



Kinetic studies of carbon nanofibre and hydrogen evolution via ethane decomposition over fresh and steam regenerated Ni/La₂O₃ catalyst

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ABSTRACT

The co-precipitated Ni/La₂O₃ catalyst had low total surface area and adsorption–desorption isotherm of nearly type II. The X-ray diffractogram demonstrates that NiO, LaNiO₃, and La₂O₃ were the phases present in Ni/La₂O₃ catalyst. The decomposition of ethane over Ni/La₂O₃ 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 H₂ and CH₄ 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/La₂O₃ 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.

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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 ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$, $\Delta H^\circ_{298} = 206.1 \text{ kJ mol}^{-1}$), carbon dioxide reforming ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$, $\Delta H^\circ_{298} = 247.3 \text{ kJ mol}^{-1}$), and partial oxidation ($\text{CH}_4 + (1/2)\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$, $\Delta H^\circ_{298} = -35.7 \text{ kJ mol}^{-1}$) are utilized for hydrogen and synthesis gas production.

The CO_x free hydrogen can be a clean fuel since CO₂ 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 ($\text{C}_n\text{H}_{2n+2} \rightarrow n\text{C} + (n+1)\text{H}_2$) 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 ($\text{C} + x\text{H}_2\text{O} \rightarrow \text{CO}_x + x\text{H}_2$) 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/La₂O₃ catalyst was prepared by co-precipitation technique and characterized by simultaneous thermal analysis (STA), X-ray diffraction (XRD), BET N₂ 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/La₂O₃ 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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2. Experimental

2.1. Catalyst preparation

Ni/La₂O₃ catalyst was prepared by co-precipitation technique. To 500 cm³ solution consisting of lanthanum and nickel nitrates (Merck) with a total concentration of 0.5 M at approximately 343 K was added 720 cm³ of 0.5 M sodium carbonate solution dropwise under stirring during 3 h. The stirring was continued another 20 min and the slurry was left for approximately 40 min. Then the co-precipitate was filtered, washed with hot deionized water at around 343 K, and dried at 393 K for about 20 h. The dry precipitate was calcined from room temperature up to 1073 K at a rate of 10 K min⁻¹ in static air and held at around 1073 K for 5 h to yield oxides. Nickel and sodium contents were determined by atomic absorption to be 18.5 and 0.12% respectively. The powder was pressed at 10 t pressure and the pellets were crushed and sieved to particle size of 300–350 μm.

La₂O₃ was prepared by precipitation method from solution of lanthanum nitrate with sodium carbonate and then calcination at 1073 K for 5 h. The powder was pressed and the pellets were crushed and sieved to particle size of 300–350 μm. La₂O₃ which was also provided by Aldrich was pressed and the pellets were crushed and sieved.

2.2. Catalyst characterization

Thermogravimetric studies of precipitate precursor of Ni/La₂O₃ were performed using a SDT 2960 Simultaneous DTA–TGA produced by TA Instruments. The temperature of the sample was increased linearly at a ramping rate of 10 K min⁻¹ up to 1173 K in air, monitoring the mass, temperature, and the difference in temperature between the sample and a thermally inert reference.

The X-ray diffraction (XRD) pattern was recorded on Scintag XDS 2000/USA. The radiation source was CuK_α in the 2θ range of 0.0–70°. The detector was a semiconductor detector of the type Ge (Li) crystal. The powdered sample was in a stationary state while the detector rotating through the angle θ, for scanning the diffraction angle. The diffractometer was controlled by a computer installed with DMS2000 Software.

BET surface area of calcined catalyst was performed using the ASAP 2010 Analyzers. The ASAP Analyzers utilize the principle of physical adsorption to obtain information about the surface area and porosity of a solid material. The catalyst contained in an evacuated sample tube was heated to 623 K and held at that temperature over night to remove any adsorbed gas. After cooling to cryogenic temperature, the catalyst was exposed to pure N₂ gas at a series of precisely controlled pressures. The pressure at which adsorption equilibrium occurs was measured and the universal gas law was applied to determine the quantity of gas adsorbed.

