



## The promoting effects of alkali metal oxide in side-chain alkylation of toluene with methanol over basic zeolite X



He Han<sup>a</sup>, Min Liu<sup>a</sup>, Xiaowa Nie<sup>a</sup>, Fanshu Ding<sup>a</sup>, Yiren Wang<sup>a</sup>, Junjie Li<sup>a</sup>, Xinwen Guo<sup>a,\*</sup>, Chunshan Song<sup>a,b,\*</sup>

<sup>a</sup> State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning Province, PR China

<sup>b</sup> EMS Energy Institute, PSU-DUT Joint Center for Energy Research and Department of Energy & Mineral Engineering, Pennsylvania State University, University Park, PA 16802, United States

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### ABSTRACT

The side-chain alkylation of toluene with methanol was investigated on a series of catalysts which were prepared by ion-exchange or subsequent impregnation of zeolite X with potassium hydroxide or cesium hydroxide aqueous solution. The catalysts were characterized by X-ray diffraction, scanning electron microscopy, X-ray fluorescence, Ar physical adsorption-desorption, NH<sub>3</sub> temperature-programmed desorption (TPD), CO<sub>2</sub>-TPD, pyridine adsorption Fourier-transform infrared (FT-IR) spectroscopy, FT-IR spectroscopy in O–H stretch region, thermogravimetric/differential thermal analysis, ultraviolet-Raman spectroscopy, and X-ray photoelectron spectroscopy. It was found that alkali metal oxide played extremely important roles in the modification of catalysts and in the catalytic reaction pathway. Strong basic sites were formed by modification of basic zeolite X with alkali metal oxide. These basic sites promoted the dehydrogenation of methanol to formaldehyde which was recognized as the true alkylating agent in side-chain alkylation. Consequently, side-chain alkylation of toluene with formaldehyde was enhanced. As toluene was mainly adsorbed and activated on alkali metal cations bonded on the zeolite framework, the synergistic effects between alkali metal oxide and alkali metal cations were proposed. One of the possible reaction pathways for side-chain alkylation of toluene with methanol over basic zeolite was described. Alkali metal ion-exchanged zeolite X modified with alkali metal oxide demonstrated relatively high side-chain alkylation activity. However, the improvement of styrene selectivity faced with great challenges.

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### 1. Introduction

Styrene is an important monomer used in the manufacture of many polymers. At present styrene is produced globally on a scale of ~18.5 million tons [1]. Current methods for the large-scale production of styrene involve multiple steps, typically beginning with benzene alkylation with ethylene using Friedel-Crafts or zeolite catalysts followed by energy-intensive dehydrogenation of ethylbenzene [2]. An alternative method for the production of styrene is a direct and single-step side-chain alkylation of toluene with

methanol [3]. Numerous academic papers or patents disclosed this reaction and the catalysts preparation methods [2–10]. However, this process has generally been characterized by having low conversion of toluene in addition to having low selectivity to styrene [11].

Basic faujasite (X or Y) has been shown as suitable catalysts for the side-chain alkylation of toluene with methanol [5,9,12]. One of the most widely applied methods for making the catalyst is the ion-exchange of sodium cations of faujasite by the more electropositive cations (K<sup>+</sup>, Rb<sup>+</sup> or Cs<sup>+</sup>). The effects of alkali metal cations on the basicity of the zeolites and the activity for this reaction have been studied extensively [8,10,13–15]. Another route for modification of faujasites is the impregnation of faujasites by alkali metal hydroxides or acetates followed by calcination, which brings about the formation of basic guest-compounds consisting of alkali metal oxide clusters in the zeolite cavities [6]. However, scarce attention

\* Corresponding authors. State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning Province, PR China.

E-mail addresses: [guoxw@dlut.edu.cn](mailto:guoxw@dlut.edu.cn) (X. Guo), [csong@psu.edu](mailto:csong@psu.edu) (C. Song).

has been given to the promoting effects of alkali metal oxide on this reaction.

In the earlier studies, Engelhardt et al. [4] found that high selectivity for ethylbenzene formation was achieved on zeolites in the K or Cs form containing excess alkali hydroxides. They inferred that relatively small amounts of occluded alkali hydroxides deposited on the zeolite surface may act as sites for hydrogenation. Mielczarski et al. [5] investigated the infrared spectra of adsorbed species over zeolites NaX, ion-exchanged CsNaX and cesium acetate impregnated CsNaY (CsAce/CsNaY) during side-chain alkylation of toluene with methanol to form styrene. They found that zeolites with no acidity (CsAce/CsNaY) decomposed methanol to CO and CO<sub>2</sub> while zeolites with some acidity (CsNaX) converted methanol to formaldehyde. Acid sites probably stabilized the formation of formaldehyde. However, they were not necessary for side-chain alkylation of toluene to occur. Hunger et al. [6] used <sup>133</sup>Cs and <sup>13</sup>C MAS NMR spectroscopy to investigate the side-chain alkylation of toluene with methanol over cesium ion-exchanged zeolites Y with and without subsequent impregnation with cesium hydroxide. They found that the oxide guest compound had a high dispersion on the zeolite host and intensively influenced the intrinsic base strength of the host framework. In addition, the dehydrogenation of methanol to formaldehyde proceeded both on non-impregnated catalyst (at 673 K) and on impregnated CsNaY zeolites (at 573 K). They also observed the signals of formate species in this process and indicated that the formate species could play an active role as alkylating agent in the side-chain alkylation of toluene. Alabi et al. [7] investigated the effects of modification of cesium ion-exchanged zeolite X with Cs<sub>2</sub>O on the catalytic activity in the side-chain alkylation of toluene to styrene and ethylbenzene. They found that the toluene conversion increased, but the selectivity to styrene decreased on modification of Cs-X with Cs<sub>2</sub>O. Infrared spectroscopy of adsorbed pyridine and CO<sub>2</sub> indicated that the basic properties were markedly enhanced, but acidic properties were not changed by modification of Cs-X with Cs<sub>2</sub>O. They suggested that the enhancement of toluene conversion was due to the generation of strong basic sites which promoted the activation of toluene by an abstraction of a proton from methyl group.

