makes barrier for the path A. That of CH_3O-NO_2 as well as R^2-R^1 groups affects easiness of rotation for the path B. It is easily expected that **1** has the lowest barrier in the three molecules because both R^1 and R^2 are hydrogens. The methyl substitution on C_β (**2**) gives additional barrier by 2-3 kcal/mol to that for **1**. Because of having methyl and isopropyl groups, **5** has the highest energy barrier for the rotation. The energy height for the path B is lower than that for the path A for **5**. The conformer **b**, therefore, forms through the path B in the nitro olefins having bulky substitutents on R^1 and R^2.

The magnitude of the hyperconjugative interaction between the C_α anion and the C-O σ^* orbitals are largely related to the easiness of the process.[16] As discussed above, MNDO calculations underestimate the interaction. The energy barriers for th paths A and B are, probably, larger than those calculated with the semiempirical method. Unfortunately, the MNDO calculations could not describe the absolute difference of the barrier height between **3** and **4** or **5**, i.e., the intermediate with R^2 = Me is calculated to have a barrier similar to those for R^2 = Et and i-Pr. This is probably an artifact resulting from crude calculations. The smaller substituent is expected to give lower barrier than those for larger substituents seen in the relation between **1** and **2** of Figure 6. If this is true in the difference between **3** and **5**, we can expect that the anti/syn ratio of the methyl system is worse than that for the ethyl system. The anti/syn ratios for **3**, **4**, and **5** are 85/15, 98/2, and 98/2, respectively.

Experimental Section

Nitro olefins were prepared from dehydration of corresponding nitro alcohols. ^1H NMR spectra were recorded on Hitachi R-250H at 250 MHz. GLC analyses were carried out on Simadzu GC-8A.

Preparation of β-Nitro Ethers: *anti*-2-Methoxy-3-nitrobutane (13). To a solution of sodium methoxide, which was in situ generated from sodium hydride (60%, 606 mg) and methanol (1 mL), in THF (10 mL) was added 2-nitro-2-butene (525 mg, 5.2 mmol), and the resulting solution was stirred for 24 h at room temperature. The reaction mixture was cooled at -78 °C, and acetic acid was added (1 mL) and stirred for additional 1 h. Then the solution was poured into water, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine one time and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo after filtration, and the residue was subjected to column chromatography (silica gel/hexane-ethyl acetate, 20:1) to give **13** in 46% yield (317 mg). The anti/syn ratio was determined by GLC analysis: ^1H NMR ($CDCl_3$) δ 1.22 (d, J = 6.1 Hz, 3 H), 1.53 (d, J = 6.7 Hz, 3 H), 3.36 (s, 3 H), 3.89 (dq, J = 4.9, 6.2 Hz, 1 H), 4.48 (dq, J = 4.8, 6.8 Hz, 1 H).

The other β-nitro ethers were prepared via the same procedure. The spectral data were as following. ***anti*-2-Methoxy-3-nitropentane (14)**: ^1H NMR ($CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3 H), 1.22 (d, J - 6.1 Hz, 3 H), 1.88-2.09 (m, 2 H), 3.38 (s, 3 H), 3.64 (quint, J = 6.1 Hz, 1 H), 4.34 (ddd, J = 3.6 Hz, J = 6.1, 10.4 Hz, 1 H). ***anti*-2-Methoxy-4-methyl-3-nitropentane (15)**: ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 6.7 Hz, 6 H), 1.26 (d, J = 6.1 Hz, 3 H), 2.33 (m, J = 6.7 Hz, 1 H), 3.40 (s, 3 H), 3.71 (quint, J = 6.1 Hz, 1 H), 4.41 (dd, J = 6.1 Hz, J = 7.9 Hz, 1 H).

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Electrocatalytic Hydrogenation Using Precious Metal Microparticles in Redox-Active Polymer Films

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Glassy carbon felt electrodes have been modified by electrodeposition of poly(pyrrole-viologen) films (derived from *N,N'*-dialkyl-4,4'-bipyridinium salts), followed by electroprecipitation of precious metal (Pt, Pd, Rh, or Ru) microparticles. The resulting electrodes have been proved to be active for the electrocatalytic hydrogenation of conjugated enones (2-cyclohexen-1-one, cryptone, carvone, isophorone), styrene, and benzonitrile in aqueous media (pH 1). Despite low loadings of metal catalysts, high electric and products yields and a long term stability of these cathodes have been observed. The influence of the metal loading and the polymer structure on the catalytic efficiency as well as the selectivity obtained according to the metal catalyst used have been studied. Comparison with results previously reported for other catalytic cathodes like Pt/Pt, Pd/C, or Raney nickel electrodes proves the high efficiency of these metal microparticles within redox polymer film based electrodes.

