NOVEL PROCESS FOR STYRENE FROM ETHYLBENZENE WITH CARBON DIOXIDE

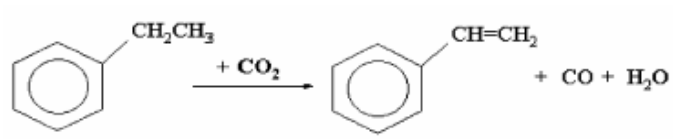
Sang-Eon Park[a] and Jong-San Chang[b]

[a]Department of Chemistry, Inha University, Incheon 402-751, Korea
[b]Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology (KRICT), Taejon 305-600, Korea

Introduction

The utilization of carbon dioxide, which is known as a main contributor to the greenhouse effect, has been of global interest from both fundamental and practical viewpoints in green chemistry.[1] The application of supercritical CO_2 is one of the most exciting ideas to replace volatile organic solvents in green chemistry approach.[2] As another way of the utilization, it is worthwhile to note that carbon dioxide can be used as an oxygen source or oxidant. It has been proposed that carbon dioxide plays a role as the soft oxidant to abstract hydrogen from simple or functionalized hydrocarbons through the catalytic activation of carbon dioxide to form CO and oxygen species.[3-7]

Vapor-phase dehydrogenation of ethylbenzene (EBDH) is a representative process to produce styrene (SM), an important monomer for synthetic polymers. This is one of the ten most important industrial processes. However, it is thermodynamically limited and, moreover, very energy - consuming process. As an alternative way, the oxidative dehydrogenation of ethylbenzene (EB) has been proposed to be free from thermodynamic limitation regarding conversion, operating at lower temperatures with an exothermic reaction.[8] However, this process with use of strong oxidant, oxygen, suffers from loss of selectivity for styrene due to the production of carbon oxides and oxygenates. Recently, the utilization of carbon dioxide as an oxidant for the EBDH has been attempted to explore new technology for producing styrene selectively. We have recently developed a novel process for dehydrogenation of ethylbenzene to produce styrene using carbon dioxide as soft oxidant, so-called $SODECO_2$ (Styrene Production via Oxidative Dehydrogenation of Ethylbenzene with Carbon Dioxide as Soft Oxidant) process. This work deals with characteristics of this novel process.



Results and Discussion

The EBDH reaction is generally carried out in vapor phase at 600 - 650°C under steam. The important roles of steam in the industrial dehydrogenation of EB are classified as follows: providing heat to the endothermic dehydrogenation, diluting EB in order to increase equilibrium conversion, and preventing coke deposition on the catalyst.[11] Although steam is widely used in the EB dehydrogentaion due to these beneficial roles, the use of steam has a drawback of losing latent heat of condensation during subsequent separation particularly in a mass process.[11,12] Characteristics of steam and carbon dioxide are summarized in Table 1. It is easily presumable that carbon dioxide can play the same beneficial roles of steam mentioned above.

Table 1. Comparison of Carrier Gases for Dehydrogenation of Hydrocarbons

Characteristics	Steam	Carbon Dioxide
Function	Not oxidant Diluent	Soft oxidant Diluent
Heat capacity	Medium (37.0 J/mol·K at 673K)	High (49.1 J/mol·K at 673K)
Advantage	High selectivity Catalyst stability Coke resistance Keeping oxidation state	High selectivity Activity enhancement Equilibrium shift Cheap carrier gas
Disadvantage	Expensive diluent Highly endothermic High latent heat High operation cost	Not commercialized Endothermic Catalyst deactivation

In the case of steam as diluent, it has been pointed out that the present commercial processes require an excess of superheated steam (steam/EB = 7 - 12 mol/mol), so that they consume a large amount of latent heat of steam upon condensation at a liquid-gas separator following a reactor.[9] Moreover, in conventional dehydrogenation units, selectivity and conversion are linked so that high conversion and high selectivity cannot be achieved simultaneously. To achieve high selectivity, conventional plants are limited to less than 70 % conversion. For overcoming these drawbacks, the ABB/UOP SMART™ (Styrene Monomer Advanced Reheat Technology) process has been recently proposed (*See* http://www.uop.com/petrochemicals/processes_products/smart_sm_intro.htm). The major reactions in the process are the EBDH to styrene and the subsequent oxidation of the hydrogen produced in the first reaction. This hydrogen is reacted with oxygen over a highly selective catalyst. In the process, the removal of hydrogen from the process substantially increases single-pass EB conversions while maintaining high SM selectivity.

