OXIDATIVE CO₂ REFORMING OF METHANE ON ALUMINA-SUPPORTED Co-Ni CATALYST

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Summary

CO₂ reforming of CH₄ in the presence of O₂ in the feed has been investigated in a fixed bed reactor containing a Co-Ni catalyst. Increasing O₂ partial pressures increased CH₄ consumption before leveling out at O₂:CH₄ = 1. Although CO production decreased with O₂ addition, H₂ formation initially rose to a maximum before a slow decline. The H₂:CO product ratio increased from 0.9 for pure CO₂ reforming to a plateau of 1.4 as O₂ partial pressures increased to equimolar level in the feed. The complete consumption of O₂ in the final product stream means that the oxidative CO₂ reforming of CH₄ can be used to generate ideal syngas composition for Fischer-Tropsch synthesis. In particular, the overall reaction was exothermic and the post-reaction analysis revealed minimal carbon deposition. Thus, this form of reactor operation is energetically attractive and provided efficient carbon utilization.

Keywords
Hydrogen production, reaction path analysis, sustainability, CO₂ utilization.

1. Introduction
Synthesis gas (H₂/CO) is primarily produced from catalytic steam reforming of natural gas over nickel-based catalysts. With increasing concern on the rise of anthropogenic greenhouse gas emissions, there has been renewed interest in the replacement of steam as a reactant with carbon dioxide. The main limitations of CO₂ and steam reforming, however, are high energy consumption and tendency for carbon deposition leading to catalyst deactivation. To overcome these problems, the coupling of CO₂ reforming with partial oxidation has been investigated¹⁻³, but most other researchers have focused on autothermal steam reforming. This work therefore aims to investigate the effects of the co-feeding various amounts of O₂ during the CO₂ reforming reaction in order to minimize carbon deposition and energy utilisation. Previous studies in our laboratory have shown that alumina-supported Co-Ni catalysts exhibit synergistic effects during hydrocarbon reforming and superior coking resistance compared to Ni/Al₂O₃⁴⁻⁵.

2. Experimental
5Co-15Ni/80Al₂O₃ was prepared via double impregnation of aqueous Co(NO₃)₂ and Ni(NO₃)₂ on γ-alumina, dried overnight at 393 K and calcined for 5 h at 1073 K. BET surface area was measured using Quantachrome Autosorb-1 unit for N₂ adsorption at 77 K. Temperature-programmed calcination and reduction analyses were done in a Thermocahn TherMax 200 system, in 55 ml min⁻¹ of air and 50% H₂/Ar respectively. Total carbon content was determined using a Shimadzu TOC Analyser 5000A. A Micrometrics Autochem 2910 was used to perform H₂-chemisorption. The catalysts were reduced in-situ in a stainless steel fixed bed reactor in 50 ml min⁻¹ of 50% H₂/N₂ at 5 K min⁻¹, and held at 1063 K for 2 h. Reaction runs were conducted at gas-hourly space velocity of 20,000 h⁻¹ to avoid transport intrusions.

3. Results and Discussion

Fig. 1. Derivative weight profiles during (a) calcination, and (b) reduction

Fig. 1(a) shows the derivative weight profile during temperature-programmed calcination. The main peak at about 473 K, along with the shoulder at 500 K
corresponds to the decomposition of metal nitrates to their respective oxides. The broad shoulder at 560 K indicates the formation of the metal aluminate phase (NiAl2O4 and CoAl2O4). The H2-TPR profile (cf. Fig. 1b) implicates the reduction of Co3O4 to CoO and NiO to Ni (at 435 K) and NiCo2O4 to Ni and CoO, at 600 K. The peaks at 740 K and 973 K represent the reduction of CoO to Co and the metal aluminates phase respectively. Physiochemical properties of the catalyst are summarized in Table 1.

Table 1. Physiochemical properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>BET Area (m2 g⁻¹)</td>
<td>110.8</td>
</tr>
<tr>
<td>Pore Volume (cm³ g⁻¹)</td>
<td>0.4962</td>
</tr>
<tr>
<td>Metal Dispersion (%)</td>
<td>0.58</td>
</tr>
<tr>
<td>Metal Surface Area (m² g⁻¹)</td>
<td>0.776</td>
</tr>
<tr>
<td>Active Particle Size (nm)</td>
<td>173.8</td>
</tr>
</tbody>
</table>

Fig. 2. Effect of O₂ addition on (a) consumption and (b) production rates. Reactions were conducted at 923 K and PCH₄ = PCO₂ = 0.2 atm.

Fig. 3. CH₄ conversion and H₂/CO ratio

Figs. 2 (a & b) show that CH₄ consumption rate increased with increasing O₂ partial pressure while CO₂ utilization rate decreased even more rapidly suggesting that CH₄ partial oxidation became more prominent as O₂ content in feed increased. On the other hand, CO₂ consumption rate decreased reflecting a net formation of CO₂ at higher O₂ concentration. Similarly, CO formation rate decreased with increased O₂ partial pressures. H₂ formation rate reached a maximum at PO₂ = 0.1 atm, before a gentle decline. Although H₂ production started dropping at PO₂ > 0.1 atm, H₂:CO ratio (cf. Fig. 3) increased to 1.4, suggesting that the rate of CO oxidation is more rapid than that of H₂. The product gas is also suitable as feed for olefin production via Fischer Tropsch synthesis. The calculated heats of reactions (ΔHr) for the CO₂ reforming and partial oxidation reactions at 923 K are +257.3 kJ mol⁻¹ and -26.5 kJ mol⁻¹ respectively. However, experimental ΔHr for CO₂ reforming was determined to be +240.2 kJ mol⁻¹; at PO₂ = 0.1 atm it was +14.7 kJ mol⁻¹, and at PO₂ = 0.2 atm the overall reaction is exothermic with ΔHr = -132.2 kJ mol⁻¹. The strong exothermicity at high O₂ partial pressures suggests the occurrence of multiple oxidation reactions (such as CH₄ partial oxidation, H₂ and CO oxidation). In addition, decreased coke deposition is evident with O₂ addition since the spent catalysts of stoichiometric CO₂ reforming had total carbon content of 46%, compared to < 2% when O₂ was added.

4. Conclusions

This study has demonstrated the beneficial effects of co-feeding small amounts of O₂ during CO₂ reforming of CH₄. O₂ addition resulted in improved CH₄ reaction rate and H₂:CO ratio with attendant negligible coke deposition. Moreover, the increase in overall reaction exothermicity shows that by manipulating the amounts of O₂ added, the thermal behavior of the reactions may be controlled.

References