



Synthesis of zirconia-immobilized copper chelates for catalytic decomposition of hydrogen peroxide and the oxidation of polycyclic aromatic hydrocarbons

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ABSTRACT

Chelating sorbents with diethylenetriaminepenta(methylene-phosphonic acid) (DTPMPA) and ethylenediaminetetraacetic acid ligands immobilized on zirconia matrix were prepared and subsequently saturated with Cu(II). All the Cu chelates catalyzed decomposition of H₂O₂ yielding highly reactive hydroxyl radicals. All of them were also able to catalyze degradation of polycyclic aromatic hydrocarbons (anthracene, benzo[a]pyrene and benzo[b]fluoranthene). The most effective DTPMPA-based catalysts G-32 and G-35 (10 mg ml⁻¹ with 100 mmol H₂O₂) caused almost complete decomposition of 15 ppm anthracene and benzo[a]pyrene during a five day catalytic cycle at 30 °C. Anthracene-1,4-dione was the main product of anthracene oxidation by all catalysts. The catalysts were active in several cycles without regeneration.

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1. Introduction

Removal of nonpolar contaminants including polycyclic aromatic hydrocarbons (PAHs) is difficult, since such wastes, e.g., the extracts of contaminated soils, are not readily degraded by conventional methods and must be sometimes treated with organic solvents due to limited water-solubility of PAHs (Sims and Overcash, 1983).

In addition to the use of microbial degradation or the utilization of isolated enzymes (Baldrian et al., 2000; Paszczynski and Crawford, 2000; Baborová et al., 2006), alternative chemical and physico-chemical approaches for PAH degradation have been proposed. These include, e.g., the treatment with ultraviolet light (Jang and McDow, 1997; An and Carraway, 2002; Ao et al., 2003), ultrasonic treatment (Little et al., 2002), ozonation (Yao et al., 1998; Goi and Trapido, 2004), or gamma radiolysis (O'Shea et al., 2002); most of them are of limited use due to high energy demand and/or the need of special equipment.

In our previous works we described several copper-based Fenton-like metal/ligand systems for homogeneous catalytic decomposition of hydrogen peroxide and production of hydroxyl radicals (Gabriel et al., 2000, 2004). The main shortcoming of homogeneous catalytic processes ensues from the requirement for catalyst recovery or separation. In many cases, catalyst separa-

tion from the reaction mixture is technically and economically unfeasible. Moreover, many active homogeneous catalysts, including transition metal ions and their complexes are toxic and thus represent a potential environmental problem. Under these circumstances, it is desirable to develop heterogeneous catalytic procedures where the catalysts are easily separable.

Recently, heterogeneous wet peroxidation systems have been described. The systems based on ion-exchange binding that include metal- or metal complex-loaded ion exchangers (Salem, 2000; El-Safty et al., 2001; Crowther and Larachi, 2003; Gemeay et al., 2003), metal-pillared clays (Guo and Al-Dahhan, 2003; Caudo et al., 2007) or zeolite-immobilized metal ions (Centi et al., 2000; Fajerwerg et al., 2000; Kuznetsova et al., 2004) usually suffer from leaching of bound metals or metal-complexes and systems in the form of a slurry are not always easy to separate. The applicability of the systems using metals nonspecifically bound to polymeric support (Jose et al., 2003; Gupta et al., 2003a,b) or polymeric metal chelates (Baldrian et al., 2005) on the other hand may be limited by the fact that the carrier itself can be also oxidatively attacked by the produced reactive oxygen species. This can result in an irreversible loss of metal binding capacity of the ion exchanger (Baldrian et al., 2005).

