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Silica Nanoparticle Hyperbranched Polyglycerolsulfuric Acid: The Chemoselective, Efficient, Green and Reusable Nanocatalyst for the Alcohol Oxidation

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ABSTRACT

Nano SiO_2/hyperbranched polyglycerol (HPG)/SO_3H catalyst was readily prepared for first time from inexpensive starting materials in aqueous media which catalyzed the synthesis of benzoic acid. FTIR spectra, X-ray diffraction (XRD) and transmission electron micrographs (TEM) was employed to characterize the properties of the synthesized nano SiO_2/HPG/SO_3H. High catalytic activity and ease of recovery from the reaction mixture using filtration and several reuse times without significant losses in performance are additional eco-friendly attributes of this catalytic system.

KEYWORDS: Silica Nanoparticle; Nanocatalyst; Oxidation; Green Chemistry; Solvent Free.

1. INTRODUCTION

Acidic catalysts have been used, mainly in industry, for producing more than 1×10^8 Mt/year of products. Among acidic catalysts, the most commonly used are HF, H_2SO_4, $HClO_4$ and H_3PO_4 (in liquid form or supported on Kieselguhr). Solid acids have many advantages such as ease of handling, decreasing reactor and plant corrosion problems and environmentally safe disposal [1,2]. Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes [3]. Green chemistry has been defined as a set of principles that reduce or eliminate the use or generation of hazardous substances. In addition, there is current research and general interest in heterogeneous systems because of their importance in industry and in developing technologies [4]. Heterogeneous organic reactions have proven useful to chemists in the laboratory as well as in the industrial context. These reactions are effected by the reagents immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of the good dispersion of active reagent sites, associated selectivity and easier work-up [5].

Nanoparticles have emerged as sustainable alternatives to conventional materials, as robust, high surface area heterogeneous catalysts [6-10] and catalyst supports [11-16]. The nano-sized particles increase the exposed surface area of the active component of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically andmimicking the homogeneous catalysts. However, their insolubility in reaction solvents renders them easily separable from the reaction mixture like heterogeneous catalysts, which in turn makes the product isolation stage effortless. Also, the activity and selectivity of nano-catalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology.

Engaged in the development of greener and sustainable pathways for organic transformations, nanomaterial and nano-catalysis [17-23], here we report a facile approach to prepare n-propylsulfonat-grafted multicarboxylic hyperbranched polyglycerol (HPG)-coated SiO_2 hybrid support for first time which catalyzed the reduction of alcohol oxidation in aqueous media.

2. EXPERIMENTAL

2.1. Materials and Methods

Chemical materials were purchased from Fluka and Merck in high purity. Melting points were determined in open capillaries using an Electrothermal 9100 apparatus and are uncorrected. FTIR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission modein spectroscopic grade KBr pellets for all the powders. The particle size and structure of nano particle was observed by using a Philips CM10 transmission electron microscope operating at 100 KV. Powder X-ray diffraction data were obtained using Bruker D8 Advance model with Cu Kα radition. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10 °C min^{-1} under nitrogen. ^1H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.46 MHz, BRUKER DRX-400 AVANCE spectrometer at 400.22 and 100.63 MHz, respectively. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Mass spectra were recorded on Shimadzu GCMS-QP5050 Mass Spectrometer.

2.2. General Procedure for the Preparation of Nano SiO_2

The synthesis of nano SiO_2 was achieved by the ammonia-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) in a mixed solvent of deionized water and ethanol using PEG as the surfactant agent in the process at room temperature. In a typical procedure, 100 mL ethanol and 20 mL deionized water were mixed together in a beaker and then 1.0 g of PEG (MW 6000) was dispersed in to the mixture by ultrasonication. After adding ammonia water (2.5 mL), tetraethyl orthosilicate (TEOS, 2 mL) was added to the reaction solution and the pH value was controlled in the range $12 \leq pH \leq 13$. The resulting dispersion was under mechanically stirred continuously for 20 h at room temperature. The resultant products were collected and washed with ethanol and deionized water in sequence and then dried under vacuum at 60 °C for 2 h for further use. During this period, the pH value was adjusted by ammonia water and kept in the range $12 \leq pH \leq 13$.

2.3. General Procedure for the Preparation of Nano SiO_2/HPG

2 mmol of nano SiO_2 were dispersed in a mixture of 80 mL of toluene and 1.0 mmol of potassium methylate (CH_3OK), followed by the addition of 10 mL of anhydrous dioxane. 2.0 g of Glycidol was added dropwise over a period of 1 h. After vigorous stirring for 2 h, the final suspension was repeatedly washed, filtered for several times and dried at 60 °C in the air.

