

Selective conversion of ethylbenzene into styrene over K_2O/TiO_2-ZrO_2 catalysts: Unified effects of K_2O and CO_2

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Abstract

By varying the composition of TiO_2 and ZrO_2 , various TiO_2-ZrO_2 mixed oxide catalysts were prepared by co-precipitation method using ammonium hydroxide as a hydrolyzing agent. Similarly, TiO_2 and ZrO_2 isolated oxides were also prepared for the purpose of comparison. 60 mol% TiO_2 + 40 mol% ZrO_2 mixed oxide catalyst (here after simply termed as TiO_2-ZrO_2) was impregnated with different amounts of potassium oxide (K_2O). These catalysts were characterized by BET surface area, X-ray diffraction (XRD) and temperature programmed desorption of NH_3 . K_2O/TiO_2-ZrO_2 catalysts exhibited high performance towards the selective conversion of ethylbenzene into styrene in the presence of CO_2 , wherein K_2O improved the conversion of ethylbenzene and selectivity of styrene acting as a basic promoter, similarly CO_2 enhanced both conversion and selectivity acting as an oxidant as well as a diluent. The unified promotional effects of K_2O and CO_2 improved the conversion of ethylbenzene up to 60–65% at 95–99% selectivity levels of styrene.

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1. Introduction

Currently, more than 80% of styrene is produced based on the catalytic dehydrogenation of ethylbenzene at high temperatures (>600 °C) with promoted iron oxide catalysts in the presence of large excess of superheated steam. The major disadvantage of this process is its reversible reaction, which imposing a thermodynamic limitation [1]. Low conversion of ethylbenzene, low selectivity of styrene and high energy consumption of the present process has been the driving force for the exploration of alternative technologies [1]. Developments are going on to increase the conversion and selectivity by the removal of the reaction product hydrogen and thereby shifting the thermodynamic equilibrium towards products direction. The oxidative dehydrogenation of ethylbenzene has been proposed to be free from thermodynamic limitations regarding conversion and operating at lower temperatures with an exothermic reaction, but the low selectivity of styrene is the major drawback of this process [2].

Alternatively, it has been realized that the carbon dioxide (CO_2) utilization as a diluent as well as a mild oxidant will be the technologically important advancement. Because, CO_2 utilization offers several advantages, like acceleration of the reaction rate, enhancement in the product selectivity, diminishing of thermodynamic limitations, suppression of total oxidation, prolonging of catalyst life, prevention of hotspots and so on. Hence, several research groups including us have been exploring the possibility of CO_2 utilization in the dehydrogenation of ethylbenzene over different catalysts such as F_2O_3 , V_2O_5 , Sb_2O_5 , Cr_2O_3 , CuO , CeO_2 , ZrO_2 , La_2O_3 , alkali metals, etc., on different supports [3–10]. Among these reports, Sakurai et al. [3] found that the conversion of ethylbenzene in the presence of CO_2 is 14% higher than in the presence of argon over carbon supported V_2O_5 catalysts. Sugino et al. [6] reported that the active carbon supported and alkali metal oxide promoted iron catalysts showed better activity in the presence of CO_2 . Mimura et al. [7] realized that 10% Fe_2O_3/Al_2O_3 with proper amount of CaO is highly effective in the presence of CO_2 . Sun et al. [11] demonstrated that the selectivity of styrene can be improved to 95–99% at the conversion levels of 50% over chromium promoted and alumina supported vanadium catalysts

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in the presence of CO₂. We investigated the dehydrogenation of ethylbenzene with CO₂ over a ZSM-5 supported iron oxide catalyst and found that ethylbenzene was predominantly converted into styrene via an oxidative manner, wherein CO₂ played the role of an oxidant in order to improve catalytic activity as well as coke resistance of the catalyst remarkably [9,10]. The role of CO₂ has thoroughly been investigated over alumina supported vanadium catalysts with a wide varieties of promoters [12–15].