The convenient way to overcome this problem is the use of inorganic supports. As they themselves are mostly not catalytically active it is necessary to find appropriate immobilization chemistry for binding of metal chelates to their surface. Functionalized inorganic chromatographic materials used for separation based on

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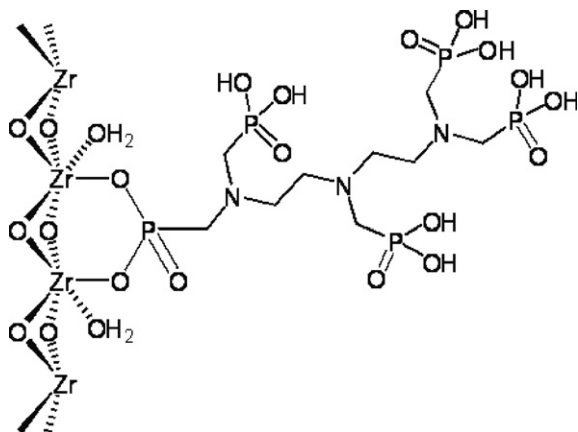


Fig. 1. The structure of diethylenetriaminepenta(methylene-phosphonic acid) chelated on the coordinatively unsaturated Zr(IV) atoms at a ZrO_2 matrix surface.

interaction can offer the desired properties. Matrices on silica (SiO_2) and zirconia (ZrO_2) (Trudinger et al., 1990; Dun and Zhao, 2005), magnesia–zirconia ($\text{MgO} \cdot \text{ZrO}_2$), and ceria–zirconia ($\text{CeO}_2 \cdot \text{ZrO}_2$)₆ basis are used for this purpose. Functionalization of silica by silanization with 3-aminopropyl trimethoxy silane for binding catalytically active metal chelate is not sufficiently stable. Zirconia was therefore chosen in the present study. Its preparation and functionalization for the given purpose is also easier. It uses for functionalization a very stable coordination bond of the Zr(IV) atoms on the matrix surface and monophosphonate (Bellezza et al., 2005) or even stronger coordination bond to di- or polyphosphonate chelating agents (Clausen and Carr, 1998; Subramanian and Sarkar, 2003) (Fig. 1). Appropriate chelating groups are iminodiacetic and its phosphonic analogue. Reagents having two or more such groupings are then bound through one of them to zirconia support and residual form chelates with transition metals catalytically active in Fenton-like reactions (e.g., Cu, Co or Fe).

Two approaches for the preparation of zirconia with chelating groups were used. “Sol–gel” – method consists of the hydrolysis and precipitation of zirconyl chloride with water and ammonia in the presence of a chelating reagent (Wang et al., 1997). In the second method zirconia is prepared from zirconyl chloride by precipitation with sodium hydroxide (Chuah and Jaenicke, 1997) and the product is then treated with chelating reagents. Cu chelates were prepared in both cases by reaction of zirconia–chelating conjugates reagent with Cu(II) salt.

The aim of this work was to develop a functional heterogeneous catalyst for the decomposition of hydrogen peroxide and to test its ability to decompose polycyclic aromatic hydrocarbons as model xenobiotic organic compounds.

2. Experimental

2.1. Preparation of heterogeneous catalyst

Zirconyl chloride octahydrate (98%), diethylenetriaminepenta(methylene-phosphonic acid, heptasodium salt (Na_7DTPMPA ; 250 mg ml^{-1} in H_2O , 55% purity) and ethylenediaminetetraacetic acid, disodium salt dihydrate (Na_2EDTA ; 99.0) were purchased from Sigma–Aldrich.

The “sol–gel” preparation of ZrO_2 -A-EDTA: A solution of 1.00 g zirconyl chloride octahydrate in 2 ml water was heated at 60 °C for 15 min and this solution was then added under vigorous stirring to 13 ml of 0.067 M Na_2EDTA + 0.4 M ammonia warmed up to 60 °C in a 100-ml three necked reactor. The slurry was heated and stirred for another 2.5 h. After cooling, the product was filtered

off, thoroughly washed with distilled water until chlorides in eluate disappeared and dried in vacuo at 50 °C for 2 h. ZrO_2 -A-DTPMPA was prepared in the same way as by ZrO_2 -A-EDTA; 13 ml of 0.0185 M Na_7DTPMPA + 0.4 M ammonia was taken instead of Na_2EDTA .

