



## Effect of Pt and Pd promoter on Ni supported catalysts—A TPR/TPO/TPD and microcalorimetry study

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### ABSTRACT

The promoting effect of Pt and Pd in bimetallic Ni–Pt and Ni–Pd catalysts supported on alumina nano-fibre (Alnf) were tested for the liquid phase reforming of sorbitol to produce hydrogen. The mono- and bimetallic catalysts were studied by different characterisation techniques such as: temperature programmed reduction, oxidation, CO desorption, microcalorimetry, TEM and STEM/EDX. Although bimetallic catalysts have long been the subject of great interest because of their exceptional properties compared to the monometallic catalysts, the reason behind their improved activity is still a question of debate. Experimental evidence showed that the addition of both Pt and Pd—even in a very small fraction—to the Ni catalyst increases its reducibility significantly. The TEM and STEM/EDX analysis confirmed that Pt and Ni are present as alloys in nano-sized rod shaped particles. At the same time it was found that the CO differential heat of adsorption is appreciably lowered in the bimetallic catalysts. This is substantial because reducing the CO binding strength can avoid the poisoning of the active metal sites. As a result, we demonstrate that the rate of H<sub>2</sub> formation from sorbitol reforming was 3 to 5 times higher for bimetallic catalysts when compared to the monometallic catalysts.

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### 1. Introduction

Due to rising fuel prices, efforts to improve catalysts for production of alternative fuels have increased in the last few years. Hydrogen production from biomass is one of the most prevailing research areas in this regard. Hydrogen is considered one of the best alternative fuels because of its environmental benefits and high efficiency for energy production in fuel cells. However, hydrogen as a fuel will be able to reduce greenhouse gas emissions only when the source of hydrogen is environmentally benign such as water or biomass. But since water electrolysis is an energy-intensive process it requires a cheap and renewal source of electricity for it to be efficient. Currently photovoltaic cells, however, are not a viable energy source for water electrolysis. The focus is thus on biomass, which is cheap and abundant. Its high water content makes it unsuitable for gasification or steam reforming, but reforming of the biomass in the liquid phase is possible. After the introduction of aqueous phase reforming of alcohols and ethylene glycol [1–3], further studies [4] suggested that hydrogen can be directly produced from aqueous solutions of sugar or sugar alcohols.

From our previous studies [5] and the literature [6–8] we observed that the activity of the catalyst can be greatly enhanced

using a bimetallic catalyst. It has also been suggested that the addition of noble metals to a Ni catalyst may reduce coke deposition and therefore provide stability [9]. The Ni–Pt system in particular has been extensively studied because of its synergetic catalytic effect [10–13]. Reducibility and kinetic studies for various reactions on Ni–Pt system supported on silica and alumina have also been reported [10,11,14–16]. Ko et al. [17] conducted CO chemisorption on mono- and bimetallic catalysts of Ni and Pt supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to study preferential oxidation (PROX) of CO in hydrogen rich stream. Their study showed that under the same pre-treatment condition Ni–Pt bimetallic catalysts had higher number of active sites. Moreover, the activity and selectivity of the bimetallic catalyst per unit site of the catalyst was also found to be higher for the PROX reaction. However, the reason for this was not clear beyond the enhanced reducibility of bimetallic catalysts. One of the reasons could be that the catalyst was more resistant to oxidation under the reaction condition [25]. It may also be possible that CO adsorption is altered on bimetallic catalysts due to surface heterogeneity creating favourable reaction conditions. Several probe molecules and surface reactions have been conducted to study adsorption behaviour of bimetallic catalysts [18–20]. However, the effect of noble metals on the CO chemisorption properties of the bimetallic supported catalysts has been less understood. In this study we aim to correlate the effect of the noble metal promoters such as Pt and Pd on Ni, using temperature programmed reduction (TPR), oxidation (TPO) and CO desorption (TPD). Heat-

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flow microcalorimetry was employed to determine the strength of CO interaction on these catalysts. CO interaction with the catalyst is of high importance because a strong interaction can lead to catalyst poisoning [21]. It has been suggested that weaker interaction can decrease the heat of adsorption of CO and hydrogen chemisorption, thereby increasing the fraction of the surface available for the reforming reaction [22]. Reducing the amount of precious noble metal content also reduces the cost of the catalysts.

## 2. Experiments and methods

### 2.1. Catalyst preparation

The catalysts used in this study were prepared using the wet impregnation technique. Hydrogen hexachloroplatinate(IV) (8% solution in water, Aldrich) was used as a precursor for the platinum catalyst, while nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Univar) as a source of nickel and palladium(II) nitrate solution (10 wt%  $\text{Pd}(\text{NO}_3)_2$  solution in 10 wt% nitric acid, Aldrich) for palladium catalysts. The impregnated Pt, Pd and Ni catalysts were prepared by adding appropriate amounts of solution of precursor to the support with constant stirring at 60 °C for 6 h. The catalysts were then dried overnight at 90 °C followed by calcination at 500 °C. Pt, Pd and Ni were supported on high surface area alumina nano-fibre (Alnf). For alumina nano-fibre preparation, glycerol was mixed with an appropriate amount of acid solution of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and then a basic solution of  $\text{NaAlO}_2$  was added drop-wise. The final pH of the solution was maintained at 6. The precipitate was collected by centrifugation. The precipitate was then washed several times to remove  $\text{Na}^+$  and  $\text{Cl}^-$  ions. The washed cake was then mixed with PEO surfactant Tergitol 15TS-7. After prolonged stirring and ageing at 100 °C the resultant supernatant liquid was thrown and the white cake was dried in air and calcined at 500 °C for 20 h.

