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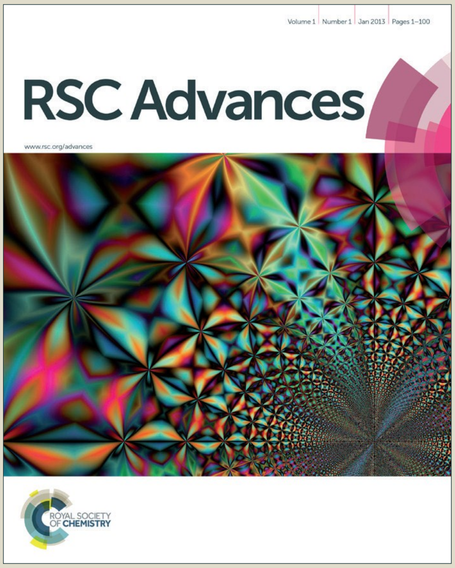

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Catalytic Property of N-hydroxyphthalimide Immobilized on A Novel Porous Organic Polymer in Oxidation of Toluene by Molecular Oxygen

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Abstract: By molecule designing, based on micro-sized macroporous silica mold, N-hydroxyphthalimide (NHPI) was synthesized and immobilized on a novel porous organic polymers (POPs) polystyrene (pSt). The POPs pSt was prepared by surface-initiated graft polymerization and etched away the silica matrix. Subsequently, based on 1,4-dichloro methoxy butane used as chloromethylation reagent, chloromethylation POPs was obtained through Friedel-Crafts alkylation reaction. Next phthalic anhydride was bonded onto the POPs through the esterification reaction, which was carried out between the chloromethyl groups on POPs and the carboxyl group of trimellitic anhydride (TMA), obtaining the products POPs-PA. And then the bonded phthalic anhydride (PA) reacted with hydroxylamine hydrochloride, NHPI-immobilized heterogeneous material pSt/NHPI was obtained. The products obtained were fully characterized. Finally, a co-catalyst system was constituted by solid catalyst pSt/NHPI and a little of $Co(OAc)_2$, which was used in the oxidation reaction processes of toluene with molecular oxygen as oxidant at lower temperature and ordinary pressure of oxygen. The experimental results showed that the co-catalyst system can make toluene deeply oxidized into benzoic acid, and this combination catalyst also possessed high catalytic activity, excellent catalytic selectivity and recyclability.

Keywords: Silica gel particles; Porous organic polymer; N-hydroxyphthalimide; Immobilization; molecular oxygen; catalytic oxidation

Benzoic acid is an important feedstock， which has been widely used in various areas, such as an intermediate for caprolactam, dyes and perfume, an auxiliary agent for rubber industry, and also an agent for preservative or intermediate reaction[1-3]. Up to now, the production of benzoic acid is heavily relied on the oxidation of toluene, which requires expensive reagents and harsh conditions[4,5]. Therefore, the direct green oxidation of toluene to benzoic acid with air or molecular oxygen has attached extensive attention. At present, several sophisticated oxidation catalyst systems which are able to use molecular oxygen as the end oxidant have been introduced[6-10]. The combination of N-hydroxyphthalimide (NHPI) and some mediators is attractive and promising for the oxidation of alcohols in homogeneous catalyst systems[11-14]. Moreover, it is difficult to separate and recover NHPI after the reaction, whereas immobilizing NHPI catalyst on solid supports can overcome this shortcoming. Now the heterogenization of homogeneous catalysts has become a hot subject, whereas the research in immobilized NHPI is scarce[15-18]. In this study, NHPI is immobilized on a new POPs pSt.

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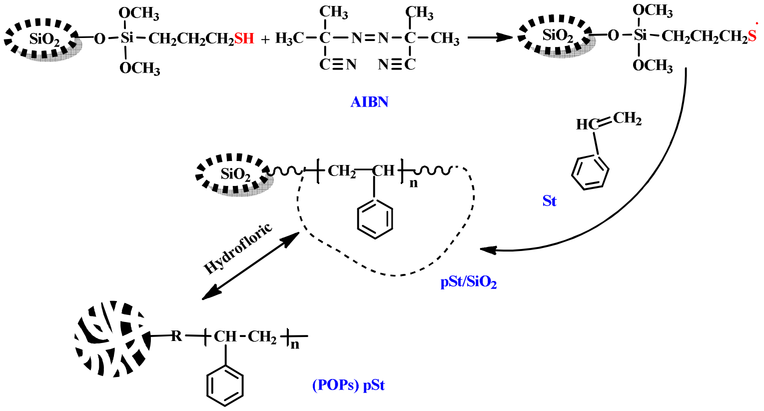
Porous organic polymers (POPs) have attracted tremendous attention in both academia and industry owing to their unique functionalization and relatively excellent stability, and have widely applied in gas storage, separation and catalysis[19-22]. As is known to all, silica gel (SiO_2) exhibiting excellent mechanical property and fine thermal and chemical stability, such as relatively good stability, a great large pore surface area, good adsorption capacity and an ordered pore arrangement[23,24], has emerged as an inorganic solid support and has been widely used in polymer composites. However, many researches focus on its external surface but neglect to utilize its abundant pore structure[25-27], herein, a new porous organic frameworks have been designed and synthesized through novel and convenient method base on silica gel particles.