Recently, in one of our recent reports the enhanced activity of ZrO₂ in the presence of CO₂ has been described [16]. In another report, we illustrated the significant enhancement in the catalytic activity of ZrO₂ when it is mixed with MnO₂ [17]. Apart from MnO₂-ZrO₂ mixed oxide catalyst system, we found that CeO₂-ZrO₂ mixed oxide catalyst supported on SBA-15 showed remarkable catalytic activity in the presence CO₂ [18]. These two series of mixed oxide catalysts showed superior activity to their individual oxides (ZrO₂, TiO₂ and CeO₂). Based on these results TiO₂-ZrO₂ mixed oxide catalysts has been investigated. Furthermore, we found that these TiO₂-ZrO₂ mixed oxide catalysts can be further improved up to the stage of complete suppression of by-products by neutralizing the strong acidic sites by K₂O addition. TiO₂-ZrO₂ mixed oxide catalyst system with K₂O promoter has not yet been reported for the dehydrogenation of ethylbenzene to styrene in the presence of CO₂.

Hence, in the present report, the preparation, characterization and catalytic performance of K₂O/TiO₂-ZrO₂ catalysts for the selective dehydrogenation of ethylbenzene into styrene emphasizing the synergistic influence of K₂O and CO₂ have been delineated.

2. Experimental

2.1. Preparation of the catalysts

Various loadings of TiO₂-ZrO₂ mixed oxide catalysts were prepared by co-precipitation method. In a typical experiment, by taking the requisite amounts of zirconyl(IV) nitrate hydrate (Acros Organics, USA, 99.5%) and titanium(IV) chloride (Yakuri Pure Chemicals Co. Ltd., Japan), homogeneous 0.1 M aqueous mixed salt solution was made under mechanical stirring. To this homogeneous salt solution requisite amount of ammonium hydroxide (DC Chemicals Co. Ltd., Korea, Assay 25.0–28.0%) was added until the pH of the solution reached to 8 under constant mechanical stirring at room temperature. The resultant white precipitate was separated by filtration under reduced pressures and washed with de-ionized water several times until the complete removal of chloride ions, followed by drying at 120 °C for 12 h and calcination at 600 °C for 6 h in a muffle furnace. TiO₂-ZrO₂ mixed oxide was impregnated with 1, 2, 3 and 4 wt.% K₂O wherein, potassium carbonate (Aldrich, USA) was used as a precursor for K₂O promoter. After the impregnation, all these samples were dried at 120 °C for 12 h, and calcined at 600 °C for 6 h in static air atmosphere.

2.2. Catalytic activity test

The catalytic activity studies were performed in a fixed bed down flow stainless steel reactor (i.d. 4.5 mm and length 300 mm) under atmospheric pressure. In a typical experiment, approximately 1.0 g of the catalyst sample was loaded with the support of quartz wool and subjected to the catalyst pretreatment at 600 °C for 0.5 h in the flow of N₂ (20 ml/min). After the completion of the pretreatment, the reaction was conducted at different temperatures either in the flow of N₂ or CO₂. Ethylbenzene was introduced by a peristaltic pump with a feed rate of 9.8 mmol/h along with either CO₂ or N₂. Products were analyzed by a gas chromatogram (Younglin Instrument, Acme 6000 series, Korea) equipped with TCD and FID.

2.3. Catalyst characterization

BET surface areas of the catalysts were determined using Chemisorp 2705 unit (Micromeritics Instrument Co., USA). All the samples were pretreated at 200 °C for 4 h before measurement. N₂ was used as an adsorbate gas and the measurements were performed at 77 K.

X-ray diffraction patterns were recorded using a Rigaku, Miniflex, diffractometer with a nickel filtered Cu K α radiation of wave length 1.5418 Å at a voltage of 40 kV and a current of 100 mA up to 80° of 2 θ range for the verification of structural aspects of TiO₂, ZrO₂, TiO₂-ZrO₂ and K₂O/TiO₂-ZrO₂ catalysts.

