

Synthesis and characterization of a new platinum supported catalyst based on poly-(acrylamide-co-[3-(acryloylamino) propyltrimethylammoniumchloride]) as carrier

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Abstract

In the following the synthesis of a new platinum supported catalyst founded upon the title copolymer is described. Adsorption of hexachloroplatinic acid through an ion exchange process followed by reduction in hydrogen leads to a catalyst which is useful in various heterogeneous gas phase reactions. Using several copolymers in different monomer proportions, it is demonstrated that a polymer carrier of composition 90% acrylamide and 10% quaternary compound is the most active one. On the basis of results obtained by use of X-ray photoelectron spectroscopy the presence of Pt⁰ and Pt²⁺ species on the surface of the carrier is proved. It is shown that both species are influenced by amide and quaternary groups of the support. Taking the catalytic activity of samples which differ in the Pt⁰ and Pt²⁺ content into consideration, it is demonstrated that platinum in the zerovalent state is active in the reactions.

Keywords: Polymer anchored catalysts; Platinum catalysts; X-ray photoelectron spectroscopy

1. Introduction

Since the first investigations of Akamatsu et al [1], deposition of transition metal atoms, e.g. platinum, on polymer surfaces with amide groups has received wide attention. Particularly, the use of supported nylon carriers in the hydrogenation of benzene has been investigated intensively [2–5]. In all examinations the authors found a quite different reaction behavior in comparison to catalysts based on oxide, e.g. aluminum oxide.

In most of the studies it was suggested that platinum influenced by a nitrogen functionality acts as the active species. Nevertheless the oxidation state of the active sites is discussed controversial in the literature. Harrison and Rase supposed that a monatomic dispersion of metallic platinum is the reason for catalytic activity [6]. In opposition to this statement, many authors assume that platinum in a positive oxidation state is active in the reactions [2,4,5,7]. The research of Teichner et al. is in contradiction to this. They support the existence of metallic platinum, but not atomically dispersed [3].

During the intensive research on nylon carriers, various attempts were made to improve the

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low activity of the supported catalysts. The carrier materials were changed in order to obtain an ordered distribution of the platinum on the surface of the support. Using polyacrylamide, polyacrylonitrile, polyacrylamideoxime and several ion exchange resins, no improvement of catalytic activity was reached [2]. This may be caused by the fact that most of the chosen polymers were not soluble in the solvents used for the preparation of the catalyst. Therefore a homogeneous dispersion of the active compound on the polymer is not very probable. The fact that most of the applied polymers have more adsorption sites than necessary to anchor the metallic precursor also seems to be disadvantageous for a regular distribution of the metal compound.

Taking this into consideration, a cationic, water soluble polyelectrolyte is used to anchor the metal salt in this study. We will show that this polyelectrolyte will be capable not only of ion exchange (quaternary ammonium group) but also of complexation (amide group). The work along this direction was successful in so far as the cationic group enables a definite anchoring of the metal salt. After complexation of the precursor through an amide group of the same

copolymer unit, this preparation leads to a homogeneous dispersion of the active compound.

2. Experimental

2.1. Materials

The polymer carriers investigated were statistical copolymers of acrylamide (Aam) and 3-(acryloylamino)propyltrimethylammoniumchloride (TCA) in different monomer proportions. They were synthesized by radical polymerization from aqueous solution at Chemische Fabrik Stockhausen (Krefeld, Germany). The structural formulae of the polyelectrolyte is listed in Scheme 1.

The average molecular weights of the carriers (M_w : $\sim 10^6$) were measured by a static and a dynamic method using gel permeation chromatography and low angle light scattering [8]. The polymers were purified by ultrafiltration using a Minitian system with four polysulfon plates (10000 nm).

