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Heterogeneous catalysts obtained by incorporation of polymer-supported phosphonates into silica used in oxidation reactions

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Summary

The synthesis of copolymers functionalized with phosphonate groups, incorporation of them into ordered meso-macroporous silica, characterization and evaluation of the obtained materials as catalysts in oxidation of cyclohexene are presented. The catalysts obtained are very active and selective in epoxidation of cyclohexene using hydrogen peroxide as an environmentally friendly oxidant.

Introduction

Mesoporous oxide materials with macroporous structures are of interest as potential catalysts, sorbents and supports [1-3]. These materials are used to obtain new and efficient catalysts by incorporation of various catalytic active species [4]. Polymer-supported reagents are used in catalysis [5-7], organic synthesis [8], environmental [9] separations [10] and as polycationic biocides [11]. Their applications are the results of the functionalization groups. The functionalization of polymers with phosphonate groups is one of the possibilities [12-15]. Phosphonates are chelating agents and absorbents with many technical and industrial applications [15-17]. Polymers with phosphorous-based ligands display selectivity for metal ions [10, 15]. As organophosphorous ligands they are used for metal ion separations [15] and to obtain very active and selective catalysts in epoxidation of alkenes by metal complexes [18, 19].

In this paper we report the synthesis of composite materials from copolymers functionalized with phosphonate groups incorporated into meso-macroporous silica, and the characterization and evaluation of the obtained materials as catalysts in oxidation of cyclohexene. The novelty of the research consists in incorporation of copolymers functionalized with phosphonates into macro pores of silica with bimodal porous structure.

Experimental

Materials

The reagents used for preparation of the materials were tetramethylortosilicate (TMOS) (Merck), TRITON X-100 (T, Aldrich), polyoxyethylenetridecyl ether ($C_{13}(EO)_6$) (C_{13}, Aldrich), tungstic acid (Aldrich), tetrabutylammonium hydroxide (Aldrich), hydrochloric acid ((Merck), hydrogen peroxide (Aldrich), cyclohexene (Merck), trimethyl phosphite (Merck), triethyl phosphite (Fluka), tri-isopropyl phosphite (Pierce), tributhyl phosphite (Fluka), 1,2-dichloromethane (Chimopar), ethanol (Chimopar), ethyl ether (Chimopar), and chloromethylated styrene-divinylbenzene copolymer (CCVictoria). Peroxotungstic acid $H_2W_2O_{11}$ was obtained from 2.1 g of H_2WO_4 and 10 g of H_2O_2 at 333 K.

Procedure

Synthesis of the phosphonate grafted on styrene-divinylbenzene copolymers

The properties of the chloromethylated styrene-divinylbenzene copolymers used as starting materials are presented in Table 1.

5-g sample of copolymer and 50 ml of solvent (Dioxane) was added to a 250 ml round bottom flask fitted with a reflux condenser, mechanical stirrer at thermometer. The mixture was stirred for 2 h at room temperature to allow the copolymer beads to swell and then the phosphite was added. The molar ratio of chloromethyl groups: trialkylphosphite was 1:1.3. The mixture was maintained under stirring for 24 h at 373 K. After cooling, the polymer beads were separated by filtration, washed with ethanol (3x20 ml), 1, 2-dicloromethane (3x20 ml) and ethyl ether (3x20 ml), and dried under a 2KPa vacuum at 323 K for 24 h.

Table 1. The characteristics of the styrene-7% divinylbenzene chloromethylated copolymer used in polymer-analogous reactions.

