Highly Ordered Mesoporous Organosilica–titania with Ionic Liquid Framework as Very Efficient Nanocatalyst for Green Oxidation of Alcohols

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Abstract: Preparation, characterization and catalytic application of a novel ordered mesoporous organosilica–titania with ionic liquid framework (ILNOS-Ti) is developed. The ILNOS-Ti was prepared by surfactant directed simultaneous hydrolysis and condensation of alkyl-imidazolium ionic liquid and tetramethoxysilane followed by treatment with tetrabutylorthotitanate (TBOT) under moderate conditions. The chemical and physical properties of the material were investigated using TG, EDX, DRIFT, TEM, SEM, small angle XRD and nitrogen adsorption-desorption analyses. The ILNOS-Ti was applied as efficient nanocatalyst for the green oxidation of alcohols in the presence of hydrogen peroxide under mild conditions. The corresponding carbonyl products were obtained in high yield. The stability, recoverability and reusability of the designed nanocatalyst were also studied under applied reaction conditions.

Keywords: Organosilica-titania, ionic liquid, nanocatalyst, oxidation, alcohols

1. Introduction

Transition metal catalyzed oxidation of alcohols to their corresponding carbonyl compounds is one of the most significant organic transformations from both laboratorial and industrial point of view, due to key role of this process in the production of intermediates of valuable compounds such as pharmaceuticals, agricultural chemicals and fine chemicals [1-3]. In traditional, this reaction has been widely developed using a lot of transition metal catalysts such as $\text{Pd}(\text{OAc})_2/\text{pyridine}$, $\text{Pd}(\text{OAc})_2/(\text{ligand})_2$, $\text{CuBr}\cdot\text{Me}_2\text{S}$, $[\text{VO}(\text{acac})_2]$, $\text{K}_2[\text{OsO}_2(\text{OH})_4]$, nickel phosphine, *etc* under homogeneous conditions [4-14]. However, these homogeneous catalytic systems suffer from problems of product separation, catalyst recovery, moderate chemoselectivity, high reaction temperature as well as the use of organic solvents and stoichiometric amounts of inorganic oxidants, which are highly toxic and environmentally polluting and increasing environmental concerns [15-17]. Therefore, more recently the use of heterogeneous metal catalysts together with “green oxidants” such as molecular oxygen or hydrogen peroxide is an attractive alternative method because its potential for simple catalyst recovery and product separation, minimization of metal-based waste, generation of water as the sole by-product and so on [18-26]. Especially, heterogeneous ordered mesoporous organosilicas supported metal catalysts combined with environmentally friendly oxidants are major challenges of exploratory research in the oxidation processes [27-30]. Among these, titanium containing ordered mesoporous materials have been very interesting and employed as powerful catalysts in the various oxidation reactions such as alcohol oxidation, epoxidation, hydroxylation, *etc.* using hydrogen peroxide as green oxidant [31-37]. Kang and co-workers reported Ti-MCM41 and Ti-MCM48 catalysts with remarkable activities in the epoxidation of alkenes using H_2O_2 oxidant [38]. Titanium containing ethane bridged hybrid mesoporous silsesquioxane was applied in the ammoximation of ketones using aqueous hydrogen peroxide oxidant [39]. The most advantage of the latter catalyst was its high activity and retention of the mesostructure after removal of the organic ethylene bridge by calcination at high temperature. Organic-inorganic hybrid Ti-SBA-15 materials were synthesized from titanocene dichloride in the presence of non-ionic

