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Nano-$TiCl_4.SiO_2$: A Versatile and Efficient Catalyst for Synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes

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Abstract

Nano-silica supported titanium tetrachloride ($TiCl_4.SiO_2$) was prepared and used as an acid catalyst for the 14-aryl or alkyl-14*H*-dibenzo[*a,,j*]xanthenesreaction under solvent-free conditions. Compared to the classical 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenesreaction conditions, this method consistently has the advantage of excellent yields, mild reaction conditions, ease of workup, survival of different functional groups and short reaction times.

1. Introduction

Heterogeneous catalysis dominates the industrial scenery mainly due to the facility of recovery and reuse of solid insoluble catalysts [1, 2].Titanium tetrachloride as a powerful Lewis acid is a liquid which is highly volatile, corrosive and difficult to handle. It hydrolyses to produce HCl in the presence of moisture. Silica-supported $TiCl_4$ have several advantages as catalysts which make them economically and environmentally attractive. They have very strong Brønsted acidity approaching the superacid region and this acid–base property can be varied over a wide range by changing the chemical composition. It can be stored at an ambient temperature for months without losing its catalytic activity. This catalyst does not need special precautions for preparation, handling, or storage.

The preparation of benzoxanthenes is important due to their broad spectrum of biological and therapeutic properties such as antiviral [3], antibacterial [4] and anti-inflammatory [5] activities. They have efficiency in photodynamic therapy [6] and in antagonism of the paralyzing action of zoxazolamine [7]. Further, these compounds can be employed as dyes [8], pH-sensitive fluorescent materials for visualization of biomolecules [9] and in laser technologies [10].

For the construction of xanthenes and benzoxanthenes, various procedures are available including the cyclo-acylation of carbamates [11], trapping of benzynes by phenol [12], cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone [13], cyclodehydrations [14] and reaction of aldehydes with β-naphthol [15].

Previously, this procedure has been catalyzed with acids such as silica sulfuric acid [16, 17] Dowex-50W [18], $NH_4H_2PO_4$ [19], $HClO_4$–SiO_2[20], PW acid [21], cyanuric chloride [22], $Yb(OTf)_3$ [23], and polyphosphoric acid (PPA/SiO_2) [24].

2. Experimental procedure

The chemicals were used from Merck Company without any additional purification. The products were characterized by FT-IR (ATR), ^{1}H-NMR, and a comparison of their physical properties with those reported in the literature. FT-IR (ATR) spectra were run on a Bruker, Eqinox 55 spectrometer. A Bruker (DRX-400 Avance) NMR was used to record the ^{1}H NMR spectra. The X-ray diffraction (XRD) patterns of materials were recorded by employing a Philips Xpert MPD diffractometer equipped with a Cu Kα anode (λ = 1.54 A°) in the 2θ range from 10 to 80°. The SEM of nano particles determined with VEGA/TESCAN scanning electron microscope and TEM photograph was prepared by Leo 912AB OMEGA microscope.

A mixture of 2-naphthol (2 mmol), aldehyde (1 mmol), and 50% nano-$TiCl_4.SiO_2$ (0.05 g) was heated at 90°C. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was washed with hot ethanol and filtered to recover the catalyst. The filtrate was cold to obtain the pure 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthene derivatives in 85–97% yields.

3. Results and discussion

Nano-$TiCl_4.SiO_2$[25, 26] as an efficient and reusable acidic catalyst is synthesized *via* reaction of nano-silica gel with $TiCl_4$ in chloroform at room temperature. For the identification of the structure of nano-$TiCl_4.SiO_2$, we studied IR spectra of SiO2, nano-$TiCl_4.SiO_2$ and $TiCl_4$ (Fig. 1). In all of the spectra, very broad OH stretching bands are observed with a strong intermolecular hydrogen bonding. In FT-IR spectra of nano-$TiCl_4.SiO_2$ and SiO2, the absorption bands for Si-OH and Si-O-Si appear in ~700 cm^{-1} and ~1100 cm^{-1} respectively. The absorption band of Ti-Cl appear in 1600 cm^{-1} in $TiCl_4$ spectrum. In FT-IR spectrum of nano-$TiCl_4.SiO_2$, the O-Ti-Cl, Si-OH and Si-O-Si absorption bands are observedin 900, 700 and 1100 cm^{-1} respectively. In this study on nano-$TiCl_4.SiO_2$ structure led to more exactly configuration containing SiO_2-$TiCl_3$ (19%) and SiO_2-$TiCl_2$-SiO_2 (81%) (Scheme 1).

