Journal of Molecular Catalysis A: Chemical 350 (2011) 16–25

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Solvent free synthesis of quinoxalines, dipyridophenazines and chalcones under microwave irradiation with sulfated Degussa titania as a novel solid acid catalyst

B. Krishnakumar, M. Swaminathan*

Department of Chemistry, Annamalai University, Annamalainagar, Tamil Nadu 608 002, India

ARTICLE INFO

Article history:
Received 2 July 2011
Received in revised form 29 August 2011
Accepted 29 August 2011
Available online 3 September 2011

Keywords:
Sulfated TiO_2–P25
Quinoxaline
Dipyridophenazine
Chalcone
Microwave

ABSTRACT

Sulfated TiO_2–P25 (Degussa titania) has been prepared by sol–gel method using H_2SO_4 and characterized by FT-IR, XRD, FE-SEM, EDS, HR-TEM, XPS, DRS and BET surface area measurements. Sulfate loading by H_2SO_4 increases the Lewis acidity of Degussa tiatania. This catalyst gives an excellent yield with less reaction time and is an inexpensive and easily recyclable solid acid catalyst for the synthesis of quinaxalines, dipyridophenazines and chalcones under microwave irradiation.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous catalysts dominate the industrial scenery mainly due to the facility of recovery and reusability [1]. A number of organic transformations have been studied with these catalysts leading to better regio and stereo selectivity [2,3]. In general, metal oxides have been used extensively either as such or as supports in conjunction with other active components for many industrial oxidation, reduction and acid–base catalyzed reaction. Among the semiconductor oxides TiO_2 has been widely used as a benchmark catalyst due to its good photocatalytic activity, low cost and long term stability. TiO_2–P25, is a mixture of anatase and rutile forms of TiO_2 (80:20) specially made for photocatalysis by Degussa company, France. This catalyst with high surface area has been widely used because of its relatively high level of activity in many photocatalytic reactions [4]. Catalytic efficiencies of most of the developed new photocatalysts are usually compared with this specially made catalyst. Furthermore this catalyst is very cheap and available in large quantities. We have earlier reported the application of sulfated titania obtained from H_2SO_4 and prepared TiO_2 (anatase form) for the synthesis of quinoxalines, dipyridiphenazines, chalcones and for N-formylation of amines [1,5,6]. It was found that TiO_2–P25 was more efficient than TiO_2 in N-fomylation reaction [6]. This prompted us to prepare sulfated TiO_2–P25 and to test its catalytic efficiency. Pyridine adsorption method [7] reveals that the surface acidity of sulfated TiO_2–P25 is 4.25 times higher than TiO_2–P25 [8]. This shows that TiO_2–P25–SO_4^{2-} has more acidic sites when compared to TiO_2–P25.

Quinoxalines are known for their pharmacological activities [9–13]. Dipyridophenazines have been used as ligands for the formation of metal–ligand complexes with attractive features [14]. The most common method of preparation of quinoxalines is the double condensation of an aryl 1,2-diamine with a 1,2-dicarbonyl compound in refluxing ethanol or acetic acid for 2–12 h giving 34–85% yield [14–16].

Lewis acids and many other catalysts including gallium(III) triflate [17], montmorillonite K10 [18], sulfamic acid [19], cupric sulfate pentahydrate [20], Zn (L-proline) [21], I_2 [22,23], Ni nanoparticles [24], cellulose sulfuric acid (CSA) [25], silica sulfuric acid (SSA) [26], sulfated titania [1,8], Zn^{2+}-montmorillonite K10 clay [27] and methanol/acetic acid [28] have been used for the preparation of quinoxalines and dipyridophenazines. Chalcones were used as key precursors in the synthesis of a large array of biologically important heterocycles [29–31]. α,α′-Bis(substituted benzylidene)cycloalkanones, obtained by the crossed aldol condensation between cycloalkanone and benzaldehydes have been used as precursors for the synthesis of bioactive pyrimidine derivatives. These compounds have gained much importance as they are used as agrochemical, pharmaceutical and perfume intermediates [32]. Hence, the synthesis of chalcones has generated vast interest to organic/medicinal chemists. Acid and base catalyzed methodologies have been reported for the synthesis of chalcones [33–41]. But the reported procedures for quinoxalines and chalcones have

* Corresponding author. Tel.: +91 4144 225072; fax: +91 4144 225072.
E-mail address: chemres50@gmail.com (M. Swaminathan).

1381-1169/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2011.08.026

several disadvantages such as long reaction times (14 h–5 days), difficulty in the catalyst preparation, high temperature, use of special apparatus, costly reagents, etc. High temperature and long reaction time may lead to the formation of the side products and necessitated elaborative work up in the purification processes. Synthesis of these compounds using the recyclable heterogeneous photocatalysts will be more economical and eco-friendly.

We had reported the synthesis of quinoxalines and dipyridophenazines using TiO_2–P25–SO_4^{2-} at room temperature in the solvent ethanol [8]. It has been well established that microwaves shorten the reaction time and improve product yields without the use of solvents [42–44]. So, we tried the synthesis of quinoxaline and dipyridopyridine derivatives and chalcones under irradiation with microwaves. Herein we report a recyclable, easily separable, eco-friendly and highly effective catalytic system TiO_2–P25–SO_4^{2-} for the synthesis of quinoxalines, dipyridophenazines and chalcones (mono- and di-) under microwave irradiation.

2. Experimental

2.1. Materials

1,2-Phenylenediamine, substituted diamines, benzil, Acetophenones, benzaldehydes, and cyclohexanone (Aldrich chemicals) were used as received. A gift sample of TiO_2–P25 was obtained from Degussa (Germany). It is an 80:20 mixture of anatase and rutile with the particle size of 30 nm and BET specific area 50 $m^2\,g^{-1}$. H_2SO_4 (Fischer 98%) was used as received. 1,10-Phenanthroline-5,6-dione was prepared according to the literature procedure [15].

2.2. Preparation of sulfate loaded TiO_2–P25

About 2.7 g of TiO_2–P25 was suspended in 100 mL of 2-propanol and to this solution 3.2 mL of 1 M H_2SO_4 was added drop wise under vigorous stirring. The resulting colloidal suspension was stirred for 4 h. The gel obtained was filtered, washed and dried in an air oven at 100 °C for 12 h. Addition of $BaCl_2$ to filtrate gave no precipitate indicating that all the sulfate ions were completely loaded on the gel. This catalyst contained 5 wt% of SO_4^{2-}. Sulfate content of the catalyst was determined from the amount of H_2SO_4 taken for the preparation of the catalyst.

