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# A Study of Platinum-Poly{acrylamide-co-[3-(acryloylamino)-propyltrimethylammoniumchloride]} Catalysts: Catalytic Behaviour in the Cyclohexene Hydrogenation Reaction

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**The preparation of platinum-poly{acrylamide-co-[3-(acryloylamino)-propyltrimethylammoniumchloride]} catalysts is described. The influence of copolymer proportion and average molecular weight on the activity in the gas phase hydrogenation of cyclohexene has been analyzed. Copolymers of the composition 90% acrylamide/10% quaternary compound and molecular weights around 919,000 g/mol proved to have the highest efficiency. Cyclohexane and benzene were found as reaction products. The nature of the active species was investigated with FTIR measurements of adsorbed carbon monoxide. Platinum in the zero-valent state, electronically influenced by the carrier, was identified as the agent responsible for the hydrogenation properties of the catalyst. Selectivities are given for some additional test reactions.**

## INTRODUCTION

During the last 35 years, several articles dealing with the use of polymers as supports for platinum have been published. One of the first investigations was carried out by Akamatsu *et al.* (1, 2), who connected $K_2PtCl_6$ to silk fibroin fibers. After reduction, these catalysts showed some unique features in hydrogenation reactions. Harrison and Rase (3) employed various nylons instead of silk. They assumed that the zero-valent noble metal was associated with the amide groups. Nevertheless, Rasadkina and co-authors formulated a $Pt^{2+}$ nylon complex (4, 5). Dini *et al.* (6) suggested a catalytic species with a platinum atom complexed by two chlorine atoms and two amide groups. A good summary underlining the problems of determining the active species was published by Teichner *et al.* (7). By utilization of ESR they investigated that the amide function transferred electrons to the zero-valent platinum atom (8). Using XPS, Sermon and Azhari found zero-valent, as well as divalent Pt in a recent study (9). They ascribed the peculiar hydrogenation properties to a complex of $Pt^{2+}$ exclusively.

A different possibility to bind platinum is the use of polyelectrolytes or ion exchange resins, instead of applying amide groups. Sabadie and Descotes (10) reported the synthesis of a catalyst made from $K_2PtCl_4$ and Amberlyst A27. The reactions of various transition metal complexes with water-soluble polyelectrolytes based on copolymers of aminoalkyl methacrylates containing a sulfur atom were studied by Simanova *et al.* (11).

In this context it is quite surprising that most authors used polymers to anchor the active compound that they themselves had synthesized. For industrial applications, the use of commercially available polymers would be more convenient. Therefore, the authors report in this article the use of a commercial polyelectrolyte with amide functions as a support for platinum.

## EXPERIMENTAL

### *Materials*

(a) *Polymers.* Poly{acrylamide-co-[3-(acryloylamino)-propyltrimethylammoniumchloride]} was kindly supplied in various proportions (90/10, 70/30, 40/60, 20/80) by Chemische Fabrik Stockhausen GmbH, Krefeld, Germany. For each of the four compositions the average molecular weight varied from 70,000 to 3,125,000 g/mol. The polymers were purified by ultrafiltration.

(b) $H_2PtCl_6 \cdot 6\,H_2O$ was kindly provided by Degussa AG.

(c) Cyclohexene was obtained from Merck (>99%).

(d) Hydrogen (≥99.999% v/v) was used as supplied (Messer Griesheim GmbH).

(e) Carbon monoxide (≥99.97% v/v) was used as supplied (Messer Griesheim GmbH).

### *Catalyst Preparation*

(a) *Polymer catalysts.* 200 mg of the polymer were dissolved in 30–50 ml doubly-distilled water (depending on the molecular weight of the polymer). An aqueous solution of hexachloroplatinic acid containing 6 mg platinum was added and the whole mixture was stirred for three

