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Effect of Fe Additives on the Catalytic Performance of Ion-Exchanged CsX Zeolites for Side-Chain Alkylation of Toluene with Methanol

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Abstract: The side-chain alkylation of toluene with methanol was investigated over some Fe-modified Cs ion-exchanged X zeolite (CsX) catalysts prepared via the impregnation method using different iron sources. The adsorption/activation behaviors of the reactants on the surface of the catalysts were studied by in situ Fourier-transform infrared (FT-IR) spectroscopy and temperature programmed desorption (TPD) mass measurements. Modification of CsX with a small amount of FeCl₃ could result in a considerable decrease in catalytic activity, due mainly to the remarkable decrease in the density of acidic and basic sites of the catalysts. Interestingly, the Fe(NO₃)₃-modified CsX with an optimum Fe loading of 0.15 wt.% shows improved catalytic activity and high yield compared to the side-chain alkylation products. Modification of CsX with Fe(NO₃)₃ could also result in a decrease in basic sites of the catalyst. However, such a change does not bring an obvious negative effect on the adsorption/activation of toluene, while it could effectively inhibit the generation of the undesired bidentate formate. Furthermore, the introduced FeO_x species (derived from the decomposition of Fe(NO₃)₃) may also act as new Lewis acidic sites to participate in the activation of methanol and to stabilize the formed active intermediates (i.e., unidentate formate). Therefore, modification of CsX with a suitable amount of Fe(NO₃)₃ may adjust its adsorption/activation ability for reagents by changing the acid–base properties of the catalyst, which can finally enhance the catalytic performance for the side-chain alkylation of toluene with methanol.

Keywords: toluene; methanol; side-chain alkylation; iron (Fe); CsX zeolite

1. Introduction

Styrene is an industrially essential chemical that is used for the synthesis of various polymers. Traditionally, styrene is synthesized via two subsequent catalytic reactions: the alkylation of benzene with ethylene to synthesize ethylbenzene, and the dehydrogenation of ethylbenzene to styrene. However, this method has some disadvantages, such as a high energy consumption, complicated operation process, and high cost of production. Therefore, recent studies focused on developing more simple and efficient ways to synthesize styrene. The side-chain alkylation of toluene with methanol is a very attractive reaction since it may offer an alternative method to produce styrene and ethylbenzene [1–5]. For this process, a variety of solid catalysts with different acid–base properties

were investigated, including alkali metal ion-exchanged zeolites [6–10], alkaline porous CaO [11], Cs-containing microporous carbon [12], MgO encapsulated mesoporous zeolites [13], and layered double hydroxides (LDHs) [14]. As a representative catalyst system, Cs ion-exchanged X zeolites (CsX) received considerable attention for their relatively high catalytic activity and selectivity to styrene [8,9,15]. More interestingly, it was found that the catalytic performance of CsX may be further improved by modification with some additives [9,16,17].

For instance, it was reported that modification of CsX with Cs₂O could enhance the toluene conversion due to the generation of strong basic sites which promote the activation of toluene via the abstraction of a proton from the methyl group [7,18]. Hattori and coworkers reported that metal borate-modified CsX showed improved catalytic activity and selectivity compared to styrene owing to the ability of borates to selectively form formaldehyde from methanol [7,9]. Han et al. [17] gave a similar speculation after studying the side-chain alkylation reaction over composite catalysts composed of CsX and sodium borate (Na₂B₄O₇) or CuO/SiO₂. In another work reported by Wieland et al. [2], they proposed that impregnating boric acid on CsX could effectively promote the side-chain alkylation activity by neutralizing some unfavorable strong basic sites, which are the main active centers for rapidly decomposing methanol to byproducts like CO and H₂. In our recent work [19], it was found that the modification of CsX with boron phosphate can improve the catalytic activity for the side-chain alkylation of toluene with methanol. The introduction of BPO₄ can bring more weak acidic sites and decrease the concentration of basic sites of the catalysts, which can inhibit the generation of the unfavorable bidentate formate, thus finally resulting in the improvement of the catalytic performance of the catalyst. Currently, it is still a very attractive subject to search easily available and efficient additives for enhancing the side-chain alkylation performance of the CsX catalysts, and to understand the effect of the additives on the acidic–basic properties of the catalysts, as well as on the adsorption/activation ability for methanol and/or toluene.

In this work, some Fe-modified CsX catalysts were prepared by using two kinds of iron resources, Fe(NO₃)₃ and FeCl₃, as additives. Their catalytic properties were investigated for the side-chain alkylation of toluene with methanol. By combining a variety of characterization means, including the in situ Fourier-transform infrared spectra (FT-IR) and temperature programmed desorption (TPD) techniques (monitored by a mass spectrometer), the effects of different Fe additives on the acidic–basic property and the adsorption/activation ability of the CsX catalysts were studied for getting some useful information to understand the enhanced role of Fe additives in the side-chain alkylation of toluene with methanol.

2. Results

2.1. Catalytic Performance

The catalytic properties of CsX and the Fe-modified CsX catalysts for the side-chain alkylation of toluene with methanol are shown in Table 1. The major reaction products are ethylbenzene and styrene, while the byproducts include carbon monoxide, hydrogen, carbon dioxide, xylenes, trimethylbenzene, benzene, and C1–C3-light hydrocarbons.

A 6.5% conversion of toluene is obtained over CsX with 19.2% selectivity to styrene and 78.0% selectivity to ethylbenzene. Varying the addition amounts of iron (Fe(NO₃)₃ or FeCl₃) in the range of 0.08–0.50 wt.% brings significant changes in toluene conversion and selectivity to styrene. For the Fe(NO₃)₃-modified catalysts (nFe/CsX-I), introduction of a small amount of Fe species could improve the catalytic activities of the CsX catalysts. Among them, 0.15Fe/CsX-I, derived from the impregnation of CsX with 0.15 wt.% iron, exhibits the highest toluene conversion (8.0%) with 84.5% selectivity of ethylbenzene and 12.4% selectivity of styrene. With further increasing iron contents, the conversion of toluene decreases gradually, and a 4.9% conversion of toluene is obtained when the iron loading reaches 0.50 wt.%.

