Propane Conversion in the Presence of Alumina-Based Aerogel

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Abstract—Features of propane conversion for selective olefin production in the presence of nanofibrous aerogel materials have been studied. The effect of modification of aerogel alumina with titania and silica on the catalytic activity and the olefin selectivity in propane conversion at atmospheric pressure has been shown. Low-temperature nitrogen adsorption has revealed that these catalysts have a developed specific surface area of about 300 m²/g; water vapor adsorption at 293 K has shown that materials of this type contain 0.2–0.6 mmol/g of acid sites. X-ray diffraction analysis and transmission electron microscopy have revealed that the synthesized materials are an amorphous aerogel with tangled fibers with a thickness of ~6 nm.

Keywords: propane conversion, ethylene, propylene, alumina, titania, silica **DOI:** 10.1134/S0965544119010109

INTRODUCTION

Light olefins (ethylene and propylene) are the most important intermediates for heavy organic synthesis and polymer production [1]. On an industrial scale, these products are mostly synthesized by straight-run gasoline pyrolysis [2]. Currently, the fraction of global propane production in the composition of natural and associated petroleum gas increases; therefore, propane is an attractive feedstock for the production of light olefins. The catalytic conversion of propane can occur via two routes:

(i) propane dehydrogenation to propylene:

$$C_3H_8 \rightarrow C_3H_6 + H_2,$$

 $\Delta H^\circ = 124 \text{ kJ/mol, and}$

(ii) propane cracking to ethylene and methane:

 $C_3H_8 \rightarrow CH_4 + C_2H_4$, $\Delta H^\circ = -56 \text{ kJ/mol.}$

It is currently believed that effective hydrocarbon cracking catalysts are systems based on ultrastable zeolites, in which the zeolite in a cation-decationated form is stabilized at a temperature of $500-550^{\circ}$ C and a partial pressure of water vapors below 0.8 atm [3, 4]. A disadvantage of this method is a low SiO₂/Al₂O₃ ratio and, accordingly, low thermal stability and catalytic properties of the resulting zeolite. For example, propane conversion in the presence of catalysts based on a modified ZSM-5 zeolite was studied. It was shown that these systems provide an olefin selectivity of 62% [5, 7]. In general, oxide catalyst systems are effective catalysts in propane conversion to olefins. Features of propane conversion in the presence of samarium vanadite and samarium vanadate synthesized by the solid-phase synthesis method were studied in [8]. It was shown that $SmVO_3$ catalyzes mostly the propane cracking to form methane and ethylene, while $SmVO_4$ equally accelerates both the cracking and dehydrogenation of propane.

The use of contact systems in which the reaction mixture is forcibly transported through the catalyst pores and the reaction for high-temperature processes occurs mostly in the diffusion region leads to an increase in the process rate [9, 10], which can significantly decrease the probability of occurrence of side processes, namely, the formation of tar and coke in the catalysts. Diffusion limitations can be decreased by the use of fibrous materials, particularly those based on various nanowires.

Propane conversion is mediated, along with alumina, by other oxides and/or their mixtures. The oxides that are most commonly used in this reaction are titania and silica. Therefore, it was of interest to synthesize catalytically active composite materials of the aerogel type based on nanofibrous alumina modified with titania and silica in propane conversion and study the features of this process in the presence of the synthesized catalyst systems.

EXPERIMENTAL

The nanofibrous aerogel was prepared by wet air oxidation of metallic aluminum diffusing through a mercury amalgam layer on the surface of an aluminum plate in a specially constructed reactor [11]. Aluminum plates with a size of $100 \times 100 \times 1$ mm, which were produced by OOO Lab-3 in accordance with Specifications TU 6-00-00205133-63-97 (purity of 99.999%), after the formation of a mercury amalgam layer on their surface, were placed into the reactor chamber and held at 20°C and a humidity of 70% for 5 h. Under these conditions, the average growth rate of the nanofibrous alumina aerogel was 1 cm h^{-1} . The alumina synthesized by this method contained 40–43 wt % of water and has an amorphous structure. The density of the freshly prepared alumina-based nanofibrous aerogel was 0.004 g/cm³.

