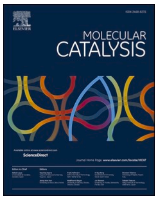
Molecular Catalysis 503 (2021) 111440

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis



Selective aerobic oxidation of toluene to benzaldehyde catalyzed by covalently anchored N-hydroxyphthalimide and cobaltous ions

Jinyang Xu, Guojun Shi *, Yuxin Liang, Qiuting Lu, Lijun Ji

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, Jiangsu Province, People's Republic of China

ARTICLE INFO

Keywords:
Toluene
Benzaldehyde
Selective oxidation
N-hydroxyphthalimide
Covalent anchoring

ABSTRACT

Selective oxidation of toluene to benzaldehyde via dioxygen is of great significance industrially but suffers from a severely low selectivity due to a much higher reactivity of the desired product than the reactant. A combination of homogeneous N-hydroxyphthalimide (NHPI) and cobaltous ions was found active and selective for the transformation from toluene to benzaldehyde in the presence of hexafloropropan-2-ol. In this work, homogeneous NHPI was covalently anchored onto the surface of commercial mesoporous SiO_2 to facilitate the separation and recovery of the catalyst, aiming at a possible industrial application. The grafting bonds were well confirmed by FT-IR, TGA and XP spectra, and the density of $>$ N—OH groups anchored was up to 0.6 mmol/g in the immobilized NHPI catalysts. The resulting catalysts exhibited an excellent activity for selective oxidation of toluene to benzaldehyde, and there was no appreciable loss in catalytic activity observed after repeated evaluations, suggesting a promising prospect for its further investigation and possible application.

1. Introduction

Selective transformation of toluene into benzaldehyde is attracting an increasing attention due to the versatile applications of the desired product [[1–6]]. However, the traditional production of benzaldehyde proceeds via chlorination of toluene and subsequent hydrolysis industrially, suffering from a severe corrosion of equipment and a chlorination contamination of the product. It is important to note the product benzaldehyde containing chlorine cannot be used for foods and medicines [7]. Therefore, a highly efficient and environmentally friendly process for the production of chlorine-free benzaldehyde has been expected.

Some methods, such as oxidation of benzyl alcohol [8], styrene [9] or toluene [10] and reduction of benzoic acid [11], were tried to prepare benzaldehyde, among which the direct oxidation of toluene to benzaldehyde, especially when molecular oxygen was used as the oxidant, exhibited greater potential in industrial application due to the cost and availability of the raw material [12]. However, a huge challenge rises when the direct oxidation of toluene is used for the production of the desired benzaldehyde, which is the fact that the aimed product benzaldehyde is much more active than the starting material toluene under reaction conditions and easily is deeply oxidized to benzoic acid, CO_x, etc. [13]. Furthermore, the C(sp^3)–H bonds of toluene are unreactive under mild conditions due to a spin-flip restriction between it and the ground triplet state molecular oxygen [14], and thus the oxygenation of the substrate usually proceeds at an elevated temperature, pressure, etc., leading to a terribly low selectivity to benzaldehyde [15,16].

N-hydroxyphthalimide (NHPI) can be activated to generate phthalimide N-oxyl (PINO) free radicals, which can catalyze oxidative dehydrogenation of N-heterocycles [17], oxidative acylation of arenes [18], the transformation from olefins to carbonyl products by oxidation cleavage of C=C double bonds [19], and the oxidation of saturated C—H bonds to alcohols, aldehydes, acids or esters [20,21] using molecular oxygen. Compared with tetramethylpiperidine-N-oxyl (TEMPO), PINO exhibited high catalytic activity for C—H bonds oxidation due to the presence of its adjacent electrophilic cuyl [22,23]. The electron-withdrawing capability of the adjacent cuyl enhances the bond dissociation energy (BDE) O—H in NHPI and facilitates the H-abstraction of the resulting N-oxyl (PINO) [22,23]. Moreover, the adjacent cuyl can also promote the generation the production of the transition state complex via a polar effect [22,23]. The PINO free radical can be generated by means of a single electron transfer to transition metal cations with a high valence [24,25] or dioxygen at an elevated temperature [18,19], H-abstraction of metal-oxygen complex radical [20],

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[*] Corresponding author. Permanent address: School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, Jiangsu Province, People's Republic of China.

E-mail address: gjshi@yzu.edu.cn (G. Shi).

https://doi.org/10.1016/j.mcat.2021.111440
Received 26 September 2020; Received in revised form 25 January 2021; Accepted 26 January 2021

acylperoxy radical [26] or $NO_2^{\bullet}$ radical [27]. The strongly electrophilic PINO radical involves the transformations of substrates to the desired product via H-abstraction [18, 28,29,30], electrophilic addition [19], etc. to promote the related transformations. It is Ishii and his co-workers who firstly developed NHPI/Co(II) as catalysts for selective oxidation of toluene in acetic acid and achieved a high degree of transformation of toluene at room temperature [31]. However, the predominating product from toluene in Ishii and coworkers' researches was benzoic acid and the selectivity to the desired benzaldehyde was only ca. 3%.

The newest breakthrough in selective oxidation of toluene to benzaldehyde was made by Pappo's group [32]. They found that the presence of hexafluoropropan-2-ol (HFIP) markedly enhanced the selectivity to benzaldehyde even at a high toluene conversion using the homogeneous NHPI/Co(II) catalysts. The surprising effect of HFIP on the selective production of benzaldehyde from toluene was attributed to the formation of intermolecular hydrogen bonds between HFIP and the aimed benzaldehyde based on the NMR analysis and theroretical calculation [32]. It was found that the hydrogen bonds formed enhanced the bond dissociation energy (BDE) of aldehydic C—H bond and thus inhibited its successive cleavage and the formation of the over-oxidized product benzoic acid.

The combination of NHPI/Co(II) with HFIP was praised as "a surprisingly simple and remarkably elegant solution to the partial oxidation of toluene to benzaldehyde" [33]. However, a difficulty in the separation, recovery and reuse of the homogeneous NHPI and cobaltous ions will be encountered when the route is considered for possible industrial production [34]. Moreover, NHPI is easily decomposed under reaction conditions and the resulting trace of by-products will lead to a contamination of the desired products and thus more work has to be devoted to their purification [16]. A reliable immoblization of the homogeneous catalyst NHPI will facilitate its separation, recovery and reuse and inhibit its decomposition to some extent. Thus, the remaining question is how to attach the NHPI molecules to the suitable supports with an excellent textural properties and to realize a high catalytic activity for direct oxidation of toluene to benzaldehyde using molecular oxygen.