We propose here another process using carbon dioxide in order to solve the problems due to use of steam such as high-energy consumption and thermodynamic limitation. The main concept of this new technology is started from the utilization of carbon dioxide as the soft oxidant in oxidative catalysis. We pay attention to the possibility to utilize oxygen atoms of a carbon dioxide molecule as the oxidant to abstract hydrogen atom in dehydrogenation of hydrocarbons because the C-H bond dissociation through the hydrogen abstraction with oxygen species is generally accepted to be the rate-determining step in dehydrogenation of hydrocarbons. Thus, the main role of CO_2 in the process is illustrated to play the function of hydrogen abstraction from ethyl group of ethylbenzene, leading to the enhanced activity as well as selectivity over the catalysts that are capable of activating CO_2 to generate atomic surface oxygen.

Besides the role of CO_2, another important thing to consider for the CO_2 utilization is how to and where to bring a large amount of CO_2 with high concentration. Fortunately, there are many processes to produce CO_2 by-product with relatively high concentration in petrochemical industry, for example, gas-phase partial oxidation, reforming, etc. Based on these ideas, we propose the new process for producing styrene, so-called the $SODECO_2$. In addition to the above advantages, it is advantageous in the $SODECO_2$ process that very cheap carbon dioxide thus obtained from by-product of petrochemical oxidation or reforming process is utilized without further purification instead of using expensive steam diluent. Subsequent advantages of the process are: (1) energy saving by the replacement of steam which

requires high loss of latent heat of water, (2) easy retrofit of current steam processes, and (3) lower reaction temperature due to the ability of equilibrium alleviation, etc. Figure 1 shows the schematic diagram of the $SODECO_2$ process that was constructed based on the above concepts.

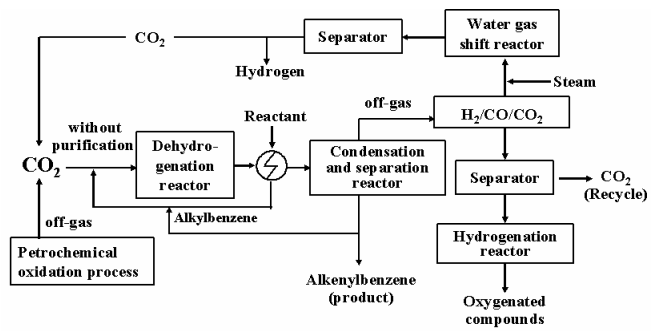


Figure 1. Schematic diagram of the $SODECO_2$ process.

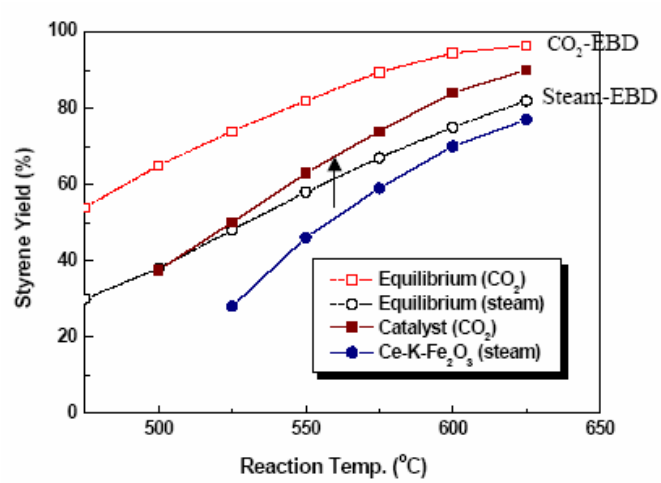


Figure 2. Catalytic activities of CO_2-EBD and commercial steam-EBD catalysts. Reaction conditions: Temp. = 600°C, LHSV = 1.0 h^{-1}, CO_2/EB = 1/1. Reaction condition: P = 0.75 atm, LHSV = 1.0 h^{-1}, CO_2/EB = 5/1 (CO2 Cat.) H_2O/EB = 10/1 (Steam Cat.) Catalyst volume = 100 ml. For CO_2-EBD reaction, CO_2 conversion = 42% at 560°C.

