Carbon Dioxide as an Oxidizing (Dehydrogenating) Agent

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There have been several publications on the reaction of two greenhouse gases, carbon dioxide and methane, to form hydrogen and carbon monoxide (synthesis gas), valuable reactants for conversion to fuels and chemicals. Our attention was brought to the fact that CO_2 is a weak oxidizing or dehydrogenation compound. [Oxidation is equivalent to dehydrogenation.] We have therefore carried out research on using CO_2 as a reagent for the dehydrogenation of hydrocarbons, a manner of using this greenhouse gas as a reactant while providing useful, environmentally clean products with a possible saving in energy.

Dehydrogenation of hydrocarbons requires high temperatures due to thermodynamic limitations. A high steam-to hydrocarbon ratio is used to supply heat for the reactions, dilute the reactants to increase equilibrium conversion and avoid coke deposition on the catalyst. CO_2 could play a role similar to steam in these reactions. Utilization of CO_2 in the dehydrogenation of hydrocarbons could be used to produce chemicals efficiently and, at the same time, convert this greenhouse gas to valuable carbon monoxide (CO) gas.

Styrene, a high volume, high value chemical, is a raw material for polymers; it is produced by dehydrogenation of ethylbenzene in the presence of steam and a catalyst. The problems encountered in ethylbenzene dehydrogenation are similar to those generally met in the dehydrogenation of hydrocarbons. High steam-to-hydrocarbon ratios (7 to 12) and high temperatures (above 600°C) are used in commercial plants. A new process using CO_2 instead of steam has been reported. A comparable yield of styrene was obtained at 580°C (50° lower than the commercial process). The energy consumption using CO_2 instead of steam is 1.9×10^8 cal/t-styrene, only 12.7% of the energy consumption of the commercial process (15.0×10^8 cal/t-styrene).

Commercial catalysts for dehydrogenation of ethylbenzene are not suitable for this new process; new catalysts are under investigation.

A series of catalysts on various supports were prepared by incipient wetness techniques, drying and calcinations. Catalyst performance was measured in a continuous

reactor. 0.5g of catalyst, mixed with 1g of quartz sand, was loaded into a tubular reactor. Ethylbenzene was introduced with a syringe pump and vaporized before entering the reactor. CO_2/ethylbenzene ratios were maintained at 10 in most experiments. A LHSV of one for ethylbenzene was used. The products were analyzed online using two gas chromatographs.
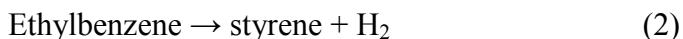
Thermodynamic calculations were conducted for this reaction system. Coupling the reverse water gas shift reaction with the dehydrogenation of ethylbenzene is not favored for lowering the standard free energy for styrene production. However, higher concentrations of CO_2 will shift the equilibrium to obtain high conversions of styrene. Equilibrium conversion for the dehydrogenation of ethylbenzene was about 15% higher in the presence of CO_2 than that in steam. From thermodynamic results, a similar conversion could obtained at 50°C lower in the presence of CO_2.

Some reaction results at 550°C are listed in Table 1. The table shows that Al_2O_3 is a better support for iron catalyst than is SiO_2. In some cases, potassium promotion was favorable. Active carbon (AC) supported iron catalysts had very high initial activities but the catalysts deactivated rapidly.

A $Pt/WO_3/ZrO_2$ catalyst showed comparable activity for the dehydrogenation of ethylbenzene in the presence of CO_2. All three components in this catalyst are essential because activities of Pt and WO_3/ZrO_2 were very low. The activity increased with increase in WO_3 concentration in the $Pt/WO_3/ZrO_2$ catalyst.

Figure 1 shows the effect of CO_2 on the dehydrogenation of ethylbenzene. Obviously, CO_2 improves the activity and stability of Fe/Al_2O_3 catalysts. Similar effects were observed with $Pt/WO_3/ZrO_2$ and Fe/AC catalysts. It can also be seen from Table 1 that a substantial amount of valuable CO is produced when CO_2 is used in the dehydrogenation reaction.

