

# Microporous poly-(*N,N*-dimethyl-acrylamide)–(1-methacryloyl-ethylene-2-sulphonate)–(*N,N'*-methylene-bis-acrylamide) resins as hydrophilic supports for metal catalysts

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## Abstract

The synthesis of poly-(*N,N*-dimethyl-acrylamide)–(1-methacryloyl-ethylene-2-sulphonate) (M4K) with 4 mol.% of *N,N'*-methylene-bis-acrylamide (MBAA) as crosslinker, and of poly-(*N,N*-dimethyl-acrylamide)–(1-methacryloyl-ethylene-2-sulphonic acid) (M4A) with 4 mol.% MBAA is described. Polymerization was performed under gamma rays irradiation of a water solution of monomers (M4K), or of the monomer mixture (M4A), at room temperature. High affinity to protonic solvents was observed for both materials. Palladium catalysts were prepared from M4K through ion-exchange with  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  and from M4A through ion-exchange with palladium acetate; the subsequent Pd(II) reduction with sodium borohydride in ethanol yielded the final catalysts with a uniform distribution of metal throughout the resin particles. The average size of metal crystallites obtained by X-ray diffraction was about 4 nm and did not show any dependence on metal content in the polymer in the range from 0.5 to 8.8 w/w % of metal. The rate of hydrogenation of *p*-nitrotoluene and cyclohexene in catalytic tests with 1 and 0.5 w/w % Pd catalysts was proportional to the metal content in catalysts, which confirmed a very good accessibility of these supports. Catalysts with low metal content also exhibit a significant deactivation in the course of the hydrogenation of *p*-nitrotoluene to *p*-toluidine in methanol under ambient conditions.

**Keywords:** Accessibility; Acrylamide–methacryloyl derivatized resins; Catalyst deactivation; Cyclohexene; Gamma rays; Hydrogenation;  $\text{NaBH}_4$ ; *p*-Nitrotoluene; Palladium; Swellability; X-ray diffraction

## 1. Introduction

Macromolecular supports for metal catalysts are becoming more and more popular due to the

possibility of controlling in a simple way their morphology [1] and, in general, their physico-chemical properties [2], as well as the metal concentration and distribution in the particle, and the size of crystallites [3]. Mainly styrene-based sulphonated resins are employed in industrial proc-

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esses [4], but also other polymers, e.g. nylon (for Ru and Pt catalysts) [5] and crosslinked copolymers of dimethylacrylamide with functionalized monomers [1], are interesting for potential applications.

Hydrophilicity of the support can play important role for the selectivity in a complex reaction system, e.g. the partial hydrogenation of benzene over ruthenium supported on various hydroxides and oxides [6]. Syntheses of polymeric supports from functionalized monomers enable simple controlling of hydrophilicity using different ratio of hydrophilic and hydrophobic monomers. We described recently palladium catalysts supported on poly-(*N,N*-dimethyl-acrylamide)–(*p*-styryl-sulphonate)–(*N,N'*-methylene-bis-acrylamide) resin as promising catalysts for reactions in water or alcohols as media [7]. Benzene ring in the latter resin lowers hydrophilicity of the support, therefore we extended our work to anionic resins prepared from non-styrene based functionalized monomers. One of such monomer is 1-methacryloyl-ethylene-2-sulphonic acid and salts of this acid.

We report here on the copolymerization of the *N,N*-dimethyl-acrylamide with either potassium 1-methacryloyl-ethylene-2-sulphonate or 1-methacryloyl-ethylene-2-sulphonic acid, with *N,N'*-methylene-bis-acrylamide as crosslinker, as well as on the preparation and characterization of palladium catalysts based on these new polymers. Hydrogenation of *p*-nitrotoluene to *p*-toluidine and of cyclohexene to cyclohexane were chosen as model catalytic reactions.

## 2. Experimental

### 2.1. Materials

Reagent-grade *N,N'*-methylene-bis-acrylamide (MBAA) and *N,N*-dimethyl-acrylamide (DMAA) were obtained from Aldrich; reagent-grade 1-methacryloyl-ethylene-2-sulphonic acid and potassium 1-methacryloyl-ethylene-2-sulphonate were supplied by Strem; *p*-nitrotoluene,

methanol (MeOH), ethyl acetate (EAC), diethyl ether (DETE) and dichloromethane (DCM) were supplied by Carlo Erba (RPE reagents). Pure ethanol (EtOH), tetrahydrofuran (THF), toluene (TOL), acetone (AC), cyclohexene and sodium borohydride were purchased from Aldrich.  $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$  was from Strem and palladium acetate was from Fluka. All the products were employed as received, apart from *p*-nitrotoluene and cyclohexene which were purified prior to use by sublimation under reduced pressure and by distillation, respectively.

