Catalysis Letters 69 (2000) 93–101

Oxidative dehydrogenation of 4-vinylcyclohexene into styrene over ZrO_2 catalyst promoted with Fe_2O_3 and CaO

Yong-Suk Choi[a], Yong-Ki Park[a], Jong-San Chang[a], Sang-Eon Park[a,*] and Anthony K. Cheetham[b]

[a] *Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology, PO Box 107, Taejon 305-606, Korea*
[b] *Material Research Laboratory, University of California, Santa Barbara, CA 93106, USA*

Received 27 March 2000; accepted 17 July 2000

The oxidative dehydrogenation of 4-vinylcyclohexene (VCH) into styrene was carried out in the presence of oxygen over a ZrO_2 catalyst promoted with Fe_2O_3 and CaO. Intrinsically, ZrO_2 showed high dehydrogenation activity, which resulted in 80% styrene selectivity with 45% conversion at 425 °C and LHSV 3 h^{-1}. When the ZrO_2 was further promoted with calcium and iron, $CaO/Fe_2O_3/ZrO_2$, the highest styrene selectivity of 88.9% was obtained as well as the lowest deactivation. The deactivation of catalyst was prohibited properly through the introduction of oxygen in the reactant together with the modification of Fe_2O_3/ZrO_2 with CaO. The $CaO/Fe_2O_3/ZrO_2$ showed constant catalytic activity and selectivity for more than 50 h without deactivation. The selectivity of styrene was strongly influenced by the mole ratio of O_2/VCH and 95% selectivity with 80% conversion was obtained at O_2/VCH mole ratio of 6 over Fe_2O_3/ZrO_2. It is thought that the oxidative dehydrogenation proceeds through the dehydrogenation (DH) of ring-hydrocarbon of VCH followed by selective combustion of hydrogen (SHC) and the high selectivity of styrene was achieved by the bi-functional role of ZrO_2 for DH and SHC reactions.

Keywords: oxidative dehydrogenation, deactivation, VCH, styrene, ZrO_2, Fe_2O_3, CaO

1. Introduction

Currently, more than 80% of world's 1,3-butadiene (BD) is extracted from crude C_4 effluents made from the steam cracking of heavy hydrocarbon feedstocks such as naphtha in the production of ethylene. The growth rate of BD production in ethylene plants is estimated to be 28% greater than the BD demand, which has resulted in a global BD surplus. Several years ago, Dow Chemical has introduced a new two-step process to produce styrene from BD via 4-vinylcyclohexene (VCH) [1]. Styrene is an important monomer for the production of polymers such as polystyrene and styrene–butadiene rubber and this new process will offer an alternative for the production of styrene monomer from BD when the market for BD does not justify extraction for current needs. To produce styrene from BD, the first step entails a liquid phase cyclodimerization of BD into VCH through Diels–Alder reaction over copper-loaded zeolite catalyst [2–4], and then secondly the produced VCH is converted into styrene in a gas-phase oxidative dehydrogenation reaction using other heterogeneous catalysts such as tin–antimony oxide or heteropolyacids [5,6].

According to Hucul et al. [5], tin–antimony oxide is a very effective catalyst for the oxidative dehydrogenation of VCH into styrene with 93% selectivity and 91% styrene yield at 380 °C and LHSV 0.5 h^{-1}. However, even in oxidative dehydrogenation, deactivation is so severe that water should be added to the feed stream at a water to VCH ratio of 12 : 1 for a lifetime of the catalyst of more than 1 000 h. Recently, Neumann et al. proposed a new oxidative dehydrogenation catalyst, $PV_2Mo_{10}O_{40}^{5-}$/carbon working in the feed stream containing oxygen and VCH without water but this catalyst also suffered from severe deactivation [6]. 80% conversion of VCH with 50% styrene selectivity could be achieved even at 260 °C and high LHSV of 2.9 h^{-1} but the activity maintained only for 4 h.

In this study, we tried to circumvent these problems in the production of styrene from VCH by introducing a zirconia-based catalyst effective for oxidative dehydrogenation. According to our previous study [7], iron-oxide-promoted zirconia having high surface area showed enhanced dehydrogenation activity in ethylbenzene dehydrogenation into styrene in mild oxidizing atmosphere of CO_2. Due to the similarity between these two dehydrogenations processes leading to the same final product styrene, oxidative dehydrogenation of VCH was carried out using the same catalyst as in ethylbenzene dehydrogenation. The zirconia-based catalyst showed excellent catalytic performance for the selective production of styrene and furthermore the deactivation of the catalyst could be overcome using oxygen as an oxidant instead of CO_2.

2. Experimental

2.1. Catalyst preparation

ZrO_2 (XZO674/04, 33 m^2/g) and Ce–ZrO_2 (XZO802/01, Zr/Ce = 4–5.6, 57 m^2/g) supplied by MEL Chemicals Co.

---

[*] To whom correspondence should be addressed.

were used after calcining at 500 °C for 5 h and all the other chemicals were used in analytical grade without further purification. Described in our previous paper [8], iron oxide supported ZrO_2 catalysts were prepared by deposition of an aqueous suspension of iron(II) sulfate heptahydrate onto ZrO_2 at 60 °C and pH = 10–11 under N_2 atmosphere to avoid oxidation. Iron sulfate aqueous solution was made by dissolving iron(II) sulfate heptahydrate in 100 ml of distilled water purged with nitrogen for 1 h to remove dissolved oxygen. The ZrO_2 was dispersed in another 100 ml of distilled water purged with nitrogen and then poured into the prepared iron sulfate solution. To precipitate iron as $Fe(OH)_2$ on the support, the pH of the solution was adjusted at 10–11 by adding 25% ammonia solution. The precipitated solid product was filtered and washed thoroughly with 2 l of distilled water. The filtrate was dried in vacuum at 70 °C and then calcined under N_2 flow at 500 °C for 3 h. Loading of iron oxide on the prepared catalysts ranged from 2 to 5 wt%. For CaO promotion, ZrO_2 was precipitated with aqueous calcium nitrate solution corresponding to 1 wt% CaO at 60 °C and pH 10–11 and then treated the same way as iron-oxide-promoted zirconia except drying at 110 °C.

