

Co-SBA-15-Immobilized NDHPI as a New Composite Catalyst for Toluene Aerobic Oxidation

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Abstract A new composite catalyst was constructed by immobilizing active site N,N-dihydroxypyromellitimide (NDHPI) on the co-catalyst Co-doped mesoporous sieve SBA-15 through the chemical bond with the 3-(glycidoxypropyl) trimethoxysilicane used as the silylation agent. The catalyst was characterized by various means. The new catalyst showed significantly higher activity in toluene aerobic oxidation at 90 °C with acetonitrile as a solvent or under solvent-free condition compared with the NDHPI and cocatalyst independent system. The effects of the reaction conditions such as temperature, oxygen pressure, catalyst amount on the toluene oxidation over the immobilized catalyst were also investigated. After reuse for three times, the composite catalyst kept the activity without loss of Co from SBA-15.

Graphical Abstract A new composite catalyst was constructed by immobilizing active site N,N-dihydroxypyromellitimide (NDHPI) on the co-catalyst Co-doped mesoporous sieve SBA-15 through the chemical bond with the 3-(glycidoxypropyl) trimethoxysilicane used as the silylation agent. The catalyst was characterized by various means. The catalytic performance of the composite was evaluated in toluene aerobic oxidation and the reuseability of the catalyst was also investigated.



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1 Introduction

Benzaldehyde and benzyl alcohol are important organic value-added intermediates that are widely used in dyes, pharmaceuticals, food stuff and other industries [1–4].

Benzaldehyde is mainly produced from toluene chlorination followed by hydrolysis in the domestic industry, which is a serious polluting process and should be modified in terms of production cost. Compared with the traditional preparation method, the direct oxidization of toluene to benzaldehyde and benzyl alcohol with molecular oxygen used as an oxidant is an environmental-friendly synthesis route. However, the majority of the oxidation process proceeds under harsh conditions such as high temperature, high pressure, large energy consumption, and limitation due to the recycle of transition metal catalysts [5, 6]. In industry, liquid-phase toluene oxidation in the SINA process is carried out at 165 °C and 1.0 MPa with Co(OAc)₂ used as the catalyst. This route has a toluene conversion rate of 14–15% and a benzoic acid selectivity of 92–93%, only a small amount of byproducts (e.g. benzaldehyde and benzyl alcohol) [3, 7]. With the growing market demand for benzaldehyde and benzyl alcohol, it is urgent to develop a new toluene catalytic oxidation system for selective formation of these two substances [5, 8-10]. As reported, a liquid-phase air oxidation of toluene to benzaldehyde and benzyl alcohol in the solvent-free or promoter-free condition and using cobalt tetraphenylporphyrin as the catalyst has a conversion rate of 8.9% and total selectivity of 60% at 160 °C, 0.8 MPa, and 0.04 m^3/h airflow [8]. The manganese tetraphenylporphyrin supported on chitosan used as a catalyst for toluene catalytic oxidation yielded a 5.9% conversion and 96% selectivity at 195 °C and 0.6 MPa [11]. As is well-known, benzaldehyde and benzyl alcohol are more susceptible to secondary oxidation to benzoic acid, so reducing the reaction temperature may be an effective way to improve the selectivity of intermediates from the dynamic perspective.

