ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 5, pp. 880−883. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © S.M. Gadzhizade, S.A. Dzhamalova, N.A. Aliev, A.A. Kasimov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 5, pp. 826−829.

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

A Study of the Reaction of Propane Dehydrogenation on a Cr,Co,Ni,Bi,K/γ-Al_2O_3 Catalyst in the Presence of Atmospheric Oxygen

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Received December 3, 2008

Abstract—Effect of the C_3H_8 dehydrogenation temperature (560–650°C) and oxygen on the rates of C_3H_8 conversion and C_3H_6 formation was studied using a catalyst prepared under lowered or atmospheric pressure.

DOI: 10.1134/S1070427209050255

Propylene is one of the most important raw materials in modern petrochemical industry. It is used to manufacture glycerol, acrolein, isopropanol, acetone, polypropylene, propylene oxide, etc. The wide industrial use of propylene results in that close attention is being given by researchers to development of catalysts and processes for production of propylene [1, 2].

Propylene is manufactured on a large industrial scale by pyrolysis of oil fractions. Thus, synthesis of propylene is rather closely tied with manufacture of the main product, ethylene. The yield of propylene in pyrolysis is insufficiently high, being only about 10% even in the so-called "propylene" mode. The production volume fails to satisfy the steadily increasing industrial demand for propylene.

The demand for propylene has become higher than that for ethylene. The total world's demand for propylene will double in the nearest 20 years to become 140 million tons by 2020.

In recent years, a considerable attention has been given to studies in the field of synthesis of propylene by catalytic dehydrogenation of propane. A negative factor in processes of propane dehydrogenation in the oxygen-free mode is thermodynamic limitation on the yield of propylene and periodicity of the process [3].

To lift the thermodynamic limitations on the yield of propylene and to perform the process on a permanent basis, many modern studies have been oriented to development of processes for oxidative dehydrogenation of propane. Extensive studies of oxidative dehydrogenation of C_3H_8 on V/Al and V–K/Al_2O_3 catalysts have been performed by Resini et al. [4]. At temperatures of 350–500°C, contact time of 0.2–0.3 s, and $O_2 : C_3H_8$ molar ratios of 1 : 1 to 1 : 5, the yield of C_3H_8 in the presence of oxygen is within the range 6.4–17.5% at a selectivity of 34.1–48.5%.

On a catalyst containing Pt supported by Al_2O_3, the conversion of C_3H_8 at temperatures of 200–360°C is 40% at a selectivity of 20% [5], and on a V_2O_5/Al_2O_3 catalyst at a temperature of 690°C, the conversion of C_3H_8 is 8.5% at a selectivity of 31.8%. In recent years, extensive studies devoted to development of new high-efficiency catalysts and processes for propane dehydrogenation have been carried out at Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan [6].

Oxygen is delivered in amounts of 0.1 to 0.5 mol per mole of a raw material in the presence of an inert diluent, nitrogen, taken in an amount of 15 mol per mole of the raw material. In the course of the C_3H_8 dehydrogenation reaction, a 100% conversion of oxygen is observed.

EXPERIMENTAL

Our study was performed in a flow-through stainless steel reactor. The catalyst was prepared as follows: γ-Al_2O_3 (specific surface area 93.0 m2, bulk density 0.6 g cm^{-3}) was preliminarily dried at 120°C and calcined at 300–400°C and then impregnated with solutions of the salts $Ni(NO_3)_3 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, KNO_3,

$Co(NO_3)_3 \cdot 6H_2O$, and $Bi(NO_3)_3 \cdot 5H_2O$. The resulting mass was evaporated to a paste-like state and then dried in air at 80–120°C for 4 h. After the drying, the catalyst was calcined in a vacuum (residual pressure 15–20 mm Hg) at 600–620°C for 5–6 h, with temperature raised at a rate of 50 deg h–1. For comparison, the above catalyst samples were also prepared under atmospheric pressure [7]. The amount of the catalyst was maintained constant: 12 cm^3 at a catalyst bed height of 6 cm.

We suggest to deposit salts of the active components on a crushed support and then to mold the catalyst and perform drying and calcination by the recommended scheme, which provides a homogeneous distribution of the active component over the catalyst surface.

The catalyst prepared under lowered pressure has a number of advantages over that synthesized at atmospheric pressure. For example, this catalyst has a larger specific surface area (Table 1) and a narrow pore radius distribution (70–80% of the total pore volume is constituted by pores with radii of 6–12 nm), which positively affects the choice of optimal conditions for the process. Therefore, we compared catalysts prepared under different conditions, but at the same temperature and constant time of drying and calcination. To select the optimal catalyst composition, we took one-, two-, three-, four-, and five-component systems. The catalyst prepared under lowered pressure contained reduced and oxidized forms of compounds of the starting components (as indicated by X-ray phase analysis and electronic diffuse reflectance spectra). It also contains such compounds as $NiAl_2O_4$, $CoAl_2O_4$, and $K_2Cr_2O_7$ in substantially greater amounts, compared with the catalyst prepared under atmospheric pressure conditions.

