Dehydrogenation of Ethylbenzene to Styrene with CO_2 over TiO_2-ZrO_2 Bifunctional Catalyst

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Received April 4, 2006

In the dehydrogenation of ethylbenzene to styrene, CO_2 could play a role as an oxidant to increase conversion of ethylbenzene and stability as well over TiO_2-ZrO_2 mixed oxide catalysts. TiO_2-ZrO_2 catalysts were prepared by co-precipitation method and were characterized by BET surface area, bulk density, X-ray diffraction, temperature programmed desorption of NH_3 and CO_2. These catalysts were found to be X-ray amorphous with enhanced surface areas and acid-base properties both in number and strength when compared to the respective oxides (TiO_2 and CO_2). These catalysts were found to be highly active (> 50% conversion), selective (> 98%) and catalytically stable (10 h of time-on-stream) at 600 °C for the dehydrogenation of ethylbenzene to styrene. However, in the nitrogen stream, both activity and stability were rather lower than those in the stream with CO_2. The TiO_2-ZrO_2 catalysts were catalytically superior to the simple oxide catalysts such as TiO_2 and ZrO_2. The synergistic effect of CO_2 has clearly been observed in directing the product selectivity and prolonging catalytic activity.

Key Words : Dehydrogenation, Styrene, CO_2, TiO_2-ZrO_2, Catalysis

Introduction

The utilization of CO_2, which is a main contributor to the greenhouse effect, has been of global interest from both fundamental and practical viewpoints in green and sustainable chemistry. In particular, it is worthwhile to note that CO_2 could be used as an oxygen source or oxidant and can be considered as a nontraditional mild oxidant and oxygen transfer agent. Commercially, styrene is still being produced from ethylbenzene over iron based catalysts in the presence of super heated steam, since; steam plays a prominent role in shifting of the reaction equilibrium towards products, prolonging the catalyst activity and most significantly acts as a heat carrier. However, the usage of large volume of super heated steam is one of the drawbacks of the present technology. Recently, much attention has been paid for the effective utilization of CO_2 as a substitute to steam.[1-4] However, the present commercial catalyst is ineffective in the presence of CO_2. The indispensable requirement is the selection of a catalyst system which can activate CO_2. The acidic properties of CO_2 necessitate the choice of a catalyst with basic properties. Additionally, the catalytic system should be capable of activating the ethylbenzene with specific acidic sites. Accordingly, in our earlier publication, the concept of acid-base bi-functional catalysis has been investigated for the dehydrogenation of ethylbenzene over amphoteric ZrO_2 in the presence of CO_2.[5]

It is well known that mixing the pure oxides is a beneficial way either to modulate the properties of the component oxides or to create new active sites. Several theories have been proposed, for the enhanced acid-base properties and their activities.[6-9] Accordingly, mixing of TiO_2 and ZrO_2 exhibit high surface area, profound surface acid-base proper-

ties, enhanced hydrothermal and mechanical robustness.[10-12] Consequently, TiO_2-ZrO_2 mixed oxides are proved to be highly active and selective catalysts for several reactions such as isomerization of cyclohexane oxides,[13,14] hydrogenation of carboxylic acids to alcohols,[15] epoxidation of cyclooctene,[16] dehydation of methanol to dimethyl ether and isopropanol to propene.[17,18] Particularly, TiO_2-ZrO_2 catalysts were used for the oxidative and non-oxidative dehydrogenation of ethylbenzene and cyclohexane.[10-12,19] However, TiO_2-ZrO_2 mixed oxide catalysts were not thoroughly been investigated for the dehydrogenation of ethylbenzene to styrene using CO_2 as a soft oxidant.

In the present investigation, catalytic activity of individual oxides and mixed TiO_2-ZrO_2 oxides in the dehydrogenation of ethyl benzene to styrene has been described. Structure activity relationships are summarized with the help of XRD characterization and also the activity with respect to TPD of NH_3 and CO_2 has been described. A comparative study has been made in the presence and absence of CO_2. In order to elucidate the stability of the catalyst the reaction has been studied at moderate to elevated temperatures.