Acidity measurements were performed by temperature programmed desorption of NH₃ using Chemisorp 2705 unit (Micromeritics Instrument Co.) equipped with thermal conductivity detector (TCD). Typically, ca. 50 mg of catalyst was pretreated in flowing helium at 500 °C for 1 h, cooled to 100 °C and allowed to expose 5% NH₃ in helium gas mixture with a flow rate of 20 ml/min for 30 min and subsequently the adsorbed NH₃ was purged with helium gas at the same temperature for 1 h to remove the physisorbed NH₃. The chemisorbed NH₃ was measured in flowing helium gas with the flow rate of 20 ml/min from 100 to 800 °C with the heating rate of 10 °C/min.

3. Results and discussion

3.1. Physico-chemical properties of the catalysts

The TiO₂-ZrO₂ mixed oxide catalyst exhibited high surface area, amorphous phase and profound acid–base bi-functional properties. Similar observation was reported by several authors at various ratios of TiO₂-ZrO₂ mixed oxide catalysts [19–21]. The BET surface areas and the crystalline phases are depicted in Table 1. The estimated BET surface area of TiO₂-ZrO₂ is 135 m²/g.

By the addition of 1, 2, 3 and 4 wt.% of K₂O to TiO₂-ZrO₂ the BET surface areas have been decreased to 118, 108, 96 and 89 m²/g, respectively, which are shown in Table 1. The diminishing trend in the BET surface areas with the increased amount of K₂O might be due to the blockage of certain pores. Mao et al. [21] reported that the surface area of TiO₂-ZrO₂ was dra-

Table 1
BET surface areas and crystalline phases of the catalysts

Catalyst	A_{BET} (m ² /g)	Crystalline phase
TiO ₂	5	TiO ₂ -rutile
ZrO ₂	25	ZrO ₂ -monoclinic
TiO ₂ -ZrO ₂	135	TiO ₂ -anatase
1% K ₂ O/TiO ₂ -ZrO ₂	118	TiO ₂ -anatase
2% K ₂ O/TiO ₂ -ZrO ₂	108	TiO ₂ -anatase
3% K ₂ O/TiO ₂ -ZrO ₂	96	TiO ₂ -anatase
4% K ₂ O/TiO ₂ -ZrO ₂	89	TiO ₂ -anatase

K₂O loading is in wt. %.

matically decreased from 103 to 45.9 m²/g by the addition of 8% B₂O₃ to TiO₂-ZrO₂. This behavior was explained on the basis of the blockage of micropores that are present in the TiO₂-ZrO₂ mixed oxide. The XRD data depicted in Table 1 and shown in Fig. 1 have clearly been indicating the monoclinic phase of ZrO₂, rutile phase of TiO₂ and amorphous phase of TiO₂-ZrO₂ mixed oxide catalyst.

The change of phases from crystalline to amorphous has been reported by several authors during the stages of TiO₂-ZrO₂ mixed oxide preparation [22,23]. Although the TiO₂-ZrO₂ mixed oxide is in the amorphous phase, its K₂O promoted counterparts exhibited crystalline behavior with the anatase phase of TiO₂ as shown in Fig. 2. Due to the K₂O addition, anatase TiO₂ phase separation has been observed. Neither ZrO₂ crystalline phases nor TiO₂ rutile phase has been observed from the XRD results.

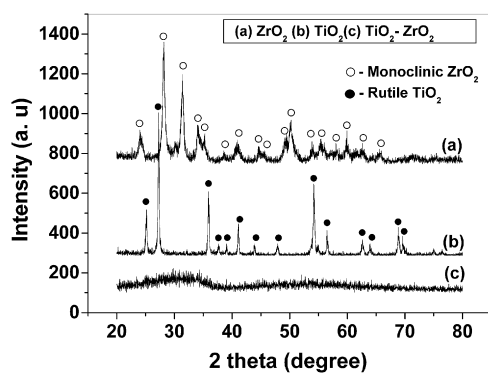


Fig. 1. XRD patterns of: (a) ZrO₂, (b) TiO₂ and (c) TiO₂-ZrO₂ mixed oxide.