$K_2Cr_2O_7$ is a strong oxidizing agent that easily releases oxygen in the dehydrogenation mode; $NiAl_2O_4$ is a good binder.

We studied dehydrogenation of propane to propylene in the presence of atmospheric oxygen and nitrogen taken as diluent in an amount of 15 mol per mole of a raw material. Oxygen was introduced in an amount of 0.1 mol per mole of propane.

At 620°C, the yield of propylene is 63–65% at a selectivity of 88–90% in the oxidative dehydrogenation mode. In the absence of oxygen, the yield of propylene is about 50% at a selectivity of 90–92%.

At temperatures of 600–620°C, we studied the effect of the molar ratio of oxygen on the yield of propylene and on the process selectivity.

Table 1. Characteristic of the Cr,Co,Ni,Bi,K/γ-Al_2O_3 catalyst

Parameter	Synthesis conditions	
	lowered pressure	atmospheric pressure
Grain size, mm	2–3	2–3
Specific surface area, $m^2\ g^{-1}$	125.2	60.0
Pore volume, $cm^3\ g^{-1}$	0,18	0.16
Bulk density, g cm^{-3}	0.714	0.84

A characteristic feature of preparation of all the known catalysts is that the drying and calcination in molding of the active paste of a catalyst are performed under atmospheric pressure.

Using the Cr,Co,Ni,Bi,K/γ-Al_2O_3 catalyst we developed, we studied the effect of the reaction temperature and the molar ratio of oxygen to an inert gas (nitrogen) on the yield of propylene. The effect of temperature (560–650°C) was analyzed at a volumetric flow rate of the starting fraction ($C_3H_8 + O_2 + N_2$) of about 885.8 h^{-1} and a molar ratio of oxygen to propane of 0.11–0.12; the amount of nitrogen was within 10.1–16.6 mol per mole of propane.

The conversion rates of the hydrocarbons (C_3H_8, C_3H_6) and oxygen and the formation rate of C_3H_6 were determined.

The time of contact between the raw material vapor and the catalyst was determined with allowance for the change in the volume of the vapor of the raw material ($C_3H_8 + O_2 + N_2$) and reaction products upon a change in the reaction temperature. Maintaining constant the amount of the starting propane, oxygen, and nitrogen, we varied the reaction temperature from 560 to 650°C. For example, at delivery rates of propane, oxygen, and nitrogen of 0.6, 0.063, and 9.967 l h^{-1}, respectively (linear flow velocity of about 3.04 cm s^{-1}), raising the reaction temperature from 560 to 650°C leads to a decrease in the time of contact from 1.92 to 1.67 s.

The effect of the reaction temperature was analyzed in such a way that the concentration of propane at the entry into the reaction zone was 0.00285 M in the entire temperature range studied.

Table 2 lists the rates of C_3H_8 conversion and formation of C_3H_6 and by-products of the reaction [H_2, $\Sigma(C_1 + C_2)$, CO_2, H_2O, and O_2] in relation to temperature (560–650°C) at a constant O_2 concentration in the reaction

volume (~0.0003 M) and constant propane concentration (0.00285 M).

As can be seen in Table 2, the rate of C_3H_8 conversion steadily grows with temperature; in this case, the rate of C_3H_8 formation increases from 0.995×10^{-4} mol l_{ox}^{-1} s^{-1} at 560°C to 4.995×10^{-4} mol l_{ox}^{-1} s^{-1} at 640°C. Then, the rate of C_3H_6 formation decreases to 4.995×10^{-4} mol l_{ox}^{-1} s^{-1} at 650°C, with the rate of hydrogen formation increasing to 4.98 mol l_{ox}^{-1} s^{-1}. The C_3H_6 formation rate falls at temperatures higher than 640°C because propylene undergoes thermal decomposition to a substantially greater extent, compared with its formation.

As C_3H_8 is formed, the thermal cracking rate increases, which becomes noticeable at 590°C. Beginning with this temperature, the formation rate of low-molecular hydrocarbons $\Sigma(C_1 + C_2)$ produced in decomposition of hydrocarbons sharply increases. In the course of the conversion, the concentration of C_3H_8 in the gas decreases and, consequently, so does the rate of its decomposition. However, as the concentration of C_3H_8 decreases, that of C_3H_6 increases, and, the higher the temperature, the more substantial the faster the formation of low-molecular hydrocarbons.