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**TABLE 1**

**Physico-Chemical Properties of the Investigated Catalysts**

| Copolymer proportion AAM/TCA | Average molecular weight (g/mol) | Pt content (%) | Surface area ($m^2/g$) | Pore volume (ml/g) |
|---|---|---|---|---|
| 90/10 | 70,000 | 2.3 | 8.30 | 1.58 |
| 90/10 | 227,000 | 2.4 | 8.71 | 1.69 |
| 90/10 | 919,000 | 2.5 | 8.86 | 1.81 |
| 90/10 | 1,111,000 | 2.4 | 8.41 | 1.62 |
| 90/10 | 3,053,000 | 2.5 | 6.40 | 1.53 |
| 70/30 | 3,196,000 | 2.7 | 3.83 | 1.27 |
| 40/60 | 2,805,000 | 2.8 | 3.11 | 0.46 |
| 20/80 | 3,125,000 | 2.9 | 3.04 | 0.31 |

days. The polymer/platinum complex was precipitated subsequently with an alcoholic $CaCl_2$ solution, filtered, washed copiously with methanol, followed by drying at room temperature under reduced pressure. The catalyst was activated by reducing it in a hydrogen flow (1.2 L/h) for 2 h at 180°C. Without this last step no activity in any reaction could be observed.

Samples of the catalyst were treated with boiling $H_2SO_4/H_2O_2$ and then AAS was used to calculate the amount of platinum. The results of these investigations are given in Table 1.

(b) *Pt/$Al_2O_3$ catalyst.* $Al_2O_3$ was prepared via hydrolysis of aluminum isopropylate (12). According to Jayaman *et al.* (13) the main fraction of the product consists of the $\gamma$-modification. The impregnation of the oxide was achieved in a similar way as outlined under (a). $Al_2O_3$ was added to an aqueous solution of the platinum salt containing a metal content suited to give a catalyst with 2.5% Pt. After three days of stirring, the filtrate was dried at 120°C. The reduction was carried out in a hydrogen stream at 400°C for 2 h.

### *Experimental Procedure*

The hydrogenation reaction was carried out in an ordinary flow-type tubular reactor, temperature-controlled by an oven coupled with a thermoregulator, where 20 mg of the catalyst were placed on a porous glass frit. Cyclohexene was fed into a hydrogen stream from a saturator thermostated at 10°C (partial pressure =60 hPa). Products have been determined by an on-line gas chromatograph (Perkin Elmer Sigma 4) with a dimethylpolysiloxane column held at 40°C. All presented results refer to steady state conditions.

### *Physico-Chemical Characterization*

The surface areas of the catalysts were determined by the BET method using large amounts of substance (up to 10 g) because of the relatively small specific surface areas and $N_2$ as adsorbate. Pore volume measurements have been performed by a procedure described by Mottlau and Fisher (14). The results are reported in Table 1.

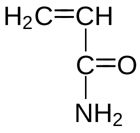
### *FTIR Spectroscopic Measurements*

In order to examine the character of the active species, a silicon disc was coated with a thin film of the impregnated polymer and reduced at 180°C in a hydrogen atmosphere. After definite periods carbon monoxide was added and the IR-bands of platinum-bound CO were measured on a Bio-Rad FTS-40 spectrometer with an effective resolution of $0.5\ cm^{-1}$.

The same procedure was also used with reduction in carbon monoxide. The measured bands for both reducing agents proved to be the same (15). Since measuring in a pure CO atmosphere was more convenient to handle, this way of studying the reduction process has been preferred.

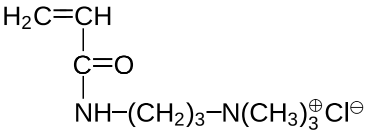
## RESULTS

The authors used statistic copolymers based on acrylamide as carriers for dispersed platinum particles. These copolymers consisted of acrylamide (AAM) and 3-(acryloylamino)propyltrimethylammoniumchloride (TCA) in various proportions and different molecular weights. If it is assumed that the metal precursor is connected to two quaternary groups (16), a theoretical platinum content of 5 wt% (90/10) or higher (70/30, 40/60, 20/80) could be achieved.



