Applied Catalysis A: General 443–444 (2012) 214–220

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Side-chain alkylation of toluene with methanol to styrene over cesium ion-exchanged zeolite X modified with metal borates

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ARTICLE INFO

Article history:
Received 18 June 2012
Received in revised form 1 August 2012
Accepted 2 August 2012
Available online 10 August 2012

Keywords:
Styrene
Toluene
Methanol
Side-chain alkylation
Metal borate-modified cesium ion-exchanged zeolite

ABSTRACT

Cesium ion-exchanged zeolite X (Cs-X) was modified with metal borates to prepare efficient catalysts for side-chain alkylation of toluene with methanol to styrene. The catalytic behavior of Cs-X was improved by the modification with metal borates such as zirconium borate, zinc borate, copper borate and lanthanum borate. Modification was performed by mechanical mixing of Cs-X and a metal borate in dry state followed by calcination. Significant enhancement of activity was observed for modification with zirconium borate and zinc borate. The selectivity to styrene was increased by modification with all metal borates. Modification with metal component or boron alone was not so effective as that with metal borate. The highest activity was obtained with the Cs-X modified with 10 wt% zirconium borate and calcined at 773 K. The high activity of metal borate-modified Cs-X is due to the ability to selectively form formaldehyde from methanol, which is suggested by appearance of clear IR peak at 1690 cm^{-1} assigned to unidentate formate species on adsorption of methanol. The basic sites and acidic sites of Cs-X were slightly weakened by modification with metal borates. It was revealed that mechanical mixing of Cs-X and metal borates followed by calcination is a good method to prepare Cs-X modified with both metal components and boron.

1. Introduction

Styrene is currently produced by two steps: alkylation of benzene with ethylene to ethylbenzene, and dehydrogenation of ethylbenzene to styrene. Since the dehydrogenation step is energy intensive, alternate process to produce styrene is desired to be developed.

One of the possible alternate routes to styrene is the side-chain alkylation of toluene with methanol to styrene in one step. The reaction has been known since 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]. Soon after the report of 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 zeolites X and Y [2]. 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. The idea that formaldehyde is the actual alkylating agent of toluene is widely accepted [3–9]. Ethylbenzene is simultaneously produced with styrene in all the cases reported. Ethylbenzene is suggested to result from hydrogenation of styrene [2,8,10]. For the industrial purpose, a high selectivity of styrene relative to ethylbenzene is desirable.

Two functions are required for the catalyst active for the side-chain alkylation: dehydrogenation of methanol to formaldehyde and activation of the methyl group of toluene. 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 [8].

Enhancements of catalytic activity and selectivity for styrene were attempted by modification of Cs-X with various compounds. Positive effects of modification with B component have been reported in literature [9,11] as well as in patents [12–14]. In addition to B, several metal components were proposed to have promoting effect on the alkylation. The metal components proposed to be effective so far include Ca, Mn, Ni, Cu, Zn, Ag, Ce, Cr, and Fe. The oxide forms of these metal components are either methanol decomposition catalysts or basic in character. Referring to the development of solid base catalysts, there will be such metal components other than those described above that have possibility to be effective in enhancing the catalytic activity of Cs-X by addition together with B. It is worthy to examine metal components which have not been examined so far.

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http://dx.doi.org/10.1016/j.apcata.2012.08.003

Since many metal borates are insoluble in water, B component and metal components are normally added by successive impregnation; impregnation with aqueous H_3BO_3 followed by impregnation with aqueous metal salts soluble in water. Unique method for addition of B component and metal component was disclosed in a patent in which Cs-X and a metal borate were mechanically mixed in a dry state [15]. The catalysts prepared from Cs-X and borates of Mg, Ca, Al, Mn, Fe, Co, Ni, and Cu by the mechanical mixing showed a high selectivity for styrene as compared to non-modified Cs-X.

In the present study, we have prepared Cs-X based catalysts from novel metal borates, Zr and La as metal components, by mechanical mixing and examined for their catalytic activities for side-chain alkylation of toluene with methanol. The catalyst containing Zr and B showed the highest activity, its activity being twice as high as that of Cs-X. The selectivity for styrene (styrene/(styrene + ethylbenzene)) exceeded 90%.

2. Experimental methods

2.1. Catalyst preparation

The base catalyst of Cs-X was prepared from NaX (Junsei Chemicals, Japan) by ion-exchanged with Cs^+. Cesium hydroxide (Alfa Aesar) was used as a source of Cs^+ according to Engelhardt et al. [16]. The NaX has Si/Al ratio of 1.24 and surface area of 527 m^2/g. In 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 an aqueous solution of the cesium hydroxide (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 reverse 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.

