

## Synthesis of 1-benzoylpyrene using silica-supported phosphotungstic heteropoly acid as an efficient and reusable catalyst

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(Received 10 December 2011 • accepted 18 March 2012)

**Abstract**—A novel one-pot catalytic synthesis of 1-benzoylpyrene through acylation of pyrene with benzoic anhydride catalyzed by several heteropoly acids (HPAs) was investigated. Pure 1-benzoylpyrene was obtained and its structure was identified by GC/MS, FT-IR and <sup>1</sup>H NMR spectra. Silica-supported phosphotungstic heteropoly acid (PW/SiO<sub>2</sub>) was found to be the most active catalyst in the acylation. The yield and the selectivity of 1-benzoylpyrene were up to 62.5% and 100%, respectively. The effects of experimental parameters on the catalytic acylation reaction, and the possibility of reusability of PW/SiO<sub>2</sub> catalyst were studied. PW/SiO<sub>2</sub> catalyst is easily separable from the reaction mixture and reusable without loss of its activity.

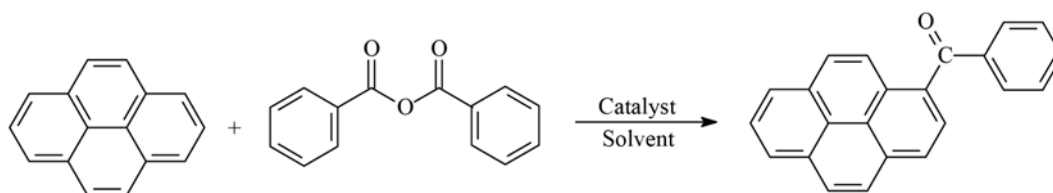
Key words: 1-Benzoylpyrene, Friedel-Crafts Acylation, Pyrene, Heteropoly Acids, Catalysis

### INTRODUCTION

The Friedel-Crafts acylation of aromatic compounds is the most important route for the synthesis of aromatic ketones that are intermediates in manufacturing fine and specialty chemicals as well as Pharmaceuticals [1]. The acylation of aromatics has been generally carried out with homogeneous lewis acid-type catalysts (anhydrous metal halides such as AlCl<sub>3</sub> and FeCl<sub>3</sub>) and acyl halides as acylating agents. The overall process produces a significant amount of undesirable products and destroys the catalyst. In view of the increasingly strict environmental legislation, the application of heterogeneous catalysis has become attractive. In recent several decades, considerable effort has been put into developing heterogeneously catalyzed Friedel-Crafts and other organic reaction using solid acid catalysts such as zeolites, clays, Nafion-H, mesoporous superacidic catalyst, and so forth [2-4]. Heteropoly acids (HPAs) are another type of promising solid acid catalysts for aromatic Friedel-Crafts acylation. HPAs with Keggin structure are the most studied class within polyoxometalates, because they possess relatively high acidity and thermal stability [5]. Supported HPAs are important for many applications, because bulk HPAs have low specific structure area (1-10 m<sup>2</sup>/g). It is important to increase the surface area or even better to increase the number of accessible acid sites of the HPA. This can

be achieved by dispersing the HPA on solid support with high surface area [6,7]. For heterogeneous systems, it is possible to control solid strength by supporting HPAs on different carriers. An immobilization of HPAs on a number of porous supports such as silica, active carbon, montmorillonite K-10, zeolite, etc. was therefore extensively studied [8]. But SiO<sub>2</sub>, which is relatively inert towards HPAs, is the most often used [9]. Furthermore, supported HPA catalysts are more easily separated and recovered from reaction mixtures, and reused than bulk HPAs. To date, Friedel-Crafts acylations of benzene, naphthalene, and their derivatives catalyzed by HPAs have been paid many efforts [10-12]. However, only a few reports have been published for the acylation of polyaromatics over HPAs [10,13]. To the best of our knowledge, no acylation of pyrene catalyzed by supported HPAs has been reported.

In our laboratory, the acylation of polyaromatics catalyzed by chloroaluminate-based ionic liquids had already been studied [14]. In continuation of our work in studying the acylation of polyaromatics with green method, herein we firstly report the synthesis of 1-benzoylpyrene, which could be used as new fine chemical, through acylation of pyrene with benzoic anhydride catalyzed by silica-supported phosphotungstic heteropoly acid (PW/SiO<sub>2</sub>) (Scheme 1) under different experimental conditions. The PW/SiO<sub>2</sub> catalyst was facily isolated from the products and effectively recycled.