2.4. General Procedure for the Preparation of Nano SiO_2/HPG/SO_3H

Nano SiO_2/HPG (6 g) was suspended in 600 mL of 0.1 M toluene solution of 1,3-propanesultone and the colloidal solution was refluxed for 48 h. The n-propylsulfonated nano SiO_2/HPG was isolated and purified by repeated washing (first in ethanol and then in deionized water) and centrifugation.

2.5. General Procedure for the reduction of alcohol oxidation

A mixture of benzyl alcohol (1 mmol) and K_2CO_3 (5 mmol), deionized water (5 ml) and nano SiO_2/HPG/SO_3H (0.0009 g) was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the product was extracted with ethyl acetate (2×10 ml). The organic layer was dried (Na_2SO_4), evaporated and the crude product was purified by flash column chromatography (ethyl acetate/n-hexane, 1:20) to provide the pure product.

2.6. Selected Spectroscopic data

Benzoic acid: Mp 122–125 °C; ^1H NMR ($CDCl_3$): δ=7.53 (t, 2H, J=16 Hz), 7.61 (t, 1H, J=8 Hz), 7.94 (d, 2H, J=4 Hz); 13.01 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ=128.5, 129.2, 130.7, 132.6, 167.3.

3. RESULTS AND DISCUSSION

Due to the reasonable needs to clean and green recovery of the heterogenous catalyst, we synthesized nano SiO_2/HPG/SO_3H as a new catalyst by a direct method through the ring opening reaction of 1,3-propanesultone with nano SiO_2/HPG in refluxing toluene. The synthesized nano SiO_2/HPG/SO_3H was then characterized by different methods such as XRD, TEM, SEM, FTIR and TGA.

For ion-exchange pH analysis of the catalyst, to an aqueous solution of NaCl (0.1 M, 5 mL) with a primary pH 5.93, the catalyst (50 mg) was added and the resulting mixture was stirred for 1 h after which the pH of solution decreased to 2.25. This is equal to a loading of 5.6 mmol SO_3H g^{-1}.

The formation of hierarchic structure of SiO_2/HPG/SO_3H nano particles can be illustrated by Fig. 1. The influence of pH on nano size is illustrated in Fig. 2.

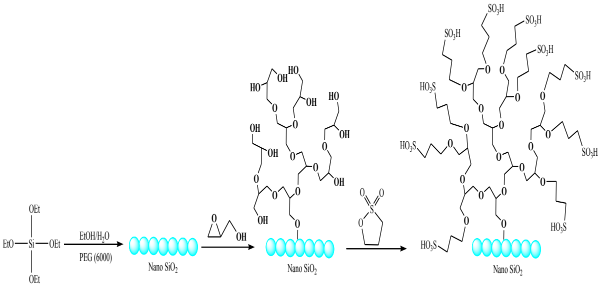

Fig. 1. Schematic illustration of the synthesis for SiO_2/HPG/SO_3H nanoparticles.

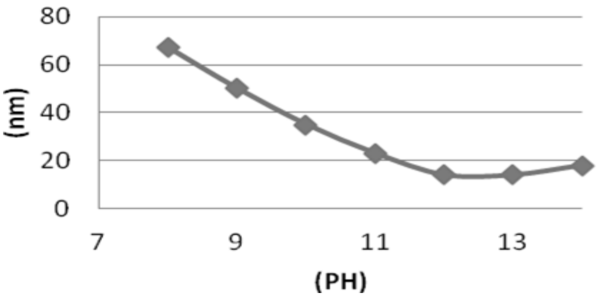

Fig. 2. Influence of pH on the size of nano SiO_2.

The nano size of SiO_2 decreases with the increase of pH and remains almost invariable (13 nm) when pH are in the range $12 \leq pH \leq 13$. Different from previous work, PEG was used as surfactant agent in the process. First, primary SiO_2 nanoparticles in solution with the assistance of PEG. Then surface modified SiO_2 nanoparticles by PEG molecule chains aggregate into smaller particles. The morphology and size of SiO_2 nanoparticles is dependent on the PEG and can be observed with the transmission electron microscope (Fig. 3a and b).

The characterization of the nano SiO_2 with and without the assistance of PEG showed the same particle size and morphology by transmission electron microscopy and agglomeration of silica without the PEG can be seen (TEM; Fig. 3b). The average size of nano SiO_2 is about 10 - 15 nm (Fig. 3a). TEM and SEM images of nano SiO_2/HPG/SO_3H are shown in (Fig. 3c and 3d). The average size of nano SiO_2/HPG/SO_3H is about 15-18 nm.

