Journal of University of Science and Technology Beijing
Vol.8(2001), No.3, p.185

Effects of Catalyst and Additive Containing Li, Na, or Ca on Reduction of Iron Oxide/Carbon Composite Pellets

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(Received 2000-10-08)

Abstract: The catalyst containing 0.69% (mass fraction) of Li^+, Na^+, or Ca^{2+} were synthesized, and the catalytic effect on the reduction of iron oxide/carbon composite pellets were investigated by comparing with that of additive at 850 ℃. The effect of the catalyst was greater than that of the additive, it can be considered that catalyst promoted the formation of iron nucleus early on reduction processes of iron oxide/carbon composite pellets. In addition, both effects of catalyst and additive increased after added carbon powder into the pellets, but the extent of increase decreased when the carbon powder exceeded a suitable content (about 4%), this amount is less than that of carbon needed theoretically on the reduction from hematite to iron.

Key words: iron oxide; carbon; reduction; catalyst; pellets; additive

[*This work was financially supported by the National Natural Science Foundation of China, Contract No. 59774022.*]

1 Introduction

Thermodynamically, the reduction of hematite to iron can occur at temperature over 710 ℃ under the condition of carbon excess, but almost direct reduction is usually in progress at higher temperature because the reduction rate of iron oxides at lower temperature is slower, it results in the increase of carbon dioxides and deterioration of environment, and so on. Recently, the attention has been paid on the application of catalysts and additives for the increase of reaction rate of reduction at lower temperature. F. Nakiboglu et al. reported that reduction rate could be increased by adding a little of alkali metal and alkali earth metal into iron oxide [1–3]. Observations by previous workers also had shown that some interfaces contribute to the reduction of iron oxides [4], but the research about the catalytic mechanisms of alkali metal, alkali earth metal, and interface was not very enough for the applications of catalyst on the reduction of iron oxide/carbon composite pellets. Therefore, the effect of catalyst and additive containing alkali metal or alkali earth metal, as well as the effect of interfaces on the reduction of iron oxide/carbon composite pellets were experimentally investigated for determining these catalytic mechanisms.

2 Experimental Method

2.1 Synthesis Catalyst

Raw materials consist of analytical reagents of Fe_2O_3, $CaCl_2$, NaCl, LiCl, and spectra pure powder of carbon; the mixing ratio of samples is shown in **table 1**.

Table 1 The mixing ratio of raw materials of catalysts (mass fraction) %

Catalyst	I	II	III	IV
Raw materials	Fe_2O_3 : $CaCl_2$: C	Fe_2O_3 : NaCl : C	Fe_2O_3 : LiCl : C	Fe_2O_3 : C
Mixing ratio / %	71 : 24 : 5	71 : 24 : 5	71 : 24 : 5	93 : 7

The well-mixed sample of 5 g was pressed to form a cylinder of 10 mm in diameter in a matrix under the pressure of 16.7 MPa. The sample with a basket of Fe-Cr-Al was put in a vertical furnace with the working tube of 40mm in diameter, and was reduced in mixture gas of 50% CO and 50% CO_2 (volume fraction) for 3 h at 850 ℃ under the flow rate of 5.0×10^{-6} m^3/s and the pressure of 1.013×10^5Pa. After reduction, the sample was raised up at the upper part of the working tube, and cooled down to room temperature; afterwards the sample was ground and determined by X-ray diffraction.

2.2 Determination of catalytic property

For comparison of catalytic effect, the catalyst and additive were added separately in 0.69% (mass fraction) of alkali metal or alkali earth metal into the mixtures of hematite and carbon [2], the compositions of samples are listed in **table 2**, the samples were mixed and pressed to form pellets with a cylinder of 10 mm in diameter.

Table 2 Composition of samples for comparison of catalytic property

Adding sorts	m_H / g	m_a / g	w_c / %				
Catalyst I	5.000	0.289	0	2	4	6	8
Additive I	5.000	0.096	0	2	4	6	8
Catalyst II	5.000	0.268	0	2	4	6	8
Additive II	5.000	0.088	0	2	4	6	8
Catalyst III	5.000	0.593	0	2	4	6	8
Catalyst IV	5.000	0.289	0	2	4	6	8

Note: m_H—mass of hematite; m_a—mass of catalyst or additive added in pellets; w_c —mass fraction of carbon added separately in pellets.

