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Combined CO_2 reforming and partial oxidation of *n*-heptane on noble metal zirconia catalysts

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Abstract

The combined CO_2 reforming and partial oxidation (POX) of *n*-heptane was studied on various noble metal zirconia catalysts between 700 and 900 °C. The activity order of the metals was Rh > Pd > Ir > Pt. Selectivity to syngas increased with the activity of the catalysts but the H_2 to CO molar ratio decreased. The activity and selectivity of the 0.25 wt% Rh/ZrO_2 catalyst were close to the performance of a commercial 15 wt% NiO/Al_2O_3 catalyst. The conversions and product compositions were compared to the calculated thermodynamic equilibria.

Keywords: *n*-Heptane; CO_2 reforming; Dry reforming; Partial oxidation; Autothermal reforming; Synthesis gas; Noble metal; Zirconia

1. Introduction

CO_2 reforming is a promising route to produce valuable synthesis gas (syngas) consisting of hydrogen and carbon monoxide from the cheap environmentally harmful raw material for being upgraded to, e.g. aldehydes and further to resins and adhesives. Challenges in CO_2 reforming are the highly endothermic nature of the reaction and the catalyst deactivation by carbon deposition [1]. However, novel methods have been developed to make CO_2 reforming more feasible through catalyst development and combining it with partial oxidation (POX).

The CO_2 reforming of methane (Eq. (1)) has been extensively studied and commercialised [2]. Other possible raw materials are higher hydrocarbons such as traffic fuel gasoline [3], which is less studied. However, the traditional CO_2 reforming catalysts containing nickel are poisoned by sulphur [4] in fuels. In addition, the catalyst coking is more severe with higher hydrocarbons [5].

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO; \quad \Delta H^\circ_{298\,K} = +247\,kJ/mol \qquad (1)$$

These challenges can be solved with more stable but also more expensive noble metal catalysts. The activity of the 1 wt% noble metal catalysts supported by alumina-stabilised magnesia in CO_2 reforming of methane [1] has been observed to decrease in the order of Rh > Ir > Pt > Pd. Souza and Schmal [6] have obtained good results with platinum catalysts in combined CO_2 reforming and partial oxidation of methane. A 0.9 wt% platinum catalyst with zirconia support [7] has been observed to be much more stable than a catalyst with alumina support in CO_2 reforming of methane.

In the autothermal reforming reaction CO_2 reforming and partial oxidation are combined so that the total reaction is thermoneutral. Thus, no outside heating is required. However, according to thermodynamics oxygen decreases the conversion of carbon dioxide. Therefore, the amount of oxygen should be lower than required for the autothermal operation.

In this work, the combined CO_2 reforming (Eq. (2)) and POX (Eq. (3)) reaction of gasoline was studied with *n*-heptane as the model compound. The performance of various zirconia supported noble metal catalysts were compared to a

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commercial nickel catalyst and the product compositions to the thermodynamic equilibria.

$$C_7H_{16} + 7CO_2 \rightleftharpoons 8H_2 + 14CO; \quad \Delta H^\circ_{298\,K} = +1395\,kJ/mol \tag{2}$$

$$C_7H_{16} + 3.5O_2 \rightleftharpoons 8H_2 + 7CO; \quad \Delta H^\circ_{298\,K} = -586\,kJ/mol \tag{3}$$

2. Experimental

Noble metal catalysts were prepared by impregnating the support ZrO_2 (MEL Chemicals EC0100E/8) with aqueous metal precursor solutions. The support material was ground to the particle size of 0.250–0.355 mm and calcined at 900 °C for 16 h. The BET surface area was 21.5 m^2/g. The precursors were rhodium nitrate (Sigma–Aldrich), palladium nitrate (Alfa-Aesar), hexachloroiridium acid (Sigma–Aldrich), platinum nitrate, Pt(n), (Johnson-Matthey), tetraamineplatinum nitrate, Pt(a), (Strem Chemicals) and hexachloroplatinum acid, Pt(c), (Merck). The catalysts were dried for 4 h at room temperature and overnight at 100 °C. In the calcination of the catalysts the furnace was heated with the rate of 80 °C/h and kept at 700 °C for 1 h. A commercial 15 wt% NiO/Al_2O_3 catalyst with the particle size of 0.2–0.3 mm was used for comparison. The noble metal characterisation results [8] including the metal contents analysed with an atomic absorption spectrometer (AAS) and the metal dispersions determined with the Coulter Omnisorp 100 CX are shown in Table 1.

