

RESEARCH PAPER

Solvent-Free Synthesis of Azo Dyes Based on β -Naphthol Using Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ by Grinding Method

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ABSTRACT

Azo compounds in addition to common uses in science and technology, is used as optical materials in the processing of molecular data, ion sensors, and biological applications. Primary aromatic amines are diazotized in an acid, and the subsequent coupling process can produce azo dyes. Supported Ti(V) catalyst is a powerful Lewis acid that is used to promote organic reactions. In this work, azo dyes were effectively synthesized using Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ as a solid acid reagent. The heterogeneous nanoparticles were fully characterized by FT-IR, XRD, XRF, EDS, TGA, FESEM, TEM and BET techniques. This solid acid reagent enhances the coupling reaction of β -naphthol with aryl diazonium salt to form diazo dyes under solvent free grinding conditions. In this protocol, many aromatic amines with electron withdrawing or electron releasing groups are used to form azo dyes. Azo dye products are characterized by FT-IR and NMR spectroscopy. This new synthetic method has the advantages of short reaction times, easy work-up and high yields.

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INTRODUCTION

Azo compounds are attractive targets for organic synthesis methodology due to their widespread applications in many fields of technology and medicine [1-5]. Prior to the mid- nineteenth century, materials with coloring properties were extracted mainly from natural sources, mainly from animals or vegetables. However, natural colors were almost completely replaced by the synthetic colors at the beginning of the twentieth century. Today, almost, all dyes and pigments on the market, with the exception of some inorganic pigments, are synthetic materials. Hundreds of new color combinations enter the market every year and become a series of different application

[6, 7].

According to the classification of dyes, 60-70% of them is azo compounds, in addition to common uses in science and technology, is used as optical materials in the processing of molecular data, ion sensors, and biological applications [8, 9]. The azo dye molecule contains one or more π systems that can produce different colors by changing the electron donor or electron acceptor functional groups. Traditionally, primary aromatic amines are diazotized in concentrated sulfuric acid, and the subsequent coupling process can only continue under acidic conditions. Previously, some acidic catalysts such as Nano- Fe_3O_4 encapsulated-silica supported boron trifluorid [10], silica sulfuric acid

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[11], Nano-CuFe₂O₄-supported sulfonic acid [12], Nano BF₃·SiO₂ [13], kaolin-SO₃H [14], Nano silica chromic acid [15], has been used to synthesize azo dyes.

Supported Ti(V) catalyst is a powerful Lewis acid that is used to promote organic reactions [16-20]. In this research, we have prepared Nano- γ -Al₂O₃/Ti(IV) as a solid acid, characterize its structure, and use it in the synthesis of azo dyes. A schematic diagram of the proposed method is shown in Fig. 1.

MATERIALS AND METHODS

All chemical reagents were purchased from Fluka, Merck and Aldrich chemical companies and were used without any further purification. All of the products are known compounds which were characterized by comparison of their spectral (FTIR and ¹H NMR), and physical data with authentic samples. ¹H NMR spectra were recorded

on a Bruker DRX-400 Avance spectrometer in CDCl₃ and DMSO-d₆ as solvents and chemical shift are expressed in δ ppm relative to tetramethyl silane. IR spectra were determined on a Nicolet Magna series FT-IR 550 spectrometer using KBr pellets. Thin layer chromatography (TLC) on commercial aluminium-backed plates of silica gel 60 F₂₅₄ was used to monitor the progress of the reactions. Melting points were obtained with a micro melting point apparatus (Electrothermal, Mk3). The XRD patterns were collected on a Philips Xpert MPD diffractometer equipped with a Cu K α anode ($\lambda=1.54 \text{ \AA}$) in the 2θ range from 10 to 80°. Elemental composition was investigated by XRF BRUKER S4 EXPLORER. Average size of Nano- γ -Al₂O₃/Ti(IV) was analyzed by FESEM and TEM using a Mira 3-XMU and Philips CM120 with a LaB6 cathode and accelerating voltage of 120 kv, respectively. Brunauer–Emmett–Teller (BET) surface area analysis of nano- γ -Al₂O₃/Ti(IV) was

