

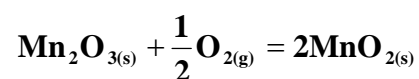
STUDY ON OXIDIZING DYNAMICS OF INDUSTRIAL WASTE MANGANESE DUST

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ABSTRACT

A great amount of waste Mn dust is brought about by producing ferro-manganese alloy, whose main composition are Mn_2O_3 and Mn_3O_4 . In order to utilize the waste Mn dust and protect the environment, they would be oxidized to MnO_2 , which will be used as support-combustion agent for pulverized coal injecting into blast furnace. This paper has examined the reaction mechanism and the controlled step in the oxidation:



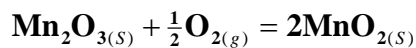
The results show that the reaction rate and ratio are low, on which the temperature and the oxygen partial pressure have a little effect. It is also found that the reaction is controlled by oxygen absorption on the surface of Mn_2O_3 particles and that the expression of the reaction rate is:

$$\frac{d\alpha}{dt} = 1.37 \times 10^{-2} \exp\left(-\frac{32000}{RT}\right)(100 - \alpha)P_{O_2}^{0.4}$$

1. INTRODUCTION

A great amount of waste Mn dust is brought by producing ferro-manganese alloy, whose main compositions are Mn_2O_3 and Mn_3O_4 , and of which the Mn content is over 60 percent. At present, factories merely dispose of the waste Mn dust by piling up simply. In order to make the waste Mn dust as a resource and protect the environment, the problem how to utilize the waste dust has to be settled urgently. The previous studies^[1] indicate that MnO_2 helps coal powder to burn very well, but Mn_3O_4 does little. So if the waste dust would be oxidized to MnO_2 , which will be used as support-combustion agent for pulverized coal injecting into blast furnace. Thus, not only the waste material can be utilized again, also the effect of pulverized coal injecting will be strengthened.

For inquiring into the feasibility of oxidizing waste dust commercially, in view of



this paper has determined the oxidation rate of Mn_2O_3 , examined the reaction mechanism and the controlled step in the oxidation.

2. EXPERIMENTS

2.1 Preparation for Samples

Based on the thermodynamical calculation, the Mn_2O_3 sample was obtained by roasting chemical reagent MnO_2 at 680 in the air for 10 hours. Their particle sizes were below 0.45mm. Being analyzed by X-ray diffraction, the content of Mn_2O_3 was over 97 percent.

2.2 Experimental Apparatus and Method

The autoclave, which could stand high pressure 20MPa, was used as a reactor for the oxidation experiment. The schematic diagram of experiment apparatus can be seen in Fig.1. All the crucibles were underwent the constant mass treatment by heating for 4 hours at $1133 \pm 20K$ in Muffle furnace.

The experiment adopted mass increment method, which examined the oxidation ratio of Mn_2O_3 under given conditions, i. e. fixed time, constant temperature and oxygen partial pressure by weighing the mass increment of samples before and after reaction. The experimental conditions were showed in table 1.

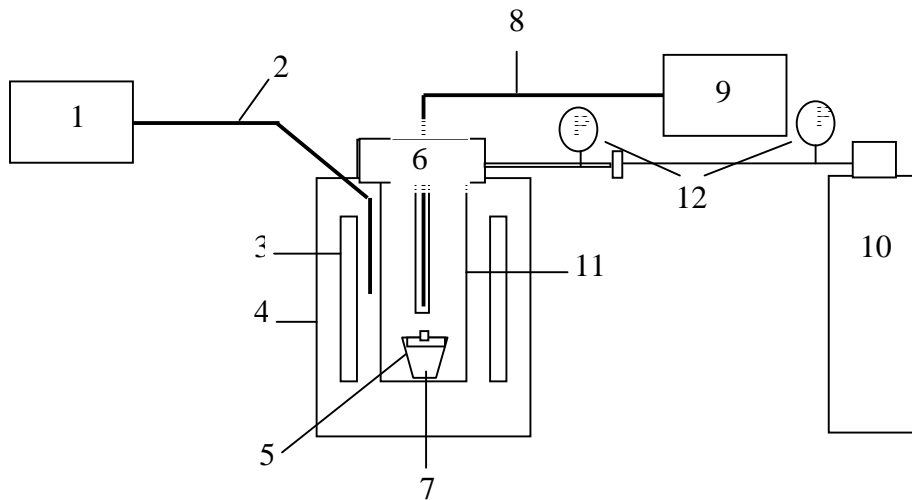


Fig.1 Schematic view of experiment apparatus

- | | |
|--|---|
| 1. Autoclave temperature controller | 2. Thermocouple for temperature control |
| 3. Heating elements | 4. Outer covering of autoclave |
| 5. Crucible | 6. Air-tight ring flange |
| 7. Mn ₂ O ₃ sample | 8. Thermocouple for temperature measure |
| 9. XMZ temperature numeral shower | 10. Oxygen cylinder |
| 11. Autoclave | 12. Pressure gauge |