### 2.2. Apparatus

SEM and XRMA analyses were carried out by means of a Cambridge Stereoscan 250 EDX PW 9800 apparatus. X-ray diffraction measurements were performed by a DRON UM1 diffractometer with a  $\text{Co}_{K\alpha}$  X-ray source. Profiles of Pd(111) reflections were recorded with an angular step  $0.04^\circ 2\theta$  and time on the step 30 s and 10 s for 0.5 and 1, and 8 w/w % Pd catalysts, respectively. Elemental analyses (C, H, N, S) were carried out by means of a Carlo Erba 1106 analyzer. Atomic absorption measurements (K, Pd) were performed with a Perkin Elmer 3030 atomic absorption spectrometer. Samples (ca. 100 mg) were digested in 1 cm<sup>3</sup> of concentrated nitric acid, 1 cm<sup>3</sup> of concentrated sulphuric acid and 5 cm<sup>3</sup> of concentrated hydrogen peroxide, and the solution obtained after the mineralization was diluted to the concentration suitable for atomic absorption measurements.

### 2.3. Synthesis

The ion exchange resin denoted as M4K was prepared from the following monomers:

- (i) *N,N*-dimethyl-acrylamide (DMAA)
- (ii) *N,N'*-methylene-bis-acrylamide (MBAA)
- (iii) potassium 1-methacryloyl-ethylene-2-sulphonate (MESK)

The copolymerization was performed in concentrated water solution, upon gamma ray irradiation [7]. 4.76 g of DMMA, 4.93 g of MESK and

Table 1  
Content of elements in P4N

Sample		Element				
		C	H	N	S	K
M4K	calc. (%)	44.22	6.17	7.43	7.15	8.72
	found (%)	46.07	6.50	8.13	6.40	7.82
M4A	calc. (%)	49.47	7.17	8.70	7.07	–
	found (%)	47.31	7.60	8.60	6.78	–

0.438 g of MBAA were dissolved at 40°C in 5.00 g of water in a 20 cm<sup>3</sup> Pyrex cylindrical probe under nitrogen. The closed probe was exposed to gamma rays from a <sup>60</sup>Co at 0.5 Gy/s for 72 h at 18°C. After breaking the probe, a cylindrical white rod was obtained. The rod was rinsed in deionized water and cut into slices of about 2 mm thickness, which were washed and decanted with water, methanol and again with water, each washing lasting ca. 30 min, with stirring. The polymer was rinsed with methanol and dried at 60°C, 5 kPa, for 24 h to constant weight (9.78 g, 96.6% polymerization yield). The analytical data are collected in Table 1. The solution obtained upon collecting all the filtrates was analyzed for the content of potassium.

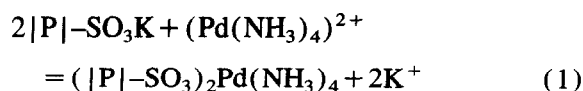
The ion exchange resin denoted as M4A was prepared from the following monomers:

- (i) *N,N*-dimethyl-acrylamide (DMAA)
- (ii) *N,N'*-methylene-bis-acrylamide (MBAA)
- (iii) 1-methacryloyl-ethylene-2-sulphonic acid (MESA)

The synthesis was performed as above, utilizing 5.60 g of DMMA, 4.00 g of MESA and 0.46 g of MBAA (yield 9.61 g, 95.5%). The analytical data are collected in Table 1. A part of the polymer chain without cations is represented in Fig. 1.

The obtained resin was conveniently powdered by suspending the perfectly dry material in water and letting it to swell and self-break for about one day. This procedure was repeated three times.

Incorporation of Pd(II) into the resin M4K was performed through the ion exchange:



The ion-exchange was carried out using Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, as described in Ref. [7]. A slightly yellow particles were obtained after the ion-exchange, washing and drying. Analysis showed that palladium occupied more than 90% of cationic positions in the polymer, if the metal is supposed to be present in the resin as Pd(II).

The reduction of Pd(II) to Pd(0) was performed with NaBH<sub>4</sub> 0.066 M in ethanol (10 times excess). A catalyst with 7.2 wt.% palladium content (M4KPd8) was prepared in this way.

