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Indium oxide nanoparticles embedded in TUD-1 as a highly selective catalyst for toluene to benzaldehyde oxidation using TBHP as oxidant

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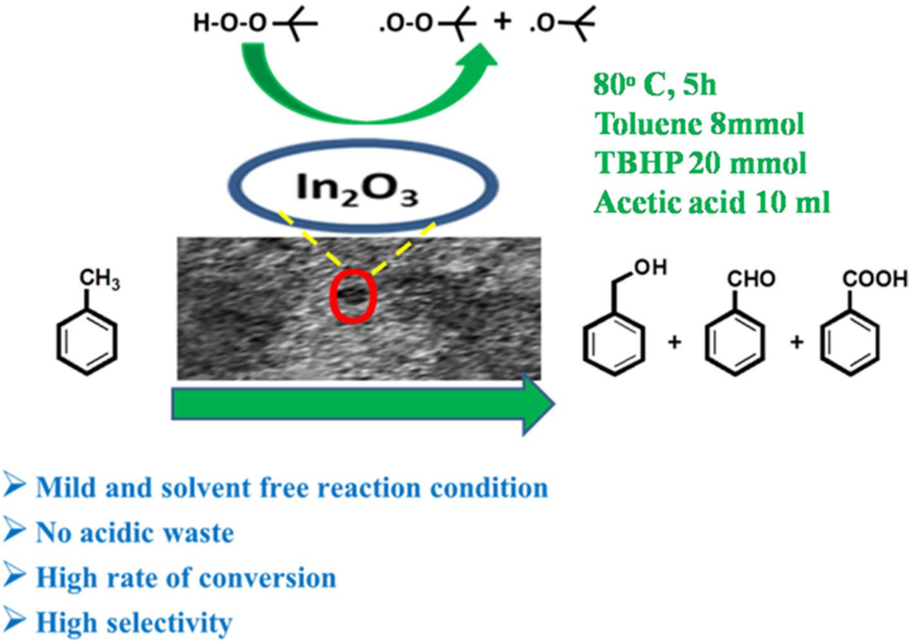
Abstract

C–H activation reaction is one of the most challenging reactions in the present scenario. The green synthesis of benzaldehyde from toluene using TBHP in a sustainable amount as an oxidant over indium-incorporated TUD-1 is performed in the present study. In(1)-TUD-1 (In/Si = 1/100 mol ratio) shows 48% toluene conversion and 83% benzaldehyde selectivity using acetic acid as solvent. The catalyst was recyclable up to five times. A plausible reaction mechanism is also proposed based on the characterization results.

Graphic abstract



Keywords Benzaldehyde · Indium · Mesoporous silica · TBHP · Toluene oxidation

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Introduction

The selective liquid phase oxidation of hydrocarbons to the analogous oxygen-carrying compounds has the potential to simplify the synthesis of complex molecules greatly and has remained a most promising and challenging reaction in both academic and industry circles (Luo et al. 2013). Selective oxidation of C–H bond is still an unsolved problem as the intermediates such as alcohol and aldehydes are more responsive to secondary oxidation to form carboxylic acid which lowers the selectivity (Kantam et al. 2002). Oxygenated products are the indispensable intermediates for agrochemicals, pharmaceuticals, fine chemicals, fragrances, polymers and many chemical feedstocks (Saravanamurugan et al. 2004; Rao et al. 2009). Many researchers have been devoted to the design and synthesis of new reagents and catalysts which can convert these unreactive C–H bonds into C=O. Toluene has a great significance among various hydrocarbons and which on oxidation produces benzyl alcohol, benzaldehyde and benzoic acid. Amidst the oxidized products, benzaldehyde is the most prudent product but it is very prone to oxidation to form benzoic acid. In most of the oxidation reactions, higher oxidation state of metal reagents like manganese, osmium and chromium are used as oxidants in stoichiometric amounts (Visuvamithiran et al. 2013; Brutchey et al. 2005). The above reagents produce huge volumes of organic wastes which are environment unfriendly. Transition metal catalysis has emerged as a powerful tool for C–H activation, but the techniques are accompanied by drawbacks such as low selectivity and use of large amount of solvents and bromides (Zhao et al. 2004; Qian et al. 2005; Maksimchuk et al. 2012). Supported Au–Pd nanoparticles show quite a better result in this aspect (Saiman et al. 2012). Many metals-incorporated metal oxides and zeolites have also been used (Saravanamurugan et al. 2004). Despite notable recent efforts, the development of general and mild strategies is very indispensable in the field of C–H activation.

