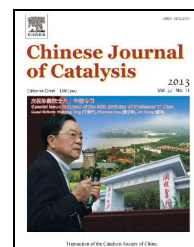


available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/chnjc](http://www.elsevier.com/locate/chnjc)

Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

## Catalytic conversion of methyl chloride to lower olefins over modified H-ZSM-34

Ting Xu, Hang Song, Weiping Deng<sup>#</sup>, Qinghong Zhang, Ye Wang<sup>\*</sup>

State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China

### ARTICLE INFO

#### Article history:

Received 4 July 2013

Accepted 16 August 2013

Published 20 November 2013

#### Keywords:

Methyl chloride

Lower olefins

H-ZSM-34

Ethylenediaminetetraacetate treatment

Cerium modification

Acidity

### ABSTRACT

Among several typical zeolites, H-ZSM-34 was found to be an efficient catalyst for the conversion of methyl chloride to lower olefins, i.e., ethylene, propylene, and butenes. Treatment of H-ZSM-34 with a Na<sub>2</sub>H<sub>2</sub>EDTA (EDTA = ethylenediaminetetraacetate) aqueous solution followed by ion exchange and calcination enhanced the catalytic performance significantly. The selectivity to lower olefins increased significantly for certain Na<sub>2</sub>H<sub>2</sub>EDTA aqueous solution concentrations; when the H-ZSM-34 catalyst was treated with a 0.1 mol/L Na<sub>2</sub>H<sub>2</sub>EDTA solution, the selectivity and yield of C<sub>2</sub>–C<sub>4</sub> olefins reached 82% and 61%, respectively, at 673 K and a CH<sub>3</sub>Cl partial pressure of 9.2 kPa. The modification of H-ZSM-34 with Ce ions improved C<sub>2</sub>–C<sub>4</sub> olefin selectivity and yield. Catalyst characterization suggests that treatment with Na<sub>2</sub>H<sub>2</sub>EDTA or modification by Ce decreases the acidity of H-ZSM-34. The weakened acidity of the treated or modified H-ZSM-34 may suppress the hydrogen transfer reaction and prevent lower olefins from further transformation to paraffins.

© 2013, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

### 1. Introduction

Lower olefins, in particular ethylene and propylene, are among the most important building-block chemicals. Ethylene and propylene are primarily produced from petroleum via steam cracking of naphtha. The demand for the lower olefins has grown rapidly in recent years. There is a strong incentive to develop non-petroleum routes for the production of lower olefins to reduce reliance on diminishing petroleum sources. The production of lower olefins via novel routes such as the dehydrogenation of lower paraffins [1] and the methanol-to-olefins (MTO) process [2,3] has attracted much attention.

Methane is the main constituent of natural gas, coal-bed gas,

shale gas, landfill gas, biogas, and methane hydrates. The transformation of abundant and affordable methane resources to key building-block chemicals such as lower olefins is one of the most important research goals in catalysis. Current technology for chemical use of methane involves high-temperature steam reforming to produce syngas and the subsequent conversion to methanol, followed by methanol transformation to chemicals (e.g., propylene and ethylene). However, steam reforming of methane is an energy- and cost-intensive process [4]. Many studies have been devoted to the direct transformation of methane to chemicals such as methanol, formaldehyde, and ethylene, but yields of desired products are low [4–9]. The development of novel catalytic routes for the trans-

<sup>\*</sup> Corresponding author. Tel: +86-592-2186156; Fax: +86-592-2183047; E-mail: wangye@xmu.edu.cn

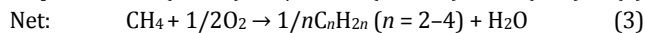
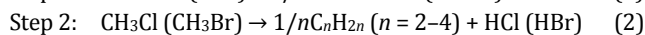
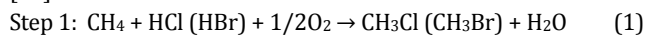
<sup>#</sup> Corresponding author. Tel: +86-592-2180480; Fax: +86-592-2183047; E-mail: dengwp@xmu.edu.cn

This work was supported by the National Basic Research Program of China (2010CB732303), the National Natural Science Foundation of China (21173174, 20923004, 21033006, and 21161130522), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1036).

DOI: 10.1016/S1872-2067(12)60681-0 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 34, No. 11, November 2013

formation of methane to building-block chemicals is of high significance from a practical and fundamental point of view.

Recently, we reported a two-step route for the conversion of methane to lower olefins, particularly  $C_3H_6$ , via  $CH_3Cl$  or  $CH_3Br$  [10].



The HCl or HBr generated in the second step can be used directly in the first step, and the net reaction is the oxidative dehydrogenation of methane to lower olefins, i.e., Eq. (3).

The key to realizing this novel two-step route is to develop efficient catalysts for both steps. Some catalysts such as Ru/SiO<sub>2</sub> [11], Rh/SiO<sub>2</sub> [12], FePO<sub>4</sub>/SiO<sub>2</sub> [13], LaOCl [14–16], and CeO<sub>2</sub> [10] have been studied for use in Step 1, i.e., the oxidative chlorination or bromination of methane to  $CH_3Cl$  or  $CH_3Br$  by HCl or HBr in the presence of O<sub>2</sub>. This work is devoted to studying catalysts for Step 2.

Some studies have investigated catalysts for the conversion of methyl halides to light olefins. H-SAPO-34 is an efficient catalyst for the MTO process [2,3,17–19]. Because of the chemical similarities between methyl halides and methanol, H-SAPO-34 has been employed mainly as a catalyst for the formation of light olefins in methyl halide conversion [20–25]. We have demonstrated that H-ZSM-5 is a highly efficient catalyst for the conversion of methyl halides ( $CH_3Cl$  and  $CH_3Br$ ) to  $C_2$ – $C_4$  olefins, particularly  $C_3H_6$ , after modification such as by NH<sub>4</sub>F treatment [10,26].

