

Promoting Effects of Carbon Dioxide on Dehydrogenation of Propane over a SiO₂-supported Cr₂O₃ Catalyst

Isao Takahara* and Masahiro Saito*

National Institute for Resources and Environment (NIRE), 16-3 Onogawa, Tsukuba, Ibaraki 305

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The effects of carbon dioxide in the dehydrogenation of C₃H₈ to produce C₃H₆ were investigated over several Cr₂O₃ catalysts supported on Al₂O₃, active carbon and SiO₂. Carbon dioxide exerted promoting effects only on SiO₂-supported Cr₂O₃ catalyst. The promoting effects of carbon dioxide over a Cr₂O₃/SiO₂ catalyst were to enhance the yield of C₃H₆ 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 CO₂ to produce methanol, hydrocarbons, etc., and the CO₂ reforming of methane to syngas have been extensively studied. Furthermore, it has been reported that CO₂ has several promoting effects on the conversion of hydrocarbons, for example, oxidative coupling of methane,¹ aromatization of propane² and dehydrogenation of ethylbenzene.³ The authors have investigated the effect of CO₂ on the dehydrogenation of propane over supported Cr₂O₃ catalysts, and found that CO₂ has promoting effects on a silica-supported Cr₂O₃ catalysts, as described in this paper.

Several supported Cr₂O₃ catalysts were prepared by a impregnation method using an aqueous solution of chromium nitrate. The supports used were γ-Al₂O₃, active carbon (AC) and SiO₂. 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 Cr₂O₃/Al₂O₃ and Cr₂O₃/AC showed the diffraction lines ascribed only to the phases of respective supports. In the case of Cr₂O₃/SiO₂, a Cr₂O₃ phase and an amorphous SiO₂ phase were observed. The dehydrogenation of C₃H₈ was conducted under atmospheric pressure of C₃H₈ + CO₂(Ar) at 823 K by using a fixed bed flow reactor.

The main products of the conversion of C₃H₈ in the presence of Ar were C₃H₆ and H₂, while those in the presence of CO₂ were C₃H₆, H₂, and CO, as shown in Table 1. Since the selectivities for C₃H₆ were more than 90%, the dehydrogenation of C₃H₈ to C₃H₆ should be the main reaction both in the presence

of CO₂ and in the absence of CO₂. The yield of H₂ + CO was found higher than C₃H₆ 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 CO₂ reforming of C₃H₈ (reaction 4) as shown below.

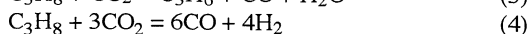


Figure 1 shows the change in catalytic activities of several supported Cr₂O₃ catalysts with time on stream. The activity of the Cr₂O₃/Al₂O₃ catalyst were much lower in the presence of CO₂

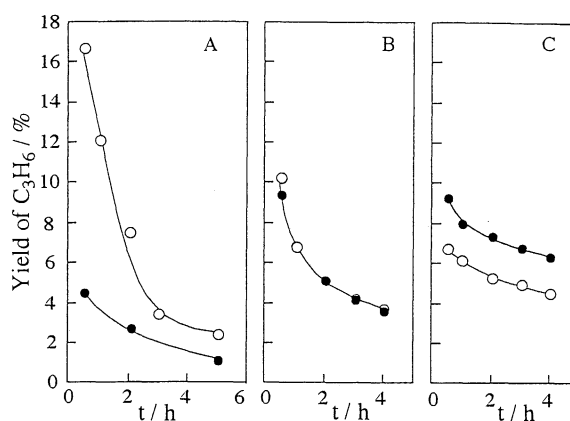


Figure 1. Catalytic activities of several supported Cr₂O₃ catalysts as a function of time on stream. Catalyst: A=Cr₂O₃(15 wt%)/Al₂O₃, B=Cr₂O₃(5 wt%)/AC, C=Cr₂O₃(5 wt%)/SiO₂. Reaction conditions: 823 K, W/F=2 g-cat•h/mol, Feed gas ratio: C₃H₈/CO₂=1/1(●), C₃H₈/Ar=1/1(O).

Table 1. Products of the conversions of C₃H₈ in the presence and in the absence of CO₂ over several supported Cr₂O₃ catalysts^a

Catalyst	Feed gas ^b	Yield / %			Selectivity / %			
		C ₃ H ₆	H ₂	CO	C ₃ H ₆	CH ₄	C ₂ H ₆	C ₂ H ₄
Cr ₂ O ₃ (15wt%)/Al ₂ O ₃	C ₃ H ₈ /Ar	16.5	21.2	-	95.5	2.1	1.6	0.8
	C ₃ H ₈ /CO ₂	4.3	3.6	3.9	91.3	6.4	0.7	1.6
Cr ₂ O ₃ (5wt%)/AC	C ₃ H ₈ /Ar	10.1	12.2	-	94.4	2.3	1.2	2.1
	C ₃ H ₈ /CO ₂	9.3	5.1	6.4	93.6	2.9	1.3	2.1
Cr ₂ O ₃ (5wt%)/SiO ₂	C ₃ H ₈ /Ar	6.5	7.2	-	90.4	2.7	2.7	3.5
	C ₃ H 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: C₃H₈/CO₂(Ar)=1/1(molar ratio).