2.3. Apparatus

The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of BET equation using a micrometrics ASAP 2020 V3.00 H. Powder X-ray diffraction patterns were obtained using X'Per PRO diffractometer equipped with a CuK_α radiation (wavelength 1.5406 Å) at 2.2 kW max. Peak positions were compared with the standard files to identify the crystalline phase. Avatar-330 FT-IR spectrophotometer was used for recording IR spectra. Higher resolution transmission electron microscope (HR-TEM) images were recorded using a JEOL JEML-3010 high-resolution transmission electron microscope. The working voltage of TEM was 300 keV. The morphology of catalyst was examined using a JEOL JSM-6701F cold field emission scanning electron microscope (FE-SEM). Before FE-SEM measurements, the samples were mounted on a gold platform placed in the scanning electron microscope for subsequent analysis at various magnifications. Proton and carbon NMR spectra were recorded on a BRUKER AVIII FT-NMR spectrometer operating at 500 MHz for all the samples. For GC analysis, Perkin-Elmer GC-9000 with a capillary column of DB-5 and flame ionization detector was used. GC/MS analysis was carried out using GC model: Varian GC-MS-Saturn 2200 Thermo, capillary column VF5MS (5% phenyl-95% methylpolysiloxane), 30 m length, 0.25 mm internal diameter, 0.25 μm film thickness, temperature of column range from 50 to 280 °C (10 °C min^{-1}) and injector temperature 250 °C. Microwave LG ECN:MG-395 WA/01, MOD: MG-395 WA model was used.

2.4. Preparation of quinoxaline and dipyridophenazine derivatives

To a mixture of an *o*-phenylenediamine (1 mmol) and 1,2-dicarbonyl compound (1 mmol) in dry media, 0.1 g of TiO_2–P25–SO_4^{2-} was added and the mixture was irradiated under micro oven at 480 W for 1 min. Completion of the reaction was tested by thin layer chromatography (TLC). After completion of the reaction, ethyl acetate was added to the solidified mixture and the insoluble catalyst was separated by filtration. The filtrate was dried over anhydrous Na_2SO_4. The solvent was evaporated to get the products. Then it was subjected to GC and GC–MS analysis for the determination of the yield of the products. The structures of products had been confirmed by FT-IR, ^1H NMR, ^{13}C NMR and GC–MS analysis. A variety of substituted 1,2-phenylenediamines were condensed with benzil and 1,10-phenanthroline-5,6-dione.

2.5. Preparation of 1,3-diphenylprop-2-en-1-one

To a mixture of acetophenone (1 mmol) and benzaldehyde (1.1 mmol) in dry media, 0.1 g of TiO_2–P25–SO_4^{2-} was added and the mixture was irradiated under micro oven at 480 W for 1 min. Completion of the reaction was tested by TLC. After completion of the reaction, products were separated and identified by the same procedure described in Section 2.4.

2.6. 2,3-Diphenylquinoxaline, ***3a***

m.p. = 125–126 °C; IR (KBr) (cm^{-1}) = 3055, 2921, 1542, 1344, 768, 696; ^1H NMR ($CDCl_3$, 500 MHz) δ = 8.19 (dd, 2H), 7.76 (dd, 2H), 7.5 (m, 4H), 7.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = aromatic carbons are observed at 128.30, 128.83, 129.05, 129.23, 129.87, 129.99, 134.90, 139.10, 141.24 and 153.49 (C=N); GC–MS (m/z) = 282.3 (M^+).

2.7. Dipyrido[3,2-a:2′,3′-c]phenazine, ***4a***

m.p. = 246–247 °C; IR (KBr) (cm^{-1}) = 3073, 2852, 1577, 1498, 1415, 1361, 1337, 739, 669; ^1H NMR ($CDCl_3$, 500 MHz) δ = 9.65 (2d, 2H), 9.27 (d, 2H), 8.36 (t, 2H), 7.94 (q, 2H), 7.82 (q, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = aromatic carbons are observed at 124.17, 127.62, 129.56, 130.69, 133.81, 141.14, 142.51, 148.40 (C=N of pyridine ring) and 152.53 (C=N of phenazine ring); GC–MS (m/z) = 282.1 (M^+).

2.8. 1,3-Diphenylprop-2-en-1-one, ***5a***

m.p. = 56–58 °C; IR (KBr) (cm^{-1}): 3058, 3019 (aromatic C(H str.), 1660 (C=O str.), 1571 (C=C str.), 1493, 1338, 1216, 1074 (other str. frequencies); ^1H NMR ($CDCl_3$, 500 MHz) δ = 7.84 (d, J = 15.5, 1Hβ), 7.55 (d, J = 15.5, 1Hα), 8.05 (m, 2H), 7.65–7.40 (other aromatic protons, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 190.43 (C=O), 132.82 (Cβ), 122.12 (Cα), 144.79–128.50 (aromatic carbons); GC–MS (m/z): 208.9 (M^+).

3. Results and discussion

3.1. Catalyst characterization

5 wt% sulfate loaded Degussa titania (TiO_2–P25–SO_4^{2-}) has been characterized by FT-IR, XRD, FE-SEM, EDS, HR-TEM, XPS, DRS and BET surface area measurements.

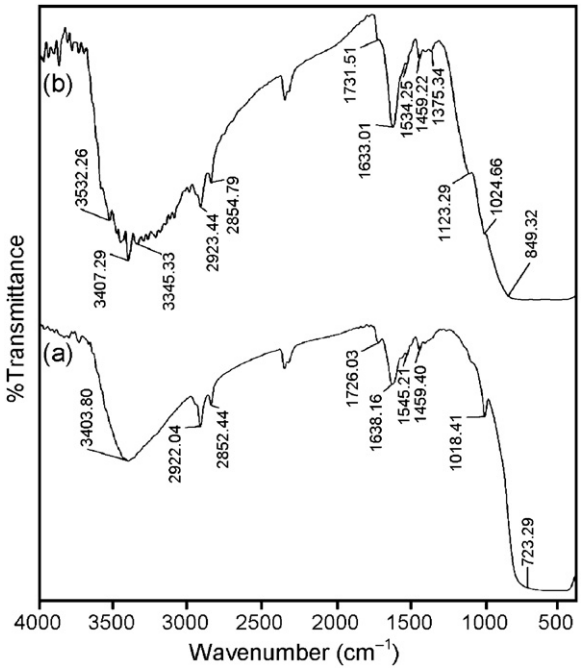


Fig. 1. FT-IR spectra of: (a) TiO_2–P25 and (b) TiO_2–P25–SO_4^{2-}.

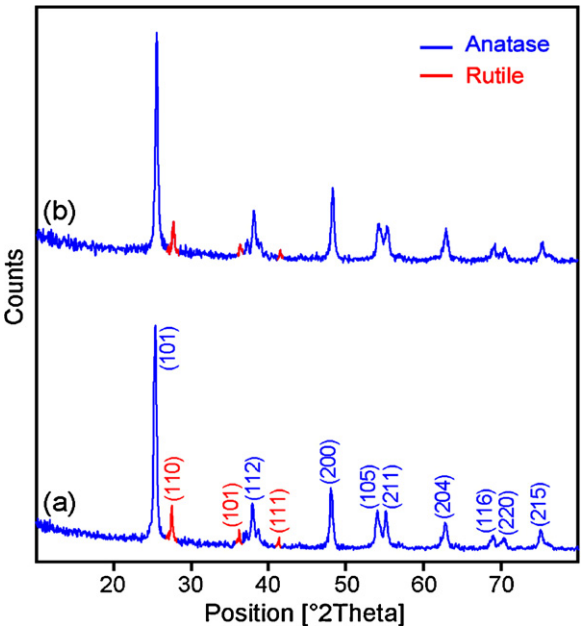


Fig. 2. XRD patterns of: (a) TiO_2–P25 and (b) TiO_2–P25–SO_4^{2-}.

