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CO_2 utilization as an oxidant in the dehydrogenation of ethylbenzene to styrene over MnO_2-ZrO_2 catalysts

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Abstract

MnO_2-ZrO_2 binary oxide catalytic system was applied for the effective utilization of CO_2 as an oxidant in the ethylbenzene dehydrogenation (EBD) to styrene monomer (SM). MnO_2-ZrO_2 oxides were prepared by co-precipitation method and characterized as solid solution mixture having surface area more than 100^2 g^{-1}. 10% MnO_2-ZrO_2 mixed oxide catalyst exhibited conversion of 73% with the selectivity of 98% at 650 °C. The MnO_2-ZrO_2 binary oxides were X-ray amorphous whereas the individual oxides (MnO_2 and ZrO_2) having much lower surface areas were crystalline in nature. As a result, MnO_2-ZrO_2 binary oxides exhibited greatly elevated catalytic activity for the conversion of ethylbenzene (EB) than those of individual oxides in the presence of CO_2. However, in the absence of CO_2 poor catalytic activity and stabilities were observed. Gradual enhancement of activities were demonstrated in the higher CO_2 to EB ratios. Hence, CO_2 had a profound role as a soft oxidant by improving both activity and stability in the EBD over MnO_2-ZrO_2 mixed oxide catalysts.

Keywords: Ethylbenzene; Styrene; Dehydrogenation; MnO_2-ZrO_2 mixed oxides; CO_2

1. Introduction

Ethylbenzene dehydrogenation (EBD) is a representative process for the production of styrene (SM), an important monomer for synthetic polymers. This is one of the ten most important industrial petrochemical processes. However, the present industrial process is thermodynamically limited, energy consuming, super heated steam obligatory, coke-deactivating, partially active, and poorly selective [1]. Alternatively, oxidative EBD has been proposed in order to circumvent some of the cited difficulties [2]. However, in the oxidative dehydrogenation process the usage of O_2 (strong oxidant) produces unwanted by-products (oxygenates) along with SM resulting in low selectivity of SM [3]. Hence, alternative oxidative EBD with CO_2 oxidant has been emerging as a potential process [4–6], because CO_2 utilization offer several advantages in catalysis such as acceleration of the reaction rate, enhancement in product selectivity, alleviation of thermodynamic equilibrium limitations, suppression of total oxidation, prolonging of catalyst life, and prevention of hot spots on the catalyst surface. Based on these unique characteristics it has been coined as a soft oxidant [7,8].

Since the present commercial iron based catalysts are ineffective for the EBD in the presence of CO_2, intensive explorations have emerged recently in order to develop compatible catalytic systems that can operate effectively with CO_2. Mimura et al. [9–11] and Badstube et al. [12,13] have investigated Al_2O_3 and active carbon (AC) supported alkali metal promoted iron oxide based catalysts, respectively, for EBD in the presence of CO_2. The effective utilization of CO_2 was accomplished in our earlier publications over zeolite and ZrO_2 supported iron oxides [8,14], Al_2O_3 supported vanadium and vanadium-antimony oxide catalysts [15–17]. In our recent report, the influence of CO_2 over ZrO_2 has been described, wherein enhancement in conversion of EB as well as selectivity towards SM in presence of CO_2 oxidant was observed [18]. Furthermore, catalytic activity of ZrO_2 has been significantly improved when it was mixed with TiO_2 [19]. Presently, the study has been extended to MnO_2-ZrO_2 mixed oxides, based on our results on TiO_2-ZrO_2 mixed oxide catalysts. In the present publication, apart from the general catalytic activity studies of MnO_2-ZrO_2 mixed oxides in the dehydrogenation of EB to SM, the role of CO_2 as a soft oxidant has been delineated.

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2. Experimental

2.1. Catalyst preparation

MnO_2-ZrO_2 mixed oxides were prepared by co-precipitation method taking zirconyl nitrate and manganese nitrate as precursors and aqueous ammonia solution was used as a hydrolyzing agent. In a typical experiment, 0.1 M mixed aqueous solution of respective precursors was stirred at room temperature for 0.5 h. After attainment of homogeneous solution, requisite amount of aqueous ammonia solution was added until the pH of the solution reached 9 and the stirring was continued further 1 h followed by aging at 100 °C for 12 h. The resultant precipitate was filtered off under reduced pressure and washed thoroughly with water and dried at 120 °C for 12 h in oven and finally calcined at 550 °C for 6 h in a muffle furnace. Individual oxides (MnO_2 and ZrO_2) were prepared adopting the same procedure. In order to find out the EBD activity on MnO_2 and ZrO_2 solid solution, 50% MnO_2-ZrO_2 mixed oxide was further calcined at 650, 750 and 850 °C.

