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Pathway to Ethylbenzene Formation in Side-Chain Alkylation of Toluene with Methanol Over Cesium Ion-Exchanged Zeolite X

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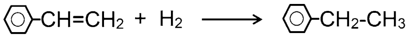
Abstract To control the styrene to ethylbenzene ratio in the products of side-chain alkylation of toluene with methanol over Cs-X-based catalysts, pathway to ethylbenzene was examined. Styrene underwent transfer hydrogenation with methanol much faster than hydrogenation with hydrogen to ethylbenzene. Addition of Cs_2O and ZrB_2O_5 to Cs-X enhanced and suppressed, respectively, the transfer hydrogenation.

Keywords Ethylbenzene · Styrene · Methanol · Toluene · Transfer hydrogenation · Side-chain alkylation

1 Introduction

Selectivity in alkylation of toluene with methanol is determined by acid–base properties of the catalyst. While ring alkylation takes place over acidic catalysts to xylenes, side-chain alkylation takes place over basic catalysts to styrene and ethylbenzene. It is widely accepted that the formation of styrene in the side-chain alkylation over basic catalyst results from dehydrogenation of methanol to formaldehyde which undergoes aldol-type condensation with toluene to form styrene [1, 2]. In addition to styrene, significant quantities of ethylbenzene are also produced in all the results reported so far. However, the pathway of the ethylbenzene formation has not been extensively studied. Elucidation of the pathway to ethylbenzene is important in controlling the styrene/ethylbenzene ratio in the products in side-chain alkylation of toluene with methanol. The formation of ethylbenzene is undesirable for an industrial purpose.

The pathways to ethylbenzene proposed so far are (1) hydrogenation of styrene, (2) direct methylation of toluene with methanol, (3) hydrogenolysis of 2-phenylethanol which is formed by aldol-type addition of toluene to formaldehyde, and (4) transfer hydrogenation of styrene with methanol as shown below.



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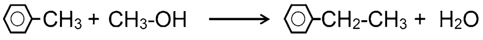

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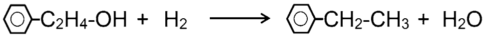

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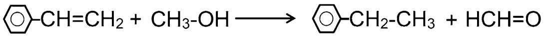

(4)

The pathway (1) was first proposed by Sidorenko et al. [1], and later supported by Yashima et al. [2] on the basis of the experimental observation that the selectivity for styrene was reduced in a hydrogen stream as compared to

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that in a nitrogen stream over Rb-X and K-X. The H_2 used for the hydrogenation of styrene originated from decomposition of methanol to acetaldehyde and CO. Decrease in styrene production in an H_2 stream was also observed for Cs-X modified with Cu and B [3]. This pathway has been often cited [4–9], though the evidences to support this pathway were not presented.

The pathway (2) was also proposed by Yashima et al. [2] to explain the observation that the ethylbenzene/styrene ratio was higher when methanol was used as an alkylating reagent than when formaldehyde was used. They claimed that when methanol is used, the direct methylation of toluene with methanol might occur in addition to the aldol-type condensation to increase the ethylbenzene/styrene ratio in the products.

The pathway (3) was proposed by Sooknoi and Dwyer [9] as one of the possible pathways to styrene without experimental support.

The pathway (4) was proposed by Garces et al. [10]. They reported that styrene was readily hydrogenated with methanol, but only minor amount of ethylbenzene was produced with hydrogen over Cs ion-exchanged X and carbon modified with Cs and B [10]. However, no experimental data were given. Although this pathway has not been taken into account in most of the references on the side-chain alkylation, this pathway should be examined as a possible one since transfer hydrogenation with alcohols is frequently observed over solid base catalysts. In the transfer hydrogenation with alcohols, alcohols transfer their two hydrogen atoms to other molecules such as olefins, ketones and nitriles, and the alcohols convert into aldehydes or ketones [11].

In the present study, the pathway to ethylbenzene was examined by carrying out the following reactions (a), (b) and (c).

