

Nano silica chromic acid/wet SiO₂ and NaNO₂ as an efficient reagent system for synthesis of azo dyes based on 1-naphthol at room temperature and solvent-free conditions

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ABSTRACT

A convenient, rapid, and one-pot method for the synthesis of azo dyes has been developed. In this protocol, diazotization reagent (ArN₂⁺-CrO₃-SiO₂) was prepared via grinding of aromatic amines, NaNO₂, wet SiO₂ and nano silica chromic acid (Nano-SCA) 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 ArN₂⁺-CrO₃-SiO₂ with 1-naphthoxide in good to excellent yields. Mild and heterogeneous reaction conditions, high stability of diazonium salt, easy procedure, short reaction time and high yields are some important advantages of this protocol.

Keywords: Azo dyes, Nano silica chromic acid, 1-Naphthol, Solvent-free condition, Diazonium salt.

1. 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 temperature and immediately are degraded. 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 chromic acid (Nano-SCA), is a solid acid which can be used for different reactions either as

reagent or as catalyst under heterogeneous conditions. Collective nano-SCA and wet SiO₂ 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 SCA/wet SiO₂, NaNO₂ and 1-naphthol in solvent free and room temperature conditions.

2. Experimental

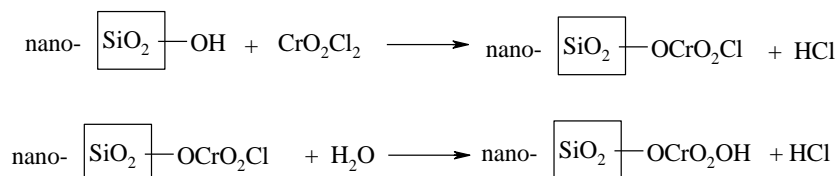
The chemicals used in the synthesis of all dyes were obtained from Merck chemical company and were used without further purification. ¹H and ¹³C NMR spectra were recorded on Bruker 400 ultra-shield NMR spectrometer (CDCl₃ and acetone-d₆) FT-IR spectra were recorded on a magna-550 Nicolet. The Scanning Electron Microscope (SEM) picture of nano-SCA is recorded with 15000 X.

2.1. Preparation of nano silica chromic acid

A 500 mL suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting HCl gas over an adsorbing solution (*i. e.* water) was used. It was

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Scheme 1. Preparation of nano solid acid and HCl.

charged with nano silica gel (5 g). Then chromyl chloride (10 g) was added drop wise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately. After the addition was complete the mixture was shaken for 30 min. Nano silica chromic acid as a dark brown solid, 12 g, was obtained.

2.2. Preparation of azo dyes

10 mmol of aniline derivative and 10 mmol of NaNO₂ were added in 500 mg of nano-SCA and 1000 mg wet SiO₂ (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 dyes were achieved in good to excellent yields (71-91%)

The Selected spectral data:

Entry 1, Table 1: IR (KBr) cm⁻¹: 3441, 3033, 1635, 1444, 1526, 1352, 1188, 1266, 756, 827. ¹H NMR (400 MHz, CDCl₃, ppm) δ: 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). ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 161.33, 160.67, 141.84, 136.71, 133.31, 129.53, 128.33, 128.15, 124.80, 122.19, 122.06, 121.61, 114.78, 55.64.

Entry 5, Table 1: IR (KBr) cm⁻¹: 3431, 3031, 1617, 1482, 1225, 1273, 873, 775. ¹H NMR (400 MHz, CDCl₃, ppm) δ: 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), ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 177.88, 144.80, 140.06, 133.61,

130.08, 129.59, 128.86, 128.62, 128.07, 127.42, 125.72, 124.82, 121.73, 118.60.

Entry 7, Table 1: IR (KBr) cm⁻¹: 3441, 3033, 1611, 1444, 1526, 1352, 1188, 1266. ¹H NMR (400 MHz, CDCl₃, ppm), δ: 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, 1H), 7.12 (t, *J*=8 Hz, 1H), 6.63 (d, *J*=7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 168.40, 143.59, 138.86, 138.36, 133.55, 130.19, 129.79, 128.59, 128.50, 128.03, 125.32, 124.00, 121.64, 119.18, 21.30.

