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Strongly acidic mesoporous aluminosilicates prepared from zeolite seeds: acylation of anisole with octanyl chloride

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Abstract

Ultrastable acidic mesoporous aluminosilicates (MCM-48-S, MCM-48-SH, MCM-41-S) with mesostructures, strong acidity, and high hydrothermal stability was synthesized from assembly of cetyltriammonium bromide (CTAB) and pre-formed zeolite Beta seed. The catalytic application of the solid acid catalysts (HMCM-41-S and HMCM-48-SH) was demonstrated with the Friedel–Crafts acylation of aromatics. High conversion (>90%) and high selectivity (100%) were obtained.

Keywords: Zeolite seed; Mesoporous aluminosilicates; Acylation; Anisole

1. Introduction

Mesoporous aluminosilicates have attracted much recent attention because of their potential use as versatile catalysts and catalyst supports, especially for large molecules [1]. Compared with conventional zeolites, MCM-41 and MCM-48 have weaker acidity and much less hydrothermal stability which limit their catalytic applications. The relatively low acidity of mesoporous materials such as MCM-41, as compared to zeolites, can be attributed to the amorphous nature of the pore walls.

Recently, two research groups succeeded in synthesizing mesoporous aluminosilicates with high acidity and hydrothermal stability [2–4]. The success relies on the formation of better-structured wall with pre-formed zeolitic nanocluster. They used zeolite seeds made from quaternary alkyl ammonium salts as silica precursor to make the mesoporous materials with surfactants as templates. The success relies on formation of better-structured wall with pre-formed zeolitic nanocluster. The mesotructures reported for these type of stable acidic mesoporous materials are hexagonal [2–4], cellular foam [5], and large-pore hexagonal [6]. The strategy of prior developments of zeolite nanocluster for making mesoporous silica is robust and general. Recently, we have reported the corresponding three-dimensional bicontinuous cubic (*Ia3d*), denoted as, MCM-48-S [7]. We employed the beta-zeolite seeds, which were produced by using tetraethylammonium hydroxide (TEAOH) as the structure-directing agent, as the silica source. A similar method of preparing MCM-48 with enhanced acidity has also been reported [8]. These materials possess very high hydrothermal stability and strong acidity.

The new materials will be useful in many catalytic applications taking advantage of its stronger acidity. Up to the present, the test reactions are mostly cracking reactions, cumene cracking [2] or tri-isopropylbenzne [3,9,10]. Those reactions normally require acidic sites of intermediate strength. It would be desirable to extend applications where stronger acidity and mesoporosity are required.

The Friedel–Crafts acylation of aromatics is a widely used reaction for the production of many pharmaceutical, agrichemical, and fragrant compounds [11]. The acid catalyzed acylation of aromatics is the main route for the formation of aromatic ketone, an important intermediate in the pharmaceutical and flavor industry. Conventional Friedel–Crafts methodology calls for Lewis acids such as metal halides and some strong Brønsted acids such as polyphosphoric and sulfuric acid as the catalysts [11]. In order to eliminate the corrosion and environmental problems, many efforts are being made to find solid acid catalysts which can successfully

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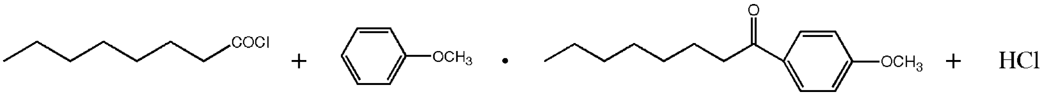
carry out acylation with a more environmental-friendly technology [12–15].

In this paper to study the acylation reaction of anisole with octanoyl chloride as in



(1)

It is known that zeolite Beta is an effective catalyst for the acylation of aromatic compounds. Thus it is desirable to carry out the reaction on the mesoporous aluminosilicates, MCM-41-S and MCM-48-S, made from zeolite Beta seeds. Previously, the acylation of anisole by octanoic acid has been investigated on BEA coating of structured supports [16] and acid leached zeolite Beta [17]. It is proposed that the catalysis occurred on strong Lewis acid sites on the zeolite Beta and the mesoporosity enhanced the catalytic action. The acylation reaction catalyzed by solid acid seems to be internal diffusion-limited in zeolites [15]. The use of mesoporous solid acids would improve the transport of the reactants, especially for the relatively large molecules as octanoyl chloride used in this work.

