PHOTOASSISTED PRODUCTION OF $O_2^{-\bullet}$ AND H_2 IN AQUEOUS MEDIUM STIMULATED BY POLYTHIOPHENE IN ZSM-5 ZEOLITE CHANNELS

Gabriel ČÍK[a,]*, František ŠERŠEŇ[b] and Alena BUMBÁLOVÁ[c]

[a] Department of Environmental Science, Slovak University of Technology, 812 37 Bratislava, Slovak Republic; e-mail: cik@chelin.chtf.stuba.sk
[b] Institute of Chemistry, Faculty of Natural Sciences, Comenius University, 842 15 Bratislava, Slovak Republic; e-mail: sersen@fns.uniba.sk
[c] Department of Pharmaceutical Analysis and Nuclear Pharmacy, Faculty of Pharmacy, Comenius University, 832 32 Bratislava, Slovak Republic

Received May 11, 1998
Accepted October 12, 1998

The formation of reactive oxygen species due to irradiation by a visible light of the polythiophene deposited in ZSM-5 zeolite channels in aqueous medium has been studied. Polymerization of thiophene was carried out in zeolite channels after the ion-exchange reaction of Na^+ for Fe^{3+}. By means of EPR spectroscopy, the temporarily generated $^1O_2$ in irradiated aqueous medium was proved. The formation of $O_2^{-\bullet}$ was confirmed by the reduction of Fe^{3+}-cytochrome *c*. Irradiation led to the water reduction to hydrogen.

Key words: ZSM-5 zeolites; Polythiophenes; Reactive oxygen species; Water photoreduction; Water photolysis; Photochemistry.

Reactive oxygen species play an important part in the photoassisted decomposition of water, in the mineralization induced by water and air pollution on inorganic semiconductors[1–5] (TiO_2, ZnO, ZrO, *etc*.), and in the environmental chemistry[6].

Since radiation is absorbed by inorganic semiconductors only in the limited part of the UV-VIS spectrum ($\lambda_{max} < 400$ nm), the researchers' effort is aimed at the preparation of the spectrally sensibilized ($\lambda_{max} > 400$ nm) and photostable system[7]. The new possibility to prepare stable photoactive systems characterized by the radiation absorption in a visible part of the electromagnetic spectrum is offered by heterogenic systems based on natural and synthetic zeolites. Zeolites are crystalline aluminosilicates, the basic crystalline framework of which is composed of the AlO_4^{5-} and SiO_4^{4-} tetrahedrons. Tetrahedrons constitute of the typical zeolite structure with a system of cages and channels of various dimensions. Their composition may be expressed by the following general formula: $M_x[(Al_2O_3)_x(SiO_2)_y]\cdot n\ (H_2O)$, where x and y represent the total number of tetrahedrons in a basic cell. Since the Al-tetrahedron is carrying one negative charge, this must be compensated for the M^+ cation which is not bound by a covalent bond and therefore can be very easily replaced by the other metal element[8]. Zeolites of the Y-type have been recently used as a carrying matrix to stabilize the $Ru(bpy)_3^{3+}$ complex in studying the oxidation of water to oxygen[9]. In recent years, photocatalytic effects have also been studied on organic semiconductors, among which polythiophene (PT) and its derivatives occupy an important position[10]. Polythiophene is an environmentally stable conjugated polymer which gives rise to polaron states (cation-radicals) through photoactivation when rapid subsequent reactions are stimulated by a released electron[10,11].