The preparation of the Pd form of the resin M4A was performed through the route involving ion exchange with palladium acetate [6]. Since M4A was directly obtained in the acid form, palladium acetate was a more convenient starting material in this case, although some spontaneous reduction of the metal occurs. Reduction of the metal was performed as indicated above. Three catalysts with palladium contents of 0.58 (M4APd05), 1.3 (M4APd1), and 8.8% w/w (M4APd8) were prepared. The value 8.8% w/w of palladium corresponds to the maximum when palladium occupies two cationic position during ion exchange.

All materials were sieved to separate fractions of different particle sizes to be used in the characterization procedures.

#### 2.4. Swelling behaviour

The solvent compatibility of M4K and M4A was determined by measuring their bulk expanded

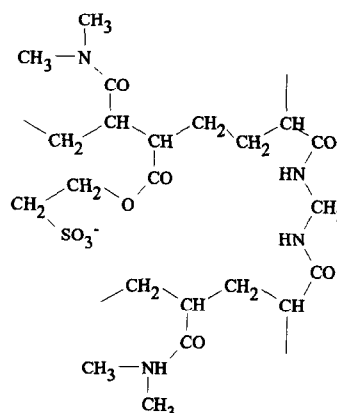


Fig. 1. Schematic representation of the backbone of M4A and M4K resins.

volumes [2]. To evaluate the effect of the incorporation of Pd(II) on this parameter, the Pd-charged resin M4KPd8 was also measured prior to reduction. For details of the measurement procedure, see Ref. [7].

### 2.5. Catalytic tests

Catalytic hydrogenation tests with *p*-nitrotoluene were carried out in a batch, vigorously shaken three-necked reactors (frequency about 1.3 Hz), at room temperature and 0.1 MPa, as described in Ref. [7].

Catalytic tests with cyclohexene were carried out in a 50 cm<sup>3</sup> glass-lined stainless steel reactor connected with a flexible metal capillary to an apparatus for measuring the hydrogen consumption at constant pressure [8]. Experiments were performed at room temperature and 0.5 MPa. Typically, 10 ml of a 1 M solution of cyclohexene in

methanol were employed, with an amount of catalyst yielding an analytical Pd concentration equal to 0.5 mM. The reactor was filled with reactants, catalyst and hydrogen, immersed in an oil bath and vigorously agitated using a mechanical shaker (frequency about 6 Hz).

### 3. Results and discussion

The analytical data referring to resin M4K and M4A are collected in Table 1. As the consequence of non-quantitative polymerization, the analytical figures are slightly different from the theoretical values.

XRMA pictures of M4K and M4A are reported in Fig. 2 and Fig. 3. A perfectly homogeneous distribution of potassium (in the case of M4K) and sulphur throughout a section of a resin particle is apparent. The lateral resolution power of the

