Temperature-programmed reduction of nickel steam reforming catalyst with glucose

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ABSTRACT

Temperature-programmed reduction (TPR) of a NiO/α-Al$_2$O$_3$ steam reforming catalyst with glucose under a N$_2$ flow was investigated using TGA-FTIR technique. A series of catalyst samples obtained at different temperatures during the TPR were characterised by XRD, CHN elemental analysis, SEM-EDX and TPO. Results showed that the whole TPR covering from room temperature to 900 °C consisted of two reactive processes. They were glucose pyrolysis producing carbonaceous materials (char), and NiO reduction by the char resulting in CO$_2$ as a main product. When the initial mass ratio of glucose to the catalyst was 1:10, the catalyst could be completely reduced without carbon remaining. Moreover, two mass loss peaks were observed at around 440 °C and 670 °C, respectively, during the reduction. Based on the experiments of char characterisation, H$_2$ TPR and excess glucose TPR, a two-stage reduction mechanism was proposed. The first reduction stage was attributed to a solid reaction between NiO and char. The second stage was assigned to NiO being reduced by the CO produced by char gasification with CO$_2$. Their apparent activation energies were 197 ± 19 kJ/mol and 316 ± 17 kJ/mol, respectively, estimated using the Kissinger method.

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1. Introduction

Chemical looping reforming (CLR) is a novel reforming technology for syngas production from hydrocarbons with low heat demand [1–5]. A typical CLR process is performed by circulating oxygen carrier (normally supported metal oxide) between two reactors. In a fuel reactor, the oxygen carrier is first reduced by fuel, and then catalyses steam reforming of fuel [6]. In an air reactor, the reduced oxygen carrier is re-oxidized and then sent back to the fuel reactor for a new cycle. The heat required for the steam reforming is supplied by the internal combustion. A key issue for CLR technology is the selection of suitable oxygen carriers. Supported NiO has been suggested as a promising oxygen carrier due to its high reduction reactivity and adequate catalytic activity on steam reforming [6–8].

In fact, alumina supported NiO (NiO/α-Al$_2$O$_3$) is a common catalyst for industrial steam reforming process [9]. It has also been selected as a model steam reforming catalyst in some research [10,11]. Similar to other transition metal catalysts, the NiO catalyst requires reduction to give active phase (i.e. metallic Ni) prior

to their use [12]. In industry, the catalyst reduction is usually conducted with either hydrogen-containing gases or natural gas-steam mixtures. Reduction conditions are important as they have influences on subsequent catalytic activity [10]. For instance, high temperatures and rapid reduction may result in lower Ni dispersions and less activity, the introduction of carbon or sulphur may accelerate catalyst deactivation [13,14]. Therefore, reduction mechanisms and possible affecting factors have been extensively investigated using hydrogen or light hydrocarbons as reducing agents [15–22].

Richardson et al. [10,11,16] carried out a series of studies on H$_2$ reduction of NiO/α-Al$_2$O$_3$ catalysts. A reduction mechanism was proposed as follows. (1) Hydrogen is dissociated, first on NiO and then rapidly on the surface of Ni clusters as they become available. (2) Hydrogen atoms rupture Ni—O bonds, producing Ni^0 atoms and H$_2$O molecules. This process is retarded or accelerated by foreign cations in NiO lattice or on vicinal surface. (3) Nickel atoms diffuse across the support surface away from reduction centres. Water retained on the surface retards nucleation by limiting the diffusion. (4) Nickel atoms nucleate into metallic clusters, after an induction period if the overall reduction rate is low (e.g. at low temperatures). (5) Nickel clusters grow into crystallites. In addition to chemical reaction, nucleation and mass transfer, the fate and activity of radicals formed by the dissociation of reductant molecules

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also play a role in determining reduction kinetics, as suggested by Syed-Hassan et al. [18,23].

The conventional fuel for syngas generation by steam reforming or CLR is natural gas. There is a growing interest in exploiting biomass as substitute of fossil fuel to produce fuels and chemicals. Some bio-liquids such as bio-diesel and bio-ethanol could be utilized as transport fuels after a simple pre-treatment. In contrast, bio-oil must be upgraded by complex chemical processes (e.g. hydrodeoxygenation, zeolite upgrading [24]) if it is to be used in vehicles, which increases energetic and economic costs. This is determined by the properties of bio-oil that include high oxygen content, complex composition, low heating value, high viscosity, incomplete volatility, and chemical instability. Alternatively, bio-oil can be converted into syngas by steam reforming [25,26]. The conversion of bio-liquids to syngas is a promising route to utilize biomass resources as syngas has a wide application (the production of ammonia, methanol, alkanes and hydrogen), although the storage of syngas is not as easy as that for liquid fuels. Syngas production by bio-oil steam reforming followed by water gas shift has been considered as a promising way for sustainable H_2 production, which is of importance to accomplish 'hydrogen economy' in future.

Some bio-liquids (e.g. sunflower oil [2], waste cooking oil [27,28], scrap tyre oil [29], and bio-oil [30]) have been tested in a CLR process. Feasibility of bio-oil CLR was proved but bottlenecks still existed. For scrap tyre pyrolysis oil in which a considerable amount of sulphur was present [29], the H_2 yield decreased as the cycle number increased. Analysis of the reacted catalyst indicated this was most likely due to catalyst deactivation by carbon deposition and sulphur poisoning. Catalyst deactivation upon cycling was also observed during the CLR of biomass pyrolysis oil as indicated by the drop in fuel conversion [30]. The reduction rate of catalyst also decreased with cycling. Solutions to these problems include preparing catalysts more tolerant to carbon deposition, pre-treating feedstock to remove sulphur, and investigating the mechanism of catalyst reduction with bio-feedstock.

