

Catalytic Reduction of Carbon Dioxide on Zn-loaded HZSM-5
Accompanying Aromatization of Propane

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CO₂ was successfully reduced on a Zn/HZSM-5 catalyst accompanying the conversion of C₃H₈ into more valuable products. Further, CO₂ was found to suppress the formation of lower alkanes and the deposition of coke.

Catalytic reduction of CO₂ attracts much attention as a possible technology for the chemical fixation of CO₂. However, hydrogenation of CO₂ requires the production of H₂, which in turn requires much energy. The catalytic reduction of CO₂ by hydrocarbon, such as CO₂-reforming of CH₄,¹⁾ is attractive in this respect. If valuable products can be formed from hydrocarbon, the reaction will be more advantageous. We have reported that the reduction of CO₂ accompanying the dehydrogenation of C₃H₈ to C₃H₆ is possible on oxide catalysts such as Ga₂O₃, ZnO and so on.²⁾

In this letter, we report that CO₂ can be reduced on Zn-loaded HZSM-5 accompanying the aromatization of C₃H₈. The aromatization of lower alkane is known to produce C₆-C₈ aromatics with the formation of H₂ and lower alkanes on HZSM-5 and pentasil type metal-silicates containing Ga, Zn, Pt, and so on.³⁾

Zn/HZSM-5 catalyst was prepared by refluxing an aqueous solution of Zn(NO₃)₂ with HZSM-5 (Si/Al=46.6) powders for 24h, followed by evaporation-to-dryness and calcination at 823K. Zn content was 10 wt%. The catalytic test was conducted by using a conventional flow reaction apparatus. W/F was 2.0 g h mol⁻¹, and C₃H₈/CO₂/N₂ ratio was 2/5/5 or 2/0/10.

As shown in Table 1, the reaction of C₃H₈ alone gave the product distribution which agrees well with those reported:³⁾ major products are aromatics and lower aliphatics, and the formation of H₂ was confirmed gas-chromatographically. Low conversion and high selectivity to alkenes at high temperature may be attributed to the deactivation by coke deposition, because the used catalyst was highly darkened. In the reaction of C₃H₈ + CO₂, a significant amount of CO is formed, confirming the reduction of CO₂.

Table 1. Reactions of C_3H_8 and $C_3H_8 + CO_2$ on a Zn/HZSM-5 catalyst

Temperature / K	C_3H_8 reaction				$C_3H_8 + CO_2$ reaction			
	723	773	823	873	723	773	823	873
C_3H_8 conv. / %	15.0	41.6	51.0	26.2	12.2	37.0	68.4	53.0
CO_2 conv. / %	-	-	-	-	0.7	3.8	9.1	11.0
CO yield / %	-	-	-	-	0.8	4.3	13.1	15.3
Hydrocarbon product distribution (C%)								
$CH_4 + C_2H_6$	18.5	27.9	23.1	7.2	10.3	18.7	25.0	11.6
$C_2H_4 + C_3H_6$	32.6	19.0	25.8	66.4	45.7	29.1	21.9	47.7
C_4^+	8.1	3.5	2.2	2.4	7.8	5.1	2.3	1.8
Aromatics	40.8	49.6	48.8	24.0	36.2	47.0	50.8	38.8

probably, through the reverse water gas shift conversion. Low conversion of CO_2 , which is partly due to high concentration of CO_2 in feed stream, indicates low catalytic activity for the reduction of CO_2 : it was estimated that about 30% of produced H_2 was used for the reduction of CO_2 at 773K.

At low temperature, the selectivity of $CH_4 + C_2H_6$ is decreased by the introduction of CO_2 , which may be due to the consumption of H_2 . While at high temperature where the coke deposition seems serious, CO_2 increases the conversion of C_3H_8 , suggesting that the coke deposition is suppressed. Higher yield of CO than the conversion of CO_2 suggests that CO_2 may gasify the deposited coke. This was confirmed through the formation of CO on the introduction of CO_2 onto the catalyst with deposited coke. This gasification by CO_2 may suppress the accumulation of deposited coke resulting in less deactivation.

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