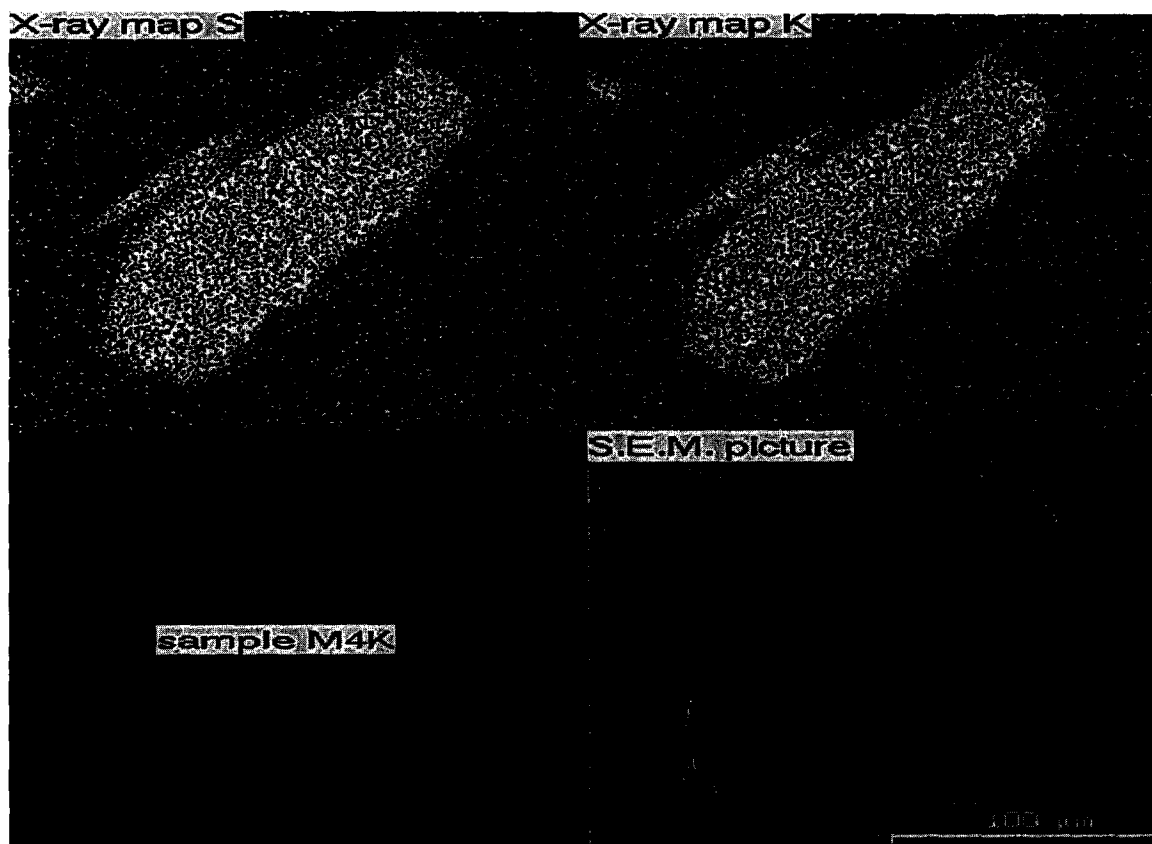


Fig. 2. SEM and XRM maps of sulphur and potassium in M4K.

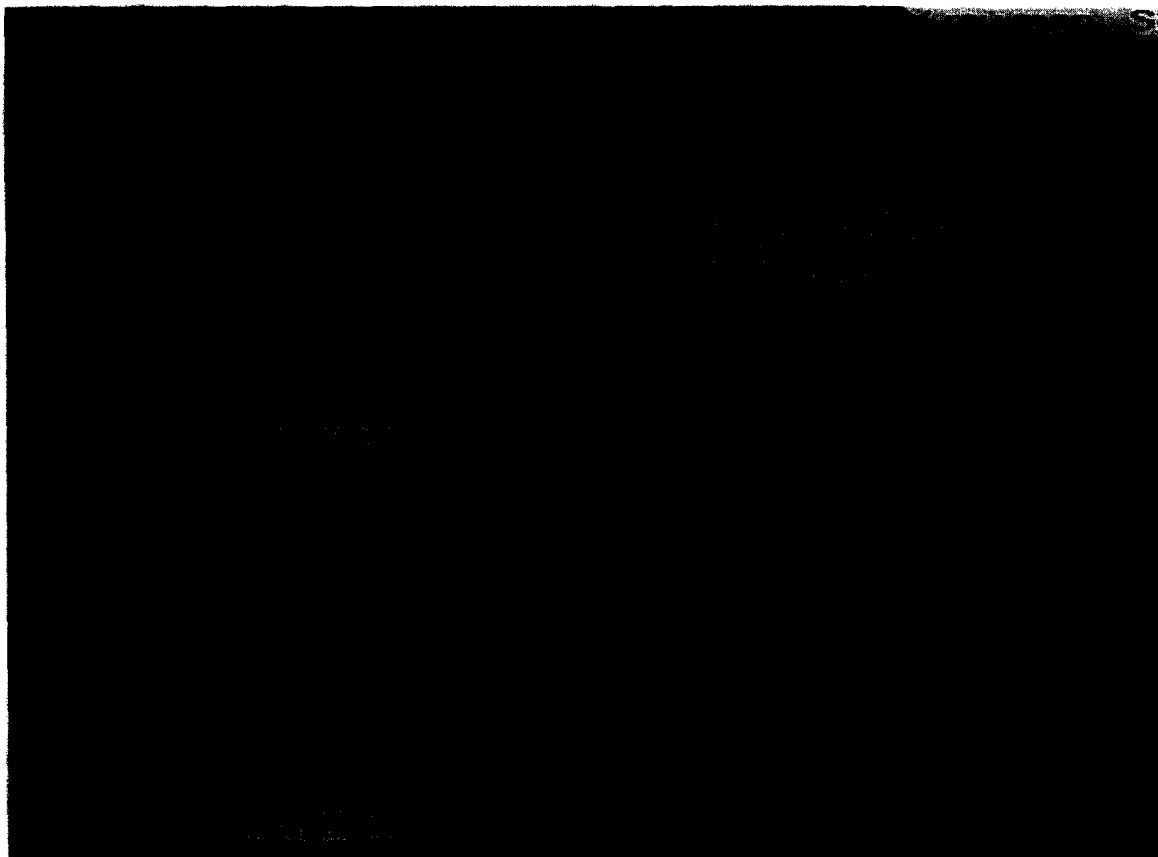


Fig. 3. SEM and XRM maps of sulphur in M4A.

microprobe analytical apparatus is estimated to be  $1 \mu\text{m}^2$ .