Introduction

Electrocatalytic hydrogenation has never achieved the same success as catalytic hydrogenation even in the laboratory, despite the advantage of very mild conditions (room temperature and atmospheric pressure) normaly employed in electrochemical synthesis. In electrocatalytic hydrogenation, chemisorbed (active) hydrogen is formed directly at the electrode surface. Thus, the kinetic barrier for dissociation and mass transport of poorly soluble molecular hydrogen are bypassed and the reaction conditions are much milder than in regular catalytic hydrogenation. In comparison with conventional electrosynthesis, electrocatalytic hydrogenation offers selective and unusual

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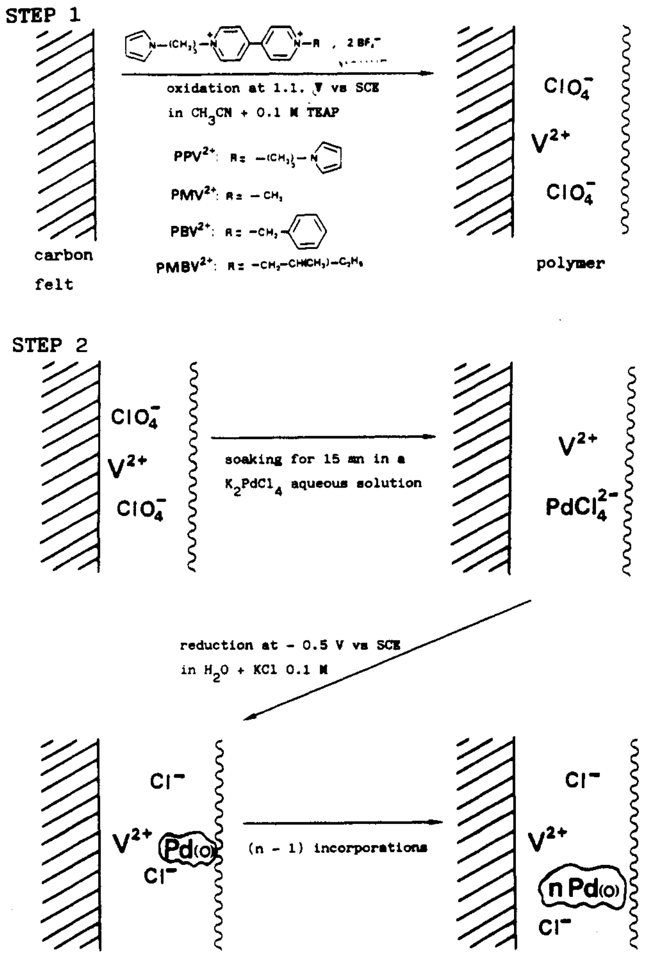
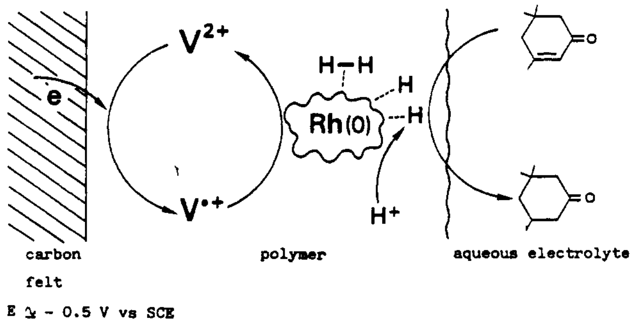
Scheme I. Preparation of a Catalytic Electrode for Hydrogenation (V^{2+}: Viologen Units Linked to the Polypyrrole Film)



reductions, at much less negative potentials than when the initial step is electron transfer, i.e., reduces the energy consumption.

The lack of interest for electrocatalytic hydrogenation can be mainly attributed to the poor activity of catalytic electrodes, which involve very low current densities for efficient reactions. Even so, several electrosynthetic reactions of potential interest have been reported, using hydrogen active powder cathodes such as Raney nickel,[1,2] Devarda copper,[2] and palladium or platinum on carbon.[3] However, these cathodes are not practical because of their powdery nature.