Dehydrogenation of ethylbenzene could involve the following reactions:

$$CO_2 + ethylbenzene \rightarrow CO + styrene + H_2O \qquad (1)$$

$$Ethylbenzene \rightarrow styrene + H_2 \qquad (2)$$

$$H_2 + CO_2 \rightarrow CO + H_2O \qquad (3)$$

CO could be produced either by reaction (1) or by a combination of reactions (2) and (3). A study of the reverse water gas shift reactions shows that reaction (3) is

approaching thermodynamic equilibrium at 550°C. It is difficult to distinguish these two routes. From the promotion effect of CO_2 on this reaction, one can conclude that CO_2 is involved in the activation of ethylbenzene. CO_2, as a weak oxidant, would react with the weak bonds in adsorbed ethylbenzene to increase the oxidation rate.

Carbon dioxide could also be used in the dehydrogenation of isobutane to isobutene. Our search for improved catalysts for incorporating CO_2 into dehydrogenation processes to produce high values chemicals is nearing completion.

Figure 1. Effect of CO_2 on Dehydrogenation of Ethylbenzene with Fe/Al$_2$O$_3$ Catalyst
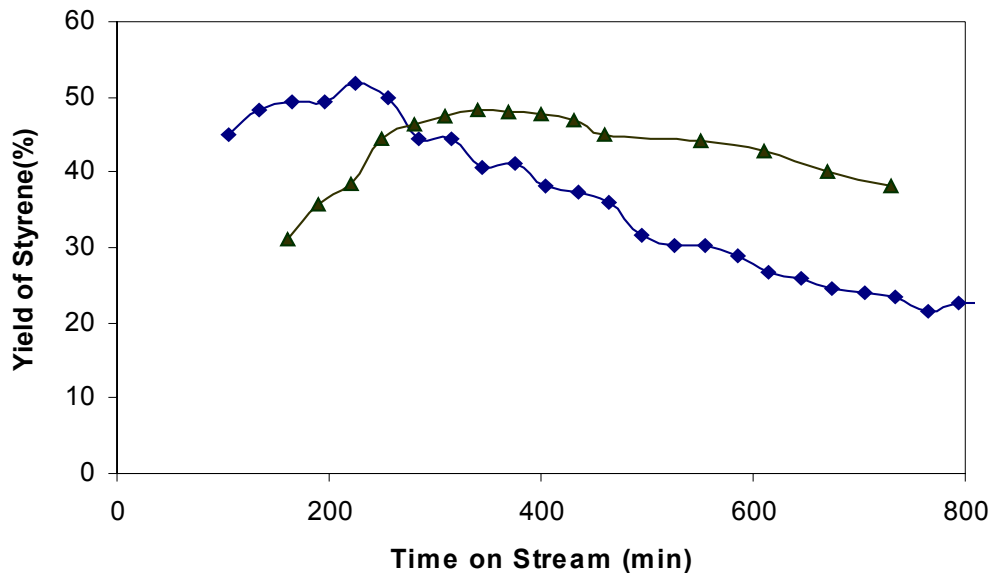
Table 1. Dehydrogenation of Ethylbenzene on Various Catalysts.

Catalyst	TOS (min)	Conversion (%)	Yield of Styrene (%)	Selectivity to Styrene (%)	Yield of CO (%)
Fe/Al$_2$O$_3$	50	42.8	39.9	93.3	NA
	200	27.9	27.8	97.9	NA
	500	22.6	22.6	100	NA
KFe/Al$_2$O$_3$	50	33.3	31.2	93.6	4.6
	200	47.3	47.3	100	43.6
	500	42.3	42.3	100	37.1
KFe/SiO$_2$	35	1.08	1.08	100	0
	200	1.34	1.34	100	0
	500	1.59	1.59	100	0.02
Fe/AC	60	27.8	67.8	93.9	NA
	200	58.3	41.4	99.3	NA
	500	21.2	18.8	100	NA
KFe/AC	60	27.4	63.4	76.8	85.5
	200	71.5	28.5	100	32.4
PtWO3/ZrO$_2$ (No CO$_2$)	60	62.7	37.3	100	-
	200	72.9	27.1	100	-
	500	80.0	20.0	100	-

Reaction conditions:
Temperature:550°C, WHSV of ethylbenzene:1, CO$_2$/ethylbenzene:10