2.2. Catalytic reactions

The oxidative dehydrogenation reaction of VCH was carried out in a conventional fixed-bed microreactor made of quartz in the temperature range of 300–600 °C and 1 bar. 300 mg of catalyst was placed in the reactor and then pretreated with He at 600 °C for 1 h. After pretreatment, the reaction was carried out while introducing a mixture of VCH and oxygen in helium balance. The VCH corresponding to the LHSV of 0.5–1.0 h^{-1} was injected with a syringe pump and then vaporized for the mixing with gases. For the analysis of products a gas chromatograph (HP 5890) equipped with FID detector and DB-wax capillary column (60 m × 0.317, 0.5 μm) was used.

2.3. Characterization

The physical and chemical properties of the prepared catalysts were analyzed by XPS, UV/VIS-DRS, EPR, XRD, BET, and TPD. The details of the analytic methods and the results are described well in our previous paper [7].

3. Results and discussion

3.1. Oxidative dehydrogenation of VCH into styrene

As described in our previous paper [7], zirconia promoted with iron oxide showed enhanced dehydrogenation activity in oxidative dehydrogenation of ethylbenzene to styrene especially in mild oxidizing atmosphere of CO_2. Due to the similarity of dehydrogenation leading to the same final product of styrene, this catalyst was applied for the oxidative dehydrogenation of VCH in the same mild oxidizing atmosphere of CO_2. However, as shown in figure 1, the selectivity of styrene in mild oxidizing atmosphere of CO_2 was not so high as in ethylbenzene dehydrogenation. Instead of the desirable product styrene, ethylbenzene was formed predominantly. This means that the dehydrogenation processes of VCH and ethylbenzene look similar apparently leading to the final product styrene but they have quite different histories for dehydrogenation due to the difference of locations to be dehydrogenated. In the case of ethylbenzene, because all of the cyclic hydrocarbons are already dehydrogenated to form stable aromatic, only the branched ethyl group needs to be dehydrogenated. However, VCH is in opposite situation to that of ethylbenzene. The branched ethyl group of VCH is already dehydrogenated and only dehydrogenation of cyclic hydrocarbon is required. Therefore, the poor selectivity of styrene in oxidative dehydrogenation of VCH with CO_2 might be caused by the different reactivities of cyclic and branched hydrocarbons for dehydrogenation. So, we required a different strategy to achieve high styrene selectivity while suppressing ethylbenzene formation in VCH dehydrogenation.

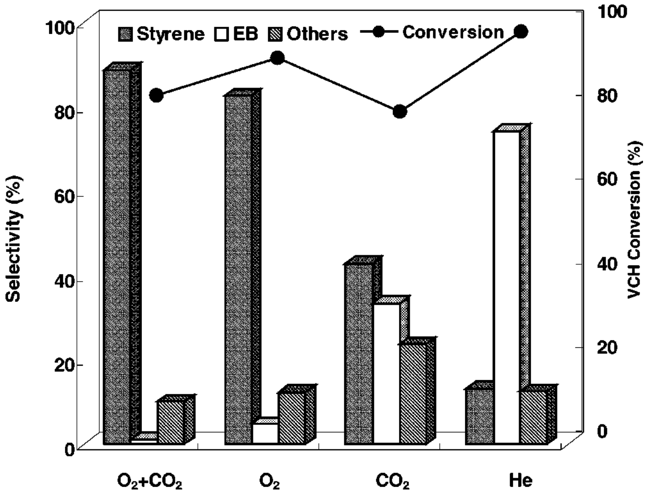
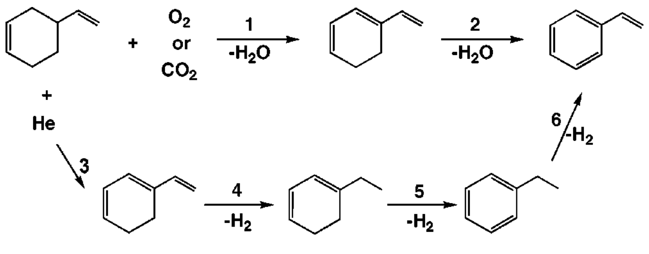


Figure 1. Dehydrogenation of VCH over 1 wt% CaO/2 wt% Fe_2O_3/ZrO_2 in different reaction atmospheres: 30 ml/min He; 7 ml/min CO_2 + 23 ml/min He; 12 ml/min air+18 ml/min He; and 12 ml/min air+7 ml/min CO_2 + 11 ml/min He. Reaction conditions: VCH = 0.3 ml/h, T = 400 °C, P = 1 atm, and LHSV = 1 h^{-1}.

It is well known that cyclic compounds such as cyclohexane could be dehydrogenated more easily than alkyl hydrocarbons such as ethane and propane. As an example, cyclohexane could be dehydrogenated into benzene in the temperature range of 300–500 °C but at least 600 °C is required for propane dehydrogenation to propylene [9,10]. Furthermore, the dehydrogenation activity of alkyl hydrocarbon is strongly influenced by the carbon number. So, different from propane, 800 °C is required to dehydrogenate ethane into ethylene even in oxidizing atmosphere [11,12]. The different reactivity of these functional groups could be seen also clearly in the hydrogenation reaction. As an example, ethylene could be hydrogenated to ethane



Scheme 1.

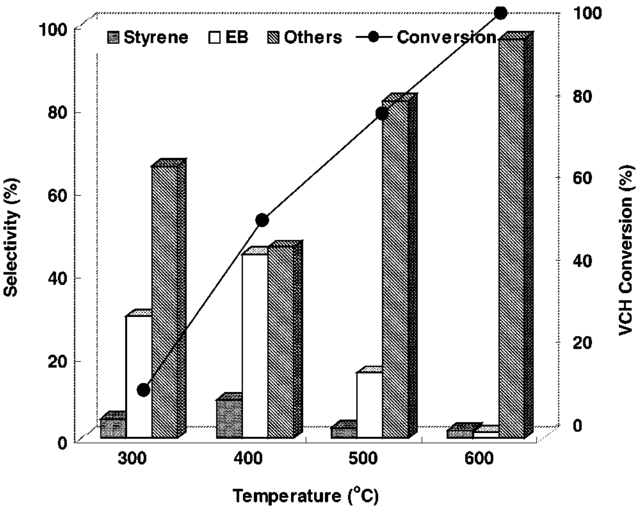


Figure 2. Dehydrogenation of VCH over 2 wt% Fe_2O_3/ZrO_2 in inert atmosphere without oxygen at various temperatures. Reaction conditions: reactant = 0.3 ml/h VCH + 30 ml/min He, $P = 1$ atm, and LHSV = 3 h^{-1}.

