Catalysis Letters Vol. 101, Nos. 1–2, May 2005 (© 2005)
DOI: 10.1007/s10562-004-3749-6

Effect of supports on catalytic activity of chromium oxide-based catalysts in the dehydrogenation of propane with CO_2

Małgorzata Kocoń, Piotr Michorczyk*, and Jan Ogonowski

Institute of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland

Received 24 November 2004; accepted 3 December 2004

Dehydrogenation of propane in the presence and absence of CO_2 over CrO_x/SiO_2 and CrO_x/Al_2O_3 catalysts with Cr loading between 0.7–20.4 wt% was discussed. It was found that the nature of support strongly effects on the catalytic performance in the dehydrogenation with CO_2. Over the CrO_x/SiO_2 catalyst CO_2 enhance the propene yield, whereas over the CrO_x/Al_2O_3 catalyst the yield and selectivity of propene in the presence of CO_2 strongly decrease. The effect of steam on catalytic performance of the tested catalysts was also discussed.

KEY WORDS: propane; dehydrogenation with CO_2; supported chromium oxide catalysts.

1. Introduction

In the last decade several research groups found that introduction of CO_2 into the feed gas improved catalysts performance in the dehydrogenation of hydrocarbons. These results concern mainly the dehydrogenation of ethane [1–5], propane [4,6–9], butanes [4,9,10] and ethylbenzene [11–15] in the presence of CO_2. The generally accepted role of carbon dioxide in the dehydrogenation of hydrocarbons is removal of hydrogen and suppression of coke deposition on the catalyst surface. However, the pathway of hydrogen removal is still not clear. It is proposed that carbon dioxide can react directly with hydrogen to make the water gas ($CO + H_2O$) or can act as a mild oxidant in the oxidative dehydrogenation. It is difficult to estimate which of the pathways predominates. The oxidative pathway has been proposed for dehydrogenation of hydrocarbons over vanadium, chromium, cerium and iron oxide catalysts, whereas over gallium oxide the non-redox pathway is more likely.

It has been recognized that acidic nature as well as redox one is an important property of CO_2. Few studies have been reported that the acidic property of CO_2 plays some important role in the dehydrogenation of hydrocarbons with CO_2, especially in the determination of the yield of reaction product [16].

In the present work, we have studied the dehydrogenation of propane to propene in the presence of CO_2 over chromium oxide-based catalysts supported on two very different oxide supports (SiO_2 and Al_2O_3).

2. Experimental

2.1. Preparation of catalysts

Two kinds of oxides were used as supports; γ-Al_2O_3 (BET surface 155 m^2/g, 507C Aldrich), SiO_2 (BET surface 304 m^2/g, POCH Poland). Supported catalysts were prepared by impregnation technique from an aqueous solution of $Cr(NO_3)_3$ (POCH, Poland). The chromium loading in the catalyst was regulated by varying the concentration of chromium salt in the impregnation solution. The solutions were mixed with the supports (SiO_2, Al_2O_3), followed by evaporation under constant stirring and calcined at 923 K for 3 h in air. The notations such $(0.7)CrO_x/SiO_2$ or $(0.7)CrO_x/Al_2O_3$ were employed for the chromium oxide-based catalysts supported on SiO_2 and Al_2O_3, respectively, with the value in parenthesis indicating the Cr loading.

2.2. Temperature-programmed reduction-H_2

Temperature-programmed reduction (TPR) of the catalyst was performed by using a $He + H_2$ (90/10 vol%) gas mixture. The flow rate of the carrier gas was 30 ml/min. 200 mg sample was used and heated (10 K/min) to the final temperature of 873 K. The H_2 consumption was measured by a thermal conductivity detector.

2.3. Catalytic tests

The dehydrogenation of propane to propene in the presence or absence of CO_2 was carried out at atmospheric pressure in a flow-type stainless steel reactor, packed with 0.5 g of the catalyst. The feed was a mixture

---

* To whom correspondence should be addressed.
E-mail: pmichor@usk.pk.edu.pl

1011-372X/05/0500–0053/0 © 2005 Springer Science+Business Media, Inc.

of 12.5 vol% of propane and 87.5 vol% of carbon dioxide (or helium). The total flow rate was 30 ml/min. The catalysts were first preheated in a helium stream at 873 K and then the reaction was started at 673–873 K temperature range. The reverse water–gas shift reactions were conducted under the same conditions, by replacing propane with hydrogen. The reactants and products were analysed online using two gas chromatographs. One of them was equipped with a 3 m glass column (3 mm i.d.), packed with Porapak Q and a flame ionization detector. This chromatograph was used to analyse hydrocarbons C_1–C_3. The second chromatograph was equipped with a 3 m stainless steel column of the same diameter, packed with Carboxen 1000 and, a thermal conductivity detector (for CO, H_2 and CO_2 analyses).