The combined CO_2 reforming and POX reaction and thermal experiments of *n*-heptane (Fluka, ≥99.5%) were carried out in a fixed bed flow reactor of quartz glass with an inner diameter of 9 mm. There was a smaller quartz glass tube with an outer diameter of 3 mm inside the reactor for the thermocouple. The reactor was heated by a three-zone tube furnace.

Reaction products were analysed with Fourier transform infrared (FT-IR) Spectrometer GASMET Cr-2000. It was equipped with a Peltier cooled mercury cadmium telluride (MCT) detector and multicomponent analysis software. The temperature of the sample cell was set to 230 °C. The interferometer beamsplitter material and window material was ZnSe. The interferometer resolution was 8 cm^{-1}. The Rh–Au coated sample cell had a path length of 0.4 m and volume of 0.2 dm^3.

Table 1
Metal contents and dispersions [7] calculated with the adsorption stoichiometry of 1 for carbon monoxide

Catalyst	Content (wt%)	Surface concentration[a] (atoms/nm^2)	Dispersion (%)
$Rh(n)/ZrO_2$	0.25	0.7	≥80.7[b]
$Pd(n)/ZrO_2$	0.41	1.1	81.5
$Ir(c)/ZrO_2$	n.a.	0.7[c]	22.6[c]
$Pt(a)/ZrO_2$	0.46	0.7	12.7
$Pt(n)/ZrO_2$	0.45	0.6	36.1
$Pt(c)/ZrO_2$	0.46	0.7	52.6

Abbreviations: n, nitrate precursor; c, hexachloro acid precursor; a, tetraamine nitrate precursor.
n.a., not available.

[a] The BET surface area was 21.5 m^2/g.

[b] Dispersion of 161.3% with the stoichiometry of 1 suggests the formation of rhodium dicarbonyls [10] with the stoichiometry of 0.5.

[c] Calculated with the metal content of 0.5 wt%.

The experiments were carried out between 700 and 900 °C under atmospheric pressure. The *n*-heptane content was 0.4 mol% in argon. The O_2 to *n*-heptane molar ratio of 1.4 was lower than the ratio of 2.5 in autothermal reforming. Carbon dioxide was fed in three-fold stoichiometric excess with the CO_2 to *n*-heptane molar ratio of 21 in order to reduce the catalyst deactivation by coking [9]. The amount of the catalysts was 0.1 g and the total feed rate was 1 $dm_n^3\,min^{-1}$. The Rh catalyst was tested also after reduction at 900 °C for 1.5 h with the total flow of 0.20 $dm_n^3\,min^{-1}$ and the H_2/Ar molar ratio of 1. Thermal reactions of *n*-heptane and carbon dioxide were studied with an empty reactor between 600 and 870 °C and with zirconia support between 700 and 900 °C.

Thermodynamic equilibria of the reaction mixture consisting of *n*-heptane, lighter hydrocarbons, carbon dioxide, carbon monoxide, oxygen, hydrogen and water were calculated with the HSC Chemistry 5.11 program [10]. Calculations of conversions and product compositions were based on moles.

3. Results and discussion

3.1. Thermodynamics in the combined CO_2 reforming and POX reaction

The typical side reactions of the CO_2 reforming are the Boudouard reaction (Eq. (4)), the water-gas shift (WGS) reaction (Eq. (5)) and the methanation reaction or reverse steam reforming of methane (Eq. (6)).

$$2CO \rightleftharpoons C + CO_2; \quad \Delta H^\circ_{298\,K} = -172\,kJ/mol \tag{4}$$

$$H_2O + CO \rightleftharpoons H_2 + CO_2; \quad \Delta H^\circ_{298\,K} = -41\,kJ/mol \tag{5}$$

$$3H_2 + CO \rightleftharpoons CH_4 + H_2O; \quad \Delta H^\circ_{298\,K} = -206\,kJ/mol \tag{6}$$