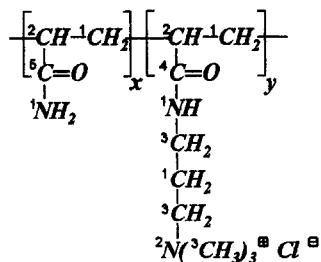
Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, purity > 99%, Degussa) as supporting material, and the reagents for the catalytic reaction (see

Table 1

Catalytic activity in several reactions of poly-{acrylamide-co-[3-(acryloylamino)propyltrimethylammoniumchloride]} in the proportion 90% Aam and 10% TCA

Substrate	Pressure (hPa)	Catalyst (mg)	Flow (ml/min)	Temp. ^a (°C)	Yield (%)	Products (%)
Hexene	117	20	50	120	75	hexane
					15	<i>t</i> -hexene
					5	<i>c</i> -hexene
Cyclohexene	60	20	50	160	72	cyclohexane
					10	benzene
Benzene	58	50	10	160	12	cyclohexane
Nitrobenzene	12	50	10	140	92	aniline
Chlorobenzene	56	50	10	160	6	benzene
					50	benzene
					18	cyclohexane
Acetaldehyde	560	50	10	160	—	—
Crotonaldehyde	60	50	10	160	4	butyraldehyde
Mesityloxide	53	50	10	160	—	—
Benzaldehyde	33	50	10	160	4	cyclohexylcarbald.
Styrene	30	50	10	140	50	ethylbenzene

^a Temperature at maximum conversion.



Scheme 1. Superscript numbers refer to Table 3.

Table 1, purity > 99%, Merck) were used without further purification.

2.2. Preparation of the catalysts

Loading of the polymers with hexachloroplatinic acid was carried out according to the general procedure outlined below.

200 mg of the polymer was dissolved in 30–50 ml water. After complete dissolution, an aqueous solution of the platinum salt (platinum content 6 mg ~ 3% platinum on the carrier) was added. This step was followed by stirring the solution for 20 h. During this time, the ion exchange of Cl^- against PtCl_6^{2-} reached equilibrium. The polymers thus loaded were precipitated by adding 200 ml of a solution of calcium chloride in methanol. Subsequently, the catalyst was washed with methanol and dried at room temperature under reduced pressure. Finally the loaded polymer was reduced in a hydrogen atmosphere for two hours at 180°C. Without this last preparation step, the catalysts were not active in any reaction.

2.3. Catalytic reaction experiments

The catalytic reaction experiments were carried out in a flow microreactor connected to a gas chromatograph. The reactor consisted of a glass tube (length: 28 cm, diameter: 0.7 cm), which was heated by an oven coupled with a thermoregulator. The liquid reactant was held in a thermostated evaporator and vaporized into a stream of dried and deoxygenated hydrogen gas which bubbled through the reactant. Usually

20–50 mg of the catalyst powder was placed in the reactor and held in place by means of a porous glass frit. A flow rate of 10–50 ml/min was used. In a typical catalysis experiment the product stream was sampled periodically for the online GC analysis. Products were separated using a dimethylpolysiloxan column. As gas chromatograph, a Sigma 4 from Perkin Elmer, equipped with a flame ionization detector, was used.

2.4. Characterization by X-ray photoelectron spectroscopy

All X-ray photoelectron spectra were obtained from a VG-Instruments ESCALAB 5 (Mg(K α) radiation ($E = 1253.6$ eV)). The lowest binding energy component of the C 1s signal was assigned to be 285.0 eV for charging reference.

Using polymers prepared by the procedure described above, problems arose, caused by the low platinum content and the porosity of the carrier. Therefore the preparation process was modified and the platinum content increased up to 11%. For X-ray photoelectron spectroscopy analysis, the polymer–metal solution was coated as a thin film on a gold sheet. After evaporation of the solvent in an oven, the samples were analyzed. To ensure a high dispersion of the metal a polymer in the proportion 20% acrylamide and 80% quaternary compound was used as carrier.

2.5. Characterization by FTIR-spectroscopy

In order to confirm the results of the XPS investigations, the absorption frequencies of platinum bound CO have been investigated. The studies were carried out in the range 1000–4000 cm^{-1} . For the measurements the loaded polymer was coated as a thin film on a silicon disk. To cover the polymer-bonded platinum with CO the polymer film was reduced in a carbon monoxide atmosphere at 180°C. For these experiments we used a Bio-Rad FTS-40 spectrometer and an effective resolution of 0.5 cm^{-1} .

3. Results and discussion

3.1. X-ray photoelectron spectroscopy (XPS)

Fig. 1 shows platinum spectra for platinum foil (a), polymer loaded with hexachloroplatinic acid before reduction (b) and after reduction with hydrogen for 6 h (c) and 12 h (d). The spectrum of the platinum foil (a) was recorded for reference. The spectrum (a) consists of two peaks separated by 3.35 eV. The higher binding energy peak is caused by Pt $4f_{5/2}$ electrons, the lower binding energy peak by Pt $4f_{7/2}$ electrons. The area ratio Pt $4f_{7/2}$:Pt $4f_{5/2}$ is 1.27.

