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Communication

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Chem. Mater., **Just Accepted Manuscript** • DOI: 10.1021/acs.chemmater.7b00249 • Publication Date (Web): 16 Mar 2017

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Self-encapsulation of heteropolyacids in a 3D-ordered coke framework for heterogeneous catalysis in homogeneous way

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ABSTRACT: *Heterogenization of homogeneous catalysts is highly important for modern industry; however, existing methods cannot preserve catalysts in the native state without leaching. The most promising approach implies the encapsulation of homogeneous catalysts into the porous non-soluble shell. This work expands the technique for heterogenization of heteropolyacids (HPAs) by self-encapsulation into porous 3D nanocapsules during the coke formation. We have shown that by a proper choice of the ordered template a stable material can be synthesized. HPA, being locked inside the carbonaceous shells, is fully accessible for reagents enabling the use of fixed bed reactor. The described approach opens new perspectives for application of homogeneous catalysts in the heterogeneous context.*

Catalytic processes play a major role in many fields of industry, including the production of fuels, chemicals, drugs, and polymers. Generally, the catalysts used for these processes could be separated into two complementary classes, namely, heterogeneous catalysts (zeolites, metal oxides, supported metal particles, mineral acids on oxides) and homogeneous catalysts (mineral acids, alkali, salts, metallocomplexes), that find their application in different processes under various conditions. While heterogeneous catalysts are easy to separate, regenerate, and recycle, homogeneous ones typically provide higher activity and selectivity in the reactions. However, complex recycling procedures for homogeneous catalysts after reaction lead to the increase of the cost of the process, as well as the contamination of the reaction product, therefore limiting the industrial application of the process by non-continuous batch reactor technologies.[1] Merging these two classes of catalysts will introduce a new type of catalysts that combine the advantages of homogeneous and heterogeneous catalytic systems.[2-4] Thus, the search for the efficient technology of the heterogenization of homogeneous catalytic system is of high importance for the modern industry.

In particular, the main efforts in this field are focused on the immobilization of homogeneous catalysts on the surface of different non-soluble supports. Various methods including covalent grafting, encapsulations into inorganic matrixes, electrostatic interaction, coating, etc. have been proposed for different homogeneous catalysts.[5-8] However, such methods have a number of disadvantages, including the loss of catalytic activity, low stability towards leaching, diffusion limitations etc. Besides, in spite of the great technological interest, generally applicable methods for the immobilization of homogeneous catalysts are lacking. We expect that the development of a new material with high permeable properties and uniform continuous shell around homogeneous catalyst is a promising strategy for heterogenization.

Recently, we have reported on the development of a novel strategy for the encapsulation of heteropolyacids into the amorphous carbonaceous framework.[9] However, the encapsulation efficiency as well as accessibility to the reacting molecules were insufficient for the application as an effective heterogeneous catalyst.

Herein, we report a successful design of a 3D-ordered carbonaceous framework without drawbacks of the former method for encapsulation of heteropolyacid (HPA) catalysts.[10-14] This is one of the most frequently studied classes of materials, with numerous alternative methods for the immobilization of HPAs suggested in the literature. HPAs exhibit remarkable chemical properties such as strong Brønsted acidity, fast and reversible multi-stage redox activity, and high thermal and hydrolytic stability, making them attractive for catalytic applications, such as esterification, hydration, and oxidation.[12] However, high solubility in polar solvents limits their application in industry. We demonstrate that selective building of the coke layer over the active sites of HPA catalyst deposited on the structured support with well-defined size and shape enables the preparation of a 3D material with homogeneous catalyst inside, and does not lead to diffusional limitation in mass transfer of reactants and products through the walls of these nanoreactors.

