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Kinetic studies of carbon nanofibre and hydrogen evolution via ethane decomposition over fresh and steam regenerated Ni/La_2O_3 catalyst

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ABSTRACT

The co-precipitated Ni/La_2O_3 catalyst had low total surface area and adsorption–desorption isotherm of nearly type II. The X-ray diffractogram demonstrates that NiO, $LaNiO_3$, and La_2O_3 were the phases present in Ni/La_2O_3 catalyst. The decomposition of ethane over Ni/La_2O_3 catalyst has been investigated using temperature-programmed reaction (TPRn). TPRn profile exhibited both low temperature and high temperature range of carbon deposition and indicated the production of H_2 and CH_4 in the gas phase from decomposition of ethane. Methane may be evolved from hydrogenation of surface methyl group from the decay of ethylidyne intermediate. The content, type of carbon, and kinetics of reaction of carbon with oxygen were determined by using temperature-programmed oxidation (TPO). Succeeding the regeneration of Ni/La_2O_3 catalyst after carbon deposition for three times with steam, this catalyst exhibited the similar TPRn spectra and had still initial activity toward ethane decomposition and carbon nanofibres production. Results of isothermal gasification of carbon nanofibres with steam at temperatures of 823–923 K showed that most of the carbon nanofibres are removed during reaction with steam.

1. Introduction

The mixture of hydrogen and carbon monoxide called synthesis gas has been a feedstock for chemicals and synthetic fuels. The different chemical processes, i.e., steam reforming ($CH_4 + H_2O \rightarrow CO + 3H_2$, $\Delta H^\circ_{298} = 206.1\ kJ\ mol^{-1}$), carbon dioxide reforming ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$, $\Delta H^\circ_{298} = 247.3\ kJ\ mol^{-1}$), and partial oxidation ($CH_4 + (1/2)O_2 \rightarrow CO + 2H_2$, $\Delta H^\circ_{298} = -35.7\ kJ\ mol^{-1}$) are utilized for hydrogen and synthesis gas production.

The CO_x free hydrogen can be a clean fuel since CO_2 and other environmental pollutants are not emitted when it is combusted or used in fuel cells. The hydrogen produced by all of these processes contains a large amount of CO, which must be converted to carbon dioxide through a water–gas shift reaction. Recently, stepwise steam reforming of hydrocarbons has been employed for the production of CO_x free hydrogen for fuel cell applications [1–5]. This method comprises of two steps, the catalytic decomposition of hydrocarbons in the first step ($C_nH_{2n+2} \rightarrow nC + (n+1)H_2$) to produce CO_x free hydrogen and surface carbon in the form of nanofibres, which allows the catalyst to be active for an extended period of time without deactivation and gasification of carbon with steam ($C + xH_2O \rightarrow CO_x + xH_2$) in the second step. The nanofibre carbon is also useful for various industrial processes. Steam gasification also produces hydrogen, improving the overall hydrogen production.

Ni-based catalysts are also active for the stepwise steam reforming of hydrocarbon. There is evidence in the literature that the use of lanthanide oxides as promoters [6–9] or supports [10,11] for steam reforming process may improve the catalyst resistance to carbon deposition. Part of the effect may be due to enhanced adsorption of water and carbon gasification. Therefore, in this work Ni/La_2O_3 catalyst was prepared by co-precipitation technique and characterized by simultaneous thermal analysis (STA), X-ray diffraction (XRD), BET N_2 adsorption method, and temperature-programmed reduction (TPR). We studied the kinetic of decomposition of ethane as an alternative approach for hydrogen and carbon nanofibres formation on fresh and steam regenerated Ni/La_2O_3 catalyst using temperature-programmed reaction (TPRn). The effect of the regeneration steps on activity and carbon formation was investigated. The carbon deposits on the fresh catalyst were characterized by transmission electron microscopy (TEM). The content, type of carbon, and kinetics of reaction of carbon with oxygen were determined by using temperature-programmed oxidation (TPO). We further examined isothermal steam gasification of the deposited carbon.

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