ELSEVIER

Catalysis Today 45 (1998) 55–59

CATALYSIS TODAY

Promoting effects of CO_2 on dehydrogenation of propane over a SiO_2-supported Cr_2O_3 catalyst

I. Takahara[a,*], W.-C. Chang[b], N. Mimura[a], M. Saito[a]

[a] *National Institute for Resources and Environment (NIRE), 16-3 Onogawa, Tsukuba-shi, Ibaraki 305, Japan*
[b] *JKF (Japan-Korea Industrial Technology Co-operation Foundation) researcher, 16-3 Onogawa, Tsukuba-shi, Ibaraki 305, Japan*

Abstract

The effects of carbon dioxide on 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 catalysts. 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. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Dehydrogenation; Propane; Carbon dioxide; Chromium oxide

1. Introduction

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 ethylbenzene [3,4]. The authors have investigated the effect of CO_2 on the dehydrogenation of propane over several supported Cr_2O_3 catalysts, and found that CO_2 has promoting effects on silica-supported Cr_2O_3 catalysts.

2. Experimental

Several supported Cr_2O_3 catalysts were prepared by an 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 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 post-reactor XRD was performed. In Cr_2O_3/Al_2O_3 and Cr_2O_3/AC, the observed patterns were not changed, but the diffraction of Cr_2O_3 was increased slightly in Cr_2O_3/SiO_2. The dehydrogenation of C_3H_8 was conducted under atmospheric pressure of $C_3H_8+CO_2(Ar)$ at 823 K by using a fixed bed flow reactor. TPR/D studies were carried out to elucidate the behavior of Cr_2O_3 in the catalyst during treatment with H_2 and

---

*Corresponding author. Tel.: +81-298-58-8174; fax: +81-298-58-8176; e-mail: pl959@nire.go.jp

PII: S0920-5861(98)00245-4

CO_2. A pulse reaction technique was also employed for examining the initial activity of the catalyst.

3. Results and discussion

3.1. *Effects of CO_2 on dehydrogenation of C_3H_8*

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 to be 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:

$$C_3H_8 = C_3H_6 + H_2 \tag{1}$$

$$CO_2 + H_2 = CO + H_2O \tag{2}$$

$$C_3H_8 + CO_2 = C_3H_6 + CO + H_2O \tag{3}$$

$$C_3H_8 + 3CO_2 = 6CO + 4H_2 \tag{4}$$

Fig. 1 shows the activities of several supported Cr_2O_3 catalysts for the dehydrogenation of C_3H_8 in the presence of CO_2 as well as in the absence of CO_2. The activity of the Cr_2O_3/Al_2O_3 catalyst was much lower in the presence of CO_2 than that in the absence of 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 in the absence of CO_2.

Fig. 2 shows the selectivities for H_2 and CO as a function of C_3H_6 yield. In the case of Cr_2O_3/Al_2O_3 catalyst, the selectivity for H_2 decreased with an increase in C_3H_6 yield, whereas the selectivity for CO increased with an increase in C_3H_6 yield, as shown in Fig. 2(A). On the other hand, the selectivities of Cr_2O_3/SiO_2 catalyst for CO and H_2 did not change irrespective of C_3H_6 yield, as shown in Fig. 2(B). These findings suggest that CO might be formed via successive reactions (1) and (2) over Cr_2O_3/Al_2O_3 catalyst, whereas both the reactions (1) and (3) could take place simultaneously over Cr_2O_3/SiO_2 catalyst.

In order to study the contribution of CO_2 in the conversion of C_3H_8 to C_3H_6 over a Cr_2O_3/SiO_2 catalyst, catalytic tests with alternate feeds of C_3H_8/Ar and C_3H_8/CO_2/Ar were carried out. The results shown in Fig. 3 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 over a Cr_2O_3/SiO_2 catalyst.