For the preparation of regio-regular PTs, it is possible to use synthetic zeolites whose cavity and channel dimensions permit the strong polymer chain anchoring after the polymerization reaction. This kind of reaction is studied mostly on the Y-type and ZSM-5 zeolites[8,12]. The polymerization (oligomerization) reaction is caused by oxidation with transition metals (Cu^{2+}, Fe^{3+}) after the ion-exchange reactions for Na^+. The aim of our work was to prepare PT in ZSM-5 zeolite channels in the presence of Fe^{3+} ions and, by means of the heterogeneous Fe-ZSM-5–PT system, to study photophysical changes in aqueous medium proceeding along the polymer chain owing to irradiation by a visible light of the electromagnetic spectrum. In this work, our objective is to study the production of reactive oxygen species formed during the photoassisted reaction of the polythiophene, deposited in channels of the ZSM-5 zeolite in aqueous medium. It has been found that these changes are accompanied by the generation of oxygen superoxide $O_2^{-\bullet}$ and by the formation of H_2.

EXPERIMENTAL

Polymerization of thiophene was performed in Na-ZSM-5 zeolite channels (VURUP Co., Slovak Republic) according to refs[8,12]. The used zeolite was of the following composition (molar ratio): $Na_2O : CaO : Al_2O_3 : SiO_2 = 0.61 : 0.34 : 1.0 : 43.6$. The treatment of zeolite with Fe^{3+} ions was carried out with aqueous solution of $FeCl_3$ in an ion-exchange reaction[8,13]. The exchanged Fe^{3+}-ZSM-5 was prepared by refluxing (6 h) 5 g of the zeolite with 100 cm^3 of aqueous 0.3 M $FeCl_3\cdot 6\ H_2O$ (Aldrich). Following the exchange reaction the sample was filtered and dispersed twice in distilled water to remove an excess of Fe^{3+} before being dried in a desiccator.

The diffusion reflectance UV-VIS spectrum was measured with an M-40 apparatus (Zeiss, Germany) and the transformation of data to Kubelka–Munk parameters was carried out. Barium sulfate was used as a standard. The diffusion reflectance FT-IR spectra were measured with a

PU-9900 instrument (Philips Analytical). The inorganic composition of the zeolite sample was analyzed by the radionuclide X-ray fluorescence method. Irradiation of an element was excited by a radionuclide γ-radiation source ^{238}Pu having the half-time of conversion 86.4 years, energy 12–22 keV and activity 1 110 MBq. The spectrum of the sample developed after the interaction with the radionuclide source was measured using the semiconductor Si/Li detector connected with a multi-channel analyzer ORTEC (EG&G ORTEC, U.S.A.). The analysis of the untreated as well as treated zeolite sample showed the following contents of elements (μg g^{-1}): Na-ZSM-5 (Fe 39.2; Cu less than 1; Zn 104.3; Mn less than 1; Pb less than 1); Fe-ZSM-5 (Fe 285.6; Cu 15.5; Zn 77.7; Mn 36.7; Pb less than 0.5). EPR spectra were measured with an ERS-230 apparatus (ZWG, Academy of Sciences, Germany) in the X-region at the microwave output 5 mW and at the modulation amplitude 0.5 mT. As an $^1O_2$ detector, 2,2,6,6-tetramethylpiperidine (TEMP; synthesized by Dr D. Végh, Department of Organic Chemistry, Slovak University of Technology, 99.3%) was used. As a spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, Sigma) was used. Irradiation of the sample (water suspension of the treated zeolite) was accomplished by a metal-halogen lamp (250 W, Tesla, ≈60 W m^{-2}) from the distance of 50 cm through a 5-cm water filter in the cavity of the EPR apparatus at 25 °C. pH of water suspension was 5.63. In order to determine the content of the generated H_2, a special closed reactor was used, the mixture of liberated gases being analyzed with a gas chromatograph MCH-112 (Chemoprojekt, Czech Republic). Molecular sieve 5A and He (20 cm^3 min^{-1}) as a carrier were used.

