Role of Silica–Alumina Catalyst Texture
in the Reaction of Propane Oxidative Dehydrogenation
in the Presence of Sulfur Dioxide

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Abstract—The effects of preparation conditions, component ratio, and pretreatment temperature (1000–1550°C) of silica–alumina samples on their phase composition, texture characteristics, and catalytic properties are studied in the reaction of the oxidative dehydrogenation of propane by sulfur dioxide. It is shown that the samples contain individual silicon and aluminum oxides. The product of their interaction (mullite) is formed only at 1550°C. Mesoporous and macroporous catalysts with mono- and polydispersed pore distributions over sizes are obtained. It is found that the porous structure of the catalyst plays a key role in the process of the oxidative dehydrogenation of propane in the presence of sulfur dioxide at 600–700°C. The apparent rate of propylene formation increases with an increase in the pore volume with radii between 10 and 100 nm. Propane is transformed into propylene more selectively on the catalyst where the pores with radii of 10–100 nm dominate; narrower pores (< 10 nm) are favorable for the formation of coke and complete oxidation products.

INTRODUCTION

It is known [1, 2] that, in the process of propane oxidative dehydrogenation by sulfur dioxide on carbon, the formation of oxidative condensation products (OCP) containing C, H, O, and S is observed. These products are themselves more catalytically active toward propylene formation than initial catalysts. The properties OCP depend on the nature of oxide: OCP/Al_2O_3 is more active toward propane conversion than OCP/SiO_2, but the latter are more selective toward propylene [1]. Therefore, silica–alumina composites are possibly able to provide a more efficient combination of desired properties.

The goal of this work is the study of the effects of the preparation procedure, component ratio, and the aluminum-silicon catalyst treatment temperature on the reaction of propane oxidative dehydrogenation to propylene in the presence of sulfur dioxide.

EXPERIMENTAL

Silica–alumina catalysts were prepared by wet mixing of initial reactants in the desired ratio at a desired wetness with the further formation in tubes with a diameter of 2.8–3.0 mm and a length of 4–5 mm, drying at 110°C for 12 h, and calcination at 1000–1550°C. Four series of samples were prepared, which differed in the nature of aluminum-containing material: (I) pseudoboehmite aluminum hydroxide, (II) a mixture of pseudoboehmite and hydrargillite aluminum hydroxides, (III) thermochemically activated hydrargillite, which is an amorphous mixture of hydrargillite and boehmite, and (IV) alumina prepared by the plasmo-

chemical method (a mixture of α-Al_2O_3 (3–5%) plasmochemical alumina (Al_2O_{3plasm}) with a disordered lattice close to δ-Al_2O_3). According to the electron microscopic data, this oxide consists of the particles with sizes varying over wide ranges from several fractions to several tens of micrometers. The particles differed in the shapes—from globular to spherical. As a silicon-containing material, we used aerosil A-175.

Catalysts were analyzed for the concentrations of silicon and aluminum according to the procedure described in [3]. X-ray phase analyses of the samples were carried out using an HZG-4C diffractometer and CuK_α monochromatic irradiation. The specific surface area of the samples were determined by the method argon thermal desorption [4] with an accuracy of ±10%. The porosity was measured before and after the reaction by the method of mercury porosimetry using a Pore Sizer 9300 instrument. To exclude the effect of capillary condensation between 0.5–1.0-mm granules in spent catalysts samples, the pores with sizes larger than 10 000 nm were excluded from consideration. The amounts OCP were determined by an increase in the sample weight.