even at room temperature over a Pt catalyst but more than 300 °C is required for benzene to cyclohexane [13,14]. This means that the dehydrogenation of an alkyl group is more difficult than that of a cyclic one but the opposite trend exists in the hydrogenation process. So, for the selective production of styrene the cyclic hydrocarbon of VCH has to be dehydrogenated while blocking the dehydrogenated ethyl group from hydrogenation such as the proposed pathway of $1 \rightarrow 2$ of scheme 1. If the ethyl group is not protected properly during the dehydrogenation then the ethylbenzene will be formed preferentially through the hydrogenation of the ethyl group by the hydrogen abstracted from cyclic hydrocarbons (the pathway of $3 \rightarrow 4 \rightarrow 5$ of scheme 1). As discussed before, once the ethyl group is hydrogenated then it is impossible to dehydrogenate it at the given dehydrogenation temperature of VCH, 400 °C, because at least 500 °C is required for its dehydrogenation (pathway 6). One more thing to be considered in the dehydrogenation of VCH is that the reaction temperature could not be increased above 450 °C due to its decomposition into light hydrocarbons (figure 2). Even in mild oxidizing atmosphere of CO_2, more than 80% of VCH decomposed into light hydrocarbons above 500 °C. This means that intrinsically the dehydrogenation of VCH should be carried out below 500 °C at which the dehydrogenation of the ethyl group is possible. So, the only way to achieve high styrene selectivity is to protect the ethyl group from re-hydrogenation during the dehydrogenation process of ring hydrocarbons of VCH. The suitability of this strategy could be seen also from the ethylbenzene dehydrogenation. Because the ring hydrocarbons of ethylbenzene are already dehydrogenated to form a stable aromatic, it is not necessary to consider the re-hydrogenation of the less reactive aromatic ring during the dehydrogenation of the ethyl group. So, even at a rather high temperature of 600 °C, high selectivity of styrene is ensured with low production of by-products. However, as the cracking and hydrogenolysis reactions become pronounced in this temperature region, the mild oxidizing atmosphere of CO_2 brings improvement for styrene selectivity through the selective removal of H_2 by CO_2 while preventing cracking or hydrogenolysis [15].

Comparing to the dehydrogenation of ethylbenzene, the role of oxidant is more important in the oxidative dehydrogenation of VCH due to the temperature limited under 450 °C. In the dehydrogenation temperature of VCH, the oxidizing power of CO_2 was not enough to combust the hydrogen produced in the dehydrogenation of ring hydrocarbons of VCH. So, a stronger oxidant such as oxygen was required to remove effectively the abstracted hydrogen. As shown in figure 1, when the dehydrogenation of VCH was carried out in oxygen atmosphere, the selectivity of styrene increased from 10 to 80% while the decrease of ethylbenzene from 80 to 5%. Furthermore, when CO_2 was introduced together with oxygen the highest selectivity of styrene was obtained. The selectivity of styrene is well correlated with the strength of the oxidant. It is thought that as the reaction atmosphere is changed from inert helium to oxygen, the dehydrogenation pathway changed from $3 \rightarrow 4 \rightarrow 5 \rightarrow 6$ to $1 \rightarrow 2$ of proposed scheme 1. Different from the strong dependence of selectivity, the conversion was not much influenced by the reaction atmosphere and the same level of conversion was obtained at the same space velocity of VCH. This means that firstly the dehydrogenation proceeds through the same pathway regardless of reaction environment such as step 1 or 3 of scheme 1 but different pathways are followed after the dehydrogenation depending on the reaction environments. That is, it is thought that the oxygen is mainly involved in the combustion process of hydrogen abstracted from ring hydrocarbons of VCH rather than the initial step of dehydrogenation of VCH.

The role of oxidant could be further evidenced by the dependence on space velocity of activity and selectivity. As shown in figure 3, the conversion of VCH increased monotonically depending on the space velocity but the product distribution was not influenced by the space velocity. This will provide another evidence to support reaction pathway $1 \rightarrow 2$ of scheme 1 in the oxidative dehydrogenation of VCH. If the dehydrogenation proceeds through the pathway $3 \rightarrow 4 \rightarrow 5 \rightarrow 6$ then the selectivity of styrene should be increased as the space velocity of VCH increases through the further conversion of ethylbenzene into styrene. One more thing to be considered in figure 3 is that the reaction proceeds mainly through $1 \rightarrow 2$ of scheme 1 because

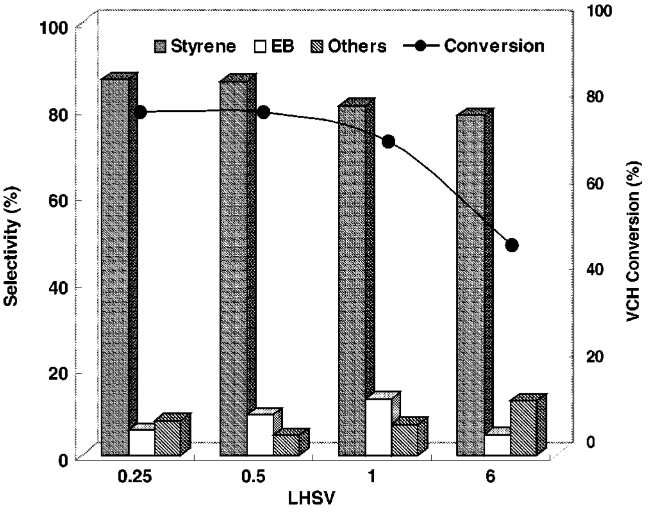


Figure 3. The dependence of activity and selectivity on the space velocity of VCH over 1 wt% CaO/2 wt% Fe_2O_3/ZrO_2. Reaction conditions: reactant = 12 ml/min air + 18 ml/min He, O_2/VCH ratio = 6, $P = 1$ atm, and $T = 400\,^{\circ}$C.

