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Superacidic catalysts for alkylation of benzene by olefins

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Objectives

The objectives of the project are the synthesis of superacidic porous catalysts containing embedded phosphotungstic acid (PTA) and their use in catalytic alkylation of aromatic compounds by higher olefins. The novelty of this work is covalent immobilization of PTA clusters to the surface of silica gel for prevention of their leaching from the catalyst. On the first step, the activities of obtained catalysts were tested in liquid-phase alkylation of 1,3,5-trimethylbenzene by 1-decene (Fig. 1). These results were compared to the results of alkylation on non-immobilized PTA and zeolites.

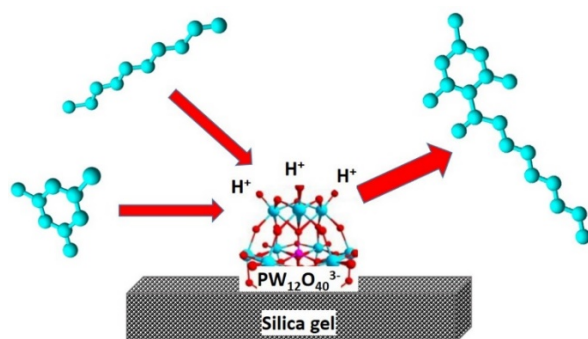


Figure 1. Alkylation of 1,3,5-trimethylbenzene by 1-decene on H-PTA/SiO₂.

Synthesis and characterization

In the first part of the study, the catalysts were synthesized by the sol-gel method. Tetraethoxysilane and PTA were precursors in the synthesis. Four various surfactants (Pluronic P123, dodecylamine, sodium dodecylsulfate and trimethylstearylammmonium chloride) were used as pore-forming agents. Co-condensation of precursors enabled covalent embedding of a PTA into the support matrix. The use of surfactants resulted in increased surface area of the materials, thus improving their catalytic activity.

TEM images revealed mesoporous structure showing particles with a range of sizes between 100 nm to 1 μ m. Dark spherical spots indicate the presence of embedded PTA clusters (Fig. 2). Obtained FT-IR spectra of the synthesized catalysts contained characteristic band of PTA at 963 cm⁻¹, presence of silica gel was indicated by peaks at 805 ($\beta_{\text{Si-O-Si}}$) and 1088 ($\nu_{\text{Si-O-Si}}$) (Fig. 3). Mesoporous material had high BET surface area and high concentration of acidic catalytic sites. Thermoanalysis showed that the obtained material is thermally stable up to 500 °C (Fig. 4). Dynamic light scattering study revealed that obtained samples had particle sizes in the range of 260-360 nm. (Fig. 5).

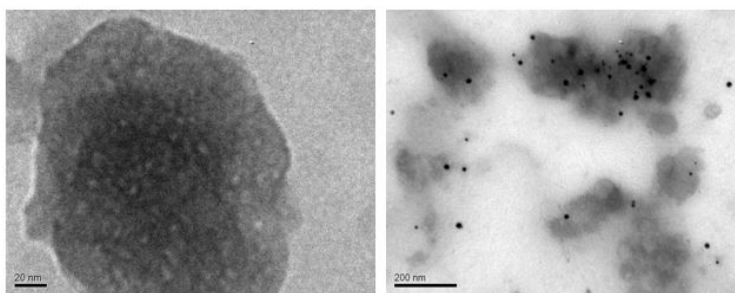


Figure 2. TEM images of the obtained material.

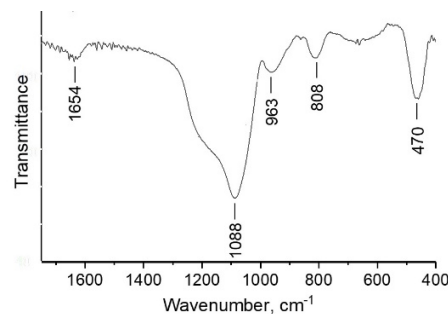


Figure 3. FT-IR spectra of H-PTA/SiO₂.

Alkylation study

The reaction between 1,3,5-trimethylbenzene and 1-decene was carried out in liquid-phase at 100-160°C. Composition of the product was determined by gas chromatography. The catalyst obtained with Pluronic

P123 as a template (**1**) demonstrated the highest activity and resulted in 90% conversion of 1-decene into the products. Its cesium salt appeared much less active. It was also determined that this catalyst was more effective than zeolite HY (Fig. 6).