Scheme II. Catalytic Hydrogenation of Isophorone on a C/Poly(pyrrole–viologen)–Rh(0) Electrode



On the other hand, it has been demonstrated that the deposition of noble metal microparticles in polymeric films such as viologen- and cobaltocenium-based redox polymers,[4] poly(vinylacetic acid),[5] poly(3-methylthiophene),[6] poly(4-vinylpyridine),[7] Nafion,[8] polyaniline,[9] or poly(mercaptohydroquinone or benzoquinone),[10] results in improved photo- or electrocatalytic generation of hydrogen in aqueous media. We found recently that carbon electrodes modified by poly(pyrrole–viologen) films containing Pd(0) and Rh(0) microparticles are excellent catalytic electrodes for the electrohydrogenation of organic compounds owing to their reproductibility and long term and strong activity.[11] These cathodes appear to be an interesting alternative to powder electrodes and electrocatalytic surface like rhodium[12] or nickel[13] on carbon, or platinized platinum.[14] It should be noted that recently the electrocatalytic hydrogenation of 2-cyclohexen-1-one on graphite coated by a Nafion film containing nickel microparticles has been briefly reported.[15]

In this paper, we report some attractive features of poly(pyrrole–viologen) films containing metal microparticles as electrode materials for catalytic hydrogenation. The influence of the nature and the concentration of the metal catalyst as well as the effect of the polymer structure on the efficiency and selectivity of these cathodes have been examined for the reduction of selected unsaturated organic substrates. The paper concludes with a brief comparison with other catalytic cathodes.

Results and Discussion

The preparation and the working principle of C/poly(pyrrole–viologen)–metal catalytic cathodes are depicted in a straightforward way in Schemes I and II. Poly(pyr-

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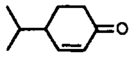
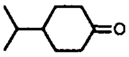
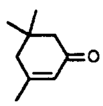
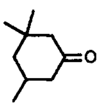
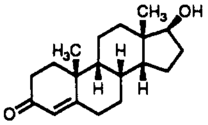
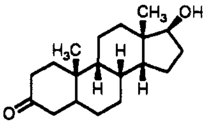
Table I. Electrochemical Hydrogenation on C/Poly PPV^{2+}–Metal Electrodes[a]

entry	substrate	init amt, mmol	metal cat. (μmol)	consmd current, electron molecule^{-1}	product	yield,[b] % (current effcncy, %)[c]
1		15	Pd (33)	2		100 (100)
2		15	Pd (33)	2		13 (10)
3			Rh (9)	2		37 (37)
4			Rh (31)	2		63 (63)
5				4		90 (45)
6			Rh (48)	2		73 (73)
7	$PhCH{=}CH_2$	10	Pd (42)	2	$PhCH_2CH_3$	65 (65)
8			Pt (45)	2		58 (58)
9			Rh (43)	2		56 (56)
10	$PhC{\equiv}N$	10	Pd (17)	4	$PhCH_2NH_2$	68 (68)[d]
11			Pt (45)	4		9 (9)[d]
12			Rh (48)	4		30 (30)[d]
13		3.5	Pd (50)	2	 $5\alpha/5\beta = 0.85$[e]	38 (38)
14			Pt (48)	2	$5\alpha/5\beta = 0.64$[e]	37 (37)
15				10		99 (20)
16			Rh (35)	2	$5\alpha/5\beta = 1.04$[e]	32 (32)

[a] All experiments were carried out in 80 mL of water/methanol mixtures containing 0.1 M KCl, pH 1; the electrode potential was adjusted to keep an electrolysis current in the vicinity of 100 mA. [b] VPC yields unless otherwise noted. [c] Yield and current efficiency are in percent. [d] HPLC yield. [e] Determined by VPC (SE 30 column).

role–viologen) films (polyV^{2+}) were prepared by oxidative electropolymerization of viologen monomers[16] (Scheme I, step 1). Pt(0), Pd(0), Rh(0), and Ru(0) microparticles were incorporated in the polymer by anion exchange, using $PtCl_4^{2-}$, $PdCl_4^{2-}$, $RhCl_6^{3-}$, and $RuCl_6^{3-}$ respectively, followed by an electrochemical reduction[4,11] (Scheme I, step 2). The cathodic charge passed was used to determine the metal loading. This procedure can be repeated several times to increase the amount of metal in the polymer. Typical, each impregnation procedure results in the incorporation of a maximum of 2 atoms of Pd(0) or Pt(0) per 3 viologen units. The incorporation of Rh(0) and Ru(0) appeared less efficient, owing to the bigger size and the higher charge of their corresponding anions.

