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Combined CO_2 reforming and partial oxidation of fuel compounds

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CO_2 reforming and the combined CO_2 reforming and partial oxidation reaction of selected fuel compounds were studied on a commercial 15 wt% NiO/Al_2O_3 catalyst and a 0.25 wt% Rh/ZrO_2 catalyst at 600–900 °C. Oxygen reduced the energy requirement and catalyst coking. Ethanol was a more suitable starting material than the hydrocarbons.

KEY WORDS: CO_2 reforming; partial oxidation; hydrocarbon; ethanol; rhodium; zirconia.

Abbreviations: C7: *n*-heptane; GHSV: gas hourly space velocity (h^{-1}); Hc: cracking products (smaller hydrocarbons); POX: partial oxidation; *T*: temperature (°C)

1. Introduction

In CO_2 reforming, a valuable raw material for the chemical industry, synthesis gas (syngas), is produced from carbon dioxide and hydrocarbon. The syngas, which consists of hydrogen and carbon monoxide, can be upgraded, for example, to aldehydes and further to resins and adhesives. The CO_2 reforming of methane has been extensively studied and commercialised [1].

Two significant challenges in CO_2 reforming are the highly endothermic nature of the reaction and the catalyst deactivation by carbon deposition [2]. In addition to this, the traditional CO_2 reforming catalysts containing nickel are poisoned by the sulphur [3] present in fuels. Furthermore, the catalyst coking is more severe with higher hydrocarbons [4]. One approach to solving these problems is to use more stable noble metal catalysts and combine CO_2 reforming with partial oxidation (POX).

Several studies have been published on combined CO_2 reforming and POX of methane [5–7]. The addition of oxygen to the feed increased both methane conversion and the stability of supported Pt catalysts [5]. On a Pt/ZrO_2 catalyst, higher yield of syngas was obtained at lower temperatures with than without oxygen [8]. Furthermore, a 24 wt% Co/γ-Al_2O_3 catalyst that was unstable in CO_2 reforming was active and stable in the combined CO_2 reforming and POX reaction [6]. In addition, the H_2 to CO ratio in the product gas can be controlled by adjusting the ratio of oxygen to carbon dioxide [7]. In the presence of oxygen, part of the methane is first combusted to carbon dioxide and steam, and then CO_2/steam reforming of the rest of the methane occurs [8]. In the autothermal reforming reaction, CO_2 reforming (equation 1) and partial oxidation (equation 2) are combined so that the total reaction (equation 3) is thermoneutral.

Higher hydrocarbons such as gasoline [9] are less well studied than methane. Solymosi *et al.* investigated CO_2 reforming of ethane [10] and propane [11, 12] on supported noble metal catalysts. CO_2 reforming of ethane was fast above 427 °C on a 2 wt% Rh/ZSM-5 catalyst, and hydrogen and carbon monoxide were formed with a molar ratio of 0.3–0.6. The catalyst was significantly deactivated at the stoichiometric ratio of CO_2 to ethane, but deactivation was decreased with use of a large excess of carbon dioxide. In the CO_2 reforming of propane the activity order of platinum metals was $Ru > Rh > Pd > Pt = Ir$. The Ru catalyst also gave the highest H_2 to CO ratio, 0.62. The order of activity for Rh catalyst supports was $Al_2O_3 > TiO_2 > MgO > SiO_2$, and the H_2 to CO ratio was the highest, 0.53–0.64, with the Rh/TiO_2 catalyst. Panczyk *et al.* [13] observed that molybdenum modification of Ni/Al_2O_3 catalyst and increase in the CO_2/C ratio decrease carbon deposition on the catalyst in the CO_2 reforming of butane. In studies on CO_2 reforming of *n*-heptane on 23% Ni/Al_2O_3, 0.2% Ru/La_2O_3 and 1% Ru/Al_2O_3 catalysts, Fujimura *et al.* [14] found the Ni catalyst to be the most active, but it was deactivated by whisker carbon formation.

In this work, the combined CO_2 reforming and POX reaction was studied on a commercial nickel catalyst with *n*-heptane as a model compound for gasoline. In addition, the reaction of *n*-heptane was compared with the reactions of other fuel compounds on a Rh/ZrO_2 catalyst. Methane was a model compound for natural gas and *n*-dodecane a model compound for diesel. Since liquid fuels contain aromatic compounds in addition to

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aliphatic compounds [15], toluene was studied as a model for aromatic compounds. Ethanol was studied as an example of a biofuel. The product distributions were compared with the calculated thermodynamic equilibria.

