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Nano Silica/ HIO_4 as a Green and Reusable Catalyst for Synthesis of 2-Naphthol Azo Dyes under Grinding Conditions

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Abstract:

Nanosilica periodic acid (nano-SPIA) is found to be a new, powerful, and reusable heterogeneous catalyst for the rapid synthesis of 2-naphtholazo dyes via diazotization of aromatic amines and followsazo coupling with 2-naphthol under solvent-free conditions at room temperature by grinding. Eco-friendly, heterogeneous reaction conditions, high stability of diazonium salt, simple experimental procedures, and high yields are some of the important advantages of this method.

Keywords: *Nanosilica periodic acid, Azo dye, Diazonium salt, 2-naphthol, Solvent free.*

1. INRODUCTION

Azo dyes contain at least one nitrogen–nitrogen double bond (N=N); however, many different structures are possible. Monoazo dyes have only one N=N double bond, whereas diazo and triazo dyes contain two and three N=N double bonds, respectively [1]. Azo dyes also have some applications in high-technology fields: electronic devices, linear and nonlinear optics, reprography, sensors, and biomedicine [2-5]. Diazonium salts are prepared by a reaction of nitrosonium ion (NO^+) and aniline derivatives at a low temperature (0–5 °C) in the presence of liquid acids. NO^+ is achieved via a reaction of sodium nitrite and strong acid [6]. Diazonium salts that are formed by the reaction of sodium nitrite, aniline derivatives, and strong liquid acids are unstable at room temperature and immediately decompose. A few reports are available for reactions involving stable diazonium salts at room temperature using solid acids and supported reagents [7]. Many studies have reported the diazotization of aniline derivatives by solid acids such as silica sulfuric acid [8], clay [9], lead and triethylammoniumformate [10], *p*-toluenesulfonic acid [11], and ionic liquid [12]. Azo dyes can alsobe obtained under solvent-free condition [13,14]. Synthesis of azo compounds with nanosized iron-promoted reductive coupling of aromatic nitro compounds has been reported [15]. Here, we wish to report a convenient and one-pot method for diazotization and diazo coupling reactions by using nano-SPIA under solvent-free conditions at room temperature by grinding.

2. EXPERIMENTAL

2.1. Materials

Nano-silica gel and other chemicals were purchased from Aldrich, Merck, and Fluka chemical companies. All products were known and identified by a comparison of their physical and spectroscopic data with those of authentic samples.

2.2. Apparatus

IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR spectrophotometer. ^1H NMR and ^{13}CNMR spectra were recorded on a Bruker DRX-400 Avance spectrometer with tetramethylsilaneserving as an internal reference. Scanning Electron Microscopy (SEM) of nano particles was performed with a VEGA/TESCAN scanning electron microscope. Transmission Electron Microscopy (TEM) was performed on a Philips CM10-HT100KV microscope. The X-ray diffraction (XRD) patterns of materials were recorded by employing a Philips Xpert MPD diffractometer that was equipped with a Cu Kαanode (λ = 1.54 Å) in the 2θ range from 5 to 80°. Melting points were determinedon the Yanagimoto micro melting point apparatus. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

2.3. Preparation of nano silica periodic acid (nano-SPIA)

10 mL of 70% aqueous solution $HIO_4$was added to 1 g of nanosilicagel and stirred for 30 minutes. After filtration from unreacted periodic acid, the solution was heated at 50°C for 1 h under vacuum to afford nano-SPIA as a free flowing powder [16].

2.4. Typical Procedure

A mixture of aniline (1 mmol, 0.093g), nano-SPIA (0.05 g), and sodium nitrite (2 mmol, 0.138 g) was ground in a mortar for 10 minutes to obtain a homogeneous mixture. Then, two drops of water were gradually added to this mixture and the mixture was ground for 10 minutes until the gas evolution was completely finished. 2-Naphthol (1 mmol) was added to the diazonium salt and ground for 10 min. The progress of the reaction was monitored by thin-layer chromatography (TLC) using a mixture of ethyl acetate and n-hexane (1:9 v/v) as solvent. Further purification of the product was performed by flash column chromatography using n-hexane and ethyl acetate. The related dye was obtained in 91% yield.

