



## Step-by-step design of novel biomimetic nanoreactors based on amphiphilic calix[4]arene immobilized on polymer or mineral platforms for destruction of ecological toxicants

Lucia Zakharova\*, Yuliana Kudryashova, Alsu Ibragimova, Elmira Vasilieva, Farida Valeeva, Elena Popova, Svetlana Solovieva, Igor Antipin, Yulia Ganeeva, Tatiana Yusupova, Alexander Konovalov

A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Scientific Center of the Russian Academy of Sciences, 8, ul. Akad. Arbuzov, Kazan, 420088, Russia

### ARTICLE INFO

#### Article history:

Received 18 November 2011

Received in revised form

26 December 2011

Accepted 4 January 2012

#### Keywords:

Phosphorus acid esters

Ecological toxicants

Destruction

Supramolecular catalysis

### ABSTRACT

The effective supramolecular catalysts based on amphiphilic calix[4]arene functionalized by iso-nonyl groups at the upper rim and polyoxyethylene groups at the lower rim (9CO9) are developed for the destruction of toxic phosphorus acid esters. In the microheterogeneous 9CO9–polyethyleneimine (PEI)–lanthanum salt systems, a step-by-step enhancement of the catalytic activity was accomplished and a ca. 200-fold acceleration of hydrolysis is reached. The effect is contributed by the superposition of the factors of micellar catalysis (the concentration of reagents and changes in their microenvironment) and homogeneous catalytic mechanisms, in particular the general basic catalysis by aminogroups of PEI and the electrophilic catalysis by the La(III) ions. A further increase in the catalytic performance is achieved through the covalent immobilization of 9CO9 on the mesoporous silica. An inhibition/catalysis inversion occurs upon transferring from the single 9CO9 solution to the supported 9CO9/SiO<sub>2</sub> particles.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

The supramolecular design of functional nanosystems (sensors, nanocontainers, catalysts, etc.) is based on the “bottom-up” strategy, which makes it possible to develop soft materials with an impulse responsive behavior by means of the self-assembling of amphiphiles. Microheterogeneous and nanostructured systems are generally polyfunctional and may be used for important practical applications including environmental aspects [1–8]. Our studies are focused on the design of supramolecular catalysts for the hydrolytic cleavage of ester bonds [9–13]. Catalysis in constrained systems is known to be widely used for the effective destruction of ecological toxicants, such as phosphorus acid esters [9–16], which are widely used as pesticides, drugs, and nerve gases [17].

Supramolecular catalysts are considered to be simple synthetic analogues of biocatalysts modeling the multifactor mechanism of their action [13], including effects of concentrating the reagents and the changes in their microenvironment in combination with the contribution of homogeneous catalysis by functional groups lying in vicinity of the active center of ferments. This underlies considerable accelerations of enzymatic reactions reaching more than ten orders of magnitude. A crucial role in mechanisms of

biocatalysts belongs to the pre-organization of reagents at the active center of ferments, which results in the formation of the ferment–substrate complex thereby providing the approach of reagents and their favorable orientation. Taking this into account, the search for novel amphiphilic agents should be considered a challenging task. Included in the important building blocks for the design of supramolecular systems are amphiphilic calixarenes [18–21], which combine the functions of surfactants and the cyclophane platform. Therefore they are capable of self-assembling in aqueous solutions through different mechanisms, i.e., (i) contributed by the hydrophobic effect, which is typical for surfactants, (ii) involving the calixarene cavity (the so-called inclusive interactions); (iii) multi-centered interactions contributed by CH– $\pi$ , the Van der Waals forces, etc. [22–29]. The attractiveness of calixarenes for supramolecular design is due to their facile functionalization at both upper and lower rims. From the viewpoint of the development of catalysts, the calixarene platform with covalently bound functional groups provides the way for the immobilization of catalytically active centers on a macrocyclic matrix, thereby allowing the first level of pre-organization.

