

Dehydrogenation of propane in the presence of CO₂ on Cr(3%)/SiO₂ catalyst under supercritical conditions

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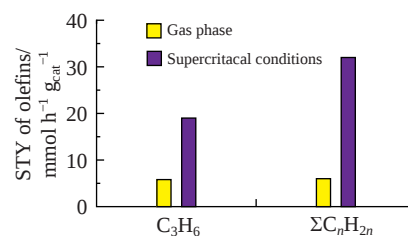
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The propane dehydrogenation reaction was carried out in the presence of CO₂ on a Cr(3%)/SiO₂ catalyst under supercritical conditions. Dependences of the propane conversion, product selectivity, and olefin productivity on the C₃H₈:CO₂ ratio and reagent consumption were revealed. It was found that the application of supercritical conditions resulted in the increase in propylene productivity by a factor of three and overall olefin productivity by a factor of five as compared to a conventional reaction in the gas phase.



Keywords: supercritical carbon dioxide, dehydrogenation, carbon dioxide, propane to propylene, utilization of carbon dioxide.

Oxidative dehydrogenation of propane in the presence of CO₂ can resolve two urgent problems in the chemical industry. The first of them is related to the increase in consumption of propylene, so there is a need for the reliable source of cheap and readily available raw materials and more efficient propylene production technologies. The second one arises from the global problem of CO₂ utilization, which is among the major greenhouse gases.^{1,2}

For the successful oxidative dehydrogenation of propane to propylene in the presence of carbon dioxide, a catalyst should be capable of activating the inert CO₂ molecule. The highest catalytic activity in this reaction has been demonstrated by supported chromium-containing catalysts.^{3–11} However, the catalytic effectiveness depends on the chromium content, the support nature, and the reaction conditions. In the series of chromium-containing catalysts on various oxide supports, the CrO_x/SiO₂ catalyst exhibited the best catalytic activity.¹² In the comparative analysis of physical-chemical properties of amorphous silica with different texture characteristics and of catalysts prepared on these supports

[Cr(2–10%)/SiO₂], the dependence of catalytic activity on the specific surface area and the diameter of support pores has been recently established.¹³

Investigation of the Cr(3%)/SiO₂ catalyst sample by the XRD and UV-VIS diffuse-reflectance spectroscopy before and after the catalytic tests revealed that the deposition of heavy reaction products occurred on the surface over time, thereby blocking the active centers of catalyst.¹³

It has been found that in catalytic reactions carried out under supercritical conditions, the productivity towards the major products is improved due to an increased density of the reaction medium,¹⁴ and the processes of coke deposition on the catalyst surface are suppressed.^{15–18} Recently, the hydrogenation reaction of CO₂ under supercritical conditions on various CuO–ZnO–Al₂O₃, Fe/TiO₂ and Fe/SiO₂ catalysts has been reported,^{19–21} and an increase in the catalyst productivity, a decrease in the deposition of solid reaction products on the catalyst surface and an increase in the catalyst operating time were observed as compared to the gas-phase

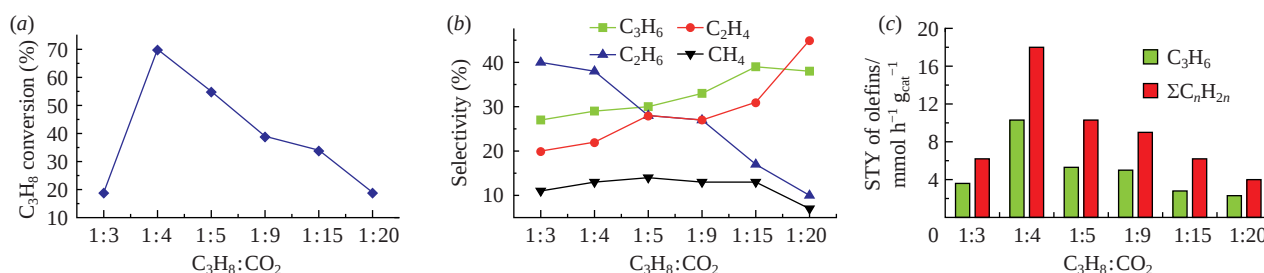


Figure 1 Dependences of (a) the propane conversion, (b) the product selectivity and (c) the productivity of propylene and total olefins vs. the molar ratios of reactants in the propane dehydrogenation under supercritical conditions (600 °C, V = 1.3 mmol min⁻¹).

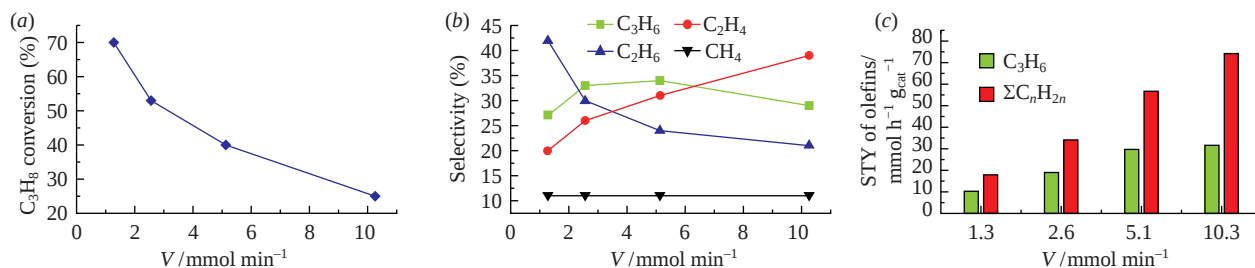


Figure 2 Dependences of (a) the propane conversion, (b) the product selectivity and (c) the productivity of propylene and total olefins vs. the flow rate of reaction mixture in the propane dehydrogenation under supercritical conditions (600 °C, C₃H₈:CO₂ = 1:4).