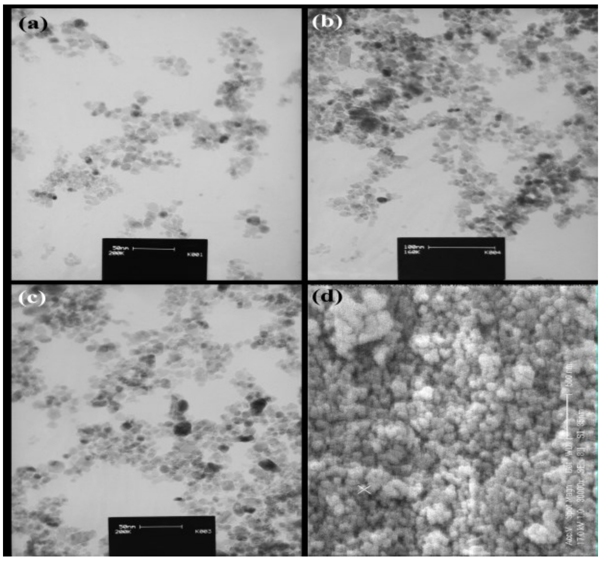

Fig. 3. (a) TEM images of nano SiO_2 with the assistance of PEG; (b) TEM images of nano SiO_2 without the assistance of PEG; (c) TEM images of nano SiO_2/HPG/SO_3H; (d) SEM image of nano SiO_2/HPG/SO_3H.

This structure was further supported by the FT-IR spectra. The IR band at 3440 cm^{-1} could be assigned to the stretching vibrations of Si-OH groups in the structure of amorphous SiO_2. The very strong and broad IR band at 1095 cm^{-1} with a shoulder at 1103 cm^{-1} is usually assigned to the TO and LO modes of the Si-O-Si asymmetric stretching vibrations. The IR band at 802 cm^{-1} can be assigned to Si-O-Si symmetric stretching vibrations, whereas the IR band at 495 cm^{-1} is due to O-Si-O bending vibrations (Fig. 4a). After the polymerization, a new band of C-H groups at 2870 cm^{-1} appeared in the FT-IR spectrum. For nano SiO_2/HPG/SO_3H, two obvious bands at 1593 and 3425 cm^{-1} associated with carbonyl groups and O-H stretching appeared (Fig. 4b). In their work, an amorphous peak was centered at $2\theta = 23^{o}$. The broad band at 2θ=15.0°–30.0° can be assigned to the amorphous SiO_2 shell (JCPDS No. 29-0085), (Fig. 4c). The thermal behavior of nano SiO_2/HPG/SO_3H is shown in Fig. 5. A significant decrease in the weight percentage of the nano SiO_2/HPG/SO_3H at about 130 °C is related to desorption of water molecules from the catalyst surface. This was evaluated to be 1-2% according to the TG analysis. In addition, the analysis showed two other decreasing peaks. First peak appears at temperature around 200-400 °C due to the decomposition of SO_3H. This is followed by a second peak at 450-600 °C, corresponding to the loss of the organic spacer group.

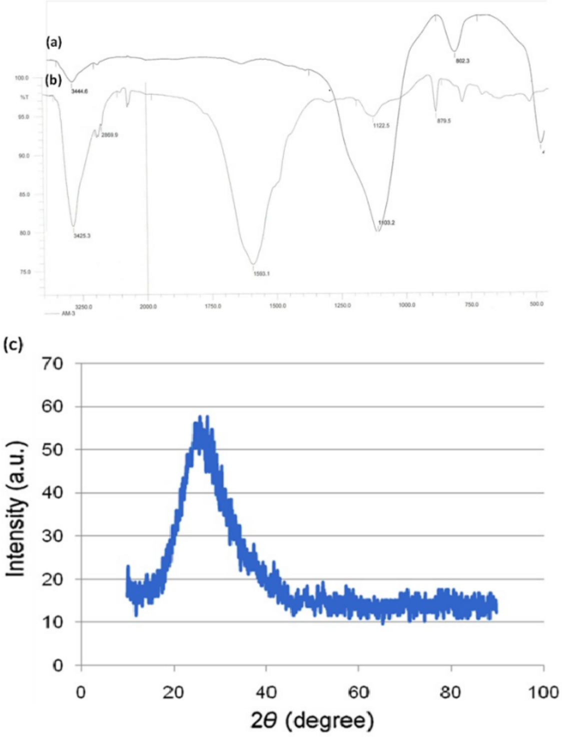

Fig. 4. FTIR spectra of (a) nano silica; (b) nano SiO_2/HPG/SO_3H; (c) XRD analysis of nano SiO_2/HPG/SO_3H.

