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Nano silica chromic acid/wet SiO_2 and $NaNO_2$ as an efficient reagent for one-pot synthesis of azo dyes based on 2-naphthol at room temperature under 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 (ArN_2^+ $^-CrO_3$–SiO_2) was prepared via grinding of aromatic amines, $NaNO_2$, wet SiO_2 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 ArN_2^+ $^-CrO_3$–SiO_2 with 2-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 silica chromic acid, 2-Naphthol, Solvent-free condition, Diazonium salt**.**

Introduction

Azo dyes are formed via condensation of diazonium salts with a strong nucleophile such as naphthoxide. One of the most important dye classes, is the azo ones which contain about half of the dyes used in industry. 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 aniline derivatives, sodium nitrite 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 environmentally safe disposal, ease of handling, decreasing reactor and plant corrosion problems. 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 catalyst or as reagent under heterogeneous conditions. Collective nano-SCA and wet SiO_2 would be a superior proton source and is comparable with other solid acids such as silica sulfuric acid, silica chloride, nafion-H, and etc. [8-13]. In this paper, we wish to present a simple one-pot protocol for synthesis of azo dyes using nano-SCA, wet SiO_2, $NaNO_2$ and 2-naphthol under solvent free conditions at room temperature.

Results and discussion

Nano-SCA is formed *via* the reaction between nano silicagel (mesh 20 nm) and chromyl chloride, CrO_2Cl_2. Then HCl and SiO_2-CrO_3H which are formed *in-situ* by the reaction between Nano-SCA and H_2O in wet SiO_2 (Scheme **1**) are caused by the azotization of aniline derivatives.

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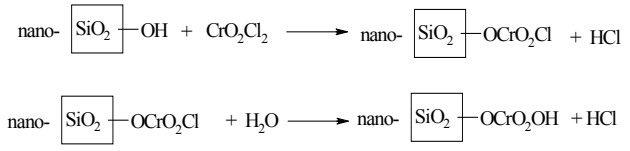


Scheme 1: preparation of nano-SCA and HCl.

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

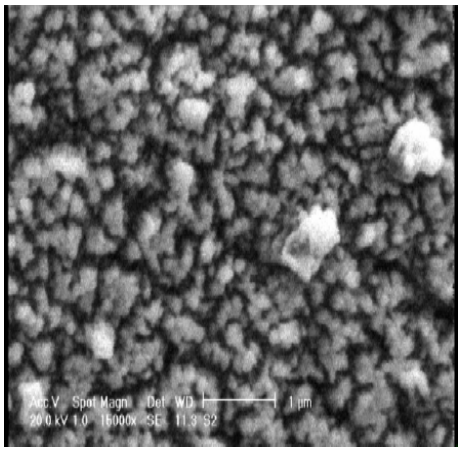
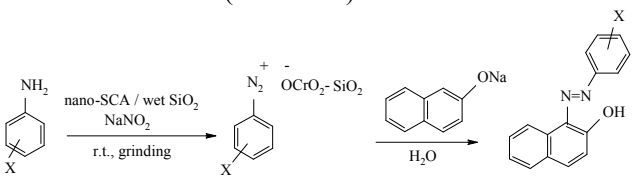


Figure 1: Scanning Electron Microscope (SEM) image of nano-SCA / Resolution 15000X

Stable polymeric diazonium salt was formed by grinding of mixture of aniline derivatives, nano-SCA, wet SiO_2 and $NaNO_2$. Azo dyes was prepared by addition of aqueous solution of 2-naphtol to the above mentioned mixture (Scheme **2**).



Scheme 2: one-pot synthesis of azo dyes based on aniline derivatives and 2-naphthol.

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-SCA (g): wet SiO_2 (g) is 1:1.5:0.05:0.10. A variety of aniline derivatives were applied for formation of corresponding azo dyes (Table **1**).

In fact, the nano silica chromic acid is an efficient and reusable catalyst which in the presence of wet SiO_2, it can release the H^+ *in situ* for making up th NO^+ from $NaNO_2$.

Then the prepared NO^+ can transform the NH_2 group to the diazonium ion. However, the reusability of the SCA was treated and shown that, four times for the reusability characteristic. Is is noted that the isolated yields for each time were decreased smoothly.

Table 1: preparation of azo dyes using nano-SCA at room temperature under solvent free conditions[a]

Entry	x	Time (sec)	Yield (%)
1	4-NO_2	60	80
2	4-COOH	50	85
3	4-SO_3H	55	85
4	2-COOH	70	80
5	H	50	80
6	2-CH_3	45	85
7	2-NO_2	80	80
8	4-Cl	50	80
9	4-CH_3	35	90
10	4-OCH_3	25	95
11	3-NO_2	75	80
12	3-CH_3	60	80
13	2-OCH_3	45	85
14	3-OCH_3	50	80
15	2-Cl	60	85
16	3-Cl	70	80

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 stereic hindrance and owing of electron-withdrawing group, 2-nitroanilin, was converted to the corresponding diazonium salt slower than the others.The structure of resulted dyes were characterized by UV, FT-IR, ^1H and ^{13}C- NMR.

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 2-naphthol using nano silica chromic acid as a solid acid at room temperature under solvent-free conditions. The yields of products were good to excellent and the reaction times were very 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 and ^{13}C NMR spectra were recorded on 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-SCA is recorded with 15000 X.

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 charged with nano silica gel (5.0 g). Then chromyl chloride (10.0 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 completed, the mixture was shaken for 30 min. Nano silica chromic acid as a dark brown solid, (12.0 g), was obtained.

