Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Modification of Cs-X for styrene production by side-chain alkylation of toluene with methanol



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ARTICLE INFO

Article history: Received 11 May 2013 Received in revised form 29 July 2013 Accepted 3 August 2013 Available online 31 August 2013

Keywords: Toluene Methanol Styrene Ethylbenzene Cesium oxide-loaded cesium ion-exchanged zeolite (Cs₂O/Cs-X) Zirconium borate

ABSTRACT

Effects of modification of cesium ion-exchanged zeolite X (Cs-X) with Cs₂O and zirconium borate (ZrB₂O₅) on the catalytic activity in the side-chain alkylation of toluene to styrene and ethylbenzene were studied to prepare an effective catalyst for styrene production. The toluene conversion to styrene and ethylbenzene increased but the selectivity to styrene decreased on modification of Cs-X with Cs₂O. For the toluene conversion, the optimum loading of Cs₂O was in the range ca. 1–5 wt%. Modification of Cs₂O/Cs-X with ZrB₂O₅ increased both toluene conversion and styrene selectivity. Characterization of acidic and basic properties by IR spectroscopy of adsorbed pyridine and CO₂ indicated that basic properties were markedly enhanced but acidic properties were not changed by modification of Cs-X with Cs₂O. It is suggested that the enhancement of toluene conversion by modification with Cs₂O is due to the generation of strong basic sites which promote the activation of toluene by an abstraction of a proton from methyl group. Modification with ZrB_2O_5 facilitates the formation of formaldehyde to increase the toluene conversion and suppresses the transfer hydrogenation of styrene with methanol, the main pathway to ethylbenzene, to increase the styrene selectivity.

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1. Introduction

Alkylation of toluene with methanol yields xylenes over acidic catalysts and styrene and ethylbenzene over basic catalysts. The former reaction is utilized for production of xylene isomers. The later reaction has been known since 1967 when Sidorenko et al. reported that K and Rb ion-exchanged zeolite X (K-X and Rb-X, respectively) catalyzed the reaction to produced styrene and ethylbenzene [1]. Recently, the side-chain alkylation of toluene with methanol has drawn attention since the reaction might be utilized for styrene production which is currently undertaken by alkylation of benzene with ethylene to ethylbenzene followed by dehydrogenation [2].

Soon after the report by Sidorenko et al., Yashima et al. studied the reaction in detail and reported that Rb-X and Cs-X were efficient catalysts as compared to other alkali ion-exchanged zeolite X and Y [3]. They also supported the reaction pathway proposed by Sidorenko et al. that methanol is first dehydrogenated to formaldehyde which undergoes aldol-type condensation with toluene to produce styrene. This mechanism is widely accepted [4-10]. Ethylbenzene produced simultaneously with styrene is suggested to result from hydrogenation of styrene [3,9,11].

Two functions are required for the catalyst active for the sidechain alkylation; dehydrogenation of methanol to formaldehyde and activation of the methyl group of toluene probably by abstraction of an H⁺. Both functions are related to the basic sites of the catalyst. It was suggested that the dehydrogenation of methanol might proceed on less basic sites and the activation of toluene might proceed on more strongly basic sites [9].

In order to enhance the activity of Cs-X, different kinds of modifications have been attempted on Cs-X. Different kinds of metal components were added to Cs-X. Cu and Ag were reported to be effective metal components [11]. Besides the metal components, promoting effects of addition of B and P on the activity were reported in literature [10,12] and patents [13–15]. In our preceding paper, we have reported that addition of metal borates, in particular zirconium borate (ZrB₂O₅), enhanced the activity of Cs-X as well as the selectivity to styrene [16].

