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Propane Chlorination over Ruthenium Oxychloride Catalysts

N. V. Testova[a, *], **A. S. Shalygin**[a, b], **G. M. Maksimov**[a], **E. A. Paukshtis**[a, b, c], **and V. N. Parmon**[a, b, c]
[a] Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
[b] Novosibirsk State University, Novosibirsk, 630090 Russia
[c] Tomsk State University, Tomsk, 634050 Russia
*e-mail: testova@catalysis.ru

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Abstract—The gas-phase chlorination of propane over different catalysts, including those containing ruthenium oxychlorides as the active component, has been investigated. The propylene and chlorine-containing product formation selectivities in propane chlorination at 150–450°C in a fixed-bed flow reactor have been determined.

Keywords: propane chlorination, propane dehydrogenation, ruthenium catalysts

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Propylene is among the most important large-scale products of the processing of hydrocarbons derived from natural gas and petroleum. It is isolated from petroleum cracking and pyrolysis products and is also obtained by the catalytic thermal dehydrogenation of propane. Propane dehydrogenation as an industrial propylene production method has been used since 1990. At present, a number of commercial-scale processes producing propylene by catalytic propane dehydrogenation are known in the world market, the base ones being Catofin, Oleflex, STAR, and Snamprogetti/Yarsintez [1]. The direct catalytic dehydrogenation of propane is carried out in the presence of metal oxides, namely, Cr_2O_3, MoO_3, V_2O_5, TiO_2, and GeO_2. The most efficient catalyst is Cr_2O_3 supported on γ-Al_2O_3 [2–4]. The industrial processes are conducted at ~550–600°C. Under these conditions, with the chromium oxide catalyst the propylene selectivity can be as high as 82–87%, but the propane conversion is only 48–65% [1]. At high temperatures, propane dehydration is typically accompanied by intensive coke deposition. In addition, the by-products of this process contain methylacetylene, which poisons the polymerization catalysts used in the subsequent production of polypropylene [5]. The main problem in these methods of propylene production from propane is that it is necessary to conduct the process at a high temperature in order to raise the equilibrium concentration of the olefin, since the dehydrogenation reaction is endothermic:

$$C_3H_8 \rightarrow C_3H_6 + H_2, \quad \Delta_r H^\circ_{298} = 124.26 \text{ kJ/mol}.$$

This problem is being solved by developing oxidative dehydrogenation processes involving various catalysts [6, 7]. The propylene yield in oxidative propane dehydrogenation does not exceed 35% even with the best catalysts. A >40% propylene yield was attained with a Mg/Dy/Li/Cl/O mixed-oxide catalyst [8]. A high selectivity (94–96%) at 200°C was achieved with a $PtH_3PMo_{12}O_{40}$ catalyst [9] at a conversion of 20.4%.

The oxidative dehydrogenation of propane with oxygen is an exothermic process:

$$C_3H_8 + 1/2O_2 \rightarrow C_3H_6 + H_2O,$$

$$\Delta_r H^\circ_{298} = -117.58 \text{ kJ/mol}.$$

This process is accompanied by total propane oxidation to carbon oxides,

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O,$$

$$\Delta_r H^\circ_{298} = -2044.04 \text{ kJ/mol},$$

which makes difficult its commercialization because of the necessity of heat utilization.

There have been attempts to carry out propane dehydrogenation using organochlorine compounds [10, 11], sulfur-containing compounds [12–14], nitrous oxide [15, 16], CO_2 [17], and halogens [18] as gentle oxidizers. Note that employing halogens in this process was suggested more than 50 years ago. There have been thermodynamic calculations on the oxidative dehydrogenation of hydrocarbons with different halogens [18]. According to these calculations, the thermodynamically most favorable oxidizer is molecular chlorine. It was suggested that the resulting HCl be oxidized with oxygen back to Cl_2 (Deacon reaction):

$$2HCl + 1/2O_2 \rightarrow Cl_2 + H_2O,$$

$$\Delta_r H^\circ_{298} = -57.24 \text{ kJ/mol}.$$

It is assumed that propane chlorination yields propyl monochlorides according to the reaction

$$C_3H_8 + Cl_2 \rightarrow C_3H_7Cl + HCl,$$

$$\Delta_r H^\circ_{298} = -133.36 \text{ kJ/mol},$$

which are fairly readily dehydrochlorinated to propylene:

$$C_3H_7Cl \rightarrow C_3H_6 + HCl, \quad \Delta_r H^\circ_{298} = 73.01 \text{ kJ/mol}.$$