Table 1 Experimental conditions.

Temperature (K)	583	633	683	
Oxygen partial pressure (MPa)	0.5	1.0	1.5	2.0
Reaction time (hr)	2.0	4.0	6.0	8.0

3. RESULTS AND DISCUSSION

3.1 Results

Oxidation ratio α can be defined by

$$\alpha = \frac{\Delta[\text{O}]}{\Sigma\Delta[\text{O}]} \times 100\% \quad (1)$$

where, $\Delta[\text{O}]$: oxygen increment of Mn₂O₃ in real reaction;

$\Sigma\Delta[\text{O}]$: oxygen increment of Mn₂O₃ complete oxidized in terms of theory.

Put it in order, oxidation ratio $\alpha(\%)$ is written as

$$\alpha = \frac{W - W_0}{W_0 \times \frac{16}{158}} \times 100\% \quad (2)$$

where, W_0 : the mass of samples before reaction (g);

W : the mass of sample after reaction (g).

The number 16 and 158 in it stand for atomic weight of oxygen and molecular weight of Mn_2O_3 respectively.

The mass increment of Mn_2O_3 sample have been determined under the experimental conditions as Table 1. The Mn_2O_3 oxidation ration of isochronous and constant oxygen partial pressure could be calculated on the basis of experimental data and showed by Table 2.

Table 2. Oxidation ratio α under experimental conditions.

α (%)		Temp. (K)		
		583	633	683
Constant oxygen partial pressure ($P_{O_2}=1MPa$)	t=2.0hr	0.71	2.65	3.71
	t=4.0hr	1.86	3.82	4.92
	t=6.0hr	3.00	4.97	6.11
	t=8.0hr	4.12	6.11	7.29
Isochronous (t=4hr)	$P_{O_2}=0.5$ Mpa	1.49	2.63	3.57
	$P_{O_2}=1.0$ Mpa	1.86	3.82	4.92
	$P_{O_2}=1.5$ Mpa	2.43	4.23	5.76
	$P_{O_2}=2.0$ MPa	2.53	4.51	6.08

3.2 Mn_2O_3 Oxidation Rate Expression

For $Mn_2O_{3(s)} + \frac{1}{2}O_{2(g)} = 2MnO_{2(s)}$, the reaction rate expression can be represented as

$$\frac{d\alpha}{dt} = k(100 - \alpha)^n p_{O_2}^m \quad (3)$$

where, α - Mn_2O_3 oxidation ratio at the moment of t (%);

p_{O_2} - oxygen partial pressure (Pa);

k - reaction rate constant, which can be determined by Arrenius formula,

$k = A \exp(-\frac{E}{RT})$, where E is called as activation energy and A as frequency factor;

m, n - parameters awaiting determining;

t – reaction time (hr).

So the reaction rate expression (3) could be rewritten as

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (100 - \alpha)^n p_{O_2}^m \quad (4)$$

In order to determine the parameters n , m , E , A , using the formula (4), and $\frac{d\alpha}{dt}$ obtained by measurement under different experimental conditions, the parameters n , m , E , A can be determined by the method as follows.

(1) Determine parameter n

Assuming oxygen partial pressure as constant, if the values of $\ln\left(\frac{d\alpha}{dt}\right)$ are plotted against the corresponding values of $\ln(100 - \alpha)$ at each temperature, three straight lines would be obtained (Fig.2). Each slope of line stands for one parameter n at certain temperature. The mean values of slopes at different temperature equals one ($n=1$).