After that, the synthesized alumina samples were impregnated with titanium(IV) isopropoxide and triethoxychlorosilane at 373 K for 24 h. The dopant and basic alumina were taken in equal volume ratios.

This synthesis is based on the ability of both titanium(IV) isopropoxide and triethoxychlorosilane to undergo hydrolysis. The surface of the original nanofibrous aerogel contains OH groups capable of undergoing the hydrolysis reaction with the above reagents to form the respective oxides [12]:

$$n(-OH)(s) + Me(OR)_{4}(g)$$

$$\rightarrow (-O-)_{n} Me(OR)_{4-n}(s) + nROH(g),$$

$$(-O-)_{n} Me(OR)_{4-n}(s) + (4-n) H_{2}O(g)$$

$$\rightarrow (-O-)_{n} Me(OH)(s) + (4-n) ROH(g),$$

where (s) is the surface and (g) is the gas phase.

This method makes it possible to deposit both titania and silica in an amount of 5 wt %; it is not accompanied by the transition of titania and silica to the crystalline phase with subsequent reduction to a nullvalence state.

To determine the morphology of the synthesized catalysts, transmission electron microscopy (TEM) micrographs were recorded on a 200-kV JEM 2100 microscope (JEOL, Japan). To this end, the samples were placed on a substrate wetted with alcohol without any pretreatment.

X-ray diffraction (XRD) analysis of the samples was conducted on a high-precision PANalytical Empyrean X-ray diffractometer using monochromatic CuK_{α} radiation in the reflection geometry in an angular range of $2\theta = 10^{\circ}-100^{\circ}$.

To determine the presence of ions in the aerogel, elemental analysis was conducted on a Clever-31 X-ray fluorescence spectrometer.

Thermal analysis was conducted on an SDT Q600 TG/DSC/DTA synchronous thermal analyzer to determine the stability of the synthesized nanofibrous aerogel in the high-temperature region.

Parameters of the pore structure of the samples were determined from nitrogen adsorption isotherms at 77 K, which were measured on a Micromeritics ASAP 2020-MP automatic high-vacuum unit in a relative pressure range of 0.001–0.98. The samples were preevacuated to a residual pressure of less than 10 mmHg.

The specific surface area of all the samples was measured by the Brunauer–Emmett–Teller (BET) method. The surface was calculated by the comparative MP method (micropore size distribution) and the t-plot method (determination of micro- and/or mesopore volumes and specific surface area of the sample compared with the initial adsorption isotherm of a nonporous material with the same surface chemistry). The total specific surface area was determined from the slope of the initial portion of the comparative MP plot; the mesopore surface was determined from the comparative plot in the polymolecular adsorption region by the MP method. In addition, the ratio of the volume and surface of micro- and mesopores was determined by the t-plot method.

Comparative assessments of surface functional groups and the number of primary adsorption sites (PASs) of the nanofibrous aerogels were obtained from the water adsorption isotherm at 293 K on a vacuum weighing system with a McBain quartz helical spring balance with a sensitivity of 10 μ g with a weighed portion of up to 100 mg.

Catalytic tests were conducted in a U-shaped flow quartz reactor at atmospheric pressure in a wide temperature range (300-1273 K). Propane was used as the feedstock; it was supplied at a rate of 55.8 μ mol/s, which was constant in all the tests. The catalyst load was 0.05 g.

Sampling was conducted through a dosing valve; the samples were analyzed on a Kristall 2000 M chromatograph equipped with a flame ionization detector and a thermal conductivity detector; products were separated on a Porapak Q column with a length of 1.5 m and a diameter of 3 mm; the temperature of the column and the detectors was 373 and 473 K, respectively. The main products of both the thermal and catalytic conversion of propane were hydrogen, methane, ethane, ethylene, and propylene.

Propane conversion was determined upon the establishment of a steady state from the amount of reacted propane:

$$\alpha = \frac{n_{\rm fed} - n_{\rm unreact}}{n_{\rm fed}},$$

where n_{fed} is the amount of the fed propane (µmol) and n_{unreact} is the amount of unreacted propane (µmol).