The enthalpy of the overall reaction

$$C_3H_8 + Cl_2 \rightarrow 2HCl + C_3H_6,$$

$$\Delta_r H^\circ_{298} = -60.34 \text{ kJ/mol},$$

is only −60.34 kJ/mol, which mitigates the problem of utilizing the heat of reaction.

The necessity of utilizing hydrogen chloride and, accordingly, the necessity of designing a chlorine-balanced process were long a drawback of this olefin synthesis method. The resulting hydrogen chloride can be used in a number of processes, for example, acetylene hydrochlorination and ethylene oxychlorination.

Ruthenium-based catalysts approved themselves in many reactions involving chlorine, including the Deacon reaction [19–21] and methane and ethane oxychlorination [22]. It is likely that the high reactivity of the ruthenium compounds in reactions involving chlorine and organochlorine compounds is due to the fairly high chlorine affinity of ruthenium. This view is corroborated by the capacity of ruthenium(IV) ions to form various oxychlorides both in aqueous solution [23] and in the solid state. For example, it was hypothesized that the active site in the Deacon reaction over the RuO_2/TiO_2 catalyst is ruthenium oxychloride $RuO_{2-x}Cl_x$ [24].

Here, we report the activity and selectivity of a variety of HCl-resistant solid catalysts, including glass-fiber and ruthenium oxychloride–containing ones, in the reactions between propane and chlorine at 150–450°C.

EXPERIMENTAL

Catalyst Preparation

The Ru/TiO_2-1 catalyst(0.3 wt % Ru) was prepared by incipient-wetness impregnation of titanium dioxide (Degussa P-25, $S_{BET} = 57$ m^2/g, $V_{pore} = 0.36$ cm^3/g) with an aqueous hydrochloric acid solution of $K_4Cl_5RuORuCl_5$ (pH 1) at 90°C followed by drying at 110°C and calcination in air at 350°C for 2 h.

The Ru/TiO_2-2 catalyst (2.0 wt % Ru) was prepared by oxidizing Ru(III) to Ru(IV) with potassium perchlorate $KClO_4$. For this purpose, titanium dioxide was impregnated to incipient wetness with an aqueous $RuCl_3$ solution (55 g/L) and was dried in air at 60°C for 2 h. The resulting $RuCl_3/TiO_2$ sample was impregnated to incipient wetness with an aqueous solution containing $KClO_4$ (25 g/L) and KCl (16 g/L), washed with deionized water, and dried at 60°C for 2 h.

The Ru/TiO_2-3 catalyst (5.0 wt % Ru) was prepared by mechanically mixing the necessary amounts of $K_4Cl_5RuORuCl_5$ and TiO_2 until the formation of a uniform mass, which was then ground in a mortar for 1 h.

The specific surface area of all ruthenium catalysts was practically equal to that of the TiO_2 support (57 m^2/g).

The WO_3/TiO_2 (30% WO_3) catalyst with a specific surface area of 30 m^2/g was obtained by reacting aqueous solutions of the $H_4SiW_{12}O_{40} \cdot 6H_2O$ heteropoly acid (0.07 mol/L) and $TiCl_4$ (3 mol/L) followed by adding 25% aqueous NH_3 until pH 9 under stirring. The resulting paste was dried and was then calcined at 800°C for 6 h in air.

The glass-fiber catalysts ($S_{BET} \approx 1 \pm 0.5$ m^2/g) were prepared from glass cloths subjected to acid and thermal treatments followed by aluminum salt deposition. The starting materials were commercial glass cloths made from sodium silicate glass (80% SiO_2, 0.3–1.5% Al_2O_3, fiber diameter of 7–10 μm). In addition, the glass contained small amounts of calcium and iron. The cloth was leached with a 5.5% HNO_3 solution at 90°C for 60 min and was dried at 110°C. Aluminum sulfate was introduced from its aqueous solution by impregnating the leached glass fibers (GF) at 80°C. Next, the fibers were washed with deionized water to remove aluminum compounds weakly bound to the support, dried at 110°C, and calcined in air at 300°C. The resulting samples, designated GF-1 and GF-2, contained 1.8 and 0.5 wt % Al, respectively.

