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# Carbon dioxide assisted toluene side-chain alkylation with methanol over Cs-X zeolite catalyst

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ABSTRACT

Zeolite Cs-X is an acknowledged representative basic catalyst useful for side-chain alkylation of toluene with methanol. In spite of numerous investigations, still there has been long lasting challenge for achieving high selectivity for side-chain alkylated products rather than ring alkylated products. In an effort to improve the yields of side-chain alkylated products, $CO_2$ was introduced during the toluene side-chain alkylation with methanol at 425 °C over Cs loaded faujasite catalyst. The $CO_2$ addition facilitated in removing the formed hydrogen by reverse water-gas shift reaction and enhanced the product yield. Interestingly, $CO_2$ addition helped in obtaining higher yields of side-chain alkylation products including styrene/ethylbenzene and α-methylstyrene/isopropylbenzene. The $CO_2$ introduction resulted in less $H_2$ formation in the product stream during the reaction. Mesoporosity was also introduced to the zeolite X to improve the activity and product selectivity.

## 1. Introduction

Styrene is an essential ingredient for the production of many kinds of polymeric materials such as polystyrene, acrylonitrile-butadiene-styrene (ABS) thermoplastic, styrene-butadiene rubber (SBR), and other. The most conventional styrene production is based on the dehydrogenation of ethylbenzene obtained from benzene and ethylene by a well-known Friedel-Crafts alkylation process [1,2]. However, ethylbenzene dehydrogenation process suffers from problems like catalyst deactivation, leaching of potassium promoter, and high energy consumption due to high steam to ethylbenzene ratio obligation [3–5]. Toluene side-chain alkylation over basic catalysts has been studied as a potential alternative route for the production of styrene from cheap raw materials like toluene and methanol. The alternative approach was proposed by Sindorenko by using $K^+$ and $Rb^+$ ion exchanged Faujasite zeolites in 1967 [1]. A multitude of researchers have studied this reaction to obtain styrene in one step for over 50 years but there is still a lot more work to be done to achieve the satisfactory level. The toluene side-chain alkylation reaction results not only low catalytic conversion of reactants but also low selectivity of the desired styrene monomer. Therefore, for increased styrene yield many studies are under active investigation at different laboratories.

The side-chain alkylation generally proceeds on solid base catalysts [6–10]. If the catalyst acidity increases, it facilitates more alkylated toluene products such as xylene, ethyl toluene, and trimethyl-benzene through direct methylation of benzene ring [11]. Too strong acidity of the catalysts speeds up the methanol dehydration [12], and very strong basic sites enhance the decomposition of methanol into hydrogen and carbon monoxide [13]. Therefore, catalysts for toluene side-chain alkylation should have harmony between the acidity and basicity [14].The side-chain alkylation reaction generally proceeds in a two-step process. First is the dehydration of methanol to form formaldehyde, which further reacts with the toluene to produce styrene and ethylbenzene [8,15].

In general, catalyst design for side-chain alkylation is mostly confined to alkali metal modified zeolites [16]. Zeolites were primarily preferred as support materials for basic metals because of their robust nature, high thermal stability, and uniform pore structure [17]. One of the promising catalysts and widely studied is the cesium ion-exchanged or cesium oxide impregnated zeolite-X. The usefulness of MgO encapsulated mesoporous zeolite for this reaction was also explored recently by our group [18]. The MgO encapsulated in carbon templated silicalite-1 catalyst yielded up to 5% of aromatics. Alabi et al. [8] and Hattori et al. [19] have reported that impregnation of $Cs_2O$ over the cesium ion exchanged zeolite-X shows high toluene conversion because of the introduction of strong basic sites. However, the styrene selectivity was dramatically decreased in spite of no acidity change. They suggested that enhancement of catalyst basicity influences the

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activation of toluene, and the formed styrene monomer is converted to ethylbenzene due to transfer hydrogenation of styrene with methanol [19]. Zhang et al. [20] have investigated the reaction by employing $BPO_4$ modified CsX since the $BPO_4$/CsX catalyst exhibits weaker acidic sites and lower amount of basic sites in comparison to CsX. This catalyst provided high methanol utilization efficiency by way of limitation of bidentate formate generation on the catalyst surface [21]. Sooknoi and Dwyer [22] also investigated the side-chain alkylation and reported the formation of 2-phenylethanol from the reaction between toluene and formaldehyde, which undergoes hydrogenolysis to form ethylbenzene [23]. They found that ethylbenzene was the major product when the reaction was carried out over CsNaX catalyst with Cs clusters. This study revealed that Cs clusters enhance the hydrogenolysis of 2-phenylethanol. Alkylation of ethylbenzene with methanol over zeolite-X was investigated by Huang and Ko [24]. They reported that ethylbenzene with methanol can produce styrene, alpha-methyl styrene, cumene, toluene, and benzene via free radical mechanism [25]. In addition, diverse catalysts such as KX [26], metal borate modified CsX [14], aluminum and nitrogen containing solid catalysts [27], Cu and Ag deposited X [23], layered double hydroxides [28], alkali metal exchanged zeolites (X, Y, L, β) [29], and other have also been investigated for this reaction.

