.97	50
1	11.01	70	14.1	65	9.26	74	6.4	65
2	26.3	98	15.76	73	8.97	64	13.17	80
3	23.8	95	15.26	64	9.77	60	10.77	75



Fig. 11. Effect of Fe₂O₃ weight on the CO conversion at 200–500 °C for Fe₂O₃ with 75 nm crystallite size.



Fig. 12. The conversion of carbon monoxide as a function of time for different weights of Fe_2O_3 samples with crystallite size 75 nm at temperatures: (a) 200 °C and (b) 400 °C.

to 2 g shows a sharp increase in CO conversion from 62 to 90%, the same trend is shown at 500 $^{\circ}$ C with a change in conversion from 70 to 95% which indicates that maximum amount of catalyst for maximum conversion is attained with 2 g of iron oxide catalyst.

Fig. 12a and b shows CO conversion percent as a function of time for different weights of Fe_2O_3 with crystallite size of 75 nm at temperature 200 and 400 °C, respectively, from which it is clear that as time proceeds CO conversion increases for all weights and the difference in conversion extent increases as time proceeds at 200 °C. At 400 °C, all weights show almost the same CO conversion at the initial stages up to 35% then an irregular change in rate is observed till the end of the conversion. It can be noticed that 2 g Fe_2O_3 samples show high conversion while 3 g samples show the maximum rate at the final stages.

Activation energies were calculated using Arrhenius equation and the values are given in Table 1. It is clear that the activation energy is directly proportional to the percent conversion and the maximum activation energy (26.3 kJ mol⁻¹) is attained at 98% conversion for 2 g Fe₂O₃ samples with crystalline size of 75 nm while the minimum activation energy (≈ 8.2 kJ mol⁻¹) was attained for 1 g Fe₂O₃ samples with crystal size of 150 nm.

4. Conclusion

Three types of nanocrystallite iron oxide powders were prepared by co-precipitation method in different crystal size 75, 100 and 150 nm. It was observed that the maximum value of CO conversion extent decreased with the increasing of crystallite size of the prepared samples. The commercial iron oxide samples with crystallite size of 250 nm show very low response toward CO oxidation (~20% conversion extent) which reflects the effective use of nanocrystallite iron oxide samples prepared by co-precipitation method. The catalytic temperature plays a significant role in the oxidation of CO to CO₂. At relatively high temperatures of 400 and 500 °C, the conversion extents increase to 90 and 98%, respectively, for samples with 75 nm. It was observed that the response of all samples toward CO oxidation at 400 °C is better than that obtained at 500 °C which can be attributed to sintering processes at high temperature (500 °C).

The experimental data were used to study the mechanism of the catalytic oxidation reaction. The reaction was found to be first order with respect to CO. The data of CO catalytic oxidation was compared in the absence and presence of oxygen. It was found that the catalytic oxidation of CO over nanocrystallite Fe_2O_3 probably proceeded by adsorption mechanism where the reactants are adsorbed on the surface of the catalyst with breaking O–O bonds, then CO pick up the dissociated O atom forming CO_2 .

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