### 2.2. Characterisation of catalyst

Alumina nano-fibre surface area was measured using the BET technique employing nitrogen physisorption at the temperature of liquid nitrogen in a Quantachrome Autosorb-1C instrument. The

percentage of metal loading was measured by Inductively-Coupled Plasma Atomic Emission Spectrometer (ICPAES).

#### 2.2.1. TPR/TPO/TPD

Temperature programmed characterisation, such as reduction (TPR), oxidation (TPO) and desorption (TPD), was carried out using a setup illustrated in Fig. 1. Probe gases, attached to Brooks 5850E mass flow controllers of suitable flow range, were passed through a quartz glass reactor in a tube furnace. The gases were continuously sampled downstream through a 25  $\mu\text{m}$  capillary connected to a Varian leak valve. The leak valve introduced gases in a vacuum chamber attached to SRS RGA300 quadrupole mass spectrometer. Varian MiniTask, with a maximum pumping speed of 40 L/s (for nitrogen) and base pressure of  $1.5 \times 10^{-7}$  Torr, was used to evacuate the vacuum chamber. The partial pressures of the gases evolved from the sample were recorded with respect to time, which was then converted to temperature according to the ramp rate of the furnace. Partial pressures were then converted to  $\mu\text{mol}/\text{min}$  using the calibration from standard gas mixtures at a measured flow rate in ml/min. TPR was conducted with 5%  $\text{H}_2/\text{N}_2$  mixed gas at a flow rate of 50 ml/min. TPO was conducted with 2%  $\text{O}_2/\text{He}$  mixed gas at a flow rate of 50 ml/min. In both cases the temperature was raised from room temperature to 700 °C at the rate of 10 °C/min. For CO-TPD catalysts were pre-reduced in situ at 500 °C for Ni catalysts and 300 °C for Pt and Pd catalysts using ultrapure  $\text{H}_2$  at a flow rate of 80 ml/min for 5 h. The catalysts were then purged with He at 100 ml/min flow rate, at the reduction temperature for 1 h. The catalysts were cooled to room temperature and dosed with CO at 100 ml/min for 15 min. The whole system, including the catalyst, was then flushed with He at 100 ml/min for at least 1 h to remove any trace of CO. For TPD measurements the temperature was raised from room temperature to 700 °C at the rate of 10 °C/min.

#### 2.2.2. Microcalorimetry

Microcalorimetry measurements were performed at 30 °C using a Setaram BT2.15 heat-flux calorimeter. The calorimeter was connected to a high vacuum gas-handling and volumetric system employing Baratron capacitance manometers for precision pressure measurement of  $\pm 0.5 \times 10^{-4}$  Torr. The maximum apparent leak

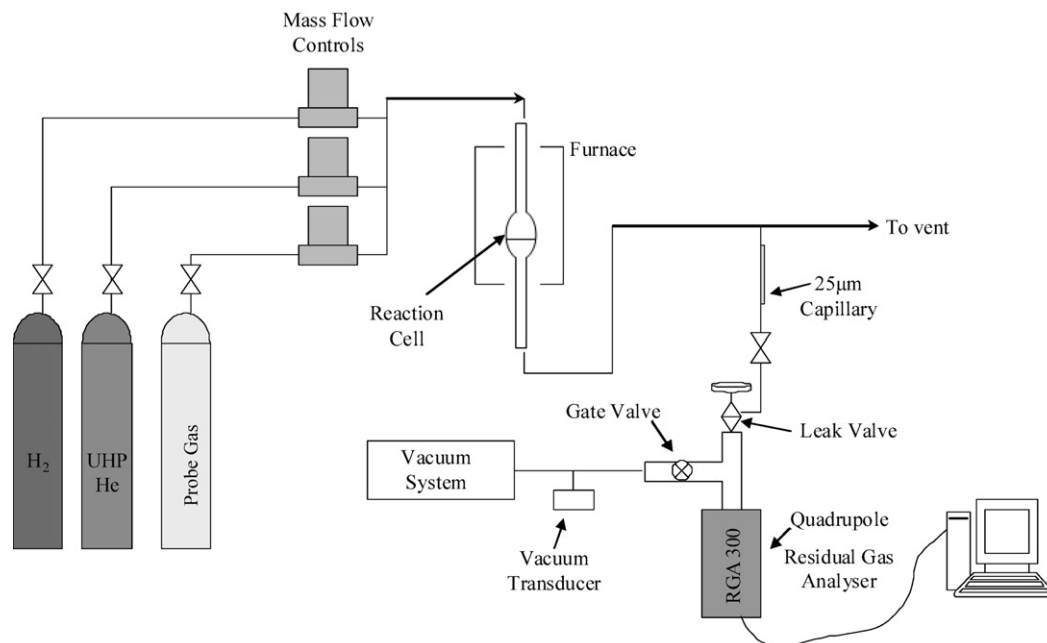


Fig. 1. Setup for temperature programmed characterisation.

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