



## Short communication

## Enhanced propene/ethene selectivity for methanol conversion over pure silica zeolite: Role of hydrogen-bonded silanol groups

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## ABSTRACT

Pure silica zeolite with MEL structure (Si-ZSM-11) was firstly reported as an efficient Methanol-to-Propene (MTP) catalyst in methanol conversion, with higher propene yield (14.0 wt.%) and propene/ethene ratio (5.9) than H-ZSM-11 zeolite with a Si/Al ratio of 26 (7.4 wt.% and 1.9, respectively). Hydrogen-bonded silanol groups in Si-ZSM-11 are weakly acidic and act as active sites in methanol conversion, predominantly promoting propene production and inhibiting side reactions.

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## 1. Introduction

The Methanol-to-Olefins (MTO) process constitutes the final step in the upgrading of natural gas, coal or biomass via syngas intermediate to polymer-grade olefins. ZSM-5 and SAPO-34 are two archetype catalysts that are used for this process and are regarded as the most effective catalysts [1,2].

Currently, ZSM-5 is the preferred catalyst in the Methanol-to-Propene (MTP) process because of its high propene yield and slow deactivation rate. Previous studies have indicated that the product distribution obtained is strongly dependent on the physical and chemical properties of the zeolite (acid strength, density of acid sites, and the channel structure), and operating conditions [3]. The MTP reactions are found to be Brønsted-acidic, and the acid catalytic activity of zeolite resides in tetrahedral framework Al atoms. The charge-compensating protons of the oxygen anions bridging between Al and Si give rise to strong Brønsted acidity [4]. That is to say that the activity of zeolite or zeotype catalyst is determined by the nature, amount, and accessibility of the acid sites, especially Brønsted acid sites [5,6]. Nevertheless, the role of the silanol groups in methanol conversion has not been reported.

Perfect silicalite should be inert and hydrophobic for the surface of pure silica zeolite being nearly completely internal and formed almost entirely by Si–O–Si bonds. When subjected to thermal treatments, partial loss of tetrahedral silicon from the framework takes place. This

loss of tetrahedral silicon results in the simultaneous generation of extra-framework species and lattice defects. Defective silicalite samples show a high density of internal OH groups, presumably located in internal cavities, generated by the absence of a relevant percentage of T sites. The presence of these hydroxylated nanocavities makes this porous material less hydrophobic than a perfect silicalite and shows interesting catalytic properties in reactions where a very mild acidity is needed. Silanol groups are crucial in determining the activity and deactivation behavior of zeolite catalysts in many reactions [7,8]. For instance, the active sites for highly rearranging cyclohexanone oxime to  $\epsilon$ -caprolactam over an MFI-type silicalite are the silanol nests in the silicalite structure [9]. Likewise, silicalite-1 is also found to be an efficient catalyst for the formation of propene by the reactions of light alkenes because of the absence of strong acid sites and the presence of weak acid sites (silanol groups) [10]. In addition, Thibault-Starzyk et al. made a direct correlation between the formation of coke and the presence of silanol defects in the isomerization of ortho-xylene over MFI zeolite, and found that coke deposits were mainly located on non-acidic silanol groups inside the micropores [11]. Thus, it is questionable whether silanol groups could promote the activity and catalytic lifetime for methanol conversion.

Recently, our research group synthesized a hierarchical ZSM-11 zeolite [12], which features intercrystalline mesopores and rod-like crystal intergrowth morphology. The material exhibits an excellent activity and high propene and gasoline selectivity in methanol conversion [13]. In this study, pure silica and ZSM-11 containing alumina (Si/Al = 26) zeolites with MEL structure and hierarchical properties (Si-ZSM-11