Impregnation is a convenient method to prepare the immobilized organic catalysts, while it often suffers from a fatal defect: the leaching of the active components. Hermans et al. tried the immobilization of NHPI on silica support by impregnation [35], and the obtained catalysts were applied to the solvent-free oxidation of cyclohexane. The immobilized NHPI was well adsorbed on support and there no apparent leaching observed under reaction conditions due to a low polarity of cyclohexane. Therefore, the prepared NHPI/SiO_2 catalysts exhibited high and steady catalytic activity for the selective oxidation of cyclohexane. However, similar results were not observed when toluene was used as the raw material for catalytic transformation on the anchored NHPI/SiO_2 catalysts prepared by impregnation [36]. As reported by Zhou et al., the immobilized NHPI/SBA-15 catalyst prepared by impregnation presented a sharp decrease in catalytic activity when it was reused in the toluene oxidation [36]. Covalent anchoring was believed more reliable for the immobilization of organic catalysts [37]. It was found that the immobilized NHPI catalysts synthesized by the binding of amide or ester bonds possessed repeatable catalytic activity in some systems [37,38,39], but the grafting bonds were easily hydrolyzed in the presence of acids [40,41].

In this work, immobilized NHPI/SiO_2 catalysts were prepared by covalent grafting in term of C—O—N bonds, and the resulting catalysts were characterized to analyze their structural and textural properties, and further used to catalyze the direct oxidation of toluene to benzaldehyde in HFIP. The properties and catalytic performance of the catalysts were discovered, and the possible mechanism of selective oxidation of toluene to benzaldehyde was probed.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Synthesis of N,N-dihydroxypyromellitimide (NDHPI)

Hydroxylamine hydrochloride (40 mmol) and triethylamine (Et_3N, 40 mmol) were dissolved in 120 ml of ethanol. After a thorough stirring (the solid was dissolved completely), 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) (20 mmol) was added to the above ethanol solution. The solution was refluxed at 80 °C for 8 h, and then deionized water (200 mL) was introduced into the solution. The resulting suspend was filtered and the obtained yellow powder was dried at 50 °C in static air. The synthetic route is shown in Fig. 1 and the prepared yellow powder was referred to as *N,N*-dihydroxypyromellitimide (NDHPI).

2.1.2. Synthesis of NHPI-GPTMS-SiO_2

The synthesized sample NDHPI (4 mmol) and 3-(glycidoxypropyl) trimethoxysilane (GPTMS) (12 mmol) were added into ethyl acetate (120 mL) under a strict stirring. The reaction mixture was refluxed for 24 h at 78 °C in the atmosphere of nitrogen. Then, the solvent was removed by rotary evaporation and the solid was washed successively with ethanol and dichloromethane. The synthetic route is shown in Fig. 2 and the intermediate synthesized was referred to as NHPI-GPTMS.

The synthesized intermediate NHPI-GPTMS (1 mmol) and commercial SiO_2 (silica gel for column chromatography, 1 g) was dispersed in toluene under a strict stirring. The prepared suspend was refluxed at 100 °C for 24 h in the atmosphere of nitrogen. Then, the resulting suspend was filtered and the resulting solid was washed using a mixed solution of diethyl ether and chloroform (1 : 1). The synthetic route is shown in Fig. 3 and the catalyst synthesized was referred to as NHPI-GPTMS-SiO_2.

2.1.3. Synthesis of SiO_2-GPTMS-NHPI

The SiO_2-GPTMS-NHPI catalyst was synthesized at the same reaction conditions, but an opposite order adopted in comparison with the catalyst NHPI-GPTMS-SiO_2.

Firstly, GPTMS was attached onto the surface of the commercial SiO_2 by a condensation reaction between the silanol of the substrate and the methoxyl of GPTMS, and the prepared intermediate was referred to as SiO_2-GPTMS (Fig. 4).

Then, the covalent attachment proceeded between the synthesized intermediate SiO_2-GPTMS and the prepared NDHPI by the formation of a C—O—N bond. The resulting catalyst was referred to as SiO_2-GPTMS-NHPI (Fig. 5).

2.2. Characterization of catalysts

FT-IR spectra were recorded on a TENSOR 27 spectrometer using a self-supporting wafer diluted by KBr with a sample concentration of 1%. ^1H NMR and/or ^{13}C NMR spectra of the intermediate GPTMS-NHPI and the catalysts SiO_2-GPTMS-NHPI and NHPI-GPTMS-SiO_2 were measured at room temperature on a solid NMR spectrometer (Bruker, Avance III, 400 W Hz). LC–MS (Therm, LCQ Deca XP MAX) was adopted to analyze the reaction solution and the purity of the synthesized NDHPI. Elemental analyses were performed on a Vario EL Cube element analyzer. Thermogravimetric analyses were carried out in a temperature range 30–800 °C with a scan rate of 10 °C/min under a N_2 atmosphere. The grafting densities of the synthesized catalysts were determined by their weight loss at a temperature range from 240 to 800 °C, which is shown in Eqn. 1. Low temperature N_2 adsorption-desorption was operated at 77 K on a Micromeritics ASAP 2010 micropore analysis system. XPS measurements were performed on an ESCALAB electron spectrometer.

$$D = (\mathrm{L} \times 1000)/\mathrm{Mw} \tag{1}$$

D: Grafting density (mmol/$g_{catalyst}$)
L: Weight loss from 240 to 800 °C (wt. %)
Mw: Relative molecular weight of the grafted organic moiety (392)

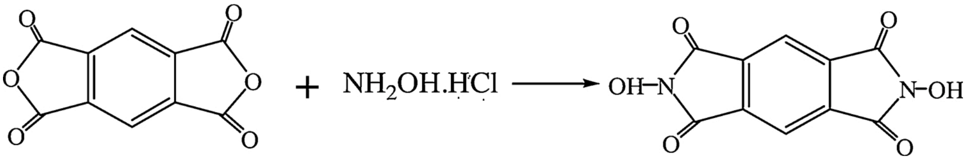

Fig. 1. Synthetic route of NDHPI.

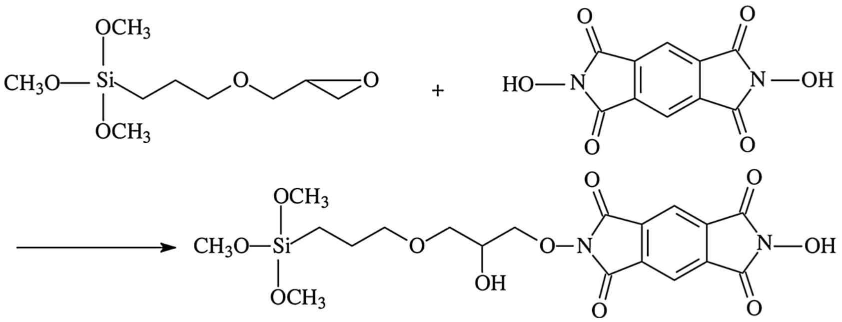

Fig. 2. Synthetic route of NHPI-GPTMS.

