



# Investigation of the promoting effect of Mn on a Pt/C catalyst for the steam and aqueous phase reforming of glycerol



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## ARTICLE INFO

### Article history:

Received 6 December 2016

Revised 23 February 2017

Accepted 5 March 2017

### Keywords:

Steam reforming

Aqueous phase reforming

Glycerol

Hydrogen

Platinum

Manganese

Activated carbon

Bimetallic catalyst

Surface Lewis acid site

## ABSTRACT

The catalytic performances in steam reforming (SR) and aqueous phase reforming (APR) of glycerol of a bimetallic Pt-Mn catalyst supported on activated carbon are investigated and correlated with the surface properties of the catalyst. Under SR conditions, Mn showed a significant promoting effect over Pt/C, both in terms of hydrogen production rate and conversion, with a higher selectivity toward the glycerol dehydration products. Upon addition of Mn the amount of strong Lewis acid sites increased, promoting the dehydration of glycerol and favoring the C–O over C–C cleavage at expenses of hydrogen selectivity. Conversely, under APR conditions, a slightly higher hydrogen selectivity and only minimal enhancement in hydrogen production were found, while the products selectivity was comparable to Pt/C. Most of Mn leached into the aqueous media, but the remaining (<5% of the fresh parent sample) might be alloyed with Pt and promote the CO desorption from neighbor Pt sites.

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## 1. Introduction

Sustainable hydrogen production will probably play a fundamental role in future economies, due to the need of clean energy vectors to meet the modern environmental requirements, and to minimize our dependence on fossil fuels [1–4]. Water and biomass are emerging as valuable candidates to replace natural gas as main feedstock for the hydrogen production, owing to their abundance, relatively low cost, and carbon neutrality. Besides promising routes such as photoelectrochemical water-splitting and enzymatic and microbiological-based technologies, which are, however, in a too early stage of development for an economically sustainable implementation, reforming of biomass-derived compounds could be a viable way for the medium-term future, since it couples a well-known technology with renewable feedstocks [2–5].

In particular, steam reforming (SR) and aqueous phase reforming (APR) have been extensively studied for the past decade, showing that high hydrogen production rates can be achieved using a large variety of organic substrates, from simple model molecules to complicated mixtures, such as bio-oil [3,5–13]. In this scenario, glycerol will become one of the most important commodities as it is the main by-product from the transesterification of vegetable oils and fats to produce biodiesel, and is a good model compound for polyols in biomass catalytic conversion processes [14–16]. Many works have been published on SR and APR of glycerol for the hydrogen production, using a variety of catalysts based on both precious and non-precious metals [11,17–24]. Ru catalysts have shown good catalytic performances because of their high C–C cleavage ability and coke resistance [18], while among non-precious metals Ni is preferred [25]. However, in order to achieve good conversion levels with these catalysts, high temperatures are generally required. Pt-based catalysts can be very active even at relatively low temperature (<300 °C), while retaining good C–C cleavage activity [25]. In order to further increase the hydrogen production up to industrial-relevant rates, the addition of promoters is a viable strategy. Kunkes et al. had studied a series of Pt-based catalysts modified with noble and non-noble metals in the

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SR reaction of glycerol, and found that at low reaction temperatures only noble metals, such as Re, had a distinct promoting effect. The superior catalytic activity of the Pt-Re/C tested in that study was ascribed to lower activation energy for CO production compared to Pt/C [24]. Besides the lack of a deeper investigation on the actual promoting mechanism, it seemed that at low temperatures only noble metals were able to promote effectively the SR of glycerol, making the development of an active non-noble metal based promoter more challenging.

To achieve that, fundamental insights into reactivity and reaction pathways can be obtained by studying the catalysts mimicking the actual working conditions. For example, an *in-operando* XAS technique was used by Dietrich et al. to study a Pt-Mo catalyst supported on carbon black for the APR reaction of glycerol. The authors found an increased glycerol conversion, but lower hydrogen selectivity, ascribed to the partial oxidation of Mo in APR conditions, which led to increased C–O cleavage activity through acid catalyzed reactions [21]. As one of the early effective industrial promoters used in particular for the naphtha reforming, Re has attracted much attention also for the reforming of other substrates other than glycerol, such as ethylene glycol, phenols, and sugars [11,12,17,24,26]. Generally, the catalytic performances of the Pt-Re catalysts increased with all the substrates, in both SR and APR. Besides the acidity induced by the partial oxidation of Re in hydrothermal conditions, which as in the case of Mo led to higher conversion levels but lower selectivity toward hydrogen, Wang and co-workers found that the enhanced performances of Pt-Re catalysts were mostly due to the facile CO desorption from the catalyst surface by spillover from Pt to adjacent  $\text{ReO}_x$  sites, thus explaining the low activation energy for CO production found by Klunkes et al. [11,17,24,27,28].