The Cs-X's modified with metal borates were prepared by grinding a mixture containing the Cs-X and a metal borate with mortar for 30 min in a dry state. A ground mixture was calcined with a slow ramp rate of 2 K/min at 773 K unless otherwise stated for 3 h. The weight % of the metal borate was 10 wt% for all the catalysts unless otherwise stated. Zinc borate ($2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$) was supplied from Wako Pure Chemicals, Ind., Japan. Zirconium borate (ZrB_2O_5), lanthanum borate ($LaBO_3$), and copper borate ($Cu(BO_2)_2$) were prepared according to the reported procedures. Zirconium borate was prepared according to Knyrim et al. from aqueous solutions of disodiumtetraborate and zirconium nitrate [17]. The precipitate was washed with water, dried and calcined at 623 K in air. Lanthanum borate was prepared according to Lin et al. from a mixture containing boron trioxide and lanthanum oxide by heating at 1373 K in argon atmosphere [18]. Copper borate was prepared from aqueous solutions of disodiumtetraborate and copper nitrate [19]. The precipitate was washed with water, dried and calcined at 723 K. Cs-X catalysts modified with zirconium borate, zinc borate, lanthanum borate, and copper borate are denoted by ZrB/Cs-X, ZnB/Cs-X, LaB/Cs-X, and CuB/Cs-X, respectively.

In addition to these Cs-X containing metal borates, three more catalysts were prepared. The first one is the Cs-X containing B without metal component which was prepared by grinding Cs-X with boric acid (B/Cs-X) in which boron was supposed to be in the form of B_2O_3. The second one is the B and Zr loaded on Cs-X by impregnation with a mixed aqueous solution of boric acid and zirconium nitrate (B-Zr/Cs-X). The slurry was aged at room temperature for 1 h under stirring conditions, and then the excess solvent was removed by heating at 363 K under vacuum in a rotary evaporator. The third one is Cs-X containing only Zr component prepared by impregnation with zirconium nitrate (Zr/Cs-X) in which Zr was supposed to be in the form of ZrO_2. These three catalysts were calcined with a slow ramp rate of 2 K/min at 773 K for 3 h. The total of the added compounds were all 10 wt% unless otherwise stated.

2.2. Reaction procedures

The catalytic runs were carried out in a fully integrated, discrete, micro-processor controlled fixed bed continuous flow reactor system (Model # 401C-0286, Autoclave Engineers). The system consists of one tubular stainless steel reactor (8 mm I.D. × 14 mm O.D. × 40 cm) attached with stainless steel one-zone furnace assembly through reactor furnace wall thermowell. The catalysts sample (400 mg) was pretreated with flowing N_2 at 723 K for 2 h, and then cooled to a reaction temperature of 698 K. The flow rates of the reactant (toluene/methanol = 6/1) and N_2 were maintained at 0.12 ml/min and 40 ml/min (STP) with high pressure feeding pump (Series III Digital HPLC Pump, Autoclave Engineers), and mass flow controller (Model # 5850S/BC, Brooks), respectively. The products were analyzed with online gas chromatograph (Agilent technologies, Model # 6890N) equipped with a WCOT fused silica capillary column coated with squalane (Varian, Cat. # CP7520, length: 100 m, ID: 0.25 mm) with FID detector. The products were identified by comparison with authentic samples. Because of FID detector, H_2, CO_2 and H_2O could not be analyzed by gas chromatography.

2.3. Characterization

IR spectra of adsorbed CO_2, pyridine and methanol were measured with *in situ* IR cell with CaF_2 windows. Samples were pressed into a thin wafer (~50 mg/20 mm dia) and placed in the cell which was attached 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 patterns were measured with RigakuMiniflix II XRD powder diffraction system, Cu K_α 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 7000×. 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, BET equation being adopted to calculate the surface areas.

TG/DTA curves were measured with Rigaku Thermo plus TG 8120 for the uncalcined samples (9.0 mg), α-Al_2O_3 being used as a reference sample. The sample was heated at a rate of 10 K/min in a static air.

3. Results

3.1. Catalytic activity

The products consisted mostly of styrene and ethylbenzene in addition to the reactants, toluene and methanol. Small hydrocarbons were detected, but their quantities were less than 5% of styrene produced. These were excluded from the product quantification.

Figs. 1 and 2 show the variations in toluene conversion and styrene selectivity, respectively, as a function of time on stream under the reaction conditions: toluene/methanol = 6/1, feed rate 0.12 ml/min, N_2 flow rate 40 ml/min, catalyst 400 mg and the reaction temperature 683 K. Since the molar ratio of toluene to methanol was 6, the attainable conversion of toluene was 16.7%.