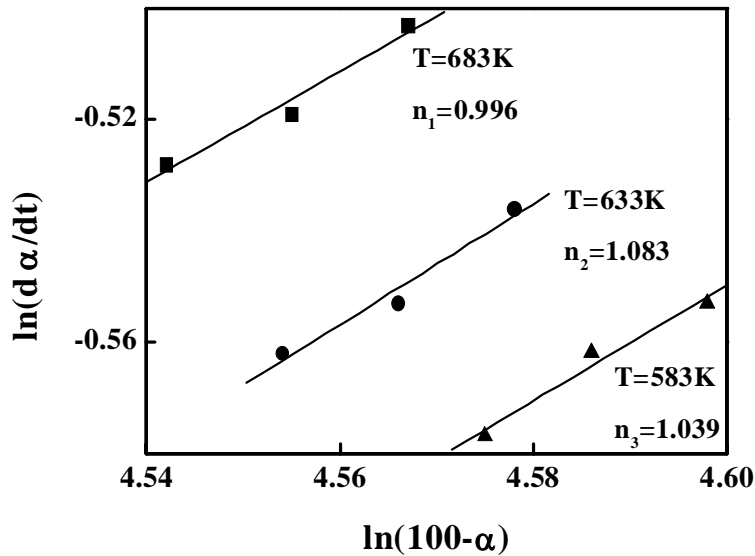


Fig.2 Relationship between $\ln\left(\frac{d\alpha}{dt}\right)$ and $\ln(100 - \alpha)$ in the Mn_2O_3 oxidation.

(2) Determine m and k

Applying $n=1$ to formula (3) and integrating it, an equation is represented as

$$\ln\left(\frac{100}{100 - \alpha}\right) = k p_{O_2}^m t$$

As it can be seen in Fig.3, three straight lines are obtained by plotting $\ln(\ln(\frac{100}{100-\alpha}))$ against $\ln p$ at each temperature. The value of parameter that $m=0.4$ is determined by the mean of their slopes.

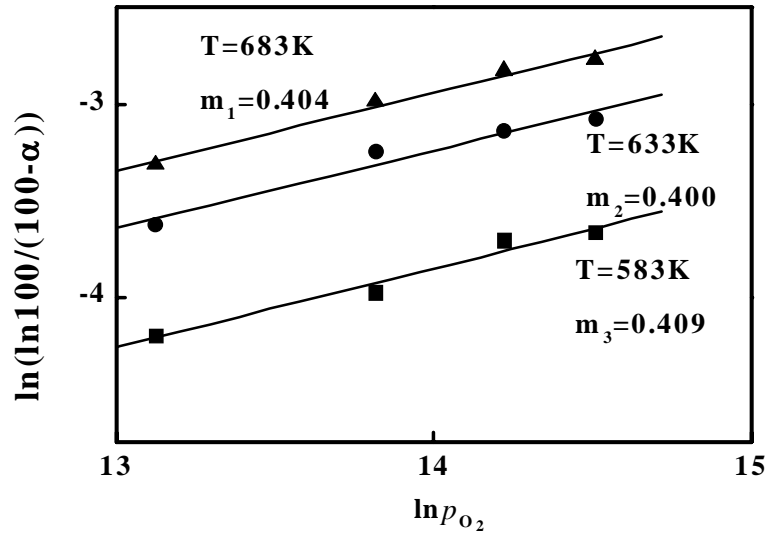


Fig.3 Relationship between $\ln(\ln(\frac{100}{100-\alpha}))$ and $\ln(p)$ in the Mn_2O_3 Oxidation.

