



# The preferential oxidation of CO in hydrogen rich streams over platinum doped nickel oxide catalysts

Ziyaad Mohamed, Venkata D.B.C. Dasireddy, Sooboo Singh, Holger B. Friedrich\*

School of Chemistry and Physics, University of KwaZulu-Natal, Durban 4000, South Africa

## ARTICLE INFO

### Article history:

Received 18 March 2015  
Received in revised form 8 June 2015  
Accepted 8 July 2015  
Available online 17 July 2015

### Keywords:

Nickel oxide/alumina  
Platinum/alumina  
Preferential oxidation  
Carbon monoxide and hydrogen

## ABSTRACT

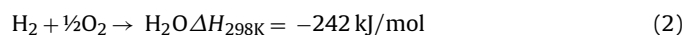
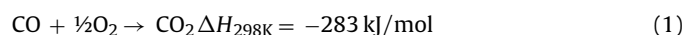
NiO/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/NiO/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the incipient wetness technique with a Ni loading of 25 wt% and Pt loading of 0.5 wt%. These catalysts were characterized by ICP-OES, XRD, BET, TPR, N<sub>2</sub> adsorption–desorption isotherms, CO chemisorption, FTIR-CO, XPS, SEM-EDX and TEM. XRD and XPS results of the catalysts showed the presence of NiO and PtO phases on the respective supports and *in situ* redox reactions showed that the catalysts underwent reversible phase changes (oxide and metallic) that were stable. FTIR-CO studies showed that the Pt containing samples exhibited both linear and bridged CO adsorption with higher intensities observed for the Pt/NiO/Al<sub>2</sub>O<sub>3</sub> catalyst. The catalysts were tested for the oxidation of CO in H<sub>2</sub> rich streams (preferential oxidation–PROX) in a continuous flow fixed bed stainless steel reactor. The NiO/Al<sub>2</sub>O<sub>3</sub> catalyst produced very low conversions of CO in the stipulated PROX temperature range and showed highest conversion of 11% with a selectivity of 25% toward CO<sub>2</sub>. The Pt/Al<sub>2</sub>O<sub>3</sub> catalyst showed improved activity within the PROX temperature range with highest CO conversion of 56% and selectivity toward CO<sub>2</sub> of 68% at 200 °C. The Pt/NiO/Al<sub>2</sub>O<sub>3</sub> catalyst revealed synergistic effects, obtaining much higher CO conversions within the PROX temperature ranges compared to both the mono-metallic catalysts. The highest CO conversion, of 99.9%, for this catalyst was at 200 °C, with a selectivity of 72.8% toward CO<sub>2</sub> using a C:O<sub>2</sub> ratio of 1:2.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrogen produced from fossil fuels has become a promising alternative to conventional fuel sources due to its low environmental impact, offering maximum power density as a fuel for proton exchange membrane fuel cell (PEMFC) applications [1–4]. One of the main concerns using hydrogen is safe storage for on-board applications, therefore on-board production following a series of catalytic reforming reactions, such as: steam reforming, autothermal reforming, partial oxidation and water-gas shift is more economically viable [5–7]. This reformat gas is supplied to the fuel cell stack for power generation [6]. However, following the water-gas shift reaction, trace amounts of CO (~1%) are still present in the feed stream [3,8–10]. This CO poisons a vital component of the PEMFC, which is the platinum electrode, leading to a loss in the fuel cell efficiency and hence its power output [6,9]. Preferential oxidation carried out after the conventional water-gas shift reaction provides a promising route for removing trace amounts of CO contaminants that may be present in the H<sub>2</sub> rich streams.

This method is effective, offering ease of implementation, cost efficiency, reliability and safety for on-board fuel processing [10,11]. The reactions that take place in the preferential oxidation (PROX) reactor are shown below [12]:



only the first reaction (Eq. (1)), the oxidation of CO to CO<sub>2</sub> is desired [12]. This reaction is usually accomplished at lower temperatures. The undesired H<sub>2</sub> oxidation reaction (Eq. (2)) is the key competitive reaction that takes place at higher temperatures and must be minimized to reduce the loss of H<sub>2</sub>, while reducing CO concentrations to acceptable levels [2]. Thermodynamically, the enthalpy of H<sub>2</sub> reacting with O<sub>2</sub> is lower than that of CO reacting with O<sub>2</sub>, however, with increasing temperature, H<sub>2</sub> prevents CO from adsorbing to some active sites of the catalyst [13]. PROX usually requires minimal amounts of surplus air corresponding to a CO/O<sub>2</sub> mole ratio or λ value of between 0.5 and 2 [12].