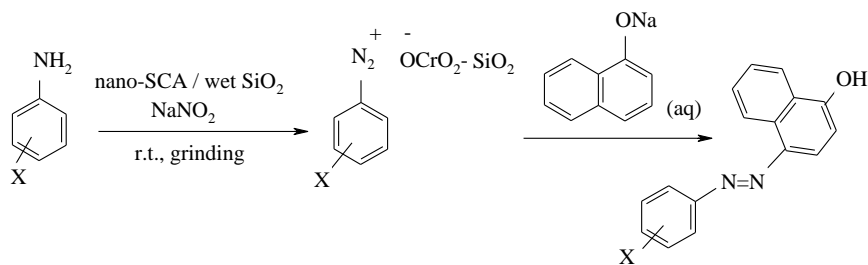
Entry 15, Table 1: IR (KBr) cm⁻¹: 3438, 3032, 1626, 1491, 1448, 1209, 1254, 1096. ¹H NMR (400 MHz, CDCl₃, ppm) δ: 16.21 (s, NH), 8.27 (d, *J*=8 Hz, 1H), 7.93 (d, *J*=8.4 Hz, 1H), 7.59 (m, 1H), 7.52 (m, 1H), 7.48 (t, *J*=8 Hz, 1H), 7.39-7.34 (m, 2 H), 7.24 (t, *J*=8 Hz, 1H), 7.04-6.8 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 170.59, 144.33, 140.10, 133.39, 133.01, 129.76, 128.94, 128.69, 128.19, 125.89, 124.33, 121.75, 119.93.

Entry 16, Table 1: IR (KBr) cm⁻¹: 3438, 3032, 1605, 1491, 1448, 1209, 1254, 1096. ¹H NMR (400 MHz, CDCl₃, ppm) δ: 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).

3. Results and Discussion

Nano-SCA is formed via the reaction between nano silica gel (mesh 20 nm) and chromyl chloride, CrO₂Cl₂. Then HCl and SiO₂-CrO₃H which are formed *in-situ* by the reaction between Nano-SCA and H₂O in wet SiO₂ (Scheme 1) are caused by the azotisation of aniline derivatives.

The Scanning Electron Microscope (SEM) picture of nano-SCA is recorded with 15000 X (Fig.1). According to SEM data, the mesh of nano-SCA is 65 nm



Scheme 2. One-pot synthesis of azo dyes based on aniline derivatives and 1-naphthol.

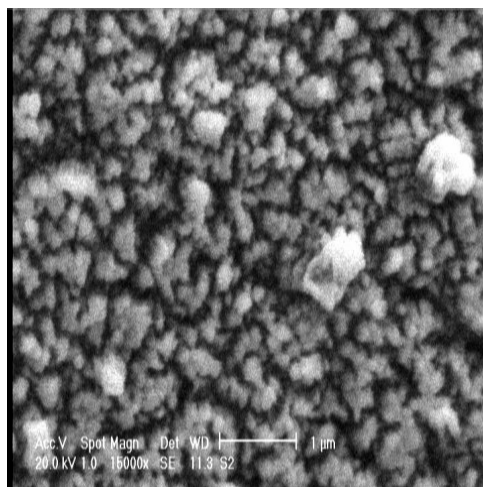


Fig.1. Scanning Electron Microscope (SEM) image of nano-SCA / Resolution 15000X.

Stable polymeric diazonium salt was formed by grinding of mixture of nano-SCA, wet SiO₂, NaNO₂ and aniline derivatives. Azo dyes were prepared by addition of aqueous solution of sodium 1-naphthoxide to the above mentioned mixture (Scheme 2). Because of polymeric

Table 1. preparation of azo dyes using nano-SCA in room temperature and solvent free condition^a

Entry	x	Time (sec)	Yield (%)
1	4-NO ₂	45	84
2	4-COOH	39	89
3	4-SO ₃ H	69	85
4	2-COOH	57	81
5	H	75	71
6	2-CH ₃	83	72
7	2-NO ₂	90	80
8	4-Cl	39	91
9	4-CH ₃	43	86
10	4-OCH ₃	40	84
11	3-NO ₂	48	83
12	3-CH ₃	78	76
13	2-OCH ₃	80	79
14	3-OCH ₃	77	78
15	2-Cl	78	73
16	3-Cl	75	79

^a. The ratio of aniline derivative (mmol): NaNO₂ (mmol): nano-SCA (g): wet SiO₂ (g) is 1:1.5:0.05:0.10.

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): NaNO₂ (mmol): nano-SCA (g): wet SiO₂ (g) is 1:1.5:0.05:0.10. 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, 2-nitroanilin, was converted to corresponding diazonium salt slower than the others. The structure of resulted dyes were characterized by, FT-IR, ¹H and ¹³C- NMR.

4. Conclusion

Nano-SCA 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 chromic 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 very short.

Acknowledgments

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