As for the FeCl₃-modified CsX catalysts (nFe/CsX-II), the addition of FeCl₃ could result in an obvious decrease in toluene conversion, but could indeed improve the selectivity of styrene. It is worth noting that the conversion of methanol decreases to ~90% when using Fe/CsX-II as a catalyst,

lower than CsX and Fe/CsX-I (97% conversion of methanol), implying that the activation ability for methanol decreases somewhat after modifying the CsX catalyst with FeCl₃.

Table 1. Catalytic properties of Fe-modified Cs ion-exchanged X zeolite (CsX) catalysts for the side-chain alkylation of toluene with methanol. ^a

Catalysts	Conversion (%) Toluene	Selectivity (%)			Yield (%) Styrene + Ethylbenzene
		Styrene	Ethylbenzene	Others ^b	
CsX	6.5	19.2	78.0	2.8	6.3
0.08 Fe/CsX-I	7.8	13.3	83.5	3.2	7.6
0.15 Fe/CsX-I	8.0	12.4	84.5	3.1	7.6
0.30 Fe/CsX-I	7.0	11.2	85.1	3.7	6.7
0.50 Fe/CsX-I	4.9	10.5	85.2	4.3	4.7
0.08 Fe/CsX-II	3.5	49.0	49.3	1.8	3.4
0.15 Fe/CsX-II	2.7	52.8	42.6	4.6	2.5
0.30 Fe/CsX-II	2.1	56.6	39.4	4.0	2.1

^a Reaction condition: reaction temperature of 435 °C, reactant space velocity of 2.0 h⁻¹, toluene/methanol ratio of 3/1, reaction time of 2 h. ^b Other byproducts include xylenes, trimethylbenzene, and benzene.

Additional experimental results suggest that the stability of the Fe(NO₃)₃-modified CsX catalyst is better than the unmodified CsX catalyst, and no obvious decrease in catalytic activity could be observed after a 6-h reaction over the catalyst of 0.15Fe/CsX, while a slight decrease for CsX could be detected after 5 h. The gradual deactivation of the CsX catalyst should be mainly caused by the rapid coke deposition over the stronger basic sites of the catalyst, and its catalytic activity could be fully recovered via calcination of the used catalyst at 600 °C under air.

The above results suggest that modification of CsX with a suitable amount of Fe(NO₃)₃ as an iron source may improve the catalytic activity for the side-chain alkylation of toluene with methanol. While the modification of CsX with a small amount of FeCl₃ can lead to a considerable decrease in toluene conversion, it can be of benefit to enhance the selectivity of styrene. For understanding the role of the different iron additives, a variety of characterization means were carried out, and the main results are given below.

2.2. Catalyst Characterization

Figure 1 shows the X-ray diffraction (XRD) patterns of the CsX, nFe/CsX-I, and nFe/CsX-II catalysts. The diffractograms of the Fe-modified CsX catalysts indicate that the faujasite (FAU) structure of the zeolites is retained after the modification. The appearance of a weak peak at about 12.3° on the pattern of CsX may be assigned to the formation of some large cesium oxide clusters on the surface of zeolite X [20]. Upon the introduction of Fe species, the signal at 12.3° decreases gradually, and is nearly undetectable when a relatively high amount of Fe species is introduced. These results suggest that some interactions between the Fe additives and the surface dispersed Cs₂O clusters should exist. The absence of diffraction peaks related to Fe-based compounds indicates the Fe species should be highly dispersed on the zeolite host. In addition, with the increase in Fe content, the intensities of the relevant diffraction peaks belonging to zeolites decrease somewhat. These phenomena can be mainly attributed to the changes in the X-ray absorption coefficients caused by the introduction of Fe-based compounds [15].

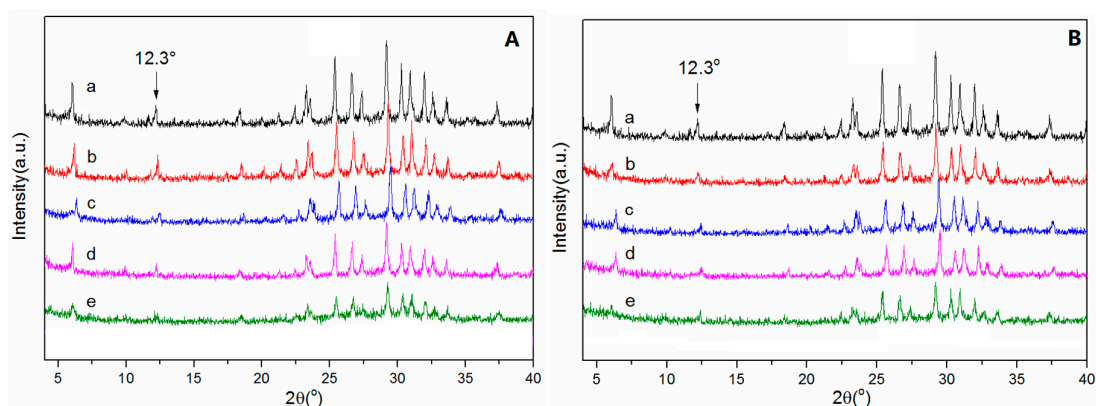


Figure 1. X-ray diffraction (XRD) patterns of the catalysts: **(A)** (a) Cs ion-exchanged X zeolite (CsX), (b) 0.08 Fe/CsX-I, (c) 0.15 Fe/CsX-I, (d) 0.30 Fe/CsX-I, (e) 0.50 Fe/CsX-I; **(B)** (a) CsX, (b) 0.08 Fe/CsX-II, (c) 0.15 Fe/CsX-II, (d) 0.30 Fe/CsX-II, (e) 0.50 Fe/CsX-II.