In this paper we will report the synthesis and characterization of MCM-41-S and MCM-48-S with the zeolite Beta seeds. The acidity and the distribution of acid sites were evaluated by temperature programmed desorption (TPD) of ammonia and X-ray photoelectron spectroscopy (XPS) of chemisorbed pyridine. Finally we report the acylation of anisole on octanoyl chloride with those catalysts.

2. Experimental

2.1. Materials and syntheses

Fumed silica (from Sigma), tetraethylammonium hydroxide (TEAOH, 20% aqueous solution from Acros), cetyltrimethylammonium bromide (C_{16}TMAB from Acros) and sodiumaluminate (from Riedel-de-Haen) were used as received.

Synthesis of pre-formed zeolitic nanocluster:zeolitic nanoclusters were prepared by mixing $NaAlO_2$, NaOH, fumed silica, TEAOH aqueous solution, and water at 50 °C for 2–5 h, then the solution was hydrothermally heated at 100 °C for 18 h. A clear solution of nanoprecursors was obtained.

Three strongly acidic mesoporous aluminosilicates denoted as MCM-48-S, MCM-48-SH, and MCM-41-S were hydrothermally synthesized by mixing the pre-formed zeolitic nanocluster and surfactant solution (C_{16}TMAB). MCM-48-S was synthesized by the reaction of zeolitic nanocluster with cetyltrimethylammonium bromide solution at 150 °C for 6–24 h. Well-ordered MCM-48-SH (the extra H denotes re-hydrothermal treatment) was obtained by adjusting the pH value of the as-synthesized MCM-48-S precursor to 10.0 with 1.2 M H_2SO_4 and then hydrothermally treating the mixture at 100 °C for 2 days. MCM-41-S was synthesized by hydrothermally treating the mixture of pre-formed zeolitic nanocluster and surfactant solution (C_{16}TMAB) at 150 °C for 2–6 h, then adjusting the pH value to 10.0 and hydrothermally treating the precursor again at 100 °C for 2 days. All the samples were collected by filtration, washed with water, dried at 100 °C oven for 6 h, and calcined at 580 °C for 6 h. For the purpose of comparison among samples, the Al/Si ratio of all samples, including the standard MCM-48, were fixed at 1/37. The molar ratios of reactants $NaAlO_2$:SiO_2:NaOH:TEAOH:C_{16}TMAB:H_2O were 1:37:1.5–9:11–22:18.3:3000–3500.

The proton form of the mesoporous materials (HMCM-48-S, HMCM-48-SH, and HMCM-41-S)was prepared at 80 °C by ion exchange with 0.1 M NH_4Cl, followed by calcination at 500 °C for 2 h.

2.2. Characterization

The powdered X-ray diffraction patterns were recorded on a Scintag X1 diffractometer using Cu Kα ($\lambda = 0.154$ nm) radiation. The N_2 adsorption–desorption isotherms were obtained on a Micromeritics ASAP 2010 sorptometer at 77 K. The infrared spectra were measured on MAGNA-IR 500 spectrometer in the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}. The NH_3-TPD-MASS curves were determined in the range 110–800 °C at a heating rate of 10 °C/min on an AutoChem 2910 and Thermo ONIX ProLab system.

X-ray photoelectron spectroscopic analyses of chemisorbed pyridine on the HMCM-48-SH catalyst were performed using a Thermo VG Scientific, ESCALAB 250 fitted with a monochromatic Al Kα radiation (1486.8 eV) X-ray source, under a residual pressure of $\sim 10^{-7}$ Pa. Calibration was achieved by setting the Si 2p binding energy at 103.0 eV. Before loading the organic base, the catalyst was pretreated at 450 °C for 12 h to remove adsorbed water and organic contaminants, and then cooled down to room temperature and impregnated with a solution of pyridine by ultrasonification. Then the materials were pretreated at 150 °C for 12 h to ensure complete chemisorbed pyridine on the surface.

