Synthesis and characterization of $\text{TiO}_2\text{--SiO}_2$ nanoparticles as catalyst for dehydrogenation of 1,4-dihydropyridines

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Abstract. Nanoparticles of binary $\text{TiO}_2\text{--SiO}_2$ mixed oxides was prepared via sol–gel method using tetraethyl-orthosilicate (TEOS) and titanium isopropoxide (TIPP) in different reaction conditions (solvent and pH) using ammonium hydroxide, acetic acid, sodium hydroxide, ethyleneglycol and polyethylene glycol followed by calcination at 850–970 °C. The morphologies, structures and chemical compositions were determined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transmission infrared spectroscopy (FTIR) techniques. The catalytic activity of the obtained nanomaterials was explored for the dehydrogenation of 1,4-dihydropyridines (1,4-DHPs). Observation of 86–100% conversion and 100% selectivity towards the formation of desired products with prepared nanoparticles will be discussed here.

Keywords. Nanoparticles; nanorods; $\text{TiO}_2\text{--SiO}_2$ mixed oxides; dehydrogenation; 1,4-dihydropyridines.

1. Introduction

Many physical and chemical properties of metal oxides can be modified by interaction with a second oxide. In 1949, Thomas suggested that binary oxides' acidity originated from the isomorphous substitution of cations in the crystal structure of one oxide by cations of different elements (Thomas 1949; Hu *et al* 2003). $\text{TiO}_2\text{--SiO}_2$ mixed oxides can be considered as attractive materials for catalytic applications due to their high catalytic activity and selectivity either as catalysts or catalyst supports (Song *et al* 2002; Kim *et al* 2004; Yang *et al* 2005). Silica-modified titanium dioxide are generally synthesized via different methods such as chemical vapour deposition (CVD) (Li *et al* 2005), sol–gel (Balachandaran *et al* 2010), hydrothermal (Sayilkan *et al* 2007), microemulsion (Kim and Kim 2005), microwave (Jung *et al* 2007), ultrasonic microemulsion (Zhu *et al* 2007) and reflux procedures (Yang *et al* 2005). Sol–gel method has emerged as a promising processing route for the synthesis of nano-sized particles due to the simplicity of sol–gel processing in addition to its high purity resulting from the availability of high purity chemicals as raw materials (Kwon *et al* 2003). The sol–gel processing allows the formation of nanoparticle oxides with controlled size, porosity and shape (coatings, fibres, powders, monoliths). Moreover, it is particularly a useful method for the preparation of multi-component oxides with a high degree of homogeneity (Lafond *et al* 2002).

Herein, we prepared $\text{TiO}_2\text{--SiO}_2$ nanoparticles via sol–gel method by changing synthesis parameters (solvent

and pH) followed by using them as catalyst for oxidative aromatization of Hantzsch 1,4-DHPS to the corresponding substituted pyridines. In fact, dihydropyridines (DHPs) are analogues of nicotinamide adenine dinucleotide hydride (NADH) coenzyme (Mauzerall and Westheimer 1955). It has been found that NADH initially undergoes oxidative aromatization to the corresponding pyridine derivatives during the metabolism by the action of cytochrome P-450, present in liver (Guenerich *et al* 1991). Some pyridine derivatives are medicinally significant compounds and used as selective human adenosine receptor modulators (Guo *et al* 2007) protein kinase C (PKC) inhibitor (Karki 2010) or for treatment of atherosclerosis and other coronary diseases, respectively (Bischhoff *et al* 1997). The oxidation of Hantzsch 1,4-DHPs provides an easy access to the pyridine derivatives with anti-hypoxic and anti-ischemic activities. Some of these derivatives also exhibit acaricidal, insecticidal, bactericidal and herbicidal activities (Raghuvanshi and Singh 2008). 1,4-DHPS have been aromatized to pyridines by various reagents such as $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (Pfister and Rapid 1990) $\text{Cu}(\text{NO}_3)_2$ (Maquestiau *et al* 1998), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Mashraqui and Karnik 1991), $\text{Mn}(\text{OAc})_3$ (Varma and Kumar 1999), $\text{Zr}(\text{NO}_3)_4$, Pd/C (Sabitha *et al* 2003), RuCl_3/O_2 (Mashraqui and Karnik 1998), CrO_2 (Ko and Kim 1999), $\text{Fe}(\text{ClO}_2)_4$ (Nakamichi *et al* 2004), $\text{Mn}(\text{TPP})\text{Cl}/(\text{Bu}_4\text{N})\text{IO}_4$ (Nasr-Esfahani *et al* 2005), $\text{Mn}(\text{pbdo})_2\text{Cl}_2/\text{MCM-41}$ or $\text{Mn}(\text{pbdo})_2\text{Cl}_2/\text{Al-MCM-41}$ (Heravi *et al* 2009), $\text{SiO}_2/\text{P}_2\text{O}_5\text{--SeO}_2$ (Paul *et al* 2007) $\text{H}_6\text{P Mo}_9\text{V}_3\text{O}_{40}$ (Heravi *et al* 2007), silica supported cobalt catalysts (Shamim *et al* 2009) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}/\text{H}_2\text{O}_2$ (Sharma *et al* 2008). Some of these methods suffer from strong oxidative

