# POLYMER OXIDATION CATALYST CONTAINING ACIDIC FUNCTIONAL GROUPS

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The catalyst containing redox sites in addition to acid functional groups was prepared by sulphonation of a macroporous chloromethylated styrene–divinylbenzene copolymer with concentrated sulphuric acid at elevated temperatures. Its activity was tested for the oxidation of 2-propanol by molecular oxygen at 120°C and was found to be comparable to that of the iridium on carbon catalyst. Neutralisation of acid functional groups by alkali metal led to proportional decrease in the oxidation activity. The results of EPR spectroscopic study of these catalysts show that the redox properties of the polymer are caused by carbon clusters which are capable of electron exchange.

In the preceding work[1] it was reported that styrene–divinylbenzene copolymers substituted with quinone groups exhibit low catalytic redox activity. This activity can be increased substantially by introducing sulphonic acid groups on the copolymer by its direct sulphonation with sulphuric acid. It was further found that sulphonic acid groups do not increase the catalytic redox activity only by their cooperation with quinone redox sites. It was observed that also in the preparation of polymer catalysts of this type involving the condensation of the starting polymer with chloromethyl methyl ether and hydroquinone catalysed by Friedel–Crafts reagents and the sulphonation of the functionalized polymers so formed with concentrated sulphuric acid at elevated temperatures, there proceeds degradation of organic macromolecules leading to formation of defects which exhibit redox capacity determinable by titration and thus also the catalytic activity[2].

As in some cases the redox capacity and catalytic activity induced by degradation of the polymer structure with Friedel–Crafts reagents and with concentrated sulphuric acid was higher than the same parameters corresponding to the content of quinone functional groups, in the present work we attempted to prepare polymer catalysts of redox type using a controlled degradation of styrene–divinylbenzene copolymers. The catalytic activity of these polymers was tested for the gas phase and liquid phase oxidation of 2-propanol by molecular oxygen.

## EXPERIMENTAL

*Starting polymers.* Macroporous styrene–divinylbenzene copolymer with 10% of divinylbenzene, containing chloromethyl groups (MK-Cl-10, specific surface 15 m$^2$/g, Cl content 15·4%) and standard styrene–divinylbenzene copolymer with 6% of divinylbenzene, containing chloromethyl groups (SK-Cl-6, specific surface 0·1 $m^2/g$, Cl content 17·1%) were produced by Spolek pro chemickou a hutní výrobu, Ústí n/L. Macroporous styrene–divinylbenzene copolymer with 10% of divinylbenzene (MK-10, specific surface 25 $m^2/g$) was supplied by Výzkumný ústav synthetických pryskyřic a laků, Pardubice. MK-Cl-10 polymer was condensed with hydroquinone by the procedure reported by Kun[3] to give the polymer MK-Hydr-10 (Cl content 7·5%).

*Sulphonation of chloromethylated copolymers and polymers formed by their condensation with hydroquinone.* Dried polymer (20 g) was allowed to swell overnight in 150 ml of sulphuric acid (96% $SO_3$ by weight). Then the temperature of the reaction mixture was increased with vigorous stirring. When it reached the sulphonation temperature it was maintained constant for appropriate time (Tables I and III). Then the mixture was cooled to ambient temperature. The excess sulphuric acid was removed by repeated decantation with distilled water. The polymer was transferred into a glass tube and washed with distilled water until the test for sulphate ions in the eluate was negative. After that the polymer was dried at 105°C to constant weight. The same procedure was used also for the sulphonation with chlorosulphonic acid.

*Sulphonation with gaseous sulphur trioxide.* The polymer (5 g) was introduced into a glass tube which was placed in an oven heated to 180°C. Sulphur trioxide was evolved by a stream of argon from oleum (50—60% $SO_3$) heated to 100°C. After 6 h, the contents of the tube were transferred into ice water and repeatedly washed until neutral reaction of the eluate. Then the polymer was dried at 105°C for 6 h *in vacuo* (5 kPa).

*Reaction of chloromethylated polymer with* $ZnCl_2$. The dry polymer (5 g) was allowed to stand overnight in a mixture of 10 ml of decane and 5 g of $ZnCl_2$. Then the temperature of the reaction mixture was increased to 180°C under stirring and maintained at this temperature for 6 h. After cooling, the polymer was washed with ethanol, placed in a glass tube and washed with distilled water. Finally, it was dried at 105°C to constant weight.

