ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/chemcomm



Journal Name

COMMUNICATION

"Fishing" of heteropolyacids into carbonaceous seine via coking

Received 00th January 20xx, Accepted 00th January 20xx Vitaly L. Sushkevich,^a Irina I. Ivanova^a, Christine Lancelot^b, Simona Moldovan^c, Ovidiu Ersen^c, Vitaly V. Ordomsky^b*

DOI: 10.1039/x0xx00000x

www.rsc.org/

The carbon encapsulated tungstophosphoric acid was synthesized by the controlled coking during gas phase reaction of formaldehyde with isobutene. As-made material showed unique stability toward leaching in the aqueous phase due to localization of HPA clusters inside of porous coke matrix with high activity in the esterification reaction.

Heteropolyacids (HPAs) are attractive metal-oxygen compounds of the transition metals (V, Nb, Mo, W) with diverse molecular structures and adjustable functionality. These nanomaterials exhibit interesting chemical properties such as strong Brönsted acidity, fast and reversible multi-stage redox activity and high thermal and hydrolytic stability, making them attractive for catalytic applications [1]. HPAs have been extensively used as the catalysts for several industrial acid-catalyzed and oxidation processes like hydration of olefins (propylene, isobutene) into alcohols [2], production of ethylacetate from ethylene and acetic acid [3], oxidation of methacrolein into methacrylic acid [4] and direct oxidation of ethylene to acetic acid [5]. However, most part of the catalytic processes use HPAs as homogeneous catalysts in liquid phase which has many drawbacks such as corrosion of equipment, recycling of the catalyst, low selectivity etc. Application of HPAs as heterogeneous catalysts for liquid reactions will result in development of green, safe and efficient processes in catalysis. However, utilization of HPAs as heterogeneous catalysts has limitations such as very low surface area (<5 m²/g), which reduces accessibility to the acidic sites, and high solubility in polar medium which makes impossible recycling of the catalyst. The solution of these problems would open new perspectives in the application of HPAs in catalysis.

There are several approaches to overcome these drawbacks which include support of HPA on high surface area oxides [6-7],

This journal is © The Royal Society of Chemistry 20xx

embedding of HPA in supports during in-situ synthesis [8] and partial neutralization of protons in HPA with formation of insoluble salts [9-10]. However, all these methods have their own weaknesses.

Deposition of HPAs over alumina, silica, zirconia, carbon increases dispersion of acid with increase of the accessibility of acid sites [11-12]. However, in the presence of polar medium the acid leached out into the reaction medium [13]. Immobilization of HPAs on the surface of supports by anchoring to isolated basic sites like AI-OH over alumina [7] or amino groups [14] might partially improve stabilization of HPA lowering their solubility but with decline of its acidity. The preparation of embedded systems by addition of HPA during sol-gel synthesis of silica leads to encapsulation of heteropolyanion to the matrix [15]. However, the necessary calcination step for the formation of pore structure destroys HPA. Exchange of the part of the protons of HPA with large cations, like Ag^+ , Cs^+ and NH_4^+ is the most efficient for HPA heterogenezation due to the formation of micro- and mesoporous salt with low solubility in polar solvents [16]. However, in order to obtain full heterogenezation of HPA the extent of ion exchange should be very high (>80 % of available acid sites) which results in significant decrease of catalyst acidity. Thus, all these methods cannot be considered as very efficient: weak interaction of HPA with supports results in its leaching whereas strong interaction leads to loss of catalyst acidity and decomposition of the structure.

The complexity of the problem motivates us to elucidate a fundamentally new approach for the heterogenezation of HPA which would keep the same acidity like in the bulk state and high accessibility to reagents. We used Keggin-type tungstophosphoric acid $H_3PW_{12}O_{40}$ (HPW) as one of the most commonly used HPA [1]. HPW has relatively large anion (~1.2 nm) which would be possible to encapsulate in the thin porous wall "sack". Our approach in this direction is founded on encapsulation of HPW in coke shell deposited in-situ during reaction. At the first step, HPW/SiO₂ catalyst was prepared by incipient wetness impregnation with high dispersion of HPW on the surface of silica globules. The as-prepared material has been used as a catalyst in the gas phase Prins reaction of formaldehyde with isobutylene