RESULTS AND DISCUSSION

Figure1 illustrates a differential diffusion reflectance spectrum after accomplishing the oxidative polymerization reaction and of zeolite, on which only Fe^{3+} ions were present. The positions of the assigned absorption maxima can be seen in Table I, in which also the characteristic polythiophene bands found in the FT-IR spectrum are demonstrated. The UV-VIS spectrum can be divided into two energetic regions: approximately up to 500 nm and above 500 nm. The positions of absorption maxima of the variously long

TABLE I
Positions of electronic absorption maxima in diffusion reflectance UV-VIS spectra and diffusion reflectance FT-IR spectra of polythiophene synthesized in ZSM-5 zeolite channels in the presence of Fe^{3+} ions

λ_{max}, nm	$\tilde{\nu}$, cm^{-1}
398	1 458.4 C=C stretching
478	1 331.1
575	
700	
876	

thiophene oligomers deposited in ZSM-5 zeolite channels are examined in detail in ref.[14]. According to this work, the neutral oligomers (T_2, T_3, T_4 and T_6) have their absorption maxima at 300 (T_2), 354 (T_3), 390 (T_4) and 434 (T_6) nm. Their oxidized forms (polarons) have absorption maxima at 407 ($T_2^{+\bullet}$), 522 ($T_3^{+\bullet}$), 614 ($T_4^{+\bullet}$) and 775 ($T_6^{+\bullet}$) nm. Dications (bipolarons) on the polymer (oligomer) chain have absorption maxima at 600 (T_6^{++}), 636 ($T_{4(1)}^{++}$), 661 (T_8^{++}), 761 (T_9^{++}), 833 ($T_{4(2)}^{++}$) and higher, in dependence on the size of the backbone (neutral) chain. Our results have shown that similar absorption maxima appear in the ZSM-5 zeolite channels also during the chemical (oxidative) oligomerization of thiophene in the presence of Fe^{3+}. This fact allows us to deduce that the neutral ($\lambda < 500$ nm) and oxidative forms ($\lambda >$ 500 nm, polarons and bipolarons of thiophene oligomers) occur in zeolite channels of the synthesized sample.

Photophysical changes of polythiophene chains in aqueous medium were studied by EPR spectrometry. In the EPR spectrum of a dry Fe-ZSM-5 zeolite (not indicated), a wide line $g \approx 2.00$ ($\Delta B_{pp} \approx 57$ mT) appeared. This signal belongs to clustered iron species present in the oxide/oxide–hydroxide impurity phases[15,16]. The same signal was registered by the authors in ref.[16] after performing the ion-exchange reaction of sodium ions for Fe^{3+} in the Y-type zeolite. In aqueous medium, the signal of iron became evidently weaker. After the oxidative polymerization of thiophene taking place in zeolite channels, a new signal with $g = 2.006$ ($\Delta B_{pp} = 0.7$ mT) appeared, which can be assigned to polarons of short polymer chains[11]. The number of spins was

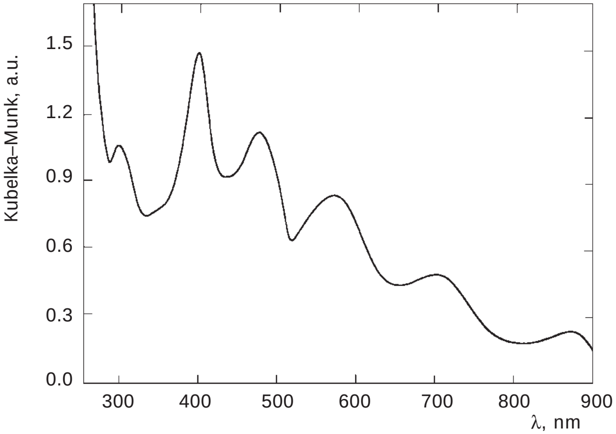

Fig. 1
Diffusion reflectance spectrum of thiophene oligomers in Fe-ZSM-5 zeolite channels