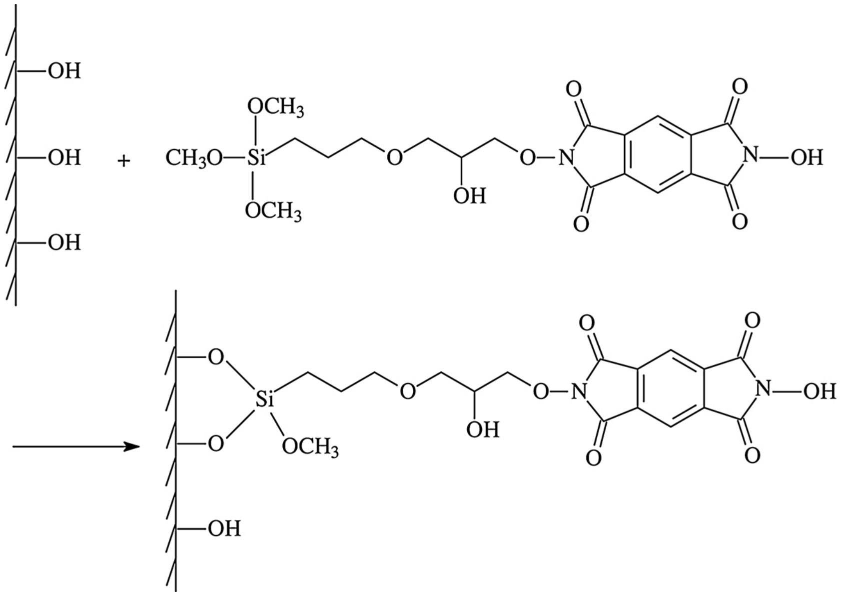

Fig. 3. Synthetic route of NHPI-GPTMS-SiO_2.

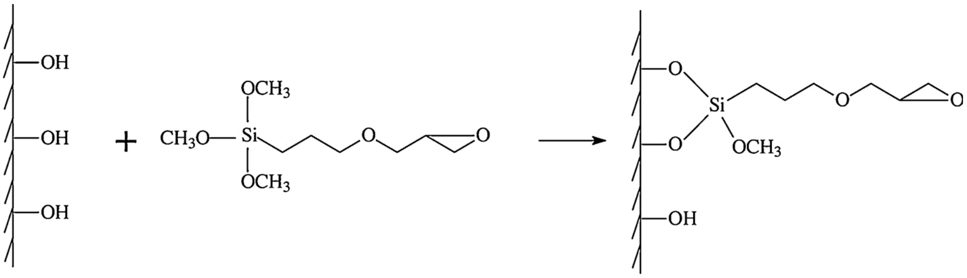

Fig. 4. Synthetic route of SiO_2-GPTMS.

2.3. Catalytic activity test

The catalytic performance of the anchored NHPI was evaluated via the selective oxidation of toluene to benzaldehyde. The reaction was carried out in a PTFE-lined autoclave (50 mL), and the reaction temperature was monitored by a thermocouple inserted in the autoclave. In a typical reaction, toluene (0.21 mL, 2.0 mmol), catalyst (0.20 g), Co $(OAc)_2 \cdot 4H_2O$ (10 mg, 0.040 mmol) and HFIP (4.2 mL, 40 mmol) were

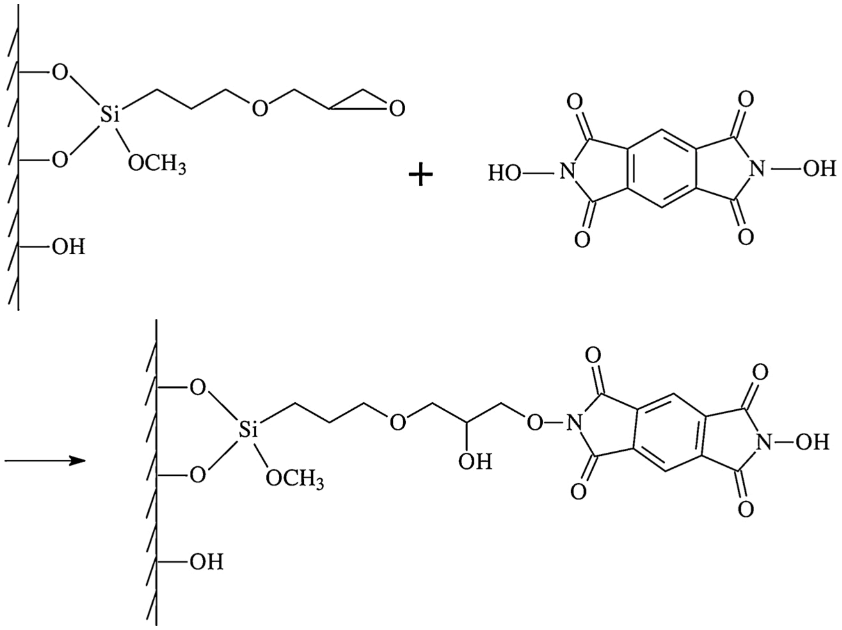

Fig. 5. Synthetic route of SiO_2-GPTMS-NHPI.

introduced into the autoclave, and the rest of the autoclave was repeatedly purged by O_2 (99.999 %) before test. The resulting reaction mixture was filtered to recycle the anchored NHPI catalyst, and the solution left was analyzed by an off-line gas chromatographer (SHIMADZU GC-2014) equipped with a SGE AC-10 capillary column and a flame ionization detector (FID). The analysis was carried out at a column temperature of 160 °C, and the components in the reaction solution were assigned by means of GC–MS (Trace-ISQ, DB-5). The quantitative calculations of conversions, selectivities and yields were performed using chlorobenzene as an internal standard with an estimated error of ca. 2%. The recycled catalyst was repeatedly washed using a mixed solution of diethyl ether and chloroform (1 : 1) followed by a drying in static air at 50 °C for 24 h. The recycled catalysts were recorded as NHPI-GPTMS-SiO_2-R_y, in which “y” denotes the times for which the catalysts were reclaimed.