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Scheme 1. Preparation and morphology of $\text{TiO}_2\text{-SiO}_2$ nanoparticles by changing synthesis parameters (pH and solvent).

Figure 1. SEM images of $\text{TiO}_2\text{-SiO}_2$ with (a) ethylene glycol; TS_{EG} , (b) acetic acid; $\text{TS}_{\text{CH}_3\text{COOH}}$, (c) NaOH; TS_{NaOH} , (d) polyethylene glycol; TS_{PEG} and (e) NH_4OH ; $\text{TS}_{\text{NH}_4\text{OH}}$.

Figure 2. TEM images of (a) TSEG and (b) TSNH₄OH.

Table 1. Effect of solvent and pH on morphology of TiO₂–SiO₂ nanoparticles.

Entry	pH	Solvent	Image
1	7	Isopropanol	
2	13	Isopropanol	
3	7	Dodecanol	
4	7	Ethanol	

conditions, tedious work up and side product formation. To my knowledge, in spite of using many reagents for dehydrogenation of DHPs, using nanoparticles as oxides or mixed oxides as catalysts for this purpose should be interesting subject for studies.

2. Experimental

Tetraethyl orthosilicate (TEOS, 98%), ammonium hydroxide (NH₄OH, 25%), acetic acid (AcOH), ethylene glycol (EG), polyethylene glycol (PEG), isopropanol, titanium isoperoxide (TIPP, 98%), sodium hydroxide (NaOH), ethanol

Figure 3. TGA of (a) TSEG, (b) TSCH₃COOH, (c) TSNaOH, (d) TSPG and (e) TSNH₄OH.

(EtOH), hydrogen peroxide (H₂O₂, 30%), benzaldehyde (PhCHO), ethyl acetoacetate (MeCOCH₂CO₂Et) and ammonium acetate (NH₄OAc) were prepared from Merck Chemical Company and used without further purification.

X-ray powder diffraction (XRD) data were recorded on a diffractometer type (Philips PW1800) at room temperature, operating at 40 kV and 30 mA, using CuKα₁ radiation ($\lambda = 1.5406 \text{ \AA}$). The nanostructures of the samples were analysed

Figure 4. X-ray powder diffraction patterns of (a) TSEG, TSCH₃COOH, TSNH₄OH (calcined at 850 °C) and TSPEG (calcined at 900 °C), (b) TSEG (calcined at 970 °C), (c) TSCH₃COOH (calcined at 970 °C), (d) TSNH₄OH (calcined at 970 °C) and TSNaOH (calcined at 850 °C) (■: anatase, ▲: cristobalite, ▼: rutile, ◆: opal).

by scanning electron microscopy (SEM; S-4160 Hitachi) and transmission electron microscopy (TEM; Philips EM 208s) at an accelerating voltage of 100 kV. Thermal studies were performed using Mettler–Toledo TGA/SDTA-851 at a heating rate of 25 °C/min, under oxygen atmosphere. FT–IR spectra were recorded on a Bruker Tensor 27 FT–IR spectrometer. Oxidative aromatization products were analysed by GC and GC–MS using an Agilent 6890 series with FID detector, HP-5, 5% phenylmethylsiloxane capillary and an Agilent 5973 network, mass selective detector, HP-5 MS 6989 network GC system, respectively.

