



Activation of carbon-supported platinum catalysts by sodium for the low-temperature water-gas shift reaction



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ABSTRACT

The activation of multi-walled carbon nanotube-supported platinum catalysts for the low-temperature water-gas shift reaction is demonstrated by the addition of sodium. Nitric acid oxidation of the carbon nanotubes allows for the addition of sodium through ion-exchange and creates anchoring sites for platinum. We show that an oxidized platinum state is stabilized by the presence of sodium. Evidence for a sodium-promoted Pt-(OH)_x active site is given through XPS analysis of the catalysts before and after reaction and confirmed by CO-TPR. Removal of the oxygen groups and partial removal of sodium by annealing the Na-modified carbon nanotubes to 800 °C in inert atmosphere creates a surface on which Pt is initially very active, but of lower stability due to the absence of a sufficient number of surface sodium anchoring sites.

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1. Introduction

The water-gas shift reaction is an essential component of reformate fuel gas upgrading processes for hydrogen production and purification [1]. When used as a part of PEM fuel cell systems, the WGS catalyst must be particularly robust due to frequent startup–shutdown cycles and potential exposure to air. Due to the susceptibility of the industrial copper catalysts to deactivation under such conditions, interest in noble metals as potential replacements has grown in recent years and many catalyst formulations have been examined [2,3].

Platinum, in particular, has been heavily studied as an alternative to the copper-based water-gas shift catalyst. Typical catalyst formulations have included Pt/CeO₂ [4,5], Pt/TiO₂ [6,7], Pt/Al₂O₃ [8,9], and Pt/ZrO₂ [10]. The activity of such materials has been linked to the oxygen defect concentration of the metal oxide support [4,11–13] and its ability to stabilize platinum in its active (Pt-O_x) state [3,14,15]. As a result, significant research efforts have focused on understanding the interaction of Pt with ceria [16] and modified ceria [17] due to the high activity (and defect concentrations) of these catalysts. Despite their high performance, ceria-based catalysts are deactivated under frequent

shutdown/restart operation [18] as a result of hydroxycarbonate formation [5] and the destabilization of the active Pt-O_x site. At high temperatures, sintering of the platinum metal and the ceria support is the main reason for deactivation [19]. Alternatives to ceria are thus actively investigated.

A new class of alkali-promoted platinum catalysts has recently emerged as an alternative to ceria-supported Pt. The addition of alkali has been shown to improve the activity of Pt on a variety of oxide supports including ZrO₂ [20,21], CeO₂ [22,23], TiO₂ [24], and Al₂O₃ [25,26]. In the presence of alkali, Pt can be used most efficiently even on an inert support like silica, as has been demonstrated by Flytzani-Stephanopoulos and co-workers [25,27].

The latter work has presented evidence that a similar mechanism to that observed on Pt/CeO₂ is also plausible for these catalysts, whereby oxygen is supplied to the active site in the form of hydroxyls, via sodium (or potassium) atoms, bound to Pt with oxygen links in a Pt-Na(K)-O_x(OH)_y cluster [25]. Water can easily be dissociated on these clusters and the CO reaction with –OH is catalyzed at low temperatures. Indeed, the apparent WGS activation energies of Pt on any oxide support are similar (~70 kJ/mol) [4,8,24,25,28], supporting the notion of a common Pt-(OH)_x site. It was also recently shown that alkali addition to encapsulated Pt@SiO₂ catalysts promotes their WGS activity and provides structural stability to platinum which allows for stable activity in cyclic operation [27].

To further probe the need for a metal oxide as a carrier for active platinum catalysts, we have examined carbon supports, on which platinum is typically inactive for the low-temperature WGS reaction. In this work, we demonstrate that we can activate platinum

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on inert carbon surfaces by the addition of alkali promoters. The remarkable improvement in activity upon the addition of sodium is thought to be directly related to the state of platinum.

Previous studies on carbon-supported platinum catalysts have shown the stabilizing and promoting effect of calcium on activated carbon-supported platinum for carbon dioxide hydrogenation [29]. Additionally, surface oxygen groups on carbon supports have been shown to have significant influence on catalytic performance in selective hydrogenation reactions [30]. Further understanding the interplay between surface oxygen groups and alkali promoters may allow for improved and more economical platinum-based catalyst design for a number of applications, such as hydrogenation [30] and oxygen reduction reactions [31,32].

Here we use a multi-step process for the synthesis of sodium-promoted platinum catalysts supported on multi-walled carbon nanotubes (MWNTs). While simple co-impregnation of Pt and Na precursors suffices to create an active catalyst, the approach followed in this work allows for the identification of the important oxygen anchoring sites on carbon surfaces. This may also be useful for the design of other dispersed M-O_x species on carbons.

2. Experimental

2.1. Catalyst preparation

The preparation of the catalyst was performed in a step-wise manner using carbon-modification techniques similar to those described by Roman-Martinez et al. [29]. A schematic of the process employed is shown in Fig. 1. A detailed description of the preparation steps is given below.