2. Experimental

CO_2 reforming and the combined CO_2 reforming and POX reaction of *n*-heptane (Fluka, ≥ 99.5%) were studied on a commercial 15 wt% NiO/Al_2O_3 catalyst with a particle size of 0.2–0.3 mm. The combined CO_2 reforming and POX reactions of methane (Aga, 99.9995%), ethanol (Altia, ≥ 99.5%), *n*-heptane, toluene (Riedel-de Haën, ≥ 99.7%) and *n*-dodecane (Aldrich, 99+) were studied on a 0.25 wt% rhodium on zirconia catalyst. The Rh catalyst was prepared by impregnating the ZrO_2 support (MEL Chemicals EC0100E/8) with aqueous rhodium nitrate solution (Sigma-Aldrich). The support material was prepared by grinding to particle size 0.250–0.355 mm and calcination at 900 °C for 16 h. The catalyst was dried for 4 h at room temperature and overnight at 100 °C. In the following calcination the furnace was heated at 80 °C/h and kept at 700 °C for 1 h. The metal content of the catalyst was determined with an atomic absorption spectrometer (ICP-AES). The BET surface area of the support was 22 m^2/g and the Rh surface concentration was 0.7 at/nm^2.

The experiments were carried out in a fixed bed flow reactor of quartz glass with an inner diameter of 9 mm. The reactor was heated by a three-zone tube furnace. Reaction products were analysed with a Fourier transform infrared (FT-IR) spectrometer GASMET Cr-2000 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. Quantitative analysis of the coke was performed by feeding 0.1 $dm_n^3\ min^{-1}$ air to the reactor at 800 °C after the experiment and integrating the peak of the generated carbon dioxide.

The CO_2 reforming and the combined CO_2 reforming and POX reaction of *n*-heptane on the Ni catalyst were carried out between 600 and 800 °C under atmospheric pressure. The *n*-heptane content was 0.4 mol% in argon. The O_2 to $C_{heptane}$ molar ratio was 0–0.9 and the CO_2 to $C_{heptane}$ molar ratio was from stoichiometric to threefold stoichiometric excess. The amount of the catalyst was 0.05–0.20 g and the total feed rate 0.8–2.0 $dm_n^3\ min^{-1}$. The GHSV was 3.2×10^5 to $15.7 \times 10^5\ h^{-1}$.

The combined CO_2 reforming and POX reactions of methane, ethanol, *n*-heptane, toluene and *n*-dodecane on the supported Rh catalyst were studied between 700 and 900 °C under atmospheric pressure. The fuel carbon content was 2.7 mol% in argon. The CO_2 to C_{fuel} molar ratio was increased to 3 in order to reduce the catalyst deactivation by coking [3]. The O_2 to C_{fuel} molar ratio of 0.2 was lower than the ratio in autothermal reforming. The amount of the catalyst was 0.1 g and the total feed rate was 1 $dm_n^3\ min^{-1}$. Thus, the GHSV was $6.4 \times 10^5\ h^{-1}$. The effect of reduction of the catalyst before the experiment was studied with methane and Ar:H_2 1:1 mol/mol total feed rate of 0.2 $dm_n^3\ min^{-1}$.

Thermodynamic equilibria of reaction mixtures consisting of fuel compound, carbon dioxide, carbon monoxide, oxygen, hydrogen and water were calculated with the HSC Chemistry 5.11 program [16].

3. Results and discussion

3.1. Thermodynamics of the combined CO_2 reforming and POX reaction

CO_2 reforming of *n*-heptane is thermodynamically favourable above 450 °C (equation 1). CO_2 reforming of *n*-dodecane (equation 2) is thermodynamically favourable above 423 °C, whereas CO_2 reforming of toluene (equation 3) requires temperatures above 498 °C. CO_2 reforming of methane (equation 4) only becomes feasible at a much higher temperature, 642 °C. The reaction of ethanol (equation 5) proceeds at lowest temperature, 318 °C.

$$C_7H_{16} + 7CO_2 \rightleftharpoons 8H_2 + 14CO; \quad \Delta H^0_{298\,K} = +1395\,kJ/mol \tag{1}$$

$$C_{12}H_{26} + 12CO_2 \rightleftharpoons 13H_2 + 24CO; \quad \Delta H^0_{298\,K} = +2422\,kJ/mol \tag{2}$$

$$C_7H_8 + 7CO_2 \rightleftharpoons 4H_2 + 14CO; \quad \Delta H^0_{298\,K} = +1157\,kJ/mol \tag{3}$$

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO; \quad \Delta H^0_{298K} = +247\,kJ/mol \tag{4}$$

$$C_2H_5OH + CO_2 \rightleftharpoons 3H_2 + 3CO; \quad \Delta H^0_{298\,K} = +297\,kJ/mol \tag{5}$$

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 equations for the autothermal reforming of *n*-heptane (equation 6), *n*-dodecane (equation 7), toluene (equation 8) and methane (equation 9) at 800 °C were obtained by the thermodynamic calculations. Table 1 shows the thermodynamic equilibrium values at 800 °C for carbon dioxide conversion and the product compositions obtained with threefold excess of carbon dioxide and lower amount of oxygen (O_2/C_{fuel} = 0.2 mol/mol) than in autothermal reforming. The autothermal reac-