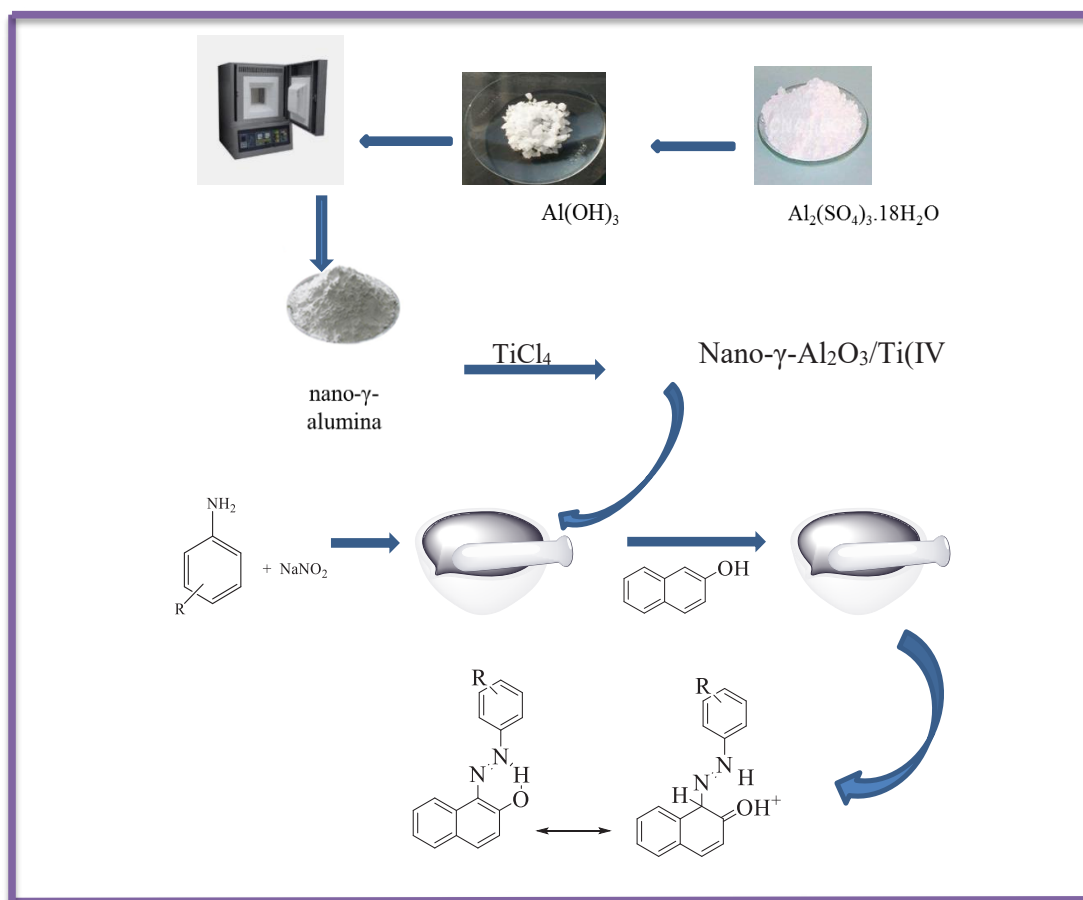


Fig. 1. Schematic diagram of the proposed method

done with Micromeritics, Tristar II 3020 analyzer. Quantitative elemental information (EDS) of Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ alumina was measured by EDS instrument, Phenom pro X.

Preparation of Nano- γ - Al_2O_3 and Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$

NaOH (600 ml, 1 M), was added drop-wise to a slurry containing $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (66 g). The mixture was stirred at room temperature. The resulted suspension was filtered to obtain the white solid Al(OH)_3 . The solid were washed with distilled water until no more sulfate ions were detected in the washings. After that NaOH (100 ml, 1 M) was added to a beaker containing Al(OH)_3 (20 g) to produce NaAl(OH)_4 . Then PEG 4000 (0.3%) was added to solution and it was neutralized with HCl (0.1 M), to pH 8 until Al(OH)_3 produced again. The obtained precipitate filtered and washed with distilled water. The dried solid was calcined in the furnace at 800 °C for 3 hours through atmospheric air to produce nano- γ - Al_2O_3 powder.

Follow the procedure below to prepare Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$. To a mixture of nano- γ - Al_2O_3 (1 g) and CH_2Cl_2 (10 ml), TiCl_4 (0.5 ml) was added dropwise. The resulting suspension was stirred for 1 hour at room temperature, filtered, washed with chloroform, and dried at room temperature.

Typical procedure for the diazotization and azo coupling reactions

Aromatic amines (2 mmol), Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ (0.5 g) and sodium nitrite (3 mmol) were ground in a mortar with a pestle for a few minutes. In this step, aryl diazonium salt as a yellow solid was formed. Then, 2 mmol of 2-naphthol was added to obtained diazonium salt with vigorous grinding. The progress of the reaction was monitored by TLC (Ethyl acetate–n-Hexan 7: 3). The crude product was resolved in acetone and the solid acid catalyst was separated by simple filtration. By adding water to filtrate, azo dyes as a pure orange solid were obtained. All the products were identified by a comparison of their melting points, FT-IR and ^1H NMR spectra with published data.

1-(3-Nitrophenylazo)-2-hydroxy naphthalene (Table 2, Entry 1)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3438, 1616, 1528, 1494, 1446, 1347, 1252, 1201, 834, 758, 734. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.2 (s, NH), 8.52 (t, $^3J=8.4$ Hz, 2H), 8.09 (d, $^3J=7.2$ Hz, 1H), 7.93 (s, 1H),

7.74 (d, $^3J=9.2$ Hz, 1H), 7.61 (m, $^3J=7.2$ Hz, 3H), 7.45 (d, $^3J=6.8$ Hz, 1H), 6.81 (d, $^3J=9.2$ Hz, 1H).