Figure 2 shows the SEM images of the CsX, 0.15 Fe/CsX-I, and 0.15 Fe/CsX-II catalysts. The image of the CsX catalyst contains homogeneous zeolite crystal particles with an average size of 2–3 μm . The Fe-modified CsX catalysts are composed mostly of similar zeolite crystallites, as well as a trace amounts of small particles below 0.5 μm . These small particles might contain debris of the X zeolite crystallites and the Fe-based species. Furthermore, modification of CsX with Fe species could result in a color change from white to pale yellow.

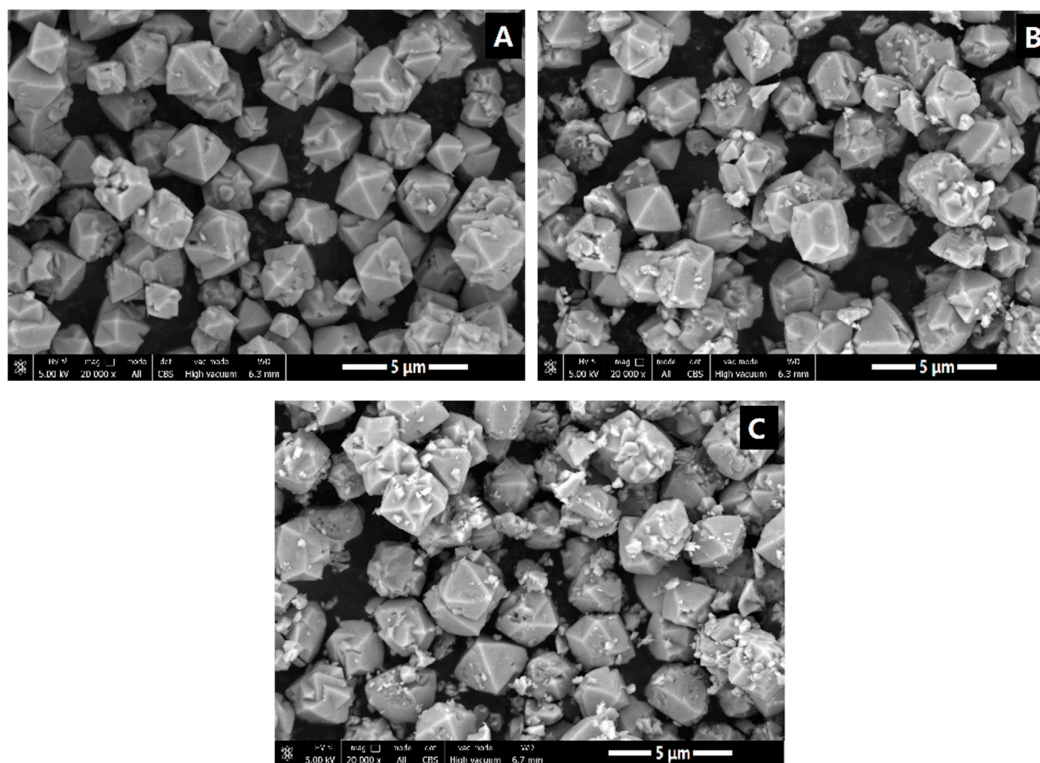


Figure 2. SEM images of catalysts: **(A)** CsX, **(B)** 0.15 Fe/CsX-I, **(C)** 0.15 Fe/CsX-II.

In addition, the energy-dispersive spectroscopy (EDS) mappings of CsX, 0.15 Fe/CsX-I, and 0.15 Fe/CsX-II catalysts are shown in Figure 3, which reveal the homogeneous distribution of Cs and Fe species within the zeolite crystals.