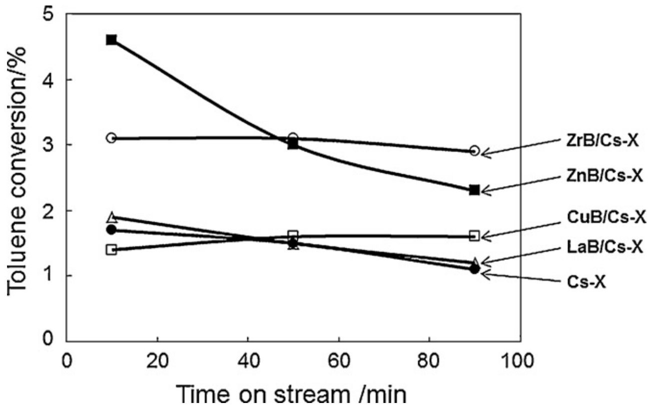

Fig. 1. Toluene conversion as a function of time on stream in side chain alkylation of toluene with methanol at 683 K over Cs-X and Cs-X's modified with metal borates.

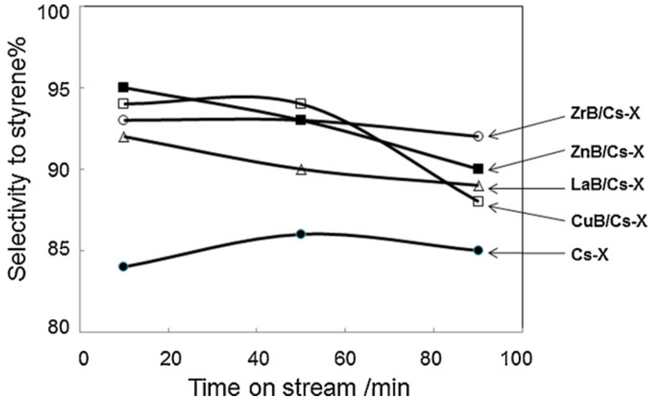

Fig. 2. Selectivity to styrene as a function of time on stream in side chain alkylation of toluene with methanol at 683 K over Cs-X and Cs-X's modified with metal borates.

Modification of Cs-X with metal borates brought about significant changes in the conversion of toluene depending on the type of borate as shown in Fig. 1. The toluene conversion for ZnB/Cs-X was high at a time on stream of 10 min, but decreased considerably with time on stream. ZrB/Cs-X showed a high conversion and did not decay with time on stream. LaB/Cs-X showed almost the same toluene conversion as non-modified Cs-X, their conversions decreased slightly with time on stream. The toluene conversion for CuB/Cs-X, on the other hand, slightly increased with time on stream and significantly exceeded that of Cs-X in 90 min.

Modification of Cs-X with metal borates resulted in distinct improvement in the selectivity for styrene as shown in Fig. 2. In particular, ZrB/Cs-X showed the selectivity higher than 92% throughout the time on stream, which was higher than the selectivity below 86% for non-modified Cs-X.

In addition to the reaction results for the catalysts shown in Fig. 1, the results for other catalysts are summarized in Table 1. Data were taken at a time on stream of 50 min. Modification with B and Zr by impregnation with a mixed aqueous solution containing boric acid and zirconium nitrate did not improve the catalytic activity of Cs-X (entry 6). The activity and selectivity were even worse than those of non-modified Cs-X. Addition of ZrO_2 alone enhanced the toluene conversion, but the selectivity of styrene was low, ethylbenzene being produced much more than styrene (entry 7). Addition of 10 wt% BO_3 alone resulted in a marked decrease in toluene conversion (entry 8), but addition of 0.8 wt% BO_3 increased the toluene conversion but decreased the styrene selectivity (entry 9).

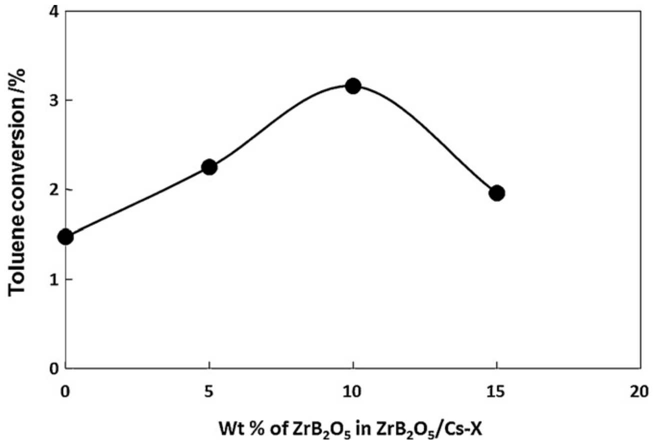

Fig. 3. Variation in toluene conversion as a function of zirconium borate loading of ZrB/Cs-X in side chain alkylation of toluene with methanol at 683 K.