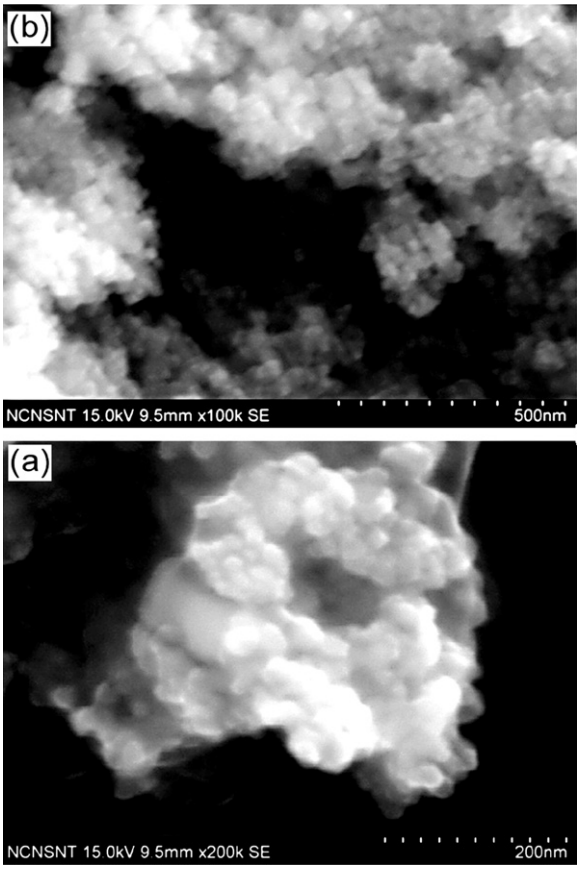


Fig. 3. FE-SEM images of: (a) TiO_2–P25–SO_4^{2-} 200k× and (b) TiO_2–P25–SO_4^{2-} 100k×.

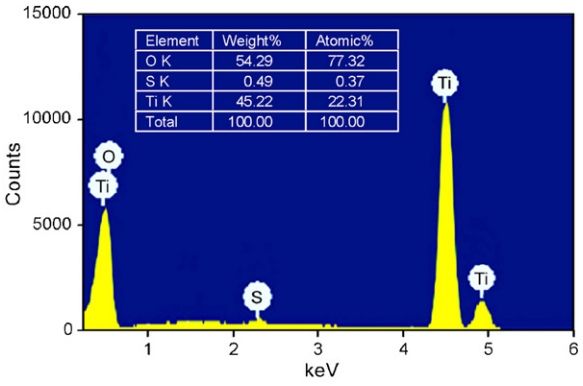


Fig. 4. EDS of TiO_2–P25–SO_4^{2-}.

3.1.1. FT-IR analysis

FT-IR spectra for the pure TiO_2–P25 and TiO_2–P25–SO_4^{2-} samples are shown in Fig. 1(a and b). TiO_2–P25–SO_4^{2-} gives two bands at 3345 and 3532 cm^{-1} in the 3300–3600 cm^{-1} regions. It means that there are two kinds of OH bond in the sample, in which one is ascribed to adsorbed water and the other is surface hydroxyl group of TiO_2. The peak corresponding to 1375 cm^{-1} is the stretching frequency of S=O and the peaks at 1123 and 1024 cm^{-1} are the characteristic frequencies of SO_4^{2-}.

3.1.2. XRD analysis

XRD pattern of TiO_2–P25 and TiO_2–P25–SO_4^{2-} are given in Fig. 2(a and b), respectively. Since Degussa TiO_2–P25 is a mixture of 80% anatase and 20% rutile, XRD pattern shows both anatase and rutile lines. Sulfate modification does not change the phase. The average crystallite size of TiO_2–P25–SO_4^{2-}, determined using Debye–Scherrer equation, is 17.8 nm. Sulfate modification reduces the size of TiO_2–P25.

3.1.3. FE-SEM analysis

Fig. 3(a and b) shows FE-SEM images of TiO_2–P25–SO_4^{2-} with 200 and 100k magnifications. TiO_2–P25–SO_4^{2-} exhibits a cloud like structure at higher magnification of 200k (Fig. 3(a)). Small spherical shaped particles are clearly seen at both magnifications (Fig. 3(a and b)).

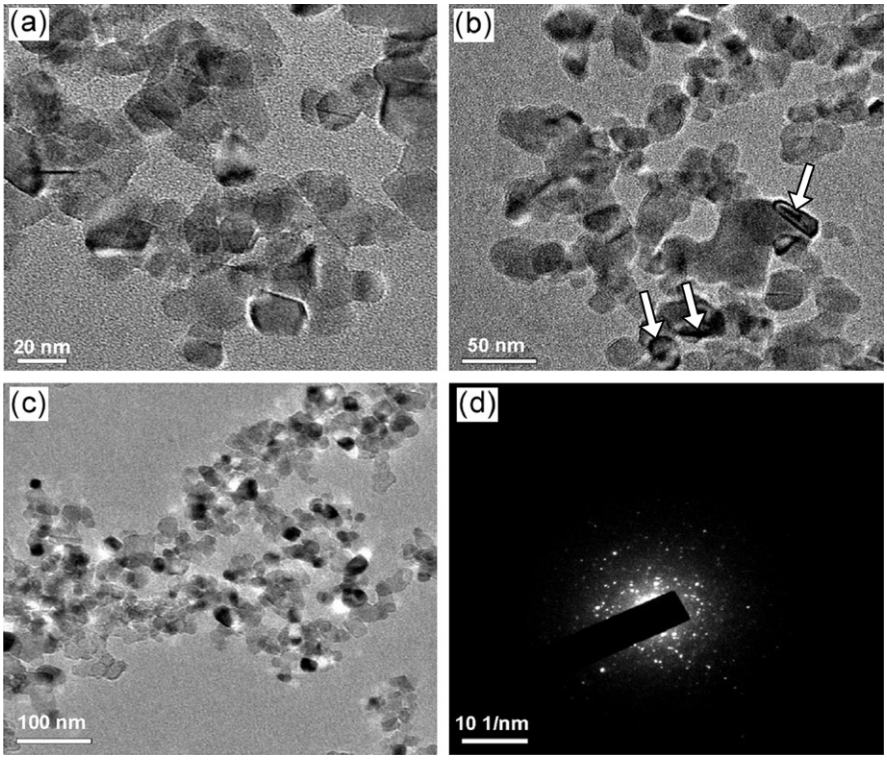


Fig. 5. HR-TEM images of TiO_2–P25–SO_4^{2-}: (a) 20 nm, (b) 50 nm (⇨ – corroded), (c) 100 nm and (d) SAED pattern.

3.1.4. EDS analysis

The EDS of TiO_2–P25–SO_4^{2-} is displayed in Fig. 4. The percentage of sulfur (0.49 wt%) in the sulfated titania at a particular region is also given in table (inset of Fig. 4). This spectrum shows the presence of sulfur.