Constructing mercapto group/AIBN(-SH/AIBN) redox initiating system, the mercapto groups on the surfaces of modified particles MPMS/SiO_2 with the decomposition of initiator AIBN in DMF solution, on which the hydrogen atom transferred to one free radical of benzoic acid so that sulfur free radicals were obtained on the surfaces of silica gel particles, and the graft polymerization of St was caused on the surface of silica gel particles, preparing the grafted particles pSt/SiO_2, then etched away the silica matrix and formed the POPs pSt. And then 1,4-bis(chloromethoxyl) butane (BCMB), trimellitic anhydride (TMA) and hydroxylamine hydrochloride were used as the reaction reagent, respectively, through three macromolecular reactions, chloromethylation reaction, esterification and acyl imidization, and eventually immobilized material pSt/NHPI was obtained. The above entire chemical process can be showed schematically in Scheme 1.

(1) Preparation of the porous organic polymers (POPs) pSt



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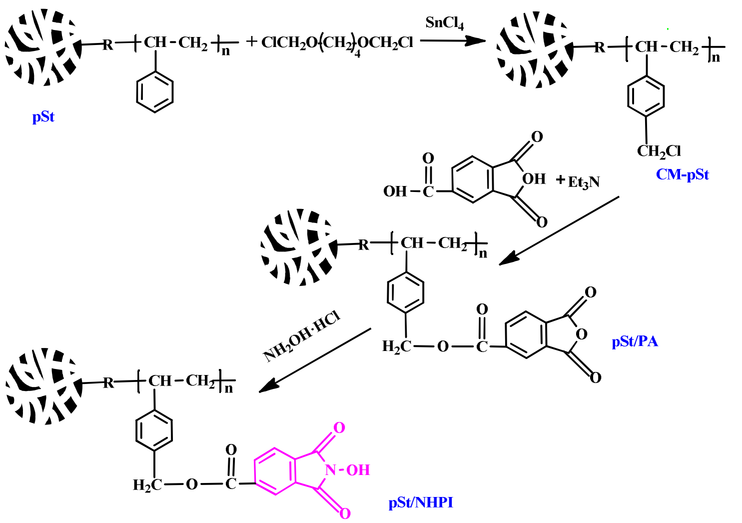

(2) Immobilization of NHPI on the POPs pSt

Scheme 1. Chemistry of preparing the heterogeneous catalyst pSt/NHPI

In this communication, the aerobic oxidation of toluene into benzoic acid working together with the co-catalyst $Co(OAc)_2$ was conducted, which used molecular oxygen as final oxidant by low-temperature and normal-pressure of oxygen operation, and the possible catalytic oxidation mechanism was discussed. The results show that it has a certain application value in the field of solid supported catalysis.

2 Experimental Section

2.1 Chemicals and materials

Silica gel (about 125 μm, Haiyang Chemical Limited Company, Qingdao, China). γ-mercaptopropyl trimethoxysilane (MPMS, Nanjing Chuangshi Chemical Aux Ltd., Jiangsu, China). Styrene (St, Suzhou Nanhang Chemical Ltd., China), purification by vacuum distillation before use. 2,2’-azobisisobutyronitrile (AIBN, 98% purity, Shanghai Zhongli Chemical Plant, Shanghai, China), purification by recrystallization from ethanol before use. Trimellitic anhydride (TMA, Tianjin Guangfu Fine Chemical Ltd., China), Toluene, Aceticacid, *N*,*N*-dimethylformamide(DMF), Dimethylacetamide(DMAC)(Tianjin Shentai Chemical Ltd., China). Transition metal salts: $Co(OAc)_2$、$CuCl_2$、$Fe(acac)_2$、$MnSO_4$ (Shanghai Jingchun Biochemical Ltd., China). Hydroxylamine hydrochloride (Ruishuo Chemical Limited Company, Shanghai, China). Other reagents were of analytical pure grade and were used without further purification.

2.2 Apparatus

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Perkin-Elmer 1700 Infrared Spectrometer (FTIR, Perkin-Elmer Company, USA); Unic-2602 UV spectrophotometer (Unic Company, Shanghai); LEO-438VP scanning electronic microscope (SEM, LEO Company, UK); STA449 thermogravimetry analyzer (TGA, Netzsch Company, German); ASPA2000 Physisorption (Micromeritics Company, USA); GC-2010 gas chromatograph (GC, Shimadzu Company, Japan). PE-2400II Elemental Analyzer (EA, Perkin-Elmer Company, USA).

2.3 Preparation and characterization of pSt/NHPI

2.3.1 General procedure for preparation of POPs pSt

According to the operation steps of Ref. [28,29], the graft polymerization of St was caused on the surface of silica gel particles, and the specific operation steps were as follows. Firstly, silica gel particles were treated for activation by using aqueous solution of hydrochloric acid as activation reagent. Secondly, activated silica gel particles were surface-modified with coupling agent MPMS, obtaining the modified products MPMS/SiO_2, whose mercapto group content was 1.08mmol/g. Using AIBN as initiator and DMF as solvent, the graft polymerization of St on the surfaces of MPMS/SiO_2 particles were carried out, obtained the grafting particles pSt/SiO_2, then transferred them into polyethylene beaker and added 30ml of 40% hydrofluoric to etch away the silica gel, and followed by washing and drying, finally, the porous organic polymers pSt was prepared. The grafting degree of the pSt/SiO_2 particles was determined by TGA.