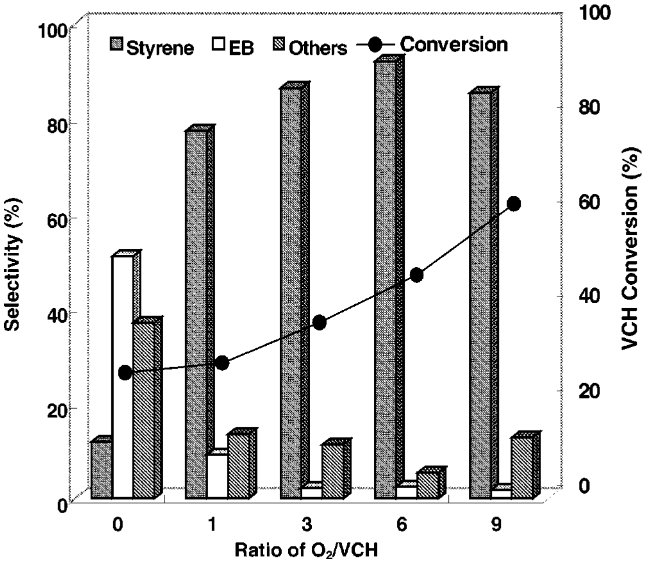


Figure 4. Oxidative dehydrogenation of VCH in the presence of oxygen over 1 wt% CaO/2 wt% Fe_2O_3/ZrO_2 at various O_2/VCH mole ratios. Reaction conditions: reactant = 0.3 ml/h VCH, $T = 375\,^{\circ}$C, $P = 1$ atm, and LHSV = 2 h^{-1}.

only small amount of by-products except ethylbenzene and styrene were not detected while changing the space velocity.

3.2. Optimum ratio of oxygen/VCH

The introduction of oxygen brought discontinuous change in styrene selectivity. By introducing oxygen at the O_2/VCH ratio of 1 over 2 wt% Fe_2O_3/ZrO_2 catalyst, the styrene selectivity was changed from 12 to 80%, which corresponds to eight times increase of selectivity compared to that in helium atmosphere (figure 4). As the ratio of O_2/VCH changed from 0 to 9, the conversion of VCH increased monotonically from 30 to 60%. This means that the more oxygen the more favorable the dehydrogenation of VCH through the combustion of generated hydrogen. However, for maximum yield of styrene there also exists an optimum concentration of oxygen because the by-product formation becomes dominant in high oxygen concentration. However, a little different result was obtained in oxidative dehydrogenation of VCH using oxygen over polyoxometalate, $PV_2Mo_{10}O_{40}^{5-}$ where both maximum activity and selectivity were obtained at the same oxygen/VCH ratio of 1.9 [6]. The difference of optimum oxygen/VCH ratio for styrene selectivity over the polyoxometalate and the zirconia catalyst might be resulted from the different oxidation ability of these two catalyst but it is not easy to explain the different dependence of activity on oxygen concentration. The linear increase of activity depending on oxygen concentration over zirconia (figure 3) could be explained by the enhanced oxidation rate by the presence of oxygen but the opposite trend over polyoxometalate should be explained differently [6].

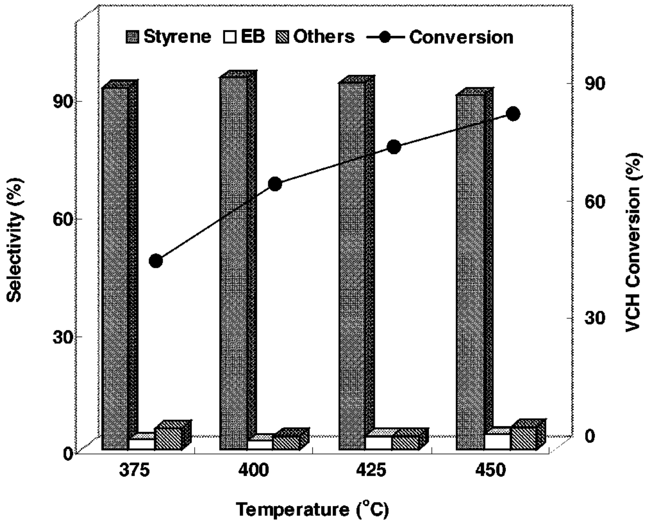


Figure 5. Oxidative dehydrogenation of VCH in the presence of oxygen over 2 wt% Fe_2O_3/ZrO_2 at various temperatures. Reaction conditions: reactant = 0.3 ml/h VCH + 12 ml/min air + 18 ml/min He, O_2/VCH ratio = 6, $P = 1$ atm, and LHSV = 2 h^{-1}.

One more interesting result in oxidative dehydrogenation of VCH over 2 wt% Fe_2O_3/ZrO_2 is that the by-product indicated as "others" in figure 5 could be suppressed to less than 5% as well as the ethylbenzene to less than 2% up to 450 °C at the high oxygen/VCH ratio of 6. This means that even if there exists excess oxygen it does not oxidize the hydrocarbons such as VCH, ethylbenzene and styrene and only reacts with the abstracted hydrogen to form water. So, it was possible to increase the dehydrogenation activity with the increase of oxygen concentration while maintaining high selectivity of styrene without by-products.

3.3. Concept of selective hydrogen combustion

As an alternative approach for the dehydrogenation of hydrocarbons, an oxidative dehydrogenation which is a combination process of dehydrogenation (DH) and selective hydrogen combustion (SHC) could be applied. In oxidative dehydrogenation of light paraffins, however, due to the difference of temperature window of DH and SHC, these two reaction steps could not be combined into one and have to be carried out separately in series such as DH → SHC → DH with appropriate temperature for each reaction, as proposed by Grasselli et al. [16,17]. Firstly, the hydrogen is produced in the DH process and then the generated hydrogen is combusted selectively by the SHC catalyst in the presence of oxygen, which results in the increased yield of dehydrogenates compared with the conventional DH process without oxygen. Conceptually, the oxidative dehydrogenation of VCH is quite similar to that of light paraffins such as propane and butane except that these two reactions are carried out in one catalyst.