2.2. Catalyst characterization

BET surface area of the catalyst was measured by nitrogen adsorption at liquid nitrogen temperature (−196 °C) using pulse chemisorb 2705 (Micromeritics Instrument Co., USA). The catalysts were evacuated for 2 h at 200 °C prior to the experiment. Bulk density was estimated on the basis of mass and volume of the catalysts.

X-ray powder diffraction patterns were recorded on a Rigaku X-ray Diffractometer (Multiflex, Japan), with Ni filtered Cu Kα radiation ($\lambda = 1.5406$ Å) operated at 50 kV and 50 mA in the 2θ range of 10–90° with scan speed of $4^\circ\ min^{-1}$.

Temperature programmed desorption (TPD) of NH_3 (5% NH_3 in helium) and CO_2 (5% CO_2 in helium) studies were performed using pulse chemisorb 2705 (Micromeritics Instrument Co., USA). In the individual TPD experiments either NH_3 or CO_2 was adsorbed at 100 °C for 30 min and purged at the same temperature with helium gas (20 ml/min) for the removal of the physisorbed gasses, followed by desorption of the gasses from 100 to 700 °C at a heating rate of 5 °C/min.

2.3. Reaction and analysis

The catalytic activity studies were performed in a fixed bed continuous flow stainless steel reactor (i.d., 4.5 mm and length, 300 mm). Typically, 1.0 g of catalyst sample was loaded into the reactor with the support of quartz wool. The reactor was heated to 600 °C in presence of N_2 flow (20 ml/min) at the rate of 2 °C/min and pretreated at this temperature for 2 h then altered to the reaction temperature and pretreated with CO_2 (20 ml/min) prior to conducting the reaction for 0.5 h. EB was introduced by a peristaltic pump with a feed flow rate of 9.8 mmol/h along with either N_2 or $N_2 + CO_2$. Unless otherwise specified contact time (W/F) is 16.73 g h/mole at 5.1 molar ratio of CO_2 to EB. Contact time (W/F) is defined as the weight of the catalyst in grams divided by the sum of the flow rates of the reactants and nitrogen in moles per hour. 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 (6 ft × 1/8″) was used for the analysis of gaseous products such as hydrogen, nitrogen, carbon monoxide, methane, and carbon dioxide. HP-innowax column (30 m long, 0.32 mm i.d. and 0.25 μm film thickness) was used for the analysis of liquid products in which, SM is the major product, and benzene, toluene, benzaldehyde, and acetophenone were minor/trace products.

Table 1
BET surface areas and bulk densities of MnO_2-ZrO_2 mixed oxide catalysts

Catalyst	Surface area (m^2/g)	Bulk density (g/cm^3)
ZrO_2	25	1.71
MnO_2	5	1.63
5% MnO_2-ZrO_2	72	1.49
10% MnO_2-ZrO_2	106	1.28
20% MnO_2-ZrO_2	108	1.21
25% MnO_2-ZrO_2	101	1.16
50% MnO_2-ZrO_2	106	0.99

3. Results and discussion

3.1. Physico-chemical properties of MnO_2-ZrO_2 mixed oxides

The surface areas of individual oxides of MnO_2, ZrO_2 and their mixed oxides (MnO_2-ZrO_2) were depicted in Table 1. The surface areas of all the mixed oxides are much higher than that of individual oxides, whereas the bulk densities are lighter than either MnO_2 or ZrO_2 (Table 1). The mixed oxides were X-ray amorphous or poorly crystalline, whereas both MnO_2 and ZrO_2 are purely crystalline (Fig. 1). The TPD of NH_3 and CO_2 of individual oxides (MnO_2 and ZrO_2) and 10% MnO_2-ZrO_2 mixed oxide reveal that the individual oxides possessed fewer number of acidic as well as basic sites than 10% MnO_2-ZrO_2 mixed oxide (Figs. 2 and 3). The mixed oxides calcined at higher temperatures (>650 °C) were transformed into crystalline materials (Fig. 4). The formation of amorphous, high