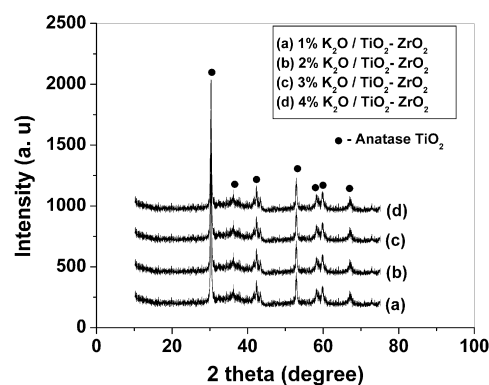


Fig. 2. XRD patterns of K₂O/TiO₂-ZrO₂ catalysts (K₂O loading is in wt. %).

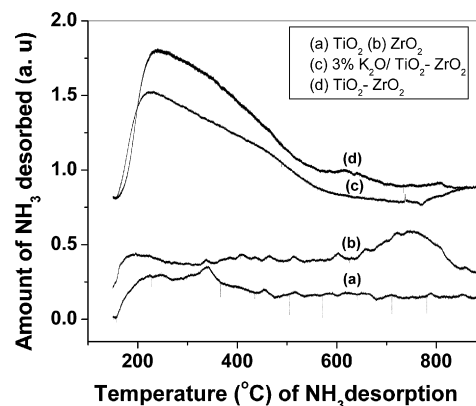


Fig. 3. TPD patterns of: (a) TiO₂, (b) ZrO₂, (c) 3% K₂O/TiO₂-ZrO₂ and (d) TiO₂-ZrO₂ (K₂O loading is in wt. %).

3.1.1. Acidic properties of the catalysts

The acidic properties have been determined by the well-known TPD technique for the best catalyst (3% K₂O/TiO₂-ZrO₂) and also for the purpose of comparison the NH₃ TPD patterns were also generated for TiO₂-ZrO₂ mixed oxide, TiO₂ and ZrO₂. As shown in Fig. 3, the NH₃ TPD patterns have been indicating that the wide distribution of acidic sites from weak to strong in isolated oxides (TiO₂ and ZrO₂) and TiO₂-ZrO₂ mixed oxide. The acidic sites in TiO₂ are much less in number, but are distributed uniformly from weak acidic sites to strong acidic sites. In ZrO₂ weak to moderate acidic sites are more or less equal in number, whereas the strong acidic sites are comparatively higher. In the case of TiO₂-ZrO₂ and 3% K₂O/TiO₂-ZrO₂ catalysts the acid site distribution and their number are entirely different from TiO₂ and ZrO₂. The number of weak to moderate acidic sites in TiO₂-ZrO₂ mixed oxide is very high, but the strong acidic sites are comparable to TiO₂ and ZrO₂. In the case of 3% K₂O/TiO₂-ZrO₂ catalyst only weak to moderated acidic sites are present. Almost all strong acidic sites and some weak to moderate acidic sites present in TiO₂-ZrO₂ have been neutralized by K₂O. Fung and Wang studied the changes in the acid base properties of TiO₂-ZrO₂ mixed oxides after K₂O addition and reported that at minimum loading of K₂O strong acids get poisoned, with the increase in K₂O loading simultaneously both moderate and weak acidic sites were neutralized [24,25].