As it is the case for the platinum foil, spectrum (b) for the polymer loaded with hexachloroplatinic acid shows two clearly separated peaks with similar separation and area ratios,

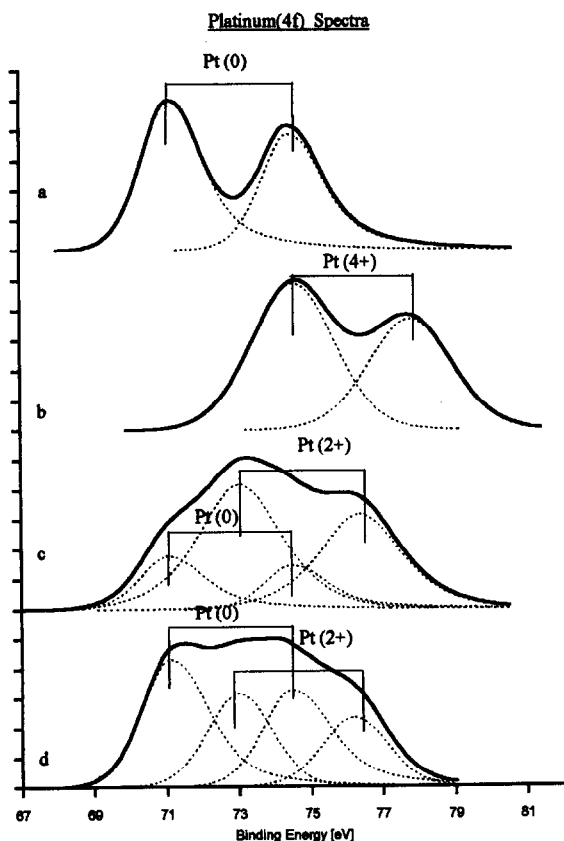


Fig. 1. Platinum 4f XPS-spectra for platinum foil (a), polymer loaded with H_2PtCl_6 (b), loaded polymer reduced for 6h (c) and loaded polymer reduced for 12 h.

Table 2

Peak deconvolution results for the platinum spectra shown in Fig. 1

	Pt ⁰		Pt ²⁺		Pt ⁴⁺	
	4f _{7/2}	4f _{5/2}	4f _{7/2}	4f _{5/2}	4f _{7/2}	4f _{5/2}
Pt foil						
BE (eV)	71.10	74.42	—	—	—	—
FWHM (eV)	2.1	2.1	—	—	—	—
Area (%)	100%		—		—	
H ₂ PtCl ₆ loaded onto the polymer						
BE (eV)	—	—	—	—	74.56	77.82
FWHM (eV)	—	—	—	—	2.7	2.7
Area (%)	—		—		100%	
Loaded polymer reduced for 6 h						
BE (eV)	71.05	74.39	73.05	76.39	—	—
FWHM (eV)	2.2	2.1	2.7	2.7	—	—
Area (%)	26.5%		73.5%		—	
Loaded polymer reduced for 12 h						
BE (eV)	71.07	74.45	73.02	76.47	—	—
FWHM (eV)	2.2	2.2	2.6	2.6	—	—
Area (%)	56.4%		43.6%		—	

but shifted to higher binding energies. These peaks are assigned to the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks for Pt⁴⁺. No reduction of the platinum took place during the loading process. After reduction of the loaded polymer with hydrogen, the shape of the platinum peaks changes dramatically (spectra c and d). One broad peak is obtained. This peak can be deconvoluted into Pt⁰ and Pt²⁺ peaks as shown in Fig. 1 and Table 2. The amount of Pt⁰ increases with reduction time. But even after 12 h reduction with hydrogen, Pt²⁺ species are still present. This is probably caused by the fact that the polymer foil used in XPS analysis is difficult to reduce in comparison to the porous material employed in catalytic experiments.

Fig. 2(A–D) shows the element regions of C (1s), N (1s), O (1s) and Cl (2p) for the pure polymer (a), the polymer loaded with hexachloroplatinic acid (b) and the polymer with hexachloroplatinic acid after reduction with hydrogen for 6 h (c).

