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Production of hydrogen by unmixed steam reforming of methane

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Abstract

Unmixed steam reforming is an alternative method of catalytic steam reforming that uses separate air and fuel–steam feeds, producing a reformate high in H_2 content using a single reactor and a variety of fuels. It claims insensitivity to carbon formation and can operate autothermally. The high H_2 content is achieved by in situ N_2 separation from the air using an oxygen transfer material (OTM), and by CO_2 capture using a solid sorbent. The OTM and CO_2 sorbent are regenerated during the fuel–steam feed and the air feed, respectively, within the same reactor. This paper describes the steps taken to choose a suitable CO_2-sorbent material for this process when using methane fuel with the help of microreactor tests, and the study of the carbonation efficiency and regeneration ability of the materials tested. Elemental balances from bench scale experiments using the best OTM in the absence of the CO_2 sorbent allow identifying the sequence of the chemical reaction mechanism. The effect of reactor temperature between 600 and 800 °C on the process outputs is investigated. Temperatures of 600 and 800 °C under the fuel–steam feed were each found to offer a different set of desirable outputs. Two stages during the fuel–steam feed were characterised by a different set of global reactions, an initial stage where the OTM is reduced directly by methane, and indirectly by hydrogen produced by methane thermal decomposition, in the second stage, steam reforming takes over once sufficient OTM has been reduced. The implications of these stages on the process desirable outputs such as efficiency of reactants conversion, reformate gas quality, and transient effects are discussed.
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1. Introduction

Unmixed steam reforming, henceforth called 'USR', first appeared in the mainstream scientific literature through the two publications Kumar et al. (1999) and Lyon and Cole (2000). It offers an alternative method for the autothermal production of a hydrogen-rich reformate (more than 90% dry). It relies on alternated feeds of air and of a mixture of vapourised fuel and steam to create a cyclic process. During USR, the fuel–steam feed and the air feed do not mix, contrary to conventional autothermal catalytic steam reforming, where pure oxygen is relied on for partial oxidation of the fuel and providing heat for the endothermic steam reforming reaction. Instead, the USR process makes use of an oxygen 'mass transfer' material or OTM, here chosen to be reduced nickel supported on alumina. Although various reactor and flow configurations are possible with USR, a plug flow fixed bed reactor is used in the present study, where the bed materials are crushed to 1–2 mm size. The OTM is able to store oxygen exothermically by forming the NiO on the support when subjected to an air flow, thus heating up the reactor bed evenly over its cross-section, and allowing the inert N_2 component to evolve separately from the reformate. The oxide then regenerates to metallic Ni by reduction when it is exposed to the subsequent fuel and steam feed, responsible for the main steam reforming reaction. When a CO_2-sorbent material is used in combination with the OTM, the catalytic reaction of steam reforming proceeding under the fuel–steam feed on the hot Ni–OTM catalyst bed occurs alongside CO_2 capture. This results in further purification of the reformate as well as favouring the water gas shift reaction towards H_2 production. The reformate can reach more than 90% content in H_2 (dry) as a result of the combined in situ N_2 and CO_2 separations and the increased WGS. Some of the heat liberated under the following air flow is then utilised to decompose the carbonate present, thereby regenerating the CO_2 sorbent for the

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next cycle while the Ni–OTM oxidises. The evolutions of CO, CO_2, and H_2, proceed under the fuel–steam feed. Under air feed, the reactor effluent is an oxygen-depleted and CO_2-laden air stream. When using one fixed bed reactor, the production of hydrogen is therefore intermittent. For the process to continuously produce hydrogen, two identical reactor beds would need to run in parallel, each operating in a different half cycle. Alternative ways of continuously producing H_2 with a single reactor could also involve the use of a rotating bed travelling through air feed then fuel–steam feed zones. USR has previously been demonstrated using methane and diesel fuels (Kumar et al., 1999; Lyon and Cole, 2000). Over subsequent years, DOE reports and conference presentations appeared in the literature as research and development continued from the original work and the terminology of autothermal cyclic reforming (Kumar et al., 2004), as well as unmixed fuel processing were also used in this context (Zamansky, 2002; Rizeq et al., 2003). Close relatives of USR are chemical looping combustion (Ishida et al., 1987; Son and Kim, 2006), and coal hybrid combustion–gasification chemical looping (current work by the US' DOE National Energy Technology Laboratory).