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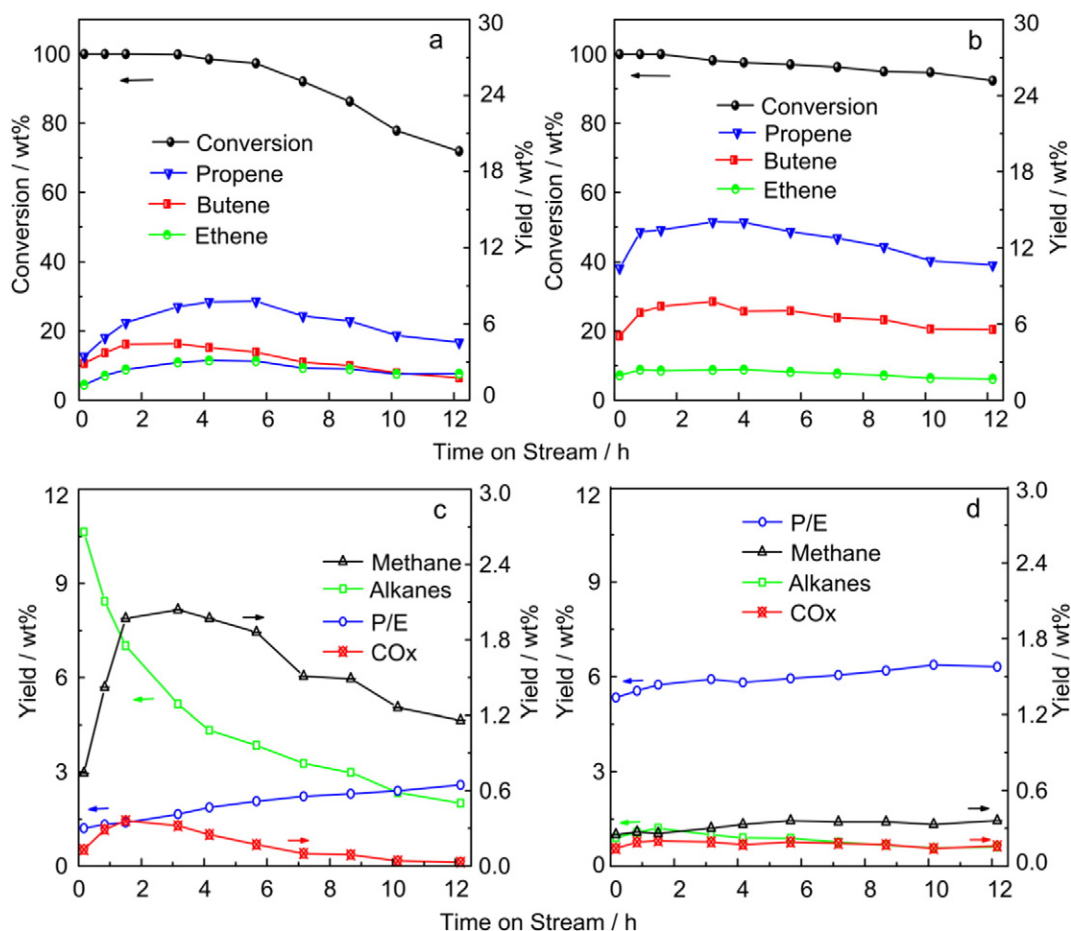


Fig. 1. Methanol conversion and product distribution vs. time over H-ZSM-11 (a and c) and Si-ZSM-11 (b and d).

and H-ZSM-11, respectively) were compared to investigate whether the reaction performance and deactivation behaviors are affected by the silanol groups.

## 2. Experimental

### 2.1. Catalyst preparation

Hierarchical ZSM-11 zeolite was prepared according to the method described in Ref. [14]. The synthesis of pure silica ZSM-11 zeolite followed the same procedure except for the fact that no  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  was added. The details about the experimental procedures were given in the Supporting information. The two zeolites were denoted as H-ZSM-11 and Si-ZSM-11, where the Si/Al ratio of H-ZSM-11 is 26. The resultant H-ZSM-11 zeolite was modified by sodium through wet impregnation. The desired samples obtained were denoted as H-11-X (X = 0.5, 1.0, 2.0, 5.0). X indicates the mass percentage of Na/zeolite.

### 2.2. Catalyst characterization

The samples were characterized by X-ray diffraction patterns on the X'Pert PRO MPD (PANalytical Co.) diffractometer, thermogravimetry (TG) and differential thermal analysis (DTA) (NETZSCH Proteus STA449C), scanning electron microscopy (S-4800), X-ray fluorescence spectroscopy (Axios Advanced X-ray Spectrometer),  $^{29}\text{Si}$  nuclear magnetic resonance (Bruker AV-400), nitrogen adsorption-desorption (Quantachrome) and infrared spectra (Nicolet Co, USA). Adsorption of pyridine was performed at room temperature. CO probe molecules were adsorbed at 100 K and a partial pressure of 70 mbar.

The description about the experimental procedures was given in the Supporting information.

### 2.3. Catalytic testing

The catalytic testing was carried out at 450 °C in a fixed-bed micro-reactor under atmospheric pressure. In a typical experiment, 1 g catalyst with particle size of 0.25–0.42 mm was packed between two layers of quartz sands in the reactor. The pure methanol solution was introduced into the system by a HPLC infusion pump at a fixed rate of 0.164 g/min. The weight hourly space velocity (WHSV) for methanol in the study was  $9.8 \text{ h}^{-1}$  with  $\text{N}_2$  (21 mL/min) as carrier gas. The analysis method and equipment for the products were listed in the Supporting information.

## 3. Results and discussions

Si-ZSM-11 catalyst showed a high catalytic activity and low deactivation rate in converting methanol to propene. Fig. 1 presents the methanol conversion levels and product yields with time on stream at 450 °C. Both catalysts demonstrated almost 100% initial methanol conversion. After 12 h on stream, the Si-ZSM-11 catalyst lost merely 8% activity,

**Table 1**  
Textural properties and chemical composition of the zeolites.

Samples	Surface area ( $\text{m}^2/\text{g}$ )			Pore volume ( $\text{cm}^3/\text{g}$ )			Elemental analysis (wt.%)		
	$S_{\text{Ext}}$	$S_{\text{Micro}}$	$S_{\text{BET}}$	$V_{\text{micro}}$	$V_{\text{meso}}$	$V_{\text{T}}$	Si	O	Al
H-ZSM-11	72	341	413	0.137	0.099	0.236	45.45	52.75	1.74
Si-ZSM-11	53	355	408	0.140	0.066	0.206	46.28	53.66	0.00

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