Because the nano-$TiCl_4.SiO_2$ produces HCl in water, we have determined the concentration of the acidic aqueous solution by titration. We have found that 0.1 g of catalyst produced a 0.0064 M aqueous solution. For the determination of the loading amount of Ti on 0.1 g of nano-$TiCl_4.SiO_2$, we have extracted Ti from the catalyst using EDTA solution (0.004 M) at pH of 4.

The standard solutions of titanium (IV) were prepared by dissolving a proper amount of $TiCl_4$ in acetone. Determination of the extracted Ti was carried out by an atomic absorption spectrometer with a hollow cathode lamp at a wavelength of 346 nm using C_2H_2/N_2O flame. The calibration equation for titanium was found as A=0.012C-0.1895 (R^2=0.9998). In this equation, A and C are the absorbance and concentration (mg L^{-1}) of titanium respectively. The calculated loading amount of Ti in catalyst is 7 mgg^{-1}.

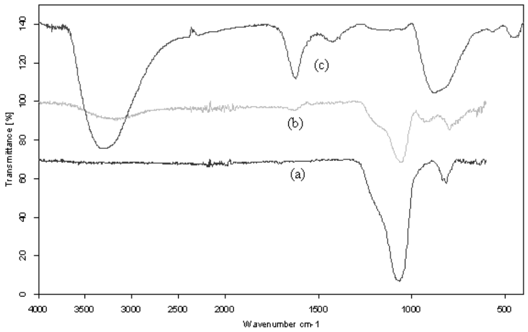
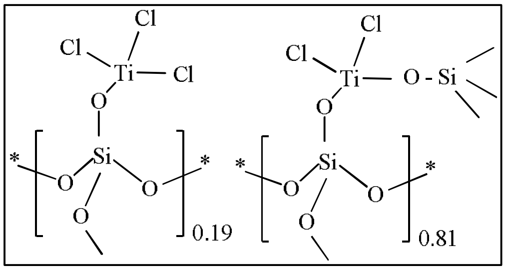


Fig. 1. FT-IR spectrum of: (a)SiO_2, (b)nano-$TiCl_4.SiO_2$, and (c) $TiCl_4$.



Scheme 1. Suggested structure for nano-$TiCl_4.SiO_2$.

The dimensions of nanoparticles were observed with the transmiThe scanning electron microscopy (SEM). The particle sizes of the commercial silica gel and synthesizednano-$TiCl_4.SiO_2$ were about 16-24 nm and 37-41 nm (Fig.2) respectively.

The X-ray diffraction (XRD) patterns of nano-SiO_2 and nano-$TiCl_4.SiO_2$ are shown inFig. 3. The XRD pattern of Nano-SiO_2has a strong peak in 2θ value of 21.8024° with FWHM equal to 0.1771. According to XRD pattern of nano-$TiCl_4.SiO_2$, the values of 2θ and FWHM are shown in Table 1.

In continuation of our investigations on solid acids in organic synthesis [27, 28],we have applied the nano-$TiCl_4.SiO_2$ for the synthesis of 14-phenyl-14*H*-dibenzo[*a*,*j*]xanthene. The reaction between benzaldehye and 2-naphthol was examined to optimize the reaction condition (Scheme 2). Reaction in different conditions in the presence of $TiCl_4.SiO_2$ revealed that the best condition for all the reaction was a solvent-free one at 90°C (Table 2, Entry 6).

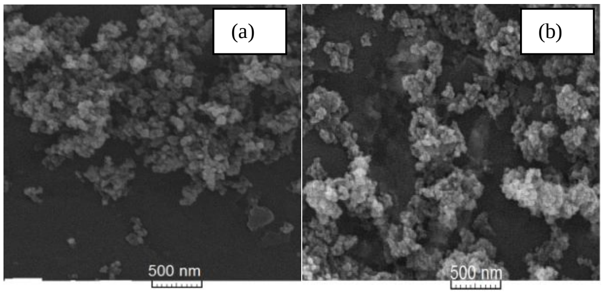


Fig. 2. SEM photograph of (a) nano-SiO_2 and (b) nano-$TiCl_4.SiO_2$.