In these films, the viologen groups ensure a stable transport of electrons at a potential (>−0.5 V vs SCE) where the reduction of protons is thermodynamically viable for pH < 4.[4] This reduction is catalyzed by the metal microparticles on which the hydrogen formed is adsorbed and the organic substrate hydrogenated (Scheme II). These cathodes have shown long term stability.[11a] They have been reused numerous times for more than 1 year without significant loss of activity.

As in catalytic hydrogenation where catalysts and operating environment have important bearing on the outcome of reduction, it is obvious that the catalytic efficiency of these electrodes will be dependent on the nature and the amount of the metal catalyst dispersed in the polymer, as well as on the structure (permeability, environment of catalytic sites) of the polymeric matrix.

Metal Catalyst Effects. Several relevant examples are presented in Table I. While cryptone appeared easy to reduce by using Pd(0) as catalyst (Table I, entry 1), in the same conditions the more hindered isophorone was hydrogenated with a low current yield (13%, entry 2). Better results could be obtained by using lower amounts of Rh(0) (entries 3 to 5) instead of Pd(0). To our knowledge, no study has been made about the comparative activity of palladium and rhodium toward the catalytic hydrogenation of isophorone. The fact that C/poly(pyrrole–viologen)–Rh(0) cathodes appear in this particular case more active than those containing Pd(0) indicates that rhodium interacts more strongly than palladium with the olefinic part of isophorone. The metal loading also has a pronounced effect on the catalyic efficiency of these cathodes. The current yield increased with the amount of Rh(0) in the polymer, to reach a maximum of 73% (entry 6). This yield could not be improved by using a higher Rh(0) loading. This result can be explained by the increase of the active surface of the catalyst located within the polymer matrix. A larger area of Rh(0) is then available as well for protons reduction and hydrogen production, as for substrate adsorption and hydrogenation. However, at very high loadings full utilization of the catalyst is not obtained, due to some limitations like electron transport or substrate permeation through the polymer film.

As pointed out previously,[11b] an interesting feature of these cathodes is that it is possible to choose the metal catalyst to achieve some selectivity for the hydrogenation. Carvone (1), which has two different carbon–carbon double bonds, was taken as an example to test the activity of Pd(0)-, Rh(0)-, and Ru(0)-containing poly(pyrrole–viologen) films (Table II). It appears that carvone is preferably reduced to carvotanacetone (3) with Rh(0). Only traces of dihydrocarvone (2) have been detected. This is not surprising, since rhodium has already been found to be a superior catalyst, compared with palladium, for the hydrogenation of a vinylic olefin.[17] Ru(0) shows the same

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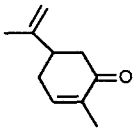
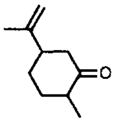
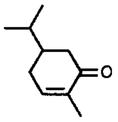
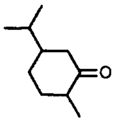
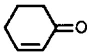
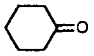
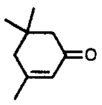
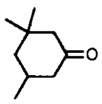
Table II. Hydrogenation of Carvone[a]



		yield,[b] %			
metal catalyst (amt, μmol)	consmd current, electron molecule^{-1}	 **2**	 **3**	 **4**	total current effcncy
Pd (50)	2	37	8	20	85
Rh (34)	2	2	46	22	90
	4	0	31	64	80
Ru (23)	2	1	22	9	41

[a] 15 mmol in water/ethanol equimolar mixtures; see Table I for others experimental conditions. [b] Determined by VPC.

Table III. Catalytic Efficiency of Cathodes Prepared by the Incorporation of Pd(0)[a] **in Different Poly(pyrrole–viologen) Films**[b,c]

substrate	consmd current, electron molecule^{-1}	product	polyPMV^{2+}	yield,[d] % (current efficiency, %) polyPBV^{2+}	polyPMBV^{2+}	polyPPV^{2+}
 [e]	2		96 (96)	89 (86)	93 (93)	91 (91)
 [f]	10		38 (7.5)	40 (8)	92 (18)	70 (14)

[a] 40 μmol. [b] Obtained by electropolymerization of monomers described in Scheme I; films contained around 20 μmol of viologen units. [c] See Table I for other experimental conditions. [d] VPC yields. [e] 10 mmol. [f] 5 mmol.

selectivity and a lower activity than Rh(0). In contrast, dihydrocarvone (2) is the main product obtained with Pd(0) as catalyst. However, the regioselectivity in these hydrogenations is not complete since significant amounts of carvomenthone (4) resulting from the reduction of the two carbon–carbon double bonds of carvone were produced, even when only 2 electrons per molecule of substrate have been passed. Increasing the charge passed resulted in an increase of carvomenthone production at the expense of carvotanacetone or dihydrocarvone (see, for example, in Table II the reduction with 4 electrons per molecule of carvone with Rh(0) as catalyst).