The carbon 1s peak is deconvoluted into five peaks for the species indicated in Scheme 1. Only small changes in the peak shape and area

ratios can be recognized between the three spectra (Fig. 2A; Table 3). The loading of the polymer with hexachloroplatinic acid and the reduction of the polymer do not influence the C 1s XPS signal. So the polymer itself is not altered during the preparation process and no reduction of the C=O groups of the polymer took place.

In contrast to platinum catalysts supported by polyamide-6 [7], a significant change can be seen in the nitrogen spectra (Fig. 2B; Table 3). The N 1s signal for the pure polymer consists of two peaks. One for the amide groups (399.9 eV), and one for the quaternary ammonia group (402.7 eV). When hexachloroplatinic acid is loaded onto the polymer, the overall peak shape of the N 1s signal changes and the spectrum cannot be deconvoluted using two peaks only. A third peak at 400.8 eV is necessary to fit the signal. We believe this third peak is due to Pt⁴⁺ binding to amide and (or) quaternary groups. About 15% of the nitrogen functions are affected by platinum. Taking the amount of platinum which is loaded onto the polymer into consideration, a stabilization of the platinum through two quaternary and one (or more) amide group seems to be possible. The platinum complex remains stable even after reduction to Pt²⁺ and Pt⁰ as changes in the XPS signal are only minor.

The O 1s (Fig. 2C, Table 3) signal is broad in all cases. It probably consists of two peaks. One for the C=O group and one from residual water, since the polymer is hygroscopic. The signal does not change during the loading and reduction processes. This can be due to the reason that the C=O group is not affected by the platinum.

For the chlorine signal of the pure polymer (labeled peak 1 in Fig. 2D) one can see the Cl 2p_{1/2} peak as a shoulder of the Cl 2p_{3/2} peak. Peak deconvolution gives a separation of 1.6 eV and an area ratio Cl 2p_{3/2}:Cl 2p_{1/2} of 1.95. After loading the polymer with hexachloroplatinic acid additional peaks from the PtCl₆²⁻ (peak 2) can be seen. The spectrum changes to a broad asymmetric peak.

As a conclusion of the above XPS-data, the following statements can be made:

1. After loading of the polymer with H₂PtCl₆ at room temperature, only Pt⁴⁺ species are present on the polymer. A partial or complete reduction of the platinum during the loading or drying process (as reported for drying at 150°C [7]) does not occur.

2. The platinum binds to amide and quaternary groups of the polymer as can be seen from the change in the N 1s XPS signal.

3. After reduction, Pt²⁺ and Pt⁰ species are present. The amount of Pt⁰ increases with re-

Table 3
Peak deconvolution results for the detailed spectra shown in Fig. 2 (numbers refer to Scheme 1 and Fig. 2)

	C 1s					N 1s			Cl ₁		Cl ₂		O 1s
	1	2	3	4	5	1	2	new	2p _{3/2}	2p _{1/2}	2p _{3/2}	2p _{1/2}	
Polymer without Pt													
BE (eV)	285.00	285.30	285.82	287.82	288.6	399.87	402.72	—	197.40	199.04	—	—	532.38
FWHM (eV)	2.0	1.9	2.3	2.2	2.3	1.7	1.8	—	1.7	1.6	—	—	2.5
Area (%)	24.0%	13.0%	49.4%	10.6%	3.0%	58.1%	41.9%	—	100%				
H ₂ PtCl ₆ loaded onto the polymer													
BE (eV)	285.00	285.40	286.00	288.00	288.60	399.88	402.70	400.80	197.30	198.90	198.51	200.12	532.40
FWHM (eV)	2.0	2.0	2.4	2.4	2.3	2.0	2.0	1.8	1.7	1.7	1.8	1.8	2.9
Area (%)	22.3%	12.6%	51.1%	10.5%	3.5%	53.1%	31.3%	15.6%	43.2%		56.8%		
Loaded polymer reduced for 6 h													
BE (eV)	285.00	285.36	286.13	288.13	288.73	399.82	402.73	400.82	197.28	198.90	198.73	200.36	532.37
FWHM (eV)	2.0	2.0	2.4	2.3	2.2	1.9	2.0	1.9	1.6	1.7	2.0	2.0	2.7
Area (%)	23.1%	13.0%	49.5%	10.8%	3.6%	50.9%	34.2%	14.9%	44.7%		55.3%		