The transmission electron microscopy (TEM) and energy dispersive analysis of X-ray (EDAX) from small areas/particles in the specimen were carried out using Philips EM 400 and CM 200. The specimen for transmission electron microscopy and energy dispersive analysis of X-ray examinations was prepared by ultrasonic dispersion of the fine powder of coked catalyst in acetone. Then a drop of the resulting suspension was applied on a holey carbon film supported by a copper grid. The acetone was evaporated to dryness. A specimen was loaded into a specimen rod and was inserted into the microscope via the airlock.

2.3. Temperature-programmed techniques

A multipurpose microreactor system was used to carry out in situ all temperature-programmed techniques [12]. The system

includes a gas handling panel, a tubular reactor, and a quadrupole mass spectrometer (Hiden Analytical, Warrington, England). The mass spectrometer is controlled by an IBM PC, which allows it to monitor up to 16 masses in the range of 1–200 atomic mass units continuously with both temperature and time. The reactor was made from stainless steel tubing with an outer diameter of 1/4 in. (6 mm) and approximately 24 cm in length. 0.200 g of a catalyst was loaded into the reactor and stainless steel wool was used to hold the catalyst in the correct position of the reactor. The reactor was positioned vertically in an electric cylindrical furnace controlled by a temperature controller. A thermocouple, chrome-alumel type, was put in the centre of the catalyst in order to measure an accurate temperature of the catalyst. The temperature of the catalyst was controlled from room temperature up to 1073 K in a temperature-programmed mode by a Newtronics Controller (Micro 96). A bubbler was used to produce a mixture of steam in helium by passing helium, 25 cm³ min⁻¹ and 1 bar, through deionized liquid water at 297 K.

2.3.1. Temperature-programmed heating (TPH)

The study of the catalyst requires a clean surface. Therefore, degassing of the Ni/La₂O₃ catalyst was performed by flowing pure helium, 25 cm³ min⁻¹ and 1 bar pressure, over 0.200 g of the catalyst, which was loaded in the microreactor tube while increasing its temperature. The temperature was programmed to increase at 5 K min⁻¹ to 923 K and allowed to dwell at that temperature for 2 h for complete removal of any adsorbed materials.

2.3.2. Temperature-programmed reduction (TPR)

After degassing the fresh catalyst in a helium stream or after oxidation of regenerated catalyst, the catalyst was cooled to ambient temperature under helium stream. The TPR experiment was carried out by heating the catalyst from 313 to 923 K linearly at a rate of 5 K min⁻¹ under the flow of 5% hydrogen in helium with flow rate of around 25 cm³ min⁻¹ and pressure of 1 bar. The catalyst was kept in contact with hydrogen gas at 923 K for 2 h for complete reduction. The hydrogen consumption and the water production were recorded by mass spectrometer. Next, a flow of helium at a flow rate of about 25 cm³ min⁻¹ and pressure of 1 bar was used for 30 min to flush out all residual hydrogen gas including any physically or chemically adsorbed hydrogen. The catalyst was cooled to ambient temperature under the flowing helium.

2.3.3. Temperature-programmed reaction (TPRn)

Subsequent pre-treatment and reduction of fresh or reduction of regenerated Ni/La₂O₃ catalyst, 5% ethane in helium with a flow rate of about 26 cm³ min⁻¹ and pressure of 1 bar was switched into the reactor. The temperature was increased at a nearly linear rate of 5 K min⁻¹ from 313 K up to 823 K while monitoring the reactant and products gases during the decomposition reaction by a mass spectrometer.

2.3.4. Isothermal gasification of carbon with steam

Following carbon deposition by exposure of fresh or regenerated Ni/La₂O₃ catalyst to ethane gas, the carrier gas was changed to helium with a flow rate of about 25 cm³ min⁻¹ and pressure of 1 bar at 823 K. The catalyst was kept in contact with helium gas for around 30 min and the temperature of the reactor was put at the temperature (823–923 K), which the gasification of carbon was performed. After 15 min the helium gas, 25 cm³ min⁻¹ and 1 bar, was passed through a bubbler, which contained deionized liquid water at 297 K for about 150 min while observing the effluent gas composition during the isothermal gasification of carbon with steam by mass spectrometer.

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