3. Results and discussion

3.1. Structural and textural properties of catalysts

The FT-IR spectra of the immobilized N-hydroxyphthalimide (NHPI) catalysts are shown in Fig. 6. 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) presented strong absorption peaks at ca. 1855 cm^{-1} and 1780 cm^{-1} due to the asymmetric and symmetric strengthening vibration of carboxyls of the anhydride, and another strong peak at ca. 1231 cm^{-1} can be ascribed to the characteristic absorption of the C—O—C bonds in PMDA (Fig. 6A). The absorption peak at 1231 cm^{-1} disappeared and the absorption peaks of carboxyls in anhydride were red-shifted to 1780 cm^{-1} and 1712 cm^{-1} after imidization. Furthermore, the resulting product by imidization of PMDA exhibited strong IR absorption at ca. 3508 cm^{-1} and 3401 cm^{-1}, which can be attributed to the asymmetric and symmetric stretching vibrations of the NO—H. These indicated that the PMDA was completely converted into the desired product *N,N*-dihydroxypyromellitimide (NDHPI) by hydroxylamine hydrochloride and triethylamine. The purity of the synthesized was also probed by LC—MS by dissolving the synthesized NDHPI in *N,N*-dimethylformamide (DMF). NDHPI was found the predominant component in the solution, indicating that the precursor PMDA was well converted into NDHPI. The results is well in line with its FT-IR spectrum and can be attributed to superfluous hydroxylamine hydrochloride used in the synthesis. For the intermediate NHPI-GPTMS synthesized by the grafting of NDHPI with 3-(glycidoxypropyl) trimethoxysilane (GPTMS), its FT-IR spectrum presented all absorption peaks of NDHPI and GPTMS in Fig. 6B, suggesting a successful anchoring reaction.

The synthesized intermediate NHPI-GPTMS was further covalently bonded to the support SiO_2 and the FT-IR spectrum of the synthesized catalyst NHPI-GPTMS-SiO_2 is shown in Fig. 6C. It was noted that the peaks at 1100, 960 and 800 cm^{-1} can be ascribed to the characteristic absorption peaks of the SiO_2 support, and peaks at 1700, 1780, 3448 and 3529 cm^{-1} to the immobilized NHPI, which confirmed that NHPI was covalently anchored to the support successfully.

It is worthwhile to note the catalyst SiO_2-GPTMS-NHPI, which was synthesized via a completely opposite sequence in comparison with its counterpart NHPI-GPTMS-SiO_2, indicated nearly same FT-IR absorption peaks as those of NHPI-GPTMS-SiO_2 in Fig. 6D. This indicates that the aimed catalyst can be synthesized according to different sequences and combinations. In addition, the FT-IR absorption spectra of the catalyst reclaimed from the catalytic reaction were compared with that of the fresh one (Fig. 6E). It was found that the recycled NHPI-GPTMS-SiO_2 catalysts exhibited nearly same characteristic absorption as the fresh one, which suggested that the binding bonds and active functional groups are relatively stable under adopted test conditions.

The ^{13}C NMR spectra of the catalysts SiO_2-GPTMS-NHPI, NHPI-GPTMS-SiO_2 and the intermediate NHPI-GPTMS are presented in Figs. 7 and S1. The ^{13}C NMR spectrum of the synthesized catalyst SiO_2-GPTMS-NHPI can be assigned to the NDHPI moiety (C1–C10) and the GPTMS one (C11–C18), indicating a successful chemical binding (Fig. 7). The intermediate NHPI-GPTMS and the catalyst NHPI-GPTMS-SiO_2 presented similar ^{13}C NMR spectra (Fig. S1). They can be assigned to the GPTMS-NHPI chain section, but a weaker response from the GPTMS moiety was observed. This might be attributed to the former, SiO_2-GPTMS-NHPI, possessed superfluous anchored GPTMS due to an opposite anchoring sequence.

The contents of C, H and N in the fresh and the catalyst recycled after catalytic tests were determined by elemental analysis and the results are shown in Table 1. It is clear that there was no obvious loss of C and H elements in the recycled NHPI-GPTMS-SiO_2 catalyst from reaction with HFIP as the solvent in comparison with the refresh catalyst, indicating excellent stability of the grafting chains (entry 1–3). However, a loss of N element was observed in the recycled NHPI-GPTMS-SiO_2 catalyst,

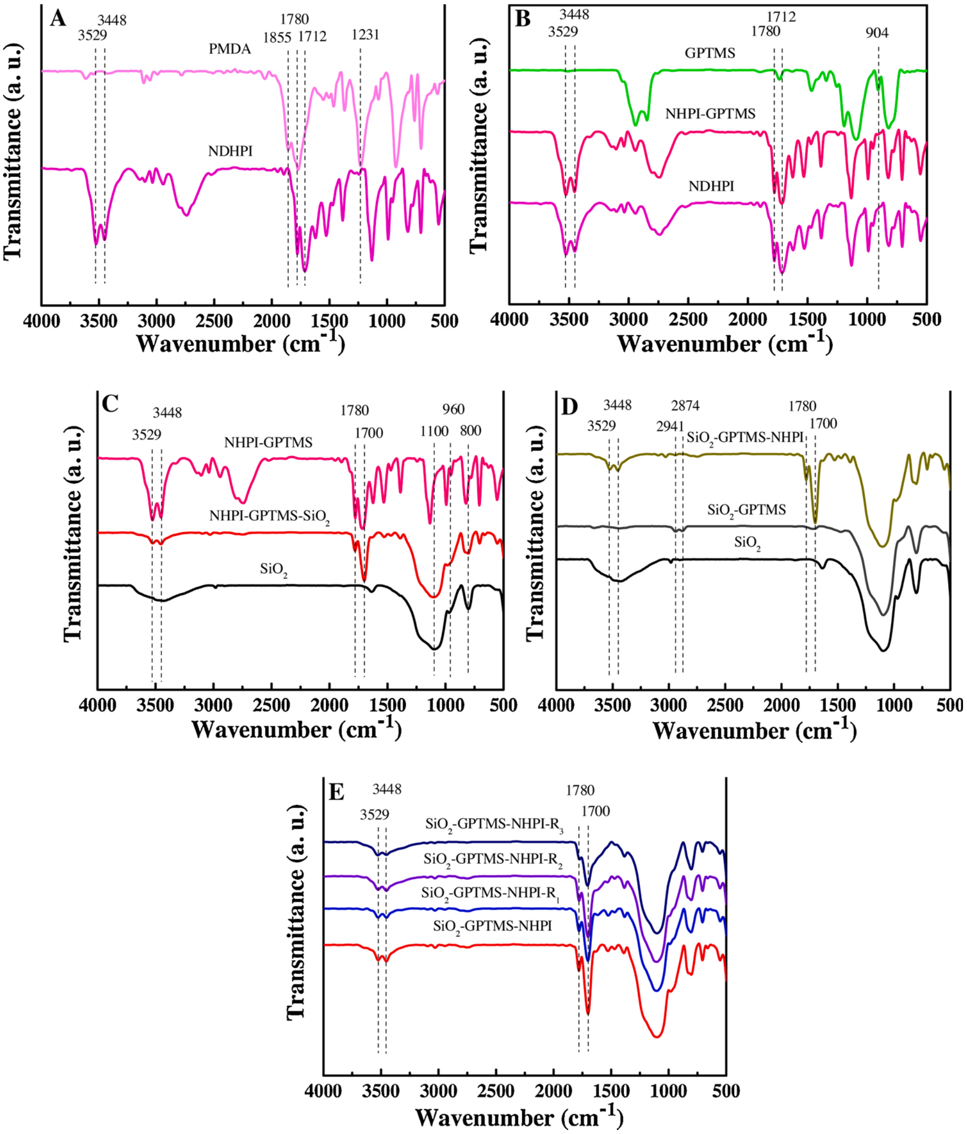

Fig. 6. FT-IR spectra of (A) 1,2,4,5-Benzenetetracarboxylic anhydride (PMDA) and *N,N*-dihydroxypyromellitimide (NDHPI); (B) 3-(glycidoxypropyl) trimethoxysilane (GPTMS), NHPI-GPTMS and NDHPI; (C) NHPI-GPTMS, NHPI-GPTMS-SiO$_2$ and SiO$_2$; (D) SiO$_2$-GPTMS-NHPI, SiO$_2$-GPTMS and SiO$_2$; and (E) NHPI-GPTMS-SiO$_2$, NHPI-GPTMS-SiO$_2$-R$_1$, NHPI-GPTMS-SiO$_2$-R$_2$ and NHPI-GPTMS-SiO$_2$-R$_3$.

