CATALYTIC DEHYDROGENATION OF AROMATIC HYDROCARBON WITH CARBON DIOXIDE AS AN OXIDANT

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Introduction

For the mitigation of global warming due to carbon dioxide, catalytic conversion of CO$_2$ has been extensively studied for last decade. Most of studies on this field have been concentrated on the utilization of carbon dioxide as a carbon source through catalytic reduction processes with various kinds of reductants. Particularly, hydrogen has long been used to abstract the oxygen atom of CO$_2$ for catalytic conversion into useful chemicals. However, catalytic hydrogenation is confronted with some limitations to be commercialized because in most cases the cost of hydrogen from conventional sources such as steam reforming of hydrocarbons is not cheaper than that of chemicals obtained from catalytic hydrogenation. However, the utilization of CO$_2$ as a mild oxidant and an oxygen transfer agent is recently attracting considerable attention. This approach is expected to open new technology for CO$_2$ utilization. It has been proposed that the oxygen species of carbon dioxide is useful for oxidative conversions of hydrocarbons. Krylov and Mamedov have studied on the oxidative conversions of alkanes, alkenes, and alcohols with carbon dioxide over Mn oxide-based catalysts. Yoo et al. showed that Fe/Mo/borosilicate catalyst could activate CO$_2$ which could be functioning as a promoter and co-oxidant for the gas-phase oxidation of alkylaromatics with oxygen as well.

Styrene is commercially produced by dehydrogenation of ethylbenzene (EB) using potassium-promoted iron oxide catalysts with a large excess of superheated steam. However, the use of steam has a drawback of losing latent heat of condensation during subsequent separation in the commercial process. The energy consumption required for the EB dehydrogenation using carbon dioxide is estimated to be much lower than that for the currently operating process using steam. In addition to energy saving, the use of CO$_2$ with replacement of steam can give a beneficial advantage to the oxidative reactions of aromatic hydrocarbons. However, carbon dioxide can be utilized as both oxidant and diluent since it can release oxygen as surface oxygen species upon activation on reduced or oxygen-deficient catalyst surface and it has high heat capacity. It can be confirmed that CO$_2$ plays a key role as oxidant and diluent in EB dehydrogenation as the soft oxidant and diluent to the promotional effect of excess carbon dioxide to the oxidative activity and preventing coke formation.

\[
\text{CH}_3\text{CH}_3 + \text{CO}_2 \rightarrow \text{CH}=\text{CH}_2 + \text{CO} + \text{H}_2\text{O}
\]

This work deals with dehydrogenation of aromatic hydrocarbons, especially ethylbenzene using CO$_2$ as an oxidant. We suggest catalysts to exhibit high activity and excellent selectivity for styrene with the help of carbon dioxide as an oxidant.

Experimental

Catalyst Preparation. γ-Al$_2$O$_3$-supported iron oxide catalyst (Fe/γ-Al$_2$O$_3$) was prepared by depositing iron(II) sulfate solution onto supports at the temperature range 60 - 70°C under nitrogen atmosphere to prevent the dissolution of oxygen. It was precipitated at pH = 10 - 11 with ammonia water. The precipitates were filtered, dried at 80°C in vacuum oven, and calcined under a nitrogen stream at 700°C for 4 h. Al$_2$O$_3$-supported vanadium oxide (V$_2$O$_5$/Al$_2$O$_3$) or vanadium-antimony binary oxide (V-SbO$_x$/Al$_2$O$_3$) catalysts were prepared by impregnation of aqueous solutions of ammonium metavanadate and antimony (III) chloride onto activated alumina. The impregnated sample was dried at 100°C and then calcined in air at 600°C for 4 h. For V$_2$O$_5$/Al$_2$O$_3$, the content of V$_2$O$_5$ was 20.0 wt%. For V-SbO$_x$/Al$_2$O$_3$, the content of V$_2$O$_5$ and Sb$_2$O$_3$ was 7.5 wt% and 15.5 wt%, respectively.

Catalytic Measurement. The EB dehydrogenation into styrene was carried out in a micro-activity test unit (Zeton, MAT 2000) with a fixed bed reactor at 600°C under atmospheric pressure. A sample of 1g was placed on a fritted metal disk in the reactor. Before reaction, the catalyst was treated in a nitrogen stream from RT to 600°C with a heating rate of 10°C/min. Ethylbenzene was introduced by syringe pump and supplied into the reactor by a carrier gas with flow rate of 20 ml/min. The liquid and gas products were analyzed by GC (Donam Corp., DS6200) equipped with FID and TCD, respectively. Effluent gases from the reactor were analyzed by a gas chromatograph (Chrompack CP9001) equipped with a thermal conductivity detector (TCD).

Results and Discussion

Steam is generally utilized as diluent in dehydrogenation of aromatic hydrocarbons and oxygen works as strong oxidant in oxidative reactions of aromatic hydrocarbons. However, carbon dioxide can be utilized as both oxidant and diluent since it can release oxygen as surface oxygen species upon activation on reduced or oxygen-deficient catalyst surface and it has high heat capacity. It can be confirmed that CO$_2$ plays a key role as oxidant and diluent in EB dehydrogenation using carbon dioxide instead of steam. Table 1 displays the effect of carrier gas in EB dehydrogenation over 5 wt% Fe/γ-Al$_2$O$_3$ catalyst. It is clearly seen that carbon dioxide works very well in EB dehydrogenation as the soft oxidant and diluent to increase the conversion as well as selectivity. The order of catalytic activity and selectivity for styrene according to carrier gas was CO$_2$ > N$_2$ > H$_2$O. Such dependence of the activity on carrier gas is just contrary to that of commercial catalyst. Considering that conversion of CO$_2$ took place together with EB conversion, the enhancement of the dehydrogenation activity and the selectivity is certainly ascribed to the promotional effect of excess carbon dioxide to the oxidative process. This result implies that the initial hydrogen abstraction at benzyl C-H bond of EB was much facilitated by carbon dioxide.