$H_2C{=}CH{-}C({=}O){-}NH_2$

AAM



$H_2C{=}CH{-}C({=}O){-}NH{-}(CH_2)_3{-}N(CH_3)_3^{\oplus}Cl^{\ominus}$

TCA

### *Copolymer Proportion, Average Molecular Weight, and Activity*

In order to determine the dependence of copolymer proportion upon activity, total conversion of cyclohexene at 180°C and $H_2$ flow rate of 10 ml/min was measured with catalysts having similar molecular weights and varying in the amount of TCA contained in the carrier. The results of these experiments are presented in Fig. 1. They lead to the conclusion that relatively small quantities of TCA (10%) are essential to obtain a high activity. Catalysts made out of the homopolymers proved to show almost no conversion.

Figure 2 presents the total conversion of cyclohexene at 180°C and 10 ml/min as a function of average molecular weight (copolymer proportion 90/10). It is evident that average molecular weights around 919,000 g/mol deliver the greatest yields of hydrogenation products.

Given these facts, for the following investigations we employed exclusively copolymers of the proportion 90/10 and an average molecular weight of 919,000 g/mol.

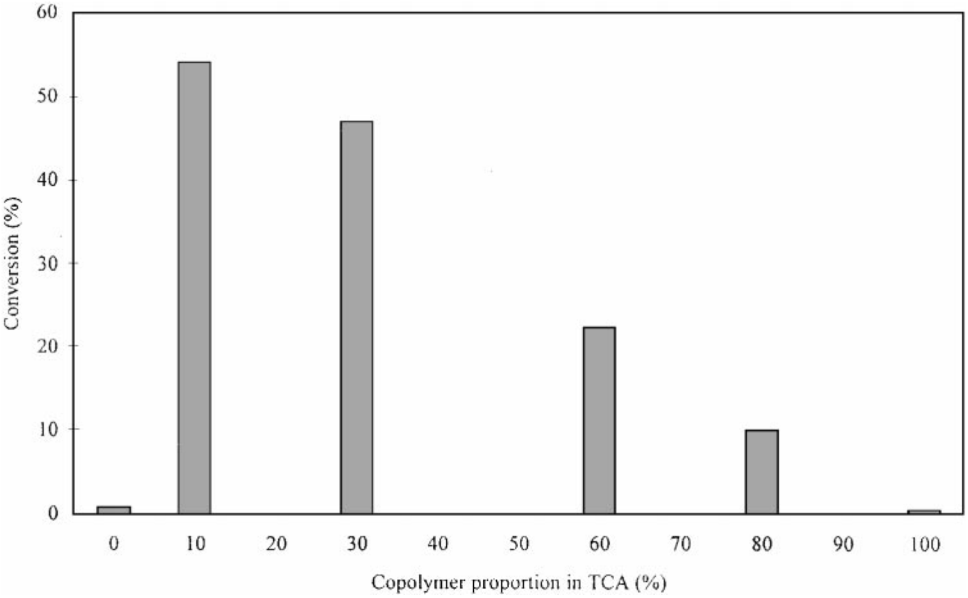


**FIG. 1.** Total conversion of cyclohexene at 180°C as a function of copolymer proportion. All samples have the same average molecular weight.

*Selectivity*

Figure 3 shows the total conversion of cyclohexene and the selectivities, as percentage values, over a temperature range from 60 to 180°C. The activity maximum at around 160°C and its levelling off are typical for our polymer catalyst. This behaviour was observed in every reaction we examined (see also below).

Cyclohexane and benzene were identified as the only products. The formation of benzene begins at 130°C and the maximum selectivity of 10% is relatively high. For the platinum/alumina catalyst benzene formation was not observed below 220°C. Under the same condition used with the polymer catalysts total conversion to cyclohexane took place in the considered temperature interval.

In Fig. 4 one can see the thermodynamic equilibrium constants calculated with Ulich's second approximation (17). It is evident that cyclohexane is the favoured product in the investigated temperature range. The dehydrogenation of cyclohexene or cyclohexane is very unlikely. Hence, the only way to build the aromatic product might be the disproportionation of cyclohexene into cyclohexane and benzene (and possibly hydrogen).