Properties	
Specific surface area: S, m^2/g	30
Porous volume: Vp, cm^3/g	0.450
Mean particle radius, Rm, A°	170
Distribution of the particle radius, %	
0-15 A°	0.93
15-50 A°	0.15
50-100 A°	4.75
100-200 A°	35.13
200-300 A°	25.61
> 300 A°	33.43
%Cl[a]	16.56
G_F[b],mmoles Cl/g copolymer	4.72
x[c]	0.640
r[d]	0.07

[a] The total chlorine content; [b] Functionalization degree; [c] Fraction of styrene (S) units bearing pendant –CH_2Cl groups (Fi); [d] Fraction of divinylbenzen (DVB) units

Incorporation of the polymer-supported phosphonate

Incorporation of the polymer-supported phosphonates (PSP) in silica was performed by surfactant techniques and hydrothermal treatment using molar composition of 1.0 SiO_2: 0.02 PSP: 0.1 C_{13}(T): 1.0 $C_{10}H_{22}$: 15.4 H_2O. The corresponding quantity of the polymer-supported phosphonate was added to a mixture of surfactant, water and decan. The pH of surfactant and water mixture was adjusted to 2 with HCl. After 3 h stirring, 10.96 g TMOS was added. The gel obtained was aged 24 hr at room temperature, sealed into Teflon-lined steel autoclaves and heated 5 days at 353 K. The solid products were recovered by filtration, washed with water and dried 12 h at 333 K in air.

Phosphonotungstic complexes

The phosphonic complexes with tungsten (2.4-0.1 mmol W/g) were obtained by shaking for several hours samples of polymer-supported phosphonates (PSP) or polymer-supported phosphonates incorporated into silica (SP) with an excess of tetrabutylammonium salt of peroxotungstic acid in dioxane solution [18]. A quantity of the SP materials were calcined in air at 823 K.

Characterization

The obtained materials were characterized by X- ray diffraction (Philips PW 170 diffractometer), Fourier transform infrared spectroscopy (Spectrum 2000, Perkin Elmer), scanning electron microscopy (SEM) (Philips XL-20 microscope), TEM (Philips Tecnai microscope). The amount of W in the catalysts and BET surface area of the samples thermal treated at 823 K were determined by atomic adsorption (Solaar 969 (TJA Solution)) and nitrogen adsorption-desorption (Micromeritics), respectively. The phosphorus content of the polymer-supported phosphonates was obtained by adsorption in water of P_2O_5 obtained from a sample of the final product precisely weighed and burnt out in an oxygen atmosphere. The solution obtained was titrated with an aqueous solution of cerium (III) 0.005 M in the presence of Eryochrome Black T as indicator [11, 13].

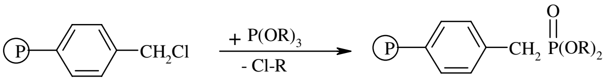
Catalytic oxidation

The epoxidation of cyclohexene was performed using a 25 ml thermostated reactor with a condenser and a magnetic stirrer. Cyclohexene (2.6 ml), dioxane (5.4 ml) and 70 mg PS and PSP catalysts were added; the system was purged for 15 min and then heated at 303K or 343 K; then the flow of nitrogen was stopped and 30 % aqueous solution of hydrogen peroxide (5.7 ml) was introduced dropwise. After reactions, the catalysts were separated by centrifugation and the filtered solids were used again. The oxidation products were analyzed by gas chromatography and hydrogen peroxide consummation was determined by iodometric titration. The selectivity in epoxycyclohexane (S_{epoxid}) was calculated as % of cyclohexane transformed in epoxide.

Results and discussion

Synthesis and characterization

The polymer-supported phosphonate groups were functionalized with different radicals by Michaels-Arbuzov polymer-analogous reactions:



(1)

where: R = Me, Et, iso-Pr, n-Bu

The formation of C-P(O)(OR)$_2$ phosphonate groups was confirmed by IR spectroscopy. IR spectra of the polymer support and polymer-supported phosphonate show that the intensity of chloromethyl absorption band (δCH_2Cl) at 1430 cm^{-1} decreases after Michaelis-Arbuzov reaction of the chloromethyl groups and the intensity of the absorption band at 1260 cm^{-1}, attributed to the valence vibration of P=O, increases. The apparition of the absorption band at 1060 cm^{-1} was attributed to the valence vibration of P-O-C bond.