2.1 Preparation of TiO₂–SiO₂ mixed oxides with different templates: general procedure

TiO₂–SiO₂ was prepared using PEG, EG, AcOH, NH₄OH and NaOH reagents. TIPP (10 mmol, 3 mL in 30 mL isopropanol) was added dropwise to TEOS (20 mmol, 6 mL in 30 mL isopropanol). 30 mmol of the reagent (with the exception that 0.1 mmol of polyethylene glycol in 30 mL water was used) was then added and the mixture was stirred for

Figure 5. FT–IR spectra of TSNH₄OH (a) before calcination, (b) after calcination at 850 °C and (c) reused as catalyst.

Scheme 2. Aromatization of 1,4-DHPs with TiO₂–SiO₂ nanoparticles.

10 min. The resultant sol was dispersed by means of ultrasonic within 20 min, followed by drying at room temperature overnight and calcined at 850–970 °C for 5 h.

2.2 Catalytic test

1,4-DHPs with R=H, Me or Ph (0.09 mmol), prepared based on the reported procedure (Zolfigol and Safaiee 2004), was added to a suspended solution of TiO₂–SiO₂ (0.01 g in 15 mL EtOH), followed by the addition of H₂O₂ (2 mL, 30%). The resultant mixture was stirred at 60 °C for several hours. The progress of the reaction was monitored by TLC. The catalyst

Table 2. Effect of time and amount of catalyst on aromatization of 1,4-DHP.

Entry	Time(h)	Amount (mg)	Conversion (%)	Selectivity (%)
1	1	30	25	100
2	3	30	58	100
3	5	30	92	100
4	5	3	85	100
5	5	5	87	100
6	5	10	96	100

Conditions: 0.09 mmol of 1,4-DHP was used, catalyst (TS_{NaOH}), solvent (EtOH, 10 mL), H₂O₂ (30%, 2 mL).

was then separated from the solution by centrifuge and the solution was subjected to GC and GC–MASS analyses.

3. Results and discussion

TiO₂–SiO₂ mixed oxides as nanoparticles or nanorods were prepared based on scheme 1 by changing synthesis parameters (solvent and pH) with acetic acid, ethylene glycol (EG), polyethylene glycol (PEG), sodium hydroxide and ammonium hydroxide were designated as TS_{CH₃COOH}, TS_{EG}, TS_{PEG}, TS_{NaOH} and TS_{NH₄OH}, respectively.

Typical SEM and TEM images of the prepared TiO₂/SiO₂ nanoparticles at 850 °C are presented in figures 1 and 2, respectively. With the exception of TS_{NaOH}, which is formed as nanorods on the basis of SEM images, TS_{CH₃COOH}, TS_{EG}, TS_{PEG}, and TS_{NH₄OH} are produced as nanoparticles. TEM images with ethylene glycol and NH₄OH are shown in figure 2. As seen, both are spherical with the average particle size of 20 and 8 nm, respectively.

The effect of solvent and pH on morphology of TiO₂–SiO₂ nanoparticles are shown in table 1. As seen in this table, morphology of TiO₂–SiO₂ with isopropanol as solvent and NaOH as nanorods, but changing the pH from 7–13, nanorods converted to spherical particles. In the case of dodecanol as solvent no distinct morphology was observed, but using ethanol as solvent, the morphology changed to nanoparticles. Therefore, for studying the role of other materials such as CH₃COOH, EG, PEG, NH₄OH, the desired reactions were carried out in isopropanol at pH = 7.

TGA curves of TS_{CH₃COOH}, TS_{EG}, TS_{PEG}, TS_{NaOH} and TS_{NH₄OH} are presented in figures 3(a–e), respectively. Two weight losses are observed, the first one is in the range of room temperature to 200 °C, due to the evaporation of the physically adsorbed water and isopropanol. The second stage is from 200–1000 °C, which indicates decomposition

of organic molecules (Yang *et al* 2005; Sirimahachai *et al* 2010).

