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Back Reactions in Thermochemical Cycle based on Carboreduction of ZnO.

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High temperature thermochemical endothermic processes can use concentrated solar radiation as the energy source for splitting water and production of hydrogen. The carboreduction of zinc oxide is an example for such processes. The product is zinc, which can be used for hydrogen production via hydrolysis. The product of hydrolysis is the zinc oxide, which is recycled to the solar reactor. This cycle can be used for conversion, storage and transportation of solar energy. The solar contribution is high and can reach almost 60%.

It was found that the mechanism of carboreduction of ZnO assumes two gas-solid chain reactions with intermediate formation of CO and CO_2 :

$$ZnO+CO = Zn+CO_2 \quad (1)$$

$$CO_2+C = 2CO \quad (2)$$

The first reaction is reduction of ZnO with CO and the second one is gasification of carbon with CO_2. Problems arise because the principal reaction (1) tends to reverse at low temperatures and condensation of zinc is difficult. So, the kinetics of the back reactions in gas and liquid phases is very important for practical realization of this energy cycle.

In the present work the kinetics of oxidation of liquid zinc was investigated by bubbling of CO_2/CO mixture in molten zinc. Experimental set up was constructed in laboratory. The reactor was made from quartz. After preheating up to the reaction temperature the oxidant is introduced to liquid zinc through the quartz dip tube (diameter 4-10 mm). The experiments were carried out in the temperature range of 450-500^{o}C with pure CO and CO_2/CO mixtures at CO_2 concentrations of 2-45% mole. The experiments with pure CO were conducted to estimate the rate of Boudouard reaction. The results show that the conversion of CO to CO_2 was very low; in the order of 10^{-4}. Consequently, the rate of Boudouard reaction in the present of zinc is low, and zinc (also ZnO) has no catalytic properties affecting the Boudouard reaction. The experiments were carried out at different CO_2 concentrations and constant flow rate. At low CO_2 concentrations the reaction rate is quite proportional to the concentration of the oxidant. At CO_2 mole fraction lager than 0.25 the reaction order is close to zero, which is in agreement with data that appear in literature. The kinetic equation $Wsp= k\ PCO_2/\ (1+bCO_2)$ is proposed and the rate constants and activation energy were determined from the experimental data. The limiting step at low concentration of CO_2 is the reaction on the gas-metal boundary. It can be concluded that if solar carboreduction of ZnO takes place at temperatures such as 1250-1300 ^{o}C, the rate of the back reactions in the cooler/condenser is expected to be low.