Promoting Effects of Carbon Dioxide on Dehydrogenation of Propane over a SiO_2-supported Cr_2O_3 Catalyst

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The effects of carbon dioxide in the dehydrogenation of C_3H_8 to produce C_3H_6 were investigated over several Cr_2O_3 catalysts supported on Al_2O_3, active carbon and SiO_2. Carbon dioxide exerted promoting effects only on SiO_2-supported Cr_2O_3 catalyst. The promoting effects of carbon dioxide over a Cr_2O_3/ SiO_2 catalyst were to enhance the yield of C_3H_6 and to suppress the catalyst deactivation.

The utilization of carbon dioxide has recently received much attention since the global warming mainly due to carbon dioxide was recognized as one of the most serious problems in the world. The catalytic hydrogenation of CO_2 to produce methanol, hydrocarbons, etc., and the CO_2 reforming of methane to syngas have been extensively studied. Furthermore, it has been reported that CO_2 has several promoting effects on the conversion of hydrocarbons, for example, oxidative coupling of methane,[1] aromatization of propane[2] and dehydrogenation of ethylbenzen.[3,4] The authors have investigated the effect of CO_2 on the dehydrogenation of propane over supported Cr_2O_3 catalysts, and found that CO_2 has promoting effects on a silica-supported Cr_2O_3 catalysts, as described in this paper.

Several supported Cr_2O_3 catalysts were prepared by a impregnation method using an aqueous solution of chromium nitrate. The supports used were γ-Al_2O_3, active carbon (AC) and SiO_2. The catalysts prepared were calcined at 823 K in air for 2 h. The catalysts were characterized by X-ray diffraction (XRD). The XRD patterns of Cr_2O_3/Al_2O_3 and Cr_2O_3/AC showed the diffraction lines ascribed only to the phases of respective supports. In the case of Cr_2O_3/SiO_2, a Cr_2O_3 phase and an amorphous SiO_2 phase were observed. The dehydrogenation of C_3H_8 was conducted under atomospheric pressure of C_3H_8 + CO_2(Ar) at 823 K by using a fixed bed flow reactor.

The main products of the conversion of C_3H_8 in the presence of Ar were C_3H_6 and H_2, while those in the presence of CO_2 were C_3H_6, H_2, and CO, as shown in Table 1. Since the selectivities for C_3H_6 were more than 90%, the dehydrogenation of C_3H_8 to C_3H_6 should be the main reaction both in the presence of CO_2 and in the absence of CO_2. The yield of H_2 + CO was found higher than C_3H_6 yield over all catalysts used in the present study. There might be three possible routes for CO formation; the first one via the successive reactions 1 and 2, the second one via the reaction 3 and the third one via CO_2 reforming of C_3H_8 (reaction 4) as shown below.

$$C_3H_8 = C_3H_6 + H_2 \quad (1)$$
$$CO_2 + H_2 = CO + H_2O \quad (2)$$
$$C_3H_8 + CO_2 = C_3H_6 + CO + H_2O \quad (3)$$
$$C_3H_8 + 3CO_2 = 6CO + 4H_2 \quad (4)$$

Figure 1 shows the change in catalytic activities of several supported Cr_2O_3 catalysts with time on stream. The activity of the Cr_2O_3/Al_2O_3 catalyst were much lower in the presence of CO_2

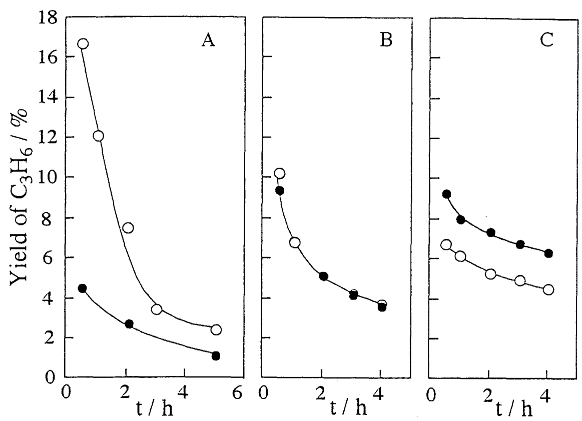

Figure1. Catalytic activities of several supported Cr_2O_3 catalysts as a function of time on stream.
Catalyst : A=Cr_2O_3(15 wt%)/Al_2O_3, B=Cr_2O_3(5 wt%)/AC, C=Cr_2O_3(5 wt%)/SiO_2,
Reaction conditions: 823 K, W/F=2 g-cat•h/mol,
Feed gas ratio: C_3H_8/CO_2=1/1(●), C_3H_8/Ar=1/1(O).