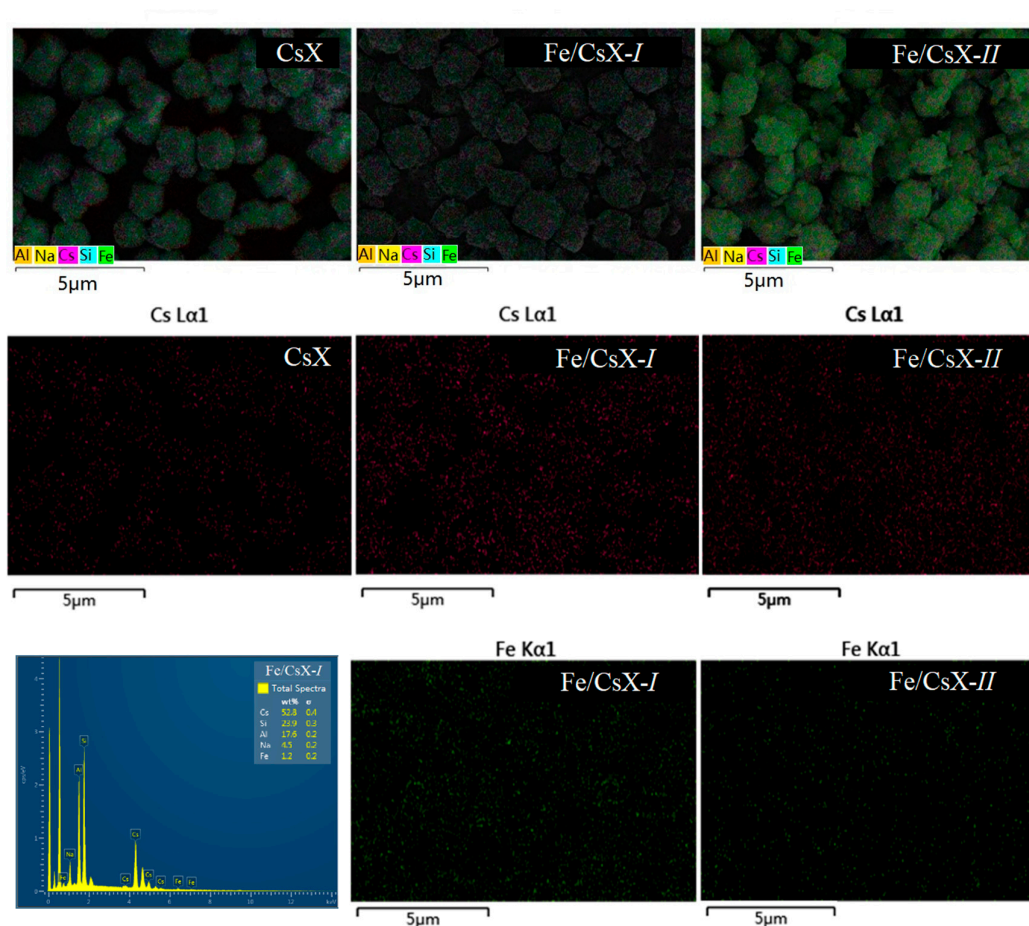


Figure 3. The Cs and Fe element distributions on CsX, 0.15 Fe/CsX-I, and 0.15 Fe/CsX-II derived from the energy-dispersive spectroscopy (EDS) mapping.

The textural parameters of the representative catalysts are listed in Table 2. There is no obvious change in the specific surface areas and the pore parameters between the CsX catalyst and the Fe-modified CsX catalysts due mainly to the relatively low Fe loading. The relatively consistent textural parameters of these catalysts provide further evidence that the crystal structure of X zeolites is maintained after introducing a certain amount of Fe species.

Table 2. The textural parameters of different catalysts. BET—Brunauer–Emmett–Teller.

Catalysts	BET Surface Area (m ² /g)	Micropore Area (m ² /g)	External Surface Area (m ² /g)	Micropore Volume (cm ³ /g)	Total Pore Volume (cm ³ /g)	Average Pore Width (nm)
CsX	324	301	23	0.14	0.17	1.9
0.15 Fe/CsX-I	329	307	22	0.15	0.18	2.0
0.15 Fe/CsX-II	308	282	24	0.13	0.16	1.9

The NH₃-TPD profiles of CsX, 0.15 Fe/CsX-I, and 0.15 Fe/CsX-II are shown in Figure 4A. One major desorption peak of NH₃ at around 210 °C is observed for all the catalysts, which is an indication of the presence of acidic sites with moderate strength. The peak area of NH₃ desorption decreases obviously after the introduction of Fe species. For 0.15 Fe/CsX-I, the peak position shifts slightly toward higher temperatures, indicating the appearance of some new acidic centers related to Fe species. Figure 4B illustrates the CO₂-TPD profiles of the representative catalysts, which shows a broad CO₂ desorption peak at around 200 °C, corresponding to basic centers with intermediate strength. Introducing a small amount of Fe species (0.15 wt.%) results in a decrease in the number of basic sites. Compared with the Fe(NO₃)₃-modified CsX catalyst, a more significant decrease can be

observed on the FeCl_3 -modified CsX catalyst. For the Cs ion-exchanged X catalyst, it is well known that the basic sites are mainly related to the framework oxygen species of X zeolites, as well as the oxygen species of Cs_2O . Our current results suggest that modification of CsX with a certain amount iron salts ($\text{Fe}(\text{NO}_3)_3$ or FeCl_3) could decrease the numbers of both the acidic and basic centers of the catalysts. Such changes should mainly originate from the interaction between the introduced Fe species and the acid–basic sites in the CsX catalyst [21,22].

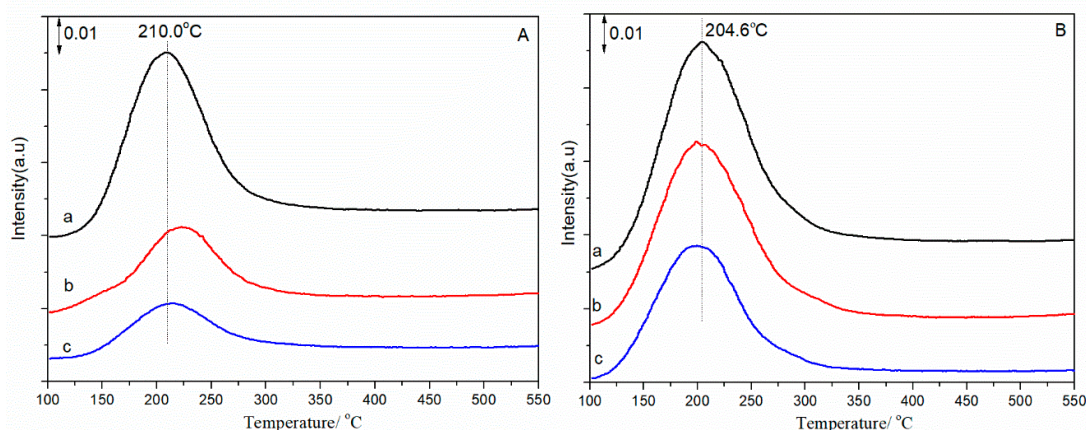


Figure 4. Profiles of (A) NH_3 temperature programmed desorption (TPD) and (B) CO_2 -TPD for catalysts: (a) CsX, (b) 0.15 Fe/CsX-I, (c) 0.15 Fe/CsX-II.

For 0.15 Fe/CsX-II, the obvious decrease in basic sites should be an indication that FeCl_3 has a stronger ability to neutralize or cover more basic sites in the CsX catalyst [21,23]. Previous literature results already revealed that the basic sites of CsX zeolites are the main active sites for the side alkylation reaction of toluene with methanol [15–17,24–26]. Therefore, the significant decrease in catalytic activity of the FeCl_3 -modified CsX should be due mainly to the considerable loss in the number of basic sites.