The solvent compatibility of M4K and M4A were quantitatively evaluated by bulk expanded volume measurements which are given in Fig. 4,

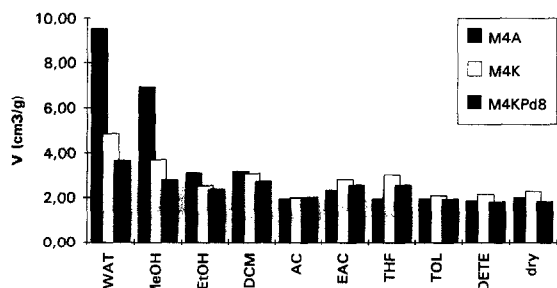


Fig. 4. Specific bulk expanded volumes of M4A, M4K, M4KPd8 in various swelling agents. The size of particles was in the range 0.05–0.25 mm, the average diameter of the equivalent sphere was 0.12 mm. WAT –water, MeOH –methanol, EtOH –ethanol, DCM –dichloromethane, AC – acetone, EAC –ethyl acetate, THF – tetrahydrofuran, TOL –toluene, DETE –diethyl ether, dry-specific volume of the dry sample.

together with the values for M4KPd8 prior to reduction.

Both resins exhibit marked hydrophilic character, particularly evident in the case of M4A. Water, methanol and ethanol appear to be suitable working media for chemical applications of these materials. As previously reported, we observe significant lowering of the swelling volume on going from M4K to the Pd-charged resin M4KPd8 prior to reduction. This can be attributed to the crosslinking effect of Pd(II) [7].

The distribution of metal after the reduction of Pd(II) to Pd(0) depends on the ratio of the diffusion rate of the reducing agent to that of metal cation to be reduced [3,7]. In other words, if the inner space of the ion-exchange resin is well accessible, the reducing agent easily reaches the cationic positions, the metal cations are reduced nearby the anionic sites, and a uniform distribution of metal crystallites is obtained. According to