In addition to SAPO-34 and H-ZSM-5, H-ZSM-34 is also a promising catalyst for the formation of lower olefins. ZSM-34 zeolite, which is an intergrowth of erionite and offretite, has an open micropore size of ~0.50 nm [27,28]. The pore size for ZSM-34 is between that for SAPO-34 (0.38–0.42 nm) and ZSM-5 (0.52–0.56 nm). Several research groups have reported that H-ZSM-34 exhibits unique product selectivities for the conversion of methanol to olefins [29–31]. In this paper, for the first time, we report on the catalytic behavior of H-ZSM-34 for the conversion of  $CH_3Cl$  to lower olefins, which is key in the two-step production of lower olefins from methane [10]. The modification of H-ZSM-34 to enhance its catalytic performance and the key factors determining the catalytic behavior will also be discussed.

## 2. Experimental

### 2.1. Catalyst preparation

Zeolites including H-ZSM-5, SAPO-34, SAPO-11, H- $\beta$ , H-MOR, and HY were purchased from Nankai University Catalyst Co. Na-ZSM-34 was synthesized using an organic template-free procedure reported by Xiao and co-workers [28]. In brief, 3.5 g NaAlO<sub>2</sub>, 7 g NaOH, 22 g KOH, and 67.5 g aqueous silica gel (40%) were stirred and aged at room temperature for 72 h and produced a clear solution denoted as L seed. NaOH (5.54 g) and fumed silica (28.85 g) were added to 83 mL water and stirred for 5 h. Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O (2.71 g) and the L seed (13.5 mL) were introduced into the mixture, followed by further stirring for 13

h. The mixture was transferred into an autoclave to crystallize at 393 K for 7 d. The product was collected by filtration, washing, and drying followed by calcination at 823 K in air for 5 h to obtain Na-ZSM-34. H-form ZSM-34 zeolite was prepared by the ion exchange of Na-ZSM-34 using NH<sub>4</sub>NO<sub>3</sub> aqueous solution. Typically, 1.0 g powdered Na-ZSM-34 was added to 50 mL NH<sub>4</sub>NO<sub>3</sub> aqueous solution (1.0 mol/L) and the suspension was stirred at 353 K for 3 h. After filtration and washing, the sample was dried at 373 K. This ion-exchange procedure was repeated three times, and the product was calcined at 823 K in air for 6 h to obtain H-ZSM-34.

The procedure for treating H-ZSM-5 with Na<sub>2</sub>H<sub>2</sub>EDTA (EDTA = ethylenediaminetetraacetate) is as follows. Typically, powdered H-ZSM-34 (2.0 g) was immersed into an aqueous solution of Na<sub>2</sub>H<sub>2</sub>EDTA (100 mL, 0–0.3 mol/L) and the suspension refluxed at 373 K. The solid product was recovered by filtration, washing with deionized water, and drying at 373 K. Ion exchange of the Na<sup>+</sup> in the treated zeolite with NH<sub>4</sub><sup>+</sup> was performed by adding the treated zeolite into an aqueous NH<sub>4</sub>NO<sub>3</sub> solution (50 mL, 1.0 mol/L), followed by washing and drying at 373 K. The ion exchange was repeated three times. Na<sub>2</sub>H<sub>2</sub>EDTA-treated H-ZSM-34 was obtained after calcination at 823 K in air for 6 h, and the sample was denoted H-ZSM-34-EDTA or H-ZSM-34-EDTA-*x*, where *x* is the concentration of Na<sub>2</sub>H<sub>2</sub>EDTA.

Rare earth metal ion-modified H-ZSM-34 samples were also synthesized using a procedure similar to that for the synthesis of parent H-ZSM-34, with the introduction of rare earth metal salts into the mixture of NaOH, fumed silica, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O before hydrothermal synthesis for Na-ZSM-34. The sample obtained was denoted RE-H-ZSM-34 (RE represents a rare earth metal). The molar ratio of RE to Al in this series of samples was controlled at 0.080.

### 2.2. Catalyst characterization

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed with an Agilent ICP-MS 4500 to measure catalyst composition. Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical X'pert Pro diffractometer with Cu K $\alpha$  radiation (40 kV, 30 mA). Ar physisorption was used to gain information about the pore structure of catalysts and was performed at 87 K on a Micromeritics ASAP-2010M instrument. The pore size distribution in the microporous region was evaluated by the Horváth-Kawazoe (HK) method.

NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) was performed on a Micromeritics AutoChem 2920 II instrument to measure the acidity. Typically, the sample loaded in a quartz reactor was pretreated with high-purity He gas at 673 K for 1 h. After cooling to 373 K, NH<sub>3</sub> adsorption was performed by switching the He flow to a 10% NH<sub>3</sub>/He gas flow and maintained at 373 K for 1 h. The gas phase or weakly adsorbed NH<sub>3</sub> molecules were purged by high-purity He at the same temperature. NH<sub>3</sub>-TPD was performed in the He flow by raising the temperature to 1073 K at 10 K/min. The desorbed NH<sub>3</sub> molecules were detected by a ThermoStar GSD 301 T2 mass spectrometer with signal of *m/e* = 16.

Download English Version:

<https://daneshyari.com/en/article/59909>

Download Persian Version:

<https://daneshyari.com/article/59909>

[Daneshyari.com](https://daneshyari.com)