Early studies on PROX conducted by Oh and Sinkevitch [14] assessed the performance of a number of noble metals supported on alumina, and some transition metal based catalysts. Their results showed that among all the catalyst types tested, Pt, Ru and Rh were

\* Corresponding author. Fax : +27 31 260 3091.  
E-mail address: [friedric@ukzn.ac.za](mailto:friedric@ukzn.ac.za) (H.B. Friedrich).

the most efficient catalysts with regards to selectivity toward CO<sub>2</sub>. Following this work, many catalytic formulations have been tested for the PROX reaction and among all the metals, Au, Rh, Ru, Pt, Ir and Pd supported on Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub>, ZnO, TiO<sub>2</sub> and SiO<sub>2</sub> showed good activity within the desired temperature ranges [3,15–18]. However, when using precious metal catalysts for the PROX reaction, high costs and limited durability are of main concern, therefore, research at present is directed toward alternative, more cost effective catalysts that show similar activity toward the PROX reaction [19]. These could make use of cheaper metals and also include a low content of noble metal, instead of using them as the bulk catalyst.

Several Pt catalytic system have already been investigated for the PROX reaction and Pt catalysts are also known to function well in fuel processors, working at high temperatures, and they are resistant toward catalyst deactivation [4,11]. Many efforts have also been made at improving the selectivity and activity of Pt catalysts by adding an additional metal. These minimize the adsorption of CO which tends to block the adsorption sites of O<sub>2</sub> on the Pt, making CO oxidation more difficult.

Ko *et al.* [20] reported that mono-metallic Pt catalysts usually exhibit noticeable PROX activity above 150 °C. Their findings also indicated that PROX activity at lower temperatures could be enhanced by the addition of a second metal such as Fe, Co, Ni, Mn or alkali metals. These authors found that the addition of Ni to the catalyst was more effective over a wide temperature range and showed higher CO conversion and selectivity toward CO<sub>2</sub>.

These results motivated our study in utilising a low Pt content, instead of using it as a bulk catalyst, toward developing a relatively inexpensive catalyst containing Ni which is used in one or more of the on-board reforming steps (steam reforming and partial oxidation) [21,22]. In this study a 25 wt% NiO/Al<sub>2</sub>O<sub>3</sub> catalyst was synthesized, characterized and tested for PROX activity within the stipulated temperature ranges. To this catalyst 0.5 wt% Pt was added and the material characterized and tested.

## 2. Experimental

### 2.1. Catalyst synthesis

The  $\gamma$ -aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) support was purchased from Alfa Aesar, Karlsruhe, Germany. The NiO/Al<sub>2</sub>O<sub>3</sub> (25 wt%) denoted as Ni–Al, Pt/Al<sub>2</sub>O<sub>3</sub> (0.5 wt%) denoted as Pt–Al and the Pt/NiO/Al<sub>2</sub>O<sub>3</sub> denoted as Pt–Ni–Al catalysts were prepared by the incipient wetness technique adopted from literature [23]. For the Ni–Al catalysts, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma–Aldrich, 98%) was dissolved in a minimum amount of deionized water and added to a slurry of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and deionized water, with vigorous stirring at room temperature for an hour. Water was evaporated on a hot plate at 80 °C until a paste was obtained. The paste was oven dried overnight at 110 °C, thereafter calcined at 500 °C. For the Pt–Al catalyst, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (BDH Chemicals, 40%) was used for the synthesis (as described for the Ni–Al catalyst) and calcined at 300 °C. The Pt–Ni–Al catalyst was prepared by adding H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O dissolved in a minimum amount of deionized water to a slurry of deionised water and the Ni–Al catalyst and calcined at 300 °C.