3.2. Dehydrogenation of ethylbenzene

3.2.1. Influence of TiO₂ loading

The influence of TiO₂ content in TiO₂-ZrO₂ mixed oxide catalysts including TiO₂ and ZrO₂ for the dehydrogenation of ethylbenzene into styrene have been shown in Fig. 4. The catalytic performance of ZrO₂ and TiO₂ is inferior to all the TiO₂-ZrO₂ mixed oxide catalysts. The enhancement in catalytic activity of TiO₂-ZrO₂ mixed oxide catalysts might be due to huge hike in weak to moderate acidic sites compared to either TiO₂ or ZrO₂ and other changes in the physico-chemical properties such as BET surface area and crystalline properties. Among the various mixed oxide catalysts TiO₂-ZrO₂ mixed oxide catalyst showed highest activity towards the conversion of ethylbenzene. Based on the high performance of

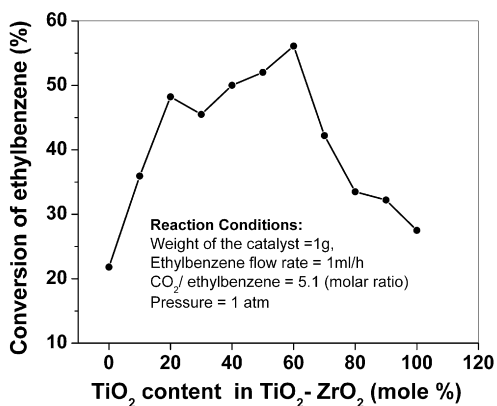


Fig. 4. Effect of TiO₂ content in TiO₂-ZrO₂ for the conversion of ethylbenzene at 600 °C.

TiO₂-ZrO₂ mixed oxide catalyst; it has been utilized for further studies.

3.2.2. Influence of K₂O on TiO₂-ZrO₂ mixed oxide catalyst

Physico-chemical and catalytic properties have been changed significantly due to K₂O addition to TiO₂-ZrO₂ mixed oxide catalyst. From Fig. 5 it is clear that the K₂O promoter has a substantial positive influence in converting ethylbenzene over TiO₂-ZrO₂ catalyst in the presence of CO₂. The catalytic activity of unpromoted TiO₂-ZrO₂ mixed oxide catalyst is higher in the first 2 h of time on stream, but latter on its activity has shown a marginal diminishing trend due to coke deposition. Contrarily, the activity of K₂O promoted TiO₂-ZrO₂ catalysts has continuously been increasing with the increase in reaction time up to 7 h of time on stream. The maximum conversion on 3% K₂O/TiO₂-ZrO₂ is 57.39%, but on TiO₂-ZrO₂ catalyst it is only 46.97%. The difference in the maximum conversion of ethylbenzene over K₂O promoted and unpromoted TiO₂-ZrO₂ is 10.42%. In other words, the hike in the conversion of ethylbenzene is 10.42% due to usage of K₂O promoter under the specified reaction conditions. The catalytic activities of K₂O/TiO₂-ZrO₂ catalysts in the first 2 h of time on stream are much lower than that of TiO₂-ZrO₂

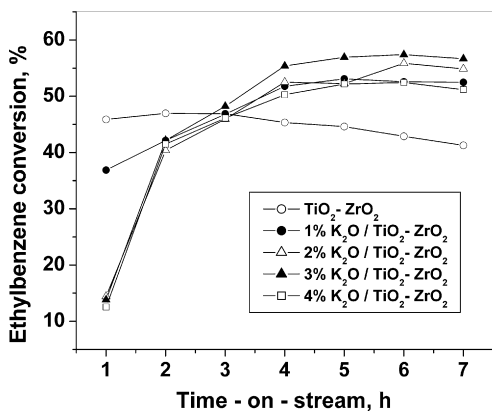


Fig. 5. Conversion of ethylbenzene with respect to time on stream (K₂O loading is in wt.%). Reaction conditions: weight of the catalyst, 1.0 g; ethylbenzene flow rate, 1 ml/h; CO₂/EB, 5.1 (molar ratio); pressure, 1 atm; temperature, 550 °C.

mixed oxide catalyst, but after third hour of time on stream the catalytic activity has been increased significantly. The initial low activities of K₂O/TiO₂-ZrO₂ catalysts are unclear. However, it has been reported that the initial low activity of certain catalysts in the oxidative dehydrogenation of ethylbenzene in presence of CO₂ [26].