2.3. The Adsorption and Desorption Behaviors of the Reagents on the Catalysts

In order to understand the main reason for why the two types of Fe-modified catalysts showed different catalytic activity and selectivity in the side-chain alkylation reaction, the adsorption/desorption properties of 0.15 Fe/CsX-I and 0.15 Fe/CsX-II for methanol or toluene were investigated by using in situ FT-IR measurement and TPD mass techniques.

The FT-IR spectra of methanol adsorbed on CsX at 140 °C are shown in Figure 5. The strong band at 1693 cm^{-1} is attributed to the $\text{C}=\text{O}$ stretching vibration of formaldehyde [27]. The sharp band at 1290 cm^{-1} should be also related to formaldehyde, due to its relative intensity being consistent with the signal of 1693 cm^{-1} at different operation conditions. The two bands appearing at 1649 and 1379 cm^{-1} could be assigned to the stretching vibrations of $\text{C}=\text{O}$ and $\text{C}-\text{O}$ in surface-adsorbed unidentate formate [27,28], while the signals at 1609 and 1339 cm^{-1} (weak) are assigned to asymmetric and symmetric $\text{O}-\text{C}-\text{O}$ stretching modes of the adsorbed bidentate formate [27]. Previous literature works revealed that unidentate formate derived from the further activation of formaldehyde is the main active intermediate for the side-chain alkylation reaction, while bidentate formate is an undesirable intermediate, which is mainly related to the formation of CO and H_2 [29].

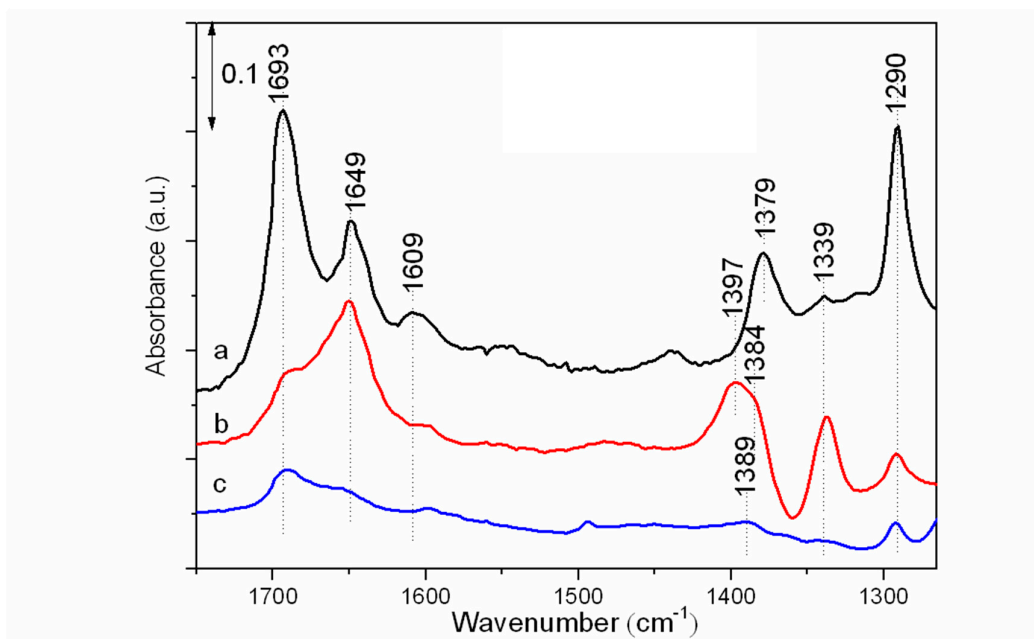


Figure 5. Fourier-transform infrared (FT-IR) spectra of surface species remaining on (a) CsX, (b) 0.15 Fe/CsX-I, and (c) 0.15 Fe/CsX-II after exposure to 1000 Pa methanol at 50 °C for 30 min and subsequent sequential evacuation at 140 °C.

Compared with the CsX catalyst, the FT-IR spectra of the surface-adsorbed species exhibit obvious changes over 0.15 Fe/CsX-I and 0.15 Fe/CsX-II. The intensities of the two bands at 1693 and 1290 cm^{-1} related to formaldehyde decrease significantly in the spectrum of 0.15 Fe/CsX-I. The band at 1650 cm^{-1} ($\nu_{\text{C=O}}$ unidentate formate) is also observed for 0.15 Fe/CsX-I, but the signal of bidentate formate (1609 cm^{-1}) is nearly undetectable. These results suggest that modification of CsX with a small amount of $\text{Fe}(\text{NO}_3)_3$ (i.e., 0.15 wt.% Fe) is favorable for the formation of the unidentate formate, while it can significantly inhibit the formation of bidentate formate.

In the case of 0.15 Fe/CsX-II, the intensities of the bands 1693 and 1290 cm^{-1} are also significantly reduced, indicating that only a small amount of formaldehyde is generated after the adsorption of methanol. Meanwhile, the stretching vibration bands 1649 cm^{-1} and 1609 cm^{-1} are absent in the methanol adsorbed spectrum. These results suggest that the amount of adsorbed formaldehyde, which derives from the activation of methanol, decreases significantly after adding a small amount of FeCl_3 (0.15 wt.% Fe) into the CsX catalyst. Moreover, the formation of formates is also considerably suppressed over the FeCl_3 -modified CsX catalyst.