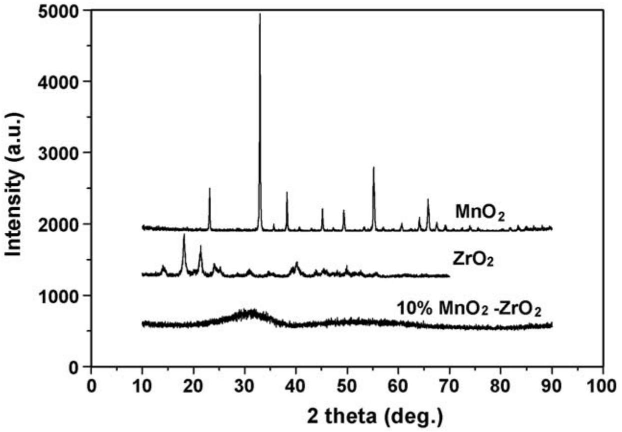

Fig. 1. XRD patterns of MnO_2, ZrO_2 and 10% MnO_2-ZrO_2 calcined at 550 °C.

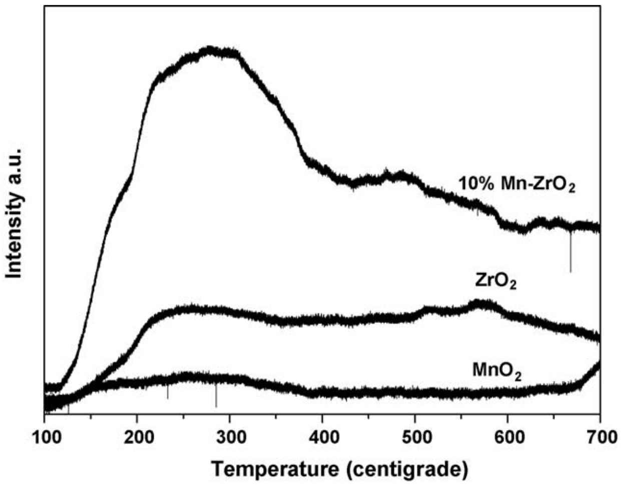

Fig. 2. NH_3 TPD patterns of MnO_2, ZrO_2 and 10% MnO_2-ZrO_2.

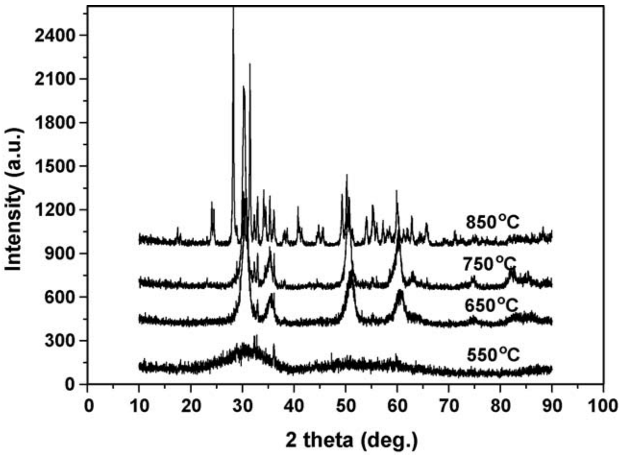

Fig. 4. XRD patterns of 50% MnO_2-ZrO_2 calcined at different temperatures.

surface area, and low density mixed oxide of ZrO_2 based binary oxides during the stages of preparation are reported [19,20]. In accordance with our previous publication, ZrO_2 contributes towards the activation of CO_2 based on its crystallographic phases [18] and acid–base capacities [20]. The addition of MnO_2, chosen not only for the enhancement in acid base properties of mixed oxide but also for its redox properties [21], anticipated the improved performance for the dehydrogenation of EB to SM in presence of CO_2.

3.2. Catalytic activity

EBD over MnO_2, ZrO_2, and 10% MnO_2-ZrO_2 mixed oxide in the presence of CO_2 was shown in the Fig. 5. The superior activity of MnO_2-ZrO_2 mixed oxide over its respective individual oxides might be due to generation of active sites during the stages of mixed oxide catalyst preparation as described above. Mimura and Saito also reported that either Al_2O_3 or Fe_2O_3 is inferior to Fe_2O_3/Al_2O_3 catalysts for the EBD in the presence of CO_2 and explained that special interaction between iron oxide and alumina might be necessary for higher activity [9]. EB conversion on MnO_2 was higher than ZrO_2 but the average selectivity (total 6 h selectivity averaged) was lower. The combination of redox and acid base bi-functional mechanism might be responsible for the higher activity of MnO_2-ZrO_2 mixed oxides. However, further studies are necessary for the elucidation of the mechanism. Marginal decrease in activity of MnO_2, ZrO_2, and MnO_2-ZrO_2 mixed oxide might be due to coke deposition.