*Measurements of activity in gas phase.* These were carried out in a glass flow reactor which was directly connected to a gas chromatograph *via* a feeding valve. 2-Propanol was feeded as liquid to an evaporator in which it was mixed with oxygen and the reaction mixture was passed over the catalyst. The products were analysed gas chromatographically at 76°C with the use of a column (4 × 1 400 mm) filled with 6% diglycerol + 6% poly(ethylene glycol 300) on Chromosorb. The weighed amount of the catalyst (1 g) was first dried at the reaction temperature (120°C) for 1 h in a stream of dry nitrogen and then it was oxidized by oxygen (50 ml/min flow rate for 2 h). Only after this treatment the oxidation of 2-propanol was commenced (propanol flow rate $3{\cdot}12 . 10^{-2}$ mol/h; $O_2$: 2-propanol molar ratio = 1).

*Measurements of activity in liquid phase.* For this purpose, a 5 ml-titanium autoclave connected to a shaking device was used. The body of the autoclave was equipped with a heating mantel provided with measuring and controlling thermocouples. The upper part of the autoclave was equipped with a capillary tube for oxygen inlet and with a silicon rubber stopcock serving for removal of samples by chromatographic microsyringe. The weighed amount of the dry catalyst (0·5) was mixed with 2·5 ml of 2-propanol in the autoclave and this was then closed. After pressurizing with oxygen to 0·8 MPa, the autoclave was heated to the reaction temperature. (120°C) under shaking. The reaction time was calculated from the beginning of heating.

*Determination of the redox capacity of polymers.* Weighed sample (1—2 g) was introduced into a glass tube and washed with 250 ml of 1N-$H_2SO_4$. The reduction was carried out by 100 ml of 1·5% solution of $TiCl_3$ in 1N-$H_2SO_4$, followed by washing with 300 ml of 1N-$H_2SO_4$. The oxidation was performed by using 150 ml of 0·1N-$Fe_2(SO_4)_3$ solution in 1N-$H_2SO_4$. Fe(II) ions formed by the reduction were determined by manganometric titration.

TABLE I

Properties of Catalysts Prepared by Sulphonation of MK-Cl-10

| Sulphonation temp., °C | Sulphonation time h | Cl content, % | Specific surface $m^2/g$ | Titration exchange capacity mequiv $H^+/g$ | Sulphur content-by titration % | Sulphur content-by analysis % | Titration redox capacity mmol H/g | Catalytic activity in gas phase % acetone | Catalytic activity in liquid phase, % acetone | EPR signal |
|---|---|---|---|---|---|---|---|---|---|---|
| 60 | 6 | 4·3 | 362 | 1·0 | 3·2 | — | 0·14 | 1·5 | 0·74 | 4 700 |
| 120 | 6 | 1·2 | 168 | 2·77 | 8·88 | 16·54 | 0·31 | 1·5 | — | 11 500 |
| 150 | 6 | 0·38 | 187 | 2·48 | 7·95 | 14·72 | 1·02 | 5·0 | 3·6 | 15 800 |
| | | 0·22 | 22 | 2·60 | — | — | 1·68 | 9·0 | — | 50 800 |
| 180 | 6 | 0·32 | 25 | 2·23 | 7·15 | 10·87 | 2·39 | 9·0 | 3·6 | 23 800 |
| | | | 15·7 | 2·54 | 8·20 | 14·1 | 2·24 | 6·4 | 3·5 | 793 100 |
| 180 | 4 | — | 12·9 | 2·44 | 7·8 | 12·17 | 2·1 | 2·4 | 3·7 | 983 000 |
| 180 | 2 | — | 23·7 | 2·44 | 7·8 | 14·7 | 1·42 | 4·6 | 4·1 | 644 600 |
| 180 | 20[a] | — | — | 1·54 | 4·9 | 8·11 | 1·1 | 0·54 | 7·3 | — |
| 200 | 1 | — | 1·0 | 2·39 | 7·6 | 10·1 | 1·37 | 2·1 | 2·9 | 1 741 800 |
| 220 | 3 | — | 0·1 | 2·13 | 6·8 | 7·13 | 1·64 | 0 | 9·3 | 1 558 500 |

[a] After 6 h, $H_2SO_4$ was replaced by fresh one.