Table 1. Products of the conversions of C_3H_8 in the presence and in the absence of CO_2 over several supported Cr_2O_3 catalysts[a]

Catalyst	Feed gas[b]	Yield / %			Selectivity / %			
		C_3H_6	H_2	CO	C_3H_6	CH_4	C_2H_6	C_2H_4
Cr_2O_3(15wt%)/Al_2O_3	C_3H_8/Ar	16.5	21.2	-	95.5	2.1	1.6	0.8
	C_3H_8/CO_2	4.3	3.6	3.9	91.3	6.4	0.7	1.6
Cr_2O_3(5wt%)/AC	C_3H_8/Ar	10.1	12.2	-	94.4	2.3	1.2	2.1
	C_3H_8/CO_2	9.3	5.1	6.4	93.6	2.9	1.3	2.1
Cr_2O_3(5wt%)/SiO_2	C_3H_8/Ar	6.5	7.2	-	90.4	2.7	2.7	3.5
	C_3H_8/CO_2	9.1	8.0	3.1	94.0	1.8	1.8	1.6

[a] Reaction conditions: 823 K, W/F=2 g-cat•h/mol.
[b] Composition of the feed gas: C_3H_8/CO_2(Ar)=1/1(molar ratio).

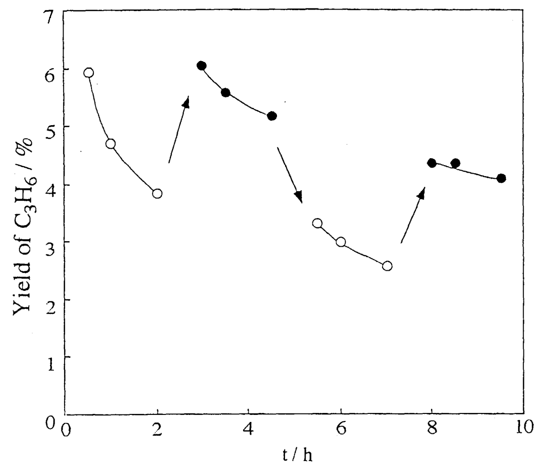

Figure2. Change in the C_3H_6 yield with alternate feeds of C_3H_8/Ar and C_3H_8/CO_2/Ar over a Cr_2O_3/SiO_2.
Reaction conditions: 823 K, W/F=0.62 g-cat•h/mol,
Feed gas: C_3H_8/CO_2/Ar =1/2/7(●), C_3H_8/Ar =1/9(O).

than that without CO_2. The activity of the Cr_2O_3/AC was independent of the presence of CO_2. On the other hand, the activity of Cr_2O_3/SiO_2 catalyst in the presence of CO_2 was surprisingly found to be 40% higher than that without CO_2.

In order to study the contribution of CO_2 in the conversion of C_3H_8 to C_3H_6, catalytic tests with alternate feeds of C_3H_8/Ar and C_3H_8/ CO_2/Ar over a Cr_2O_3/SiO_2 catalyst were carried out. The results shown in Figure 2 clearly indicate that the presence of CO_2 markedly improved the yield of C_3H_6. This catalytic performance is a proof that CO_2 plays a promoting role in the conversion of C_3H_8 to C_3H_6. Although further detailed studies are under achievement, the boundaries between Cr_2O_3 and SiO_2 might have an important role in the promoting effect of CO_2.

The effect of CO_2 addition on the deactivation of a Cr_2O_3/SiO_2 catalyst. was also examined (Figure 3). In this case, the catalyst weight for the dehydrogenation of C_3H_8 withourt CO_2 was 50% larger than that for the reaction in the absence of CO_2 in order to obtain the same initial yield of C_3H_6 in the both reactions. The decrease in the yield of $C_3H_6$was found much less in the presence of CO_2 than in the absence of CO_2. At the time on

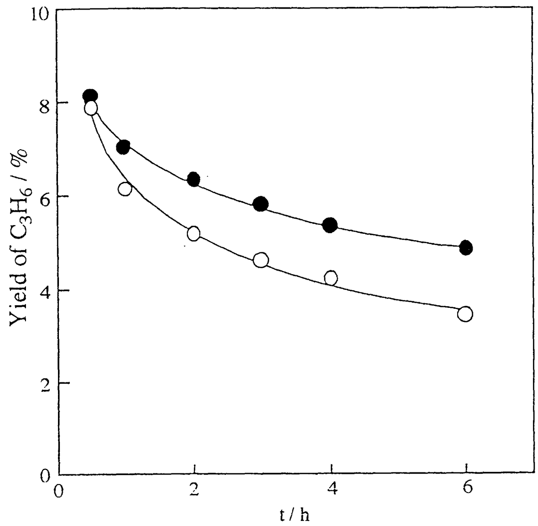

Figure3. Effect of CO_2 on the deactivation of a Cr_2O_3(5 wt%)/SiO_2.
Reaction conditions: 823 K,
Feed gas : C_3H_8/CO_2/Ar =1/2/7(●, W/F=0.62 g-cat•h/mol), C_3H_8/Ar =1/9(O, W/F=0.93 g-cat•h/mol).

stream of 6 h, the yield of C_3H_6 in the presence of CO_2 was about 40% higher than that without CO_2. This finding suggests that the addition of CO_2 could suppress the deactivation of the catalyst.

In summary, the promoting effects of CO_2 over a Cr_2O_3/SiO_2 catalyst were to enhance the yield of C_3H_6 and to suppress the catalyst deactivation.

References

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