The catalytic properties of samples in propane oxidative dehydrogenation to propylene in the presence of sulfur dioxide were studied in a flow setup at an atmospheric pressure at 600–700°C and a contact time of τ = 10 s. A reaction mixture containing 10 vol % C_3H_8, 10, 10 vol % SO_2, and 80 vol % He passed through a catalyst bed with 0.5–1.0-mm granules and a total volume of 1 cm^3 placed into a quartz reactor (an inner diameter of 3.5 mm and a reaction zone volume of 2.6 cm^3). To diminish the contribution from homogeneous reac-

Table 1. Effect of preparation procedure and phase composition of silica–alumina samples

Sample	Series	SiO$_2$ concentration, mol %	T_{tret}, °C	Phase composition		
				Al$_2$O$_3$	SiO$_2$	Si$_2$Al$_6$O$_{13}$
1	I	19	1000	δ, α (10%)	Amorphous	–
2	I	"	1250	δ, α (40%)	Amorphous	–
3	I	"	"	δ, α (48%)	Amorphous	–
4	II	"	"	δ, α (45%)	α-Cristobalite	–
5	II	"	"	δ, α (42%)	α-Cristobalite	–
6	I	"	1550	α	–	+
7	I	"	"	α	–	+
8	III	"	"	α	–	+
9	III	"	"	α	–	+
10	IV	10	1000	δ-like, α (10%)	Amorphous	–
11	IV	19	"	δ-like, α (5%)	Amorphous	–
12	IV	36	"	δ-like, α (3%)	Amorphous	–
13	IV	19	"	δ-like, α (6%)	Amorphous	–
14	IV	19	1250	δ-like, α (65%)	α-Cristobalite	–

tions, the empty volume of the reactor was packed with quartz glass (0.25–0.5-m fraction) [5]. The compositions of the initial mixture and reaction products were analyzed by chromatography.

RESULTS AND DISCUSSION

Phase composition. According to X-ray phase analysis data described in Table 1, silica–alumina samples contain alumina and silica, as well as the product of their interaction, mullite. The amounts of these phases are determined by the nature of aluminum-containing starting material, component ratio, and treatment temperature (T_{treat}). Alumina in the samples calcined at 1000°C are mainly in the form of δ-Al$_2$O$_3$ and δ-Al$_2$O$_3$-like, and α-Al$_2$O$_3$ (small amount) phases. An increase in the calcination temperature changes the ratio of phases and increases the concentration of α-Al$_2$O$_3$. Upon calcination at 1550°C, alumina is only present in the form of the α-phase. Silicon dioxide is present in all samples calcined at 1000°C in the X-ray amorphous state. With an increase in the treatment temperature to 1250°C, silica is crystallized to form α-cristobalite in the samples of series II and IV. In the samples of series I, silica remains in the amorphous state. Upon calcination at 1550°C, silicon dioxide is absent. It is known that the stable phase of α-cristobalite is formed by the treatment of pure silica gel only at 1470°C [6]. The appearance of SiO$_2$ at 1250°C in the series II and IV is associated with the presence of sodium oxide in the starting material. Sodium oxide accelerates polymorphous transformations of silica. Mullite (Si$_2$Al$_6$O$_{13}$) is formed only after calcination at 1550°C, independently of the nature of aluminum-containing starting material used in the sample preparation.

Textural characteristics of samples. Together with phase transformations, samples change their specific surface areas and pore structures. The specific surface area decreases with an increase in the treatment temperatures and with the replacement of aluminum hydroxide (series I) by alumina (series IV) (Table 2).

Because the pore structures of the compositions obtained by the method of wet mixing may include pores of three types (pores of initial species, pores formed by a "binding agent", and pores between particles [7]), the pore size distribution can be changed by changing the nature of the initial aluminum-containing material. Indeed, Tables 1 and 2 show that the pore size distribution does depend on the nature of a starting material and their treatment temperature. We obtained the samples characterized by different meso- and macropore structures with mono- and polydispersed distributions of pore sizes. In the process of propane oxidative dehydrogenation, the products of oxidative condensation are deposited on the catalyst surface (Table 2). After the reaction, their amount ranges from 1.4 to 34 wt % after 6 h depending on the sample. The deposition of OCP depends on the initial specific surface area and pore volume: at a specific surface area of 34 and 3 m^2/g (samples 3–5), the amount of coke is 6.5–26 wt %; an increase in the pore volume by a factor of ~4 (samples 1 and 13) does not change the amount of OCP (21 wt %). It was shown earlier [8] that, on silica–alumina samples, coke is formed on certain surface sites, which are OH groups attached to silicon. The choice of the a starting material, as well as changing the concentration of SiO$_2$ and catalyst treatment temperature, change the concentration of these OH groups, and hence, the amount of OCP. On the samples calcined at 1550°C, the concentration of surface OH groups is