The influence of MnO_2 and ZrO_2 composition in the EBD with time on stream in the presence of CO_2 was shown in Fig. 6. Almost all the studied compositions were catalytically active with little variation. However, 10% MnO_2-ZrO_2 mixed oxide catalyst was found to be the best. It showed that the contribution of the ZrO_2 surface was clearly necessary for the effective activation of CO_2.

In order to find out the role of pretreatment, the catalyst was treated with CO_2 (20 ml/min) at the reaction temperature at different lengths of time from 0.5 to 12 h (Fig. 7). The catalysts

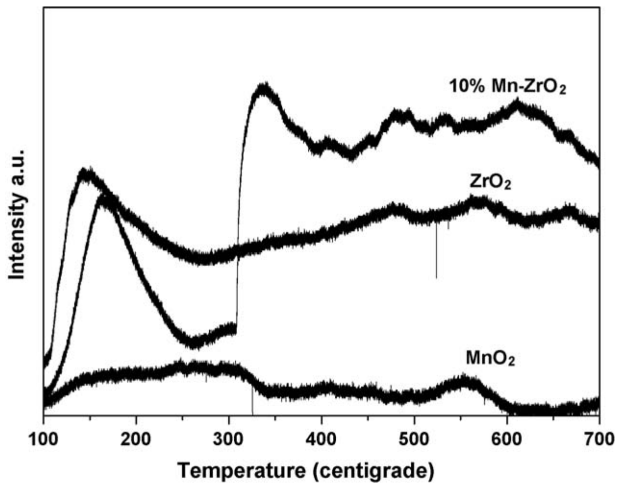

Fig. 3. CO_2 TPD patterns of MnO_2, ZrO_2 and 10% MnO_2-ZrO_2.

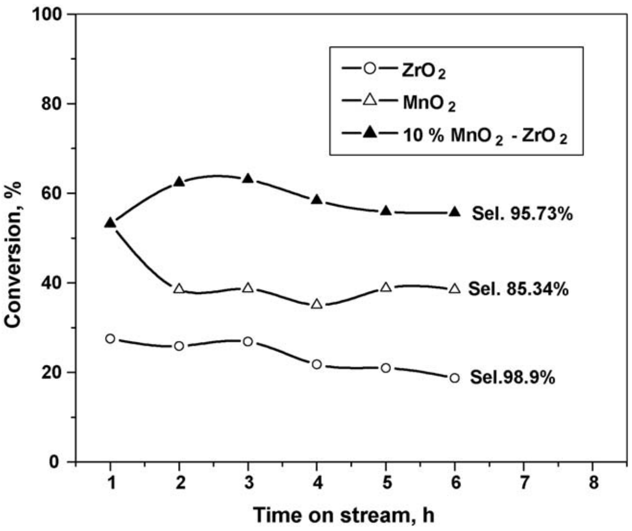

Fig. 5. EBD activity of MnO_2, ZrO_2, and 10% MnO_2-ZrO_2 mixed oxide catalyst. Reaction conditions: catalyst weight = 1.0 g, temperature = 600 °C, CO_2/EB = 5.1(molar ratio), W/F = 16.73 g_{cat} h/mole.