*Other properties.* Exchange capacity was determined by usual way[4], the chlorine content was analysed by Schöninger's method and the specific surface was determined by the method proposed by Nelson and Eggertsen[5,6].

## RESULTS AND DISCUSSION

MK-Cl-10 polymer was used as the starting polymer, since macroporous types proved to be advantageous in our earlier works[1,2]. The properties of the catalysts obtained by sulphonation of this polymer under different conditions are given in Table I. Besides the values presented in this Table also the degree of the degradation of polymer mass was followed based on the weight of the polymer. In the course of the action of sulphuric acid nearly all the chlorine present in the polymer is cleaved off. It was found that the treatment of the polymer with sulphuric acid at temperatures up to 180°C results only in minimal loss of the organic mass of the polymer and the weight of the worked up sample increases due to the higher molecular weight of the sulphonic acid group as compared to that of chlorine. However, at a temperature of 220°C, there proceeds already the considerable degradation or organic macromolecules, since the weight of the obtained polymer decreases and after sulphonation for 6 h, all the polymer is decomposed to soluble and gel-like fragments. At 250°C this process proceeds at a very fast rate, so that the insoluble polymer is difficult to obtain. Hence, the temperature 180°C is the upper limit for achieving the acceptable yield of the desired catalysts.

TABLE II

Properties of Catalysts Prepared by Treating MK-Cl-10 with Different Agents for 6 h

| Agent | $H_2SO_4$ | $ZnCl_2$ | $HClSO_3$ | $SO_3$ |
|---|---|---|---|---|
| Treatment temp. | 180 | 180 | 140 | 180 |
| Exchange capacity, mequiv $H^+$/g | 2·23 | 0 | 3·52 | 1·83 |
| Sulphur content corresponding to exchange capacity | 7·15 | 0 | 11·3 | 5·87 |
| Analytical sulphur content | 10·87 | 0 | 21·39 | — |
| Chloride content | 0·32 | 10·5 | 3·07 | — |
| Redox capacity | 2·39 | 0·01 | — | — |
| Catalytic activity in gas phase % of acetone | 9·0 | 0 | 2·0 | 1·2 |
| Catalytic activity in liquid phase % of acetone | 3·6 | 0 | 0·6 | 5·9[a] |
| Specific surface | — | 214 | — | — |
| EPR signal | 23 800 | 722 | 171 200 | 1 084 400 |

[a] In dioxane.

TABLE III

Properties of Catalysts Prepared by Sulphonation of Different Polymers at 180°C

| Starting polymer | MK-10 | SK-Cl-6 | MK-Cl-10 | MK-Hydr-10 | MK-Hydr-10 |
|---|---|---|---|---|---|
| Reaction time | 6 | 6 | 6 | 6 | 18[a] |
| Specific surface | 0·1 | 0·1 | 25 | 27 | — |
| Exchange capacity, mequiv $H^+$/g | 4·70 | 0·26 | 2·23 | 3·34 | 1·59 |
| Sulphur content corresponding to exchange capacity | 15·0 | 0·83 | 7·15 | 10·7 | 5·05 |
| Analytical sulphur content | 25·8 | 1·24 | 10·87 | 10·12 | 8·52 |
| Chlorine content | — | 12·7 | 0·32 | 0·62 | — |
| Redox capacity | 0·99 | 0·15 | 2·39 | 2·49 | 1·47 |
| Catalytic activity in gas phase % of acetone | 3·0 | 0 | 9·0 | 13·2 | 2·6 |
| Catalytic activity in liquid phase % of acetone | 7·7 | 0·85 | 3·6 | 7·7 | 13·3 |
| EPR signal | 162 400 | 13 500 | 23 800 | 122 500 | — |

[a] After 6 h, $H_2SO_4$ was replaced by fresh one.

