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Liquid-phase cascade acylation/dehydration over various zeolite catalysts to synthesize 2-methylanthraquinone through an efficient one-pot strategy

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ABSTRACT

Liquid-phase cascade acylation/dehydration reactions over various zeolite catalysts were performed to synthesize 2-methylanthraquinone (2-MAQ). Many characterization techniques such as NH_3-TPD, pyridine-IR, BET, XRD, SEM, TEM, XRF, and TGA have been employed to study the relationship between the catalytic behavior and the nature of catalysts. The present work provides evidence that the acidity, pore size, particle size, and surface area of zeolites strongly affect both the catalytic properties and the coke formation. Moreover, it is discovered that the reaction activity of phthalic acid (PA) is higher than that of phthalic anhydride, and the yield of 2-MAQ reached 82.2% when PA was used, which opened a new avenue for one-pot synthesizing 2-MAQ by using PA as an acylation reagent. The catalyst can be recycled four times only with a slight decrease in activity. The nano-sized H-beta zeolite could be a promising liquid-phase cascade acylation/dehydration catalyst for clean one-pot synthesis of 2-MAQ.

1. Introduction

2-MAQ is a very significant building block for the synthesis of dyes and pigments [1,2], pharmaceuticals [3,4], agrochemicals (i.e. insecticide) [5], light-emitting devices [6], additives of paper making [7], as well as potentially useful as a significant insecticide, since it is postulated as the chemical which gives teak its resistance to insect and fungal attacks. Three industrialized synthetic routes for producing 2-MAQ have been developed: phthalic anhydride (PHA) method, anthracene oxidation method, and naphthoquinone method [1]. From the viewpoint of the low production cost, abundant raw materials, and a facile operation process, the PHA method exhibited immense application prospects. However, in the traditional synthetic process, $AlCl_3$ is used as the catalyst for the acylation of benzene and its derivatives with PHA to produce 2-(4′-alkylbenzoyl) benzoic acid and its derivatives (2-RBBA) [8], followed by the concentrated H_2SO_4-catalyzed dehydration of 2-RBBA to obtain anthraquinones [9,10]. In the above-mentioned two-step synthetic strategy, a large amount of $AlCl_3$ and concentrated H_2SO_4 are employed, which give rise to many problems concerning the handing, health, safety, corrosion, and waste disposal of the catalysts. In order to overcome these problems, there is urgent need to develop a green and effectual heterogeneous catalytic one-pot synthetic protocol to replace the conventional two-step route. Of most of interest is the fact that heterogeneous catalysis provides a new dimension for synthetic organic chemistry in terms of facile operation, safety, non-corrosion, high selectivity, small work-up, and little effluent pollution. Using a solid acid catalyst might be a very promising way to synthesize 2-MAQ and its derivatives considering their catalytic activity, selectivity, and reusability. Generally, solid acids were employed to promote the dehydration process for anthraquinone production via the dehydration of 2-RBBA, but not for the acylation of aromatics with PHA to yield 2-RBBA [11–14].

In our previous work, the 2-ethylanthraquinone had already been synthesized via H-beta zeolite-catalyzed dehydration process using 2-(4′-ethylbenzoyl) benzonic acid (2-EBBA) [15]. However, the use of 2-EBBA is required as a starting material, which was as-synthesized by the $AlCl_3$-catalyzed acylation of ethylbenzene with PHA. In this process, the $AlCl_3$ was not eliminated, and the environmental issue still remains to be solved. Nevertheless, rare reports concerning the solid acid catalyst-promoted direct one-pot synthesis of anthraquinones can be found, which exhibits novelty, although the solid acids including zeolites and mesoporous catalysts catalyzed acylation are very well known [16–19].

H-beta zeolite, which possesses 3-dimensional 12-membered-ring pore openings, is an intergrowth hybrid of two distinct but

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closely related structures that have tetragonal and monoclinic crystalline structures [20]. Due to its special pore system and surface acidity, H-beta zeolite had attracted much attention in the synthesis of many fine chemicals [21–26]. As an acylating catalyst, H-beta has been applied in the synthesis of many different aromatic or diphenyl ketone compounds [27,28]. Moreover, it was also reported that anthraquinone was synthesized by the gas-phase reaction between benzene and PHA over metal salt-modified zeolites at 823 K. The reaction atmosphere was diluted with N_2 and CO_2, and thus 65% conversion of PHA and 92% selectivity of anthraquinone were achieved [29]. Russian scientist, Kikhtyanin also reported the gas–solid reaction [30].

We had also studied the anthraquinone production over zeolite and modified zeolite in gas–solid phase [31]. The 59.1% conversion of PHA and 94.3% selectivity to the desired product can be obtained under optimal conditions. However, many inherent disadvantages such as dangerous operation, high energy consumption, high-level equipment, and rigorous reaction conditions exist with respect to the above-mentioned gas-phase methods, as well as difficult handling and control issues. The gas–solid phase reaction cannot satisfy the requirement of industrial production. Therefore, in our research group, we are currently focusing on liquid-phase one-pot reaction to yield anthraquinone and its derivatives under milder reaction conditions.