Experimental

Catalyst preparation. TiO_2-ZrO_2 mixed oxide catalysts were prepared by co-precipitation method. In a typical experiment, requisite amount of zirconyl (IV) nitrate hydrate (Acros Organics, USA, 99.5%) and titanium (IV) chloride (Yakuri Pure Chemicals, Co, Ltd, Japan) were dissolved in de-ionized H_2O and stirred until the solution become homogeneous followed by the addition of requisite amount of aqueous ammonium solution (DC Chemicals Co., Ltd, Korea, 25.0-28.0%) until the solution pH = 7-8. The

resultant white precipitate was separated by filtration under reduced pressures and washed with de-ionized H_2O several times until the complete removal of chloride and nitrate ions followed by drying at 120 ^oC for 12 h and calcined at 550 ^oC for 6 h in a muffle furnace. In order to find out the formation of $TiZrO_4$ phase and its catalytic behavior the 60% TiO_2-ZrO_2 mixed oxide was further calcined at 650, 750 and 850 ^oC for 6 h respectively.

Surface area and bulk density. BET surface areas of the catalysts were determined using Chemisorp 2705 unit (Micromeritics Instrument. Co., USA). All the samples were pretreated at 200 ^oC for 4 h before measurement. N_2 was used as an adsorbate gas and the measurements were performed at 77 K. Bulk densities were estimated on the basis of mass and volume of the catalysts.

X-ray diffraction. X-ray powder diffraction patterns were recorded on a Rigaku X-Ray Diffractometer (Multiflex, Shimodzu, Japan) with Ni filtered Cu K$_\alpha$ radiation (λ = 1.5406 Å) operated at 50 kV and 50 mA in the 2θ range of 10 to 90° with a scan speed of 4°/min.

TPD of NH_3 and CO_2. Acidity and basicity of the mixed oxide catalysts were performed by temperature programmed desorption of NH_3 and CO_2 respectively, using Chemisorp 2705 unit (Micromeritics Instrument. Co., USA) equipped with thermal conductivity detector (TCD). Typically, *c.a.* 50 mg of catalyst was pretreated in flowing He at 500 ^oC for 1 h, cooled to 100 ^oC and allowed to expose 5% NH_3 in helium gas mixture with a flow rate 20 mL/min for 30 min and subsequently the adsorbed NH_3 was purged with helium at the same temperature for 1 h to remove the physisorbed NH_3. The chemisorbed NH_3 was measured in flowing helium with the flow rate of 20 mL/min from 100 ^oC to 500 ^oC with the heating rate of 10 ^oC/min.

Catalytic activity. The catalytic activity studies were performed in a fixed bed down flow reactor (i.d. 4.5 mm and length 300 mm) under atmospheric pressure. 1.0 g of catalyst sample was loaded into reactor with the support of quartz wool. The pretreatment of the catalyst was conducted at 600 ^oC in the flow of N_2 (20 mL/min) for 2 h and altered to the reaction temperature and conducted the reaction by switching over to CO_2 flow. Ethylbenzene was introduced by a peristaltic pump with a feed rate of 9.8 mmol/h along with either CO_2 or N_2. Gaseous and liquid products were analyzed simultaneously by on-line GC (Younlin Instrument, Acme 6000 series, Korea) equipped with TCD and FID. Poropak N 80/100 column (6ft × 1/8") was used for the analysis of gaseous products such as hydrogen, nitrogen, carbon monoxide, methane and carbon dioxide. Innowax widebore column (30 meters long, 0.32 mm I. D and 0.25 μm film thickness) was used for the analysis of liquid products, in which, styrene was the major product and benzene, toluene, benzaldehyde and acetophenone were minor/trace products.

Results and Discussion

TiO_2-ZrO_2 mixed oxide catalysts. The BET surface areas of mixed oxides (TiO_2-ZrO_2) and the individual oxides (TiO_2 and ZrO_2) were summarized in Table 1. The BET surface area of either TiO_2 (15 m^2/g) or ZrO_2 (25 m^2/g) is much lower than that of all the loadings of their mixed oxides. Addition of TiO_2 to ZrO_2, sharp increase in surface area was observed and reached a maximum of 130 m^2/g at 40% TiO_2-ZrO_2 and it is almost same up to 60% TiO_2-ZrO_2 catalyst. Further increase in TiO_2 loading slow decrease in surface area was observed, which is an agreement with the results of Mao *et al.*[20] The bulk densities of mixed oxides were lower than that of pure TiO_2 or ZrO_2; this behavior may be explained on the basis of particle size. The high surface areas of the mixed oxides calcined at 550 ^oC are obviously in the amorphous nature. Similar observation was put forward by several authors.[21-23]