$1.3 \cdot 10^{19}$ spin g^{-1}. This signal maintained its stability also in aqueous medium. The irradiation with a visible light in aqueous medium caused the EPR signal of polarons to grow (Fig. 2). This suggests that the concentration of the oxidized oligomeric species of thiophene (polarons) increases with the time of illumination – similarly to what was observed in the non-aqueous medium[11]. When the zeolite without PT was irradiated, no changes were noticed in the EPR signal assigned to Fe^{3+}. If thiophene oligomers were also present in zeolite channels, the signal of Fe^{3+} was not changed by irradiation either. After the application of TEMP to $^1O_2$ detection, the EPR signal belonging to its oxidized form (TEMPO, 2,2,6,6-tetramethylpiperidine-*N*-oxyl, Fig. 3) was recorded during the irradiation of Fe-ZSM-5–PT water suspension in the sample. This signal represents, in all probability, an adduct of TEMP and $^1O_2$. When DMPO was used, the polaron signal of polythiophene disappeared and only the signal characteristic of the DMPO adduct and that of the organic radical (DMPO-R) appeared without observing the adduct with an active oxygen intermediate. DMPO could not be used for detection of $O_2^{-\bullet}$ radicals because DMPO probably quenches the active form of polythiophene. Figure 3 reveals that the signal intensity of TEMPO has an increasing tendency depending on the time of the irradiation. In view of the fact that the size of the molecule of TEMP exceeds the size of the openings in ZSM-5 zeolite channels (0.53 × 0.56 and 0.51 × 0.55 nm), it should be admitted that the indicated reaction proceeds, above all, in the entrance of the channels or on the zeolite "external" surface near the channel openings as well.

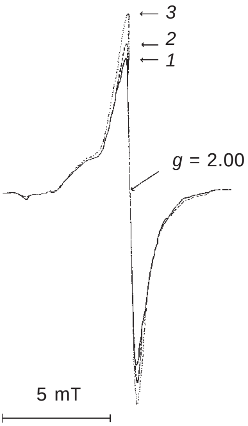

FIG. 2
Growth of the EPR signal of polarons of thiophene oligomers depending on irradiation time: *1* 0 min; *2* 10 min; *3* 15 min (sample containing $5 \cdot 10^{-5}$ dm^3 water and 1 mg Fe-zeolite with polythiophene)

Using gas chromatography, it was found that gases evolved during the irradiation of Fe-ZSM-5–PT water suspension contained hydrogen, the amounts of which were 624 and 449 μmol in two independent samples after four hours of irradiation. The question whether the decomposition of water also gives rise to oxygen cannot be answered because our experimental equipment has not allowed us so far to express the unambiguous standpoint. The problem rests upon the fact that it is very difficult to remove oxygen absorbed on the zeolite surface. However, the growth rate of the EPR signal of polaron states was found to decrease after bubbling nitrogen through water suspension. It was also ascertained that the production of TEMPO was reduced (this is not documented in the figure) in the samples bubbled through with nitrogen after the irradiation. This suggests that oxygen may have an important role in the assumed mechanism of water decomposition. If we consider that the number of spins in the organic component of the system was growing during irradiation and the Fe^{3+} signal did not change, we can accept the idea that the photoactivation of PT leads to the subsequent transfer of the electron which, in the next step, participates in water reduction. Then, for the basic mechanism, the following reactions can be preliminarily proposed[1,6,17].

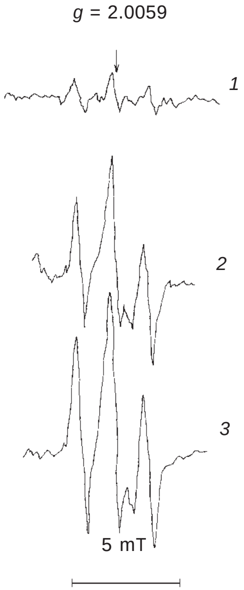

FIG. 3
Temporal dependence of the growth of the EPR signal of 2,2,6,6-tetramethylpiperidine and $O_2^{-\bullet}$ produced during the irradiation of the Fe-ZSM-5 zeolite with polythiophene in its channels (sample containing $5 \cdot 10^{-5}$ dm^3 water, $1.1 \cdot 10^{-6}$ mol TEMP and 1 mg Fe-zeolite with polythiophene); irradiation time: *1* 0 min, *2* 10 min, *3* 15 min