The hydrogenation of a bulky α,β-unsaturated carbonyl compound like testosterone (Table I, entries 13–16) reveals some interesting features. Yields were similar with Pd(0), Pt(0), and Rh(0). Quantitative hydrogenation could be carried with a current yield around 20% (entry 15). These rather low yields reflect the difficult access of the bulky testosterone molecules to the metal sites located in the polymer layer. This leads to the loss of hydrogen produced on catalytic sites. This hydrogenation is selective, since less than 1% of the carbonyl group was reduced, whatever the metal used. This behavior is similar to that observed for the reduction of cyclohexen-2-one derivatives like cryptone, isophorone, and carvone. The influence of the catalyst is only appreciable on the comparative yield of α and β isomers. They were formed in a ratio that depends on the metal used. While an equimolar mixture of α and β isomers was obtained with Rh(0) (entry 16), an slight excess of the β isomer was formed with Pd(0) (entry 13) and especially with Pt(0) (entry 14). This poor selectivity is reminiscent of the known distribution of products in the palladium-catalyzed hydrogenation of steroidal enones, where varying proportions of isomers are produced.[18]

Influence of the Structure of the Polymer. Catalytic efficiencies of various cathodes built by incorporation of the same amount of Pd(0) in different poly(pyrrole–viologen) films have been compared by using the reduction of 2-cyclohexen-1-one and isophorone as test reactions. Results are presented in Table III.

2-Cyclohexen-1-one was readily hydrogenated into cyclohexanone with high yields (current yield: 86–96%) whatever the polymer used. In contrast, important differences were observed with the reduction of the more hindered isophorone, with current yields from 7.5 to 18%. The best result was obtained with the polyPMBV^{2+} film, which gave a product yield of 92% when 10 electrons per molecule have been passed (current efficiency: 18%). This activity is surprisingly high, as compared with those observed (two times lower) for polyPMV^{2+} and polyPBV^{2+} films. They simply differ by a substituent at the 1′-position of the viologen unit, namely, a methyl or a benzyl group in place of an isopentyl substituent. Thus, the polymer structure has a significant effect on the catalytic efficiency of these modified electrodes. These observations can be rationalized by taking into account the permeability of the different polymer layers to substrate molecules and the steric hindrance around the metal sites. As compared to the small methyl substituent and the rigid benzyl substituent, the isopentyl group could be responsable of more permeable polymer matrixes, which allow a favorable accommodation of isophorone molecules around the catalytic sites.

However it is noteworthy that high yields were also obtained with the electrode based on the electropolym-

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[18] Loewenthal, H. J. E. *Tetrahedron* **1959**, *6*, 269–303.

Table IV. Hydrogenation of 2-Cyclohexen-1-one to Cyclohexanone on Different Catalytic Cathodes

entry	cathode (amt of cat.)	electrolyte	proton source	amt of substr, mmol	potential, V vs SCE	current[a] effcncy, %	selectivity[b]	ref
1	Pd (4mg) in polyV^{2+}	H_2O/EtOH (1:1) + 0.5 M KCl	HCl	10	−0.5	90	100	this work[c]
2	Raney Ni (500 mg)	THF/H_2O (9:1) + 1 M $NaClO_4$	pivalic acid	3	*d*	66	91	3
3			H_2O			8	100	
4	Pd (15 mg) on C powder		pivalic acid			84	98	
5			H_2O			88	100	
6	Pt (15 mg) on C powder		pivalic acid			79	82	
7			H_2O			48	85	
8	Ni (2.2 mg) in Nafion	H_2O + 1 M $NaClO_4$	H_2O	2	−1.2	75	72	15

[a] Current efficiency for the formation of cyclohexanone, at passage of 2 × 96 500 C mol^{-1} of charge, with a current of 100 mA. [b] Selectivity for the formation of cyclohexanone to all products. [c] See Table III. [d] Not given.