The methanol TPD profiles over CsX and the Fe-modified CsX catalysts are shown in Figure 6. The gas phase analysis based on a quadrupole mass spectrometer reveals the presence of H_2 , CH_4 , CO, and HCHO during the temperature programmed desorption process of methanol. It can be seen that the gas products start to appear at 314 °C on the CsX catalyst (see Figure 7A). The intensities of CH_4 and HCHO reach the maximum at around 410 °C. The signal of CO_2 starts at 349 °C, showing two maxima peaks at 397 and 511 °C, respectively. The profiles of CO and H_2 also exhibit two maxima peaks at 410 and 520 °C, respectively. These results suggest that at least two kinds of active sites (basic centers) are present on the surface of CsX catalyst, which could participate in the activation of methanol separately. As for 0.15 Fe/CsX-I, the decomposition of methanol starts at about 330 °C, slightly higher than that of CsX. Additionally, the TPD profiles show only one single maximum peak for each product. These results imply that the addition of Fe species could cover or neutralize some stronger basic sites for methanol activation. The concentrations of CH_4 and HCHO reach the maximum at around 426 °C, and gaseous CO_2 is detected with a maximum at 522 °C. The peaks of CO and H_2 appear at 480 °C in the desorption profiles. For the catalyst of 0.15 Fe/CsX-II, gaseous CO and H_2 are detected at around 400 °C, while a CO_2 peak appears at 470 °C. Gas phase analysis results

reveal that 0.15 Fe/CsX-II has a much lower ability for methanol activation compared to CsX and 0.15 Fe/CsX-I catalysts.

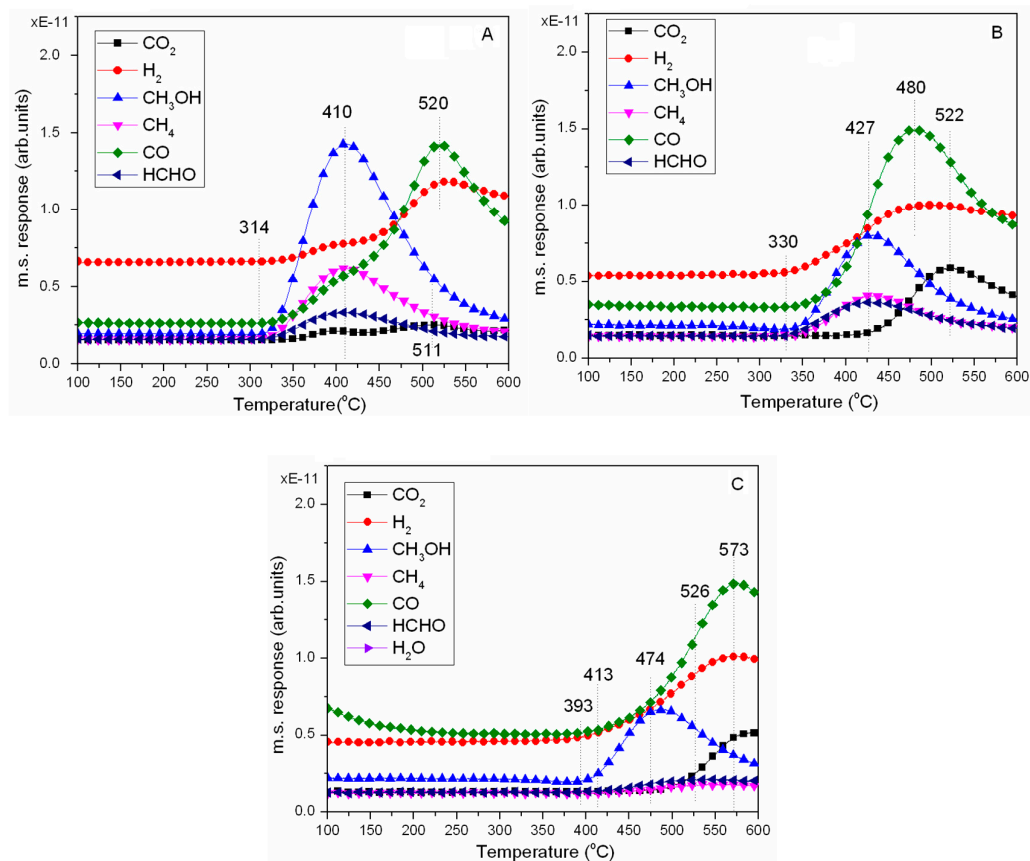


Figure 6. The methanol TPD profiles over various catalysts: (A) CsX, (B) 0.15 Fe/CsX-I, (C) 0.15 FeCsX-II.

For the side-chain alkylation of toluene with methanol, it is believed that the formation of undesirable CO_x (CO and CO_2) is mainly facilitated by the stronger basic sites existing on the CsX catalyst through the following steps: methanol dehydrogenation occurs on the basic sites to intermediately form formaldehyde (HCHO); then, HCHO is transformed to surface formates, which subsequently decompose into H_2 , CO_2 , and CO. Moreover, the further methanization of CO with H_2 is responsible for the formation of CH_4 [30]. In our case, the introduction of $\text{Fe}(\text{NO}_3)_3$ into the CsX catalyst can efficiently inhibit the undesirable decomposition of methanol, while loading with FeCl_3 can significantly suppress the formation of the intermediates like formaldehyde and/or formates.

The FT-IR spectra of the toluene adsorption on various catalysts are compiled in Figure 7. For CsX, the bands observed at 1596 and 1493 cm^{-1} can be assigned to the stretching vibrations of C–C and C=C in surface-adsorbed toluene [31,32]. The two bands at 3047 and 3019 cm^{-1} are related to the C–H stretching vibration bands of the aromatic ring. The peaks appearing at 2915 and 2865 cm^{-1} are attributed to the C–H stretching of the methyl group of toluene [33]. These results suggest that toluene could be physically adsorbed on the surface of CsX catalyst [34]. For the two Fe-modified CsX catalysts, the main signals related to the C–H stretching vibrations of the aromatic ring and the methyl group are quite similar to the CsX catalysts, indicating that the activating ability for toluene does not have obvious changes after introducing a small amount of Fe additives into the CsX catalyst.