$$\mathrm{PT} \xrightarrow{h\nu} \mathrm{PT}^{*} \longrightarrow [\mathrm{PT}^{+\bullet} + \mathrm{e}] \longrightarrow \mathrm{O}_2^{-\bullet} \qquad k = 1.9 \cdot 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \qquad (1)$$

$$\mathrm{PT} \xrightarrow{h\nu} \mathrm{PT}^{*} \xrightarrow{\mathrm{O_2(H_2O)}} [\mathrm{PT}^{+\delta} \ldots\ldots\ {}^1\mathrm{O}_2^{-\delta}] \longrightarrow \mathrm{PT}^{+\bullet} + \mathrm{O}_2^{-\bullet} \qquad (2)$$

$$\begin{tikzcd}
\mathrm{PT} \arrow[r, "h\nu"] & \mathrm{PT}^{*} \arrow[r, "\mathrm{H_2O}"] & \mathrm{PT}^{+\bullet} + \mathrm{e} \arrow[d, "\mathrm{H}^{+}"] & & \\
 & & \mathrm{H}^{\bullet} & k = 2.3 \cdot 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} & (3)
\end{tikzcd}$$

$$\mathrm{H}^{\bullet} + \mathrm{H}^{\bullet} \longrightarrow \mathrm{H}_2 \qquad k = 1.0 \cdot 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \qquad (4)$$

Both the detected $^1O_2$ followed by its transition to $O_2^{-\bullet}$ and the H_2 generated in the evolved gases entitle us to take into account the earlier mentioned reactions. We suppose that in the first step of light reaction an interaction between the excited polythiophene and O_2 occurs with the production of $^1O_2$, which is proved by the appearence of the EPR signal of TEMPO. The second step is the production of $O_2^{-\bullet}$ during the reaction (*2*). The production of $O_2^{-\bullet}$ during the irradiation of thiophene trimer (of 2,2′:5′,2″-terthiophene) in aqueous medium was studied in ref.[17]. The authors have proved that the photoactivation of 2,2′:5′,2″-terthiophene results in the generation of $O_2^{-\bullet}$ directly in water. We, too, have proved the generation of $O_2^{-\bullet}$, namely by the reduction of Fe^{3+}-cytochrome *c* to Fe^{2+}, which is described in ref.[17].

After completing the irradiation, the EPR signal assigned to the oxidized states of thiophene oligomers (polarons) became gradually weaker, which confirms that Fe^{2+} ions produced in the oxidative polymerization enter, in all probability, the dark reactions. On the basis of this fact it is possible to assume that a drop in the number of spins of the organic component found during the dark reaction is brought about by participation of Fe^{2+} in the reaction with polythiophene polarons.

CONCLUSIONS

The polymerization of thiophene in pentasile type ZSM-5 (Fe^{3+}-ZSM-5) zeolite channels permits one to synthesize the low-molecular polythiophenes with a different proportion of neutral and oxidized (polaron) species. The polaron states of thiophene oligomers are stable in zeolite channels also in aqueous medium. By irradiation of deposited neutral thiophene oligomers in the zeolite in aqueous medium the concentration of polaron states increases. The concomitant feature of the electron transfer from a neutral oligomeric form is the growth of the EPR signals of cation-radicals (polarons) as well as the production of the superoxide oxygen ($O_2^{-\bullet}$). It has been found that irradiation leads to the reduction of water to hydrogen.

The autors thank Dr D. Végh for providing a sample of TEMP. The work has been supported by the Commission of the European Community under the project No. IC 15-CT97-0703 and the projects of Ministry of Education of the Slovak Republic (No. 95/51/95200 and No. 1/40113/97).

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