surfactants in acidic media [40]. Post-synthesis silylation procedures enhanced the catalytic activity of these materials in the epoxidation of 1-octene with hydrogen peroxide. Titanium species were also incorporated into ethane-based PMO materials with uniform hexagonal arrangement and used in the oxidation of alkenes [41]. Mesoporous silica–titania material was also prepared, characterized and applied as catalyst in the mild oxidation of sulfur compounds [42]. Although the abovementioned studies gave remarkable results of Ti-containing mesoporous organosilica catalysts in the oxidation processes using hydrogen peroxide as oxidant, however, the most of these have problems of high reaction temperature and the use of toxic organic solvents. Moreover, in spite of remarkable properties and importance of ionic liquid based materials in the organic processes, there is no report in the preparation of Ti-containing ionic liquid based ordered nanoporous organosilicas in the literature. Accordingly, herein we wish to disclose the preparation and characterization of ionic liquid based nanoporous organosilica chemically supported titanium (ILNOS-Ti) catalyst as well as study its catalytic application in the green oxidation of alcohols using H_2O_2 oxidant under ambient temperature (Scheme 1). The stability and recoverability of the catalyst under applied conditions have also been studied.

2. Experimental Section

2.1. Chemicals: Triblock copolymer pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, purity $\geq 99\%$) tetramethylorthosilicate (TMOS, purity $\geq 99\%$), sodium imidazolid (95%), 3-(chloropropyl)-trimethoxysilane (97%) and tetrabutylorthotitanate $[\text{Ti}(\text{O}^t\text{Bu})_4]$, purity $\geq 97\%$ were purchased from Sigma-Aldrich and used without further purification. Other chemicals including KCl (purity $\geq 99\%$), HCl (37%), H_2O_2 (30 wt.%), 1-phenylethanol (98%), 1-phenyl-1-propanol (98%), benzhydrol (98%), 4-chlorobenzhydrol (98%), 2-octanol (98%), cyclooctanol (95%), cycloheptanol (97%), cyclohexanol (99%) and cyclopentanol (99%) were purchased from Merck company and used as received. All solvents such as toluene (purity $> 99\%$), ethanol (purity $> 99\%$) and acetonitrile (purity $> 99\%$) were purchased from Merck company and used as received.

2.2. Procedure for the preparation of ILNOS

ILNOS was synthesized using triblock copolymer pluronic P123 surfactant, imidazolium ionic liquid and TMOS under acidic conditions according to our previous report [27a]. For this, firstly, the 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride ionic liquid was synthesized by treatment of sodium imidazolid (5 mmol) with 3-(chloropropyl)-trimethoxysilane (10 mmol) under argon atmosphere at 100 °C for 40 h [27a]. The ionic liquid based nanoporous organosilica (ILNOS) was then prepared as following. In a typical preparation, P123 (2.1 g) and KCl (9 g) were completely dissolved in a solution of deionized water (13.1 g) and HCl (2M, 28.8 g) at 40 °C for 3 h. Then, a methanol solution of 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride (1.1 g) and TMOS (3.4 g) was added into the reaction vessel and the it was stirred at the same temperature for 36 h. Next, the resulting mixture was statically heated at 100 °C for 72 h. The obtained product was filtered, washed with deionized water and dried in room temperature. The pluronic P123 surfactant was removed by Soxhlet apparatus using ethanol (150 mL) and concentrated HCl (5 mL) for 24 h. The final material was dried at 70 °C for 20 h and denoted as ILNOS [27a].

2.3. Procedure for the preparation of ILNOS-Ti

In order to prepare ILNOS-Ti, the surface of the ILNOS was modified by $\text{Ti}(\text{O}^i\text{Bu})_4$ *via* a coating procedure. For this, the ILNOS (1 g) was dispersed in 15 mL of super dry toluene under argon atmosphere and concurrently $\text{Ti}(\text{O}^i\text{Bu})_4$ (0.5 mL, 1.4 mmol) was added. This was stirred at reflux conditions. After 1 hour, the second amount of $\text{Ti}(\text{O}^i\text{Bu})_4$ (0.5 mL, 1.4 mmol) was added. The titanium source was added step by step and drop-wise. After 1 hour, a mixture of deionized water and pure ethanol (1:1, 20 mL) was added to the reaction vessel and stirring was continued for 2 hours. The resulting mixture was filtered and washed completely with deionized water and pure ethanol. The final

material was dried at 90 °C to deliver a white powder denoted ILNOS-Ti. The loading of the titanium was obtained to be 2.2 mmol/g by the means of the Ti-content obtained from inductively coupled plasma/optical emission spectroscopy (ICP-OES). This demonstrated that more than 78% of titanium was successfully coated onto material surface.

