

[54] **PRODUCTION OF RUTILE AND IRON FROM ILMENITE**

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[63] Continuation-in-part of Ser. No. 2,659, Jan. 13, 1970, abandoned.

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[58] Field of Search..... **2/659; 75/121, .5 AA, 75/.513 A, 1; 423/417**

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[57]

ABSTRACT

Ilmenite is treated with a reducing agent to selectively reduce iron oxide to metallic iron. The product is then treated with carbon monoxide in the presence of ammonium polysulfide solution to form iron carbonyl, which is removed by volatilization leaving rutile. The iron carbonyl is then decomposed to produce metallic iron.

5 Claims, No Drawings

PRODUCTION OF RUTILE AND IRON FROM ILMENITE

This application is a continuation-in-part of application Serial No. 2,659, filed Jan. 13, 1970 and now abandoned.

In many prior art processes for producing rutile from ilmenite, the iron oxide in the ilmenite is selectively reduced to metallic iron, and the iron is then removed by converting it to iron oxide, ferrous salts, or ferric salts. Such processes are disclosed, e.g., in U. S. Pat. Nos. 3,112,178; 3,252,787 and 3,257,198. The fundamental disadvantage of these processes is that the iron compounds produced have less value than metallic iron, and are a disposal problem or else require further processing steps to produce metallic iron. U. S. Pat. No. 1,789,813 discloses treatment of iron oxide-containing materials with carbon monoxide to convert the iron to the carbonyl, removal of the carbonyl from the reaction zone and decomposition of the carbonyl to yield metallic iron. However, in the absence of a suitable catalyst, this process has been found to be impractical since the rate of reaction between the iron and the carbon monoxide is too slow. Moreover, the particular catalyst employed has been found to be critical in obtaining a reaction rate suitable for an economically feasible process.

It has now been found, according to the process of the invention, that ilmenite may be treated to yield a high-grade rutile ore and iron by means of a process comprising selective reduction of iron oxide in the ilmenite to metallic iron, followed by treatment with CO, in the presence of ammonium polysulfide solution as catalyst, to form the volatile iron carbonyl which is then removed from the reaction zone and subsequently decomposed to produce metallic iron and CO.

Reduction of the ilmenite is accomplished by means of conventional procedures, e.g., treatment with hydrogen for about 1 to 3 hours, preferably about 2 hours, at a temperature of about 750° to 1,000°C, preferably about 860°C. Treatment with coke for about 2 to 6 hours, preferably about 4 hours, at about 900° to 1,200°C, preferably about 1,100°C, is also effective. Other conventional reducing agents such as carbon, coal or carbon monoxide may also be used. Optimum amounts of reducing agent, as well as optimum temperature and time of treatment, will obviously vary considerably with the type of reducing agent, specific type of ore treated, state of subdivision of the ore, desired purity of the product (rutile ore), etc., and are best determined experimentally. For a few ores, it may be advantageous to preoxidize the ilmenite, prior to reduction, to convert any ferrous iron to ferric iron. This can be conveniently done by heating the ilmenite for about 1 to 3 hours in an atmosphere of air or oxygen, at a temperature of about 500° to 1,000°C, preferably about 750°C.

The reduced ilmenite is then treated with CO, in the presence of a catalyst comprising ammonium polysulfide solution, for about 2 to 4 hours at a temperature of about 100° to 200°C, preferably about 110° to 150°C, and a pressure of about 1 to 200 atmospheres, preferably about 60 to 100 atmospheres. Again, optimum reaction conditions will depend on the above variables and are best determined experimentally.

The carbonyl formed is predominantly the pentacarbonyl, i.e., $\text{Fe}(\text{CO})_5$, and the amount of CO required is approximately the stoichiometric amount for formation

of this compound. Greater than stoichiometric amounts may, however, be used to speed the reaction, while lesser amounts may be adequate if complete removal of iron is not required. The CO reactant will generally be most conveniently and efficiently supplied as a flowing stream, the flowrate being adjusted to supply the required amount of CO.

The catalyst preferably consists essentially of an aqueous ammonium polysulfide solution, although other catalysts such as other sulfur compounds, sulfur, ammonia, other ammonia compounds, etc. may be present in minor amounts. The ammonium polysulfide solution consists of an aqueous solution having a concentration of $(\text{NH}_4)_2\text{S}$ of about 20 to 24 weight percent, plus excess dissolved sulfur in an amount of about 5 to 6 weight percent. This solution is employed as catalyst in an amount of about 0.05 to 0.08 ml for each gram of the reduced ilmenite.

It has also been found that best results are achieved when the catalyst is introduced into the reaction zone in such manner that the catalyst solution does not contact the reduced ilmenite, only vaporized catalyst thereby contacting the reduced ilmenite. This may be readily accomplished by introducing the catalyst solution into the reaction zone in a separate vessel, or by addition of the catalyst to the reaction vessel with the reduced ilmenite contained in a separate vessel, e.g., a ceramic boat, as in the examples below.

The iron carbonyl is volatile at the temperature employed in its formation and, therefore, its removal from the reaction zone is readily accomplished by sweeping with a flowing stream of gas. This gas usually most conveniently consists of a portion of the CO gas stream used for supplying the CO reactant. Thus, the flowing stream of CO serves both to supply the reactant CO and sweep the product $\text{Fe}(\text{CO})_5$ from the reaction zone.

