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

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CO_2 was successfully reduced on a Zn/HZSM-5 catalyst accompanying the conversion of C_3H_8 into more valuable products. Further, CO_2 was found to suppress the formation of lower alkanes and the deposition of coke.

Catalytic reduction of CO_2 attracts much attention as a possible technology for the chemical fixation of CO_2. However, hydrogenation of CO_2 requires the production of H_2, which in turn requires much energy. The catalytic reduction of CO_2 by hydrocarbon, such as CO_2-reforming of CH_4,[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 CO_2 accompanying the dehydrogenation of C_3H_8 to C_3H_6 is possible on oxide catalysts such as Ga_2O_3, ZnO and so on.[2]

In this letter, we report that CO_2 can be reduced on Zn-loaded HZSM-5 accompanying the aromatization of C_3H_8. The aromatization of lower alkane is known to produce C_6-C_8 aromatics with the formation of H_2 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 $Zn(NO_3)_2$ 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 $C_3H_8/CO_2/N_2$ ratio was 2/5/5 or 2/0/10.

As shown in Table 1, the reaction of C_3H_8 alone gave the product distribution which agrees well with those reported:[3] major products are aromatics and lower aliphatics, and the formation of H_2 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 C_3H_8 + CO_2, a significant amount of CO is formed, confirming the reduction of CO_2,

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

	C_3H_8 reaction				C_3H_8 + CO_2 reaction			
Temperature / K	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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