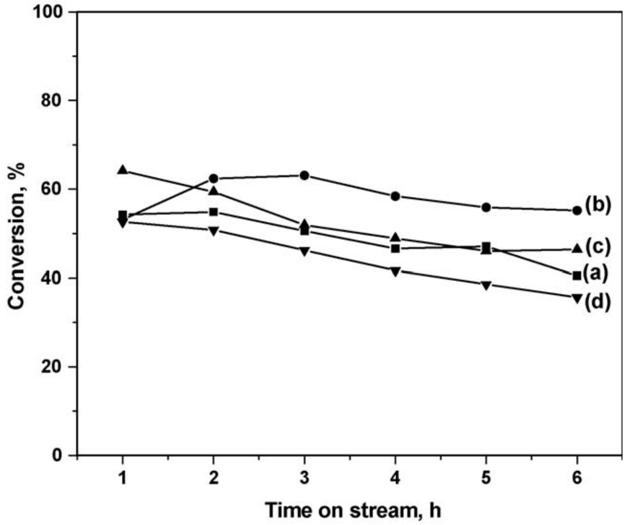

Fig. 6. EBD activity over different loadings MnO_2-ZrO_2 mixed oxide catalysts (a) 5% MnO_2-ZrO_2; (b) 10% MnO_2-ZrO_2; (c) 20% MnO_2-ZrO_2; (d) 50% MnO_2-ZrO_2. Reaction conditions: catalyst weight = 1.0 g, temperature = 600 °C, CO_2/EB = 5.1 (molar ratio), W/F = 16.73 g_{cat} h/mole.

pretreated with CO_2 for 0.5–1 h showed marginal hike in activity. The reason for the small hike in activity with CO_2 pretreatment might be adsorption of certain amount of CO_2 facilitates the reaction instead of competitive adsorption of both EB and CO_2 at a time. The catalysts pretreated for more than 1 h showed reduction in activity, but the total deactivation has not been detected even after 12 h pretreatment with CO_2. The decrease in activity with longer pretreatment periods might be due to neutralization of some of the active basic sites by CO_2.

The catalytic activity of 50% MnO_2-ZrO_2 mixed oxides calcined at different temperatures for the EBD in presence of CO_2 was shown in Fig. 8. The MnO_2-ZrO_2 mixed oxide calcined at 550 °C exhibited higher conversion and selectivity. The catalytic activity decreased with increased calcination temperatures. The change in phases from amorphous to crystalline (Fig. 4) drastically decreased the EB conversion and SM selectivity.

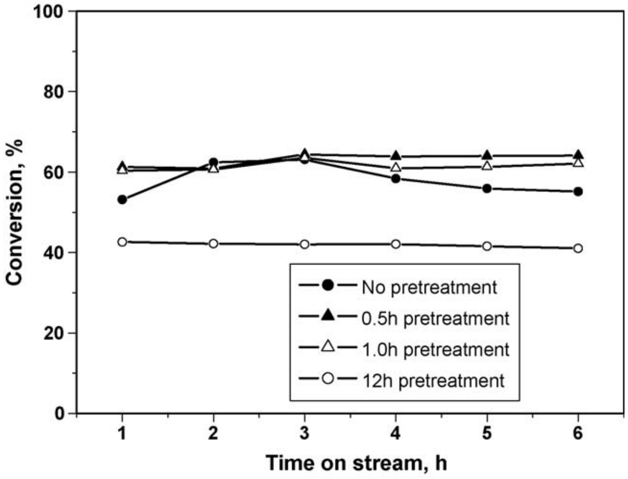

Fig. 7. EBD activity with respect to pretreatment temperature over 10.% MnO_2-ZrO_2 mixed oxide catalyst. Reaction conditions: catalyst weight = 1.0 g, temperature = 600°, CO_2/EB = 5.1 (molar ratio), W/F = 16.73 g h/mole.

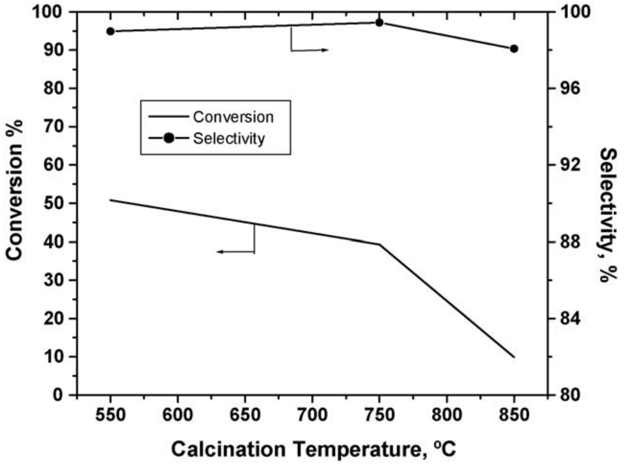

Fig. 8. EBD activity with respect to calcination temperature over 50.% MnO_2-ZrO_2 mixed oxide catalyst. Reaction conditions: catalyst weight = 1.0 g, temperature = 600°, CO_2/EB = 5.1 (molar ratio), W/F = 16.73 g h/mole.

