

PRF # 55931-UR5

Project title: Room temperature Friedel-Crafts alkylation using magnetic nanoparticle catalysts in oscillating magnetic fields

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The goal of this project is to study a new type of a heterogeneous catalyst activation method. To test the new idea a series of $-\text{SO}_3\text{H}$ group attached silica coated magnetic CoFe_2O_4 nanoparticles are prepared and used as catalysts for Friedel-Crafts alkylation under the influence of 20-500 Hz oscillating magnetic fields.

Synthesis of magnetic nanoparticles with imidazolium ionic groups and sulfonic acid functions (MNPSiIMSO₃H)

The ionic groups such as imidazolium cation with counter ions chloride, cyanide and acetate are known to interact with substrates by dipolar interactions. The incorporation of these ionic liquid moieties between magnetic nanoparticle and active acidic catalyst site can be used to enhance the activity of a catalyst. Our earlier studies on sulfonic acid functionalized acidic ionic liquid modified silica catalysts have shown that this type of solid acid catalysts are very effective catalysts in the acid catalyzed processes such as the hydrolysis of polysaccharides [1]. Therefore it would be appealing to study synergistic effect of imidazolium cation and sulfonic acid group immobilized on magnetic field driven nanoparticle catalysts. The synthesis and testing of this class of magnetic nanoparticle catalysts is a major task in the proposed project. As suggested in the proposal, we have synthesized these catalysts during this reporting period, using the reaction scheme shown in Figure 1.

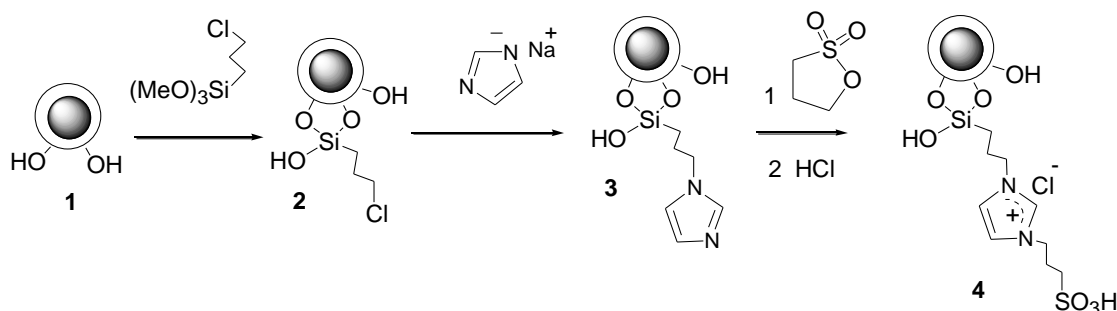


Figure 1. Synthesis of magnetic nanoparticle catalyst (MNPSiIMSO₃H, 4)

First the silica coated magnetic nanoparticles (1) were reacted with (3-chloropropyl) trimethoxysilane in refluxing toluene to incorporate chloropropyl group to the magnetic nanoparticle surface. Then a suspension of the chloropropyl attached nanoparticles (2) was treated with the sodium salt of imidazole for the nucleophilic substitution of chlorine with imidazole group. The initial attempts of this reaction in THF medium resulted poor conversions of about 15% and then change of solvent to DMSO resulted improvements in the conversion to approximately 50%, but further attempts to achieve complete conversions of chlorine substituted nanoparticles to imidazole substituted nanoparticles (3) were not successful. In an alternative route, we have attempted to prepare the product 3 by the synthesis of 1-[3-(trimethoxysilyl)propyl]-1*H*-imidazole first and then reacting with silica coated magnetic nanoparticles. However, this route also failed to give complete incorporation of imidazole group on to the surface of the magnetic nanoparticles. Next the reaction of 3 with 1,3-propane sultone at 80 °C, for 24 h followed by acidification with conc. HCl gave the imidazolium group and sulfonic acid attached MNPSiIMSO₃H catalyst 4. In order to test the catalytic activity of the new imidazolium - sulfonic acid groups attached MNPSiIMSO₃H the initial experiments were carried out for the phenol alkylation reaction as shown in Figure 2. The reaction vial with phenol : *t*-butanol = 1 : 3 mole mixture and MNPSiIMSO₃H (2 mol%) was placed ~ 1 mm from the rotating magnet and the speed of the motor was controlled using a DC power regulator to give a 40 Hz oscillating field. The temperature inside the solution remained close to room temperature in equilibrium throughout the reaction period. At the end of the reaction period, MNPSiIMSO₃H catalyst was removed by a strong neodymium permanent magnet and the product was analyzed by GC and ¹H NMR.