In the present paper, the liquid-phase cascade reactions including acylation of toluene with PHA (or PA) and the consecutive dehydration over various zeolites are studied. The merits of a green, low cost, facile operation, and safety allow it to be a clean, effectual, and practical route to produce 2-MAQ (Scheme 1). Effects of zeolite structure and pre-treatment conditions, reaction parameters, besides zeolite particle size in the catalytic performance for the cascade acylation/dehydration reaction to synthesize 2-MAQ were investigated. The nano-sized H-beta zeolite indicated excellent catalytic properties for synthesizing the desired products. The 70.1% yield and the 93.3% selectivity of 2-MAQ were achieved over the nano-sized H-beta zeolite catalyst. In order to probe into the reason for nano-sized H-beta having good catalytic performance, both micro-sized H-beta (commercially available catalyst) and nano-sized one (prepared in our lab) were fully characterized by employing BET, XRD, TEM, SEM, NH_3-TPD, pyridine-IR, XRF, and TGA technologies.

Although 75.1% conversion of PHA (over nano-sized H-beta) can be achieved, there is still about 25% of PHA remaining which is unconverted. For raw material recycling, the unreacted PHA needs to be separated from the reaction mixture by the aqueous alkaline and consecutive acid treatment. In the separation process, the PHA was transformed into PA. In order to lower production cost and safety (transforming PA into PHA is a dangerous and high energy-consuming process), we attempted to directly use the PA as an acylation reagent for synthesizing 2-MAQ; and surprising results were discovered. Not only may the PA be used as an acylation reagent for 2-MAQ production, but also the reaction activity of PA is higher than that of PHA, and a higher yield of 2-MAQ was achieved when using PA as the acylation reagent, which opens a new avenue for synthesizing anthraquinone and its derivatives. The relationships between the catalytic performance and the nature of zeolites were also explored.

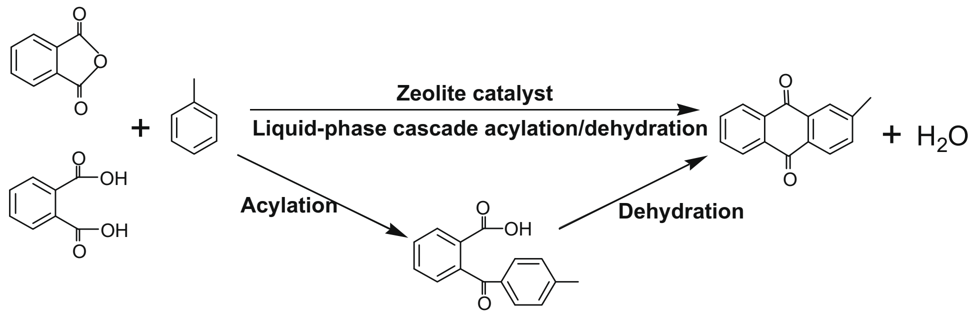
2. Experimental

2.1. Catalyst preparation

A H-Y (SiO_2/Al_2O_3 = 5.5) zeolite was prepared by calcining NH_4-Y (obtained from the Chinese Changling Catalysis Group) at 823 K for 4 h in air. Na-form M, ZSM-5, and micro-sized beta zeolites (provided by China Petroleum and Chemical Corp., Department of Catalysis Chemistry and Engineering, DUT and China Fushun Institute of Petroleum and Petrochemicals, respectively); these were ion-exchanged with NH_4NO_3 aqueous solution (0.4 M) at 353 K for 2 h to obtain the NH_4-form samples, which were converted into H-form zeolites through the consecutive drying (393 K for 12 h) and calcination process (at designed temperature for 5 h). The nano-sized Na-beta zeolite catalyst was synthesized on the basis of Refs. [32,33], and the H-form nano-sized beta zeolite was obtained based on the above-mentioned ion-exchange process.

2.2. Catalyst characterization

BET surface areas were measured by N_2 physisorption at 77 K using an AUTOSORB-1 (Quantachrome, USA) instrument. Prior to analyses, samples were degassed for more than 4 h at 623 K. X-ray powder diffraction patterns of the samples were recorded with a Rigaku D/max-2400 apparatus using CuKα radiation. XRF (SRS3400X) was used to determine the amount of sodium component of zeolite and molar ratio of SiO_2/Al_2O_3. The morphology of the nano-sized H-beta zeolite was examined by transmission electron microscopy (JEM-2000EX), and ethanol was used as a dispersant, allowing the sample to be well dispersed by ultrasonic. A SEM image of micro-sized H-beta zeolite was taken by a Hitachi S4800 scanning electron microscope. NH_3-TPD experiments were performed on an in-house constructed system equipped with a thermal conductivity detector (TCD) to quantitatively determine the desorbed ammonia; the signal was calibrated using standards. A quartz U-tube was loaded with 200 mg zeolite sample which was pretreated at 813 K for 3 h in Helium, then cooled to 423 K with Helium flowing and saturated with NH_3 until equilibrium. It was then purged with Helium (30 mL min^{-1}) at 873 K for 3 h, then cooled to 423 K and saturated with NH_3 until equilibrium. It was then purged with Helium again until the baseline was stable. NH_3-TPD was then promptly started by increasing temperature from 423 to 873 K at a ramp rate of 15 K min^{-1}. Pyridine FT-IR adsorption (Nicolet Impact 410) was used to measure the natural