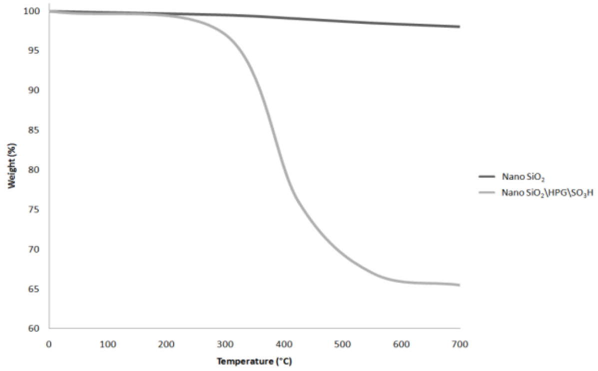

Fig. 5. TGA diagram of nano SiO_2/HPG/SO_3H.

The catalytic potential of the nano SiO_2/HPG/SO_3H was evaluated in condensation reactions. In order to optimize the reaction conditions, we examined reduction of benzyl alcohol oxidation as a model compoundusing under various reaction conditions in terms of temperature, time, amount catalyst, solvent, and product yield (Table 1). Catalytic amount of nano SiO_2/HPG/SO_3H (0.0009 g) and K_2CO_3 (5 mmol) in water at room temperature was found to be ideal the reaction conditions for the complete reduction of alcohol oxidation (Table 1, entrie 6). Three separated reactions were examined in the absence of anycatalyst and in the presence of nano SiO_2 and nano SiO_2/HPG. The results of these studies showed that lesser of the desired product was formed (Table 1, entries 16-18). A similar reaction in the presence of H_2SO_4 as a non-supported catalyst gave the desired product in moderate yield (64 %) due to the formation of by-products (Table 1, entry 19). This result indicated that the catalytic efficiency of H_2SO_4 was increased by immobilization onto nano SiO_2.

It is important to note that the heterogeneous property of nano SiO_2/HPG/SO_3H facilitates its efficient recovery from the reaction mixture during work-up procedure. The activity of the recycled catalyst was also examined under the optimized conditions. After the completion of reaction, the catalyst was separated by filtration, washed with methanol and dried at the pump. The recovered catalyst was reused for ten consecutive cycles without any significant loss in catalytic activity (Fig. 6). The TEM images of the reused catalyst (Fig. 7) also indicated that no detectable changes of the catalyst occurredduring the reaction and the recycling stages. The nano SiO_2/HPG/SO_3H before use does not result in the change of the morphology and size of the obtained nano SiO_2/HPG/SO_3H after reuse ten times.

To show the unique catalytic behavior of nano SiO_2/HPG/SO_3H in these reactions, we have performed the alcohol oxidation in the presence of [RuHCl(CO)(PPh_3)$_3$]/DPSO, CuCl/tBuOOH, PS-TEMPO/NaClO, Pt-C/Air, TPAP/NMO, $KMnO_4$, OsO_4 and CAN (Table 2). As it is evident from table 2, nano SiO_2/HPG/SO_3H is the most effective catalyst for this purpose, leading to the alcohol oxidation in a lesser time with better yield and reduces the amount of catalyst.

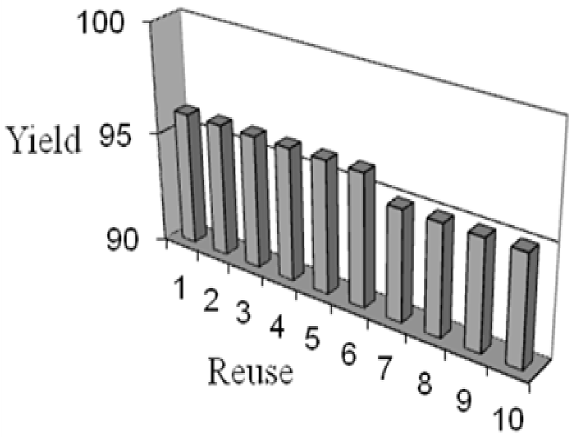

Fig. 6. Reuses performance of the catalysts.