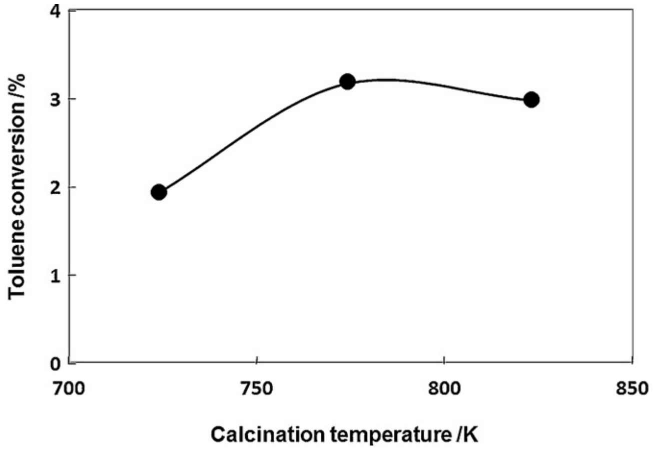

Fig. 4. Variation in toluene conversion as a function of calcination temperature of ZrB/Cs-X in side chain alkylation of toluene with methanol at 683 K.

The effect of zirconium borate loading on the toluene conversion was examined, and the results are shown in Fig. 3. The maximum toluene conversion was obtained with 10 wt% zirconium borate loaded Cs-X, that is ZrB/Cs-X.

The effect of calcination temperature of ZrB/Cs-X on the toluene conversion was examined, and the results are shown in Fig. 4. The maximum toluene conversion was observed when calcined at 773 K.

3.2. Characterization

3.2.1. Surface area

Surface areas are summarized in Table 2. Since the weight of the zeolite unit cell increased by ion-exchange of Na with Cs and addition of other components, the normalized surface areas as defined below were calculated and included in Table 2.

$$\text{Normalized surface area} = \frac{\text{measured surface area} \times \text{unit cell weight of zeolite X containing Cs and borate}}{\text{unit cell weight of Na-X}}$$

Table 1
Catalytic activities for alkylation of toluene with methanol at 683 K.

Entry	Catalyst	Methanol conv. (%)[f]	Toluene conv. (%)[g]	EB select. (%)[h]	ST select. (%)[i]	ST yield (%)[j]
1	Cs-X	36.8	1.5	13.8	86.2	1.3
2	ZrB/Cs-X[a]	45.2	3.1	6.8	93.2	2.9
3	LaB/Cs-X[a]	27.9	1.5	9.9	90.1	1.4
4	ZnB/Cs-X[a]	37.6	3.0	6.6	93.4	2.8
5	CuB/Cs-X[a]	44.9	1.6	6.1	93.9	1.5
6	B-Zr/Cs-X[b]	37.3	1.1	33.8	66.2	0.7
7	Zr/Cs-X[c]	31.3	1.8	87.0	13.0	0.2
8	B/Cs-X[d]	7.9	0.3	0	100	0.3
9	B(0.8)/Cs-X[e]	34.0	1.8	30.4	69.6	1.3

[a] Prepared by mechanical mixing with metal borates.
[b] Prepared by co-impregnation method with H_3BO_3 aq. and $Zr(NO_3)_4$ aq.
[c] Prepared by impregnation with $Zr(NO_3)_4$ aq.
[d] Prepared by mechanical mixing with H_3BO_3.
[e] Containing 0.8 wt% H_3BO_3 prepared by impregnation.
[f] Methanol conv. = {1 − (methanol recovered)/(methanol fed)} × 100%.
[g] Toluene conv. = {1 − (toluene in products)/(toluene fed)} × 100%.
[h] EB select. = ethylbenzene/(ethylbenzene + styrene) × 100%.
[i] ST select. = styrene/(ethylbenzene + styrene) × 100%.
[j] ST yield = (toluene conv.) × styrene/(total hydrocarbon products) × 100%.

The normalized surface area of Cs-X was close to that of Na-X indicating crystalline structure was retained after ion-exchange with Cs. For LaB/Cs-X, ZrB/Cs-X and CuB/Cs-X, addition of the borates followed by calcination at 773 K resulted in a decrease in surface area by about 14–20%. For ZnB/Cs-X, however, distinct decrease in surface area was observed, the normalized surface area of ZnB/Cs-X was less than a half of the original one. Although addition of 0.8% H_3BO_3 did not decrease much, addition of 10% H_3BO_3 decreased the surface area to 8% of the original one.

3.2.2. *XRD*

Fig. 5 shows XRD patterns of Cs-X, LaB/Cs-X, ZrB/Cs-X and ZnB/Cs-X. All samples retain crystalline structure of FAU, but the intensity of diffraction peaks decreased in the order of Cs-X, ZrB/Cs-X, LaB/Cs-X and ZnB/Cs-X. This order is the same order of decrease in the surface area.

3.2.3. *SEM*

SEM images for Cs-X and ZrB/Cs-X are shown in Figs. 6 and 7, respectively. Cs-X is composed mostly of crystallites in the range 1–3 μm, while ZrB/Cs-X is composed of crystallites in the range 1–3 μm and small particles of 0.1–1 μm attached to the larger crystallites.