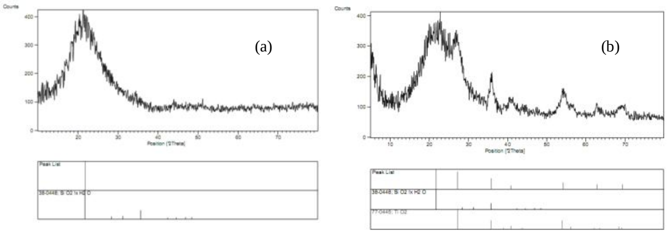


Fig. 3. X-ray diffraction (XRD) pattern of a) nano-SiO_2 and b) nano-$TiCl_4.SiO_2$.

Transmission electron microscopy (TEM) picture of nano-$TiCl_4.SiO_2$ were shown in Fig. 4. The particle size in (TEM) pattern is calculated between 14-20 nm.

Table 1. Nano-$TiCl_4.SiO_2$ reflexes in XRD diffractogram

Ent.	Pos [°2Th.]	FWHM [°2Th.]	Particle size (A°)
1	21.7587	0.3542	22.0
2	27.1424	1.6531	5.0
3	35.8287	0.4723	17.0
4	40.8394	1.1808	7.0
5	54.1881	1.1808	7.5
6	62.8214	0.7085	13.0
7	69.3466	2.3040	4.0

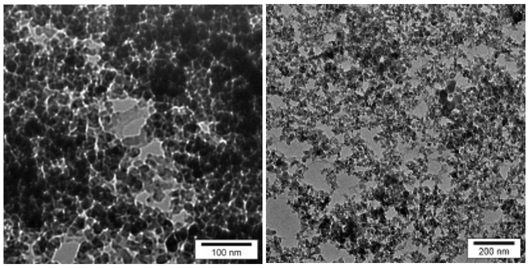
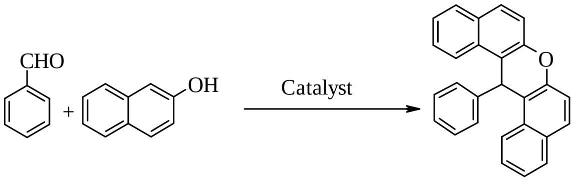


Fig.4. TEM photograph of nano-$TiCl_4.SiO_2$.

We have repeated the above mentioned reaction with 50% nano-$TiCl_4.SiO_2$ and found that 0.05 g of catalyst is necessary (Table 2, Entry 12).To examine the reusability of nano-$TiCl_4.SiO_2$in a solvent-free condition, after each run, the product was dissolved to $CHCl_3$ and filtered. The catalyst residue was washed with acetone and reused. Treatment with acetone removes the tar from the catalyst surface more efficiently (Table 2, Entries 14 and 15). The catalyst was reusable although a gradual declinewas observed in its activity. All of the products were known and characterized by FT-IR, ^{1}H-NMR, and the physical properties of those reported in the literature.



Scheme 2. Synthesis of 14-phenyl-14*H*-dibenzo[*a*,*j*]xanthenes.

According to the obtained best condition, we have applied 2-naphthol and various aldehydes, for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthene derivatives (scheme 3 and Table 3).

Table 2. Synthesis of 14-(phenyl)-dibenzo[*a*,*j*]xanthene under various conditions[a]