Preparation of ZrO_2 -A-EDTA-Cu (G-31): 0.5 g ZrO_2 -A-EDTA was shaken in an Erlenmeyer flask with 45 ml of 0.1 M CuSO_4 solution for 6 h. The slurry was then filtered, thoroughly washed with water and dried in vacuo at 50 °C for 2 h. ZrO_2 -A-DTPMPA-Cu (G-32) was prepared analogously to ZrO_2 -A-DTPMPA.

The preparation of zirconia by precipitation with sodium hydroxide (ZrO_2 -B): A solution of 4.00 g zirconyl chloride octahydrate in 20.0 ml of distilled water was dropwise added (1 ml min^{-1} ; peristaltic pump) under vigorous stirring to 7.44 ml of 1 M NaOH solution at room temperature. The suspension formed was heated at 100 °C for 12 h, vacuum-filtered after cooling and washed with 1 M ammonium nitrate and water until chlorides in eluate disappeared. The product was dried at 100 °C for 10 h and calcinated at 500 °C in a muffle oven for 12 h.

Modification of ZrO_2 -B with chelating reagents and preparation of Cu chelates: ZrO_2 -B-EDTA-Cu (G-34): 0.60 g ZrO_2 -B was shaken in an Erlenmeyer flask with 7.5 ml of 0.1 M Na_2EDTA solution for 6 h. The solid was vacuum-filtered, thoroughly washed with water and shaken with 45 ml of 0.1 M CuSO_4 solution for 6 h. The product was collected by vacuum filtration, thoroughly washed and dried under vacuum at 50 °C for 2 h.

Preparation of ZrO_2 -B-DTPMPA-Cu (G-35): For preparation, see above; 0.1 M Na_7DTPMPA was used instead of 0.1 M Na_2EDTA .

2.2. Catalytic systems

In the experiments with hydrogen peroxide decomposition 1% (w/v) G-31, G-32, G-34 or G-35 (pH 4.0–4.7) were combined with 0.1 M hydrogen peroxide in water. The reaction proceeded at 30 °C in the dark with slow agitation. Controls did not contain any catalyst. In experiments with PAH degradation, 1% (w/v) catalysts were mixed with 0.1 M hydrogen peroxide in water–acetone (1:1 v/v) containing 15 ppm anthracene, benzo[a]pyrene, benzo[b]fluoranthene or anthracene-1,4-dione. In another experiment, a mixture of anthracene, benzo[a]pyrene, benzo[b]fluoranthene 15 ppm each with the H_2O_2 solution was used. The reaction proceeded at 30 °C in the dark with slow agitation. Controls for evaluation of adsorption of PAH on catalyst were without hydrogen peroxide. Controls of noncatalyzed oxidation by hydrogen peroxide were without catalyst. At each sampling time, the catalyst was separated by centrifugation (~30 s) and the supernatant was immediately used for analysis. It was decided not to stop the reaction by addition of a quenching agent because this would interfere with analyses of the reaction mixture. In the experiments dealing with the pH dependence of H_2O_2 decomposition, the pH values of catalysts in 0.02 M NaCl were adjusted with HCl and NaOH, respectively, to pH 2–10 before hydrogen peroxide addition. The catalysts separated after reaction were washed with 0.02 M aqueous NaCl for further use.

2.3. High performance liquid chromatography

The degradation of PAH was followed by RP-HPLC. The analyses were performed on a Waters Alliance HPLC system (Waters, USA) equipped with a diode array detector 2996 using the LiChrospher PAH column, (250 mm × 4 mm, particle diameter 5 μm ; Merck, Germany). An acetonitrile–water (9:1) mixture was used as mobile phase in isocratic mode, flow rate 1 ml min^{-1} . The analyses were performed at 35 °C with diode array detector/UV detection of the compounds. The quantification proceeded at 230 nm (benzo[b]fluoranthene) and 250 nm (anthracene, anthracene-1,4-dione and

benzo[a]pyrene), respectively. All compounds were eluted from the column during a 30-min run under the conditions described.