The amounts of aluminum and ruthenium in the catalysts were determined by inductively coupled plasma atomic emission spectroscopy on an Optima 4300 DV spectrometer (PerkinElmer, United States).

The reference samples were the porous carbon sorbent Sibunit (Institute of Hydrocarbons Processing, Siberian Branch, Russian Academy of Sciences, Russia) with $S_{BET} = 590$ m^2/g according to argon adsorption data and $V_{pore} = 0.860$ cm^3/g and quartz sand obtained by grinding quartz glass.

Catalytic Tests

Catalytic experiments were carried out at atmospheric pressure in a tubular flow reactor (quartz tube 200 mm in length and 7 mm in inner diameter) with a fixed catalyst bed. The reactor was heated in a tubular electric furnace to 150–450°C. The weight of the catalyst placed in the reactor was 1.0 g. Glass-fiber samples, which were loose balls of fibers, were compacted to the minimum possible volume after being placed in the reactor. The quartz sand and Sibunit samples were powders (0.25–0.50 mm size fraction).

Propane and argon (99.9% pure) were delivered from cylinders using a gas flow controller. Chlorine, obtained in an electrolyzer, was fed into the reactor as a chlorine–argon mixture. All pipelines and spaces intended for chlorine were protected against light. The amount of chlorine obtained was determined with an accuracy of ±2% from the electrochemical equivalent of chlorine and the amount of electricity that had been passed through the electrolyte (saturated sodium chloride solution). Propane and chlorine were fed at a rate of 200 and 50 (100) h^{-1}, respectively; argon, at a rate of 400 h^{-1}. The molar ratio of the gases in the reaction mixture was $C_3H_8 : Cl_2 : Ar = 2 : 0.5\ (1) : 4$. The total GHSV of the gas mixture fed to the catalyst bed was 650–700 h^{-1}. The gaseous products were sampled at the reactor outlet. The reaction products were analyzed on a Tsvet-570 chromatograph (Tsvet, Russia using a special-purpose capillary column (20 m × 0.32 mm) with DVB-PLOT as the stationary phase and a flame-ionization detector.

The propane conversion (X) and the ith product formation selectivity (S_i) were calculated via the formulas

$$X = 100(C_{\text{in}} - C_{\text{out}})/C_{\text{in}}, \tag{1}$$

$$S_i = 100C_i/(C_{\text{in}} - C_{\text{out}}), \tag{2}$$

where C_{in} and C_{out} are the propane concentrations in the gas stream at the reactor inlet and outlet, respectively, and C_i is the concentration of the ith product at the reactor outlet. If necessary, a correction for the change in the volume of the reaction products was applied.

In the gas-phase chlorination of propane,

$$C_3H_8 + Cl_2 \rightarrow C_3H_7Cl + HCl$$

only one-half of the chlorine atoms are involved in the formation of the chlorinated hydrocarbon, while the others turn into hydrogen chloride. Therefore, if the reaction is performed using excess hydrocarbon at $C_3H_8/Cl_2 = 4$ ($C_3H_8/Cl_2 = 2$ in some runs), then, even if the entire chlorine is consumed and only the monochlorinated hydrocarbon is formed, the propane conversion will not exceed 25% (and 50%, respectively) and will be still lower if the reaction yields more deeply chlorinated compounds.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of the propane conversion and the propylene, 1- and 2-choloropropane, and 1,2-dichloropropane formation selectivities for each of the catalysts examined. Below 300°C, the propane conversion for all catalysts is insignificant. The major product forming over Sibunit is 2-chloropropane. Quartz sand shows approximately equal 1- and 2-chloropropane formation selectivities. The products forming over the glass fibers (GF-1 and GF-2) and WO_3/TiO_2 are dominated by 1-chloropropane. In the presence of Ru/TiO_2-1, the reaction in this temperature range yields dichloropropane and a minor amount of 1-chloropropane.