The course of sulphonation depends upon a number of factors which can be controlled only with difficulty, so that the properties of the products obtained vary considerably. This demonstrates itself in the specific surface, the catalytic activity and also in EPR signal. In spite of these fluctuations, one can state that the products with highest catalytic activity are obtained at 180°C for the sulphonation carried out for 6 h. Differences in the catalytic activity in the gas and liquid phase oxidation will likely depend on the accessibility of the active sites of the catalyst in both media, which relates mainly to the specific surface in the case of the gas phase reaction and to the swelling ability of the polymer mass in the case of the liquid phase oxidation. In our previous works[1,2] we have assumed the cooperation of sulphonic acid groups and active redox sites in the catalytic reaction. As the necessary condition for this cooperative effect will be certain steric demands and since it is not clear whether all the redox sites determinable by titration in the liquid phase are catalytically active, one cannot expect a straightforward correlation of the exchange and redox capacity with the catalytic activity.

The values of EPR signal are the measure of the degradation of the polymer mass, which agrees with the conditions used to synthesize these catalysts. Similarly to the redox sites determinable by titration, also the sites giving EPR signal are not obviously catalytically active in all cases, since there is no direct proportionality between their amount and the catalytic activity of the polymer.

Titration exchange capacity of all the polymers listed in Table I is lower than that of sulphonated styrene–divinylbenzene copolymers with 10% of divinylbenzene, although their polymer structure is identical and they contain, furthermore, only chloromethyl group. It was also found that the sulphur content in these polymers is greater than is the number of sulphonic acid groups determinable by titration. The relationship between sulphur-containing groups which can be determined by acid-base titration and the other sulphur present in the polymers studied at different temperatures of sulphonation is shown in Fig. 1. In order to get a deeper insight into processes taking place during treatment with sulphuric acid, we analysed also the gaseous products in the course of the reaction up to maximal temperature. These analyses were made with the use of Finnigan 3000 mass spectrometer. The results are shown in Fig. 2. They indicate that at temperatures below 100°C sulphuric acid reacts exclusively with chloromethyl group of the polymer to produce hydrogen chloride. This process is very fast, so that in about 20–30 min all the chlorine of the polymers evolves into the gas phase. The chloromethyl group seems thus to be one of the sites on the polymer which is subjected to attack by sulphuric acid. Sulphur dioxide and carbon dioxide begin to be present in greater amounts only at temperatures above 110°C. Their formation demonstrates the decomposition of both the starting polymer and the reacting sulphuric acid.

All the results just discussed allow to conclude that the mode of sulphuric acid action changes with temperature. Instead of acting as the sulphonating agent, other reactions are preferred, such as formation of sulphones, dehydrogenation and oxidation. It is known that sulphonation is reversible reaction. The high concentration of sulphonium ions results in displacement of hydrogen atoms attached to benzene ring, whereas the high proton concentration, obtained by diluting sulphuric acid with group by hydrogen, and that especially at high temperatures[7,8]. Furthermore, water, brings about the reverse reaction, *i.e.* the replacement of the sulphonic acid at higher temperatures sulphuric acid acts also as oxidizing agent, which is demonstrated by dehydrogenation of organic polymer to produce the more cross-linked structure with lower hydrogen content. This process can lead eventually even to formation of carbon clusters, and by oxidation of carbon atoms to formation of carbon dioxide, sulphuric acid being at the same time reduced to sulphur dioxide or to other low valent sulphur compounds. The difference found between the exchange capacity determining the number of sulphonic acid groups and the total content of sulphur occurs in the polymer shows that the considerable amount of sulphur is present in the polymer in the form other than as sulphonic acid groups, likely in the form of sulphone bridges or fragments containing bound sulphur.

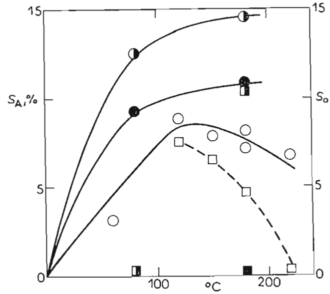

FIG. 1

Dependence of Sulphur Content in Catalysts on Temperature of Sulphonation of Starting Polymers

$S_A$ Sulphur corresponding to sulphonic acid groups determined by titration ○, $S_0$ the residual sulphur to the analytical value □; empty marks MK-Cl-10, halved marks MK-10, full marks MK-Hydr-10.