3.1.5. HR-TEM analysis

HR-TEM images with different magnification of TiO_2–P25–SO_4^{2-} are shown in Fig. 5(a–c). TiO_2–P25–SO_4^{2-} particles are in the range from 20 to 100 nm. It can be seen from Fig. 5(b) that the particles are slightly corroded by sulfuric acid. This is indicated in the figure by the arrow. Selected area electron diffraction (SAED) pattern is shown in Fig. 5(d).

3.1.6. XPS analysis

The XPS survey spectrum (Fig. 6(a)) of the TiO_2–P25–SO_4^{2-} indicates the peaks of elements Ti, O, C and S. The carbon peak is attributed to the residual carbon from the sample and adventitious hydrocarbon from XPS instrument itself. Fig. 6(b–d) shows the binding energies of Ti, O and S, respectively. Binding energy peaks of Ti2p photoelectron peak occur at 458.8 and 464.5 eV (Fig. 6(b)). Normally, the Ti2p line in the case of pure TiO_2 samples can be observed at 458.5 eV [45,46]. A slight shift to (0.3 eV) higher binding energy is seen in sulfated catalyst. The O1s signal (Fig. 6(c)) shows two peaks at 530.0 and 531.7 eV. The main peak at 530.0 could be ascribed to lattice oxygen in TiO_2, while the signal at *ca.* 531.7 eV could be associated to oxygen in sulfate [47] and the binding energy of the S2p photoelectron peak is observed at 165.0 eV (Fig. 6(d)).

3.1.7. Diffuse reflectance spectra

The diffuse reflectance spectra TiO_2–P25 and TiO_2–P25–SO_4^{2-} are displayed in Fig. 7(a and b), respectively. There is a slight increase in absorbance from 350 nm to entire visible region in TiO_2–P25–SO_4^{2-}. The increase in absorbance in entire visible region reveals that this catalyst is more active in solar light.

Table 1
Surface properties of TiO_2–P25–SO_4^{2-}.

Properties	Values
BET surface area	49.8 $m^2\ g^{-1}$
Maximum pore volume	0.357201 $cm^3\ g^{-1}$
Molecular cross-sectional area	0.1620 nm^2

3.1.8. BET surface area analysis

In general the surface area of the catalysts is the most important factor influencing the catalytic activity. The surface area of TiO_2–P25–SO_4^{2-} was determined using the nitrogen gas adsorption method. The BET surface, pore volume and pore diameter of TiO_2–P25–SO_4^{2-} are given in Table 1. BET surface area of TiO_2–P25–SO_4^{2-} (49.8 $m^2\ g^{-1}$) is almost same as the surface area of TiO_2–P25 (50 $m^2\ g^{-1}$).

3.2. Quinoxaline and dipyridophenazine derivatives

In our earlier report the condensation reaction of 1,2-phenylenediamine (*o*PD) **1a** and benzil **2a** was reported in the presence of TiO_2–P25–SO_4^{2-} with different concentrations of sulfate at room temperature for 5 min in ethanol medium [8]. Same reaction when performed under microwave irradiation in dry media (Scheme 1) gives 99% yield of product quinoxaline in 1 min. Structure of this quinoxaline was confirmed by spectral and GC–MS data. Only 40% of product was obtained when a mixture of 1,2-phenylenediamine **1a** (1 mmol) and benzil **2a** (1 mmol) was irradiated in micro oven without catalyst (480 W) for 1 min. This condensation reaction of *o*PD and benzil in the presence of different catalysts are compared and the results are summarized in Table 2. It clearly indicates that this method is better than the previously reported methods for the synthesis of quinoxaline derivatives.

Table 2
Comparison of condensation reaction of *o*-Phenylenediamine and benzil in the presence of different catalysts.

Entry	Solvent	Reaction conditions	Time (min)	Yield	Reference
1	Ethanol/H_2O	$Ga(OTf)_3$/RT	5/30	>99/85	[17]
2	H_2O	montmorillonite K10/RT	2.5 h	>99	[18]
3	MeOH	SA/RT	5	>99	[19]
4	MeOH/H_2O	$CuSO_4{\cdot}5H_2O$/RT	5/15	97/96	[20]
5	Acetic acid	L–proline/RT	5	96	[21]
6	DMSO	I_2/RT	35	95	[22]
7	CH_3CN	I_2/RT	3	98	[23]
8	CH_3CN	Ni nanoparticle/RT	20	96	[24]
9	Ethanol/H_2O	CSA/RT	60 min/2.3 h	93/72	[25]
10	Ethanol	SSA/RT	15	98	[26]
11	Ethanol/H_2O	TiO_2–P25–SO_4^{2-}/RT	5/15	98/90.4	[8]
12	Ethanol/H_2O	TiO_2–SO_4^{2-}/RT	5/10	99.2/97.3	[1]
13	H_2O–CH_3CN	Zn^{2+}–montmorillonite K10/RT	2.5 h	89	[27]
14	MeOH	acetic acid/MW	5	99	[28]
15	Solvent free	TiO_2–P25–SO_4^{2-}/MW	1	99.0	Present work

SA = sulfamic acid, CSA = cellulose sulfuric acid, SSA = silica sulfuric acid, RT = room temperature, MW = microwave irradiation.