XRD patterns of TiO_2, ZrO_2 and 50% TiO_2 –ZrO_2 calcined at 550 ^oC were shown in Figure 1. The XRD pattern of pure ZrO_2 was in monoclinic phase and pure TiO_2 show mostly anatase phase whereas the mixed oxides (40-60% TiO_2-ZrO_2) was found to be X-ray amorphous. These results were in agreement with the XRD results of Zou and Lin.[23] The XRD patterns of all the mixed oxides depicted in Figure 2, the XRD patterns of 10 and 20% TiO_2-ZrO_2 mixed oxides

Table 1. BET surface areas and bulk densities of TiO_2-ZrO_2 mixed oxides

Catalyst	BET surface area (m^2/g)	Bulk density (g/cm^3)
TiO_2	15	1.71
ZrO_2	25	1.89
10% TiO_2–ZrO_2	79	1.02
20% TiO_2– ZrO_2	116	1.01
30% TiO_2–ZrO_2	126	0.96
40% TiO_2–ZrO_2	130	0.81
50% TiO_2–ZrO_2	129	0.79
60% TiO_2–ZrO_2	135	0.76
70% TiO_2–ZrO_2	122	0.91
80% TiO_2–ZrO_2	109	0.89
90% TiO_2–ZrO_2	111	0.92
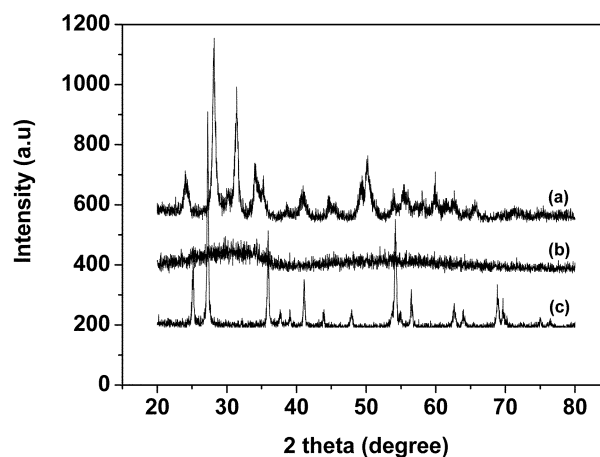
Figure 1. XRD patterns of pure (a) ZrO_2 and (b) 50% TiO_2-ZrO_2 mixed oxide and pure (c) TiO_2 calcined at 550 ^oC.
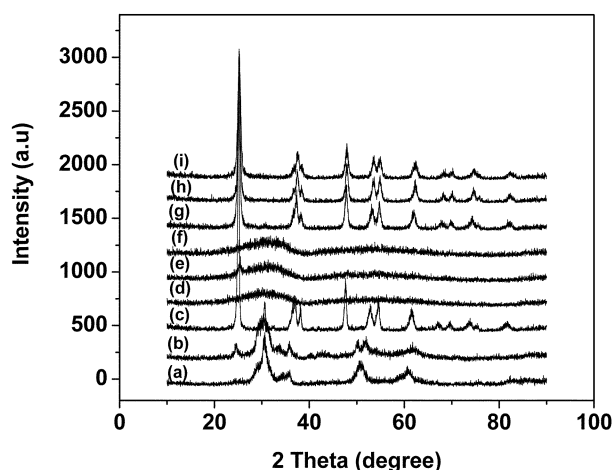
Figure 2. XRD patterns of different compositions of TiO_2-ZrO_2 mixed oxides. (a) 10%TiO_2-ZrO_2; (b) 20% TiO_2-ZrO_2; (c) 30% TiO_2-ZrO_2; (d) 40% TiO_2-ZrO_2; (e) 50% TiO_2-ZrO_2; (f) 60% TiO_2-ZrO_2; (g) 70% TiO_2-ZrO_2; (h) 80% TiO_2-ZrO_2; (i) 90% TiO_2-ZrO_2.