Silica materials have received enormous attention for their distinctive physico-chemical properties like high thermal stability, high specific surface area, ready surface modification, corrosion resistance and environment friendly (Lai 2013). It also enhances the stability of metal oxide nanoparticles. Mesoporous silica-supported metal catalysts like Metal-TUD-1 (Co, Ti, Cr, Fe, Mn) (Anand et al. 2009; Wang et al. 2018) catalyzed aerobic oxidation of cyclohexane using radical initiators like TBHP and CHHP. Vanadium phosphate containing KIT-6 using H_2O_2 did not perform so well (Rezaei et al. 2017). NDHPI on SBA-15 carrier was used as a catalyst for toluene to benzaldehyde oxidation (Zhou et al. 2016). Indium-incorporated silica for C–H activation has not been explored well till now.

Our primary clear need is the development of an environmentally benign catalyst which can produce benzaldehyde selectively from toluene under very mild reaction conditions. Instead of choosing any transition metal, we have chosen post-transition metal like indium. Indium salts are very stable to water and air, less toxic, more abundant and cheaper compared to transition metals, easy to handle and also very well known for its Lewis acidity in its +3 oxidation state. We here for the first time report the utilization of indium-incorporated TUD-1 with two different indium loadings for toluene to benzaldehyde using TBHP as single oxygen donor under very mild reaction conditions. We have also studied the effect of aging time and temperature on the catalytic activity. The catalysts were characterized by N_2 physisorption, HRTEM, UV–Vis, pyridine IR and O_2 pulse chemisorption, EDX and elemental mapping techniques. Among the indium-loaded catalysts In-TUD-1 (In = 1 and 4 mol%), In(1)-TUD-1 shows higher catalytic activity, i.e., 48% toluene conversion and 83% benzaldehyde selectivity using acetic acid as solvent.

Experimental

Materials and methods

Catalyst synthesis procedure

Different indium-loaded In-TUD-1 catalysts were synthesized by sol–gel procedure as reported in literature. Tetraethyl orthosilicate (TEOS, 98%, Acros Organics) was added to the aqueous solution of indium nitrate (99.9%, Sigma-Aldrich) in deionized water with continuous stirring. Triethanolamine (TEA, 99%, Acros Organics) was added dropwise to the mixture. The entire mixture was stirred for 10 min followed by the addition of tetraethylammonium hydroxide (TEAOH, 20% aqueous solution), (Merck Germany). The resulting gel composition of the mixture is TEOS: $In(NO_3)_3$:TEA: H_2O: TEAOH = 1: x: 2: 11: 1 ($x = 0.01$, 0.04). At room temperature, the complete mixture was stirred for 24 h and the synthesized gel was dried at 110 °C for 24 h in a static oven. In the end, the dried material was calcined in a muffle furnace at 700 °C for 10 h with a temperature ramp of 1 °C/min.

To study the effect of aging time and temperature on the catalytic activity, we synthesized two other catalysts. The first one is by varying aging temperature, i.e., 80 °C for 24 h and the latter one is by varying time of 14 h at 110 °C. In both the cases, indium loading of 1 mol% was kept constant and the catalysts are labeled as In(1)-TUD-1-80C and In(1)-TUD-1-14H, respectively. The details of the synthesized procedures are depicted in supporting information as (catalyst preparation).

Catalyst characterizations

The nitrogen adsorption–desorption isotherms of the prepared catalysts were measured at liquid nitrogen temperature at − 196 °C with a Quantachrome NOVA 3200, USA. Pretreatment of the samples was done at 200 °C for 3 h under high vacuum. The surface area was calculated by Brunauer–Emmett–Teller (BET) equation and pore size distribution was calculated by the BJH method. The HRTEM image of the prepared catalysts was obtained on JEOL JEM 2100 microscope (USA) operated at 200 kV acceleration voltage using lacey carbon-coated Cu grid of 300 mesh size. The UV–Visible (UV–Vis) was performed in Varian Cary 500 (Shimadzu) spectrophotometer in the wavelength range of 200–800 nm. The pulse chemisorption was performed using 5% oxygen in helium for 2 h during pretreatment followed by flushing at 200 °C. During analysis, 5% O_2/He was dosed by 2750 loop of volume 0.5 cm^3. The chemisorption was performed at room temperature. FTIR analysis of the samples was performed using Agilent Cary 600 series with praying mantis setup. Before pyridine treatment, the catalysts were dried at 100 °C in a hot air oven. The catalysts (50 mg each) were taken in sample cups and pyridine (0.1 cc) was added to it. To remove the extra or physisorbed pyridine, the sample cups were kept in a hot air oven at 100 °C. The samples were used at room temperature and IR spectra were taken in the spectral range of 1700–1400 cm^{-1} with 64 scan and at a resolution of 8 cm^{-1} using KBr background. EDX and elemental mapping were carried out by S-3400N model Hitachi instrument.

