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Nano silica gel supported perchloric acid/wet SiO_2: an efficient reagent for one-pot synthesis of azo dyes based on 1-naphthol in room temperature and solvent-free conditions

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Abstract: A convenient, rapid, and one-pot method for the synthesis of azo dyes based on 1-naphthol has been developed. In this protocol, diazotization reagent (ArN_2^+ $^-ClO_4$/nano SiO_2) was prepared via grinding of aromatic amines, $NaNO_2$, wet SiO_2 and nano silicagel supported perchloric acid (nano-SPCA) without solvent at room temperature. The obtained diazotization reagent was sufficiently stable to be kept at room temperature in the dry state for long time. Azo dyes were prepared by coupling of ArN_2^+ $^-ClO_4$/nano SiO_2 with 1-naphthol in good to excellent yields. Mild and heterogeneous reaction conditions, high stability of diazonium salt, easy procedure, short time of reaction and high yields are some important advantages of this protocol.

Keywords: azo dyes, nano silicagel, perchloric acid, 1-naphthol, solvent-free condition, diazonium salt.

Introduction

One of the most important dye classes is the azo ones which contain about half of the dyes used in industry. Azo dyes are formed *via* condensation of diazonium salts with a strong nucleophile such as naphthoxide. Diazonium salts are prepared by reaction of nitrosonium ion (NO^+) and aniline derivatives in low temperature (0-5 °C). NO^+ is achieved *via* reaction of sodium nitrite and strong acid [1, 2]. Diazonium salts which are formed by the reaction of sodium nitrite, aniline derivatives and strong liquid acids, are unstable in room tempetature and immediately are degradated. In contrast, applying of solid acid instead of liquid acid is caused by the stability of diazonium salts [3-5]. Solid acids have many advantages such as ease of handling, decreasing reactor and plant corrosion problems, and environmentally safe disposal. Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes [6, 7]. Nano silica gel supported perchloric acid (nano S-PCA) is a solid acid which can be used for different reactions either as reagent or as catalyst under heterogeneous conditions. Collective nano S-PCA and wet SiO_2 would be a superior proton source and is comparable with other solid acids such as nafion-H, silica sulfuric acid, silica chloride and etc. [8-13]. In this article, we wish to present a simple one-pot protocol for synthesis of azo dyes using nano-SPCA (40%) /wet SiO_2, $NaNO_2$ and 1-naphthol in solvent free and room temperature conditions.

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Results and discussion

Nano-SPCA is formed *via* the attraction between nano silica gel (mesh 20 nm) and perchloric acid. Then H^+ and SiO_2-ClO_4^- which are formed *in situ* by the reaction between nano-SPCA and H_2O in wet SiO_2 are caused by the diazotization of aniline derivatives.

The Scanning Electron Microscope (SEM) picture of nano-SPCA is recorded with 15000 X (Figure **1**). According to SEM data, the mesh of nano-SPCA is 60 nm.

Stable polymeric diazonium salt was formed by grinding of mixture of nano-SPCA wet SiO_2, $NaNO_2$ and aniline derivatives. Azo dyes were prepared by

addition of aqueous solution of 1-naphtol to the above mentioned mixture (Scheme **1**).

