DRY REFORMING OF METHANE TO SYNTHESIS GAS OVER K, Ce, Mn PROMOTED Ni/Al_2O_3 CATALYSTS

by

NANDINI A.

DEPARTMENT OF CHEMICAL ENGINEERING

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DEDICATED

TO

MY BELOVED FAMILY

CERTIFICATE

This is to certify that the thesis entitled, **"DRY REFORMING OF METHANE TO SYNTHESIS GAS OVER K, Ce, Mn PROMOTED Ni/Al_2O_3 CATALYSTS"** being submitted by **Mrs. Nandini A.** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by her under our guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

Pant

(Dr. K. K. Pant)

Associate Professor

Department of Chemical Engineering

Indian Institute of Technology, Delhi

New Delhi-110016

S C Dhingra

(Prof. S. C. Dhingra)

Professor

Department of Chemical Engineering

Indian Institute of Technology, Delhi

New Delhi-110016

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Nandini P.

(NANDINI A.)

ABSTRACT

Carbon dioxide reforming of methane into synthesis gas (syngas), which converts two of the cheapest carbon-containing gases (CH_4 and CO_2) into a useful chemical product, has received considerable attention during recent years. The reaction is particularly interesting when natural gas is composed of methane and CO_2. In the present investigation catalytic reforming of methane with carbon dioxide into syngas over Ni/γ-Al_2O_3 catalysts modified by potassium, MnO and CeO_2 has been studied. The catalysts were prepared by wet impregnation technique and were characterized by N_2 adsorption/desorption isotherm, BET surface area, pore volume, BJH pore size distribution measurements, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, temperature programmed studies and pulse chemisorption. The performance of these catalysts was evaluated by conducting the reforming reaction in a fixed bed reactor. The amount of carbon deposited on the catalysts during an experimental run was determined by oxidation in air conducted in a thermogravimetric analyzer. Results of the investigation suggested that stable Ni/Al_2O_3 catalysts for the carbon dioxide reforming of methane can be prepared by the addition of both potassium and CeO_2 (or MnO) as promoters. The results of the various characterization techniques were used to relate the observed catalytic activity and stability to the catalyst property. The stability and lower amounts of coking on promoted catalysts were attributed to partial coverage of the surface of nickel by patches of promoters, strong metal-support interaction and to their increased CO_2 adsorption.

For the stable 13.5Ni-2K/10CeO_2-Al_2O_3 catalyst, the effect of reaction temperature, contact time and feed ratio on conversion and product yield was studied. It was found

that the conversion and product yield increased with increasing reaction temperature and $W/F_{CH4,0}$ and reached equilibrium at $W/F_{CH4,0} = 1.7$ $kg_{cat}.h/kg_{methane}$. Conversion of CH_4 increased with the increase in feed ratio of CO_2/CH_4. An equimolar amount of H_2 and CO was produced at a CO_2/CH_4 ratio of 1.0. At a higher feed ratio, the yield of H_2 decreased because some H_2 reacted with excess CO_2 through the reverse water-gas shift reaction. The kinetic behaviour of the 13.5Ni-2K/10CeO_2-Al_2O_3 catalyst in the reforming reaction was investigated as functions of temperature and of partial pressures of CH_4 and CO_2. The apparent activation energy for CH_4 & CO_2 consumption and H_2 & CO production were 46.1±2.5, 46.2±2.4, 54.0±2.6 and 47.4±1.7 kJ/mol, respectively. It was found that an increase of the H_2 partial pressure leads to a continuous enhancement of the rate of CO formation and CO_2 consumption, due to the simultaneous occurrence of the water-gas shift reaction; whereas methane conversion remained almost constant. The rate of methane consumption is strongly affected by the partial pressure of methane. Variation of the CO_2 partial pressure has a strong influence on the rate of methane consumption at low partial pressures of 0-0.1 atm, while it is insensitive to CO_2 partial pressure at high pressures. The dependencies of the rates of H_2 & CO formation and CH_4 & CO_2 consumption on the feed partial pressure of CH_4 and CO_2 were determined using a power rate law: $r_i = kp_{CH_4}^{a} p_{CO_2}^{b}$. The results suggested strong adsorption of CO_2 on the catalyst surface, (i.e. surface of the catalyst is favourably saturated with carbon dioxide), thus decreasing CO disproportionation.

A mechanism of the CH_4/CO_2 reaction has been proposed based on the experimental results and literature review. The proposed mechanism for the CH_4-CO_2 reforming reaction assumes that (i) CH_4 decomposition and CH_xO decomposition are the slow kinetic steps; (ii) CO_2 participates in the reaction mechanism through the reverse water-gas shift to produce surface OH groups, and (iii) surface OH groups react with adsorbed CH_x intermediates to yield methyl formate intermediate, CH_xO, which decomposes to yield H_2 and CO. The kinetic model, which is based on this mechanism, predicts satisfactorily the kinetic results. The activation energy for methane adsorption and dissociation was estimated to be 107.2±3.0 kJ/mol.

The activity of 13.5Ni-2K/10CeO_2-Al_2O_3 catalyst was also tested for 60 h time on stream (TOS) for the dry reforming of methane at three different temperatures (650, 700 and 750 °C). No appreciable deactivation was observed for the catalyst at all the three temperatures for the 60 h run. Results of the deactivation study suggested that both CH_4 cracking and CO disproportionation contribute to coke deposition. The spent catalysts were characterized by BET surface area, XRD, TEM and XPS analysis to understand the morphology of the coke deposited on the catalyst. XRD patterns showed that carbon formed on 13.5Ni-2K/10CeO_2-Al_2O_3 after 60 h TOS at 700 and 750 °C dispersed well and could not be observed, while after 60 h TOS at 650 °C, mainly graphitic carbon (peak at $2\theta = 26.3°$) formed. XPS characterization demonstrated the existence of mainly two kinds of carbon species, graphitic (-C-C-) and oxidized carbons (-C-CO-, CO_3^-). The qualitative analysis of coke deposited on the catalyst suggested that some carbon species formed on the surface of the catalyst must be involved in the reaction to produce CO. A large part of the graphitic carbon deposited on the catalyst surface was of the filamentous form with nickel on top of these carbon filaments. This form of graphitic carbon is more active in the reforming reaction of methane, probably due to its close contact with nickel particles. The activation energy value for coke oxidation for the 13.5Ni-2K/10CeO_2-Al_2O_3 catalyst was estimated to be in the range of 110-160 kJ/mol.

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