3.3. Effects of reaction conditions

EB conversion and SM selectivity as a function of reaction temperature, was shown in Fig. 9. The conversion of EB increased monotonically with increase in reaction temperature from 450 to 650 °C. Surprisingly the selectivity to SM was maintained at 98% at higher temperatures (600 and 650 °C). Sugino et al. reported that the conversion of EB increased sharply with reaction temperature over active carbon supported iron catalyst wherein the yield of SM was 20% at 500 °C and rose to 47% at 600 °C but the selectivity dropped from 99 to 85% [22]. In a recent report [23], decrease in SM selectivity with reaction temperature over Cr-MCM-41 was mainly due to

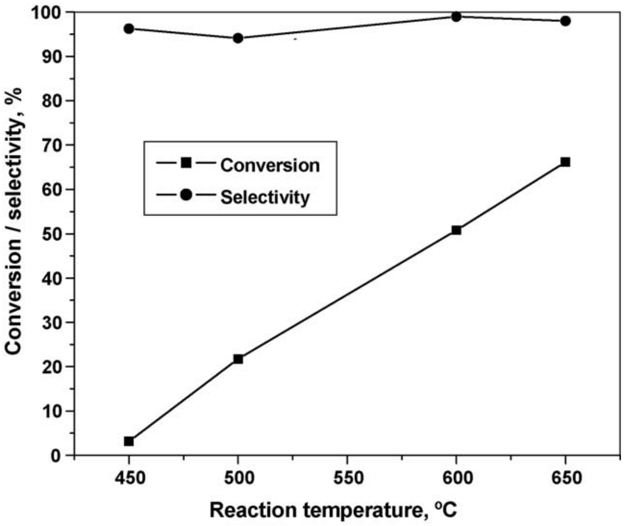

Fig. 9. EBD activity on 50% MnO_2-ZrO_2 mixed oxide catalyst with respect to reaction temperature. Reaction conditions: catalyst weight = 1.0 g, CO_2/EB = 5.1 (molar ratio), W/F = 16.73 g h/mole.

Table 2
EBD activity on 25% MnO_2-ZrO_2 in the presence and absence of CO_2

TOS (h)	CO_2			
	Presence		Absence	
	EB conversion (%)	SM selectivity (%)	EB conversion (%)	SM selectivity (%)
1	30.21	98.68	33.72	95.46
2	45.38	98.29	53.33	99.04
3	53.82	98.85	53.41	98.71
4	51.06	99.12	46.50	99.18
5	48.61	98.79	44.28	99.14
6	46.88	98.96	45.67	99.17
7	44.21	99.38	38.94	98.92
8	43.29	98.81	37.94	98.21
9	40.80	98.08	37.33	98.93
10	39.25	97.88	36.53	98.80

Reaction conditions: temperature = 600 °C, pressure = 1 atm, catalyst weight = 1.0 g, CO_2 or N_2/EB = 5.1 (molar ratio), W/F = 16.73 g h/mole.

enhancement in benzene and toluene formation. The sharp increase, in EB conversion with reaction temperatures over MnO_2-ZrO_2 mixed oxides was observed. Similar behavior in EB conversion with reaction temperature was reported in earlier publications [22,23].

The effect of contact time (W/F) on the conversion of EB was shown in Fig. 10. The data were obtained by varying the weight of the catalyst keeping the flow rates of EB as well as CO_2 constant at 10.2 molar ratios of CO_2 to EB. The conversion of EB was 46.81% at the contact time of 8.37 g h/mole. The EB conversion was considerably increased to 72.81% with increase in contact time to 16.73 g h/mole. Further increase of contact time to 25.1 and 33.46 g h/mole, increased EB conversions to 75.33 and 78.15%, respectively. However as this increase in contact time did not influence the EB conversion considerably, the contact time was fixed at 16.73 g h/mole.