^{a.} Dr V.L. Sushkevich, Prof. I.I. Ivanova, Department of Chemistry Lomonosov Moscow State University, Leninskye Gory 1, bld. 3, 119991 Moscow, Russia

^{b.} Dr. V.V. Ordomsky, Dr. C. Lancelot, Unité de Catalyse et de Chimie du Solide UMR 8181 CNRS, Ecole Centrale de Lille, Université de Lille Bât. C3, 59655 Villeneuve d'Ascq, France Fax: (+33) 03 20 43 69 53 E-mail: vitaly.ordomsky@univ-lille1.fr

^c Dr. S. Moldovan, Dr. O. Ersen, Department of Surfaces and Interfaces (DSI), 23, rue du Loess BP 43, F-67034 Strasbourg, France

Electronic Supplementary Information (ESI) available: [Preparation of catalyst, catalytic tests, physicochemical analysis, N_2 adsorption]. See DOI: 10.1039/x0xx00000x

HPW clusters.

COMMUNICATION

Journal Name

(Figure 1) during isoprene synthesis with formation of coke shell on the surface of the catalyst (HPW/SiO₂@C). Finally, the encapsulated HPA (HPW@C) was prepared by removal of silica matrix by treatment of HPW/SiO₂@C with HF water solution.



Figure 1. Scheme of the synthesis of HPW@C catalyst

In proposed scheme the selection of the reaction used for the controlled coking plays a key role. It should provide closed circuit uniform carbonaceous shell around heteropolyacid clusters without poisoning of active sites.

In our previous work [17,18] it was shown that the reaction of isobutene and formaldehyde on acid sites leads to the formation of high amount of carbonaceous deposits on the catalysts, which does not poison active sites, in contrast, acid protons interacts with coke providing unique properties of the "working" active sites for selective synthesis of isoprene. So, this behavior was considered as the pathway for controlled coking of HPA with the formation of stable encapsulated material.

The catalyst characterization results are shown in Table 1. Deposition of HPW on silica via impregnation gives the material with the loading close to the expected. Coking of HPW/SiO₂ in the mixture of isobutene and formaldehyde leads to slight decrease of HPW content due to increase of the amount of coke accumulated on the material. Removal of silica by treatment of HPW/SiO2@C catalyst in aqueous HF solution does not lead to significant increase of the HPW content as it could be expected. Thus, besides silica significant amount of HPW has been leached out during HF treatment. Taking into account that the amount of carbon should be the same before and after treatment only 15 wt. % of HPW has been encapsulated in carbon shell. It might be explained by incomplete coverage of HPW by coke deposits. The increase of the percentage of encapsulated HPW might be attained by further optimization of the conditions of carbonization, type of support and amount of HPW supported on silica.

In order to confirm full heterogenezation of the rest heteropolyacid the sample HPW@C has been treated in Soxhlet extractor with ethanol overnight. Sample after extraction was designated as HPW@C-ext. The analysis of HPW content and coke amount indicates on the high stability of HPW inside of carbon matrix toward leaching.

Table 1. Physica	I characteristics	of materials
------------------	-------------------	--------------

Material	HPA content, wt%	Weight loss, % ^a	BET surface area, m²/g	Average pore diameter, Å
SiO ₂	-	-	64	340
HPW/SiO ₂	19.8	-	70	400
HPW/SiO2@C	17.8	11.1	70	310
HPW@C	16.5	79.0	210	100
HPW@C-ext	16.3	79.2	210	100

^a measured by TGA experiment in flow of air.