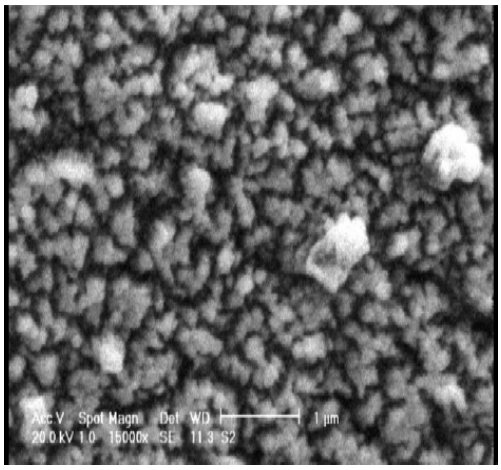
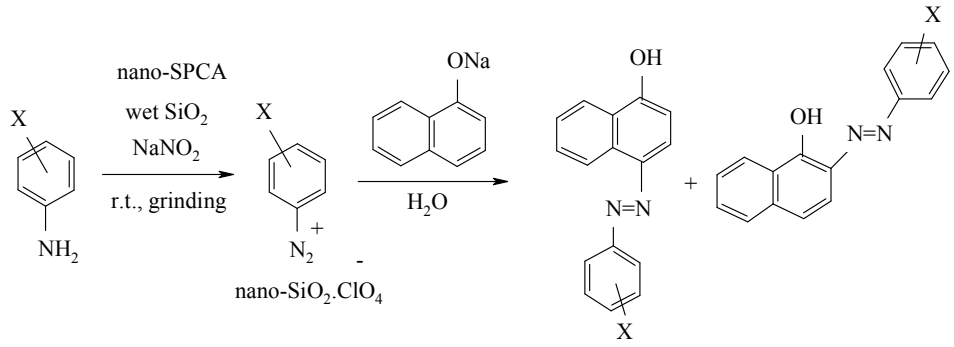


Figure 1. Scanning Electron Microscope (SEM) image of nano-SPCA / Resolution 15000X



Scheme 1

Table 1: Preparation of azo dyes using nano-SPCA at room temperature and solvent free conditions[a]

Entry	x	Time (sec)	Yield (%)
1	4-NO_2	60	80
2	4-COOH	60	85
3	4-SO_3H	80	80
4	2-COOH	70	75
5	H	60	70
6	2-CH_3	40	90
7	2-NO_2	80	70
8	4-Cl	55	85
9	4-CH_3	55	85
10	4-OCH_3	30	95
11	3-NO_2	90	70
12	3-CH_3	70	70
13	2-OCH_3	45	85
14	3-OCH_3	65	80
15	2-Cl	60	70
16	3-Cl	85	75

[a]The ratio of aniline derivatives (mmol): $NaNO_2$ (mmol): nano-SPCA (g): wet SiO_2 (g) is 1:1.5:0.05 (20mol%):0.15.

Because of polymeric diazonium salt stability, the reaction was carried out in room temperature without any degradation. According to formation of azo dye from aniline, the best ratio of aniline (mmol): $NaNO_2$ (mmol): nano-SPCA(40%) (g): wet SiO_2 (g) is 1:1.5:0.05 (20mol%):0.15. A variety of aniline derivatives were applied for formation of corresponding azo dyes (Table **1**).

The reaction was clean and the purification of product is straightforward with excellent yields, especially solid aniline derivatives. Anilines containing electron-releasing groups were converted to the diazonium salt faster than electron-withdrawing groups. Especially steric hindrance and owing of electron-withdrawing group, 3-nitroanilin, was converted to the corresponding diazonium salt slower than the others. The structure of resulted dyes were characterized by, FT-IR, ^1H and ^{13}C- NMR.

Conclusion

Nano-SPCA is non-corrosive and safe solid acid with easy separation and recovery from reaction mixture. We have synthesized azo dyes based on 1-naphthol using nano silica gel supported perchloric acid as a solid acid at room temperature and solvent-free conditions. The yields of products were good to excellent and the reaction times were short.

Experimental

Materials and instruments

The chemicals used in the synthesis of all dyes were obtained from Merck chemical company and were used without further purification. ^1H & ^{13}C NMR spectra Bruker 400 ultra-shield NMR spectrometer ($CDCl_3$ and aceton-d_6) FT-IR spectra were recorded on a magna-550 Nicolet. The Scanning Electron Microscope (SEM) picture of nano-SPCA is recorded with 15000 X.

Preparation of nano-SPCA

A 250 mL flask equipped with a constant-pressure dropping funnel was used. It was charged with nano silica gel (5 g). Then perchloric acid (10 mL) was added drop wise over a period of 20 min at room temperature. After the addition was completed the mixture was shaken for 30 minutes. Excess of perchloric acid was separated and the moist solid bed put in an oven at 50 °C for 1 hour. Nano-SPCA as a white solid (8 g) was obtained. The titration of 1 g nano-SPCA with 0.1 M, NaOH has shown that the acidic capacity of catalyst is 4 mmol H^+ in 1 g of polymeric catalyst.

