Electrochemical Evidence of Strong Electronic Interaction of PtRu on Carbon Nanotubes with High Density of Defects
Electrochemical Evidence of Strong Electronic Interaction of PtRu on Carbon Nanotubes with High Density of Defects

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We show that carbon nanotubes (CNTs) with high density of defects can present a strong electronic interaction with nanoparticles of Pt–Ru with average particle size of 3.5 ± 0.8 nm. Depending on the Pt–Ru loading on the CNTs, CO and methanol oxidation reactions suggest there is a charge transfer between Pt–Ru that in turn provokes a decrease in the electronic interaction taking place between Ru and Pt in the PtRu alloy. The CO stripping potentials were observed at about 0.65 and 0.5 V for Pt–Ru/CNT electrodes with Pt–Ru loadings of 10 and 20, and 30 wt %, respectively.

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Experimental

The carbon fibers studied in this work were synthesized via methanol chemical vapor deposition on Mn, Co catalysts using zeolite substrates at 650°C, as described elsewhere.12,13 Before impregnation with the Pt–Ru nanoparticles, the fibers and the zeolite were purified in concentrated HCl/HF under reflux, rinsed several times with Millipore water, and dried under vacuum at 100°C. This chemical treatment was applied to eliminate the catalyst particles used in the CNT growth, as detected by energy-dispersive X-ray (EDX). The CNTs were prepared once only because our reactor method after pre-evacuation for 3 h at 150°C.

All electrochemical measurements were carried out using a three-electrode cell at 25°C under argon flux. A platinumized platinum gauze and a reversible hydrogen electrode (RHE) were used as counter and reference electrodes, respectively. A mirror-finished polished glassy carbon disk electrode (Sigradur G from Hochtemperatur Werkstoffe GmbH, 9 mm diam) was used as a substrate for the thin-film Pt–Ru/CSCNT electrodes in the electrochemical measurements. The thin-film electrodes were prepared using the method developed by Schmidt et al.19 In short, the catalyst loading was ultraconsistently dispersed in water (2 mgcat mL−1), and 40 μL of the suspension was pipetted onto the substrate. After evaporation of the solvent under argon flow, a diluted Nafton solu-
oxidation of adsorbed CO to CO\textsubscript{2}. CO dissolved in the electrolyte was removed by degassing the electrolyte with N\textsubscript{2} for 30 min. For the CO stripping, CO was bubbled into the electrochemical cell and the potential was set to 0.9 V vs RHE at a scan rate of 20 mV s\textsuperscript{-1}. Potentials higher than 0.9 V were avoided in order to prevent ruthenium dissolution.

Before the CO stripping and methanol oxidation reactions were studied, the thin-film electrodes were cycled between 0.07 and 0.9 V vs RHE in an oxygen-free solution of 0.5 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} in order to control the system cleanliness. For the CO stripping, CO was bubbled into the electrochemical cell and the potential was set to 70 mV for 15 min to ensure CO adsorption. This potential was chosen to control the system cleanliness. For the CO stripping, CO was bubbled into the electrochemical cell and the potential was set to 0.9 V vs RHE at a scan rate of 20 mV s\textsuperscript{-1}. Potentials higher than 0.9 V were avoided in order to prevent ruthenium dissolution. Subsequently, the electrode (rotating disk configuration) was transferred to a second cell containing a 2 mol L\textsuperscript{-1} CH\textsubscript{3}OH + 0.5 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} solution, and the behavior of the catalysts was studied by cyclic voltammetry and chronoamperometry. The chronoamperometric currents were recorded for 30 min at a potential of 0.5 V. To determine the electroactive area of the electrodes, the value of 420 \mu C cm\textsuperscript{-2} was used as the oxidation charge of one monolayer of adsorbed CO on a smooth Pt surface.

Results and Discussion

Figures 1A-C show TEM images of CSCNT and the Pt–Ru/CSCNT catalysts prepared with three different metal loadings, i.e., 10, 20, and 30 wt %. In all cases there are truncated conical graphene layers stacked with a hollow central channel in them (Fig. 1D). The surface of the CSCNT is rich in dangling bonds or defects because each base of the cone defines an edge, as opposed to multiwalled carbon nanotubes where the walls are planar. In the CSCNTs, the truncated conical graphenes are connected by van der Waals forces in such a way that it is possible to insert chemical species into the gaps.