The conversion, yield and selectivity were calculated by the following equation:

$$\text{Conversion } (\%) = (n_g \,/\, \text{ff}(n_{pa}+n_g)) \times 100$$
$$\text{Yield } (\%) = (n_{pe}/(n_{pa}+n_g)) \times 100$$
$$\text{Selectivity } (\%) = (n_{pe}/n_g) \times 100$$

where n_{pe}, n_{pa} are the number of moles of propene and propane at the exit of the reactor, respectively, n_g is the number of moles of propane converted into the gaseous products (propene, ethane, ethene and methane). The calculations do not consider the conversion of propane to coke, as its instantaneous formation is time dependent and difficult to estimate.

3. Results and discussion

3.1. TPR results

The TPR curves of the catalysts are given in figure 1. Bulk Cr_2O_3 shows a peak around 543 K. The samples of the (3.4)CrO_x/SiO_2 and (3.4)CrO_x/Al_2O_3 catalysts exhibit only one reduction maximum at about 680 and 590 K, respffectively. These results suggest that the oxygen is more strongly bound in the supported chromium catalysts than in bulk Cr_2O_3.

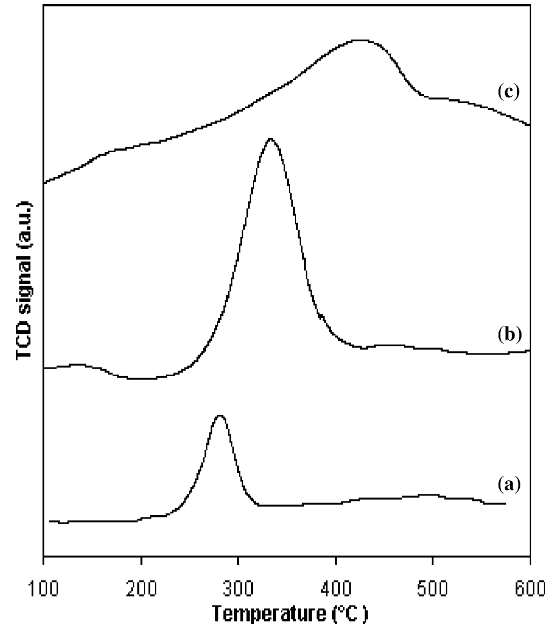

Figure 1. TPR profiles for bulk Cr_2O_3 (a), CrO_x/Al_2O_3 (b) and CrO_x/SiO_2 (c).

3.2. *Effect of temperature and feed composition*

The effect of temperature on propene yield and selectivity is shown in figure 2. In all cases the yield of propene increased with temperature, but the detailed behavior varied with a type of support and the feed composition.

Figure 2a shows the changes in the yield and selectivity of propene as a function of temperature over the (3.4)CrO_x/SiO_2 catalyst. Both in the presence and absence of carbon dioxide the yield of propene increased with temperature, while the selectivity was high at low

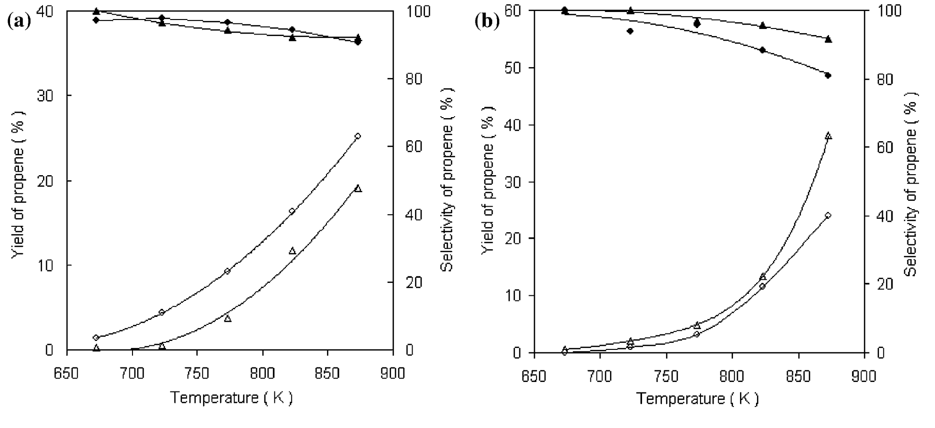

Figure 2. The catalytic performance of (3.4)CrO_x/SiO_2 (a) and (3.4)CrO_x/Al_2O_3 (b) catalysts in the dehydrogenation of propane in the presence (O) and absence of (δ) CO_2 as a function of temperature. Open symbols: propene yield; solid symbols: propene selectivity. Reaction conditions: $C_3H_8/CO_2(He)$ = 1/7 (molar ratio); total flow rate = 30 ml/min; catalyst weight = 0.5 g, reaction time 0.2 h.