Figure 3. XRD patterns of 50% TiO_2-ZrO_2 at different calcination temperatures. (a) 550 $^{\circ}$C; (b) 650 $^{\circ}$C; (c) 750 $^{\circ}$C; (d) 850 $^{\circ}$C.

were exhibited poorly crystalline with tetragonal phase of ZrO_2. Surprisingly, under similar preparation conditions pure ZrO_2 was in the monoclinic phase whereas with 10-20 %TiO_2 component ZrO_2 was stabilized as tetragonal phase. Further increase of TiO_2 (30%) component in the TiO_2-ZrO_2 mixed oxide showed highly crystalline with TiO_2 anatase phase predominantly. 40 to 60% TiO_2-ZrO_2 mixed oxides were found to be X-ray amorphous. High TiO_2 loading mixed oxide were found to highly crystalline with anatase TiO_2 phase. The XRD patterns of 60% TiO_2-ZrO_2 mixed oxide calcined at different temperatures were shown in Figure 3. The XRD pattern of 60% TiO_2-ZrO_2 calcined at 550 $^{\circ}$C was in the amorphous phase whereas, the same mixed oxide catalyst further calcined at 650, 750 and 850 $^{\circ}$C showed highly crystalline order due to the formation of $TiZrO_4$ phase (2θ = 24.7 and 30.7°). As reported,[24,25] the formation of $TiZrO_4$ solid solution at high temperature calcined TiO_2-ZrO_2 mixed oxides was obvious, hence our XRD results were well matched.

Measurement of acidity and basicity by the TPD of NH₃ and CO₂. The TPD profiles of NH_3 (Fig. 4) showed that the acid strength was in the order ZrO_2 < TiO_2 < TiO_2-ZrO_2. The acid strength distributions were obtained by analyzing the TPD profiles of NH_3, following the procedure proposed by Berteau and Delmon,[26] wherein, based on the desorption temperature of NH_3 the acidic sites were classified as 3 categories. The amount of NH_3 desorbed below 200 $^{\circ}$C is the measure of weak acidic sites, followed by desorbed in the temperature range of 200-350 $^{\circ}$C is medium acidic sites and desorbed above 350 $^{\circ}$C is strong acid sites. The NH_3 TPD profiles of ZrO_2 and TO_2 were distributed over the temperature from 150 to 500 $^{\circ}$C which indicate that the acid strength was distributed from weak to strong uniformly. However, there was slightly higher number of acid sites in the TiO_2 than that of ZrO_2. In the case of TiO_2-ZrO_2 mixed oxide the NH_3 TPD peak maximum was at 225 $^{\circ}$C, and also it was distributed in a wide range from 175 to 450 $^{\circ}$C with
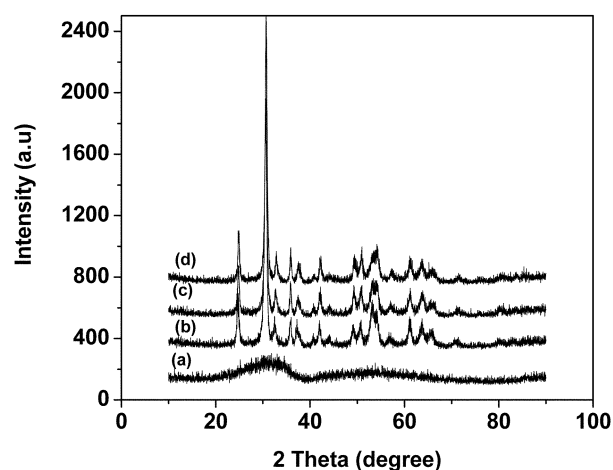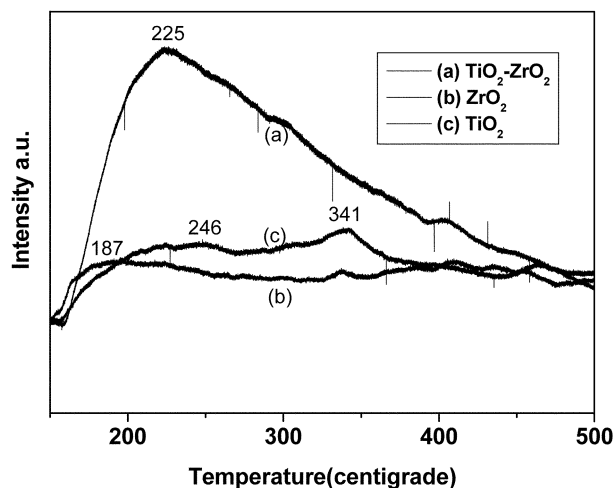