Since the side-chain alkylation of toluene involves basic sites, modification of basic properties is expected to alter the catalytic activity. It was reported that impregnation of Cs-X with Cs compound to add Cs ions in excess of the ion-exchanged capacity increased the basic properties of Cs-X [6,17–19]. The resulting



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^{0920-5861/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.cattod.2013.08.004

catalysts, Cs₂O/Cs-X, showed higher activity than Cs-X for many base-catalyzed reactions such as 2-propanol dehydrogenation [20], 1-butene isomerization [19,21–23], and Knoevenagel condensation [24–26]. It is interesting to see how the addition of Cs₂O to Cs-X affects the catalytic properties in the side-chain alkylation of toluene.

The catalytic activities of $Cs_2O/Cs-X$ for side-chain alkylation of toluene with methanol were reported by Lacroix et al. [11], Engelhardt et al. [27] and Hathaway and Davis [6]. All of them reported that the toluene conversion and selectivity to ethylbenzene were increased by addition of Cs_2O to Cs-X. However, they examined only a limited number of catalysts; no systematic study has been reported to elucidate optimum loading of Cs_2O .

In the present study, $Cs_2O/Cs-X$ catalysts with different loadings of Cs_2O were prepared to examine their catalytic behaviors in side-chain alkylation of toluene together with basic properties. Increased toluene conversion was obtained with the catalyst loaded with Cs_2O loading in a range ca. 1–4 wt%. An increase in the activity seems to result from generation of strong basic sites by modification with Cs_2O . Modification of $Cs_2O/Cs-X$ with ZrB_2O_5 further enhanced the toluene conversion as well as styrene selectivity; 10 wt% ZrB_2O_5 being the optimum amount of addition for activity and 15 wt% or more for styrene selectivity.

2. Experimental methods

2.1. Catalyst preparation

The Na-X (Junsei Chemical Co., Si/Al = 1.24) was ion-exchanged with Cs⁺ to prepare Cs-X. CsOH was used as a source of Cs⁺ according to Engelhardt et al. [27]. Into an aqueous solution of CsOH (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 an aqueous solution of the CsOH (75 ml, 0.5 M), stirred and stand for ca. 8 h. The immersion and filtration procedures were repeated two more time (total 4 times). The resulting slurry was filtered. To minimize the ion-exchange of Cs⁺ with H⁺ during washing with water, the resulting cake was immersed in 100 ml water and filtered. The filtered cake was dried in an oven at 353 K and calcined at 753 K for 3 h in air.

Cs-X containing Cs in excess of ion exchange capacity (Cs₂O/Cs-X) was prepared by incipient wetness impregnation of Cs-X with CsOH aq. solution. The loading of Cs₂O was adjusted by the concentration of CsOH aq. solution. After impregnation, the catalysts were dried at 353 K and calcined at 773 K for 3 h in air. The catalysts were designated as Cs₂O(*D*)/Cs-X, where *D* referred to the weight % of Cs₂O in the catalyst.

The Cs-X's modified with ZrB_2O_5 were prepared by grinding a mixture containing the Cs-X and ZrB_2O_5 borate with a mortar for 30 min in a dry state [28]. A ground mixture was calcined with a slow ramp rate of 2 K/min at 773 K for 3 h. ZrB_2O_5 was prepared from aqueous solutions of disodiumtetraborate and zirconium nitrate according to Knyrim et al. [29]. The precipitate was washed with water, dried and calcined at 623 K in air. The Cs-X's modified with ZrB_2O_5 were designated as $ZrB(E) Cs_2O(D)/Cs-X$, where *E* referred to the weight % of ZrB_2O_5 .

2.2. Reaction procedures

A fixed bed continuous flow reactor system (Model # 401C-0286, Autoclave Engineers) was employed for carrying out the reaction. The catalyst sample (400 mg) was pretreated in a flowing N₂ at 723 K for 2 h, then cooled to a reaction temperature of 683 K. A mixture containing toluene and methanol in 6/1 mole ratio was fed at 0.12 ml/min into an N₂ flowing at 40 ml/min (STP). The products

were analyzed with online gas chromatograph equipped with a WCOT fused silica capillary column coated with squalane (Varian, Cat. # CP7520, length: 100 m, ID: 0.25 mm) and FID detector. The products were identified by comparison with authentic samples. Because of FID detector, H_2 , CO and H_2O could not be analyzed by gas chromatography.