Table 1
Conversions and product compositions for the combined CO_2 reforming and POX of various fuel compounds

Hydrocarbon	T (°C)	Conversion (%)			Product composition (%)			H_2/CO
		Fuel[a]	Fuel, cracking[b]	CO_2	Syngas	H_2O	Cracking products[b]	
Methane	800[c]	48	–	14 (46)	77 (82)	23 (18)	–	0.49 (0.54)
	800	42	–	9 (46)	89 (82)	11 (18)	–	0.82 (0.54)
	900	66	–	27 (49)	87 (80)	13 (20)	–	0.76 (0.48)
Heptane	700	88	4	19 (33)	93 (84)	7 (13)	1	0.63 (0.33)
	800	99	8	23 (39)	88 (85)	10 (15)	2	0.60 (0.30)
	900	100	6	27 (42)	85 (83)	14 (17)	2	0.38 (0.27)
Dodecane	700	59	21	5 (36)	87 (87)	7 (12)	6	0.60 (0.35)
	800	100	35	15 (39)	89 (85)	6 (15)	5	0.55 (0.30)
	900	100	39	22 (42)	88 (84)	6 (16)	5	0.48 (0.26)
Toluene	700	55	62	1 (32)	71 (91)	7 (9)	22	– (0.19)
	800	92	4	22 (34)	94 (89)	5 (11)	1	0.24 (0.16)
	900	100	10	26 (35)	92 (88)	7 (12)	1	0.18 (0.14)
Ethanol	700	83	8	4 (38)	82 (87)	11 (12)	7	1.29 (0.75)
	800	99	5	20 (47)	86 (86)	9 (14)	5	1.12 (0.69)
	900	100	5	20 (52)	86 (86)	8 (15)	5	1.05 (0.63)

GHSV = 6.4×10^5 h^{-1}, $CO_2/C_{fuel} = 3$ and $O_2/C_{fuel} = 0.2$. Thermodynamic values in parenthesis.
[a] Thermodynamic value 100% for all.
[b] Thermodynamic value 0% for all.
[c] Catalyst reduced.

tion of ethanol could not be calculated by comparing the enthalpies of POX and CO_2 reforming because the POX of ethanol is endothermic ($\Delta H_{1073\ K}{}^0 = 30$ kJ/mol).

$$C_7H_{16} + 2CO_2 + 2.5O_2 \rightleftharpoons 8H_2 + 9CO; \quad \Delta H^0_{1073\,K} = \sim 0\,\text{kJ/mol} \tag{6}$$

$$C_{12}H_{26} + 2.9CO_2 + 4.5O_2 \rightleftharpoons 13H_2 + 14.9CO; \quad \Delta H^0_{1073\,K} = \sim 0\,\text{kJ/mol} \tag{7}$$

$$C_7H_8 + 2.9CO_2 + 2.1O_2 \rightleftharpoons 4H_2 + 9.9CO; \quad \Delta \text{H}^0_{1073\,K} = \sim 0\,\text{kJ/mol} \tag{8}$$

$$CH_4 + 0.08CO_2 + 0.46O_2 \rightleftharpoons 2H_2 + 1.08CO; \quad \Delta \text{H}^0_{1073\,K} = \sim 0\,\text{kJ/mol} \tag{9}$$

The typical side reactions of CO_2 reforming are the reverse Boudouard reaction (equation 10), the water–gas shift (WGS) reaction (equation 11) and the methanation reaction, or reverse steam reforming of methane (equation 12). At high temperatures, the thermodynamic equilibria of the reactions favour carbon dioxide consumption and carbon monoxide formation.

$$C + CO_2 \rightleftharpoons 2CO; \quad \Delta H^0_{298\,K} = +172\,\text{kJ/mol} \tag{10}$$

$$H_2O + CO \rightleftharpoons H_2 + CO_2; \quad \Delta H^0_{298\,K} = -41\,\text{kJ/mol} \tag{11}$$

$$3H_2 + CO \rightleftharpoons CH_4 + H_2O; \quad \Delta H^0_{298\,K} = -206\,\text{kJ/mol} \tag{12}$$

The equilibrium of the methanation reaction means that the temperature should be above 616 °C to ensure that the syngas product does not react further to water and methane. Reaction temperatures higher than 703 °C favour the reverse Boudouard reaction. And above 815 °C, hydrogen in addition to carbon dioxide is consumed in the reverse WGS reaction. Thus, the temperature should be optimised according to which is considered more important, the conversion of carbon dioxide or the H_2 to CO molar ratio.