Figure 4. TPD patterns of NH_3 for ZrO_2, TiO_2 and 50% TiO_2-ZrO_2 mixed oxide catalyst.

high signal intensity. This peculiar behavior in NH_3 TPD of TiO_2-ZrO_2 could be explained that the new acidic sites were generated due to mixing of TiO_2 and ZrO_2 similar to the enhancement in surface area (Table 1). This peculiarity could also be observed from the generation of amorphous nature of mixed oxide during the stages of preparation (Fig. 1). Similarly, Zou and Lin[21] reported that the TiO_2-ZrO_2 mixed oxides not only exhibit higher acidity but also have a large number of acid sites than the pure oxides.

The basic properties were investigated using the TPD of CO_2. The TPD profiles of CO_2 for TiO_2-ZrO_2 mixed oxide and the individual oxides (TiO_2 and ZrO_2) were shown in Figure 5. The CO_2 TPD profiles demonstrate that the strength and number of basic sites of TiO_2-ZrO_2 mixed oxide were much higher than that of its individual oxides (TiO_2 and ZrO_2). The temperature maxima for ZrO_2, TiO_2 and TiO_2-ZrO_2 are 140, 145 and 187 $^{\circ}$C respectively. The shift of peak maxima from lower to higher temperature was an indication of increase in basic strength. The TPD profile of TiO_2-ZrO_2 possessed 2 peak maxima at 187, 453 $^{\circ}$C. It is clearly been indicating that the basic sites were generated during the
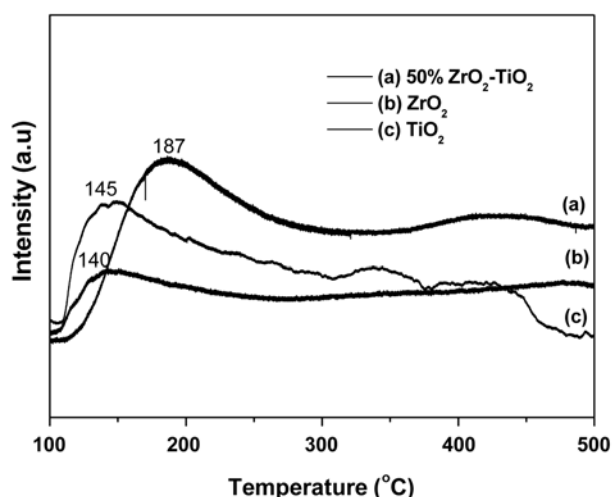
Figure 5. TPD patterns of CO_2 for ZrO_2, TiO_2 and 50% TiO_2-ZrO_2 mixed oxide catalyst.

stages of catalyst preparation.

Catalytic activity. The catalytic activity data of individual oxides (TiO_2 and ZrO_2) and 50% TiO_2-ZrO_2) the mixed oxide obtained at 550 °C in the presence of CO_2 for the dehydrogenation of ethylbenzene to styrene was displayed in Table 1. It indicates that the both TiO_2 and ZrO_2 were not only active for this reaction but also selective towards the production of styrene. However, these two oxides individually exhibited inferior activity in comparison with their respective mixed oxide. The catalytic activity of TiO_2-ZrO_2 mixed oxide catalyst was almost doubled either in the conversion or in the yields of styrene under similar reaction conditions. Surprisingly, the surface area of TiO_2-ZrO_2 mixed oxide catalyst was also much higher than that of its individual oxides prepared under similar conditions (Table 1). Similarly, Maity *et al.*[22] reported that the TiO_2-ZrO_2 mixed oxides prepared by homogeneous precipitation method exhibited higher surface area than its individual oxides and
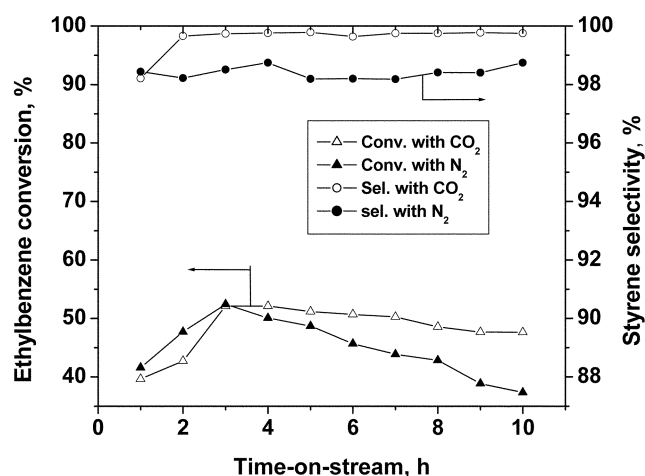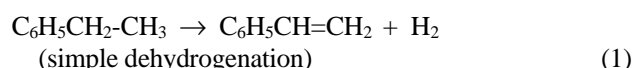