(a) The hydrogenation of styrene with hydrogen and with methanol.
(b) Toluene side-chain alkylation in a nitrogen stream and in a hydrogen stream.
(c) Toluene side-chain alkylation with different toluene/methanol ratio.

Based on the results, it is concluded that ethylbenzene is mainly formed through the transfer hydrogenation of styrene with methanol, though hydrogenation of styrene with hydrogen occurs to a smaller extent.

2 Experimental

2.1 Preparation of Catalysts

The base catalyst of cesium ion-exchanged X (Cs-X) was prepared from NaX (Junsei Chemicals, Japan) by ion-exchanged with Cs^+ ions as described in our preceding paper [12]. Cesium hydroxide was used as a source of Cs^+ according to Engelhardt et al. [6]. The NaX has Si/Al ratio of 1.24 and surface area of 527 m^2 g^{-1}. Into an aqueous solution of cesium hydroxide (75 ml, 0.5 *M*), NaX (15 g) was immersed, stirred for 5 min and stand for ca. 8 h. The slurry was filtered with Buchner funnel. The filtered cake was again immersed in the aqueous solution of cesium hydroxide, stirred and stood for ca. 8 h. The immersion and filtration procedures were repeated two more times (total 4 times). The resulting slurry was filtered and rinsed with a 75 ml of the aqueous solution of cesium hydroxide. The resulting filtered cake was immersed in a deionized water (100 ml) followed by filtering and washing with a small amount of water (20 ml) to minimize the back ion-exchange of Cs^+ with H^+ during washing with water. The filtered cake was dried in an oven at 353 K and calcined at 753 K for 3 h in air. The ion exchange percent was 54 %. BET surface area was 373 m^2 g^{-1}.

The catalyst that occludes Cs_2O in the pores of Cs-X was prepared by impregnation of the Cs-X with cesium hydroxide aqueous solution by incipient wetness. The content of Cs_2O occluded in the pores other than ion exchanged Cs^+ ions was 4.1 wt% Cs_2O which is equivalent to 0.6 Cs atom per super cage. The catalyst was denoted as Cs_2O/Cs-X. BET surface area of Cs_2O/Cs-X was 308 m^2 g^{-1}.

The Cs-X modified with zirconium borate (ZrB_2O_5) was prepared by grinding a mixture containing the Cs-X and ZrB_2O_5 with mortar for 30 min in a dry state [12]. A ground mixture was calcined with a slow ramp rate of 2 K min^{-1} at 773 K for 3 h. The wt% of ZrB_2O_5 was 10 wt%. The catalyst was denoted as ZrB/Cs-X. Zirconium borate was prepared according to Knyrim et al. [13] from aqueous solutions of disodiumtetraborate and zirconium nitrate. The precipitate was washed with water, dried and calcined at 623 K in air. BET surface area of ZrB/Cs-X was 286 m^2 g^{-1}.

2.2 Reaction Procedures

A flow type reactor (Model # 401C-0286, Autoclave Engineers) was employed for carrying out three types of reactions; toluene side-chain alkylation with methanol, hydrogenation of styrene with hydrogen, and transfer hydrogenation of styrene with methanol. A catalyst sample (400 mg) was placed in the reactor and pretreated in a nitrogen stream at 723 K for 1 h prior to the reaction.

For the side-chain alkylation, a mixture containing toluene and methanol in 6:1 molar ratio was fed at the rate of 0.12 ml min^{-1} into a nitrogen or hydrogen flowing at 40 ml min^{-1} (STP). The partial pressures of nitrogen, toluene (or hydrogen) and methanol were 378, 326 and 55 Torr (1 Torr = 133.3 Pa), respectively. For some experiments, a mixture containing toluene and methanol in 1:1 molar ratio was used, where the partial pressures of N_2, toluene and methanol were 324, 218 and 218 Torr, respectively.