The catalytic activity comparison of various loadings of K₂O promoter on TiO₂-ZrO₂ can be seen from Fig. 5, wherein, the increase of ethylbenzene conversion with increase in K₂O loading from 1 to 3% has been noticed. But the activity of 4% K₂O loaded catalyst is inferior to 3% K₂O loaded TiO₂-ZrO₂ catalyst. Based on these results, 3% K₂O loading can be considered as the optimum loading on TiO₂-ZrO₂ catalyst for the higher conversion of ethylbenzene. In the present context the role of K₂O promoter is not yet fully understood.

However, it can be assumed that K₂O acts as an electronic promoter. Other possibility is that the crystallites of TiO₂ anatase phase that is separated from the mixed oxide phase might be contributing for the enhancement in the conversion of ethylbenzene. Alternatively, acid–base active site compatibility might have taken place due to neutralization of strong acidic sites that are present in the TiO₂-ZrO₂ mixed oxide catalyst as observed from the TPD results (Fig. 3) and also the other possibility is that K₂O promoter as a basic oxide might be facilitating the activation of CO₂. However, it is difficult to draw any conclusion at the present moment regarding the enhancement in activity with the K₂O promoter.

3.2.3. Combined influence of K₂O and CO₂ on the dehydrogenation of ethylbenzene over TiO₂-ZrO₂ mixed oxide catalyst

To examine the combined influence of K₂O and CO₂ in the dehydrogenation of ethylbenzene four separate experiments were conducted under similar reaction conditions by changing the reaction environment with and without CO₂ over TiO₂-ZrO₂ mixed oxide catalyst and 3% K₂O/TiO₂-ZrO₂ catalyst, respectively, and the results are displayed in Fig. 6. The conversion of ethylbenzene over TiO₂-ZrO₂ in the nitrogen atmosphere is 52.19%, which has been significantly increased to 60.59%

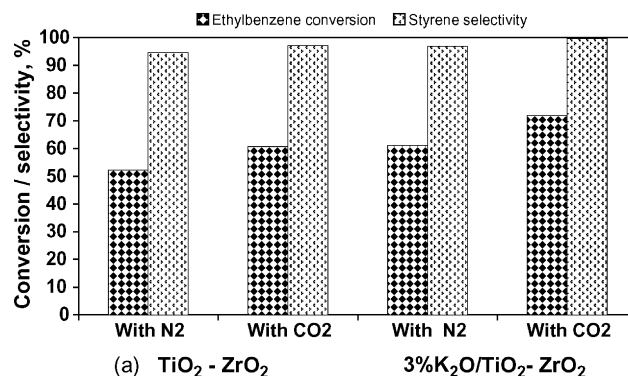


Fig. 6. Influence of catalytic activity with respect to reaction environment over: (a) TiO₂-ZrO₂ with N₂ and CO₂, (b) 3% K₂O/TiO₂-ZrO₂ with N₂ and CO₂ (K₂O loading is in wt.%). Reaction conditions: weight of the catalyst, 1.0 g; WHSV, 1.16 h⁻¹; CO₂/EB, 5.1 (molar ratio); pressure, 1 atm; temperature, 660 °C.

