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## CATALYSIS

# Gas-Phase Oxidation of Propylene into Acetone on a $V_2O_5/TiO_2$ Catalyst: Effect of Pressure and Role of Water

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**Abstract**—Positive effect of raising the pressure and water content in the reaction mixture in the oxidative conversion of propylene into acetone on a $V_2O_5/TiO_2$ catalyst was observed. It was shown that the reaction occurs via intermediate formation of isopropanol, which id produced in situ as a result of the acid-catalyzed hydration of propylene and, under certain conditions, may be the main product.

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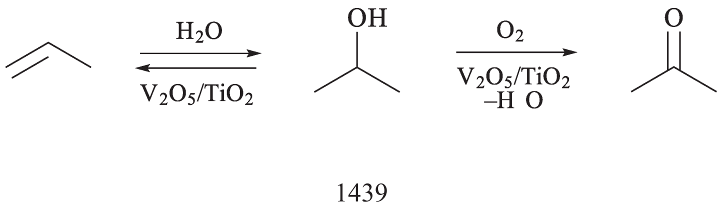
More than one fourth of the basic products of the chemical industry are obtained with the use of catalytic oxidative processes, the share of which is steadily increasing. Molecular oxygen (air) is the most readily available, inexpensive, and ecologically safe chemical oxidizing agent, and oxidation catalysts are most-in-demand and surpass in application even polymerization catalysts. The oxidative conversion of propylene into acetone is of particular interest as an atomically efficient way to obtain this compound and markedly surpasses in this regard the conventional cumene method [1]. It is known that propylene reacts with molecular oxygen in a flow-through gas-phase mode on supported heteropolyacid catalysts under atmospheric pressure and temperature of 150 to 190°C [2, 3]. However, the achievable selectivity of the reaction toward acetone (84%) at a propylene conversion of less than 18% is of no practical significance because of the low output capacity of the process. A more successful case was the application of a supported oxide vanadium catalyst $V_2O_5/TiO_2$. This provides under the optimal conditions a selectivity of 94% toward acetone at a propylene conversion of 32% [4]. It has also been shown that, as the content of water in the reaction mixture is raised to ~20%, the yield of acetone grows and the decrease in the catalytic activity with the process duration is slower [5]. The positive effect of water was attributed to its direct involvement in the hydration of propylene to give isopropanol, which is rapidly oxidized to acetone in the second stage of the reaction (see scheme). Indeed, isopropanol was found among the reaction products in trace amounts [4, 5]. It should be noted in this context that $V_2O_5/TiO_2$ is not only an efficient oxidation catalyst [6, 7], but can also be regarded as a solid acid [8]. It is also known that the acid-catalyzed hydration of propylene is a reversible reaction in the inert atmosphere and a shift of the reaction equilibrium toward formation of isopropanol is promoted by an increase in pressure [9].

The scheme of the supposed sequence of stages in the oxidative conversion of propylene into acetone is as follows



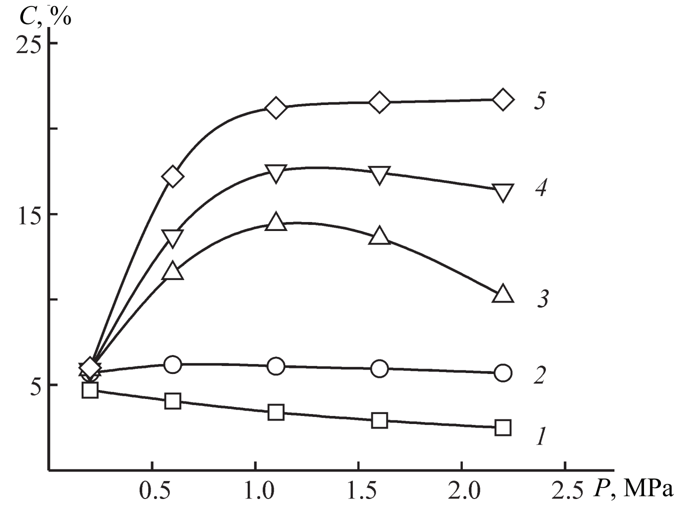


**Fig. 1.** Conversion C of propylene vs. the gas mixture pressure *P*. Starting mixture $C_3H_6/O_2/H_2O/N_2$ in ratio of 6 : 4 : 10 : 80 vol %. *R* (°C): (*1*) 179, (*2*) 180, (*3*) 190, (*4*) 205, (*5*) 215.

