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Simple hydrothermal synthesis of sphere-like TiO₂ nanoparticles and their functionalization with 1,4-butane sultone as a new heterogeneous catalyst

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Abstract For the first time, anatase TiO_2 nanoparticles with high specific surface area have been synthesized by hydrothermal method using titanium (IV) ethoxide solution. Nanocrystalline titania-based sulfonic acid (nano- TiO_2 -Bu-SO₃H (n-TBSA)) was successfully prepared by the reaction of nano-TiO₂ and 1,4-butane sultone. The samples were characterized using FT-IR, XRD, TGA, EDX, FESEM, TEM, BET and BJH analysis. The present catalytic system can be applied in multicomponent reaction for the synthesis of 1-amidoalkyl-2-naphthols and 1,8-dioxooctahydro-xanthenes. The simple preparation, chemical stability, product selectivity and the recyclability of the catalyst make it eco-friendly and economical worthwhile.

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Graphical Abstract



Keywords Nano-TiO₂–Bu–SO₃H (n-TBSA) \cdot Heterogeneous catalyst \cdot Interphase catalyst \cdot 1-Amidoalkyl-2-naphthols \cdot 1,8-Dioxo-octahydroxanthenes \cdot Reusability

Introduction

Rising environmental pollution and global anxiety resulted in the innovation of alternative methods for the production of safe chemicals. Because of constant demand in renewable energy and sustainable environment, development of novel heterogeneous catalyst instead of homogeneous catalyst in various chemical transformations has attracted increasing interest. Compared with homogeneous catalysts, heterogeneous catalysis has emerged as a useful tool to reduce waste production with regard to the simplicity of the process, easy and safe handling, avoidance of the use of toxic solvents, separation and recycling of the catalysts and eliminating problems with corrosion, toxicity and environmental harm [1–3]. An important strategy to transform a homogeneous catalyst into a heterogeneous one is to immobilize one or more components of the catalytic systems onto a broad solid surface area through an organic entity (flexible spacer) to create new organic-inorganic hybrid (interphase) catalysts. This interphase nanocatalyst has advantages of both of homogeneous and heterogeneous catalyst due to the mobility of reactive center, easy separation and recovery [4–7]. Among heterogeneous catalysts,

nanocrystalline metal oxides seem to be attractive nanocatalysts in organic syntheses due to their broad reactive surfaces with higher potential for selectivity, reusability and benign character in the context of green chemistry [8-10]. Recently, developing of novel strategies for obtaining size- and shape-controllable nanomaterials is an important topic in the science of the chemistry [11]. In nature, TiO_2 is known to exist in three different crystalline forms, brookite, rutile and anatase. Anatase TiO₂ has attracted particular attention due to its promising applications in photovoltaic cells, dye-sensitized solar cells, sensors and photocatalysis because of its superior activity compared to the other phases [12–16]. Nanocrystalline titanium has emerged as efficient and inexpensive support for the synthesis of heterogeneous catalyst owing to its unique properties [17]. However, further efforts are necessary in the design of new heterogeneous catalysts using titanium dioxide as efficient supports to achieve excellent catalytic activity and selectivity in multicomponent reaction.

Multicomponent reactions (MCRs) along with advantages of efficiency, atom economy and simplicity are arguably one of the most important protocols in organic synthesis that have attracted considerable attention for a long time [18, 19]. Therefore, synthesis of heterocyclic compounds through multicomponent reactions, environmentally benign procedures and utilizing green reusable catalysts is a prominent subject of interest.

Considering the above facts and in the course of our interest to develop eco-friendly new heterogeneous catalysts in organic synthesis [20–24], the synthesis of TiO_2 nanoparticles under hydrothermal conditions is presented in the first part of the present work. Then, chemically bound adsorbed sulfonic acid on TiO_2 (TiO_2 –Bu–SO₃H (n-TBSA)) was prepared as a new organic–inorganic hybrid acid catalysts by the reaction of 1,4-butane sultone and TiO_2 (Scheme 1). Furthermore, the catalytic activity of nanocatalyst was applied to effective synthesis of 1-amidoalkyl-2-naphthols and 1,8-dioxo-octahydro-xanthenes under solvent-free conditions.