2.3.2 Immobilization of NHPI on the POPs pSt

(1) Chloromethylation of the POPs

According to the procedure ascribed in Ref.[30], using self-made 1,4-bis(chloromethoxyl) butane (BCMB) as the chloromethylation reagent and adopting $SnCl_4$ as Lewis acid catalysts, the reaction was performed at room temperature in a dichloromethane solvent for 9h. The amount of the chlorine content on the product CM-pSt was determined by Calorimeter and Volhard method.

(2) Bonding of phthalic anhydride on CM-pSt

0.5g of CM-pSt were placed in a four-necked flask equipped with a mechanical agitator and a reflux condenser, followed by adding 30mL of DMF as solvent and soaking for 5h. And then 1.3g of TMA was dissolved in 10mL of DMF, and the mixture was added into the flask. Afterwards, 0.5mL of triethylamine (Et_3N) as catalyst was added into the reaction system, the esterification reaction between chloromethyl groups on CM-pSt and the carboxyl group of TMA was performed at 85℃ for 5h. After reaction finished, the concentrations of TMA in the supernatants were measured by ultraviolet spectrophotometry at 291 nm, which showed that the conversion of chloromethyl of CM-pSt can reaches 70%. The product pSt/PA was fully washed with DMF and aether in turn for several times, and then filtrated and dried under vacuum.

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(3) Synchronously synthesizing and immobilizing NHPI on pSt/PA

In a four-necked flask, 1g of pSt/PA was dipped in 30 mL of pyridine for 5h in order to fully swell the polymeride, followed by adding 0.8g of hydroxylamine hydrochloride as reaction reagent. The reaction between the bonded phthalic anhydride (PA) and hydroxylamine hydrochloride was conducted at 90℃ with stirring for 15 h. After the reaction, the product was acidized by adding diluted hydrochloric acid. The resultant product was washed repeatedly with distilled water and ethanol, collected by filtering and dried under vacuum. Finally, the heterogeneous catalyst pSt/NHPI was obtained, on which the immobilization amount (*Q*) of NHPI was measured by weighing method, and it was 2.25mmol/g.

$$Q = (m_2 - m_1)/M * 1000$$

In this formula, m_1 and m_2 are the quality of pSt/PA and pSt/NHPI (g), and M is the sum of molar mass of N and H atoms, which is about 15 g/mol.

2.4 Catalytic oxidation of toluene with molecular oxygen

The catalytic oxidation of toluene at the presence of molecular O_2 was conducted in a reactor equipped with a mechanical stirrer, thermometer, O_2 inlet and reflux condenser, then 40 mL of aceticacid and 1.0 g of pSt/NHPI were added and dissolved for 5h, and followed by adding 2ml of toluene and 0.04g of $Co(OAc)_2$ as the co-catalyst. Oxygen at the fixed flow rate which was 16 mL/min was passed into the reaction system. The oxidation reaction was carried out at 80℃ and continuously stirred for 30 h. Samples of the reaction mixture were taken at fixed time intervals, and then measured by a gas chromatograph with the internal standard method (N_2 as carrier gas, PEG-20M Capillary Column and FID detection), showing that benzoic acid was the main product and a small amount of byproduct benzaldehyde. After the oxidation reaction, the heterogeneous catalyst pSt/NHPI was soaked, washed with distilled water and ethanol in turn to completely remove the organic matter physically attached on the particles, and dried under vacuum. The recovered particles were reused in the oxidation reaction of toluene under the same conditions to examine their recycling performance.

3. Results and Discussion

3.1 Synthesis of NHPI catalyst

Constructing mercapto group/AIBN(-SH/AIBN) redox initiating system, and the graft polymerization of St was caused on the surface of silica gel particles, preparing the grafted particles pSt/SiO_2, followed by adding hydrofluoric acid to dissolve the silica gel, and then synchronously synthesized and immobilized NHPI on the POPs via several steps of polymer reaction, resulting in the heterogeneous catalyst particles pSt/NHPI.

3.1.1 Effects of main factors on the immobilization of NHPI

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The NHPI-immobilized heterogeneous catalyst was prepared via three macromolecular reaction steps. The chloromethylation of the phenyl on the polymer has been fully examined by our group, and the optimum reaction conditions were determined, the reaction of the bonded phthalic anhydride (PA) with hydroxylamine hydrochloride was also a mature chemical reaction, however, the reaction of CM-pSt with TMA was a key step. So in this study the effect of reaction parameters on the high bonded amount of phthalic anhydride (PA) was investigated, the optimum reaction conditions were established.

By fixing the other reaction conditions, Figure 1 gives the rate of concentration chloromethyl group conversion (CGC) change versus time at different temperatures. The results clearly showed that the esterification reaction rate increased with temperature, because the chloromethyl group conversion at 85℃ was very close to that at 90℃, a suitable reaction temperature was 85℃.