Scheme 1. Friedel-Crafts acylation of pyrene to 1-benzoylpyrene.

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## EXPERIMENTAL

### 1. Materials

Pyrene (98%) from Sinopharm Chemical Reagent Co., Ltd.,  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 20\text{H}_2\text{O}$  (PW),  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$  (SiW),  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 18\text{H}_2\text{O}$  (PMo), silica ( $\phi$  0.05-0.20 mm) from Aladdin reagent Co., were used. All other chemicals used in this study were commercially available and were used without further purification.

### 2. Catalyst Preparation

Prior to use, the silica support was washed with nitric acid, then with distilled water and finally calcined at 700 °C overnight. The supported acid was prepared by incipient wetness impregnation with stoichiometrically weighed amounts of HPA and silica. After mixing thoroughly the aqueous slurry for 2 h and evaporating at 110 °C to dryness, the supported catalyst was further heated at 150 °C for 3 h.

### 3. Catalyst Characterization

Surface area and porosity of catalysts were measured by nitrogen physisorption on a Micromeritics NOVA 2000 instrument. FT-IR spectra were recorded with KBr pellets using a Nexus 470 FT-IR spectrometer. The phase purity and crystal structure of the obtained samples were examined by X-ray diffraction (XRD) using D8 Advance X-ray diffraction equipped with Cu-K $\alpha$  radiation ( $\lambda$  1.5406 Å), employing a scanning rate of 0.02° s<sup>-1</sup> in the 2 $\theta$  range from 5 to 80°.

### 4. Typical Procedure for the Synthesis of 1-Benzoylpyrene

A mixture of pyrene (0.5 mmol), benzoic anhydride (2 mmol), and 1,2-dichloroethane (15 mL) in the presence of an appropriate amount of catalyst was stirred at the desired temperature. Progress of the reaction was monitored by GC. After completion of the reaction, the mixture was washed with 1,2-dichloroethane and filtered, after removal of solvent from the filtrate through distilling, and the crude desired product as yellow solid was washed with distilled water and petroleum ether, respectively, then recrystallized from acetone to give the pure product as yellow flake crystal. Qualitative and quantitative analyses were conducted with GC/MS (HP 6890), <sup>1</sup>H NMR (Bruker 2AR300) and FT-IR (Nexus 470), respectively.

The spectral data for the desired product 1-benzoylpyrene: GC/MS, m/z (%): 306 (M<sup>+</sup>, 100.0), 229 (79.4), 201 (91.3), 105 (14.6), 77 (25.1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz),  $\delta$ : 2.915 (s, 4H), 8.049-8.086 (m, 2H, J=8.068), 8.165-8.185 (t, 2H, J=8.170 Hz), 8.224-8.271 (m, 3H), 8.387-8.403 (d, 1H, J=4 Hz), 9.061-9.080 (d, 1H, J=4.75 Hz); FT-IR (KBr), cm<sup>-1</sup>: 3010 (Ar-H), 2980 (C-H), 1600-1450 (Ar), 1664 (C=O), 1380 (CH<sub>3</sub>).

## RESULTS AND DISCUSSION

### 1. Catalyst Characterization

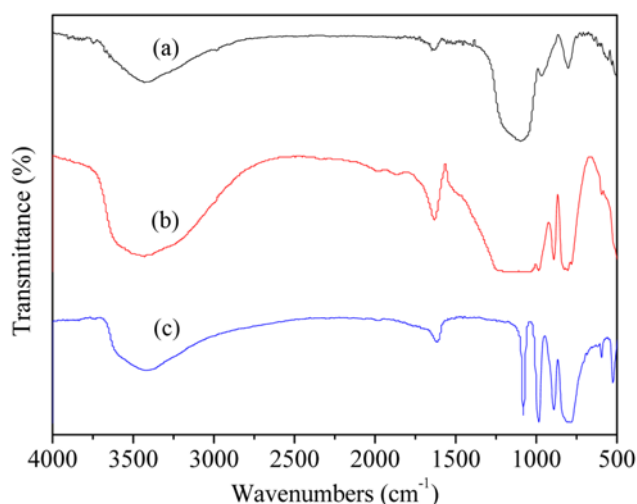
The BET surface areas and pore volume of silica, bulk and silica-supported PW catalysts are listed in Table 1.