2.5. The spectral data of some representative products

Compound 3a: UV-Vis: λ_{max} (nm in $CHCl_3$)= 490 and 318.IR (KBr, cm^{-1}): 3434 (w), 3031 (w), 1617 (s), 1447 (s), 1207, 1261 (s), 839 (s), 751 (s).^{1}HNMR ($CDCl_3$, 400 MHz) δ (ppm):16.05 (s, 1 H, NH/OH), 8.37(d, *J*=8 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 Hz, 1 H), 7.36(t, *J*=8Hz, 1 H), 7.30(t, *J*=7.2Hz, 2 H), 7.21(t, *J*=8 Hz, 1 H), 7.11(t, *J*=7.2 Hz, 1 H), 6.68(d, *J*=9.2 Hz, 1 H). ^{13}CNMR ($CDCl_3$, 100 MHz) 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.

Compound 3c: UV-Vis: λ_{max} (nm in $CHCl_3$)= 490 and 324.IR (KBr, cm^{-1}): 3432 (w), 2931 (m), 1621 (s), 1492 (s), 1451 (s), 1210, 1255 (s), 821 (s), 749 (s).^{1}HNMR ($CDCl_3$, 400 MHz) δ (ppm): 15.60 (s, 1H, NH/OH), 8.65 (d, *J*=8 Hz 1 H), 7.95(d, *J*=9.6 Hz, 1 H), 7.88(d, *J*=8.6 Hz, 2 H), 7.78(d, *J*=7.6 Hz, 1 H), 7.74(d, *J*=8.6 Hz, 2 H), 7.61(t, *J*=7.6 Hz, 1 H), 7.46(t, *J*=7.6Hz, 1 H), 6.94(d, *J*=9.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.59, 144.33, 140.10, 133.39, 133.01, 129.76, 128.94, 128.69, 128.19, 126.42, 125.89, 124.33, 121.75, and 119.93.

Compound 3h: UV-Vis: λ_{max} (nm in $CHCl_3$)= 496 and 322. IR (KBr, cm^{-1}): 3437 (w), 3030 (w), 2935 (m), 1616 (s), 1501 (s), 1447 (s), 1207, 1266 (s), 814 (s), 748 (s).^{1}HNMR ($CDCl_3$), 400 MHz) δ (ppm): 16.2 (s, 1 H, NH/OH), 8.62(d, *J*=8 Hz, 1 H), 7.74(d, *J*=9.6 Hz, 1 H), 7.69(d, *J*=8 Hz, 2 H), 7.64(d, *J*=8 Hz 1 H), 7.57(t, *J*=7.6Hz, 1 H), 7.40(t, *J*=7.6Hz, 1 H), 7.30(d, *J*=8 Hz, 2 H), 6.94(d, *J*=9.6 Hz, 1 H), 2.43(s, 3 H). ^{13}CNMR ($CDCl_3$, 100 MHz) δ (ppm):168.56, 143.51, 138.92, 138.35, 133.54, 130.20, 129.77, 128.61, 128.52, 128.02, 125.34, 124.04, 121.64, 119.15, and 21.32.

Compound 3i: UV-Vis: λ_{max} (nm in $CHCl_3$)=488 and 320. IR (KBr, cm^{-1}):3433 (w),3025,2938, 1601 (s), 1521 (s), 1441 (s), 1159, 1246 (s), 828 (s), 753 (s).^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 15.73 (s, 1H, NH/OH), 8.73(d, *J*=8.4 Hz, 1 H), 7.85(d, *J*=9.2 Hz, 2 H), 7.78(d, *J*=9.2 Hz, 1 H), 7.71(d, *J*=8.4 Hz, 1 H), 7.6(t, *J*=8 Hz, 1 H), 7.41(t, *J*=8Hz, 1 H), 7.06(d, *J*=9.2 Hz, 2 H), 7.04(d, *J*=9.2 Hz, 1 H), 3.91(s, 3 H). ^{13}CNMR ($CDCl_3$, 100 MHz) δ (ppm): 161.33, 160.67, 141.84, 136.71, 133.31, 129.53, 128.33, 128.15, 127.11 124.80, 122.19, 122.06, 121.61, 114.78, 55.64.