3.2. *Effect of conditions on the CO_2 reforming of n-heptane on a commercial 15 wt% NiO/Al_2O_3 catalyst*

The commercial 15 wt% NiO/Al_2O_3 catalyst showed activity towards CO_2 reforming even at low temperatures at which no thermal cracking occurred. Thermal experiments were described earlier [17]. As can be seen in figure 1, *n*-heptane conversion was 100% at 750 °C, whereas without the catalyst a temperature of 870 °C was required. Carbon dioxide conversion of 37% was obtained at 750 °C, but remained below 1% in thermal experiments, in which neither carbon monoxide nor water was formed. The water–gas shift reaction did not reach the thermodynamic equilibrium.

The stoichiometric CO_2 to $C_{heptane}$ molar ratio (equation 1) was observed to be too small for CO_2 reforming. Coking of the catalyst was pronounced and *n*-heptane cracking conversion high. A ratio of 2 was suitable; the cracking conversion was then less than 1%. The CO_2 to $C_{heptane}$ ratio of 3 was chosen for the studies to reduce the coking of the catalyst.

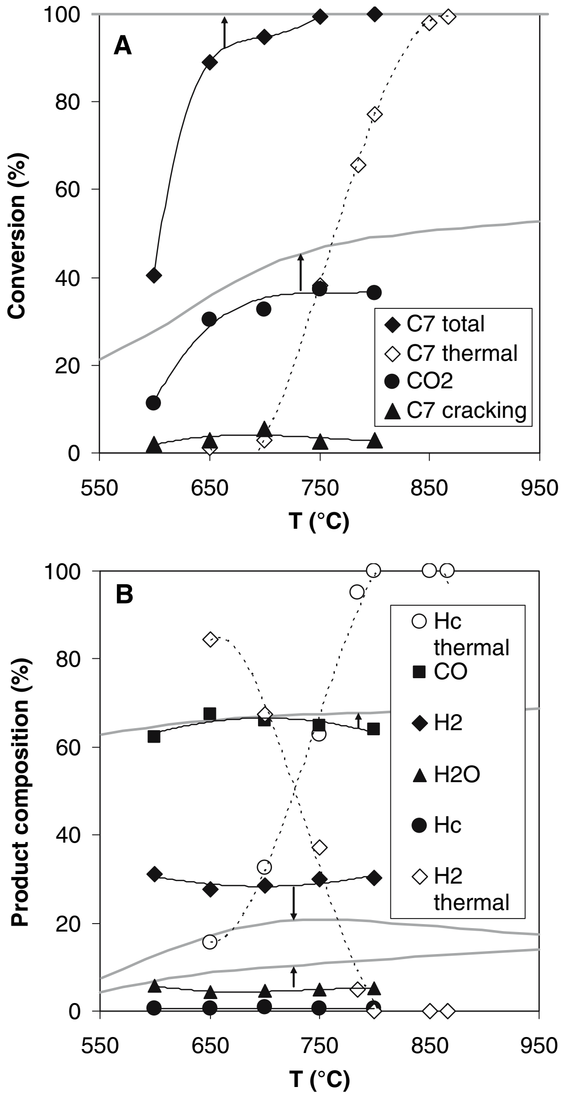

Figure 1. *n*-Heptane total and cracking conversions and carbon dioxide conversion (A) and product compositions (B) as a function of temperature in thermal experiments without catalyst and in the combined CO_2 reforming and POX reaction on the commercial 15 wt% Ni/Al_2O_3 catalyst (GHSV = 8.0×10^5 h^{-1}). CO_2/C_{fuel} = 3. Thicker curves represent thermodynamic equilibria. Hc: smaller hydrocarbons.

As expected, CO_2 conversion decreased when a small amount of oxygen ($O_2/C_{heptane}$ = 0.2 mol/mol) was added to the feed (figure 2). In contrast to the methane reforming [5], hydrocarbon conversion was not enhanced by oxygen but remained the same. Reactions did not reach the calculated thermodynamic equilibria, but the conversions and product compositions followed the trends of the equilibria. Above 630 °C the carbon dioxide conversion was lower in the presence than the absence of oxygen. The addition of oxygen had a clear effect on the coking of the catalyst. Without oxygen the amount of coke was 3.6 mg C/g catalyst after the 4-h experiment at 800 °C. In the corresponding experiment with oxygen the amount of coke was only 1.6 mg C/g catalyst.