As shown in figures 6(a) and 7(a), all of the zirconia-based catalysts revealed the same DH activity in the temperature window of 300–400 °C and the dependence of activity on temperature was quite similar regardless of the presence of oxygen. However, there was a quantum change of styrene selectivity by the presence of oxygen. This means that the dehydrogenation of VCH proceeds in the same mechanism over zirconia-based catalysts independent of oxygen but the selectivity is strongly influenced by the presence of hydrogen generated during the DH process. Grasselli et al. also found that the hydrogen generated by dehydrogenation plays an important role in deciding the

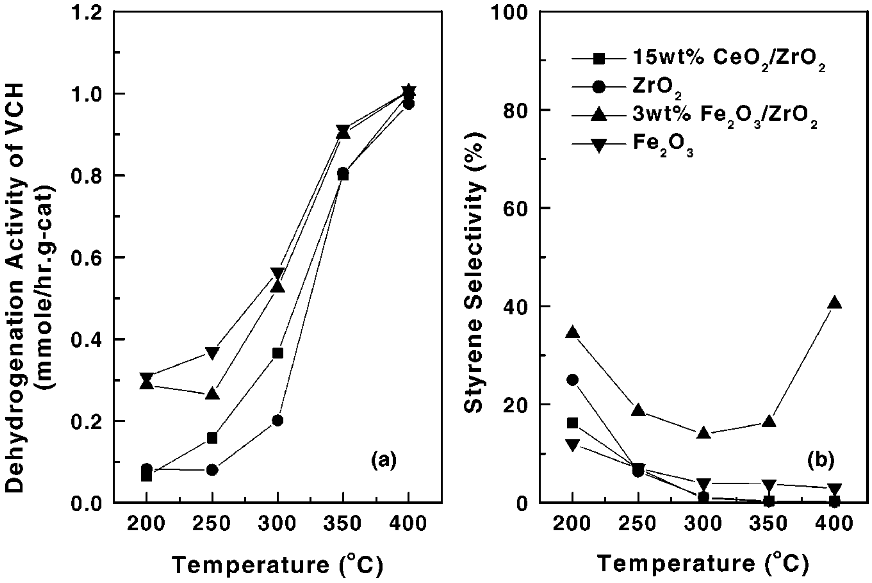


Figure 6. Dehydrogenation of VCH over zirconia-based catalysts in inert helium atmosphere at various temperatures. Reaction conditions: reactant = 0.3 ml/h VCH + 30 ml/min He, $P = 1$ atm, and LHSV = 0.75 h^{-1}.

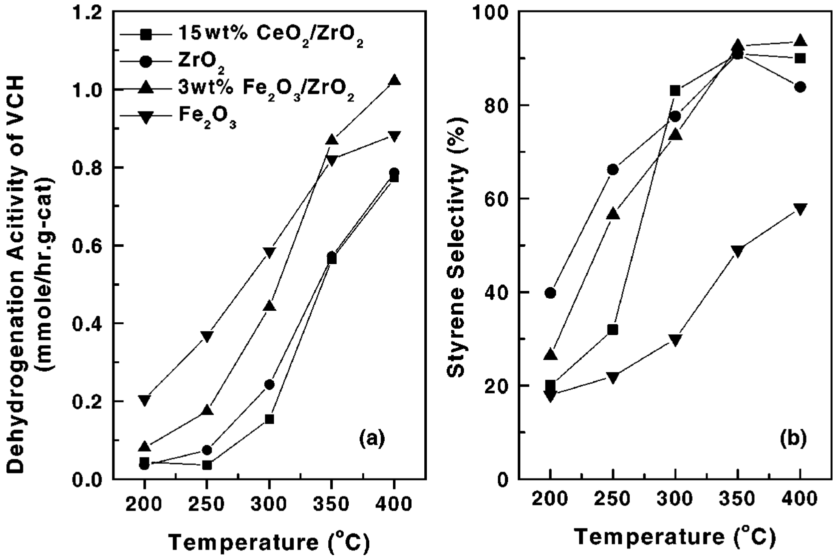


Figure 7. Oxidative dehydrogenation of VCH over zirconia-based catalysts in oxygen atmosphere at various temperatures. Reaction conditions: reactant = 0.3 ml/h VCH + 12 ml/min air + 18 ml/min He, O_2/VCH ratio = 6, $P = 1$ atm, and LHSV = 0.75 h^{-1}.

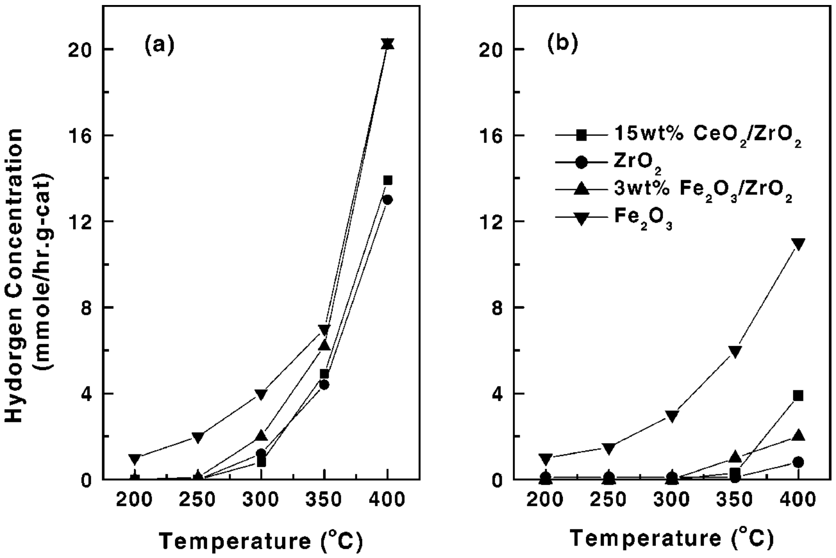


Figure 8. The profile of hydrogen concentration in different dehydrogenation process of VCH over zirconia-based catalysts: (a) in inert helium atmosphere and (b) in oxygen atmosphere. LHSV was 0.75. Reaction was carried out in the same conditions as in figures 6 and 7.