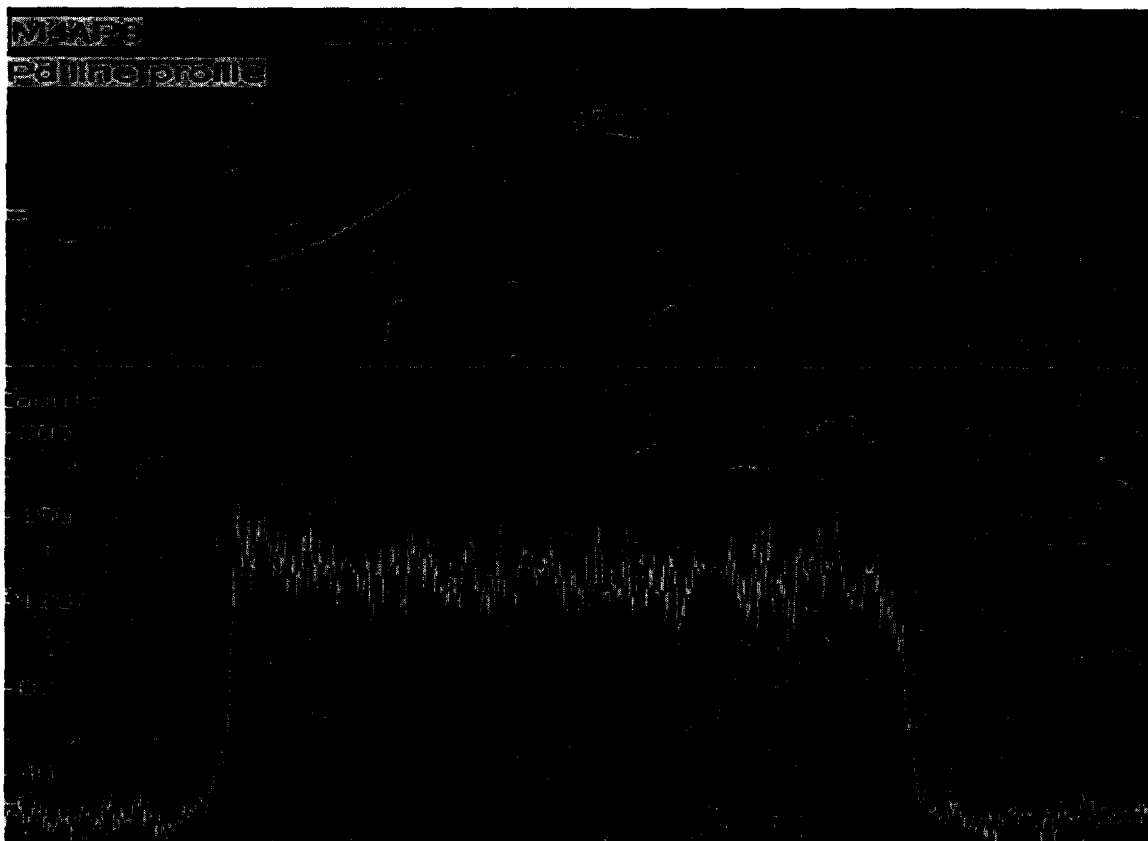


Fig. 5. Palladium distribution line profile in M4APd8.

this explanation, achievement of the uniform distribution of reduced metal is more difficult in supports with high concentration of Pd(II) than in the case of low concentration. Inspection of X-ray maps and line profiles of M4APd8 (Fig. 5), M4APd1, M4APd05 and M4KPd8 revealed the uniform distribution of reduced metal obtained under the employed reduction conditions.

The size of the metal crystallites was evaluated by X-ray diffraction measurements [9]. Diffraction patterns given in Fig. 6 indicate proportionality of intensity of the signal to the metal content, but also a decrease of precision for lower metal contents, especially for M4APd05. In spite of this, using a pseudo Voigt function [10] for data profile treatment (smooth curves in Fig. 6), quantities for evaluation of the size were estimated with less than 10 per cent relative error for all profiles. The average diameter of crystallites was calculated from the full width of the half of the maxi-

imum of breadth (FWHM) using the standard Sherrer equation [9] with the classical value of Sherrer's constant  $k=0.9$ . Due to the high value of the integral breadth of the profile (more than  $2^\circ 2\theta$  in all cases), instrumental corrections were omitted. Values of 4.13, 4.2 and 4.04 nm were determined for the M4APd05, M4APd1 and

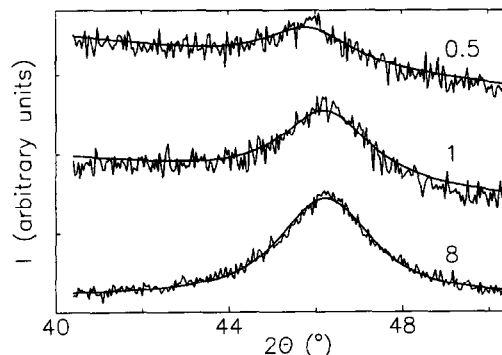


Fig. 6. X-ray powder diffraction patterns of palladium in M4A based catalysts and curve smoothing by Voigt function. Numbers over the curves denote the content of palladium in the catalysts.

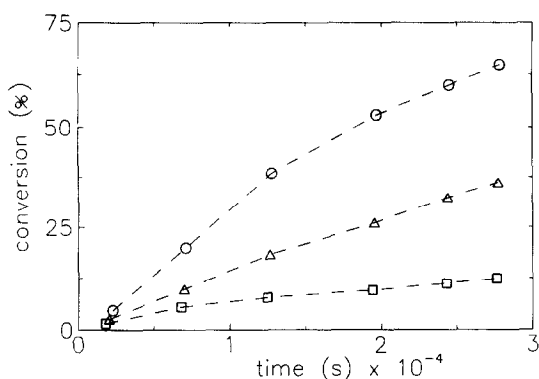


Fig. 7. Conversion of *p*-nitrotoluene vs. time on M4A-based palladium catalysts. Symbols as in Table 2.

M4APd8 catalysts, respectively. Thus, we can consider the same size of crystallites for all catalysts.

The catalytic potentialities of the M4A-based catalysts were tested in the hydrogenation of *p*-nitrotoluene (PNT) to *p*-toluidine at ambient conditions, in methanol, in a shaken batch vessel. Preliminary tests showed that under employed reaction conditions, transport of hydrogen from gas to liquid phase and transport of reactants to the surface of catalyst did not play significant restrictions for the rate of process. In order to evaluate the accessibility of the inner space of the catalyst particles, experiments with the same amount of catalyst were performed, and therefore the analytical concentration of palladium varied with the metal content of the catalyst. Results are reported in Fig. 7 and in Table 2.

