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Electrocatalytic hydrogenation of phenol on dispersed Pt: Effect of metal electrochemically active surface area and electrode material

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The influence of the electrochemically active surface area on the electrocatalytic activity for phenol hydrogenation has been investigated. It is shown that the current efficiency of the reaction does not change significantly for Pt loadings between 2% and 30% whereas a significant decrease in activity is observed for 60% Pt loading. This is used to classify this reaction in terms of its sensitivity. The influence of the electrode material and the alloying component on both current efficiency and on the reaction selectivity is determined. The material and the alloying component which exhibited the best efficiency and selectivity are deduced.

1. Introduction

Catalytic reactions have been divided into two types in terms of their sensitivity [1]. The first type would be the facile or structure-insensitive reactions for which the specific activity of the catalyst does not change with the catalyst preparation or its particle size or electrochemically active surface area [2] whereas the second type corresponds to structure sensitive or demanding reactions which are sensitive to these parameters. In the case of electrocatalytic reactions, the electroreduction of oxygen in a particle range of below 5 nm [3], the oxidation of adsorbed hydrogen atoms [4] and the oxidation of propane [6] on platinum have been reported as demanding reactions. On the other hand, the oxidation of molecular hydrogen [5, 6] and the hydrogen evolution reaction have been reported as facile reactions [6]. Recently, we reported the electrocatalytic hydrogenation of phenol on dispersed Pt on Vulcan-72 electrodes [7]. The influence of the electrode material on the current efficiency and the selectivity of the reaction was also studied [8–10]. Most of the studies on the electrocatalytic hydrogenation of phenol have been realized on platinized platinum (Pt/Pt) electrodes. In one work the effect of the electrode material was studied by using electrodeposited Pt, Rh or Pd on carbon rods [11]. In the same study, it was shown that the highest electrocatalytic activity corresponded to Rh and the lowest to Pd. This work was not devoted to the hydrogenation of phenol on noble metals dispersed onto carbon. However, the effect of the electrode material and alloying component on the efficiency and selectivity of the reaction is lacking in the literature. In this paper we investigated the effect of the electrochemically active surface area on the electrocatalytic activity of dispersed Pt electrodes for phenol hydrogenation. The influence of the electrode material and alloying component on the current efficiency and the selectivity of the reaction are also studied.

2. Experimental details

Dispersed Pt was obtained by precipitating Pt from a chloroplatinic acid solution by the addition of sodium formate in the presence of Vulcan XC-72R carbon (Cabot Canada). The metal particle size was varied by preparing catalysts containing different Pt:C ratios. Pt alloys were purchased from E-TEK Inc. and characterized by X-ray diffraction (XRD) analysis. The details of the electrode preparation and electrochemical cell are given elsewhere [7, 12]. The catholyte and anolyte consisted of H_2SO_4 0.05 M. 470 mg of phenol was added to 100 ml of catholyte. All the electrolysis were carried out at a total cell current of 40 mA and 60 °C (±2 °C) using a Kepco current supply and a 640 ESC coulometer. The electrochemically active surface areas were determined by cyclic voltammetry using a PAR 270 potentiostat monitored by M270 cyclic voltammetry software. XRD analysis were performed with a Siemens KV IV diffractometer using CuK_α and a scan speed of 1° $\min^{-1}$. Reaction products and current efficiencies were determined by their FTIR spectra (Perkin Elmer system 2000) and gas chromatography (Hewlett Packard 5890 series II). The electron micrographs were obtained by mounting the powder on a copper grid and using a Jeol FX2000 model. The image analysis software by IBAS Kontron was used to determine the particle size distribution and the average particle size.

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Table 1. Some physico-chemical characteristics of Pt/C and Pt/Pt electrodes

Electrode	*Pt/C 2%*	*Pt/C 5%*	*Pt/C 10%*	*Pt/C 20%*	*Pt/C 30%*	*Pt/C 60%*	*Pt/Pt 100%*
S_{CV}^* (m^2/g_{Pt}) ± 5%	139	90	44	35	15	13	16
Partical size (nm) ± 5%	2.75†	3.15†	3.26†	3.77†	3.79†	5.58†	17.6‡
$S_{TEM}^§$ (m^2/g_{Pt}) ± 5%	101	89	86	74	73	50	

* Electrochemically active surface area determined by cyclic voltammetry.

† Determined from TEM micrographs.

‡ Determined from TEM micrographs.

§ Specific surface area determined from TEM average particle diameter.