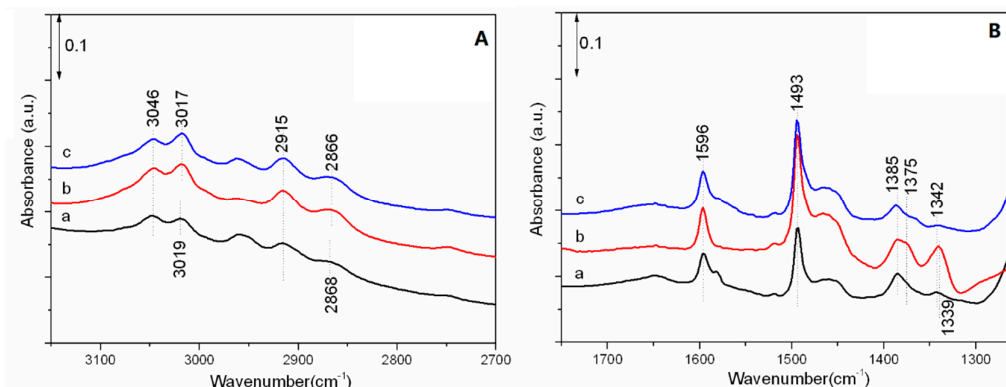


Figure 7. FT-IR spectra of surface species remaining on (a) CsX, (b) 0.15 Fe/CsX-I, and (c) 0.15 Fe/CsX-II after exposure to 1000 Pa toluene at 50 °C for 30 min and subsequent sequential evacuation at 140 °C, (A) Wavenumber range in 3150–2700 cm^{-1} , (B) Wavenumber range in 1750–1250 cm^{-1} .

The temperature programmed desorption of toluene over the catalysts is shown in Figure 8. For all the catalysts, a weak shoulder peak appears at around 108 °C, while the main desorption peak is detected at about 260 °C. Compared with CsX, the main peak shifts slightly toward lower temperatures for 0.15 Fe/CsX-I and 0.15 Fe/CsX-II catalysts. Furthermore, the total amounts of the desorbed toluene follow the order of CsX > 0.15 Fe/CsX-I > 0.15 Fe/CsX-II. These results suggest that the adsorption ability for toluene decreases a little bit after introducing a small amount of Fe species into the CsX catalyst.

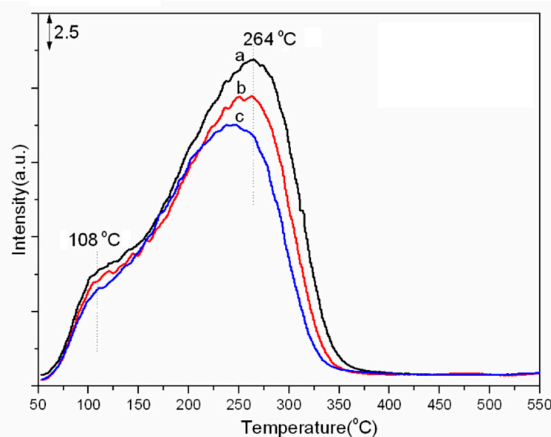


Figure 8. Temperature programmed desorption of toluene over catalysts: (a) CsX, (b) 0.15 Fe/CsX-I, and (c) 0.15 Fe/CsX-II.

3. Discussion

Previous studies revealed that a typical side-chain alkylation catalyst should have basic sites with sufficient strength for achieving the decomposition of methanol to an alkylating agent (like formaldehyde and unidentate formate), and should also have other acidic–basic sites for adsorbing toluene and polarizing its methyl group [8,24,35]. Early works also suggested that the presence of a high density of basic sites in the CsX catalyst is related to the transformation of the unidentate formate to bidentate formate, an unfavorable intermediate to be easily transferred to CO and H_2 , thus decreasing the utilization of methanol and the yield of side-chain products [29]. Such a problem may be solved to some extent by modification of the ion-exchanged CsX catalyst with additives like boron acid, phosphorous acid, or the corresponding salts through adjusting the acidic–basic properties of the catalyst [7,9,19].

In the present work, a variety of characterization results including TPD and FT-IR measurements suggest that the addition of a small amount of $\text{Fe}(\text{NO}_3)_3$ into the CsX catalyst could cover some basic sites of the catalyst, bringing a certain amount of new Lewis acidic sites of FeO_x (derived from the decomposition of $\text{Fe}(\text{NO}_3)_3$). Compared with the unmodified CsX catalyst, the $\text{Fe}(\text{NO}_3)_3$ -modified catalyst shows better capability in activating methanol to generate real alkylation agents or intermediates (i.e., formaldehyde and unidentate formate), and in inhibiting the formation of the unfavorable intermediate of bidentate formate. Therefore, the role of Fe additive in enhancing the catalytic property of CsX catalyst should also be due mainly to it covering some unfavorable stronger basic sites, similar to the previously reported additive of BPO_4 [19]. Additionally, early work reported that the addition of Fe species into Mobil-five (MFI)-type zeolite catalysts may also influence the activation ability of toluene in the alkylation reaction, and the introduced Fe_2O_3 could induce the formation of formate via chemisorption of methanol at temperatures above 400 K [36–38]. Hence, it seems reasonable to propose that the introduced FeO_x (derived from the decomposition of $\text{Fe}(\text{NO}_3)_3$), which uniformly distributed on the surface of CsX catalyst, may also act as an efficient active site to directly participate in the adsorption/activation of methanol and toluene.

It should be mentioned here that, although the catalytic activity of 0.15 Fe/CsX-I is lower than the literature-reported ZrB_2O_5 - or BPO_4 -modified CsX catalysts [9,19], it is still a relatively active catalyst in comparison with other additive-modified CsX catalysts, like $\text{Cs}_2\text{O}/\text{CsX}$ [7], $\text{Na}_2\text{B}_4\text{O}_7/\text{CsX}$ [17], and ZnO/CsX [39], suggesting that $\text{Fe}(\text{NO}_3)_3$ could functionalize as an effective additive to improve the catalytic performance of the ion-exchanged CsX catalyst. A undesirable feature of the $\text{Fe}(\text{NO}_3)_3$ -modified CsX catalyst is that it exhibits relatively low selectivity to styrene, and high selectivity to ethylbenzene. Previous literature results revealed that the reaction of styrene with methanol or hydrogen (decomposed product) is the main pathway to generate ethylbenzene [24,40]. Therefore, the high ethylbenzene selectivity of the $\text{Fe}(\text{NO}_3)_3$ -modified CsX catalyst should be an indication that the introduced Fe species may also enhance the hydrogenation ability of the catalyst. Further work is still required to improve the catalytic activity and styrene selectivity of the Fe-based CsX catalyst, i.e., by introducing a second ingredient, which is currently underway.

