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Dehydrogenation of propane in the presence and absence of CO_2 over β-Ga_2O_3 supported chromium oxide catalysts

P. Michorczyk,[a],* K. Góra-Marek,[b] and J. Ogonowski[a]

[a]Institute of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland
[b]Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

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The dehydrogenation of propane to propene in the presence and absence of CO_2 over β-Ga_2O_3 supported chromium oxide catalysts has been studied. The effect of chromium content and feed composition on the dehydrogenation of propane has been investigated. It has been found that deposition of chromium oxide enhances the dehydrogenation activity and resistance to coke deposition. Moreover, it has been shown that CO_2 promotes the dehydrogenation of propane above 848 K. At that temperature in the presence of CO_2 both the yield of propene and conversion of propane were higher than in the inert gas atmosphere.

KEY WORDS: gallium and chromium oxides; dehydrogenation with CO_2; propene.

1. Introduction

The dehydrogenation of propane in the presence of CO_2 has been recently studied as an alternative way for obtaining propene with simultaneous conversion of CO_2 to CO, which is more useful raw material for a number of chemical processes. Several different bulk and supported oxide catalysts have been tested in this reaction. Different oxides (Ga, Cr, V, Fe, Zr and Zn) were used as active components [1–10] and potassium oxide was introduced as promoter [7,8]. Inorganic oxides (SiO_2, Al_2O_3) [1–3], mesoporous materials (MCM-41) [4] and carbonaceous materials (diamond, active carbon) [1,5] were used as the supports. Among them, chromium and gallium oxides based materials seem to be promising catalysts due to their high dehydrogenation activity and selectivity. These observations led us to conclusion that it is worthwhile to extend catalytic studies giving more attention to the catalysts containing both of the latter mentioned materials. In this communication, we report the results obtained in the dehydrogenation of propane in the presence and absence of CO_2 over β-Ga_2O_3 supported chromium oxide catalysts. The β polymorph of Ga_2O_3 was taken as the active support due to its high dehydrogenation activity, thermal stability, and relatively high specific surface area.

2. Experimental

2.1. Preparation and characterization of catalysts

Bulk β-Ga_2O_3 was obtained by thermal decomposition of $Ga(NO_3)_3 \cdot 8H_2O$ at 923 K for 6 h in air atmosphere. The chromium containing catalysts were prepared by impregnation technique from an aqueous solution of $Cr(NO_3)_3$. The chromium content in the catalysts was regulated by varying the concentration of chromium salt in the impregnation solutions. The solutions were mixed with β-Ga_2O_3 and evaporation under constant stirring. After the impregnation, the catalysts were dried at 423 K for 2 h and calcined at 923 K for 3 h in air atmosphere. The notation such $Cr(3.4)O/Ga_2O_3$ was employed for the chromium oxide-based catalyst supported on β-Ga_2O_3, with the value in parenthesis indicating the Cr content (wt%).

Specific surface areas of the obtained materials were determined by the BET method using Ar as adsorbate at 77 K.

The number and strength of Lewis acid sites were determined by adsorption of pyridine after activation of the samples in vacuum (10^{-6} mbar) at 723 K for 1 h. An excess of pyridine was adsorbed at 440 K and next the physisorbed phase has been removed by evacuation at the same temperature. The adsorbed pyridine was subsequently desorbed at 570 K, and the ratios A_{570}/A_{440} (where A_{440} and A_{570} are the intensities of IR bands of pyridine bonded to Lewis sites after the evacuation at 440 K and 570 K, respectively) were taken as the measure of the acid strength of the Lewis acid sites. The spectra were recorded on a Bruker Equinox 55 IR spectrometer with resolution of 2 cm^{-1} and were normalized to the 10 mg of sample.

2.2. Catalytic tests

The catalytic tests were carried out in a flow-type quartz reactor packed with 500 mg of catalyst (grain size

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

0.2–0.3 mm). The feed was a mixture of C_3H_8:He(CO_2) at the molar ratio 1:7. The total flow rate of the feed was 30 ml/min. The reactants and products collected during 10 min on stream were analyzed using two gas chromatographs. One of them was equipped with a column packed with Porapak Q and a flame ionization detector (for hydrocarbon analyses). The other GC was equipped with a column packed with Carboxen 1000 and, a thermal conductivity detector (for H_2, CO and CO_2 analyses).

Coke amounts were estimated from amounts of CO_2 and CO evolved during oxidative regeneration of the catalysts at 873 K.

3. Results and discussion

3.1. *Effect of chromium content*

Table 1 lists the average conversion of propane and the distribution of products in the dehydrogenation of propane as a function of chromium content.