3. Results and discussion

3.1. *Effect of the particle size or the electrochemically active surface area*

Figure 1 shows the current efficiencies (CE) for the electrocatalytic hydrogenation of phenol on 2% Pt/C-based electrode containing 4 mg of platinum prepared from catalysts with different Pt loadings. The last point with a Pt content of 100% corresponds to a platinized platinum (Pt/Pt) electrode with 4 mg of electrodeposited Pt. Electrodes prepared from catalysts with Pt loadings ranging from 2% to 30% present high current efficiencies (between 63% and 73%) whereas the Pt/C electrode prepared from 60% Pt/C catalyst and the Pt/Pt electrode present much lower current efficiencies (24% and 8%, respectively). The differences in the current efficiencies may be attributed to the physico-chemical characteristics of the electrodes or to their electrochemically active surface area. The X-ray photoelectron spectroscopy (XPS) and XRD analysis showed no apparent differences in terms of chemical composition or crystallographic orientation between Pt/C and Pt/Pt electrodes or amongst Pt/C electrodes of different Pt loadings [13]. The electrochemically active surface areas determined from the coulombic charge associated with the hydrogen adsorption peaks are presented in Table 1. When the platinum loading decreases the electrochemically active surface area increases. This may be due to a decrease in the platinum particle size. Transmission electron microscopy (TEM) and XRD analysis were used to study the variation of the Pt particle size as a function of its loading in the catalyst. Figure 2 shows a bright field electron micrograph of the 2% Pt supported on carbon. The platinum appears as small dark particles uniformly distributed on carbon particles. The TEM photographs were further analysed to estimate the distribution and the average particle size. For each catalyst at least 300 particles were considered for the determination of the average particle diameter. In the case of 2% Pt/C, although the particle size may vary between 1.0 and 5.5 nm, approximately 80% are between 1.0 and 4.0 nm with an average particle size of 2.75. The average particle size for platinum catalysts with higher platinum loadings are presented in Table 1. As expected, the particle size increases as the platinum to carbon ratio increases. The specific surface areas of the electrodes calculated from TEM data are

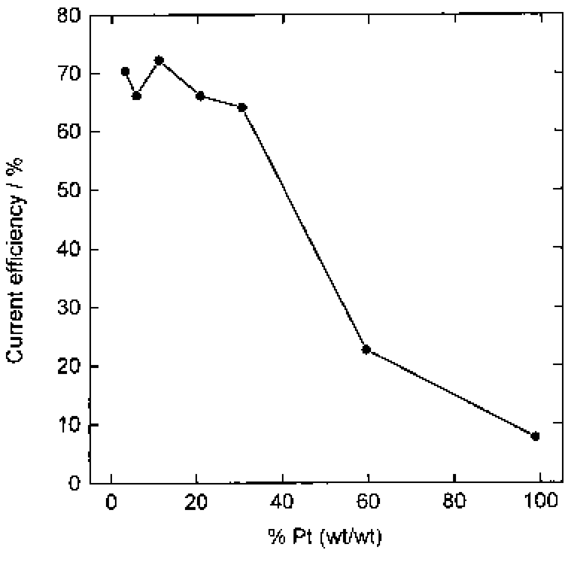

Fig. 1. Current efficiency (%) for phenol electrocatalytic hydrogenation as a function of the Pt loading in the catalyst.

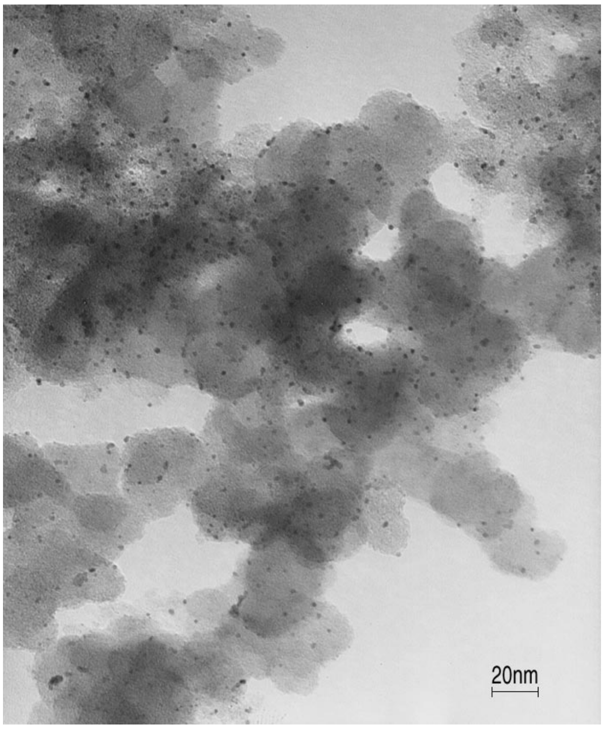

Fig. 2. Bright field electron micrograph of 2% Pt on carbon catalyst.

