

Short communication

# Hydrophobic aluminosilicate zeolites as highly efficient catalysts for the dehydration of alcohols

Shaodan Xu<sup>a,b,\*</sup>, Huadong Sheng<sup>a</sup>, Tao Ye<sup>a,c</sup>, Dan Hu<sup>a</sup>, Shangfu Liao<sup>a,\*</sup><sup>a</sup> Zhejiang Institute of Quality Inspection Science, Hangzhou 310018, China<sup>b</sup> Key Laboratory of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310027, China<sup>c</sup> MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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## ABSTRACT

Efficient dehydration of alcohols to olefins, acting as a control step in the upgrading of phenolic biofuel into alkane fuels, is an important topic in biomass conversion. Here, we report the design and synthesis of hydrophobic aluminosilicate ZSM-5 zeolites by an organosilane-modification approach (ZSM-5-OS). Water-droplet contact angle tests confirm the formation of hydrophobic surface after the modification. Interestingly, the obtained ZSM-5-OS catalysts exhibit excellent catalytic properties in dehydration of various alcohols into the corresponding olefins in water solvent. The approach reported in this work would be potentially important for developing more efficient catalysts for biomass conversion in the future.

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## 1. Introduction

The fast pyrolysis of lignocellulosic biomass, which is regarded as a renewable feedstock, has attracted much attention for the production of phenolic bio-oil as a promising alternative to fossil fuels [1–8]. However, the direct use of the as-prepared phenolic bio-oil is impossible, because of the unfavorable features of high oxygen content, low energy density, low stability, and high viscosity [9–14]. In order to solve these problems, the upgrading of phenolic bio-oil by hydrodeoxygenation strategy has been developed to obtain high-quality alkane-oil [10,15]. Typically, the hydrogenation process over combined metal (e.g. Ru, Pt) and acid catalysts (e.g. HCl, acid resins, zeolites) contains consecutive steps including hydrogenation of phenolic molecules to alcohols, dehydration of alcohols to olefins, and hydrogenation of olefins to alkanes. In this process, the hydrogenation and dehydration reactions occurred on the metal and acid sites, respectively. Particularly, the step of acid-catalyzed alcohol dehydration is greatly important for the cleavage of C–O bonds, which is reported to be a rate-control step in the bio-oil upgrading process [9]. Therefore, developing highly efficient catalyst for dehydration of alcohols in water solvent is important for obtaining high-quality alkane-oils from biomass [16–20].

Recently, many homogeneous acid catalysts have been found to be active for the dehydration of alcohols, including phosphoric acid and acidic ionic liquids [9,21]. However, their homogeneous feature produces difficulty in catalyst separation and regeneration from the reaction system. More recently, aluminosilicate zeolites (e.g. ZSM-5, Beta) as typical examples of solid acids have been employed to catalyze the dehydration of alcohols in bio-oil upgrading [22–25]. Because of the obvious advantages of high stability, abundant acidic sites, and heterogeneous feature, zeolites are regarded to be one of the most promising catalysts for the dehydration of alcohols. However, it should be noted that the catalytic activity of aluminosilicate zeolites still could not satisfy all the requirements of an efficient catalyst, even some methods have already been used to enhance the zeolite activity, high reaction temperature ( $\geq 150$  °C) was still necessary to obtain the olefin products [22,25].

In this work, we report an efficient approach method to enhance the catalytic activities of aluminosilicate zeolite in dehydration of alcohols into olefins by improving the zeolite hydrophobicity. The hydrophobic zeolites were synthesized by an organosilane-modification approach (ZSM-5-OS). The ZSM-5-OS catalysts with hydrophobic surface could promote the fast diffusion of water species from the acid sites, and motivate the reaction balance to the formation of olefin products, giving 10-fold higher activities than the conventional ZSM-5 catalyst. More importantly, the ZSM-5-OS catalyst is stable and shows high activities even after several recycling steps. Furthermore, by combining with Ru nanoparticles, the obtained Ru/ZSM-5-OS catalysts are highly efficient for the direct hydrodeoxygenation of phenolic molecules into alkanes, because of the efficiency of hydrophobic ZSM-5-OS catalysts for

\* Corresponding authors at: Zhejiang Institute of Quality Inspection Science, Hangzhou 310018, China.

E-mail addresses: [xushaodan6677@126.com](mailto:xushaodan6677@126.com) (S. Xu), [liaoshangfu057@163.com](mailto:liaoshangfu057@163.com) (S. Liao).

dehydration of alcohols, which is a key step in the hydrodeoxygenation processes.

## 2. Experimental

### 2.1. Sample preparation

All reagents were of analytical grade and used as purchased without further purification. The zeolites are all in H-form.

#### 2.1.1. Synthesis of ZSM-5 zeolite

As a typical run, 8 ml of tetrapropyl ammonium hydroxide (TPAOH, 20 wt.%) and 0.09 g of sodium aluminate ( $\text{NaAlO}_2$ ) were added into 20 ml of water. After stirring at room temperature for 2 h, 7 ml of tetraethyl orthosilicate (TEOS) was added and the resulted mixture was stirred overnight. Then the gel was transferred into an autoclave to crystallize at 180 °C for 3 days. After filtrating, drying, and calcining at 550 °C for 4 h, the ZSM-5 zeolite was obtained.

#### 2.1.2. Synthesis of ZSM-5-OS samples

As a typical run, 1 g of ZSM-5 was dried at 120 °C under vacuum for 3 h, followed by the addition of 50 ml of anhydrous toluene containing 1.2 g of organosilane. The mixtures were refluxed overnight and collected by rotary evaporation, followed by washing with a large amount of anhydrous toluene and ethanol. The sample obtained was designated as ZSM-5-OS. The experiments above were carried out in anhydrous conditions to avoid the reaction between organosilane and  $\text{H}_2\text{O}$ .