The phosphorus content in the functionalized copolymers was used in order to determine their functionalization degrees [13].

The fraction of repetitive units functionalized with phosphonate groups was determined by accepting the statistical structure of the repetitive of final copolymer presented in Figure 1.

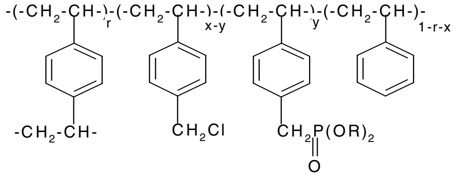


Figure 1. Statistical structure of the repeat unit of the functionalized copolymer [13]

The main characteristics of the copolymer functionalized with phosphonate groups are presented in Table 2.

Table 2. Characteristics of phosphonate groups grafted on styrene-divinylbenzene copolymers.

No.	Code	Phosphite	P content (%)	y^a	G_F^b Mmoles/g
1	Me	$(CH_3O)_3P$	4.07	0.19	1.25
2	Et	$(C_2H_5O)_3P$	4.40	0.22	1.38
3	IP	$(iC_3H_7O)_3P$	4.18	0.22	1.35
4	Bu	$(nC_4H_9O)_3P$	3.37	0.17	1.03

a. $y = \dfrac{\%P \cdot M_{mi}}{100 \cdot n_P \cdot A_P - \%P \cdot (M_{SFf} - M_{SFi})}$, $M_{mi} = r \cdot M_{DVB} + x \cdot M_{SFi} + (1 - r - x) \cdot M_S$;

b. $G_F = \dfrac{y}{M_{mf}}$, $M_{mf} = r \cdot M_{DVB} + (x - y) \cdot M_{SFi} + y \cdot M_{SFf} + (1 - r - x) \cdot M_S$.

The degrees of functionalization with phosphonate groups are relatively high, ranging from 1 – 1.4 mmoles of functional groups / g of copolymer, ensuring a sufficient concentration of active centers per unit mass of the copolymer and being suited for application as catalytic agent.

The analysis of the statistical structure of the repetitive unit of the final copolymer revealed that 17-22% of the aromatic rings are bearing phosphonate groups. Moreover, it should be noted that in the initial copolymer, 64% of the aromatic rings were functionalized with chloromethyl groups and 36% (100%-64%) of the aromatic rings of the initial polymer were not functionalized.

Incorporation into silica

Using the procedures described in the experimental section, phosphonates and phosphonotungstic complexes incorporated into hierarchically ordered silica with meso- and macropores were obtained. The hierarchical structure of the materials can be directly visualized by scanning electron microscopy (Figure 2). The morphology of the particles show a regular array of the mesoporous particles and macropores

