# Catalysts synthesized by selective deposition of Fe onto Pt for the water-gas shift reaction

Isaias Barbosa Aragao[a,b], Insoo Ro[b], Yifei Liu[b], Madelyn Ball[b], George W. Huber[b], Daniela Zanchet[a,*], James A. Dumesic[b,*]

[a] Institute of Chemistry, University of Campinas (UNICAMP), P.O. Box 6154, 13083-970 Campinas, São Paulo, Brazil
[b] Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, United States

## ARTICLE INFO

## ABSTRACT

FePt bimetallic catalysts with intimate contact between the two metals were synthesized by controlled surface reactions (CSR) of (cyclohexadiene)iron tricarbonyl with hydrogen-treated supported Pt nanoparticles. Adsorption of the iron precursor on a Pt/SiO$_2$ catalyst was studied, showing that the Fe loading could be increased by performing multiple CSR cycles, and the efficiency of this process was linked to the renewal of adsorption sites by a reducing pretreatment. The catalytic activity of these bimetallic catalysts for the water gas shift reaction was improved due to promotion by iron, likely linked to H$_2$O activation on FeO$_x$ species at or near the Pt surface, mostly in the (II) oxidation state.

## 1. Introduction

The catalytic properties of bimetallic systems can present chemical and physical behaviors that are more than just a sum of their separate parts [1], leading to orders of magnitude enhancement in activities and selectivities compared to their monometallic counterparts [2–4]. However, the creation of a narrow distribution of surface sites represents a challenge for typical deposition methods, which often create a wide composition range, making it difficult to rationalize the system and elucidate the nature of the active sites.

The synthesis of bimetallic catalyst systems has been explored in the literature using colloidal methods [5] and heterometallic clusters [6–11]. Some of the limitations of these approaches include the presence of strongly bonded capping molecules, e.g., organic acids or amines, to the surface of the nanoparticles (NPs), or atmosphere-sensitive reactions for the synthesis of precursors. A method employing controlled surface reactions (CSR) represents an alternative to overcome some of these issues by selectively depositing a commercial organometallic complex on the surface of preformed NPs [12–16]. The CSR method has been successfully applied to synthesize bimetallic systems, revealing promotion effects that can be several orders of magnitude higher than the monometallic unpromoted catalysts. In the case of carbon-supported MoPt catalysts made by the CSR approach, for example, there was a 4000 fold increase in activity for the water gas shift reaction (WGSR), raising the potentiality of the method [12].

One bimetallic system of particular interest in which the CSR method could be successfully explored is FePt, which has shown excellent performance in several key reactions [17–19]. For example, Zhang et al. [17] studied the oxidation of CO in H$_2$-rich gas mixtures (PROX-CO) and showed that Fe-decorated Pt NPs became more active at low temperatures due to the change in reaction mechanism. While Pt NPs follow a competitive Langmuir-Hinshelwood mechanism, the presence of Fe moieties leads to a non-competitive bi-functional mechanism, by preferentially activating the O$_2$. This change in mechanism due to the oxophyllic properties of the FeO$_x$ moieties is ubiquitous [20–22] and has also been shown on other Fe bimetallic systems [23,24].

For the WGSR, in which H$_2$O activation is a rate limiting step for several systems, different bimetallic systems have already been studied [25–31] aiming to improve selectivity and conversion. In this paper, we explore the CSR method to synthesize FePt catalysts for the WGSR. In particular, a detailed study on the parameters that affect the Fe deposition was performed, shedding light on the requisites to selectively deposit the iron moieties on Pt NPs.