selectivity [17]. So, the hydrogen concentration was monitored while carrying out the reaction in the same conditions as in figures 6 and 7 and the result is shown in figure 8. In inert helium atmosphere, a considerable amount of hydrogen was formed over all of the zirconia-based catalysts such as ZrO_2, $CeZrO_2$, and Fe_2O_3/ZrO_2 above 300 °C but in the presence of oxygen, its concentration was very low (figure 8 (a) and (b)). That is, when the oxygen was introduced in the dehydrogenation process of VCH, the hydrogen concentration maintained its very low level over the whole temperature range of reaction due to the selective removal of it by combustion. This means that the selective removal of hydrogen by combustion is very decisive to achieve high styrene selectivity (see the results of figures 6(b), 7(b), and 8(b)). The oxidative dehydrogenation activity of iron oxide was also investigated and compared with those of zirconia-based catalysts. Iron oxide showed high dehydrogenation activity and comparable to that of zirconia. However, it showed quite poor styrene selectivity even in the presence of oxygen. Figure 8 revealed further evidence for a poor selectivity of styrene over iron oxide catalyst. That is, iron oxide is an efficient dehydrogenation catalyst to dehydrogenate VCH but its oxidation ability is not enough to convert produced hydrogen for the selective production of styrene, which resulted in low styrene selectivity together with high hydrogen concentration in the products.

So, to ensure high selectivity of styrene, the catalyst has to provide enough combustion activity for the removal of hydrogen at the given DH temperature. The light-off temperatures of hydrogen over zirconia-based catalysts were measured in the flowing of hydrogen and oxygen mixture at O_2/H_2 ratio of 6 (figure 9). All of the zirconia-based catalysts showed superior combustion activity even from 200 °C and their combustion completed above 300 °C. The combustion activity is very high and comparable or superior to that of mixed metal oxide catalysts such as In_2O_3/ZrO_2 and Fe/Sn/Sb oxide proposed by Grasselli et al. [16] and Hucul et al. [5].

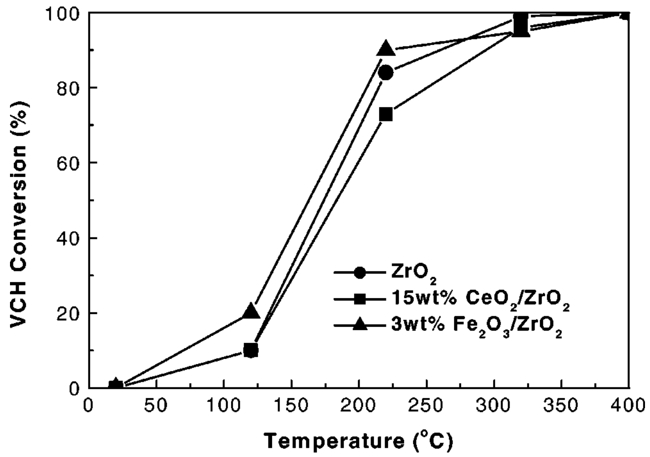


Figure 9. Hydrogen combustion of zirconia-based catalysts in oxygen atmosphere without VCH. Reaction conditions: 6 ml/min O_2 and 1 ml/min H_2 was introduced over 0.3 g of catalyst.

As shown in figures 6(a) and 9, the combustion temperature of hydrogen over zirconia catalyst is in quite similar range of dehydrogenation temperature of VCH. The zirconia-based catalysts have dual catalytic functions of dehydrogenation and hydrogen combustion at the same temperature region. That is, due to the coincidence of the temperature window for dehydrogenation and combustion, it was possible to achieve high styrene yield just by introducing oxygen in the dehydrogenation process of VCH over the zirconia-based catalysts. Another requirement to achieve high styrene selectivity is that in this temperature region only the hydrogen has to be combusted selectively without oxidizing hydrocarbons. If not selective, then hydrocarbons will be converted into other oxygenated hydrocarbons or CO and CO_2. However, all of the zirconia-based catalysts were very selective for hydrogen combustion up to 400 °C and the hydrocarbons were preserved not to be oxidized into other by-products. From these results, it could be suggested that zirconia is a quite suitable catalyst for the oxidative dehydrogenation of VCH satisfying all of the required catalytic functions such as DH and SHC.

3.4. Influence of promoters

To investigate the influence of promoters in the oxidative dehydrogenation of VCH over the zirconia catalyst, it was further modified with cerium and iron oxides and the results are shown in table 1. When the zirconia was modified with 15 wt% CeO_2, it showed higher dehydrogenation activity than ZrO_2, especially at lower temperature, but in the point of view of styrene selectivity it was not as high as expected; 45.8% conversion with 46.5% styrene over $CeZrO_2$ while 26.1% conversion with 78.2% styrene over ZrO_2 at 400 °C, LHSV $= 3\ h^{-1}$ and O_2/VCH $= 3$ (table 1). The other characteristic of $CeZrO_2$ is that the selectivity of styrene is more sensitively dependent on the temperature than that of ZrO_2 and so the reaction temperature could not be increased as high as for ZrO_2; 78.2% styrene at 400 °C and 78.3% at 450 °C over ZrO_2 but 46.5% styrene at 400 °C and 34.6% at 450 °C over $CeZrO_2$ (table 1). This means that at high temperature $CeZrO_2$ is not selective for the combustion of hydrogen and hydrocarbons also oxidized. This non-selective combustion over $CeZrO_2$ could be explained by the enhanced oxidation ability caused by the ceria promoter. According to the previous results, ceria has multiple, stable oxidation states of 3+ and 4+, which allow it to undergo oxidation and reduction relatively easily through its oxygen storage function, the taking up of oxygen under oxidizing conditions and releasing it under reducing conditions [18,19].

