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Research paper

# Improvement of the catalytic activity of MCM-48 synthesized from metakaolinite in the alkylation of phenol with *tert*-butyl alcohol

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ABSTRACT

M/MCM-48 (M and MCM-48 represent metakaolinite and Mobile composite of matter) mesoporous molecular sieves with good thermal and hydrothermal stabilities were synthesized by a hydrothermal method using metakaolinite as partial Si and Al sources. The samples were characterized by X-ray diffraction (XRD), $NH_3$ temperature-programmed desorption ($NH_3$-TPD), thermal gravimetric-differential scanning calorimeter (TG-DSC), transmission electron microscopy (TEM), Fourier transform-infrared (FT-IR) and $N_2$ physical adsorption. The effect of crystallization time and temperature on the synthesis of M/MCM-48 was investigated. The catalytic activity of M/MCM-48 was evaluated by the alkylation of phenol with *tert*-butyl alcohol (TBA). M/MCM-48 with long-range ordering was synthesized at the crystallization temperature of 120 °C for 36 h. The H-M/MCM-48, H-Al/MCM-48 and H-MCM-48 catalysts (H represents the protonated sample) were prepared *via* an ion-exchanged method. Under comparable conditions, H-M/MCM-48 exhibited a higher catalytic activity than H-MCM-48. A maximum phenol conversion of 73.4% with a 4-*tert*-butylphenol selectivity of 70.0% was achieved over the H-M/MCM-48 catalyst at the reaction temperature of 140 °C.

## 1. Introduction

Alkylation of phenol with *tert*-butyl alcohol has attracted researchers' attention owing to the fact that butylated phenols, such as 2-t-butyl phenol (2-TBP), 4-t-butyl phenol (4-TBP) and 2,4-di-t-butyl phenol (2,4-DTBP), have been widely used for the production of phenol resins, antioxidants, agrochemicals, and rubber chemicals (Bhatt and Patel, 2011; Hello et al., 2014). The alkylation reaction was conventionally catalyzed by homogenous acid catalysts, such as Lewis acids $AlCl_3$, $BF_3$ and $FeCl_3$ (Shinde et al., 2004) and Brönsted acids $H_3PO_4$, $H_2SO_4$ and $HClO_4$ (Carlton, 1948). However, these catalysts have some disadvantages such as toxicity, corrosiveness and low selectivity (Yadav and Kamble, 2012). To overcome these hindrances, environmentally friendly heterogeneous solid acid catalysts have been exploited (Chen et al., 2007; Sheng et al., 2012). The alkylation reaction could be effectively catalyzed by cation-exchanged resins, zeolites, clay-based catalysts and mesoporous molecular sieves (Sakthivel et al., 2003).

M41S (mesostructured silicates) mesoporous materials, discovered in 1992 (Kresge et al., 1992), have attracted considerable attention due to their high surface areas and large pore sizes. Recently, the catalytic activities of mesoporous solid acid catalysts have been evaluated by the alkylation of phenol with *tert*-butyl alcohol (Kumar et al., 2006) and the results revealed that mesoporous solid acid catalysts could effectively catalyze the alkylation of phenol with *tert*-butyl alcohol.

MCM-48 (Mobile composite of matter), a member of the M41S family, can be used as a catalyst or catalyst support (Huang et al., 2008). However, owing to its poor hydrothermal stability and weak acidity, the catalytic application of pure silica MCM-48 mesoporous molecular sieve is limited. In order to overcome these drawbacks, numerous efforts have been devoted to improve the hydrothermal stability by the addition of salts (Wang et al., 2006), controlling pH value in the buffer system and post-synthesis hydrothermal restructuring (Xia and Mokaya, 2004). Furthermore, the catalytic activity can be improved by doping heteroatoms, importing heteropolyacids and adding zeolite secondary building units (Zhang et al., 2008).

Kaolinite with high contents of $SiO_2$ and $Al_2O_3$ and low cost has larger reserves in nature. It can be used as an alternative Si and Al source for the synthesis of zeolites. The inert Si and Al in the framework can be activated by the calcination of kaolinite at high temperature. Metakaolinite is derived from kaolinite dehydroxylation at 450–980 °C. To the best of our knowledge, using metakaolinite as an additive for the synthesis of MCM-48 has not been reported.

