

Oxidations of Allylic and Benzylic Alcohols under Inductively-Heated Flow Conditions with Gold-Doped Superparamagnetic Nanostructured Particles as Catalyst and Oxygen as Oxidant

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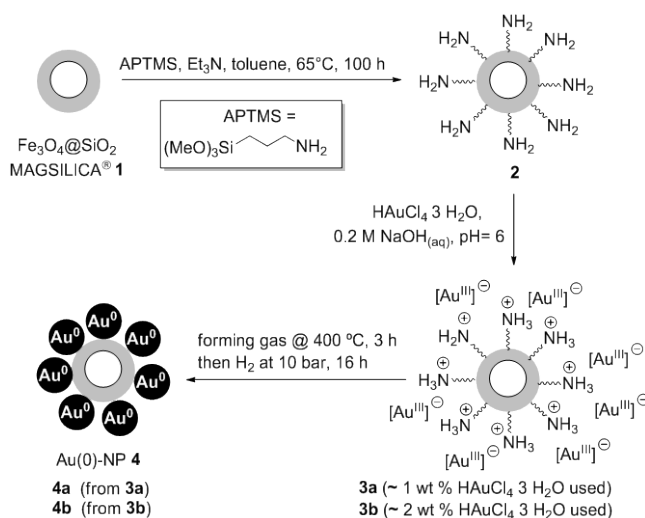
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Abstract: A continuous flow protocol for the oxidation of alcohols to aldehydes and ketones, respectively, using oxygen gas or atmospheric air is reported. The key features of this work are gold nanoparticles that are attached to the surface of nanostructured core shell particles composed of an Fe₃O₄-containing core and a silica shell. These nanostructured particles exert superparamagnetic properties and thus inductively heat up in an external oscillating electromagnetic field, conditions under which the gold catalyst is able to perform these oxidation reactions.

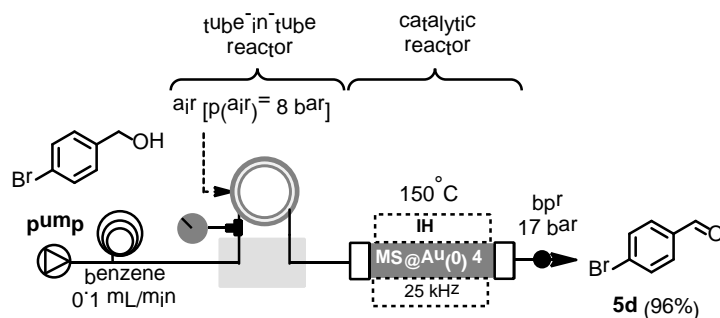
In our research, we relied on the uptake of Au³⁺ ions from an aqueous HAuCl₄ solution onto amino-functionalized, silica-coated nanostructured magnetic particles **2**. The loading was achieved at pH= 6 and yielded nanostructured particles **3**. This was followed by metal reduction under forming gas at 400 °C and further reduction in an autoclave under hydrogen atmosphere to furnish the desired gold-doped core-shell particle **4** (Scheme 1). We prepared two different types of particles that differed in the amount of HAuCl₄ employed during immobilization (**2**→**3**). Catalysts **4a** and **4b** differed in the amount and size of gold nanoparticles present on the silica surface. We used nanostructured, superparamagnetic nanoparticles **1** as supporting material, composed of an Fe₃O₄-containing core and a SiO₂ shell. These particles were functionalized by coupling of (3-aminopropyl) trimethoxysilane (APTMS) to the silica coating. The basic amino groups in **2** facilitated loading of the anionic Au complex [Au(OH)_xCl_{4-x}]⁻ to yield **3**. In our hands this protocol was superior to the adsorption of gold on SiO₂ surfaces. From X-ray absorption near edge structure analysis, Rossi et al. concluded that amino groups grafted on solid supports interact more strongly with metal ions than gold that is simply adsorbed on the surface of non-functionalized supports.

Scheme 1. Preparation of nanostructured, gold-doped particles **4** (MAGSILICA®).



Essentially, we aimed to carry out a scale up study to demonstrate the practicability of this catalytic system. Therefore, a PEEK reactor was filled with 2.0 g of catalyst **4a** (24.0 mg Au) and 1.0 g of MAGSILICA® **1**. Thus, 4-bromobenzyl alcohol (2.5 g 13.37 mmol) was dissolved in 50 mL benzene and the solution was pumped through the reactor at a flow rate of 0.1 mL/min. Several reaction parameters were changed towards higher productivity. The concentration of the reaction mixture was increased threefold and the flow rate was doubled while catalyst loading was only increased by a factor of four. The desired product was isolated in 92% yield. The same transformation was repeated using pressured air instead of oxygen gas. Gratifyingly, the catalyst also showed high activity with atmospheric oxygen as oxidant and the product was isolated in 96% yield (Scheme 2).

Scheme 2: Oxidation of 4-bromobenzyl alcohol with atmospheric oxygen as oxidant.^[a,b]



Reaction conditions: ^a 4-Bromobenzyl alcohol (100 mg, 0.54 mmol) in benzene (4 mL); ^b catalyst **4a** (2.0g, 24.0 mg Au), 150 °C and MAGSILICA® (1.0 g).

In conclusion, we report on the design of nanostructured core shell particles based on iron oxide (primarily Fe₃O₄) and a silica shell that are doped with gold nanoparticles (< 10 nm).^[40] This nanostructured architecture allows rapid heating in direct proximity of the heterogenic catalytically active gold nanoparticles under inductive heating conditions and using them in O₂-promoted oxidations of primary and secondary alcohols, which provided aldehydes and ketones, respectively.

The catalytic samples were mixed with nanostructured core-shell iron oxide and used as catalytic fixed bed materials in mesofluidic PEEK reactors. The processes were conducted under high pressure/high temperature conditions and provided in almost all cases complete conversion in a single pass. The catalytically active nanoparticles show excellent distribution across the nanostructured surface of the core shell nanoparticles with sizes below 10 nm and low polydispersity. Catalyst leaching is negligible with less than 0.0015% over 12 hours of operation. The high activity of the catalyst was demonstrated after upscaling as well as when exchanging oxygen gas by atmospheric oxygen as oxidant. It is important to note that no overoxidation occurred during the flow-process. We are certain that the catalyst architecture and the technical set-up has potential applications for continuous oxygen-promoted oxidations in technical processes.

Manuscript accepted for publication: *Advances in Synthesis & Catalysis*, 2014.