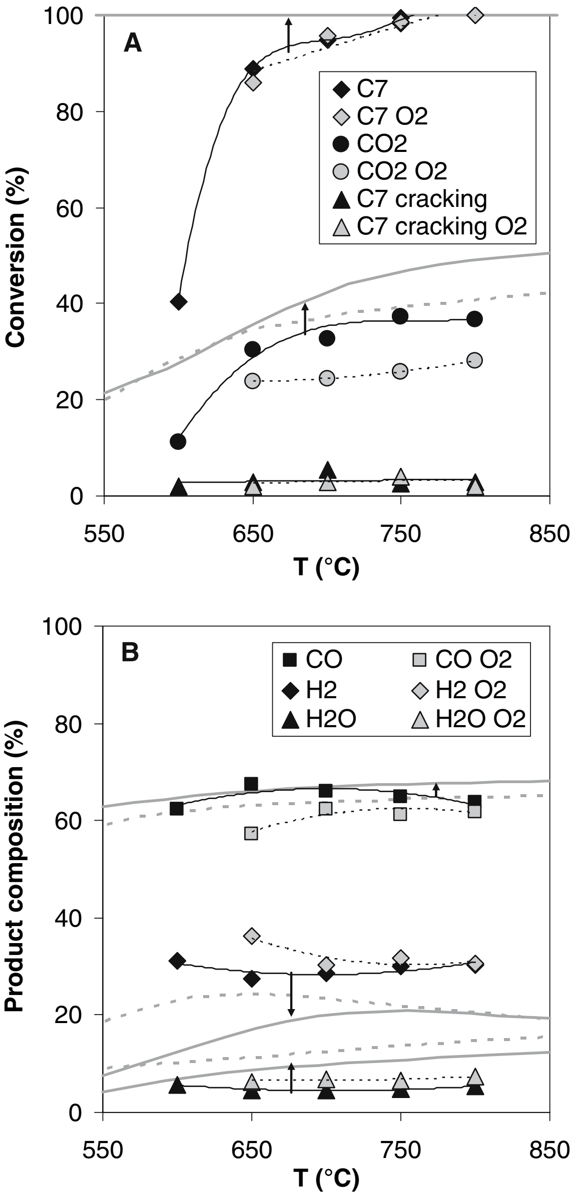

Figure 2. *n*-Heptane total and cracking conversions and carbon dioxide conversion (A) and product composition (B) as a function of temperature in CO_2 reforming and in combined CO_2 reforming and POX (O_2/C_{fuel} = 0.2) on the commercial 15 wt% Ni/Al_2O_3 catalyst at 800 °C. GHSV = 8.0×10^5 h^{-1}, CO_2/C_{fuel} = 3. Thicker curves represent thermodynamic equilibria.

The effect of oxygen was studied at 800 °C and the results are shown in figure 3. CO_2 conversion decreased with the amount of oxygen. At the same time, syngas selectivity decreased because less carbon monoxide was formed and hydrogen was bonded to oxygen to form water. At high oxygen concentration, when the conversion of carbon dioxide obtained a negative value, the total conversion of *n*-heptane decreased from 100% to 84% and the cracking conversion was 17%.

The reforming activity can also be seen from the temperature profiles of the furnace and the reactor at

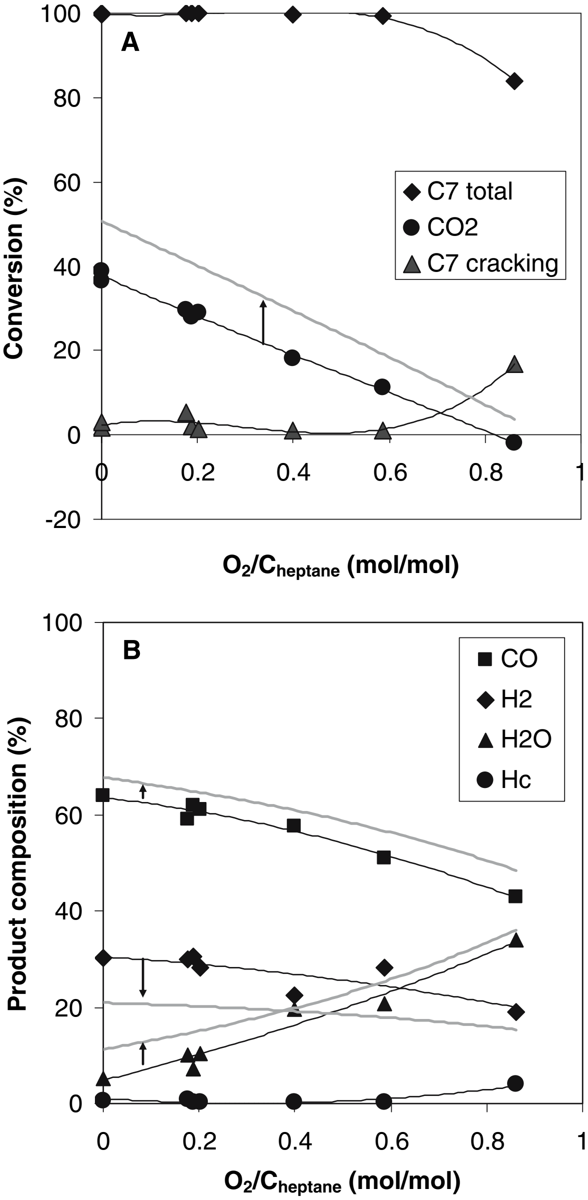

Figure 3. n-Heptane total and cracking conversions and carbon dioxide conversion (A) and product compositions (B) as a function of the O_2 to $C_{heptane}$ molar ratio in combined CO_2 reforming and POX on the commercial 15 wt% Ni/Al_2O_3 catalyst at 800 °C. GHSV = $8.0 \times 10^5\ h^{-1}$, CO_2/C_{fuel} = 3. Thicker curves represent thermodynamic equilibria. Hc: smaller hydrocarbons.