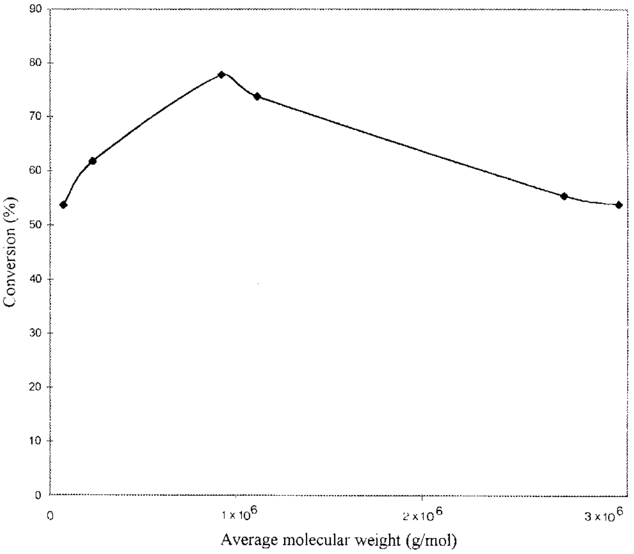


**FIG. 2.** Total conversion of cyclohexene at 180°C as a function of average molecular weight. All samples have the proportion 90% AAM/10% TCA.

*Additional Reactions*

With the intention to check out the catalytic properties of the polymer-supported platinum, a number of different hydrogenation reactions have been examined. Table 2 gives the data for the chosen reactions, which were carried out at 160°C with 50 mg catalyst and a $H_2$ flow rate of 10 ml/min. The given conversions refer to steady state conditions of the same catalyst used in the reaction of cyclohexene (90/10, $M_w = 919{,}000$ g/mol). Interestingly, it was the superior one also for these additional substrates.

The catalyst seems to be well suited for hydrogenation of double bonds without reducing aromatic ring systems. Dehydrohalogenation is another interesting application, which could be used to remove chlorine from chlorobenzenes in waste gases. The hydrogenation of aromatic nitro compounds could also be easily achieved. In no case has a reduction of a carbonyl function been observed.

$Pt/Al_2O_3$ yields in all cases totally hydrogenated substances as main products, i.e. cyclohexane, ethylcyclohexane, and (saturated) alcohols.

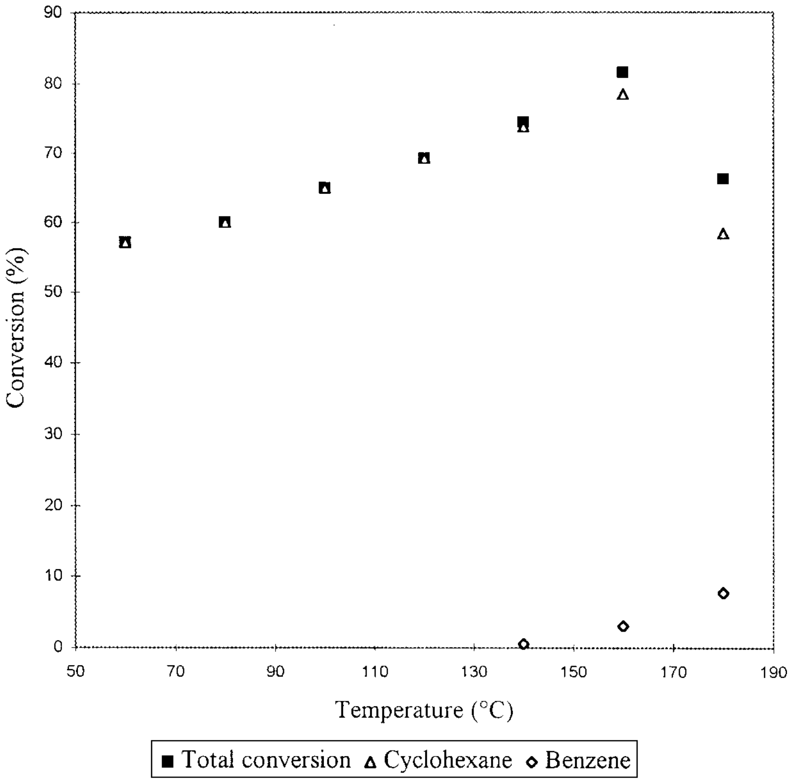


**FIG. 3.** Dependence of activity and selectivity on temperature for a catalyst with molecular weight 918,900 g/mol and proportion 90% AAM/10% TCA.