At high temperatures the thermodynamic equilibria of the side reactions favour carbon dioxide consumption and carbon monoxide formation. CO_2 reforming of *n*-heptane is thermodynamically favourable above 450 °C. However, due to the equilibrium of the methanation reaction the temperature should be above 616 °C. Furthermore, the reaction temperatures higher than 703 °C are suitable for coke removal by the reverse Boudouard reaction. Above 815 °C hydrogen in addition to carbon dioxide is consumed in the reverse WGS reaction. Thus, the temperature should be optimised according what is considered more important, the conversion of carbon dioxide or the H_2 to CO molar ratio.

In the combined CO_2 reforming and POX reaction oxygen can react to water and carbon dioxide in total oxidation in addition to carbon monoxide. The reaction equation for the autothermal reforming of *n*-heptane (Eq. (7)) was obtained by the thermodynamic calculations.

$$C_7H_{16} + 2CO_2 + 2.5O_2 \rightleftharpoons 8H_2 + 9CO; \quad \Delta H^\circ_{298\,K} = \sim 0\,\mathrm{kJ/mol} \qquad (7)$$

According to thermodynamic calculations the H_2 to CO molar ratio is 0.84 and the carbon dioxide conversion is 89% at 800 °C with stoichiometric oxygen and carbon dioxide amounts. The product composition is 96% syngas, 3% methane and 1% water. With the three-fold excess of carbon dioxide the H_2 to CO molar ratio is considerably lower, 0.32, and the carbon dioxide conversion is the stoichiometric maximum, 33%, at 800 °C. The product composition is 81% syngas and 19% water. Under the conditions of the experiments, with the three-fold excess of carbon dioxide and the lower oxygen amount, the H_2 to CO molar ratio is still lower, 0.30. However, the carbon dioxide conversion is higher, 39%, at 800 °C due to the reverse WGS reaction. In addition, the product composition is better, 85% syngas and 15% water.

3.2. Thermal experiments of n-heptane and carbon dioxide

In the thermal experiments the *n*-heptane conversion increased from 0 to 100% between 650 and 870 °C in the empty reactor in absence of oxygen. At 800 °C it was 75%. Results of the experiments with ZrO_2 were similar to the results with the empty reactor. The *n*-heptane conversion was higher with oxygen, 87% (67% cracking) at 800 °C. The carbon dioxide conversion was less than 1% with and without oxygen.

n-Heptane was cracked to smaller hydrocarbons and ethene was the predominant product in absence of oxygen. The product composition at 800 °C is shown in Fig. 1. Only a small amount of carbon monoxide was observed with ZrO_2 in absence of oxygen. In presence of oxygen partial and total oxidation of *n*-heptane and the reverse WGS reaction took place. The product contained 37% syngas and 9% water. The H_2 to CO molar ratio of 2.9 was larger than the stoichiometric ratio of 1.1 for the POX reaction, because there was not enough oxygen for the stoichiometric POX reaction, which requires an O_2 to *n*-heptane molar ratio of 3.5. In addition, hydrogen is formed also in the thermal cracking of *n*-heptane in presence of oxygen. The methane to ethene molar ratio at 800 °C was the same, 0.24, with and without oxygen.

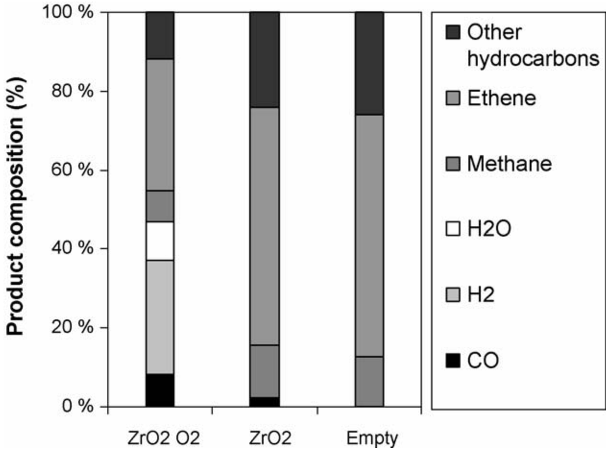

Fig. 1. Product composition in experiments without catalyst at 800 °C.

