

A solid sulfonic acid catalyst for the solvent free alkylation of phenol

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ABSTRACT

Silica extracted from rice husk ash was functionalized with 3-mercaptopropyltrimethoxysilane (MPTMS) and then oxidized to sulfonic acid at room temperature and pressure. The FT-IR analysis shows bands at 1354–1166 cm^{-1} due to the asymmetric and symmetric stretching of SO_2 group. The ^{13}C CP MAS NMR of $\text{RHAPrSO}_3\text{H}$ showed chemical shifts at 58.6, 12.1 and 23.0 ppm attributed to the three carbon atoms of the propyl chain. The pyridine acidity test showed strong bands at 1510, 1541 cm^{-1} in the FT-IR spectrum attributed to the Brønsted acid sites. In the alkylation of phenol using $\text{RHAPrSO}_3\text{H}$, a conversion of ca. 75% was achieved at the reaction temperature of 120 °C. The catalyst could be regenerated by washing and drying at 185 °C for 24 h. The catalyst was reused several times without loss of catalytic activity.

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1. Introduction

Friedel–Crafts alkylation of phenol with *tert*-butyl alcohol (TBA) is a valuable process for fine chemicals synthesis (Scheme 1) which is important for both industrial and academic study. The *tert*-butyl phenol products are used as raw materials for the manufacture of a variety of resins, durable surface coatings, varnishes, wire enamels, printing inks, surface-active agents, rubber chemicals, antioxidants, fungicides and petroleum additives [1,2]. Approximately half-million tons of *tert*-butyl phenol, *i.e.*: 4-*tert*-butyl phenol (4-TBP), 2,4-ditertbutylphenol (2,4-DTBP), are used in different areas of industry [3–5]. 4-TBP is used to manufacture various antioxidants, varnishes and lacquer resins, fragrances and protecting agents for plastic [6]. 2,4-DTBP is largely used to produce substituted triaryl phosphates [7]. Literature review reveals that these alkylation reactions are mostly carried out in the gas phase with high conversion of phenol [8,9]. However, gas phase reactions usually involve high temperature and pressure leading to high cost. Very few studies on the solvent state alkylation of phenol with TBA have been published [4,10]. These solvent state reactions usually show very low conversions, *i.e.* less than 50%. It will therefore be advantageous to find new catalysts and milder experimental conditions to enhance and improve product yield.

Rice husk (RH) is a by-product of the rice milling industry. These husks cause serious disposal and pollution problems. However, due to the presence of a high content of silica in these husks, it was thought advantageous to use the silica as a support for

heterogeneous catalysts. The controlled burning of RH in air leads to the formation of rice husk ash (RHA). The silica content of the ash was found to be $\geq 95\%$. Many catalysts have been prepared via sol-gel technique using silica from RHA as a support. These catalysts were used successfully in esterification [11], alkylation [12], cyclization [13], and CO_2 utilization [14].

Several types of sulfonic acid-functionalized silica have been reported which exhibited excellent activity for different reactions. These catalysts have been used for Friedel–Crafts alkylation [15], esterification [16,17], acetalization [18], and condensation reactions [19]. These reported methods for the preparation of the catalysts suffer from drawbacks such as low yield of catalyst, harsh reaction conditions, multiple steps, long reaction time, non-environmental friendly organic solvents and costly chemicals. However, herein we report a simple procedure to functionalize RHA with MPTMS to form silica with surface $-\text{CH}_2-\text{SH}$ group in a one-pot synthesis [20]. In this work the functionalized $-\text{CH}_2-\text{SH}$ group was oxidized to sulfonic acid, $-\text{CH}_2-\text{SO}_3\text{H}$ with hydrogen peroxide at room temperature. This procedure is environmental friendly, cheap, time saving and used non-toxic chemicals. We found this catalyst to be very active for the alkylation reaction. Herein we report the preparation, characterization and the catalytic activity of this catalyst.