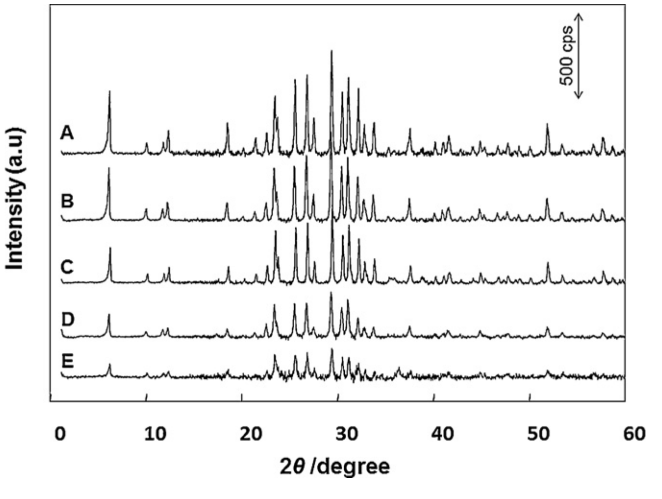

Fig. 5. XRD patterns of Cs-X and Cs-X's modified with metal borates. (A) Cs-X, (B) ZrB/Cs-X, (C) CuB/Cs-X, (D) LaB/Cs-X and (E) ZnB/Cs-X.

Table 2
Surface areas of catalysts.

Catalyst	BET surface area (m^2/g)	Normalized surface area (m^2/g)
Na-X	527	527
Cs-X	373	513
ZrB(5%)/Cs-X	317	459
ZrB/Cs-X	286	438
ZrB(15%)/Cs-X	234	378
LaB/Cs-X	260	398
ZnB/Cs-X	137	209
CuB/Cs-X	299	457
B-Zr/Cs-X	196	300
Zr/Cs-X	195	299
B/Cs-X	27	41
B(0.8%)/Cs-X	319	444

3.2.4. *TG/DTA*

TG/DTA curves for ZrB/Cs-X are shown in Fig. 8. Weight loss observed in the range ~500 K accompanied by endothermic heat is ascribed to desorption of physically adsorbed water. Above 500 K, gradual changes in weight and heat were observed, which could be ascribed to desorption of chemisorbed water and carbon dioxide.

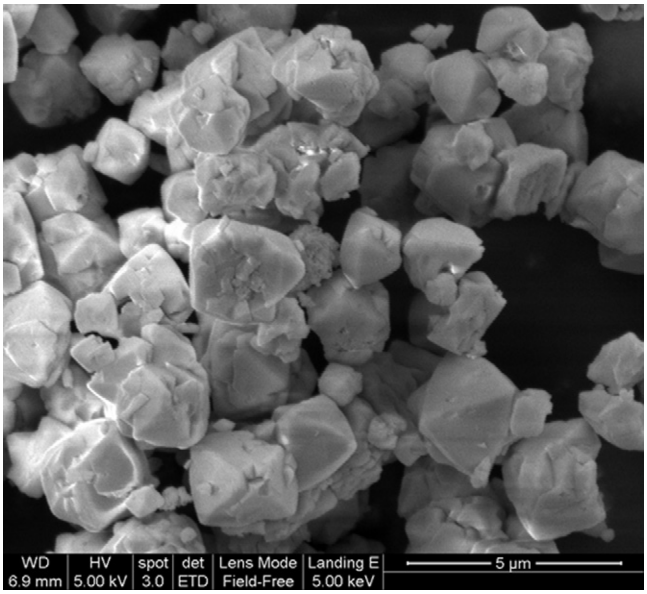

Fig. 6. SEM image of Cs-X.

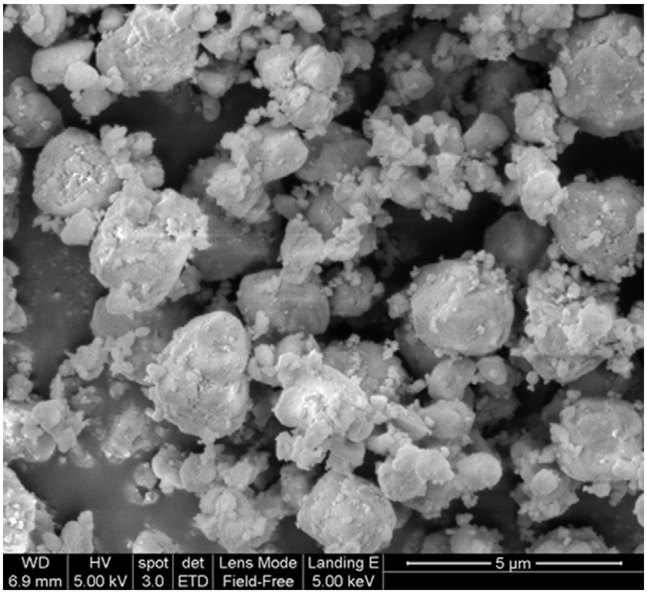

Fig. 7. SEM image of ZrB/Cs-X.

