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Production of hydrogen over bimetallic Pt–Ni/δ-Al_2O_3: II. Indirect partial oxidation of LPG

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Indirect partial oxidation (IPOX) of a 75:25 propane:*n*-butane mixture, which was used as a model for LPG, was studied over the bimetallic 0.2 wt%Pt–15 wt%Ni/δ-Al_2O_3 catalyst in 623–743 K temperature range. The effects of steam to carbon ratio (S/C), carbon to oxygen ratio(C/O_2) and residence time (W/F (g cat-h/mol LPG)) on the hydrogen production activity, selectivity and product distribution were studied in detail. The results are compared with the results obtained in the IPOX of pure propane. An Increasing Temperature Program (ITP) was applied during all experiments and the results showed that the presence of *n*-butane in the feed enhances hydrogen production activity and selectivity. Considering the well established distribution network of LPG and the superior performance of the bimetallic Pt–Ni catalyst in the IPOX of LPG, Pt–Ni system seems a very promising catalyst alternative to be used in commercial fuel processors.

KEY WORDS: autothermal reforming; indirect partial oxidation; hydrogen production; Pt–Ni catalysts; LPG.

1. Introduction

The stringent environmental regulations impose the use of fuel cell systems in generating energy for both mobile and stationary applications. For example, the common use of fuel cell-electric motor combinations in vehicles must be enforced within the next five to ten years in areas that suffer heavily from air pollution. In both mobile and stationary applications, pure hydrogen feed is needed for fuel cell operation, considering the fact that the other fuel alternative, methanol, is hazardous, causes inefficiency in operation and does not have a proper distribution network. Hydrogen feed for fuel cells must either be supplied from a storage tank or be produced on site/on board. The former needs safe and economically feasible storage technologies which can only be developed in the mid- to long-term, comparing the targeted 6.5 wt% hydrogen storage capacity at ambient temperature with the currently obtained ca. 1 wt% storage level [1]. Thus, hydrogen production from hydrocarbons on board the vehicle for mobile fuel cell applications and on site for immobile fuel cell applications via using efficient fuel processors is a very reliable short-term solution. At that point, the hydrocarbons that already have well established distribution networks are the best choices for fuel. The two possible options are natural gas, which is mostly methane, and LPG, which is a mixture of propane and butane; as a result, the design and development of reforming catalysts for these hydrocarbon feeds is of crucial importance.

The most important catalytic reaction in a fuel processor is to convert hydrocarbons to hydrogen, which can be achieved via several catalytic reactions including steam reforming and direct or indirect partial oxidation. The high activity and selectivity obtained at the reforming stage reduce the need for additional reactions that follow hydrogen production in the fuel processors; these reactions are water-gas shift (WGS) and preferential oxidation (PROX), both of which are solid-catalyzed.

In indirect partial oxidation (IPOX), which is the combination of steam reforming (SR) and total oxidation (TOX), the strongly exothermic TOX reaction supplies the heat that is needed by the endothermic SR reaction. Previous reports in the literature indicate that a dual-bed configuration or a single-bed comprising physical mixture of TOX and SR catalysts (Pt and Ni respectively) are both inferior in performance to a single bed of bimetallic catalyst in the IPOX of methane [2,3] and propane [4]. This has been explained by the utilization of bimetallic catalyst particles as efficient micro heat exchangers in supplying SR sites with the heat produced on TOX sites [4,5].

The well-established distribution network and safe storage methods make LPG a very promising candidate for use as a hydrocarbon feed in fuel processors. On the other hand, although investigations on the autothermal reforming of ethane [6], propane [4,6–8], *n*-octane [9], and other hydrocarbons [10] are available, not enough attention has been given to the catalytic conversion of LPG. In our previous studies, a bimetallic Pt–Ni/Al_2O_3 catalyst was tested in SR [11,12] and TOX [5,12] of propane and butane and recently in IPOX of propane

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[4]. The performance of the bimetallic catalyst in IPOX of propane was found superior compared to those of the monometallic catalysts reported in literature [4,7].