erization of the PPV^{2+} monomer, which contains two pyrrole groups, thus giving more dense polymer films. Consequently, an easy access of substrate molecules to catalytic sites is not the only parameter to take into consideration to explain differences in catalytic activities of the various polymer matrixes. The efficiency of the polyPPV^{2+}–Pd(0) film could be due to the reticulate nature of the film, which could prevent the aggregation of metal microparticles into clusters of bigger size and keep available a large area of metal, thus leading to cathodes having a good efficiency. At the present time, these hypotheses need to be proved by a carefull study of the physical properties of these electrodes, especially about size and dispersion of metal microparticles in the polymer layer. Whrighton and co-workers have made an extensive use of the Auger depth profile technique to establish the structure of poly(siloxane–viologen) films, confined on gold,[4a] silicium,[4b] or platinum[4b] surfaces, in which palladium microparticles have been dispersed via incorporation of $PdCl_4^{2-}$ anions, followed by their reduction to Pd(0). These interfaces must be similar to our poly(pyrrole–viologen–Pd(0)) films, prepared by using the same procedure for the incorporation of palladium. They found that Pd(0) was distributed throughout the polymer layer, with an apparently significant accumulation at the metal or semiconductor/polymer interface and at the outermost surface of the polymer overcoat. Unfortunately, no information is available about the exact size of metal clusters dispersed in the polymer layer. Scanning and transmission electron microscopy would provide valuable informations about the influence of the polymer structure on the incorporation of metal catalyst, in relation to the efficiency of the resulting cathodes. Experiments are in progress to characterize in such a way these different interfaces.

Comparison with Other Catalytic Cathodes. We have compared some of our results with those reported in the literature about electrocatalytic hydrogenation of selected substrates on different kinds of catalytic cathodes.

In this field, the reduction of 2-cyclohexen-1-one to cyclohexanone has been widely studied on various electrodes. Typical results are collected in Table IV. It appears that Pd(0) microparticles in poly(pyrrole–viologen) films (entry 1) gave a more effective and selective hydrogenation than other cathodes. No cyclohexanol was formed and current efficiencies were above 90%. With Raney nickel powder on a nickel plate, a weak organic acid as protons source is required to reach a good current efficiency. However, under these conditions some cyclohexanol was formed[3] (entry 2). By using water as a proton source the current efficiency drops down to 8% (entry 3). So, the best powdery electrode appears to be palladium deposited on carbon powder, which gave 88% of current efficiency with 100% of selectivity (entry 5). However, a rather large amount of powder (300 mg containing 15 mg of Pd) is needed to obtain this activity.[3]

Electrodes prepared by electrodeposition of Ni(0) microparticles in Nafion films are also attractive (entry 8). They are easier to handle than Raney nickel powder electrodes and show marked ability for hydrogenation, despite the small amount of catalyst used. However, a quick decrease in their activity was observed when they were reused.[15]

The high catalytic efficiency of metal microparticles in polymer films respective to that of solid metal electrodes is clearly demonstrated with the hydrogenation of styrene and benzonitrile. Their reduction on carbon electrodes modified with poly(pyrrole–viologen) films containing Pd (Table I, entries 7 and 10) and Pt (Table I, entries 8 and 11) and platinized platinum Pt/Pt or palladized carbon Pd/C[14b] have been compared. While C/polyPPV^{2+}–Pt(0) and –Pd(0) electrodes readily hydrogenate styrene to ethylbenzene, a Pt/Pt electrode (in CH_3OH/CH_3ONa) was ineffective. However, it should be noted that Pd/C and C/polyPPV^{2+}–Pd(0) electrodes have similar efficiencies for this reduction, giving 64 and 65% of current efficiency, respectively. On the other hand, it is noteworthy that benzonitrile could not be hydrogenated at platinized platinum and palladized carbon,[14b] while Pd (entry 10) and Pt (entry 11) in polyPPV^{2+} films support its conversion to benzylamine. This reduction occured in a fair yield only at Pd (68%, entry 10).

Conclusion

One of the aims of organic electrochemical research is to achieve synthesis of general interest. In this context, our study demonstrates that redox polymeric materials incorporating noble metal particulates offer an unique opportunity to prepare efficient and easy-to-handle cathodes for the electrocatalytic hydrogenation of organic compounds. Although the course of these reductions resembles that taken by normal catalytic hydrogenation with heterogeneous catalysts and elemental hydrogen, the electrochemical formation of active hydrogen directly on catalytic sites allow hydrogenation in milder reaction conditions.

