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Pt nanoclusters stabilized by N-doped carbon nanofibers for hydrogen production from formic acid

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ABSTRACT

The activities of Pt catalysts on carbon nanofibers with different nitrogen contents were compared for hydrogen production by formic acid decomposition. The catalysts contained a fraction of Pt clusters with a mean size of 1.0–2.3 nm and possibly a considerable fraction of Pt clusters with a diameter of less than 0.75 nm that were invisible by transmission electron microscopy. The activities of N-doped catalysts with low Pt contents ($\leqslant$1 wt.%) were 10 times higher than the activities of undoped catalysts. The N-doped catalysts demonstrated an improved selectivity to hydrogen and an increased resistance to CO inhibition. However, they were inactive for ethylene hydrogenation. These results are explained by the presence of electron-deficient, two-dimensional sub-nm sized Pt clusters stabilized by pyridinic nitrogen on vacancy sites. In accordance, the Pt-$4f_{7/2}$ binding energies measured by X-ray photoelectron spectroscopy were 0.6 eV higher for the N-doped samples than for the undoped ones.

1. Introduction

It has been shown recently that formic acid can be produced from biomass [1]. Hydrogen production by the catalytic decomposition of formic acid has generated much interest due to the possible application of formic acid as a source of molecular hydrogen [2–8] or as a hydrogenating agent [9,10]. The decomposition reaction has been used for over a century as a model reaction to distinguish catalysts favoring dehydrogenation (giving H_2 and CO_2) from those favoring dehydration (giving H_2O and CO). In current studies of formic acid decomposition, the main target is highly selective hydrogen production under mild reaction conditions.

Recently, Ojeda and Iglesia [6] concluded from their studies with Au/Al_2O_3 catalysts that Au species invisible by transmission electron microscopy (TEM) could be important for vapor-phase formic acid decomposition. Bi et al. [5] confirmed that samples with Au species of about 0.8 nm size supported on zirconia are several times more active than equivalent samples with Au particles of about 1.8 nm size in the liquid-phase decomposition of formic acid in the presence of water, triethylamine, or sodium formate. Finally,

in a very recent paper, Yi et al. [11] demonstrated that atomically dispersed Au species on ceria are extremely active, resistant to CO, and selective in vapor-phase formic acid decomposition.

Stabilization of isolated metal atoms and sub-nm clusters in order to prevent sintering is a problem. Carbon nanotubes and carbon nanofibers are considered to be potential materials for use as catalyst supports owing to their unique structural and textural characteristics and to the possibility of controlling their properties during synthesis [12–15]. Doping of the carbon-based supports with nitrogen is a possible way to stabilize supported nanosized metals [16–23].

Platinum is one of the best metals for electrocatalytic reactions such as methanol or hydrogen oxidation as well as oxygen reduction. Nitrogen doping gives a considerable enhancement in the electrocatalytic activity of Pt [20,21,24]. These electrocatalysts normally contain large amount of Pt (5–60 wt.%) and typical mean Pt particle sizes are 2–6 nm. However, the use of nitrogen-doped carbons as supports for heterogeneous catalysts has had little attention until now, although this topic is expected to develop [16]. Recently, we showed that N-doping of carbon nanofibers leads to some increase in the catalytic activity of 10 wt.% Pt samples in CO oxidation [13] and to an increased activity and stability of Ru catalysts in phenol wet air oxidation [25]. Kondo et al. [26] reported an increased durability of the Pt clusters supported on

N-doped graphite in H_2–D_2 exchange reaction as compared to those on undoped graphite.

In the present work, small concentrations of Pt (0.3 and 1 wt.%) were deposited on both N-doped and undoped carbon nanofibers to obtain Pt with very small mean particle sizes ⩽1.8 nm. The performance of these catalysts was compared with the performance of catalysts with 10 wt.% Pt on the same supports and with Pt powder. We showed for the first time that the catalysts doped by nitrogen gave significantly improved rates of hydrogen production from formic acid, higher selectivity to hydrogen and enhanced resistance to CO compared with the undoped catalysts, whereas they gave strongly decreased rates for ethylene hydrogenation. These observations are explained by suggesting that a considerable fraction of the Pt species is present in the form of electron-deficient, two-dimensional sub-nm Pt clusters invisible by regular TEM (<15 atoms), that these interacting strongly with the N-doped support, and that these Pt species were active in formic acid decomposition while being inactive in ethylene hydrogenation. The particle sizes and electronic properties of the Pt were characterized by TEM and X-ray photoelectron spectroscopy (XPS), respectively. The results of the literature density functional theory (DFT) calculations were used to help explain the results.

2. Experimental

Carbon nanofibers (N-CNFs) with 0, 3.4, and 7.5 wt.% N and with a helical morphology and a herringbone structure were synthesized by decomposition of an ethylene/ammonia mixture (0, 50, and 75 wt.% NH_3) over the 65 wt.% Ni/25 wt.% Cu/10 wt.% Al_2O_3 catalyst for 1 h at 823 K [13,14]. To remove the catalyst used in the decomposition, all the obtained materials were treated with concentrated HCl several times for several weeks at room temperature and then with a boiling 2 M HCl for 30 min. To remove Cl till its absence in the solution shown with an $AgNO_3$ probe, boiling in water for several times was used. The materials were dried in Ar flow at 443 K. The obtained supports 0N-CNFs (0 wt.% N), 3.4N-CNFs (3.4 wt.% N), and 7.5N-CNFs (7.5 wt.% N) had Brunauer–Emmett–Teller (BET) surface areas of 220, 290, and 200 $m^2\,g^{-1}$, respectively.