Table 2. Textural characteristics of the samples before and after 6-h service under the conditions of propane oxidative dehydrogenation reaction

Sample	Series	S_{sp}, m²/g before	S_{sp}, m²/g after	V, cm³/g before	V, cm³/g after	OCP concentration, wt %	4–10 nm before	4–10 nm after	10–100 nm before	10–100 nm after	100–1000 nm before	100–1000 nm after	>1000 nm before	>1000 nm after
1	I	180	105	0.53	0.400	21	0.53	0.354	0	0.029	0	0	0	0.017
2	I	49	39	0.30	0.171	34	0.2	0.089	0.1	0.060	0	0.001	0	0.021
3	I	31	28	0.24	0.267	6.5	0	0.027	0.24	0.236	0	0	0	0.004
4	II	34	30	0.48	0.282	26	0.18	0.067	0.21	0.139	0.09	0.050	0	0.027
5	II	36	27	0.77	0.332	22	0.05	0.045	0.22	0.186	0.11	0.044	0.39	0.056
6	I	5	7	0.28	0.192	2.3	0	0.003	0.28	0.161	0	0.025	0	0.004
7	I	5	8	0.20	0.247	2.2	0	0.002	0.2	0.220	0	0.013	0	0.013
8	III	4	5	0.32	0.288	1.4	0	0.002	0.03	0.078	0.29	0.197	0	0.012
9	III	2	7	0.40	0.359	1.5	0	0.014	0.01	0.037	0.39	0.187	0	0.121
10	IV	83	–	1.14	–	–	0.15	–	0.43	–	0.49	–	0.07	–
11	IV	47	38	1.58	1.162	–	0.19	0.045	0.47	0.428	0.59	0.583	0.33	0.106
12	IV	70	–	1.40	–	–	0.13	–	0.92	–	0.32	–	0.03	–
13	IV	66	54	1.93	1.112	21	0.17	0.058	0.85	0.556	0.66	0.415	0.25	0.084
14	IV	16	–	1.81	–	–	0.2	–	0.43	–	0.87	–	0.31	–

much lower than in the samples calcined at a lower temperature. The amount of OCP is lower by an order of magnitude on the former samples (samples 6–9).

Coke deposits change the textural characteristics of silica–alumina samples (Table 2). The specific surface area of silica–alumina samples calcined at 1000–1250°C decreases during the reaction, and a decrease in S_{sp} depends on the sample series. The specific surface area of samples calcined at 1550°C increases by a factor of ~1.4–3. With some exceptions, the overall pore volume of silica–alumina samples also decreases after 6 h of catalyst service. Simultaneously, the pore size distribution changes (Table 2): all samples reveal polydispersed distribution of pores over sizes. This fact suggests that OCP substantially affect the textural properties of the samples. The maximal decrease in the overall pore volume, which is probably due to site blocking by OCP, is observed in the samples containing thin pores with radii from 4 to 10 nm.

Catalytic properties of samples. It is known that at high temperatures, the oxidation of propane can occur via heterogeneous, heterogeneous–homogeneous, and homogeneous mechanisms, depending on the reaction conditions and catalyst nature. Changes in the volume of the reaction zone and the catalyst-free volume of the reactor [5] allowed us to determine conditions at which the contribution of the homogeneous process is minimal. Table 3 shows that the propane conversion x is very small in the absence of the catalyst even if the conditions are optimal. Therefore, we neglected the homogeneous component of the process.