The catalytic activity of 25% MnO_2-ZrO_2 mixed oxide catalyst for EBD in the presence of CO_2 and its absence was shown in Table 2. The selectivity of SM is always constant at about 98% under either N_2 or CO_2 atmosphere, whereas the conversion under CO_2 atmosphere was higher than under N_2 atmosphere except for the first 2 h of time on stream. The initial low activity was observed with CO_2 when the catalyst was not pretreated with CO_2. The constant selectivity with decreasing conversion under N_2 atmosphere represents that both the yields of SM as well as by-products were diminished with the time on stream. In other words, the catalyst deactivation rate was more under N_2 atmosphere rather than CO_2 atmosphere. It can be explained that the catalyst deactivation might be taking place due to coke deposition. In the presence of CO_2, certain amount of coke might be converting into CO [24]. As a result the rate of catalyst deactivation decreases. Similar catalytic behavior in the presence of CO_2 over Cr/Cab-O-Sil catalyst for the EBD was reported [24]. The maximum difference in conversion of EB was 5% over 10% MnO_2-ZrO_2 mixed oxide catalyst at 600 °C in the presence of CO_2 than that in the absence of CO_2. The yield of SM in the presence of CO_2 was 2.5 times higher than that in the absence of CO_2 at 550 °C over V/MgO catalyst [25].

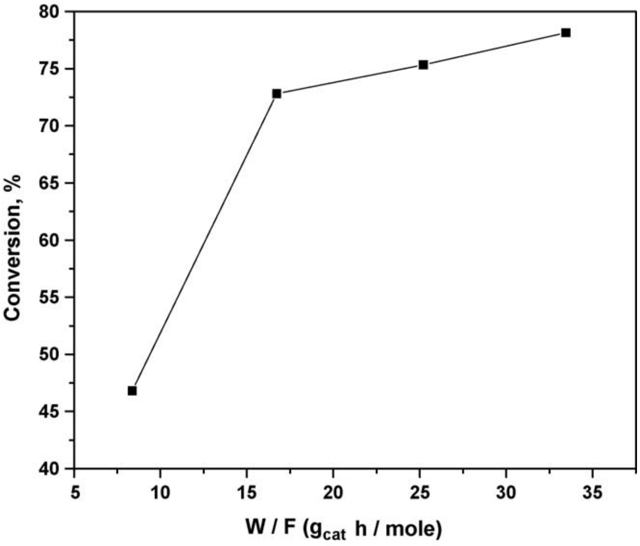

Fig. 10. Variation of EBD activity with contact time over 10% MnO_2-ZrO_2 mixed oxide. Reaction conditions: catalyst weight = 1.0 g, temperature = 650 °C. CO_2/EB = 10.2 (molar ratio).

The influence of CO_2 was also determined by varying the feed composition of CO_2 and EB. The conversion of EB at different feed ratios of CO_2 to EB over 10% MnO_2-ZrO_2 mixed oxide catalyst at 650 °C was depicted in Fig. 11. The conversion of EB in the absence of CO_2 was 64.25%, which was increased to 72.82% when N_2 (N_2/EB = 10.2) was replaced by CO_2 (CO_2/EB = 10.2) in the feed. The increase in the conversion of EB was observed with increase in the amount of CO_2 in the feed up to CO_2 to EB ratio of 10.2. At a CO_2 to EB ratio of 15.3, the conversion of EB was decreased. Similar trend was observed in the catalytic activity pattern of activated carbon supported iron catalysts for the dehydrogenation of EB [12]. It seems that optimum concentration of surface CO_2 could be required to get high stability and activity due to the competitive adsorption of CO_2 and EB onto the catalyst surface. Therefore, 10% MnO_2-ZrO_2 mixed oxide catalyst showed the optimum activity and stability at the CO_2 to EB ratio of 10.2 due to the adequate balance for the adsorption and activation of CO_2 and EB.

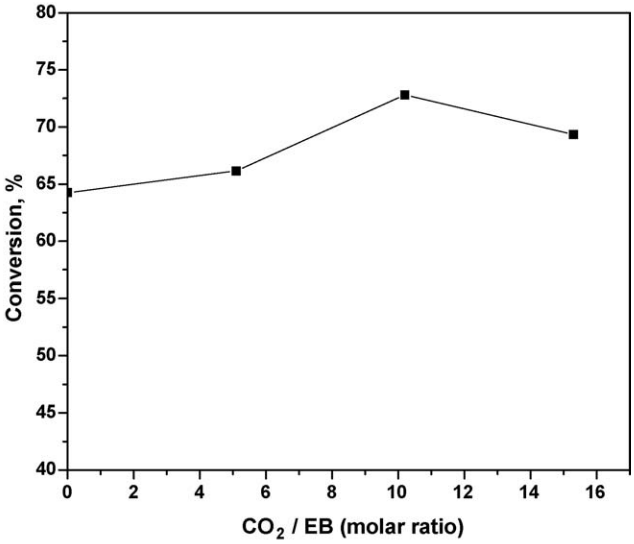

Fig. 11. EB conversions on 10% MnO_2-ZrO_2 with respect to feed ratio (CO_2/EB). Reaction conditions: catalyst weight = 1.0 g, temperature = 650 °C, W/F = 16.73 g_{cat} h/mole.