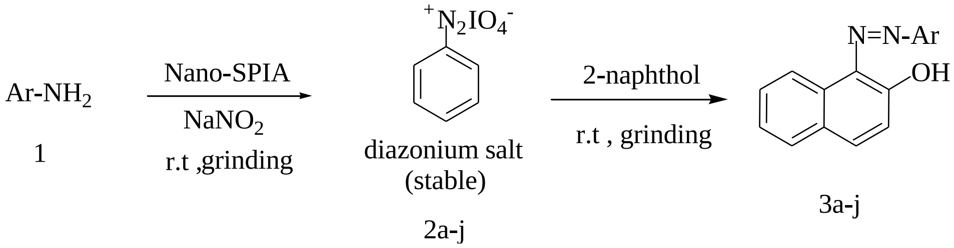
3. RESULTS AND DISCUSSION

In continuation of our previous research conducted on the synthesis and application of solid acid catalysts and supported reagents in organic syntheses [17–28], we have studied the conversion of primary aromatic amines to the related azo dyes in the presence of nano-SPIA. According to this protocol, a stable diazonium salt was formed under solvent-free conditions at room temperature (Scheme 1).

We have prepared nano-SPIA by reacting nanosilicagel with a 70% aqueous solution of HIO_4.According to the SEM and TEM images and XRD pattern, the particle size of nano-SPIA is 35 nm (Figure1).

By mixing aniline (1 mmol) and sodium nitrite (1 mmol) in the presence of various amounts of nano-SPIA, we have obtained the related diazonium salt in 91% yield using 0.05 g of nano-SPIA (Table 1, Entry 4).

After preparation of diazonium salts, 2-naphthol (1mmol) was added to them and stirred for 10 minutes. The whole process of diazotization lasts 30 minutes. The crude product was extracted with dichloromethane. Then, the solvent was evaporated by a rotary evaporator at reduced pressure and the crude product was purified by flash column chromatography. Through this procedure, azo dyes were obtained in good to excellent yields (Table 2).



Scheme 1. *Azo dye preparation based on 2-naphthol in the presence of nano-SPIA*

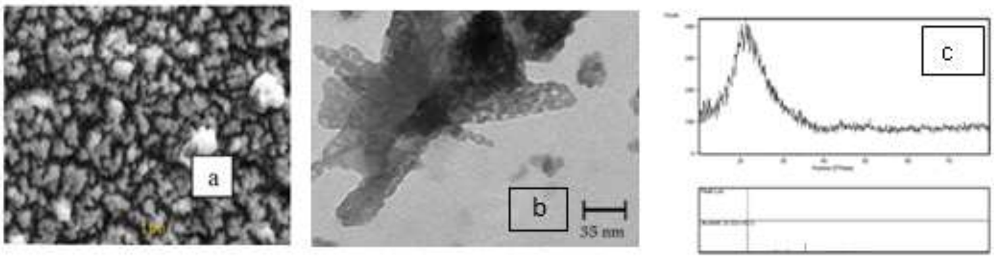


Figure 1. *The SEM(a) and TEM(b)images and XRD (c) pattern ofnano-SPIA*

Table 1. *Preparation of phenyldiazoniumperiodate in the presence of various amounts of nano-SPIA*[a]

Ent.	Time (min)	Catalyst (g)	Yield (%)
1	45	0.03	45
2	40	0.04	60
3	35	0.045	75
4	30	0.05	91
5	30	0.06	91

[a] Aniline (1 mmol) and sodium nitrite (2 mmol) were used

***Table 2**. Preparation of azo dyes based on 2-naphthol in the presence of nano-SPIAat room temperature* [a]

Entry	Amine	Product	Yield (%)	M.P.	
				Found	Reported [30]
1	aniline	3a	91	136	134
2	4-chloro aniline	3b	93	159	161
3	4-bromo aniline	3c	87	152	154
4	2-nitro aniline	3d	90	248	245
5	4-nitro aniline	3e	96	259	256
6	2-chloro aniline	3f	82	164	166
7	2-metyl aniline	3g	85	131	131
8	4-metyl aniline	3h	86	145	142
9	p-anisidine	3i	90	177	180
10	3,4-Methoxy aniline	3j	75	197	198

[a] The ratio of amine (mmol), $NaNO_2$ (mmol), 2-naphthol (mmol), and nano-SPIA (g) is 1:2:1:0.05