### 2.2. Catalyst characterization

#### 2.2.1. Inductively coupled plasma-optical emission spectroscopy

The elemental composition of the fresh catalysts was determined using an Optima 5300 DV PerkinElmer Optical Emission Spectrometer. Accurately weighed catalyst samples (0.50 g), were dissolved in 5 mL HNO<sub>3</sub> and digested using a PerkinElmer Multi-wave microwave sample preparation system operating at 600 W.

Standards solutions for Ni and Pt (Industrial Analytical, RSA) were prepared ranging from 0 to 100 ppm.

#### 2.2.2. Physisorption–N<sub>2</sub> adsorption–desorption and pore size distribution (PSD)

The fresh and used catalyst samples (~0.2 g) were degassed under a steady stream of nitrogen using a Micromeritics Flow Prep 060 Sample degas system. A temperature ramp of 2 °C per min was applied until a final temperature of 200 °C was reached and the samples were kept constant at this temperature overnight. Thereafter, samples were analysed using a Micromeritics TriStar II Surface Area Analyser. The same instrument was used to determine the pore size distributions using the method of Barret, Joyner and Halenda (BJH).

#### 2.2.3. Powder and *in situ* X-ray diffraction

Powder X-ray diffraction (XRD) patterns of the fresh and used catalysts were recorded on a Bruker D8 Advance instrument with Difractplus XRD Commander Software and a Bruker VANTEC detector. The radiation source used was Cu K $\alpha$  (wavelength of 0.1540 nm), operating on a long focus line with a voltage and amperage of 40 kV and 40 mA respectively. The catalysts were scanned in a 2 $\theta$  range from 2° to 90° at 0.5° per minute. For *in situ* redox experiments, 5% H<sub>2</sub> in nitrogen was used as the reducing gas and air as the oxidizing gas. The temperature was ramped from room temperature to 600 °C at 50 °C increments and gradually cooled to 100 °C.

#### 2.2.4. Temperature programmed techniques

Temperature programmed reduction (TPR) profiles were obtained using a Micromeritics Autochem II Chemisorption Analyzer. Approximately 0.05 g of the fresh calcined catalyst sample was placed in a U shaped quartz tube. Prior to reduction, the catalysts were pre-treated by heating to 400 °C under a stream of argon (30 mL/min) for 30 min and the temperature was decreased to 90 °C under the same stream of argon. The reduction experiments were carried out using 5 vol.% H<sub>2</sub> in Ar as the reducing agent with a flow rate of 30 mL/min to a temperature of 1000 °C ramped at 10 °C/min.

#### 2.2.5. CO Chemisorption

Fresh catalyst samples (~0.15 g) were degassed under a flow of N<sub>2</sub> from room temperature to 200 °C and then kept under vacuum for 12 h using a Micromeritics Flow Prep 060 Sample Degas System. Samples were analysed using a Micromeritics ASAP 2020 instrument. Samples loaded in a quartz tube were initially reduced with H<sub>2</sub> at 700 °C for 2 h. The chemisorption of CO on the materials was analysed at 35 °C within a pressure range of 200–400 mmHg. The metal dispersions and crystallite sizes were calculated from the CO adsorption data using a stoichiometric ratio of 1.

#### 2.2.6. FTIR CO

FTIR–CO measurements were recorded using a Bruker Tensor 27 with Harrick DRIFTS accessory and Harrick high temperature reaction chamber. The catalyst samples were compressed into self-supporting wafers (~20 mg/cm<sup>2</sup>) and mounted in the IR cell which allowed both heating (200 °C) and cooling (RT) *in situ* under atmospheric pressures. The fresh catalyst samples were degassed under Ar (30 mL/min) at 200 °C for 6 h prior to each experiment. CO gas was pulsed through a VICI loop size of 100  $\mu$ L over the samples at 35 °C and 200 °C and flushed out with Ar between each pulse.

#### 2.2.7. X-ray photon spectroscopy (XPS)

A Kratos Axis Ultra DLD spectrometer, fitted with an achromatic Al K source operated at 120W was used for XPS analysis. During the analysis, the pressure in the chamber was maintained around  $1 \times 10^{-9}$  mbar. The acquisition of survey and detailed regional scans

Download English Version:

<https://daneshyari.com/en/article/45289>

Download Persian Version:

<https://daneshyari.com/article/45289>

[Daneshyari.com](https://daneshyari.com)