The mean particle size of the well-dispersed Pt–Ru particles supported on the CSCNTs was determined using the relation \( d_{\text{TEM}} = (\sum n_{i}d_{i})/n \), where \( n_{i}, d_{i}, \) and \( n \) are the number, particle diameter, and the total number of particles, respectively. The mean particle size was 3.5 ± 0.8, 4.0 ± 0.8, and 3.7 ± 0.7 nm for the 10, 20, and 30 wt % catalysts, respectively. The average diameter of the particles and the error were obtained from several pictures that are not shown here. The zones with smaller agglomeration were chosen for determination of the parameters \( n_{i} \) and \( d_{i} \).

These results suggest that the catalyst particle size distribution on the various Pt–Ru/CSCNT catalysts used in this work are similar, independent of the Pt–Ru loading, as expected from the microemulsion method. This is because the water-to-surfactant ratio \( (\omega_{0}) \) was kept constant during the synthesis of the Pt–Ru nanoparticles.

To determine the Pt/Ru atomic ratio in the Pt–Ru alloy obtained by the microemulsion method, all samples were characterized by XRD and EDX. Figure 2 shows the X-ray patterns of the Pt–Ru/CSCNT catalysts as well as the pattern for the CSCNTs carbon nanotubes and Pt/C E-TEK. The X-ray diffractograms of the CSCNTs displayed 2 intense peaks at around 2\theta = 26° (not shown) and 43°, and 2 other less intense peaks at around 2\theta = 53 and 78.5°, which can be attributed to the CSCNT structures. Neither the diffraction peak at 2\theta = 28°, corresponding to the most intense diffraction peak associated with tetragonal RuO\textsubscript{2}, nor hexagonal close-packed ruthenium phases were observed. To evaluate the degree of Pt–Ru alloy in the fcc structure, we calculated the lattice parameter \( (a_{\text{fcc}}) \) by using the (220) diffraction peaks. The \( a_{\text{fcc}} \) values obtained for the Pt–Ru/CSCNT catalysts were 0.3881 nm for 10%, 0.3868 nm for 20%, and 0.3860 nm for 30% metal loading. As for the 20% Pt\textsubscript{50}Ru\textsubscript{50}/C E-TEK, the lattice constant was 0.3887 nm. The \( a_{\text{fcc}} \) obtained for the Pt–Ru/CSCNT catalysts are in good agreement with the value of the Pt–Ru/CSCNT catalysts.

![Figure 1](image1.png)

**Figure 1.** TEM micrographs of (A) 10% Pt–Ru/CSCNTs, (B) 20% Pt–Ru/CSCNTs, (C) 30% Pt–Ru/CSCNTs, and (D) HRTEM of stacked cones of the typical tube present in the powder after purification in HF/HCl.

![Figure 2](image2.png)

**Figure 2.** X-ray diffractograms of (a) CSCNTs, (b) 10% Pt–Ru/CSCNTs, (c) 20% Pt–Ru/CSCNTs, (d) 30% Pt–Ru/CSCNTs, (e) 20% Pt–Ru/C E-TEK, and (f) 20% Pt/C E-TEK.
bulk Pt$_{38}$-Ru$_{52}$ alloy (0.38624 nm) determined by Gasteiger et al.\textsuperscript{18}

EDX analyses thus confirm that the microemulsion method predominantly yields catalysts with composition Pt$_{50}$Ru$_{50}$.