which can be attributed to the desorption of N-containing species such as GPTMS-NDHPI that was adsorbed on the surface of the support and hadn't been washed completely in the process of synthesis (Fig. S2). Additionally, the SiO$_2$-GPTMS-NHPI catalyst synthesized via a completely opposite sequence presented a lower N content, which might be ascribed to the more difficult imidization on the immobilized catalyst compared with the anhydride dissolved in homogeneous solvent (entry 4).

Thermal stability and concentration of the grafted organic moiety were analyzed and calculated by thermogravimetric analysis (TGA) at a temperature range of 30–800 °C in nitrogen, and the TGA and differential thermogravimetric (DTG) curves are shown in Fig. 8. The predominant weight loss of the support SiO$_2$ was observed before 120 °C due to the desorption of physisorbed water, and a very slow trend of weight loss with an increasing temperature can be ascribed to the removal of surface hydroxyl groups of the support. Compared to the support SiO$_2$, the synthesized fresh catalyst NHPI-GPTMS-SiO$_2$ presented two stages of weight loss in the temperature region of 30–240 °C and 240–800 °C, respectively. The former could be attributed to the removal of the physisorbed and structural water, and latter may arise from the breakage and decomposition of the grafting chains dominantly. The grafting density was calculated according to Fig. 3 and the weight loss in the region from 240 to 800 °C, and 0.63 mmol/g of grafting density was resulted in. The result is roughly in line with the elemental analysis shown in Table 1. In consideration of adsorption of N-containing species on the surface of the catalyst, the recycled catalyst NHPI-GPTMS-SiO$_2$-R$_4$ is adopted to calculate grafting density with 1.2 mmol/g of N (Table 1, entry 3), and a grafting density of 0.6 mmol/g was obtained because there are two N atoms in every grafting chain. It is also important to note the recycled catalyst almost exhibited the same weight loss curves (TGA and DTG) if the difference in initial content of physisorbed water is considered, which clearly indicated that the synthesized NHPI-GPTMS-SiO$_2$ is stable under applied reaction conditions (HFIP as the solvent).

The core level N 1s XP spectrum of *N,N*-dihydroxypyromellitimide (NDHPI) was compared with that of the synthesized NHPI-GPTMS-SiO$_2$ catalyst and they are presented in Fig. 9. NDHPI exhibited a perfectly symmetric N 1s spectrum centered at 400.7 eV. It is noted that the synthesized NHPI-GPTMS-SiO$_2$ catalyst presented an additional peak at 401.2 eV besides the peak at 400.7 eV, which suggested a successful

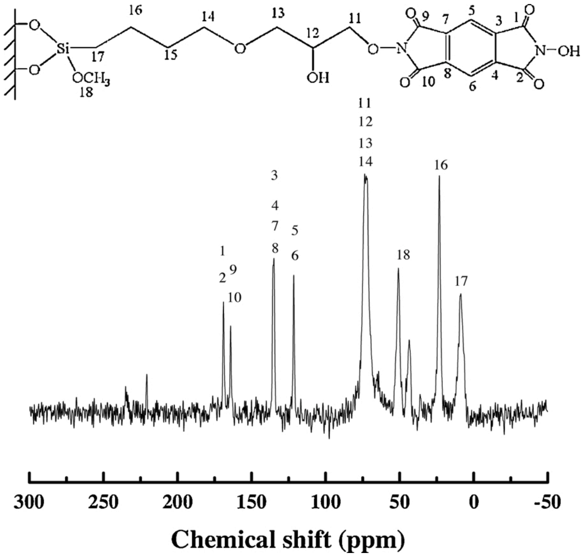

Fig. 7. ^{13}C NMR spectrum of SiO_2-GPTMS-NHPI.

Table 1
Contents of C, H and N in the fresh and recycled catalysts determined by elemental analysis.

Entry	Catalyst	C (mmol/g)	H (mmol/g)	N (mmol/g)
1	NHPI-GPTMS-SiO_2	11.3	19.0	2.0
2	NHPI-GPTMS-SiO_2-R_1	11.0	18.9	1.7
3	NHPI-GPTMS-SiO_2-R_4	10.1	21.2	1.2
4	SiO_2-GPTMS-NHPI	11.6	22.4	0.8

covalent grafting of N—OH with the epoxy functional group of GPTMS. The slightly higher binding energy of N 1S in the grafting bond might be attributed to the enhanced electron-deficient environment, and the similar peak areas of the N atoms with two different chemical states in their XP spectra suggested that the synthesis of the catalyst followed the route shown in Figs. 1–3.

The textural properties of the synthesized fresh catalyst were compared with those of the support SiO_2 (Table 2). An apparent decrease in specific surface area, pore volume and pore diameter were observed after grafting the NHPI to the support, which can be ascribed to the coverage and/or blockage of the grafting organic moiety for the substrate. It is also important to note that the recycled catalyst from catalytic reaction in HFIP didn't present severe decrease in its textural properties, indicating that the grafting chains might be well remained during the catalytic test.

3.2. Toluene oxidation performance of catalysts

Catalytic performance of the synthesized catalysts and related intermediates were evaluated via selective oxidation of toluene to benzaldehyde using molecular oxygen and the results are summarized in Table 3. There was no conversion of toluene observed under applied reaction conditions in the absence of catalysts (entry 1). At the same time, the cobaltous acetate (entry 2), the support SiO_2 (entry 3) and grafting chain (GPTMS) (entry 4) presented no activity for toluene oxidation. The synthesized catalysts NHPI-GPTMS-SiO_2 exhibited a toluene conversion of 5.8 % and a selectivity to benzaldehyde of 82.7 % in the absence of initiator under the adopted experimental conditions, indicating that the immobilized NHPI catalyst synthesized in present work is capable of catalyzing selective oxidation of toluene to benzaldehyde (entry 5).

