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Hydrogenation of α, β unsaturated aldehydes over polycrystalline, (111) and (100) preferentially oriented Pt nanoparticles supported on carbon

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Abstract

The influence of the shape/surface structure of Pt nanoparticles on the selective hydrogenation of crotonaldehyde and cinnamaldehyde has been studied. (111) and (100) preferentially oriented Pt nanoparticles (10 nm) as well as polyoriented Pt nanoparticles (3 nm) were synthesized, characterized (by TEM, cyclic voltammetry and adsorption microcalorimetry) and their catalytic properties evaluated. TEM analysis provided information about the size and shape of the Pt nanoparticles, whereas cyclic voltammetry allowed gaining qualitative and quantitative information about their surface structure. Thus, small Pt nanoparticles (≈3 nm) were revealed to have a polyoriented surface, containing high ratio of corner and edges atoms to terrace atoms, whereas large Pt nanoparticles (≈10 nm) were shown to have larger Pt domains with (100) and (111) surface structures. Microcalorimetric results for CO adsorption showed higher values of initial heat for polyoriented Pt/C compared to preferentially oriented samples, thus accounting for a higher amount of highly unsaturated surface platinum atoms for Pt/C, in agreement with cyclic voltammetry. The catalytic performances of the samples showed a strong structure-sensitive character for both reactions, with TOF values following the trend Pt(100)/C > Pt(111)/C > Pt/C. Moreover, Pt(111)/C showed higher selectivities to unsaturated alcohol than Pt(100)/C and Pt/C samples.

Keywords: Nanoparticles; Platinum; Unsaturated aldehydes; Preferential surface orientation

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1. Introduction

The influence of the surface structure of a metal particle on its catalytic and electrocatalytic properties has been extensively reported [1–3]. Nevertheless, in the case of nanoparticles, the effect of the surface structure has been generally related to the so-called "size effect." Thus, some reactions have been shown to be strongly dependent on the particle size, whereas others are independent of the particle size. Boudart, in 1969, classified the first type of reactions as structure sensitive, and the second type as structure insensitive [4]. Later studies related the structure sensitive character of a given reaction to the structure sensitive character of the chemical bond formed between the reactant and the catalyst surface, the strength of which is affected by the local surface structure (relative concentration of steps, terraces, etc.) [5]. Nevertheless, the effect of metal nanoparticle size on catalytic or electrocatalytic activities is better understood at present than the influence of the shape/surface structure, since size control of the nanoparticles has generally been easier than shape/surface structure control. In spite of that, some papers have demonstrated that it is possible to synthesize quasi-monodispersed Pt nanoparticles of controlled particle shape and that the catalytic or electrocatalytic properties of these nanoparticles are under shape/surface structure control. Thus, El-Sayed et al. have reported about the effect of the shape of Pt nanoparticles on their catalytic properties [6–11]. Reactions such as propylene hydrogenation, electron-transfer and Suzuki reactions have revealed the importance of controlling the shape of the nanoparticles. Somorjai et al. have also shown the importance of the shape/surface structure using ethylene hydrogenation and carbon monoxide adsorption and oxidation as surface reaction probes [12,13]. Aldaz et al. have

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also reported the influence of the particle shape/surface structure on the electrocatalytic properties of Pt nanoparticles using ammonia oxidation and carbon monoxide adsorption–oxidation as model reactions [14,15].

From the point of view of the synthesis, and since the pioneer work of El-Sayed et al. [16], some contributions have appeared in relation to the preparation of nanoparticles with controlled shape [17–19]. These new methodologies have been mainly focused on the synthesis of Au and Pt nanoparticles with preferential shape/surface structure, due to the great number of reactions where this kind of materials can be employed.

An interesting model reaction is the hydrogenation of α,β-unsaturated aldehydes (acrolein, crotonaldehyde, cinnamaldehyde, etc.). Here, the selective hydrogenation of the carbonyl group, which is preferred because the unsaturated alcohols are valuable intermediates for the production of perfumes and pharmaceuticals, is very complicate, and with usual hydrogenation catalysts complete hydrogenation (both C=C and C=O groups) to yield the primary alcohol or selective hydrogenation of the olefin bond to give the saturated aldehyde are often obtained. Low selectivity toward crotyl alcohol is generally obtained with Pt supported catalysts, although it can be increased by using different approaches, such as an increment of the platinum particle size and by the use as support of a reducible oxide such as TiO_2 [20–22]. An increase in selectivity toward the unsaturated alcohol in the liquid phase hydrogenation of crotonaldehyde over Pt nanoparticles supported on SiO_2 and Al_2O_3 (from 9 to 35%) has been obtained by increasing their particle sizes (from 2 to 6 nm) [21]. It has been shown that the selectivity to the primary products, butyraldehyde and crotyl alcohol, critically depends on the Pt particle size [20]. The presence of a high fraction of Pt(111) surfaces in large Pt nanoparticles favors the adsorption of crotonaldehyde via the carbonyl bond, this leading to its preferential hydrogenation to yield the unsaturated alcohol, the product of interest. On the other hand, both double bonds can be adsorbed without any restriction on Pt(100) and on edges and corners [20]. Under these conditions, the saturated aldehyde is preferentially produced, as the hydrogenation of the C=C bond is favored by both thermodynamic and kinetics reasons. In this way, the synthesis of well-defined shape Pt nanoparticles represents a key point for the design of more active and selective catalysts for this kind of reactions.