Hydrogenation of styrene was carried out using different hydrogenating agents; hydrogen and methanol. For the hydrogenation of styrene with hydrogen, a benzene solution containing 5 mol% styrene was fed at the rate of 0.12 ml min^{-1} into a hydrogen carrier flowing at 40 ml min^{-1} (STP). The partial pressures of hydrogen, benzene and styrene were 392, 368 and 20 Torr, respectively. For the hydrogenation of styrene with methanol (transfer hydrogenation), a mixture containing styrene (4.3 mol%), methanol (17 mol%) and benzene (78.7 mol%) was fed at the rate of 0.12 ml min^{-1} into an N_2 carrier flowing at 40 ml min^{-1} (STP). The partial pressures of nitrogen, benzene, methanol and styrene were 348, 324, 70 and 18 Torr, respectively. The products were analyzed by on-line gas chromatography. All the reactions were carried out at 683 K.

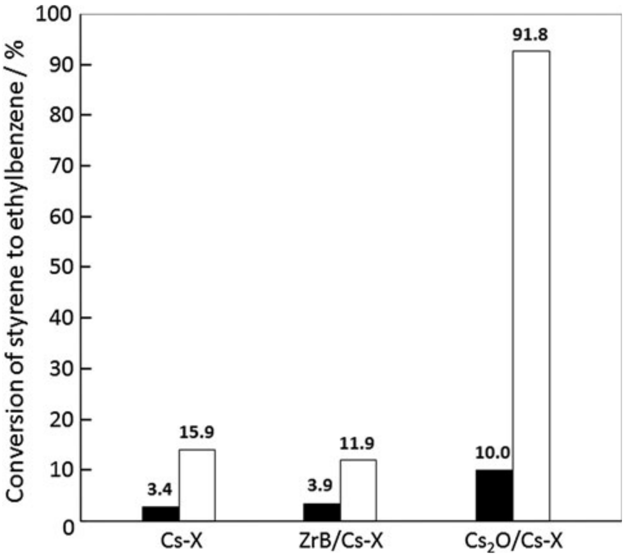

Fig. 1 Conversions of styrene to ethylbenzene in hydrogenation with H_2 (*filled square*) and in transfer hydrogenation with methanol (*unfilled square*) over Cs-X, ZrB/Cs-X and Cs_2O/Cs-X

3 Results

3.1 Reactions of Styrene with Hydrogen and with Methanol

In the reaction of styrene with hydrogen or methanol, only ethylbenzene was formed, no other products being detected. Since cyclohexane and cyclohexene were not produced, hydrogenation of diluent benzene did not occur. Formaldehyde, CO and hydrogen which might be formed as products of transfer hydrogenation by methanol and the following decomposition could not be detected by gas chromatography.

Figure 1 shows the conversions of styrene in the hydrogenation with hydrogen and the transfer hydrogenation with methanol over Cs-X, ZrB/Cs-X and Cs_2O/Cs-X. The data plotted were taken at a time on stream of 90 min. For all catalysts, the transfer hydrogenation proceeded faster than the hydrogenation. In particular, Cs_2O/Cs-X exhibited a high activity for the transfer hydrogenation, the formation of ethylbenzene being almost saturated (91.8 %). The hydrogenation of styrene was slow, but was not so slow as to be excluded from the reaction mechanisms of the side-chain alkylation.

Addition of ZrB_2O_5 to Cs-X suppressed the transfer hydrogenation to a significant extent (15.9–11.9 %) but increased the hydrogenation to a small extent (3.4–3.9 %). On the other hand, addition of Cs_2O to Cs-X caused an increase in activity for both the hydrogenation and the transfer hydrogenation. In particular, an increase in the transfer hydrogenation was large.

3.2 Side-Chain Alkylation of Toluene with Methanol in Nitrogen and in Hydrogen

Table 1 shows the results of the reaction of toluene with methanol in nitrogen and in hydrogen over Cs-X and Cs_2O/Cs-X. For all catalysts, the toluene conversion did not change much, and the ethylbenzene selectivity decreased. The increase in the ethylbenzene selectivity indicated that hydrogenation of styrene with hydrogen was taking place in the reaction in hydrogen.

The last column in Table 1 lists the methanol conversion. As already reported in the preceding paper [12], methanol consumed in the reaction exceeded the toluene converted, indicating that methanol decomposition to CO and hydrogen occurred to a considerable extent.