With the aim of developing industrial-grade catalysts at lower costs, new and cheaper promoters are required. Recently, manganese has been proposed as effective promoter for Pt- and Ni-based catalysts, in both the SR and APR of oxygenates, showing remarkable performances in terms of improved hydrogen production rates [10,29]. Interestingly, Mn is an effective promoter for the CO oxidation reaction due to its good redox properties and high oxygen storage capability. These peculiar features could be useful for the production of  $\text{H}_2$  with lower levels of CO, which is poisonous for many noble metals, and in particular Pt [30,31]. There is, however, a lack of understanding of the actual promotion mechanism of Mn in reforming reactions and about the impact of water on the bimetallic catalyst whether it is fed in the vapor or in the liquid phase. In this work, a Pt-Mn catalyst supported on activated carbon is studied in both SR and APR of glycerol and compared with monometallic Pt/C. The fresh catalysts were characterized by CO chemisorption, hydrogen temperature programmed reduction, high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) together with energy dispersive X-ray analysis (EDX) analysis. In order to investigate the surface properties of the catalysts simulating reforming conditions with particular focus on the acidic properties, pretreatments with steam were carried out before attenuated total reflection infrared spectroscopy (ATR-IR) with pyridine as probe molecule and ammonia temperature programmed desorption ( $\text{NH}_3$ -TPD) experiments.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation method using an activated carbon support (TA60, PICATAL) previously dried overnight at 110 °C. Tetraammineplatinum (II) nitrate

hexahydrate ( $(\text{NH}_3)_4\text{Pt}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich) and manganese nitrate tetrahydrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , Sigma-Aldrich) were used as metal precursors. The impregnated samples were dried overnight at room temperature and calcined at 260 °C for 2 h in air. The bimetallic catalyst (Pt-Mn/C) was prepared by co-impregnation of the two metal salts, followed by the same drying and calcination steps. The Pt/Mn molar ratio was 1, with the Pt being the 2 wt.%.

### 2.2. Catalyst characterization

#### 2.2.1. Physical adsorption and chemisorption

Specific surface areas were measured by nitrogen physisorption isotherms at –196 °C using the BET method (Tristar II, Micromeritics), outgassing the samples at 110 °C for 2 h before each measurement.

The metal loadings were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) after microwave digestion of the samples in aqua regia.

CO-pulse chemisorption was performed on an Autochem II (Micromeritics). The samples were first reduced with 10 vol.%  $\text{H}_2/\text{Ar}$  at 280 °C for 1 h and then purged for 30 min with He before being cooled to 40 °C. A series of CO pulses were then introduced until saturation. Pt dispersion was evaluated by processing the thermal conductivity detector (TCD) signals, assuming a Pt/CO stoichiometry of 1.

$\text{H}_2$ -TPR experiments were carried out on the same apparatus. Prior to each analysis, the samples were pretreated in flowing He for 1 h at 110 °C, and then cooled down to room temperature. A temperature ramp of 10 °C  $\text{min}^{-1}$  and a 10 vol.%  $\text{H}_2/\text{Ar}$  flow were used in all the experiments.

CO- and  $\text{NH}_3$ -TPD experiments were performed again by using the Autochem II (Micromeritics) apparatus. The samples were first reduced at 280 °C with a 10 vol.%  $\text{H}_2/\text{Ar}$  flow, and then cooled to 225 °C under He flow. Subsequently, steam pulses were introduced for about 1 h by flowing He through a water bubbler, followed by cooling to 40 °C, and then purged for 1 h. After 1 h under CO or  $\text{NH}_3$  flow (50  $\text{mL min}^{-1}$ ), the samples were purged with He for 1 h at room temperature. Finally, the samples were heated up with a ramp rate of 10 °C  $\text{min}^{-1}$  to 500 °C in He flow. CO desorption curves were obtained by processing the TCD signals, while the amount of desorbed  $\text{NH}_3$  was calculated by integrating the mass signals (ThermoStar Quadropole Mass Spectrometer from Pfeiffer Vacuum).

#### 2.2.2. Electron microscopy

Electron micrographs were carried out with a Zeiss LIBRA 200FE, equipped with 200 kV FEG, in-column second-generation omega filter for energy selective spectroscopy (EELS) and imaging (ESI), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM)-STEM facility and EDX probe for chemical analysis. All the samples were reduced at 260 °C for 1 h with 10 vol.%  $\text{H}_2/\text{Ar}$  flow (50  $\text{mL min}^{-1}$ ) before performing the analyses. Prior to the introduction in the instrument, the samples were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited on a holey carbon gold grid (300 mesh). The histograms of the metal particle size distribution for the samples were obtained by counting at least 500 particles onto the micrographs. The mean particle diameter ( $d_m$ ) was calculated by using the formula  $d_m = \frac{\sum d_i n_i}{\sum n_i}$ , where  $n_i$  is the number of particles with diameter  $d_i$ .

#### 2.2.3. ATR-IR

Detailed ATR-IR experiments are described in our previous report [17]. The Internal Reflection Element (IRE) was coated by suspending 5 mg of catalyst in 1 mL of Milli-Q water, and sonicat-

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