1-(2-Nitrophenylazo)-2-hydroxy naphthalene (Table 2, Entry 2)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3426, 1606, 1568, 1480, 1448, 1313, 1192, 1127, 842, 744. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.6 (s, NH), 8.43 (br. s, 1H), 8.31 (br. s, 1H), 7.74 (d, $^3J=6.0$ Hz, 2H), 7.65 (br. s, 1H), 7.51 (d, $^3J=8.0$ Hz, 2H), 7.42 (s, 2H), 6.70 (br. s, 1H).

1-(4-Nitrophenylazo)-2-hydroxy naphthalene (Table 2, Entry 3)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3436, 1594, 1501, 1452, 1331, 1201, 1152, 1104, 837, 748. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.2 (s, NH), 8.42 (d, $^3J=7.6$ Hz, 1H), 8.33 (d, $^3J=8.4$ Hz, 1H), 7.61 (d, $^3J=8.8$ Hz, 4H), 7.56 (d, $^3J=7.2$ Hz, 2H), 7.44 (d, $^3J=6.8$ Hz, 1H), 6.70 (d, $^3J=9.2$ Hz, 1H).

1-(2-Chlorophenylazo)-2-hydroxy naphthalene (Table 2, Entry 4)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3439, 1617, 1554, 1499, 1447, 1258, 1207, 1142, 840, 752. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.5 (s, NH), 8.52 (s, 1H), 8.13 (s, 1H), 7.70 (d, $^3J=8.8$ Hz, 1H), 7.56 (s, 2H), 7.44 (dd, $^3J=8$ Hz, 3H), 7.19 (d, $^3J=7.6$ Hz, 1H), 6.83 (s, 1H).

1-(4-Chlorophenylazo)-2-hydroxy naphthalene (Table 2, Entry 5)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3436, 1620, 1561, 1489, 1446, 1252, 1209, 1090, 821, 749, 497. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.1 (s, NH), 8.56 (d, $^3J=8.0$ Hz, 1H), 7.75 (d, $^3J=9.2$ Hz, 1H), 7.70 (d, $^3J=8.8$ Hz, 2H), 7.63 (d, $^3J=8.0$ Hz, 1H), 7.57 (t, $^3J=8.4$ Hz, 1H), 7.46 (d, $^3J=8.4$ Hz, 1H), 7.41 (d, $^3J=8.0$ Hz, 1H), 7.35(s, 1H), 6.90 (d, $^3J=9.6$ Hz, 1H). λ_{max} (nm)= 484 (π - π^* , N=N).

1-(2-Methoxyphenylazo)-2-hydroxy naphthalene (Table 2, Entry 6)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3434, 1615, 1551, 1485, 1444, 1391, 1249, 1204, 1148, 1104, 1020, 837, 746. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.65 (s, NH), 8.52 (s, 1H), 8.07 (s, 1H), 7.67 (d, $^3J=4.8$ Hz, 1H), 7.54 (d, $^3J=4.4$ Hz, 3H), 7.37 (d, $^3J=4.8$ Hz, 1H), 7.10 (d, $^3J=4.8$ Hz, 1H), 7.01 (s, 1H), 6.80 (dd, $^3J=4.8$ Hz, 1H), 4.03 (s, 3H, Ar-OCH₃).

1-(2-Methylphenylazo)-2-hydroxy naphthalene

(Table 2, Entry 7)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3435, 1618, 1554, 1504, 1450, 1255, 1205, 1151, 839, 753. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.7 (s, NH), 8.6 (br. s, 1H), 8.1 (br. s, 1H), 7.75 (br. s, 1H), 7.61 (br. s, 3H), 7.40 (br. s, 3H), 6.9 (br. s, 1H), 2.56 (s, 3H, Ar- CH_3).

1-(2, 4-Dimethylphenylazo)-2-hydroxy naphthalene (Table 2, Entry 8)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3435, 1612, 1554, 1497, 1299, 1206, 1148, 815, 749. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.7 (s, NH), 8.6 (br. s, 1H), 7.9 (br. s, 1H), 7.84 (br. s, 1H), 7.63 (br. s, 3H), 7.11 (br. s, 3H), 6.94 (br. s, 1H), 2.53 (s, 3H, Ar- CH_3), 2.38 (s, 3H, Ar- CH_3).

1-(3-Hydroxyphenylazo)-2-hydroxy naphthalene (Table 2, Entry 9)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3385, 1599, 1540, 1449, 1268, 864, 489. ^1H NMR (400 MHz, DMSO, ppm) δ : 8.15 (d, $^3J=8.1$ Hz, 1H), 7.7 (d, $^3J=7.7$ Hz, 1H), 7.3 (m, 2H), 7.1 (m, 2H), 6.8 (d, $^3J=6.8$ Hz, 1H), 6.7 (t, $^3J=6.7$ Hz, 1H), 5.97 (t, $^3J=5.9$ Hz, 2H), 5.9 (d, $^3J=5.9$ Hz, 1H), 4.85 (s, 1H, NH), 4 (s, 1H, OH).