2.3. Catalytic reaction–acylation of anisole with octanoyl chloride on mesoporous materials

The catalytic reaction was operated (Eq. (1)) in a slurry system (with a reaction volume of 25 ml) with a batch reflux configuration. The system was purged with nitrogen to expel air and moisture. The concentration of octanoyl chloride in anisole was 0.2 mol/l, and the amount of catalyst (mesoporous material) used was 0.15 g. Tetradecane was added as

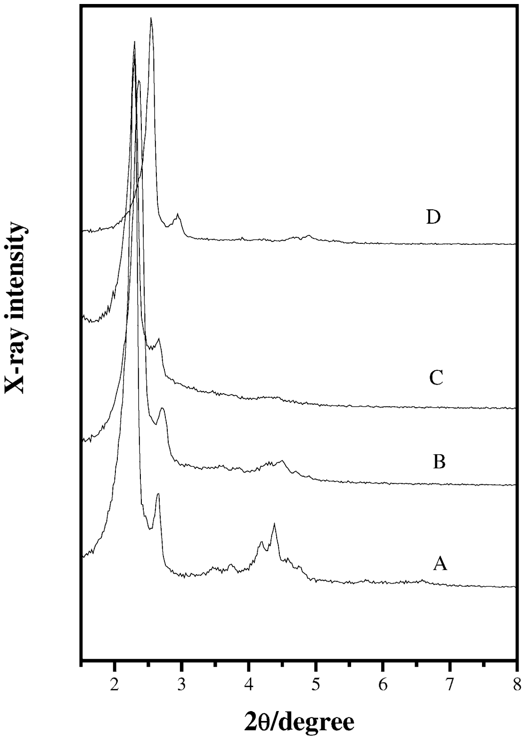


Fig. 1. The XRD patterns of MCM-48-SH (A) calcined; (B), (C) soaked in boiling water for 5 and 10 days; (D) treated in 800 °C steam for 4 h.

a GC internal standard. The reaction temperature was taken as the refluxing temperature of anisole (155 °C). Reaction mixture was sampled with a syringe every 30–60 min and GC analyzed.

3. Results and discussion

3.1. Synthesis and characterization

Fig. 1A is the XRD pattern of MCM-48-SH which shows a well-defined set of diffraction peaks that were assigned to the (2 1 1), (2 2 0), (3 2 1), (4 0 0), (4 2 0), (3 2 2), (4 2 2), and (4 3 1) peaks of the cubic space group *Ia3d*. We did not find any diffraction peak in the region of higher angles ($2\theta = 10$–$40°$) (not shown here), and this implied that the material is a pure phase. The MCM-48-SH materials possess excellent hydrothermal stability. They show well-ordered cubic (*Ia3d*) mesostructures even after soaked in boiling water for 10 days (Fig. 1C) or after treated in 800 °C steam for 4 h (Fig. 1D). There is only limited decay of structure. Table 1 lists the physical properties of the products that were treated in boiling water for different time. The MCM-48-SH possesses a BET surface area around 1152 m^2/g, a high pore volume about 1.06 cm^3/g, and the average pore diameter is about 27 Å. The BET surface area and pore volume of MCM-48-SH show smaller reduction (15–20%) after treated in 800 °C 20% steam for 4 h or after 5-day hydrothermal treatment and it stays nearly the same to 10 days. The wall thickness slowly increases as the time of re-hydrothermal treatment increases. Previously Ryoo and coworkers showed that the hydrothermal stability of MCM-48 could be improved by treating the as-synthesized sample in hot NaCl solution for prolonged period (up to 20 days) [18]. However, their hydrothermal stability test in boiling water was for only 12 h.

Fig. 2 is the XRD pattern of MCM-41-S that shows good hexagonal phase (*P6mm*). It exhibits the same high hydrothermal stability as MCM-48-SH Fig. 2C and D). The sample has a BET surface area around 1155 m^2/g, a high pore volume about 1.11 cm^3/g, and the average pore diameter is about 25 Å (Table 1). These physical data of mesoporousity are close to those reported by Zhang et al. [3] for MAS-5, with one major difference. We further took the IR spectrum (Fig. 3) of MCM-48-S. The sharp absorption peaks at 500–550 cm^{-1} observed indicate the presence of five-member ring structure for the siloxane connections [3] that is characteristic of the zeolite seeds. In contrast, the standard MCM-48 synthesized from aluminate silicates does not possess this special feature in IR. We measured the MAS NMR chemical shift of the tetrahedral site of ^{27}Al (figure not shown here) for MCM-48-S at 53.8 ppm which is close to that of zeolite BEA (at 54.5 ppm). From the ^{27}Al NMR data, we can also account for the special strong wall structure.

