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Simple method for functionalization of silica with alkyl silane and organic ligands

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ABSTRACT

3–(chloropropyl)triethoxysilane (CPTES) with imidazole and sodium silicate from rice husk ash (RHA) successfully reacted within a short time in one–pot synthesis in purely homogenous method. A similar procedure was used for the immobilization of melamine and saccharine to demonstrate a generally applicable method. No reflux was needed, and a green solvent was used as the reaction medium. The surface areas of the prepared materials were very high compared with the materials which have similar structure prepared by the traditional method. The TGA/DTA confirmed that all the materials were highly stable. The FT-IR shows that all expected the functional groups were present. The HRTEM showed that the materials had ordered mesoporous straight-channels which were like the MCM-41. The synthesis procedure is simple, repeatable with different organic ligands and does not require toxic solvents or multiple steps with high products yield.

1. Introduction

The silica attached to organic ligands in its structure had been well studied by many scholars (Brunel, 1999; Bae et al., 2000; Airoldi and Arakaki, 2001). The modification process of silica with organic functional groups could lead to changes in the shape and chemical properties of the resulting composite material. Modification of the silica surface is important as it can be used for the synthesis of different catalysts having very specific activity and selectivity.

The functionalization of silica with specific organic functional groups can be carried out by immobilizing silica with organic ligands using different chemical techniques. Silanol groups in silica have the ability to react with silylating agents and make the silica much more amenable for further reaction (Cestari et al., 2001). There are many different methods for the reaction of silica with silylating agents. One of the more popular methods is the direct reaction of tetraalkoxysilane, $Si(OR)_4$ and the coupling agent $(RO)_3Si(CH_2)_3X$, in the presence of an acid or a base catalyst (El-Nahhal and El–Ashgar, 2007; Cestari and Airoldi, 1997). Silylating agents have two different procedures for the reaction with silica. The first procedure is to react the silylating agents with the ligand complex and then to immobilize the resulting ligand with the preformed silica in a heterogeneous reaction. The second procedure is to treat the post–polysiloxane with the complex group. Both these procedures have been well studied by many scholars (Hoegaerts et al., 2000; Prado and Airoldi, 2001). From the literature, the main disadvantages of these procedures were (a) the long reaction times and (b) the use of hazardous solvents/chemicals. Therefore, the designing of a simple and more direct procedure is required to synthesize silica-silylating agent's material.

CPTES was usually used as the anchoring agent for modifying the silica in a heterogeneous reaction. Bae et al. (2000), Hoegaerts et al. (2000), Shi and Wei (2008) used toluene as a solvent with reflux for more than 23 h. The reaction was followed by soxhlet purification using an organic solvent like toluene. Brunel (1999) had also used toluene when he functionalized silica with CPTES at 120 °C with a total reaction time of approximately 14 h. Alcântara et al. (2007) took approximately 72 h for silica modification with 3–(chloropropyl)trimethoxysilane at 150 °C. Recently, a very simple technique to immobilize CPTES onto the silica network was reported by Adam et al. (2009a).

In our previous studies, imidazole (Adam et al., 2013), melamine (Adam et al., 2010), and saccharine Adam et al. (2009b) were reacted with silica. The reaction procedures for immobilizing these ligands onto RHACCl (rice husk ash with -CH_2Cl end groups) were done via multiple steps in a heterogeneous way. The first step was to immobilize the anchoring agent, CPTES (silylating agent) onto silica. Then, in the second step the silica is ready to be anchored (immobilized) with other organic moiety or ligands by a simple S_N1 substitution reaction. In this step toluene was used as the solvent and continuous reflux was

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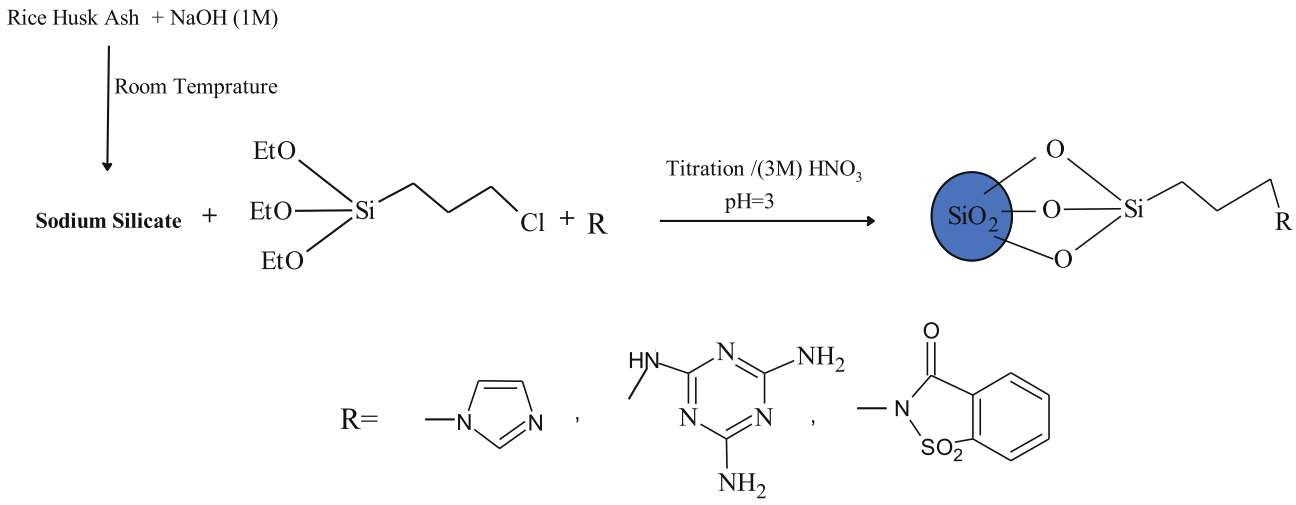