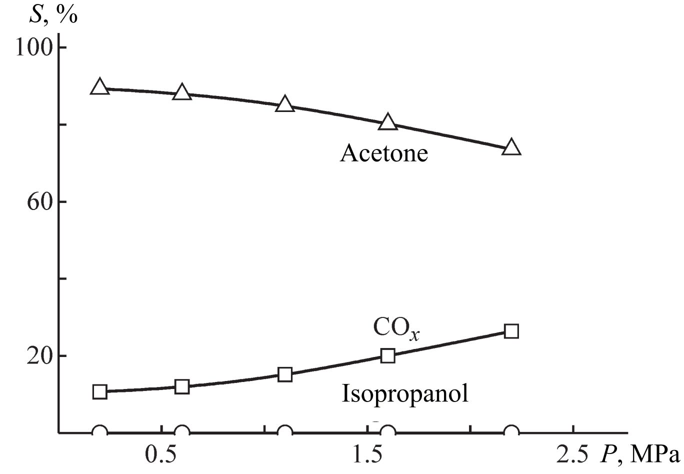


**Fig. 2.** Selectivity *S* toward reaction products vs. pressure *P*. $T = 190°C$, starting mixture $C_3H_6/O_2/H_2O/N_2$ in ratio of 6 : 4 : 10 : 80 vol %.

It would be reasonable to assume that the intensification of the first stage of the reaction by raising the pressure and optimizing the relative amounts of propylene and water will, on the whole, positively affect the oxidative conversion of propylene into acetone. In reversible processes, such as hydration of alkenes, raising the pressure can shift the chemical equilibrium in accordance with the Le Chatelier principle and accelerate the successive reactions, which are exceedingly slow at low pressures. Another important consequence of an increase in pressure is that the concentration of gaseous reagents grows, which favors a faster rate of their interaction and, on the whole, makes higher the specific output capacity of a catalyst.

The goal of our study was to evaluate the influence exerted by the pressure and the reaction mixture composition on the course of the reaction of propylene with oxygen and water on the $V_2O_5/TiO_2$ catalyst.

## EXPERIMENTAL

A sample with 20% $V_2O_5/TiO_2$ ($S_{BET} = 111$ m$^2$ g$^{-1}$) was produced by impregnation of $TiO_2$ (anatase, Alfa Aesar, Germany, specific surface area 350 m$^2$ g$^{-1}$) with an aqueous solution of vanadyl oxalate, prepared from $V_2O_5$ (>99.6%, Reakhim, Russia) and oxalic acid (>97%, Reakhim, Russia), followed by drying in air at 110°C for 24 h and calcination in a flow of air (50 mL min–1) for 4 h at 400°C. The resulting catalyst was characterized by X-ray diffraction (XRD) analysis, IR spectroscopy, temperature-programmed reduction of $H_2$, and differential dissolution method [10].

The reactions of gas-phase oxidation of propylene were performed in a tubular steel reactor with inner diameter of 10 mm in the flow-through mode with a fixed catalyst bed (sample volume 2 mL). The volumetric delivery rate of the $C_3H_6/O_2/H_2O/N_2$ mixtures of various compositions was 4500 h$^{-1}$. The temperature within the reactor was measured (with accuracy of ±1°) with a thermocouple placed in the catalyst bed.

Prior to measuring the kinetic characteristics of the reactions, we activated the catalyst for 1 h in the reactor at 400°C in a flow of $O_2$/He (1 : 3). Then, the reaction mixture was passed for 1 h through the reactor cooled to the required temperature to reach steady-state conditions.

Based on published data [2–5], we performed the catalytic reactions with propylene in the temperature range 170–215°C. The total pressure of the gas mixture was varied from 0.2 to 2.2 MPa. The reaction mixtures were subjected to an on-line chromatographic analysis, as this was done in [11, 12]. The absence of a homogeneous oxidation of propylene under these conditions was confirmed by runs in a reactor having no catalyst.

## RESULTS AND DISCUSSION

Figure 1 shows how the conversion of propylene depends on pressure at varied temperature for the starting

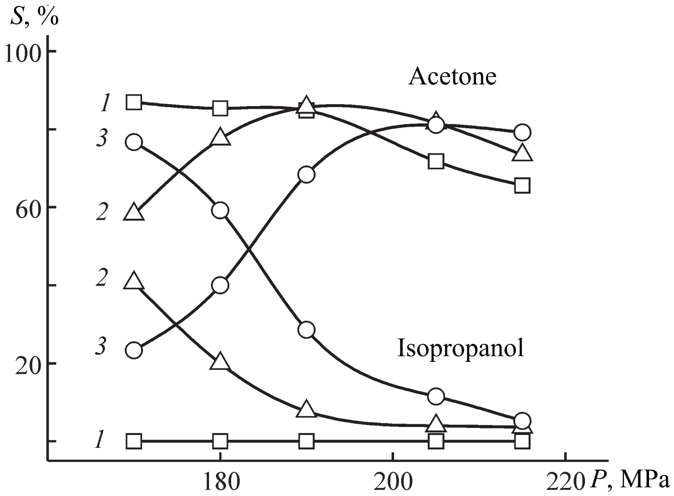


**Fig. 3.** Selectivity *S* toward reaction products vs. temperature *T*, *P* = 1.1 MPa. Starting mixture $C_3H_6/O_2/H_2O/N_2$ in ratios (vol %): (*1*) 6/4/10/80, (*2*) 6/4/30/60, (*3*) 6/4/50/40; the same for Fig. 4.

