

## The Effects of CO<sub>2</sub> Addition on the Partial Oxidation of Heptane for Hydrogen Generation

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**Abstract:** The effects of CO<sub>2</sub> on the partial oxidation of heptane for hydrogen generation have been studied. Based on the experimental results and thermodynamic equilibrium calculations, the validity of CO<sub>2</sub> addition to weaken the hot spots, and the feasibility of the autothermal operation are discussed.

**Keywords:** Autothermal operation, heptane conversion, CO<sub>2</sub>, hydrogen production.

The rapid growing fuel cell technology is merited for its environmental compatibility and high efficiency of fuel to electricity<sup>1</sup>. The study on hydrogen production has been stimulated by the increasing demand of hydrogen in the fuel cell technology, as well as in the refinery industry<sup>2-4</sup>. Among several hydrogen-rich materials, gasoline has advantages of higher energy density and the availability of the infrastructure. Generally, steam reforming, partial oxidation and autothermal processes are considered for hydrogen production, and the partial oxidation process is favored for the rapid response system and merited for the simplification of the reformer<sup>2</sup>. The possibility of partial oxidation of heptane (as the typical component of gasoline) for hydrogen generation has been investigated as the first step<sup>5</sup>. However, the partial oxidation process is an exothermic reaction (equation (1)), which could lead to sudden rise of the temperature in catalysts bed, namely, caused the hot-spot problem. The active metal would sinter and it was favorable for carbon deposition, when the hot spots were existing<sup>5</sup>. Theoretically, the addition of CO<sub>2</sub> or H<sub>2</sub>O is helpful to avoid the hot-spot problem or even makes the reaction autothermally<sup>2</sup>, because steam reforming and CO<sub>2</sub> reforming of hydrocarbon both are strong endothermic (equation (2),(3)) reactions:



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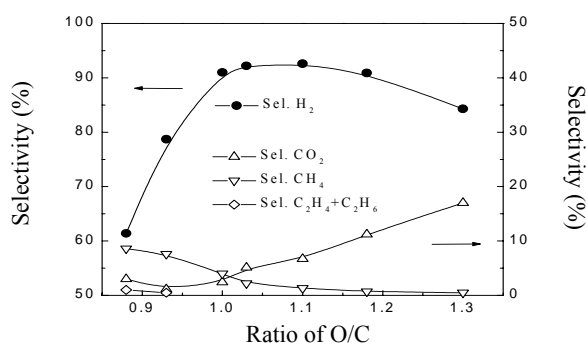


The mixed reforming of hydrocarbon with oxygen and H<sub>2</sub>O has been studied widely for the aim at autothermally operation<sup>4</sup>, whereas the mixed reforming of higher hydrocarbon with oxygen and CO<sub>2</sub> is lacked of investigation. CO<sub>2</sub> could be supplied conveniently by the the water-gas shift reaction (CO+H<sub>2</sub>O=CO<sub>2</sub>+H<sub>2</sub>), which is used to clean up CO after the reforming reaction for PEMFC<sup>2</sup>. Additionally, the addition of CO<sub>2</sub> is beneficial to the environmental protection<sup>4</sup>. Therefore, here we present a primary study on the CO<sub>2</sub> addition effects during the partial oxidation of heptane (POH) reaction for the hydrogen generation. A simple discussion is also developed based on experimental results and thermodynamic equilibrium calculations.

Reactions were carried out in a fixed-bed quartz reactor at atmospheric pressure. Saturated heptane vapor is delivered into the micro-reactor by helium, and the products are analyzed by an online HP4890 GC. All the equilibrium results presented in this paper are calculated *via* the HSC software package (Outokumpu Research Oy, 1991)<sup>6</sup>. The NiLiLa/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared *via* an impregnation method, which has been described detailed elsewhere<sup>5</sup>.

The effects of O/C (molar ratio, if not specified) on POH reaction have been investigated firstly, results are shown in **Figure 1**. Differing from the partial oxidation of methane reaction, the maximum hydrogen selectivity of POH can be obtained when the O/C is higher than 1.0. The lower hydrogen selectivity is due to carbon deposition at O/C=1.0, which has been discussed in detail<sup>5</sup>. The mixed reforming of *n*-heptane with O<sub>2</sub>+CO<sub>2</sub> (defined as MRH) was then studied. The results are shown in **Table 1**.

**Figure 1** Influences of O/C ratio on the performance of partial oxidation of heptane (800°C, GHSV=3.8x10<sup>4</sup> L kg<sup>-1</sup>h<sup>-1</sup>, C<sub>7</sub>H<sub>16</sub>/He=1/5.8)



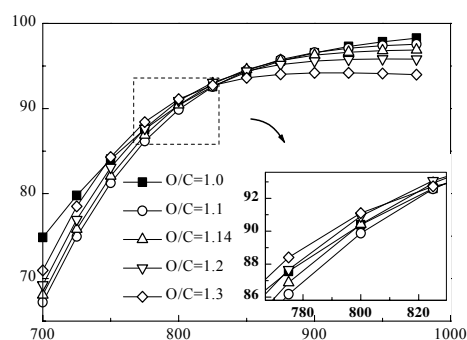
**Table 1** The influences of O(O<sub>2</sub>)/C(C<sub>7</sub>)\* on the MRH reaction

O(O <sub>2</sub> )/C(C <sub>7</sub> )	Conv.CO <sub>2</sub>	Sel.CO	Sel.H <sub>2</sub>	Sel.CH <sub>4</sub>	H <sub>2</sub> /CO
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1.04	35.7%	98.5%	90.6%	1.5%	1.11
1.00	62.4%	95.4%	88.6%	4.6%	1.06