different oxygen concentrations (figure 4). If the temperature in the bed is lower than in the furnace, as in the case of no oxygen and low concentration of oxygen ($O_2/C_{heptane}$ = 0.2 mol/mol), the total reaction is endothermic and the CO_2 reforming reaction takes place. A higher bed temperature than furnace temperature means that exothermal oxidation reactions are predominant, as with the oxygen amount of the stoichiometric POX reaction with and without carbon dioxide. At nearly autothermal conditions ($O_2/C_{heptane}$ = 0.4 mol/mol) there was only a slight difference between the temperatures of the furnace and the reactor.

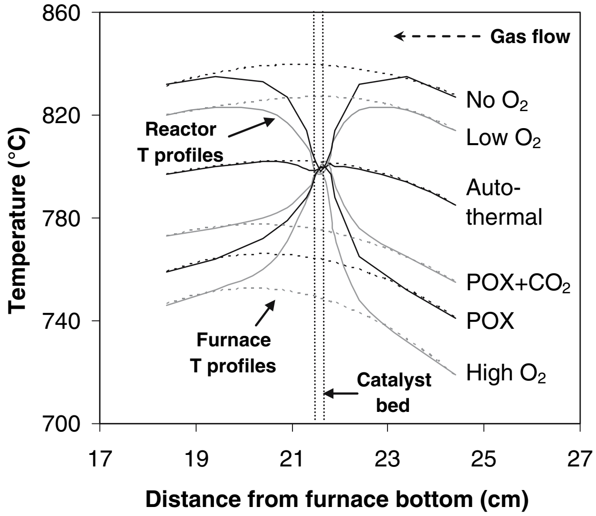

Figure 4. Temperature profiles of the furnace (dashed lines) and the reactor (solid lines) in the combined CO_2 reforming and POX reaction of n-heptane with various amounts of oxygen on the commercial 15 wt% Ni/Al_2O_3 catalyst at 800 °C. GHSV = $8.0 \times 10^5\ h^{-1}$, CO_2/C_{fuel} = 3.

The effect of space velocity was studied with a small amount of oxygen ($O_2/C_{heptane}$ = 0.2 mol/mol) at 800 °C. When the space velocity was decreased, the reactions approached the thermodynamic equilibria, as expected.

3.3. *Combined CO_2 reforming and POX reaction of fuels on 0.25 wt% Rh/ZrO_2 catalyst*

The 0.25 wt% Rh/ZrO_2 catalyst was chosen for the comparison of different fuel compounds in the combined CO_2 reforming and POX reaction. The choice was made on the basis of our earlier study on noble metal catalysts [17] in which the activity and selectivity of the 0.25 wt% Rh catalyst were found approach the performance of the commercial Ni catalyst. The total and cracking conversions of fuel compounds, carbon dioxide conversions and coke amounts at 800 °C are shown in figure 5. The product compositions are presented in figure 6. All the results are given in Table 1 together with the thermodynamic values. With all fuel compounds, less carbon monoxide and water and more hydrogen were formed relative to the thermodynamic values, indicating that the WGS reaction did not reach equilibrium. Temperature profiles of the furnace and the reactor in the combined CO_2 reforming and POX reaction at 800 °C are shown in figure 7. In contrast to the earlier comparison of catalysts [17], where the energy demand increased with the activity of the catalyst, no clear relationship was apparent between the energy demand and the fuel compound reactivity. This was due to the different thermodynamics of the reactions.

n-Heptane was more suitable for the combined CO_2 reforming and POX reaction than were the other