In this study, LPG, which is a mixture of propane and *n*-butane, was used as the hydrocarbon feed in IPOX over bimetallic 0.2 wt%Pt–15 wt%Ni/δ-Al_2O_3. The reaction tests were conducted in the 623–243 K interval. LPG was obtained by mixing propane with *n*-butane using a 75:25 ratio which approximates the propane-rich LPG available in several regions of the world. The reactor effluent was tested at 20 K intervals of temperature increase. The effects of other parameters, such as steam to carbon ratio, carbon to oxygen ratio and W/F (g cat-h/mol LPG) on the hydrogen production activity and selectivity were also investigated. Autothermal conditions were obtained during IPOX experiments for various feed mixtures. The test results were compared with the results of our study on the IPOX of propane [4]; the comparison clearly indicates better performance in the IPOX of LPG i.e. higher hydrogen production with higher H_2/CO ratio on the Pt–Ni system. This may be explained by the fact that the presence of *n*-butane leads to a larger amount of heat production in TOX and, as a consequence, enhances SR and the accompanying water-gas shift (WGS) reaction.

2. Experimental

2.1. Catalyst preparation

The thermally stable δ-Al_2O_3 support was obtained by drying γ-Al_2O_3 (Alcoa) at 423 K for 2 h and then calcination at 1173 K for 4 h. The monometallic 15 wt%Ni/δ-Al_2O_3 catalyst was prepared by the incipient-to-wetness impregnation technique using aqueous precursor solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Merck). The resulting slurry that was formed after ultrasonic mixing of the precursor solution and the support under vacuum for 1.5 h was then dried overnight at 393 K and then calcined at 873 K for 4 h. The bimetallic catalyst was prepared by the sequential impregnation technique using an aqueous solution of Pt, namely $Pt(NH_3)_4(NO_3)_2$ (Aldrich), over the initially prepared and calcined NiO/δ-Al_2O_3 sample. The metal loading was 0.2 wt% for platinum. Upon Pt impregnation, the final slurry was dried at 393 K and re-calcined at 773 K for 4 h.

2.2. Reaction system

Reaction tests were conducted in stainless steel tubular down-flow microreactors. In all experiments, 150 mg of fresh catalyst packed inside a 6 mm ID stainless steel micro-reactor was used. The temperature of the catalyst bed was controlled with ±0.1 K precision via a programmable temperature controller (Shimaden FP-21). Prior to reaction tests, the catalysts were reduced in 20 ml/min of pure hydrogen flow at 773 K for 4 h. The flow rates of the gases (dry air, hydrogen, propane, *n*-butane, nitrogen) were controlled by Omega and Aalborg mass flow controllers. The flow rate of water was controlled by a Jasco PU-1580 HPLC pump, and the water was evaporated before it was introduced into the feed gas mixture. The transfer lines of the reaction system were heated for preventing condensation.

2.3. Reaction conditions

The experiments were carried out in the temperature range of 623–743 K by using an increasing temperature program (ITP). In designing experiments, carbon/oxygen, steam/carbon and W/F (g cat-h/mol LPG) ratios were used as the reaction parameters. The reaction was studied at 20 K intervals within the temperature range. The hydrocarbon, dry air and steam flow rates were adjusted according to the assigned carbon/oxygen ratios ($1.50 < C/O_2 < 2.70$) and residence times ($0.51 < W/F < 1.37$). The total inflow was varied between 110 ml/min and 293 ml/min. High flow rates were preferred to eliminate temperature rises and hot-spots that may occur due to the exothermicity of oxidation reactions. The details of the experimental conditions studied are given in table 1.