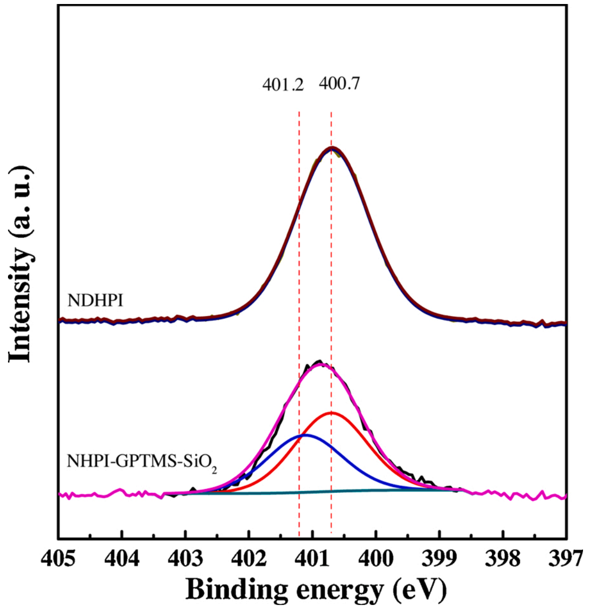

Fig. 9. Core level N 1s XP spectra of NDHPI and NHPI-GPTMS-SiO_2.

Table 2
Textural properties of SiO_2, NHPI-GPTMS-SiO_2 and NHPI-GPTMS-SiO_2-R_1.

Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
SiO_2	372	0.85	9.3
NHPI-GPTMS-SiO_2	236	0.57	7.2
NHPI-GPTMS-SiO_2-R_1	217	0.55	7.8

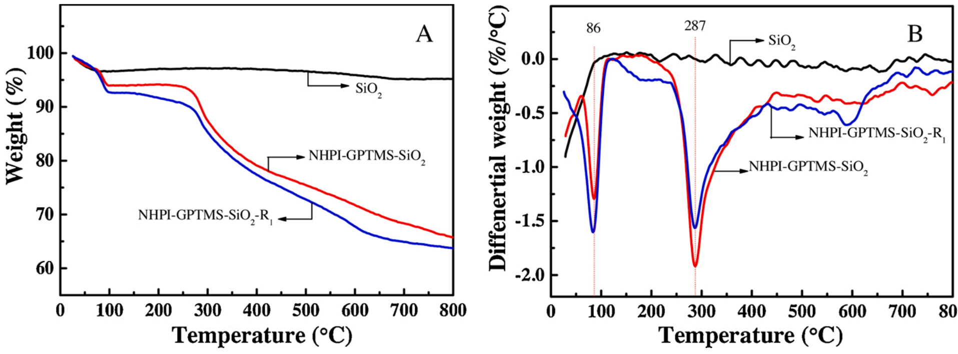

Fig. 8. TGA (A) and DTG (B) curves of SiO_2, NHPI-GPTMS-SiO_2 and NHPI-GPTMS-SiO_2-R_1 recycled from the catalytic reaction for toluene oxidation in HFIP.

Table 3
Reaction results of the toluene oxidation catalyzed by different catalysts in HFIP.[a].

Entry	Catalyst	Conv. (%)	Selectivity (%)			
			Benzaldehyde	Benzyl alcohol	Benzoic acid	Others
1	None	0	–	–	–	–
2	$Co(OAc)_2$	0	–	–	–	–
3	SiO_2, $Co(OAc)_2$	0	–	–	–	–
4	GPTMS, $Co(OAc)_2$	0	–	–	–	–
5	NHPI-GPTMS-SiO_2	5.8	82.7	13.2	4.1	0
6	NHPI-GPTMS-SiO_2, $Co(OAc)_2$	14.1	73.1	21.9	4.9	0.1
7	NDHPI, $Co(OAc)_2$	17.9	54.8	19.0	25.7	0.5
8	SiO_2-GPTMS-NHPI, $Co(OAc)_2$	10.4	62.6	22.7	14.1	0.6
9[b]	NHPI-GPTMS-SiO_2, CoO/SiO_2	7.9	78.0	22.0	0	0

[a] Reaction conditions: toluene (2 mmol), O_2 (2 MPa), HFIP (40 mmol), NHPI-GPTMS-SiO_2 or SiO_2-GPTMS-NHPI or SiO_2 (0.2 g), GPTMS (0.2 mmol), NDHPI (0.1 mmol), $Co(OAc)_2$ (0.040 mmol)90 °C, 5 h. [b] CoO/SiO_2 (5.5 mg or 0.040 mmol Co) prepared by coprecipitation.

The introduction of the initiator $Co(OAc)_2$ markedly promoted the reaction, and a toluene conversion of 14.1 % and a selectivity to benzaldehyde of 73.1 % were observed (entry 6), which can be attributed to the synergistically catalytic role of cobaltous ions and N-oxyl on the selective oxidation of toluene to benzaldehyde [13,31,42]. This work was designed to selectively catalyze toluene oxidation by heterogeneous NHPI catalyst synthesized. This will make it possible to carry out the transformation by a fixed-bed flowing reactor, and thus significantly reduce the loss and possible contamination to environment. The transformation from toluene to benzaldehyde is not a high value-added protocol because the aimed product is a bulk chemical with a relatively low value. However, the heterogenization of the active homogeneous catalyst for selective oxidation of benzylic C—H bonds may be valuable for the synthesis of other value-added organic intermediates. And the immobilized catalysts synthesized and the reaction chemistry of toluene over them would provide a guideline for the selective oxidation of benzylic C—H to aldehydes, alcohols, carboxylic acids, ketones, hydroperoxides, etc. As an example, the transformation from m-phenoxytoluene to m-phenoxybenzaldehyde might proceed on the basis of the conversion of benzylic C—H bonds.

Homogeneous NDHPI, the precursor of the immobilized NHPI catalyst, presented a slightly higher activity in the presence of the initiator $Co(OAc)_2$, which is not strange because its higher mobile capability and accessibility to the initiator and the reactant(s) in comparison with the immobilized N-oxyl catalyst (entry 7). Additionally, another catalyst synthesized in a completely opposite order, SiO_2-GPTMS-NHPI (entry 8), gave a lower toluene conversion in terms of a same mass of catalyst in comparison with its counterpart NHPI-GPTMS-SiO_2, which can be ascribed to a lower grafting density of N-oxyl (Table 1).