Using the derived experimental data, the activation energies for propane conversion in the presence of various catalyst systems were calculated. To this end, the

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Fig. 1. Transmission electron microscopy images at a resolution of 100 nm for samples: (a) Al_2O_3 , (b) TiO_2/Al_2O_3 , and (c) SiO_2/Al_2O_3 .

dependences of the logarithm of the reaction rate on the reciprocal of temperature were studied.

RESULTS AND DISCUSSION

Figure 1 shows TEM images of the synthesized materials; it is evident that the synthesized aerogels are composed of tangled nanowires with a diameter of 5-6 nm.

The XRD patterns of the aerogel materials (Fig. 2) do not exhibit reflections corresponding to the diffraction pattern of X-ray amorphous substances. In addition, it was found that the nanofibrous aerogel samples contain only aluminum, titanium, and silicon ions; other ions capable of affecting the physicochemical and catalytic properties of the studied materials were not detected.

According to thermal analysis, in a temperature range of $20-1200^{\circ}$ C, nanofibrous alumina does not undergo phase transitions. In the low-temperature region of $80-200^{\circ}$ C, only a loss of adsorption water was detected; other changes were not registered.

All the synthesized materials can be attributed to mesoporous adsorbents; only nanofibrous alumina contained a small amount of micropores (Table 1). For the comparative assessment of the surface functional groups and the number of PASs in the synthesized nanofibrous aerogel samples, water adsorption isotherms at 293 K were recorded (Fig. 3).

In the extremely low relative filling region, the isotherms have a convex portion. The description of these portions by the Langmuir equation makes it possible to determine the number of PASs for the adsorption of water molecules (Table 2). In all the cases, the number of PASs was determined according to the comparative plots of water vapor adsorption.

According to the concept of PASs [13], in the initial region of relative pressures, the adsorption of water molecules occurs on oxygen-containing surface functional groups. The presence of acidic oxygen complexes in the catalysts increases the adsorption and facilitates the micropore filling. The chemical state of the surface plays a significant—commonly decisive—role in the water vapor adsorption. The presence of nonacid oxygen complexes does not affect the surface polarity of the catalyst and does not enhance the water vapor adsorption.

Analysis of the water vapor adsorption isotherms shows that the number of PASs slightly decreases in the case of deposition of titania on nanofibrous alu-

Catalyst	S _{BET} , m²/g	$V_{\rm o}, {\rm cm}^3/{\rm g}$ $S_{\rm micr}, {\rm m}^2/{\rm g}$	$V_{\rm BJH}$, cm ³ /g desorption/adsorption	2 _{xo} , nm	2_{xoBJH} , nm desorption/adsorption	$S_{\rm ME},$ m ² /g	$S_{ m MP},\ m^2/g$
Al ₂ O ₃	253	0.011/29.5	0.58/0.56	6.7	9.7/10.0	223	196
TiO ₂ /Al ₂ O ₃	310	_	0.68/0.67	8.1	9.96/10.24	386	—
SiO ₂ /Al ₂ O ₃	219	_	0.50/0.48	8.3	11.10/12.41	185	—

Table 1. Parameters of the pore structure of the nanofibrous aerogel catalysts studied

 S_{BET} is the specific surface area; V_{o} and S_{micr} is the volume and apparent surface area of micropores in the samples, respectively; V_{BJH} is the mesopore volume; 2_{xo} is the pore size (two half-widths for the slit model 2_{xo}) determined in the BET region and in the capillary condensation region from the desorption branch in terms of the Barrett–Joyner–Halenda (BJH) model; $2x_{\text{oBJH}}$ is the average pore size in the capillary condensation region determined by the BJH method; S_{MF} is the mesopore surface; and S_{MP} is the micropore surface area.