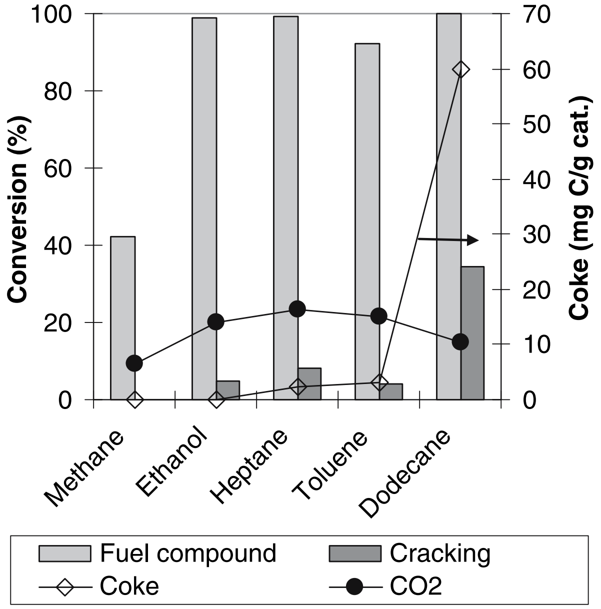

Figure 5. Total and cracking conversions of fuel compounds, carbon dioxide conversions and coke amounts in the combined CO_2 reforming and POX reaction of various hydrocarbons at 800 °C. GHSV = 6.4 × 10^5 h^{-1}, CO_2/C_{fuel} = 3 and O_2/C_{fuel} = 0.2.

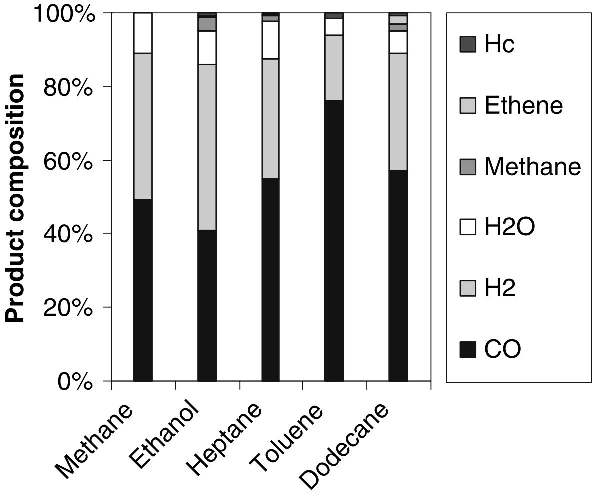

Figure 6. Product compositions in the combined CO_2 reforming and POX reaction of various fuel compounds at 800 °C. GHSV = 6.4 × 10^5 h^{-1}, CO_2/C_{fuel} = 3 and O_2/C_{fuel} = 0.2.

hydrocarbons at the selected O_2/C_{fuel} ratio. The catalyst was coked only slightly: the amount of carbon deposition was 2.3 mg C/g catalyst. The reaction of *n*-heptane also gave the best carbon dioxide conversions, 23% at 800 °C and 27% at 900 °C. Although the best product composition, 93% syngas, was obtained at 700 °C, *n*-heptane conversion was then only 88%. At 800 °C the product composition was almost as good and *n*-heptane conversion was 99%. At 900 °C the H_2 to CO molar ratio was only 0.38 and considerably lower than at lower temperatures due to the reverse WGS reaction.

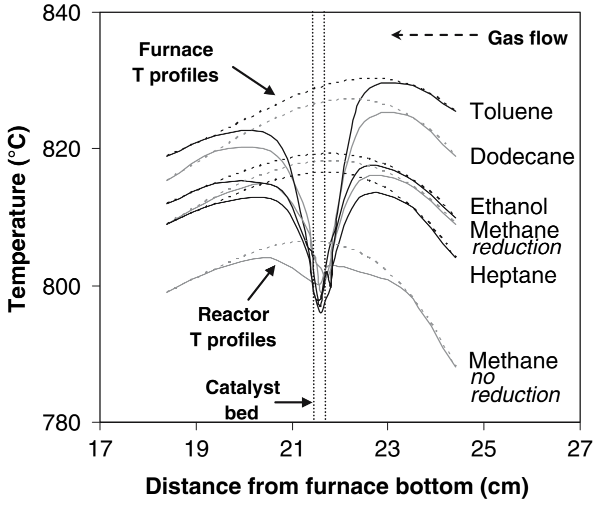

Figure 7. Temperature profiles of the furnace (dashed lines) and the reactor (solid lines) in the combined CO_2 reforming and POX reaction of various fuel compounds at 800 °C. GHSV = 6.4 × 10^5 h^{-1}, CO_2/C_{fuel} = 3 and O_2/C_{fuel} = 0.2.

Methane required the highest temperature of all compounds tested. Methane did not, however, coke the catalyst. Methane conversions were very low compared with the thermodynamic values and the conversions of other compounds. Higher conversions require lower total feed rates as shown in the studies of Souza *et al.* [5] and O'Connor *et al.* [8]. However, the highest conversion of carbon dioxide in this study, 27%, was achieved also with methane at 900 °C. In addition, there was only slightly less syngas in the product than at 800 °C. The conversion of methane was still low however, only 66%. Reduction of the catalyst increased the conversion only a few percentage units but sharply decreased the H_2 to water molar ratio. Thus, considerably less syngas was produced, and the H_2 to CO molar ratio was clearly lower.