TEM analysis confirms the encapsulation of HPW into carbon shell in HPW@C sample. Before silica leaching by HF (Figure 2a) TEM measurements show uniform distribution of coke and HPA on the surface of the support. Unfortunately due to the low contrast with silica it is not possible to locate HPW clusters distributed on the parent material. The earlier studies have shown that heteropolyacid presents on the surface of silica in pseudoliquid state due to amorphous secondary structure [19]. At the same time, Figure 2b shows the presence of small HPW clusters with the sizes in the range of 3-15 nm uniformly distributed in the carbon matrix. HPW units might flock together to form clusters in the rigid structure of carbon matrix after washing out silica. It should be noted that the contour of carbon shell in HPW@C sample resembles the contour of silica globules (Figure 2a,b). This observation shows that carbon layer is not strictly localized around HPA clusters but forms continuous shell on the surface of HPA supported over silica globules (Figure 1). Indeed, uniform coverage of silica support by pseudo-liquid HPW film should result in the synthesis of continuous carbon layer on the surface of silica. Variation of silica morphology could be used for preparation of material with different textural properties of carbon shell. In order to get more information about carbon shell, the HPW@C catalyst was studied by EFTEM (energy filtered TEM) using the "three windows method" on the carbon edge, as detailed in the Supplementary Information (SI). Both the zero loss TEM image and the carbon map displayed Figure 2c and d, respectively, show 10-15 nm thick coke shell around empty space with the



Figure 2. TEM image of HPW/SiO₂@C (a), HPW@C (b). (c) Zero loss TEM image of HPW@C and (d) EFTEM micrograph of carbon. The black and white arrows point to the carbon shell and HPW clusters, respectively.

The HPW immobilized inside might be used as catalyst only if carbon layer is porous enough with access of the molecules of reagents to the HPW active sites. The textural properties of the materials prepared by impregnation before HPW/SiO₂ and after carbidization HPW/SiO₂@C are quite close to those of the bulk silica (Table 1, Figure S1, SI). Nitrogen adsorption/desorption

Journal Name

isotherms demonstrate high adsorption at p/p₀=0.9-1 which might be explained by filling of interparticle volume. It is interesting to note that removal of silica resulted in completely different form of adsorption isotherm with large size hysteresis loop (Figure S1, SI) pointing on the formation of pores with average diameter 100 Å.

The state of HPW and nature of coke deposit was evaluated by MAS NMR measurements (Figure 3). Deposition of HPA on silica leads to slight shift of ³¹P signal from -15.3 to -15.1 ppm, probably due to the interaction of HPA with surface silanol groups. This shift is higher for HPW@C material (-14.9 ppm). Note that ³¹P signal for HPW@C material is much broader in comparison with bulk and silica supported HPA. These observations point on the interaction of HPW with the carbon layer which is stronger in the case of HPW@C. This behavior might be related to the structure of coke deposits. ¹³C MAS NMR spectra of HPW/SiO₂@C and HPW@C samples reveal the presence of signals at 18, 36 and 129 ppm. The peaks at 18 and 36 ppm could be attributed to saturated atoms of branched aliphatic carbons, whereas the intense broad peak at 128.9 ppm is due to olefinic carbon atoms [20]. These results are in line with our previous work [17] and it could be suggested that in HPW@C material heteropolyacid protons interact with C=C double bonds of the coke shell. Based on NMR results and chemistry of the reaction the coke deposits should have the linear chains containing both isoprene and butylene units [17]. The high concentration of mobile acid sites in pseudo-liquid HPW distributed on the surface of silica provides high density of oligomer chains on the surface. These polymer chains should be intertwined forming thick shell (Figure 1, 2) leading to the high stability of this coke layer during extraction of HPA.



Figure 3. ³¹P (a) and ¹³C (b) MAS NMR spectra for materials studied.

To establish that the incorporation of the HPA into the carbonaceous shell of the material does not inhibit its catalytic properties, a series of experiments were undertaken using a catalytic benchmark reaction of esterification of acetic acid by ethanol. The reaction was carried out in liquid phase to simultaneous test the stability of the material towards heteropolyacid leaching. At the moment, this process is carried out in industry over HPA in the vapor phase to avoid the leaching of the catalyst which significantly restricts its economic efficiency. Addition of bulk HPW to the reaction mixture of ethanol with acetic acid dramatically increases the reaction rate in comparison with the blank experiment. The addition of HPW@C catalyst with equal amount of HPW gives almost twice lower catalytic activity in comparison with homogeneous catalyst. It might be due to the external diffusional limitations in HPW@C in comparison with homogeneous HPW uniformly distributed in the reactor. The

HPW@C-ext sample demonstrated the same catalytic activity as non-extracted HPW@C. This observation confirms the unique stability of HPW in the coke matrix towards leaching with polar solvents. Finally, to check the concept of use of the catalyst in heterogeneous mode the HPW@C-ext sample has been filtered from the reaction mixture, washed with ethanol and used for the second run. The catalyst demonstrated the full retention of the

COMMUNICATION



activity in comparison with the parent sample. The data confirms

that encapsulated HPW@C retains acid properties with full

recyclability in the liquid phase reactions.