also listed in Table 1. The following relation was used to calculate these values:

$$S = \frac{6 \times 10^3}{\rho d} \qquad (1)$$

where ρ is the platinum density, d is the particle diameter in nanometre and S is the specific surface area in m^2 per g_{Pt}. As seen from Table 1, the platinum surface areas determined by CV and TEM are different. These discrepancies may be considered in terms of several limitations that apply to the CV and TEM techniques, as indicated elsewhere [14–19]. In particular, if TEM techniques are used, the total area of the Pt on the carbon is considered in the calculation, thereby including the area partially blocked as a consequence of anchoring the Pt on the carbon substrate. Nonetheless, in the case of platinized platinum, the value of 17.6 nm is in good agreement with the measured electrochemically active surface area (16 m^2 per g_{Pt}) and with the reported value in other studies [20]. The current efficiencies presented in Fig. 1 correspond to electrodes with the same amount of platinum (2%) but prepared from catalysts of different Pt particle size. To study the effect of the electrochemically surface area on the current efficiency, hydrogenation was performed on electrodes with the same electrochemically surface area prepared from catalysts with different Pt loadings. Figure 3 shows the current efficiencies of the electrodes with a real electrochemically surface area of 0.2 m^2 as a function of the Pt loading in the original catalyst used to prepare the electrode. Again the electrode prepared from the catalyst containing 60% Pt has a much lower current efficiency (40%) than those made from a catalyst with a lower Pt loading. Therefore, the decrease in the electrochemically surface area alone can not explain the observed decrease in the current efficiency. On the other hand, no apparent difference in surface composition (other than the ratio between Pt and C), chemical state of Pt or crystallographic orientation among the electrodes was detected by XPS or XRD analysis [13]. Consequently, a fundamental question arises: is the difference in electrocatalytic performance for phenol hydrogenation related to the metal particle size or electrochemically active surface area? It has been suggested that the particle size or electrochemically active surface area effect on the electrocatalytic properties of the oxygen reduction reaction would be observed for electrocatalysts containing particles smaller than 4 nm where the most variation in the fraction of atoms at vertices, edges or link sites is expected [5, 6, 21–25]. However, Figure 1 shows that the current efficiency of phenol hydrogenation does not change significantly for electrodes with platinum loadings of 2% to 30%. This may be an indication that phenol hydrogenation on highly dispersed Pt electrodes is not a structure-sensitive reaction. Effectively, between 2% and 30% platinum loadings, the variation of the electrochemically active surface area is significant, but the current efficiency of phenol hydrogenation is practically constant.

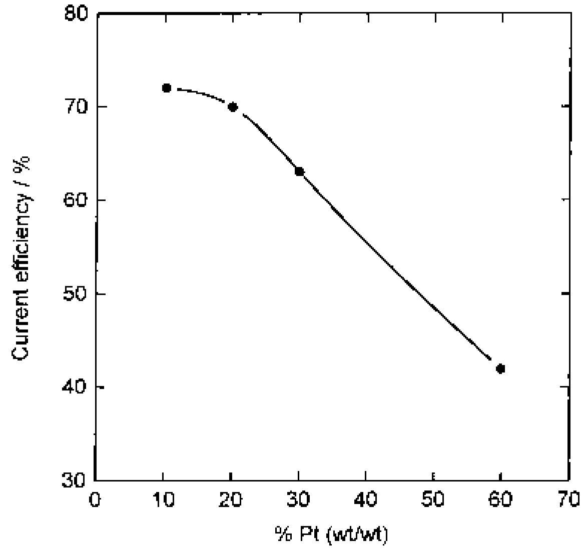

Fig. 3. Current efficiency (%) for phenol electrocatalytic hydrogenation as a function of the Pt loading in the catalyst used to prepare electrodes with a real electrochemically surface area of 0.2 m^2.