## 2. Experimental

SiO$_2$ (Davisil grade 646, Sigma-Aldrich) was used as support for the catalysts. It was crushed and sieved to 60–100 mesh (0.150 − 0.250 mm), then stirred with 20% HNO$_3$ for 3 h, vacuum filtered, washed until pH 7 with milli-Q grade H$_2$O, and dried overnight at 383 K before use. Alumina (γ-Al$_2$O$_3$, CATALOX SBA-200) and titania

(TiO₂, P25, Degussa) were used as received. (Cyclohexadiene)iron tricarbonyl ($C_6H_8Fe(CO)_3$, Strem Chemicals, 98%), and anhydrous *n*-pentane (Sigma-Aldrich) were used without further purification, handled and stored under inert gas inside a glovebox. Chloroplatinic acid hexahydrate ($H_2PtCl_6·6H_2O$, Sigma-Aldrich, ≥ 37.50% Pt basis) and iron(III) nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$, Strem, 98 + %) were used as precursors for incipient wetness impregnation (IWI).

## 2.1. Synthesis

A monometallic catalyst containing 5 wt% Pt, which will be referred as 5Pt/SiO₂, was synthesized by IWI, as described elsewhere [12]. Briefly, 1.2 mL of a solution containing the desired amount of Pt precursor to achieve 5 wt% was added to each gram of SiO₂. The solid was dried at 383 K for 3 h, and the final solid was reduced at 533 K (1 K min⁻¹) for 4 h under 100 mL min⁻¹ of H₂ (Industrial grade, Airgas) and passivated at room temperature under 100 mL min⁻¹ of 1% O₂/He. A Pt/C monometallic catalyst was synthesized following the same procedure.

The CSR method was used to prepare bimetallic catalysts [13]. In a typical synthesis, using Schlenck line techniques and a glove box, 0.7 g of 5Pt/SiO₂ catalyst was reduced at 573 K for 4 h (1 K min⁻¹) under 100 mL min⁻¹ of H₂. Then, 3.5 g of pentane solution containing 0.714 mg gcat⁻¹ of (cyclohexadiene)iron tricarbonyl (equivalent to 0.05:1 Fe:Pt, 0.07 wt% of Fe) was added and left stirring for 2 h. The excess solvent was removed, the residue was vacuum dried, and the remaining solid was reduced again at 573 K. At this stage, the sample was passivated at room temperature under 100 mL min⁻¹ of 1% O₂/He to produce the final catalyst or reduced again and transferred to the glove box to perform a new CSR cycle targeting higher Fe loadings. A hydrogen pretreatment step was performed between cycles, unless noted otherwise. After the final passivation step, the sample was handled under ambient conditions.

A batch of catalyst was prepared without any hydrogen pretreatment to evaluate the influence of this procedure on adsorption of the precursor. In this case, the pre-reduced Pt/SiO₂ catalyst was degassed overnight under vacuum at room temperature, followed by refilling with Ar and precursor deposition.

Catalysts made by CSR on Pt/SiO₂ were denoted as Pt₁Fe_A/SiO₂_BC, in which A corresponds to the final 1 Pt: A Fe molar ratio (nominal values from 0.05 to 0.2) and B is the number of cycles (1–6) performed to achieve that Fe loading; for example, Pt₁Fe₀.₂/SiO₂_4C was prepared by 4 cycles using 0.05 equivalents of Fe, with a final ratio of 0.2. In the case of Pt₁Fe₀.₂/SiO₂_1C, the solvent was evaporated so the desired Fe:Pt ratio could be achieved using one cycle. The catalyst composition was determined by ion coupled plasma-atomic emission spectroscopy (ICP-AES). The CSR method was applied to the Pt/C catalyst to produce the Pt₁Fe₀.₂/C_1C catalyst. The same CSR procedure was applied to the SiO₂ support to produce Fe/SiO₂, in which the amount of Fe was equivalent to Pt₁Fe₀.₂/SiO₂_1C. Control experiments were carried out in which the CSR method was used for SiO₂, TiO₂, and γ-Al₂O₃. For comparison, a bimetallic FePt catalyst was prepared by IWI (IWI-Pt₁Fe₀.₂/SiO₂), where the desired amount of iron nitrate was added to Pt/SiO₂, and the solid was dried overnight and calcined for 4 h at 563 K under air (1 K min⁻¹).