The activity was expressed by the conversion of toluene defined by

Conversion of toluene (%) =
$$\left\{\frac{1 - [\text{toluene outlet}]}{[\text{toluene inlet}]}\right\} \times 100\%$$

The styrene selectivity was defined by

Styrene selectivity (%) =
$$\left\{ \frac{[\text{styrene}]}{[\text{styrene}] + [\text{toluene}]} \right\} \times 100\%$$

For the hydrogenation of styrene with hydrogen, a benzene solution containing 5 mol% styrene was fed at the rate of 0.12 ml/min into a hydrogen carrier flowing at 40 ml/min (STP). 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 into an N₂ carrier flowing at 40 ml/min (STP). The amount of catalyst and the reaction temperature were the same as those for the side-chain alkylation, 400 mg and 683 K, respectively.

2.3. Characterization

IR spectra of adsorbed CO_2 and pyridine were measured with in situ IR cell with CaF_2 windows. Samples were pressed into a thin wafer (\sim 50 mg/20 mm dia) and placed in the cell which was connected to a vacuum system. The samples were pretreated at 723 K for 2 h in a vacuum prior to exposure to the adsorbate. All spectra were measured at room temperature.

Powder XRD patters were measured with Rigaku Miniflix II XRD powder diffraction system, Cu-K $_{\alpha}$ being used as a radiation source at 30 kV and 15 mA.

SEM images were measured with a JEOL JSM-5800 scanning microscope. Magnification was 5000. Before taking SEM photographs, the samples were loaded on sample holder, held with conductive aluminum tape and coated with a film of gold in vacuo with Cressington sputter ion-coater for 20 s with 15 mA current.

Surface areas were measured by N_2 adsorption at 77 K, the BET equation being adopted to calculate the surface areas. Samples were pretreated at 573 K in a vacuum prior to the measurement.

3. Results and discussion

3.1. Morphology and acid-base properties of modified Cs-X

3.1.1. BET

The BET surface areas of the catalysts are listed in Table 1. Since the weight of the zeolite unit cell increased by ionexchange of Na with Cs and addition of other components, the normalized surface areas as defined below were calculated and included in Table 1.Normalized surface area = $(\underline{\text{measured surface area}}) \times (\underline{\text{unit cell weight of Zeolite X containing Cs and borate}})}_{\text{unit cell weight of Na-X}}$

The normalized surface areas decreased with the loading of Cs_2O , in particular, for the sample containing 7.8 wt% Cs_2O . However, crystalline structure was retained for Cs_2O loaded Cs-X by XRD measurements (not shown). It was reported on the basis of ¹³³Cs and ²³Na MAS NMR study that all Cs species added to Cs-X were occluded in the zeolite cavities in the form of Cs_2O for the catalysts containing less than 2.9 Cs atoms per supercage (14.9 wt% Cs_2O), while parts of Cs_2O were located on the outer surface of the zeolite crystals for the catalysts containing more than 5.1 Cs atoms

Table 1	
Surface areas of catalysts	s.

Catalyst	Cs ₂ O wt%	ZrB ₂ O ₅ wt%	BET surface area (m ² /g)	Normalized BET surface area (m ² /g)
Na-X	0	0	527	527
Cs-X	0	0	373	511
Cs ₂ O(1.1)/Cs-X	1.1	0	367	507
Cs ₂ O(2.1)/Cs-X	2.1	0	332	465
Cs ₂ O(4.1)/Cs-X	4.1	0	308	440
Cs ₂ O(7.8)/Cs-X	7.8	0	187	279
ZrB(5)/Cs ₂ O(4.1)/Cs-X	4.1	5	317	453
ZrB(10)/Cs ₂ O(4.1)/Cs-X	4.1	10	201	319
ZrB(15)/Cs ₂ O(4.1)/Cs-X	4.1	15	159	267
ZrB_2O_5	-	100	8.1	-

per supercage $(23.6 \text{ wt\% } \text{Cs}_2\text{O})$ [30]. The Cs₂O contents used in the present study were below 14.9 wt%. Accordingly, it is suggested that all Cs₂O species were occluded inside the cavities. A marked decrease in surface area for Cs₂O(7.8)/Cs-X is due to the filling some of the cavities of the Cs₂O(7.8)/Cs-X with Cs₂O species.