Different from ceria, when the zirconia is modified with 2 wt% Fe_2O_3, 30% improvement of dehydrogenation activity was possible, which resulted in the increase of styrene selectivity (figure 7 and table 1). In inert helium atmosphere, more enhanced dehydrogenation activity and styrene selectivity were observed over Fe_2O_3/ZrO_2 than over any other catalysts (figure 6). However, in oxygen atmosphere, only increased activity was observed over Fe_2O_3/ZrO_2 with similar selectivity of styrene with other catalysts (figure 7). This means that the Fe_2O_3 mainly affect the dehydrogenation step of VCH rather than the selective combustion of hydrogen produced in the dehydrogenation step. Wu also found the synergistic effect of dehydrogenation in the dehydrogenation of ethylbenzene over a Fe_2O_3–ZrO_2 catalyst [20]. They found an improvement of acidity and basicity as well as of surface area by the co-presence of Fe_2O_3 and ZrO_2 and these properties were well correlated with the dehydrogenation activity of ethylbenzene. So, the increased activity and selectivity in

Table 1

The activity and selectivity in oxidative dehydrogenation of VCH over various zirconia-based catalysts.[a]

Catalyst	Temperature (°C)	VCH conversion (%)	Selectivity (%)			
			Styrene	Ethtylbenzene	Benzene	Others
ZrO_2	375	14.2	66.9	7.0	3.5	22.5
	400	26.1	78.2	6.1	4.2	11.5
	425	44.2	82.4	6.8	3.6	7.2
	450	54.4	78.3	7.7	3.5	10.5
15 wt% CeO_2/ZrO_2	375	43.1	59.2	31.1	2.3	7.4
	400	45.8	46.5	42.6	2.4	8.5
	425	49.2	33.7	51.8	3.0	11.5
	450	56.7	34.6	48.9	3.2	13.3
2 wt% Fe_2O_3/ZrO_2	375	26.6	83.2	3.4	1.9	11.6
	400	34.5	86.3	3.0	2.0	8.7
	425	33.8	79.0	4.2	2.8	14.1
	450	29.4	55.2	8.4	5.2	31.2
1 wt% CaO/ 2 wt% Fe_2O_3/ZrO_2	375	36.6	87.3	1.7	2.3	8.7
	400	45.2	88.9	1.3	2.5	7.4
	425	48.9	85.0	3.0	3.6	8.3
	450	52.1	82.5	3.6	4.5	10.4
3 wt% Fe_2O_3/ 15 wt% CeO_2/ZrO_2	375	48.9	67.1	29.5	1.4	2.0
	400	48.1	77.3	16.0	2.1	4.6
	425	53.7	82.1	9.6	2.5	5.8
	450	57.4	75.0	10.4	3.3	11.3
$0.15Fe_2O_3/SbO/9SnO_2$[b]	380	97.2	96.8	–	–	–

[a] Reaction conditions: reactant = 0.3 ml/h VCH + 6 ml/min air + 24 ml/min He, O_2/VCH ratio = 3, $P = 1$ atm, and LHSV $= 3\ h^{-1}$.

[b] This result is taken from [5]. Reaction conditions: VCH/$H_2O/O_2/N_2$ = 1/14.4/1.5/19.9 and LHSV $= 0.3\ h^{-1}$.

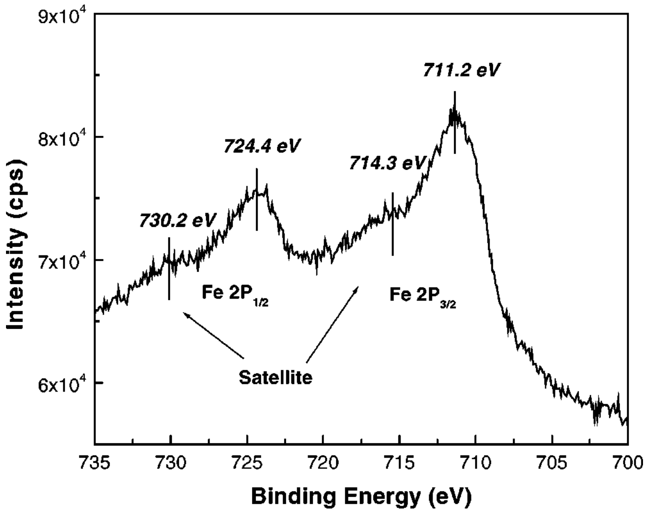


Figure 10. XPS spectra of 2 wt% Fe_2O_3/ZrO_2 catalyst after pretreated in vacuum at 500 °C for 1.5 h and then followed by air flowing at 400 °C for 2 h.

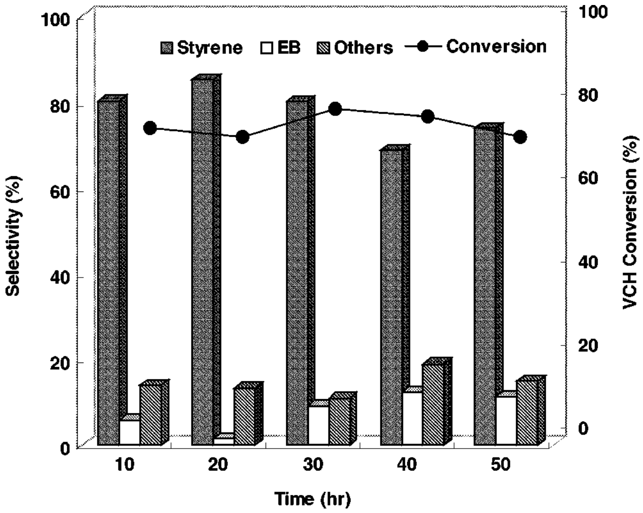


Figure 11. The deactivation mode of 1 wt% CaO/2 wt% Fe_2O_3/ZrO_2 catalyst in oxidative dehydrogenation of VCH by oxygen. Reaction conditions: reactant $=$ 0.3 ml/h VCH $+$ 12 ml/min air $+$ 24 ml/min He, O_2/VCH ratio $= 6$, $T = 375\,^{\circ}C$, $P = 1$ atm, and LHSV $= 2\ h^{-1}$.

oxidative dehydrogenation of VCH over Fe_2O_3–ZrO_2 also could be explained by the increased basicity and surface area caused by Fe_2O_3. The XPS spectra of figure 10 describe the binding energy (BE) of Fe $2p_{1/2}$ and $2p_{3/2}$ of the Fe_2O_3–ZrO_2 catalyst. There exist one broad peak for Fe $2p_{3/2}$ at 711.2 eV and another for Fe $2p_{1/2}$ at 724.4 eV, together with a shake-up satellite at 715.8 eV. The BEs of iron oxides are so close that it is not easy to discriminate by XPS but according to Muhler et al. the BEs of 709.9, 710.5, and 711.1 eV could be assigned to FeO, Fe_3O_4, and Fe_2O_3, respectively [21]. Hirano also assigned the peaks in the range of 710.8–711.3 eV to Fe_2O_3 and 710.0–710.3 eV to Fe_3O_4 [22]. Kuivila et al. identified that a broad shake-up satellite centered at 719.8 eV is a characteristic peak from Fe(III) species and at 715 eV from Fe(II) species independent of coordination state of iron compounds [23]. According to the Mössbauer spectroscopic study of Fe_2O_3–ZrO_2 by Boot, the Fe_2O_3 on ZrO_2 exists as well-dispersed α-Fe_2O_3 [24]. From the XPS result in this study and references, it is thought that most of the iron oxide on zirconia exists as well-dispersed Fe_2O_3.