Two gas chromatographs operating in parallel were used for product analysis. Hydrocarbons and CO_2 were analyzed in a Shimadzu GC-14A gas chromatograph equipped with a Porapak Q column. Fixed gases (H_2, O_2, N_2, and CH_4) were analyzed in a Shimadzu GC-8A gas chromatograph equipped with a Molecular Sieve 5A column. Two salt-ice traps were used to remove water vapor from the stream analyzed by Molecular Sieve 5A. Transfer lines of the reactor and analysis systems were kept at 398 K to prevent possible condensation. Blank tests confirmed that the stainless steel reactor, alumina and glasswool were inert under the reaction conditions.

Table 1

The reaction conditions and thermo-neutral points for IPOX of LPG in the 623–243 K temperature range

Exp. No.	Feed composition*	C/O_2	S/C	W/F (g cat-h/mol HC)	Thermo-neutral point (K)
1	1.0 : 1.5 : 16.1 : 5.7	2.12	5	1.37	
2	1.0 : 1.5 : 16.1 : 5.7	2.12	5	1.12	644; 666
3	1.0 : 2.2 : 16.4 : 8.2	1.50	5	0.51	643; 668
4	1.0 : 1.5 : 16.1 : 5.7	2.12	5	0.51	640; 658
5	1.0 : 1.2 : 16.1 : 4.5	2.70	5	0.51	

*Feed composition is given as the molar ratios of the reactant gases and inerts (HCmixture:O_2:Steam:Inert).

3. Results and discussion

A bimetallic 0.2 wt%Pt–15 wt%Ni/δAl_2O_3 catalyst was prepared and tested in the IPOX of LPG having a 75:25 propane:*n*-butane composition. The detailed surface characterization of the bimetallic Pt–Ni catalyst reported previously [4] has shown that (i) Pt rich Pt and Ni islands are formed on the catalyst surface where Pt centers, which dominantly catalyze exothermic TOX, are in the very close neighborhood of the Ni sites, which dominantly catalyze endothermic SR, as confirmed by SEM/SEM-BCI analyses, and (ii) there is no Pt–Ni alloy formation either locally or in the bulk as confirmed by EDAX and XRD, respectively.

3.1. Preliminary reaction tests

Preliminary tests were conducted for defining the intervals of each reaction parameter that did not lead to coke deposition during reaction. Carbon/oxygen ratios were kept outside explosion limits throughout the experiments. The range of steam/carbon ratios investigated for the LPG feed indicated that coke deposition was observed at a steam/carbon ratio of 3.2 for the carbon/oxygen ratio of 2. Thus, the steam/carbon ratio was kept constant at 5 at all times in order to prevent catalyst deactivation due to coke deposition.

The decreasing temperature progression (DTP) starting from 743 K down to 623 K also led to coke deposition on the catalyst surface for various combinations of W/F and carbon/oxygen ratios. This was due to the very fast total oxidation at high temperatures which caused an increase in temperature of the catalyst bed immediately above 800 K as soon as the hydrocarbon mixture was fed to the reactor. Therefore, experiments on the IPOX of LPG were conducted only with the increasing temperature progression (ITP).

3.2. Indirect partial oxidation of LPG

The reaction conditions and the temperatures at which thermo-neutral conditions were observed in the IPOX of LPG are given in Table 1. Thermo-neutrality was obtained around 650 K for $1.50 < C/O_2 < 2.12$ where the S/C ratio was fixed at 5 and W/F was changed between 0.51 and 2.12 g cat-h/mol LPG. Thermoneutral points were defined as the conditions at which constant reactor temperature was observed for at least 30 min without any external heat supply [4]. At thermoneutral points, the heat produced by total oxidation is at least equal to the sum of the heat absorbed by steam reforming and the heat loss from the system. Thus, these points are characteristic for the particular system used in the IPOX of LPG. LPG conversions were nearly 100 per cent throughout the temperature range for all experiments.