Bulk PW showed very low surface areas as well as very low porosity (Table 1, Entry 2), as expected. The surface area and pore volume of silica-supported PW (Table 1, Entries 3-5) decreased remarkably compared to their parent support (Table 1, Entry 1), but still showed very high values. The reduction in the surface area and pore volume of supported catalysts may be due to the blockage of smaller pores by active species.

The IR absorption bands assigned to the Keggin anion (800-1,100

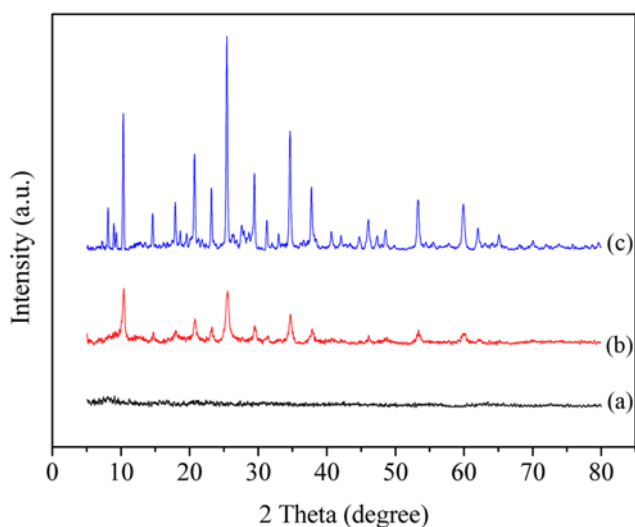
**Table 1. Specific surface area of silica, bulk and silica-supported PW**

Entry	Catalyst	$S_{BET}$ (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
1	SiO <sub>2</sub>	323.67	1.55
2	PW	9.09	0.01
3	30%PW/SiO <sub>2</sub>	228.06	0.58
4	40%PW/SiO <sub>2</sub>	195.23	0.45
5	50%PW/SiO <sub>2</sub>	151.64	0.42



**Fig. 1. IR spectra: (a) SiO<sub>2</sub>; (b) 40% PW/SiO<sub>2</sub>; (c) PW.**

cm<sup>-1</sup>) in bulk and silica-supported PW (40% PW/SiO<sub>2</sub>) are seen in Fig. 1. A shoulder of silica band appeared at approximately 1,200 cm<sup>-1</sup>, partially superseding PW 1,080 cm<sup>-1</sup> stretching (Fig. 1(b)). Due to strong absorption of silica in the region of the Keggin anion “fingerprint”, some of its characteristic absorption bands become unclear; however, some could still be detected for the supported catalyst, Fig. 1(b), as that band at 890 cm<sup>-1</sup>, typical of the Keggin anion and not observed in the silica spectrum. The band around 1,080 cm<sup>-1</sup> is attributed to the stretching vibration of P-O, that at 985 cm<sup>-1</sup>



**Fig. 2. X-rays diffractograms: (a) SiO<sub>2</sub>; (b) 40% PW/SiO<sub>2</sub>; (c) PW.**

to the stretching vibration of  $W=O$ , and  $805\text{ cm}^{-1}$  to the stretching vibrations of  $W-O-W$ .

The XRD measurement for the supported catalysts was carried out in the present work. Fig. 2(a)-(c) presents the typical XRD patterns of silica, silica-supported PW (40% PW/SiO<sub>2</sub>), and PW, respectively. As shown in Fig. 2(b), some of the diffraction peaks of crystalline PW are not evident in the 40% PW/SiO<sub>2</sub> sample as compared to those of the bulk PW (Fig. 2(c)), revealing that PW has been finely deposited onto the silica surface. Our results are analogous with the observation by Blasco et al. [15].

## 2. Effects of HPAs

At first the acylation reaction of pyrene with benzoic anhydride was performed in the presence of PW, PMo, and SiW (Table 2, entries 1-3). The results showed that the strongest acid, PW, is the most efficient catalyst, as expected, closely followed by SiW, which is a slightly weaker acid than PW. In contrast, PMo shows a very poor performance. This is probably due to reduction of this HPA by the reaction medium [16]. Catalytic activities of the three silica-supported HPAs were also investigated. PW/SiO<sub>2</sub> caused the reaction efficiently compared with PMo/SiO<sub>2</sub>, and SiW/SiO<sub>2</sub> (Table 2, entries 4-6), which is in agreement with the corresponding bulk HPAs. The experimental results demonstrated that the silica-supported acidic HPAs had better catalytic activities than their respective bulk HPAs in the acylation of pyrene to benzoylpyrene. Among all the investigated catalysts, 40%PW/SiO<sub>2</sub> exhibited the best catalytic activity with a yield of 62.5% and a selectivity of 100% for 1-benzoylpyrene (Table 2, Entry 4). All the reactions were carried out under the optimum conditions. Based on above observations, 40 wt% PW on silica was chosen as the suitable catalyst for more investigations.