XRD patterns of calcined TiO₂–SiO₂ nanoparticles at 850 and 970 °C for TS_{CH₃COOH}, TS_{EG} and TS_{PEG}, TS_{NaOH} and TS_{NH₄OH} are shown in figures 4(a–d). Based on the obtained results, XRD patterns of the calcined TS_{CH₃COOH}, TS_{PEG} and TS_{EG} at 850 °C are similar and show characteristic peaks of anatase at 2θ 25.21, 38.66, 48.10, 54.53, 62.56, 69.65, 75.41, 82.77 (JCPDS card no. 21-1272) on amorphous silica (figure 4(a)). Increasing the calcined temperature up to 970 °C for TS_{EG} indicates the anatase and rutile phases (figure 4(b)) with 2θ: 27.62, 36.32, 39.40, 41.41, 44.22, 54.53, 56.80, 62.96, 64.30, 69.25, 70 (JCPDS card no. 12-1276) on the cristobalite silica with 2θ 22 (JCPDS card no. 39-1425) and XRD pattern of TS_{CH₃COOH} shows formation of rutile phase and no anatase was detected (figure 4(c)). XRD patterns of TS_{NH₄OH} (at 970 °C) shows formation of anatase (61%) and rutile (31%) (figure 4(d)). It was also found that XRD pattern of TS_{NaOH} at 850 °C is similar to TS_{NH₄OH} at 970 °C.

FTIR spectra of TS_{NH₄OH} before and after calcinations at 850 °C are shown in figures 5(a–b). The broad bands appearing at 3500–3400 cm^{−1} may be attributed to the surface OH groups of TS_{NH₄OH} or adsorbed water (figure 5(a)). After calcination, intensity of this broad band decreases (figure 5(b)) and observation of bands at 1140, 1100, 1040, 945 and 795 cm^{−1}, 600–400 cm^{−1} are due to Si–O–Si (Aziz and Sopyan 2009; Nilchi *et al* 2010; Hilonga *et al* 2010), and Si–O–Ti or Ti–O–Ti vibrations (Smitha *et al* 2010), respectively. FT–IR spectra of calcined TS_{CH₃COOH}, TS_{NaOH}, TS_{EG} and TS_{PEG} at 850 °C are similar to that of TS_{NH₄OH}.

3.1 Catalytic activity

The prepared TS_{CH₃COOH}, TS_{NH₄OH}, TS_{EG}, TS_{PEG} and TS_{NaOH} as nanoparticles or nanorods were found as environmentally benign and effective catalyst for aromatization of Hantzsch 1,4-DHPs. Initially, diethyl 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate was examined as the representative 1,4-DHP for testing the catalytic experiments (scheme 2). The aromatization reaction of 1,4 DHP was carried out using TS_{NaOH} as model catalyst.

The effect of time and the amount of catalyst on aromatization of 1,4-DHP are given in table 2. The aromatization of 1,4-DHP was carried out in the presence of 30 mg of catalyst at different times, in order to choose the best reaction time. As can be seen, when R is Ph, DHP is mostly aromatized after 5 h, beyond which no considerable dehydrogenation occurs during the next 2 h. After optimization of the reaction time, reaction was carried out with 3, 5 and 10 mG catalyst, the conversion were increased from 86–96% with 100% selectivity, therefore, the rest of reactions were carried out with 10 mG catalyst within 5 h.

In order to see catalytic activity of the prepared nanospecies of TiO₂/SiO₂ on aromatization of 1,4-DHPs,

Table 3. Effect of prepared Ti–Si mixed oxides nanoparticles as catalyst for aromatization of 1,4-DHP.

Entry	Nanocatalyst	Conversion (%)	Selectivity (%)	Ti (%)	Si (%)
1	TS _{EG}	90	100	26.76	24.70
2	TS _{PEG}	86	100	25.65	25.78
3	TS _{NH₄OH}	100	100	33.24	22.39
4	TS _{CH₃COOH}	94	100	26.32	24.37
5	TS _{NaOH}	96	100	27.51	23.58

Conditions: substrate (0.09 mmol), catalyst (10 mg), solvent (EtOH, 10 mL), H₂O₂ (2 mL, 30%), 60°C, 5 h.

Table 4. Optimized reaction condition for aromatization of 1,4-DHPs derivatives with TS_{NH₄OH} effect.