The initial reaction rate turned out to be proportional to the metal content in the case of M4APd05 and M4APd1 which is documented by values 5.61 and 7.44 for the ratio  $(\xi_v)/[Pd] \times 10^2$ . The value 1.65 in the case of M4APd8

shows on significant internal diffusional restrictions in this catalyst. Unfortunately, a reliable comparison of the hydrogenation rates is prevented by effective catalyst deactivation. In fact, these catalysts are seen to undergo rapid deactivation under the employed conditions: 100% conversion was reached only with M4APd8, while in the case of M4APd05 it was about 30% after 30 h. M4APd8 was still active in the first recycle, though appreciably less than in the first run; M4APd1 was considerably less active, and M4APd05 practically inactive. Chromatographic analysis of reaction mixture showed that in all samples amounts of intermediates did not exceed 1% of the initial concentration of PNT. Thus, the deactivation occurs as the consequence of leaching of palladium from the support. The content of palladium in our catalysts was lowered to the values 0.5 and 6.5% w/w of Pd in M4APd1 and M4APd8, respectively, after 2 runs. In the sample of M4APd05 the content of palladium was practically zero. We tried to find some quantitative data about hydrogenation of *p*-nitrotoluene in literature, but we were not successful. However, there was some information about deactivation of Pd/C catalyst during hydrogenation of 2,4-dinitrotoluene (DNT) [11–13]. Janssen et al. [12,13] determined values of parameters in Langmuir–Hinshelwood model from which the rate of the formation of 4-hydroxylamine-2-nitrotoluene (important intermediate) can be calculated ( $0.0144 [\text{mol}_{\text{DNT}} \text{kg}_{\text{cat}}^{-1} \text{s}^{-1}]$  or  $0.0015 [\text{mol dm}^{-3} \text{s}^{-1} \text{M}^{-1}]$  for the molar concentration of palladium [M]). The value 0.0015 is close to values given in Table 2, so our catalysts seem to

Table 2

Initial rates ( $\xi_v$ ) in hydrogenation of *p*-nitrotoluene

Catalyst	$\xi_v \times 10^6$ ( $\text{mol dm}^{-3} \text{s}^{-1}$ )	[Pd] (mM)	$(\xi_v)/[Pd] \times 10^2$ ( $\text{mol dm}^{-3} \text{s}^{-1} \text{M}^{-1}$ )	Relevant symbol in Fig. 7
M4APd8	34.1	2.07	1.65	circle
M4APd1	17.1	0.31	5.61	triangle
M4APd05	9.3	0.125	7.44	square

Room temperature, 0.1 MPa, 1 M *p*-nitrotoluene in methanol, size of particles 0.3–1 mm, [Pd] –molar concentration of palladium in reaction mixture. Conversion curves are in Fig. 7.

be of comparable activity. However, deactivation during the hydrogenation of nitrocompounds might not be an unavoidable nuisance of our dimethylacrylamide-based resin. It is worthwhile to mention that deactivation strongly depends on the nature of the support and can be very low using some other microporous anionic resins, e.g. dimethylacrylamide–styrene sulphonate resins [7] or interpenetrating polymers [14].

In order to overcome the problem of catalyst deactivation, and to obtain data for a reliable comparison of the activities of our catalysts, we performed additional catalytic tests using the hydrogenation of cyclohexene as model reaction. The preliminary tests showed much higher rate of hydrogenation than it was in the hydrogenation of *p*-nitrotoluene (approximately 50 times). The rate increased with increasing pressure of hydrogen in the range from 0.1 to 1.5 MPa. The tests reported below were performed at ambient temperature and 0.5 MPa keeping constant concentration of palladium in the reaction mixture in all runs (0.5 mM). Deactivation was absent and the catalysts maintained their activity upon recycling: the conversion curves for the first and second run were very close to each other, the variance in the conversion values being less than 5%. Table 3 and Fig. 8 and Fig. 9 summarize results.

Under employed conditions transport of hydrogen from gas to liquid phase did not restrict the process. However, transport from liquid phase to the surface of catalyst and diffusion of components into the catalyst influenced the rate of the process significantly when the catalyst contained higher amount of palladium. The straight-line shape of the conversion curves for both experiments M4APd8 with bigger particles, and M4APd8 with smaller ones indicates that the constant rate is given by a constant driving force for the supply of hydrogen from the bulk liquid to the surface of catalyst. The constant driving force is caused by concentration of hydrogen on the surface close to zero (very fast consumption of hydrogen coming to the catalyst) and constant concentration in bulk liquid supposed to be hydrogen saturated. When the concentration of palla-

Table 3  
Initial rates ( $\xi_v$ ) in hydrogenation of cyclohexene

Catalyst	$d$ (mm)	$\xi_v \times 10^4$ (mol dm <sup>-3</sup> s <sup>-1</sup> )	Relevant symbols in Fig. 8 and Fig. 9
M4APd8	0.3–1	2.06	circle
M4APd8	0.1–0.3	3.27	filled circle
M4APd1	0.3–1	9.82	triangle
M4APd05	0.3–1	11.7	square
M4APd05	0.1–0.3	13.6	diamond
M4APd05	<0.1	12.8	filled square
M4APd05 <sup>a</sup>	<0.1	26.4	asterisk

Room temperature, 0.5 MPa, 1 M cyclohexene in methanol. [Pd] 0.5 mM in each run,  $d$  – size of particles. Conversion curves are in Fig. 8.