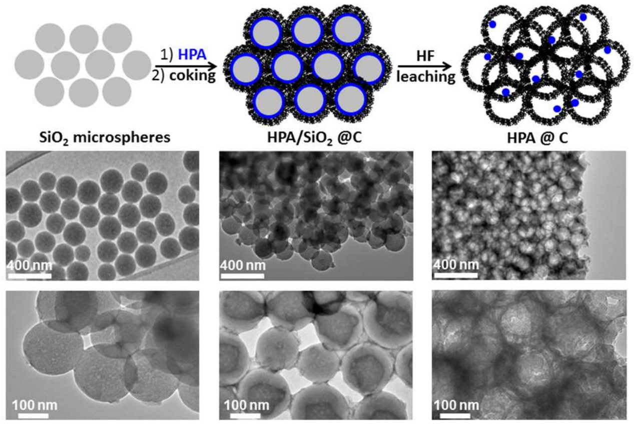


Figure 1. General scheme of the synthetic process and TEM images of the products obtained after each step. From left to right: in the first step, colloidal silica spheres of approximately 170 nm were obtained from the water solution. These spheres were doped with HPW (HPA/SiO_2@C) by incipient wetness impregnation and coked in the mixture of isobutene and formaldehyde to form monodisperse silica spheres covered with carbonaceous deposits. Finally, the silica was leached out by HF treatment and HPW particles encapsulated in aggregated coke shells were obtained (HPA@C).

The system was realized by combining two synthetic procedures. It is known that HPA can be uniformly distributed on the surface of silica leading to the formation of the pseudo-liquid layer, which continuously covers the entire surface of the support.[13-14] On the other hand, we have recently discovered that Prins condensation of isobutene with formaldehyde over the acid solid catalysts leads to the formation of the high amount of coke with porous structure.[9,15-17] These two factors form the basis for the design of the leaching-stable catalysts with HPA particles encapsulated into the carbonaceous shell. Importantly, our strategy implies the selective self-encapsulation of HPA via coke forming directly over the acid sites of HPA particles, in contrast to the previously suggested nanocasting methods with carbonization of sucrose, resorcinol, etc. as a carbon precursors.[18]

The pathway leading to the catalytic composite is shown schematically in Figure 1, in combination with TEM images of the product after each step.

We used silica microspheres with the diameter of 170 nm dispersed in water as the template for the synthesis of the carbonaceous capsules. Careful evaporation of water does not lead to aggregation or sintering of silica; all particles showed identical size and shape as confirmed by TEM measurements (Figure 1). At the next step, dry silica microspheres were impregnated with water solution of tungsten phosphoric acid (HPW), and dried at 393K, yielding the samples with HPA distributed on the surface of SiO_2. Next, the obtained materials were coked in the mixture of isobutene and formaldehyde at 573K for 3h, leading to the carbon coated silica microspheres with HPA inside. As evidenced by TEM, this procedure retained the parent structure of silica spheres without destruction and deformation. However, the treatment of the catalyst in a isobutene/formaldehyde mixture at high temperature led to the filling of interglobular space with coke (Figure 1, center).

Finally, silica was removed out of the composite by the treatment with an HF solution (40 wt%) at 323K. The TEM images (Figure 1, right) show that after this step, 3D carbonaceous shells were formed with capsules resembling silica globules. The thickness of the wall of a coke layer is about 10 nm.

It should be mentioned, that the stability and shape of the carbonaceous shells are strongly governed by the size of the silica microspheres used for synthesis. In particular, application of small sized 10 nm SiO_2 leads to the formation of continuous carbon material without legible shell structure (Figure S1), with low amount of HPA encapsulated in the shell. For silica spheres with the diameter of 1000 nm, a significant destruction of the material at the HF treatment step was observed (Figure S2). This is the result of low stability of large thin shells collapsing when the silica support is removed.

Table 1. Materials characteristics

Catalyst	Content, wt%		Surface area, $m^2 \cdot g^{-1}$	Weight loss, %[a]
	HPA	SiO_2		
HPA/SiO_2	19.0	81.0	14	n/a
HPA/SiO_2 after catalytic test	1.2	98.8	-	-
HPA/SiO_2@C	-	-	15	6.2
HPA@C	39.7	0.2	115	60.1
HPA@C after catalytic test	39.5	0.2	n/a	n/a

[a] Measured by TGA in a flow of air (Figure S3)

The treatment in an HF solution can, along with silica, leach the HPA, which is not fully encapsulated into the carbonaceous shell. According to the elemental analysis, a significant amount of HPA has been leached out during the HF treatment, with encapsulation of 35% of initial amount of HPA (Table 1). However, it is significantly higher than observed over amorphous silica catalyst with encapsulation of only 15% of HPA.[9] This indicates that application of ordered silica materials results in a higher efficiency for encapsulation of HPA, possibly due to the formation of a less defected coke layer structure over the silica microspheres, compared to amorphous silica gels.