Catalytic activity studies

In a two-necked round-bottom flask, toluene (*8* mmol) and 70% *t*-butyl hydroperoxide (20 mmol) and 10 ml of acetic acid as solvent were added. The mixture was shaken in molecular level followed by stirring in a thermostated oil bath maintained at 80 °C and 100 mg of catalyst was added to it. Before performing the reaction, the catalyst was dried for 3 h at 100 °C in a hot air oven. The round-bottomed flask was fitted with a condenser. Aliquots were taken at regular intervals of time to check the progress of the reaction. After completion of the reaction, the catalyst was separated by filtration and the reaction mixture was extracted with ethyl acetate and dried with anhydrous Na_2SO_4. The products were analyzed with a gas chromatograph (Agilent 7890B) fitted with a FFAP capillary column (30 m × 32 mm × 0.25 µm) and an FID detector. Temperature used was from 120 °C (2 min) to 230 °C at a heating rate of 20 °C/min.

Results and discussion

Characterization results

BET surface area and porosity measurement, XRD, HRTEM, EDX and STEM, FTIR, NH_3-TPD, H_2-TPR and O_2-TPO techniques have been depicted thoroughly in our previous paper (Rahman et al. 2015). The characterization techniques revealed that In(1)-TUD-1 (In = 1 mol%) shows higher surface area and larger pore diameter, better dispersion of metal nanoparticles over the surface of TUD-1, more reducible In_2O_3, more oxygen uptake and lower surface acidity compared to In(4)-TUD-1 (In = 4 mol%).

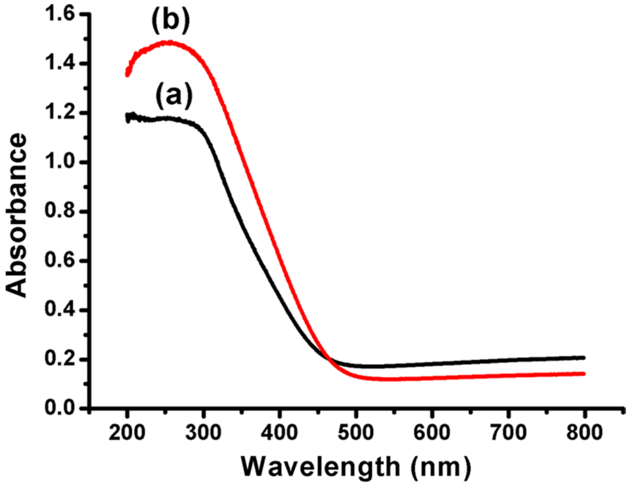


Fig. 1 UV-Vis spectra of a In(1)-TUD-1 and b In(4)-TUD-1

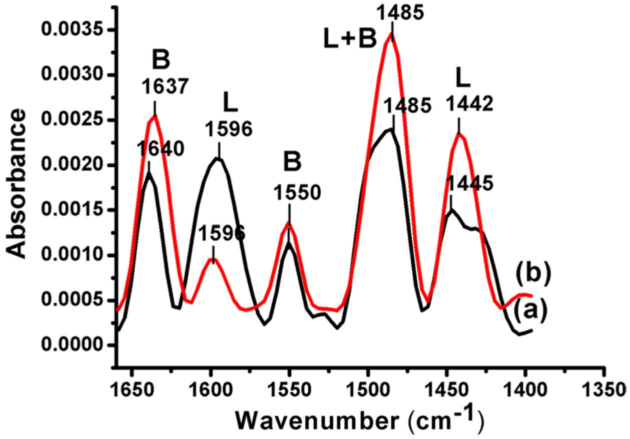


Fig. 2 Infrared spectra of pyridine adsorbed at 298 K on fresh a In(1)-TUD-1and, b In(4)-TUD-1. *L* Lewis acid site, *B* Bronsted acid site, *L+B* Lewis+Bronsted acid site

The UV–Vis spectra of the synthesized catalysts have been represented in Fig. 1. The absorption band at 250 nm instead of at 330 nm indicates the presence of In_2O_3 nanoparticles which may be due to the weak quantum confinement effect. With increasing indium loading, the peak is intensified and shifted to a higher wavelength (Kumar et al. 2016).

Figure 2 depicts the pyridine-adsorbed FTIR spectra of the fresh samples at 298 K. The absorption peaks at 1640, 1550 cm^{-1} correspond to the pyridine adsorbed in Bronsted acid sites and peaks at 1596, 1445 cm^{-1} correspond to pyridine adsorbed in Lewis acid sites. Peak at 1485 infers to pyridine adsorbed in both the Bronsted and Lewis acid sites. Bronsted acid sites are more populated for In(4)-TUD-1 (Reddy et al. 2009). The percentage of acidic and basic sites is depicted in Table S1.