*Reduction of the Catalysts*

The reduction of unreduced polymer catalysts was studied by FTIR measurements (see Experimental section). After 30-min exposure to carbon monoxide, a strong band at 2091 $cm^{-1}$ appeared. In the following time, this band decreased and two new ones formed simultaneously at 2043 and 2023 $cm^{-1}$. No change in the IR spectrum could be detected after the first band disappeared. It is noteworthy that an isosbestic point at 2070 $cm^{-1}$ was passed through during the reduction process.

Catalysts made out of the homopolymers showed nearly identical frequencies, with the exception that the last CO band was missing for the acrylamide-supported platinum. The intensities of the signals around 2040 and 2020 $cm^{-1}$ for the copolymer- and the TCA homopolymer catalyst were of comparable size.

Table 3 gives a summary of the FTIR spectroscopic results.

**TABLE 2**

**Results from Additional Reactions at 160°C**

| Educt | Partial pressure (hPa) | Products | |
|---|---|---|---|
| Benzene | 58 | 12% cyclohexane | |
| Styrene | 30 | 50% ethylbenzene | |
| Chlorobenzene | 56 | 50% benzene | 18% cyclohexane |
| Nitrobenzene | 12 | 92% aniline | 6% benzene |
| Benzaldehyde | 33 | 4% cyclohexylcarbaldehyde | |
| Acetaldehyde | 560 | No conversion | |
| Crotonaldehyde | 60 | 4% butyraldehyde | |
| Mesityl oxide | 53 | No conversion | |

## DISCUSSION

The results obtained indicate that platinum catalysts based on poly{acrylamide-co-[3-(acryloylamino)propyltrimethylammoniumchloride]} possess some interesting properties. The unusual abilities may be ascribed to the structural and electronic state of the catalyst.

The FTIR measurements reveal that two states are passed through during the reduction. These states have to belong to divalent and zero-valent platinum since

**TABLE 3**

**Wavenumber Values of Platinum-Bound CO**

| Sample | After 30 min ($cm^{-1}$) | After 90 min ($cm^{-1}$) | |
|---|---|---|---|
| AAM-homopolymer | 2093 | 2042 | — |
| TCA-homopolymer | 2087 | 2040 | 2024 |
| 90/10 copolymer | 2091 | 2043 | 2023 |