## 3. Effect of PW Loading on Silica

PW/SiO<sub>2</sub> with different weight percentage of PW to SiO<sub>2</sub> (PW Loading on Silica) was examined as evidenced in Fig. 3. Both yield and selectivity of 1-benzoylpyrene increased with the loading, passing a maximum at about 40 wt% loading. It is because HPAs strongly interact with supports at low loading levels, while the bulk properties of HPAs prevail at higher loading [17]. Based on above observations, 40 wt% PW on silica was chosen as the suitable catalyst for more investigations.

## 4. Effect of PW/SiO<sub>2</sub> Amount

The effect of 40 wt% PW/SiO<sub>2</sub> amount (mol percentage of PW

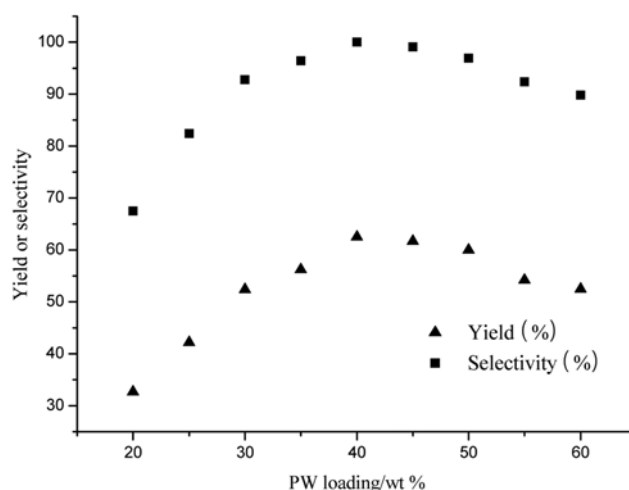
**Table 2. Efficacies of different HPAs in the acylation of pyrene to 1-benzoylpyrene**

Entry	Catalyst	Catalyst amount <sup>a</sup> (mol%)	Yield <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
1	PW	5	57.8	100
2	SiW	5	52.6	100
3	PMo	5	4.2	8.5
4	40% PW/SiO <sub>2</sub>	5	62.5	100
5	40% SiW/SiO <sub>2</sub>	5	58.6	100
6	40% PMo/SiO <sub>2</sub>	5	9.5	18.6

Reaction conditions: pyrene, 0.5 mmol; benzoic anhydride, 2 mmol; reaction temperature, 75 °C; reaction time, 40 min; solvent, CH<sub>2</sub>Cl-CH<sub>2</sub>Cl (15 mL)

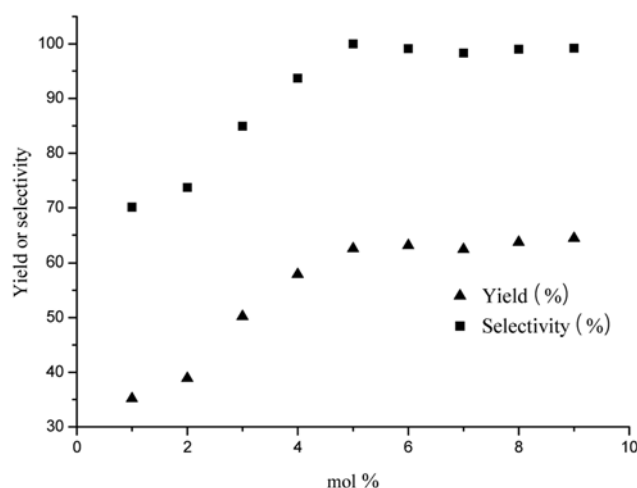
<sup>a</sup>Mol percentage of HPA to pyrene

<sup>b</sup>The yield and selectivity were determined by GC



**Fig. 3. Effect of PW loading on the acylation of pyrene to 1-benzoylpyrene.**

Reaction conditions: pyrene, 0.5 mmol; benzoic anhydride, 2 mmol; PW/SiO<sub>2</sub>, 5 mol%; reaction temperature, 75 °C; reaction time, 40 min; solvent, CH<sub>2</sub>Cl-CH<sub>2</sub>Cl (15 mL).