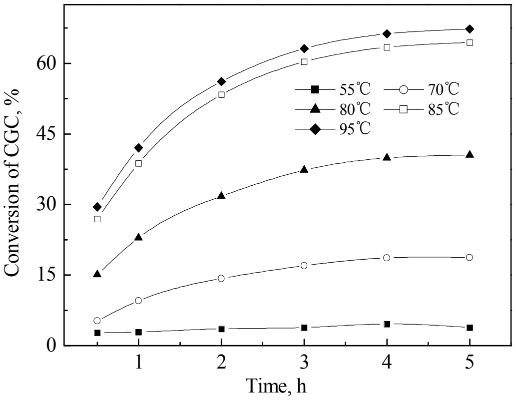

Figure 1. Variation of chloromethyl group conversion rate of CM-pSt at different temperatures

Table 1. Dielectric constant data for various solvents

Solvent	DMAC	DMF	DMAC/Dioxane[a] (V/V=1:1)	DMF/Dioxane[a] (V/V=1:1)
Dielectric constant ε (25℃)	37.8	36.7	20.0	19.5

[a] The dielectric constant of the mixied solvent was calculated according to molar ration of the two solvents.

Table 2. Effect of reaction conditions on the esterification reaction

Entry	Temperature(℃)	Catalyst[b]	Solvent	Reaction time(h)	CGC(%)
1	85	Et$_3$N	DMF/Dioxane[a]	5	57.3
2	85	Et$_3$N	DMAC/Dioxane[a]	5	59.5
3	85	Et$_3$N	DMF	5	65.5

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4	85	Et_3N	DMAC	5	68.2
5	85	Bu_3N	DMAC	5	61.9
6	85	NaOH	DMAC	5	46.2
7	85	Na_2CO_3	DMAC	5	34.6

[a] The volume ratio of two solvents was 1:1.

[b] The used amount of catalyst in this reaction were 15mmol. Et_3N (Triethylamine), Bu_3N (Tri-n-butylamine).

In the presence of HCl agent, the reaction between chloromethyl group of CM-pSt and carboxy of TMA is a nucleophilic substitution reaction. Carboxy hydroxyl loses hydrogen proton and translates into a carboxylic acid anion as a nucleophilic attack group, while chloromethyl loses chlorine translates into carbenium ion which is closely associated with the polarity of the solvent. A higher solvent polarity gives a stronger dipole-dipole interaction of solvent and nucleophilic reagent, which is helpful for removing the chlorine atom and attacking the carboxylic acid anion. Obviously, the polarity of the solvents can promote the nucleophilic substitution reaction. Based on this, DMAC should be selected as the suitable solvent. At the same time, the suitable catalyst was Et_3N which can be well dissolved in the reaction system.

3.1.2 Characterization of functional particles pSt/NHPI

As shown in Figure 2, the chemical modification of SiO_2 was confirmed by IR spectroscopy.

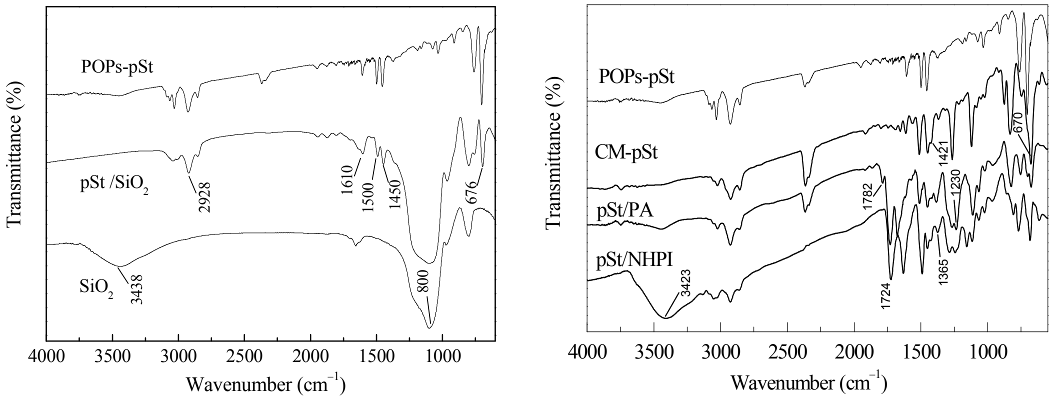

Figure 2. IR spectra of the reactants

In the spectrum of SiO_2 at 3438 cm^{-1}, 1126 cm^{-1}, around 800 cm^{-1} are observed, these bands are assigned to the silanol groups as well as the adsorbed water, the antisymmetric stretching vibration absorption of Si-O-Si bond and the symmetrical stretching vibration absorption of Si-O bond. In the spectrum of pSt/SiO_2, the characteristic absorption of the methylene groups of the main chain of the polymer appeared at 2928 cm^{-1}, while the peaks at 1610 cm^{-1}, 1500 cm^{-1}, 1450 cm^{-1} and 674 cm^{-1} are ascribed to skeleton vibration of benzene ring on polystyrene. In the spectrum of POPs-pSt, it can be