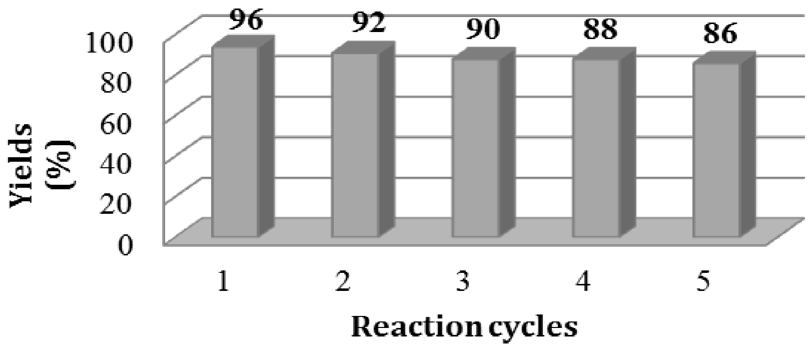


***Figure 2.** The reusability of catalyst*

The reusability of nano-SPIA for preparation of product (3e) was checked several times without exhibiting any important decrease in catalytic activity (Figure 2).

For investigating the stability of the diazonium salts, some aryl diazonium nano-silica periodates were stored in a desicator at room temperature. After the specified time points, 2-naphtholwas added to each salt and the reaction mixture was ground at room temperature for 10 minutes. The products were extracted and the yields of azo dyes were compared with the product provided with the related fresh diazonium salts (Table 3). As shown in Table 3, aryl diazonium nano-silica periodate with electron-withdrawing groups on the aromatic ring are more stable than those with electron donating groups because of the instability of the resulting aryl cation. We have also compared the stability of diazonium silica periodateswith diazoniumnano-silica periodates and found that the diazonium silica periodates have less stability (Table 4).

The efficiency of Nano Silica/HIO_4 catalyst in comparison with that of various catalysts and reagents was also examined (Table 5). Nano Silica/HIO_4 was found to be the most efficient of all catalysts that were tested, in terms of yields.

In ^1H NMR spectrum of compound 3h, the signal of OH/NH proton appeared at δ =15-16 ppm due to a bifurcated intramolecular hydrogen bond that is an example of a hydrogen bond involving one proton and two acceptors. The signal of the three aliphatic protons (CH_3) was shown at δ=2.43 ppm. A doublet of doublet signal around δ=7.3–7.69 ppm was assigned to the protons of the aromatic rings (Figure 3). On the other hand, in^{13}C

NMR spectrum of compound 3h, the signals around δ= 119.15–168.56 ppm are assigned to the carbons of the aromatic rings. The signal of the aliphatic carbon (CH_3) is shown at δ=21.32 ppm (Figure 4).

***Table 3**. The stability study of the catalyst some aryl diazoniumnanosilicaperiodate at room temperature*[a]

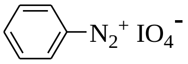
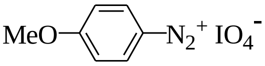
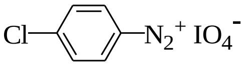
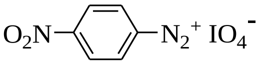
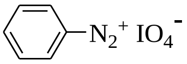
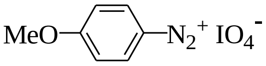
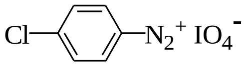
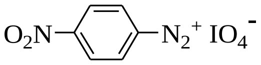
Diazonium salt	Prduct	Yield (%) after						
		30 min	1 day	2 days	3 days	4 days	5 days	6 days
	3a	91	88	85	80	75	52	35
	3i	90	85	80	76	61	50	30
	3b	93	90	86	81	77	70	65
	3e	96	93	90	85	79	73	69

***Table 4**. The stability study of the catalyst of some aryl diazonium silica periodate at room temperature*

Diazonium salt	Prduct	Yield (%) after						
		30 min	1 day	2 days	3 days	4 days	5 days	6days
	3a	85	73	50	43	25	20	-
	3i	80	75	43	32	22	-	-
	3b	83	78	74	70	48	37	24
	3e	89	80	73	69	51	30	25

[a] The yields refer to the isolated pure products after adding 2-naphthol to their relateddiazonium salts within the specified time

***Table 5**. The synthesis of a zo dyes using different catalysts or reagents in comparison with nano silica/ HIO_4.*

Entry	Catalyst or reagents	Yields (%)[a]
1	Polymer/HIO_4	95[31]
2	Silica/H_2SO_4	83[8]
3	Nano SiO_2-CrO_3H	80[32]
4	HCl/$NaNO_2$	67 [33]
5	[H-NMP] HSO_4	88[34]
6	Our work	96

[a] Isolated yields and 1-((4-nitrophenyl) diazenyl) naphthalen-2-ol (3e) was synthesized

[b] Compound3a was prepared.