It should be noted that the rate of oxygen loss, $W(O_2)$, increases up to a temperature of 620°C, and then stabilizes at 0.615×10^{-4} mol l_{ox}^{-1} s^{-1}. This means that oxygen is fully bound below 620°C. As a result, the rate of H_2O formation markedly decreases, from 0.8×10^{-4} to 0.51×10^{-4} mol l_{ox}^{-1} s^{-1}, although the amount of hydrogen formed in the process increases from 0.1546 to 0.482 l h^{-1}.

Such a sharp decrease in the rate of H_2O formation is, presumably, due also to the reaction of water present in the reaction volume with coke deposits on the catalyst to give CO and the CO_2:

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$H_2O + \text{“C”} \rightarrow CO + H_2$$

$$2CO + O_2 \rightarrow 2CO_2$$

It should be noted that the formation rate of decomposition products grows from 0.9×10^{-4} to 1.45×10^{-4} mol l_{ox}^{-1} s^{-1} as temperature is raised from 560 to 650°C. The decomposition of both the starting (C_3H_8) and target (C_3H_6) hydrocarbons occurs both on the coke-free part of the catalyst and on that coked in the process.

It follows from these data that, as temperature is raised in the presence of atmospheric oxygen introduced in amounts of 0.5, 0.3, and 0.1 mol per mole of a raw material, the yield of C_3H_6 grows and the process selectivity falls, with the latter being the more pronounced, the greater

Table 2. Rates W of conversion of C_3H_8 and O_2 and formation of H_2, $\Sigma(C_1 + C_2)$, CO_2, and H_2O at different reaction temperatures. Delivery rates (l h^{-1}): C_3H_8 0.6, O_2 0.063, ΣN_2 0.967

Temperature, °C	$W \times 10^{-4}$, mol l_{ox}^{-1} s^{-1}						
	H_2	ΣC_1+C_2	CO_2	C_3H_8	C_3H_6	H_2O	O_2
560	1.598	0.041	0.114	1.891	1.829	0.372	0.310
600	3.089	0.279	0.217	3.524	3.276	0.506	0.470
610	3.356	0.317	0.238	3.971	3.689	0.752	0.615
620	3.927	0.471	0.248	4.298	3.896	0.796	–
640	4,898	1,137	0.362	5.219	4.351	0.579	–
650	4.981	1.447	0.393	5.238	4.154	0.506	–

Table 3. Rates of C_3H_6 formation and C_3H_8 conversion

Amount of oxygen, mol O_2 per mole of C_3H_8	Rates of C_3H_6 formation and C_3H_8 conversion, mol l_{ox}^{-1} s^{-1}		$W(C_3H_6)_{form}/W(C_3H_8)_{conv}$	Temperature, °C	Yield of C_3H_6, mol %	
	$W(C_3H_6)_{form}$	$W(C_3H_8)_{conv}$			C_3H_8 prop.	C_3H_8 decomp.
0.5	2.474	4.032	0.6136	620	42.3	61.4
0.3	3.185	4.165	0.7647	620	51.9	76.6
0.1	3.896	4.298	0.9065	620	62.8	90.6

amount of oxygen is introduced. However, at any amount of oxygen delivered to the reaction zone, the maximum yield of C_3H_6 is observed at temperatures of 620–630°C at an acceptable selectivity. The highest yield of C_3H_6 and an acceptable process selectivity are observed upon introduction of 0.1 mol of oxygen per mole of a raw material. The yield of C_3H_6 at 620°C is about 63% at a selectivity of 90.6%.

Based on these data, we conclude that the optimal temperature of the reaction of C_3H_8 dehydrogenation is $T \rightarrow 620$°C.

Table 3 lists the rates of C_3H_6 formation and C_3H_8 conversion. It follows from the data in Table 3 that, as the amount of introduced oxygen decreases (0.5–0.1 mol mol^{-1}), the observed rate of C_3H_6 formation grows faster than falls the rate of C_3H_8 conversion. This occurs because the deep oxidation of C_3H_6 to CO_2 becomes less pronounced upon introduction of larger amounts of oxygen.

CONCLUSIONS

(1) When a catalyst is prepared under lower pressure conditions ($P_{res} \approx$ 15–20 mm Hg), pores with a narrow radius distribution are formed, with 70–80% of pores constituted by those with radii of 6–12 nm.

(2) A catalyst prepared under lowered-pressure conditions contains oxidized and reduced forms of metals and compounds $NiAl_2O_4$, $CoAl_2O_4$, and $K_2Cr_2O_7$.

(3) The activity of the catalyst prepared under lowered-pressure conditions is 63–65% at a selectivity of 90–91%.

(4) The rates of C_3H_6 formation and C_3H_8 conversion were determined in relation to temperature and amount of oxygen introduced.

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