The pellet was put into the furnace and reduced for 30 min at 850 ℃ under the CO flow of 3.0×10^{-6} m^3/s and the pressure of 1.013×10^5Pa. After reaching the reduction time, the pellet was raised up to the upper part of the working tube and cooled down to room temperature. Eventually, the reduction rate of iron oxide was calculated according to the contents of the total iron and the carbon remained from the chemical analysis of pellet, the reduction ratio, R, was given by

$$R=\frac{100}{[\mathrm{O}]_b}\cdot\left(1-[\mathrm{C}]_b-\frac{[\mathrm{Fe}]_b(1-[\mathrm{C}]_a)}{[\mathrm{Fe}]_a}\right) \quad (1)$$

where $[\,]_b$ and $[\,]_a$ were the mass ratios of the element in the brackets [ ] before and after the reaction respectively.

3 Results and Discussion

The experimental results for the effects of catalyst, additive and interface on the reduction of iron oxide/carbon composite pellets are summarized in **table 3**. It indicates the differential change of reduction rate with the increase of carbon content by dR/dC. Further, the integral change is shown in **figure 1**.

Table 3 Effects of catalyst, additive and carbon content on reduction ratio of pellets

Experimental Conditions		w_c / % 0	2	4	6	8
Non-addition	R / %	50.0	52.5	56.5	58.5	60.1
	dR / dC	—	1.25	2.00	1.00	0.80
Catalyst I	R / %	57.5	61.1	74.5	75.5	76.5
	dR / dC	—	1.80	6.70	0.50	0.50
Catalyst II	R / %	59.1	67.5	87.5	90.1	84.2
	dR / dC	—	4.20	10.00	1.30	−2.95
Catalyst III	R / %	58.2	63.5	84.5	87.5	86.3
	dR / dC	—	2.65	10.50	1.50	−0.60
Catalyst IV	R / %	55.3	57.9	60.3	61.3	61.5
	dR / dC	—	1.30	1.20	0.50	0.01
Additive I	R / %	52.0	57.4	68.1	72.0	72.5
	dR / dC	—	2.70	5.35	1.95	0.25
Additive II	R / %	56.5	61.3	70.0	72.1	71.2
	dR / dC	—	2.40	4.35	1.05	−0.45

Figure 1 shows that the reduction ratio increased after added carbon into pellets, this is because CO can be formed by the Boudouard reaction in pellets, which results in the decrease of the diffusion resistance of CO. But the effects of catalyst, additive, non-addition on the reduction of pellets were different, e.g. the effects of catalyst II and catalyst III were the greatest, oppositely, that of catalyst IV was the smallest. It indicated that they maybe have different mechanisms on catalysis of pellet reduction.

X-ray diffraction patterns of catalysts are given in **figure 2**, in which a lot of wustite existed in mineralogical composition of catalysts. According to the comparison of experimental results of catalyst IV addition

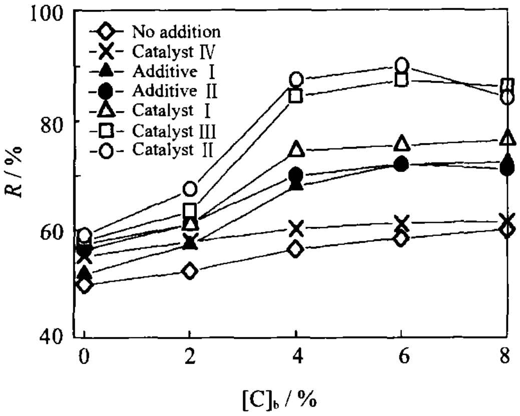

Figure 1 Comparison of the integral changes of pellet reductionafter added catalyst and additive at 850 ℃ for 30 min.

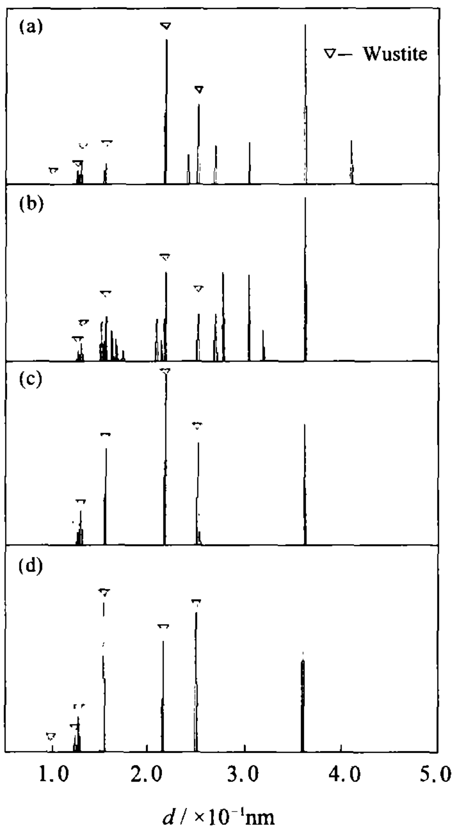

Figure 2 X-ray diffraction of the catalysts, (a) Catalyst I; (b) Catalyst II; (c) Catalyst III; (d) Catalyst IV.