4. Materials and Methods

4.1. Catalyst Preparation

The commercial NaX zeolites ($\text{Si}/\text{Al} = 1.5$), purchased from NanKai Catalyst Company, were calcined at 550 °C for 6 h in a muffle furnace before the ion-exchange procedure. The CsX catalysts were typically prepared as follows: NaX zeolites (6 g) were ion-exchanged with 0.2 mol/L (450 mL) aqueous solutions of CsNO_3 (from Alading) to replace the Na^+ with Cs^+ for 2 h at 70 °C. The filtered cake was washed with distilled water three times on a vacuum filter and dried in an oven at 100 °C overnight. The resulting samples were then calcined at 600 °C (heating rate of 2 °C/min) for 4 h in flowing air to get Cs ion-exchanged X zeolites (CsX).

Iron-modified CsX catalysts were prepared by incipient wetness impregnation with an aqueous solution of $\text{Fe}(\text{NO}_3)_3$ or FeCl_3 . The contents of Fe were adjusted by changing the concentration of the Fe salt aqueous solution. After impregnation, the resultant catalysts were dried at 100 °C and subsequently calcined at 600 °C in air for 4 h. The iron-modified catalysts were designated as nFe/CsX-I and nFe/CsX-II, where n refers to the wt.% of iron in the catalysts, and I and II indicate the iron sources of $\text{Fe}(\text{NO}_3)_3$ and FeCl_3 , respectively.

4.2. Catalytic Experiments

The catalytic reactions were carried out in a quartz fixed-bed reactor (8 mm inner diameter (ID)) under atmospheric pressure. About 0.5 g of catalyst (40–60 mesh) was packed into the constant temperature zone. Before the reaction, the catalysts were activated at 450 °C with a heating rate of 10 °C/min for 2 h in a stream of air (30 mL/min), and then cooled down to 435 °C. A liquid mixture of toluene and methanol (molar ratio 3/1) was pumped at a rate of 1.2 mL/h in a flowing N_2 stream (20

mL/min). The products were analyzed by a gas chromatograph (BF3420A) connected to a free fatty acid phase (FFAP) capillary column.

4.3. Characterization of Catalyst

Brunauer–Emmett–Teller (BET) surface areas and pore volumes of the samples were measured by N₂ adsorption at −196 °C using a Micromeritics ASAP 2010N analyzer (Micromeritics instrument Ltd. Shanghai, China). The samples were pretreated under a vacuum at 250 °C for 12 h prior to the measurement. The temperature programmed desorption (TPD) of CO₂ and NH₃ was used to determine the properties of base and acid. The fresh sample (50 mg, 40–60 mesh) was calcined at 550 °C for 1 h in He flow, then cooled down to 100 °C in order to adsorb CO₂ or NH₃ for 0.5 h. After the excess CO₂ or NH₃ was removed by flowing He for 1 h at 100 °C, the temperature programmed desorption was carried out at a rate of 10 °C/min in He (30 mL/min), and the desorbed CO₂ or NH₃ was monitored online by a thermal conductivity detector (Micromeritics instrument Ltd. Shanghai, China). The toluene TPD was also obtained using the abovementioned method. Methanol decomposition and desorption were monitored by a quadrupole mass spectrometer (Omni Star™, Pfeiffer Vacuum Co., Ltd. Shanghai, China). TPD and thermal evolution profiles were recorded by monitoring the intensity of different *m/e* fragments as a function of temperature. The crystal structures of samples were characterized on a Shimadzu XRD-6000 diffractometer (40 kV and 30 mA) (Shimadzu Global Laboratory Consumables Co., Ltd., Shanghai, China) using Ni-filtered Cu K α radiation. Scanning electron microscope (SEM) images and EDS mapping were measured with a Hitachi X-65.

The adsorption/activation behaviors of methanol, toluene, or the mixture of toluene/methanol (molar ratio of 3/1) were studied by using an in situ Fourier-transform infrared (FT-IR) spectrometer (Thermo Scientific Nicolet™ 6700, Thermo Electron Instruments Co., Shanghai, China). The catalyst powder was pressed into a thin self-supporting wafer (~15 mg, and 13 mm diameter) and placed in the infrared cell equipped with a CaF₂ window, which was attached to a vacuum system. Before the measurement, the samples were evacuated under vacuum at 300 °C for 1 h and cooled down to 50 °C. Subsequently, the samples were exposed to reactants (10 mbar) until equilibration for adsorption at 50 °C, and then desorbed under vacuum at 140 °C for 30 min. The corresponding FT-IR spectra were recorded upon decreasing the temperature to 50 °C again.

5. Conclusions

In the present study, the side-chain alkylation of toluene with methanol was investigated over two kinds of iron-modified CsX catalysts. Modification with appropriate amounts of FeO_x (derived from Fe(NO₃)₃) has a positive effect on improving the catalytic activity of the CsX catalyst. The introduced FeO_x could cover some unfavorable basic sites, thus inhibiting the generation of undesirable bidentate formate. Furthermore, the surface dispersed FeO_x species may also act as new Lewis acidic sites to participate in the adsorption/activation of toluene, and to stabilize the alkylation intermediate of unidentate formate, finally resulting in an improvement of the catalytic activity of the CsX catalyst for the side-chain alkylation reaction.

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