1-(4-Hydroxyphenylazo)-2-hydroxy naphthalene (Table 2, Entry 10)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3426, 1595, 1445, 1264, 836. ^1H NMR (400 MHz, DMSO, ppm) δ : 8.45 (d, $^3J=8.4$ Hz, 1H), 8.1 (d, $^3J=8.1$ Hz, 1H), 7.15 (t, $^3J=7.14$ Hz, 1H), 7.05 (d, $^3J=7.06$ Hz, 1H), 6.75 (t,

$^3J=6.7$ Hz, 1H), 6.7 (d, $^3J=6.7$ Hz, 1H), 6.45 (d, $^3J=6.4$ Hz, 2H), 6.4 (d, $^3J=6.3$ Hz, 2H), 4.5 (s, 1H, NH), 3.5 (s, 1H, OH).

1-(4-Methylphenylazo)-2-hydroxy naphthalene (Table 2, Entry 11)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3435, 1616, 1556, 1500, 1446, 1265, 1207, 1140, 815, 748, 498. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.2 (s, NH), 8.4 (d, $^3J=8.0$ Hz, 1H), 7.74 (d, $^3J=9.4$ Hz, 1H), 7.69 (d, $^3J=8.0$ Hz, 2H), 7.21 (d, $^3J=8.4$ Hz, 1H), 7.57 (t, $^3J=7.6$ Hz, 1H), 7.40 (t, $^3J=7.6$ Hz, 1H), 7.30 (d, $^3J=8.0$ Hz, 2H), 6.94 (d, $^3J=9.2$ Hz, 1H), 2.39 (s, 3H, Ar- CH_3).

1-(Phenylazo)-2-hydroxy naphthalene (Table 2, Entry 12)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3439, 1617, 1554, 1499, 1447, 1258, 1207, 1142, 840, 752. ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 16.3 (s, NH), 8.58 (d, $^3J=8.0$ Hz, 1H), 7.74 (t, $^3J=8.0$ Hz, 3H), 7.61 (d, $^3J=7.6$ Hz, 1H), 7.57 (t, $^3J=7.6$ Hz, 1H), 7.49 (t, $^3J=7.2$ Hz, 2H), 7.41 (t, $^3J=7.2$ Hz, 1H), 7.33 (t, $^3J=6.8$ Hz, 1H), 6.88 (d, $^3J=8.8$ Hz, 1H).

1-(1-Naphthylazo)-2-hydroxy naphthalene (Table 2, Entry 13)

FT-IR (KBr)/ $\bar{\nu}$ (cm^{-1}): 3442, 3336, 3031, 2889, 1625, 1513, 1431, 1384, 1270, 1176, 813, 768, 568. ^1H NMR (400 MHz, DMSO, ppm) δ : 8.1 (d, $^3J=8.05$ Hz, 1H), 7.7 (m, 1H), 7.6 (d, $^3J=7.6$ Hz, 1H), 7.3 (m, 6H), 7.15 (br. t, 1H), 7.05 (d, $^3J=7$ Hz, 1H),

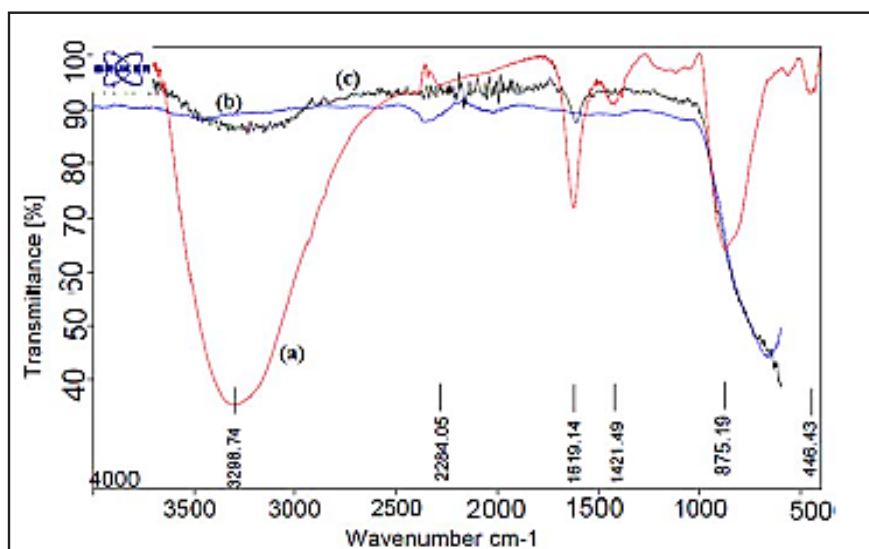


Fig. 2. FT-IR spectra of a) $\text{TiCl}_4(\text{aq})$, b) Nano- γ - Al_2O_3 and c), Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$.

6.65 (d, ³J=6.6 Hz, 1H), 5.7 (s, 1H, NH).