3.2.5. IR study

Fig. 9 shows IR spectra of CO_2 adsorbed on Cs-X and ZrB/Cs-X followed by evacuation at 373 K and 523 K. Two bands at 1480 and 1650 cm^{-1} appeared on Cs-X after evacuation at 373 K are assigned to bidentate carbonate. No bands assigned to other carbonates such as unidentate carbonate and bicarbonate were observed. By evacuation at 523 K, these bands were eliminated. Because of strong band below 1500 cm^{-1} due to the presence of B, only one band at 1650 cm^{-1} was observable for ZrB/Cs-X. The band was assigned to bidentate carbonate. The intensity of the band at 1650 cm^{-1} is slightly weaker for ZrB/Cs-X than for Cs-X. The basic sites on Cs-X were slightly weakened by modification with zirconium borate. A small difference in O—H stretching region between Cs-X and ZrB/Cs-X was noted. The intensity of the band at 3740 cm^{-1} was weaker for ZrB/Cs-X than for Cs-X. Zirconium borate may interact with OH groups of Cs-X.

Fig. 10 shows IR spectra of pyridine adsorbed on Cs-X and ZrB/Cs-X followed by evacuation at 473 and 523 K. No bands assigned to pyridinium ion were observed at 1540 cm^{-1} for both Cs-X and ZrB/Cs-X. No protonic acid sites exist on both catalysts. As compared the band intensity at 1580 cm^{-1} which is due to Lewis acid sites, the intensity was weaker for ZrB/Cs-X than for Cs-X. The band position, however, was the same for the two samples. The number of Lewis acid sites is slightly reduced by modification with zirconium borate. It should be noted that Lewis acid sites on which pyridine can be retained after evacuation at 523 K exist on the surfaces of Cs-X and ZrB/Cs-X.

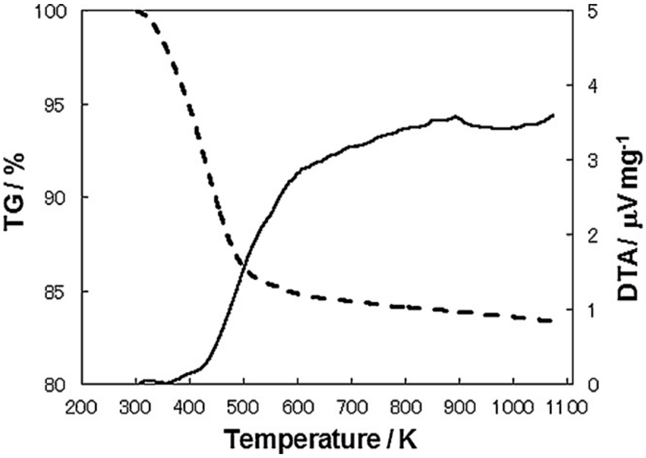

Fig. 8. TG/DTA of ZrB/Cs-X. Dotted line, TG; solid line, DTA.

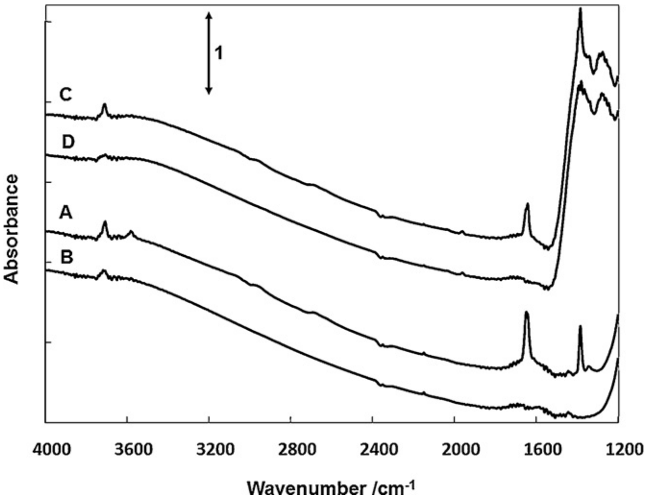

Fig. 9. IR spectra of CO_2 adsorbed on Cs-X and ZrB/Cs-X. (A and B) CO_2 adsorbed on Cs-X and evacuated at 373 K and 523 K, respectively; (C and D) CO_2 adsorbed on ZrB/Cs-X and evacuated at 373 K and 523 K, respectively.