<sup>a</sup> 1 mM of palladium in the reaction mixture.

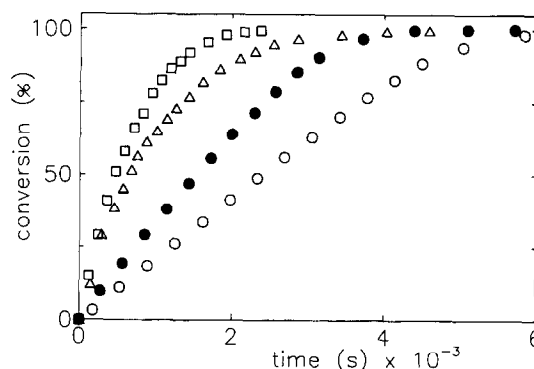


Fig. 8. Conversion of cyclohexene vs. time with M4A-based palladium catalysts. Symbols as in Table 3.

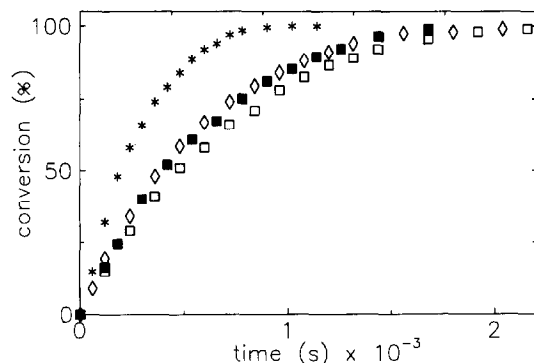


Fig. 9. Conversion of cyclohexene vs. time with M4APd05 catalyst. Symbols as in Table 3.

dium in the catalyst is lowered, internal diffusion starts to play a role as it is seen from results for the M4APd1 catalyst. In the case of M4APd05, we believe to have achieved the kinetic regime only when the particle size of the catalyst was lower than 0.3 mm. In fact, the observed initial



reaction rate was the same for both small ( $0.1 < d < 0.3$  mm) and very small ( $d < 0.1$  mm) particles. Moreover, upon doubling the analytical metal concentration (1 mM) we observed a double initial rate in the case of very small particles (Table 3). This circumstance rules out any influence of the gas–liquid transport on the reaction rate and confirms the achievement of the kinetic regime. Conversion curves for M4APd05 catalyst show also a dependence of the rate on the concentration of cyclohexene. We suppose that this is due to the small value of the adsorption constant of cyclohexene on the surface (as in case of 1-hexene [15]), henceforth the majority of surface is not occupied by cyclohexene and the kinetics stemming from the Langmuir–Hinshelwood model [16] cannot be reduced to the form with the zero order to cyclohexene.

Mass-transfer hindrances were apparently controlling the overall rate of the process also in all experiments with M4KPd8 catalyst.

All these experiments proved the good accessibility of the interior space of M4A based catalysts and high activity of palladium crystallites inside them. The concentration of metal less than 1% w/w is sufficient to obtain a catalyst of the acceptable activity.

#### 4. Conclusions

Gamma ray initialized polymerization of *N,N*-dimethyl-acrylamide, *N,N'*-methylene-bis-acrylamide, potassium 1-methacryloyl-ethylene-2-sulphonate (or sulphonic acid) was successful and resulted in the preparation of strongly hydrophilic microporous anionic resins. Palladium catalysts based on these resins demonstrated their ability in promoting hydrogenation reactions. It was observed that the higher the metal content in the catalyst the higher the reaction rate, which demonstrates a good interior accessibility of the support. The average diameter of metal crystallites in M4A based catalysts does not depend on metal concentration and it is equal to the value about 4 nm.

In accord with literature data, deactivation of Pd catalysts during hydrogenation of *p*-nitrotoluene was observed. This phenomenon is probably caused by the good swellability of resins in methanol and a consequent good accessibility of metal crystallites resulting in relatively fast dissolution of metal [11] and loss of activity, which is well documented for catalysts with low content of metal.

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