Earlier, we proposed the step-by-step design of supramolecular catalysts (nanoreactors) based on amphiphiles by means of the successive introduction of building blocks capable of self-assembly or bearing catalytic groups [9–12]. In the framework of this approach, polyethyleneimine (PEI) was used as a key component capable of binding the reagents through a multi-centered sorption

\* Corresponding author. Tel.: +7 843 2 73 22 93; fax: +7 843 2 73 22 53.

E-mail address: [lucia@iopc.ru](mailto:lucia@iopc.ru) (L. Zakharova).

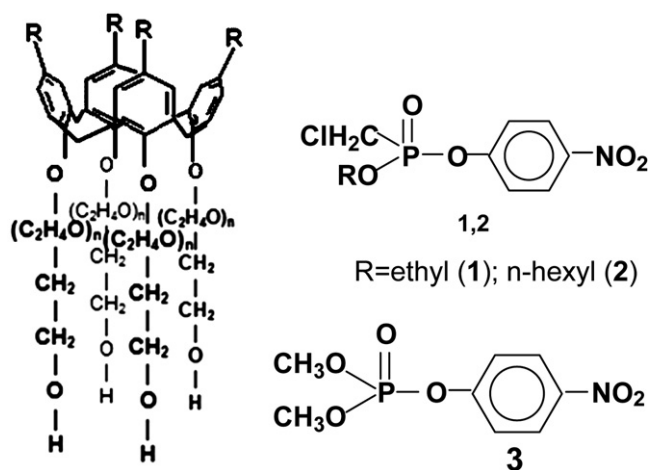


Fig. 1. Structural formulas of oxyethylated calixarene ( $R=i$ -nonyl,  $n=8$ ) and substrates 1–3.

mechanism and bearing amino groups catalyzing the hydrolysis of ester bonds via a general base mechanism. Besides, the addition of polymers to the solution of amphiphiles makes it possible to form a new type of catalysts, namely nanocontainers immobilized on a neutral or catalytically active (as in the case of PEI) matrix. These systems present the higher level of pre-organization modeling the multifactor mechanism of enzyme catalysis. In continuations of our interest in the reactivity in the supramolecular systems, herein we focus on the development of the immobilized supramolecular catalysts for toxic phosphorus acid esters. The novelty proposed in this study is concerned with the use of calix[4]arene bearing iso-nonyl groups at the upper rim and polyoxyethylene groups at the lower rim (9CO9) (Fig. 1) as amphiphilic building blocks. Polyoxyethylated calixarenes are structural macrocyclic analogues of nonionic surfactants capable of associating in aqueous solutions [30]. They were patented as effective non-toxic nanocontainers for a wide series of biologically active compounds [31]. The present work reports on the step-by-step design of the supramolecular catalyst for the hydrolysis of phosphorus acid esters 1–3 (Fig. 1) involving the parallel monitoring of the structural behavior and catalytic properties of the system. The effectiveness of microheterogeneous and supported supramolecular catalysts are assumed to be compared. To this end the immobilization of the calix[4]arene will be carried out on the hydrophilic polymer polyethyleneimine (non-covalent fixation) or the mineral support based on the  $SiO_2$  matrix (covalent fixation).

## 2. Material and methods

### 2.1. Synthesis

9CO9 was synthesized according to the published procedure [29].

Mesoporous  $SiO_2$  was synthesized according to a known procedure [32]. Briefly, 205 ml of  $NH_4OH$  (25 wt.% solution) were mixed with 270 ml of distilled water; then 2.0 g of cetyltrimethylammonium bromide (CTAB) were added into the solution with stirring and heating. When the solution became homogenous, 10 ml of tetraethoxysilane (TEOS) were introduced giving rise to a white slurry. After 2 h, the resulting product was filtered, washed with distilled water, dried at ambient temperature, and followed by calcination in air at  $550^\circ C$  for 4 h.