Preparation of azo dyes

10 mmol of aniline derivative and 15 mmol of $NaNO_2$ were added in 500 mg of nano-SPCA and 1500 mg wet SiO_2 (50% w/w) and grinded. The diazonium salt was prepared in short time (Table **1**). 10 mL of acetone was added to mixture and filtered and washed with acetone (2.5 mL). A solution of 10 mmol of 1- naphthol in 10 mL of 10% sodium hydroxide solution was prepared and slowly added in to the diazonium salt with stirring in short time at room temperature. The obtained dye was dissolved in acetone and filtered. By evaporation of solvent, the solid dye was achieved in good to excellent yields (70-95%).

Selected spectral data:

Entry 1, Table 1, isomer 2: IR (KBr) cm^{-1}: 3441, 3033, 1635, 1444, 1526, 1352, 1188, 1266, 756, 827. ^1H NMR (400 MHz, $CDCl_3$): 15.69 (s, NH), 8.18 (d, *J*=7.6 Hz, 1H), 8.11 (d, *J*=9.2 Hz, 2H), 7.50 (m, 1H), 7.48 (t, *J*=7.6 Hz, 1H). 7.43 (d, *J*=9.2 Hz, 2H), 7.32 (t, *J*=7.6 Hz, 1H), 6.89 (d, *J*=9.6 Hz, 1H), 6.82 (d, *J*=9.6 Hz, 1H).

Entry 5, Table 1, isomer 2: IR (KBr) cm^{-1}: 3431, 3031, 1617, 1482, 1225, 1273, 873, 775. ^1H NMR (400 MHz, $CDCl_3$): 15.81 (s, NH), 8.21 (d, J=8 Hz, 1H), 7.51 (d, J=8 Hz, 1H), 7.44 (t, J=8 Hz, 2H), 7.36 (d, J=8.4 Hz, 2H), 7.29 (t, J=7.6 Hz, 2H), 7.21 (t, J=8 Hz, 1H), 6.83-6.97 (m, 2H).

Entry 7, Table 1, isomer 2: IR (KBr) cm^{-1}: 3441, 3033, 1611, 1444, 1526, 1352, 1188, 1266,^1H NMR (400 MHz, $CDCl_3$), 15.79 (s, NH), 8.25 (brs, 1H), 8.18 (d, J=8 Hz, 1H), 7.97 (d, J=8.4 Hz, 1H), 7.60 (d, J=7.2 Hz, 1H) 7.55 (t, J=8.4 Hz, 1H), 7.52 (m, 1H), 7.33 (t, J=8 Hz, 1H), 7.32 (d, J=8.4 Hz, 1 H), 7.12 (t, J=8 Hz, 1H), 6.63 (d, J=7.2 Hz, 1H).

Entry 15, Table 1, isomer 2: IR (KBr) cm^{-1}: 3438, 3032, 1626, 1491, 1448, 1209, 1254, 1096.^1H NMR (400 MHz, $CDCl_3$), 16.21 (s, NH), 8.27 (d, J=8 Hz, 1H), 7.93 (d, J=8.4 Hz, 1H), 7.59 (m, 1H), 7.52 (m, 1H), 7.48 (t, J=8 Hz, 1H), 7.39-7.34 (m, 2 H), 7.24 (t, J=8 Hz, 1H), 7.04-6.8 (m, J=9.2 Hz, 2H).

Entry 16, Table 1, isomer 2: IR (KBr) cm^{-1}: 3438, 3032, 1605, 1491, 1448, 1209, 1254, 1096^1H NMR (400 MHz, $CDCl_3$), 16.02 (s, NH), 8.25 (s, 1H), 8.24 (d, J=8.6 Hz, 1H), 7.68 (d, J=8.6 Hz, 1H), 7.60 (m, 1H), 7.53 (t, J=8.6 Hz, 1H), 7.50 (m, 1H), 7.48 (t, J=7.1 Hz, 1H), 7.32 (t, J=7.1 Hz, 1H), 6.83 (m, 2H).

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