Scheme 1. Liquid-phase cascade acylation/dehydration over zeolite catalysts to replace traditional two-step route for the synthesis of 2-MAQ.

acidic sites. The zeolite catalyst was finely ground and pressed into a self-supporting wafer (ca. 8–10 mg cm^{-2}), placed into quartz IR CaF_2 windows, pretreated in situ in a 30 mL min^{-1} of He from room temperature to 773 K with a ramp rate of 10 K min^{-1}, and then evacuated at 773 K and 5×10^{-3} Pa for 90 min. The cell was cooled to room temperature and saturated with pyridine. After removing of the excess pyridine, the spectrum was recorded. Then the sample was evacuated at different temperatures (473 K, 573 K, and 673 K) for 30 min; the corresponding spectrum was recorded to distinguish the acid sites with different strengths. The relation intensities of vibration band of 1540 cm^{-1} and 1450 cm^{-1} were assigned to the relative concentration of Bronsted and Lewis acid sites, respectively. TGA experiments were performed on a SDTA851 (Mettlter-Toledo, Switzerland) TGA instrument.

2.3. Catalytic reactions

The experiments for liquid-phase one-pot synthesis of 2-MAQ by combining the acylation of toluene with PHA and consecutive dehydration through dehydration was performed in the stainless steel autoclave with electro-magnetic stirrer in a batch mode. In a typical experiment, the PHA (PA), toluene, and zeolite catalyst (activated at 773 K for 1 h before use) are added into autoclave with a continuous magnetic stirring. The mixture was heated to the designed temperature, and held for 1–9 h at this temperature. The mixture was cooled to room temperature after the reaction was accomplished; the zeolite catalyst was filtered off from the mixture, and then fully washed with 1,4-dioxane. The product mixture was obtained by combining the filtrate and the washing liquid. The solid cake (products and unreacted PHA) was obtained by evaporating the toluene (the excess raw material) and 1,4-dioxane from the above-mentioned mixture, as well as water produced in the reaction, with a rotating evaporator. The solid cake was dried in the vacuum, and then dissolved in the 1,4-dioxane. The sample was analyzed on a liquid-chromatogram (Agilent 1100) equipped with a ZOBA×SB-C18 (250 × 4.6 mm) column at room temperature. The mobile phase was a mixture of H_2O and CH_3OH with a proper ratio, flowing at a rate of 1.0 mL min^{-1}, with HPLC collected at UV 257 nm wavelength. The calibration curves were linear for PHA ($r = 0.9994$) and 2-MAQ ($r = 0.9963$). Typical HPLC can be seen in Supplementary material. The weights of PHA and 2-MAQ were calculated based on their peak areas and the correction factors. The conversion of PHA was calculated by weight percent of the consumed PHA in the total PHA amount; the selectivity to 2-MAQ was calculated by weight percent of the desired product in total products. The yield included in this paper was the HPLC yield, which was calculated based on the conversion of PHA and the selectivity of the desired products. The separated solid was washed with alkaline solution to remove the unreacted PHA, and then the product was obtained by recrystallization. The separated product was further characterized by employing ^{1}H NMR and ESI–MS (see Supplementary material), as well as the melting point measurement.

3. Results and discussion

The micro-sized and nano-sized H-form zeolite-catalyzed liquid-phase one-pot synthetic route was employed to produce 2-MAQ (Scheme 1). The present method could be a green and effectual approach to replace both the traditional two-step routes and the one-pot gas-phase route. By using the proposed liquid-phase one-pot cascade reaction route, the heavy effluent pollution and complex handling could be eliminated. The products were separated from the reaction mixture (see Section 2). Both separated product and reaction mixture were characterized by various techniques such as ^{1}H NMR, HPLC, and ESI–MS (see the results in Supplementary material). ESI–MS indicates that dimethylanthraquinone and the uncyclized 2-RBBA are the main side products, with 99.0% purity of 2-MAQ obtainable via the purification process. From the characterization results, the desired product, 2-MAQ can be synthesized via a one-pot synthetic protocol of the present paper. We believe that this developed simpler, cheaper, and ecologically safer one-pot route of synthesizing 2-MAQ has great potential in industrialized application. In the following sections, the effects of the zeolite structure and pre-treatment conditions, reaction parameters, acylation reagent, zeolite particle size on the catalytic performance are presented, as well as the recycled performance of nano-H-beta was investigated.

3.1. Effects of zeolite structure and pre-treatment conditions

3.1.1. Effects of zeolite types

The acylation of toluene with PHA has been performed over the four H-form zeolites with different structures, H-beta, H-Y, H-MOR, and H-ZSM-5, to produce 2-MAQ. The results are presented in Table 1.