1-(4-Ethylphenylazo)-2-hydroxy naphthalene
(Table 2, Entry 14)

FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3436, 2956, 1618, 1558, 1504, 1446, 1307, 1253, 1206, 1141, 827, 752, 517. ¹H NMR (400 MHz, CDCl₃, ppm) δ : 16.2 (s, NH), 8.62 (d, ³J=8.4 Hz, 1H), 7.74 (d, ³J=8.8 Hz, 1H), 7.71 (d, ³J=8.8 Hz, 1H), 7.64 (d, ³J=8.4 Hz, 1H), 7.57 (br. t, 1H), 7.40 (br. t, 1H), 7.33 (d, ³J=6.4 Hz, 3H), 6.94 (d, ³J=8.8 Hz, 1H), 2.72 (q, ³J=7.6 Hz, 2H, Ar-CH₂CH₃), 1.29 (t, ³J=7.6 Hz, 3H, Ar-CH₂CH₃).

1-(4-Bromophenylazo)-2-hydroxy naphthalene
(Table 2, Entry 15)

FT-IR (KBr)/ $\bar{\nu}$ (cm⁻¹): 3435, 1619, 1560, 1489, 1251, 1208, 1145, 1069, 819, 750, 495. ¹H NMR (400 MHz, CDCl₃, ppm) δ : 16.1 (s, NH), 8.54 (br. s, 1H), 7.73 (d, ³J=8.4 Hz, 1H), 7.60 (br. s, 6H), 7.41 (d, ³J=9.2 Hz, 1H), 6.87 (br. s, 1H).

RESULTS AND DISCUSSION

In continuation of our research on the applications of solid acids in organic synthesis, we have synthesized, Nano- γ -Al₂O₃/Ti(IV) as a new heterogeneous acidic reagent and investigated its efficiency in azo dyes preparation at room temperature under grinding conditions.

For identification of the structure of, Nano- γ -Al₂O₃/Ti(IV), we have studied FT-IR (ATR) spectra of TiCl₄ (aq), nano- γ -Al₂O₃ and, Nano- γ -Al₂O₃/Ti(IV)

(Fig. 2). In TiCl₄ (aq) spectrum, a broad band at 3298 (H₂O), a middle band at 1619 (Ti-Cl) and a strong band at 875 cm⁻¹ (Ti-O) were observed (Fig 2a). In nano- γ -Al₂O₃ FT-IR spectrum, a very strong band at 600-1000cm⁻¹ (Al-O) was observed (Figure 2b), Nano- γ -Al₂O₃/Ti(IV), in addition to γ -Al₂O₃ signal, two additional bands at 1619 and 3298 show binding of TiCl₄ to γ -Al₂O₃ (Fig 2 c).

The FE-SEM images of the, Nano- γ -Al₂O₃/Ti(IV) and Nano- γ -Al₂O₃ Nanoparticles are displayed in Fig 3.

They exhibit irregular spherical shape for Nano particles below 50 nm. Energy-Dispersive X-ray Spectroscopy (EDS) of, Nano- γ -Al₂O₃/Ti(IV) was measured by EDS instrument provided the presence of the expected elements in the structure of this catalyst and confirmed supporting of TiCl₄ on Nano- γ -Al₂O₃ (Fig 4). The elemental compositions of Nano- γ -Al₂O₃/Ti(IV) were found to be 58.5, 29.9 and 6.5% for O, Al and Ti, respectively.

The X-ray diffraction (XRD) pattern of, Nano- γ -Al₂O₃/Ti(IV) is shown in Fig 5. According to XRD pattern of catalyst, the values of 2 θ and FWHM are shown in Table 1. The signals at 2 θ equal to 37 (b), 45 (c) and 67 (d) are shown Nano- γ -Al₂O₃ structure. According to XRD pattern, the two additional signals at 2 θ equal to 32 (a) and 75 (e) with FWHM equal to 0.236 and 1.152 respectively, are shown the presence of bonded Ti to Nano- γ -Al₂O₃ (Fig 5).

The specific surface area of catalyst was

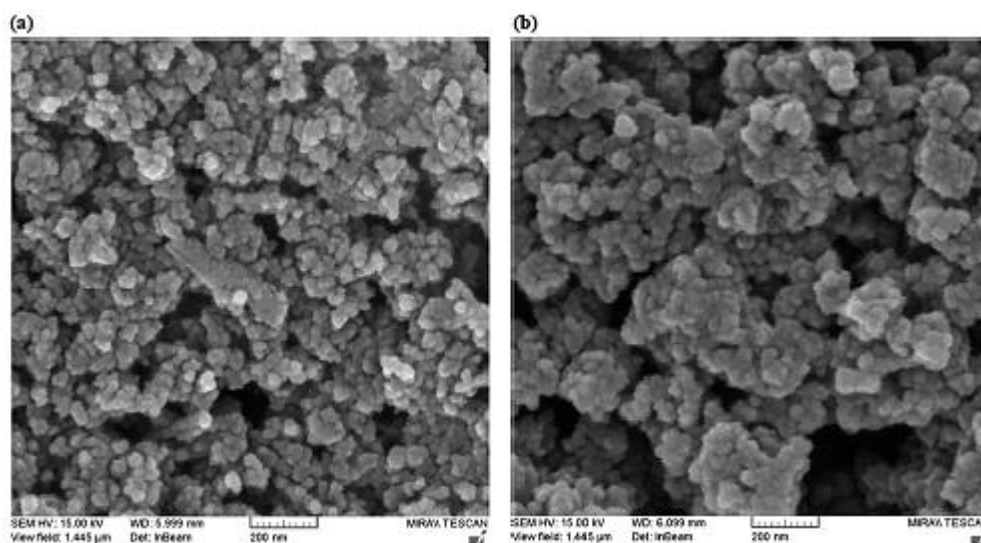


Fig. 3. The FE-SEM image of a), Nano- γ -Al₂O₃/Ti(IV) and b) N- γ -Al₂O₃.