Carbon dioxide has received a lot of attention as safe, cheap, renewable, and environmental friendly feedstock in recent years [30]. However, due to its high thermal stability and stable oxidation state [31], utilization is not easy for industrial applications. Therefore, unprecedented research activity is being carried out to find novel technologies for $CO_2$ utilization. We have extensively investigated the feasibility and cost effectiveness of styrene production from ethylbenzene dehydrogenation by utilizing $CO_2$ as a soft oxidant and reached closer to commercialization [30,32–38]. The interaction between $CO_2$ and the catalyst promotes the ethylbenzene conversion and catalyst stability [39,40]. The $CO_2$ in the dehydrogenation reaction can effectively remove the formed hydrogen [41,42] through reverse water-gas shift reaction [43], and also help decoking reaction [42]. In the present work, we made an attempt to explore the influence of $CO_2$ in the side-chain alkylation of toluene with methanol over cesium modified zeolite-X catalyst obtained by a microwave-assisted synthesis method [44–47].

## 2. Experiment

### 2.1. Catalyst preparation

*Cesium ion exchange:* Cs-X was obtained by an aqueous ion exchange of commercially available sodium form of zeolite-X (Sigma-Aldrich, Si/Al = 2.4). The Cs-ion exchange was carried out using 5 g of Na-X and 50 ml of 0.5 M cesium hydroxide solution (Sigma-Aldrich, 50 wt.% in $H_2O$, 99.9%). The ion exchange lasted for 6 h at ambient temperature by the normal procedure of soaking. Following the exchange, the sample was filtered off with 400 ml of deionized water. The filtered slurry was dried at 80 °C for 12 h, and then it was calcined in a muffle furnace at 480 °C for 4 h. The above process was repeated one more time to obtain the final cesium ion exchanged Cs-X catalyst. The addition of $Cs_2O$ (2 wt.%) to Cs-X was performed by impregnation of Cs-X ($Cs_2O$/Cs-X) with cesium hydroxide solution. After impregnation, the sample was dried in the oven at 80 °C and calcined at 480 °C for 4 h in air atmosphere.

*Hierarchical FAU:* Calcined Na-X was used as the parent sample for post-synthetic treatment step. The dealumination was conducted with ethylene diaminetetra acetic acid disodium salt dihydrate ($Na_2H_2EDTA$, Sigma-Aldrich, ≥ 99%) in a microwave reactor (Microsynth, Milestone). To an aqueous 0.3 M of 30 ml $Na_2H_2EDTA$ solution, 1 g of Na-X sample was added. The obtained mixture was transferred to the microwave vessel and heated by microwave irradiation at 120 °C for 1 h. After which the solid was separated by centrifugation. The resulting solid (EDTA-Na-X) was dried at 80 °C for 12 h and then calcined in a muffle furnace at 480 °C for 4 h. The cesium ion exchange to this sample was carried out by following the same steps as described above to obtain the EDTA-Cs-X.

### 2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the synthesized catalysts were obtained on a Rigaku Miniflex diffractometer with Cu Kα radiation source at 30 kV and 15 mA. Surface area measurements were made using the Micromeritics ASAP 2050 gas adsorption analyzer. The t-plot method was applied to calculate the external surface area. Before the measurements, samples were out gassed at 200 °C for 4 h. Temperature-programmed desorption (TPD) analysis of $NH_3$ and $CO_2$ as probe molecules was carried out on a Micromeritics ASAP 2950 instrument. The $NH_3$ and $CO_2$ TPD curves were obtained by thermal conductivity detector to investigate the surface acidity and basicity of the catalysts. Thermogravimetric/differential thermal analysis (TG/DTA) was performed with a Bruker TG-DTA 2000 SA instrument in the range of 35–800 °C under air flow. From the obtained TG/DTA curves, the amount of coke deposited on the catalyst surface during the reaction was estimated.

### 2.3. Catalyst testing

Catalytic activity was evaluated towards toluene side-chain alkylation in a fixed-bed micro reactor with 1/4 inch stainless steel tube at atmospheric pressure. Around 200 mg of catalyst was secured between the quartz wool plugs and activated at 480 °C for 1 h under helium flow. The activated catalyst was cooled to the desired reaction temperature. Pre-mixed solution of toluene and methanol with 2:1 mole ratio was used as the reactant. The mixture was fed into the reactor through preheated (200 °C) stainless steel tube for vaporization with a weight hourly space velocity (WHSV) of 2.1 $h^{-1}$. He or $CO_2$ were used as the carrier gases at a flow rate of 15 ml/min. Qualitative and quantitative analysis of the reaction products were carried out by a gas chromatograph (ACME 6000, Young Lin Instruments). Liquid products were analyzed by using DB-Wax capillary column (60 m length, inner diameter 0.32 mm, stationary phase thickness 0.25 mm) and flame ionization detector, and the gas phase products were analyzed by another gas chromatograph equipped with Carboxen 1000 packed column (60/80 mesh, 4 ft × 1/8 in. ss) and thermal conductivity detector. The toluene conversion, product selectivity, and product yield were estimated by the following equations:

$$C_T(\%) = \frac{\sum y_{i.o}}{y_{Tol.o} + \sum y_{i.o}} \times 100$$

$$S_i(\%) = \frac{y_{i.o}}{\sum y_{i.o}} \times 100$$

$$Y_I\ (\%) = C_T \times S_i$$

where $y_{Tol.o}$ and$y_{i.o}$ are the outlet molar fraction of toluene and aromatic products respectively.

## 3. Results and discussion

### 3.1. Characterization of catalysts

XRD patterns of various samples synthesized in this study are shown in Fig. 1. As can be noted from this figure, all samples maintained the FAU crystalline structure after cesium ion exchange and microwave treatment with $Na_2H_2EDTA$. However, the EDTA-Na-X sample peak intensity has decreased, and the zeolite crystal structure has partially been damaged by dealumination [46]. Cation size difference between