From Table 1, H-beta zeolite catalyst appears to be the best active catalyst in terms of both conversion of PHA and selectivity to 2-MAQ. H-Y and H-MOR zeolite catalysts exhibit a slightly lower conversion of PHA and a very low selectivity to 2-MAQ, while H-ZSM-5 zeolite catalyst exhibits very poor catalytic properties in both conversion of PHA and selectivity to 2-MAQ; the side products might be produced by isomerization, disproportionation, cracking, and polymerization. These results may be attributed to the different structure and surface acidic properties of the catalysts. Due to the interconnected channel architecture, H-beta and HY zeolites allow for an easier diffusion of the products than H-MOR. However, compared with that of H-beta, the lower Si/Al ratio of H-Y will lead to a higher hydrophilicity, which may absorb some produced water. As a result, the H-Y zeolite is passivated by the absorbed water. The higher hydrophobic H-beta zeolite is favorable for the reaction. For the H-ZSM-5, due to its tiny pore size, the reaction probably occurred only on the external surface. Fig. 1 presents the NH_3-TPD profiles for four types of zeolites.

From Fig. 1, it can be observed that these profiles consist of two peaks: one appears at a low temperature range around 523 K and the other appears at a high temperature range around 673 K for H-Y, H-beta, and H-ZSM-5, or 843 K for H-MOR catalysts. The low and the high temperature regions can be assigned to the weak and the strong acid sites, respectively. The zeolites (H-Y and H-MOR) with lower molar ratio of SiO_2/Al_2O_3 possess more and stronger acid sites than H-beta zeolite catalyst, which may lead to more side reactions; as a result, very poor selectivity of 2-MAQ appears over both HY and HM. Although the H-ZSM-5 zeolite with higher molar ratio of SiO_2/Al_2O_3 has a similar surface acidic properties; again, its tiny pore size leads to very low activity and selectivity.

Table 1
Effects of zeolite structure on the catalytic performance.[a]

Catalyst[b]	Pore size (nm)	Conversion (%)	Selectivity (%)	Yield (%)[c]
H-beta (22)	0.75 × 0.67	52.6	86.2	45.3
H-Y (5.5)	0.74 × 0.74	44.3	25.8	11.5
H-MOR (10)	0.65 × 0.70	41.1	29.5	12.1
H-ZSM-5 (76)	0.56 × 0.53	15.4	3.6	0.6

[a] Reaction conditions: 0.05 mol PHA, 3:1 N_{rea} (denoted as molar ratio of toluene to PHA), 0.27 W_{cat} (denoted as dosage of catalyst, which is calculated with respect to the weight ratio of catalyst to PHA), and 5 h t_R (denoted as reaction time) at 523 K.
[b] The number in parentheses is the molar ratio of SiO_2 to Al_2O_3.
[c] HPLC yield.

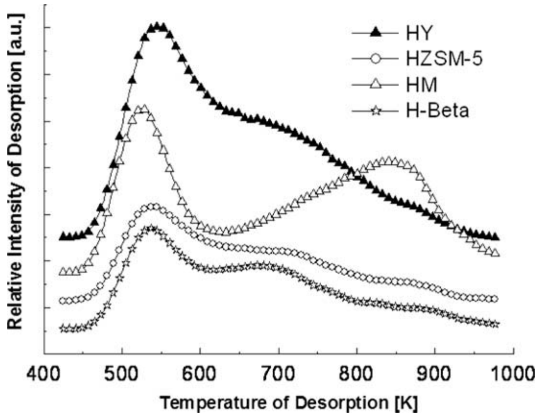


Fig. 1. NH_3-TPD profiles for the four zeolite catalysts.

Based on the above-mentioned analysis, H-beta is a good choice for synthesizing 2-MAQ.

3.1.2. Effects of calcination temperature

The calcination temperature (denoted as T_C) plays an important role in adjusting surface acidic properties and crystalline structure, which affects catalytic performance. By using H-form zeolite H-beta-1 as a catalyst (obtained from Na-form beta zeolite via once ion-exchange process), the effects of the T_C on both catalytic performance and C_R (denoted as relative crystallinity) were investigated; Table 2 presents the results.

In order to explore the relationship between the catalytic behavior and the acidity of the four H-beta zeolites, the catalysts were characterized by NH_3-TPD technique. Fig. 2 gives the characterization results.

Table 2
Effects of T_C on the C_R and catalytic performance.[a]

T_C (K)	C_R[b] (%)	Conversion (%)	Selectivity (%)	Yield (%)
723	100	60.6	91.4	55.4
823	95.1	66.4	93.7	62.2
923	91.5	64.6	91.8	58.9
1023	84.8	63.0	87.3	46.3

[a] Reaction conditions: 0.05 mol PHA, 3:1 N_{rea}, 0.27 W_{cat}, and 5 h t_R at 523 K, 0.7 MPa, H-beta-1.
[b] C_R is denoted as relative crystallinity, which is calculated based on XRD spectra profile.

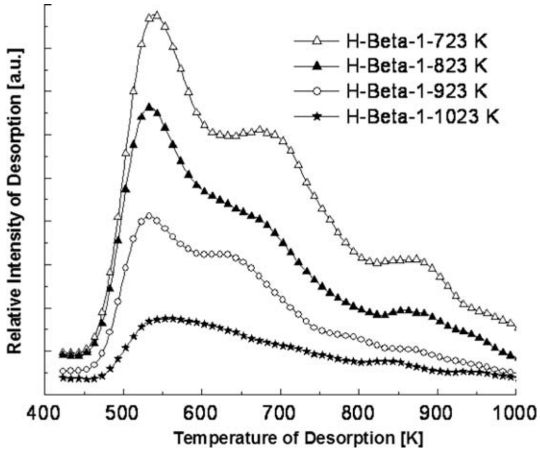


Fig. 2. NH_3-TPD profiles of the H-beta-1 zeolites with various calcination temperatures.