In the study of solid catalysts, the reaction rate is usually a specific value that refers to the unit surface area [9]. However, it was found recently that the specific catalyst activity in a number of reactions occurring via a heterogeneous–homogeneous mechanism is basically determined by the value of the total surface area if a series of similar catalysts are considered. The specific activity is describable by the law $r_{sp} = A/(1 + BS)$, where S is the total surface area, A and B are the constants [10, 11]. Figure 1 shows the dependence of the apparent specific rate of propane conversion in the reaction of propane oxidative dehydrogenation at 640 and 700°C. The specific activity of the samples is inversely proportional to the total surface area and agrees well with the above regularities. At 600 and 550°C, no such regularities were observed. Therefore, the homogeneous component of the reaction is absent. Process acceleration due to the chain reaction at a higher temperature and its transfer to the pore volume should correlate with the value of the free volume inside the catalyst. The catalysts with a higher surface area usually have pores with larger diameters, and the radical decay on the surface should dominate over chain propagation in the pore volume. Taking into account the above law, we further considered the reaction rate relatively to a sample weight in further studies of the effects of the size and volume of pores on the catalyst activity and selectivity.

Propane oxidative dehydrogenation by sulfur dioxide at 600–700°C over the catalysts under study occurs via a complicated heterogeneous–homogeneous mechanism. This reaction is accompanied by the formation

of a series of products: C_3H_8 transforms into C_3H_6, C_2H_6, C_2H_4, CH_4, CO, CO_2, and coke; SO_2 transforms into H_2S, H_2O, and S. Table 3 shows how the catalytic properties of samples with the same composition change depending on the pore structure. Samples 1, 7, and 8 have a monodispersed pore structure with dominant pore radii of 7, 80, and 200 nm, respectively. Sample 11 has a polydispersed pore distribution over sizes depending on the reaction temperature and contact time during the initial period of the reaction. It is seen that the pore structure of the samples affects the reaction direction at different temperatures. Sample 1 with fine pores differs from the others in its behavior. At 600–700°C, it forms the maximal amount of carbon oxides and coke (the lowest balance with respect to carbon is observed). With an increase in the reaction temperature, falls the yield of propylene to zero at 700°C. The main products formed on samples 7 and 8 at 600 and 640°C are propylene and ethylene. At 700°C, the selectivity to propylene decreases and the yields of ethylene, methane and CO increases. Sample 11 has polydispersed pore-size distribution over sizes. The selectivity to propylene is maximal at 640°C. The yields of ethylene, methane, and CO are higher at 700°C. At 600°C, carbon oxides are the main products of the reaction. A decrease in the contact time leads to a substantial decrease in the conversion of propane. The selectivity to olefins increases. We may assume that the process of propane oxidative dehydrogenation is accompanied by
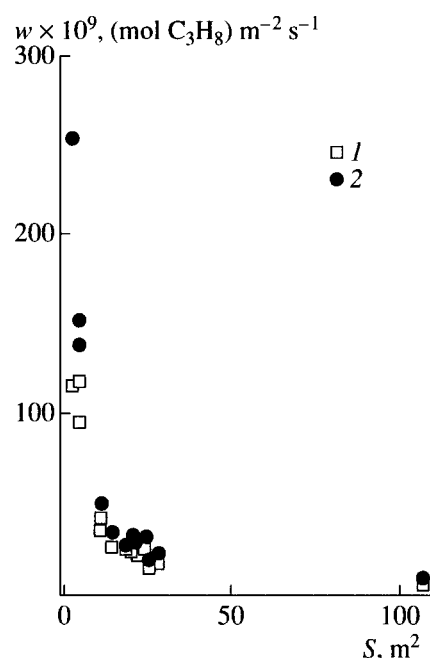