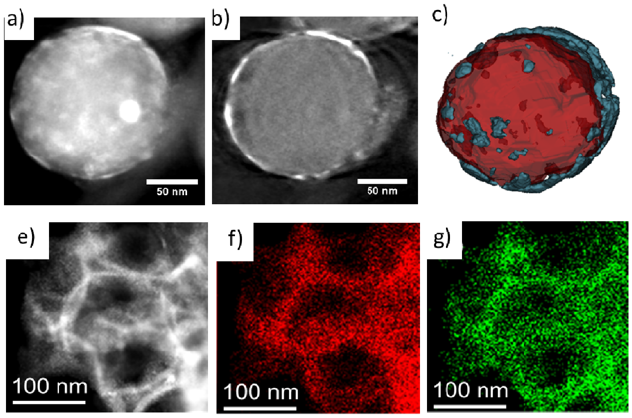


Figure 2. Top: STEM-HAADF tomography of a HPA/SiO2@C particle: a) typical STEM-HAADF image from the tilt series used to calculate the reconstruction; b) slice redrawn from the reconstructed volume; c) 3D model of the particle based on STEM-HAADF electron tomography experiment. Bottom: EDX mapping of a representative aggregate of the HPA@C material for W (f) and C (g). The data shows the location of heteropolyacid layers on the internal surface of carbonaceous nanoshell in HPA/SiO_2@C. The HPA is distributed inside of the shells after silica removal in HPA@C.

To gain further insight into the 3D position of the HPA species within the carbonaceous shell, as well as the spatial distribution of HPA particles with respect to the internal surface, STEM-HAADF and STEM-EDX analysis for HPA/SiO_2@C and HPA@C sample have been acquired. As expected, the deposition of HPA leads to the formation of a thin film on the surface of silica microspheres (Figure 2). Removal of silica by the HF treatment leads to redistribution of HPA in the capsule. STEM-EDX analysis indicates that the majority of HPA is localized along with the wall of the carbonaceous shell. The removal of ethanol during drying of the sample in a TEM holder should lead to the stacking of HPA anions in the coke shell. However, liquid phase should lead again to the redistribution of HPA in the capsule volume.

In further experiments, the state of HPA and nature of the carbonaceous shell were determined, and main characteristics are summarized in Figure 3. The powder XRD patterns (Figure 3a) show typical features of a crystalline material, which can be identified as a $H_3PW_{12}O_{40}\cdot 6H_2O$ phase.[19] No peaks due to the HPA decomposition products were observed. Broadening of the XRD reflections compared to the bulk $H_3PW_{12}O_{40}$ indicates the small size of HPA nanocrystals due to the high dispersion of HPA in the carbon shell. The broad peak spawning from 10 to 40 degrees could be attributed to the amorphous carbon.

The ^{31}P NMR spectrum of the HPA@C material reveals the presence of one signal at –16.1 ppm due to the phosphorus atoms in the HPA structure similar to bulk HPA (Figure 3b).[17] Broadening of the peak is the result of the weak interaction of HPA with the carbonaceous shell. No signals due to other phosphorus species are found in the spectra, indicating the high stability of $H_3PW_{12}O_{40}$ during the synthesis procedure.

Evaluation of the chemical composition of carbonaceous shell made by ^{13}C MAS NMR reveals the presence of signals at 17, 52, and 129 ppm (Figure 3c). The peak centered at 17 ppm could be attributed to the saturated atoms of branched aliphatic carbons, whereas the intense broad peak at 129 ppm is due to olefinic carbon atoms. The signal at 52 ppm could correspond to carbon atoms in C-O methoxy groups of the coke or side products of formaldehyde conversion over HPA. These results are in line with our previous works.[15-17] Based on the NMR results and the chemistry of the reaction, the coke deposits should have linear chains containing both isoprene and isobutylene units, as shown in Scheme 1.