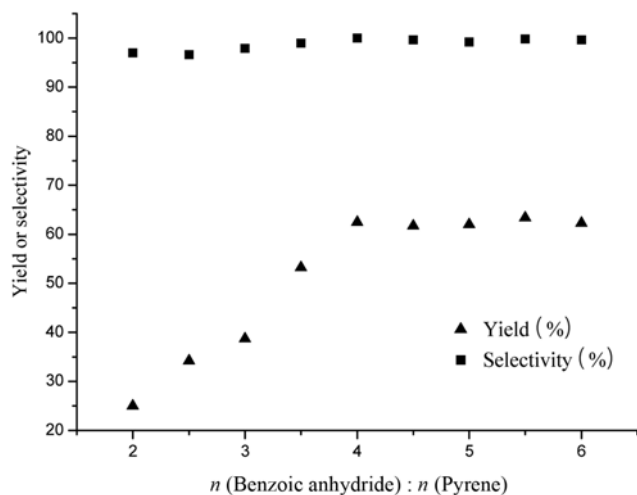
**Fig. 4. Effects of PW/SiO<sub>2</sub> amount on the acylation of pyrene to 1-benzoylpyrene.**

Reaction conditions: pyrene, 0.5 mmol; benzoic anhydride, 2 mmol; PW loading, 40% (w/w); reaction temperature, 75 °C; reaction time, 40 min; solvent, CH<sub>2</sub>Cl-CH<sub>2</sub>Cl (15 mL).

to pyrene) on the acylation of pyrene to 1-benzoylpyrene was tested and the results are displayed in Fig. 4. The yield and selectivity of 1-benzoylpyrene markedly changed with catalyst amount up to 5 mol%. Further addition of catalyst had no improvements in the yield and selectivity. This was because beyond a certain dosage, there exist an excess of catalyst sites over what is actually required by the reactant molecules, and hence, the additional catalyst does not increase the rate of the reaction [18].

## 5. Effect of Molar Ratio of Benzoic Anhydride to Pyrene

Fig. 5 shows the results at various mole ratios of benzoic anhydride to pyrene from 2 to 6. It is found that the yield of 1-benzoylpyrene was significantly improved with increasing the molar ratio benzoic anhydride to pyrene from 2 to 4; but then no longer has an obvious increase as further increasing the mole ratios from



**Fig. 5.** Effects of molar ratio of reactants on the acylation of pyrene to 1-benzoylpyrene.

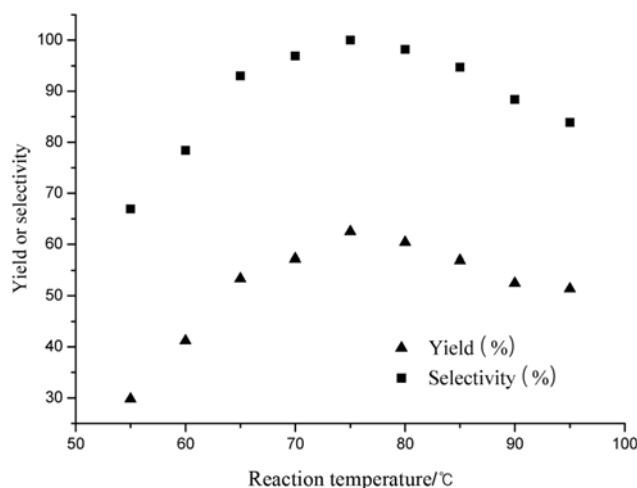
Reaction conditions: pyrene, 0.5 mmol; 40% PW/SiO<sub>2</sub>, 5 mol %; reaction temperature, 75 °C; reaction time, 40 min; solvent, CH<sub>2</sub>Cl-CH<sub>2</sub>Cl (15 mL).

4 to 6. However, the mole ratio of benzoic anhydride to pyrene has no noticeable influence on the selectivity towards 1-benzoylpyrene. A molar ratio of benzoic anhydride to pyrene of 4 favors the formation of 1-benzoylpyrene.