and non-addition, it is understood that the reduction ratio of pellets increases after adds catalyst IV. This can be explained that the wustite in the catalyst reacted with hematite in the pellet as follows:

$$FeO + Fe_2O_3 \rightarrow Fe_3O_4 \quad (2)$$

to form the interfaces between Fe_2O_3 and Fe_3O_4, FeO and Fe_3O_4. It resulted in the decrease of lattice conversion energy from hematite to magnetite and from magnetite to wustite, and promoted the reduction of iron oxide. That dR/dC of the pellet after added catalyst IV was smaller than that of the pellet of non-addition in table 3, can be explained that the effect of reaction (2) is weakened relatively with the increase of carbon content in pellets.

The increase of the reduction rate of pellets after added catalyst I, catalyst II, catalyst III, additive I, or additive II, is shown in figure 1. It is considered that the alkali metal or alkali earth metal promoted the Boudouard reaction, and resulted in the increase of reduction rate of iron oxides, this is identical with previous experimental result [5]. But how to explain the different effect between catalyst and additive on the reduction of pellets is the key of problems.

The lattice parameter of wustite was calculated from the results of X-ray diffraction and equation (3) and listed in **table 4**. Table 4 indicates that the lattice parameters of wustite in catalyst I, catalyst II, and catalyst III, are greater than that of wustite in catalyst IV. This shows that Na^+, Li^+ or Ca^{2+} ion entered into the lattice of wustite. Therefore, the increase of reduction rate for pellets can be considered that the wustite in catalyst reduced early to iron in the reduction process of pellets because that bigger ions as Na^+, Li^+ or Ca^{2+} entered into the lattice of wustite, and resulted in lowering the wustite stability, moreover, the iron also had the effect of catalyst for the Boudouard reaction [6] in pellets. The catalytic effect on the reduction of pellets is identical with the increases of lattice parameter of wustite in catalyst, i.e. the effect of catalyst II was the greatest, that of catalyst III and I were secondly, and that of catalyst IV was the smallest.

Table 4 Lattice parameters (*a*) of the wustite in catalysts

Catalyst	I	II	III	IV
$a / \times 10^{-1}$ nm	4.3064	4.3161	4.3073	4.3062

$$\sin^2\theta = (\lambda / 2a)^2 (h^2 + k^2 + l^2) \quad (3)$$

In addition, table 3 shows that the values of dR/dC increased with the increase of carbon content when less than 4%, but when more than the carbon content, the values of dR/dC were closed to zero for pellets after added catalyst or additive. Therefore, there is a suitable amount of carbon content, e.g. about 4%, for the reduction of pellets under this experimental condition. It can be considered that the suitable amount is the transform point from carbon content controlling rate step to non-carbon content controlling rate step for the Boudouard reaction in the reduction of pellets, and this value is less than the amount of carbon needed theoretically on the reduction from hematite to iron.

4 Conclusions

(1) The reduction rate of iron oxide/carbon compos-

ite pellets can be improved by adding catalyst or additive containing Li^+, Na^+, or Ca^{2+}, but the effect of the catalyst is greater than that of the additive on the reduction of iron oxides. This is because that Li^+, Na^+, or Ca^{2+} entered into the lattice of wustite in catalyst, which resulted in the formation of iron early in the process of reduction of iron oxide/carbon composite pellets.

(2) The wustite in catalyst also promoted the reduction of iron oxide/carbon composite pellet, but the effect decreased with the increase of carbon content in the pellet. This can be considered that the wustite in the catalyst reacted with hematite in the pellet to form interfaces between Fe_2O_3 and Fe_3O_4, FeO and Fe_3O_4, which resulted in the decrease of lattice conversion energies from hematite to magnetite and from magnetite to wustite, and promoted the reduction of iron oxide, but the increase of carbon content decreased the interfaces formed.

(3) There was a suitable amount of carbon added in iron oxide/carbon composite pellet after added catalyst or additive. The suitable amount was about 4%, which is less than that of carbon calculated theoretically according to reduction from hematite to iron by carbon.

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