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Highly selective aqueous phase hydrogenation of phenols over nanostructured RuO_2 on MCM-41 catalysts

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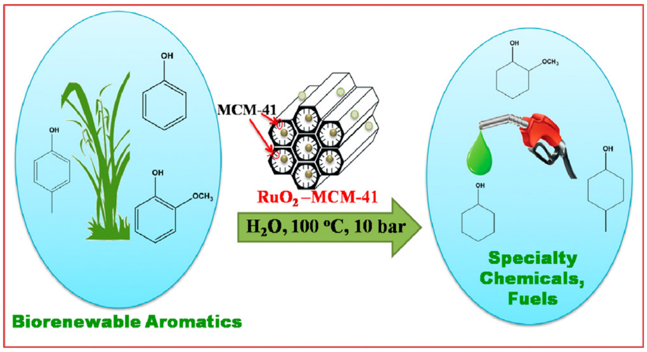
GRAPHICAL ABSTRACT



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ABSTRACT

Selective aqueous phase hydrogenation of phenol as well as its derivatives is important for the synthesis of chemical intermediates which are crucial for the manufacture of high-tonnage commodities and a multitude of value added platform chemicals. Herein, we report a facile catalyst made of highly dispersed small RuO_2 nanoparticles supported on mesoporous MCM-41 using one-pot approach. The optimal $5RuO_2$-MCM-41 catalyst with particle size 6-8 nm showed excellent activity and selectivity in aqueous phase hydrogenation of phenol and other functionalized substrates, which are building blocks of lignin, to corresponding cyclohexanol products without any additives. These catalysts showed better stability and can be reused several times without any significant drop in activity which proves the heterogeneity of the immobilized oxide catalyst.

1. Introduction

Catalytic transformations of biorenewable aromatics to value added chemicals and fuels through economic and energy efficient process have currently attracted considerable attention. Global demand for polymers like nylon-6, nylon-6,6, and also the depletion in the products derived from non-renewable energy sources has forced to identify a renewable feedstock that replace the existing materials [1–3]. Lignocellulosic biomass is considered as the most accessible renewable feedstock for a variety of fine chemicals and biofuels [4]. Among which, lignin accounts for the second most abundant biomass in nature [5], which after depolymerization yields highly oxygenated aromatic monomers mainly, phenolic compounds [6]. By utilizing both heterogeneous and homogeneous catalysts of transition metals, including Pd [7], Ru [8], Pt [9], biomass derived phenolic bio-oil components (phenols, guaiacols

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and syringols) are transformed to their corresponding cycloalkanes with high selectivity. Selective hydrogenation of phenols are desirable strategy to yield a variety of products involving cycloketones, cycloalcohols, arenes, cycloalkanes and methane which are key intermediates to higher value commodities.

Generally, the phenol hydrogenation reactions are carried out in the vapor phase at elevated temperatures and pressures over supported Pd catalysts, but they suffers deactivation due to coke formation [10]. Later on, many researchers have contributed to the liquid phase hydrogenation reaction of phenol using Pd [11], Pt [12], Rh [13] catalysts on different supports for improving the activity. Previous investigations suggest that the metal sites facilitate the activation of H_2 and basic sites in support adsorb phenol during hydrogenation reactions. Depending on the geometry of phenol adsorption on different sites on the support, the product selectivity can be tuned [14]. Designing a heterogeneous catalyst using ruthenium nanoparticles is of great interest due to its excellent intrinsic ability for hydrogenation reactions [15–17] and cost effective compared to other noble metals like Pd. A detailed insight in to the literature reveals that, to date, there are very few efforts to utilize ruthenium as a catalyst to selectively hydrogenate phenolic entities. In the recent past, studies on ruthenium catalysts has been a subject of great interest to hydrogenate arenes [6], hydrodeoxygenation of lignin derived phenols [8], and selective hydrogenolysis of phenols [18], since they contributes to the concept of chemicals from nature. Main shortcoming with Ru based catalysts is the metal detachment from the support and resulting in leaching which reduces the efficiency of the catalyst in liquid phase phenol hydrogenation. Hence it is challenging to develop a stable, highly efficient and selective catalyst for phenol hydrogenation in liquid phase. By tuning the size and shape of the nanoparticles and the properties of the support, the catalytic performance can be improved by achieving better physical and chemical reactivity [19]. Somorjai et al. has proved the remarkable size dependence of Ru NP on the CO oxidation reactivity where 6 nm catalyst showed 8-fold higher activity compared to 2 nm particles [20]. The catalytic activity trend by nanoparticles with different size has been subject of interest due to its practical and fundamental perspective. It can predict the structure sensitivity of catalytic reaction since particle size varies the surface atomic structure, oxidation state, metal-support interaction and the electronic state which influences the nature of active sites that tunes the product selectivity and conversion [21].