2.4. Electron paramagnetic resonance (EPR) measurements

EPR spectra were recorded with on E-540 Spectrometer X-Band (Bruker, Germany). The following conditions were used while recording the spectra: microwave power 20 mW, modulation amplitude 0.2 mT, attenuation 20 dB, time constant 0.5 s, scan speed 0.3 mT min^{-1} , calibration standard $\text{Cr}^{3+}/\text{MgO}$ and 25°C . The WinEPR (Bruker, Germany) program was used for spectra recording, handling and evaluation. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was used as a radical trapping agent. The reaction system of the EPR experiments is described in the legend to Fig. 4. The catalyst was applied in the form of slurry after H_2O_2 and DMPO addition.

2.5. Assay of hydrogen peroxide, hydroxyl radicals and metal ions

The concentration of H_2O_2 was assayed using the Xylenol Orange and sorbitol method (Wolff, 1994). The method based on the reaction of deoxyribose with $\cdot\text{OH}$ radicals was used to detect the production of $\cdot\text{OH}$ radicals by the catalyst (Aruoma, 1994). The reaction mixture consisted the catalyst (10 mg ml^{-1}), hydrogen peroxide (0.1 M) and deoxyribose (0.0028 M). Aliquots (500 μl) of the reaction mixture were taken and the reaction was stopped by the addition of 500 μl thiobarbituric acid (1 mg ml^{-1} in 0.05 M NaOH) and 500 μl of trichloroacetic acid (2.8 mg ml^{-1}). The deoxyribose degradation product reacted with thiobarbituric acid during 30 min treatment at 80°C , with the resulting formation of a pink color. The product of the reaction was quantified by spectrophotometry ($\lambda = 532 \text{ nm}$) after dilution with an equal amount of water. The amount of $\cdot\text{OH}$ radicals detected was expressed in arbitrary units (a.u.).

Concentrations of metal ions were analyzed with a flame atomic absorption spectrophotometer (AAS, Aurora Instruments, Canada) after appropriate dilution of liquid samples or after microwave digestion of solid samples in a $\text{HNO}_3/\text{H}_2\text{O}_2$ mixture.

3. Results

3.1. Properties of the catalyst

The content of Cu in the conjugates of zirconia with chelating agents depends especially on the surface area of zirconia and therefore on the particle size distribution and porosity. Preparation of zirconia is a complex multistep process influenced by many parameters. As the evaluation criterion of the catalyst preparation procedures we have chosen the content of Cu in the conjugates. A markedly higher Cu binding capacity was achieved by precipitation of zirconia in the presence of chelating agent and ammonia, in the sol-gel process: the Cu(II) content in individual catalysts was (in $\mu\text{mol g}^{-1}$ dry mass): 233 in G-31, 623 in G-32, 146 in G-34, and 382 in G-35. The Cu contents are higher in such cases than for precipitation of zirconia with sodium hydroxide followed by digestion of hydrated zirconia, even though the latter process was classified as forming a high surface area (Chuah and Jaenicke, 1997). The conjugates of DTPMPA with iminophosphonate grouping bound more Cu(II) than EDTA conjugates with both types of zirconia matrices. The pH of the reaction mixture was 4.9 for G-31, 4.6 for G-32, 4.8 for G-34 and 5.2 for G-35. In repeated catalytic cycles, the catalysts G-34 and G-35 lost less than 1% of the bound Cu(II) per cycle while the metal loss from the catalysts prepared by the sol-gel process – G-31 and G-32 – was slightly higher (2–3%). The performance of used catalysts could be recovered by their treatment with CuSO_4 solution when necessary (see Section 2.1).

All the catalysts at 10 mg ml^{-1} were able to decompose 0.1 M hydrogen peroxide within 120 h (Fig. 2). G-31 and G-34 decomposed more than 50% of hydrogen peroxide within the first two hours of treatment. The catalysts performed four catalytic cycles without a notable decrease in efficiency (Fig. 3). The decomposition of hydrogen peroxide was accompanied by the production of hydroxyl radicals. The highest production of $\cdot\text{OH}$ radicals was detected during the first two hours of hydrogen peroxide decomposition. The peak production of hydroxyl radicals differed among the catalysts and reached 192 a.u. in G-35, approximately twice as much as in the other catalytic systems (94 a.u. in G-32, 75 a.u. in G-34 and 69 in G-31). Spin-trapping experiments with DMPO also confirmed the production of hydroxyl radicals by the heterogeneous catalysts (Fig. 4). It seems that the metal ions on the surface of the catalysts first form a complex with hydrogen peroxide. The hydroxyl radical formed within the bound complex and can later oxidize different organic compounds. The formation of ligand-metal-radical complexes follows from the slight difference in