It is clearly seen that with the increase of the calcination temperature, both the C_R and the total acid sites decrease, which may be attributed to the aluminum ion and the hydroxide ion being dislocated from the framework of H-beta zeolite. The H-beta calcined at 823 K (H-beta-1-823) exhibits the best catalytic properties. About 66.4% conversion of PHA and 93.7% selectivity of 2-MAQ was observed. Although H-beta-1-723 catalyst possesses the most amount of both moderate and strong acid sites, both the catalytic activity and the selectivity over H-beta-1-723 are worse than those over other catalysts. It is concluded that the desired reaction requires acidic active sites in proper amounts and strength.

3.1.3. Effects of ion-exchange times

Na-form beta zeolite can be converted into H-form through an ion-exchange process. Effects of ion-exchange times (2 h at 353 K for every ion-exchange process) of beta zeolite in its catalytic performance and ion-exchange degree were investigated; Table 3 shows the experimental results. From Table 3, it can be observed that the ion-exchange times have a considerable effect on the catalytic properties. Na-form zeolite can be completely converted into H-form zeolite if the ion-exchange processes were performed twice (H-beta-2); the Na^+ content can be detected by XRF characterization techniques. Compared with H-beta-1, H-beta-2 exhibits better activity and selectivity. With the ion-exchange times being further increased, only slight increase in conversion, but sharp decrease in selectivity was observed.

Table 3
Effect of the ion-exchange times on the ion-exchanged degree and catalytic performance.[a]

H-beta-*n*[b]	*IED*[c] (%)	Conversion (%)	Selectivity (%)	Yield (%)
H-beta-1	68.3	42.6	65.3	27.8
H-beta-2	100	61.3	87.6	53.7
H-beta-3	100	63.4	74.7	47.4
H-beta-4	100	65.3	56.5	36.9
H-beta-5	100	67.6	48.3	32.6

[a] Reaction conditions: 0.05 mol PHA, 3:1 N_{rea}, 0.27 W_{cat}, and 5 h t_R at 523 K, 823 K T_C for H-beta.
[b] *n* is denoted as the ion-exchange times.
[c] *IED* is denoted as ion-exchange degree.

This result can be explained by the NH_3-TPD profiles (Fig. 3) and the relative concentration ratio of B/L acid site determined by pyridine-IR for H-beta-*n* zeolite catalysts (Table 4). The pyridine-IR spectra were collected at different desorption temperatures (423 K, 573 K, and 723 K) after the pyridine adsorption and consec-

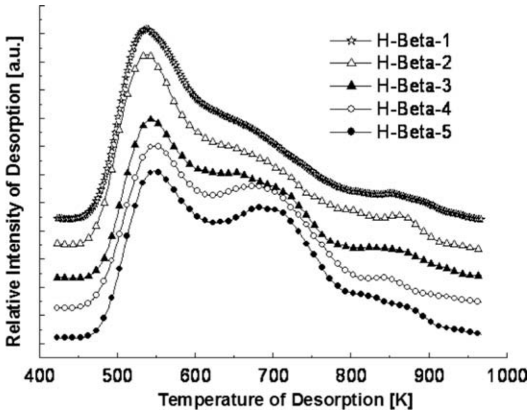


Fig. 3. NH_3-TPD profiles of H-beta-*n* zeolite catalysts.

Table 4
Comparison of B/L acid site ratio determined by pyridine-IR for H-beta zeolites.

H-beta-*n*[a]	B/L acid site at various desorption temperature[b] (K)		
	423	573	723
H-beta-1	3.93	3.05	1.76
H-beta-2	2.40	2.67	1.79
H-beta-3	1.86	2.50	2.33
H-beta-4	1.56	2.04	3.15
H-beta-5	1.44	3.9	3.01

[a] *n* is denoted as the ion-exchange times.

[b] B/L is calculated by the equation of 1.5 × (A_B/A_L) where A_B/A_L is the absorbance ratio [34].

utive purging process (see Section 2). From Fig. 3, it can be seen that with the increase in ion-exchange times, weak acid sites decrease, but moderate and strong ones increase. The higher catalytic activity of H-beta zeolite catalyst is due to the more moderate acid sites, but too many moderate and strong acid sites may lead to a decrease in selectivity. From Table 4, it can be observed that H-beta zeolite contains both B and L acid sites, with more B acid sites than L ones. From Table 3, it can be concluded that the moderate-strength acid sites are the best for the desired reaction, with a proper B/L ratio. The strong B acid sites may result in many side reactions such as cracking and polymerization. The H-beta-2 calcined at 823 K was sieved as a promising catalyst for the further studies. The 823 K calcination temperature and two times ion-exchanged zeolite catalysts were used to study the effects of reaction parameters, acylation reagent, and particle size of H-beta on the catalytic performance in one-pot synthesizing 2-MAQ, besides the reusability of the catalyst.