Fig. 1. Specific rate of propane conversion (at x = 60–70%) vs. total catalyst surface area during the initial period of catalyst service at (*1*) 640 and (*2*) 700°C.

dehydrogenation, cracking, coke formation, and complete oxidation. The presence of pores with $r < 10$ nm is favorable for coking and oxidation. Pores with r = 10–100 nm and possibly pores with r = 100–1000 nm

Table 3. Catalytic properties of silica–alumina samples with various porous structures

Sample	T, °C	τ, s	x, %	Selectivity, %						Carbon balance*
				C_3H_6	C_2H_4	C_2H_6	CH_4	CO	CO_2	
1	600	10	51.9	30.5	4.2	0.3	6.8	16.1	42	55
	640	"	72.8	15.5	11.2	1.2	15.4	26.2	30.9	48
	700	"	100	–	4.1	6.7	31.7	13.7	45.8	38
7	600	10	31.6	63.7	10.6	–	5.9	0.6	7.9	76
	640	"	59.6	61.4	14.2	–	6.8	4.7	9.6	82
	700	"	86.7	47.6	25.5	0.9	14.2	1.3	11.7	74
8	600	10	35.2	58.6	7.2	–	2.2	7.3	14.5	71
	640	"	65	63.7	13.4	–	7	4.2	5.5	78
	700	"	91.5	34.1	18.8	1.7	19.8	8.0	18.3	63
11	600	10	54.7	39.8	3.3	–	1.8	7.2	32.6	85
	640	10	69.3	54.7	18.5	–	9.7	8.2	8.9	76
	640	5	30.7	63.8	22.9	–	7.5	3.2	4.2	84
	640	2.5	19.5	63.9	23.1	–	11.5	1.9	4.2	85
	700	10	98.9	35.9	31.6	3.0	24.8	15.0	7.2	75
Without a catalyst**	600	–	~0.5	64	13	–	6	–	16	98
	640	–	2.2	53.9	16.8	–	9.7	–	13.5	95
	700	–	4.8	40.6	28.3	–	15.9	–	9.1	93

* Carbon balance was calculated from the gaseous products.

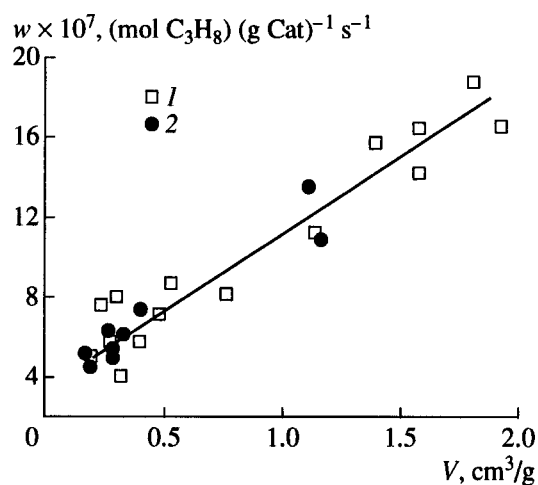** Reactor was filled with quartz glass particles with diameters of 0.25–0.5 mm.

$w \times 10^7$, (mol C_3H_8) (g Cat)$^{-1}$ s^{-1}

Fig. 2. Apparent propane conversion rate (at $x = 60$–70%) vs. total pore volume (*1*) during the initial period of catalyst service and (*2*) after 6 h at 640°C.
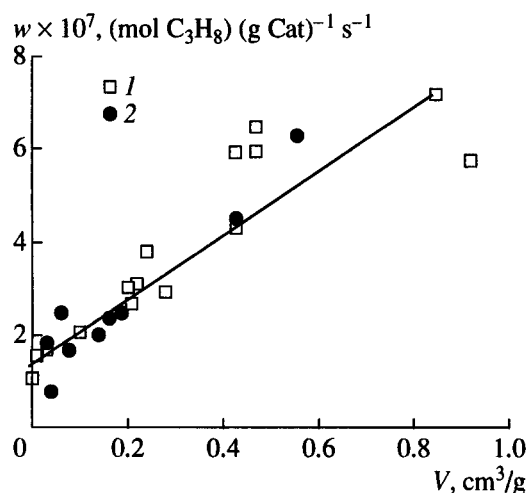
$w \times 10^7$, (mol C_3H_8) (g Cat)$^{-1}$ s^{-1}