Compared to hydrogen active powder or solid metal electrodes, C/poly(pyrrole–viologen)–metal cathodes appear more selective and efficient. In addition, they have shown a long term stability. As a matter of fact, by imbedding the metal particles in polymeric films, the loss of catalytic activity due to physical or chemical loss of the catalyst can be suppressed.[5-7]

Extension of this work will require us to try to establish the relationship between the structure of the polymer matrix, the physical properties of the dispersed metal, and the catalytic activity of the resulting cathode. More efficient use of embedded catalysts may perhaps be observed by enhancing film porosity. It has been demonstrated that the size of the anions incorporated in polypyrrole films during electropolymerization determine their porosity.[19] An attractive approach to the increase of the efficiency of these cathodes for the hydrogenation of bulky or hindered substrates will be to electropolymerize pyrrole–viologen monomers in the presence of a large anion supporting electrolyte.

Experimental Section

Potassium tetrachloroplatinate, tetrachloropalladate, and hexachlororuthenate and sodium hexachlororhodate were purchased from Aldrich. Organic reagents were obtained from Aldrich or Fluka, except for the products resulting from the hydrogenation of carvone[20] and testosterone,[21] which were kindly supplied by C. Petrier. Acetonitrile (Rathburn HPLC grade S), potassium chloride, hydrochloric acid, and ethanol (Prolabo) were used as received. Tetraethylammonium perchlorate (Fluka) was recrystallized from water and dried under vacuum at 80 °C for 3 days. Water was doubly distilled in a quartz apparatus.

The electrochemical equipment was described previously.[22] All experiments were run under an argon atmosphere and under a fume cupboard to to evacuate hydrogen gas evolved in nonquantitative experiments.

Monomers. 1,1′-Bis(3-(pyrrol-1-yl)propan-1-yl)-4,4′-bipyridinium (PPV^{2+}),[16b] 1-(3-(pyrrol-1-yl)propan-1-yl)-1′-methyl-4,4′-bipyridinium (PMV^{2+}),[16a] and 1-(3-(pyrrol-1-yl)propan-1-yl)-1′-benzyl-4,4′-bipyridinium (PBV^{2+})[16c] as their tetrafluoroborate salts were synthesized as reported previously.

1-(3-(Pyrrol-1-yl)propan-1-yl)-1′-(2-methylbutan-1-yl)-4,4′-bipyridinium ditetrafluoroborate ($PMBV^{2+}$) was prepared by refluxing for 15 h in 4 mL of MeCN a 4-fold molar excess of 1-(3-bromopropan-1-yl)pyrrole (1.13 g, 4 equiv) with 4-(4′-pyridyl)-1-(2-methylbutan-1-yl)-pyridinium tetrafluoroborate (MBV^+, 0.48 g, 1.5 mmol). The resulting precipitate was filtered off, washed with ether, dissolved in 1:1 $H_2O/EtOH$, and passed through an anion exchange column (Amberlite IRA-93 from Fluka) in BF_4^- form. The solvent was removed under reduced pressure, followed by addition of 2 mL of EtOH. The precipitate that resulted upon addition of ether was filtered off to yield $PMBV^{2+}(BF_4^-)_2$ (252 mg, 33%): ^1H NMR (80 MHz, CD_3OD) δ 1.06 (m, 6 H), 1.49–2.43 (series of m, 3 H), 2.48 (m, 2 H), 4.18 (t, 2 H, $J = 7$ Hz), 4.72 (m, 4 H), 6.00 (t, 2 H, $J = 2$ Hz), 6.71 (t, 2 H, $J = 2$ Hz), 8.63 (m, 4 H), 9.20 (m, 4 H); mass spectrum (FAB), *m/e* (positive mode) 335 (C^{2+}), 422 ($C^{2+}BF_4^-$).

$MBV^+BF_4^-$ was synthesized by stirring for 1 night at room temperature a solution of 4,4′-bipyridine (1.37 g, 8.8 mmol) and 1-iodo-2-methylbutane (1.45 g, 7.3 mmol) in 4 mL of benzene. The resulting precipitate of MBV^+I^- was filtered off and transformed to its tetrafluoroborate derivative in the same way as above (yield 522 mg, 23%).

