

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/Al₂O₃^{4,5}.

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

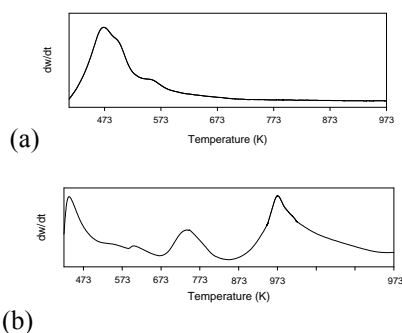


Fig. 1. Derivative weight profiles during (a) calcination, and (b) reduction

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

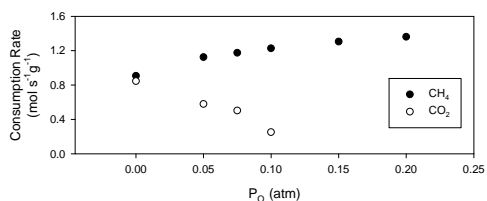
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corresponds to the decomposition of metal nitrates to their respective oxides. The broad shoulder at 560 K indicates the formation of the metal aluminate phase (NiAl_2O_4 and CoAl_2O_4). The H_2 -TPR profile (cf. Fig. 1b) implicates the reduction of Co_3O_4 to CoO and NiO to Ni (at 435 K) and NiCo_2O_4 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

BET Area ($\text{m}^2 \text{g}^{-1}$)	110.8
Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	0.4962
Metal Dispersion (%)	0.58
Metal Surface Area ($\text{m}^2 \text{g}^{-1}$)	0.776
Active Particle Size (nm)	173.8

(a)



(b)

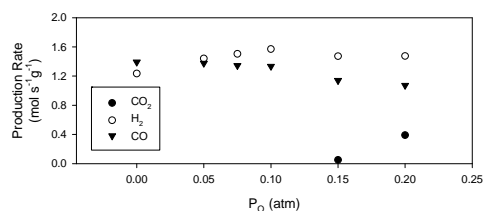


Fig. 2. Effect of O_2 addition on (a) consumption and (b) production rates. Reactions were conducted at 923 K and $P_{\text{CH}_4} = P_{\text{CO}_2} = 0.2$ atm.

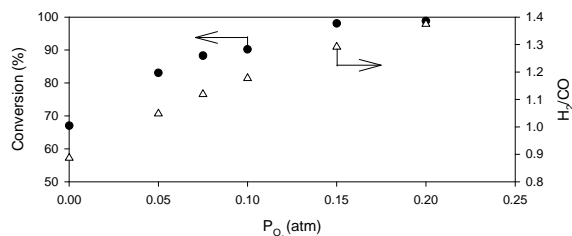


Fig. 3. CH_4 conversion and H_2/CO ratio

Figs. 2 (a & b) show that CH_4 consumption rate increased with increasing O_2 partial pressure while CO_2 utilization rate decreased even more rapidly suggesting that CH_4 partial oxidation became more prominent as O_2 content in feed increased. On the other hand, CO_2 consumption rate decreased reflecting a net formation of CO_2 at higher O_2 concentration. Similarly, CO formation rate decreased with increased O_2 partial pressures. H_2 formation rate reached a maximum at $P_{\text{O}_2} = 0.1$ atm, before a gentle decline. Although H_2 production started dropping at $P_{\text{O}_2} >$

0.1 atm, H_2/CO ratio (cf. Fig. 3) increased to 1.4, suggesting that the rate of CO oxidation is more rapid than that of H_2 . The product gas is also suitable as feed for olefin production via Fischer Tropsch synthesis. The calculated heats of reactions (ΔH_r) for the CO_2 reforming and partial oxidation reactions at 923 K are $+257.3 \text{ kJ mol}^{-1}$ and $-26.5 \text{ kJ mol}^{-1}$ respectively. However, experimental ΔH_r for CO_2 reforming was determined to be $+240.2 \text{ kJ mol}^{-1}$; at $P_{\text{O}_2} = 0.1$ atm it was $+14.7 \text{ kJ mol}^{-1}$, and at $P_{\text{O}_2} = 0.2$ atm the overall reaction is exothermic with $\Delta H_r = -132.2 \text{ kJ mol}^{-1}$. The strong exothermicity at high O_2 partial pressures suggests the occurrence of multiple oxidation reactions (such as CH_4 partial oxidation, H_2 and CO oxidation). In addition, decreased coke deposition is evident with O_2 addition since the spent catalysts of stoichiometric CO_2 reforming had total carbon content of 46%, compared to $< 2\%$ when O_2 was added.

4. Conclusions

This study has demonstrated the beneficial effects of co-feeding small amounts of O_2 during CO_2 reforming of CH_4 . O_2 addition resulted in improved CH_4 reaction rate and H_2/CO ratio with attendant negligible coke deposition. Moreover, the increase in overall reaction exothermicity shows that by manipulating the amounts of O_2 added, the thermal behavior of the reactions may be controlled.

References

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