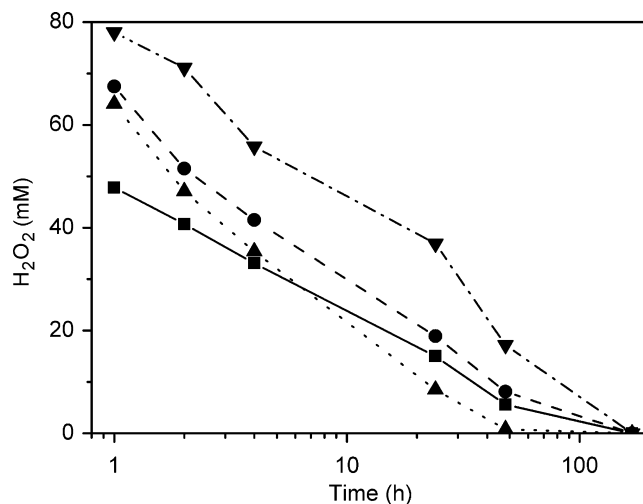


Fig. 2. The time course of hydrogen peroxide concentration during the treatment with 1% (w/v) catalysts and 0.1 M hydrogen peroxide. Catalyst: G-31 (squares), G-32 (circles), G-34 (triangles), G-35 (inverted triangles).

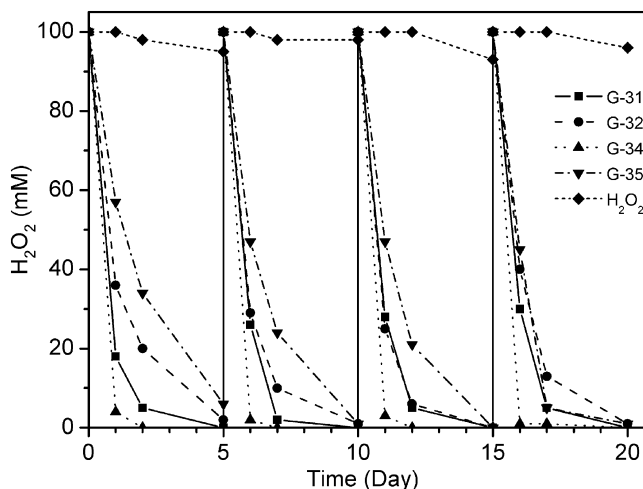


Fig. 3. Hydrogen peroxide content in reaction mixtures during four sequential catalytic cycles. one hundred ppm of hydrogen peroxide was incubated with 1% (w/v) heterogeneous catalysts at 30°C , one cycle lasted for five days. Catalyst: G-31 (squares), G-32 (circles), G-34 (triangles), G-35 (inverted triangles), H_2O_2 + no catalyst (diamonds).

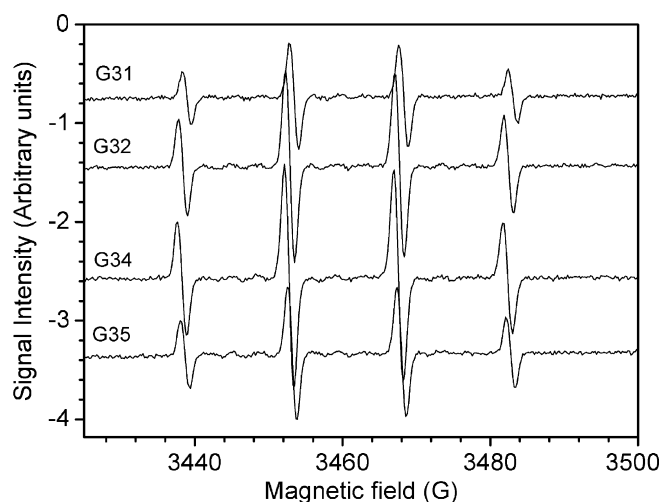


Fig. 4. EPR spectra of spin adducts of DMPO produced by heterogeneous catalysts G-31, G-32, G-34 and G-35. The reaction was initiated by the addition of H_2O_2 . The reaction mixture contained 1% (w/v) catalysts, 0.1 M H_2O_2 and 0.3 M DMPO and proceeded at 30 °C in the dark.