3.1.2. SEM

Fig. 1 shows SEM images of Cs₂O(4.1)/Cs-X (A) and ZrB(10)/Cs₂O(4.1)/Cs-X (B), SEM images of Cs-X (C) and ZrB(10)/Cs-X (B) which were reported in our preceding paper are also shown for comparison [16]. SEM images of Cs₂O/Cs-X and Cs-X are similar, and those of ZrB(10)/Cs₂O(4.1)/Cs-X and ZrB(10)/Cs-X are similar. Cs-X and Cs₂O(4.1)/Cs-X were composed mostly of crystallites in the range 1–3 μ m, while ZrB(10)/Cs-X and ZrB(10)/Cs₂O(4.1)/Cs-X were composed of crystallites in the range 1–3 μ m and small particles of 0.1–1 μ m attached to the larger crystallites. It is likely that the small particles attached to the larger crystallites are ZrB₂O₅ particles.

3.1.3. Basicity and acidity

Changes in basicity and acidity with modification of Cs-X with Cs₂O were studied by IR of adsorbed CO₂ and pyridine, respectively.

Fig. 2 shows IR spectra of CO₂ adsorbed on Cs-X and Cs₂O(4.1)/Cs-X. The spectra on Cs-X were taken from our preceding paper [16] and shown together in Fig. 2 for comparison with those on Cs₂O/Cs-X. No carbonates remained on the surface of Cs-X after pretreatment in a vacuum at 723 K. Two bands appeared at 1380 and 1650 cm⁻¹ after evacuation of the CO₂ adsorbed-Cs-X at 373 K. These bands are ascribed to the bidentate carbonate [31]. The bidentate carbonate was eliminated by evacuation at 523 K. The basic sites on Cs-X were in such a strength that they cannot retain CO₂ after evacuation at 523 K. CO₂ was adsorbed much stronger on $Cs_2O(4.1)/Cs-X$ than on Cs-X. After pretreatment at 723 K, a broad band was observable at about $1400 \,\mathrm{cm}^{-1}$. This broad band is composed of different carbonates. The carbonates consisted mainly of ionic carbonate (CO_3^{2-}) having a peak at about 1400 cm⁻¹ and unidentate carbonate having peaks at about 1420 and 1380 cm⁻¹. The carbonates formed during preparation partly remained on the surface after the pretreatment at 723 K. Four bands appeared at 1380, 1440, 1650 and $1680 \,\mathrm{cm^{-1}}$ after evacuation of the CO₂ adsorbed-Cs₂O(4.1)/Cs-X at 373 K. The two bands at 1380 and 1650 cm⁻¹ were the same as those observed for Cs-X, and assigned to bidendate carbonate [31]. The band intensity was much stronger for Cs₂O(4.1)/Cs-X than for Cs-X. Two bands at 1440 and 1680 cm⁻¹ were observed only for $Cs_2O(4.1)/Cs-X$. Since splitting of the bands was 240 cm⁻¹, these bands could be assigned to a hydrogencarbonate different from the carbonate showing bands at 1380 and 1650 cm⁻¹ [31,32]. The bands at 1440 and 1680 cm⁻¹ were eliminated on evacuation at 523 K. The bands at 1380 and 1650 cm⁻¹ remained a little after evacuation at 523 K.