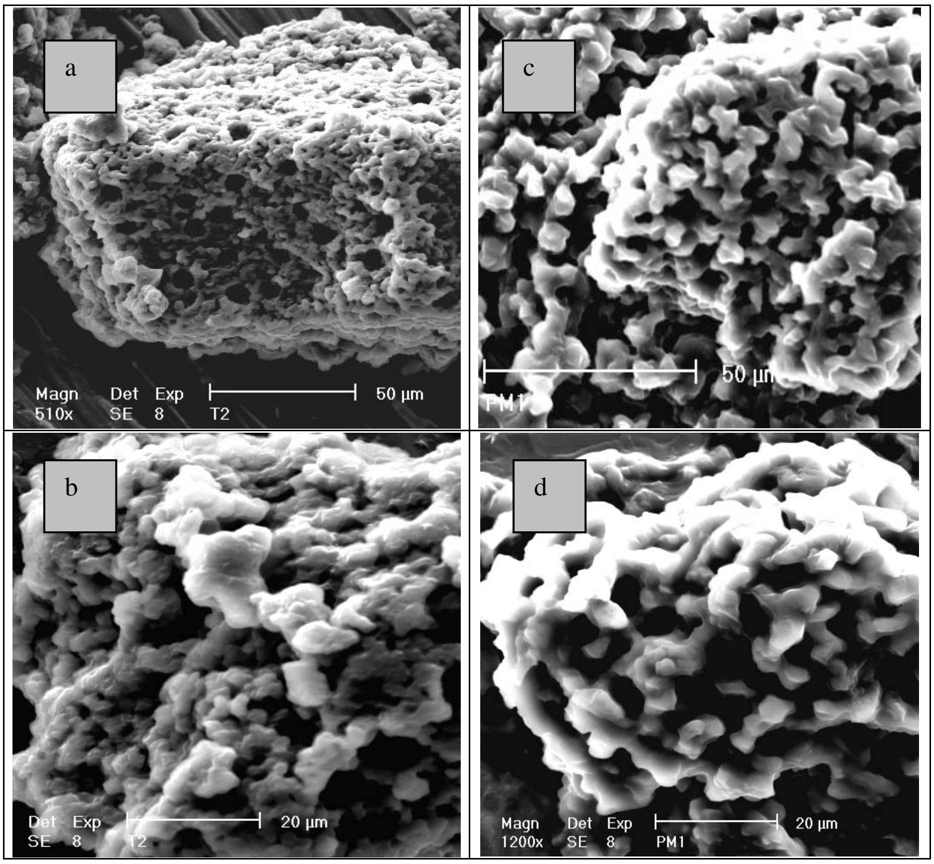


Figure 2. SEM images of the meso-macroporous silica containing polymer-supported phosphonates (a,b: compound no.2 in Table 2 with C13; c,d: compound no.2 in Table 2 with TRYTON)

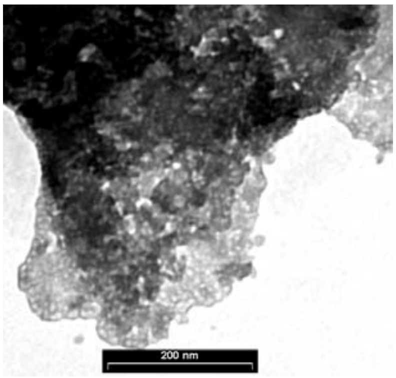


Figure 3. TEM image of the meso-macroporous silica containing polymer-supported phosphonates with triethyl radical synthesized with TRYTON surfactant

between 5-10 μm. Structure and morphology of the silica–phosphonate materials obtained by TRITON X-100 and polyoxyethylenetridecyl ether are similarly. The XRD patterns exhibit a single broad reflection extending from 20-35° (2θ) indicating the amorphous nature of our samples.

The ordered structure of mesoporous silica with macropores is also demonstrated from the TEM pictures (Figure 3).

The BET specific surface area of silica with polymer-supported phosphonates is very high (Table 4). The pore size distributions curve obtained by BJH method[20] (Barrett-Joiner-Halenda) using adsorption branch of the isotherms are centered at around 3.7 nm. The macropores were confirmed by SEM and TEM images (Figs. 2, 3).

IR-spectra of the polymer-supported phosphonates containing ordered silica (Figure 4) show the presence of P=O, W=O and P-O-C bonds. Bands of the peroxotungstic species were found at 952-969 cm^{-1}, γ (W=O).

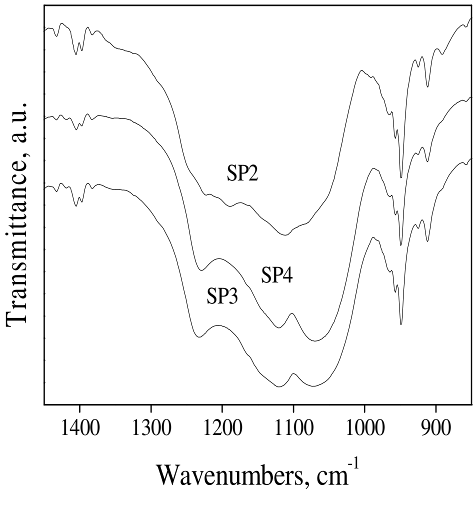
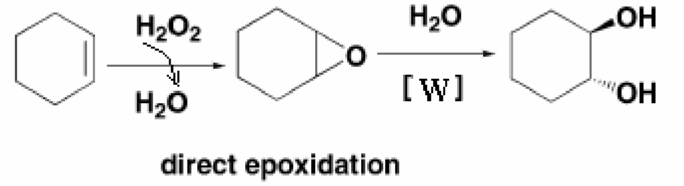