3.3 Effects of Toluene to Methanol Ratio on the Styrene Selectivity in Side-Chain Alkylation

The toluene/methanol mole ratio exerted significant effect on both the activity and the ethylbenzene selectivity. The results of the reactions carried out with different toluene/methanol mole ratios over Cs-X and Cs_2O/Cs-X in nitrogen are given in Table 1 (entry 1 and 5 for Cs-X, and entry 3 and 6 for Cs_2O/Cs-X). As the toluene/methanol ratio decreased from 6/1 to 1/1, the ethylbenzene selectivity increased both for Cs-X (from 19.9 to 28.6 %) and for Cs_2O/Cs-X (87.8 to 90.2 %). At the same time, the toluene conversion increased by about twice for both Cs-X and Cs_2O/Cs-X (from 1.1 to 2.7 % and 3.3–7.4 %, respectively).

Table 1 Results of side-chain alkylation of toluene with methanol in H_2 and in N_2

Catalyst	Carrier gas	Tol/MeOH	Tol_{conv} (%)	EB_{select} (%)	$MeOH_{conv}$(%)
Cs-X	N_2	6/1	1.0	19.9	36.3
Cs-X	H_2	6/1	1.2	26.2	40.5
Cs_2O/Cs-X	N_2	6/1	3.3	87.8	74.2
Cs_2O/Cs-X	H_2	6/1	3.0	91.8	74.0
Cs-X	N_2	1/1	2.7	28.6	36.4
Cs_2O/Cs-X	N_2	1/1	7.4	90.2	45.0

Tol/MeOH molar ratio of toluene to methanol in reactant, Tol_{conv} toluene conversion, EB_{select} ethylbenzene selectivity = [ethylbenzene]/[ethylbenzene + styrene] × 100, $MeOH_{conv}$ methanol conversion

4 Discussion

All the results obtained in the present study strongly suggest that the formation of ehylbenzene in the side-chain alkylation of toluene with methanol results mainly from the transfer hydrogenation of styrene with methanol. Although the hydrogenation of styrene with H_2 could not be excluded, its contribution to ethylbenzene formation is small as compared to the transfer hydrogenation with methanol.

As shown in Fig. 1, the transfer hydrogenation of styrene with methanol proceeded faster than the hydrogenation of styrene with hydrogen. This result coincides with what Garces et al. [10] described for Cs ion exchanged zeolite X and carbon containing Cs and B, though they did not present the data. The rates of the transfer hydrogenation with methanol and the hydrogenation with hydrogen varied with the type of catalyst. The rate of the transfer hydrogenation was particularly high for Cs_2O/Cs-X. The high ethylbenzene selectivity observed over Cs_2O/Cs-X in the side-chain alkylation of toluene with methanol is suggested to be due to the fast transfer hydrogenation of styrene with methanol.

The results shown in Fig. 1 were obtained under a methanol partial pressure of 70 Torr for the hydrogen transfer, and a hydrogen partial pressure of 392 Torr for the hydrogenation. In the side-chain alkylation of toluene with methanol (toluene/methanol = 6/1) in a nitrogen stream, the partial pressures of methanol and hydrogen were 55 and less than 103 Torr, respectively. The value 103 Torr was calculated on the assumption that all methanol converted to CO and hydrogen. The actual hydrogen pressure in the side-chain alkylation should be less than 103 Torr, and was much smaller than that used in the hydrogenation of styrene. Therefore, the ratio of the hydrogenation to the transfer hydrogenation in the side-chain alkylation should be smaller than those for the reactions from which the data shown in Fig. 1 were obtained.

As the toluene/methanol ratio in the reaction mixture decreased from 6/1 to 1/1, the ethylbenzene selectivity increased for both Cs-X and Cs_2O/Cs-X. The effect of the toluene/methanol ratio on the styrene selectivity can be understood if the formation of ethylbenzene is mainly through the transfer hydrogenation with methanol. The partial pressure of methanol was higher in the reaction with 1/1 toluene/methanol mixture (218 Torr) than with 6/1 mixture (55 Torr). Increase in the methanol partial pressure would facilitate the transfer hydrogenation of styrene with methanol, resulting in an increase in the formation of ethylbenzene. The observed results suggest that the transfer hydrogenation with methanol is the main pathway to ethylbenzene in the side-chain alkylation. The higher styrene selectivity for higher toluene/methanol ratio was also reported for Rb-X [2].