Distinct difference in IR spectrum between Cs-X and ZrB/Cs-X was observed when the catalysts were exposed to 133 Pa methanol at 623 K and cooled down to room temperature. Fig. 11 shows the spectra observed. Two bands were observable at 1610 cm^{-1} and 1670 cm^{-1} which were assigned to bidentate formate and unidentate formate, respectively [4]. On Cs-X, a strong band assigned to bidentate formate was observed, while the band to unidentate formate was very weak. On ZrB/Cs-X, in contrast, strong band assigned to unidentate formate appeared as well as the band to bidentate formate.

4. Discussion

4.1. Catalytic activity

Addition of metal components together with B to Cs-X has been reported in literature and patents. Lacroix et al. observed improved

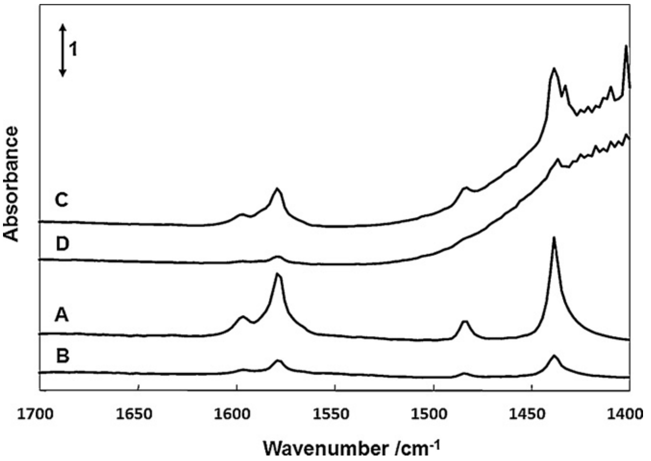

Fig. 10. IR spectra of pyridine adsorbed on Cs-X and ZrB/Cs-X. (A and B) Pyridine adsorbed on Cs-X and evacuated at 473 K and 523 K, respectively; (C and D) pyridine adsorbed on ZrB/Cs-X and evacuated at 473 K and 523 K, respectively.

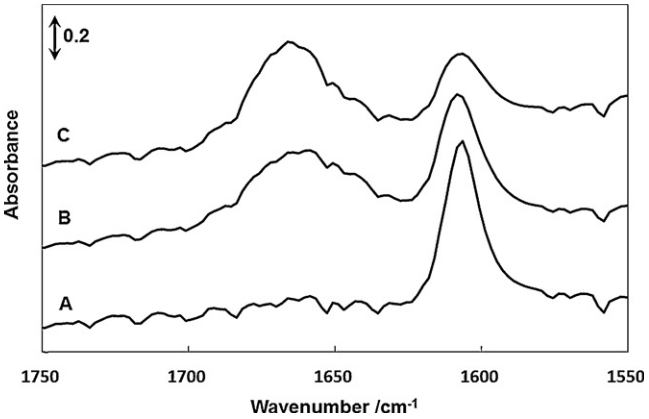

Fig. 11. IR spectra of surface species remaining on (A) Cs-X, (B) ZrB/Cs-X and (C) ZnB/Cs-X after exposure to 133 Pa methanol at 623 K followed by cooling down to room temperature.

activity for Cs-X loaded with Cu and Ag and B doped Cs-X [10]. Addition of Cu and Ag was done separately from addition of B to Cs-X. They used aqueous solutions of metal components and boric acid. Addition of the two components was done by two steps in most cases: addition of B in the first step and addition of metal component in the second step. One exception can be found in a patent [15]. The patent used metal borates to add two components in one step. A mixture containing metal borate and Cs-X was mixed with kneader in dry state and calcined. The patent reported high activities of Cs-X's mixed with several metal borates. As metallic components, Mn, Zn, Ca, Ni, Cu were used. Although all the catalysts showed higher activities than Cs-X, the reaction conditions were not described in detail.

The present study confirmed that addition of metal components and B by mechanical mixing of metal borates in a dry state is a good way to prepare the Cs-X containing both metal components and B. Among the catalysts prepared based on the Cs-X, the best catalyst was the Cs-X modified with 10 wt% zirconium borate by means of mechanical mixing of Cs-X and zirconium borate followed by calcination at 773 K. Addition of Zr and B separately from zirconium nitrate and from boric acid aqueous solutions did not result in the formation of efficient catalyst as compared to addition of zirconium borate in a dry state. Addition of Zr has never examined before.

Addition of B to Cs-X has been widely adopted in patents, but has rarely been studied in literature. One of the studies was reported by Wieland et al. [7]. Addition of B to Cs-X promoted the side-chain alkylation. Role of B was proposed to suppress the decomposition of methanol into CO and H_2. The optimum loading was reported to be 0.8 wt% H_3BO_3.