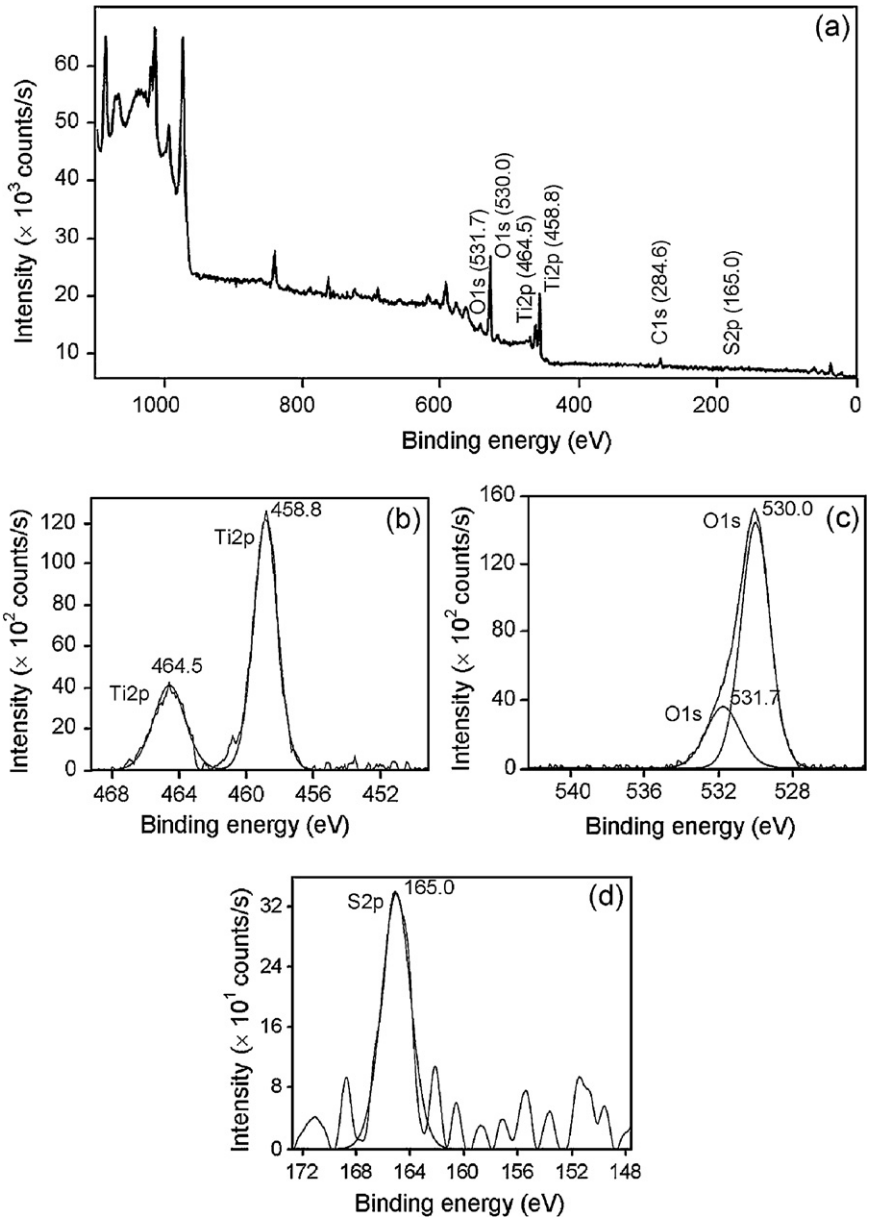
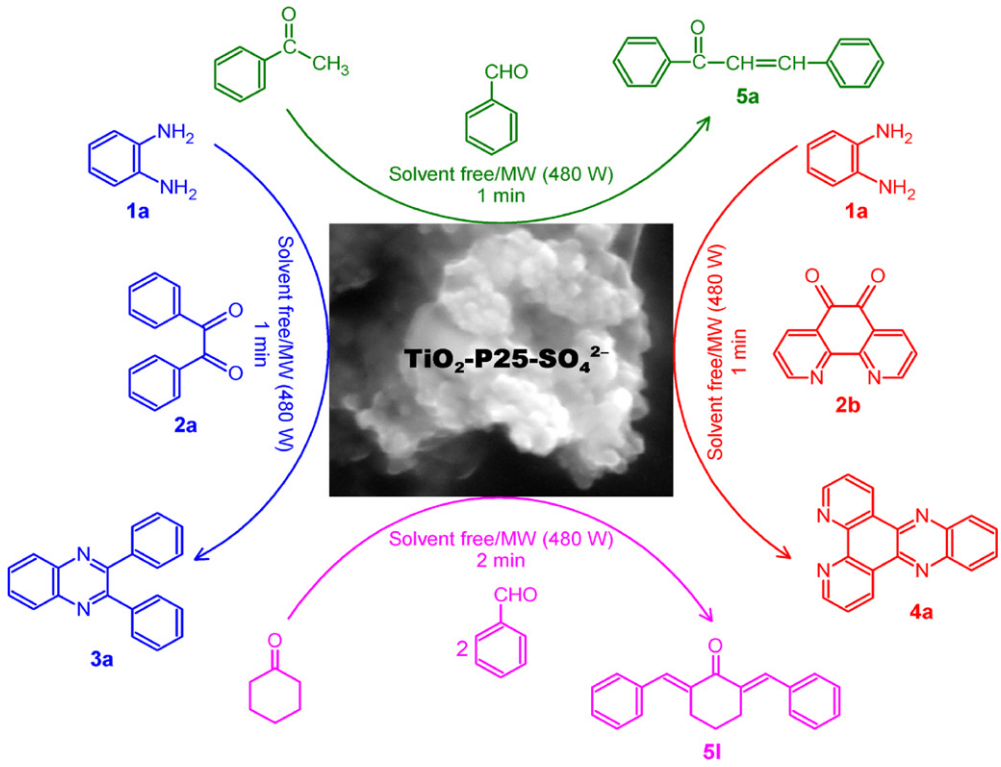


Fig. 6. XPS of TiO_2–P25–SO_4^{2-}: (a) survey spectrum, (b) Ti2p peak, (c) O1s peak and (d) S2p peak.



Scheme 1. Organic transformations catalyzed by TiO_2–P25–SO_4^{2-} under microwave irradiation.

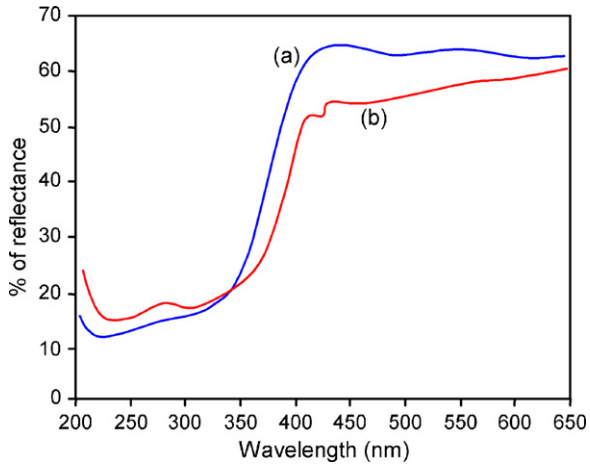


Fig. 7. DRS of: (a) TiO_2–P25 and (b) TiO_2–P25–SO_4^{2-}.

To find out the scope of this new protocol, we used various substituted 1,2-phenylenediamines and the results obtained are summarized in Table 3. This method was also applied for the condensation of 1,2-phenylenediamine with 1,10-phenanthroline-5,6-dione **2b** (Scheme 1) under the same conditions used for quinoxalines and the product dipyrido[3,2-a:2′,3′-c]phenazine **4a** was obtained in excellent yield (99.0%) within 1 min (Table 4, entry 1). Structure of this product was confirmed by spectral and GC–MS data. All the reactions with substituted 1,2-phenylenediamines proceeded very cleanly with microwave irradiation and no undesirable side products were formed, but the yields were highly dependent on substituents. Analysis of results presented Tables 3 and 4 show that electron-donating groups at the phenyl ring of 1,2-diamine favor the formation of product (Table 3, entry 2; Table 4, entry 2), while, electron-withdrawing groups such as fluoro, chloro and carboxy slightly decrease the product yields (Table 3, entries 3–5; Table 4, entries 3–5) with longer reaction times. Substrate with the strong electron-withdrawing NO_2 group gave moderate yield even with 10 min irradiation (Table 3, entry 6 – 80.0%; Table 4, entry 6 – 85%). At room temperature in ethanol, NO_2 substituted *o*PD gave trace of product in both condensation reactions [8]. 2,3-Diaminopydrine and aliphatic diamine (ethylene diamine) also gave good yields (Table 3, entries 7 and 8; Table 4, entries 7 and 8).