In consideration of the possible contamination of the initiator homogeneous $Co(OAc)_2$ to the products, the supported cobaltous ion catalyst synthesized by co-precipitation was used to catalyze toluene oxidation in the presence of NHPI-GPTMS-SiO_2 and HFIP (entry 9, Table 1). Compared with the combined NHPI-GPTMS-SiO_2/$Co(OAc)_2$ (entry 6), the entirely heterogeneous combination, NHPI-GPTMS-SiO_2/CoO/SiO_2, showed a toluene conversion of 7.9 % and a selectivity to benzaldehyde to 78.0 %. The heterogeneous combination facilitate the complete separation of catalysts from the reaction mixture and the purification of the products. What is more, this indicated that the anchored NHPI and the supported Co ions are accessible to each other and the both can synergistically catalyze the selective oxidation of toluene to benzaldehyde in the presence of HFIP. The decrease in the reactivity of toluene, compared with the combined NHPI-GPTMS-SiO_2/$Co(OAc)_2$ catalyst (entry 6), can be attributed to less accessibility of the supported cobaltous ions with the bound NHPI and/or reactant(s).

HFIP is a distinctive solvent for selective oxidation of toluene to benzaldehyde and was well investigated when homogeneous NHPI was used as the catalyst for toluene oxidation [13,42]. However, it keeps unknown that how the solvents affect the reactivity of toluene and its selectivity on covalent-anchored NHPI catalyst. Effect of solvents on toluene oxidation on the combination NHPI-GPTMS-SiO_2/$Co(OAc)_2$ is summarized in Table S1. There was little toluene observed under solvent-free conditions (entry 1). More than 80 % of conversion was found when acetonitrile and acetic acid were used as solvents and the predominant product was benzoic acid (entry 2, 3). Toluene was selectively converted into the desired benzaldehyde in the presence of HFIP, but a lower conversion was observed (entry 4). The reactivity of toluene in different solvents indicated that the covalently anchored NHPI are active in the presence of solvent selected, the fluctuation in conversions and selectivities need to further investigation.

Effect of reaction temperature and time on the toluene oxidation catalyzed synergistically by NHPI-GPTMS-SiO_2 and $Co(OAc)_2$ in HFIP was examined, and the results are presented in Fig. 10 and Table 4, respectively. There was no apparent toluene conversion observed at a reaction temperature lower than 50 °C. The conversion of toluene and the yield of benzaldehyde was significantly increased while increasing the reaction temperature from 50 to 90 °C. However, too high reaction temperature led to a decrease in catalytic activity for toluene oxidation, which might be attributed to the loss of phthalimide N-oxyl radical (PINO) due to the increased reaction temperature.

As was shown in Table 4, benzaldehyde and benzyl alcohol were produced and there was no benzoic acid obtained at the early stage of the reaction (1 h). This suggested that benzaldehyde and benzyl alcohol might be produced from toluene directly, but benzoic acid not. The toluene conversion was found a nearly linear increase when the reaction time extended to 10 h. At the same time, the selectivity to benzaldehyde presented a decreasing trend due to its over-oxidation to benzoic acid. It was noted that the conversion only presented a very slow increase when the reaction time was further extended from 10 to 15 h, indicating a severe loss of the activity of the catalyst. This might be ascribed to the

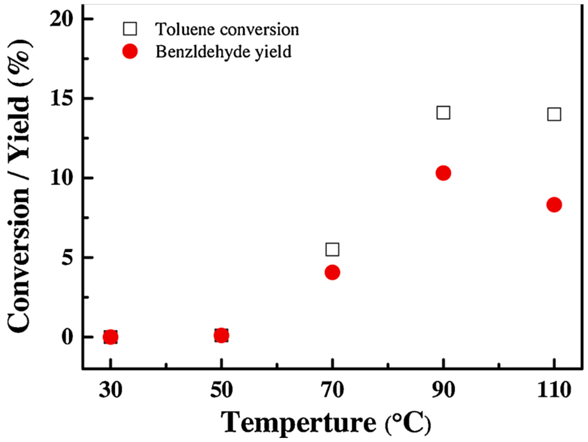

Fig. 10. Effects of reaction temperature on the toluene oxidation to benzaldehyde catalyzed synergistically by NHPI-GPTMS-SiO_2 and $Co(OAc)_2$ in HFIP.

Table 4
Effects of reaction time on the toluene oxidation catalyzed synergistically by NHPI-GPTMS-SiO_2 and $Co(OAc)_2$ in HFIP.

Reaction time (h)	Conv. (%)	Selectivity (%)			
		Benzaldehyde	Benzyl alcohol	Benzoic acid	Others
1	2.7	76.9	23.1	0	0
2	6.0	77.7	22.1	0	0.2
5	14.1	73.1	21.9	4.9	0.1
10	29.8	48.4	15.7	35.7	0.2
15	30.3	47.9	15.0	37.0	0.1

Reaction conditions: toluene (2 mmol), NHPI-GPTMS-SiO_2 (0.2 g), $Co(OAc)_2$ (0.04 mmol), O_2 (2 MPa), HFIP (40 mmol), 90 °C.

accumulation of water as a byproduct in the autoclave [43]. NHPI will be converted into N-oxyl anion instead of N-oxyl radical in the presence of water, which is a strong acceptor of proton [43]. The removal of the water is possible when the reaction proceed via a fixed-bed flowing reactor.

In order to probe how the benzaldehyde, benzyl alcohol and benzoic acid were produced from toluene, the control experiments were performed and the results are presented in Table 5. A very low conversion was observed when benzyl alcohol was used as the starting material, which indicates that benzyl alcohol is not reactive under the applied reaction conditions. In consideration of a high selectivity to benzaldehyde at the initial stage of toluene oxidation (Table 4), it was further confirmed that benzaldehyde was predominantly produced from toluene directly. It is interesting to note that toluene was produced from benzyl alcohol under the applied experimental conditions. This should be attributed to the disproportionation of benzyl alcohol, which was reported by Hutchings' group [44]. Benzaldehyde of 57.1 % was converted and the sole product was benzoic acid, indicating that the produced benzaldehyde will be partially further over-oxidized in spite of the presence of inhibiting agent HFIP. In addition, benzaldehyde and benzyl alcohol were catalytically oxidized used homogeneous NHPI, and the results were compared with those from the heterogeneous catalyst NHPI-GPTMS-SiO_2. A big difference in conversion and selectivities was found when benzyl alcohol was used as the starting material, which might be attributed to the discrepancy of the catalytic properties between the homogeneous and heterogeneous NHPI and need to further investigation.

A possible reaction network of the toluene oxidation catalyzed synergistically by NHPI-GPTMS-SiO_2 and $Co(OAc)_2$ in HFIP is proposed according to the catalytic results presented in Tables 3–5 and shown in Fig. 11. Under applied experimental conditions, benzyl alcohol and benzaldehyde can be directly produced from toluene, but benzoic acid arose from the oxidation of benzaldehyde, not from benzyl alcohol or toluene directly. Benzyl alcohol can be converted into benzaldehyde directly by oxidation, and can be also transformed into toluene and benzaldehyde by disproportionation [[44–47]].