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	Surface area (m^2/g)	Feed gas[b]	Yield (%)			Selectivity[e] (%)				Carbon balance (%)
			C_3H_6[c]	H_2[c]	CO[d]	C_3H_6	CH_4	C_2H_6	C_2H_4	
Cr_2O_3 (5 wt%)/Al_2O_3	170	C_3H_8/Ar	12.7	15.6	–	96.5	1.6	1.2	0.7	98.4
		C_3H_8/CO_2	3.3	2.6	2.8	92.9	5.0	0.5	1.6	97.9
Cr_2O_3 (5 wt%)/AC	910	C_3H_8/Ar	10.1	12.2	–	94.4	2.3	1.2	2.1	97.1
		C_3H_8/CO_2	9.3	5.1	6.4	93.6	3.0	1.3	2.1	95.0
Cr_2O_3 (5 wt%)/SiO_2	430	C_3H_8/Ar	6.5	7.2	–	90.4	3.4	2.7	3.5	95.2
		C_3H_8/CO_2	9.1	8.0	3.1	94.0	2.6	1.8	1.6	96.0

[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).

[c] (100×moles of C_3H_6 or moles of H_2)/(moles of C_3H_8 at the inlet).

[d] (100×moles of CO)/(moles of CO_2 at the inlet).

[e] Selectivity=(100×number of carbon atoms per molecule of a product×moles of a product)/(total number of carbon atoms in the hydrocarbon products).

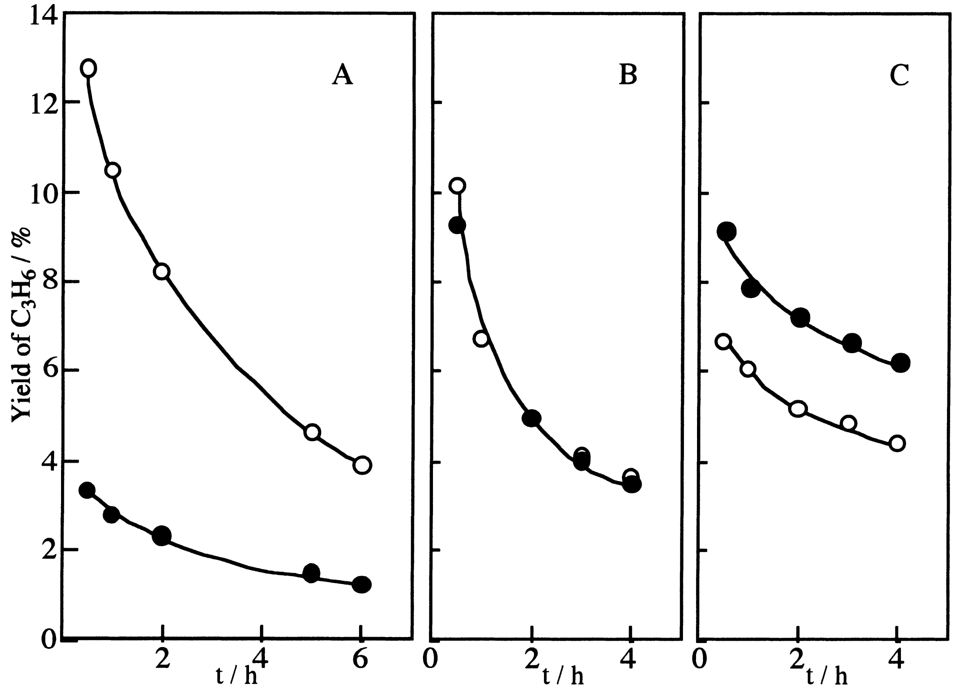

Fig. 1. Catalytic activities of several supported Cr_2O_3 catalysts as a function of time on stream: (A) Cr_2O_3 (5 wt%)/Al_2O_3; (B) Cr_2O_3 (5 wt%)/AC; (C) Cr_2O_3 (5 wt%)/SiO_2; 823 K; $W/F=2$ g-cat h/mol; feed gas: $C_3H_8/CO_2=1/1$ (●); $C_3H_8/Ar=1/1$ (○).