HPW bulk HPW@C HPW@C- HPW@C- No catalyst extr 1run extr 2 run

Figure 4. Ethanol conversion after 3 h of reaction with acetic acid (T=333 K, 10 g ethanol, 10 g acetic acid, 0.1 g HPW).

To conclude, the new strategy has been proposed for heterogenezation of HPA by controlled coking of silica supported HPA catalyst with subsequent leaching of silica matrix. This material present uniformly distributed HPA clusters inside of large close circuit porous carbon shell. Extraction and reusability tests confirmed the unique activity and stability of HPA in reaction conditions towards leaching. In comparison with other encapsulation methods HPA retains its acidic properties and chemical structure with simple reusability advantage of heterogeneous catalyst. Described approach can be extensively expanded on all HPA with different structures and chemical composition which brings new perspectives in application of heteropolyacids in catalysis.

The authors gratefully acknowledge the support of the French National Research Agency (CATSYN-BIOFUELS, ANR-12-BS07-0029). V.L. Sushkevich and I.I. Ivanova thank the Russian Science Foundation for the financial support (Grant №14-23-00094).

Notes and references

- 1 I.V. Kozhevnikov, Catal. Rev. Sci. Eng., 1995, **37**, 311.
- 2 Y. Onoue, Y. Mizutani, S. Akiyama, Y. Izumi, Chem. Tech., 1978, **8**, 432.
- 3 Suzuki T, Yoshikawa H, Abe K, Sano K (1994) WO Patent WO0022803 to Showa Denko KK.
- 4 M. Wada M (1990), Shokubai, 1990, **32**, 223.
- 5 K. Sano, H. Uchida, S. Wakabayashi, Catal. Surv. Jpn., 1999, **3**, 55.

- K.M. Rao, R. Gobetto, A. Ianibello, A. Zecchina, J. Catal. 1989, 119, 512.
- 7 P. Madhusudhan Rao, A. Wolfson, S. Kababya, S. Vega, M.V. Landau, J. Catal., 2005, **232**, 210.
- 8 A. Lapkin, B. Bozkaya, T. Mays, L. Borello, K. Edler, B. Crittenden, Catal. Today 2003, **81**, 611.
- 9 M. Misono, Chem. Commun. 2001, 1141.
- 10 T. Ito, K. Inumaru, M. Misono, Chem. Mater. 2001, **13**, 824.
- 11 L.R. Pizzio, C.V. Caceres, M.N. Blanco, Appl. Catal A 1998, 167, 283
- 12 J.G. Hernandez-Cortez, T. Lopez, M.E. Manriquez, R. Gomez, J. Navarrete, J. Sol–Gel Sci. Technol. 2003, **26**, 213.
- 13 P. Vazquez, L. Pizzio, G. Romanelli, J. Autino, C. Caceres, M. Blanco, Appl. Catal. A 2002, **235**, 233.
- 14 R. Gao, Q. Zhu, W.-L. Dai, W.-L., K. Fan, RSC Advances 2012, 2, 6087.
- 15 J.G. Hernandez-Cortez, T. Lopez, M.E. Manriquez, R. Gomez, J. Navarrete, J. Sol–Gel Sci. Technol., 2003, **26**, 213.
- 16 T. Okuhara, M. Kimura, T. Kawai, Z. Xu, T. Nakato, Catal. Today 1998, 45, 73.
- 17 I. Ivanova, V. Sushkevich, Yu. Kolyagin, V. Ordomsky, Angew. Chem. Int. Ed., 2013, **52**, 12961.
- 18 V.L. Sushkevich, V.V. Ordomsky, V.V. Ivanova, Appl. Catal. A 2012, **441-442**, 21.
- 19 S. Shikata, M. Misono, Chem. Commun. 1998, 1293.
- 20 E. Breitmaier, W. Voelter, Carbon-13 NMR Spectroscopy: High resolution methods and applications in organic and biochemistry, VCH, New York, **1990**, p. 515.

Journal Name