Platinum (0.3, 1, and 10 wt.%) was deposited by homogeneous precipitation from H_2PtCl_6 with NaOH. A known amount of acid was added to the water suspension of carbon support and stirred for 60 min at room temperature. Then, a stoichiometric amount of 0.5 M solution of NaOH was added dropwise at room temperature. The mixture was stirred and heated for 1.5 h at 343 K. The pH reached 8 at the end. This was followed by filtration and careful washing of the material in distilled water, drying and reduction in a 30 vol.% H_2/Ar mixture for 1 h at 523 K. A Pt black powder with a BET surface area of 30 $m^2\,g^{-1}$ was purchased from Alfa Aesar.

TEM images and energy-dispersive X-ray spectroscopy (EDS) data were obtained using a JEOL JEM-2010 microscope with accelerating voltage 200 kV. A high-angle annular dark field scanning transmission electron microscopic (HAADF/STEM) study was performed using a JEOL JEM-2100F microscope. At least 100 particles were used to calculate a mean Pt particle size for each of the samples. X-ray photoelectron spectra were recorded on an ES-300 photoelectron spectrometer (KRATOS Analytical) with an Al Kα source (1486.6 eV). The binding energy of Au-$4f_{7/2}$ at 84.0 eV was used for the spectra calibration. Special experiments on the determining of the Pt state in the 1Pt/7.5N-CNFs sample before and after reduction in hydrogen were performed at the BESSY II Synchrotron Centre (Berlin). The reduction in hydrogen was performed at 2.5×10^{-5} mbar for 2 h at 573 K. The sample was not contacted with air after the reduction. In this case, the radiation energy was 650 eV, and the spectrometer resolution was higher than that obtained with the KRATOS spectrometer.

Vapor-phase formic acid decomposition (2.0 vol.% HCOOH/He) and ethylene hydrogenation (0.5 vol.% C_2H_4/1 vol.% H_2/He) were performed with 7 mg of catalysts in a fixed-bed quartz reactor of 4 mm internal diameter. A total flow rate of 51 $cm^3\,min^{-1}$ was applied in all experiments. Formic acid (Sigma–Aldrich, 98–100%) was introduced into the system using a syringe pump (Sage). The activity data were collected at steady state after 1-h catalyst reduction (1 vol.% H_2/Ar) at 573 K followed by cooling in He to the reaction temperature. To prevent sintering, the Pt powder was reduced in the same H_2/Ar mixture during the temperature ramp of 20 K min^{-1} to 573 K. The sample was cooled in He immediately after reaching this temperature.

A 2.5 vol.% CO/He mixture with the same total flow rate as He was used for the CO effect study. The amounts of catalysts in these experiments were 7 and 30 mg for the N-doped and undoped samples, respectively. The reactants and products were analyzed by a gas chromatograph (HP-5890) fitted with a Porapak-Q column and a thermal conductivity detector [4,9]. Activation energies and turnover frequencies were determined at low conversions in the range of temperatures 343–483 K.

3. Results

3.1. Electron microscopy study

To determine the mean particle size in the synthesized catalysts, they were characterized by TEM (Figs. S1 and S2 in Supplementary Material, Table 1). The mean particle sizes for the 0.3 and 1 wt.% Pt catalysts were generally in the range 1.0–1.8 nm and were lower than those for the 10 wt.% Pt samples (1.6–2.3 nm), and some Pt-supported catalysts on N-doped carbons reported earlier in the literature [20]. The catalysts with 1 wt.% Pt without nitrogen (1Pt/0N-CNFs) and with 7.5 wt.% N (1Pt/7.5N-CNFs) possessed quite similar mean particle sizes (1.2–1.3 nm) and equal standard size deviations. An increase in Pt content in the catalysts with 7.5 wt.% N from 1 wt.% (1Pt/7.5N-CNFs) to 10 wt.% (10Pt/7.5N-CNFs) led to an increase in the mean particle size from 1.2 to 1.6 nm (Fig. S2 and Table 1). The mean particle size in the catalysts with 10 wt.% Pt decreased with nitrogen doping from 2.3 to 1.6 nm.

As the mean particle size for the 0.3 and 1 wt.% Pt catalysts was close to the sensitivity of the used TEM, an EDS/TEM study of the 1Pt/7.5N-CNFs and 1Pt/0N-CNFs samples was carried out, and some results are shown in Fig. S3. This study demonstrated the presence of several regions in the samples, where Pt particles were not clearly seen by TEM. However, Pt was seen in these regions by EDS. This generally indicates that a fraction of TEM-invisible Pt species exists in the catalysts. The invisible Pt could be present as sub-nm sized clusters or even in an atomically dispersed state. To confirm this, a study with more sensitive HAADF/STEM method was performed (Fig. 1 and Table 1). Two samples with 1 wt.% Pt after the reaction and one with 0.3 wt.% Pt before the reaction were taken for this research. The mean particle sizes determined by HAADF/STEM were quite similar to those obtained by TEM (Table 1); however, the shapes of particle size distributions were very different. The measurements by HAADF/STEM demonstrated much stronger left-hand part in the distributions than in those determined by TEM. This has to be explained by higher sensitivity of this method to smaller particles (0.75–1 nm). Particles smaller than 0.75 nm can hardly be seen by this method either. No difference in the samples before and after the reaction was found.

The shape of the distributions characterized by the most intensive left-hand bar may indicate that a considerable fraction of clusters with a size of <0.75 nm (<15 atoms) is present in the studied samples. This is in agreement with the EDS/TEM studies (Fig. S3), indicating the presence of TEM-invisible clusters or atoms. This