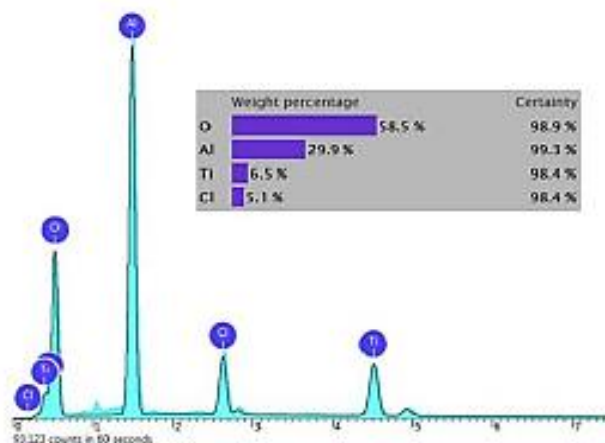


Fig. 4. EDS analysis diagram of Nano- γ -Al₂O₃/Ti(IV).

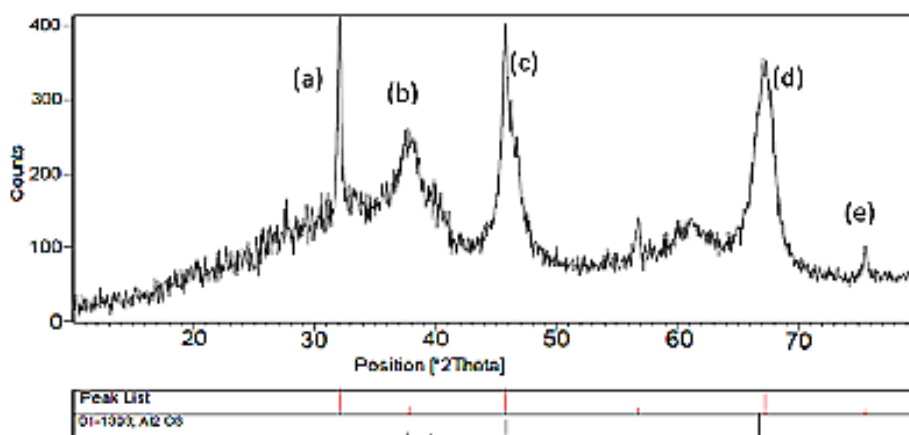


Fig. 5. XRD patterns of Nano- γ -Al₂O₃/Ti(IV).

Table 1. XRD analysis of nano- γ -Al₂O₃/Ti(IV).

No.	1	2	3	4	5
Pos. [2 θ]	31.900	37.676	45.666	67.253	75.537
FWHM [2 θ]	0.236	1.574	0.393	0.472	1.152

measured by Brunauer–Emmett–Teller (BET) theory. Single point surface area at P/P₀ = 0.184317546 is 73.9645 m²/g and BET surface area is 75.592 m²/g. The N₂ adsorption isotherm of catalyst is depicted in Fig 6.

Thermal gravimetric analysis (TG-DTA) pattern

of, Nano- γ -Al₂O₃/Ti(IV) was detected by heating from 50°C to 400 °C and then cooling until 165°C (Fig 7).

Nano- γ -Al₂O₃/Ti(IV) is stable until 392 °C and only 10.5 % of its weight was reduced due to the removal of catalyst moisture. The char yield of the

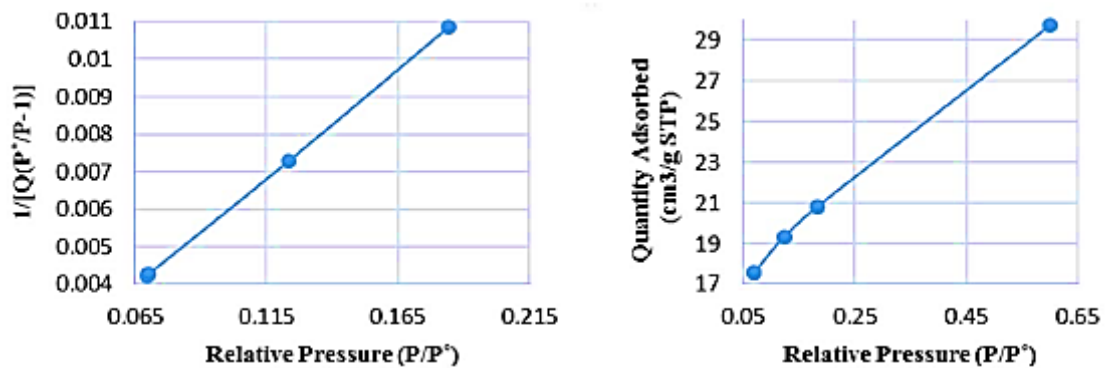


Fig. 6. Nitrogen adsorption isotherm at 77 K on Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$.