Above 300°C, for all catalysts an increase in the propane conversion is accompanied by propylene formation and by the disappearance of 2-chloropropane. As the temperature is raised to 400°C, the 1-chloropropane formation selectivity for quartz sand and Sibunit remains practically invariable, while in the case of GF-1 and WO_3/TiO_2 1-chloropropane disappears as well, but at a lower rate than 2-chloropropane. The dichloropropane formation selectivity above 300°C is low. The GF-2 sample (with a lower aluminum content) is characterized by a lower propylene selectivity. This is likely due to the fact that monochloropropane dehydrochlorination over this catalyst occurs at a lower rate because the catalyst is less acidic than GF-1 [25].

We believe that, in the case of quartz sand and Sibunit, propylene formation taking place with an increasing temperature is mainly due to 1-chloropropane dehydrochlorination. With the glass-fiber catalysts, the increase in the propylene formation selectivity as a result of an increasing temperature is accompanied by a decrease in both the 1- and 2-chloropropane selectivities. A similar increase in the olefin concentration caused by an increasing temperature was earlier observed in ethane chlorination [26, 27] and propylene oxychlorination [28].

The products forming over the Ru/TiO_2-1 catalyst at lower temperatures are dominated by 1,2-dichloropropane. The dehydrochlorination of this compounds van yield methyacetylene or monochloropropylene; however, the proportions of these products at high temperatures are negligibly small. This fact suggests that, in the case of the Ru/TiO_2-1 catalyst, propylene can result not only from consecutive chlorination and dehydrochlorination reactions but also from the direct oxidative dehydrogenation of propane by molecular chlorine, a reaction similar to the oxidative dehydrogenation of propane with oxygen [29]. As the temperature is raised, the propane conversion increases and, since the entire chlorine is converted even at low temperatures, the propylene formation selectivity does not decrease.

The temperature dependences of the propylene formation selectivity for the catalysts examined are plotted in Fig. 2. Clearly, the selectivity is determined by the nature of the catalyst. The highest selectivity (96.7%) is observed for the Ru/TiO_2-1 catalyst above 400°C.

Raising the chlorine concentration in the feed by a factor of 2 (to $C_3H_8/Cl_2 = 2$) increases the propane conversion to 50% and causes the formation of considerable amounts of chloropropylenes. The table lists propane conversion, propylene selectivity and yield, and chlorinated product selectivity data for the ruthenium-containing catalysts in propane chlorination at 300°C and above for the $C_3H_8 : Cl_2 : Ar = 2 : 1 : 4$ molar ratios in the feed. Under these conditions, the propylene yield reaches 45%, while the maximum possible yield is 50%.

A comparison of the results obtained for the ruthenium-containing samples demonstrates that, with Ru/TiO_2-1 prepared by impregnation, the propylene formation selectivity at 400°C reaches 94.6% and is well above the propylene formation selectivity observed for the mechanical mixture of the initial components in Ru/TiO_2-3 (78.7%) at similar propylene conversion values.

For the Ru/TiO_2-2 sample, which was prepared by ruthenium oxychloride formation during the impreg-