Results and discussion

Catalyst characterization

FT-IR spectroscopy

FT-IR spectra for the pure nano-TiO₂ and nano-TiO₂-Bu-SO₃H samples are presented in Fig. 1. In the case of nano-TiO₂, the peaks positioned at 3426 and 1645 $\rm cm^{-1}$ are related to the -OH stretching and bending vibrations of the adsorbed water, respectively. The presence of a welldefined band positioned at 611 cm⁻¹ is related to the Ti–O stretching and Ti-O-Ti bending which characterizes the formation of the anatase structure of TiO₂ [25]. This result is in accordance with that obtained from the XRD studies. The spectrum of functionalized nano-TiO₂ by sulfonic acid displays almost the same pattern as that of pristine nano- TiO_2 , but the band at 3427 cm⁻¹ is flattened in sulfonated nano-TiO₂ which can be attributed to the modification of nano-TiO2. Also, CH stretching vibrations were observed at 2945 and 2918 cm^{-1} and the peaks positioned at 1228, 1151 and 1041 cm^{-1} are related to the stretching frequency of S-O and S=O in SO₃H [26]. This result shows modification of nano-TiO₂ using 1,4-butane sultone.

X-ray diffraction (XRD) analysis

Figure 2a shows the XRD pattern of TiO₂ nanoparticle before modification process, presenting the characteristic peaks of anatase structure. The pattern indicates a crystallized structure with the peak positions of 2θ : 25.3°, 36.3°, 37.6°, 39.3°, 48.0°, 54.2°, 55.0°, 62.5°, 68.8°, 75.5° and 82.7°, which are assigned to the (101), (103), (004), (112), (200), (105), (211), (204), (220), (215) and (303) crystallographic faces of anatase TiO₂ (ICCD no. 21-1272) [27]. The crystal size of the TiO₂ nanoparticles was also determined from X-ray pattern using the Scherrer formula given as $t = 0.9\lambda/B_{1/2}\cos\theta$, that t is the average crystal size, λ the X-ray wavelength used (1.54 Å), $B_{1/2}$ the angular line width at half maximum intensity and θ the Bragg's angle. The average crystal size of the TiO₂



Fig. 1 FT-IR spectra of a nano-TiO₂ and b nano-TiO₂-Bu-SO₃H



Scheme 1 Synthesis of nano-TiO2-Bu-SO3H



Fig. 2 X-ray diffraction patterns of a nano-TiO_2 and b nano-TiO_2–Bu–SO_3H

nanoparticles for $2\theta = 26.06^{\circ}$ is calculated to be around 14.9 nm. This was coincident with the results obtained from the TEM analysis. In Fig. 2b, it can be seen that the diffraction peaks of nano-TiO₂–Bu–SO₃H are similar to those of the parent TiO₂ nanoparticles, which suggest that the phase structure of the synthesized nanoparticle is well retained after modification.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of nano-TiO₂-Bu- SO_3H in comparison with nano-TiO₂ is displayed in Fig. 3. The TGA curve of nano-TiO₂ (Fig. 3a) exhibits a weight loss below 100 °C which corresponds to the loss of the physically adsorbed water and then a steady weight loss in the range of 150-700 °C, which possibly corresponds the to the dehydroxylation of nano-TiO₂. For the n-TBSA, the TGA curve (Fig. 3b) seems to indicate two-stage decomposition. One initial weight loss assigned to the loss of the physically adsorbed water below 120 °C and the other that started at approximately 216 up to 700 °C assigned to the decomposition of the covalently bound organic group. Also from the TGA, it was found that catalyst has a great thermal stability (until 150 °C) confirming that it could be safely used in organic reactions at temperatures up to 140 °C [17].

SEM analysis

According to the FESEM analysis (Fig. 4), it was observed the synthesized nano-TiO₂ (Fig. 4a–c) and n-TBSA (Fig. 4d–f) were homogeneous spherical-shaped particles. It is clear that the primary surface morphology of the assynthesized TiO₂ has been changed after functionalization



Fig. 3 TGA curve of a nano-TiO₂ and b nano-TiO₂-Bu-SO₃H

with organic group resulted in the formation of larger clusters of the obtained TiO_2 nanoparticle.

