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The effect of the catalytic layer design on oxidative dehydrogenation of propane over monoliths at short contact times

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Abstract

Main factors determining performance of straight channel corundum monolith supported catalysts in the autothermal reaction of propane oxidative dehydrogenation at short contact times are verified. It was made possible by using a unique design of the catalytic reactor which allows an independent tuning of the gas preheat temperature and the catalyst temperature. It is also equipped with a cooled sampler to cut any homogeneous reactions after the catalyst layer. The effects of the front and back thermal shields, feed rate, relative contact time and the void space between the catalytic monoliths or after them are elucidated. The performance of the monolithic catalyst is compared with that crushed and packed into a granulated layer. A substantial impact of the homogeneous gas-phase reactions on the propane conversion and product selectivities is demonstrated. In turn, their share depends upon the longitudinal temperature gradient within the monolithic layer as determined by the heat generation in the inlet part due to propane combustion by oxygen, its transfer along the monolith layer and consumption in the rear part of the monolith in the absence of oxygen through endothermic reactions of dehydrogenation, cracking and steam reforming. In the autothermal mode of the propane oxidative dehydrogenation at short contact times on monolithic catalysts, the effect of those factors is as important as that of the catalyst and feed chemical composition.

Keywords: Propane oxidative dehydrogenation; Short contact times; Monolithic corundum supported catalysts; Catalytic layer design; Gas-phase reactions and heat transfer

1. Introduction

The autothermal oxidative dehydrogenation of paraffins at short contact times over Pt-supported monolithic catalysts was recently shown to be quite efficient in the olefins, especially ethylene, production [1–6]. For the propane oxidative dehydrogenation, the propylene yields are not sufficiently high to satisfy demands of the industrial catalytic processes due to propylene cracking into ethylene and methane [7]. Tuning the chemical composition of supported monolithic honeycomb catalyst and the feed composition was shown to improve propylene selectivity and yield as compared with earlier reported values [8,9]. For reactor scale-up, the problem of the catalytic layer configuration affecting the mass and heat transfer must be dealt with as well. Furthermore, homogeneous or surface-enhanced homogeneous reactions are expected to appreciably affect the propylene yield. However, these questions were earlier not addressed properly for the case of experiments conducted with monolithic catalysts operating at short contact times in the autothermal mode. Hence, the present research aims primarily at filling these gaps in fundamentals of propane oxidative dehydrogenation at short contact times on honeycomb corundum monolith supported catalysts with active components based upon platinum–tin or complex framework zirconium phosphates containing Co or Mn.

2. Experimental

2.1. Catalysts preparation

As supports, proprietary corundum monoliths with wall thickness 0.25 mm and channel sizes ca. 1 mm with specific surface area in the range of 5–10 m^2/g annealed at 1300 °C were used.

The platinum–tin containing catalysts with 2–3 wt.% platinum loading and the Pt:Sn ratio equal to 1:5 were prepared as in [8].

To prepare sols of complex phosphates of zirconium and Co (Mn) corresponding to the formula $M_xZr_4(PO_4)_6$ ($x =$ 1, 2), a stoichiometric amount of cobalt (manganese) nitrate was added to 1 M solution of $ZrOCl_2$ and this mixture was

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titrated with the dropwise addition of a stoichiometric volume of the 1 M $(NH_4)_2HPO_4$ while the solution was constantly stirred. Corundum micromonoliths were impregnated by these sols and then purged by compressed air to remove their excess capable to plug the channels. Catalysts were calcined at 900 °C, phosphate content was ∼2 wt.%. Then some samples were impregnated with aqueous solutions of H_2PtCl_6 (Pt loading ∼0.5 wt.%) and calcined at 700 °C.

2.2. Experimental set-up

A proprietary tubular reactor (Fig. 1) was used to test the monolithic catalysts. The construction of the reactor allows to independently tune the gas preheat temperature and the catalyst temperature using two heaters (Fig. 1). The first heater ensures the feed stream preheat to desired temperatures (usually around 300 °C). The second heater was used to compensate the heat losses from the catalyst, and, hence, to independently control the catalyst temperature measured at the end of the catalytic monolith by a thermocouple inserted into the plugged monolith channel (T_{cat}). For tuning the longitudinal temperature profile, in some experiments the reactor was additionally equipped with a heat exchanger allowing to cool the rear part of the monolithic catalyst. To take probes of the gas phase immediately after the catalyst (or at any required distance from the catalytic monolith), a specially designed tube sampler kept at a constant temperature to prevent the water condensation and cut any homogeneous post-catalyst reactions was used. In some experiments, the reactor was modified by inserting into it a water-cooled metallic heat exchanger as a support for the monolithic piece thus, ensuring an efficient heat removal from the rear part of the catalyst.

