

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 $-SO_3H$ 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 sulfonic acid functions

We have synthesized two new sulfonic acid group functionalized magnetic nanoparticle catalysts and characterized during this period. The incorporation of the ionic liquid moieties between magnetic nanoparticle and active acidic catalyst site can be used to enhance the activity of a catalyst. In addition we have synthesized a second catalyst with sulfonic acid group directly connected to the magnetic nanoparticle surface for comparison. The synthesis and testing of ionic liquid class of magnetic nanoparticle catalysts is a major task in the proposed project and these catalysts were prepared using the reaction scheme shown in Figure 1.

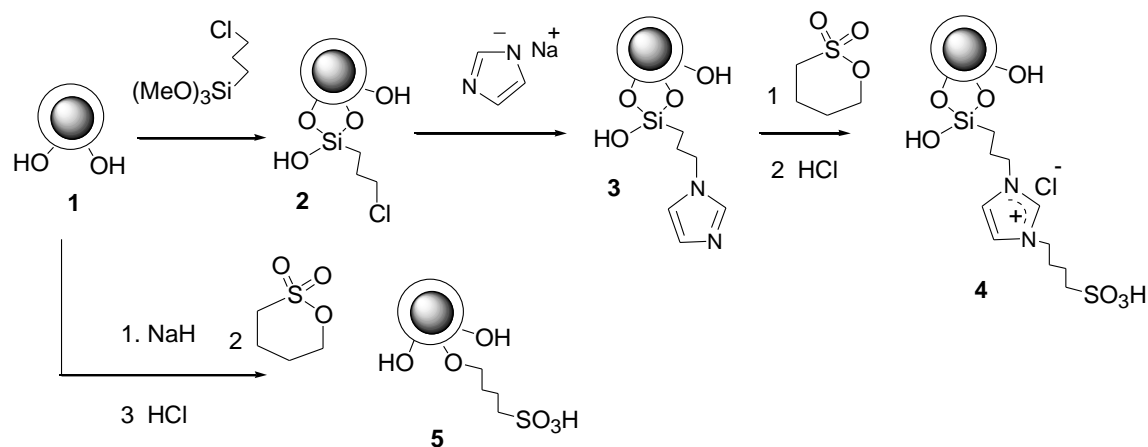


Figure 1. Synthesis of sulfonic acid functionalized magnetic nanoparticle catalysts **4** and **5**

In the synthesis of ionic liquid group containing catalyst **4**, 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 use of DMSO as a solvent resulted improvements in the conversion to approximately 65%, but further attempts to achieve complete conversions of chlorine substituted nanoparticles to imidazole substituted nanoparticles (**3**) were not successful. In the next step the reaction of **3** with 1,4-butanediol sulfone at 80 °C, for 24 h followed by acidification with conc. HCl gave the imidazolium group and sulfonic acid attached catalyst **4**.

The second catalyst **5** was synthesized by reaction of the sodium form of **1** with 1,4-butanediol sulfone at 80 °C, for 24 h followed by acidification with conc. HCl.

These two catalysts were tested in the alkylation of benzene and anisole under a 40 Hz oscillating magnetic field created by the mechanical rotation of a strong Neodymium magnet at 23 °C as shown Figure 2. The reaction vial with benzene : 1-decene = 1 : 3 mole mixture with catalyst **4** or **5** (2 % loading) was exposed to 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, catalyst was removed by a strong neodymium permanent magnet and the product was analyzed by GC and 1H NMR. In a second series of experiments benzene was replaced with anisole and the experiments were repeated with anisole : 1-decene = 1 : 3 mole mixture with catalyst **4** and **5** (2 % loading).