The study of the reaction mixture after the reaction showed the presence of all isomers of alkylated 1,3,5-trimethylbenzenes but a linear alkylbenzene was the major product. It was also found that 1-decene isomerized producing a mixture of isomeric decenes.

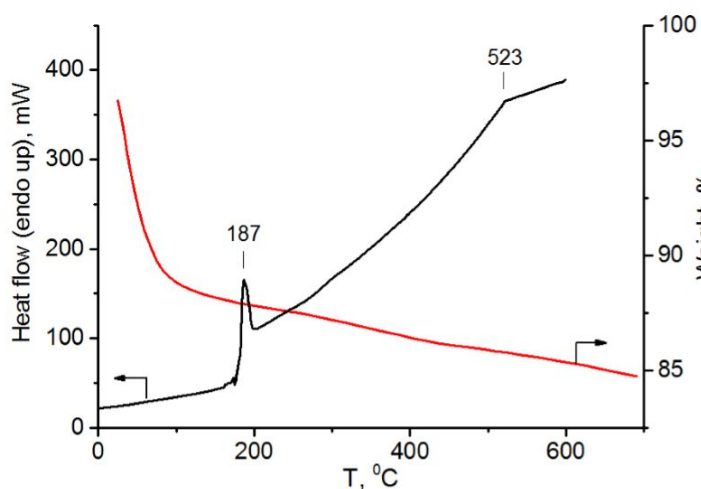


Figure 4. DSC and TGA curves of H-PTA/SiO₂.

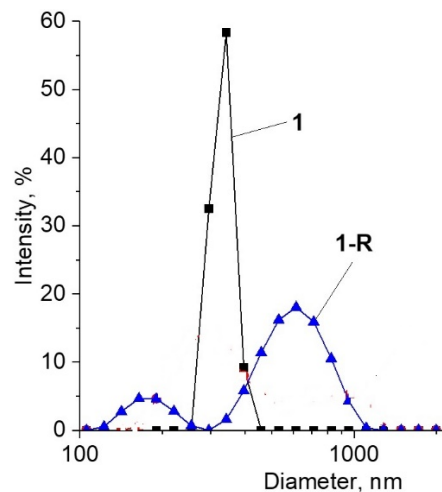


Figure 5. Particle size distribution of H-PTA/SiO₂ before (1) and after (1-R) catalysis.

Recycling of the obtained catalyst resulted in slight decrease of the surface area and acidity. This could be due to the partial pore blocking by carbon deposits. However, unchanged contents of tungsten indicated that no leaching of PTA occurred. Observed decrease of 1-decene conversion is the subject of the future study with objective to determine the optimal regeneration conditions.

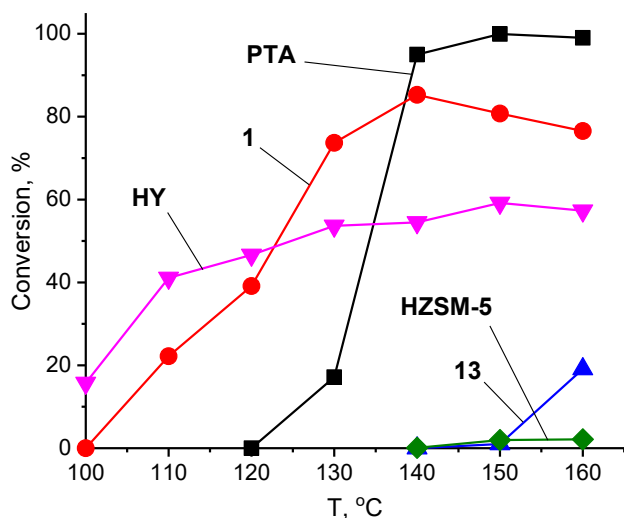


Figure 6. Catalytic activity of pure PTA, H-PTA/SiO₂ and Cs-PTA/SiO₂ in comparison with zeolites HY and HZSM-5.

Student participation, publications and presentations

Two students worked on this project during 2018-2019 academic year. The results of their research has been presented at 8 local, national and international conferences. In addition, a paper based on results of the first step was published:

A. Kuvayskaya, S. Garcia, R. Mohseni, A. Vasiliev. Superacidic mesoporous catalysts containing embedded heteropolyacids. *Catal. Lett.* 149 (2019) 1983-1990

Plan of research for the 2nd year

It was found that the most effective catalyst was prepared with the use of Pluronic P123 as a pore-forming agent. Future research will be devoted to the study of its catalytic activity in alkylation of benzene in gas phase.