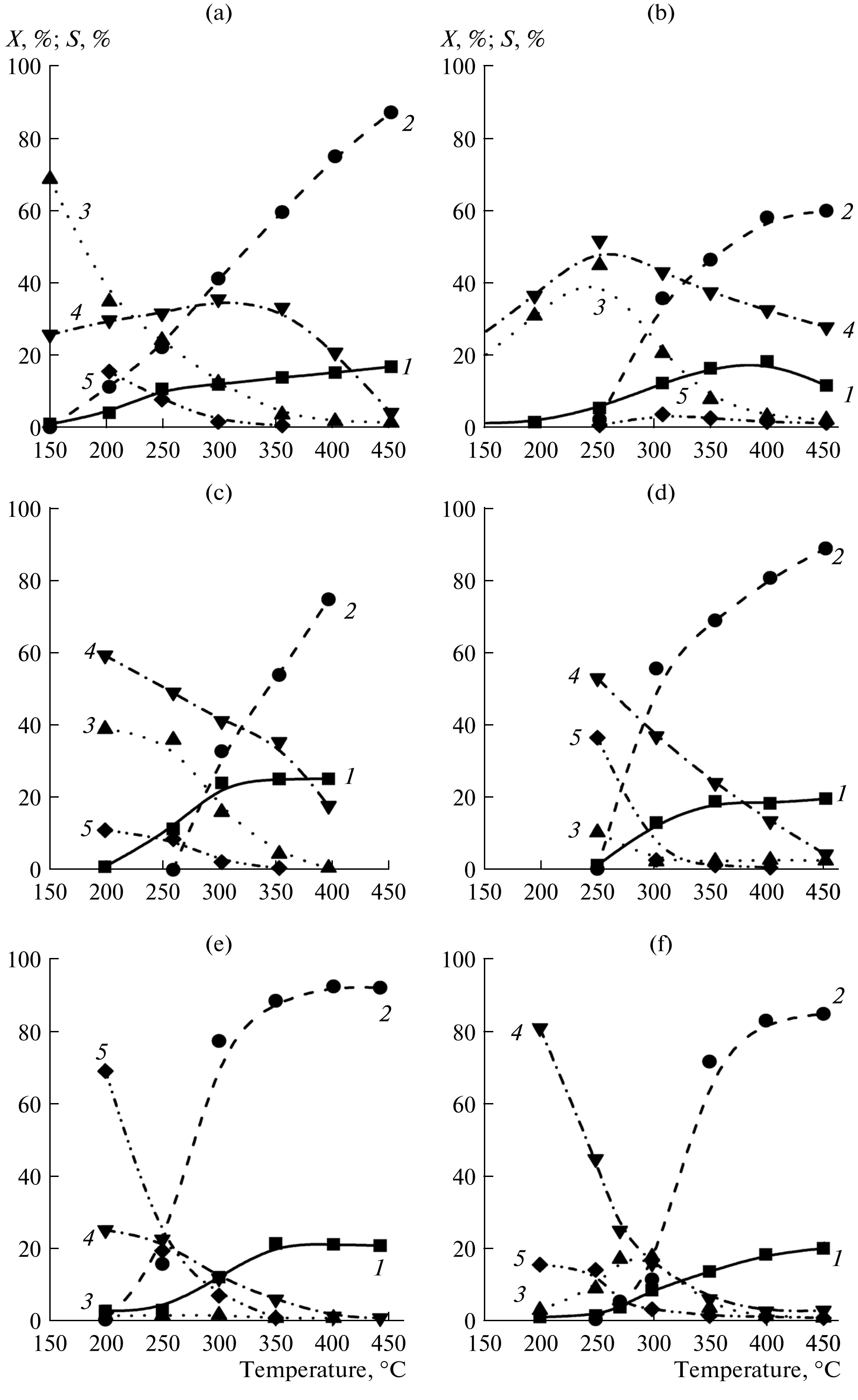

Fig. 1. Temperature dependences of (*1*) propane conversion, (*2*) propylene selectivity, (*3*) 2-chloropropane selectivity, (*4*) 1-chloropropane selectivity, and (*5*) 1,2-dichloropropane selectivity in propane chlorination over various catalysts: (a) Sibunit, (b) quartz, (c) GF-2, (d) GF-1, (e) Ru/TiO_2-1, and (f) WO_3/TiO_2. The molar ratio of the components in the feed is $C_3H_8 : Cl_2 : Ar = 2 : 0.5 : 4$.

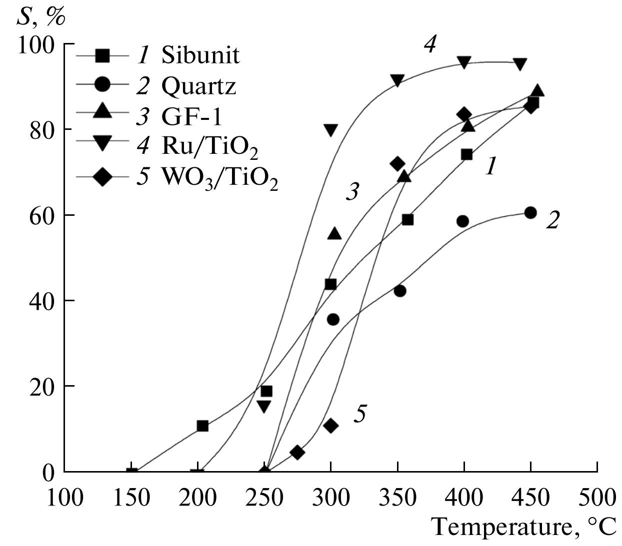

Fig. 2. Temperature dependences of the propylene formation selectivity in propane chlorination over various catalysts. The molar ratio of the components in the feed is $C_3H_8 : Cl_2 : Ar = 2 : 0.5 : 4$.