A number of advantages are claimed for the USR process: (i) production of H_2-rich reformate (ca. 90% dry H_2) with a single reactor, (ii) potential for autothermal operation without the need for pure oxygen that would require a costly air separator pre-processing stage, (iii) improved heat transfer characteristics that allow down-scaling up of the process to a point, increasing its potential for distributed power generation if coupled with an intermediate temperature solid oxide fuel cell, or with a molten carbonate fuel cell, (iv) low cost reactor materials due to a hotter reactor centre and colder walls, (v) compactness of the process due to coupling of the endothermic and exothermic reactions within the reactor rather than relying on external heating, (vi) separation of CO_2-containing effluent from the H_2-rich reformate with potential for cheaper purification downstream technologies, (vii) insensitivity to coking, (viii) insensitivity to sulphur (as claimed by Lyon and Cole, 2000), finally, and related to the last two points, (ix) fuel feedstock-flexibility (gas and liquid). Currently there are adaptations of the principle of USR to pulverised coal using circulating fluidised bed technologies which draw similarities with chemical looping combustion (Rizeq et al., 2003).

The cycle of reactions involved in the methane unmixed reforming process is shown below and includes some reactions that were identified during the present investigation in addition to those mentioned in the literature.

1.1. First half of cycle: air feed

The main reactions are

Oxidation of the supported OTM and separation of N_2 from air:

$$Ni_{(S)} + 0.5(O_2 + 3.762N_2) \Rightarrow NiO_{(S)} + 1.881N_2 \quad (\Delta H < 0,\ \text{exothermic}). \tag{R1.1}$$

Reaction (R1.1) heats up the OTM's bed and some of its heat is used in the regeneration of the CO_2 sorbent:

Regeneration of the sorbent: $$MCO_{3(S)} \Rightarrow MO_{(S)} + CO_2 \quad (\Delta H > 0,\ \text{endothermic}). \tag{R1.2}$$

In addition to Reactions (R1.1) and (R1.2), identified in Lyon and Cole (2000) as the reactions at work under air flow, Reactions (R1.3) and (R1.4) were found to play a significant role during the present work:

Carbon complete oxidation: $$C_{(S)} + O_2 \Rightarrow CO_2 \quad (\Delta H < 0,\ \text{exothermic}), \tag{R1.3}$$

Carbon partial oxidation: $$C_{(S)} + 0.5O_2 \Rightarrow CO \quad (\Delta H < 0,\ \text{exothermic}). \tag{R1.4}$$

The gas product from this half cycle is N_2 rich containing CO_2 and unreacted O_2.

1.2. Second half of cycle: fuel–steam feed

The vapourised fuel and steam mixture encounters the hot reactor bed and the following global reaction occurs:

$$\begin{aligned} &MO_{(S)} + NiO_{(S)} + \text{fuel} + H_2O \\ &\quad \to (MCO_{3(S)} + Ni_{(S)}) + (C_{(S)}, CO, CO_2, H_2O) + H_2 \\ &\qquad (\Delta H > 0,\ \text{endothermic}). \end{aligned} \tag{R2}$$

Reaction (R2) is the overall reaction, it can be split up into the global reactions below:

Steam reforming: $$CH_4 + H_2O \to CO + 3H_2 \quad (\Delta H > 0, \text{endothermic}), \tag{R2.1}$$

Water gas shift reaction: $$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (\Delta H < 0,\ \text{exothermic}), \tag{R2.2}$$

Carbonation of CO_2 sorbent: $$MO_{(S)} + CO_2 \to MCO_{3(S)} \quad (\Delta H < 0,\ \text{exothermic}), \tag{R2.3}$$

OTM reduction with methane (unmixed combustion of methane):

$$CH_4 + 4NiO_{(S)} \to CO_2 + 2H_2O + 4Ni_{(S)} \quad (\Delta H > 0,\ \text{endothermic}), \tag{R2.4}$$

OTM reduction with H_2: $$H_2 + NiO_{(S)} \to Ni_{(S)} + H_2O \quad (\Delta H < 0,\ \text{exothermic}), \tag{R2.5}$$

Thermal decomposition of methane: $$CH_4 \to C_{(S)} + 2H_2 \quad (\Delta H > 0,\ \text{endothermic}). \tag{R2.6}$$

The main mechanism of unmixed reforming is illustrated in Fig. 1.

Similar processes such as chemical looping combustion and sorption-enhanced gasification or reforming in circulated fluidised beds offer similarities of chemical mechanism to unmixed combustion, although these terms seem to have been so far applied to interconnected fluidised or circulating beds through which the OTM and/or the CO_2 sorbent circulate undergoing redox or absorption/desorption stages. Since the birth of chemical looping combustion (Richter and Knoche, 1983;