TEM analysis

Figure 5 shows the TEM images of the TiO_2 nanoparticle. It was found that the as-synthesized nanomaterial has spherical morphology. According to the TEM images, it is also clear that the morphology, size and distribution of the nanoparticles are almost homogeneous. This figure also indicates the average particle size distribution of nano-TiO₂ was in the range of 10–15 nm.

Figure 6 shows TEM images of the modified TiO_2 nanomaterial. It was found that the morphology of the obtained material was still spherical. However, Fig. 6c shows that the size of the as-synthesized nanomaterial is not homogeneous and there are different kinds of the nanomaterial in view of their sizes. It also indicated that the average particle size distribution was in the range of 15–20 nm.

BET and BJH analysis

The surface area, pore volume and pore size of the synthesized powders were calculated using the Brunauer– Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) equations, respectively. Prior to N₂-physical adsorption measurements, the samples were degassed at 150 °C for 120 min in the nitrogen atmosphere. The specific surface area (SBET) of the obtained materials was determined with adsorption–desorption isotherms of N₂ at 77 K. The surface area, pore volumes and pore diameters of the synthesized materials are summarized in Table 1. Besides, Table 2 shows the textural properties of the as-prepared materials.



Fig. 4 SEM images of a-c nano-TiO₂ and d-f nano-TiO₂-Bu-SO₃H

XRD energy-dispersive X-ray spectroscopy (EDX) analysis

The elemental composition of nano-TiO₂–Bu–SO₃H from EDX analysis also indicated the presence of Ti, O, S and C elements (Fig. 7), and the percent of elements is shown in Table 3.

PH analysis of catalyst

The optimum concentration of H^+ of nano-TiO₂–Bu–SO₃H was determined by acid–base potentiometric titration of the aqueous suspension of the weighed amount of thoroughly washed catalyst with standard NaOH solution. At first, 100 mg nano-TiO₂–Bu–SO₃H was dispersed in 20 ml H₂O by ultrasonic bath for 60 min at room temperature after which the pH of solution was 3.36. The amount of the acid was neutralized by addition of standard NaOH solution (0.088 N) to the equivalence point of titration. The required volume of NaOH to this point was 0.5 ml. This is equal to a loading of 0.44 mmol H⁺/g.

Catalytic activity of nano-TiO₂–Bu–SO₃H in one-pot multicomponent reactions

On the basis of the information obtained from the above mentioned studies, catalytic activity of n-TBSA was examined in multicomponent reactions for the synthesis of heterocyclic compounds such as 1-amidoalkyl-2-naphthol and 1,8-dioxo-octahydro-xanthene derivatives. All products were characterized by spectral data and compared with their physical data with the literature.

Synthesis of 1-amidoalkyl-2-naphthol derivatives

The catalytic activity of n-TBSA was assessed in the synthesis of 1-amidoalkyl-2-naphthols 4. Initially, the reaction of benzaldehyde 1, β -naphthol 3 and benzamide 2 (mole ratio 1:1:1.2) was considered as the model reaction (Scheme 2).

To select an appropriate amount of catalyst on the catalytic performance, the model reaction was also carried out in the presence of various molar ratios of n-TBSA and the best yield was observed when the reactions were performed by using of 3 mol% of n-TBSA (Table 4, entry 5). Through examination, it was found that the reaction did not proceed in the absence of the catalyst in any temperature (Table 4, entries 1–3). To find out the best operative reaction temperature, the reaction was carried out under varying reaction temperature with 3 mol% of n-TBSA under solvent-free conditions (Table 4, entries 5, 7–8). Thus, 100 °C was selected as the optimum temperature.

To investigate the effect of the solvent on the catalytic reaction, the model reaction in the presence of 3 mol% of n-TBSA was carried out in several solvents such as ethanol, methanol, water, THF and toluene and in a solvent-free condition (Table 4, entries 5, 9–13).

It was found that ethanol is better than other solvents for this reaction but the best yield obtained under solventfree conditions (Table 4, entry 5).

Having established efficient optimized conditions for the synthesis of 1-amidoalky-2-naphthols, a range of aryl aldehydes were subjected to react with 2 and 3 to generate 4a–n in high to moderate yields. The results are summarized in Table 5. The products were characterized by IR, ¹H NMR and ¹³C NMR spectroscopy, and also by comparison with authentic samples.