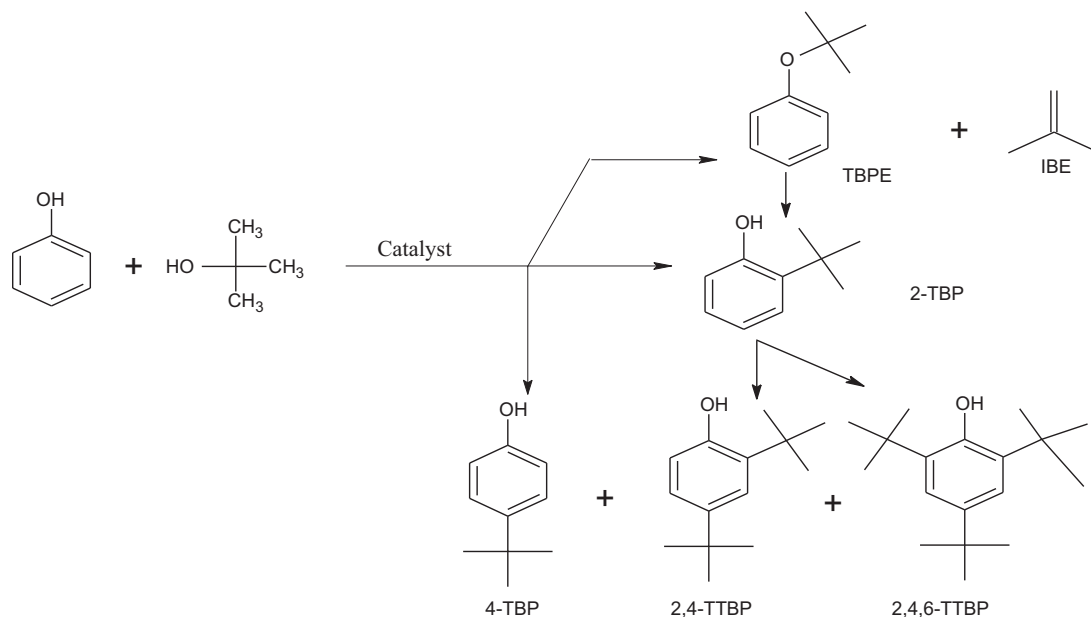
2. Materials and methods

2.1. Raw materials

The chemicals used in this study were sodium hydroxide (System, 99%), 3-mercaptopropyltrimethoxysilane (MPTMS) (Merck, 95%), nitric acid (System, 65%), toluene (J.T. Baker,

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Scheme 1. The possible products of *tert*-butylation of phenol [12].

99.8%), hydrogen peroxide (J.T. Baker, 30%), TBA (Merck, 99%), 2-propanol (Unvasol, 99%), phenol (Scharlau, 99.5%), acetonitrile (Qrec, 99.9%), acetophenone (Nacalai tesque, 99.9%). These were used without further purification. The RH was collected from a rice mill in Penang, Malaysia. All other chemicals used were AR grade or of high purity and were used directly without further purification.

2.2. Extraction and modification of silica from RHA

2.2.1. Sources of silica

The RHA was chosen as the source of amorphous silica [21] as it was available in abundance. The silica was extracted from RH according to a reported method [22,23].

2.2.2. Preparation of solid silica-based sulfonic acid

The silica was immobilized with MPTMS according to a reported method [20] and the sample was labeled as RHAPrSH. The oxidation of the thiol group was also carried out according to a reported method [24,25]. In general, the thiol group of the modified silica (RHAPrSH, 3.0 g) was oxidized with 30% H₂O₂ solution (15 mL) and concentrated H₂SO₄ (two drops) in ethanol (15 mL) for 24 h at room temperature and the solid was filtered off and washed three times with de-ionized water (50 mL). In order to ensure that all the -SH groups were oxidized, the solid was suspended in 30 mL of 0.05 M H₂SO₄ solution for 5 h [26]. The solid was then filtered off and washed thoroughly with distilled water and dried at 110 °C overnight. About 2.7 g of the product was collected.

2.3. Sample characterization

The RHAPrSO₃H was characterized by Powder X-ray diffraction (Siemens diffractometer, D5000, Kristalloflex). The nitrogen adsorption porosimetry was carried out on an automatic physisorption porosimeter (Autosorb-1 CLP, Quantachrom, USA). The FT-IR spectra were recorded on a PerkinElmer spectrometer (System 2000). The CP/MAS NMR of ²⁹Si and ¹³C were obtained using a Bruker (DSX-300) machine. The scanning electron microscopy (SEM) (Leica Cambridge S360) and energy dispersive spectrometry (EDX) (Edax Falcon System) was used to study the

morphology of the catalysts. The TEM micrographs were obtained using Philips CM12 equipment.

2.4. The surface acidity of RHAPrSO₃H

The sample together with a beaker of pyridine was placed in a desiccator equipped with a valve connection to a membrane vacuum pump (AMB Greiffenberger Antriebstechnik, model MZ2C, CE 2002/06). The system was evacuated for 1 h at a rate of 1.7 m³/h. The system was then closed and the desiccator was kept under vacuum for 48 h to equilibrate with the pyridine vapor. The atmosphere in the desiccator was evacuated again for 1 h at the same pumping rate. The sample was then removed and analyzed by FT-IR using KBr disk. The spectrum was recorded in absorption mode.

2.5. Cation exchange capacity (CEC)

Sodium chloride 1.0 g (17 mmol) was dissolved in 25 mL of distilled water in a conical flask with a magnetic stirrer. A 1.0 g (±10 mg) sample of RHAPrSO₃H was added and left to stir for 30 min. This was followed by 2–3 drops of phenolphthalein and the sample was titrated with standard NaOH solution. An average of 3 separate titrations was performed to obtain an average value for the CEC of RHAPrSO₃H [27].

2.6. Alkylation reaction procedure

The alkylation was carried out in liquid phase under argon in a 50 mL round bottom flask, equipped with a magnetic stirrer and water condenser. The water for the condenser was chilled to 2–3 °C in ice. A pump (Astro 500 liquid filter) was used to circulate this chilled water through the condenser to minimize the evaporation of TBA. Phenol (3.7 g, 0.04 mol) was transferred to the round bottom flask containing 0.15 g of the catalyst (pre-dried at 110 °C for 24 h and cooled in a desiccator to minimize moisture content). After the reaction temperature reached 120 °C, TBA (7.6 mL, 0.08 mol) was added. The reaction mixture was refluxed for 6 h. Samples for analysis (~0.50 mL) were withdrawn at regular intervals from the reaction mixture and 20 μL of acetonitrile (as internal standard for TBA) or acetophenone (as internal standard

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