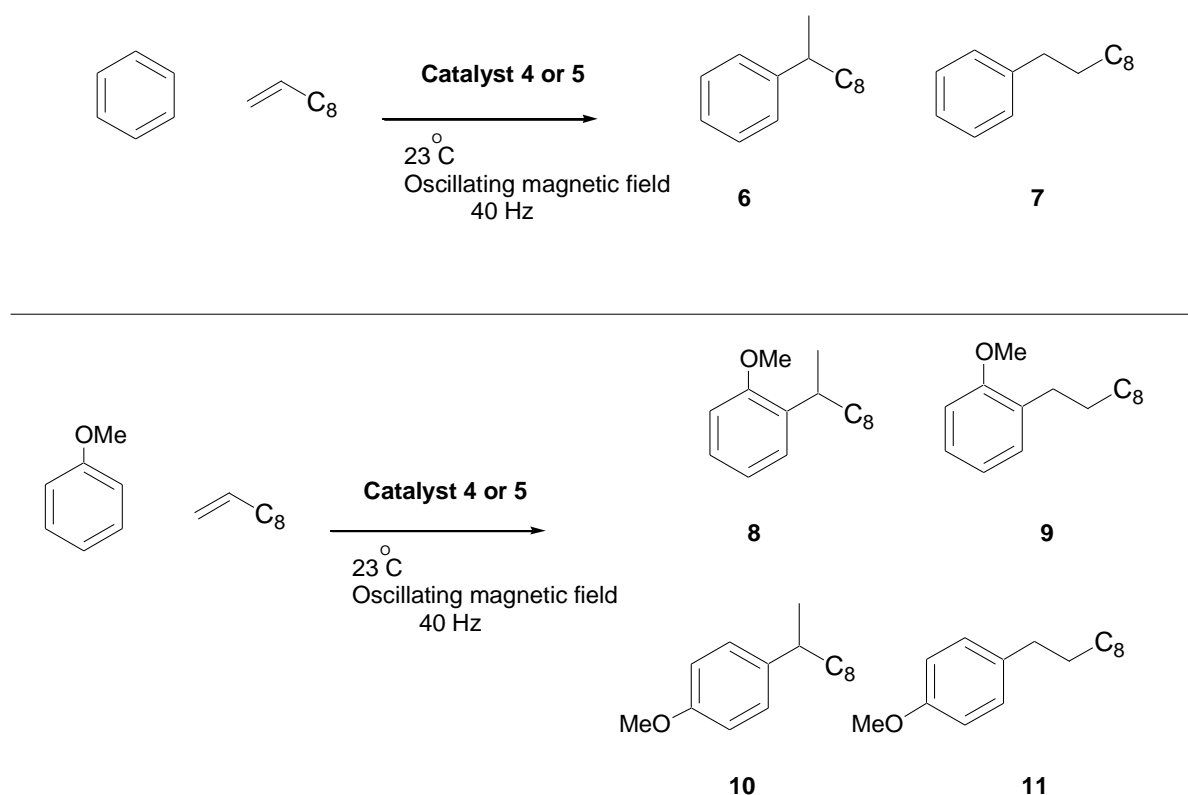


Figure 2. Alkylation of benzene and anisole using imidazolium ionic liquid group + sulfonic acid function attached magnetic nanoparticle catalyst **4** and sulfonic acid group attached magnetic nanoparticle catalyst **5**, under 40 Hz oscillating magnetic field created by the mechanical rotation of a strong Neodymium magnet at 23 °C.

Table 1. Comparison of the catalytic activities of **4** and **5** in the alkylation of benzene and anisole using oscillating field generated by rotation of a CMS Magnetics N45 Neodymium cube magnet at 40 Hz at 23 °C.

Reactants (mole ratio)	Catalyst	Time (h)	% Conversion
benzene : 1-decene (1 : 3)	4 (2 mol %)	12.0	< 1
benzene : 1-decene (1 : 3)	5 (2 mol %)	12.0	0
anisole : 1-decene (1 : 3)	4 (2 mol %)	12.0	8
anisole : 1-decene (1 : 3)	5 (2 mol %)	12.0	6
anisole : 1-decene (1 : 3)	4 (2 mol %)	24.0	11
anisole : 1-decene (1 : 3)	5 (2 mol %)	24.0	7

The alkylation of less reactive benzene gave only traces of products with catalyst **4**, and no products were observed with catalyst **5**. In the alkylation of more reactive anisole, catalyst **4** produced a conversion of 8 % after 12 h, and comparatively lower conversions were observed with catalyst **5**. This again proved the superior catalytic activity of the ionic liquid loaded catalysts as we have observed in our previous work on similar systems. The extension of time to 24 h could produce only small enhancements in conversions as shown the last two entries in the Table 1. We are currently analyzing the mixtures produced to determine the compositions of **8**, **9**, **10** and **11** in the reactions.

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 methods of increasing the oscillating frequency of the magnetic field also in attempts to improve the alkylation yields.

Involvement of undergraduate and graduate students in research

One Prairie View A&M chemistry major undergraduate students worked on the project during the regular semesters in 2018-19 reporting period. One graduate student also worked on the project during the reporting period.