An increase in the ethylbenzene selectivity in the reaction of toluene with methanol under a hydrogen stream was reported by Yashima et al. [2] and Lacroix et al. [3]. On the basis of the results, Yashima et al. proposed that ethylbenzene was produced primarily by the hydrogenation of styrene with the hydrogen formed from decomposition of methanol. Since then, the hydrogenation of styrene with hydrogen has been most frequently cited as a main route to ethylbenzene formation. In the present study too, the increase in the ethylbenzene selectivity was observed under a hydrogen stream. Contribution of the hydrogenation of styrene with hydrogen to the ethylbenzene formation should exist. The contribution, however, is estimated to be small as compared to that of the transfer hydrogenation with methanol because the hydrogenation of styrene with hydrogen is slow as compared with the transfer hydrogenation with methanol.

The possibility of direct methylation of toluene to ethylbenzene seems to be low. The direct methylation was proposed by Yashima et al. [2] as one of the possible ways to explain the observation that the ethylbenzene/styrene ratio was higher when methanol was used as an alkylating reagent than when formaldehyde was used. The possible mechanism for the direct methylation would involve the reaction of benzyl anions formed from toluene with methyl cations formed from methanol. If methyl cations were formed, the ring methylation of toluene would have occurred to form xylene isomers. The formation of xylene isomers was not observed. Accordingly, the direct methylation is not plausible over Cs-X based catalysts. The high ethylbenzene/styrene ratio observed when methanol was used as an alkylating agent can be explained by the occurrence of the transfer hydrogenation of styrene with methanol.

Addition of Cs_2O to Cs-X caused an increase in the toluene conversion and the ethylene selectivity, which was also reported by Lacroix et al. [3], Engelhardt et al. [6] and Hathaway and Davis [14]. In the present study, it was shown that the activity for the transfer hydrogenation of styrene with methanol was markedly increased by the addition of Cs_2O to Cs-X as shown in Fig. 1. It is suggested that a high ethylbenzene selectivity (low styrene selectivity) in the side-chain alkylation results from a high activity of Cs_2O/Cs-X for the transfer hydrogenation. As addition of Cs_2O to Cs-X was reported to result in the increase in the strength of basic sites [15], the increase in the transfer hydrogenation is likely to result from the increase in the basic strength.

Effects of the addition of B components to the catalyst on the activity for side-chain alkylation have been reported in both literature and patents [16–19]. It was reported that addition of B to catalyst suppressed the decomposition of methanol, and, therefore, increased the total yield of styrene and ethylbenzene [18, 19]. In our previous paper, we reported that ZrB_2O_5 was the best additive in increasing the activity and the styrene selectivity [12]. In the present study, we observed that the conversions of styrene to ethylbenzene in the transfer hydrogenation of styrene with methanol were 15.9 % over Cs-X and 11.9 % over ZrB/Cs-X. The addition of ZrB_2O_5 to Cs-X suppressed the transfer hydrogenation of styrene with methanol, which resulted in the high styrene selectivity in the side-chain alkylation of toluene with methanol, though the reason of the suppression effect of ZrB_2O_5 addition is not clear at present.

5 Conclusions

1. Ethylbenzene is mainly formed through the transfer hydrogenation of styrene with methanol in the side-chain alkylation of toluene with methanol over Cs-X based catalysts; the contribution of the hydrogenation of styrene with hydrogen to ethybenzene formation is small.
2. The addition of Cs_2O to Cs-X enhances the activity for the transfer hydrogenation of styrene with methanol, which results in a high ethylbenzene selectivity in the side-chain alkylation.
3. The addition of zirconium borate to Cs-X suppresses the transfer hydrogenation of styrene with methanol.

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