For fixed steam/carbon and carbon/oxygen ratios (Exps. 1, 2 and 4 in table 1), a decrease in the residence time (i.e. increase in the total flowrate) led to a considerable increase in the hydrogen production, especially when W/F was very low (figure 1). The increase in hydrogen production with a decrease in W/F can be explained by the limited residence time of carbon monoxide and hydrogen on the catalyst surface that prevents methanation. The results are parallel to those obtained when pure propane was used as the hydrocarbon feed [4], and to those reported in the literature [6] where IPOX of propane on Ni/Al_2O_3 was studied. The results obtained in the IPOX of LPG indicate that low W/F values should be preferred for higher hydrogen productivity.

When the results of Exps. 3, 4, 5 were compared, the expectation was to observe an increasing trend in hydrogen production with a decrease in the carbon/oxygen ratio. However, as indicated by the results in Figure 2a, this was not the case although the hydrogen production levels were not very different. An explanation may be extracted from the methane production levels obtained in these experiments. Figure 2b shows that methane production increases with carbon/oxygen ratio, as in the case of propane IPOX [4]. The high methane production level in Exp. 5, which may be due to enhanced levels of carbon monoxide hydrogenation, may have led to a decrease in hydrogen productivity.

The hydrogen/carbon monoxide production ratio was found to decrease with temperature. On the other hand, neither the increase in the W/F nor the carbon/oxygen ratios seem to affect H_2/CO production ratio with a specific trend (figures 1 and 2a; table 1). The results reported in the literature do not indicate a clear relation either: hydrogen selectivity was reported to decrease with oxygen/*n*-octane ratio when *n*-octane was used as the hydrocarbon feed [8] whereas it was found to increase with increasing oxygen/methane ratio when methane was used as the hydrocarbon feed [6].

For the sake of making sound comparisons, the W/F and C/O_2 ratios used in the IPOX of LPG in this study

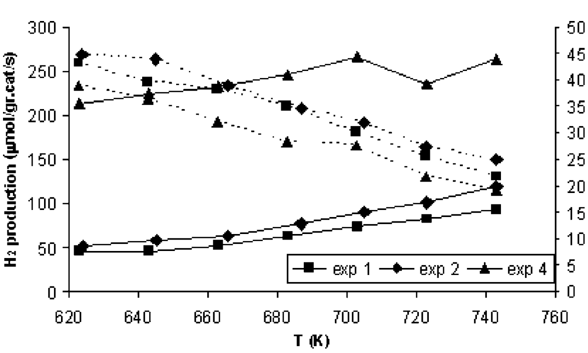

Figure 1. Hydrogen production activity increases with a decrease in W/F. The most probable reason is the limited residence of H_2 produced and CO on the catalyst surface that limits back-methanation. The close H_2/CO values, which do not show any clear relation with W/F, support that explanation. (Exp. 1: W/F = 1.37; Exp. 2: W/F = 1.12; Exp. 4: W/F = 0.51) (- - - - - - - - hydrogen production; H_2/CO).