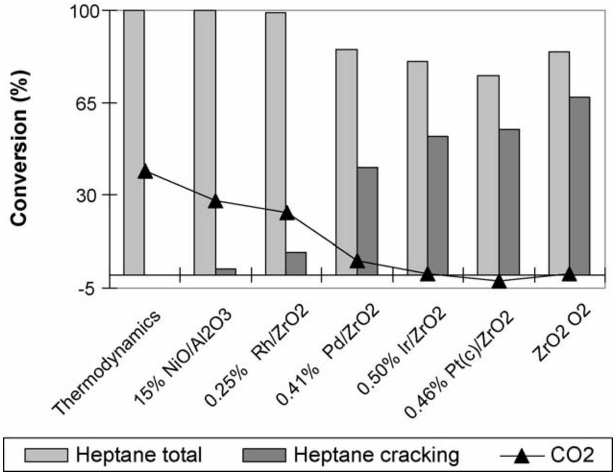

Fig. 2. *n*-Heptane total and cracking conversions and carbon dioxide conversion in the combined CO_2 reforming and POX reaction of *n*-heptane with various catalysts at 800 °C.

3.3. Noble metal catalyst comparison in the combined CO_2 reforming and POX reaction

The 0.25 wt% Rh/ZrO_2 catalyst was the most active noble metal catalyst (Fig. 2) in the combined CO_2 reforming and POX reaction of *n*-heptane. Due to the smaller molar mass the Rh catalyst had the same molar amount of metal as the Pt catalysts. In addition, it had a high metal dispersion. The 0.41 wt% Pd/ZrO_2 catalyst showed lower activity although its dispersion, 82%, was also high and metal content nearly two-fold compared to the Rh catalyst. The Pt/ZrO_2 catalysts were slightly active only at high temperatures. Even the Pt(c) catalyst with the highest dispersion of 53% was poor. The activity of the Ir/ZrO_2 catalyst was between the Pd and Pt catalysts. The dispersion of iridium had been calculated with the targeted metal content of 0.5 wt% and the result was low, 23%.

Selectivity to syngas increased with the activity of the catalysts but the H_2 to CO molar ratio decreased (Fig. 3), because hydrogen is formed in cracking and carbon monoxide is formed mainly with catalyst. Reactions on the noble metal catalysts remained further from the thermodynamic equilibria than that on the Ni catalyst due to the lower activity and thus the higher degree of cracking. With the active Ni and Rh catalysts the conversion of carbon dioxide and the amounts of carbon monoxide and water increased and the amount of hydrogen decreased with increasing temperature (Fig. 4). This was in agreement with the thermodynamic calculations. The WGS reaction did not reach the thermodynamic equilibrium in the reaction conditions. Less hydrogen and carbon dioxide were converted to water and carbon monoxide than expected according to thermodynamics.

The activity order of the catalysts can also be seen from the temperature profiles of the furnace and the reactor in Fig. 5.

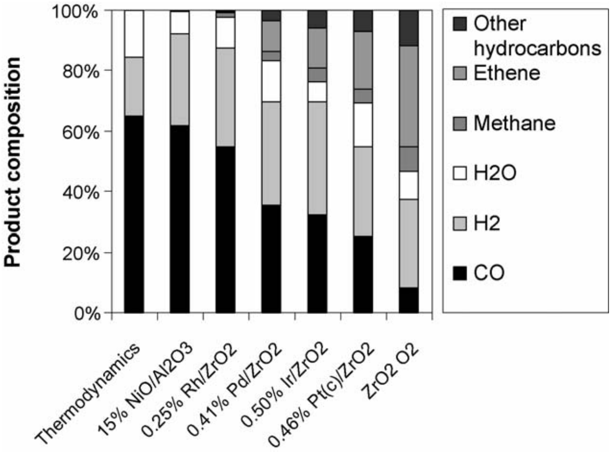

Fig. 3. Product compositions in the combined CO_2 reforming and POX reaction of *n*-heptane with various catalysts at 800 °C.

