Catalytic Combustion of Light Hydrocarbons under Fuel-Rich Conditions

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Introduction
The integration of fuel processors, the catalytic units that can convert fossil fuels to hydrogen-rich streams, with hydrogen fuel cells is considered as a promising solution to the problems related to the availability, distribution and storage of hydrogen. Recent computer-based studies have demonstrated the possibility of efficient hydrogen production on-board the vehicles through catalytic indirect partial oxidation (total oxidation followed by steam reforming) of propane, a major constituent of LPG [1]. The model catalyst was bimetallic and included Pt (specific for exothermic total oxidation) and Ni (specific for endothermic hydrogen producing steam reforming) metals over the same support in order to drive micro level energy exchange between the reactions, leading to elevated amounts of hydrogen produced. In this work, total oxidation of propane and n-butane (second major hydrocarbon in LPG) are investigated under fuel-rich conditions, i.e. at a set of fuel:oxygen ratios above the stoichiometric values, which can be found from the following reactions as 0.20 for propane and 0.15 for n-butane:

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\begin{align*}
\text{C}_3\text{H}_8 + 5\text{O}_2 &= 3\text{CO}_2 + 4\text{H}_2\text{O} \\
n\text{-C}_4\text{H}_{10} + 6.5\text{O}_2 &= 4\text{CO}_2 + 5\text{H}_2\text{O}
\end{align*}
\]

Supported monometallic Pt/Al₂O₃ and Ni/Al₂O₃ prepared by incipient-to-wetness impregnation technique and bimetallic Pt-Ni/Al₂O₃ prepared by sequential impregnation technique are the catalysts of interest. The metal contents are 0.2 per cent (by weight) Pt and 15 per cent Ni. The catalytic activities are monitored through a series of reaction tests conducted in a continuous flow fixed-bed microreactor system equipped with mass flow and temperature controllers. Pretreatment of the catalysts at 500°C for 4h under 20 ml/min hydrogen flow is followed by reaction at temperatures increasing from 150°C to 385°C at a rate of 1°C/min. Inlet composition is set as H:C:O₂:N₂ (ml/min)=1:x:139-x and total inlet flow is kept constant at 140 ml/min with x depending on the fuel:oxygen ratio. Product analysis is conducted through two gas chromatographs equipped with Porapak Q and Molecular Sieve 5A columns for hydrocarbon and fixed gas analysis, respectively. The catalyst samples are characterized by electron microscopy studies using a Philips XL30 ESEM-FEG system.

Results and Discussion
The effect of fuel:oxygen ratios on the total oxidation activities obtained over Pt, Ni and Pt-Ni catalysts are shown in Table 1. Catalytic activities are expressed in terms of light-off temperatures, which are defined as the temperatures at which 10 per cent conversion is obtained.
The results of n-butane oxidation indicate that the activities of the catalysts follow the order of Pt>Pt-Ni>Ni. Such an order is expected since Pt-based catalysts are known to be active in alkane oxidation [2], and poor activities of Ni are reported [3]. This trend is also confirmed by the fact that the light-off temperatures are lowered by ca. 50°C when Pt metal is added to Ni even at quantities as low as 0.2 per cent. Although the amount of Pt metal is same in Pt/Al₂O₃ and Pt-Ni/Al₂O₃ catalysts, the former exhibits much higher activities. This difference can be explained by the degree of Pt dispersion. Electron microscopy studies showed that the particle size of Pt metal in Pt and Pt-Ni catalysts was in the range of 0.01-0.06 µm and of 0.07-0.30 µm, respectively. The studies also demonstrated big platinum clusters settled over Pt-Ni surface and the relatively small, well-dispersed Pt particles over Pt/Al₂O₃ surface. Light-off temperatures follow a unique pattern in propane and in n-butane oxidation over Pt-Ni/Al₂O₃ catalyst. As the amount of oxygen in the feed is reduced, i.e. fuel:oxygen ratio is increased, the temperature decreased down to a certain value (266°C-propane, 259°C-n-butane) and started to increase again. Formation of minimum values are due to possible synergistic interactions between Pt and Ni sites and Pt is likely to dominate in these interactions. The latter can be explained using the oxidation mechanism over Pt, which is based on the site competition between adsorbed oxygen and adsorbed hydrocarbon. It is reported that the sticking probability of hydrocarbons to Pt surface increases with the carbon number of the alkane [2]. Thus, the quantity of oxygen required to compete with n-butane is expected to be greater than that required in the case of propane. As a result, the fuel:oxygen ratio at which the light-off temperature is minimum is lower in n-butane oxidation ([n-C₄H₁₀:O₂]min=1.02, [C₃H₈:O₂]min=1.86).

References