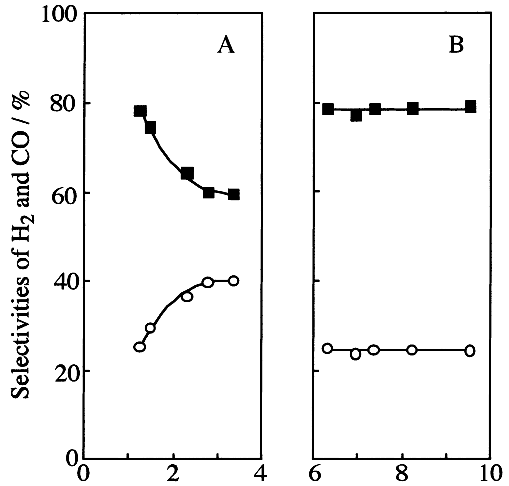

Fig. 2. Selectivities of H_2 and CO in the reaction of $C_3H_8+CO_2$ as a function of C_3H_6 yield: (A) Cr_2O_3 (5 wt%)/Al_2O_3; (B) Cr_2O_3 (5 wt%)/SiO_2; selectivity: H_2 (■); CO (○); 823 K; $W/F=2$ g-cat h/mol; feed gas: $C_3H_8/CO_2=1/1$.

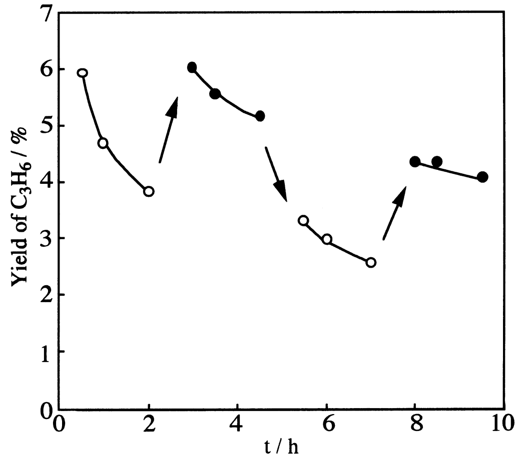

Fig. 3. Change in the C_3H_6 yield with alternate feeds of C_3H_8/Ar and C_3H_8/CO_2/Ar over a Cr_2O_3/SiO_2: 823 K; $W/F=0.62$ g-cat h/mol; feed gas: $C_3H_8/CO_2/Ar=1/2/7$ (●); $C_3H_8/Ar=1/9$ (○).

Furthermore, the ratio of C_3H_6 yield in the reaction in the presence of CO_2 to that in the absence of CO_2 decreased with increasing Cr_2O_3 content in the Cr_2O_3/SiO_2 catalyst, as shown in Fig. 4. This suggests that

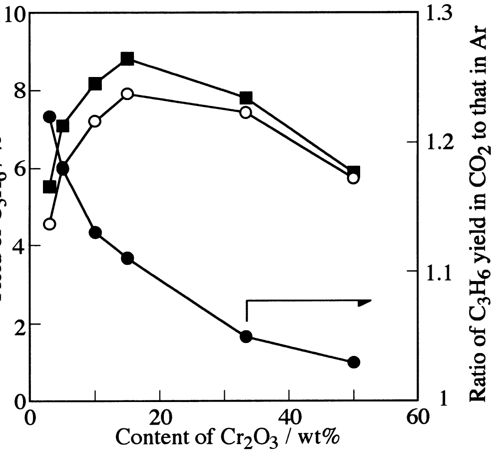

Fig. 4. Yield of C_3H_6 in the dehydrogenation of C_3H_8 in the presence of CO_2 (■) and in the absence of CO_2 (○), and their ratio (●) as a function of Cr_2O_3 content on a Cr_2O_3/SiO_2: 823 K; $C_3H_8/CO_2(Ar)=1/1$; *W*/*F*=2 g-cat h/mol.

the boundaries between Cr_2O_3 and SiO_2 particles 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 (Fig. 5). The reaction conditions for both the cases with and without CO_2 were the same except the catalyst weight, which was 50% larger in the case of the reaction without CO_2, in order to obtain the same initial yield of C_3H_6. 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. This finding suggests that the addition of CO_2 could suppress the deactivation of the catalyst.