The acidity of the samples was determined by measuring the NH_3-TPD-MASS desorption curves of the H-form of

Table 1
Comparison of physical characteristics of various products treating in boiling water for different time

Samples treated in boiling water	Surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)	a_0 (Å)	*h* (Å)
MCM-48	1322	23.5	0.87	89.4	17.2
Untreated MCM-41-S	1155	25.0	1.11	92.5	17.4
For 5 days	960	23.0	0.85	91.0	18.6
For 10 days	855	19.5	0.59	94.0	20.8
800 °C 20% steam for 4 h	847	18	0.46	83.8	18.1
Untreated MCM-48-SH	1152	27.0	1.06	94.0	17.0
For 5 days	970	23.0	0.86	91.6	18.2
For 10 days	914	21.0	0.75	94.0	19.9
800 °C 20% steam for 4 h	978	18.0	0.53	85.1	18.6

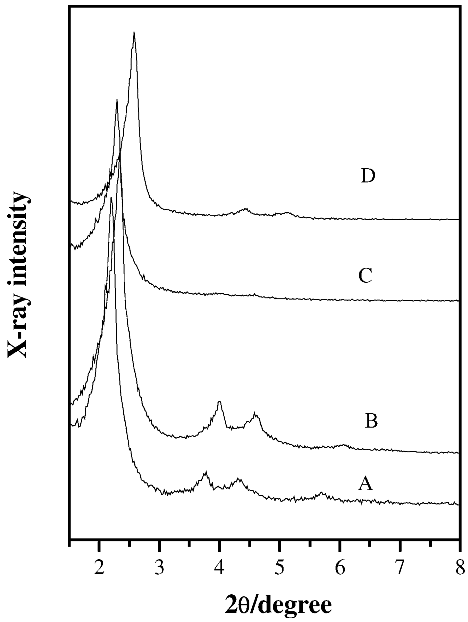


Fig. 2. The XRD patterns of MCM-41-S (A) as synthesized; (B) calcined; (C) soaked in boiling water for 10 days; (D) treated in 800 °C steam for 4 h.

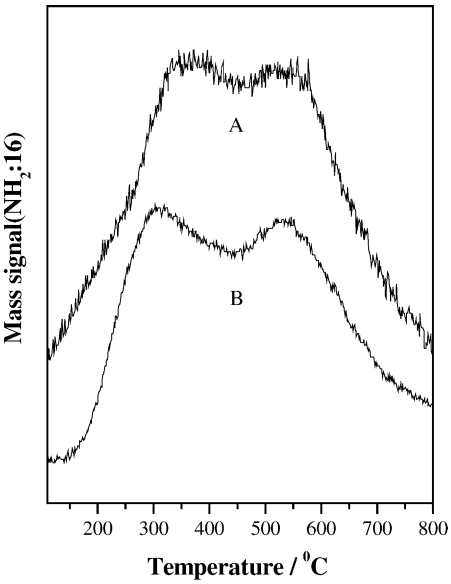


Fig. 4. The NH_3-TPD-MASS curves of samples (A) HMCM-41-S; (B) HMCM-48-SH.

MCM-48-SH and MCM-41-S (Fig. 4). NH_3-desorption lasts until a fairly high temperature of 500 °C, much higher than that of typical MCM-48 at 320 °C [3]. The high temperature for NH_3 desorption is similar to the desorption temperature of the acidic HZSM-5. We thus have a fairly acidic mesoporous aluminosilicates in MCM-48-SH and MCM-41-S.

In the 1970s, Defosse and Canesson [19] used X-ray photoelectron spectroscopy (XPS) technology to study the nature and strength of acid sites present in zeolite Y by determining the position and intensity of the N 1s peak of an adsorbed organic base. Since then, several workers have extended this technique to study of other zeolitic materials [20,21]. Santiesteban et al. [22] have used this technology to study the nature and relative strength of acid sites of WO_x/ZrO_2 catalysts. XPS should be a suitable technique to determine the nature (Brønsted and/or Lewis) and relative strength of acid sites of our mesoporous materials. The XPS spectra were recorded in the 390–415 eV regions to determine the binding of N 1S electron in the sample. Fig. 5 shows the N 1s XPS spectrum obtained on the HMCM-48-SH catalyst loaded with pyridine. The spectra can be de-convoluted into three bands (50% Gaussian, 50% Lorentzian) as shown in Fig. 5 and Table 2. We use the previous assignment [22] of peak I corresponding to a strong Brønsted acid site, peak II corresponding to a weak Brønsted acid site and peak III corresponding to a strong Lewis acid site. The data indicate that weak Brønsted acid site and Lewis site are the predominant acid sites on the surface of the HMCM-48-SH (both are