temperature but it gradually decreased with increasing temperature. Over the whole temperature range the yield of propene was higher in the presence of CO_2 then its absence. On the other hand, over the (3.4)CrOx/Al_2O_3 catalyst carbon dioxide exerts an adverse effect on the yield and selectivity of propene (figure 2b). The introduction of CO_2 to the feed decreased the selectivity and yield of propene.

The effect of feed composition on the dehydrogenation activity of the (3.4)CrO_x/SiO_2 and (3.4)CrO_x/Al_2O_3 catalysts is shown in figure 3. The promoting effect of CO_2 on propene yield was only observed on silica supported catalyst. CO_2 does not promote dehydrogenation of propane over the (3.4)CrO_x/Al_2O_3 catalyst. Moreover, the yield and selectivity of propene markedly decreased in the presence of carbon dioxide.

Figure 4 shows the influences of steam on yield and selectivity of propene over (3.4)CrO_x/SiO_2 and (3.4)CrO_x/Al_2O_3 catalysts. The introduction steam to the reaction zone strongly decreased dehydrogenation activity of the tested catalysts.

The steam effect is irreversible in the case of (3.4)CrO_x/SiO_2 catalyst, whereas over the (3.4)CrO_x/Al_2O_3 catalyst it is reversible and similar to that of CO_2. It has to be pointed out that this effect is unfavorable, however unavoidable in the reaction with CO_2, because the water is produced by the reactions (1) and (2).

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (1)$$

$$C_3H_8 + CO_2 \rightleftharpoons C_3H_6 + CO + H_2O \qquad (2)$$

The catalytic properties of the supported chromium catalysts are strongly affected by the acidity/basicity of the oxide support. It is proposed that poisonous effect of CO_2 on the dehydrogenation activity of CrO_x/Al_2O_3 catalyst is due to the basicity of Al_2O_3 [17]. However, Nakagawa *et al.* [16] suggested that in the dehydrogenation of ethane with CO_2, the decrease of the ethene yield over Ga_2O_3/Al_2O_3 catalyst is caused by modification of acidity of the catalyst surface with water. This

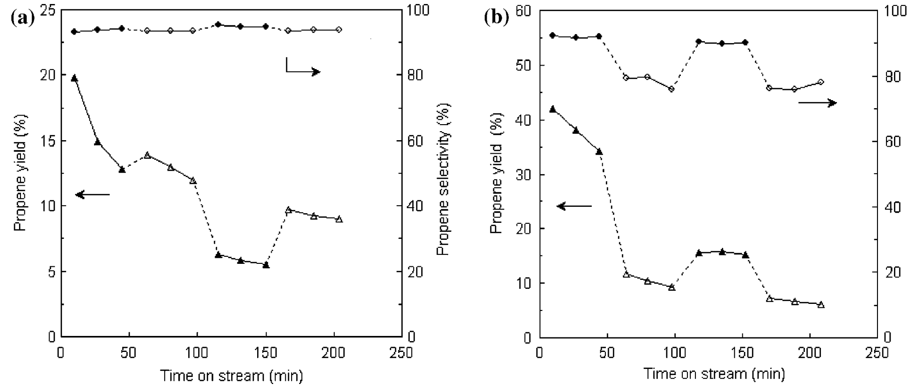

Figure 3. The effect of feed composition on propene yield and selectivity over (3.4)CrO_x/SiO_2 (a) and (3.4)CrO_x/Al_2O_3 (b) catalysts at 873 K. Propene selectivity (○) and yield (δ). Solid symbols: reaction in He; open symbols: reaction in CO_2. Reaction conditions: $C_3H_8/CO_2(He) = 1/7$ (molar ratio); total flow rate = 30 ml/min; catalyst weight = 0.5 g.