N-hydroxyphthalimide (NHPI) and its analogues are known as radical-generating agents, the O-H bonds break down easily to form phthalimide N-oxyl (PINO) radicals. Under mild conditions, PINO abstracts a hydrogen atom from the substrate to activate the carbon hydrogen bond, thus promoting the oxidation of hydrocarbon [12–15]. Together with the non-toxicity and availability, it attracts attention from researchers. As reported, a newly-developed oxidizing system NHPI/O2/Co(II) is able to efficiently catalyze the oxidation of various organic compounds under mild conditions and at moderate oxygen pressure and temperature [16]. Metal salts as co-catalysts play an important role in the NHPI-catalyzed oxidation with molecular oxygen. Owing to large dosage repuired and dissolubility in polar solvents, more attention has been paid to the reuse of NHPI immobilization in recent years. NHPI has been immobilized on silica gels [17], in ionic liquid [18], aminiomethyl polystyrene and chloromethyl polystyrenevia amide or ester bonds [6]. Since metal co-catalyst also needs to be reused, immobilization of the metal contents such as M/ZSM-5 [19] and Cosalen/SiO₂ [20] with NHPI were used in the hydrocarbon and alkylarene oxidation. We believe that binding the active site NHPI and co-catalyst metal component together can actually realize the reuse of the catalytic system. NHPI incorporated onto Cu-BTC metal-organic frameworks (BTC = benzene-1,3,5tricarboxylic acid) for toluene aerobic oxidation [21] was a meaningful attempt, but was limited by low activity. We previously immobilized N,N-dihydroxypyromellitimide (NDHPI) on pre-grafted glycidoxypropyl chains of SBA-15, and thereby improved the catalytic performance in the toluene aerobic oxidation with Cosalen as a co-catalyst under mild reaction conditions. It is noticeable that the toluene conversion rate decreased sharply in the absence of Cosalen [3], but Cosalen is limited by low recyclability and a strong tendency to form dimers, resulting in deactivation [22]. In this work, NDHPI was immobilized on the Codoped mesoporous sieve SBA-15 through chemical bonding. Then the new composite catalyst was used in toluene aerobic oxidation and its reusability was investigated.

2 Experimental

2.1 Preparation of Catalysts

2.1.1 Preparation of Co-SBA-15

In a typical procedure, P123 [triblock copolymer $(PEO_{20}PPO_{70}PEO_{20})$] (3.98 g) and Co(OAc)₂·4H₂O (0.25 g) were dissolved in a HCl solution (120 mL, pH 1) under stirring at 40 °C to form a homogeneous mixture. Then the mixture was added with tetraethoxysilane (TEOS) (9 mL) under vigorous stirring for 24 h, then transferred to a Teflon reaction kettle, and crystallized at 100 °C for 24 h. The mixture was stirred and evaporated to a viscous material, which was then dried overnight at 100 °C. Finally, the polymeric structure-directing agent was removed by calcination at 550 °C for 6 h. The resulting carrier was coded as Co-SBA-15.

2.1.2 Preparation of NDHPI-Epoxy/Co-SBA-15

First, NDHPI was synthesized according to a reported method [23]. Then NDHPI (1.00 g) and 3-(glycidoxypropyl) trimethoxysilicane (GPTMS) (2.83 g) were added into ethyl acetate (120 mL). The mixture was refluxed under a nitrogen atmosphere and at 80 °C for 24 h. After reaction, the resulting mixture was centrifuged and the precipitate was washed with dichloromethane (150 mL) to form NDHPI-epoxy. Secondly, Co-SBA-15 (4.00 g) was suspended in ethyl acetate (120 mL). The mixture was stirred fully, added with the NDHPI-epoxy (1.84 g), and refluxed for 24 h. After cooling to room temperature, the solids were collected by filtering and washed with an ether and chloroform mixed solution (volume ratio is 1:1) for several times. Finally, the resulting product was vacuum-dried at 50 °C for 24 h to form NDHPI-epoxy/Co-SBA-15 (Scheme 1).

2.2 Characterization of Catalysts

Fourier transformed infrared spectra (FTIR) of the catalysts were recorded on a Thermo Nicolet 380 spectrometer in KBr disks. Their porous structures were determined by analyzing the nitrogen adsorptions at 77 K in a NOVA-2200e Quanta chrome apparatus. Scanning electron microscopy (SEM) images were recorded on a Jeol JSM-6610LV instrument equipped with a tungsten filament at 30 kV. Transmission electron microscopy (TEM) images were taken on a JEM-2100 microscope. Cross-polarization magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectra were recorded on an Agilent DD2500 instrument at a frequency of 99.29 MHz. The elemental composition was characterized with X-ray photoelectron spectroscopy (XPS) in Kratos AXIS UltraDLD. A Thermo Jarrell Asch IRIS Advantage 1000 inductively coupled plasma (ICP)-atomic spectroscopy was used to analyze metal Co contents. CHN elemental analysis was carried out on Elementar Vario EL ananlyzer.