In the present work, metakaolinite-incorporated M/MCM-48, pure silica MCM-48 and Al-incorporated Al/MCM-48 were synthesized. H-M/MCM-48, H-Al/MCM-48 and H-MCM-48 were also prepared by the

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ion exchange method. The thermal and hydrothermal stabilities of M/MCM-48 were investigated. The catalytic activities of the catalysts for the alkylation of phenol with *tert*-butyl alcohol were evaluated.

## 2. Experimental

### 2.1. Materials

All the chemicals of analytical grade were purchased from Shanghai Chemical Reagent Co., Ltd. Metakaolinite was purchased from Shanxi Hequ Zhengyang Kaolin Co., Ltd. with the chemical composition (mass %) of $SiO_2$ 52, $Al_2O_3$ 45, $Fe_2O_3$ 0.4, $TiO_2$ 1.5, CaO 0.3, MgO 0.2, $K_2O$ 0.05, $Na_2O$ 0.15, and MnO 0.004. To ensure that the raw material was metakaolinite, the purchased metakaolinite was heated at 750 °C for 2 h before use.

### 2.2. Synthesis of M/MCM-48

M/MCM-48 samples were synthesized by the hydrothermal method (Kresge et al., 1992). Typically, 0.9 g of NaOH and 0.19 g of NaF were dissolved in 50 g distilled water, and then 10.61 g of cetyltrimethylammonium bromide (CTAB) was added to the mixture under stirring at 35 °C for 50 min. After that, 10 g of tetraethylorthosilicate (TEOS) was slowly added and stirred for 60 min. Then, 1 g of metakaolinite was added into the above gelatinous solution under stirring for 2 h. The mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and crystallized at 100–160 °C for 24–72 h in an oven. The samples were filtered, washed with distilled water, and dried at 80 °C for 24 h, denoted as s-M/MCM-48. The s-M/MCM-48 samples were heated to 550 °C at a heating rate of 2 °C $min^{-1}$ and kept at 550 °C for 6 h in air, denoted as M/MCM-48.

For comparison, pure silica MCM-48 and Al/MCM-48 samples were also synthesized using the same method but without metakaolinite and with $Al_2(SO_4)_3 \cdot 18H_2O$ (0.84 g), respectively. Al contents in M/MCM-48 and Al/MCM-48 samples determined by inductive coupled plasma (ICP) technique (Vista-MAX, Varian) were 5.92% and 5.96%, respectively.

The M/MCM-48, Al/MCM-48 and MCM-48 samples were protonated by repeating ion exchange by using 0.5 mol $L^{-1}$ $NH_4NO_3$ solution at 80 °C for 2 h and followed by calcination at 550 °C for 2 h, denoted as H-M/MCM-48, H-Al/MCM-48 and H-MCM-48, correspondingly.

### 2.3. Thermal and hydrothermal stability tests

For thermal stability tests, 0.3 g of M/MCM-48 was calcined at 700, 800 and 900 °C for 4 h, denoted as M/MCM-48-700, M/MCM-48-800 and M/MCM-48-900. For the hydrothermal stability tests, 0.5 g of M/MCM-48 was added into a 100 mL Teflon-lined stainless autoclave and hydrothermally treated at 100 °C for 24, 48 and 72 h, designated as M/MCM-48-24, M/MCM-48-48 and M/MCM-48-72.

