Nickel catalyst auto-reduction during steam reforming of bio-oil model compound acetic acid

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ABSTRACT

Transition metal catalysts widely used in refineries are provided as oxides and require pre-reduction to become activated. The auto-reduction of a NiO/Al_2O_3 catalyst with acetic acid (HAc) followed by HAc steam reforming was investigated in a packed bed reactor. Effects of temperature and molar steam to carbon ratio (S/C) on reduction kinetics and catalyst performance were analysed. Results showed that a steady steam reforming regime along with complete NiO reduction could be obtained after a coexistence stage of reduction and reforming. A 2D nucleation and nuclei growth model fitted the NiO auto-reduction. The maximum reduction rate constant was attained at S/C = 2. Steam reforming activity of the auto-reduced catalyst was just below that of the H_2-reduced catalyst, probably attributed to denser carbon filament formation and larger loss of active Ni. Despite this, a H_2 yield of 76.4% of the equilibrium value and HAc conversion of 88.97% were achieved at 750 °C and S/C = 3.

1. Introduction

Hydrogen production has attracted global attention because of hydrogen's growing application in proton exchange membrane fuel cells. At present, hydrogen generation processes including catalytic steam reforming of natural gas or naphtha, partial oxidation of heavy oil and steam gasification of coal have been well established. However, the reduction of fossil fuel stocks and the release of greenhouse gases caused by these processes have spurred research into sustainable and environmentally friendly hydrogen production routes. One promising route is to produce hydrogen from terrestrial biomass via fast pyrolysis followed by catalytic steam reforming of bio-oil or its fractions [1,2]. Depending on biomass feedstock and pyrolysis conditions employed, the composition of bio-oil is varied but mainly consists of

oxygenated hydrocarbons, such as acids, ketones, alcohols, phenols and sugars [2,3]. In order to get a better understanding of the chemical process during steam reforming of the whole bio-oil, a number of studies have focused on steam reforming of bio-oil model compounds [4–8], especially acetic acid (HAc) [9–14] due to its high content in bio-oil.

The steam reforming reaction is normally catalysed by supported transition metal catalysts (such as Co or Ni) or noble metal catalysts (Pt, Rh). For HAc steam reforming, a Ni based catalyst was found to have better stability and activity than other transition metal catalysts [11] and exhibited catalytic activity similar to that of noble metal catalysts [12]. To prevent potentially hazardous exothermic oxidation during transport or storage, transition metal catalysts are provided by manufacturers in the form of oxides instead of their active metallic state. Hence, they require to be reduced just prior to

being used in steam reforming. In industry, this is achieved by subjecting the catalyst to a gaseous flow of H_2, NH_3, or CH_4, depending on their local availability [15]. In the latter case, a careful protocol of starting conditions with large excess of steam is recommended to avoid carbon deposits from CH_4 decomposition, which cause loss of active surface area [16]. Such a catalyst activation step does not only represent a starting regime which potentially relies on fossil feedstock (since both H_2 and NH_3 are at present produced at commercial scale mainly from natural gas) but also increase operational complexity, with its associated safety hazards. The present work intends to integrate catalyst reduction and steam reforming in one process (termed 'integrated process'). In this process, the oxidised catalyst is initially automatically reduced by reforming fuel in a period termed 'auto-reduction', and then sustains the steam reforming reaction. In particular, whether HAc, as a bio-oil model compound, has the ability to perform the reduction step will be investigated. To the authors' knowledge, little research has been done on the reduction of metal oxides by oxygenated hydrocarbons, although reduction with simple molecules such as H_2 [17–19], CH_4 [20–22] and CO [23] have been studied in the fields of metallurgy, catalysis and chemical looping technology.