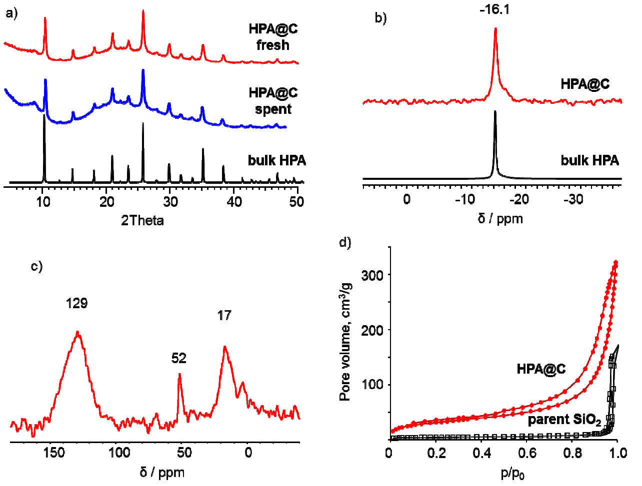
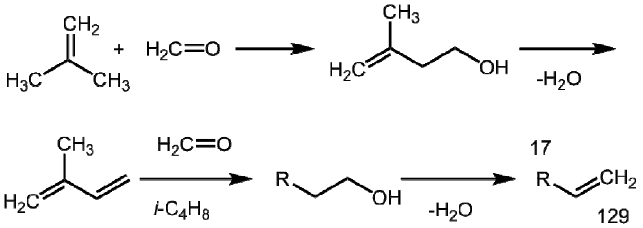


Figure 3. a) XRD patterns and b) ^{31}P MAS NMR spectra of HPA@C material compared with bulk HPA; c) ^{13}C MAS NMR spectrum of HPA@C material; d) N_2 adsorption/desorption isotherms at 77K for parent silica and HPA@C.

These "polymer" chains are intertwined, forming a thin shell (Figure 1) leading to the high stability of the coke layer, and porous enough to allow the reactive molecules penetrate through the walls of the shell. Nitrogen adsorption-desorption isotherm confirms high porosity of the shell; the high adsorption at relative pressures p/p_0 within 0.7-0.9 corresponds to the filling the capsule's internal volume. These data are in line with the TEM measurements showing the formation of thin shell walls that are permeable for small molecules. It should be noted that parent silica globules do not show high porosity; the small surface area of 14 $m^2\cdot g^{-1}$ is due to the interglobular space in the dry material (Figure 3d).



Scheme 1. Prins condensation of isobutene with formaldehyde, leading to the formation of carbonaceous deposits. Numbers show the ^{13}C NMR signals of the corresponding carbon atoms, observed for HPA@C material (Figure 3c).

Summarizing, the HPA particles are effectively encapsulated into the 3D carbonaceous framework and accessible for molecules. As such, good performance can be expected in heterogeneous catalytic reactions. One of the model reactions investigated over HPA catalysts is the dehydration of tert-butanol.[20-21] To study the activity and stability towards leaching of as-synthesized encapsulated materials, the reaction was carried out in the fixed bed reactor under the atmospheric pressure and the temperature of 351K. The reaction conditions were selected to avoid fast catalysts deactivation due to coking; therefore only the leaching of active HPA could lead to the decrease of tert-butanol conversion. Furthermore, under these conditions a fraction of water and tert-butanol is presented in the liquid phase, enabling HPA's dissolution during the reaction. The results were compared with the benchmark HPA/SiO_2 and HPA/C catalysts prepared by the incipient wetness impregnation of amorphous silica and carbon black with the water solution of tungsten phosphorus heteropolyacid.

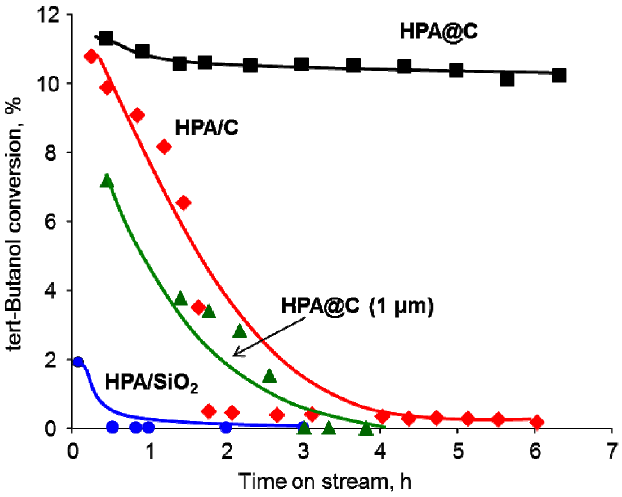


Figure 4. Catalytic performance of different samples in the reaction of tert-butanol dehydration into isobutene in a fixed bed reactor. The activity of the catalysts was measured in a plug-flow reactor using 13 mg of catalyst in a mixture of 7.5% tert-BuOH in He with a weight hourly space velocity of 8 g h^{-1} g^{-1}, T = 351K.