4. Conclusions

MnO_2-ZrO_2 mixed oxide catalysts were demonstrated to be highly active in the dehydrogenation of EB to SM in the presence of CO_2. The best results were obtained over 10% of MnO_2 loaded on ZrO_2 catalyst at 650 °C with a conversion of 73% and the selectivity to styrene was about 98%. CO_2 attributed to the enhancement in catalytic activity by the oxidative conversion as well as catalytic life by suppressing the coke deposition.

Acknowledgement

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References

[1] F. Cavani, F. Trifiro, Appl. Catal. 133 (1995) 215.
[2] W.S. Chang, Y.Z. Chen, B.L. Yang, Appl. Catal. 124 (1995) 221.
[3] I.P. Belomestnykh, E.A. Skrigan, N.N. Rozhdestvenskaya, G.V. Isagulіants, Stud. Surf. Sci. Catal. 72 (1992) 453.
[4] S. Sato, M. Ohhara, T. Sodesawa, F. Nozaki, Appl. Catal. 37 (1988) 207.
[5] M. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga, T. Suzuki, Appl. Catal. 121 (1995) 125.
[6] N. Mimura, I. Takahara, M. Saito, T. Hattori, K. Ohkuma, M. Ando, Catal. Today 45 (1998) 62.
[7] S.-E. Park, J.-S. Chang, M.S. Park, Prepr. Am. Chem. Soc. Div. Fuel Chem. 41 (1996) 1387.
[8] J.-S. Chang, S.-E. Park, M.S. Park, Chem. Lett. (1997) 1121.
[9] N. Mimura, M. Saito, Catal Today 55 (2000) 173.
[10] N. Mimura, M. Saito, Catal. Lett. 58 (1999) 59.
[11] M. Saito, H. Kimura, N. Mimura, J. Wu, K. Murata, Appl. Catal. 239 (2003) 71.
[12] T. Badstube, H. Papp, P. Kustrowski, R. Dziembaj, Catal. Lett. 55 (1998) 169.
[13] R. Dziembaj, P. Kustrowski, T. Badstube, H. Papp, Top. Catal. 11/12 (2000) 317.
[14] J.-S. Chang, D.-Y. Hong, Y.-K. Park, S.-E. Park, Stud. Surf. Sci. Catal. 153 (2004) 347.
[15] V.P. Vislovskiy, J.-S. Chang, M.-S. Park, S.-E. Park, Catal. Commun. 3 (2002) 227.
[16] J.-S. Chang, V.P. Vislovskiy, M.-S. Park, D.-Y. Hong, J.S. Yoo, S.-E. Park, Green Chem. 5 (2003) 587.
[17] M.-S. Park, V.P. Vislovskiy, J.-S. Chang, Y.-G. Shul, J.S. Yoo, S.-E. Park, Catal. Today 87 (2003) 205.
[18] J.-N. Park, J. Noh, J.-S. Chang, S.-E. Park, Catal. Lett. 65 (2000) 75.
[19] D. Raju Burri, K.-M. Choi, S.-C. Han, Y.- H. Lee, A. Burri, S.-E. Park, unpublished results.
[20] M.E. Manriquez, T. Lopez, R. Gomez, J. Navarrete, J. Mol. Catal. 220 (2004) 229.
[21] O.V. Krylov, A.K. Mamedov, S.R. Mirazabekova, Catal. Today 24 (1995) 371.
[22] M. Sugino, H. Shimada, T. Turada, H. Miura, N. Ekenaga, T. Suzuki, Appl. Catal. 121 (1995) 125.
[23] Y. Ohishi, T. Kawabata, T. Shishido, T. Takaki, Q. Zhang, Y. Wang, K. Takehira, J. Mol. Catal. 230 (2005) 49.
[24] J. Ren, W.-Y. Lee, K.-C. Xie, Catal. Lett. 93 (2004) 31.
[25] Y. Sakurai, T. Suzaki, K. Nakagawa, N. Ikenaga, H. Aota, T. Suzuki, J. Catal. 209 (2002) 16.