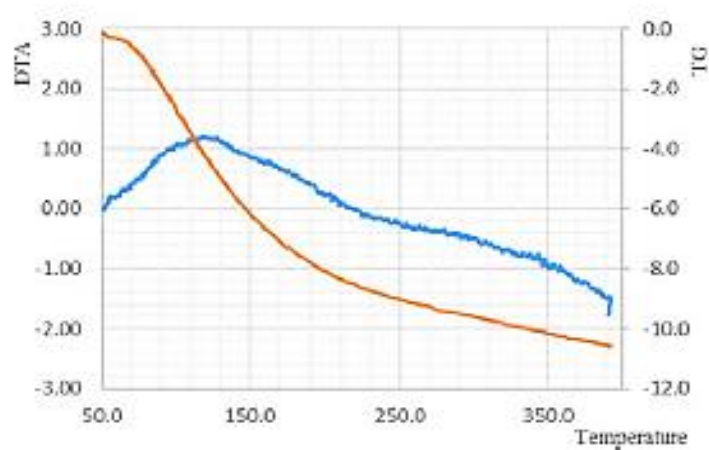


Fig. 7. Thermal gravimetric analysis (TG-DTG) pattern of Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$.

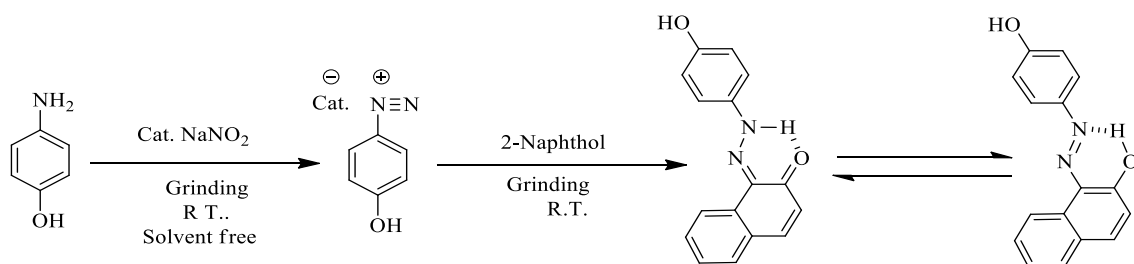


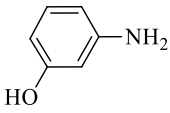
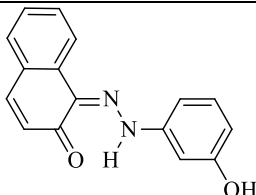
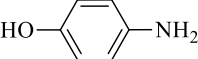
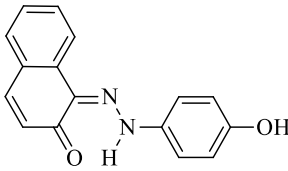
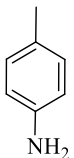
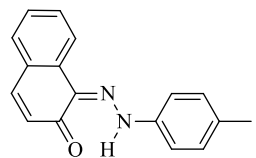
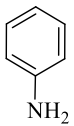
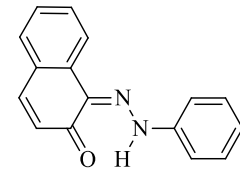
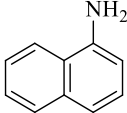
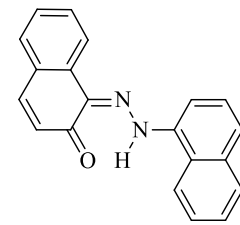
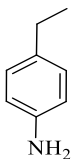
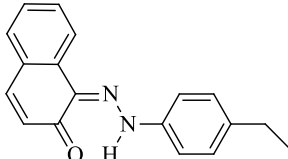
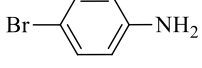
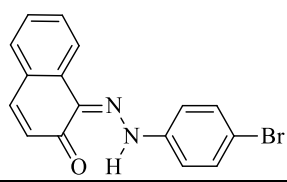
Fig. 8. Synthesis of azo dyes using acid catalyst at room temperature.

catalyst in 392°C is 89.5%. According to the TG-DTA diagram of, Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ and our study, it was revealed that this reagent is suitable for organic reactions until 400 °C.

In our opinion, Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ can catalyze

many organic reactions. This work, we wish to report a simple technique for the synthesis azo dyes based on β -naphthol using Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ as a heterogeneous reagent in a green approach and solvent free by grinding method

Entry	Aryl amine	Product	Yield ^b	M.P. °C		Ref.
				Found	Reported	
1			78	201-203	206-207	13
2			85	220-222	216-218	13
3			80	240-242	235-237	13
4			88	169-170	172-174	13
5			83	161-163	187-189	13
6			80	180-182	181-183	13
7			88	150-152	157-159	13
8			87	180-182	184-186	13

9			86	134-136	134	21
10			89	183-185	186	21
11			88	118-120	116-118	13
12			88	130-132	130-131	12
13			65	139-140	141-144	22
14			89	80-82	89-91	13
15			85	188-190	196-198	13

*Reaction conditions: Aromatic amines (2 mmol), sodium nitrite (3 mmol), β -naphthol (0.5 mmol) and, Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ (0.5 g) under grinding method

^bIsolated yields

(Fig. 8). Our methodology has advantages such as short reaction time, no time consuming workup, no hazardous solvent and no column chromatography purification. The reaction gave

quantitative yields and products formed smoothly under green reaction condition. The results of the synthesis of azo dyes by Nano- γ - $\text{Al}_2\text{O}_3/\text{Ti(IV)}$ are summarized in Table 2.