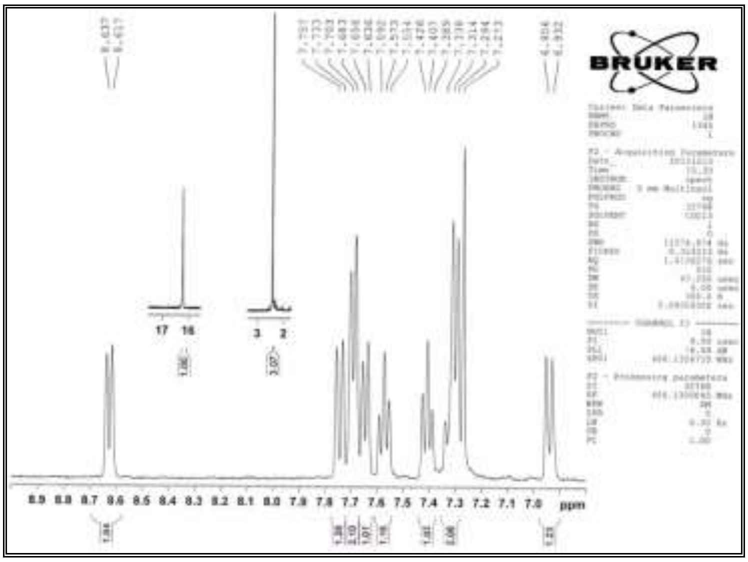


Figure 3. *^{1}H NMR spectrum of 1-(2-(4-methylphenyl)diazenyl) naphthalene-2-ol*

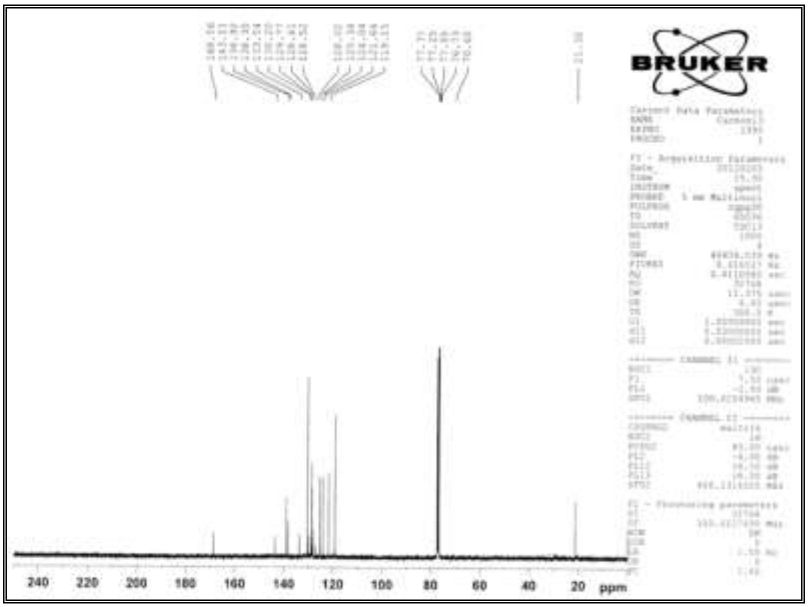


Figure 4. *^{13}C NMR spectrum of 1-(2-(4-methylphenyl) diazenyl)naphthalene-2-ol*

4. CONCLUSION

Various aromatic amines, including electron-withdrawing and electron-donating groups, were rapidly and efficiently converted to the related azo dyes under solvent-free condition at room temperature. Especially nano-SPIA proved to be a suitable catalyst and afforded the highest stability of diazonium salts and yields. One reason for this behavior may be related to the number of available 2 active sites, which, in turn, increases the catalytic activity. The solvent-free conditions employed in the present method make it (solvent-free condition at room temperature) environmentally friendly as well as useful for industrial applications. This method is a novel, efficient, and environmentally benign route for solvent-free synthesis of azo dyes. Furthermore, it is characterized by mildness, short reaction time, being a valuable effective process, its ease of handling, and involving a simple experimental procedure, which prove advantageous.

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