CO_2 hydrogenation during $FeCO_3$ (Siderite) reduction

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The catalytic hydrogenation of carbon dioxide, makes use of CO_2 as a huge carbon resource for chemical hydrogen storage. Iron is frequently used as a catalyst. The hydrogenation of CO_2 has been greatly investigated with synthetically produced iron catalysts.

In our project, we focused on the hydrogenation of CO_2 combined with the reduction of siderite. $FeCO_3$ (Siderite) is a major raw material in the iron production. The metallurgical state-of-the-art processing of siderite consists of calcining of $FeCO_3$ in a sinter plant to hematite (Fe_2O_3), which then reacts with CO to form a pig iron smelter in the blast furnace. H_2 reduces iron carbonate directly to elemental iron or iron oxide (Wustite), and CO_2 is partially hydrogenated to methane and carbon monoxide. The experiments were conducted in a tubular reactor on bench scale. The temperature range was 350°C to 500°C, the pressure range was from ambient pressure to 1.5 MPa. Through variation of the reaction parameters (temperature, pressure, hydrogen atmosphere) the effect of operation conditions on the product yield was investigated. While reduction of iron carbonate in nitrogen produces magnetite (Fe_3O_4), CO_2 and CO according to (Eq. 1), H_2 atmosphere enables formation of wustite (FeO) (Eq. 2), elemental iron (Eq. 3), as well as CO_2 (Eq. 3), CO (Eq. 4) and CH_4 (Eq. 5).

$$FeCO_3 \xrightarrow{Q,N_2} \frac{1}{3}\ Fe_3O_4 + \frac{2}{3}\ CO_2 + \frac{1}{3}\ CO \quad (1)$$

$$FeCO_3 \xrightarrow{Q,H_2} FeO + CO_2 \quad (2)$$

$$FeCO_3 + H_2 \overset{Q}{\rightarrow} Fe + CO_2 + H_2O \quad (3)$$

$$FeCO_3 + 2\ H_2 \overset{Q}{\rightarrow} Fe + CO + 2\ H_2O \quad (4)$$

$$FeCO_3 + 5\ H_2 \overset{Q}{\rightarrow} Fe + CH_4 + 3\ H_2O \quad (5)$$

High pressures and low temperatures facilitate methane formation, while at elevated temperature and low pressure CO plus CO_2 formation is preferred.

The direct reduction of iron carbonate with H_2 to elemental iron consumes less reducing agent and emits less CO_2 compared with the state-of-the-art technology of calcining in the sinter plant and reduction of hematite/magnetite in the blast furnace.