Figure 6. Catalytic activity on 50% TiO_2-ZrO_2 mixed oxide catalyst in the presence and absence of the CO_2. Reaction conditions: T = 600 °C, P = 1 atm, W/F = 16.73 g cat, h/mole, CO_2/ EB = N_2/EB = 5.1 (molar ratio).

also claimed that these mixed oxides possess both acidic and basic sites. These catalytic results are suggesting that the compatible catalytic sites were generated during the stages of TiO_2-ZrO_2 mixed oxide catalyst preparation. In a recent review by Reddy and Khan[27] explained that that there is a correlation between dehydrogenation of ethylbenzene activity and acid - base property where in Zr ion act as Lewis acid site and Ti ion as a base site.
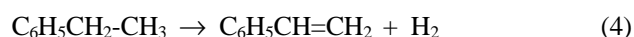
The formation of amorphous TiO_2-ZrO_2 mixed oxide (Figs. 1-3), enhancement in surface areas (Table 1), and the hike in acidic and basic sites number and strength (Figs. 4 and 5) might be the reasons for the higher catalytic activity of these mixed oxides towards conversion of ethylbenzene and styrene selectivity than those of their individual oxides. It is evident that the dehydrogenation of ethyl benzene to styrene followed the acid-base bi-functional mechanism.

The time on stream study on TiO_2-ZrO_2 mixed oxide catalyst in the presence and absence of CO_2 clearly been indicating its potential role in directing the product formation and catalytic stability at 600 °C (Fig. 6). The conversion of ethylbenzene was initially lower in the presence of CO_2 than its absence. Mimura *et al.* has already been reported the lower initial activity in presence of CO_2 than in the presence of helium for the dehydrogenation ethylbenzene over Fe_2O_3/ Al_2O_3 catalyst.[28] This anomaly might be due to the presence of large number of OH groups initially on the surface of the catalyst and the competitive adsorption of ethylbenzene and CO_2 rather than ordered. Third hour onwards there was a significant difference in the ethylbenzene conversion as well as in catalytic stability, suggesting that simple dehydrogenation of ethylbenzene was taking place in the absence of CO_2 (equation 1) where as in the presence of CO_2 reverse water gas shift reaction (equation 2) was coupling with the simple dehydrogenation.

$$C_6H_5CH_2\text{-}CH_3 \rightarrow C_6H_5CH=CH_2 + H_2$$
$$\text{(simple dehydrogenation)} \qquad (1)$$

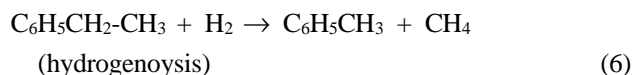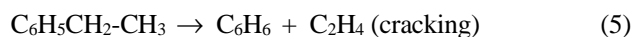$$H_2 + CO_2 \rightarrow CO + H_2O \text{ (RWGS)} \qquad (2)$$

Recently, Cavani and Trifiro reported that the oxidation of hydrogen by CO_2 shifts the dehydrogenation equilibrium to achieve higher yields by increasing the conversion as well as selectivity.[29] In a recent study by Sun *et al.*,[30] coupling the reverse water gas shift reaction with the ethylbenzene dehydrogenation, the role of CO_2 has clearly been explained with illustrated mechanistic aspects.