#### 6. Effect of Reaction Temperature and Reaction Time

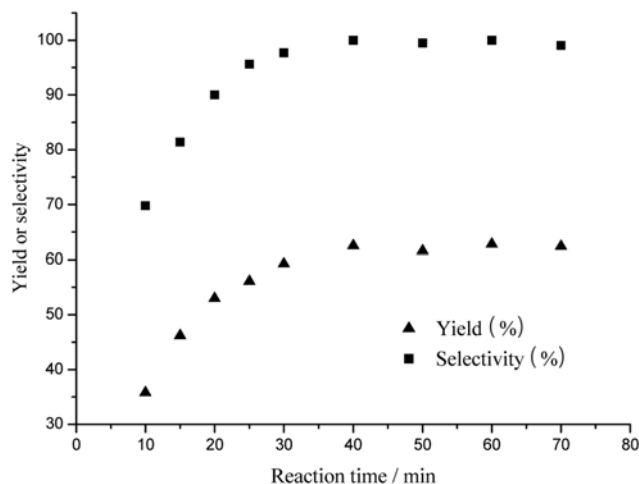
The effect of reaction temperature on both yield and selectivity of 1-benzoylpyrene was investigated at reaction temperatures ranging from 55 to 95 °C (Fig. 6).

The results show that the yield and selectivity of 1-benzoylpyrene rapidly increased with increasing the reaction temperature from 55 to 75 °C. However, as a result of the exothermic nature of the reaction, an obvious decrease in yield and selectivity of desired product occurred when the reaction temperature was further increased. The



**Fig. 6.** Effects of reaction temperature on the acylation of pyrene to 1-benzoylpyrene.

Reaction conditions: pyrene, 0.5 mmol; benzoic anhydride, 2 mmol; 40% PW/SiO<sub>2</sub>, 5 mol%; reaction time, 40 min; solvent, CH<sub>2</sub>Cl-CH<sub>2</sub>Cl (15 mL).



**Fig. 7.** Effects of reaction time on the acylation of pyrene to 1-benzoylpyrene.

Reaction conditions: pyrene, 0.5 mmol; benzoic anhydride, 2 mmol; 40% PW/SiO<sub>2</sub>, 5 mol%; reaction temperature, 75 °C; solvent, CH<sub>2</sub>Cl-CH<sub>2</sub>Cl (15 mL).

suitable reaction temperature was 75 °C.

The effect of reaction time was studied in a range of 10-70 min (Fig. 7). The results show that increasing the reaction time from 10 to 40 min caused a noticeable increase in the yield and selectivity of 1-benzoylpyrene; then the yield and the selectivity no longer had obvious increase as further increasing the reaction time from 40 to 70 min.

#### 7. Reusability of PW/SiO<sub>2</sub>

To investigate the possibility of reusability of PW/SiO<sub>2</sub> (40 wt%), a recycle experiment was conducted. After reaction, PW/SiO<sub>2</sub> was recovered by filtering, thoroughly washed with CH<sub>2</sub>Cl-CH<sub>2</sub>Cl and dried in an oven at 120 °C for 2 h, to remove the adsorbed reactants or products. The results of the acylation catalyzed by the recycled PW/SiO<sub>2</sub> are listed in Table 3.

After 40 wt% of PW/SiO<sub>2</sub> ran five times, the yield and selectivity of 1-benzoylpyrene were only slightly lowered as compared to the fresh catalyst, which may be mainly caused by PW leaching during dichloromethane elution. The experimental results indicate that PW/SiO<sub>2</sub> is a recyclable and environmentally benign catalyst in the synthesis of 1-benzoylpyrene.

## CONCLUSIONS

1-Benzoylpyrene was for the first time synthesized directly through acylation of pyrene with benzoic anhydride catalyzed by PW/SiO<sub>2</sub>

**Table 3.** Results of repeated use of PW/SiO<sub>2</sub> catalyst

Run	1	2	3	4	5
Yield/%	62.5	61.4	60.2	58.6	57.2
Selectivity/%	100	100	98.5	96.7	93.5

Reaction conditions: pyrene, 0.5 mmol; benzoic anhydride, 2 mmol; 40% PW/SiO<sub>2</sub>, 5 mol%; reaction temperature, 75 °C; reaction time, 40 min; solvent, CH<sub>2</sub>Cl-CH<sub>2</sub>Cl (15 mL)

catalyst. PW/SiO<sub>2</sub> was found to be a highly efficient, reusable, inexpensive and ecofriendly solid acid catalyst for the synthesis of 1-benzoylpyrene. Excellent selectivity and yield of the desired product, mild reaction conditions, short time, simple experimental procedure and product isolation make this protocol complementary to the existing methods.

#### ACKNOWLEDGEMENTS

This work was supported in part by the National Natural Science Foundation of China (No. 20207003). The authors are grateful for the financial support.

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