Product $\text{Fe}(\text{CO})_5$ is conducted to a separate vessel where it is decomposed to yield powdered, plate, or chip metallic iron and CO, the latter being recirculated to the carbonylation reaction. Decomposition is accomplished by maintaining the separate vessel at higher temperature or lower pressure, or a combination of the two. Temperature of about 280° to 350°C, preferably about 300°C, and a reduced flow rate, i.e., longer residence time, are desirable. Simultaneous reduction of the pressure by any amount will usually speed the decomposition of the carbonyl.

The invention will be more specifically illustrated by the following examples.

EXAMPLES 1 to 9

In each of these examples about 11.4 grams of ilmenite, containing about 25 percent iron, was ground to a particle size of minus 100 mesh and placed in a ceramic boat in a high pressure cylindrical reactor at a temperature of 860°C. Hydrogen was then introduced to the reactor at atmospheric pressure and a flow rate of 150 ml/min STP for a period of 2 hours.

Hydrogen flow was then stopped and the reactor cooled to room temperature. The weight of the reduced ilmenite was about 10 grams. Aqueous ammonium polysulfide solution (APS) containing 20 weight percent $(\text{NH}_4)_2\text{S}$, plus 5 to 6 weight percent excess dissolved sulfur, was then added to the reactor in the amount shown in Table 1, without actually contacting the reduced ilmenite in the ceramic boat. Carbon mon-

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oxide gas was then introduced to the reactor at the pressure and temperature given in Table 1 and a flow rate of 150 ml/min STP for a period of 2 hours. Excess CO and $\text{Fe}(\text{CO})_5$, formed by reaction with metallic iron from the hydrogen reduction, were conducted from the reactor to a Vycor vessel maintained at a temperature of 300°C and a pressure of 1 atmosphere to decompose the $\text{Fe}(\text{CO})_5$. Results, in terms of percent of iron removed, are given in Table 1.

Example 10

In this example ammonia was employed as catalyst. Initial reduction of the ilmenite was accomplished as in examples 1 to 9. The reaction vessel was then evacuated and ammonia admitted at 1 atmosphere pressure for about 1 minute. CO was then admitted until the pressure was 1,000 psig and continued at a flow rate of 150 ml/min STP for a period of 2 hours. Decomposition of $\text{Fe}(\text{CO})_5$ was accomplished as in examples 1 to 9 and results are shown in Table 1.

Examples 11 to 20

In these examples powdered elemental sulfur was employed as catalyst. Initial reduction was accomplished as in the preceding examples. Powdered sulfur, in the amount shown in Table 1, was then mixed with 10 grams of the reduced ilmenite and placed in the ceramic boat. The reaction vessel was then evacuated (except in Example 11) and CO admitted to a pressure of 1200 psig and continued at a flow rate of 150 ml/min STP for a period of 2 hours. In Example 11, the reaction vessel was not evacuated before the CO flow was started.

Again, decomposition of the $\text{Fe}(\text{CO})_5$ was as in the preceding examples and results are shown in Table 1.

The marked superiority of the ammonium polysulfide solution as catalyst is evident from the data of Table 1.

TABLE 1

CO pressure,	Temp.	Percent of total
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Example	Catalyst	psig	°C	iron removed
	ml			
1	APS 0.16	1,400	143	44
2	Do.	1,400	142	47
3	Do.	1,400	142	43
4	APS 0.48	1,400	140	70
5	Do.	1,400	140	66
6	Do.	1,400	140	70
7	APS 0.64	1,400	127	93
8	Do.	1,200	125	91
9	Do.	1,000	115	92
10	NH_3 , 1 atm.	1,000	118	3
	gm			
11	Sulfur, 0.075	1,200	129	2
12	Sulfur, 0.038	1,200	123	2
13	Sulfur, 0.075	1,200	125	9
14	Sulfur, 0.12	1,200	124	18
15	Sulfur, 0.15	1,200	127	28
16	Sulfur, 0.175	1,200	130	21
17	Sulfur, 0.20	1,200	130	26
18	Sulfur, 0.25	1,200	125	20
19	Sulfur, 0.30	1,200	125	7
20	Sulfur, 0.50	1,200	125	7

We claim:

1. A method for producing rutile from ilmenite comprising selectively reducing iron oxide in the ilmenite to metallic iron, reacting the reduced product at a temperature of about 100° to 200°C with carbon monoxide in the presence of a catalyst consisting of ammonium polysulfide solution, said solution being disposed out of contact with the reduced ilmenite, to convert the metallic iron to volatile iron carbonyl, removing the iron carbonyl from the reaction zone, and decomposing the carbonyl to metallic iron and carbon monoxide.

2. The method of claim 1 in which the reduction is preceded by an oxidation step to convert any ferrous iron to ferric iron.

3. The method of claim 1 in which the reduction is accomplished with hydrogen.

4. The method of claim 1 in which the reduction is accomplished with coke.

5. The method of claim 1 in which the carbonyl is decomposed at a temperature of about 280° to 350°C.

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