In addition to propene, products attributed to cracking such, as ethene, ethane and methane as well as products of deep oxidation of propane, carbon oxides (<0.02% not shown in table 1), were detected in the gaseous products flow. The results presented in the table confirm high dehydrogenation activity of bulk β-Ga_2O_3 reported previously [9,10]. It is clear that the deposition of chromium oxide on the surface of β-Ga_2O_3 enhances the average yield of propene. With the increase of Cr content up to 6.8 wt%, the average yield of propene gradually increases, and then declines, which can be caused partially by the lower surface area of the catalyst with the highest Cr content. The average selectivity to products varies with Cr content. In the case of propene the selectivity changes between 84% and 88%, whereas the average selectivity to coke gradually decreases with increase of Cr content.

Based on the analogy between Ga_2O_3 and Al_2O_3, we suggest that deposition of chromium oxide on the surface of β-Ga_2O_3 generates surface Cr^{3+} species highly active in the dehydrogenation process. Such species have been previously proposed as the active sites for the dehydrogenation of light alkanes in the case of CrO_x/Al_2O_3 [11,12]. Moreover, the deposition of Cr decreases the strength of Lewis acid sites on the surface of the catalyst, which was confirmed by quantitative IR studies of pyridine adsorption (figure 1).

3.2. *Effect of CO_2*

The effect of reaction temperature on the dehydrogenation of propane in the presence and absence of CO_2 is shown in figure 2. The average conversion of propane in the presence of CO_2 is lower at temperature below 823 K, however, the conversion increases steeply with temperature and exceeds the value obtained in He atmosphere above 848 K.

In inert atmosphere, the average conversion of propane gradually increases up to 848 K and then rises insignificantly with the further increase of the reaction temperature. In the presence of CO_2 the average yield of propene increments in the whole temperature range, while in the absence of CO_2 it increases linearly up to 848 K and then declined. The average selectivity of propene both in the presence and absence of CO_2 decreases with temperature. However, at higher

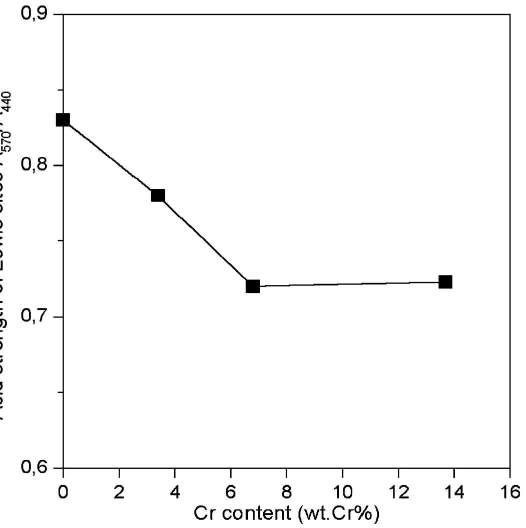

Figure 1. The strength of Lewis acid sites in β-Ga_2O_3 supported chromium oxide catalysts as a function of chromium content.

Table 1

Dehydrogenation of propane over β-Ga_2O_3 supported chromium oxide catalysts at 823 K[a]

Catalyst	Surface area (m^2/g)	Conversion (%) C_3H_8	Yield (%) C_3H_6	Selectivity (%)				
				C_3H_6	C_2H_6	C_2H_4	CH_4	Coke[b]
β-Ga_2O_3	39	25.0	21.6	86.3	1.1	1.6	1.4	9.5
Cr(3.4)O/Ga_2O_3	35	31.5	26.2	83.4	2.3	1.7	3.4	9.2
Cr(6.8)O/Ga_2O_3	36	33.7	28.5	84.7	1.6	1.3	3.5	8.9
Cr(13.7)O/Ga_2O_3	29	30.5	26.8	87.6	1.0	1.3	3.0	7.0

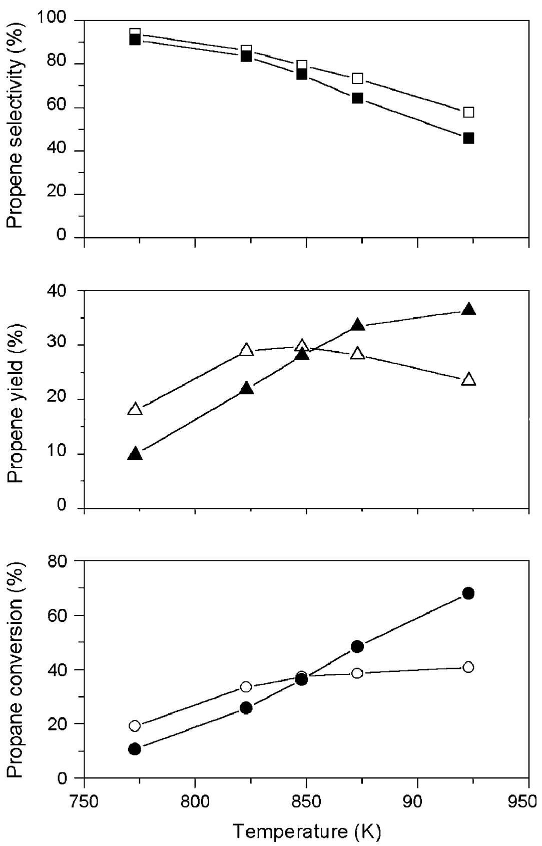

Figure 2. The effect of reaction temperature on averages propane conversion (○), propene yield (Δ) and selectivity (□) over Cr(6.8)O/Ga_2O_3 catalyst in the presence (solid symbols) and absence (open symbols) of CO_2.

temperatures the decrease was more significant in the presence of CO_2.