Several authors proposed the mechanism of ethylbenzene dehydrogenation to styrene monomer in the presence of CO_2[32-36] in which, redox sites were prevailed either with single step pathway (equation 3) or dual step pathway (equations 4 and 2).

$$C_6H_5CH_2\text{-}CH_3 + CO_2 \rightarrow C_6H_5CH=CH_2 + H_2O \qquad (3)$$

$$C_6H_5CH_2\text{-}CH_3 \rightarrow C_6H_5CH=CH_2 + H_2 \qquad (4)$$

Styrene selectivity point of view, TiO_2-ZrO_2 mixed oxide was superior which might be due to catalytic site compatibility. The commonly observed by-products such as benzene

and toluene produced by cracking and hydrogenolysis (equation 5, 6) respectively in the dehydrogenation of ethylbenzene were minimal even at high temperatures suggesting that the catalytic sites responsible for these reactions might be differ from those of ethylbenzene dehydrogenation or strength insufficiency.

$$C_6H_5CH_2\text{-}CH_3 \rightarrow C_6H_6 + C_2H_4 \text{ (cracking)} \quad (5)$$

$$C_6H_5CH_2\text{-}CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$$
$$\text{(hydrogenoysis)} \quad (6)$$

The stable activity of TiO_2-ZrO_2 mixed oxide catalysts in the dehydrogenation of ethylbenzene to styrene even at elevated temperatures in the presence of CO_2 was observed. Mimura *et al.*[28] observed that the rapid deactivation of the Fe_2O_3/Al_2O_3 catalyst during the dehydrogenation in the presence of helium, whereas the deactivation of the catalyst was hardly observed during the dehydrogenation in the presence of CO_2 and concluded that the CO_2 suppressed the deactivation of the catalyst during the dehydrogenation of ethylbenzene. It could be explained that the coke deposition on the surface of the catalyst was lower in the presence of CO_2 than that of its absence (Table 1).

The catalytic activity of various TiO_2-ZrO_2 mixed oxides was depicted in Figure 7. Among which 60% TiO_2-ZrO_2 exhibited superior activity than that of other loadings. The same catalyst was calcined at higher temperatures and confirmed the formation of $TiZriO_4$ and conducted the reaction using these $TiZrO_4$ containing TiO_2-ZrO_2 mixed oxide catalysts and found that there was no significant increase in activity.

The dehydrogenation of ethylbenzene over 50% TiO_2-ZrO_2 mixed oxide at various reaction temperatures was showed in the Figure 8. The catalytic activity at 400 °C was almost negligible, whereas at 500 °C it attained considerable conversion levels (about 17%), there after a significant increase was observed. At normal industrial operating
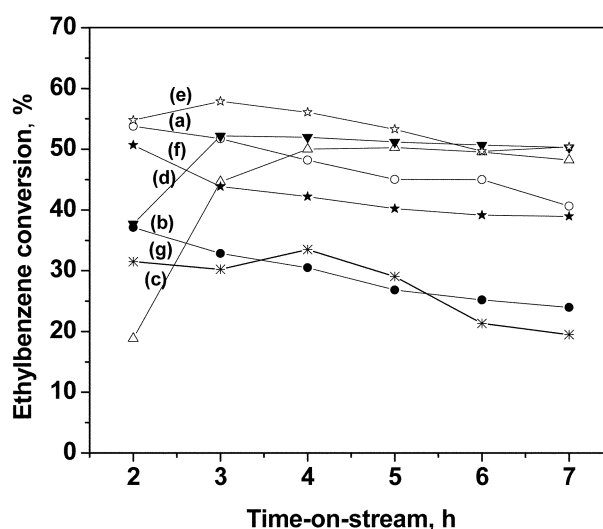

Figure 7. Variation of catalytic activity with at different loadings. (a) 20% TiO_2-ZrO_2; (b) 30% TiO_2-ZrO_2; (c) 40% TiO_2-ZrO_2; (d) 50% TiO_2-ZrO_2; (e) 60% TiO_2-ZrO_2; (f) 70% TiO_2-ZrO_2; (g) 80% TiO_2-ZrO_2. Reaction conditions: T = 600 °C, P = 1 atm, W/F = 16.73 g cat, h/mole, $CO_2/EB = N_2/EB = 5.1$ (molar ratio).

temperature (about 650 °C), the conversion was about 57% and in particular, selectivity towards styrene (96%) is remarkable at this higher temperature (Fig. 8).

