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Research article

A study on catalytic hydrogen production: Thermodynamic and experimental analysis of serial OSR-PROX system

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ABSTRACT

Steady state performance of OSR and serial OSR-PROX reactors were investigated. OSR of methane/propane and PROX were conducted over novel Pt-Ni/δ-Al_2O_3 and Pt-Sn/AC catalysts, respectively. OSR (623–773 K) and PROX (383–388 K) reactors' temperature combination, S/C ratio (2.25–6) in the OSR feed, and W/F_{O_2} ratio (1.5–12.2 mg-cat·min/μmol) in the PROX feed, *which was adjusted through oxygen addition to OSR outlet at rates on the basis of CO molar flow in the OSR outlet*, were used as the experimental parameters. Simultaneous use of high temperature and high S/C ratio led to increased H_2 and H_2/CO ratios, and decreased CH_4 and CO_2 concentrations in OSR product. In serial tests, the highest achieved H_2 concentration was 66% (dry based inert free) at S/C ratio of 6 at 723 K, while the lowest CO concentration was 700 ppm at OSR-PROX temperature combination of 723 & 383 K. Maximum achieved methane and propane conversions at 723 K were 70% and 100%, respectively. Oxygen fed to OSR was totally consumed in all tests. OSR temperature of 723 K, S/C ratio of 5, PROX temperature of 383 K and W/F_{O_2} ratio of 1.53 in the PROX feed were the optimal parameters targeting high H_2/CO product ratio. The experimental product distribution trends were consistent with the results of the thermodynamic equilibrium calculations.

1. Introduction

The use of combined Fuel Processor-PEM Fuel Cell (FP-PEMFC) systems in small scale stationary applications is expected to be an essential element of smart grid systems owing to their non-intermittent energy production. Those systems produce fully renewable energy when bio-methane is used as FP's hydrocarbon feed.

A typical fuel processor includes mainly three units, in which reforming, water gas shift (WGS) and preferential oxidation (PROX) reactions are conducted in series. In the oxidative steam reformer (OSR), where hydrocarbon fuel, oxygen and water are fed to the reactor, endothermic steam reforming and exothermic oxidation reactions take place simultaneously producing a gas rich in H_2, but the product stream contains side products, like CO and CO_2. The following intermediate WGS unit is used for suppressing CO level while enriching the stream in H_2. At the final stage, PROX unit is used for decreasing CO to ppm levels to obtain PEM-grade H_2. As the part of our studies on fuel processing reactions, our novel bimetallic system designed for OSR reaction has been tested for different operating conditions. The results of our previous studies [1–4] clearly revealed high temperature shift (HTS) activity of the OSR catalyst (Pt-Ni/δ-Al_2O_3) for the tested temperature and S/C feed ratios leading to very low CO concentrations in the OSR product. Additionally, our recent study on PROX performance of AC supported Pt-Sn system indicated that higher than 96% CO conversion was possible under realistic feed conditions [5].

In the fuel cell part, there have been studies by other groups on reducing the amount and strength of CO adsorption on the catalyst surface and on increasing the CO tolerance of PEM fuel cell anode to higher than 200 ppm via alloying Pt with other metals like Ru, Sn, Rh, Mo, etc. Additional advantage of alloying Pt with a second element in the anode catalyst is cost reduction through decreasing the Pt loading. The operation of PEM fuel cells at higher temperatures via using both different membranes and bimetallic Pt based anode catalysts enables them to tolerate higher concentrations of CO in the feed stream [6–13].

The aim of the current study is to find out whether the use of a very simple, two reactor OSR-PROX system has a potential to be used in hydrogen production from methane and propane for PEM fuel cell applications. The reaction tests were conducted in a Fuel Processor Prototype (FPP) which was designed and constructed in our laboratory. Individual and serial tests were performed at different OSR and OSR-

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PROX reactors' temperature combinations for different steam to carbon ratios in the OSR feed and for different oxygen to carbon monoxide ratios in the PROX feed by oxygen addition to OSR outlet at rates determined on the basis of CO molar flow in the OSR outlet. Novel Pt-Ni/δ-Al_2O_3 and Pt-Sn/AC catalysts were used in OSR and PROX reactors, respectively. The study also covers a comprehensive thermodynamic analysis aiming to calculate equilibrium compositions of methane and propane OSR products for various feed compositions to confirm the experimental product distribution trends.