Figure 4. IR spectra of the silica containing polymer-supported phosphonates with triethyl phosphite (SP2), tri-isoprophyl phosphite (SP3), tributhyl phosphite (SP4) radicals

The adsorption band at 1260 cm^{-1} is shifted toward lower wave number due the interaction of P=O with silica. The intensity of these bands decreases for the incorporated polymer-supported phosphonates with triethyl phosphite radicals and for all the complexed polymers.

Catalytic evaluation

The ability of the newly synthesized supported phosphotungstic complexes to catalyze the epoxidation of cyclohexene was examined at two different temperatures in the presence of hydrogen peroxide. The results reported in Tables 3 and 4 show a high selectivity in epoxide above 90 % in most cases. Another product was diol. The reaction pathway proposed for oxidation of cyclohexene is a direct epoxidation (1):



(1)

A high conversion was obtained for the polymer-supported phosphonate functionalized with tributhyl phosphite. The conversion increases with temperature for all the catalysts. H_2O_2 efficiency (amount of H_2O_2 used in cyclohexene epoxidation/amount of H_2O_2 transformed) was high for all the catalysts (around 36-48 %).

Table 3. Catalytic activity of PSP catalysts in epoxidation of cyclohexene

Catalyst[a]	mmolW/g	T (K)	C^b (%)	$S_{epoxide}{}^c$ (%)
WPSP1	1.53	323	84	91
WPSP2	1.34	323	90	95
WPSP2	1.34	303	79	96
WPSP3	1.23	323	92	98
WPSP4	1.03	303	86	92
WPSP4	1.03	323	97	98
WPSP4	2.4	323	99	98

[a] (WPSP1-4)-polymer-supported phosphotungstic (code 1-4: 1-Me, 2-Et, 3-IP, 4-Bu (see table 2)) [b] % conversion of cyclohexene; [c] % of epoxycyclohexane; reaction time-28 h

Table 4. Surface area and catalytic activity of the SP catalysts in epoxidation of cyclohexene

Catalyst[a]	mmolW/g	S_{BET}, m^2/g	T (K)	C^b (%)	C^c (%)	$S_{epoxide}{}^d$ (%)
WSP1	0.20	634	323	82	61	94
WSP2	0.18	602	323	88	56	96
WSP2	0.18	602	303	71	48	98
WSP3	0.14	584	323	89	54	98
WSP4	0.10	590	303	84	45	92
WSP4	0.10	590	323	96	51	99
WSP4	0.30	590	323	98	58	99

[a] (WSP1-4)-polymer-supported phosphotungstic incorporated into bimodal porous silica (code 1-4: 1-Me, 2-Et, 3-IP, 4-Bu (see table 2)) [b] % conversion of cyclohexene for as-synthesized catalysts; [c] % conversion of cyclohexene for calcined catalysts [d] % of epoxycyclohexane; reaction time-28 h