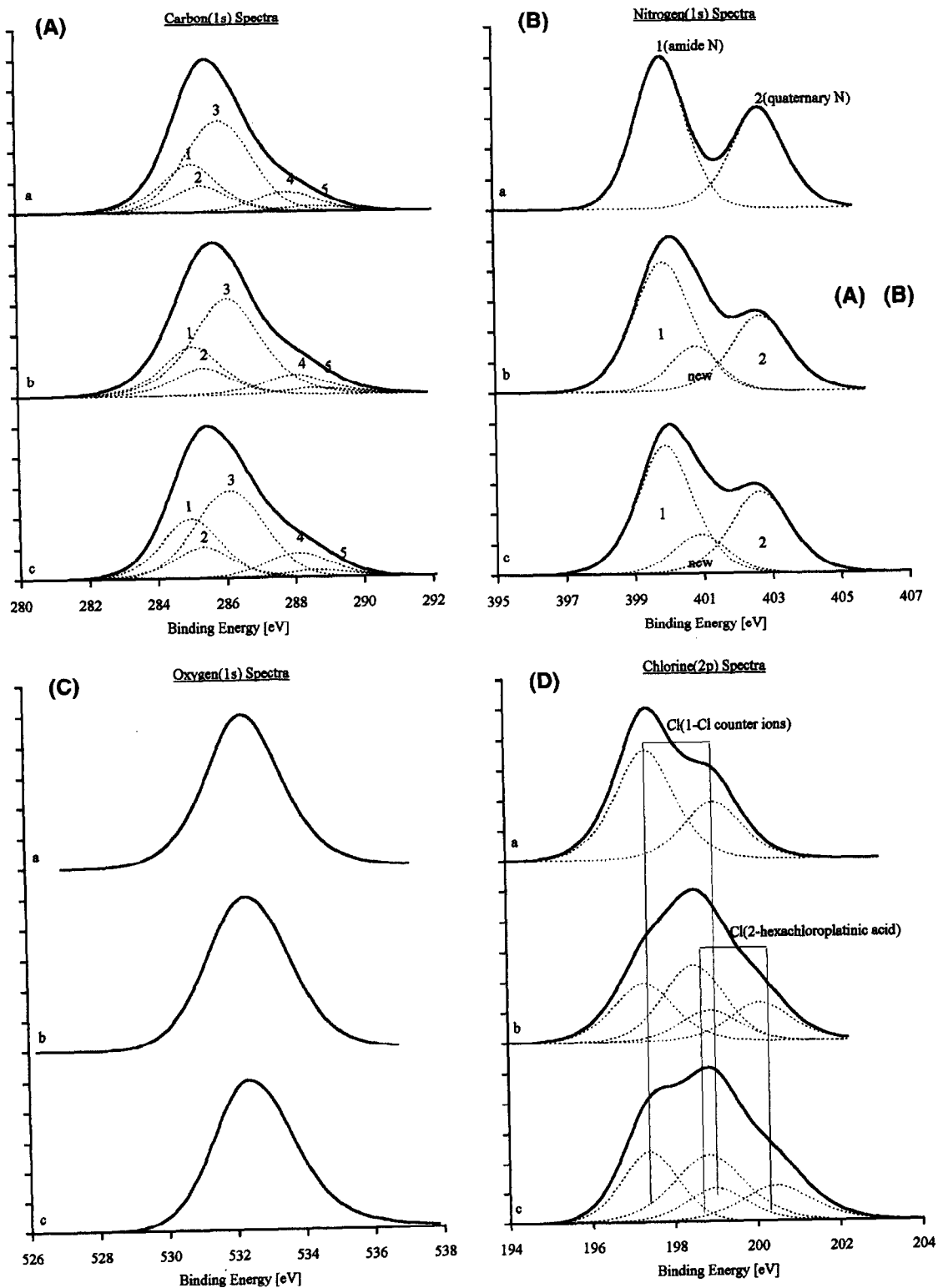


Fig. 2. Element XPS-spectra of C 1s (A), N 1s (B), O 1s (C) and Cl 2p (D) for pure polymer (a), polymer loaded with H_2PtCl_6 (b) and loaded polymer reduced for 6 h (c).

duction time, but even after long reduction time Pt^{2+} is still present. Since the catalytic activity in the different reactions (see below) is also increased with reduction time, Pt^0 is supposed to be the catalytic active species.

