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Reforming reactions of acetic acid on nickel catalysts over a wide temperature range

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Abstract

Catalytic steam reforming of bio-oil, a liquid derived from pyrolysis of biomass, may be a viable process of renewable hydrogen production. Acetic acid is one of the major constituents of bio-oil, and for this reason, it is used as a model compound to study its reaction network under steam reforming conditions over Al_2O_3 and La_2O_3, and Ni catalyst supported on La_2O_3/Al_2O_3 carrier, employing transient and steady-state techniques. It is found that acetic acid interacts strongly with the Al_2O_3 carrier and less strongly with La_2O_3. Decomposition reactions as well as the ketonization reaction take place, especially at intermediate temperatures. In the presence of Ni, catalytic activity is shifted toward lower temperatures. Nickel promotes steam reforming reactions and retards the rate of carbon deposition onto the catalyst surface. It is also found that carbon formation is affected by reaction temperature, the HAc/H_2O ratio and catalyst composition. Carbon deposition is favoured at low reaction temperatures and at high HAc/H_2O ratio.

Keywords: Steam reforming; Hydrogen production; Bio-oil; Acetic acid; Nickel catalysts; Temperature programmed reaction; Temperature programmed desorption

1. Introduction

Hydrogen, in combination with fuel cells, is being considered as an environmentally friendly source of energy for automotive as well as stationary applications. Hydrogen has the significant advantage of producing no air or other pollutants in its transformation to energy, while fuel cells, which operate primarily on hydrogen, offer enhanced efficiency in power generation. At present, hydrogen is produced almost entirely from fossil fuels such as natural gas, naphtha and coal, following processes which are well established. In such cases, however, the amount of carbon dioxide which is released into the atmosphere during hydrogen production is only marginally smaller than that formed by direct combustion of the same fuels, on the basis of equal power generation. On the other hand, use of hydrogen produced by renewable sources, such as biomass, can reduce substantially the amount of CO_2 released. Thus, the use of biomass as an alternative energy source, with essentially zero CO_2 impact, could play a major role in reducing global CO_2 emissions [1–5].

For the past few decades, renewable biomass has been considered as potential feedstock for gasification processes to produce syngas (a mixture of hydrogen and carbon monoxide). However, the economics of current syngas production processes favour the use of hydrocarbons and inexpensive coal. Recently, the use of bio-ethanol as an intermediate in the hydrogen from biomass production process has been proposed [6–8]. Similarly, the direct, liquid phase conversion of sugars to hydrogen has also been proposed [4]. All of these processes have advantages and disadvantages. The optimal process may depend on the particular application, geographic location of its implementation, state of the art of enabling technologies and state of technological development of the process.

An alternative approach to the production of hydrogen from biomass may be a process involving fast pyrolysis of biomass to generate a liquid product, bio-oil, and reforming of bio-oil so as to produce a gaseous stream rich in hydrogen [5,9–15]. Moreover, an integrated process, in which biomass is partially used to produce more valuable materials or chemicals, while the residual fractions are utilized for the generation of

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hydrogen, may be economically viable in today's energy market [5].

Although the molecular composition of pyrolysis oil varies significantly with the type of biomass and pyrolysis conditions used (pyrolysis severity and media), its major components are oxygenates belonging to the following groups: acids, aldehydes, alcohols, ketones and substituted furans derived from cellulose and hemi-cellulose and phenolic and cyclic oxygenates derived from lignin [9,16–18]. These molecules are not thermally stable at typical reforming temperatures, while some of them may not even be stable at much lower temperatures [16,18]. Thus, there is a significant competition between catalytic reforming reactions and thermal decomposition for most oxygenates [9].

To address issues of activity, selectivity and lifetime of a catalyst, a better understanding of the reaction network of both the thermally induced cracking/decomposition and the catalytic steam reforming reactions of oxygenates, as a function of reaction temperature, is required. Thus, purpose of the present investigation is to study the reaction patterns of thermal cracking and reforming of major constituents of bio-oil, with respect to reaction temperature and catalytic material. Acetic acid (HAc) is one of the major components of bio-oil [16,17,19], and for this reason was selected as representative model compound for this purpose.