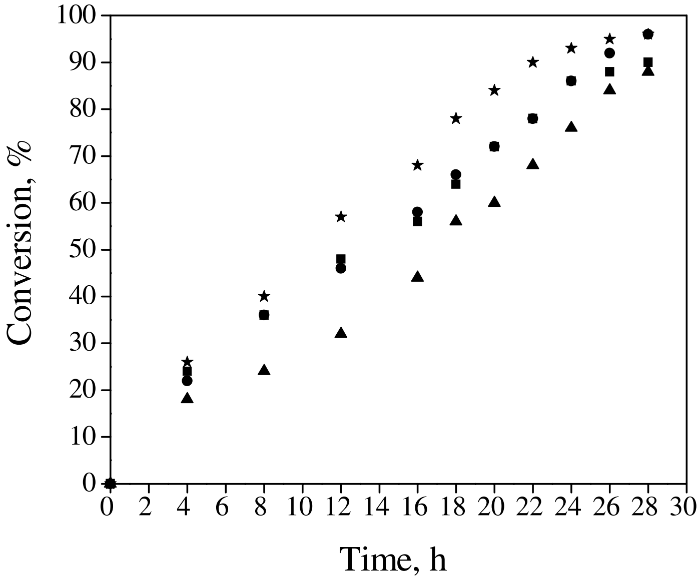


Figure 6. Conversion of cyclohexene vs. reaction time for ■WPSP2, ★WPSP4, ▲WSP2 and ● WSP4 catalysts

A brief kinetic study on the epoxidation of cyclohexene in the presence of supported phosphotungstic complexes at 323 K was investigated up to about 28 h by analyzing of reaction mixture at regular intervals of time. For all the catalysts the conversion increases almost linearly in the first few hours (Figure 6). The highest conversion was obtained at the longest reaction time, which was 28 hours.

One of the main objectives of incorporation of polymer-supported phosphonates into silica was to evaluate the potential of the catalysts for practical applications. When compared the polymer-supported phosphotungstic (WPSP) with polymer-supported phosphotungstic incorporated into bimodal porous silica (WSP) the selectivity and stability increased by incorporation. The catalysts were separated from the reaction mixture after each experiment by filtration, washed with solvent and dried to constant weight before using it in the subsequent run. These results show that conversion was reduced by 30% after 1-2 reaction cycles, for WPSP catalysts and after 3-4 reaction cycles, for WSP catalysts. The activity of the calcined catalyst is lower.

The presence of the surfactants in the macropores is favorable for the liquid phase transfer of H_2O_2 and can explain the high activity of the polymer-supported phosphonates incorporated into ordered porous silica in epoxidation reaction with hydrogen peroxide. The surfactant molecules and phosphonates in two liquid phase can be considered as solvent or/and phase transfer catalyst which will reduce the possible decomposition of H_2O_2 and facilitate the transport of H_2O_2 into macropores for the oxidation reaction.

Conclusions

The degrees of functionalization with phosphonate groups are relatively high, ranging from 1 – 1.4 mmoles of functional groups / g of copolymer, ensuring a sufficient concentration of active centers per unit mass of the copolymer and being suited for application as heterogeneous catalysts.

Peroxotungstic units are complexed to polymer-supported phosphonates and polymer-supported phosphonates incorporated into meso-macroporous ordered silica. The catalysts obtained are very active and selective in epoxidation of cyclohexene using hydrogen peroxide as an environmentally friendly oxidant.

Notation

x – fraction of styrene units bearing pendant $–CH_2Cl$ groups (Fi)
y – fraction of styrene units bearing pendant $–CH_2P(O)(OR)_2$ groups (Ff)
r – fraction of divinylbenzen (DVB) units
M_{mf} – average molecular weight of the repetitive unit of the final copolymer
%P – phosphorus percentage in the final copolymer
A_P – atomic weight of phosphorus
M_S – molecular weight of the repetitive unit of the styrene
M_{DVB} – molecular weight of the repetitive unit of the divinylbenzene
M_{SFi} – molecular weight of the repetitive unit of the styrene functionalized unit Fi groups
M_{SFf} – molecular weight of the repetitive unit of the styrene functionalized with Ff groups
G_F – functionalization degree
Fi – CH_2Cl groups
Ff – $CH_2P(O)(OR)_2$ groups
n_P – number of phosphorus atoms in the pendant groups
PSP – polymer-supported phosphonates
SP – polymer-supported phosphonates incorporated into silica
WPSP – polymer-supported phosphotungstic
WSP – polymer-supported phosphotungstic incorporated into bimodal porous silica

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