## 2.2. Characterization

### 2.2.1. Electronic spectroscopy

Electronic spectra (UV–vis) were acquired in a Thermo Scientific Evolution 300 UV–vis spectrometer. Samples were prepared in *n*-pentane in a glove box. Precursor adsorption (% adsorbed and amount of Fe adsorbed) was measured by the concentration of precursor in solution after the CSR procedure using a calibration curve of the absorbance maximum at 290 nm, Fig. S1.

### 2.2.2. CO-Chemisorption

The CO chemisorption studies were performed using a Micromeritics ASAP2020C apparatus. Prior to measurement of the CO uptake at 303 K, the catalyst was reduced in flowing H₂ at 573 K for 2 h. Metallic surface area was calculated assuming the adsorption of 1 CO molecule per Pt atom at the surface, as previously reported [16].

### 2.2.3. X-Ray diffraction

Powder X-Ray Diffraction (XRD) patterns were acquired on a Bruker D8 Discovery, operating with Cu-Kα micro X-ray source, with a Montel mirror, and a Vantec 500 area detector.

### 2.2.4. Atomic emission spectroscopy

ICP-AES was performed with a Perkin-Elmer Plasma 400 ICP Emission Spectrometer. Fifty mg of each sample was digested with 10 g of aqua regia overnight at 423 K in a reflux system, and then diluted with milli-Q grade water and quantified. Calibration curves were made with commercial ICP standards − Pt and Fe in hydrochloric acid from TraceCERT®, Sigma-Aldrich.

### 2.2.5. Electron microscopy

Samples were deposited on holey carbon Cu TEM grids by dropping an ethanol suspension of each sample on it, followed by plasma cleaning before analysis. A FEI Titan STEM with Cs probe aberration corrector operated at 200 kV with spatial resolution < 0.1 nm was used for scanning transmission electron microscopy (STEM) studies. High-angle annular dark-field (HAADF) images were collected with detector angle ranging from 54 to 270 mrad, probe convergence angle of 24.5 mrad, and probe current of approximately 25 pA. Energy dispersive x-ray spectroscopy (EDS) data were collected using the same microscope with an EDAX SiLi Detector. EDS point spectra were collected with a probe current ∼200-780 pA and spatial resolution ∼0.5 nm. For each sample, approximately 50 NPs were analyzed by placing the beam on individual particles and collecting EDS spectra.

### 2.2.6. X-ray absorption fine structure

*Ex situ* X-ray Absorption Fine Structure (XAFS) measurements for the Fe K-edge were carried out at the 12BM at the Advanced Photon Source (APS) at the Argonne National Laboratory. The samples were reduced in an inert cell, sealed between Kapton® tapes inside of a glovebox, and kept in a sealed vial under inert atmosphere until the measurements. The samples were mounted in a slide support and the spectra were collected in fluorescence mode using a Canberra 13-Element Ge Detector.

*In situ* XAFS measurements at the Pt L₃-edge and Fe K-edge were acquired at XAFS2 beamline at the Brazilian Synchrotron Light Laboratory (LNLS), using a homemade tubular furnace operating in transmission mode. EXAFS (Extended X-ray Absorption Fine Structure) spectra were collected before and after reduction (573 K, 2 K min⁻¹ under 100 mL min⁻¹ at 5% H₂/He) at the Pt L₃-edge at room temperature. The temperature programmed reduction profile of one of the samples was done by X-ray Absorption Near Edge Structure (TPR-XANES) at the Fe K-edge (100 mL min⁻¹ of 5% H₂/He, heating ramp to 873 K at 10 K min⁻¹, scan time = 9 min). Spectra were collected under *in situ* WGSR conditions at both edges starting from the reduced catalysts, with CO:H₂O equal to 1:3 (6.6 mL min⁻¹ of 5% CO in He, 0.99 mL min⁻¹ of H₂O, and He as balance), with total flow of 100 mL min⁻¹.

XAFS data were analyzed using DEMETER 0.9.25 package software following standard procedure [32]. To evaluate the variation of the iron oxidation state, we applied the method proposed by Capehart et al. [33], in which the average oxidation state is correlated to the absorption edge shift obtained by the integration of the vacant electronic sites above the Fermi level in comparison with the standards.