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clearly observed that the absorption peak at 800 cm^{-1} and 1126 cm^{-1} has disappeared after silica gel dissolved. In the spectrum of CM-pSt, except for the characteristic absorption bands of POPs-pSt, the appearance of two absorption bands at 1421 cm^{-1} and 670 cm^{-1} was due to the chloromethyl group –CH_2Cl. In the spectrum of pSt/PA, the adsorptions of chloromethyl group were much weakened, whereas the characteristic absorption band of ether group C-O-C appeared at 1230 cm^{-1}, also two characteristic absorption bands of cyclic anhydride appeared at 1782 cm^{-1} and 1724 cm^{-1}, which attributed to asymmetry and symmetry coupling vibration adsorption of anhydride carbonyl, respectively. In the spectrum of pSt/NHPI, the characteristic absorption band of free radicals group N-O appeared at 1365 cm^{-1}, the strong absorption band at 3443 cm^{-1} represented the -OH stretching vibration absorption, all of the above changes of spectrum data sufficiently confirmed that pSt/NHPI particles were prepared.

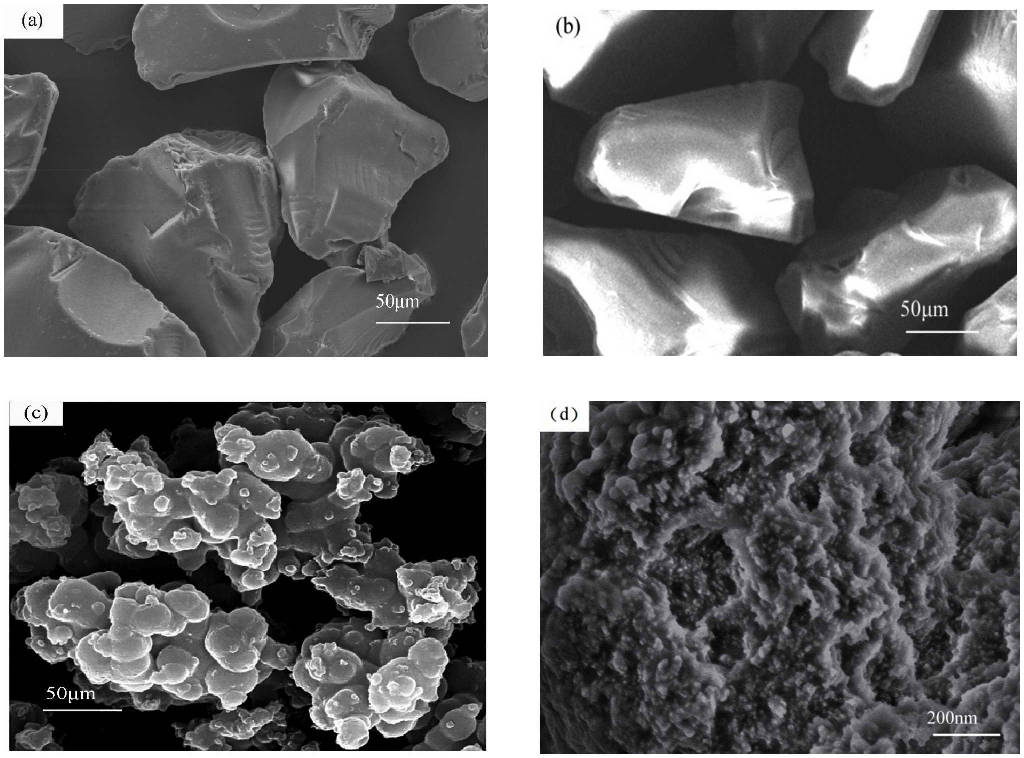

Figure 3. SEM images of four kinds of particles

(a) Silica particles SiO_2; (b) Graft particles pSt/SiO_2

(c) POPs pSt; (d) Functional POPs pSt/NHPI

Figure 3 demonstrated the change of structure of particles in the course of chemical modification of SiO_2. The surfaces of raw silica gel particles(a) were rough and scraggy, whereas the surfaces of the grafted particles pSt/SiO_2(b) became smoother and flatter. It was caused by the coating and filling up action of the functional macromolecule. It can be observed from (c) and (d) that with the corrosion of

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silica gel, the obtained polymeric network samples were composed of loosely agglomerated particles with irregular shape and a large number of hollow apertures.

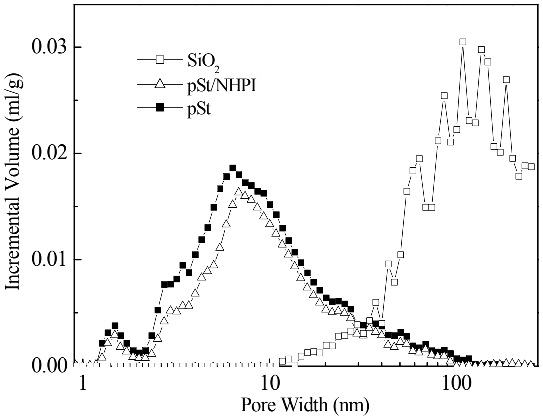

Figure 4. Pore size distribution for pSt and pSt/NHPI

The porosity parameters of the POPs were summarized in Tab.1, the porous skeleton of SiO_2 mainly composed of macropores, whereas the porous skeleton of the two POPs mainly composed of mesopores, the surface area and pore volume of the POPs decreased with NHPI immobilized. It is mainly due to the reagent NHPI bonded to the pores through several steps of polymer reaction.