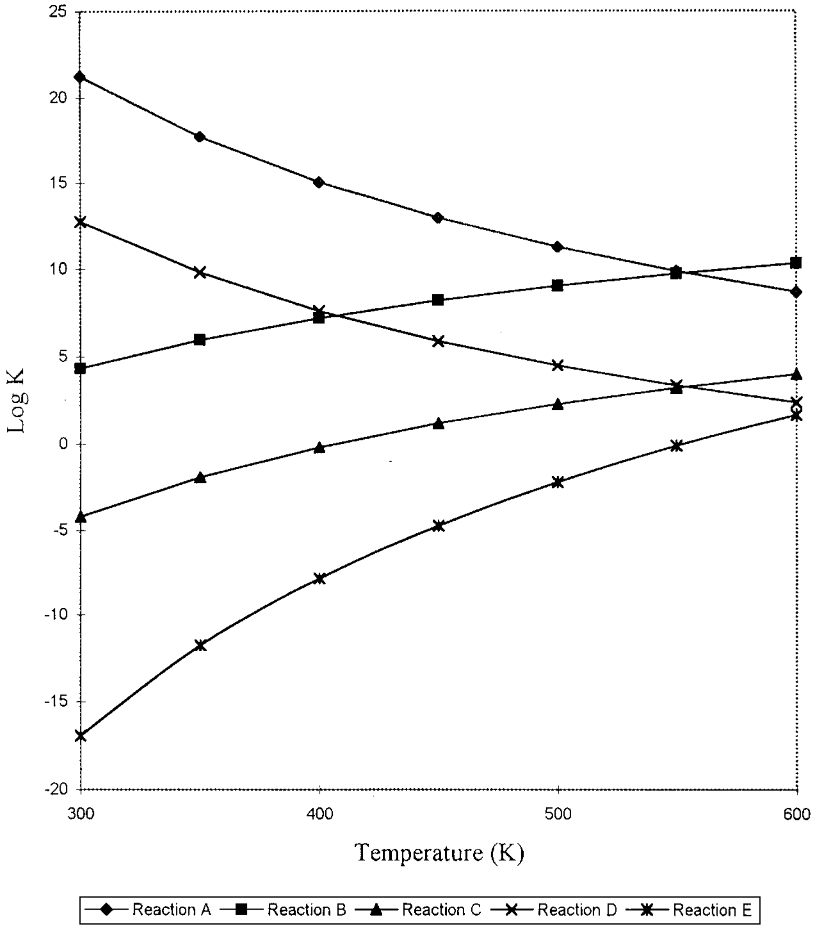


**FIG. 4.** Dependence of thermodynamic equilibrium constants on temperature for the reactions: (A) 3 cyclohexene → 2 cyclohexane + benzene; (B) 3 cyclohexene → cyclohexane + 2 benzene + 3 $H_2$; (C) cyclohexene → benzene + 2 $H_2$; (D) cyclohexene + $H_2$ → cyclohexane; (E) cyclohexane → benzene + 3 $H_2$.

hexachloro(IV)platinate has no space left for addition of carbonyl ligands.

Carbon monoxide is well known as a good probe molecule for the electronic state because the CO vibration frequencies depend on the degree of electron back-donation from the metal. For linearly bound carbon monoxide on a $Pt^0/Al_2O_3$ catalyst the literature provides data from 2090 to 2070 $cm^{-1}$ (18). Teichner *et al.* (19) found a shift of 30–50 $cm^{-1}$ for Pd/nylon catalysts in comparison to oxidic carriers. They explained this effect by a transfer of polyamide electrons to the metal. Since poly{acrylamide-co-[3-(acryloylamino)propyltrimethylammoniumchloride]} possesses C=O, as well as NH groups like nylon, this effect should play a role on the present carrier also. If this shift is subtracted from the frequencies given for $Pt^0$ on alumina, signals in the area around 2040/2020 $cm^{-1}$ will result. Therefore, these signals should represent $Pt^0$ on the copolymer carrier. Primet *et al.* (18a) reported a band above 2100 $cm^{-1}$ for carbon monoxide adsorbed on divalent platinum. Consideration of the frequency shift will deliver a signal around 2090 $cm^{-1}$. Accordingly, our band observed at 2091 $cm^{-1}$ is considered to belong to CO adsorbed on a $Pt^{2+}$-species of the copolymer catalyst. This interpretation seems to be reasonable since positively charged species always give higher CO frequencies than the neutral ones, due to their weaker electron back-donation abilities.

The band around 2090 $cm^{-1}$ totally disappeared during reduction while the signals at 2040/2020 $cm^{-1}$ increased in their intensities. We conclude that the active species of the catalyst should be zero-valent platinum.

According to literature data, the value for bridged-bound carbon monoxide is around 1850 $cm^{-1}$ (18a). Interestingly, no such band could be observed for our catalyst, even if one pays regard to a possible frequency shift. This fact might be a hint on a high degree of dispersion.

As can be seen in Table 3, the 90/10 catalyst used for the hydrogenation experiments has two bands for the zero-valent platinum. The impregnated TCA homopolymer shows the same behaviour, but acrylamide-supported platinum has only the band at 2042 $\mathrm{cm}^{-1}$. From this fact we can conclude that the active species responsible for the hydrogenation properties is connected to the quaternary ammonium group of the TCA monomer because the acrylamide catalyst shows no activity in the cyclohexene hydrogenation reaction (see Fig. 1) and the CO bands of the used active one are identical to those of TCA catalyst.