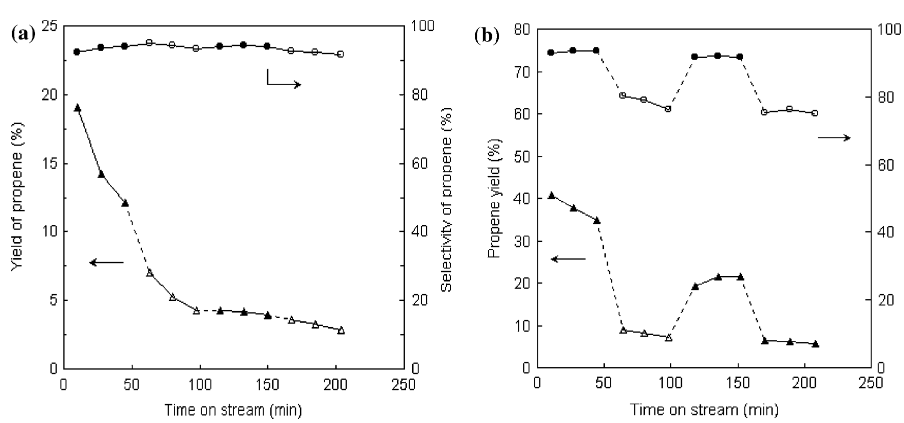

Figure 4. The effect of steam on propene yield and selectivity in the dehydrogenation of propane over (3.4)CrO_x/SiO_2 (a) and (3.4)CrO_x/Al_2O_3 (b) catalysts at 873 K. Propene selectivity (○) and yield (δ). Solid symbols: reaction in He; open symbols: reaction in wet He. Reaction conditions: $C_3H_8/CO_2(He) = 1/7$ (molar ratio); total flow rate = 30 ml/min; catalyst weight = 0.5 g.

effect could be also responsible for low activity of the CrO_x/Al_2O_3 catalyst in the dehydrogenation of propane with CO_2.

3.3. *Effect of chromium content*

Table 1 lists the propane conversion and hydrocarbons selectivity for the CrO_x/Al_2O_3 and CrO_x/SiO_2 catalysts with chromium content 0.7, 3.4 and 13.7 wt%. In addition to propene, the by-products attributed to cracking, such as ethene, ethane and methane were fund in the product flow.

The effect of the chromium loading level (0.7–20.1 wt% of Cr) on the poisoning/promoting effect of CO_2, measured as the ratio of yield in He to the yield in CO_2 (Y_{He}/Y_{CO_2}) is shown in figure 5.

Over the CrO_x/SiO_2 catalyst with increase of chromium loading the ratio Y_{He}/Y_{CO_2} increased whereas over the CrO_x/Al_2O_3 catalyst with increase in the loading level the poisoning effect of CO_2 decreased.

4. Conclusion

The results obtained prove that the nature of support strongly influences on the effect of CO_2 in the dehydrogenation of propane. The promoting effect of CO_2 on propene yield was observed on the CrO_x/SiO_2 catalyst, while on the CrO_x/Al_2O_3 catalyst, carbon dioxide did not promote dehydrogenation. It seems that CO_2 and/or the steam formed during the dehydrogenation with CO_2 change the acidity/basicity of the CrO_x/Al_2O_3 catalyst.

Acknowledgment

This research was supported in part by the Polish State Committee for Scientific Research (KBN), under Project No. PB-1089/TO9/2003/24.

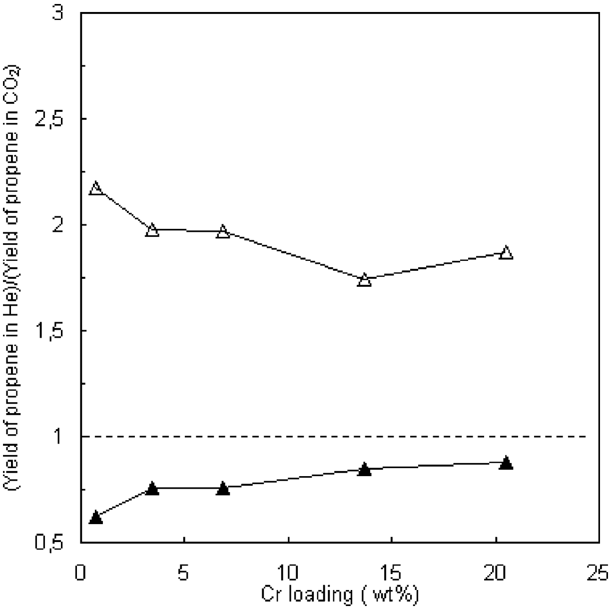

Figure 5. The ratio of propene yield in He to that in CO_2 as a function of Cr loading. Open symbols: over CrO_x/Al_2O_3 catalyst; solid symbols: over CrO_x/SiO_2.