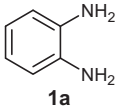
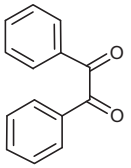
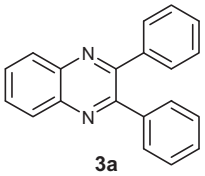
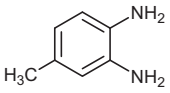
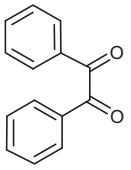
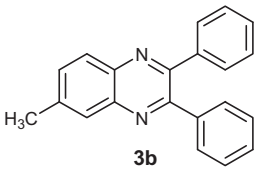
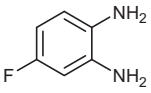
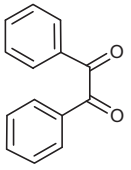
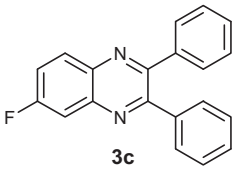
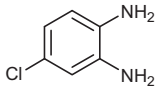
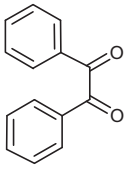
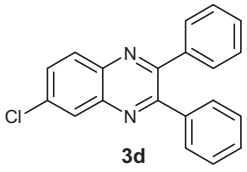
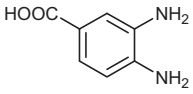
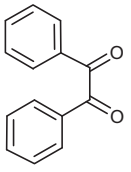
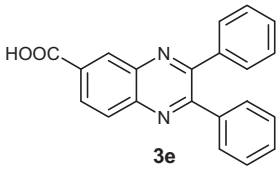
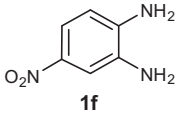
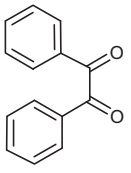
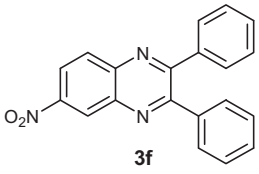
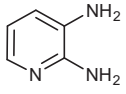
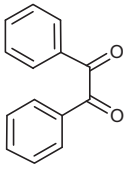
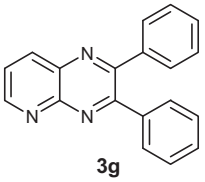
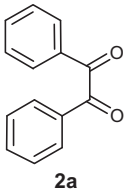
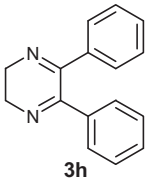
As reported earlier this condensation reaction follows the same mechanism for acid catalyzed condensation reactions [8,18]. The possibility of recycling the catalyst (TiO_2–P25–SO_4^{2-}) was examined for the reaction of *o*-phenylenediamine **1a** and benzil **2a**. When the reaction was complete, ethyl acetate was added to the solidified mixture and the insoluble catalyst was separated by filtration. The separated catalyst could be used five times without any treatment, and its catalytic activity was found to be 98% even at fifth run.

3.3. Chalcone derivatives

When a mixture of acetophenone (1 mmol) and benzaldehyde (1.1 mmol) without solvent was irradiated in micro oven (480 W) for 5 min no product was formed and further increase of irradiation time induced evaporation and charring. But the, addition of 0.1 g of TiO_2–P25–SO_4^{2-} to this mixture has initiated condensation reaction producing 99% 1,3-diphenylprop-2-en-1-one **5a** (chalcone) in 1 min (Scheme 1) (Table 5, entry 1). Structure of this product has been confirmed by spectral and GC–MS data.

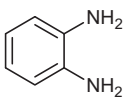
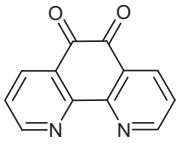
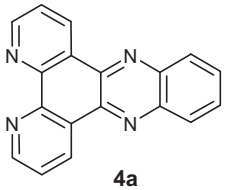
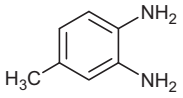
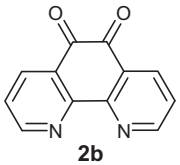
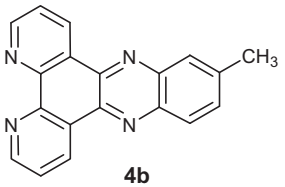
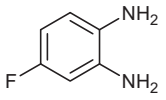
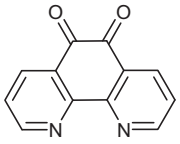
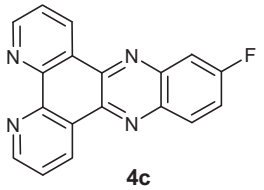
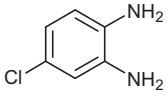
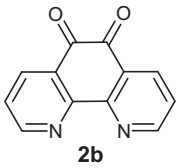
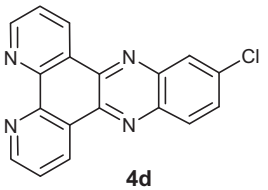
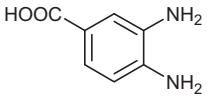
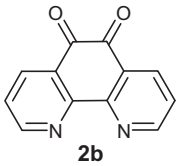
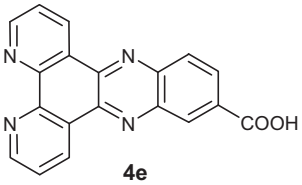
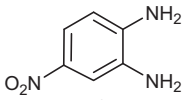
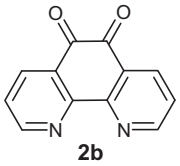
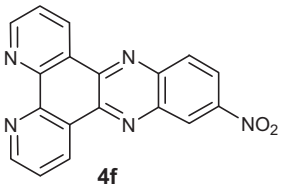
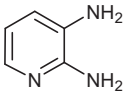
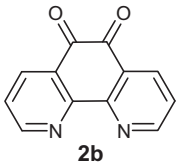
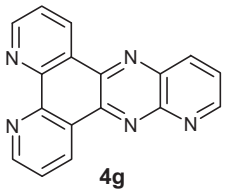
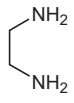
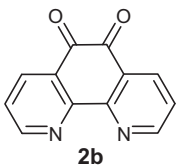
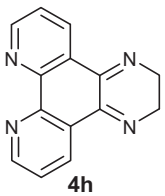
In order to show the applicability of this new protocol, we used various substituted benzaldehydes with different ketones and percentage yields of chalcones obtained are summarized in Table 5. Product yields with substituted benzaldehydes were highly dependent on the substituents. It is found that electron-donating groups at the phenyl ring of benzaldehyde favored the formation of product (Table 5, entries 2 and 3). In contrast, electron-withdrawing groups such as bromo, fluoro and chloro gave slightly lower yields (Table 5,

Table 3
Quinoxaline derivatives from different 1,2-diamines and 1,2-diketone (benzil) catalyzed by TiO_2–P25–SO_4^{2-} under microwave irradiation.