2.4. General procedure for the oxidation of alcohols using ILNOS-Ti nanocatalyst

The oxidation of alcohols was performed in a magnetically stirred round-bottomed flask fitted with a condenser and placed in a temperature controlled oil bath. It is important to note that in all experiments the mole percent of catalyst referring to the molar % content of titanium obtained using ICP analysis. Typically, the flask was charged with 1 mmol of alcohol and catalyst (1 mol%). Then, 1.5-2 mL of H₂O₂ was added slowly and drop by drop during the reaction time. The mixture was stirred at 60 °C and the reaction progress was monitored using TLC and GC (Agilent 6890N, capillary column). The carbonyl products were obtained in high to excellent yield.

2.5. Procedure for the recovery of the ILNOS-Ti catalyst

One of the main aims of this work was to develop the recoverability of the under studied catalyst. We explored the reusability of the catalyst in the model reaction of 1-phenylethanol, H₂O₂ and 1 mol % of ILNOS-Ti at 60 °C. For this, after completing of the reaction, the catalyst was easily separated from reaction mixture by centrifugation, washed with ethanol and dried at 80 °C in an oven for 3 h. The recovered catalyst was then reused under the same conditions as the first run. The study showed that the catalyst could be recovered and reused at least 14 times without significant decrease in stability and efficiency.

2.6. Procedure for the hot filtration test

To test if titanium was leaching from the solid material during the reaction, a hot filtration test was carried out. In a typical procedure, 1 mmol of 1-phenylethanol was allowed to oxidize with hydrogen peroxide in the presence of 1 mol% of catalyst at 60 °C. After about 40% of the reaction was

progressed, it was stopped and obtained mixture was hotly filtered. The catalyst-free filtrate was next heated at 60 °C in the presence of hydrogen peroxide and the reaction progress was monitored by GC. Interestingly no further oxidation was observed after 6 h. It is also important note that the ICP analysis of the filtrate showed no-leaching of titanium during reaction process.

3. Results and Discussion:

The ionic liquid based nanoporous organosilica chemically supported titanium (ILNOS-Ti) was prepared *via* surfactant directed hydrolysis and co-condensation of 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride and tetramethoxysilane (TMOS) followed by treatment with tetrabutylorthotitanate (TBOT) according to Scheme 1. This nanomaterial was characterized with several techniques such as TEM, SEM, EDX, DRIFT, small angle XRD, TG and nitrogen adsorption-desorption analyses.

The DRIFT spectrum of ILNOS-Ti is shown in Figure 1. The O–H stretching vibrations of surface hydroxyl groups and physically adsorbed water were observed as a broad peak at 3300–3450 cm^{-1} . The stretching vibration of aromatic and aliphatic C–H bonds were, respectively, appeared at 3087 and 2934 cm^{-1} . The peaks observed at 1636 and 1565 cm^{-1} were also assigned, respectively, to C=N and C=C stretching vibrations of imidazolium ring. The Si–O–Si asymmetric and symmetric stretching vibrations were appeared in the absorption range of 956–1070 cm^{-1} .

Thermal gravimetric analysis (TGA) of ILNOS-Ti was performed in a nitrogen atmosphere in the temperature range of 25–800 °C and a heating rate of 10 °C/min. The first weight loss (8.6 %) observed below 100 °C, is attributed to desorption of water and physically adsorbed solvents (ethanol or methanol). The second weight loss (2.6 %) can be corresponded to the solvents and/or surfactant template trapped in the material matrix [27a, 43, 44]. The most noticeable weight loss (about 20%) observed in the temperature range of 280–800 °C, corresponding to degradation of imidazolium ionic liquids moieties [43, 44] (Figure 2).