The electrochemical performance of the Pt–Ru/CSCNT catalysts was then probed. Figure 3 shows the CO stripping voltammograms on thin-film Pt–Ru/CSCNT and Pt–Ru/C E-TEK catalysts at a CO adsorption potential of 0.07 V and sweep rate of 20 mV s$^{-1}$ between 0.05 and 0.9 V vs RHE. These conditions allowed elimination of all adsorbed CO during the first cycle, and the current in a second cycle coincided with the baseline in the case of the pure supporting electrolyte. The voltammograms revealed that the shape and position of the CO oxidation peak depend on both the metal loading and the substrate used as support for the nanoparticles. For the Pt–Ru/CSCNT catalysts containing 20 and 30 wt % Pt–Ru, there was a cathodic shift of at least 100 mV due to CO oxidation, compared with Pt–Ru/C E-TEK. Although no variation in the position of the CO oxidation peak of the 20 and 30% Pt–Ru/CSCNT catalysts (0.51 V vs RHE) was observed, the peak shape was noticeable in the case of 30% Pt–Ru/CSCNTs compared with 20% Pt–Ru/CSCNTs and Pt–Ru/C E-TEK catalysts. Both the peak intensity and hysteresis change slightly with catalyst loading and the type of carbon support. The onset of methanol oxidation occurs at about 0.4 V for all the loadings and carbon supports. However, Fig. 4 reveals that the 20% Pt–Ru/CSCNT catalyst presents the best kinetics for methanol oxidation, because its oxidation peak is more intense than those observed for the other catalysts.

The electrochemical performances of the Pt–Ru/CSCNT catalysts containing 20 and 30% Pt–Ru were then probed. Figure 3 shows the CO stripping voltammograms on thin-film Pt–Ru/CSCNT and Pt–Ru/C E-TEK catalysts at a CO adsorption potential of 0.07 V and sweep rate of 20 mV s$^{-1}$ between 0.05 and 0.9 V vs RHE. These conditions allowed elimination of all adsorbed CO during the first cycle, and the current in a second cycle coincided with the baseline in the case of the pure supporting electrolyte. The voltammograms revealed that the shape and position of the CO oxidation peak depend on both the metal loading and the substrate used as support for the nanoparticles. For the Pt–Ru/CSCNT catalysts containing 20 and 30 wt % Pt–Ru, there was a cathodic shift of at least 100 mV due to CO oxidation, compared with Pt–Ru/C E-TEK. Although no variation in the position of the CO oxidation peak of the 20 and 30% Pt–Ru/CSCNT catalysts (0.51 V vs RHE) was observed, the peak shape was noticeable in the case of 30% Pt–Ru/CSCNTs compared with 20% Pt–Ru/CSCNTs and Pt–Ru/C E-TEK catalysts. Both the peak intensity and hysteresis change slightly with catalyst loading and the type of carbon support. The onset of methanol oxidation occurs at about 0.4 V for all the loadings and carbon supports. However, Fig. 4 reveals that the 20% Pt–Ru/CSCNT catalyst presents the best kinetics for methanol oxidation, because its oxidation peak is more intense than those observed for the other catalysts.

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Figure 4. Methanol oxidation on (a) 20% Pt–Ru/C E-TEK, (b) 20% Pt–Ru/CSCNT, (c) 30% Pt–Ru/fiber, and (d) 10% Pt–Ru/CSCNT catalysts in 0.5 mol L⁻¹ H₂SO₄ + 2 mol L⁻¹ CH₃OH at a scan rate of 20 mV s⁻¹.

Conclusions

This paper shows that the CSCNT is a carbon support that has strong electronic interaction with the Pt–Ru catalyst. The surfaces of CNTs rich in defects are very interesting for the adsorption of Pt–Ru nanoparticles, because good dispersion and low agglomeration of the Pt–Ru particles can be achieved independent of the Pt–Ru load. The electrochemical data suggest that there is a charge transfer between Ru and C that changes the activity of Pt. The CO stripping for 10% loading occurs at about 0.65 V, while for other compositions the stripping takes place at about 0.5 V. The structure of CSCNTs, composed by several open tips of CNTs or a tube with high density of defects, should lead to a more reactive surface than the walls of multiwalled or single-walled CNTs, thus increasing the interaction of carbon with other chemical species. Electronic interaction between Au and single-walled CNTs has also been detected which is strong enough to modify their electronic structure.²⁴ CSCNTs are a kind of CNT that can open new perspectives for clusters of catalyst loading because they are electronic conductors that can affect catalyst activity. In addition, the electrocatalytic activity of Pt–Ru on CNTs in the oxidation of methanol decreases in the following order: 20% Pt–Ru/CNTs > 30% Pt–Ru/CNTs > 10% Pt–Ru/CNTs. This variation suggests that there are sites that interact with Pt–Ru nanoparticles differently on the surface of CSCNTs. It is well known that the diameter and density of defects on the surface of CNTs can change with CNT length. In addition, the surface of the tubes can also contain amorphous carbon.

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