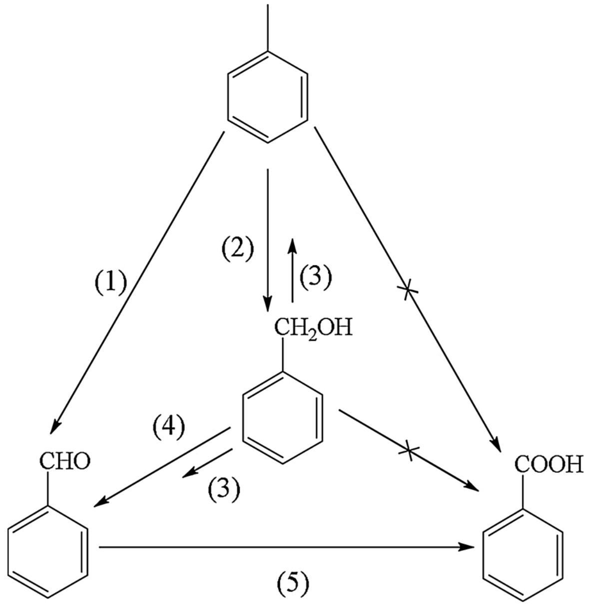

Fig. 11. The reaction network of the toluene oxidation catalyzed synergistically by NHPI-GPTMS-SiO_2 and $Co(OAc)_2$ in HFIP. (1) Toluene oxidation to benzaldehyde; (2) Toluene oxidation to benzyl alcohol; (3) Disproportionation of benzyl alcohol to toluene and benzaldehyde; (4) Benzyl alcohol oxidation to benzaldehyde; (5) Benzaldehyde oxidation to benzoic acid.

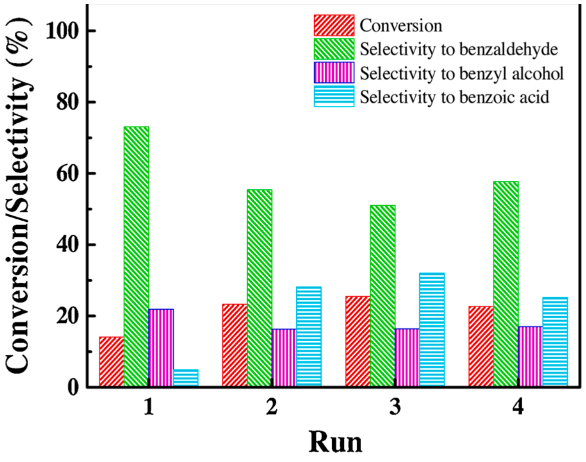

Fig. 12. Reusability of NHPI-GPTMS-SiO_2 for toluene oxidation to benzaldehyde in HFIP.

The reusability and recyclability of the NHPI-GPTMS-SiO_2 catalyst were investigated in HFIP and the results are shown in Fig. 12. It was found that that NHPI-GPTMS-SiO_2 can be recycled and reused in HFIP without the remarkable loss, and the recycled catalyst after the first run even exhibited higher catalytic activity than the fresh one. The enhancement in catalytic performance might be ascribed to the elution of covering materials on the surface of the fresh catalyst under reaction

Table 5
Oxidation reactions of different starting materials catalyzed synergistically by NHPI-GPTMS-SiO_2 and $Co(OAc)_2$ in HFIP.[a]

Starting material	Conv. (%)	Selectivity (%)				
		Toluene	Benzaldehyde	Benzyl alcohol	Benzoic acid	Others
Toluene	14.1	–	73.1	21.9	4.9	0.1
Benzyl alcohol	3.7	12.4	87.6	–	0	0
Benzaldehyde	57.1	0	–	0	100	0
Benzyl alcohol[b]	94.9	0	15.9	–	81.0	3.1[c]
Benzaldehyde[b]	43.5	0	–	0.9	95.5	3.5[c]

[a] Reaction conditions: starting material (2 mmol), NHPI-GPTMS-SiO_2 (0.2 g), $Co(OAc)_2$ (0.04 mmol), O_2 (2 MPa), HFIP (40 mmol), 90 °C, 5 h. [b] NHPI (0.20 mmol). [C] benzyl benzoate.

conditions, which is in line with the results from elemental analysis (Table 1). It is worthwhile to note that the toluene conversion and the selectivities to benzaldehyde, benzyl alcohol and benzoic acid were relatively stable, indicating an excellent reusability for toluene oxidation.

The most accepted mechanism for the toluene oxidation reaction catalyzed synergistically by NHPI and Co(OAc)$_2$ was proposed by Ishii [31]. First, Co(II) ion is oxidized to Co(III)-oxygen complex (superoxocobalt(III) or μ-peroxocobalt(III)) by molecular oxygen. NHPI then was H-abstracted by the Co(III) peroxide to generate PINO radical, which initiated the radical chain process (Fig. S3). What's more, an experiment was performed to prove that the oxidation of toluene catalyzed synergistically by NHPI-GPTMS-SiO$_2$ and Co(OAc)$_2$ in HFIP via a free radical way. By adding 2,6-di-tert-butyl-p-cresol, a typical radical scavenger, into the reaction mixture and found that the transformation of toluene was quenched.

It is worthwhile to note that a lower reactivity of toluene was observed while using immobilized NHPI as the catalyst (entry 6, Table 3) compared with the homogeneous NDHPI in terms of a same amount of N−OH. It is possible to keep accessible between the heterogeneous NHPI (or PINO) and the homogeneous cobalt complex free radical ($CoOO^{\bullet}$ or $CoO^{\bullet}$) or reactant intermediates ($PhCH_2^{\bullet}$ or $PhCH_2OO^{\bullet}$) by stirring and/or the thermal motion of the homogeneous molecules. However, a decrease in mobile ability of the immobilized NHPI (or PINO) could lead to a loss in accessibility between heterogeneous and homogeneous parts and a decrease of toluene reactivity.

4. Conclusion

NHPI was anchored onto the surface of the commercial support SiO$_2$ by covalent bonds with 3-(glycidoxypropyl) trimethoxysilane (GPTMS) as the transitional material, and the anchoring bonds were well confirmed by FT-IR, TGA and XP spectra. The synthesized immobilized NHPI catalyst (NHPI-GPTMS-SiO$_2$) was found a grafting density of > N—OH of up to ca. 0.6 mmol/g, and exhibited an excellent activity for selective oxidation of toluene to benzaldehyde. There was no apparent decrease in catalytic activity observed after repeated evaluations for the synthesized NHPI catalyst, suggesting a promising prospect for further investigation and possible application.

CRediT authorship contribution statement

Jinyang Xu: Investigation, Writing - original draft. **Guojun Shi:** Conceptualization, Methodology, Funding acquisition, Writing - review & editing. **Yuxin Liang:** Investigation. **Qiuting Lu:** Investigation. **Lijun Ji:** Methodology.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

The authors gratefully acknowledge the project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD),Government of Jiangsu Province, P. R. China.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111440.

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