Table 1. Effect of carrier gas in EB dehydrogenation over Fe/γ-Al$_2$O$_3$ catalyst$^a$

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>X(EB), %</th>
<th>S(SM), %</th>
<th>X(CO$_2$), %</th>
<th>H$_2$O/H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>63.7</td>
<td>95.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>25.0</td>
<td>88.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>68.5</td>
<td>97.2</td>
<td>47.4</td>
<td>1.7</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: Temp. = 600°C, LHSV = 1.0 h$^{-1}$, CO$_2$/N$_2$ or H$_2$O/EB = 10/1, Time-on-stream = 4 h. $^b$relative concentration to EB.
Crystalline iron oxides have not been appeared on XRD pattern of Fe/γ-Al2O3 catalyst, suggesting that iron oxide phase is amorphous and is well dispersed. Characterization results revealed that the oxidation state of iron oxide over γ-alumina is between γ-Fe2O3 and Fe3O4. These two phases in the catalyst seem to be interconvertible during EB dehydrogenation with CO2. There may be optimal population of iron oxide phase between γ-Fe2O3 and Fe3O4 to show high activity. The surface basicity upon the introduction of iron oxide onto γ-Al2O3 support was not changed so much. It is known that a Fe2O3 spinel oxide, so-called magnetite is basically oxygen deficient enough to activate carbon dioxide at elevated temperature.12 In our previous work, it has been considered that oxygen deficiency of iron oxide in the supported catalyst is one of the most important factors on promoting the catalytic activity in the presence of CO2.6 Oxygen-deficient sites of the supported iron oxide catalyst seem to produce CO efficiently from the CO2 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 supported iron oxide catalysts appears to be more efficient for the CO2 dissociation and thereby the oxidative dehydrogenation of EB. Therefore, it is assumed that high activity of Fe/γ-Al2O3 in the presence of CO2 is mainly due to the presence of Fe3+ species and its oxygen deficiency.

Figure 1 displays the catalytic results for EB dehydrogenation with CO2 over V2O5/Al2O3 and V-SbOx/Al2O3 catalysts at 600°C. These catalysts exhibited very high conversion (>75%) and high selectivity (>95%) at initial stage. However, catalytic activity of V-SbOx/Al2O3 was higher than that of V2O5/Al2O3 and, moreover, its stability was much better than that of the unpromoted one. It has been proposed that redox behavior of vanadium oxide-based catalysts played a key role in accordance with Mars-van-Krevelen mechanism in oxidative dehydrogenation of alkylaromatics.13 Likewise, EB dehydrogenation with CO2 is expected to follow the same mechanism. Vanadium oxide with V5+ is generally considered as an active component. Deactivation of supported vanadium oxide catalysts was occurred by deep reduction of V5+ into V3+ and coke formation. The introduction of Sb oxide into V2O5/Al2O3 led to preventing the deep reduction of the oxidation state of vanadium and facilitating the redox cycle, resulting in enhancement of the catalyst stability as well as the catalytic activity. Carbon dioxide for this reaction acted as the soft oxidant to provide oxygen species on reduced catalyst surface and, consequently, reoxidize the reduced vanadium species.

There are two possible pathways for EB dehydrogenation to styrene. The simple dehydrogenation of EB that produces styrene and hydrogen occurs under nitrogen or even carbon dioxide atmosphere, while the oxidative dehydrogenation of EB that produces styrene, carbon monoxide, and water occurs under carbon dioxide atmosphere. During the reaction, carbon monoxide and hydrogen in the gas phase were observed together with a trace of methane. Considering the gas product distribution, the ratio of H2O/H2 in the product stream is estimated to be 1.7 for Fe/γ-Al2O3 and 1.4 for V-SbOx/Al2O3, respectively, after 4 h on stream. The formation of water as well as carbon monoxide implies that CO2 molecule over catalyst surface is dissociated with CO and surface oxygen, which can abstract hydrogen from EB and then results in the generation of water. Taking into account the formation of large amount of water, high activity for supported iron oxide and supported vanadium catalysts under CO2 carrier may be mainly ascribed to oxygen species dissociated from carbon dioxide molecule, thus due to the promotion of the oxidative process by carbon dioxide. In other words, this indicates that carbon dioxide plays a role as an oxidant in EB dehydrogenation on supported iron oxide and vanadium oxide catalysts.

Conclusions

This work demonstrates that the utilization of carbon dioxide as an oxidant is very useful for oxidative dehydrogenation of aromatic hydrocarbon such as ethylbenzene. In dehydrogenation of ethylbenzene over supported iron oxide and vanadium oxide catalysts, carbon dioxide plays a key role as an oxidant to increase catalytic activity and selectivity to styrene.

Acknowledgment

This work was performed for the Greenhouse Gas Research Center, one of the Critical Technology-21 Programs, funded by the Ministry of Science and Technology of Korea (MOST). VPV thanks the MOST for the visiting scientist fellowship. We also thank Daebo Industries Co.(Korea) for financial support.

References