As a typical bio-feedstock for CLR, bio-oil is obtained by fast pyrolysis of biomass and comprised of numerous hydrocarbons. Most of bio-oil components have a tendency to decompose at operating temperatures (600–900 °C). Both types of pyrolysis products (volatiles and char) are potential reductant for oxygen carriers. Therefore, multiple reaction channels exist simultaneously during CLR, making research on reduction mechanism difficult.

Rather than evaluating the global reduction process during CLR, the objective of this study is to reveal the reactivity between a NiO catalyst and char from glucose pyrolysis, which is part of the complex reaction network. Glucose was selected as a model compound of biomass as it is the basic building block of cellulose and one of bio-oil components [25,26]. A slow temperature-programmed rise and a continuous flow of inert gas were employed in this study. Such a condition decoupled glucose pyrolysis and catalyst reduction, enabling the reduction to be studied separately. Reduction characteristics and mechanism were discussed. The work presented here is part of a series on the reduction of a NiO catalyst with various bio-compounds and has been covered in the thesis of the first author [8]. Such a study has an implication both for exploiting biomass resources via chemical looping technology and for gaining an insight into solid reduction mechanism.

2. Experimental

2.1. Sample preparation

The catalyst used in this study was 18 wt% NiO/α-Al$_2$O$_3$ provided by Johnson Matthey Plc. It was received as pellets and was broken into particles with a size of 0.85–2 mm prior to use. As Fig. 1 displays, the fresh catalyst particles showed uniform grey green. After being reduced by H_2, they turned to uniform black. Presumably, NiO was distributed throughout the pellet rather than like an eggshell. Glucose ($C_6H_{12}O_6$) was purchased from Fisher Scientific. The catalyst particles (2.0 g) were impregnated with a glucose aqueous solution (20 mL, 10 g/L) overnight at room temperature without stirring. Then the particles were dried at 80 °C in an oven for about 12 h and hereafter denoted as 'catalyst-G'. For control experiments, blank α-Al$_2$O$_3$ pellets (provided by TST Ltd.) were treated using the same procedure as the catalyst. The α-Al$_2$O$_3$ particles impregnated with glucose were referred to as 'Al$_2$O$_3$-G'. The NiO/α-Al$_2$O$_3$ particles without impregnation were referred to as 'fresh catalyst'.

2.2. Temperature-programmed reduction (TPR)

(1) For process analysis, the TPR of catalyst-G was performed on a TGA-FTIR instrument. A thermal gravity analyser (TGA, Stanton Redcroft TGH1000) and a Fourier transform infrared spectroscope (FTIR, Thermo Scientific Nicolet iS10) were integrated via a Nicolet transfer line. 200 mg of samples were placed in a platinum crucible and heated from ambient temperature to 900 °C at 5 °C/min under a N_2 flow of 50 mL/min. The Nicolet's OMNIC software was used to analyse FTIR spectra and create chemigrams (species evolution profile against temperature). Wavenumber ranges set for creating the chemigram of a specific compound were listed in SD1 (Supplementary Document 1). (2) For kinetics analysis, a series of TPR experiments were carried out by the TGA instrument alone. The heating rate was maintained at 5 °C/min for the process of glucose pyrolysis but changed to different values (3, 7, 10, 15 °C/min) when it came to the process of NiO reduction. (3) The H_2 TPR experiment was also performed on the TGA instrument. 20 mg of fresh catalyst were heated from ambient to 150 °C at 20 °C/min under a N_2 flow and then was kept at this temperature for 3 h to remove adsorbed moisture and air. After that, the sample was heated to 900 °C at 5 °C/min under a H_2 flow (5% H_2 in N_2, 50 mL/min) followed by naturally cooling down under a N_2 flow. (4) The excess glucose TPR experiment was conducted in the same procedure as that for catalyst-G, except that the initial mass ratio of glucose to the catalyst was 1:1.4 in contrast to the 1:10 for catalyst-G.

2.3. Sample characterisation

A series of samples were obtained at different temperatures during the TPR of catalyst-G. They were denoted as 'catalyst-G-T', where 'T' stands for the end temperature (420, 530, 670, 770 or 900 °C). They were crushed to fine powder for XRD tests, CHN elemental analysis and TPO tests but were kept as particles in SEM-EDX tests.

2.3.1. XRD and Rietveld refinement

X-ray diffraction (XRD) tests of these samples were conducted using a PANalytical X'pert MPD instrument with Cu Kα radiation. The scanning of X-ray ranged from 20° to 80° (2θ) with an increment of 0.0332°/step and a speed of 0.7 s/step. To determine crystallite sizes of Ni and NiO, Rietveld refinement of the XRD data [31] was performed using X'Pert HighScore Plus software.

2.3.2. CHN elemental analysis

The carbon and hydrogen content of these samples was determined by a CHN elemental analyser (Flash EA2000 by CE Instruments Ltd.). Around 15 mg of powder samples was put into a tin capsule. Then the tin capsule was folded properly to remove any trapped air before it was fed to the analyser. Duplicate determina-