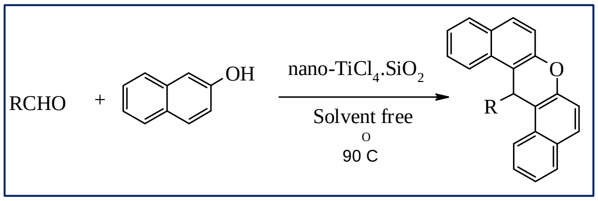
En	(g) Catalyst	Solvent	Cond.	Time(h)/ Yeild(%)$^{Ref.}$
1	50% $TiCl_4.SiO_2$ (0.1)	Chloroform	r.t	15/5
2	50% $TiCl_4.SiO_2$ (0.1)	Ethanol	r.t	15/5
3	50% $TiCl_4.SiO_2$ (0.1)	Solvent free	r.t	15/5
4	30% $TiCl_4.SiO_2$ (0.1)	Solvent free	90 °C	0.5/60
5	40% $TiCl_4.SiO_2$ (0.1)	Solvent free	90 °C	0.5/77
6	50% $TiCl_4.SiO_2$ (0.1)	Solvent free	90 °C	0.5/96
7	50% $TiCl_4.SiO_2$ (0.025)	Solvent free	90 °C	0.5/60
8	50% $TiCl_4.SiO_2$ (0.075)	Solvent free	90 °C	0.5/95
9	50%$TiCl_4.SiO_2$ (0.1)	Solvent free[b]	MM	1/60
10	50%$TiCl_4.SiO_2$ (0.1)	EtOAc[c]	Sonication	30min/74
11	50%$TiCl_4.SiO_2$ (0.1)	Solvent free[d]	MW	20min/80
12	50% nano-$TiCl_4.SiO_2$ (0.05)	Solvent free	90 °C	0.1/95
13	50% nano-$TiCl_4.SiO_2$ (0.025)	Solvent free	90 °C	0.1/89
14	50% nano-$TiCl_4.SiO_2$ (0.05), 2nd run	Solvent free	90 °C	0.5/88
15	50% nano-$TiCl_4.SiO_2$ (0.05), 3rd run	Solvent free	90 °C	1.5/80
16	Dowex-50 W	Solvent free	100 °C	2/86[18]
17	$NH_4H_2PO_4/SiO_2$	Water	Ultrasound/40 °C	40min/88[19]
18	$HClO_4$–SiO_2	Solvent-free	125 °C	8min/92[20]
19	PW acid	Solvent-free	100°C	1.5/91[21]
21	Cyanuric chloride	Solvent-free	110°C	32min/91[22]
22	$Yb(OTf)_3$	Reflux	110°C	7/89[23]
23	Silica sulfuric acid	Solvent-free	80 °C	45min/86[16]

[a] The molar ratio of 2-naphthol : benzaldehyde is 2:1

[b] using mixer mill (MM 400) in 25 Hz frequency.

[c] usingBANDELIN Sonopulse HD 3200 Ultrasonic apparatus with power equal to 20 KHz.

[d] Using microwave oven Kenwood, 1300W.



Scheme 3. Synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthene derivatives.

Table 3. Synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenesin the presence of 50% nano-TiCl$_4$.SiO$_2$.

Ent.	**R**^{a}	**Yield**^{b} **(%)**	**Mp (^{o}C)**	
			Found	**Reported**^{ref}
1	CH_3CH_2	88	149–152	150-152[16]
2	$(CH_3)_2CH$	85	156–157	155-157[17]
3	$CH_3CH_2CH_2$	89	152–154	152-154[18]
4	C_6H_5	96	184–185	185[18]
5	4-Br C_6H_5	97	296–297	297[19]
6	4-OMe	89	202-205	203-205[20]
7	3-Cl	96	209–211	210-213[21]
8	2-OMe	88	256–259	258-259[22]
9	4-Me	94	227–229	227-229[23]
10	4-Cl	97	289–290	289[24]
11	2-Cl	95	214–216	214-216[24]
12	4-NO_2	93	310–312	311-312[26]
13	3-NO_2	90	210–211	211[24]
14	3-CH_3	91	197-199	198[24]
15	3-Br	96	189-191	190-192[26]
16	2-NO_2	97	214-215	214[26]

[a] The ratio of 2-naphthol (mmol): aldehyde (mmol): 50% nano-TiCl$_4$.SiO$_2$(g) is 2:1:0.05

4. Conclusion

In conclusion, this paper demonstrates simple methods for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes using 50% nano-TiCl$_4$.SiO$_2$ as a reusable, inexpensive, and efficient catalyst. Short reaction times, high yields, scale up, and easy work-up are the advantages of this protocol.

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