Synthesis of 9CO9@ $SiO_2$ : Immobilized calixarene was prepared as reported previously [33]. Briefly, a sample of silica was dehydrated at  $250$ – $280^\circ C$  under a vacuum of 15 Torr for 10 h until the constant weight of 1.36 g was obtained. After the silica was

cooled under argon to room temperature, 1.2 mL of  $SiCl_4$  in 8 mL dichloromethane was added with dry syringe, followed by the addition of triethylamine (0.75 g in 5 mL dichloromethane). The resulting suspension was kept at room temperature for 12 h, and the solvent was subsequently evaporated in vacuum. Later 30 mL of toluene, 1.7 mL of triethylamine and a freshly prepared solution of 9CO9 (1.05 g in 20 mL toluene) were added by turns and the resulting solution was refluxed under nitrogen for a period of 20 h. The silica sample was filtered and successively washed with 125 mL of hot toluene, 25 mL of methanol, and 10 mL of water. Finally, the sample was Soxhlet-extracted with hot benzene for a period of 28 h to remove physisorbed material and dried at  $150^\circ C$  under vacuum to remove the solvent. The weight of the final product is 2.04 g. Data of elemental analysis (C, 7.99%; H, 1.1%) reveal the presence of an organic component with the  $SiO_2:9CO9$  ratio equal to 5:1. The immobilization of calixarene is supported by the dye solubilization method which shows the appearance of absorbency at  $\lambda = 495$  nm due to the solubilization of the hydrophobic dye Orange OT by the admicelles of calixarene. The IR spectra were registered on a Fourier-spectrometer "Bruker Vector 22" in the wave number range of  $400$ – $4000\text{ cm}^{-1}$ . The FTIR spectra of the modified silica sample were characterized by the appearance of new bands:  $\nu, \text{cm}^{-1}$  (KBr): 3432 (OH); 2947, 2881 (i-Nonyl).

### 2.2. Characterization of the $SiO_2$ and 9CO9@ $SiO_2$ samples

The XRD analysis and the TEM images showed that the silica sample has domains with a crystalline structure. Fig. 2 shows the TEM images of the sample characterizing the morphology and the internal structure of the sample, which are in good agreement with literary data [33]. Due to the use of the diluted CTAB solution in the synthesis of silica the structure-templating micelles are rather small and uniformly distributed in the solution. Therefore, the final product has a uniform structure without any clusters and is composed of hexagonal structural units. Morphology (Fig. 2a) confirms that there is a long-range ordered hexagonal array crystal. The lower magnification TEM image of the sample (Fig. 2b) reveals that the sample has not been agglomerated.

The pore characteristics of the silica sample determined by the absorptive methods are as follows: the adsorption pore volume is  $1.63\text{ cm}^3\text{ g}^{-1}$ , the specific surface is  $730\text{ m}^2\text{ g}^{-1}$ , and the porosity is  $0.093\text{ kg m}^3$ . According to the thermal analysis data, the water content in the pores equals 8–10 wt.%, with two types of water revealed, i.e., the weakly bound and the strongly bound water in the 1:1 ratio. This may be due to the presence of pores of different types or to the changes in the water behavior in constrained systems. The wetting enthalpy determined by calorimetry equals  $-70\text{ J g}^{-1}$  (exothermic effect). In the 9CO9@ $SiO_2$  sample the water content does not change as compared to the initial  $SiO_2$  sample, while the wetting enthalpy decreases by 2.5. The latter provides evidence for the decrease in the hydrophilicity of the silica sample modified by calixarene.

### 2.3. Reagents

Substrates 1 and 2 were prepared according to the published procedure [34]. Substrate 3 (99% grade) and branched PEI with the average molecular mass 25,000 were from Aldrich. The solution concentrations of PEI are given as the molar concentration on a monomer basis (moles of monomer per liter of solution). In the micellization and reactivity studies, a fixed PEI concentration of 0.05 M was generally used. This corresponds to  $4.3 \times 10^{-5}$  M when recalculated for the macromolecule as a whole.

Download English Version:

<https://daneshyari.com/en/article/150160>

Download Persian Version:

<https://daneshyari.com/article/150160>

[Daneshyari.com](https://daneshyari.com)