Catalyst coking is more severe with higher hydrocarbons [4] and as expected, the catalyst was heavily coked with *n*-dodecane. The amount of carbon deposited was 60 mg C/g catalyst. In addition, large amounts of cracking products were formed. The amount of syngas produced was almost the same as with *n*-heptane, however. The conversion of carbon dioxide became high only at the highest temperature tested, 22% at 900 °C.

The hydrogen to carbon monoxide molar ratio, 0.24 at 800 °C, was poor with toluene, in accordance with the low hydrogen content of the molecule. The product composition was otherwise good; the total syngas production, 94% at 800 °C and 92% at 900 °C, was better than with *n*-heptane (which gave 88% syngas at 800 °C and 85% at 900 °C). Toluene coked the catalyst slightly more than *n*-heptane. The carbon deposition was 3.1 mg C/g catalyst. In addition, according to thermodynamic calculations, toluene required higher temperature than *n*-heptane and *n*-dodecane for total conversion. The conversion of carbon dioxide was good: 22% at 800 °C and 26% at 900 °C.

Consistent with the short carbon chain, hydrogen to carbon ratio, oxygen in the molecule and calculated low energy requirement, ethanol was the best compound for the combined CO_2 reforming and POX reaction. Ethanol did not coke the catalyst. The amount of cracking products was about the same as with *n*-dodecane, but methane was the main cracking product. The H_2 to CO molar ratio was high, over one at all temperatures studied. In earlier steam reforming of ethanol [18], Rh/CeO_2, Rh/ZrO_2 and Rh/CeO_2-ZrO_2 showed high activity and selectivity towards hydrogen production.

4. Conclusions

The CO_2 reforming of fuel compounds 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 POX reduces the energy demand. In addition, oxygen reduces the catalyst deactivation by coke formation. However, it also decreases the conversion of carbon dioxide and the selectivity to synthesis gas. The amount of oxygen should therefore be lower than required for the autothermal operation, and optimisation is required to find the right amount.

It was observed that aromatic compounds such as toluene are highly stable and require high temperatures for total conversions. In addition, the H_2 to CO molar ratio is very low. Gasoline would be more suitable for the combined CO_2 reforming and POX reaction than diesel. The reaction of diesel would produce more cracking products and coke the catalyst severely. Natural gas, in turn, would require much higher temperatures for high conversions. As expected, ethanol was the most suitable compound.

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References

[1] M.C.J. Bradford and M.A. Vannice, Catal. Rev. Sci. Eng. 41 (1999) 1.

[2] J.R. Rostrup-Nielsen and J.-H. Bak Hansen, J. Catal. 144 (1993) 38.

[3] J.R. Rostrup-Nielsen, in: *Catalysis, Sciences and Technology*, Vol. 5, eds. J.R. Anderson and M. Boudart (Springer-Verlag, Berlin, 1984).

[4] K. Kochloefl, in: *Handbook of Heterogeneous Catalysis*, Vol. 4, eds. G. Ertl, H. Knözinger and J. Weitkamp (Wiley-VCH, Weinheim, 1997).

[5] M.M.V.M. Souza and M. Schmal, Appl. Catal. A: Gen. 255 (2003) 83.

[6] H.Y. Wang and E. Ruckenstein, Catal. Lett. 75 (2001) 13.

[7] E. Ruckenstein and H.Y. Wang, Catal. Lett. 73 (2001) 99.

[8] A.M. O'Connor and J.R.H. Ross, Catal. Today 46 (1998) 203.

[9] K.J. Puolakka and A.O.I. Krause, Stud. Surf. Sci. Catal. 153 (2004) 137.

[10] F. Solymosi, A. Szöke and L. Ovári, J. Catal. 186 (1999) 269.

[11] F. Solymosi and P. Tolmacsov, Catal. Lett. 83 (2002) 183.

[12] F. Solymosi, P. Tolmacsov and K. Kedves, J. Catal. 216 (2003) 377.

[13] M. Panczyk, G. Giecko, W. Gac, S. Pasieczna, B. Stasinska and T. Borowiecki, Adsorpt. Sci. Techn. 19 (2001) 455.

[14] S. Fujimura, K. Nakagawa, N. Ikenaga and T. Suzuki, Sekiyu Gakkaishi 40 (1997) 179.

[15] U.S. Environmental Agency, Gasoline composition stydy, http://www.epa.gov/earth1r6/6en/xp/lppapp6a.pdf, October 31, 2005.

[16] A. Roine, HSC Chemistry for Windows version 5.11, Outokumpu Research Oy, 2003.

[17] K.J. Puolakka, S. Juutilainen and A.O.I. Krause, Catal. Today 115 (2006) 217.

[18] C. Diagne, H. Idriss and A. Kiennemann, Catal. Commun. 3 (2002) 565.