\*O(O<sub>2</sub>): O atom supplied from O<sub>2</sub>; C(C<sub>7</sub>): C atom supplied from heptane  
(CO<sub>2</sub>/C<sub>7</sub>H<sub>16</sub>=1.05, GHSV=3.7x10<sup>4</sup>L.kg<sup>-1</sup>h<sup>-1</sup>, 800°C)

**Figure 2** The equilibrium hydrogen selectivity at different O/C ratio of CO<sub>2</sub> reforming reaction



**Table 2** The comparison of hydrogen selectivity at different O<sub>effe.</sub>/C(C<sub>7</sub>) in the mixed reaction

Ratio	CO <sub>2</sub> reforming	POH	MRH	POH*
O <sub>effe.</sub> /C(C <sub>7</sub> ) (O(O <sub>2</sub> )/C(C <sub>7</sub> ))	Sel.H <sub>2</sub> equil.	Sel.H <sub>2</sub> equil.	Sel.H <sub>2</sub> experi.	Sel.H <sub>2</sub> experi.
1.00	90.4%	90.8%	/	91.0%
1.10 (1.00)	89.9%	90.7%	88.6%	92.6%
1.14 (1.04)	90.4%	90.1%	90.6%	90.1%

\*: GHSV=3.8x10<sup>4</sup>L.kg<sup>-1</sup>h<sup>-1</sup>  
(GHSV=3.7x10<sup>4</sup>L.kg<sup>-1</sup>h<sup>-1</sup>, 800°C, CO<sub>2</sub>/C<sub>7</sub>H<sub>16</sub>=1.05)

Only methane and water have been found as the by-products during the MRH reaction. Comparing to the POH reaction, the addition of CO<sub>2</sub> has obvious effects on the hydrogen selectivity. In order to avoid carbon deposition, the O/C ratio was higher than the stoichiometric ratio. As a result, CO<sub>2</sub> are not converted completely. Additionally, CO<sub>2</sub> could supply only one oxygen atom for the oxidation of heptane refers to equation (3). The oxygen atom supplied from CO<sub>2</sub> could be calculated as follows:

$$O(\text{CO}_2) = \text{Conv}_{\text{CO}_2} M_{\text{CO}_2} / 2 \quad (5)$$

in which Conv<sub>CO<sub>2</sub></sub>: conversion of CO<sub>2</sub>, M<sub>CO<sub>2</sub></sub>: molar number of CO<sub>2</sub>, O(CO<sub>2</sub>): oxygen

atom supplied from CO<sub>2</sub>. Thus the effective O atom to heptane during the mixed reforming process should be:

$$(6) \quad O_{\text{effe.}} = O(O_2) + O(CO_2)$$

in which  $O_{\text{effe.}}$ : effective oxygen atom,  $O(O_2)$ : oxygen atom supplied from O<sub>2</sub>

The thermodynamic equilibrium selectivity of hydrogen at different ratio of O/C is shown in **Figure 2**. A turning point is appeared at about 825°C. When the temperatures are lower than 825°C, the selectivity of hydrogen increases a little with O/C, except when O/C=1.0. On the contrary, hydrogen selectivity decreases with O/C, when temperatures are higher than 825°C. The thermodynamic equilibrium hydrogen selectivity and the experimental hydrogen selectivity of different reactions are shown in **Table 2**. From **Table 2** we can find, the hydrogen selectivity of POH reaction is higher than thermodynamic equilibrium value. This fact indicates the hot spots are existed in the catalyst bed during the strong exothermic partial oxidation reactions.

Keeping the molar ratio of CO<sub>2</sub>/C<sub>7</sub>H<sub>16</sub> to be constant, the hydrogen selectivity of MRH reaction is a little lower than the equilibrium value at O(O<sub>2</sub>)/C(C<sub>7</sub>) of 1.0. The difference indicates that the CO<sub>2</sub> reforming reaction has not reached thermodynamic equilibrium during the mixed reforming reaction. Hence, the selectivity of hydrogen is lower than both POH and CO<sub>2</sub> reforming reaction even when the ratio of CO<sub>2</sub>/O<sub>2</sub> is much lower than the stoichiometric ratio for the thermoneutralitic condition (refer to equation (4)). The reasonable assume is that the CO<sub>2</sub> reforming reaction is difficult to reach equilibrium, when CO<sub>2</sub>/O<sub>2</sub> lower than the stoichiometric ratio, since the hydrogen generation rate of CO<sub>2</sub> reforming reaction is slower than partial oxidation reaction<sup>7</sup>. In other words, the CO<sub>2</sub> reforming reaction is kinetically difficult to reach the thermodynamic equilibrium at such a high reaction space velocity. However, increasing the CO<sub>2</sub>/O<sub>2</sub> would incline to carbon deposition<sup>8</sup>.

Nevertheless, when O(O<sub>2</sub>)/C(C<sub>7</sub>) is increased to 1.04 (corresponding the  $O_{\text{effe.}}/C(C_7) = 1.14$ ), the experimental value of hydrogen selectivity in MRH reaction rose a little than thermodynamic equilibrium values both of POH and CO<sub>2</sub> reforming reactions. The results imply that the proportion of CO<sub>2</sub> reforming reaction is too low to avoid completely the hot point problem. The experimental value of POH reaction at O(O<sub>2</sub>)/C(C<sub>7</sub>) of 1.14 is almost equal to the equilibrium value. It does not mean that the hot-spot problem has been solved, but only because that the stable hydrogen selectivity could be reached at high enough temperatures.

Addition of CO<sub>2</sub> into the POH process could decrease obviously the hot spots in the catalyst bed only decrease a little of hydrogen yield. However, the autothermal operation is feasible only when the reaction was operated at a lower space velocity. The related studies are underway.

## Acknowledgments

This work is financially supported by the National Ministry of Science and Technology of China (Grant No. G1999022401).

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Received 17 April, 2003