General Procedure for the Preparation of Catalytic Cathodes. Carbon felt (20 × 20 × 10 mm, RVC 4 000, 0.1 g cm^{-3}, purchased from Le Carbone Lorraine) electrodes were derivatized as described previously,[16c] by controlled potential oxidation at 1.1 V vs SCE in a 0.1 M tetraethylammonium perchlorate/CH_3CN solutions containing 2 mM monomer. The electropolymerization was continued until 2–4 × 10^{-5} mol of viologen unit has been deposited. The amount of polyviologen material was determined, after transfer of the electrode to clean electrolyte, from the charge under the first reduction peak of the viologen group ($V^{2+} \rightarrow V^{\bullet+}$) assuming 1 electron per molecule. The impregnation of polymer films with Pt(0), Pd(0), Rh(0), and Ru(0) was effected, following the procedure described previously.[11a] The C–polyV^{2+} electrode was rinsed with MeCN and H_2O and then soaked for 15 min into an aqueous solution of 20 mM metal salt (K_2PtCl_4, K_2PdCl_4, Na_3RhCl_6, or K_3RuCl_6). The electrode was then copiously rinsed with water and placed in a 0.1 M KCl solution. The potential was slowly moved to −0.7 V vs SCE, where the polyV^{2+} is fully reduced to poly$V^{\bullet+}$, which is capable of reducing the metal ions retained in the film to metals.[4b,c] The amount of metal precipitated in the polymer was estimated from the charge passed to reduce the metal salt.

General Procedure for the Hydrogenation Process. Reactions were carried out in a H-shaped three-compartment electrochemical cell at room temperature. The cathode compartment contained a magnetic bar, the carbon felt modified electrode, an SCE reference electrode, and a glass pH electrode. A platinum sheet (10 cm^2) was used as auxiliary electrode. The cell was flushed with argon. The cathode compartment was charged with 3–15 mmol of substrate (see tables) dissolved in 80 mL of water or water/ethanol mixture containing 0.1 M KCl; pH 1 was established and maintained by continuous addition of concentrated HCl. The potential of the cathode was held at −0.4 to −0.5 V vs SCE to obtain an electrolysis current of 100 mA. The reaction progress was followed by periodic withdrawals. The identification of products was based on VPC or HPLC comparisons with authentic samples; yields were determined by VPC or HPLC (external standard). HPLC analysis of benzonitrile hydrogenation was carried out by using a system consisting of a Waters 6000A pump, a Waters U6K injector, a Schoeffel UV spectrometric detector monitored at 254 nm, and a Waters Data Module integrator, on a reverse phase column Waters Radial-PAK μ-Bondapak C18 cartridge (eluent: 1% AcOH–19% EtOH–80% H_2O). All other samples were extracted with ether and analyzed by VPC on a Delsi 330 chromatograph with flame ionization detection with 10–20% Carbowax 20 M and SE-30 columns (2.5 m × 2 mm); the measurements were done on a Merk D 2000 integrator.

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Registry No. **1**, 99-49-0; **2**, 5948-04-9; **3**, 43205-82-9; **4**, 499-70-7; $PPV^{2+}\cdot 2BF_4^-$, 100809-39-0; poly($PPV^{2+}\cdot 2BF_4^-$, 100779-25-7; $PMV^{2+}\cdot 2BF_4^-$, 94343-60-9; poly($PMV^{2-}\cdot 3BF_4^-$), 94290-19-4; $PBV^{2+}\cdot 2BF_4^-$, 110559-70-1; poly($PBV^{2+}\cdot 2BF_4^-$), 110432-02-5; $PMBV^{2+}\cdot 2BF_4^-$, 129287-15-6; poly($PMBV^{2+}\cdot 2BF_2^-$), 129287-20-3; $MBV^+BF_4^-$, 129287-17-8; $PhC{\equiv}N$, 100-47-0; $PhCH_2CH_3$, 100-41-4; $PHCH_2NH_2$, 100-46-9; $PhCH{=}Ch_2$, 100-42-5; Rh, 7440-16-6; Pt, 7440-06-4; Ru, 7440-18-8; Pd, 7440-05-3; 2-cyclohexen-1-one, 930-68-7; cyclohexanone, 108-94-1; isophorone, 78-59-1; dihydroisophorone, 873-94-9; testosterone, 58-22-0; α-dihydrotestosterone, 521-18-6; β-dihydrotestosterone, 571-22-2; cryptone, 500-02-7; dihydrocryptone, 5432-85-9; 1-(3-bromopropan-1-yl)pyrrole, 100779-91-7.

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