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10000 (b) (a) 10000 9000 9000 Intensity, abs. units Intensity, abs. units 8000 8000 7000 7000 6000 6000 5000 5000 4000 4000 3000 3000 2000 2000 1000 1000 0 20 40 60 80 100 0 20 40 60 80 100 2θ , deg 2θ , deg 10000 (c) 9000 Intensity, abs. units 8000 7000 6000 5000 4000 3000 2000 1000 40 0 20 60 80 100 2θ , deg

Fig. 2. X-ray diffraction analysis of the structure of nanofibrous aerogels based on alumina for samples: (a) Al_2O_3 , (b) TiO_2/Al_2O_3 , and (c) SiO_2/Al_2O_3 .

mina and increases in the case of deposition of silica (Table 2).

Analysis of water vapor adsorption suggests that nanofibrous alumina and the modified composite materials based on it have an extremely developed adsorption capacity and a large number of PASs; these systems are superior to zeolite materials in these parameters. According to these findings, it can be assumed that the synthesized nanofibrous aerogel catalyst samples will exhibit catalytic activity.



Fig. 3. Water vapor adsorption isotherm at 293 K for samples: (1) Al_2O_3 , (2) TiO_2/Al_2O_3 , and (3) SiO_2/Al_2O_3 .

The freshly prepared nanofibrous aerogel samples were studied as catalysts in the propane conversion reaction. Nanofibrous alumina exhibited catalytic activity only in the region of high temperatures starting from 700 K (Fig. 4).

At the same time, during the thermal conversion of propane, the onset of decomposition occurred above 900 K; in this case, the main products were methane and ethane. A further increase in temperature led to an increase in propane conversion; however, the yield of heavy hydrocarbons increased owing to the polycon-densation of the resulting unsaturated and aromatic hydrocarbons, which led to tar formation in the catalyst. In a temperature range of 900–1100 K, coke formation was observed; at temperatures above 1150 K, tar formation took place.

In the presence of the titania- and silica-modified composite samples, a significant increase in the propane conversion and a change in the olefin selectivity compared with the respective parameters of nanofibrous alumina was observed (Table 3).

For the TiO₂/Al₂O₃ catalyst, the propylene selectivity achieved 47% at 1023 K. For the freshly prepared SiO₂/Al₂O₃ catalyst, in a low-temperature region of 600-823 K, the ethylene selectivity exceeds 50%; above 823 K, the propylene content in the reaction products increases; at 923 K, the propylene selectivity achieves a maximum of 64%, while the commercial

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Catalyst	Adsorption capacity, mmol/g	Amount of PASs, mmol/g	Average number of water molecules in the cluster	Specific adsorption capacity, µmol/m ²
Al ₂ O ₃	19.678	0.305	64	78
TiO ₂ /Al ₂ O ₃	10.403	0.241	43	34
SiO ₂ /Al ₂ O ₃	18.654	0.621	30	85

Table 2. Surface characteristics determined by the water adsorption method

 Pt/Al_2O_3 catalyst provides an ethylene selectivity of as low as 35% [14].

A change in selectivity in the case of modification of nanofibrous alumina with titania or silica is attributed to a change in the structure of the catalytic site. For unmodified nanofibrous aerogel alumina, this site is an -OH group chemisorbed on the aluminum atom, where the adsorption and catalytic conversion of propane take place, whereas in the case of modification with titania or silica, the resulting new catalytic site involving titania or silica facilitates the dissociative adsorption of propane to form hydrogen and propylene, as evidenced by lower values of activation energy for catalytic cracking (Table 4).

It was found [15] that the order of the reaction is within the unit, with some upward and downward deviations from the integer value. The following relationship is observed: with an increase in temperature, the order of the reaction deviates downwards. Based on the fact that propane cracking is a first-order reaction, the activation energies for the process were calculated for the test catalysts using the Arrhenius equation. It was found that the activation energy for the thermal conversion of propane is 143 kJ/mol, which is close to the published data [16]; for reaction in the presence of the catalyst based on nanofibrous aerogel alumina, the activation energy was 85–105 kJ/mol depending on the catalyst type (Table 3).