3.2. Effects of reaction parameters

3.2.1. Effects of dosage of catalyst

Table 5 gives the experimental results for the effects of dosage of catalyst (W_{cat}) by varying W_{cat} from 0.14 to 0.47.

As the W_{cat} is increased, an increase in the conversion of PHA can be observed, but no monotonous increase in selectivity. The selectivity reaches the maximum at 0.34 W_{cat}; further increase in W_{cat} leads to the decrease in selectivity. Therefore, the optimal weight ratio of catalysts is 0.34.

3.2.2. Effects of molar ratio of reagents

The effects of the molar ratio of toluene to PHA (N_{rea}) were investigated by varying the N_{rea} from 1:1 to 4.5:1; the results are presented in Table 6.

It is found that the N_{rea} has a dramatic influence on catalytic performance. PHA is assumed to adsorb stronger than toluene. By increasing the toluene bulk concentration a better balance of inner concentrations of the reactants is obtained. As a result, with the increase in N_{rea}, the conversion of PHA rapidly increased. However, with further increases in N_{rea}, the conversion of PHA decreases, which is due to too low concentration of reactant PHA diluted by too much toluene. Moreover, with the increase in N_{rea}, the selectivity to 2-MAQ increases; 91.3% selectivity can be achieved when N_{rea} is 4:1. Further increase in N_{rea} leads to a decrease in selectivity. A 65.1% maximum yield can be obtained when 4:1 N_{rea} is used.

Table 5
Effect of W_{cat} on the catalytic performance.[a]

Entry	W_{cat}	Conversion (%)	Selectivity (%)	Yield (%)
1	0.14	48.0	79.3	38.0
2	0.20	57.4	76.9	44.9
3	0.27	65.6	84.5	55.4
4	0.34	65.8	87.6	58.5
5	0.41	67.5	85.1	57.4
6	0.47	68.4	78.0	53.4

[a] Reaction conditions: 0.05 mol PHA, 3:1 N_{rea}, and 5 h t_R at 523 K.

Table 6
Effect of molar ratio toluene: PHA (N_{rea}) on the catalytic performance.[a]

Entry	N_{rea}	Conversion (%)	Selectivity (%)	Yield (%)
1	1.0	8.2	67.8	5.6
2	1.5	42.5	82.7	35.1
3	2.0	54.8	86.9	47.6
4	2.5	61.5	89.6	54.3
5	3.0	65.8	87.6	58.5
6	3.5	68.0	89.2	60.6
7	4.0	71.3	91.3	65.1
8	4.5	65.5	86.6	56.7

[a] Reaction conditions: 0.05 mol PHA, 0.34 W_{cat} and 5 h t_R at 523 K.

3.2.3. Effects of reaction temperature and reaction

Moreover, the effects of reaction temperature (T_R) and reaction time (t_R) on the catalytic properties were studied; the reaction results are presented in S6 and S7 (see Supplementary material). It is observed that both conversion of PHA and selectivity to 2-MAQ increase rapidly with the increase of reaction temperature up to 523 K, but then they drop-out beyond this. Therefore, the most suitable reaction temperature is 523 K. From S7, it is found that the conversion of PHA goes up with the increase in the reaction time. However, selectivity to 2-MAQ rapidly increases up to the highest value, but with further increase in the reaction time, the selectivity to 2-MAQ decreases markedly. Extended reaction times results in accelerated side reactions, which lead to a decrease in the selectivity to 2-MAQ. Therefore, the suitable t_R is 5 h, where a 65.1% yield can be achieved.

3.3. Effects of acylation reagents

With the product separation process being performed, the unreacted PHA can be transformed into PA. For raw material recycling, we attempted to directly use PA as an acylation reagent for synthesizing 2-MAQ. It is proposed that the liquid-phase cascade acylation/dehydration reaction of PA with toluene might take place, with some decrease in conversion, which permits the unreacted PHA to be converted into the desired products. Thus, the dangerous and energy-consumed dehydration process of PA may be avoided.

Table 7 exhibits the reaction results of toluene with PA and PHA. Surprising experimental results were observed. Not only may the PA be used as an acylation reagent for 2-MAQ production, but also the reaction activity of PA is higher than that of PHA, with a higher yield of 2-MAQ achieved when using PA as the acylation reagent, which may be due to the assistance from the second COOH group in PA in the protonation/dehydration of the first toward a (surface-bonded) active acylation species. If the reaction conditions are optimized, 82.2% yield of 2-MAQ can be achieved, which opens a new avenue for synthesizing 2-MAQ.

Table 7
Effects of acylation reagent on the catalytic performance in the one-pot synthesis of 2-MAQ.

Entry	Acylation reagent	Conversion (%)	Selectivity (%)	Yield (%)
1	PHA[a]	71.3	91.3	65.1
2	PA[b]	82.8	96.4	79.8
3	PA[c]	85.4	96.2	82.2

[a] Reaction conditions: 0.05 mol PHA, 4:1 N_{rea}, 0.34 W_{cat} and 5 h at 523 K.

[b] Reaction conditions: 0.05 mol PA, 4:1 N_{rea}, 0.34 W_{cat} and 5 h at 523 K (without optimization, the [a] conditions were used except for PHA being replaced by PA).

[c] Reaction conditions: 0.04 mol PA, 3.5:1 N_{rea}, 0.45 W_{cat} and 5 h at 523 K (the reaction conditions were optimized).