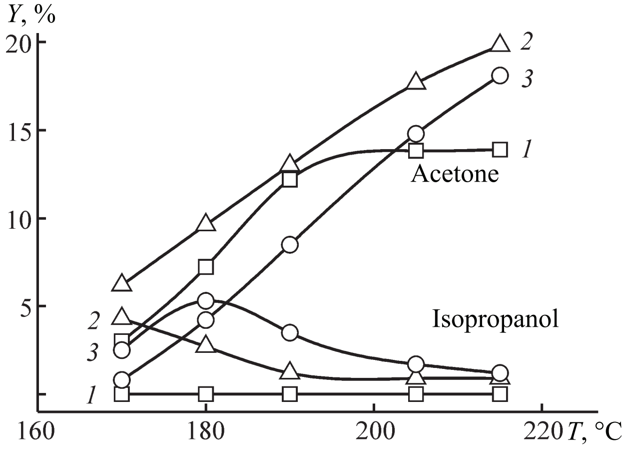


**Fig. 4.** Yield *Y* of reaction products vs. temperature *T*, *P* = 1.1 MPa.

gas mixture $C_3H_6/O_2/H_2O/N_2$ in a 6 : 4 : 10 : 80 vol % ratio, respectively. Figure 2 shows the selectivities toward the main reaction products in relation to pressure at a temperature of 190°C, which seems to be the optimal temperature for obtaining acetone under the chosen conditions. These data show that the conversion of propylene grows with pressure increasing to 1.1 MPa at an insignificant decrease in the selectivity toward acetone. Raising the pressure further, to 2.2 MPa, results in a general fall of the values of both parameters. Despite this circumstance, the output capacity of the reaction in terms of acetone at 2.2 MPa is, on average, 1.5 times that for a pressure of 1.1 MPa. Carbon oxides, CO and $CO_2$, are formed as by-products. The formation of isopropanol for the given starting mixture is at zero point, in agreement with the result of a similar reaction under atmospheric pressure [4, 5].

The effect of water on the oxidative conversion of propylene was studied for the pressure of 1.1 MPa. Figure 3 shows a temperature dependence of the selectivity of the reaction toward acetone and isopropanol for three reaction mixtures with different concentrations of water: 10, 30, and 50 vol %. It is remarkable that, as the concentration of water increases at temperatures below 200°C, the mixture outflowing from the reactor contains a substantial amount of isopropanol. Apparently, the increase in the concentration of water promotes hydration of propylene, but hinders the subsequent oxidation of isopropanol. Possibly, this is due to the competitive adsorption of water on the catalyst surface [8]. Nevertheless, the selectivity toward isopropanol substantially decreases with increasing temperature, and a proportional rise in the reaction selectivity toward acetone is observed. It is also remarkable that the maximum reaction selectivity toward acetone is also observed at high temperatures (>200°C) as the content of water is raised to 50 vol %, which is due to the suppression of reactions of deep oxidation to $CO_x$.

On the whole, raising the concentration of water in the starting mixture favors a rise in the yield of acetone with increasing temperature (Fig. 4). Nevertheless, it follows from Fig. 4 that the optimal, as regards the yield of acetone, concentration of water for the whole temperature range under study is 30%.

In conclusion, it should be noted that raising the reaction temperature further and making larger the fraction of oxygen in the starting mixture leads to a sharp rise in the yield of by-products, mostly $CO_x$. Therefore, changing these reaction parameters is inadvisable from a practical standpoint.

## CONCLUSIONS

(1) The effect of the total pressure in the range 0.2–2.2 MPa on the course of the oxidative conversion of propylene into acetone on a supported oxide catalyst of composition $V_2O_5/TiO_2$ was studied at temperatures of 170 to 213°C in reaction mixtures containing propylene, oxygen, water, and nitrogen in various ratios.

(2) It was shown that, in the general case, raising the pressure to 1.1 MPa leads to a rise in the degree of

propylene conversion and in the yield of acetone, whereas further increase in pressure leads to a decrease in these parameters. Simultaneously, the increase in pressure favors formation of deep-oxidation products, CO and $CO_2$.

(3) Raising the concentration of water in the starting mixture promotes the first stage of the reaction, conversion of propylene into isopropanol, and suppresses deep oxidation processes, which on the whole favors an increase in the yield of acetone.

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