In the presence of nanofibrous catalysts, conversion occurs mostly by the carbenium ion-mediated mechanism and the contribution of the thermal component is negligible. It is known that there is a correlation between the bond dissociation energy and the activation energy of the elementary reaction [13]. It is also known [13] that, according to the Bell–Evans–Polanyi principle, with an increase in the exothermicity of the radical process, the activation energy of the process E_a decreases. In alkanes, the primary C–H bonds are the strongest (100 kcal/mol), while the tertiary C–H bonds are the least strong (86 kcal/mol). Accordingly, the calculated apparent activation energy should not exceed the above values. The results are in good agreement with this concept.

It was found that the on-stream stability of the studied catalysts is fairly high. For these catalysts, in the catalytic conversion of propane, the on-stream time without any change in activity was 400 h at temperatures of up to 873 K and 150 h in a temperature

range of 873–1023 K. However, an increase in temperature above 1123 K led to an almost complete deactivation of the catalysts within 5 h (Fig. 5).

Up to a temperature of 873 K, the amount of carbon after 400 h on stream was about 5 wt % with respect to the loaded catalyst, whereas at 1123 K, after 5 h on stream, the carbon content was 59 wt %.

The removal of the formed carbon with an air stream at 923 K for 10 h leads to the complete restoration of the catalytic activity.

Thus, aerogel composite catalyst systems based on alumina impregnated with titania or silica are an amorphous aerogel with tangled 6-nm thick fibers. The laced structure provides an increase in the permeability of the reagents to the catalytic sites. Catalysts of this type have a developed specific surface area of about 300 m²/g and contain 0.2–0.6 mmol/g of acid sites.

The catalytic activity and olefin selectivity of the synthesized nanofibrous aerogel catalysts in the propane cracking reaction have been determined. The effect of the modification of alumina with titania and silica on the catalytic activity and olefin selectivity of the catalysts in propane cracking at atmospheric pressure has been first shown. The nanofibrous aerogel composite catalysts exhibit a high olefin selectivity at a total olefin selectivity of up to 90%. The stability of the catalysts and the possibility of their regeneration as a

Fig. 4. Temperature dependence of propane conversion: (1) without a catalyst, (2) Al_2O_3 , (3) TiO_2/Al_2O_3 , and (4) SiO_2/Al_2O_3 .

Catalyst	Temperature, K	Propane conversion, %		Selectivity, %		
			CH ₄	C_2H_4	C_2H_6	C ₃ H ₆
In the absence	723	0.1	92	8	_	_
of a catalyst	823	1.2	65	27	8	_
	923	2.1	37	19	31	13
	1023	9.0	18	19	8	55
	1123	39.2	11	28	5	56
Al ₂ O ₃	723	0.3	94	6	_	_
	823	1.0	67	17	8	8
	923	2.3	37	20	14	29
	1023	9.5	17	16	14	53
	1123	79.1	6	25	6	63
TiO ₂ /Al ₂ O ₃	723	1.7	80	12	8	_
	823	2.7	64	28	8	_
	923	3.5	55	11	6	28
	1023	48.0	15	29	9	47
	1123	85.0	23	52	7	18
SiO ₂ /Al ₂ O ₃	723	0.1	48	52	_	_
	823	0.89	20	58	22	_
	923	19.7	8	26	2	64
	1023	60.7	13	36	5	46
	1123	94.2	25	53	7	15

Table 3. Effect of temperature on the product selectivity in propane conversion

function of the contact time and temperature have been studied. The on-stream time of nanofibrous and nanocrystalline aerogel catalysts without any loss of catalytic activity is 150–400 h depending on the operating temperature. It has been found that these catalysts can be regenerated with an air stream.

Fig. 5. Dependence of the catalyst activity on the time and temperature of the test: (a) Al_2O_3 , (b) TiO_2/Al_2O_3 , and (c) SiO_2/Al_2O_3 .

Catalyst	Temperature, K	$E_{\rm a}$, kJ/mol
Without a catalyst	823-1123	143
Al ₂ O ₃	823-1123	105
TiO ₂ /Al ₂ O ₃	673–1123	85
SiO ₂ /Al ₂ O ₃	673–1123	95

Table 4. Activation energy for propane conversion, kJ/mol

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