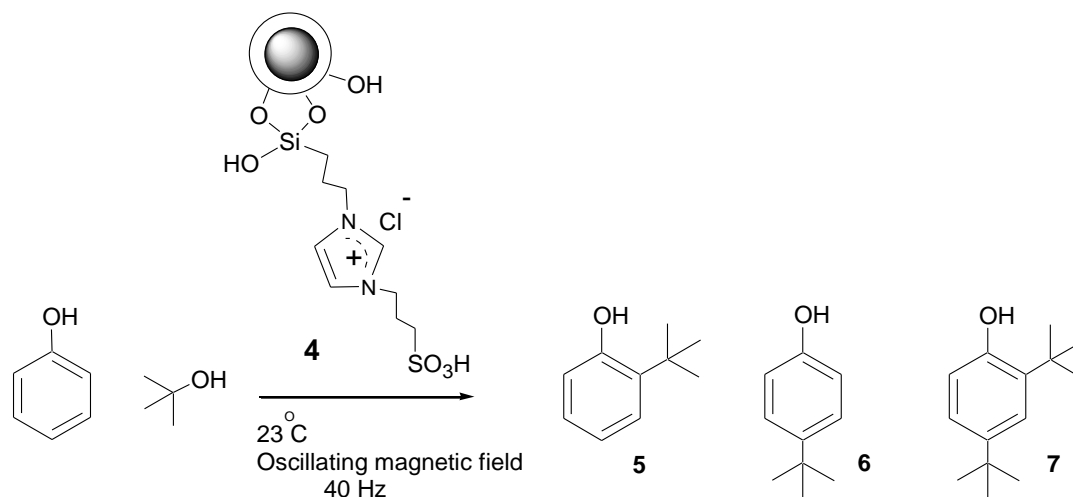


Figure 2. Alkylation of phenol with t-BuOH, using imidazolium ionic group and sulfonic acid functions attached magnetic nanoparticle catalyst (MNPSiMSO₃H, **4**) under 40 Hz oscillating magnetic field created by the mechanical rotation of a strong Neodymium magnet at 23 °C.

Table 1. Comparison of the catalytic activity MNPSiSO₃H in the alkylation of phenol with t-BuOH, using oscillating field generated by rotation of a CMS Magnetics N45 Neodymium cube magnet at 40 Hz at 23 °C.

Reaction condition	Time (h)	% yield of alkylated phenols	Product composition 5 : 6 : 7
23 °C, no magnetic field	24.0	0	-
80 °C, no magnetic field	24.0	3 ±1	2 : 2 : 5
40 Hz oscillating magnetic field, 23 °C	8.0	10 ±1	2 : 1 : 5
40 Hz oscillating magnetic field, 23 °C	24.0	12 ±1	2 : 2 : 5

The catalytic activities and alkylation yields seen in these studies are small. We are currently working on new synthetic methods for more effective immobilization of the sulfonic acid groups and imidazolium ionic liquid core groups on the magnetic nanoparticles to give higher density of catalytic sites on nanoparticle surface in order to improve the alkylation yields. In addition we are studying the effect of the oscillating frequency of the magnetic field also in attempts to improve the alkylation yields.

Involvement of undergraduate students in research

Two Prairie View A&M chemistry major undergraduate students worked part-time on the project during the regular semesters in 2017-18 reporting period. The first student, graduated with B.S. in chemistry, was accepted to a graduate program and currently studying for her Ph.D. in chemistry. The second student is a sophomore and continues to work on the project.

References:

[1] A.S. Amarasekara, O.S. Owereh, Synthesis of a sulfonic acid functionalized acidic ionic liquid modified silica catalyst and applications in the hydrolysis of cellulose, *Catalysis Communications*, 11 (2010) 1072-1075.