If the temperature is lower in the bed as with the Ni and Rh catalysts, the total reaction is endothermic and this refers to the CO_2 reforming reaction. A bed temperature higher than the furnace profile temperature means exothermic oxidation reactions are predominant, which was the case with other catalysts. The oxidation reactions were most pronounced with the Pt catalyst, which was expected because platinum is a good oxidising catalyst. In addition, the Pt and Ir catalysts had lower metal contents and dispersions than the Pd catalyst. This explains the lower activity of the Pt and Ir catalysts, which differs from the CO_2 reforming results [1].

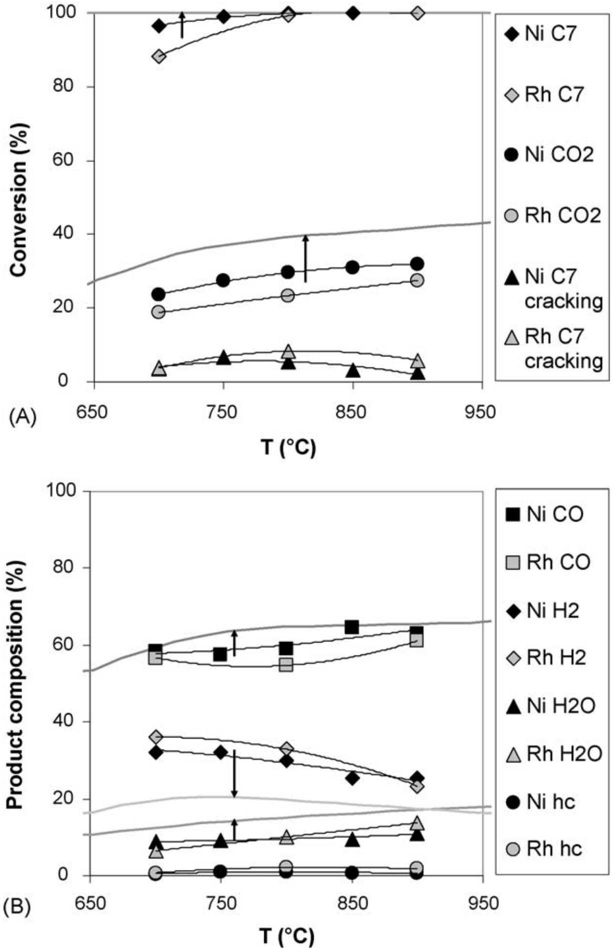

Fig. 4. *n*-Heptane (C7) total and cracking and CO_2 conversions (A) and product compositions (B) as a function of temperature in the combined CO_2 reforming and POX reaction of *n*-heptane with the 0.25% Rh/ZrO$_2$ and the 15% NiO/Al$_2$O$_3$ catalysts and according to the thermodynamic calculations (thick lines). hc, product hydrocarbons.

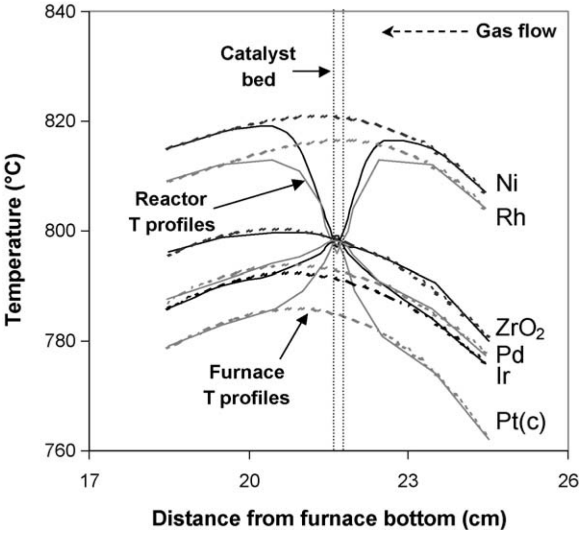

Fig. 5. Temperature profiles of the furnace (dashed line) and the reactor (solid line) in the combined CO_2 reforming and POX reaction of *n*-heptane with various catalysts at 800 °C.