O_2 pulse chemisorption study depicted in Table 1 discloses the dispersion of indium oxide nanoparticles over TUD-1 matrix. The lower dispersion may be due to stronger metal and support interaction. Better dispersion was found for lower indium-loaded catalyst compared to higher indium-loaded catalyst because in case of higher metal-loaded catalyst, agglomeration of particles and larger crystallite size was also supported by XRD and HRTEM studies.

In(1)-TUD-1-80C and In(1)-TUD-1-14H were characterized by N_2 physisorption study, HRTEM, elemental mapping and EDX. N_2 physisorption results are depicted in Table S2 and isotherms as Fig. S1, HRTEM, SAED and elemental mapping are depicted as Figs. S2, S3 and S4, respectively (Supporting Information). It was observed that In(1)-TUD-1-14H shows better catalytic activity both in terms of toluene conversion and benzaldehyde selectivity compared to In(1)-TUD-1-80C and such enhanced catalytic behavior of In(1)-TUD-1-14H can be attributed to its larger surface area and pore diameter. HRTEM micrograph confirms the sponge-like morphology and SAED pattern confirms the amorphous nature of silica. Agglomeration of indium oxide nanoparticles and lower dispersion of indium on silica were observed from HRTEM and elemental mapping, respectively, which might be the reason behind inferior catalytic activity of In(1)-TUD-1-80C compared to In(1)-TUD-1-14H. EDX result depicted in Table S3 reveals the presence of a little more amount of indium in In(1)-TUD-1-80C than In(1)-TUD-1-14H. Such a small increase in indium has been found to have no such profound effect on catalytic activity.

Table 1 O_2 pulse chemisorption study of different indium-loaded TUD-1 catalysts

Catalyst	O_2 uptake (μmol/g)	Dispersion (%)	Surface area of indium (m^2/g)	Average crystallite diameter (nm)
In(1)-TUD-1	1.02	1.99	7.94	103.3
In(4)-TUD-1	0.98	0.62	2.4	342

Indium amount was found from EDX described in our previous paper (Rahman et al. 2015)

Catalytic activity and discussion

Initially, oxidation of toluene was conducted using molecular oxygen, but no reaction occured. The reaction was also carried out using the silica support TUD-1 and 70% TBHP in water but a small amount of product was obtained. Again, the reaction was conducted using indium-incorporated TUD-1 silica using 70% TBHP in water as oxidant and it showed quite an appreciable result. The catalytic activity was optimized by varying oxidant, metal loading, temperature, time, toluene and TBHP ratio, solvent and represented in Tables 2, 3, 4, 5, 6 and 7, respectively.

Table 2 delineates the effect of oxidants on toluene oxidation. Oxidation of toluene was conducted using molecular oxygen, but no reaction was observed. We performed the reactions using both TBHP in decane (5.5 M) and 70% TBHP in water as oxidant and found that in case of both the oxidants, by increasing the metal loading, the catalytic activity increased a little in terms of conversion along with an appreciable decrease in benzaldehyde selectivity. So, we performed the other reactions using 70% TBHP in water as oxidant.

The catalytic activity studies varying the indium loading are described in Table 3. We have performed the reactions using both 70% TBHP in water as oxidant. By increasing the metal loading, the catalytic activity increased a little in terms of conversion along with an appreciable decrease in benzadehyde selectivity. In(4)-TUD-1 exhibits higher surface acidity than In(1)-TUD-1 found from NH_3-TPD and more Bronsted acid sites were observed from pyridine IR. (Martin et al. 1999) also explained very precisely that both Bronsted and Lewis acid sites are responsible for toluene chemisorption and increase in basicity of the catalyst surface by blocking the Bronsted acid site enhances the desorption rate of aldehyde. Bronsted acid sites are very necessary for

Table 2 Toluene oxidation activity using different oxidants

Catalyst	Oxidants	Toluene conversion (%)	Selectivity (%)			
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Others
In(1)-TUD-1	O_2	–	–	–	–	–
In(1)-TUD-1	**70% TBHP in water**	**42**	**20.6**	**78.2**		**< 2**
In(1)-TUD-1	TBHP in decane (5.5 M)	45	89.07	3.5	7.4	
In(4)-TUD-1	70% TBHP in water	47	31.3	64.5		< 1
In(4)-TUD-1	TBHP in decane (5.5 M)	51	93.6	2.8	3.2	< 1

Reaction conditions: toluene: 8 mmol, TBHP: 20 mmol, time: 5 h, temperature: 80 °C