The EDX analysis of the ILNOS-Ti also demonstrated the expected signals of carbon, oxygen, silicon, nitrogen, chlorine and titanium in the mass percent of 38.5, 36.5, 11.5, 2.23, 1.05 and 10.22, respectively. The abovementioned analyses are in good agreement with each other and powerfully confirm high stability as well as well immobilization and/or incorporation of ionic liquid and titanium moieties into/onto material framework.

The N₂ adsorption-desorption isotherm for ILNOS-Ti showed a sharp inflection at a relative pressure in the range of 0.6–0.8 indicating that the synthesized material has uniform ordered mesopores (Figure 4) that is very similar to well-ordered isotherm of SBA-15-type nanomaterials. This observation successfully confirms that the order of mesoporous structure of ILNOS has been maintained after titanium-coating process [43]. The BJH pore size distribution analysis of the ILNOS-Ti also showed a sharp and narrow peak centered about 9 nm confirming uniform distribution of pore sizes that is a valuable advantage in the practical chemical application of the material (Figure 5). Compared with original ILNOS, ILNOS-Ti indicated a decrease of the mean pore diameter after titanium immobilization. The BET surface area and total pore volume decreased, respectively, from 685 m²/g and 1.2 cm³/g for ILNOS to 620 and 1 for ILNOS-Ti [27]. These confirm successful immobilization of the titanium oxide particles onto ILNOS pores during coating process.

The transmission electron microscopy (TEM) image of the ILNOS-Ti was in good agreement with nitrogen-sorption analysis and showed the presence of well-ordered two-dimensional hexagonal mesopores for this nanomaterial (Figure 6). The small angle X-ray diffraction (SAXRD) pattern of the catalyst was in good agreement with TEM image and illustrated a peak with high intensity centered at $2\theta \approx 1$ (Figure 7) [43, 44]. These are characteristic of SBA-15-type mesostructures which are among the best family of nanomaterials.

To study the morphology, in the next the scanning electron microscopy (SEM) analysis was performed. This demonstrated particles with average size of 5 micrometers and a uniform rope-like morphology

(Figure 8). These type nanostructures are very good materials for catalysis, chromatography, and microelectronic applications due to their high regularity and density [45].

After successful characterization of the ILNOS-Ti, its potential catalytic ability in the oxidation of alcohols was explored. A typical procedure for the oxidation reaction was as follows: ILNOS-Ti, alcohol, solvent and oxidant were successively placed into a glass reactor. The reaction mixture was stirred at the reaction temperature and the conversion and product selectivity were periodically determined by TLC and GC. At first, the oxidation of 1-phenylethanol, as a model substrate, was carried out with ILNOS-Ti catalyst under the conditions of Table 1. As presented, the reaction progress was strongly affected with amount and kind of catalyst, temperature, solvent and oxidant. For all experiments the solvent:1-phenylethanol molar ratio was 40:1. The oxidation was hardly proceeded at room temperature in MeCN using oxygen atmosphere oxidant during 24 h (Table 1, entry 1). While, increasing the temperature to 45 °C gave 38% conversion under the same conditions and time as above (Table 1, entry 2). Oxidation in toluene scarcely proceeded under oxygen atmosphere (Table 1, entry 3). It is important to note that under solvent free media also low yield of carbonyl product was obtained in the presence of oxygen during 24 h (Table 1, entry 4). Hydrogen peroxide is particularly attractive as it has high active oxygen content, gives H₂O as the only waste product and is low-cost. In the next investigation, this was used as oxidant. Interestingly, when this oxidant was employed as dropwise in the reaction, enhanced oxidation rate in combination with perfect product selectivity was obtained in acetonitrile at 45 °C (Table 1, entry 5). Under solvent-free media the better result was obtained for 6 h under the same conditions as before (Table 1, entry 6). Increasing the temperature to 60 °C greatly enhanced the reaction efficiency, leading to a good yield of acetophenone (Table 1, entry 7). The study also showed that with increasing the amount of catalyst from 0.5 to 1 mol%, an excellent yield of carbonyl product was obtained at 60 °C and short reaction time (Table 1, entries 7-9). To study the individual impact of both ionic liquid and titanium sites during the catalysis, the efficiency of the ILNOS-Ti catalyst was compared with those of titanium-free ILNOS as well as ionic liquid-free Ti-SBA-15 and Ti-SiO₂ materials. The result showed that the ILNOS nanomaterial was very sluggish and gave only a trace amount of desired product (Table 1, entry 10)