4. The polymer backbone remains unchanged throughout the preparation process (loading with H_2PtCl_6 and reduction with H_2)

3.2. Infrared spectroscopy (FTIR)

The FTIR investigations of adsorbed CO on the supported polymer corroborate the statements made in the discussion of the XPS-data. Additionally we were able to show that the active species is the same for all monomer proportions of the carrier.

When carrying out these measurements, we first detected a CO-vibration at 2100 cm^{-1} . During the reduction this peak decreased and a new band at 2034 cm^{-1} appeared which increased by further reduction with carbon monoxide. At the end of the process we found two peaks. A very small one at 2100 cm^{-1} and a strong one at 2034 cm^{-1} . For the first peak we assume the existence of a Pt^{2+} species, for the second a Pt^0 species. In comparison with literature data of 2070 cm^{-1} for the CO-vibration of carbonyl which is bonded to zerovalent platinum dispersed on aluminum oxide [9], this position seems to be surprising. Nevertheless, this significant shift towards lower wavenumbers can be explained by an electron transfer to the metal, probably from amide groups to the platinum.

3.3. Catalytic reaction

A short synopsis of the catalytic behavior of the new catalyst system is given in Figs. 3 and 4 and Table 1.

Fig. 3 shows a typical temperature characteristic of the catalyst illustrated by conversion of 1-hexene. The leveling of the activity in the temperature range $120\text{--}140^\circ\text{C}$ was typical for the polymer catalyst and not caused by sintering

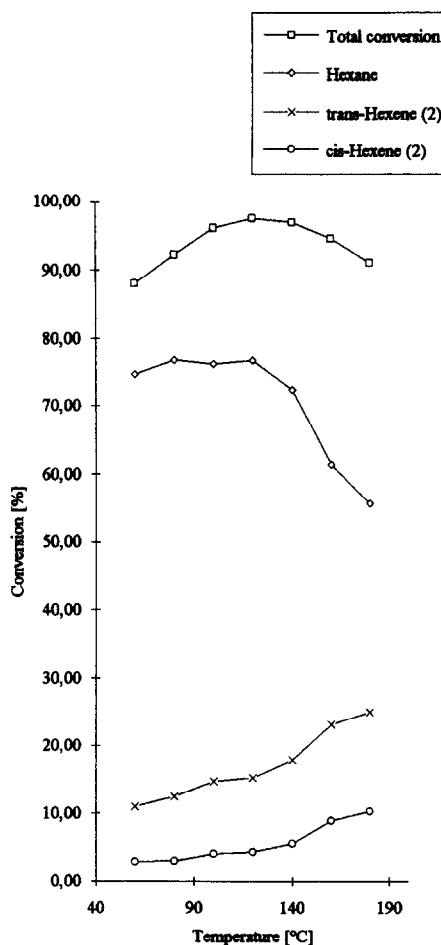


Fig. 3. Hydrogenation and isomerization activity in 1-hexene conversion of a catalyst with copolymer composition 90% acrylamide and 10% quaternary compound.

of the metal. The content of 2-hexene was unexpectedly high since the reaction was carried out under a pure hydrogen atmosphere. The *cis/trans* ratio of 0.4 found at 180°C was close to the value of 0.34 calculated for the thermodynamic equilibrium. In comparison to this behavior, we did not find any isomerization activity for platinum dispersed on alumina. Therefore we assume a different adsorption capacity for our type of catalyst. One possible explanation is the influence of related amide groups which changes the electronic state of platinum just as in the case of the nylon carriers.