Reaction performance in optimum condition are shown in bold

Table 3 Toluene oxidation activity using different indium-loaded TUD-1

Catalyst	Indium loading in (mol%)	Toluene conversion (%)	Selectivity (%)			
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Others
–	–	7	92.8	7.1		
TUD-1	–	8	92.2	7.7		
In(1)-TUD-1	1	2[a]	98.5	< 1		
In(1)-TUD-1	**1**	**42**	**20.6**	**78.2/0.53**[b]		**< 2**
In(4)-TUD-1	4	47	31.3	64.5/0.22[b]		< 1

Reaction conditions: toluene: 8 mmol, TBHP: 20 mmol, catalyst: 100 mg, temperature: 80 °C

Results in optimum conditions are represented in bold

[a] Reaction in the absence of TBHP

[b] TOF, TOF = Moles of toluene converted/moles of indium present per hour. Indium amount was found from EDX described in our previous paper (Rahman et al. 2015)

Table 4 Effect of reaction temperature on selective oxidation of toluene

Catalyst	Temperature (°C)	Toluene conversion (%)	Selectivity (%)			
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Others
In(1) TUD-1	30	29	32.6	67.2	–	–
In(1) TUD-1	**80**	**42**	**20.6**	**78.2**		**< 2**
In(1) TUD-1	100	45	17.1	62	20.7	–

Reaction conditions: toluene: 8 mmol, TBHP: 20 mmol, catalyst: 100 mg, time: 5 h

Reaction performance in optimum condition are shown in bold

Table 5 Effect of reaction time on selective oxidation of toluene

Catalyst	Time (hours)	Toluene conversion (%)	Selectivity (%)			
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Others
In(1) TUD-1	2	21	21	79	–	–
In(1) TUD-1	**5**	**42**	**20.6**	**78.2**		**< 2**
In(1) TUD-1	6	51	17.2	76.5	6.1	< 1
In(1) TUD-1	12	58	9.1	73	17.6	
In(1) TUD-1	26	59	4.5	63.1	31.9	

Reaction conditions: toluene: 8 mmol, TBHP: 20 mmol, catalyst: 100 mg, solvent: 10 ml, time: 5 h, temperature: 80 °C

Reaction performance in optimum condition are shown in bold

Table 6 Effect of toluene: TBHP molar ration on toluene oxidation

Catalyst	Toluene: TBHP molar ratio	Toluene conversion (%)	Selectivity (%)			
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Others
In(1)-TUD-1	1:1	36	25.3	73	1.2	
In(1)-TUD-1	1:1.25	38	22.6	75.3	2	< 1
In(1)-TUD-1	**1:2.5**	**42**	**20.6**	**78.2**		**< 2**
In(1)-TUD-1	1:4	45	12.1	65.8	21	<1

Reaction conditions: time: 5 h, temperature: 80 °C, catalyst: 100 mg

Reaction performance in optimum condition are shown in bold

Table 7 Effect of different solvents on toluene oxidation

Catalyst	Solvent	Toluene conversion (%)	Selectivity (%)			
			Benzyl alcohol	Benzaldehyde	Benzoic acid	Others
In(1)TUD-1	–	42	20.6	78.2		< 2
In(1)TUD-1	Ethyl acetate	43	16.5	74.5	8.2	
In(1)TUD-1	Acetonitrile	45	13.2	79.8	6.5	
In(1)TUD-1	**Acetic acid**	**48**	**14.5**	**83.2**		**< 2**
In(1)TUD-1	Ethanol	47	18.2	81.5		

Reaction conditions: toluene: 8 mmol, TBHP: 20 mmol, catalyst: 100 mg, solvent: 10 ml, time: 5 h, temperature: 80 °C

Reaction performance in optimum condition are shown in bold

toluene conversion but more Bronsted acid sites are associated with more coke deposition and catalyst deactivation (Mendez-Roman and Cardona-Martinez 1998; Bulushev et al. 2004). At higher metal loading of 4 mol%, toluene conversion should be profoundly high because of its higher acidity. As the catalyst in lower indium loading exhibits less surface acidity, so, it should show lower toluene conversion (Mal et al. 2018). Although the acidity of In(4)-TUD-1 is high, no appreciable change in toluene conversion may be due to poor metal dispersion compared to In(1)-TUD-1 was observed from XRD, HRTEM, H_2-TPR and O_2 pulse chemisorption study as well as lower surface area observed from N_2 physisorption. The decrease in benzaldehyde selectivity can be explained by the more populated Bronsted acid site which leads to deactivation of the catalyst.

Table 4 describes the effect of temperature on toluene oxidation. We started the reaction at 80 °C following the literature. By increasing the temperature from room temperature (30 °C) up to 80 °C, both the conversion and selectivity increased, but above 80 °C, toluene conversion increased but benzaldehyde selectivity decreased. Higher temperature favors total oxidation instead of partial oxidation.