confirming that the reaction is catalyzed by supported titanium species. The study also showed that both Ti-SBA-15 and Ti-SiO₂ catalysts had inferior activity as compared with that observed over ILNOS-Ti comprising the same titanium loading (Table 1, entry 9 vs. entries 11, 12). Importantly, in the latter investigation, Ti-SBA-15 gave better yield (50% yield) than Ti-SiO₂ (38%) indicating the beneficial effect of ordered mesochannels in the reaction progress. These results also strongly confirm the key role of both titanium and ionic liquid (IL) moieties in the catalytic process that may be attributed to a synergistic effect between the ILs and the immobilized titanium species [27, 43, 44]. The other positive effect of ionic liquids is due to their lipophilicity increasing substrate diffusion into mesochannels of catalyst during reaction process [27, 43, 44].

With the optimized conditions in hand, the scope of the present catalyst system toward various kinds of alcohols was examined. As presented in Table 2, this method was very effective for the oxidation of benzylic and aliphatic alcohols to their corresponding carbonyls. Secondary benzylic alcohols such as 1-phenylethanol and 1-phenyl-1-propanol were successfully oxidized to their carbonyls (Table 2, entries 1, 2). Importantly, benzhydrol and 4-chlorobenzhydrol, in spite of their steric hindrance, also were successfully oxidized and gave corresponding ketones in good yield (Table 2, entries 3, 4). It is also worth noting that the ILNOS-Ti showed an excellent activity for the oxidation of secondary aliphatic alcohols either cyclic or acyclic and delivered their corresponding ketones in high to excellent yields (Table 2, entries 5–9). These results confirm high efficiency of the ILNOS-Ti in the selective oxidation of a wide range of alcoholic compounds to their corresponding carbonyl adducts applicable in different areas of chemistry and industry world.

In the next study, the reusability of the designed catalyst was investigated in the oxidation of 1-phenylethanol as a test model. For this, after completing of the reaction, monitored by GC, the mixture was filtered and the catalyst was washed completely with ethanol. The recovered catalyst was then reused at least in 14 runs under the same conditions as the first run and furnished high yield of corresponding carbonyl product (Table 3).

A hot filtration test was then performed in the oxidation of 1-phenylethanol to verify the nature of catalyst during reaction progress (Figure 9). To do this, the oxidation was allowed to proceed to about 40% completion under optimized conditions and then it was stopped and the ILNOS-Ti nanocatalyst was removed by filtration. The filtrate was next heated at 60 °C in the presence of hydrogen peroxide, interestingly no further oxidation was observed after 6 h. In addition, it was confirmed by atomic absorption and ICP analyses that no titanium species were found in the filtrate. This is due to chemical immobilization of titanium species onto material surface. These results confirm that the designed titanium nanocatalyst is highly stable and durable during reaction process, operates in a heterogeneous manner and the applied conditions did not have negative effect in the stability of the nanomaterial.