Entry	1,2-Diamine	1,2-Diketone	Product	Time (min)	Yield[a] (%)
1	 **1a**	 **2a**	 **3a**	1	99.0
2	 **1b**	 **2a**	 **3b**	2	99.0
3	 **1c**	 **2a**	 **3c**	4	97.0
4	 **1d**	 **2a**	 **3d**	4	96.0
5	 **1e**	 **2a**	 **3e**	8	85.0
6	 **1f**	 **2a**	 **3f**	10	80.0
7	 **1g**	 **2a**	 **3g**	5	92.0
8	 **1h**	 **2a**	 **3h**	4	93.0

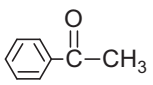
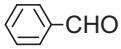
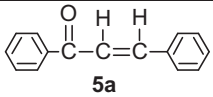
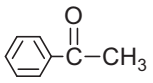
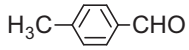
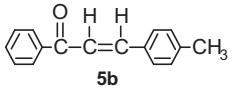
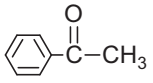
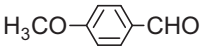
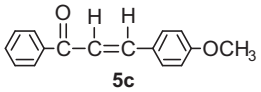
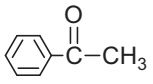
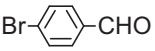
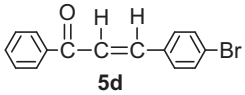
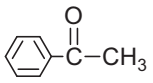
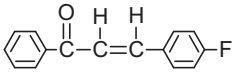
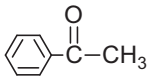
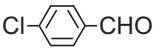
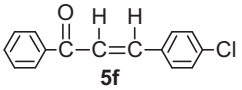
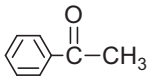
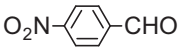
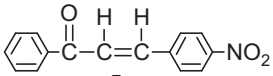
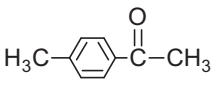
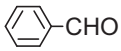
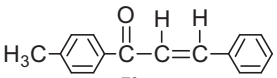
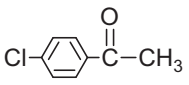
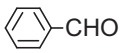
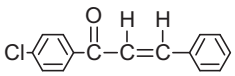
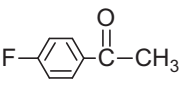
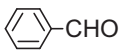
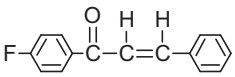
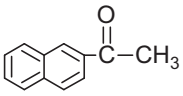
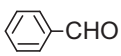
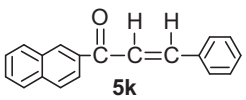
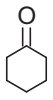
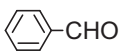
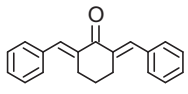
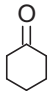
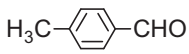
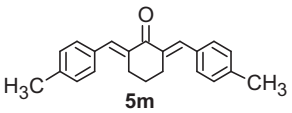
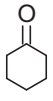
[a]Yields with respect to 1,2-diamine.

Table 4
Dipyridophenazine derivatives from different 1,2-diamines and 1,2-diketone (1,10-phenanthroline-5,6-dione) catalyzed by TiO_2–P25–SO_4^{2-} under microwave irradiation.

Entry	1,2-Diamine	1,2-Diketone	Product	Time (min)	Yield[a] (%)
1	 **1a**	 **2b**	 **4a**	1	99.0
2	 **1b**	 **2b**	 **4b**	2	99.0
3	 **1c**	 **2b**	 **4c**	3.5	97.5
4	 **1d**	 **2b**	 **4d**	3.5	97.0
5	 **1e**	 **2b**	 **4e**	7	88.0
6	 **1f**	 **2b**	 **4f**	9	85.0
7	 **1g**	 **2b**	 **4g**	4	94.0
8	 **1h**	 **2b**	 **4h**	3.5	95.0

[a]Yields with respect to 1,2-diamine.

Table 5
Percentage formation of chalcones from acetophenone, substituted acetophenones and cyclohexanone with different benzaldehydes under microwave irradiation.

Entry	Ketone	Aldehyde	Product	Time (min)	Yield[a] (%)
1			 **5a**	1	99.0
2			 **5b**	2	98.0
3			 **5c**	2	97.0
4			 **5d**	2	97.0
5			 **5e**	2	94.0
6			 **5f**	2	80.0
7			 **5g**	3.5	58.0
8			 **5h**	3.5	98.0
9			 **5i**	3.5	90.0
10			 **5j**	3.5	89.0
11			 **5k**	3.5	68.8
12			 **5l**	2	98.0
13			 **5m**	3	96.0
14			**5n**	3.5	95.0
15			**5o**	3.5	94.0

[a]Yields with respect to ketone.

entries 4–6). Substrate bearing a strong electron-withdrawing NO_2 group gave only 58% product even for 3.5 min irradiation (Table 5, entry 7).

This condensation reaction with substituted acetophenones proceeded smoothly at microwave condition without the formation of side products (Table 5, entries 8–10). 2-Acetylnaphthalene gave moderate yield of 68.0% (Table 5, entry 11). α,α′-Bis(substituted benzylidene)cycloalkanones were efficiently prepared from cyclohexanone and benzaldehydes through crossed-aldol condensation. This crossed aldol condensation was carried out under same conditions by taking 1:2 mole ratio of cyclohexanone and aldehydes in the presence of catalyst to give the desired bis(arylmethylidene)-cyclohexaones **5l–5o** in excellent yields (Scheme 1), (Table 5, entries 12–15). Mechanism of chalcone formation is similar to the mechanism proposed earlier for sulfated titania [5]. Reusability of this catalyst was tested for the reaction of benzaldehyde and acetophenone. Efficiency of this catalyst was found to be 98% even at the fifth run.

4. Conclusions

We successfully developed a simple, efficient and eco-friendly and solvent free and easy method for the synthesis of quinoxaline and dipyridophenazine derivatives from various 1,2-phenylenediamines using cheap TiO_2–P25–SO_4^{2-} as catalyst under microwave irradiation. This method gives a significant yield of quinoxaline and dipyridophenazine derivatives even with NO_2 substituted *o*PD. This catalyst was also efficient for the synthesis of chalcones and bis(substituted benzylidene)cyclohexanones by crossed aldol condensation. This reaction follows the mechanism of acid-catalyzed condensation. TiO_2–P25–SO_4^{2-} has more acidic sites when compared to TiO_2–P25. Presence of sulfur has been confirmed by FT-IR, EDS and XPS analysis. This method has the following advantages: (i) an inexpensive, green and reusable catalyst, (ii) high product yield under mild conditions and (iii) no solvent is needed. These advantages make this method as a green chemical process for the preparation of quinoxaline and dipyridophenazine, chalcones and bis(substituted benzylidene)cyclohexanones derivatives. We believe this novel methodology will find wide applications in organic synthesis.

Supporting information

GC–MS spectra (Figs. S1–S31) of all the compounds.

Acknowledgements

One of the authors M. S is thankful to CSIR, New Delhi for financial support through research grant No. 21(0799)/10/EMR-II. One of the authors B. K is thankful to CSIR, New Delhi, for the award of Senior Research Fellowship. We thank Catalysis Laboratory, IIT Madras, Chennai for BET surface area measurements. The authors also thank to Dr. T. Pradeep, IIT Madras, Chennai for the HR-TEM measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.08.026.