Synthesis of 1,8-dioxo-octahydro-xanthene derivatives

The efficiency of the obtained n-TBSA has been tested by the synthesis of 1,8-dioxo-octahydro-xanthene derivatives 6a-m under optimal conditions (3 mol% of n-TBSA in 120 °C and solvent-free condition) by condensation between aromatic aldehyde 1 (1 mmol) and dimedone 5 (2 mmol) (Scheme 3). The results are summarized in Table 6. A possible mechanism for the formation of 1,8-dioxooctahydro-xanthenes and 1-amidoalkyl-2-naphthols is shown in Scheme 4.

The efficiency of n-TBSA was compared with some other published works in the literature for the synthesis of 1-amidoalkyl-2-naphthols (Table 7). Each of these methods has their own advantages, but they often suffer from some troubles including reaction conditions, time and product yields. As can be seen in this table, the present catalyst was







 Table 1 BET data showing the textural properties of the obtained materials

Sample	BET surface area (m^2g^{-1})	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
n-TiO ₂	91.4	0.24	10.63
n-TBSA	84.8	0.21	10.36

 Table 2 BJH data showing the textural properties of the obtained materials

Property	n-TiO ₂	n-TBSA
Desorption surface area (m^2g^{-1})	131.4	126.7
Cumulative desorption pore volume (cm^3g^{-1})	0.26	0.24
Desorption pore diameter (nm)	5.29	3.53





Table 3 The percent of elements in EDX analysis

Element	Atom. C (at%)
Carbon	1.76
Oxygen	60.07
Sulfur	8.54
Titanium	29.63

found to be the most efficient catalyst for the synthesis of 1-amidoalkyl-2-naphthols.

Reusability of the catalyst

The possibility of reusing the catalyst without loss of activity is one of the most important advantages of heterogeneous catalyst from the viewpoint of green chemistry. The recovery and reusability of the catalyst was investigated in the synthesis of 1-amidoalkyl-2-naphthol. In each cycle, the n-TBSA was separated by centrifuging and washed with hot ethanol and water to ensure the organic reagents do not remain on the surface of catalyst. Then, the recovered catalyst was used in the next run. The results of five consecutive runs showed that the catalyst can be reused four times without significant loss of its activity. Moreover, the stability of catalyst was checked by XRD pattern of recycled catalyst and indicated that the catalyst was not changed after five runs (Fig. 8).

Experimental

Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck and were used as received without any further purification. Thermal analysis was done by using a thermogravimetric analyzer on a Du Pont 2000 thermal analysis apparatus at a heating rate of 5 °C min⁻¹ under air atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu Ka radiation source on a Siemens D5000 (Siemens AG, Munich, Germany) X-ray diffractometer. Field emission scanning electron microscope (FESEM) images were acquired with a Philips XL30 field emission scanning electron microscope (Philips, Amsterdam, Netherlands). TiO₂ nanoparticles were dispersed in water and cast onto a copper grid to study the sizes and morphology of the particles by TEM (transmission electron microscopy) using a Philips—CM300—150 kV microscope. The average particle size distribution was carried out using



Table 4 Optimization ofsynthesis of 1-amidoalkyl-2-naphthols

Entry	Solvent	Condition	Nano-TiO ₂ –Bu–SO ₃ H			
			Amount of catalysts (mol%)	Time (min)	Yield (%) ^a	
1	Solvent-free	r.t	_	120	NR ^b	
2	Solvent-free	50 °C	_	120	NR	
3	Solvent-free	100 °C	_	120	Trace	
4	Solvent-free	100 °C	1	20	82	
5	Solvent-free	100 °C	3	15	95	
6	Solvent-free	100 °C	5	20	90	
7	Solvent-free	80 °C	3	20	60	
8	Solvent-free	120 °C	5	20	92	
9	Ethanol	Reflux	3	120	86	
10	Methanol	Reflux	3	120	75	
11	Water	Reflux	3	120	52	
12	THF	Reflux	3	120	40	
13	Toluene	100 °C	3	120	Trace	