Entry	R	Time (h)	Conversion (%)	Selectivity (%)
1	H	3	100	100
2	Ph	5	100	100
3	CH ₃	3	100	100

Conditions: 0.09 mmol of substrate was used, TS_{NH₄OH} (10 mg), solvent (EtOH, 10 mL), H₂O₂ (30%, 2 mL).

the best reaction conditions was carried out with TS_{NaOH}, TS_{NH₄OH}, TS_{EG}, TS_{PEG} and TS_{AcOH} as catalysts (entries 1–5, table 3). As seen in table 3, TS_{NH₄OH} shows 100% conversion and selectivity towards the corresponding product. Inspection of the results reveals that the trend of Ti contents are as TS_{NaOH} (27.51%) TS_{NH₄OH} (33.245%), TS_{EG} (26.76%), TS_{PEG} (25.65%) and TS_{CH₃COOH} (26.32%). Based on the obtained results, TS_{NH₄OH} with maximum amount of Ti shows the most catalytic activity towards the corresponding products.

Notably, utilization of the used TS_{NH₄OH} nanoparticles as catalyst in the second and third aromatization reactions of DHP proceeded selectively with 95 and 92% conversions, respectively. Finally, chemical analysis of the reaction filtrate showed that about 0.02% titanium has been lost from the catalyst during the reactions. Accordingly, FT–IR spectrum of the recovered TiO₂/SiO₂ nanoparticles (figure 5(c)) was similar to that of the freshly prepared catalyst (figure 5(a)). These

evidences clearly indicate the reusability and stability of our prepared catalysis system.

The established optimized reaction conditions were then tested by DHPs for R=H, Me or Ph (scheme 2). As indicated in table 4, for R=H, Ph and Me were obtained quantitatively in 3, 5, 3 h, respectively (entries 1–3, table 4). Compared to R=H, Me (entries 1 and 3, table 4), conversion of them takes place more efficiently. The observed rate enhancement trend by changing the Ph to Me and H is in accordance with the decreasing steric hindrance at the substituted carbon. Such trend is not unexpected since approaching rate of the active catalyst for removal of the *bis*-allylic H atom located next to Ph, Me or H groups increases with decreasing steric hindrance at the *bis*-allylic carbon.

Table 5 illustrates effect of solvent on the dehydrogenation of DHPs. As seen, no reaction is observed when catalyst is used in EtOH (entry 1, table 5). Similarly, reaction is inefficient, if catalyst is used in acetic acid (entry 2, table 5).

Table 5. Effect of solvent on aromatization of DHPs.

Entry	Solvent	Time (h)	Conversion (%)	Selectivity (%)
1	EtOH	8	0	0
2	AcOH	8	37	100
3	EtOH + H ₂ O ₂	6	96	100
4	AcOH + H ₂ O ₂	3	100	100
5	EtOH + H ₂ O ₂ ^a	8	5	100
6	EtOH + H ₂ O ₂ ^b	8	5	100

Catalyst: TiO₂/SiO₂ with NaOH, 0.03 (0.5 mmol) TiO₂/SiO₂, reflux, DHP: 0.09 mmol,
^aSiO₂ was used as catalyst, ^bno catalyst was used.

Moreover, in the absence of either catalyst or SiO₂ void of TiO₂, reaction is sluggish with H₂O₂ (entries 5 and 6, table 5). On the other hand, reaction proceeds to completion when catalyst and H₂O₂ are used in EtOH or AcOH (entries 3 and 4, table 5). Therefore, presence of H₂O₂ and catalyst are vital on reaction progress. It can be concluded that TiO₂ activates the decomposition of H₂O₂.

4. Conclusions

TiO₂–SiO₂ as nanoparticles or nanorods was prepared by sol-gel method by changing synthesis parameters (pH or solvent). The particle size of the resultant was found to be about 8–60 nm. It was also realized that the morphology of the prepared TiO₂–SiO₂ with NH₄OH, acetic acid, PEG and EG are nanoparticles. In the presence of NaOH, nanorods were formed. The effect of pH, reaction time, temperature and solvent were also studied. The catalytic activity of the obtained nanomaterials on oxidative aromatization of 1,4-DHPs within 3–5 h with 86–100% conversion and 100% selectivity towards the corresponding products seems promising.

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