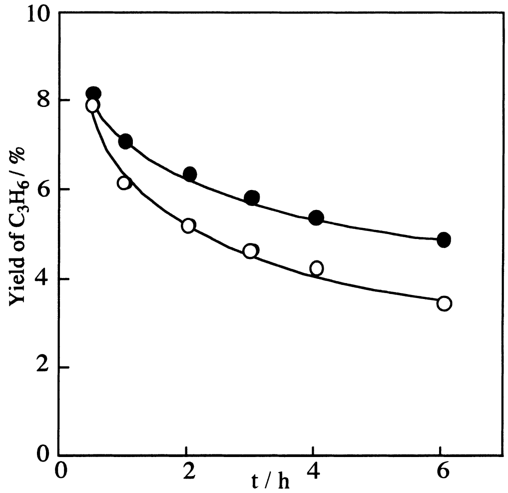

Fig. 5. Effect of CO_2 on the deactivation of Cr_2O_3 (5 wt%)/SiO_2. Reaction conditions: 823 K; (●) $C_3H_8/CO_2/Ar=1/2/7$; *W*/*F*=0.62 g-cat h/mol; (○) $C_3H_8/Ar=1/9$; *W*/*F*=0.93 g-cat h/mol.

3.2. *TPR/D result*

Fig. 6 shows TPR/D profiles during various treatments of Cr_2O_3/SiO_2 catalyst. The Cr_2O_3 was found to be reduced in a stream of H_2. And smaller peaks were observed when the catalyst, which was reduced with H_2 and then treated with CO_2, was re-reduced with H_2. This suggests that CO_2 could oxidize some part of the surface of Cr_2O_3 in the catalyst. Accordingly, these findings suggest that the surface of Cr_2O_3 on a Cr_2O_3/SiO_2 catalyst could be reduced during the dehydro-

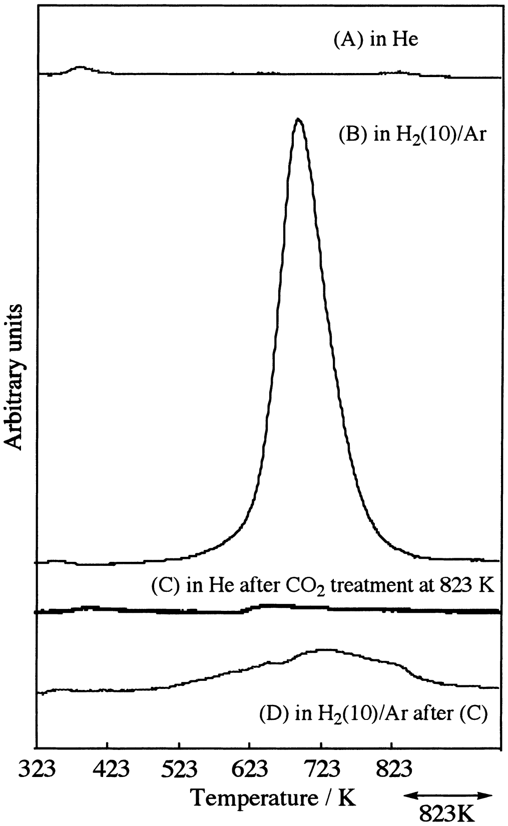

Fig. 6. TPR/D profile for treatment A→B→C→D over a Cr_2O_3/SiO_2 catalyst. Operating conditions: $H_2(10)/Ar(90)$; 10 K/min.