To check the progress of the reaction, aliquots were taken at some regular intervals of time and the catalytic activities are depicted in Table 5. With the increase of time from 2 to 12 h, gradual increase in toluene conversion and variation in product selectivity were observed. For prolonged reaction time of 26 h, benzoic acid formation increased substantially meanwhile benzyl alcohol selectivity decreased. This implies that with time, benzyl alcohol is getting further oxidized to benzoic acid which is a very stable product. Figure 3 depicts the effect of time on toluene conversion.

Table 6 delineates the impact of toluene:TBHP ratio on toluene oxidation. The molar ratio of toluene: TBHP varied as (1:1, 1:1.25, 1:2.5 and 1:4) and we observed a better result in 1:2.5 molar ratio which is 48% toluene conversion and 83% benzaldehyde selectivity. No benzoic acid was found, but a small amount of o-cresol was observed. A small increase in toluene conversion and appreciable decline in benzaldehyde selectivity were observed with toluene:TBHP (1:4) ratio. In case of toluene:TBHP ratio of 1:1 and 1:2.5, the amount of TBHP may not be sufficient for converting benzyl alcohol to benzaldehyde for which a higher amount of benzyl alcohol was found compared to benzaldehyde and no acetic acid was found. The higher amount of TBHP in the ratio of toluene: TBHP 1:4 may result in total oxidation which produced benzoic acid by total oxidation instead of partial oxidation as a result of which decrease in benzaldehyde selectivity was observed.

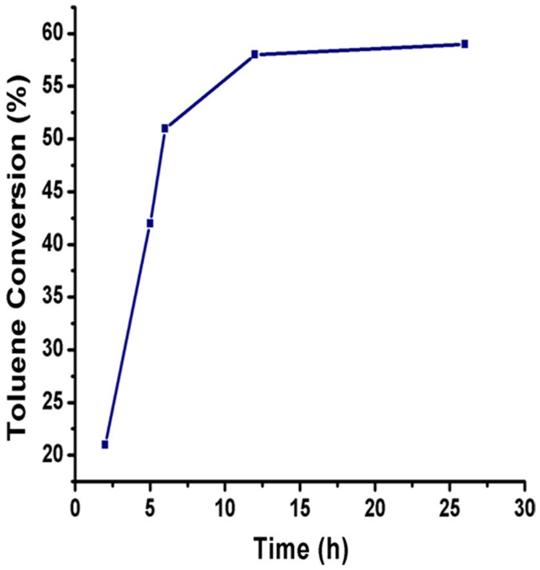


Fig. 3 Effect of reaction time on toluene conversion using In(1)-TUD-1

Again, the target of achieving optimum catalytic activity led to the use of solvents like acetic acid, acetonitrile, ethyl acetate and ethanol. We found the optimum catalytic activity, i.e., 48% toluene conversion and 83% benzaldehyde in the case of acetic acid. Acidity of the solvents is in the order acetic acid > ethanol > acetonitrile > ethyl acetate. The solvent acidity has great significance in oxyfunctionalization and with increasing solvent acidity, both the toluene conversion and benzaldehyde selectivity increased in our

Table 8 Catalyst regeneration and substrate variation

Catalyst	Substrate	Conversion (%)	Major product selectivity (%)
In(1)-TUD-1	**Toluene**	**48**	**83.2**[g]
In(1)-TUD-1	**Toluene**[a]	**47**	**84.2**[g]
In(1)-TUD-1	**Toluene**[b]	**44**	**83.3**[g]
In(1)-TUD-1	**Toluene**[c]	**40**	**80.9**[g]
In(1)-TUD-1	**Toluene**[d]	**36**	**80.5**[g]
In(1)-TUD-1	**Toluene**[e]	**28**	**78.6**[g]
In(1)-TUD-1	**Toluene**[f]	**8**	**63.5**[g]
In(1)-TUD-1	Ethylbenzene	**54**	**88**[h]
In(1)-TUD-1	Cyclohexane	**21**	**67**[i]

Reaction conditions: reactant = toluene 8 mmol; TBHP = 20 mmol; catalyst = 0.1 g; acetic acid: 10 ml, temperature = 80 °C; time = 5 h

Reaction performance in optimum condition are shown in bold

[a] First recycle

[b] Second recycle

[c] Third recycle

[d] Fourth cycle

[e] Fifth cycle

[f] Sixth cycle

[g] Benzaldehyde

[h] Acetophenone

[i] Cyclohexanone

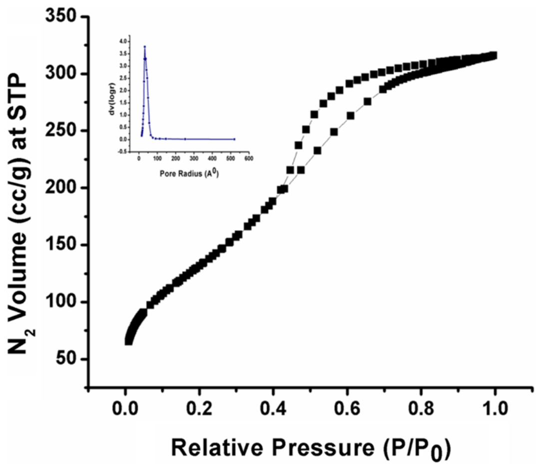


Fig. 4 N_2 physisorption isotherm and pore size distribution curve of In(1)-TUD-1 catalyst after fifth regeneration