Table 3. Textural properties of samples

Sample	A_{BET}(m^2/g)	V_{total}(cm^3/g)	Pore size distribution/%		
			micro-	meso-	macro-
SiO_2	325	0.35	1.3	15.5	83.2
POPs pSt	343	0.43	5.7	91.2	3.1
POPs pSt/NHPI	249	0.38	9.9	85.8	4.3

The thermal stabilities of the graft particles were evaluated by thermogravimetric analysis (TGA) from room temperature to 800℃ under a nitrogen atmosphere.

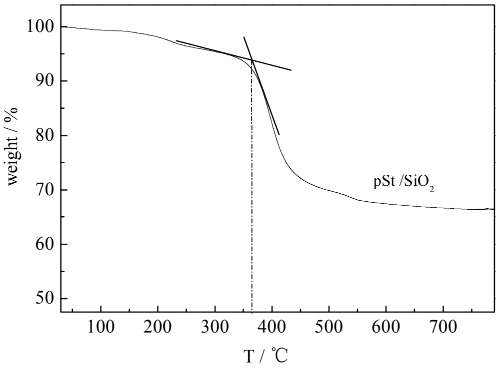

Figure 5. TGA curves of pSt/SiO_2 particles

The results were presented in Figure 5. It can be found that the graft polymer pSt/SiO_2 exhibited

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higher decomposition temperature about 380℃, indicating excellent thermal resistance to be used as supported materials.

Contents of nitrogen, carbon and hydrogen in pSt/NHPI were determined by the PE-2400II EA. The experimental conditions were as follows: The dosage of sample was 1.5mg, the temperature of combustion tube was set at 950℃, acetanilide was used as the standard sample.

Table 4. Elemental analysis

Element	C	H	N
Content (wt%)	72.84	5.10	3.11

The immobilization amount of NHPI was determined by the content of nitrogen in Table 4, and the determination result 2.23mmol/g was coincident with that of the above chemical analysis.

3.2 Catalytic characteristics of pSt/NHPI

The oxidation of toluene was catalyzed by the combination catalysts of pSt/NHPI and $Co(OAc)_2$ using molecular oxygen as final oxidant, Figure 6 showed that it can make toluene to be highly effectively transformed into benzoic acid with a yield of 48% at 80℃ in 30 h. In order to make comparison, the catalytic experiment was also carried out only using pSt/NHPI, $Co(OAc)_2$ and nothing at all, and results showed that the oxidation of toluene almost didn't occur in the three systems.

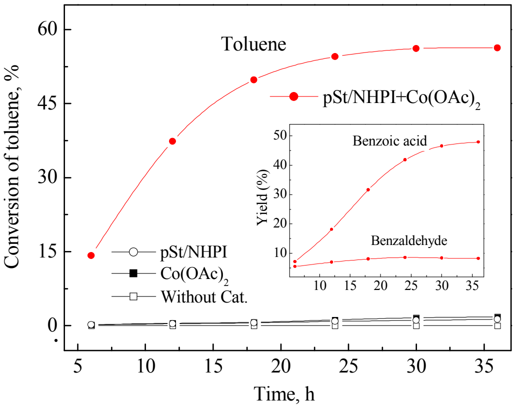

Figure 6. Variation curves of toluene conversion with time using different catalyst systems

(Temperature: 80℃, Solvent: Aceticacid)

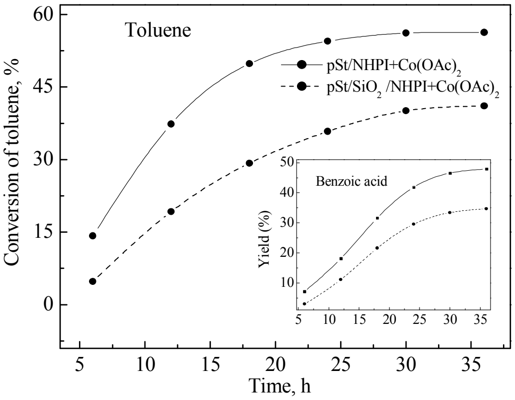

Figure 7. Effect of two particles on toluene conversion with time

(Temperature: 80℃, Solvent: Aceticacid)

The catalytic experiments also were conducted with the particles $pSt/SiO_2/NHPI$ and $Co(OAc)_2$ in Figure 7. It also can be clearly seen that the pSt/NHPI catalyst showed higher activities than the $pSt/SiO_2/NHPI$ catalyst, because the reactant concentrations between the catalysts were different. The former catalyst had more abundant pore structure, thus creating a much higher reactant concentration

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in the catalyst pores when compared with the latter. According to the Arrhenius equation, high reactant concentrations leaded to strong catalytic activity.