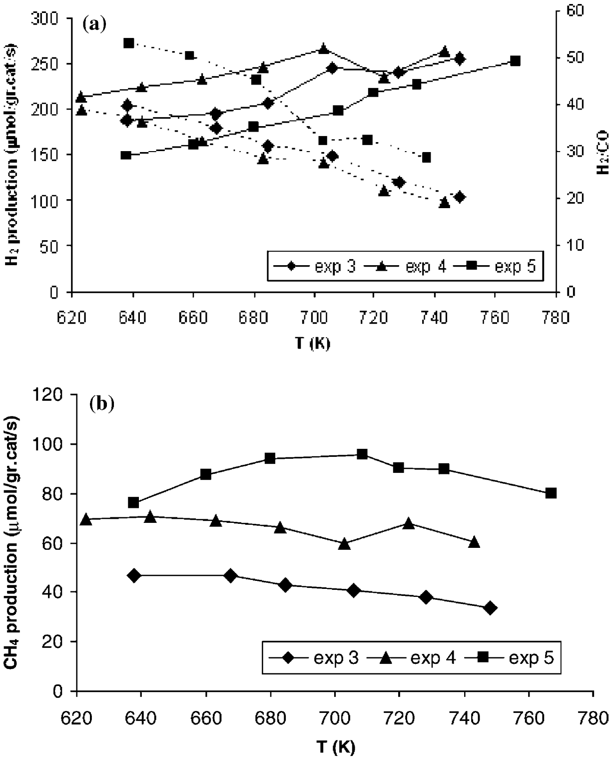

Figure 2. (a and b) Enhanced methane production rate for the set that has the highest C/O_2 ratio, exp 5, led to H_2 production rates lower than expected though its selectivity is higher. Low methane production rate has a positive effect on the H_2 production rate for $C/O_2 = 1.50$, Exp. 3. (Exp. 3: $C/O_2 = 1.50$; Exp. 4: $C/O_2 = 2.12$; Exp. 5: $C/O_2 = 2.70$) (in a: - - - - - - - - hydrogen production; b: H_2/CO).

were chosen equal to those used in our previous work on propane IPOX [4]. In both studies, 100% conversion of propane and LPG were achieved, respectively. A comparison between the results obtained from the reactions conducted with propane and LPG shows that the presence of butane clearly enhances the hydrogen/carbon monoxide ratio in the product stream (figure 3a, b, c). The presence of butane also has a clearly positive effect on the amount of hydrogen produced per hydrocarbon used (figure 3a, b, c).

The better activity and H_2 selectivity obtained on the bimetallic Pt–Ni/δ-Al_2O_3 catalyst when an LPG feed was used for IPOX can be explained as follows: in the micro characterization of the Pt–Ni/Al_2O_3 catalyst it was found that the presence of close but distinct Ni and Pt sites on the bimetallic catalyst led to the utilization of catalyst particles as micro-heat exchangers, i.e. the heat produced on Pt sites during TOX was transferred through the particle and was used by Ni sites catalyzing endothermic SR [4]. In this study, the presence of butane in LPG increased the amount of heat produced on Pt sites. This resulted from the higher oxidation enthalpy of butane compared to that of propane, and, as a consequence, a larger amount of heat was transferred to Ni sites leading to higher SR activity. The relatively easier achievement of thermoneutral conditions in the IPOX of LPG under an ITP regime and the immediate rise and blockage due to coke deposition in a DTP regime during preliminary reaction tests both support this explanation. Additionally, the better selectivity signified by the higher "H_2 produced/LPG used" ratios obtained is a clear indication of the ongoing WGS reaction over the Pt–Ni catalyst during the IPOX of LPG. It is quite clear that the WGS reaction is more pronounced when LPG is used instead of propane as the feed. This explanation is also supported by high H_2/CO ratios obtained in the product stream upon IPOX of LPG.