Reaction condition: benzaldehyde (1 mmol), β -naphthol (1 mmol), benzamide (1 mmol)

^a Isolated yields

^b No reaction was observed

Table 5n-TBSA-catalyzedone-pot synthesis of1-amidoalkyl-2-naphthols

Entry	Ar	Product	Time (min)	Yield (%) ^a	MP	MP (Refs.)
1	C ₆ H ₅	4a	10	97	235–237	235–237 [28]
2	$2-HO-C_6H_4$	4b	35	85	233-236	234–236 [28]
3	$3-HO-C_6H_4$	4c	60	80	265-267	265–267 [28]
4	$4-HO-C_6H_4$	4d	28	90	221-223	220–223 [28]
5	$2-Cl-C_6H_4$	4e	25	82	285	284–285 [<mark>28</mark>]
6	$4-Cl-C_6H_4$	4f	35	95	177-179	178 [29]
7	$(CH_3)_2NC_6H_4$	4g	60	70	220-222	220–221 [28]
8	2-MeO–C ₆ H ₄	4h	40	85	266-268	266–267 [28]
9	4-MeO–C ₆ H ₄	4i	45	80	209-211	209 [29]
10	$4\text{-Br-}C_6H_4$	4j	20	98	182-184	182–184 [<mark>30</mark>]
11	4-Me–C ₆ H ₄	4k	50	95	226-228	228 [31]
12	$4-NO_2-C_6H_4$	41	40	92	228-229	228–229 [32]
13	$3-NO_2-C_6H_4$	4m	60	95	239-241	240–242 [28]
14	4 -Fl– C_6H_4	4n	50	82	193–194	193–194 [<mark>28</mark>]

Reaction condition aromatic aldehyde (1 mmol), β -naphthol (1 mmol), benzamide (1.2 mmol), n-TBSA (3 mol%), solvent-free, 100 °C

^a Isolated yields

Scheme 3 Synthesis of 1,8-dioxo-octahydro-xanthene using of n-TBSA



Entry	Ar	Product	Time (min)	Yield (%) ^a	MP
1	C ₆ H ₅	6a	18	90	205–206 [33]
2	4-OH– 3-OMe– C ₆ H ₃	6b	30	75	225–227 [34]
3	4-НО– С ₆ Н ₄	6c	25	92	180–183 [35]
4	4 -Br– C_6H_4	6d	19	94	244–246 [35]
5	$(CH_3)_2N - C_6H_4$	6e	50	93	219–221 [35]
6	$2-Cl-C_6H_4$	6f	20	91	226–228 [33]
7	4-Cl-C ₆ H ₄	6g	15	93	233–235 [35]
8	4-Me– C ₆ H ₄	6i	30	95	210–212 [33]
9	4-NO ₂ - C ₆ H ₄	6j	15	88	227–228 [33]
10	3-NO ₂ - C ₆ H ₄	6k	30	87	170–172 [33]
11	4 -Fl– C_6H_4	61	30	93	234–235 [33]
12	4-OMe- C ₆ H ₄	6m	40	85	252–254 [33]

Reaction condition aromatic aldehyde (1 mmol), dimedone (2 mmol), n-TBSA (3 mol%), solvent-free, 120 °C

^a Isolated yields

Image software. Fourier transform infrared (FT-IR) spectra were obtained on a Shimadzu 8400 s spectrometer using KBr pressed powder disks. BET surface areas were acquired on a Beckman Coulter SA3100 surface area analyzer. The EDX characterization of the catalyst was performed using a Mira 3-XMU scanning electron microscope equipped with an energy-dispersive X-ray spectrometer operating.

¹H-NMR spectra were recorded in chloroform and dimethyl sulfoxide with TMS as an internal standard at ambient temperature on Bruker Avance 300 MHz instruments. The purity of products was checked by thin layer chromatography (TLC) on glass plates coated with silica gel 60 F254 using n-hexane/ethyl acetate mixture as mobile phase.

Catalyst preparation

Preparation of nano-TiO₂

In a typical synthetic experiment, titanium (IV) ethoxide (TEOT) (0.0047 mmol, 1.088 g) was added to 50 mL of water, and the resultant solution was transferred into a 100-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C for 24 h and then cooled to room temperature by water immediately. When the reaction was completed, a white powder was collected from the solution and washed with distilled water. The prepared powder was dried at 110 °C under normal atmospheric conditions and then calcined at 500 °C for 2 h.