2.3 Catalytic Procedures

Toluene (5.0 g), NDHPI-epoxy/Co-SBA-15 (1.43 g) and acetonitrile (4.0 g) were added into a 50-mL Teflon-lined and magnetically-stirred autoclave equipped with a block heater and a thermometer. The reaction proceeded at 90° C under an oxygen atmosphere (1.60 MPa) for 7 h. After that, the catalyst was separated by filtration, then washed

with 150 mL of chloroform and ether, and vacuum-dried at 60 °C for 24 h to form the recycled catalyst. The toluene conversion and product selectivity were calculated based on an Agilent GC-6820 instrument (HP-Innowax capillary column, 30 m×0.32 mm×0.5 μ m, flame ionization detector, N₂ as carrier gas). Cyclohexanone was used as the internal standard. The injection and detector temperatures were both 250 °C. The column was maintained initially at 80 °C for 2.5 min, then heated to 220 °C at a rate of 20 °C/ min, and kept at this temperature for 9 min.

3 Results and Discussion

3.1 Characterization of Catalysts

3.1.1 FTIR

The FTIR spectra of NDHPI, unloaded Co-SBA-15, and NDHPI-epoxy/Co-SBA-15 are shown in Fig. 1. The peaks at 1083, 792 and 461 cm^{-1} correspond to the asymmetric stretching vibration, symmetric stretching vibration and bending vibration of Si-O-Si, respectively, in the framework of Co-SBA-15. The C-H stretching peak at 2860 and 2935 cm⁻¹ both in spectrum a and b illustrated that not all of the organic template has been removed. Spectrum c shows the signals at 3508 and 3401 cm⁻¹ that are attributed to the asymmetric and symmetric stretching vibrations of the N-OH on NDHPI, respectively. In comparison of spectra c and d, the weak peaks at 3043 and 2929 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of -CH₂, respectively, which confirms the presence of glycidoxypropyl groups on NDHPI-epoxy. Nearly all absorption peaks of NDHPI-epoxy appear on spectrum e, which illustrates the successful immobilization of NDHPIepoxy on Co-SBA-15.



Scheme 1 The synthesis routes of NDHPI-epoxy/Co-SBA-15



Fig. 1 FTIR spectra of SBA-15 (*a*), Co-SBA-15 (*b*), NDHPI (*c*), NDHPI-epoxy (*d*) and NDHPI-epoxy/Co-SBA-15 (*e*)



Fig. 2 N_2 adsorption-desorption isotherms and BJH pore size distribution of Co-SBA-15 and NDHPI-epoxy/Co-SBA-15

3.1.2 N₂ Adsorption and Elemental Analysis

As showed in Fig. 2, the N_2 adsorption-desorption isotherms of Co-SBA-15 and NDHPI-epoxy/Co-SBA-15 both pertain to type IV of the International Union Pure and Applied Chemistry (IUPAC) Classification, as they have obvious H1 hysteresis loops and belong to the typical adsorption curve of mesoporous structures. The Barrett–Joyner–Halenda (BJH) pore size curves show that both Co-SBA-15 and NDHPI-epoxy/Co-SBA-15 display narrow pore size distributions with a center peak, indicating the immobilization of NDHPI did not destroy the pore structure of Co-SBA-15. After the immobilization, the specific surface area decreased from 453 to 296 m²/g and the pore volume decreased from 0.756 to 0.543 cm^3/g , which further confirm the successful immobilization of NDHPI on Co-SBA-15.

