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Immobilized phosphotungstic acid for catalytic alkylation of aromatic compounds

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Phosphotungstic acid $H_3[PW_{12}O_{40}]$ (PTA) with the Keggin structure has become well known as a solid superacid with pKa≈-13. High acidity of PTA and its good solubility in water and other polar solvents enables its use as a highly active homogeneous catalyst. However, homogeneous catalysis has various drawbacks, e.g. difficult and expensive removal of the used catalyst from the reaction mixture and its recycling. PTA also demonstrated good catalytic activity as a heterogeneous catalyst of various organic reactions, but its application is limited by solubility in polar solvents and low surface area. The objective of this work is the synthesis and study of insoluble superacidic catalysts covalently embedded into the silica matrix. The catalyst PTA/SiO_2 was synthesized by the sol-gel method. Tetraethoxysilane was co-condensed with PTA in acidic media in the presence of Pluronic P123 as a pore-forming agent. The obtained gel was air-dried and calcined at 500°C producing a mesoporous material with a significant fraction of micropores in its structure. Isotherms of adsorption/desorption of nitrogen indicated cylindrical shape of the pores with necks. Cs-exchanged material was prepared by mixing PTA/SiO_2 with a solution of CsCl. Surface acidity of the samples was determined by reversed titration. Dry samples were dispersed in a solution of pyridine in tetrahydrofuran. After equilibration, the solid phase was filtered, and the filtrate was titrated by HCl. PTA/SiO_2 has a very high adsorption capacity on pyridine, which corresponds to 15 molecules of pyridine per $[PW_{12}O_{40}]$3- anion. This number exceeded the number of available protons. The catalysts were successfully tested in the alkylation of 1, 3, 5-trimethylbenzene by octene-1 and decene-1. The use of superacidic materials in catalytic reactions can significantly improve the effectiveness of the processes.

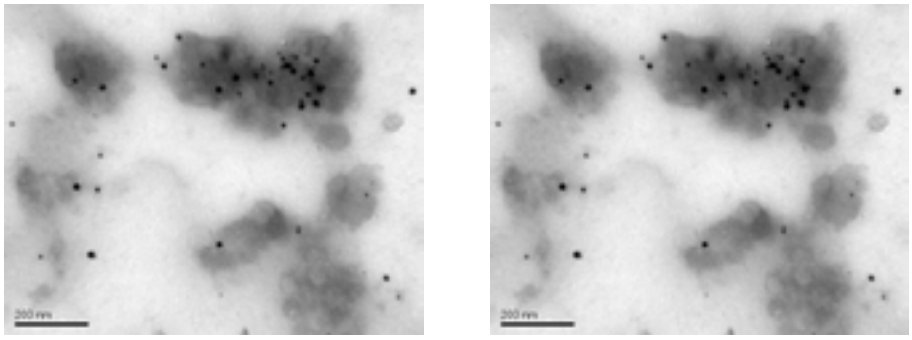

Figure 1: SEM (left) and TEM (right) images of PTA/SiO2.

Recent Publications:

1. Little I, Alorkpa E, Khan V, Povazhniy V and Vasiliev A (2018) Efficient porous adsorbent for removal of cesium from contaminated water. J. Porous Mater. 2018:1–9.
2. Seaton K, Little I, Tate C, Mohseni R, Roginskaya M, et al. (2017) Adsorption of cesium on silica gel containing embedded phosphotungstic acid. Microporous Mesoporous Mater. 244:55–66.
3. Little I, Seaton K, Alorkpa E and Vasiliev A (2017) Adsorption of cesium on bound porous materials containing embedded phosphotungstic acid. Adsorption 23:809–819.
4. Adetola O, Little I, Mohseni R, Molodyi D, Bohvan S, et al. (2017) Synthesis of mesoporous silica gels with embedded heteropolyacids. J. Sol-Gel Sci. Technol. 81:205–213.
5. Adetola O, Golovko L and Vasiliev A (2016) Modification of silica gel by heteropolyacids. Key Eng. Mater. 689:126–132.

Biography

Aleksey Vasiliev has his expertise in Material Science, Organic Chemistry and Catalysis. He has completed his PhD from the Institute of Bioorganic Chemistry and Petrochemistry in Ukraine. Then he continued his professional career in the National Technological University in Argentina, and further moved to Rutgers University (USA). Currently, he occupies the position of an Associate Professor in East Tennessee State University. In recent years, he worked in the field of mesoporous materials and their applications in adsorption and catalysis.

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