Performance characteristics of Mo–Ni/Al$_2$O$_3$ catalysts in LPG oxidative steam reforming for hydrogen production

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ABSTRACT

A 1:1 propane–butane mixture was used to study the effect of promoting 15 wt.% Ni/Al$_2$O$_3$ (15Ni) catalyst with small amounts of Mo (0.05, 0.1, 0.3, and 0.5 wt.%) for H$_2$ production during LPG oxidative steam reforming. Stability tests at 450 °C showed that lower Mo loadings (0.1 and 0.05 wt.%) had higher conversions and H$_2$ production rates than the non-promoted catalyst and a stable performance for the whole 18-h test period. TPO results showed that slightly more Ni sites were available for whisker formation over the Mo catalyst with 0.1 wt.% loading, the types of carbon resulting from cracking were the same on both promoted and non-promoted catalysts. Higher Mo loaded catalysts (0.3 and 0.5 wt.%) showed higher H$_2$ yields than the non-promoted catalysts, but lower feed-fuel conversions. XRD revealed that the loss in activity was due to oxidation of active Ni species to inactive Ni and Ni–Mo.

1. Introduction

H$_2$ is a promising fuel for producing energy in transportation and domestic applications. It can be extracted by reforming a variety of readily available hydrocarbons, such as methanol, ethanol, natural gas, gasoline, and diesel and jet fuels. Steam methane reforming (SMR) is the most common method of producing commercial, bulk H$_2$. In the last two decades other light hydrocarbons have been considered for H$_2$ production through reforming reactions. Among these is liquefied petroleum gas (LPG). LPG is a mixture of petroleum gases that exist in a liquid state at ambient temperatures under moderate pressures (less than 1.5 MPa). U.S. and Canadian LPG consist

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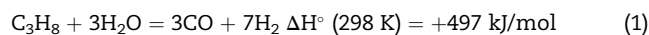primarily of propane. In many countries around the world, however, the propane content in LPG can be as low as 10%. In general, LPG is composed primarily of propane and butane along with other hydrocarbons, such as pentane, propylene, iso-butane, butylenes and ethylene. With its well established distribution network and safe storage methods, LPG has been proposed as an attractive fuel for systems in remote areas where a natural gas pipeline is not available [1]. LPG can also be used for auxiliary power units (APU).

As a mixture composed mainly of propane and butane, understanding and investigating the different reforming processes of these two gases individually are basic steps in developing LPG reforming processes and models. In addition, coming up with a reforming process that accommodates the wide range of compositions of LPG propane and butane contents is challenging. The conversion of propane or butane to H_2 can be carried out by several reaction processes, including steam reforming (SR), partial oxidation (PO), and oxidative steam reforming (OSR). Steam reforming involves the reaction of steam with a fuel in the presence of a catalyst to produce H_2 and CO:

$$C_3H_8 + 3H_2O = 3CO + 7H_2 \ \Delta H° \ (298 \ K) = +497 \ kJ/mol \quad (1)$$

$$n\text{-}C_4H_{10} + 4H_2O = 4CO + 9H_2 \ \Delta H° \ (298 \ K) = +649.9 \ kJ/mol \quad (2)$$

Partial oxidation involves the reaction of oxygen with a fuel to produce H_2 and CO when the oxygen-to-fuel ratio is less than that required for total combustion, i.e. complete conversion to CO_2 and H_2O:

$$C_3H_8 + 1.5O_2 = 3CO + 4H_2 \ \Delta H° \ (298 \ K) = -229 \ kJ/mol \quad (3)$$

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O \ \Delta H° \ (298 \ K) = -2046 \ kJ/mol \quad (4)$$
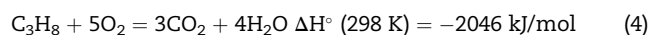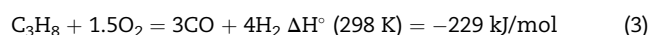
Oxidative steam reforming involves the reaction of oxygen, steam, and fuel to produce H_2 and CO_2. Equation (5) defines the idealized reaction stoichiometry for the production of H_2 from a carbonaceous fuel during OSR, where x is the oxygen-to-fuel molar ratio.

$$C_nH_mO_p + xO_2 + (2n - 2x - p)H_2O \rightarrow nCO_2 + (2n - 2x - p + 0.5m) H_2 \quad (5)$$
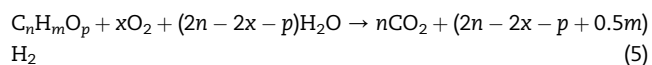
In essence, this process can be viewed as a combination of PO and SR. By adjusting the oxygen-to-carbon and the steam-to-carbon (S/C) ratios, the oxidation reactions provide the required heat for the subsequent endothermic steam reforming in the catalytic zone. However, more than 70% of the H_2 on a dry basis is produced during the steam reforming stage [2,3].