3.4. Effects of particle size of H-beta zeolites

Recently, nanomaterial and nanotechnology has received much attention for catalysis application, and studies on nano-zeolite have become popular research domains for catalysis. The above-mentioned results indicated H-beta zeolite is a promising solid acid catalyst for a green and effectual one-pot synthesis of 2-MAQ. It is proposed that nano-H-beta might be a good catalyst for a one-pot synthesis of 2-MAQ. Nano-H-beta zeolite was prepared based on Refs. [32,33]. Various characterization techniques such as TEM, SEM, XRD, XRF, BET, pyridine FT-IR, NH_3-TPD, and TGA were employed to characterize the structure and physico-chemical properties. Fig. 4 presents the XRD patterns of the nano-sized and micro-sized zeolite catalysts. The characteristic diffraction peaks at 2θ of 7.8° and 22.4° suggest that the two samples have the crystalline structure of beta with high crystallinities.

Fig. 5 gives the SEM and TEM images for micro-sized and nano-sized H-beta zeolites, respectively. The particle size of synthesized nano-sized zeolite is 20–60 nm; but about 200 nm particle size of micro-sized H-beta can be observed.

Table 8 gives the BET and XRF characterization results of both micro-sized and nano-sized H-beta zeolites. The larger surface area and pore volume (Pore vol.) of nano-sized zeolite can be observed than those of micro-sized one. The 19.4 lower $n_{Si/Al}$ of nano-sized zeolite might lead to more acid sites than those of the other one. Moreover, besides 0.4–0.8 nm pore, the 0.9–1.1 nm pore can be observed from Table 8.

Moreover, the NH_3-TPD experiments were performed to measure the surface acidic properties. Fig. 6 gives the NH_3-TPD profiles of the above-mentioned two H-beta zeolites with different structure and morphologies. The nano-sized H-beta zeolite possesses more acid sites than micro-sized one. The reactions were performed over both nano-sized and micro-sized H-beta zeolite catalysts, with the results presented in Table 9.

From Table 9, the nano-sized H-beta zeolite exhibits better catalytic performance in the one-pot synthesis of 2-MAQ than the micro-sized catalyst, which may be attributed to the former's additional surface acid sites, larger surface area and pore volume, and shorter pore channel than those of the micro-sized zeolite.

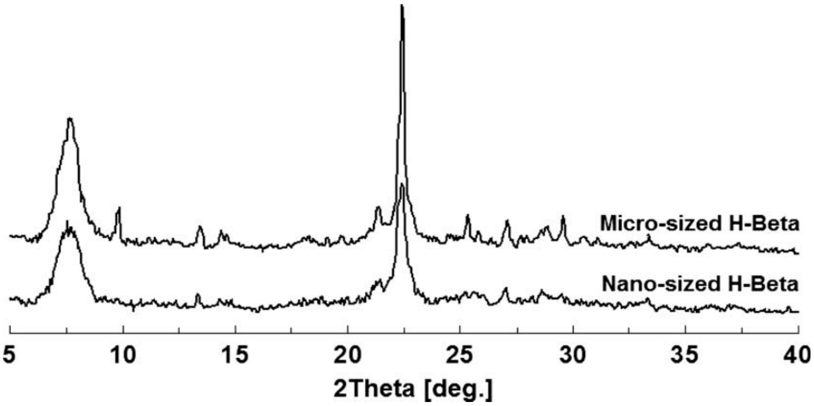


Fig. 4. XRD patterns of the nano- and the micro-sized H-beta zeolites.

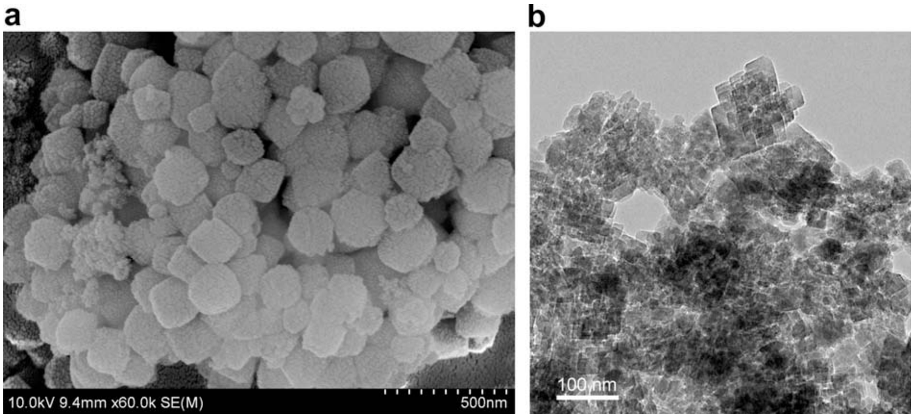


Fig. 5. SEM and TEM images for micro-sized (a) and nano-sized H-beta (b) zeolites, respectively.

Table 8
BET and XRF characterization results of both micro-sized and nano-sized H-beta zeolite catalysts.