Table 9 N_2 physisorption results of fresh and sixth cycle catalyst

Catalyst	Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (nm)
In(1)-TUD-1	688.7[a]	1.094[a]	8.30[a]
In(1)-TUD-1	500	0.048	6.36

[a] BET results reported by Rahman et al. 2015

Table 10 EDX results of fifth and sixth cycle In(1)-TUD-1 catalyst

Sample	O (at %)	Si (at %)	In (at %)	Total (at %)
In(1)-TUD-1 (fifth cycle)	83	16.53	0.04	100
In(1)-TUD-1 (sixth cycle)	85.73	14.23	0.004	100

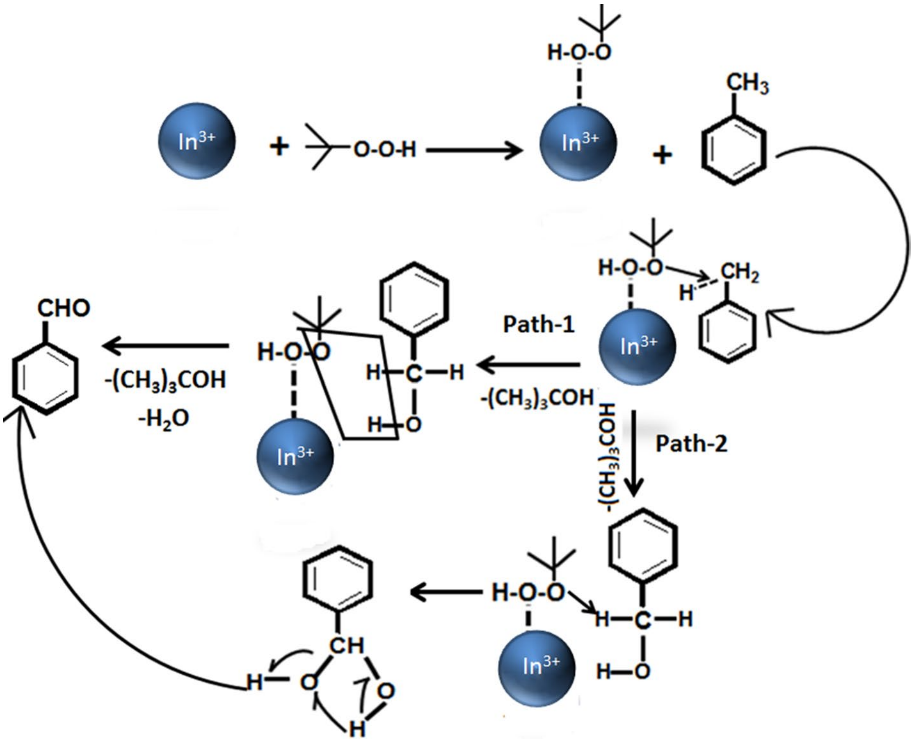
study. The effect of the solvent acidity on catalytic reaction is not clear (Bauer 2017; Velu et al. 1999; Zhang et al. 2005). Effect of solvent on toluene oxidation is represented in Table 7.

Catalyst regeneration and substrate variation

To commercialize the catalyst, catalyst recyclability is one of the essential parameters. Catalytic activities of the catalysts did not vary to a greater extent up to five cycles as represented in Table 8. The gradual decrease in conversion up to fifth cycle can be due to the leaching of metal and loss of catalyst during filtration and drying. After the fifth cycle, a sudden decline in catalytic activity was observed. To investigate the reason behind the deactivation of catalyst, the sixth cycle used catalyst was characterized by N_2 physisorption and EDX and represented as shown in Fig. 4, Tables 9 and 10, respectively. N_2 physisorption result reveals that the mesopore structure is still retained and decrease in surface area, pore volume and pore diameter may be due to the blocking of surface sites or pores of the catalyst by the reactant molecules. Again, to clear the presence of indium, EDX was performed. From the EDX results of fifth (indium 0.4 at %) and sixth cycle catalyst (indium 0.00 at 4%), we observed than an acute change in indium amount. So, we may conclude that the catalyst is stable and leaching of indium which is the active component loss may be the reason behind deactivation of the catalyst. The catalyst also induced oxyfunctionalization of ethylbenzene and cyclohexane. Acetophenone and cyclohexanone were observed to be the major products of ethylbenzene and cyclohexane oxidation, respectively.