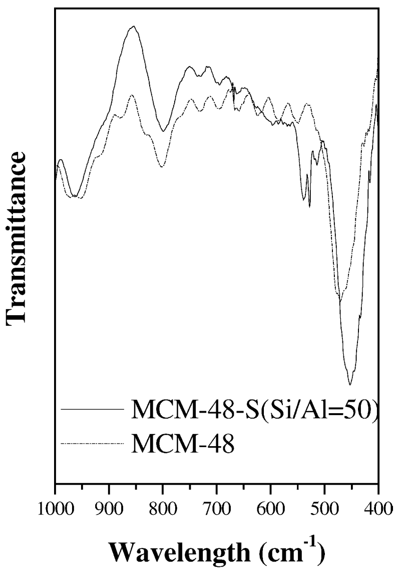


Fig. 3. Infra-red spectrum of calcined MCM-48-S and MCM-48.

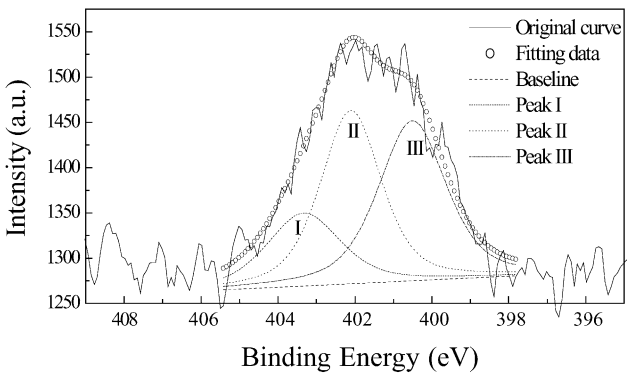


Fig. 5. N 1s photoelectron spectra of pyridine chemisorbed on HMCM-48-SH.

Table 2
Binding energies and relative concentration of N 1s components of pyridine chemisorbed on HMCM-48-SH

Component	Binding energy (eV)	Relative concentration (%)	Acid site type
Peak I	402.3	20.1	Strong Brønsted
Peak II	401.1	39.3	Weak Brønsted
Peak III	399.5	40.6	Lewis

about 40%) and strong Brønsted acid sites are about 20%. Thus the total amount of strong acids (peaks I and II) is just a little larger than that of weak Brønsted acid. This is roughly (the data is only semi-quantitative) in consistent with the two bands of acid strength observed in NH_3-TPD desorption experiment. Compared to other strong acid system, tungstated zirconia for example [22], our HMCM-48-SH materials show a much higher acid strength with high percentage of Lewis acid. The Lewis acid sites probably help more in the catalysis of acylation since this reaction is known to be well catalyzed by homogeneous Lewis acids.

3.2. Catalytic reaction

We now report the results of the catalytic reaction of Eq. (1). From the results of GC–MS analyses, the selectivity of the reaction is close to 100% for the *para*-substituted aromatic ketone. No other side-product (such as phenyl carboxylic ester or products of de-methylated anisole) was observed. Beers et al. recently reported [15] the acylation of anisole by octanoic acid with zeolite-coated monoliths as catalyst, and they always have side products with their selectivities ranging from 44% to 98% (58% to 86% for beta zeolite). The less steric hindrance in the mesopores of HMCM-41-S and HMCM-48-S, compared to zeolites, probably helps to reach the unique product of lowest energy.

As summarized in Table 3, HMCM-48-SH and HMCM-41-S exhibited much higher catalytic activity in the acylation of anisole with octanoyl chloride than MCM-48. The acidity of the standard MCM-48 is too weak to catalyze the acylation properly. Also, HMCM-48-S shows somewhat higher activity than HMCM-41-S. This is probably due to the easier transport in the bi-continuous channels of the former. More significantly, after treatment in 800 °C 20% steam for 4 h, HMCM-48-S still retains excellent catalytic activity (Fig. 6).