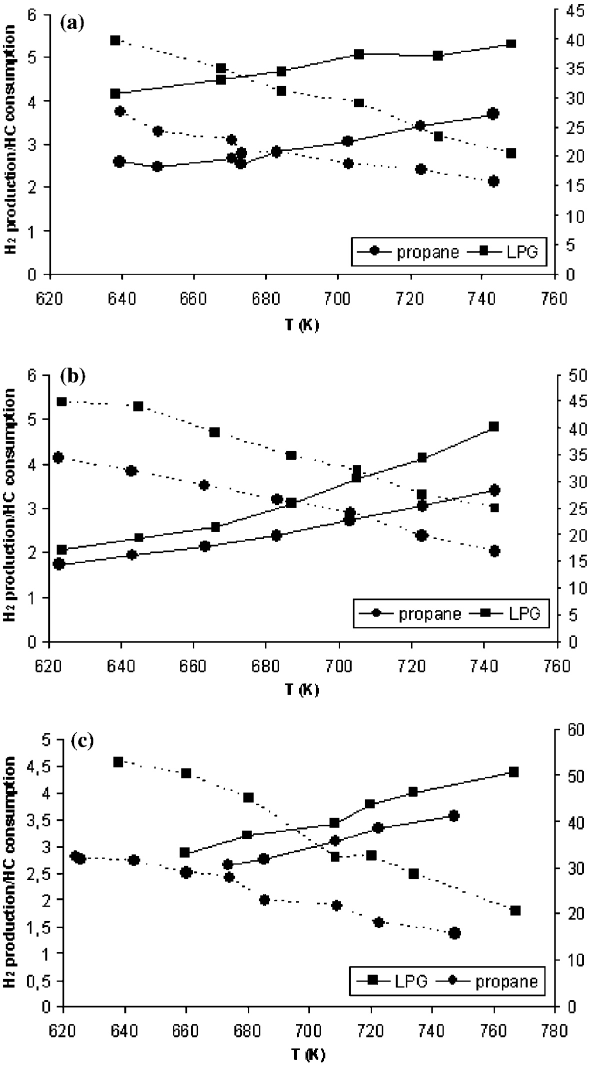

Figure 3. The activity and selectivity comparison plots for LPG and propane feeds. (a) $C/O_2 = 1.50$, $W/F = 0.51$, (b) $C/O_2 = 2.12$, $W/F = 1.12$, (c) $C/O_2 = 2.70$, $W/F = 0.51$. For all plots, $S/C = 3$ and 5 for IPOX of propane and LPG, respectively. A drastically higher H_2 production ability as well as high H_2 selectivity when LPG is used as the feed makes Pt–Ni system a promising candidate for H_2 production in commercial fuel processors. At low C/O_2 ratios, as in (a), activity difference is drastic in favor of LPG feed. The difference lessens when C/O_2 is increased (b, c). The results indicate pronounced WGS activity of the catalyst in IPOX of LPG. (- - - - - - - - H_2 production/HC consumption; H_2/CO).

At the lower C/O_2 ratio used, 1.50 in figure 3a, the H_2 production/HC consumption ratio, which shows the activity level and the product yield of the catalyst, was drastically higher for LPG. The only trend that can be extracted from Figure 3a, b and c on the relation between the C/O_2 ratio and activity and selectivity levels in the IPOX of propane and LPG is that the difference in H_2 production/HC consumption ratios for propane and LPG tests decrease as the C/O_2 ratio increases.

Considering the fact that the propane-*n*-butane mixture used in this study has a very similar composition to LPG used in several parts of the world, the results indicate that the bimetallic Pt–Ni system may be a promising catalyst candidate for use in practical applications.

3.3. Stability of the bimetallic Pt–Ni/δ-Al_2O_3 catalyst

Stability tests for the indirect partial oxidation of LPG over the bimetallic 0.2 wt%Pt–15 wt%Ni/δ-Al_2O_3 catalyst were conducted at 723 K, C/O_2 ratio of 2.70 and a W/F of 0.51 g cat-h/mol LPG, considering the superior performance of the catalyst under these conditions. 723 K was chosen as the reaction temperature since the deactivation of the catalyst is more likely to happen at this high temperature. The steam/carbon ratio was selected as 5. The bimetallic Pt–Ni catalyst was found to be very stable during the 12-h time-on-stream experiments under these conditions.

4. Conclusions

Experiments conducted on the indirect partial oxidation of LPG (75% propane-25% *n*-butane) over the bimetallic Pt–Ni/Al_2O_3 catalyst between 623–243 K have shown that both the hydrogen yield (H_2 produced per mole of hydrocarbon feed) and the hydrogen selectivity (H_2/CO ratio in the product) are substantially increased as compared to pure propane. The results obtained provide a strong indication for the potential use of the bimetallic Pt–Ni system and of LPG in commercial fuel processors designed for fuelling PEM fuel cells.

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