From the results described above, it is suggested that modification of Cs-X with Cs₂O generates both weak basic sites and strong basic sites in addition to mild basic sites present on Cs-X. Some parts of Cs species exist in the form of Cs₂CO₃. It was reported in literature that addition of Cs₂O generated strong basic sites [17,19], which was confirmed by the present study. In addition to the strong basic sites, generation of weak basic sites was observed in the present study, which has not been reported so far.

Fig. 3 shows IR spectra of pyridine adsorbed on Cs-X and $Cs_2O(4.1)/Cs-X$. Because of a strong band below 1450 cm^{-1} due to carbonate ion species, the band at 1450 cm^{-1} ascribed to pyridine coordinated to Lewis acid site was not observable for $Cs_2O(4.1)/Cs-X$. Lack on the band at 1540 cm^{-1} for both catalysts indicated that no protonic acid sites were present on both catalysts. The spectral changes with evacuation temperature were the same for both catalysts, indicating that the acid sites were not changed much by addition of Cs_2O to Cs-X. It should be noted that the acid sites which can adsorb pyridine after evacuation at 523 K exist on the surfaces of both catalysts.

3.2. Catalytic activities of modified Cs-X

3.2.1. Modified with Cs₂O

Modification of Cs-X with Cs₂O enhanced the catalytic activity of Cs-X and reduced the selectivity to styrene as shown in Fig. 4. The optimum amount of Cs₂O addition in toluene conversion was in the range ca. 1–5 wt%. The activity (toluene conversion) of the catalyst containing 2.1 wt% Cs₂O was about twice as high as that of nonadded Cs-X catalyst. Addition of 7.8 wt% Cs₂O resulted in a decrease in the activity. Unlike non-added Cs-X, Cs₂O/Cs-X produced much more ethylbenzene than styrene. The styrene selectivity dropped from 87% to 16% on addition of 1.1 wt% Cs₂O to Cs-X, though further addition of Cs₂O did not change much the styrene selectivity.

The effects of Cs_2O addition to Cs-X on the activity and selectivity observed in the present study were qualitatively similar to those reported in literature [11,6,27]. All reported that addition of Cs_2O to Cs-X resulted in an increase in the activity and reduction of styrene selectivity, though no reports described the changes in activity and selectivity with Cs_2O loading.

Modification of Cs-X with Cs₂O also affected the methanol conversion. The methanol conversion was 28.8% on Cs-X at the toluene conversion of 1.5%, while it was 60.0% on Cs₂O(4.1)/Cs-X at the toluene conversion of 2.8%. Addition of Cs₂O increased much the methanol conversion. If methanol were consumed only for the formation of styrene and ethylbenzene, the methanol conversions would have been 9% and 16.8% over Cs-X and Cs₂(4.1)/Cs-X, respectively. The differences should be due to the methanol decomposition to CO and H₂. Accordingly, the modification with Cs₂O accelerated the methanol decomposition.



Fig. 1. SEM images of (A) Cs₂O/Cs-X, (B) Zr(10)/Cs₂O(4.1)/Cs-X, (C) Cs-X, and (D) ZrB(10)/Cs-X.

3.2.2. Modification with ZrB₂O₅

Fig. 5 shows the variations in the activity and styrene selectivity as a function of ZrB_2O_5 borate loading under a reaction condition of toluene/methanol feed ratio of 6. Addition of ZrB_2O_5 to $Cs_2O(4.1)/Cs-X$ enhanced both the activity and styrene selectivity up to ZrB_2O_5 loading of 10 wt%. Further addition of ZrB_2O_5



Fig. 2. IR spectra of adsorbed CO_2 on Cs-X (a, b and c) and $Cs_2O(4.1)/Cs-X$ (d, e and f). c and f, background (pretreated at 723 K in a vacuum); a and d, CO_2 adsorbed at room temperature and evacuated at 373 K for 30 min; b and e, further evacuated at 523 K for 30 min.

decreased the activity but brought about further increase in the styrene selectivity.