3.2. *Effect of the electrode material and alloying component*

The effect of the metal catalyst was investigated by using different types of electrode material dispersed on carbon support (Vulcan XC -72). The results are listed in Table 2. All the experiments were carried out at the same conditions of current density, temperature and phenol concentration. As seen from entries 1 to 4, Pt and Rh-based electrocatalysts present higher electrocatalytic activity for phenol hydrogenation than Ru or Pd-based electrocatalysts when used at the same metal loading in the electrode (2%). Ru and Pd-based electrodes, despite their double atomic concentration compared to Pt electrode, show a much lower electrocatalytic activity (10% and 15% of current efficiency, respectively). The low activity of Pd is in agreement with results observed during the catalytic hydrogenation of phenol [26]. It was reported that when using different metals dispersed on carbon support, the catalytic activity in aqueous solution decreases in the following order: Rh>Ir>Pt>Ru>Pd. As seen from Table 2, in the case of the electrocatalytic hydrogenation, the activity follows the order: Pt ≈ Rh>Pd>Ru. Contrary to the catalytic hydrogenation, the difference in performance between dispersed Pd and dispersed Ru electrodes is not significant. However, these two electrodes present very different results in terms of the reaction product selectivity. As seen in Table 2, in the case of the Pd-based electrode, cyclohexanone is the major product of the electrolysis (entry 2) whereas in the case of Ru electrode, cyclohexanol is practically the only reaction product (entry 3). In the case of Pt electrode, the selectivity changes as a function of electrolysis time. For example, after the passage of 1.2 F mol^{-1}, the

Table 2. Current efficiencies and reaction selectivity for electrocatalytic hydrogenation of phenol on different electrode materials

Entry	*Electrode*	*Catalyst used to prepare the electrode*	*C. E.** / % ± 2%	*Selectivity*† / ± 2%
1	Pt 2%	Pt 10%	72	2.0
2	Pd 2%	Pd 10%	15	0.11
3	Ru 2%	Ru 10%	10	72
4	Rh 2%	Rh 10%	64	0.9
5	Pt 2%, Cr 0.53%	Pt/Cr 10% (50/50 a/o)	54	2.5
6	Pt 2%, V 0.52%	Pt/V 10% (50/50 a/o)	57	5.2
7	Pt 2%, Co 0.6%	Pt/Co 10% (50/50 a/o)	71	19.2
8	Pt 2%, Ir 0.2%	Pt/Ir 10% (80/20 a/o)	60	2.8
9	Pt 2%, Ir 0.2%	Pt/It 10% (80/20 a/o)	62	2.8

* Current efficiency after the passage of 1.2 Fmol^{-1}

† defined as the ratio moles of cyclohexanol : moles of cyclohexanone.

ratio between cyclohexanol and cyclohexanone is 2 (65% of cyclohexanol and 35% of cyclohexanone) whereas after passing 6 F mol^{-1} of charge, the ratio increases to 19 (95% of cyclohexanol and 5% of cyclohexanone). The same type of behaviour has been reported for the catalytic hydrogenation of phenol on Raney nickel [26]. Entries 5, 6 and 7 correspond to the electrocatalytic hydrogenation on some Pt alloys with a 1:1 ratio between Pt and a first row transition metal. It may be noted that with the same Pt loading (i.e., 2%), a lower current efficiency is obtained on Pt–Cr/C and Pt–V/C-based electrodes (entries 5 and 6, respectively) compared to Pt/C-based electrode (entry 1) and the selectivity is practically unchanged. However, in the case of the Pt–Co/C-based electrode while the observed current efficiency is as high as that of Pt/C-based electrode, a much higher selectivity for cyclohexanol formation is obtained (entry 7). Therefore, it may be seen that although the tested platinum alloys are not more active than Pt for phenol hydrogenation, the selectivity of the reaction is highly affected by the alloying component. The Pt–Co/C-based electrode presents the highest selectivity for cyclohexanol formation and Pt-Ir/C or Pt–Rh/C-based electrodes present the same efficiency and selectivity for cyclohexanol production.

4. Conclusion

The current efficiencies of the electrocatalytic hydrogenation of phenol on Pt/C-based electrodes of different particle sizes or electrochemically active surface area indicate that this reaction is not structure sensitive. The current efficiency and the selectivity of the reaction varies depending on the electrode material. The highest activity corresponds to Pt/C-based electrode whereas the most selective electrode for cyclohexanol production is obtained with Ru/C-based electrode. The Pd/C-based electrode exhibited the lowest efficiency and selectivity for the cyclohexanol formation. Among the Pt alloys tested in this work, Pt–Co/C-based electrode (Pt–Co), has the highest activity (comparable to that of Pt/C-based electrode) and the highest selectivity for cyclohexanol formation (significantly higher than that of Pt/C). The Pt–Ir/C-based electrode or the Pt–Rh/C-based electrodes exhibited the same activity and selectivity for the cyclohexanol production.

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