Thus, the aim of this work has been to study the hydrogenation of crotonaldehyde and cinnamaldehyde over polyoriented and (100) and (111) preferentially oriented carbon-supported Pt nanoparticles, in order to assess the structure sensitive character of these reactions on platinum.

2. Experimental

Two different protocols have been used to prepare Pt nanoparticles. Polyoriented Pt nanoparticles were synthesized using sodium borohydride as reducing agent in the presence of citrate and using a methodology similar to that previously reported for the preparation of gold seed nanoparticles [23]. An aqueous solution containing 2.5×10^{-4} M H_2PtCl_6 and 2.5×10^{-4} M tri-sodium citrate was prepared. Then, the desired amount of ice cold 0.1 M $NaBH_4$ solution was added all at once with continuous stirring. After 30 min, an appropriate amount of carbon black (Vulcan XC-72) was added to the solution and stirred for 2 h. Finally, two or three NaOH pellets were added to produce the precipitation of the nanoparticles on the carbon support. After complete precipitation, the supported nanoparticles were washed 3–4 times with ultra-pure water.

On the other hand, preferentially oriented nanoparticles were prepared by using the so-called colloidal method [16,17]. Briefly, a variable amount of sodium polyacrylate (PA) aqueous solution was added to a 100 ml of an aged 1×10^{-4} M solution containing the desired Pt precursor. Thus, K_2PtCl_4 was employed for the synthesis of the "(100)-Pt" nanoparticles whereas H_2PtCl_6 was used for the "(111)-Pt" nanoparticles. After 20 min of Ar bubbling, the Pt ions were reduced by bubbling H_2 for 5 min. The reaction vessel was then sealed and the solution was left overnight. After complete reduction (12–24 h), an appropriate amount of carbon (Vulcan XC-72) was added and stirred for two hours. After that, two or three NaOH pellets were added to produce the precipitation of the supported nanoparticles. After complete precipitation, the nanoparticles were washed 3–4 times with ultra-pure water. All samples were prepared to obtain a platinum loading of 5 wt%. The particle size and morphology of all the supported nanoparticle samples were characterized by transmission electron microscopy (TEM).

For the electrochemical experiments, and due to the low Pt metal loading (5 wt%), unsupported Pt nanoparticles were employed. The procedure used for the electrochemical characterization of the nanoparticles has been previously reported [24–26]. The electrochemical measurements were performed in a 0.5 M H_2SO_4 solution at room temperature. Fresh electrolyte solutions were prepared every time an experiment was carried out from Milli-Q water and Merck sulphuric acid. A three-electrode electrochemical cell was used. The electrode potential was controlled using a PGSTAT30 AUTOLAB system. The counter electrode was a gold wire. Potentials were measured against a reversible hydrogen electrode (RHE) connected to the cell through a Luggin capillary. Potentials are quoted versus this reference electrode. Before each experiment, the gold collector was mechanically polished with alumina and rinsed with ultra-pure water to eliminate the nanoparticles from previous experiments.

Differential heats of CO adsorption were measured at 300 K in a Setaram BT2.15D heat-flux microcalorimeter using the method described in detail elsewhere [27]. The microcalorimeter was connected to a high vacuum (base pressure $<10^{-5}$ Torr) volumetric system employing Baratron capacitance manometers for precision pressure measurement (0.5×10^{-4} Torr). The maximum apparent leak rate of the volumetric system (including the calorimetric cells) was 10^{-5} Torr min^{-1} in a system volume of approximately 80 cm^3 (i.e., 10^{-5} µmol min^{-1}). The procedure for microcalorimetric measurements used in this study is described below: each sample (about 0.25 g) was treated ex situ in ultrapure hydrogen (99.999% with further purification, Air Liquide) for 1 h (2 K min^{-1} ramp, 200 ml min^{-1}) at 473 K