3.5. Deactivation of catalyst

As discussed in section 1, the deactivation of catalyst is quite severe in the dehydrogenation of VCH into styrene and steam has been introduced together with the reactant to prevent it. The big advantage of zirconia-based catalysts is that they maintain dehydrogenation activity without deactivation just by introducing oxygen without water, which is a good contrast with the Fe/Sn/Sb oxide catalyst where excess water, fifteen times higher than VCH, has to be added to prevent the deactivation (figure 11). As described in table 1, when the Fe_2O_3/ZrO_2 is modified with alkali metal such as CaO, further improvement of conversion and selectivity is possible and the catalyst rarely deactivated because the metal suppresses the production of coke on the surface of catalysts. The inhibiting role of alkali metal for deactivation is well proved in the dehydrogenation of EB into styrene [25]. The deactivation of catalyst seems to be mainly caused by coke deposition from growth of polyaromatics on the catalyst surface. However, the catalytic activity under a CO_2 and O_2 stream is maintained without significant decay of the activity. This means that carbon dioxide and promoted alkali metal lead to enhancing the coke resistance to the supported iron oxide catalyst and consequently extending catalyst lifetime during the reaction.

4. Conclusion

From the oxidative dehydrogenation of VCH over zirconia-based catalysts, it was found that the ZrO_2 itself had very high intrinsic oxi-dehydrogenation activity for the selective production of styrene. When the zirconia was further modified with Fe_2O_3 and CaO, 1 wt% CaO/2 wt% Fe_2O_3/ZrO_2, the highest styrene selectivity of 88.9% was obtained. Especially, alkali metal oxide, CaO, was effective for inhibiting the deactivation of catalyst and the dehydrogenation activity was maintained for more than 50 h. The styrene selectivity was strongly influenced by the O_2/VCH ratio and maximum selectivity was obtained at 6. It is thought that the oxidative dehydrogenation of VCH over zirconia-based catalysts proceeds sequentially through the dehydrogenation of the ring-hydrocarbon of VCH followed by selective combustion of produced hydrogen by the bi-functional role of ZrO_2.

References

[1] V. Wong and S.-H. Wandg, Process Economics Program Review 94-2-4 (1996).
[2] I.E. Mawell, R.S. Downing and S.A.J. van Langen, J. Catal. 61 (1980) 485.

[3] I.E. Mawell, R.S. Downing and S.A.J. van Langen, J. Catal. 61 (1980) 493.
[4] US Patents 5 488 020; 5 329 057; 5 196 621; 4 973 568; 4 665 247.
[5] US Patent 5 336 822.
[6] R. Neumann and I. Dror, Appl. Catal. A 72 (1998) 67.
[7] J. Noh, J.-S. Chang, J.-N. Park and S.-E. Park, Appl. Catal. A (2000), submitted.
[8] J.-S. Chang, J. Noh, S.-E. Park, W.Y. Kim and C.W. Lee, Bull. Korean Chem. Soc. 19 (1998).
[9] L.I. Ali, A.-G.A. Ali, S.M. Aboul-Fotouh and A.K. Aboul-Gheit, Appl. Catal. A 177 (1999) 99.
[10] S. Miguel, A. Castro and O. Scelza, Catal. Lett. 36 (1996) 201.
[11] D.W. Flick and M.C. Huff, Catal. Lett. 47 (997) 91.
[12] C. Yokoyama, S.S. Bharadwaj and L.D. Schmidt, Catal. Lett. 38 (1996) 181.
[13] Y.-K. Park, F.H. Fabio and G.A. Somorjai, J. Catal. 178 (1998) 66.
[14] A.-G.A. Ali, L.I. Ali, S.M. Aboul-Fotouh and A.K. Aboul-Gheit, Appl. Catal. A 170 (1998) 285;
J. Wang, Q. Li and J. Yao, Appl. Catal. A 184 (1999) 181;
D. Poondi and M.A. Vannice, J. Catal. 161 (1996) 742.
[15] J.-N. Park, J. Noh, J.-S. Chang and S.-E. Park, Catal. Lett. 65 (2000) 75;
J.-S. Chang, S.-E. Park and M.S. Park, Chem. Lett. (1997) 1123.
[16] R.K. Grasselli, D.L. Stern and J.G. Tsikoyiannis, Appl. Catal. A 189 (1999) 1.
[17] J.G. Tsikoyiannis, D.L. Stern and R.K. Grasselli, J. Appl. Catal. A 189 (1999) 1.
[18] T. Shido and Y. Iwasawa, J. Catal. 136 (1992) 493.
[19] T. Bunluesin, R.J. Gorte and G.W. Graham, Appl. Catal. B 14 (1997) 105.
[20] J.-C. Wu, D.-S. Liu and A.-N. Ko, Catal. Lett. 20 (1993) 191.
[21] M. Muhler, R. Schloegl and G. Ertl, J. Catal. 138 (1992) 413.
[22] T. Hirano, Appl. Catal. 26 (1986) 81.
[23] C.S. Kuivila, J.B. Butt and P.C. Stair, Appl. Surf. Sci. 32 (1988) 99.
[24] L.A. Boot, A.J. Dillen, J.W. Geus, A.M. Kraan, A.A. Horst and F.R. Buren, Appl. Catal. 145 (1996) 389.
[25] F. Cavani and F. Trifirò, Appl. Catal. 133 (1995) 219.