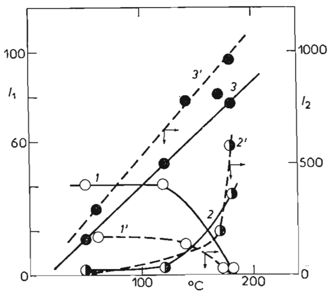

FIG. 2

Analysis of the Gas Phase in the Course of Sulphonation in Dependence on Sulphonation Temperature

$I_1$ Intensity of characteristic signals for polymer MK-Cl-10, $I_2$ intensity of characteristic signals for polymer MK-Hydr-10; content of *1*, *1'* HCl, *2*, *2'* $CO_2$, and *3*, *3'* $SO_2$.

It is known that even at lower temperatures than those used in the present work, sulphonation of styrene–divinylbenzene copolymers leads to a certain destruction of the macromolecular skeleton and thus to an increase in the specific surface of the polymer particles[9]. However, this increase is not so great as in the case of the sulphonation of the chloromethylated polymers. From Table I it is seen that the greatest increase in the specific surface takes place in the sulphonation carried out at lower temperature. The initial attack of the acid results therefore in the more subtle disturbance of the surface. At the higher temperature, at which this disturbance is greater, the specific surface decreases.

Table II summarizes the results obtained by modification of the polymer MK-Cl-10 by treatment with different agents. With regard to the oxidation activity, positive results were obtained only with the reagents introducing sulphonic acid groups into the polymer. In the case of $ZnCl_2$, the polymer was unaffected (besides a certain decrease in chlorine content) and also the catalytic activity was not observed, although the specific surface increased by one order of magnitude.

Table III presents the results obtained in the sulphonation of different polymers under conditions which were found to be optimal for MK-Cl-10. MK-10 gave a medium active catalyst which exhibited greater activity in the liquid phase oxidation. The great difference in the sulphur content based on sulphonic acid group and the total analytical sulphur content is remarkable. The sulphonation of the polymer which was structurally intact at higher temperature is obviously more oriented toward formation of other fragments that are sulphonic acid groups. Contrarily, the result obtained with MK-Hydr-10, *i.e.* with the polymer which was subjected to two Friedel–Crafts reactions with different reagents, shows that in this case the analytical sulphur content compared well with the number of sulphonic acid groups. The different course of sulphonation in the above mentioned cases is documented also by the results shown in Fig. 2. MK-Hydr-10 releases sulphur dioxide in amounts which exceed those found for the former polymer by a factor of ten. This is obviously caused by the reaction of sulphuric acid with hydroquinone groups of the polymer, reported by Tulupov[8]. The oxidation of the quinone-substituted polymer is taking place obviously even when all the hydroquinone groups are reacted, since both sulphur dioxide and carbon dioxide are evolved in amounts which exceed the number of quinone groups. It seems likely that the sulphonation of MK-Hydr-10 polymer leads to formation of the catalyst with the highest catalytic activity. The results obtained with standard polymer SK-Cl-6 prove that this type is not suitable, since gel particles do not allow sulphuric acid to act sufficiently under given experimental conditions.

Time dependence of the conversion of 2-propanol to acetone on the catalysts from Table I under constant reaction conditions is shown in Fig. 3. The steady conversion is achieved only after 40 min of the operation of the reactor. Of the catalysts studied, the most active one exhibits comparable catalytic activity with the catalyst comprising 0·5% iridium on active carbon. The latter one was studied under similar conditions by Le Nhu Thanh[10]. After steady conditions were attained, the activity of all the catalysts presented in Fig. 3 remained constant for more than 5 h. We made an attempt to influence the catalytic activity by interupting the reaction and by reoxidizing the catalyst by oxidation at the reaction temperature. The course of the conversion of 2-propanol in the initial phase of the reaction after this interruption and oxidation of the catalyst was analogous to that shown in Fig. 3 and the activity of the catalyst became constant after 40–50 min and attained the same value as before the interruption of the reaction. This process was repeated several times with the same result.