Scheme 1. The reaction sequences and the possible structure of the hybrid organo-silica materials.

necessary. The purification of these catalysts was mostly achieved with different organic solvents. The total time for producing the product was ca. 70 h. These products were then used successfully as a catalyst for different purposes, i. e acetalization of glycerol with benzaldehyde (Adam et al., 2012a), esterification (Adam et al., 2012b), glucose hydrolysis (Al-Amsyar et al., 2017), cycloaddition (Adam and Appaturi, 2013), and alkylation (Adam and Chien-Wen, 2015). However, the combine of those two steps to be one direct step in a homogeneous way is not showing in the literature according to the best of our knowledge.

Rice husk (RH) has become a cheap source of silica. Due to the high silica content in the husk, the RH became most important sources of industrial usage (Yalçin and Sevinç, 2000). The usual method to produce pure silica from RH is by burning it which leads to form a white ash (Della et al., 2002). These procedures increased environmental pollution and release different types of gases.

This work describes a simple one–pot synthesis of silica-alkyl silylating agents which allowed the immobilization of imidazole (or melamine/saccharine) onto silica from RHA within a short time. Reflux was not necessary and water as a green solvent was used as the reaction medium. The materials prepared have hexagonal straight channels which were similar the MCM-41 shapes. The prepared materials have important and unique properties due to the heterogeneous neutrality with regular surface and possible presence materials with specific functional groups which may have very specific function. Sodium silicate from RHA or from any other source was used as a starting material of the reaction. However, the ultimate aims of this study are to presence simple and easy procedures to functionalize silica with different ligands.

2. Experimental

2.1. Chemicals

All the reagents used in this study were analytical grade and used without further purification. The reagents used were imidazole (Sigma-Aldrich, 98.0%), melamine (Himedia, 99.0%), CPTES (Sigma-Aldrich, 95.0%), saccharine (Panreac, 99.0%), sodium hydroxide (Systerm, 99.0%), nitric acid (Systerm, 65.0%) and ethanol (Sigma Aldrich, 99.0%). The rice husk (RH) was collected from the rice mill in Al Muthanna governorate, south of Iraq.

2.2. Materials synthesis

The sodium silicate solution was prepared by dissolving 3.0 g of RHA into 125 mL of 1.0 M NaOH at room temperature and stirred for 1 h. 24.0 mmol of organic ligand (imidazole, melamine, and saccharine) and 24.0 mmol of CPTES were added to the sodium silicate solution. The mixture was titrated slowly with 3.0 M nitric acid with constant stirring. The white gel started to form at the pH 10.5. The titration was stopped at the pH 3 and the resulting gel was aged at room temperature for 48 h. The gel was separated by centrifugation (4000 rpm, 15 min) and then vacuum filtered, washed with distilled water for 5 times and followed by acetone. The solid product was then left at room temperature and dried in the oven at 110 °C for 24 h. The final materials were labelled in terms of the introduced ligand as Si-PrIM (IM = Imidazole), Si-PrMela (Mela = Melamine), and Si-PrSac (Sac = Saccharine). About 6.2 g of Si-PrIM, 1.12 g of Si-PrMela, and 1.95 g of Si-PrSac were collected from each preparation.

2.3. Materials characterization

The elemental analyses were carried out using CHN analyzer (Perkin Elmer-2400). The FT-IR spectra were obtained on a Shimadzu 8400s spectrophotometer. Powder XRD pattern analysis was studied by Siemens diffractometer, D5000, Kristalloflex. The surface area analysis was carried out on an automatic physisorption porosimeter (Autosorb-1 CLP, Quantachrom, USA). The surface topography images were obtained with a scanning electron microscope (SEM), model Leica Cambridge S360 and energy-dispersive X-ray spectroscopy (EDX) by Edax Falcon System. The morphology images were obtained with a high-resolution transmission electron microscope (HRTEM), model JEM 2100-F, 200 kV accelerating voltage. The TGA/DTA was performed using a dual-purpose instrument type Perkin Elmer TGA-4000.

3. Results and discussion

3.1. Material synthesis

The method describes a direct synthesis of organic ligands onto silica via alkyl silylating agent. One of the organic ligand (imidazole or melamine or saccharine) was added to the sodium silicate from RHA which contain CPTES. The reaction sequence and the possible structure of the hybrid ligand – silica materials are shown in Scheme 1.

3.2. Materials characterization

3.2.1. Elemental analysis

For the comparison reason, the CHN and EDX techniques are used for monitoring the elemental percentage of the materials. Chemical analysis results of RHA and Si-PrIM, Si-PrMela, and Si-PrSac are listed