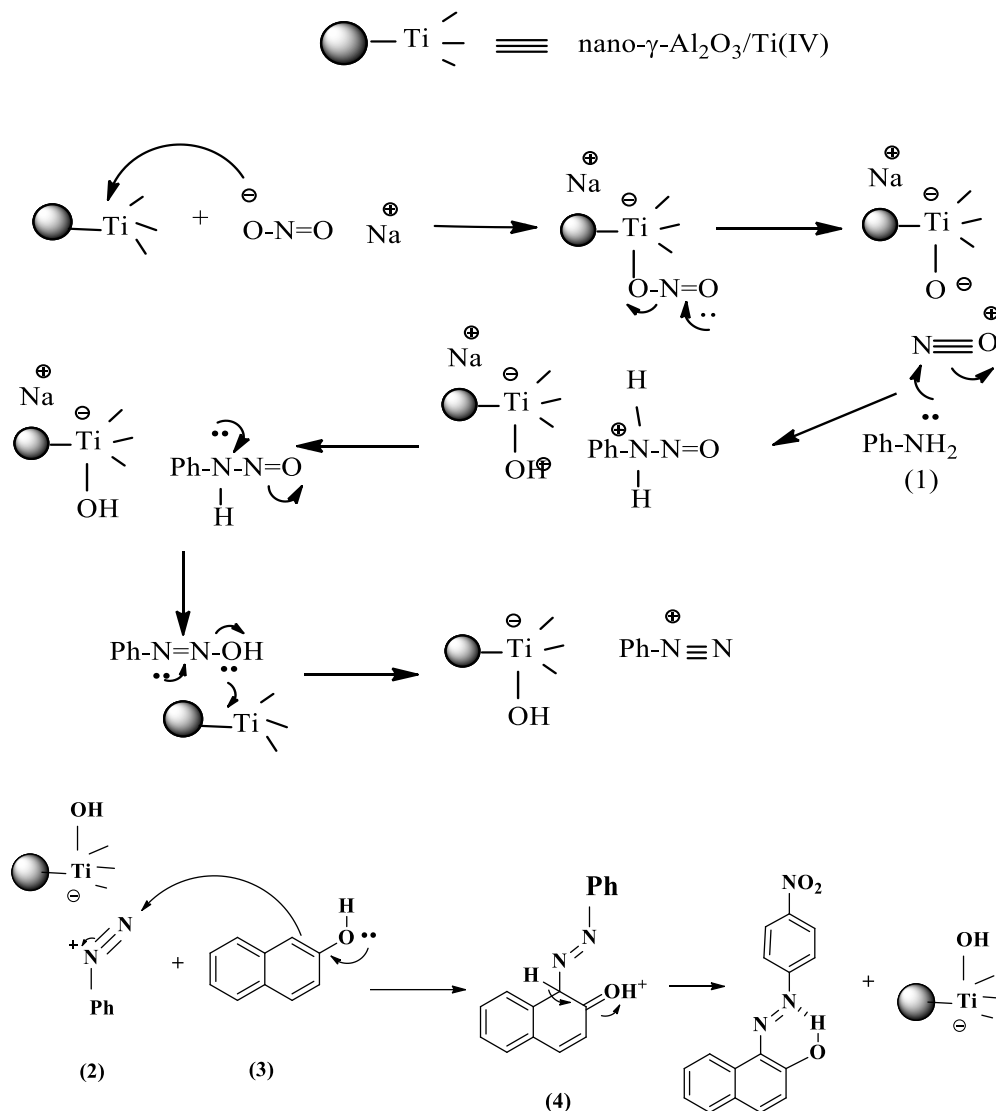


Fig. 9. Possible reaction mechanism for the synthesis of azo dyes.

The probable reaction mechanism of synthesis of azo dyes is outlined in Fig. 9. In this electrophilic aromatic substitution reaction, the primary aromatic amines (1) convert into its aryldiazonium salt. Aryldiazonium cation (2) is the electrophile and the activated β -naphthol (3) is a nucleophile. Diazonium salts are important synthetic intermediates that can undergo coupling reactions to form azo dyes (4).

CONCLUSION

In summary, we have synthesized azo dyes with using a solid acid reagent, nano- γ - $\text{Al}_2\text{O}_3/$

Ti(IV), under grinding and solvent free condition. Short reaction times, high conversions, clean reaction profiles, simple work-up, non-hazardous and excellent yields are some advantages of this protocol.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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