During our experimental work, we also found a dependence of catalytic activity on copolymer

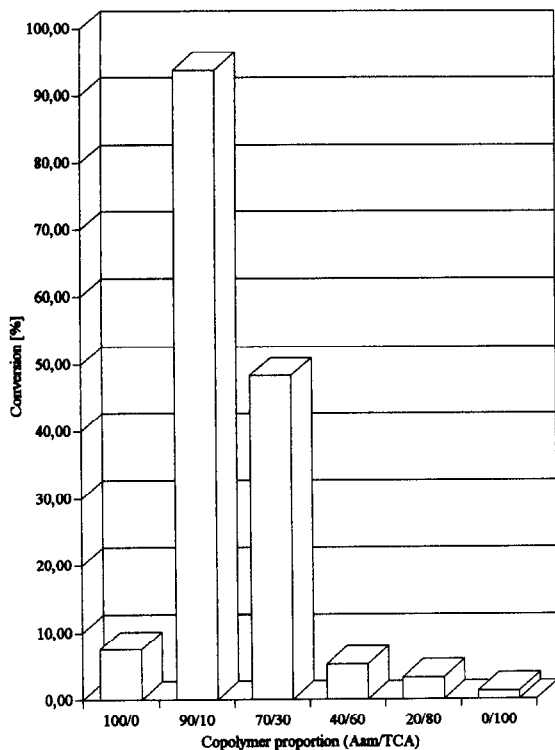


Fig. 4. Dependence of the total conversion of 1-hexene on the copolymer composition. All samples have the same average molecular weight and have been investigated at 180°C. 100/0 = polyacrylamide and 0/100 = poly-3-(acryloylamino) propyltrimethylammoniumchloride.

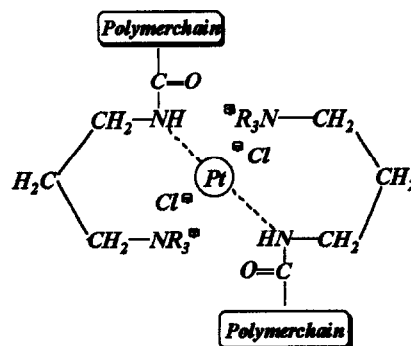
composition of the carrier. The results of these investigations are shown in Fig. 4. One notes that the supported polymers of composition 90/10 and 70/30 are the catalysts with the highest activities. The high activity of the 90/10 copolymer in comparison with the others suggests that the active compound is better dispersed in the case of this polymer. Scanning electron microscopy measurements [10] also confirm this. This is probably caused by a definite bonding of PtCl_6^{2-} through an ion exchange mechanism followed by a stabilization through amide groups of the same copolymer unit. The low activity of both homopolymers emphasizes the speculation that a homogeneous dispersion cannot be obtained if there are more adsorption sites for the precursor complex than necessary.

In order to examine the catalytic efficiency in more detail, several other reactions were stud-

ied. The results are summarized in Table 1. The findings show a good agreement with the properties reported for other catalysts based on nitrogen containing polymer carriers [1,11]. Remarkable is the high activity in hydrogenation of C=C double bonds, reduction of nitrobenzene and hydrodehalogenation. Another important feature is that the carbonyl function of aldehydes and ketones cannot be reduced. Nevertheless some differences were found in comparison to the catalytic behavior of nylon carriers reported by Sermon [4]. In the hydrogenation of benzene, we found no cyclohexene and, in the reaction of cyclohexene, we found a simultaneous disproportionation to benzene and cyclohexane.

Finally the catalytic behavior of the polymer foils used in XPS analysis were investigated in an attempt to clarify the nature of the active species. In comparison to the porous material used in the catalytic measurements, the foils showed a significantly lower activity. Since catalytic activity is also increased with Pt^0 content, the metal is supposed to be the catalytic active compound. The lower catalytic activity of the foils can then be explained by a lower number of accessible catalytic sites due to lower porosity and incomplete reduction of H_2PtCl_6 .

Taking all catalytic measurements and the results of the characterization into consideration, it is likely that the active species in our catalyst is similar to that in the catalysts based on nylon carriers. A possible structure for the



Scheme 2.

stabilization of the metal is listed in Scheme 2. It seems to be proved that the high activity of our system is caused by a better dispersion of the active compound.

4. Conclusion

The new copolymer based catalyst shows some similarity with the ones based on nylon carriers, but has a remarkably higher activity, which can be attributed to a higher dispersion of the active compound. This might be caused by a definite bonding of PtCl_6^{2-} through an ion exchange process followed by the stabilization through amide groups. With a high probability, platinum in the zerovalent state, influenced by related nitrogen functionalities, acts as the active species. But a catalytic activity of Pt^{2+} cannot be ruled out completely.

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