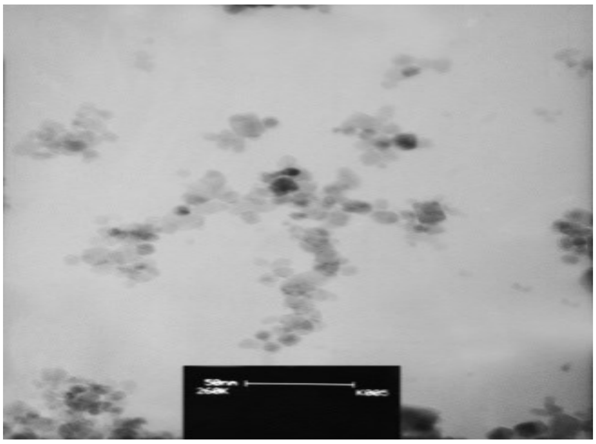

Fig. 7. TEM image of nano SiO_2/HPG/SO_3H after reuse ten times. Agglomeration of nano SiO_2/HPG/SO_3H can not be seen.

Table 1. Optimization of the reaction conditions for the reduction of benzyl alcohol oxidation in terms of temperature, amount catalyst, time and product yield.[a]

Entry	Catalyst	Solvent	Temp. (°C)	Time (min)	Amount catalyst (g)	Yield (%)[b]
1	SiO_2/HPG/SO_3H	H_2O	r.t.	20	0.0012	53
2	SiO_2/HPG/SO_3H	H_2O	r.t.	30	0.0012	79
3	SiO_2/HPG/SO_3H	H_2O	r.t.	40	0.0012	96
4	SiO_2/HPG/SO_3H	H_2O	r.t.	50	0.0012	96
5	SiO_2/HPG/SO_3H	H_2O	r.t.	40	0.001	96
6	SiO_2/HPG/SO_3H	H_2O	r.t.	40	0.0009	96
7	SiO_2/HPG/SO_3H	H_2O	r.t.	40	0.0008	87
8	SiO_2/HPG/SO_3H	H_2O	r.t.	40	0.0007	79
9	SiO_2/HPG/SO_3H	H_2O	50	40	0.0009	96
10	SiO_2/HPG/SO_3H	H_2O	100	40	0.0009	96
11	SiO_2/HPG/SO_3H	-	50	60	0.0009	69
12	SiO_2/HPG/SO_3H	EtOH	50	60	0.0009	54
13	SiO_2/HPG/SO_3H	THF	70	50	0.0009	32
14	SiO_2/HPG/SO_3H	CH_2Cl_2	40	50	0.0009	29
15	SiO_2/HPG/SO_3H	Hexane	80	50	0.0009	-
16	-	-	r.t.	40	0.0009	-
17	Nano SiO_2	-	r.t.	40	0.0009	89
18	Nano SiO_2/HPG	-	r.t.	40	0.0009	92
18	H_2SO_4	-	r.t.	40	0.0009	64

[a] Reaction conditions: benzyl alcohol (1 mmol) and K2CO3 (5 mmol), deionized water (5 ml) and nano SiO2/HPG/SO3H (0.0009 g).

[b] Isolated yields.

Table 2. Comparison of the results obtained with nano $SiO_2/HPG/SO_3H$ with some of those reported in the literature.

Entry	Catalyst	Catalyst amount	Time	Yield (%)
1	$[RuHCl(CO)(PPh_3)_3]/DPSO$	4 mol%	2.5 (h)	76-93 [24]
2	CuCl/tBuOOH	5 mol%	1-6 (h)	76-99 [25]
3	PS-TEMPO/NaClO	10 mol%	20-48 (h)	77-98 [26]
4	Pt-C/Air	1.95 wt.%	1–16 (h)	99 [27]
5	TPAP/NMO	10 mol%	-	26-100 [28]
6	$KMnO_4$	4 mmol	4-18 (h)	5-91 [29]
7	OsO_4	4 wt.%	-	50-85 [30]
8	CAN	2.2 eq	4 (h)	42-95 [31]
9	Nano $SiO_2/HPG/SO_3H$	0.0009 g	40 (min)	96

[a] Isolated yields.

4. CONCLUSION

$SiO_2/HPG/SO_3H$ nanoparticle, can be easily prepared using a polymerization method under safe conditions. The spectral and analysis data confirmed the effectiveness of the method for the preparation of $SiO_2/HPG/SO_3H$ nanoparticle by preventing the grain growth or agglomeration of the particles. The $SiO_2/HPG/SO_3H$ nanoparticle, as an effective and reusable heterogeneous catalyst, can provide an environmentally friendly alternative for the alcohol oxidation under mild conditions.

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