process. The analysis of reaction products revealed arise in the formation of olefins.^{22,23} However, there are still no published works on the dehydrogenation of propane with CO₂ under supercritical conditions. The aim of this work was to explore this reaction in the presence of CO₂ on a Cr(3%)/SiO₂ catalyst under supercritical conditions and to compare its performance with the gas-phase reaction.[†]

When propane was dehydrogenated in the presence of CO₂ in the gas phase on a Cr(3%)/SiO₂ catalyst, the propane conversion reached 67%, and the propylene selectivity was 75% at 600 °C.¹³

For the propane dehydrogenation in the presence of CO₂ under supercritical conditions, the dependence of the propane conversion and products selectivity on the C₃H₈:CO₂ ratio at 600 °C was investigated (Figure 1). Upon a decrease in the C₃H₈:CO₂ ratio, the propane conversion reached 33%, the propylene selectivity was 39%, and the H₂:CO ratio in products increased from 0.5 to 1. A further increase in the carbon dioxide content did not result in any additional growth in the propylene selectivity that remained at the level of 38% [see Figure 1(a)]; the H₂:CO ratio also did not rise. This proves the involvement of CO₂ in the direct oxidation of propane to propene (C₃H₈ + CO₂ = C₃H₆ + CO + H₂O) and the consumption of hydrogen in the reverse water shift reaction (CO₂ + H₂ = CO + H₂O), which shifts the equilibrium towards the propane dehydrogenation. Thus, in the CO₂-assisted process of propane dehydrogenation, we have obtained, along with propylene, a valuable by-product, the synthesis gas (CO + H₂), which is widely used in the chemical industry. Herewith, the variation in the C₃H₈:CO₂ ratio in the initial mixture allows one to tune the H₂:CO ratio in the products. The peculiarity of reaction is an increased ethylene selectivity, which may be due to an occurrence of the side cracking reaction (C₃H₈ → C₂H₄ + CH₄).

[†] Granulated silica gel (SiO₂, Acros) was used as the support for the preparation of catalyst samples. The pre-crushed silica gel (fraction of 0.25–0.5 mm) was dried in a drying oven at 100 °C for 6 h. The Cr(3%)/SiO₂ catalyst sample was prepared via impregnating the support with a solution of chromium nitrate in distilled water of the appropriate concentration. The sample was completely dried at 100 °C, and then calcined in air at 500 °C for 4 h.

Propane dehydrogenation into propylene in the presence of CO₂ was carried out in a flow catalytic unit with a steel reactor with an internal diameter of 4 mm. During the experiment in a gas medium, the C₃H₈ + CO₂ mixture was fed to the reactor in the volume ratio of 1:2, the total flow rate of gas mixture was 30 ml min⁻¹ (1.3 mmol min⁻¹). The catalyst loading was 1 g with a fraction of 0.25–0.5 mm. The volume hourly space velocity of the gas flow was 2000 h⁻¹.

During the experiment under supercritical conditions, the CO₂ and C₃H₈ mixture was fed into the system by a Teledyne high-pressure syringe pump at the pressure of 85 atm, and the total flow rate was varied from 1.3 to 10.3 mmol min⁻¹. The catalyst loading was 0.5 g diluted with quartz chips (0.5 g) with a fraction of 0.25–0.5 mm. Thus, the hourly space velocity of the mixture in the supercritical experiments was 2–15 times higher as compared to the gas-phase tests.

The analysis of gaseous products in the reaction was carried out online using a Crystal-5000 chromatograph equipped with thermal conductivity detectors and Heysep Q and Zeolite CaA packed columns.

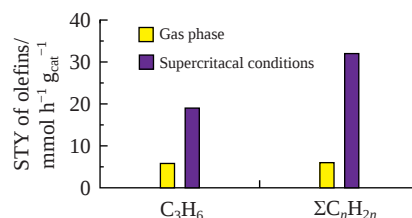


Figure 3 Space-time yields of propylene and the sum of olefins (ethylene + propylene) for the Cr(3%)/SiO₂ catalyst in the propane dehydrogenation under supercritical conditions vs. gas-phase conditions (600 °C, V = 1.3 mmol min⁻¹, C₃H₈:CO₂ = 1:3).

The productivity towards propylene and overall content of olefins were highest at the C₃H₈:CO₂ ratio of 1:4. A further increase in the CO₂ content in the reaction mixture resulted in a decreased productivity of propylene and overall olefins [see Figure 1(b)].

At the second step of catalytic investigations, the dependence of yield of the target reaction product on the flow rate was revealed (Figure 2). When propane was fed at the rate of 1.3 mmol min⁻¹, its conversion reached 70%, while a further increase in the flow rate diminished the propane conversion. Upon a rise in the reaction mixture feed rate from 1.3 mmol min⁻¹ to 5 mmol min⁻¹, the propylene selectivity was slightly increased and reached 35%; and after a further increase in the reaction mixture feed rate to 10 mmol min⁻¹, there was a slight decrease in the propylene selectivity.

In conclusion, we have performed a comparison of the experimental results of propane dehydrogenation in the presence of carbon dioxide under the supercritical conditions and in the gas phase (Figure 3). It was found that the productivity of Cr(3%)/SiO₂ catalyst under the supercritical conditions was increased by a factor of three based on the propylene content and by a factor of five based on the overall content of olefins (ethylene + propylene) as compared to the gas-phase conditions.

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