Chemical looping reforming (CLR) is an advanced autothermal reforming technology for hydrogen production, which couples endothermic steam reforming and exothermic partial oxidation of reforming fuel by alternating fuel feed and oxidant feed (usually air) [16,22,24]. A well-designed CLR process could produce a non N_2-diluted syngas with low heating demand. During CLR, a supported metal oxide is used to perform two functions: (1) oxygen transfer via redox cycling and (2) catalysing steam reforming in its reduced state. Whether the reforming fuel employed is able to cyclically reduce the metal oxide at the beginning of fuel feed to initiate catalytic steam reforming is critical. Previous studies in this area mainly focused on screening suitable metal oxides based on their reduction reactivity with CH_4 [22,25]. The reducing properties and mechanism of oxygenated hydrocarbons on

metal oxide are less investigated, but quite significant for the potential application of renewable bio-feedstock in the CLR process.

In this paper, the feasibility of a NiO/Al_2O_3 catalyst auto-reduction by reforming feedstock HAc in an integrated process is examined using a packed bed reactor. The influence of reaction temperature and molar steam to carbon ratio (S/C) on the reduction kinetics as well as the subsequent steam reforming performance of HAc is also investigated. Moreover, the difference between the integrated process and conventional steam reforming process initiated by H_2 reduction is shown and interpreted with focus on reforming activity, active Ni loss, carbon element distribution, and morphology of carbon deposits.

2. Experimental

2.1. Materials and reactor set-up

The catalyst used in this study was 18 wt% NiO on α-Al_2O_3 (NiO/Al_2O_3) provided by Johnson Matthey Plc. The catalyst was received in pellet form and was broken and sieved to particle size range of 1.0–1.4 mm prior to use. Pure α-Al_2O_3 pellets were also provided by Johnson Matthey Plc and crushed into the same particle size so as to perform a control experiment. HAc with a purity of $\geq$99% was purchased from Sigma–Aldrich.

Steam reforming experiments were conducted in a downflow packed bed reactor as shown in Fig. 1. For each run of experiment, 2 g fresh catalyst was placed in the middle of a quartz reactor, which was held inside a tube furnace. HAc aqueous solution with a given S/C ratio was injected into the reactor at a certain flow rate by a programmable syringe pump (New Era Pump Systems). The flow rate of gases (N_2 or H_2) was controlled by MKS mass flow rate controllers. The effluent was cooled via two condensers at $-7\ ^\circ$C. Condensable products and unreacted water were trapped in a condensate collector, with moisture later removed by silica gel. After that, the
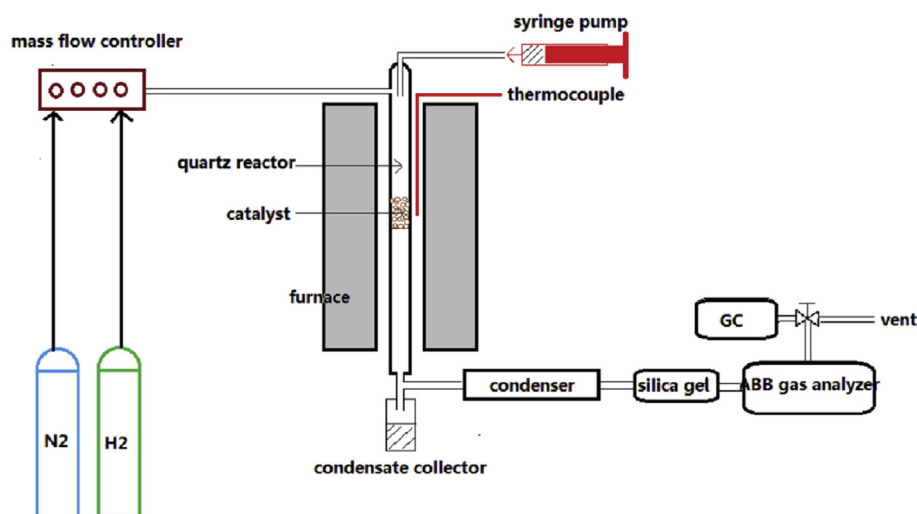

Fig. 1 – Schematic diagram of experimental set-up.