2. Experimental

2.1. Catalyst preparation

For the preparation of the bimetallic OSR catalyst (0.2wt.%Pt-10wt.%Ni/δ-Al_2O_3) first thermally stable δ-Al_2O_3 support was obtained by crushing and sieving γ-Al_2O_3 (Alfa Aesar) pellets into 354–250 μm (45–60 mesh) particle size followed by drying at 423 K for 2 h and calcination at 1173 K for 4 h. Ni/δ-Al_2O_3 catalyst was prepared by the incipient-to-wetness impregnation using aqueous solution of nickel (II) nitrate hexahydrate (Merck). The resulting slurry was then dried overnight at 383 K and calcined at 873 K for 4 h. Aqueous solution of tetraammineplatinum (II) nitrate (Aldrich) was then added to Ni/δ-Al_2O_3. The resulting slurry involving two metals was dried overnight at 383 K and finally calcined at 773 K for 4 h [1, 3].

For the preparation of the bimetallic PROX catalyst (1wt.%Pt-0.25wt.%Sn/AC) commercial activated carbon (NORIT ROX 0.8) pellets were crushed and sieved into 354–250 μm (45–60 mesh) particle size and exposed to different thermal and chemical pretreatments prior to being used as support. At first, activated carbon (AC) was treated with 2 N HCl solution in a Soxhlet apparatus under reflux for 12 h to remove some ash content and accompanying sulfur. The slurry was then rinsed and washed with DI water for 6 h to remove HCl remaining on the support surface and dried overnight at 383 K. Dried support was treated with 5 N HNO_3 solution under total reflux for 3 h. The rinsing procedure with DI water was repeated several times and the slurry was dried overnight at 383 K. Sn/AC catalyst was prepared by the incipient-to-wetness impregnation using aqueous solution of tin (IV) chloride pentahydrate (Riedel-de Haën). The resulting slurry was then dried overnight at 383 K and calcined under 50 ml/min He flow at 673 K for 2 h. Aqueous solution of hexachloroplatinic (IV) acid hexahydrate (Merck) was then added to the Sn/AC catalyst. The resulting slurry involving two metals was dried overnight at 383 K [5].

2.2. Fuel processor test prototype (FPP) and reaction conditions

The fuel processor test prototype (Fig. 1) was used for individual OSR and serial OSR-PROX reaction tests. The design and construction specifications of the FPP system were given in our previous study [3] in detail. Individual methane and propane OSR reaction tests were conducted at temperature levels of 623 K, 673 K, 723 K and 773 K for the sets with different S/C ratios in the range of 2.25–6 as given in Tables 1 and 3, respectively. Serial OSR-PROX reaction tests were performed at OSR temperature level of 723 K and PROX temperature levels of 383 K and 388 K. In the tests, oxygen was added to PROX feed, *whose addition rate was adjusted on the basis of CO molar flow in the OSR outlet*, for having W/F_{O_2} ratio in the PROX feed in the range of 1.5–12.2 mg-cat·min/μmol, as listed in Tables 2 and 4, respectively. In all catalytic performance tests, the feed stream included fixed volumetric flow rates of hydrocarbon, oxygen and helium, while the changes were made in steam flow rate, reaction temperatures, and oxygen addition to PROX feed. O_2/C ratio was fixed at 0.68 and 0.37 in the methane and propane tests, respectively, and S/C ratio levels were selected as 2.25, 3, 5 and 6. Total feed flow rate was in the range of 85–160 ml/min. Water is supplied via Jasco PU-2089 Plus HPLC pump, where the transfer line to the fuel processor inlet is heated up to 413 K and connected to the Shimaden SR91 temperature controller to enable complete vaporization of water before contacting the gas mixture. The steam flow rate is calculated by using ideal gas equation at room conditions (1 atm, 298 K), density and molecular weight of water supplied from the HPLC pump. In serial OSR-PROX reaction tests, the absence and presence of additional oxygen stream fed to the PROX reactor was also investigated. In the performance tests, product analysis was performed via on-line and real-time mass spectrometer for 2 h TOS guaranteeing that steady state condition was achieved.