Our results indicated that loading of 10 wt% H_3BO_3 strongly reduced the toluene conversion, but loading of 0.8 wt% increased the toluene conversion a little as reported by Wieland et al. [7]. The selectivity to styrene, however, reduced to 69.6%. Drastic decrease observed for 10 wt% loading of H_3BO_3 is suggested to be caused by a marked decrease in surface area; the surface area decreased to less than 10% of the original Cs-X. Since the melting point of B_2O_3 is 733 K, it is suggested that B_2O_3 melted during calcination and covered the external surface of the Cs-X crystallites, resulting in a decreased surface area as well as a low activity.

4.2. States of metallic component and boron

The states of Zr and B in ZrB/Cs-X are suggested to be mostly in the fine particles of zirconium borate dispersed on the external surface of Cs-X crystallites as shown in the SEM image (Fig. 7). The normalized surface area was 427 m^2/g which was 83% of that of Cs-X. The decrease in the surface area by 17% seems to be consistent with the dispersed model. Some of the zirconium borate particles located on the external surface of Cs-X to decrease the surface area. From TG and DTA results of ZrB/Cs-X, an occurrence of the chemical reaction of zirconium borate with Cs-X was not detected. It is plausible that fine particles of zirconium borate are dispersed on Cs-X and interact with Cs-X at the interface. Since the IR band due to OH groups was weaker for ZrB/Cs-X than for Cs-X, it is suggested that the zirconium borate particles interact with Cs-X crystallites through OH groups on the external surface of Cs-X.

4.3. Acidity and basicity

Although it was reported that balanced acidity and basicity is important for an efficient catalyst for side-chain alkylation of toluene, IR studies of adsorbed pyridine and CO_2 could not detect clear differences in acidity and basicity between Cs-X and ZrB/Cs-X. For pyridine adsorption study, only a small decrease in the band intensity was observed without change in the band position for 8a vibration mode ($\sim$1580 cm^{-1}). The band position reflects the strength of the interaction between pyridine and Lewis acid sites [20]. No change in the band position for Cs-X and ZrB/Cs-X indicates that the strength of Lewis acid sites is similar for both catalysts. Decrease in the band intensity is suggested to be due to a decrease in the number of Lewis acid sites by the addition of zirconium borate. This idea is consistent with a small decrease in the surface area for ZrB/Cs-X. The same thing can be said about basic sites. CO_2 was adsorbed as bidentate carbonate and the band position was the same for both samples. Only difference between two samples was the band intensity; the intensity was slightly weaker for ZrB/Cs-X than for Cs-X. It is suggested that the strength of basic sites is the same for both catalysts, and the number of basic sites was smaller for ZrB/Cs-X than for Cs-X.

It should be noted that the discussion about acidity and basicity described above is applicable only to relatively strong adsorption sites. Because the spectra were measured after evacuation at a high temperature, the species retained on the surface should be adsorbed on strong adsorption sites. Spectra measured after evacuation at such a low temperature as weakly adsorbed species are retained on the surface may contain information about weak acid and base sites. However, distinct information about weak acid and base sites may be difficult to obtain because the band observed after evacuation at the low temperature contains information of all the sites. Isolation of the band due only to weak sites could not be successful. The possibility cannot be excluded that addition of zirconium borate caused some changes in weak acidic and basic sites.

4.4. Interaction with methanol

In contrast to the results of IR studies of adsorbed pyridine and CO_2, a distinct difference was observed for IR study of methanol. In addition to a band ascribed to bidentate formate which was observed both for ZrB/Cs-X and Cs-X, a distinct band ascribed to unidentate formate was observed for ZrB/Cs-X at 1670 cm^{-1} when exposed to methanol near the reaction temperature. It was reported that the bidentate formate undergoes decomposition to CO and H_2, and the unidentate formate could be an intermediate for aldol-type condensation with toluene [3,4]. At least, the presence of unidentate formate indicates that formaldehyde is present in a high concentration in the gas phase. Accordingly, it is suggested that selective dehydrogenation of methanol to formaldehyde proceeds much smoother over ZrB/Cs-X than over Cs-X. The same phenomenon was observed for ZnB/Cs-X; a distinct band of the unidentate formate was observed for ZnB/Cs-X. The strong band of the unidentate formate strongly suggests the formation of formaldehyde is facilitated on ZrB/Cs-X and ZnB/Cs-X. Accordingly, a high ability of the formation of formaldehyde is suggested to be the cause of a high activity of these catalysts for the formation of styrene.

5. Conclusions

1. Metal borate modification improves the catalytic activity of Cs-X for side-chain alkylation of toluene with methanol to form styrene.
2. Among metal borates, zirconium borate is most effective.
3. Mechanical mixing of Cs-X and metal borates followed by calcination is an efficient way for the modification with metal component and boron.
4. Modification of Cs-X with metal borates facilitates the formation of formaldehyde from methanol.

Acknowledgments

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. H.H. wishes to thank the Japan Cooperation Center, Petroleum (JCCP) for financial support under the High-level Researcher Dispatching Program, JCCP.

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