In our preceding paper, we reported the effects of ZrB_2O_5 addition on the activity and selectivity of Cs-X [16]. Essentially the



Fig. 3. IR spectra of adsorbed pyridine on Cs-X (a, b and c) and Cs₂O(4.1)/Cs-X (d, e and f). c and f, background (pretreated at 723 K in a vacuum); a and d, pyridine adsorbed at room temperature and evacuated at 423 K for 30 min; b and e, further evacuated at 523 K for 30 min.



Fig. 4. Conversion of toluene (left axis) and styrene selectivity (right axis) as a function of Cs_2O loading.

same results were obtained with Cs₂O(4.1)/Cs-X; both the activity and selectivity for styrene were enhanced by addition of a proper amount of ZrB₂O₅. In both catalysts, the highest activity was observed when ZrB₂O₅ was added by 10 wt%. The activity of ZrB₂O₅-added Cs-X was not so high as compared to that of ZrB₂O₅-added Cs-X(4.1)/Cs₂O. In contrast, the styrene selectivity exceeded 90% for ZrB₂O₅-added Cs-X under the same reaction conditions, while the styrene selectivity was 36.4% for ZrB₂O₅-added Cs₂O(4.1)/Cs-X. Concerning the styrene yield (toluene conversion x styrene selectivity) for ZrB₂O₅-added Cs-X/Cs₂O, the addition of 15 wt% ZrB₂O₅ gave higher yield of styrene (yield 2.4%) than the addition of 10 wt% ZrB₂O₅ (yield 1.8%).

It was reported that addition of B component suppressed the decomposition of methanol to H₂ and CO [8]. It was also reported that addition of metal component together with B increased the activity [11]. In the preceding paper, we reported that metal borates were effective agents to prepare the Cs-X catalysts containing both metal components and B [16]. We proposed the role of metal borates as facilitation of the formation of formaldehyde from methanol. Among the metal borates, ZrB_2O_5 was most effective in promoting the activity and styrene selectivity for Cs-X based catalysts. Addition of ZrB_2O_5 had never been reported. In the present study on $Cs_2O/Cs-X$ based catalysts, it was also revealed that ZrB_2O_5 borate was an efficient additive not only to Cs-X but also to $Cs_2O/Cs-X$.

3.2.3. Toluene/methanol molar ratio

The toluene/methanol mole ratio in a feed affected much on both activity and selectivity. Fig. 6 shows the variations in the activity and styrene selectivity as a function of mole % of toluene in the feed for Cs-X and Cs₂O(4.1)/Cs-X. The maximum activity was



Fig. 5. Variations in toluene conversion and styrene selectivity as a function of $\rm ZrB_2O_5$ loading on $\rm Cs_2O(4.1)/Cs-X.$



Fig. 6. Conversion and styrene selectivity as a function of toluene mole % in the reactant mixture for $Cs_2O(4.1)/Cs-X$ (circle) and Cs-X (triangle). Upper abscissa is toluene to methanol molar ratio in the reactant.

obtained at 33.3 toluene mole %, that is toluene/methanol = 1/2, for both catalysts. The styrene selectivity, on the other hand, increased monotonically with toluene mole % for Cs-X, but kept constant for Cs₂O(4.1)/Cs-X.

It should be pointed out that the attainable conversion of toluene does not reach 100% for the reaction with a feed in which toluene/methanol is higher than unity. Toluene should remain unreacted to a certain extent even methanol were consumed all for the reaction with toluene. The attainable conversions for the feeds of toluene/methanol ratios of 1, 2, and 6 are 100, 33.3, and 16.7%, respectively.