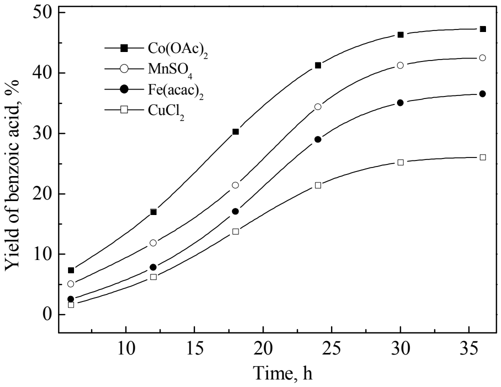

Figure 8. Variation curves of the yield of benzoic acid with time using different co-catalyst (Temperature: 80℃, Solvent: Aceticacid)

Table 5. Standard electrode potential of relevant redox couples

Entry		$\varphi^{\ominus}$/V
1	$Co^{3+}+e \rightleftharpoons Co^{2+}$	1.84
2	$Mn^{3+}+e \rightleftharpoons Mn^{2+}$	1.51
3	$Fe^{3+}+e \rightleftharpoons Fe^{2+}$	0.77
4	$Cu^{2+}+e \rightleftharpoons Cu^{+}$	0.15

The catalytic activity of several different co-catalysts was displayed in Figure 8 and its order was $Co(OAc)_2$ >$MnSO_4$ >$Fe(acac)_2$ >$CuCl_2$. For the four co-catalysts, the yield of benzoic acid increased with the advance of the reduction potential of the co-catalysts. As described in scheme 2 in the catalytic oxidation of toluene, that high valence metal ions triggers the generation of the nitrogen carbonyl cation which was a critical step.

Table 6. Effect of reaction conditions on catalytic reaction

Entry	Temperature(℃)	n(NHPI):n(Co(OAc)$_2$)	m(combination catalyst)/g	Reaction time(h)	Yield (%)
1	80	10:1	1.0	30	39.5
2	80	12:1	1.0	30	41.6
3	80	14:1	1.0	30	45.6
4	80	16:1	1.0	30	43.3
5	80	17:1	1.0	30	38.3
6	90	14:1	1.0	30	45.9
7	70	14:1	1.0	30	36.3
8	60	14:1	1.0	30	21.1
9	80	14:1	0.95	30	38.5
10	80	14:1	1.04	30	47.8
11	80	14:1	1.06	30	48.1

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As shown in Table 6, by fixing the added amount of the combination catalysts (1.0g), the mole ratio of the immobilized NHPI to $Co(OAc)_2$ was changed in series. When the molar ratio is equal to 14:1, it can make toluene to be highly effectively transformed into benzoic acid with a yield of 45.6% in 30 h. The effect of the amount of the combination catalyst in the oxidation reaction was examined. With increasing amount of co-catalysts, the yield of benzoic acid increased, so for this reaction system, the suitable amount of the combination catalyst was 1.04g in which the mole ratio of the immobilized NHPI to $Co(OAc)_2$ is 14:1. The results also clearly showed that the catalytic reaction rate increased with temperature, because the immobilized amount of NHPI at 80℃ was very close to 90℃, a suitable reaction temperature is 80℃.

3.2.1 Catalytic Selectivity.

As described above, for the catalytic oxidation of toluene with the co-catalyst system in this study, the obtained product was mainly composed of benzoic acid, and a small amount of byproduct benzaldehyde. For the oxidation system containing pSt/NHPI and $Co(OAc)_2$, Figure 9 demonstrated the changing curves of the yields of benzoic acid and benzaldehyde with time, respectively.

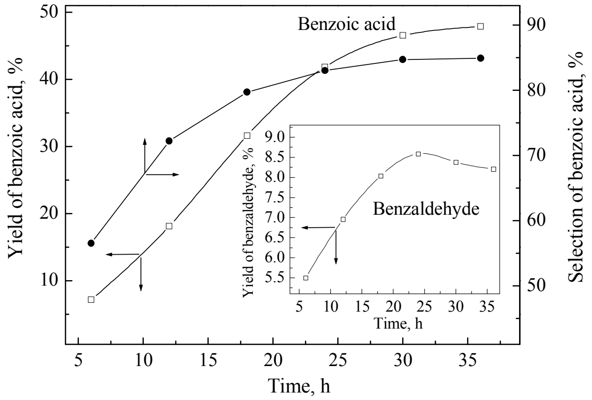

Figure 9. The yields of benzoic acid and benzaldehyde as well as selectivity of benzoic acid with time

(Temperature: 80℃, Solvent: Aceticacid)

As is shown in Figure 9. During the oxidation process of toluene, both the yield and selectivity of benzoic acid increase with time in the process. After 30 h, the yield and selectivity of benzoic acid level off, the selectivity is 86% and the yield is 48%. For the byproduct benzaldehyde, the yield increases at beginning and then declines with time, the reason for that is probably associated with the further oxidation of benzaldehyde to benzoic acid. In summary, in the oxidation of toluene by molecular oxygen, the heterogeneous catalyst pSt/NHPI in combination with a small amount of the co-catalyst $Co(OAc)_2$ has high catalytic selectivity for benzoic acid.