The insignificant effect of the reaction temperature on the average conversion of propane observed in He atmosphere is probably related to the deactivation of the catalyst by coke deposition. It is known that coke formation is accelerated at high temperatures and in the absence of gasification agents like H_2O or CO_2. Thus, increasing the reaction temperature enhances the deactivation rate and consequently the average conversion of propane increases slightly above 848 K. On the other hand, such effect is not observed in the presence of CO_2. This observation and the fact that at 848 K (where similar average conversion of propane are achieved) the amount of coke deposited during the dehydrogenation of propane in the presence of CO_2 was 40% lower than that in He, clearly show that CO_2 suppresses partially the coke deposition. There are two explanations for this phenomenon: (i) facilitation of desorption of propene by CO_2, which suppresses further deep dehydrogenation resulting in coke formation; (ii) direct reaction of CO_2 with coke (1).

$$C_{(coke)} + CO_2 = 2CO. \qquad (1)$$

The gasification effect of CO_2 seems to confirm the calculations of the CO/C_3H_6 molar ratios in the process in the presence and absence of CO_2 (figure 3). In CO_2 atmosphere, the molar ratio of CO/C_3H_6 strongly increases with temperature from 0.7 at 773 K to 3.6 at 923 K.

On the other hand, the molar ratio of H_2/C_3H_6 in the presence of CO_2 is lower than that in He, and is below 1.0 at 773–873 K (figure 3). Such results suggest that the reverse water-gas shift reaction may proceed simultaneously with dehydrogenation of propane.

$$H_2 + CO_2 = CO + H_2O. \qquad (2)$$

Both of the reactions are probably responsible for the promoting effect of CO_2 observed above 848 K.

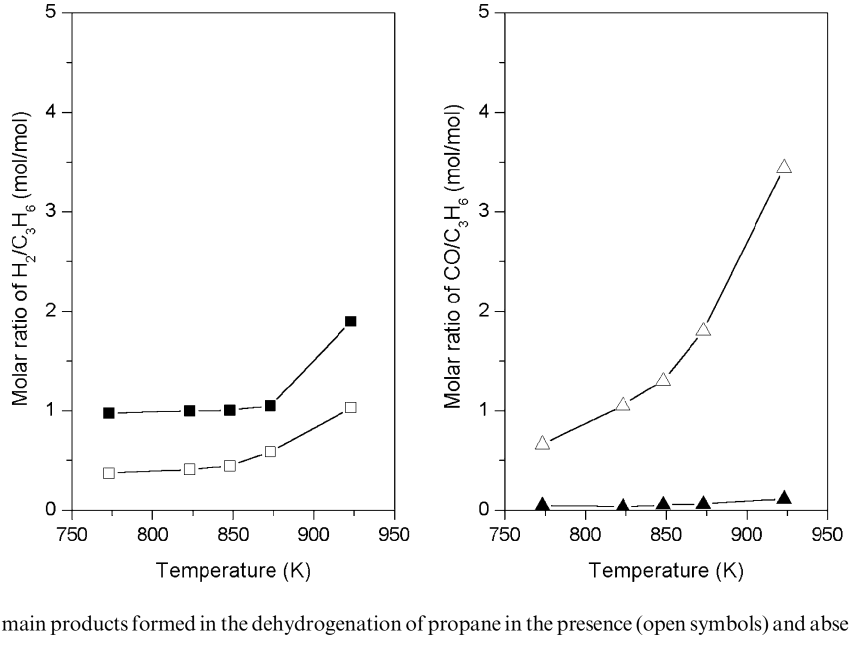

Figure 3. Molar ratio of main products formed in the dehydrogenation of propane in the presence (open symbols) and absence (solid symbols) of CO_2.

4. Conclusion

The presented results lead to the following conclusions:

- β-Ga_2O_3 supported chromium oxide materials are active and selective catalysts for dehydrogenation of propane. The high catalytic activity of these catalysts arises from the dehydrogenating properties of both gallium and chromium oxides.
- Deposition of chromium oxide on the surface of β-Ga_2O_3 enhances the resistance to coke deposition, which is caused probably by decreasing the surface acidity.
- CO_2 enhances the average yield of propene above 848 K and partially suppresses the catalyst deactivation by coke deposition.

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