In our previous work [16], the side-chain alkylation of toluene with methanol was studied on cesium ion-exchanged and cesium-impregnated zeolite X with similar cesium content, respectively. It was found that cesium ions bonded on the framework and cesium oxide formed in the pore took different roles in this reaction. The synergistic effect of cesium ions and cesium oxide was proven to be important for the formation of styrene and ethylbenzene.

In spite of the above-mentioned work, the promoting effects of alkali metal oxide in side-chain alkylation of toluene with methanol remain to be clarified. The synergistic effects of alkali metal cations bonded on the framework and alkali metal oxide distributed on the surface or in the pore in side-chain alkylation of toluene with methanol should be further investigated to exploit an effective catalyst for styrene production.

In the present study, a series of catalysts were prepared by ion-exchange and subsequent impregnation of zeolite X with potassium hydroxide or cesium hydroxide aqueous solution. The catalytic performances of side-chain alkylation of toluene with methanol over different catalysts were investigated. It was found that alkali metal oxide promoted the conversion of methanol to formaldehyde, which resulted in the enhancement of side-chain alkylation activity. However, serious methanol decomposition to CO was observed on alkali metal oxide-modified samples. The synergistic effects between alkali metal oxide and alkali metal cations were proven by correlating the catalytic performance with the various characterization results. In addition, a possible reaction

pathway of side-chain alkylation of toluene with methanol over basic zeolites was described to consider exploiting more effective catalyst for this reaction.

## 2. Experimental section

### 2.1. Materials

Zeolite NaX (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 2.48) was obtained from the Catalyst Plant of Nankai University. Potassium hydroxide (KOH, 99.99%) and cesium hydroxide monohydrate (CsOH·H<sub>2</sub>O, 99.9%) were obtained from Aladdin Industrial Corporation.

### 2.2. Catalyst preparation

Zeolite NaX was ion-exchanged with aqueous solution of different alkali cations (K<sup>+</sup> or Cs<sup>+</sup>). The procedure was described as follows: 10 g NaX was exchanged three times at 343 K for 2 h with a 0.2 M solution of alkali cation (solid/liquid ratio, 10 g/50 mL). The solid was separated from the slurry by centrifugation and washed with excess pure water each time. The material was then dried in flowing air at 373 K overnight and calcined at 813 K for 3 h. The catalyst obtained from KOH or CsOH·H<sub>2</sub>O solution was named as KX or CsX, respectively.

Subsequently, KX or CsX was modified with KOH or CsOH solution by incipient wetness impregnation, respectively. It was assumed that the added KOH (or CsOH) would be decomposed to K<sub>2</sub>O (or Cs<sub>2</sub>O) by calcination. The loading of K<sub>2</sub>O (or Cs<sub>2</sub>O) was controlled to be 6 K<sub>2</sub>O (or Cs<sub>2</sub>O) per unit cell (u.c.). After impregnation the catalysts were dried and calcined in the same conditions as ion-exchanged samples and the obtained catalysts were denoted as K<sub>2</sub>O/KX, Cs<sub>2</sub>O/KX, K<sub>2</sub>O/CsX, and Cs<sub>2</sub>O/CsX, respectively.

### 2.3. Characterization of catalysts

Powder X-ray diffraction (XRD) patterns were recorded on a SmartLab(9) diffractometer with a Cu K $\alpha$  radiation source operating at 45 kV and 200 mA. The spectra were recorded from 5° to 50° with a scanning rate of 8° min<sup>-1</sup>.

Scanning electron microscopy (SEM) images were obtained on a field-emission scanning electron microscopy (NOVA NanoSEM 450) instrument with an acceleration voltage of 10.0 kV. All the samples were sputtered with a thin film of chromium.

The chemical compositions of the samples were analyzed by X-ray fluorescence (XRF) spectroscopy on a Philips Magix-601 X-ray fluorometer.

Ar isotherms were measured in a Quantachrome autosorb-iQ2 gas adsorption analyzer at 87 K. Prior to the measurement, the samples were degassed in vacuum at 573 K for 10 h. The Brunauer-Emmett-Teller (BET) method was applied to calculate the total surface area (*S*<sub>BET</sub>), while the micropore volume was calculated by nonlocal density function theory (NLDFT) method.

Temperature-programmed desorption (TPD) of NH<sub>3</sub> and CO<sub>2</sub> was performed on a CHEMBET 3000 chemical adsorber (Quantachrome) to analyze the nature of surface acid and base sites. NH<sub>3</sub>-TPD measurements were conducted by the following procedures: About 0.1 g of the catalyst sample was purified in helium at 773 K for 1 h, cooled to 393 K, then exposed to ammonia-helium mixture (8% NH<sub>3</sub>-92% He) for 30 min. The physically adsorbed NH<sub>3</sub> was removed by helium at 393 K for 1 h. The TPD curves were obtained at a heating rate of 10 K min<sup>-1</sup> from 393 to 923 K. The desorbed ammonia was detected by gas chromatography with a thermal conductivity detector (TCD). CO<sub>2</sub>-TPD measurements were conducted the same as NH<sub>3</sub>-TPD and the adsorption gas was pure CO<sub>2</sub>.

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