Preparation of azo dyes

15 mmol of $NaNO_2$ and 10 mmol of aniline derivatives was added in 500 mg of nano-SCA and 1000 mg wet SiO_2 (50% w/w) and then was grinded. The diazonium salt was prepared in short time (Table **1**). 10 mL of acetone was added to mixture, filtered and washed with acetone (2×5 mL). A solution of 10 mmol of 2-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 (80-95%).

The spectral data of some representative products

1-(4-nitrophenyl azo)-2-naphthol (Table **1***, Entry 1):* IR (KBr) cm^{-1}: 3384, 3049, 1632, 1516, 1352, 1448, 1205, 1245, 749, 805. UV-Vis: λ_{max} $CHCl_3$= 490 nm. ^{1}H NMR (400 MHz, $CDCl_3$):16.15 (s, 1 H), 8.51 (d, *J*=8.0 Hz, 1 H) 8.39 (d, *J*=9.2 Hz , 2 H), 8.01 (d, *J*=9.2 Hz, 2 H), 7.93 (d, *J*=8.8 Hz, 2 H), 7.71 (d, *J*=7.6 Hz 1 H), 7.62 (t, *J*=8.0 Hz, 1 H), 7.53 (t, *J*=8.0 Hz,1 H), 6.72 (d, *J*=8.8 Hz,1 H).

1-(phenyl azo)-2-naphthol (Table ***1****, Entry 5):* IR (KBr) cm^{-1}: 3434, 3031, 1617, 1447, 1207, 1261, 839, 751. UV-Vis: λ_{max} $CHCl_3$= 480 nm. ^{1}H NMR (400 MHz, $CDCl_3$): 16.05 (s, 1 H), 8.37 (d, *J*=8.0 Hz, 1 H), 7.58 (d, *J*=8.4 Hz, 2 H), 7.56 (d, *J*=9.2 Hz, 1 H), 7.42 (d, *J*=8.0 Hz, 1 H), 7.36 (t, *J*=8.0 Hz, 1 H), 7.30 (t, *J*=7.2 Hz, 2 H), 7.21 (t, *J*=8.0 Hz, 1 H), 7.11 (t, *J*=7.2 Hz, 1 H), 6.68 (d, *J*=9.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):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.

1-(2-nitroPhenyl azo)-2-naphthol (Table ***1****, Entry 7):* IR (KBr) cm^{-1}: 3374, 3052, 1625, 1515, 1352, 1454, 1212, 1259, 743, 843. ^{1}H NMR (400 MHz, $CDCl_3$): 16.50 (s, 1 H), 8.58(d, *J*=8.0 Hz, 1 H), 8.51(d, *J*=8.0 Hz,1 H), 8.34 (d, *J*=8.4 Hz,1 H), 7.93 (t, *J*=8.4, 1 H), 7.89 (d, *J*=9.6 Hz,1 H), 7.78 (d, *J*=8.0 Hz, 1 H), 7.59 (t, *J*=8.0 Hz, 1 H), 7.51 (t, *J*=8.4 Hz, 1 H), 7.42 (t, *J*=8.0 Hz, 1 H), 6.67 (d, *J*=9.6 Hz, 1 H).

1-(4-chlorophenyl azo)-2-naphthol (Table ***1****, Entry 8):* IR (KBr) cm^{-1}: 3432, 3032, 1621, 1560, 1488, 1451, 1209, 1254, 1091, 821, 749. UV (λ_{max} in $CHCl_3$): 485nm. ^{1}H NMR (400 MHz, $CDCl_3$): 15.89 (s, 1 H), 8.24 (d, *J*=8.0 Hz, 1 H), 7.55 (d, *J*=9.6 Hz, 1 H), 7.50 (d, *J*=9.2 Hz, 2 H), 7.43 (d, *J*=7.6 Hz, 1 H), 7.37 (t, *J*=8.0 Hz, 1 H), 7.25 (d, *J*=9.2 Hz, 2 H), 7.22 t, *J*=8.0 Hz, 1 H), 6.69 (d, *J*=9.6 Hz, 1 H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 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.

1-(4-methylphenyl azo)-2-naphthol (Table ***1****, Entry 9):* IR (KBr) cm^{-1}: 3437, 3030, 2922, 1616, 1556, 1500, 1447, 1207, 1266, 814, 748. UV (λ_{max} in $CHCl_3$): 470nm. ^{1}H NMR (400 MHz, Acetone-d_6): 15.98 (s, 1 H), 8.66 (d, *J*=8.4 Hz, 1 H), 7.79 (d, *J*=9.2 Hz, 1 H), 7.74 (d, *J*=8.0 Hz, 2 H), 7.69 (d, *J*=8.0 Hz 1 H), 7.60 (t, *J*=8.4 Hz, 1 H), 7.44 (t, *J*=8.4 Hz, 1 H), 7.34 (d, *J*=8.0 Hz, 2 H), 6.96 (d, *J*=9.2 Hz, 1 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 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.

1-(4-methoxyphenyl azo)-2-naphthol (Table ***1****, Entry 10):* IR (KBr) cm^{-1}: 3436, 1601, 1448, 1442, 1560, 1159, 1254, 820, 749. ^{1}H NMR (400 MHz, Acetone-d_6): 15.10 (s, 1 H), 8.81 (d, *J*=8.4 Hz, 1 H), 8.01 (d, *J*=6.8 Hz, 2 H), 7.96 (d, *J*=8.8 Hz, 1 H), 7.86 (d, *J*=8.0 Hz, 1 H), 7.64 (t, *J*=8.0 Hz, 1 H), 7.47 (t, *J*=8.0 Hz, 1 H), 7.17 (d, *J*=6.8 Hz, 2 H), 7.13 (d, *J*=8.8 Hz, 1 H), 3.93 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 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.

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