Table 3
Acylation of anisole with octanoyl chloride on different materials

Catalyst	Reaction time/yield	Reaction time/yield
HMCM-48-SH	1 h/99%	–
800 °C 20% steam for 4h	2 h/74%	6 h/85%
MCM-48	1 h/0%	1 day/9%
HMCM-41-S	1 h/90%	6 h/100%
No catalyst	1 h/0%	4.5 h/0%

Conditions: batch reactor; $T = 428$ K, 0.15 g catalyst, 0.005 mol octanoylchloride, and 25 ml anisole.

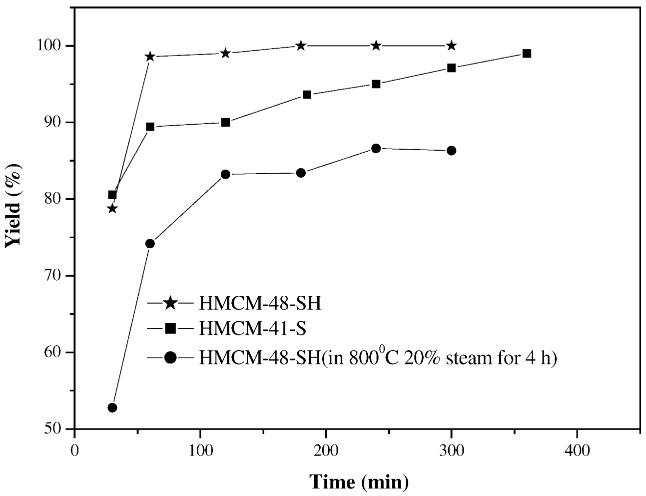


Fig. 6. Acylation of anisole with octanoyl chloride on HMCM-41-S, HMCM-SH, and HMCM-SH (treated in 800 °C steam for 4 h). Conditions: batch reactor; $T = 155$ °C, 0.15 g catalyst, 0.005 mol octanoyl chloride, and 25 ml anisole.

We next discuss the merit of using octanoyl chloride versus octanoic acid as the acylation agent. If we used octanoic acid to run the reaction, the reaction is slow and the yield reached only 20% after 26 h of reacting (Fig. 7). Why is the reaction so inefficient? Because the reaction using octanoic acid produces water. It is generally known that the presence of water can inhibit the active sites on the solid acid catalyst. Beers et al. also found the decrease of the conversion to lower than 20% when water was not removed. After applying a water-removal scheme, they were able to increase the conversion to 60% [15].

In summary, mesoporous aluminosilicates (MCM-48-S, MCM-48-SH, and MCM-41-S) with ordered structure have been synthesized using nanocluster seeds of beta zeolites. The materials possess excellent hydrothermal stability and acid strength. The combination of stability, high acid-

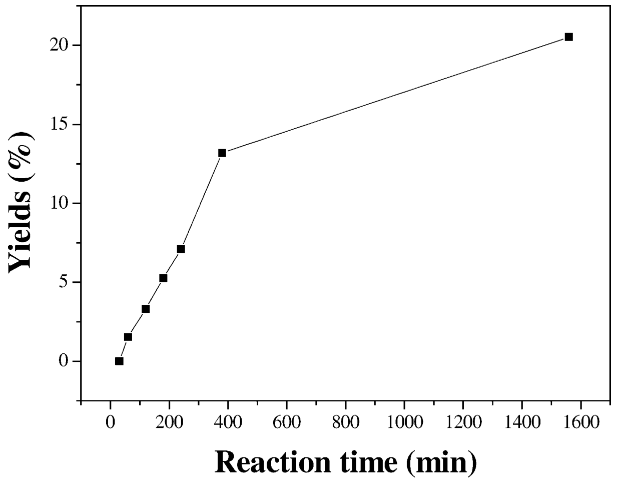


Fig. 7. Acylation of anisole with octanoic acid on HMCM-48-SH. Conditions: batch reactor; $T = 155$ °C, 0.15 g catalyst, 0.005 mol octanoic acid, and 25 ml anisole.

ity, branched channels and tunable structure order makes them excellent materials for applications in catalysis. HMCM-48-SH and HMCM-41-S exhibited higher catalytic activity in the acylation of anisole with octanoyl chloride than MCM-48, which is attributed to the stronger acid sites in HMCM-48-SH and HMCM-41-S.

Acknowledgements

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