It is quite common that as the reaction temperature increases the conversion of the reactant also increases whereas the selectivity certainly decreases. In a recent report by Sugino *et al.*,[36] as the conversion of ethylbenzene increases with increase in temperature, both the yield of styrene and its selectivity drastically decreased over active carbon supported lithium promoted iron catalyst. Similar observation was put forward by Ohishi *et al.*,[37] over chromia supported MCM-41 catalyst, in which with increasing the temperature up to 600 °C, ethylbenzene conversion linearly increased, while the selectivity to styrene gradually decreas-

Table 2. Dehydrogenation of ethylbenzene over ZrO_2, TiO_2 and 50% TiO-ZrO_2 mixed oxide

Catalyst	TiO₂			ZrO₂			TiO₂-ZrO₂		
Surface area, m²/g	15.0			25.5			129.2		
Coke, %	2.6			2.9			3.6 (4.8)[a]		
TOS, h	Conv, %	Yield, %		Conv, %	Yield, %		Conv, %	Yield, %	
	EB	SM	others	EB	SM	others	EB	ST	others
1	27.63	27.34	0.29	27.51	27.24	0.27	39.65	35.22	0.71
2	34.19	33.82	0.37	25.88	25.60	0.28	42.73	37.08	0.65
3	28.76	28.38	0.38	26.85	26.59	0.26	52.18	51.41	0.77
4	27.52	27.17	0.35	21.8	21.40	0.40	52.1	51.47	0.54
5	24.98	24.68	0.30	20.96	20.93	0.04	51.18	50.64	0.54
6	25.04	24.83	0.21	18.75	18.45	0.30	50.68	49.78	0.90
7	24.76	24.48	0.28	17.84	17.54	0.30	50.27	49.66	0.61
8	22.66	22.25	0.41	17.19	16.90	0.29	48.57	47.96	0.61
9	20.83	20.59	0.24	16.82	16.51	0.31	47.67	47.12	0.55
10	20.03	19.72	0.31	16.06	15.84	0.22	47.64	47.04	0.60

Reaction conditions: T = 600 °C, P = 1 atm, W/F = 16.73 $g_{cat.}$ h/mole, $CO_2/EB = 5.1$. [a]Coke deposition in the absence of CO_2
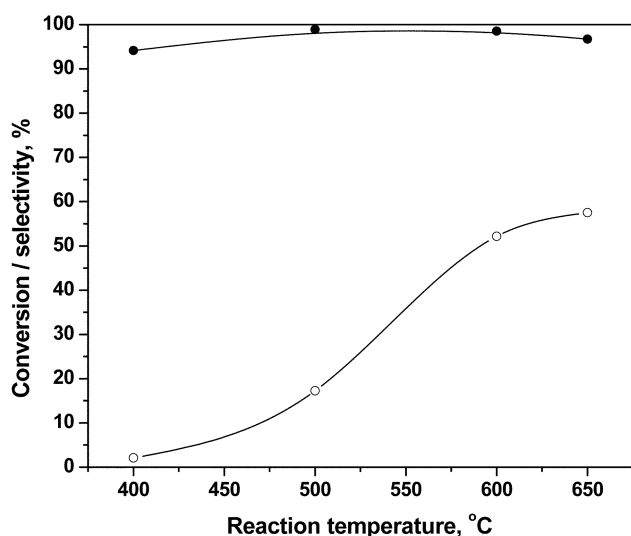
Figure 8. Conversion/selectivity as a function of reaction temperatures over 50% TiO_2-ZrO_2 catalysts. Reaction conditions: Pressure = 1 atm, W/F = 16.73 g cat.h/mol and CO_2/EB = 5.1, (○) Ethylbenzene conversion (●) Styrene selectivity.

ed and further increase of reaction temperature caused a clear decrease in the styrene monomer whereas benzene formation has significantly increased. Contrarily, in the present study, TiO_2-ZrO_2 mixed oxide catalyst exhibited the increase of conversion with increased reaction temperature without foregoing selectivity of styrene monomer. The uniqueness of TiO_2-ZrO_2 mixed oxide catalyst in maintaining higher selectivity even at higher conversion levels is the subject of interest.

Conclusions

TiO_2-ZrO_2 catalysts were highly active, selective and catalytically stable in the dehydrogenation of ethylbenzene to styrene in the presence of CO_2. The catalytic activity of TiO_2-ZrO_2 catalyst was almost doubled than those of individual oxides. The catalytic activity of TiO_2-ZrO_2 mixed oxides was superior in the presence CO_2 than its absence. The conversion of ethylbenzene increased with reaction temperature without foregoing much selectivity of styrene. The catalytic results are indicating the TiO_2-ZrO_2 catalysts are suitable for the CO_2 coupled process.

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