MWNT oxidation. Multi-walled carbon nanotubes (>95%, OD 20–30 nm, length 10–30 μm) were purchased from Cheap Tubes, Inc. Introduction of surface oxygen was performed by nitric acid oxidation. The as-received MWNTs (denoted C_N) were suspended in 70% HNO₃ (Alfa Aesar) (25 mL per gram of MWNT) and refluxed at 120 °C for 2 h (denoted 2h-C_N). After refluxing, the oxidized MWNTs were filtered and washed repeatedly with deionized water until neutral pH. The washed nanotubes were placed in a vacuum oven and dried overnight at 60 °C.

Alkali-metal ion exchange and annealing. Introduction of sodium was performed by ion-exchange, following the method used by Roman-Martinez et al. [29]. The 2h-C_N were suspended in a 1 M sodium acetate solution (50 mL per gram 2h-C_N) and refluxed at 60 °C for 24 h. Following the ion-exchange, the MWNTs were filtered, washed repeatedly with deionized water, and dried in a vacuum oven overnight at 60 °C. These materials are labeled Na-2h-C_N.

The heat-treatment of 2h-C_N and Na-2h-C_N supports was performed at 800 °C under flowing helium in a quartz packed bed reactor in order to decompose surface oxygen groups. The supports were maintained at 800 °C for 2–4 h.

Platinum deposition. Platinum was deposited on the MWNT supports by incipient wetness impregnation. Briefly, to prepare 1 g of 1 wt% Pt catalyst, 0.02 g tetraamine platinum nitrate (Alfa Aesar) was dissolved in 1.5 mL (i.e. pore volume of all supports = 1.5 mL/g) deionized water. The platinum solution was added drop-wise to the support, ensuring even distribution of the solution, until a dry paste was formed. The impregnated support was dried in a vacuum oven overnight at 60 °C. The dried samples were crushed and stored in glass vials until reaction (all catalysts were heated in He to 400 °C at a rate of 10 °C/min and held at temperature for 1 h prior to use).

2.2. Characterization

High-resolution transmission electron microscopy (HRTEM) was performed using a JEOL 2100 at an operating voltage of 200 kV.

Aberration-corrected HAADF-STEM imaging was performed using a Zeiss Libra 200 MC microscope operated at 200 kV. TEM samples were prepared by dispersing the powdered samples in ethanol and dropping onto a 200 mesh copper grid coated with a lacey carbon film. Particle sizes were estimated from the images by counting at least 200 particles.

BET surface area measurements were carried out in a Micromeritics AutoChem 2920 II system. 0.1 g of catalyst was placed in a U-shaped reactor and purged in flowing helium at 110 °C prior to BET measurement.

He-TPD was performed in a Micromeritics AutoChem 2920 II by placing 0.1–0.2 g of sample in a U-shaped quartz tube between two plugs of quartz wool, purging in helium, and linearly heating the sample at a rate of 10 °C/min in flowing helium (30 mL/min) while monitoring the gas effluent with a residual gas analyzer (SRS RGA 200).

CO-TPR was performed in a Micromeritics AutoChem 2920 II instrument on a used catalyst (following an in situ temperature-programmed surface reaction test), followed by hydration using a water-saturated helium gas flow. After cooling to room temperature, the reactor was purged with a 10% CO–He gas and heated at a rate of 10 °C/min. Effluent gases were analyzed using a residual gas analyzer (SRS RGA 200).

X-ray photoelectron spectroscopy (XPS) studies were performed using a Thermo Scientific K-Alpha operated using Al K-alpha radiation and a pass energy of 20–40 eV.

X-ray diffraction (XRD) was performed on a PANalytical X'Pert Pro using Cu K-alpha radiation, equipped with high-speed Bragg-Brentano Optics.

2.3. Activity tests

Steady-state activity tests were performed using an in-house packed-bed quartz micro-reactor operated at atmospheric pressure. The feed and product gas compositions were analyzed using an SRI 331 gas chromatograph (GC) equipped with a Carbosphere 80/100 packed column and a TCD detector. In a typical experiment, 0.1–0.2 g of catalyst was diluted with calcined quartz sand and loaded between two plugs of quartz wool. The gas composition for typical product-free activity tests was 2% CO–10% H₂O–88% He, using a flow rate of 70 mL/min.

Temperature-programmed surface reaction (TPSR) tests were performed in a Micromeritics AutoChem 2920 II system. The catalyst (0.1 g) was placed in a U-shaped reactor between two plugs of quartz wool and treated in flowing helium to 400 °C. After cooling to room temperature, a water-saturated 10% CO–He gas was flowed to the reactor (30 mL/min). The temperature was ramped linearly at 10 °C/min to 400 °C and the gas effluent analyzed by a residual gas analyzer (SRS RGA 200).

3. Results and discussion

3.1. Support characterization

The MWNT support materials were characterized at various stages of treatment by XPS and TPD in order to identify changes at the surface. The elemental compositions of the MWNT surfaces, as determined by XPS after various treatments, are shown in Table 1. The nitric acid treatment (2h-C_N) significantly increases the amount of surface oxygen (3.2 at%) compared to as-received MWNT (1.6 at%). While longer acid treatment allows for higher surface oxygen content, it is also known to cause significant structural changes to the nanotubes (e.g. opening of tips), and was therefore avoided in this study. The ion-exchange of sodium (Na-2h-C_N) onto the 2-h acid-treated MWNT results in the introduction of 0.7 at% sodium at

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