H-beta	$n_{Si/Al}$ [a]	SA1[b] ($m^2 g^{-1}$)	SA2[c] ($m^2 g^{-1}$)	Pore vol. (ml/g)	Pore size (nm)
Micro-sized	47.6	423.1	504.7	0.45	0.4–0.8
Nano-sized	19.4	498.6	704.3	1.0	0.4–0.8, 0.9–1.1

[a] Molar ratio of SiO_2 to Al_2O_3, obtained from XRF.
[b] Surface area of micro-pore.
[c] Total surface area.

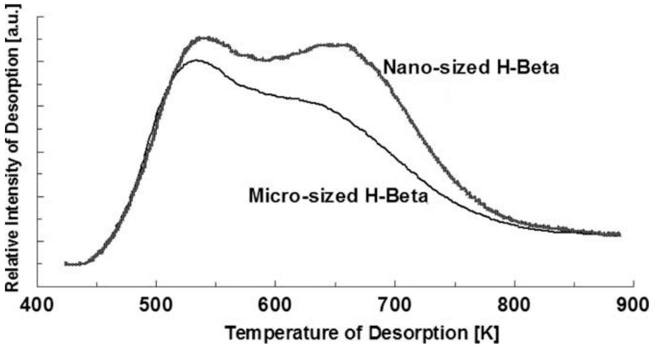


Fig. 6. NH_3-TPD profiles of the nano-sized and micro-sized H-beta zeolite catalysts.

Table 9
Effects of particle size of H-beta zeolite catalysts on the catalytic performance.[a]

Entry	Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
1	Micro-sized H-beta	71.3	91.3	65.1
2	Nano-sized H-beta	75.1	93.3	70.1

[a] Reaction conditions: 0.05 mol PHA, 4:1 N_{rea}, 0.34 W_{cat} and 5 h at 523 K.

Table 10
Reusability of the nano-sized H-beta zeolite catalyst for the one-pot synthesis of 2-MAQ.[a]

Entry	Recycling	Conversion (%)	Selectivity (%)	Yield (%)
1	Fresh	75.1	93.3	70.1
2	1^{st}	75.4	93.7	70.7
3	2^{nd}	72.7	93.8	68.2
4	3^{rd}	71.7	94.4	67.6

[a] Reaction conditions: 0.05 mol PHA, 4:1 N_{rea}, 0.34 W_{cat} and 5 h at 523 K.

3.5. Reusability of nano-sized H-beta catalyst

Of most interest in heterogeneous catalysis is from the fact that the H-beta zeolite catalyst gives a new dimension for the synthesis of fine chemicals in terms of the easy separation and facile recovery. The recovered catalyst was obtained through temperature-programed calcination from room temperature up to 823 K with a rising step of 50 K, and the acylations of toluene with PHA over fresh and recovered nano-sized H-beta zeolite catalysts. Table 10 presents the recycled results.

From Table 10, it can be observed that due to the shortened pore channel allowing materials and product to diffuse smoothly from the body of catalyst to the reaction system (which compresses the coke formation), there is no obvious decrease in conversion, but a slight increase in selectivity after the catalyst is recycled four times. TGA results show that only 9.9% weight loss for the spent nano-sized H-beta zeolite, but 12.6% weight loss for the spent micro-sized H-beta zeolite catalyst, which proves the nano-sized zeolite has good coke-resistance ability. Due to the shorter pore channel and increased pore size in nano-zeolite, the reactants and product can go through the pore smoothly, which can efficiently compress coke formation in the micro-pore of zeolite. Therefore, the nano-sized H-beta zeolite may be a promising solid acid catalyst for the one-pot synthesis of 2-MAQ.

4. Conclusions

The clean liquid-phase one-pot synthesis of 2-MAQ has been successfully accomplished through combining the acylation of toluene with PHA and consecutive dehydration over various zeolite catalysts. It is found that the zeolite acidity, pore size, particle size, and surface area strongly affect the catalytic properties of liquid-phase cascade acylation/dehydration and the coke formation. H-beta zeolite, in terms of both conversion of PHA and selectivity to 2-MAQ, was found to be better than those of other types of zeolites. The optimal reaction conditions with respect to the synthesis of 2-MAQ over H-beta zeolite catalyst are 0.34 weight ratio of H-beta zeolite to PHA, 4:1 molar ratio of toluene to PHA, at 523 K reaction temperature for 5 h. Under the optimal reaction parameters, a 65.1% yield of 2-MAQ with 91.3% selectivity can be achieved. The yield reaches 70.1% if nano-sized H-beta zeolite is employed; in addition, coke formation can be compressed if the nano-sized zeolite is used. The catalyst can be recycled three times without obvious decrease in yield. It is surprising to note that an 82.2% yield of 2-MAQ can be obtained by using PA as the acylation agent, and that PA exhibited higher reaction activity than PHA, which may be due to the assistance from the second COOH group in PA in the protonation/dehydration of the first toward an (surface-bonded) active acylation species. This work shows that the unreacted PHA can be recycled in the form of PA, which avoids a dangerous and energy-consuming process for transforming PA to PHA, as well as opening a new avenue for synthesizing 2-MAQ. Nano-sized H-beta zeolite might be a promising solid acid catalyst for a green and effectual one-pot synthesis of 2-methylanthraquinones via the liquid-phase cascade acylation/dehydration reaction.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2009.10.010.

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