Preparation of nano-TiO₂-Bu-SO₃H

Nano-TiO₂ was treated with 1 N HCl at 300 K to convert into hydrogen titanate. The surface functionalization of H⁺-titanate was performed using the surface hydroxyl groups of titanate by dehydration with 1,4-butane sultone (1,4-BS) as sulfonic acid precursors. The reactions were carried out at the refluxing temperature of toluene (383 K) for 24 h with the molar ratio of H⁺-titanate, sulfonic acid precursor and toluene of 1:0.5:15. The prepared samples were separated by centrifugation and washed with toluene. Then, the sample was dried at 383 K in vacuum oven overnight. The nanocatalyst was treated by 0.5 M H₂SO₄ before being used.

Typical procedure for the synthesis of 1-amidoalkyl-2-naphthols

The mixture of the aromatic aldehyde 1 (1 mmol), benzamide 2 (1 mmol), 2-naphthol 3 (1 mmol) and n-TBSA (0.075 g, 3 mol%) was stirred at 120 °C for the appropriate time (monitored by TLC). Then, hot ethanol (10 mL) was added and the reaction mixture was filtered. The solid catalyst was washed with ethanol and acetone (2 × 10 mL) and dried under vacuum. Pure 1-amidoalkyl-2-naphthols were afforded by evaporation of the solvent followed by recrystallization from ethanol. All products were characterized by spectral data and compared with their physical data with the literature.

Typical procedure for the synthesis of 1,8-dioxo-octahydro-xanthenes

In a round bottom flask, n-TBSA (0.075 g, 3 mol%) was added to the mixture of aromatic aldehyde 1 (1 mmol), dimedone 5 (2 mmol), at 120 °C for the appropriate time (monitored by TLC). After the completion of the reaction, hot ethanol was added to the reaction flask. The catalyst was isolated by centrifugation. Pure 1,8-dioxo-octahydroxanthenes were afforded by evaporation of the solvent followed by recrystallization from ethanol.



Scheme 4 Proposed reaction pathway for the preparation of 1,8-dioxo-octahydro-xanthenes and 1-amidoalkyl-2-naphthols catalyzed by n-TBSA

 Table 7 Comparison study of the efficiency of the n-TBSA with some different reported catalysts for the synthesis of 1-amidoalkyl-2-naphthols

Entry	Catalyst	Condition	Yield (%)	Time	Refs.
1	n-TBSA	100 °C/ solvent-free	97	10 min	This work
2	Nano- Ba ₃ (PO ₄) ₂	100 °C/ solvent-free	86	75 min	[36]
3	n-FZSA ^a	100 °C/ solvent-free	95	15 min	[37]
4	MNPs- SO ₃ H ^b	100 °C/ solvent-free	82	10 min	[38]
5	HPA/TPI- Fe ₃ O ₄ ^c	100 °C/ solvent-free	92	30 min	[28]
6	HPMO ^d	65 °C/ethyl acetate	92	3.5 h	[39]

^a Nano-Fe₃O₄@ZrO₂-SO₃H

^b Magnetic nanoparticle-supported sulfuric acid

^c H₆P₂W₁₈O₆₂/pyridino-Fe₃O₄

^d Molybdophosphoric acid (H₃[P(Mo₃O₁₀)₄])

Conclusion

To sum up, the synthesis of anatase TiO_2 nanoparticles was performed by the hydrothermal method using titanium (IV) ethoxide solution for the first time. Supported 1,4-BS on



Fig. 8 Recyclability nano-TiO₂-Bu-SO₃H after four runs

 TiO_2 results in interphase nanocatalyst for the simple, efficient and rapid one-pot synthesis of heterocyclic compound such as 1-amidoalky-2-naphthols and 1,8-dioxo-octahydro-xanthenes under solvent-free conditions. Thus, the simple and reproducible preparation, stability and reusability properties of the catalyst for up to several runs with only a minor loss in its catalytic activity indicate the potential application of this system for organic transformations.

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