The effect of the catalyst reduction on the combined CO_2 and POX reaction was studied. Reduction decreased slightly the activity of the 0.25 wt% Rh/ZrO$_2$ catalyst. It is therefore not needed and not favourable due to possible deactivation of the catalyst. Thus, with other catalysts the reduction was not tested.

3.4. Rhodium catalyst in the combined CO_2 reforming and POX reaction

The performance of the 0.25 wt% Rh/ZrO$_2$ was close to the activity of the commercial 15 wt% NiO/Al$_2$O$_3$ catalyst. The total reaction was endothermic at all studied temperatures. At 800 °C the total and cracking conversions of *n*-heptane were 99 and 8%, respectively, on the Rh catalyst compared to 100 and 5%, respectively, on the Ni catalyst. The carbon dioxide conversion was 23% for the Rh catalyst and 30% for the Ni catalyst. In addition, the H_2 to CO molar ratio was 0.49 with the Ni catalyst and 0.60 with the Rh catalyst. The product consisted of 88% syngas, 10% water and 2% smaller hydrocarbons with the Rh catalyst and 92, 7 and 1%, respectively, with the Ni catalyst. The product compositions and conversions are shown in Fig. 4 along with those calculated from the thermodynamic equilibria.

3.5. Palladium and iridium catalysts in the combined CO_2 reforming and POX reaction

In the combined CO_2 reforming and POX reaction of *n*-heptane with both the Pd/ZrO$_2$ and the Ir/ZrO$_2$ catalyst the total reaction was exothermic and the carbon dioxide conversion was slightly negative at 700 °C. This indicates that no CO_2 reforming took place. The *n*-heptane conversion was 33% (7% cracking) with the Pd catalyst and 30% (7%) with the Ir catalyst. The H_2 to CO molar ratio was 0.82 for the Pd and 1.14 for the Ir catalyst.

At 800 °C the reactions were still exothermic, but the carbon dioxide conversions were positive, 1% for the Ir catalyst and 6% for the Pd catalyst, suggesting both CO_2 reforming and partial oxidation taking place. The *n*-heptane conversion was 85% (41%) with the Pd catalyst and 81% (52%) with the Ir catalyst. The H_2 to CO molar ratios were 0.96 and 1.15 for the Pd and Ir catalysts, respectively.

At 900 °C the CO_2 reforming reaction was recognised by the endothermic nature of the reactions in addition to carbon dioxide conversions of 6% for the Ir catalyst and 9% for the Pd catalyst. The *n*-heptane total conversion for both the catalysts was 100% and the cracking conversions were 37 and 47% for the Pd and Ir catalysts, respectively. The H_2 to CO molar ratio was 0.54 for the Pd and 0.67 for the Ir catalyst. In the case of the Ir catalyst the performance could possibly be improved by changing the catalyst precursor as observed with the Pt catalysts.

3.6. Platinum catalysts in the combined CO_2 and POX reaction

With all the Pt/ZrO_2 catalysts the total reaction in the combined CO_2 and POX reaction of *n*-heptane was exothermic at 700–800 °C and slightly endothermic at 900 °C. The Pt(n) catalyst was the most active in CO_2 reforming. It gave positive carbon dioxide conversions above 700 °C whereas the Pt(a) catalyst gave positive conversion only at 900 °C and the Pt(c) catalyst only negative conversions. However, the syngas selectivities were the best with the Pt(c) catalyst and the worst with the Pt(a) catalyst.

4. Conclusions

The CO_2 reforming of *n*-heptane is a promising way of utilising carbon dioxide. However, high temperatures are required for the optimal production of synthesis gas. Combining the CO_2 reforming with partial oxidation provides a solution as the energy requirement decreases. In addition, it reduces the catalyst deactivation by coke formation.

The Rh/ZrO_2 catalyst was almost as active as the commercial Ni catalyst. Other tested noble metal catalysts had lower activities than the rhodium catalysts. Platinum as a good oxidising catalyst was not suitable for the combined CO_2 reforming and POX reaction, in which the aim is to maximise the carbon dioxide conversion.

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