3.2.2 Mechanistic studies

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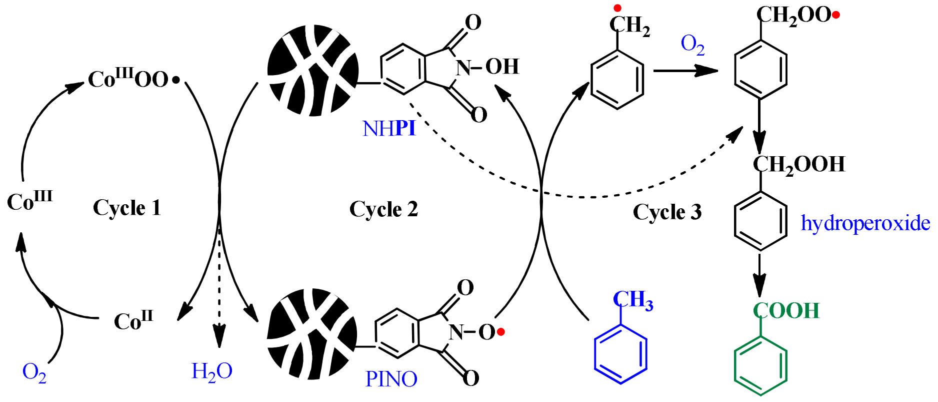
A mechanism for this catalytic oxidation is based on previous studies.[13,31,32] It can be described as a cascade of redox reactions containing three cycles which is shown in Scheme 2.



Scheme 2. Proposed mechanism for the catalytic aerobic oxidation of toluene

During the redox process, with the help of the complexation of Co(II) of Co(OAc)$_2$, a series of electron transfer is initiated with dioxygen in Cycle I. The key step in the total oxidation process is that the PINO radicals generate via the homolytic cleavage of the hydroxyl group of NHPI (Cycle I). Subsequently, the hydrogen atom of the substrate toluene is taken away by the PINO radical and formed a carbon free radical, so as to open the free radical chain reaction which includes chain initiation, propagation and termination steps. Meantime, hydroperoxide will be formed, and with its subsequent decomposition, eventually toluene is oxidized to benzoic acid and benzaldehyde. With repeating of the three cycles, toluene is continuously transformed into benzoic acid.

3.2.3 Reuse property of the catalyst

The cyclic repeated experiments were carried out by using the combination catalyst, which contained pSt/NHPI and Co(OAc)$_2$, and the supported catalyst pSt/NHPI was used in each catalytic oxidation which should be separated from the reaction mixture for reuse.

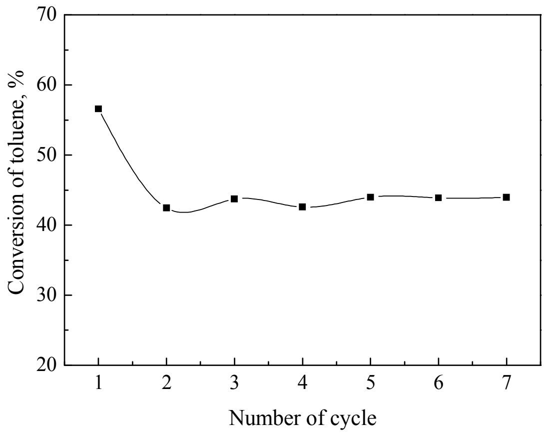


Figure 10. Effect of cycle number on catalyst activity

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(Temperature: 80℃, Solvent: Aceticacid, Reaction time: 30 h)

The experimental results were shown in Figure 10. The catalytic activity declined a little at the second recycle during the reuse of 7 times (toluene conversion fallen obviously from 56% to 43%), after that, the catalytic activity was quite stable (toluene conversion was at about 44%). In addition, the appearance of pSt/NHPI was kept well during the recycling. Therefore, it can be concluded that this immobilized catalyst has excellent reuse performance.

4. Conclusions

Via several steps of polymer reaction in this investigation, a novel porous organic polymeric support pSt for the immobilization of NHPI has been prepared. The experimental results show that the reaction of CM-pSt with TMA is a key step, the results indicate that DMAC is a suitable solvent, and the optimal reaction temperature is 80℃ in the esterification reaction. The supported catalyst pSt/NHPI could oxidate toluene into benzoic acid with the co-catalyst $Co(OAc)_2$ using molecular oxygen as final oxidant, the superiority of this catalyst over others includes a very higher catalytic activity. In summary, an efficient and convenient method is designed to support NHPI, and demonstrated the effectiveness of the heterogeneous catalyst pSt/NHPI in the catalytic oxidations of hydrocarbons.

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Graphical abstract

Catalytic Property of N-hydroxyphthalimide Immobilized on A Novel Porous Organic Polymer in Oxidation of Toluene by Molecular Oxygen

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In this work, a novel porous organic polymers(POPs) pSt has been prepared based on micro-sized macroporous silica gel and was used for the immobilization of NHPI, the obtained heterogeneous catalyst pSt/NHPI could adsorb toluene and oxidate it into benzoic acid working together with the co-catalyst Co(OAc)$_2$ by molecular oxygen. The experimental results show that this combination catalysts possess high catalytic selectivity and catalytic activity, and transforming toluene into benzoic acid with a yield of 48% in 30h.