The heterogeneous catalyst NDHPI-epoxy/Co-SBA-15 was also characterized by elemental analyses. The C, H, N mass percent were 14.14, 2.27 and 2.18%, respectively. The loading amount of NDHPI was calculated as 0.8 mmol/g. The final Co mass content was 1.53% quantified by the ICP analysis.

3.1.3 ²⁹Si(CP-MAS) NMR and XPS

The silica framework of the materials was characterized via ²⁹Si CP-MAS NMR experiments. Mesoporous silica is generally characterized by the presence of three silicon sites Q^2 , Q^3 and Q^4 , representing the species Si(OSi)₂(OH)₂, $Si(OSi)_3(OH)$ and $Si(OSi)_4$, respectively [24]. The ²⁹Si CP-MAS NMR spectrum of NDHPI-epoxy/Co-SBA-15 shows three main peaks centered at -93, -102 and -111 ppm (Fig. 3a), corresponding to Q^2 , Q^3 and Q^4 silicon resonances. The alkyl linkage to surfaces can be characterized by T^1 , T^2 and T^3 resonances, and normally, the Si–C bond resonances at -46, -56 and -67 ppm stand for the reactions of 1, 2 and 3 methoxy groups, respectively, with the silanols on surfaces [25]. As the dominant resonance is at -56 ppm, two methoxy groups of one GTPMS molecule react with the surface of Co-SBA-15, and another methoxy group is unchanged.

Figure 3b shows the XPS spectra of N1s and Co(2p) of NDHPI-epoxy/Co-SBA-15. As showed in Fig. 3b-2, the two larger bands centered at 781.3 and 797.6 eV with the respective satellites at 787.1 and 803.8 eV are related to those of Co^{2+} in CoO from the Co(2p) spectrum of the catalyst [26, 27]. The XPS spectra of N1s fit to two peaks at BE values of 400.7 and 401.3 eV (Fig. 3b-1), which are assigned to N–O–C and N–OH, respectively. However, the peak area ratio of N–O–C to N–OH is 4:1, which indicates that the majority of N–OH groups were condensed with epoxy groups after immobilization, but a small part was left for activation reaction because of the steric effect [3].

3.1.4 SEM and TEM

In the SEM images, the Co-SBA-15 (Fig. 4a) and NDHPIepoxy/Co-SBA-15 (Fig. 4b) are both wheat-like. In conclusion, the immobilization of NDHPI-epoxy did not destroy the structure of Co-SBA-15. In the TEM images, the Co-SBA-15 (Fig. 4c) has a highly-ordered two-direction hexagonal structure, which is typical of the SBA-15. After NDHPI loaded on Co-SBA-15, the structure of the carrier was clearly maintained.



Fig. 3 ²⁹Si CP-MAS NMR (a) and XPS spectra of N1s (b-1) and Co 2p (b-2) of NDHPI-epoxy/Co-SBA-15



Fig. 4 SEM and TEM images of Co-SBA-15(a, c) and NDHPI-epoxy/Co-SBA-15(b, d)

3.2 Activity Evaluation

The catalytic performance of the NDHPI-epoxy/Co-SBA-15 was evaluated in the toluene aerobic moderate oxidation at 90 °C with acetonitrile as the solvent or even

in the solvent-free condition. Some contrast tests were also carried out for comparison. All the results are listed in Table 1. Co-SBA-15 as a carrier was not reactive in the oxidation reaction. NDHPI catalyzed the toluene oxidation and the use of Cosalen improved the toluene conversion