magnetic field in the EPR spectra of hydroxyl radicals formed by different catalysts (Fig. 4) (Shah et al., 2003). In addition to hydroxyl radicals, the presence of nitroxyl radicals presumably originating from the air dissolved in water was also detected by EPR.

The decomposition of hydrogen peroxide by the catalysts was pH dependent. In general, the rate of H_2O_2 decomposition increased with increasing pH; 45–80% of H_2O_2 were decomposed at pH 2 during a 24-h treatment while it was 70–97% at pH 10 (Fig. 5). The EDTA-based catalysts were less pH-sensitive than the DTPMPA-based ones.

3.2. PAH decomposition

All the catalytic systems decomposed anthracene, benzo[a]pyrene and benzo[b]fluoranthene. The extent of degradation after five-days treatment ranged between 29% and 99% for anthracene, 52–100% for benzo[a]pyrene and 13–30% for benzo[b]fluoranthene. The DTPMPA-based catalysts G-32 and G-35 were the most efficient, causing 100% benzo[a]pyrene degradation and more than 94% anthracene degradation (Fig. 6).

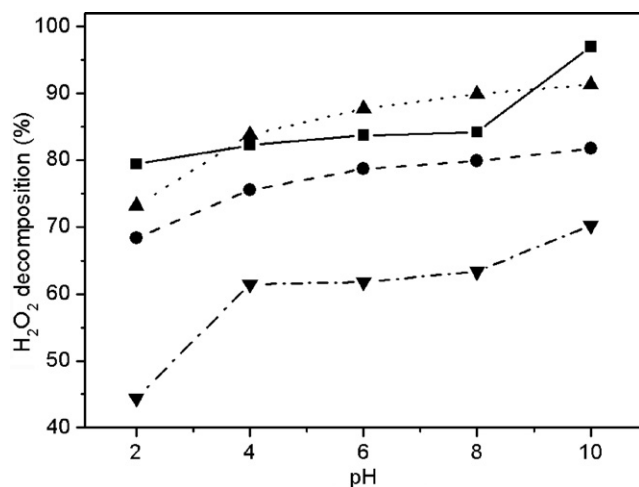


Fig. 5. The effect of pH on the H_2O_2 degradation during a 24-h treatment in the presence of 1% (w/v) catalyst and 0.1 M hydrogen peroxide. Catalyst: G-31 (squares), G-32 (circles), G-34 (triangles), G-35 (inverted triangles).

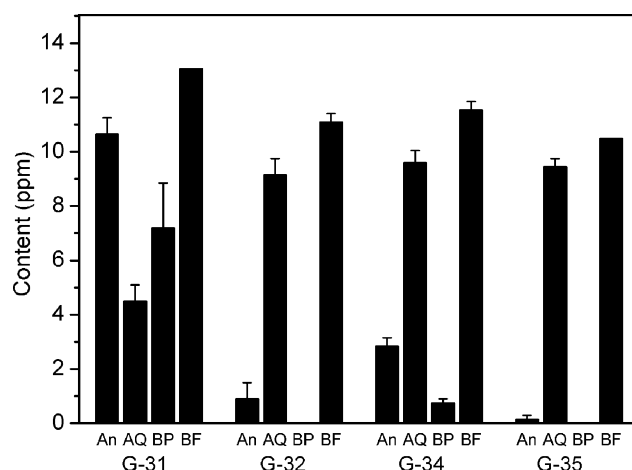


Fig. 6. The degradation of anthracene (An), benzo[a]pyrene (BP), and benzo[b]fluoranthene (BF) by heterogeneous catalysts and formation of anthracene-1,4-dione (AQ) from anthracene. Fifteen ppm of the individual compounds was incubated with 1% (w/v) heterogeneous catalysts and 0.1 M hydrogen peroxide for five days at 30 °C. The data represent averages and standard errors of three replicate reactions.