Identification of suitable solvent is significant in catalytic activity as it drastically influences the rate and selectivity in hydrogenation of phenolic compounds. The solvent for phenol hydrogenation should be stable to the catalyst and reaction conditions, dissolve and transport of H_2, retain reactants and products in solution [22]. Generally, halogenated organic compounds [23], $ScCO_2$ [24], cyclohexane [25], ionic liquids [26], water [27] are used as solvents for phenol hydrogenation, among which green solvent water have attracted great attention due to non-polluting nature of environment. Recently, Yong Wang et al. have found that hydrogenation of phenol on Pd@mpg-C_3N_4 catalyst proceeds more effectively in water than in organic solvents. Further, DFT calculations showed that water molecule can lower the activation energy for the reaction and will accelerate the proton transfer involved in the hydrogenation of phenol and cyclohexanone to cyclohexanol [28]. The complete aqueous solubility of phenol could be achieved by increase in temperature and the low aqueous solubility of products favors easy separation.

In this present work, we demonstrate a one-pot approach to synthesize finely dispersed nanostructured RuO_2 immobilized on MCM-41 with different amounts of ruthenium with a goal of engineering Ru active sites. All the Ru-oxide catalysts were well characterized and the reaction conditions were optimized systematically. The optimized 5RuO_2-MCM-41 catalyst facilitates the hydrogenation of phenol and its substrates including biomass derived phenolic compounds to give corresponding cycloalcohols selectively with high activity under mild conditions in aqueous medium. The RuO_2-MCM-41 catalyst was found to be purely heterogeneous in nature and highly stable under reducing reaction environment. Thus, we have designed cost effective, greener, reusable, one-pot RuO_2-MCM-41 heterogeneous catalyst for highly selective aqueous phase hydrogenation reactions of phenols to cycloalcohols.

2. Experimental

2.1. Materials

Ruthenium(III) chloride hydrate (99.9%), cetyltrimethyl ammonium bromide CTAB (98%), Tetraethylorthosilicate TEOS (Sigma Aldrich), Ethylenediamine (Fluka), Ethanol (Merck) and Phenol (Spectrochem), unless otherwise mentioned, reagents and solvents were purchased from Thomas Baker, Aldrich, Acros, all chemicals were used as received. All the experiments were done using ultra Millipore water.

2.2. One-pot synthesis of RuO_2 nanoparticles supported on MCM-41

Typically, 8 mmol of CTAB was dissolved in 60 mL of water under stirring at 95 °C for 15 min and calculated amount of $RuCl_3$ was added. Simultaneously, in another beaker, 2.5 ml of TEOS was added to 20 mL of ethanol mixed thoroughly and 1.5 mL of ethylenediamine was added in drops and stirred at RT for 30 min to get clear solution. The resulting clear solution was added in drop wise manner into the above metal precursor solution which is maintained at 75 °C and kept for stirring for next 2 h. The resulting reaction mixture was cooled to room temperature and aged overnight. The residue was filtered, washed thoroughly with water and ethanol to remove excess of ethylenediamine and CTAB. The obtained powder was dried at 80 °C for 12 h and calcined at 400 °C for 6 h (at a ramp rate of 2 °C/min). The Ru loading on MCM-41 was controlled to 0.5, 1, 2.5, 4, 5, and 10 wt% by changing the amount of metal precursor to explore the effect of metal content and particle size. Compared to the dry synthesis method [29], one-pot approach provides better uniform dispersion as well as controllable particle size of RuO_2 nanoparticle supported on silica materials like MCM-41.

2.3. Catalytic aqueous phase hydrogenation of phenols

The hydrogenation of phenol over RuO_2-MCM-41 catalysts was investigated in a Parr 4842 autoclave (100 mL) equipped with a mechanical stirrer and temperature controller. The reaction pot was charged with phenol (1.6 mmol), water (10 mL), and catalyst (50 mg) and the autoclave was sealed and purged twice with H_2 to exclude air. A range of experiments were carried out to optimize the reaction conditions by varying temperature, pressure, solvent, amount of catalyst and time. After reaction, the catalyst was separated by centrifugation and the product extraction was done using chloroform, the phenol conversion and selectivity were determined using GC (Agilent 7890 connected with HP5 column and FID detector) and confirmed by GC-MS (Varian connected with HP5 column) (Figure S1). The crude product in chloroform was purified using column chromatography and analyzed by ^1H NMR (Figure S2). To check reusability, after each cycle, the separated catalyst was washed repeatedly with water and acetone and dried at 100 °C for 12 h.