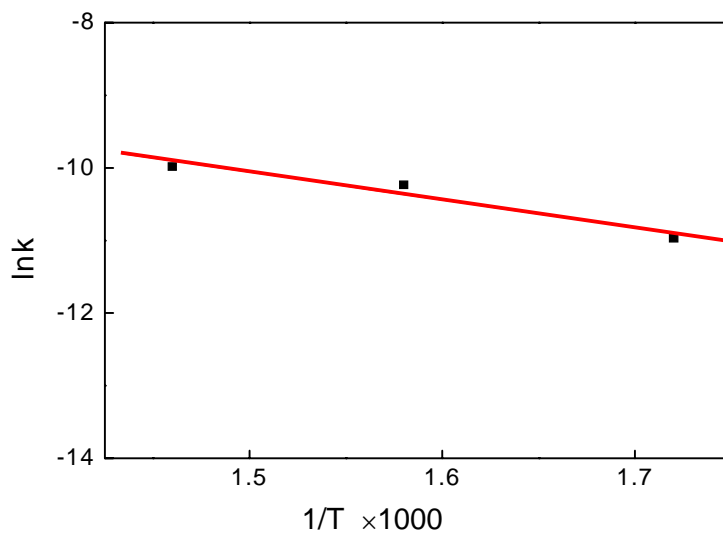


Fig.4 Effect of temperature on the reaction rate constant

Applying $n=1$, $m=0.4$ to formula (3), and according to corresponding relationship between $\frac{d\alpha}{dt}$ and α , $\ln k$ at each temperature can be calculated, which can be seen in Fig.4. And then the values of activation energy E and frequency factor A can be calculated from Fig.4, that is, $E=32000\text{J/mol}$, $A=1.37 \times 10^{-2}(\text{h}^{-1}\text{Pa}^{-0.4})$.

Thus the reaction rate constant is determined as

$$k = 1.37 \times 10^{-2} \exp\left(-\frac{32000}{RT}\right)$$

(3) Reaction rate expression

To sum up, parameters of the reaction rate expression (4), which having been determined on the basis of experimental data and the calculated results, are shown in the Table 3.

Table 3 Parameters of reaction rate expression

A ($\text{h}^{-1}\text{Pa}^{-0.4}$)	E (J/mol)	n (-)	m (-)
1.37×10^{-2}	32000	1	0.4

The reaction rate expression of $\text{Mn}_2\text{O}_3(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) = 2\text{MnO}_2(\text{s})$ is given as

$$\frac{d\alpha}{dt} = 1.37 \times 10^{-2} \exp\left(-\frac{32000}{RT}\right) (100 - \alpha) p_{\text{O}_2}^{0.4} \quad (5)$$

It can be known from formula (5) that oxidation is first-order reaction when oxygen partial pressure is fixed.

3.3 Discussion

(1) Effect of temperature on the reaction rate

Because of the relative less activation energy of Mn_2O_3 oxidation, the effect of temperature on oxidation ratio is also a little. It suggests that chemical reaction is not a controlled step.

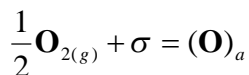
(2) Effect of oxygen partial pressure on the reaction rate

Fig.5 shows the relationship between oxidation ratio α and oxygen partial pressure. As it can be seen in the figure, the increase range of oxidation ratio is relatively great with the increase of oxygen partial pressure, while oxygen partial pressure is relatively low. But the increase range of oxidation ratio decreases gradually when continuing raising oxygen partial pressure.

(3) Controlled step in reaction

Assume that the oxidation is made up of elementary reactions as follows:

- 1) O_2 molecules are adsorbed on the surface of Mn_2O_3 particles



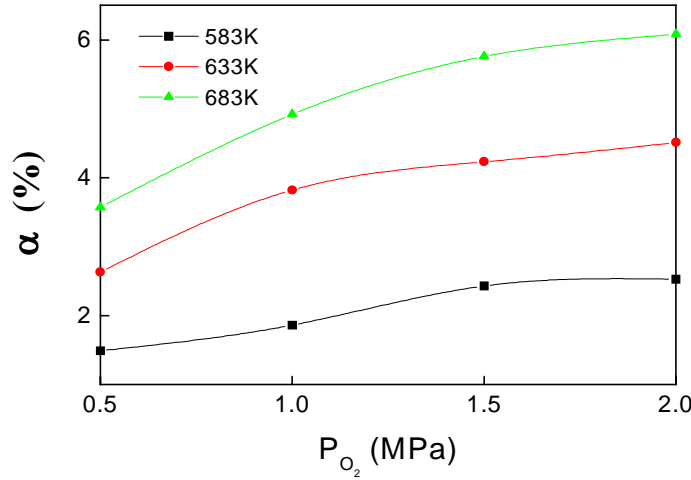
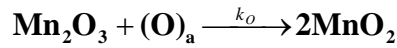


Fig.5 Effect of oxygen partial pressure on oxidation rate

2) (O)_a adsorbed will react with Mn₂O₃ on the interface and produce MnO₂



First, assume that interface chemical reaction is the controlled step, and according to L-H Model ^[2], the reaction rate expression can be given as

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k_o - \frac{1}{2} \ln p_{O_2} \quad (6)$$

Due to formula (6) not agree with experiment data, the interface chemical reaction is not controlled step in the oxidation.