Table 1

Time course of anthracene (An), benzo[b]fluoranthene (BF), benzo[a]pyrene (BP), and anthracene-1,4-dione (AQ) concentrations (in ppm) during the treatment with heterogeneous catalysts

Catalyst	Compound	Time (day)		
		1	2	5
G-31	An	12.9 ± 0.6	11.0 ± 0.0	8.9 ± 0.0
	AQ	1.1 ± 0.1	1.8 ± 0.0	1.8 ± 0.1
	BP	14.9 ± 0.4	13.5 ± 0.0	13.5 ± 0.1
	BF	14.3 ± 0.5	10.5 ± 0.2	9.0 ± 0.0
G-32	An	11.9 ± 0.2	8.7 ± 0.6	1.8 ± 0.0
	AQ	1.4 ± 0.0	2.6 ± 0.3	2.9 ± 0.2
	BP	14.8 ± 0.1	13.5 ± 0.0	12.8 ± 0.0
	BF	12.6 ± 0.0	8.8 ± 0.6	1.5 ± 0.0
G-34	An	11.1 ± 0.0	8.1 ± 0.0	4.1 ± 0.5
	AQ	1.9 ± 0.2	3.5 ± 0.2	2.6 ± 0.3
	BP	14.5 ± 0.1	13.2 ± 0.0	12.9 ± 0.0
	BF	12.0 ± 0.3	8.0 ± 0.0	3.7 ± 0.5
G-35	An	10.3 ± 0.0	7.9 ± 0.7	1.5 ± 0.1
	AQ	1.8 ± 0.1	2.9 ± 0.2	3.3 ± 0.2
	BP	14.4 ± 0.2	13.2 ± 0.2	13.2 ± 0.0
	BF	11.1 ± 0.0	8.1 ± 0.7	1.3 ± 0.2

Fifteen ppm of anthracene, benzo[b]fluoranthene and benzo[a]pyrene was incubated with 1% (w/v) catalysts and 0.1 M hydrogen peroxide for five days at 30 °C. The data are in ppm and represent averages and standard errors of three replicate reactions.

Benzo[a]pyrene and anthracene were degraded faster than benzo[b]fluoranthene in an equimolar mixture containing 15 ppm of all three PAHs. More than 90% of benzo[a] pyrene and anthracene were degraded during a five-day treatment with the most active catalysts G-32 and G-35, while the degradation of benzo[b]fluoranthene ranged only within 12–15% (Table 1). Although the oxidation proceeded at a faster rate during the first day, PAH degradation continued over the entire five-day period. After the first cycle of the PAH degradation, all the catalysts were washed extensively with a water–acetone (1:1 v/v) mixture and used for a second cycle of PAH decomposition under the same conditions. All the catalysts exhibited approximately the same PAH degradation as in the first catalytic cycle (data not shown).

Anthracene-1,4-dione was found in the reaction mixture during anthracene degradation as one of the products of anthracene oxidation. Anthracene-1,4-dione was found in all the catalytic sys-

tems tested (Table 1; Fig. 6), but not in controls (anthracene and H_2O_2 without the catalyst). Its amount was lower than the amount of decomposed anthracene, which indicates that there is probably at least one more product of anthracene degradation. Further experiments showed, that anthracene-1,4-dione is not degraded by any of the catalysts. However, since its accumulation in an equimolar mixture of three PAHs sometimes decreased with time (Table 1), it cannot be ruled out that anthracene-1,4-dione underwent further chemical reactions under these conditions. No major products were detected after degradation of benzo[a]pyrene and benzo[b]fluoranthene.