Fig. 3. Apparent rate of propylene formation (at $x = 60$–70%) vs. volume of pores with $r = 10$–100 nm at 640°C (*1*) during the initial period of catalyst service and (*2*) after 6 h.

are optimal for the formation of propylene and ethylene, whereas large transport pores does not play a critical role in the process under consideration.

Earlier, Demidov *et al.* [12] that the propane conversion and the selectivity to propylene in the process of propane oxidative dehydrogenation increase for 3–5 h. Demidov *et al.* associated this phenomenon with the accumulation of OCP. During the further 70–80 h, the activity and selectivity remained the same. The catalyst deactivation after 100 h was explained by a decrease in the volume of mesopores with $r = 10$–1000 nm. Taking these data into account, we studied the catalytic properties of silica–alumina samples with different textural characteristics at early stages of the reaction and after 6-h service at 640°C and $\tau = 10$ s. We found that, at the initial period, the conversion of propane and the selectivity to propylene are independent of the phase compo-

sition, conditions for sample preparation, and SiO_2 concentration. They only depend on the pore structure. Figure 2 shows that the higher the overall sample volume, the higher the rate of propane conversion. The apparent rate of propylene formation (Fig. 3) increases with an increase in the pore volume with $r = 10$–100 nm. After 6 h of the catalyst service, coke is formed on the surface in an amount of 1.4–34 wt % (Table 2) and changes the specific surface area, total pore volume, and their distribution over sizes. As this takes place, the dependence of the propane conversion rate and propylene yield on the pore volume does not change (Figs. 2 and 3). Thus, during the reaction, the overall pore volume decreases (sample 1). The volume of pores with 10–100 nm increases (Table 2). Correspondingly, the apparent rate of propane conversion after 6-h catalyst service decreases from 8.73×10^{-7} to 7.42×10^{-7} (mol C_3H_8) (g Cat)$^{-1}$ s^{-1}, and the apparent rate of propylene formation increases from 1.06×10^{-7} to 1.82×10^{-7} (mol C_3H_6) (g Cat)$^{-1}$ s^{-1}. The apparent rates of methane and ethylene formation change likewise. In this experiment, we did not observe correlations between the amount of coke deposited for 6 h and catalytic properties (activity and selectivity) of silica–alumina samples.

Thus, in this work we showed that the pore structure of the catalyst plays a key role in the process of propane oxidative dehydrogenation in the presence of sulfur dioxide at 600–700°C. The nature of pore distribution over sizes affects the process direction at different temperatures. Specifically, at 640°C, propane transforms into propylene more selectively in pores with $r = 10$–100 nm. Finer pores with $r < 10$ nm are favorable for the formation of coke and oxidation products. The above regularities are explainable by the fact that, in the case of a heterogeneous–homogeneous mechanism of the reaction, the portion of chemical transformations in the gas phase increases with an increase in temperature. A similar effect of pore diameter on the activity and selectivity of the catalysts was observed for methane oxidative coupling [13]. On the catalysts with pore diameters smaller than 20–50 nm (which is lower than the free path of reacting molecules), Knudsen diffusion regime was observed, and a decrease in the activity was associated with the decay of active methyl radicals in the catalyst pores. The use of the catalysts with fine pores in propane oxidative dehydrogenation leads to the retarded diffusion of initial reactants and products. An increase in the number of collisions between intermediate species in the pore volume and on the surface probably results in an increase in the rate of their oxidation into carbon oxides and olefin conversion into coke.

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