nation of the support with a $RuCl_3$ solution followed by Ru(III) oxidation to Ru(IV), after the temperature was raised from 150 to 300°C only a small amount of 1-chloropropane was detected at the reactor outlet. At 350°C, the propane conversion was substantially higher, having reached 50%, and the propylene selectivity was 88.3%. Further elevating the reactor temperature to 400°C caused a dramatic decrease in the propane conversion to 3.5%. Upon the subsequent lowering of the temperature to 350°C, the catalyst was completely deactivated. This was possibly caused by a change in the state of the catalyst, likely by the decomposition of zirconium oxychlorides. The other ruthenium catalysts did not undergo deactivation over at least 10–15 h.

The increased chloropropylene formation selectivity in the intermediate temperature range (up to 300°C) was observed only for the ruthenium- and tungsten-containing catalysts (Fig. 1). With the quartz sand, Sibunit, and glass fibers, the total chloropropylenes selectivity was no higher than 3–5%.

Thus, propane dehydrogenation with molecular chlorine over the ruthenium catalyst affords propylene at a selectivity of >95%. In addition, this catalytic process, unlike thermal dehydrogenation and oxidative dehydrogenation involving oxygen, can be carried out at a lower temperature (400°C instead of 600°C). This significantly reduces the probability of product cracking and rules out methylacetylene formation.

At 400°C, the propane conversion value is determined by the complete consumption of chlorine and depends on the C_3H_8/Cl_2 ratio in the feed. As the chlorine concentration in the feed is decreased, the propylene selectivity increases and the amount of chlorine-containing by-products decreases significantly.

CONCLUSIONS

The results of this study of propane chlorination over solid catalysts indicate the possibility of attaining a very high (>95%) propylene formation selectivity at a propane conversion of about 50%. This is observed with the ruthenium–titanium catalyst at 400°C and GHSV = 650 h^{-1}. These performance characteristics far exceed the corresponding parameters achieved in the oxidative dehydrogenation of propane. In addi-

Temperature dependences of the propane conversion, product selectivities, and propylene yield for propane chlorination over Ru/TiO_2 catalysts at component molar ratios of $C_3H_8 : Cl_2 : Ar = 2 : 1 : 4$ in the feed

Catalyst (preparation method)	Ru, %	T, °C	X, %	S, %				$\eta_{C_3H_6}$**, %
				C_3H_7Cl	$C_3H_6Cl_2$	C_3H_6	C_3H_5Cl*	
Ru/TiO_2-1 (impregnation)	0.3	300	25.3	19.9	9.2	34.5	34.2	8.7
		350	50.8	12.3	–	81.2	5.1	47.2
		400	47.6	1.1	–	94.6	3.2	45.0
Ru/TiO_2-2 (impregnation)	2.0	350	50.6	3.1	–	88.3	7.8	44.6
		400	3.5	14.6	–	64.3	6.8	2.2
		350***	0.3	70.7	–	–	21.4	0
Ru/TiO_2-3 (mechanical mixing)	5.0	300	13.0	29.7	18.0	20.6	28.9	2.7
		350	22.6	20.1	1.0	70.9	7.0	16.0
		400	46.3	17.9	0.1	78.7	2.5	36.4

* Three peaks in the chromatogram of the gas sample were assigned to chloropropylenes (on the basis of mass spectrometric data) without specifying their structure, because their mass spectra are practically indistinguishable.

** Propylene yield without dilution with argon taken into account.

*** After being heated to 400°C, the sample in the reactor was cooled to 350°C tion, use of high-temperature propane chlorination as a step in propylene production allows the by-products of the process to be easily removed.

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