4. Discussion

It was proposed, that during the Cu-mediated decomposition of hydrogen peroxide, hydroxyl radicals ($\cdot\text{OH}$) are generated in the reactions of both Cu(I) and Cu(II) with H_2O_2 (Pecci et al., 1997) while in the case of iron, the Fenton process, hydroxyl radicals are produced only in the reaction of Fe(II) and their regeneration from Fe(III) is a slow, rate-limiting process (Jose et al., 2003). As a consequence, several Cu-containing systems for catalytic decomposition of H_2O_2 have recently been described (Gabriel et al., 2000, 2004).

In heterogeneous catalysis no difference in kinetic behavior of Co-, Cu- and Fe-containing catalysts was previously observed (Baldrian et al., 2005, 2006). If we compare the activity of catalysts used in this study, the most active ones were the catalysts with the highest copper contents (G-32 and G-35), showing that the concentration of the catalytically active metal ion is of considerable importance.

The production of anthracene-1,4-dione and phthalic acid during the oxidation of anthracene with homogeneous copper-ligand-hydrogen peroxide systems was described previously (Gabriel et al., 2004). In this study, anthracene-1,4-dione was identified as a major product, but phthalic acid formation was not observed which is analogous to the situation of Cu-containing heterogeneous chelates on a polymer support (Baldrian et al., 2005). The way in which anthracene is degraded seems not to be dependent on the copper content of the catalyst only, while the concentration of anthracene-1,4-dione formed is ca. 1/3 of the concentration of anthracene consumed (see Table 1). This may indicate that the nature of the copper-chelating ligand influences the rate of formation of the oxidizing reactive oxygen species (probably mainly $\cdot\text{OH}$ and $\cdot\text{OOH}$) and probably also indirectly participates on the oxidation of anthracene by this reactive oxygen species. While copper chelate with iminodiacetic acid ligand (G-31, G-34) is nonionogenic, copper diphosphonate chelate is ionogenic because of the presence of unused phosphonate ionized OH groups in the chelate. Although phosphonate chelate is more active in formation of $\cdot\text{OH}$ than iminodiacetate type the latter is more efficient in oxidation of anthracene. Ionized neighbourhood thus probably creates unfavorable conditions for fast oxidation of anthracene by $\cdot\text{OH}$ and enables side reactions.

The use of inorganic supports for metal ions catalytically active in Fenton-like reactions can potentially overcome the problems with oxidative damage of the support, which was detected with polymeric metal chelates (Baldrian et al., 2005). However, a simple coordination of metals to inorganic carriers is not always the solution since the mixed iron oxides containing Fe, Co, Cu, and Mn were able to catalyze decolorization of synthetic dyes (Baldrian et al., 2006), but were inefficient in PAH degradation. The solution can be a combination of inorganic, chemically stable carrier as zirconia with immobilized metal chelates as used in this study. Although some metals leached from the catalyst in the first catalytic cycles, the metal loss did not affect the efficiency of the catalyst and was

reversible. The most efficient compound G-35 also exhibited a very low metal loss compared to other previously reported catalysts (Baldrian et al., 2005). The pH profile of activity is one of the most important properties of catalytic performance in water-based solutions. However, several efficient heterogeneous catalysts reported so far suffer from narrow ranges of optimum pH. The zirconia-based catalysts described here were efficient in a wide range of pH with the exception of highly acidic solutions.

Since hydroxyl radicals are produced in the catalytic decomposition of hydrogen peroxide, it is highly probable that other organic compounds (synthetic dyes, phenols, etc.) could be degraded using the catalysts. Our EPR experiments documented that UV-irradiation can further increase the production of hydroxyl radicals by the heterogeneous catalysts used in this study (data not shown).

5. Conclusions

Heterogeneous zirconia-supported metal chelates were prepared and their ability to degrade PAH was demonstrated. The catalysts retained their activity in repeated catalytic cycles and were active in a broad pH range. Compared with homogeneous catalytic processes for PAH oxidation, the catalysts described in this work offer the advantages of simple recovery from the treated solution and repeated use. The main disadvantage of homogeneous catalysis – introduction of heavy metals into treated solutions – was solved by metal immobilization. Chemical stability of the catalysts described here offers technological advantages over catalysts based on organic support which can suffer from oxidative damage.

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