3.3. Ethylbenzene formation

3.3.1. Styrene hydrogenation with H_2 and transfer hydrogenation with methanol

Styrene was allowed to react with hydrogen and with methanol to elucidate the main pathway to form ethylbenzene in side-chain alkylation of toluene with methanol over Cs-X, ZrB(10)/Cs-X, and $Cs_2O(4.1)/Cs-X$. The results are shown in Table 2. For all catalysts, the transfer hydrogenation proceeded faster than the hydrogenation. It can be concluded that ethylbenzene is formed mainly through the transfer hydrogenation of styrene with methanol, though the hydrogenation to a small extent. Although Garces et al. described that styrene was readily hydrogenated with methanol but only minor amount of ethylbenzene was produced with hydrogen over Cs-X, no experimental data were given [33].

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 Cs₂O 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.

The styrene selectivity in the side-chain alkylation increased monotonically with toluene/methanol molar ratio in the reactant

Table 2

Conversion of styrene to ethylbenzene by hydrogenation with ${\rm H}_2$ and transfer hydrogenation with methanol.

Catalyst	With H ₂ (%)	With methanol (%)
Cs-X	3.4	15.9
ZrB(10)/Cs-X	3.9	11.9
Cs ₂ O(4.1)/Cs-X	10.0	91.8



Fig. 7. Reaction mechanisms involved in side-chain alkylation of toluene with methanol.

as shown in Fig. 6. The results are interpreted by a slow transfer hydrogenation of styrene with methanol at a low partial pressure of methanol when toluene/methanol ratio is high.

3.3.2. Effects of carrier gas, N_2 and H_2

The toluene conversions and styrene selectivities in a nitrogen stream and a hydrogen streams over Cs-X and Cs₂O(4.1)/Cs-X are given in Table 3. The toluene conversion did not change much, and the styrene selectivity decreased in a hydrogen stream as compared to those in a nitrogen stream. The results indicate that the hydrogenation of styrene with hydrogen takes place. However, taking account of the results given in Table 2 that the transfer hydrogenation of styrene is much faster than the hydrogenation, the contribution of the hydrogenation of styrene is not large as compared to that of the transfer hydrogenation to ethylbenzene formation.

3.4. Effects of modification with Cs₂O and with ZrB₂O₅ borate on the activity and selectivity

The reaction of toluene with methanol to form styrene and ethylbenzene is composed of several steps in which basic sites and acidic sites are involved in different ways as shown in Fig. 7. Although it is speculative in some parts at present, the reaction is supposed to proceed as follows. Methanol undergoes dehydrogenation to form formaldehyde (step 1) and further dehydrogenation to

Table 3

Effects of carrier gas on the toluene conversion and styrene selectivity in side-chain alkylation of toluene with methanol.

Catalyst	Carrier gas	Toluene conv. (%)	Styrene select. (%)
Cs-X	N ₂	1.0	80.1
Cs-X	H ₂	1.2	73.8
Cs ₂ O(4.1)/Cs-X	N ₂	3.3	12.2
Cs ₂ O(4.1)/Cs-X	H ₂	3.0	8.2

 H_2 and CO (step 2). In both steps 1 and 2, basic sites and acid sites may participate. To proceed aldol-type condensation of formaldehyde with toluene, formaldehyde is activated by acid site to be polarized (step 3) [32], and toluene is activated by basic sites to form benzyl anion and proton (step 4). The benzyl anion attacks the polarized formaldehyde at the carbonyl $C^{\delta+}$ and the proton attacks the carbonyl O to form 2-phenylethanol (step 5) (aldoltype addition). 2-Phenylethanol undergoes dehydration to form styrene (step 6) either on acidic sites or basic sites to complete aldol-type condensation. Styrene undergoes transfer hydrogenation with methanol to ethylbenzene (step 8), and hydrogenation with H₂ formed in steps 1 and 2 (step 7). As shown in 3.3, step 8 contributes much more than step 7 to the formation of ethylbenzene. Basic sites are supposed to be involved in both the transfer hydrogenation and the hydrogenation.