Propane OSR has been studied more extensively in the literature than butane OSR. Ni-based catalysts with a variety of supports have been evaluated [4−12]. In these studies, Ni was promoted with different loadings of other transition metals mainly to improve the stability of the catalyst. Other

studies considered noble metals (Rh, Ru, Pd) on supports such as Al_2O_3, CeO_2 and MgO without Ni [13−17]. Butane OSR has gained more interest in the last few years. Again, there are studies that have evaluated Ni-based catalysts [18−21], where different supports were compared (SiO_2, TiO_2, Al_2O_3, ZrO_2, MgO, La−Al_2O_3, $CeZrO_2$ and $CeMgO_x$). Recently, Nagaoka et al. [22] compared Rh-based catalysts for butane OSR over different supports. The study was aimed at testing the ability of Rh/CeO_2, Rh/Pr_6O_{11}, and Rh/Tb_4O_7 for OSR of n-butane at room temperature. They found that only Rh/CeO_2 catalyzed the reaction, owing to the heat generated by the spontaneous oxidation of the CeO_2 species produced by prior reduction of the supported catalyst with H_2.

Propane and butane reforming has been investigated to some extent in the literature; however less attention has been paid to LPG reforming. In addition, among the LPG reforming literature, some of these studies considered pure propane as a model for LPG, which really does not represent the actual LPG compositions worldwide [23,24]. However, a few studies did consider propane/butane mixtures. After considering only propane, Çağlayan et al. [25] in a separate study investigated OSR of a 75:25 propane:butane mixture over a bimetallic Pt−Ni/Al_2O_3 catalyst. When comparing the mixture results to those with pure propane, they found that the presence of butane increased the amount of heat produced on Pt sites and hence, more heat was transferred to Ni for SR. This resulted in higher activity and H_2 yields for the butane/propane mixture. Gökaliler et al. [26] repeated the same set of experiments for a 1:1 propane:butane mixture at three S/C ratios: 5, 6 and 7. They found that although the presence of butane improved the activity and selectivity, the catalyst was exposed to more significant deactivation by coking at the moderate S/C ratios, and sustained its stability only at the highest S/C ratio. They concluded their study by recommending further work to improve the stability of the Pt−Ni catalysts, especially for butane-enriched LPG feeds.

Laosiripojana and Assabumrungrat [27] studied OSR with a 60:40 propane:butane mixture over high surface area CeO_2. They found that at 900 °C the CeO_2 catalyst had excellent resistance toward carbon deposition, compared to the conventional Ni/Al_2O_3 catalyst. They attributed this high resistance to the redox properties of CeO_2. Laosiripojana et al. [28] used the same mixture and studied partial oxidation over a Ce−ZrO_2 catalyst doped with La, Sm, Gd and Nb. They found that doping the catalyst with La, Sm and Gd considerably improved the catalytic reactivity, whereas Nb-doping reduced its reactivity. The higher reactivity of the three elements was related to their oxygen storage capacity (OSC). Laosiripojana et al. [29] continued their work with the 60:40 propane:butane LPG mixture by comparing LPG steam reforming over Ni- and Rh-based catalysts supported on Gd−CeO_2 (CGO) and Al_2O_3. The order of activity was found to be Rh/CGO > Ni/CGO = Rh/Al_2O_3 > Ni/Al_2O_3. The authors attributed the comparable activity of Ni/CGO to the precious metal Rh/Al_2O_3 catalyst to the gas−solid reactions between hydrocarbons and lattice oxygen on the CGO surface, along with the reactions taking place on the active site of Ni, which help prevent carbon deposition.

Although, numerous catalyst systems involving precious metals have been considered for LPG or propane and butane OSR, Ni-based catalysts would be a more economically