The dehydrogenation catalyst employed comprises oxygen-deficient iron oxide or vanadium oxide and promoters with transition metal oxides. In the case of iron oxide-based catalyst, oxygen-deficient iron sites can produce CO efficiently from the CO_2 dissociation, and the adsorbed oxygen on the catalyst surface can also play a role on hydrogen abstraction from EB. Dispersion of the oxygen-deficient sites or oxygen defects in the catalyst appears to be more efficient for the CO_2 dissociation and thereby the oxidative dehydrogenation of EB. In the case of vanadium oxide- based catalyst, redox behavior of vanadium oxide is found to play a key role in accordance with Mars-van-Krevelen mechanism. Carbon dioxide for this reaction is used as the soft oxidant to provide oxygen species on reduced catalyst surface and, consequently, reoxidize the reduced vanadium species. Figure 2 illustrates characteristic behavior of the dehydrogenation catalyst employed in CO_2-EBDH according to reaction temperature, clearly indicating that the designed catalyst for CO_2-EBDH can experimentally alleviate the chemical equilibrium of EBDH with steam.

The present process in this work is demonstrated under the mini-pilot plant operation equipped with the multi-tubular heat exchanger-type fixed-bed isothermal reactors. Table 2 compares the operation conditions and results of the commercial steam and $SODECO_2$ processes. Through the scale-up work for the process, using CO_2 as the oxidant high selectivity for styrene (>97%), activity enhancement (> 30%) and a drop in reaction temperature (40-50°C) through equilibrium alleviation have been accomplished and compared with conventional dehydrogenation process. Moreover, the energy consumption required for the EB dehydrogenation using carbon dioxide is estimated to be much lower (> 30%) than that for the currently operating process using steam.

Table 2. Comparison of catalyst performance between commercial and $SODECO_2$ processes.

Conditions	Commercial Process	$SODECO_2$ Process
Temp. (°C)	575-675	525-575
Pressure (atm)	75	75
LHSV (h^{-1})	0.75-1	1.0
Carrier/EB (mol)	8-12	2-10
Styrene yield (%)	60-66	55-65
SM Selectivity (%)	94.0-96.5	97.0-98.0
Catalyst lifetime	2 years	In research
By-products	H_2, BTX	BTX, CO/H_2 = 1.0-1.5

Conclusions

This work demonstrates that the utilization of carbon dioxide as soft oxidant in dehydrogenation of ethylbenzene to styrene can produce the novel process, $SODECO_2$. This process has several beneficial advantages: (1) energy saving by the replacement of steam which requires high loss of latent heat of water, (2) lower reaction temperature due to the ability of equilibrium alleviation, and (3) use of very cheap CO_2 thus obtained from by-product of petrochemical process without further purification.

Acknowledgment

This work was supported by the Korean Ministry of Science and Technology (Institutional Research Program).

References

1. Inui, T., Anpo, M., Izui, K., Yanagida, S., Yamaguchi, T. (eds.), Advances in Chemical Conversions for Mitigating Carbon Dioxide, Stud. Surf. Sci. Catal., Vol. 114, Elsevier: Amsterdam, 1998.
2. DeSimone, J.M., *Science*, 2002, **297**, 799.
3. Krylov, O.V., Mamedov, A.Kh., *Ind. Eng. Chem. Res.*, 1995, **34**, 474.
4. Chang, J.-S., Park, S.-E., Park, M.S., *Chem. Lett.*, 1997, 1123.
5. Park, S.-E., Yoo, J.S., Chang, J.-S., Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century (eds. M.M. Maroto-Valer, Y. Song, C. Song), Chapter 33, Kluwer Academic/Plenum: New York, 2002.
6. Vislovskiy, V.P., Chang, J.-S., Park, M.-S., Park, S.-E., *Catal. Commun.*, 2002, **3**, 227.
7. Chang, J.-S., Vislovskiy, V.P., Park, M.-S., Hong, D.Y., Yoo, J.S., Park, S.-E., *Green Chemistry*, 2003, **5**, 587.
8. Cavani, F., Trifiro, F., *Appl. Catal. A*, 1995, **133**, 219.
9. Mimura, N., Takahara, I., Saito, M., Hattori, T., Ohkuma, K., Ando, M., *Catal. Today*, 1998, 45, 61.