in the presence CO_2 and furthermore, the selectivity of styrene is also increased to 97.09% from 94.6%. Similarly, the conversion and the selectivity have been substantially increased even in the presence of nitrogen over 3% $\text{K}_2\text{O}/\text{TiO}_2\text{-ZrO}_2$ catalyst, which is due to the effect of K_2O promoter. The catalytic activity of 3% $\text{K}_2\text{O}/\text{TiO}_2\text{-ZrO}_2$ catalyst has dramatically increased in the presence of CO_2 , which is due to the combined promotional effects of both K_2O promoter and CO_2 . In order to explain the combined promotional effects, the data obtained over $\text{TiO}_2\text{-ZrO}_2$ catalyst in the presence of nitrogen has been compared with the data obtained on 3% $\text{K}_2\text{O}/\text{TiO}_2\text{-ZrO}_2$ catalyst in the presence of CO_2 . The conversion of ethylbenzene over $\text{TiO}_2\text{-ZrO}_2$ catalyst in the presence of nitrogen is 52.19%, which has been increased to 71.95% over 3% $\text{K}_2\text{O}/\text{TiO}_2\text{-ZrO}_2$ catalyst in the presence of CO_2 . Indeed, the hike in the conversion is 19.76%, which is exceptionally high improvement and in addition selectivity has almost reached to 100% (99.63%). Still, the conversion is much lower than the equilibrium conversions of ethylbenzene in the presence of CO_2 as reported by Qin et al. [27], wherein, it is reported that the 25.2% of ethylbenzene conversion in the simple dehydrogenation can be elevated to 82.4% at 550 °C when the ethylbenzene dehydrogenation reaction coupled with reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$). However, the data obtained over 3% $\text{K}_2\text{O}/\text{TiO}_2\text{-ZrO}_2$ catalyst is worth noting, particularly in the selectivity point of view. There are certain reports concerning the higher selectivities such as 99–100%, but at the lower conversion levels of ethylbenzene [11]. The higher selectivity of styrene over 3% $\text{K}_2\text{O}/\text{TiO}_2\text{-ZrO}_2$ catalyst can be explained mainly based on two reasons. The first one is the suppression of dealkylation products by neutralizing the strong acidic sites of $\text{TiO}_2\text{-ZrO}_2$ catalyst by optimal amount of K_2O addition as evidenced from the NH_3 TPD results that shown in Fig. 3. The second reason is that the hydrogen produced in the simple dehydrogenation is converting into water by the coupling of reverse water gas shift reaction. Hence, there is less scope for the hydrogenolysis and its subsequent reactions, consequently selectivity of styrene increased remarkably. As reported by Dulamita et al. [28], if the surface basic sites are strong enough to abstract β -hydrogen from ethylbenzene, the break of the lateral C–C bond is promoted and, therefore, the selectivity to toluene will increase. If the catalyst surface acidity is larger, α -hydrogen can be abstracted from ethylbenzene and the break of the phenyl–C bond become more probably, therefore, a higher selectivity to benzene will be obtained. The data are suggesting that the basic sites are not strong enough to convert ethylbenzene into toluene.

The high activity of the catalyst in the presence of CO_2 is due to the dissociation of CO_2 on the catalyst surface to produce active oxygen species. This oxygen species oxidizes H_2 that produced in the simple ethylbenzene dehydrogenation process into H_2O by reverse water–gas shift reaction and thereby releases the limitation of thermodynamic equilibrium. As it is evidenced from the literature, the energy required for the production of one ton styrene when coupled with reverse water gas shift reaction is CO_2 is 6.3×10^8 , whereas, in the simple dehydrogenation is 1.5×10^9 cal [26]. Due to facile conversion of ethylbenzene

into styrene in the presence of CO_2 , the selectivity of styrene increased dramatically as shown in Fig. 6.

4. Conclusions

In conclusion, 3% $\text{K}_2\text{O}/\text{TiO}_2\text{-ZrO}_2$ catalyst is promising for the selective dehydrogenation of ethylbenzene to styrene in the presence excess of CO_2 . As evidenced from the TPD of NH_3 weak to moderate acidic sites are essential for the selective production of styrene, whereas the strong acidic sites lead to the formation of by-products. 3 wt% K_2O addition to $\text{TiO}_2\text{-ZrO}_2$ mixed oxide catalyst neutralized the strong acidic sites that are responsible for coke deposition and the formation of unwanted by-products. CO_2 enhanced the conversion of ethylbenzene and styrene selectivity acting as oxidant and diluent. Hence, the unified effects of K_2O and CO_2 enhanced both the conversion of ethylbenzene and the selectivity of styrene significantly.

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