### 2.4. Characterization

Powder XRD was performed with a Rigaku D/MAX 2500PC instrument with Cu Kα radiation ($\lambda = 0.15418$ nm), operating at 40 kV, 50 mA and a slit width of 0.15 mm. XRD patterns were recorded with a step of 0.004° from 1° to 10° (2 theta) at a speed of 1° $min^{-1}$, the powder samples were uniformly placed on a glass slide. Specific surface area and pore size were measured by using a NOVA2000e analytical system. The samples were firstly degassed at 300 °C for 3 h under vacuum. And then the $N_2$ adsorption–desorption isotherms were recorded at −196 °C. $NH_3$-TPD was carried out on a TP-5000 adsorption instrument (Tianjin Xianquan Co., Ltd.). The samples (0.1 g) were pretreated in helium gas at 200 °C for 1 h. After that, the samples were ammonia-saturated at room temperature for 30 min and then flushed with helium gas at 80 °C for 40 min until the integrator baseline was stable. $NH_3$-TPD curves were obtained at a heating rate of 10 °C/min from 100 to 700 °C. TG-DSC analysis of sample (5–6 mg) was measured on a German NETZSCH-STA499 instrument in an alumina pan at a 10 °C $min^{-1}$ heating rate from room temperature to 1000 °C under a $N_2$ flow of 50 mL $min^{-1}$. TEM images were observed on a Philips TEMCNAI-12 with an acceleration voltage of 120 kV. FT-IR spectra were measured on a Nicolet Nexus FT-IR470 infrared spectrometer with the KBr pellet technique (sample/KBr, 3/100 mg), ranging from 4000 to 400 $cm^{-1}$ with the number of scans accumulated 64 and the spectral resolution of 4 $cm^{-1}$.

### 2.5. Catalytic reaction

The alkylation reaction of phenol with *tert*-butyl alcohol was carried out in a fixed-bed flow reactor. Prior to the reaction, the catalysts were activated by calcination at 550 °C in air for 10 h. 0.5 g of catalyst with particle sizes ranging from 240 to 425 μm was placed in a reaction tube. A mixed solution of phenol and *tert*-butyl alcohol with the mole ratio of 1:2 was fed into the preheated reactor using a liquid injection pump (WMCB102-A) at a flow rate of 60 mL $min^{-1}$. Before entering the reactor, the liquid mixture was heated to 80 °C. A nitrogen stream with a flow rate of 50 mL $min^{-1}$ also entered the fixed-bed flow reactor. The effluent was collected at every 2 h interval. The products were analyzed using an SP-2000 gas chromatograph fitted with a SE-54 capillary column coupled with FID.

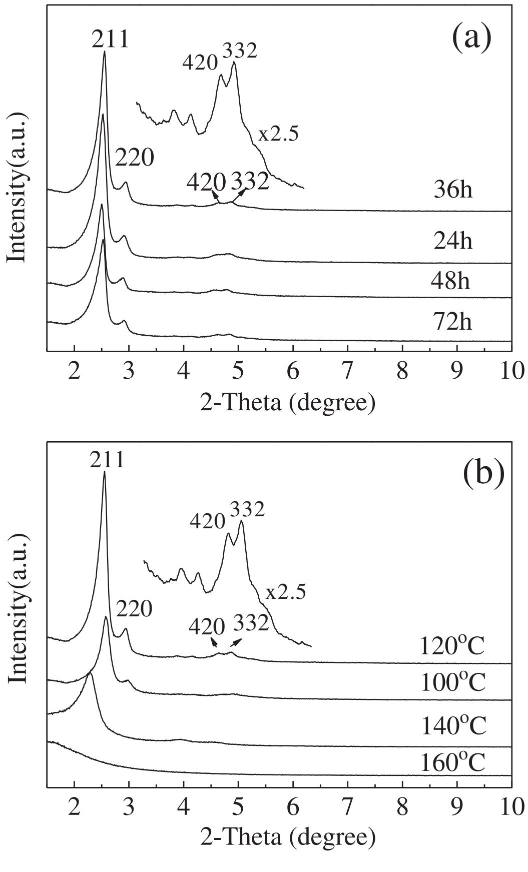

**Fig. 1.** a. XRD patterns of the samples synthesized by adding 1 g of metakaolinite in synthesis gel at the crystallization temperature of 120 °C for different crystallization times. The inset is the magnified XRD pattern. b. XRD patterns of the samples synthesized by adding 1 g of metakaolinite in synthesis gel at different crystallization temperatures for 36 h. The inset is the magnified XRD pattern.