4. Conclusion

In summary, a noble ionic liquid based ordered nanoporous organosilica supported titanium with excellent structural porosity and high efficiency was prepared and used as powerful nanocatalyst in the green oxidation of alcohols. The TEM, SAXRD and nitrogen adsorption-desorption analyses confirmed a highly ordered two-dimensional mesostructure for this material. The TGA, DRIFTS and EDX analyses also successfully showed the well incorporation and/or immobilization of expected species into material framework. The SEM image illustrated the presence of uniform rope-like particles for the ILNOS-Ti. The carbonyl products were obtained in high to excellent yield and selectivity in relatively short reaction times and moderate conditions. This nanocatalyst was successfully recovered and reused at least 14 times with remaining its activity. According to hot filtration test as well as ICP and atomic adsorption analyses the catalyst worked *via* a heterogeneous manner. Due to the aforementioned advantages of designed catalyst, some applications of this in other chemical processes are underway in our laboratory.

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Scheme 1. Preparation of the ILNOS-Ti nanocatalyst

Figure 1. DRIFT spectrum of the ILNOS-Ti

Figure 2. Thermal gravimetric analysis of the ILNOS-Ti

Figure 3. EDX spectrum of the ILNOS-Ti

Figure 4. Nitrogen adsorption-desorption isotherms of the ILNOS-Ti

Figure 5. BJH-plot of the ILNOS-Ti

Figure 6. TEM image of the ILNOS-Ti

Figure 7. Small angle XRD pattern of the nanocatalyst

Figure 8. SEM image of the ILNOS-Ti

Figure 9. Effect of removal of ILNOS-Ti on the oxidation of 1-phenylethanol. Before removal of ILNOS-Ti (◆); after removal of ILNOS-Ti (■).

Table 1. Optimization of the reaction conditions in the oxidation of 1-phenylethanol using ILNOS-Ti

Entry	Solvent	Oxidant	Catalyst (mol %)	t (°C)	Time (h)	Yield (%) ^a	TON ^b
1	CH ₃ CN	O ₂	ILNOS-Ti (0.5)	25	24	8	16
2	CH ₃ CN	O ₂	ILNOS-Ti (0.5)	45	24	38	76
3	Toluene	O ₂	ILNOS-Ti (0.5)	45	24	10	20
4	-	O ₂	ILNOS-Ti (0.5)	45	24	40	80
5	CH ₃ CN	H ₂ O ₂	ILNOS-Ti (0.5)	45	12	58	116
6	-	H ₂ O ₂	ILNOS-Ti (0.5)	45	6	65	130
7	-	H ₂ O ₂	ILNOS-Ti (0.5)	60	6	77	154
8	-	H ₂ O ₂	ILNOS-Ti (0.75)	60	6	88	117
9	-	H ₂ O ₂	ILNOS-Ti (1)	60	4	96	96.7
10	-	H ₂ O ₂	ILNOS	60	6	Trace	-
11	-	H ₂ O ₂	Ti-SBA-15 (1)	60	6	50	50
12	-	H ₂ O ₂	Ti-SiO ₂ (1)	60	6	38	38

^a GC yield. ^b Turnover number.

Table 2. Catalytic performance of ILNOS-Ti in the oxidation of alcohols^a

Entry	Substrate	Product	Time (h:min)	Yield (%) ^b	TON
1			4	96	96
2			5	96	96
3			7:30	92	93
4			7:30	90	91
5			10	86	86
6			7:30	88	88
7			7:30	90	90
8			7	92	92
9			7	89	89

^a Reaction conditions: Substrate (1 mmol), ILNOS-Ti (1 mol%), H₂O₂ (1.5-2 mL), 60 °C. ^b GC yield.

Table 3. Reusability of the ILNOS-Ti in the oxidation of 1-phenylethanol

Run	Time (h:min)	Yield (%)	Run	Time (h:min)	Yield (%)
1	4:00	96	8	4:35	91
2	4:00	96	9	4:40	89
3	4:10	95	10	4:40	86
4	4:10	95	11	4:50	85
5	4:15	93	12	4:55	83
6	4:25	90	13	5:10	80
7	4:25	90	14	5:20	80
			15	5:30	80

Graphical abstract

Preparation, characterization and catalytic application of a noble ordered mesoporous organosilica–titania with ionic liquid framework (ILNOS-Ti) is developed.