Proposed reaction mechanism

Metal nanoparticles can decompose oxidants like TBHP to form .OH and .OOH radicals (Anand et al. 2006). Early transition metals can accelerate liquid phase oxidations in their highest oxidation state, like Ti^{4+} or V^{5+}, activate peroxides for their Lewis acidity (Corma et al. 1995; Shylesh and Singh 2006). Indium in its (III) oxidation state is also well known



Scheme 1 A plausible mechanism for selective oxidation of toluene over indium-loaded TUD-1 silica (Rao et al. 2009)

for its Lewis acidity (Gandara et al. 2008). Herein, TBHP successfully performed as an oxidant in our reaction, but in the absence of metal, no appreciable amount of products formed. TBHP undergoes radical chemistry mostly. In fact, when we added a radical scavenger like quinhydrone, the reaction stopped immediately. This suggests that In-TUD-1 catalyzed reaction not surprisingly proceeds through radical intermediates or via radical chain mechanism. It is also worth mentioning that the reaction also produces t-BuOH as byproduct.

Toluene reacting with TBHP over In-TUD-1 proceeds with the generation of tertiary butyl peroxy (t-BuOO.) and tertiary butoxy (t-BuO.) radicals. In the first step, coordination of TBHP with In (III) occured. The *tert*-butyloxy radical reacts with toluene to form the benzyl radical. The formation of benzyl alcohol (I) proceeds via the formation of benzyl cation by the transfer of electron from benzyl radical to the catalyst. The benzyl cation reacts with hydroxyl anion to produce benzyl alcohol. The reduced catalyst is oxidized by TBHP. The benzyl radical combines with *tert*-butyl peroxy radical to produce benzaldehyde. It may proceed through two steps. As benzyl alcohol is hydrophilic, the presence of water near the active site allows subsequent oxidation to benzaldehyde. Benzyl alcohol rearranged to form benzaldehyde, whether by dehydration or by abstraction of hydrogen followed by rearrangement to benzyldehyde (Scheme 1).

Selective oxidation of toluene to benzaldehyde over a variety of heterogeneous catalysts has been well studied. Table 11 provides a comparison of the results achieved from our present catalyst with the other reported catalysts (Guo et al. 2005; Wang et al. 2005; Li et al. 2006). Our present catalyst exhibits a very comparable conversion and selectivity at moderate temperature with a shorter reaction time.

Conclusion

In-TUD-1 catalysts of different loading (1 and 4 mol%) were prepared by sol–gel method. In(1)-TUD-1 shows better selective oxidation of toluene to benzaldehyde using acetic acid as solvent. Elevated surface acidity of the catalyst, solvent acidity and better distribution of indium oxide nanoparticles over silica are the key enablers for better catalytic activity. Bronsted acid site is a must for toluene conversion, but an optimum Bronsted/Lewis acid site is required for selective benzaldehyde production. Interestingly, 48% toluene conversion was found in case of In(1)-TUD-1 with 83% selectivity for benzaldehyde. The present catalyst has several advantages like environment friendly, mild reaction condition, economic, simple work-up and recyclability of the catalyst up to fifth cycle.

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Table 11 A comparison table of toluene oxidation with other reported catalysts

Catalyst	Temperature/pressure	Oxidant	Conversion (%)	Selectivity (%)	References
Present catalyst	80 °C/1 atm	TBHP	41	77	Present work
Co-SBA-15	80 °C/1 atm	TBHP	7.97	63.8	Brutchey et al. 2005
Co-(II)TPP	150 °C/0.8 MPa	O_2	8.9	33	Guo et al. 2005
$MPAV_2/Nb_2O_5$	RT/1 atm	TBHP	22	76	Rao et al. 2009
V-Mo-Fe-O	80 °C/1 atm	H_2O_2	40.3	84.5	Reddy et al. 2009
Cu–Fe/TiO_2	190 °C/1 MPa	O_2	1.8	27	Wang et al. 2005
Cu–Mn (1:1)	190 °C/1 MPa	O_2	17.2	20	Li et al. 2006
C0/Mn/Br^-	110 °C/10 kg/cm^2	O_2	38.31	1.01	Kantam et al. 2002
Sil-Si-Ti(OiPr)	30 °C/1 atm	TBHP	22[a]	_	Saravanamurugan et al. 2004
1%Au–Pd/TiO_2	80 °C/1 atm	TBHP	4.4	32	Saiman et al. 2012
$MnWO_4$ nanobars	80 °C/1 atm	H_2O_2	59.5	90	Bulushev et al. 2004

[a] TBHP conversion

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