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One-step hydrocarbons steam reforming and CO_2 capture

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1. Introduction

Already in 1868 [1], H_2 was produced by the steam reforming (eq.1) of hydrocarbons in the presence of a calcium oxide, and the use of natural calcium-based sorbents as candidates to remove CO_2 in situ from reactors has been receiving increasing attention. Through simultaneous CO_2 absorption (eq.3) the equilibrium of the homogenous water gas shift reaction (eq.2) is shifted towards H_2 and CO_2 and all of the parallel reforming/gasification reactions are also influenced in favour of the desired products. Accordingly, a hydrogen-rich product gas results with reduced CO and CO_2 concentration.

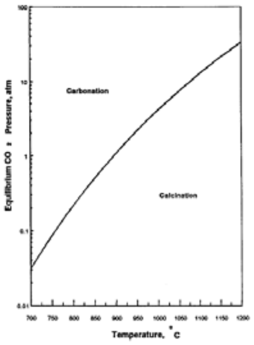

Fig. 1: Equilibrium of CO_2 pressure at a function of temperature

$$CH_xO_y + (1\text{-}y)\, H_2O \rightarrow CO + (0{,}5x + 1 - y)\, H_2 ,\Delta H_R > 0 \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 , \qquad \Delta H_R < 0 \qquad (2)$$

$$CaO + CO_2 \rightarrow CaCO_3 , \qquad \Delta H_R < 0 \qquad (3)$$

The CO_2 absorption is exothermal so that the gasification is nearly energetically self sufficient. Loaded sorbent is regenerated in a subsequent process step by adding heat. The equilibrium vapour pressure of CO_2 over CaO is given by [2]:

$$\log_{10} P_{eq}[atm] = 7.079 - \frac{8308}{T[K]}$$

The equilibrium CO_2 pressure over $CaCO_3$ as a function of temperature is shown in Figure 1. Although $CaCO_3$ decomposition in a CO_2-free atmosphere is thermodynamically favored at all temperatures shown in the figure, a temperature of at least 800°C is needed to ensure adequate decomposition kinetics [3].

2. Dolomite as CO_2 sorbent and tar reforming catalyst

A critical issue is that, although the decomposition of $CaCO_3$ is always 100%, the reactivity of CaO carbonation fell dramatically after a rapid initial reaction. Two main reasons are the loss of pore volume of the porous calcium oxide and sintering. The use of **calcinated dolomite** (CaOMgO) for CO_2 sequestration process, improve the cyclic capture. Magnesium oxide does not contribute to carbon dioxide sequestration, because magnesium carbonate decomposes at much lower temperature than calcium carbonate; however, inert MgO does contribute to stabilize the structure of the solid sorbent in a multicycle carbonation-calcination process.

It is well know that carbonate rocks, such as limestone and dolomite, also decompose tars efficiently. Purification of tarry fuel gas is a crucial step in the development of biomass gasification process; in particular, fluidized bed gasification is a promising method for the large-scale production of synthesis gas, but this method produces large amounts of undesiderable tarry materials. Therefore, catalytic elimination of the tar inside the gasifier using a cheap catalyst is the promising way to solve this problem.

To improve this catalytic activity, a variable amount of **iron** can be added by impregnation in the dolomite structure. In fact iron is known to catalyse the reactions of the main components of the fuel gas (H_2, CO, CO_2, H_2O), for example water-gas shift reaction. In addition, iron in various forms has been found to catalyse pyrolysis, tar decomposition and hydrocarbons reforming.

Iron has been less studied because of the high efficiency of nickel catalyst in hydrocarbons reforming, but it has several advantages:

- lower cost which can imply a higher metal concentration in the catalyst,
- no toxicity during mass loss in the environment.

3. Conclusion

This work-in-progress investigates the structural interactions between dolomite and iron oxides, and compares different synthesis methods, in order to obtain a **strong metal-support interaction** that should limit the known deactivation due to carbon formation and deposition, and make possible, in a cheap combined catalyst and sorbent, the one-step process of steam reforming and CO_2 separation.

References:

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[3] A. Lopez Ortiz, P. Harrison Douglas, Hydrogen production using Sorption-enhanced reaction, Industrial engineering and chemical research, 40, pp. 5102-5109.