From the kinetic curve for the oxidation of 2-propanol on catalyst 4 at 120°C (Table I) which is shown in Fig. 4 it follows that the initial reaction rate of the reaction, $r^\circ = 3{\cdot}1$ mol/h kg(cat), compares within one order of magnitude with the results obtained for the oxidation of this alcohol on iridium catalyst[10]. The values

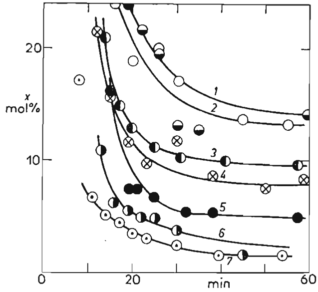

Fig. 3

Time Dependence of 2-Propanol Conversion (*x*) on Polymers Sulphonated at Different Temperatures

*1* Iridium on carbon, *2* MK-Hydr-10 sulphonated at 180°C, *3* MK-Cl-10 sulphonated at 180°C, *4* MK-Cl-10 sulphonated at 180°C, *5* MK-Cl-10 sulphonated at 150°C, *6* MK-Cl-10 sulphonated at 120°C, *7* MK-Cl-10 sulphonated at 60°C.

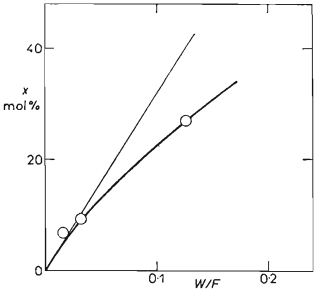

Fig. 4

Kinetic Curve for the Gas Phase Oxidation of 2-Propanol at 120°C on Polymer MK-Cl-10 Sulphonated at 180°C

*x* Conversion of 2-propanol into acetone, partial pressures of the alcohol and oxygen 50 kPa; conversions were read in 60th min of the operation of the reactor.

of the conversion in Fig. 4 were determined in 60th min of the reaction, since at the longer contact of the oxidized alcohol, the steady reaction was attained at a slower rate.

Sulphonic acid groups are prerequisite for the oxidation of 2-propanol on the catalysts studied, since the catalytic activity decreases proportionally with their neutralisation by alkali metal ions (Na), as seen from Fig. 5. The completely neutralized catalyst was inactive, although it exhibited both the redox capacity and EPR signal. The cooperation of the strong acid group in the oxidation of 2-propanol is thus common both to catalytic sites derived from organic substituents (quinones)[1] and to electron exchange sites based on carbon clusters.

Sulphonic acid groups of the catalyst catalyse also dehydration of 2-propanol to propene and dipropyl ether. This reaction proceeds at a faster rate than the oxidation and thus the conversion of the alcohol into dehydration products attains a value of about 50% for the fully sulphonated polymers. The course of the conversion in the initial phase of dehydration is the same as in the case of oxidation. This demonstrates that we deal here with parallel reactions taking place on sulphonic acid groups as common active sites.

The results discussed in the present work show that decomposition of macroporous chloromethylated styrene–divinylbenzene copolymers with sulphuric acid at elevated temperatures yields the polymer catalyst with acid and redox properties. As far as acid-base reactions are concerned, its activity is comparable with organic cation exchange resins of macroporous type. In the case of oxidation reactions, the obtained catalyst is comparable with metal catalysts. If one starts from the chloromethylated polymer which is substituted by hydroquinone prior to sulphonation, one obtains the catalyst with better oxidation properties compared to the catalyst prepared

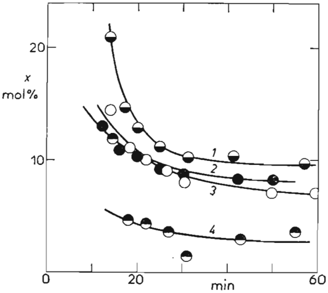

FIG. 5

Conversion of 2-Propanol ($x$) on Catalysts Neutralised to Different Degree

MK-Cl-10 Sulphonated at 180°C, contact time 0·032 kg/cat)/mol 2-propanol, the alcohol partial pressure 50 kPa, reaction temperature 120°C; *1* starting catalyst, *2* neutralised 25%, *3* 50%, *4* 75% of the acid groups of the starting polymer.

by sulphonation of the starting chloromethylated copolymer. As sulphonation of the starting styrene–divinylbenzene copolymer yields the less active catalyst than are those mentioned above, Friedel–Crafts substitution causes obviously such changes in the polymer structure which ensure formation of catalytically active redox sites on the polymer during its subsequent sulphonation at higher temperatures.

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