Silica and carbon supported HPA demonstrated fast decrease of the tert-butanol conversion after 2 h on stream (Figure 4). The HPA content for these materials dramatically decreases after catalytic tests (Tables 1), pointing to the leaching of HPA out of the catalyst being the main reason of the decreased activity. At the same time, the HPA@C sample with HPA encapsulated in the coke capsules demonstrated high activity and stability in the reaction without visible deactivation and destruction for 6 h (Figure 3a). The amount of HPA also did not significantly change after the reaction (Table 1). These results indicate that carbonaceous shell of the HPA@C sample enables the transport of tert-butanol to the protons of HPA anions, while protecting HPA from leaching.

As expected, the material synthesized from 1 μm silica did not show stable conversion of tert-butanol due to the damaged carbon shell, unable to protect HPA from leaching out (Figure 4).

The presented results of catalytic tests in fixed-bed reactor showed the high stability of encapsulated HPA towards leaching, however, the encapsulation could lead to lower activity due to the diffusional limitations for the reagents or interaction with carbon shell.[9] To access the intrinsic activity of the HPA@C catalyst, we compared its activity with bulk $H_3PW_{12}O_{40}$ in liquid phase batch reactor for the ethanol esterification with acetic acid (Figure S4). The data showed that HPA@C material possesses similar conversion of acetic acid in comparison with its homogeneous analogue hence confirming the full accessibility of HPA inside the carbonaceous shell without diffusional limitations. Furthermore, ^{31}P NMR spectrum (Figure S5) obtained for HPA@C dispersed in liquid ethanol revealed the signal at-10.9 ppm which is similar to the ethanol solution of bulk $H_3PW_{12}O_{40}$. This confirms the solvation of HPA molecules inside the shell with ethanol enabling the HPA action as the homogeneous catalyst. On contrary to the amorphous material[9] distribution of HPA inside the large ordered capsules with high external surface improve the mass transfer leading to higher activity of HPA@C.

Our results clearly show that the isolation of HPA particles in coke based carbonaceous capsules allows making heterogeneous catalysis from a soluble precursor. Indeed, the HPA presented inside the porous capsules acts as the homogeneous catalyst, but cannot leave the shell due to the large anion size. Importantly, reactants such as tert-butanol or ethanol can easily access it. In contrast to some recent HPA encapsulation strategies, the protocol reported here can be beneficial for the broad range of HPA catalysts that could be encapsulated though general coking procedure.

The here presented results describe the key steps of a flexible synthetic procedure. By a proper choice of time for coking, loading of HPA, size of silica template, and a type of the aldehyde and the olefin, the main parameters of the catalyst can be controlled, such as the thickness, the amount of HPA, and the diameter and porosity of the shell. Furthermore, the shell can be functionalized for the key-lock interaction with the reagents by use of the aldehyde and the olefins with additional functional groups. As shown in the literature, the hollow shells can be created for encapsulation of metal particles,[22-26] and our first results on the encapsulation of homogeneous catalysts constitute the basic principles for the creation of a new class of catalysts.

In conclusion, our results indicate that the self-encapsulation procedure for heteropolyacid into the ordered carbon capsules demonstrates excellent perspectives for the synthesis of the materials possessing high activity and recyclability.

ASSOCIATED CONTENT

Supporting Information. Description of synthesis procedure, TEM images, TGA and elemental analysis. This material is available free of charge via the Internet at http://pubs.acs.org

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

The authors gratefully acknowledge the Russian Science Foundation for the financial support (Grant No. 14-23-00094). This research is being performed within the ANR NANO4FUT project (ANR-16-CE06-0013-01). The authors gratefully acknowledge the support of the French National Research Agency. The TEM facility in Lille (France) is supported by the Conseil Regional du Nord-Pas de Calais, and the European Regional Development Fund (ERDF). The authors acknowledge the French electron microscopy and atom probe network, METSA.

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