Prior to the reaction tests, 150 mg of calcined OSR catalyst (0.2wt.%Pt-10wt.%Ni/δ-Al_2O_3) and 250 mg of fresh PROX catalyst (1wt.%Pt-0.25wt.%Sn/AC) were placed into the constant temperature zones of OSR and PROX microreactors, respectively. Reduction of OSR catalyst under 20 ml/min pure H_2 flow at 773 K for 4 h, and calcination and reduction of PROX catalyst, under 50 ml/min He flow at 673 K for 2 h and under 50 ml/min H_2 flow at 673 K for 10 h, respectively, were all performed in situ.

3. Results and discussion

3.1. Thermodynamic equilibrium analysis of the OSR reactions

Thermodynamic equilibrium calculations were performed to determine the operating conditions, i.e. OSR feed composition and temperature, yielding a product stream having relatively higher H_2 and lower CO, CH_4 and CO_2 concentrations. In the calculations, HSC Chemistry 5.11, which utilizes Gibbs free energy minimization, was used. In the calculations, the feed and product gases were included as species participating possible reactions as listed in Tables 5 and 7.

3.1.1. Thermodynamic equilibrium analysis of the methane OSR reaction

Methane OSR over Pt-Ni/δ-Al_2O_3 catalyst had been formerly investigated by our group and the effects of metal loadings of the catalyst, C/O_2 ratio in the feed stream and temperature were considered as the experimental parameters [14, 15]. Possible methane OSR reactions, for which temperature and feed gas composition vastly affect the extent of the contributing reactions, are given in Table 5. Highly endothermic steam reforming (CO and/or CO_2 producing SR) reactions (Table 5, Rxns #1 and #2) are accompanied by highly exothermic total (TOX) and/or partial oxidation (POX) reactions (Table 5, Rxns #3 and #4) depending on the S/C and C/O_2 ratios in the feed stream, respectively. Due to the HTS activity of the Pt-Ni/δ-Al_2O_3 catalyst [14, 15], slightly exothermic WGS reaction (Table 5, Rxn #5) is also involved in the reaction network.

Equilibrium conversion of CH_4 in OSR unit with respect to the temperature predicted by thermodynamic calculations for different S/C ratios is given in Fig. 2. The calculations were performed for a wider temperature range of 473–1073 K, compared to that was used in the current experimental study, 623–773 K, which is indicated by vertical red lines in the figures. As shown in Fig. 2, the equilibrium conversion of CH_4 reached higher than 99% at 923 K for the feed compositions given in Table 1. In addition, complete conversion of oxygen was observed for the whole temperature range and feed compositions studied. Due to the highly endothermic nature and vast extents of the SR reactions, the equilibrium conversions increased with increased temperature and increased S/C ratio in the feed stream. Raising S/C from 2.25 to 6 increased equilibrium conversion from 44% to 52% and from 74% to 91% at 623 and 773 K, respectively.

Dry based inert free equilibrium H_2, CO, CH_4 and CO_2 concentration profiles with respect to temperature and S/C ratio are shown in Fig. 3. As in the equilibrium conversion profiles, H_2 (primary product of SR reactions) and CH_4 concentrations also reached to steady state values at temperatures around 923 K. Increased temperatures and increased S/C ratios yielded higher H_2 and lower CH_4 concentrations. H_2 concentration reached a maximum value of ~72% at 873 K independent of the S/C ratio. In accordance with the equilibrium conversions given in Fig. 2,