References

[1] S. Wang, K. Murata, T. Hayakawa, S. Hamakowa and K. Suzuki, Appl. Catal. A 196 (2000) 1.
[2] R. Valenzuela, G. Buenos, V. Corberán, Y. Xu and Ch. Chen, Catal. Today 61 (2000) 43.
[3] N. Mimura, I. Takahara, M. Inaba, M. Okamoto and K. Murata, Catal. Commun. 3 (2002) 257.
[4] O. Krylov, A. Mamedov and S. Mirzabekova, Ind. Eng. Chem. Res. 34 (1995) 474.
[5] L. Xu, J. Liu, H. Yang, Y. Xu, Q. Wang and L. Lin, Catal. Lett. 62 (1999) 185.
[6] I. Takahara, W. Chang, N. Mimura and M. Saito, Catal. Today 45 (1998) 55.
[7] P. Michorczyk and J. Ogonowski, Appl. Catal. A 251 (2003) 425.
[8] K. Takehira, Y. Ohishi, T. Shishido, T. Kawabata, K. Takaki, Q. Zhang and Y. Wang, J. Catal. 224 (2004) 404.

Table 1

The dehydrogenation of propane to propene over CrO_x/SiO_2 and CrO_x/Al_2O_3 catalysts with Cr content between 0.7 and 13.7 at 873 K.[a]

Catalyst	Cr content (wt%)	Conversion (%)		Selectivity (%)			
		C_3H_8	CO_2	C_3H_6	C_2H_6	C_2H_4	CH_4
$(0.7)CrO_x/SiO_2$[b]	0.7	19.3	1.2	92.1	0.7	4.5	2.7
$(3.4)CrO_x/SiO_2$[c]	3.4	20.7	–	92.0	0.4	4.6	3.0
$(3.4)CrO_x/SiO_2$[b]	3.4	27.7	3.2	90.8	1.5	4.5	3.2
$(13.7)CrO_x/SiO_2$[b]	13.7	21.5	4.7	90.6	0.8	4.5	4.2
$(0.7)CrO_x/Al_2O_3$[b]	0.7	14.3	1.7	84.1	0.7	7.0	8.1
$(3.4)CrO_x/Al_2O_3$[c]	3.4	50.8	–	93.4	1.8	1.7	3.1
$(3.4)CrO_x/Al_2O_3$[b]	3.4	29.7	5.5	80.5	1.2	8.2	10.1
$(13.7)CrO_x/Al_2O_3$[b]	13.7	41.9	7.0	79.6	1.0	5.1	14.3

[a] Reaction conditions: 0.5 g of catalysts, total flow rate 30 ml/min, $CO_2:C_3H_8 = 7:1$, reaction time 0.2 h.
[b] Reaction in CO_2.
[c] Reaction in He.

[9] K. Nakagawa, Ch. Kajita, N. Ikenaga, M. Nishitani-Gamo, T. Ando and T. Suzuki, Catal. Today 84 (2003) 149.

[10] H. Shimada, T. Akazawa, N. Ikenaga and T. Suzuki, Appl. Catal. A 168 (1998) 243.

[11] M. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga and T. Suzuki, Appl. Catal. A 121 (1995) 125.

[12] N. Mimura and M. Saito, Catal. Today 55 (2000) 173.

[13] J. Park, J. Noh, J. Chang and S. Park, Catal. Lett. 65 (2000) 75.

[14] A. Sun, Z. Qin and J. Wang, Appl. Catal. A 234 (2002) 179.

[15] Y. Sakurai, T. Suzaki, K. Nakagawa, N. Ikenaga, H. Aota and T. Suzuki, J. Catal 209 (2002) 16.

[16] K. Nakagawa, Ch. Kajita, Y. Ide, K. Okamura, N. Ikenaga, M. Nishitani-Gamo, T. Ando, T. Kobayashi and T. Suzuki, J. Catal. 203 (2001) 87.

[17] S. Wang, K. Murata, T. Hayakawa, S. Hamakowa and fK. Suzuki, Appl. Catal. A 196 (2000) 1.

[18] C. Morterra and G. Magnacca, Catal. Today 27 (1996) 497.

[19] H. Knozinger and P. Ratnasamy, Catal. Rev. Sci. Eng. 17 (1978) 31.