Entry	Catalyst	N %	Conv. %	Selectivity %			N–OH mmol/g	TON ^g
				A	В	С		
1 ^a	Co-SBA-15	_	_	_	_	_	_	_
2 ^b	NDHPI	4.71	5.1	72.2	14.7	13.1	3.4	0.8
3	NDHPI+Cosalen	4.71	7.6	59.6	11.7	28.7	3.4	1.2
4 ^c	NDHPI/SBA-15 + Cosalen	1.98	14.8	37.3	8.7	54.0	0.7	11.6
5 ^d	NDHPI-epoxy/Co-SBA-15	2.18	22.1	24.4	5.7	69.9	0.8	15.2
6 ^e	NDHPI-epoxy/Co-SBA-15	2.62	29.9	8.4	2.3	89.3	0.9	18.3
7^{f}	B-PS-NHPI	1.13	8.5	31	52	17	0.81	6.2

Reaction conditions: 5 g (55 mmol) toluene, 2 mol% NDHPI, 0.2 mol% Cosalen, 4 g acetonitrile, 1.60 MPa O2, 90 °C, 7 h, mol%:n/n(toluene)

^aContrast test used only Co-SBA-15 as catalyst

^bIn the absence of Cosalen

^c1.43 g NDHPI/SBA-15, quoted from previous work [3]

^d1.43 g NDHPI-epoxy/Co-SBA-15 as catalyst

e1.43 g NDHPI-epoxy/Co-SBA-15, in the absence of solvent

fQuoted from reference [6]

^gTON, turn over number, moles of substrate converted per mole of N–OH

just as reported elsewhere [3]. NDHPI-epoxy/Co-SBA-15 was more active in the toluene oxidation, as it improved the toluene conversion to 22.1% and the total selectivity of benzaldehyde and benzyl alcohol to 30.1%. Surprisingly, the toluene conversion was improved to 29.9% in the absence of solvent even though the total selectivity decreased to some extent. The turnover number (TON) of the NDHPI-epoxy/Co-SBA-15 was significantly higher compared with the co-catalyst system and two references [3, 6], indicating the high efficiency of the composite catalyst, which resulted from the combined action of N–OH active site and the Co doped in the framework of SBA-15.

3.3 Effects of Reaction Conditions on the Performance of Catalyst

The effect of temperature on toluene oxidation over NDHPI-epoxy/Co-SBA-15 is shown in Fig. 5. As expected, the conversion of toluene increased with reaction temperature, however, the total selectivity of benzaldehyde and benzyl alcohol decreased all along, the selectivity of benzoic acid went up with increasing temperature. These phenomena could be explained by the followed reasons: at low temperature, the energy was not sufficient for the activation of oxygen molecules, toluene



Fig. 5 Effect of reaction temperature on oxidation of toluene. Condition: 5 g (55 mmol) toluene, 1.43 g NDHPI-epoxy/Co-SBA-15 (2 mol% NDHPI), 4 g acetonitrile, 1.60 MPa O_2 , 7 h, mol%:n(NDHPI)/n(toluene)

was hardly oxidized. As increasing temperature, oxygen molecular was apt to form the oxotransition metal reactive intermediate to oxidize toluene. So the conversion



Fig. 6 Effect of oxygen pressure on oxidation of toluene. Condition: 5 g (55 mmol) toluene, 1.43 g NDHPI-epoxy/Co-SBA-15 (2 mol% NDHPI), 4 g acetonitrile, 90 °C, 7 h, mol%:n(NDHPI)/n(toluene)

increased. Furthermore, at high temperature, benzaldehyde and benzyl alcohol were oxidized to benzoic acid easily, which decreased the total selectivity of benzaldehyde and benzyl alcohol and increased the selectivity of benzoic acid. In addition, taking the conversion of toluene and the total selectivity of benzaldehyde and benzyl alcohol into consideration, the temperature of the reaction should be kept at 90 °C.