Second, assume that gas adsorption is the controlled step, the reaction can equal



According to Langmuir adsorption expression

$$\frac{\theta}{1-\theta} = b\sqrt{p_{O_2}} \quad (8)$$

where, θ - adsorption ratio, that is, the ratio of area of having adsorbed O₂ molecules to the whole adsorbent area (-);

b – constant while temperature is fixed (-).

Consider that adsorption is the controlled step, the relationship between adsorption ratio α and oxidation ratio is given by $\theta = \frac{\alpha}{100}$.

So formula (8) can be represented by

$$\ln\left(\frac{\alpha}{100-\alpha}\right) = \ln b + \frac{1}{2} \ln p_{O_2} \quad (9)$$

Three straight lines are obtained by plotting the values of $\ln\left(\frac{\alpha}{100-\alpha}\right)$ against $\ln(p_{O_2})$ at each temperature (Fig.6).

As it can be seen in Fig.6, the slope of straight line at each temperature approximates to 0.42, which is close to 0.5, i. e. the coefficient of $\ln(p_{O_2})$ in the formula (9). So it can be deduced that the O_2 adsorption on the surface of Mn_2O_3 particles abide by Langmuir Adsorption Model and also is the controlled step in the reaction.

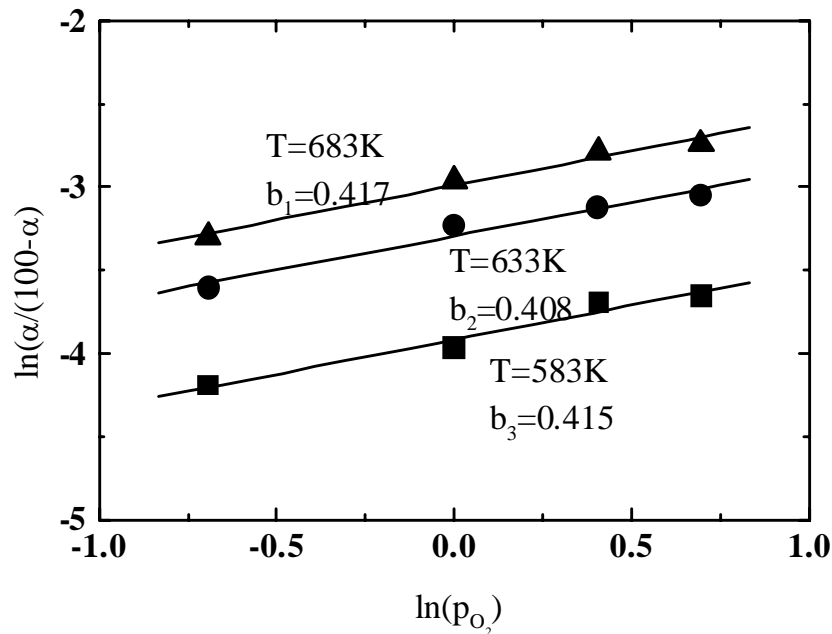
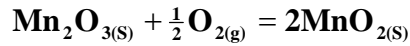


Fig.6 Relationship between $\ln\left(\frac{\alpha}{100-\alpha}\right)$ and $\ln(p_{O_2})$.

As a result of O_2 adsorption on the surface of Mn_2O_3 particles being the controlled step in the reaction, oxygen molecules cannot dissociate effectively to active oxygen atoms on the surface of Mn_2O_3 particles, which seriously hinders the further reaction. So it is the immediate cause that results in the low oxidation rate. Thus it is a study in the future that how to strengthen O_2 adsorption on the surface of Mn_2O_3 particles.

4. CONCLUSION

The reaction rate expression of Mn_2O_3 oxidation



is represented as:

$$\frac{d\alpha}{dt} = 1.37 \times 10^{-2} \exp\left(-\frac{32000}{RT}\right)(100 - \alpha)p_{\text{O}_2}^{0.4}$$

The results show that the reaction rate and ratio are lower, on which the temperature and the oxygen partial pressure have a little effect under given experiment conditions. The O_2 adsorption on the surface of Mn_2O_3 particles is the controlled step in the reaction. Though the thermo-dynamical conditions of the reaction producing Mn_2O_3 by oxidizing roasting Mn_2O_3 directly are satisfied, it would proceed very hard because of being restricted by kinetics factors. We should find out the better way to oxidize Mn_2O_3 .

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