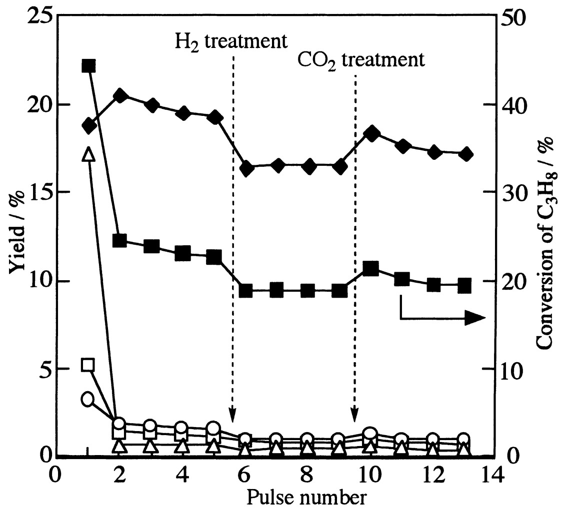

Fig. 7. Conversion of C_3H_8 and yield of hydrocarbon products as a function of the number of C_3H_8 pulse on Cr_2O_3/SiO_2. Reaction conditions: 823 K; He carrier yield: CH_4 (□); C_2H_4 (△); C_2H_6 (○); C_3H_6 (◆); conversion: C_3H_8 (■).

genation of C_3H_8 in the absence of CO_2, whereas the surface of Cr_2O_3 might be maintained partially oxidized during the reaction in the presence of CO_2.

3.3. *Pulse reaction*

A pulse reaction technique was employed for examining the initial activity of the catalyst. Fig. 7 shows the conversion of C_3H_8 and the yield of hydrocarbon products as a function of the number of C_3H_8 pulses on Cr_2O_3/SiO_2 catalyst. The yield of C_3H_6 reached a maximum of about 21% at the second pulse. After the second pulse, the yield of C_3H_6 slightly decreased with increasing pulse number. The yield of C_3H_6 decreased to 17% by the treatment of the catalyst with H_2 after fifth pulse, and remained constant from sixth pulse to ninth pulse. The treatment of the catalyst with CO_2 after ninth pulse raised the yield of C_3H_6 to 19%, but the yield of C_3H_6 gradually decreased with increasing pulse number from tenth pulse. These findings confirm that partially oxidized Cr_2O_3/SiO_2 catalyst could be more active for the dehydrogenation of C_3H_8 than a reduced catalyst. The results obtained from pulse reaction studies and from TPR/D studies might explain slower deactivation of the catalyst during the dehydrogenation in the presence of CO_2.

Furthermore, pulse reaction studies were performed for comparing between the yield of C_3H_6 during the reaction in a stream of CO_2 and in a stream of He. The C_3H_6 yield at the first pulse and the second pulse in the presence of CO_2 was found to be higher than those in the absence of CO_2. This strongly suggests that CO_2 could enhance the rate of the dehydrogenation of C_3H_8 over a Cr_2O_3/SiO_2 catalyst. This promoting effect of CO_2 might occur at the boundaries between Cr_2O_3 and SiO_2 particles.

4. Conclusion

Carbon dioxide promotion of propane dehydrogenation performance was only observed on SiO_2 supported catalysts. 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. The partially oxidized Cr_2O_3 supported on SiO_2 catalyst is active for the dehydrogenation of C_3H_8. In the presence of CO_2, the surface of Cr_2O_3/SiO_2 might be maintained to be partially oxidized during the reaction.

References

[1] T. Nishiyama, K. Aika, J. Catal. 122 (1990) 346.
[2] S. Yamauchi, A. Satsuma, T. Hattori, Y. Murakami, Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.) 37 (1994) 278.
[3] S. Sato, M. Ohhara, T. Sodesawa, F. Nozaki, Appl. Catal. 37 (1988) 207.
[4] M. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga, T. Suzuki, Appl. Catal. A 121 (1995) 125.