References

[1] B. Krishnakumar, R. Velmurugan, S. Jothivel, M. Swaminathan, Catal. Commun. 11 (2010) 997.
[2] D. Yin, D. Yin, Z. Fu, Q. Li, J. Mol. Catal. A 148 (1999) 87.
[3] J.S. Yadav, B.V.S. Reddy, K. Sadashiv, S. Raghavendra, K. Harikishan, Catal. Commun. 5 (2004) 111.
[4] M. Muruganandham, M. Swaminathan, Dyes Pigments 68 (2006) 133.
[5] B. Krishnakumar, R. Velmurugan, M. Swaminathan, Catal. Commun. 12 (2011) 375.
[6] B. Krishnakumar, M. Swaminathan, J. Mol. Catal. A 334 (2011) 98.
[7] J.M. Campelo, A. Garcia, J.M. Gutierrez, D. Luna, J.M. Marina, J. Colloid Interface Sci. 95 (1983) 544.
[8] B. Krishnakumar, M. Swaminathan, J. Organomet. Chem. 695 (2010) 2572.
[9] C.W. Lindsley, Z. Zhao, W.H. Leister, R.G. Robinson, S.F. Barnett, D. Defeo-Jones, R.E. Jones, G.D. Hartman, J.R. Huff, H.E. Huber, M.E. Duggan, Bioorg. Med. Chem. Lett. 15 (2005) 761.
[10] M. Loriga, S. Piras, P. Sanna, G. Paglietti, Farmaco 52 (1997) 157.
[11] Y.B. Kim, Y.H. Kim, J.Y. Park, S.K. Kim, Bioorg. Med. Chem. Lett. 14 (2004) 541.
[12] L.E. Seitz, W.J. Suling, R.C. Reynolds, J. Med. Chem. 45 (2002) 5604.
[13] W. He, M.R. Myers, B. Hanney, A.P. Spada, G. Bilder, H. Galzcinski, D. Amin, S. Needle, K. Page, Z. Jayyosi, M.H. Perrone, Bioorg. Med. Chem. Lett. 13 (2003) 3097.
[14] J.E. Dickeson, L.A. Summers, Aust. J. Chem. 23 (1970) 1023.
[15] M. Yamada, Y. Tanaka, Y. Yoshimoto, S. Kuroda, I. Shimao, Bull. Chem. Soc. Jpn. 65 (1992) 1006.
[16] D.J. Brown, Quinoxalines: supplement II, in: The Chemistry of Heterocyclic Compounds, John Wiley and Sons, New Jersey, 2004.
[17] J. Jing Cai, J. Ping Zou, X. Qiang Pan, W. Zhang, Tetrahedron Lett. 49 (2008) 7386.
[18] T.K. Huang, R. Wang, L. Shi, X.X. Lu, Catal. Commun. 9 (2008) 1143.
[19] H.R. Darabi, S. Mohandessi, K. Aghapoor, F. Mohsenzadeh, Catal. Commun. 8 (2007) 389.
[20] M.M. Heravi, Sh. Taheri, Kh. Bakhtiari, H.A. Oskooie, Catal. Commun. 8 (2007) 211.
[21] M.M. Heravi, M.H. Tehrani, Kh. Bakhtiari, H.A. Oskooie, Catal. Commun. 81 (2007) 341.
[22] R.S. Bhosale, S.R. Sarda, S.S. Ardhapure, W.N. Jadhav, S.R. Bhusare, R.P. Pawar, Tetrahedron Lett. 46 (2005) 7183.
[23] S.V. More, M.N.V. Sastry, C.C. Wang, C.F. Yao, Tetrahedron Lett. 46 (2005) 6345.
[24] A. Kumar, S. Kumar, A. Saxena, A. De, S. Mozumdar, Catal. Commun. 9 (2008) 778.
[25] A. Shaabani, A.H. Rezayan, M. Behnam, M. Heidary, C. R. Chim. 12 (2009) 1249.
[26] A. Shaabani, A. Maleki, Chin. J. Chem. 25 (2007) 818.
[27] A. Dhakshinamoorthy, K. Kanagaraj, K. Pitchumani, Tetrahedron Lett. 52 (2011) 69.
[28] Z. Zhao, D.D. Wisnoski, S.E. Wolkenberg, W.H. Leister, Y. Wang, C.W. Lindsley, Tetrahedron Lett. 45 (2004) 4873.
[29] A.L. Marzinzik, E.R. Felder, J. Org. Chem. 63 (1998) 723.
[30] M. Bennett, A.J. Burke, W.I. O'Sullivan, Tetrahedron 52 (1996) 7163.
[31] G. Bose, E. Mondal, A.T. Khan, M.J. Bordoloi, Tetrahedron Lett. 42 (2001) 8907.
[32] Y. Riadi, R. Mamouni, R. Azzalou, R. Boulahjar, Y. Abrouki, M. El Haddad, S. Routier, G. Guillaumet, S. Lazar, Tetrahedron Lett. 51 (2010) 6715.
[33] M. Liu, P. Wilairat, M.L. Go, J. Med. Chem. 44 (2001) 4443.
[34] J.N. Dominguez, J.E. Charris, G. Lobo, N.G. Dominguez, M.M. Moreno, F. Riggione, E. Sanchez, J. Olson, P.J. Rosenthal, Eur. J. Med. Chem. 36 (2001) 555.
[35] V.J. Ram, A.S. Saxena, S. Srivastava, S. Chandra, Bioorg. Med. Chem. Lett. 10 (2000) 2159.
[36] M.E. Zawaagstra, H. Timmerman, M. Tamura, T. Tohma, Y. Wada, K. Onogi, M.-Q. Zhang, J. Med. Chem. 40 (1997) 1075.
[37] Y. Jahng, L.X. Zhao, Y.S. Moon, A. Basnet, E.K. Kim, H.W. Chang, H.K. Ju, T.C. Jeong, E.S. Lee, Bioorg. Med. Chem. Lett. 14 (2004) 2559.
[38] A.R. Alcantara, J.M. Marinas, J.V. Sinisterra, Tetrahedron Lett. 28 (1987) 1515.
[39] J.T. Li, W.Z. Yang, S.X. Wang, S.H. Li, T.S. Li, Ultrason. Sonochem. 9 (2002) 237.
[40] N.O. Calloway, L.D. Green, J. Am. Chem. Soc. 59 (1937) 809.
[41] T. Szell, I. Sohar, Can. J. Chem. 47 (1969) 1254.
[42] K. Bougrin, A. Loupy, M. Soufiaoui, J. Photochem. Photobiol. C 6 (2005) 139.
[43] Y.H. Ju, R.S. Varma, Org. Lett. 7 (2005) 2409.
[44] G.W. Kabalka, L. Wang, V. Namboodiri, R.M. Pagni, Tetrahedron Lett. 41 (2000) 5151.
[45] B.M. Reddy, B. Chowdhury, P.G. Smirniotis, Appl. Catal. A 211 (2001) 19.
[46] B.M. Reddy, B. Chowdhury, E.P. Reddy, A. Fernandez, J. Mol. Catal. A 162 (2000) 423.
[47] G. Colon, M.C. Hidalgo, G. Munuera, I. Ferino, M.G. Cutrufello, J.A. Navio, Appl. Catal. B 63 (2006) 45.