Modification of Cs-X with Cs₂O results in the formation of strong basic sites. The strong basic sites would facilitate the activation of toluene to form benzyl anion to increase the toluene conversion. At the same time, the strong basic sites would promote step 2 to decompose methanol to CO and H₂. Also, the strong basic sites promote the transfer hydrogenation of styrene with methanol to ethylbenzene (step 8). Thereby, enhancements of the activity and the ethylbenzene selectivity were observed for Cs₂O/Cs-X. The strong basic sites of Cs₂O/Cs-X were reported to be O atoms of Cs₂O particles occluded in the cavities of Cs-X based on the ¹³⁵Cs NMR study [30].

Modification of Cs-X with ZrB_2O_5 caused enhancements of both the activity and the styrene selectivity. Changes in the strength of basic sites and acidic sites caused by the modification with ZrB_2O_5 borate could not be detected by IR of adsorbed CO_2 and pyridine. It was observed by SEM that small particles of ZrB_2O_5 are dispersed on the surfaces of Cs-X and Cs₂O/Cs-X crystallites. ZrB_2O_5 is mostly in the form of the particle, though penetration of ZrB_2O_5 into the cavities could not be excluded.

In the preceding paper, we reported that formation of unidentate formate species was observed by IR when methanol was adsorbed on ZrB/Cs-X. It was suggested that the presence of the unidentate formate indicated that formaldehyde is present in a high concentration. ZrB_2O_5 form formaldehyde from methanol. In the present study, however, the formation of unidentate formate could not be detected when methanol was adsorbed on $ZrB(10)/Cs_2O(4.1)/Cs-X$ at 623 K followed by cooling down to room temperature, the same condition we could observe the unidentate formate on ZrB/Cs-X. The formaldehyde formed on the dispersed ZrB_2O_5 particles might undergo further dehydrogenation over strong basic sites of $Cs_2O/Cs-X$, and undetectable by IR. The enhancement of activity by modification is suggested to be due to the formation of formaldehyde on the ZrB_2O_5 dispersed on the external surface of the $Cs_2O/Cs-X$ crystallites.

Enhancement of styrene selectivity caused by the modification of $Cs_2O/Cs-X$ with ZrB_2O_5 results from the suppression of the transfer hydrogenation of styrene to ethylbenzene. The suppression effect cannot be interpreted by the existence of the dispersed ZrB_2O_5 particles on the $Cs_2O/Cs-X$ surfaces. Some chemical interaction should occur between ZrB_2O_5 or elements of ZrB_2O_5 and the active sites for the transfer hydrogenation. There are, however, no data to show such interaction at present. The mechanism of the suppression effect of ZrB_2O_5 is an issue to be elucidated in future.

4. Conclusions

- 1. Modification of Cs-X with Cs₂O enhances the activity of the side-chain alkylation, which is caused by generation of strong basic sites to efficiently deprotonate toluene to form benzyl anion. Addition of ca. 1-5 wt% of Cs₂O to Cs-X gives the highest activity.
- 2. Modification of Cs-X with Cs_2O reduced the styrene selectivity, because the modification with Cs_2O facilitates the transfer hydrogenation of styrene to ethylbenzene which is the main pathway to form ethylbenzene.
- Modification of Cs₂O/Cs-X with ZrB₂O₅ enhances the activity, optimum amount of ZrB₂O₅ being 10 wt%. Enhancement of the activity by addition of ZrB₂O₅ is caused by facile formation of formaldehyde from methanol by ZrB₂O₅.
- 4. Modification of $Cs_2O/Cs-X$ with ZrB_2O_5 enhances the styrene selectivity, which is caused by suppression of the transfer hydrogenation of styrene to ethylbenzene. The styrene selectivity increases with an increase in ZrB_2O_5 loading up to 15 wt%.

Acknowledgements

The authors are grateful to King Abdulaziz City for Science & Technology (KACST) for financial support of this research through Project #AR-30-253. The authors also appreciate the support from the Ministry of Higher Education, Saudi Arabia in establishment of the Center of Research Excellence in Petroleum Refining and Petrochemicals at KFUPM.

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