For the formation of the active species the following reaction scheme can be formulated:

$$2\,\mathrm{Pol\text{-}NR_3^+Cl^-} + [\mathrm{PtCl_6}]^{2-} \rightarrow \left(\mathrm{Pol\text{-}NR_3^+}\right)_2\left[\mathrm{PtCl_6^{2-}}\right] + 2\,\mathrm{Cl^-} \qquad [1]$$

$$\left(\mathrm{Pol\text{-}NR_3^+}\right)_2\left[\mathrm{PtCl_6^{2-}}\right] + \mathrm{H_2} \rightarrow \left(\mathrm{Pol\text{-}NR_3^+}\right)_2\left[\mathrm{PtCl_4^{2-}}\right] + 2\,\mathrm{HCl} \qquad [2]$$

$$\left(\mathrm{Pol\text{-}NR_3^+}\right)_2\left[\mathrm{PtCl_4^{2-}}\right] + \mathrm{H_2} \rightarrow 2\,\mathrm{Pol\text{-}NR_3^+Cl^-} + \mathrm{Pt^0} + 2\,\mathrm{HCl}. \qquad [3]$$

In the first reaction $[\mathrm{PtCl_6^{2-}}]$ is bound to quaternary ammonium groups via an ion exchange mechanism. It is reduced to divalent platinum and in the last reaction zerovalent platinum forms on the polymer support. As described above, the carrier also interacts with the metal in form of an electron transfer. This electron transfer is possibly caused by amide or carbonyl functions.

The acrylamide homopolymer possessed signals for platinum bound carbon monoxide; as a matter of fact it also must have bound metal. An additional analysis of its platinum content revealed that it contains equal amounts of Pt like the 90/10 copolymers. This is not too surprising since the literature gives many data concerning carbonyl or amide groups binding metals, e.g. nylon catalysts. Obviously, there are at least two ways in which platinum could be bound to the copolymer carriers. However, it is more likely that the majority of the metal is connected to quaternary ammonium groups. Kudaibergenov (16) reports the connection of $[\mathrm{PtCl_6^{2-}}]$ to these via an ion exchange. Thus, the affinity of positively charged metal precursors for $\mathrm{NR_4^+}$-groups should be much higher than that for carbonyl or amide functions.

All the abovementioned results concerning the state of the active species have been confirmed by XPS measurements (20).

This is in accordance with the experimental data of the cyclohexene reaction. The acrylamide catalyst possesses no activity as a consequence of the absent quaternary ammonium group. With introduction of this group the conversion of cyclohexene increases abruptly. If only small amounts of TCA are present in the copolymer, the $\mathrm{NR_3^+}$ groups have the highest possible distance and the degree of metal dispersion is high, too. With increasing amounts of TCA the dispersion becomes lower, thus decreasing the activity as well.

Figure 2 shows a maximum activity for catalysts with an average molecular weight of 919,000 g/mol. Table 1 hints of the possibility that surface areas and pore volumes might play a role in this context, but a different effect needs to be considered. The more the molecular mass of the copolymers is increased, the greater becomes the probability of macromolecules in the form of a dense coil. As a consequence more platinum is inactively enclosed inside the polymer matrix during the precipitation step. Possibly, it requires a certain ratio between texture parameters and chain length to obtain an optimum catalyst.

In a direct comparison with $\mathrm{Pt/Al_2O_3}$ the selectivity of 10% for benzene is astonishing. As can be seen from the thermodynamic calculations (Fig. 4) the most likely way of benzene formation in the investigated temperature range consists of a disproportionation of cyclohexene. Boudart (21) reported that an intermolecular hydrogen transfer can take place between adsorbed cyclohexene molecules over platinum catalysts. The higher selectivity for benzene in contrast to an alumina support might be due to an interaction of polymer and metal. Interestingly, Sermon and Azhari (9) found only cyclohexane for a platinum/nylon catalyst in the same reaction at temperatures from 100° to 180°C.

In the additional investigated reactions, a difference between oxide and polymer carrier also occurred. While $\mathrm{Pt/Al_2O_3}$ always yielded totally hydrogenated products, the copolymer catalyst favoured partially hydrogenated ones or in case of carbonyl functions showed almost no activity. The mentioned shift of CO frequencies proves an electron transfer from the carrier to Pt. This will certainly alter the adsorption properties of platinum for the educts and consequently the activity and selectivity of the catalyst. For the reaction of chlorobenzene with hydrogen there exists evidence for the validity of this explanation. Moreau *et al.* (22) reported that in this conversion benzene forms predominantly on active sides with an electron donor character, i.e. metal with a high electron density.

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