2. Experimental

2.1. Catalyst preparation

The carriers used in the preparation of catalysts were commercial oxides such as γ-Al_2O_3 (Engelhard) and La_2O_3 (Alfa Products). The La_2O_3/Al_2O_3 support was synthesized by impregnating γ-Al_2O_3 (Engelhard) with $La(NO_3)_3$ (Alfa products). A known amount of $La(NO_3)_3$ was dissolved in water and the oxide was added to the solution under continuous stirring. The slurry was heated slowly to 90 °C and maintained at that temperature until nearly all the water evaporated. The solid residue was dried at 110 °C for 24 h and then calcined in air at 900 °C for 16 h. The La_2O_3 content of the carrier was 14 mass%.

The supported Ni catalyst, Ni/(La_2O_3/γ-Al_2O_3), was prepared by the wet impregnation method using $Ni(NO_3)_2$ (Alfa Products) as the metal precursor. The solid residue was dried at 110 °C for 24 h. The dried residue was then ground and sieved and was heated to 500 °C for 2 h for complete decomposition of nickel nitrate [7]. After this treatment, the catalyst samples were reduced at 500 °C in H_2 flow for 5 h. The nominal metal loading was 17 wt%.

2.2. Catalyst characterization

Specific surface areas of supports and catalysts were measured with the BET technique using a Micromeritics Gemini III 2375 surface analyzer, employing nitrogen physisorption at liquid nitrogen temperature. Prior to each measurement, the sample was dried at 120 °C under helium flow passing through the sample cell.

Metal dispersion of fresh catalyst was also determined by hydrogen chemisorption employing a modified Fisons Instruments (Sorptomatic 1900) apparatus. Prior to each measurement, the catalyst sample (ca. 1.0 g) was pretreated by: (a) dynamic vacuum at 250 °C for 1 h; (b) reduction with 1 bar of H_2 at 250 °C for 1 h; (c) evacuation for 30 min at 250 °C; (d) cooling to the chemisorption temperature. Hydrogen uptake at monolayer coverage of the Ni particles was obtained by extrapolation of the linear portion of the adsorption isotherm to zero pressure. The exposed surface area was calculated assuming a H:Ni stoichiometry of 1:1.

X-ray diffraction (XRD) patterns of supports and catalysts were obtained on a Philips P (PW1830/40) powder diffractometer, with a Cu Kα radiation (0.15406 nm). Scans were collected in the range of 2θ between 20° and 80° with a scanning rate of $0.05^\circ\ s^{-1}$.

2.3. Apparatus and experimental procedures

2.3.1. Transient experiments

Transient experiments were carried out in an apparatus consisting of a flow switching system, a heated reactor and an analysis system. The flow apparatus has been described in detail elsewhere [20]. The reactor consists of two 6.0 mm o.d. sections of quartz tube, which serve as inlet and outlet to and from a quartz cell of 8.0 mm o.d.. The total length of the reactor is 32.0 cm. The catalyst sample, approximately 100 mg, was placed in the cell and kept in place by means of quartz wool. The temperature of the catalyst was measured at the inlet of the catalyst bed by means of a K-type thermocouple placed within a quartz capillary well. An electric furnace controlled by a programmable controller provided heating to the reactor. Analysis of the gases was done by on-line mass spectrometer (VG Quadrupoles, Sensorlab 200D) equipped with a fast response inlet capillary/leak diaphragm system. The pressure in the main chamber was UHV level ($\approx 10^{-7}$ mbar). The desired gas mixtures were prepared in a separate apparatus by continuous blending of two streams. Calibration of the mass spectrometer signal was performed based on mixtures of known composition. For all experiments, gas phase composition was calculated from the mass spectrometer signal at *m/e* ratios of 44, 60, 58, 28, 16, 26, 27, 41 and 2 for CO_2, CH_3COOH, $(CH_3)_2CO$, CO, CH_4, C_2H_4, C_2H_6, C_3H_6 and H_2, respectively. The fragmentation of the different species was calibrated and contributions from other than the indicated ones were subtracted as well as the background level.

The experimental procedure was the following: the catalyst sample was reduced in situ under H_2 flow ($40\ cm^3\ min^{-1}$) at 750 °C for approximately 2 h. After purging with He for 15 min, the sample was cooled under He flow to room temperature. At this point ca. $30\ cm^3\ min^{-1}$ of a mixture consisting of 0.5% CH_3COOH/1.5% H_2O/He was directed into the reactor chamber. These conditions were achieved by controlling the flow of three independent He lines, two of which passed through saturators with acetic acid and water. The catalyst was kept at room temperature for the first 5 min. After this period, the reactor temperature was increased rapidly (at