The effect of oxygen pressure on oxidation of toluene was shown in Fig. 6. It was clear that the conversion increased with increasing oxygen pressure at first, while the total selectivity of benzaldehyde and benzyl alcohol decreased. In general, the higher the oxygen pressure, the higher the dioxygen solubility in the liquid phase. Hence, at a lower oxygen pressure, the concentration of O_2 in



Fig. 7 Effect of catalyst concentration (NDHPI concentration) on oxidation of toluene. Condition: 5 g (55 mmol) toluene, 4 g acetonitrile, NDHPI-epoxy/Co-SBA-15 (x mol% NDHPI), 1.60 MPa O_2 , 7 h, mol%:n(NDHPI)/n(toluene)

toluene was so low that little oxygen could be activated by catalysts, which resulted in the lower conversion. However excessive oxygen pressure could lead to oxidization of benzaldehyde and benzyl alcohol into benzoic acid. To our surprise, when the oxygen pressure increased to 2.0 MPa, the conversion of toluene decreased obviously. It may be the higher oxygen pressure accelate the reaction rate and also accelate the deactivation of catalyst caused by the products. It's worth to have an intensive study to find the reason in our following work. 1.6 MPa was a proper oxygen pressure in the present work.

Figure 7 shows the effect of the amount of catalyst on oxidation of toluene. It was clear that the conversion increased linearly with the increasing amount of catalyst. However, the total selectivity of benzaldehyde and benzyl alcohol decreased all along, the selectivity of benzoic acid went up with increasing amount of catalyst, which was mainly due to the probability of effective collision increased with catalyst amount increasing. However, with the conversion increasing, benzaldehyde and benzyl alcohol were oxidized into benzoic acid.

3.4 Catalyst Stability and Characterization of the Recycled Catalyst

To evaluate the stability of NDHPI-epoxy/Co-SBA-15 in the toluene aerobic oxidation, we recycled the catalyst and reused the catalyst two times under the same condition as the fresh catalyst. As showed in Fig. 8, the activity of the catalyst was not significantly changed and the total selectivity of benzaldehyde and benzyl alcohol stabilized after two recycles. ICP showed that the Co mass percent contents in the catalyst after zero, one and two recycles were 1.53, 1.48 and 1.61%, respectively, indicating no loss of Co from SBA-15.



Fig. 8 Results of recycle experiments in selective oxidation of toluene. 5 g toluene, 1.43 g recycled NDHPI-epoxy/Co-SBA-15, 4 g acetonitrile, 90 °C, 1.60 MPa, 7 h



Fig. 9 FT-IR spectra of NDHPI-epoxy/Co-SBA-15 (*a*), r1-NDHPI-epoxy/Co-SBA-15 (*b*) and r2-NDHPI-epoxy/Co-SBA-15 (*c*) (*r* the recycled catalyst)



Fig. 10 XRD patterns of Co-SBA-15 (*a*), NDHPI-epoxy/Co-SBA-15 (*b*), r1-NDHPI-epoxy/Co-SBA-15 (*c*) and r2-NDHPI-epoxy/Co-SBA-15 (*d*) (*r* the recycled catalyst)

The FTIR spectra of the recycled catalysts were shown in Fig. 9. It was clear that the FTIR spectra of the catalyst remained nearly unchanged after three times runs, which illustrates the structure of the catalyst was not destroyed after reaction.

The power XRD patterns of Co-SBA-15, NDHPIepoxy/Co-SBA-15 and the recycled ctalysts in Fig. 10 all showed three peaks around 2 θ angles of 0.91°, 1.48° and 1.83°, respectively, which are indexed to (100), (110) and (200) reflections of ordered hexagonal mesophase, which further confirmed that the mesoporous structure of the catalyst remained well after three runs . A composite catalyst was prepared by immobilizing NDHPI on the Co-doped mesoporous sieve SBA-15 through the chemical bond with GPTMS used as the silylation agent. The composite catalyst NDHPI-epoxy/Co-SBA-15 was characterized by various means. The existence of active site N–OH and the Co state was confirmed, and the mesoporous structure also remained. The composite catalyst was more active in the toluene aerobic moderate oxidation at 90 °C with acetonitrile as the solvent or under the solvent-free condition. The TON was significantly higher than the separate co-catalyst system. The composite catalyst kept the activity and no Co was lost from SBA-15 after three reaction runs.

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