#### 2.1.3. Synthesis of Ru/ZSM-5 and Ru/ZSM-5-OS- $\text{C}_{16}$

As a typical run, 1 g of the ZSM-5 was stirred in 50 ml of  $\text{RuCl}_3$  solution with desired Ru concentration for 12 h, followed by evaporating the excess water at 80 °C, heating at 100 °C for 12 h, and washing with a large amount of water. Then the solid powder was calcined in air at 400 °C for 2 h, and reduced by  $\text{H}_2$  at 250 °C for 2 h to obtain Ru/ZSM-5. Ru/ZSM-5-OS- $\text{C}_{16}$  was obtained by modifying Ru/ZSM-5 with *n*-hexadecyltrimethoxysilane. By ICP analysis, the Ru loadings were established at 0.78 and 0.81 wt.% for Ru/ZSM-5 and Ru/ZSM-5-OS- $\text{C}_{16}$ ,

respectively. Additionally, the dispersion of Ru atom (number of Ru atoms on the nanoparticle surface/total Ru atoms) was determined by the pulse CO adsorption tests, obtaining 23.3 and 20.1% for Ru/ZSM-5 and Ru/ZSM-5-OS- $\text{C}_{16}$ , respectively.

### 2.2. Sample characterization

X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu KR radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Si/Al ratios were determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2020 system. The contact angles of water and 1-hexene droplets on the solid surface were measured on an Optical Contact Angle Meter (SL200KB). Scanning electron microscopy (SEM) was performed using a Hitachi SU 1510. FT-IR spectra were recorded on a Bruker 66 V FTIR spectrometer. The pulse CO adsorption test was performed on FINETEC Finesorb-3010. The adsorption capacity of water and cyclohexanol was tested in a static reactor at room temperature; the solid samples were degassed at 180 °C under vacuum for 14 h before the test. 50 mg of catalyst was added into a mixture of alcohol (2 mmol) and water (10 ml). Under stirring at room temperature, the concentration of alcohol in water was analyzed by GC analysis using phenol as internal standard.

### 2.3. Catalytic tests

The dehydration reactions were performed in a 100-ml high-pressure autoclave with a magnetic stirrer (900 rpm). The substrate and powder catalyst were mixed in the reactor, then  $\text{N}_2$  was introduced and kept at desired pressure. The reaction system was heated to a given temperature. After the reaction, the product was taken out from the system and analyzed by gas chromatography (GC-17A, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17 and FFAP.

The unconverted alcohol substrate and olefin product could be quantified by using dodecane as internal standard. The alcohol

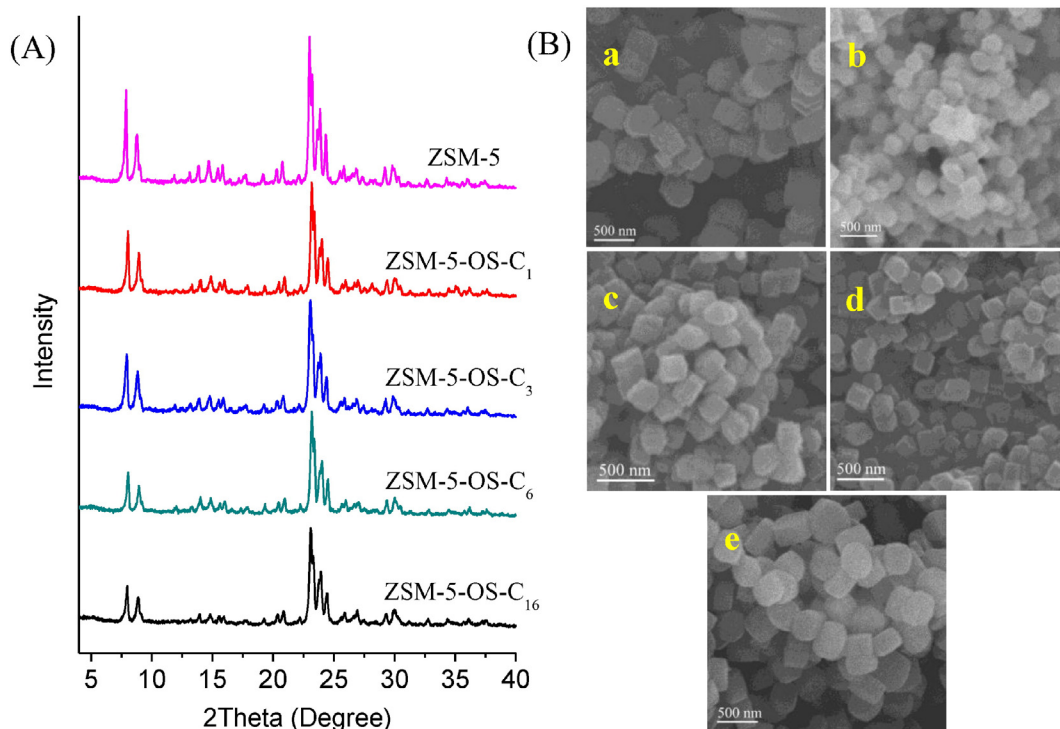


Fig. 1. (A) XRD patterns and (B) SEM images of various ZSM-5 samples. (a) Conventional ZSM-5, (b) ZSM-5-OS- $\text{C}_1$ , (c) ZSM-5-OS- $\text{C}_3$ , (d) ZSM-5-OS- $\text{C}_6$ , and (e) ZSM-5-OS- $\text{C}_{16}$ .

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