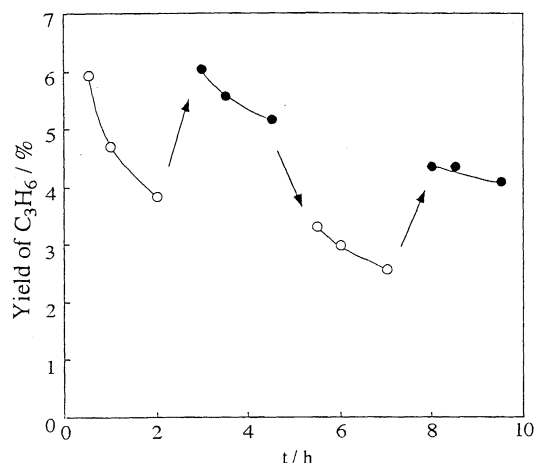


Figure 2. Change in the C₃H₆ yield with alternate feeds of C₃H₈/Ar and C₃H₈/CO₂/Ar over a Cr₂O₃/SiO₂.
Reaction conditions: 823 K, W/F=0.62 g-cat•h/mol,
Feed gas: C₃H₈/CO₂/Ar = 1/2/7 (●), C₃H₈/Ar = 1/9 (○).

than that without CO₂. The activity of the Cr₂O₃/AC was independent of the presence of CO₂. On the other hand, the activity of Cr₂O₃/SiO₂ catalyst in the presence of CO₂ was surprisingly found to be 40% higher than that without CO₂.

In order to study the contribution of CO₂ in the conversion of C₃H₈ to C₃H₆, catalytic tests with alternate feeds of C₃H₈/Ar and C₃H₈/CO₂/Ar over a Cr₂O₃/SiO₂ catalyst were carried out. The results shown in Figure 2 clearly indicate that the presence of CO₂ markedly improved the yield of C₃H₆. This catalytic performance is a proof that CO₂ plays a promoting role in the conversion of C₃H₈ to C₃H₆. Although further detailed studies are under achievement, the boundaries between Cr₂O₃ and SiO₂ might have an important role in the promoting effect of CO₂.

The effect of CO₂ addition on the deactivation of a Cr₂O₃/SiO₂ catalyst was also examined (Figure 3). In this case, the catalyst weight for the dehydrogenation of C₃H₈ without CO₂ was 50% larger than that for the reaction in the absence of CO₂ in order to obtain the same initial yield of C₃H₆ in the both reactions. The decrease in the yield of C₃H₆ was found much less in the presence of CO₂ than in the absence of CO₂. At the time on

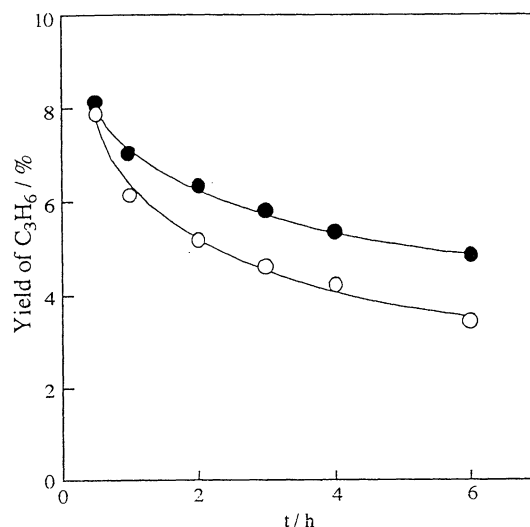


Figure 3. Effect of CO₂ on the deactivation of a Cr₂O₃(5 wt%)/SiO₂.
Reaction conditions: 823 K,
Feed gas: C₃H₈/CO₂/Ar = 1/2/7 (●, W/F=0.62 g-cat•h/mol),
C₃H₈/Ar = 1/9 (○, W/F=0.93 g-cat•h/mol).

stream of 6 h, the yield of C₃H₆ in the presence of CO₂ was about 40% higher than that without CO₂. This finding suggests that the addition of CO₂ could suppress the deactivation of the catalyst.

In summary, the promoting effects of CO₂ over a Cr₂O₃/SiO₂ catalyst were to enhance the yield of C₃H₆ and to suppress the catalyst deactivation.

References

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