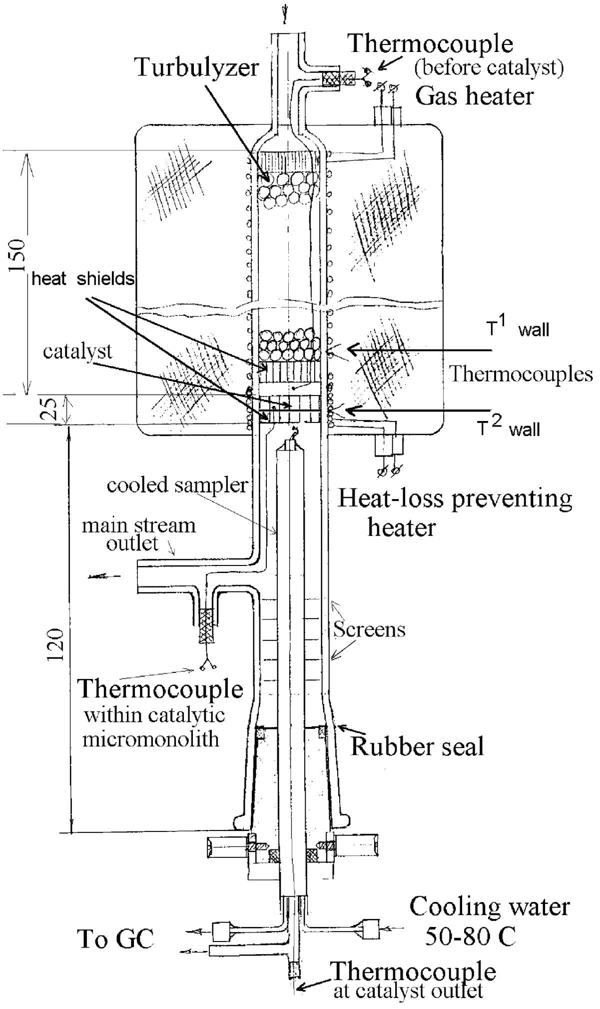

Fig. 1. The scheme of the tubular reactor.

The pieces of monolithic catalysts with diameters ca. 16 mm and thickness in the range of 2–13 mm wrapped in a silica-alumina fiber cloth for insulation and preventing the reactants bypass were placed into the quartz reactor. To minimize the heat loss, a piece of the catalytic monolith was usually placed between two heat shields made of mullite covered corundum monolithic support. This catalytic layer configuration can operate in the autothermal regime without any electrical current fed into the heating coils. In experiments conducted without the back heat shield, to cut heat losses thus keeping the autothermal regime, the probe sampler was additionally insulated by wrapping it into a ceramic fiber cloth.

To clarify the difference in performance of monolithic and granular catalysts, the same catalyst was tested as a thin-wall micromonolith and that crushed into small pieces. The testing of a crushed monolith was carried out as follows. To facilitate the assembling, a quartz ring was placed onto the back thermal shield and filled with the catalyst fraction of 0.25–0.50 mm. At the same weight, the fraction volume was only slightly (ca. 14%) bigger than that of the monolith. To prevent the gas slip between the quartz ring and the reactor wall, the ring was sealed by tightly packing a ceramic wool in that slit.

To study the role of the gas-phase reactions, the distance between the cooled sampler and the monolith end was varied from 2 to 18 mm, and the distance between two monolithic pieces placed into the reactor was changed by inserting between them the quartz rings of 4 and 8 mm length.

A feed mixture composition was controlled by using the automatic flow-meters and corresponding gas mixing devices. The feed flow rate was 5–100 L (STP) per hour (corresponding contact times were 0.03–0.8 s). The C_3H_6/O_2 ratio was varied from 1 to 2 at a nitrogen dilution of 40–60%. For tuning the feed composition, water, carbon dioxide, carbon monoxide, and hydrogen were added. The inlet and outlet gas compositions were analyzed by GC (columns with alumina, NaX, carbon) using specially designed computer programs. To estimate the components concentrations but H_2O, standards were used, while the water content was derived from the oxygen balance. The conversion and selectivity data presented in this work were calculated on the carbon or hydrogen atoms basis. Within the GC analysis uncertainty (±10%), the carbon balance was usually closed. In the most experiments, the oxygen was completely consumed at the catalyst.

Before runs, Pt-Sn based catalysts were reduced at 700 °C for 2 h in hydrogen, cooled in nitrogen to 300–350 °C, and then a reaction mixture was fed to the reactor. All other catalysts were not specially pretreated. All tested catalysts were kept at least 1 h in the reaction mixture before starting the outlet reaction mixture analysis.

3. Results and discussion

3.1. The role of the front and back heat shields

The impact of the back heat shield was studied with the Pt-Sn catalyst containing 3% Pt. The catalyst monoliths of 2 and 12.5 mm length were tested with and without the back shield. The length of the front shield was 2 mm, and that of the back shield was 5 mm. The results are presented in Table 1.

One can see that the effect of adding a back heat shield depends on the length of the monolith. In the case of a long monolith only CO_x selectivity somewhat increases correlating with the increase of the rear part temperature. It suggests that propane conversion within the long monolithic piece is only slightly affected by the back shield, which can be explained by a rather poor heat transfer along thin corundum walls.

For the short piece, addition of the back shield increases methane, ethylene and propylene selectivities whereas CO_x selectivities decline (CO selectivity remains nearly constant, while the carbon dioxide yield decreases). Note that in this case, the catalyst end temperature decreases while it is expected to increase due to a lower heat loss. It suggests that a part of propane is converted within the back heat shield via some endothermic reactions such as propane cracking, steam reforming of olefins or reaction of the surface carbon with carbon dioxide and water. The occurrence of the latter reactions is supported by the back heat shield blackening, though even after tens of hours operation in the reaction mixture, no channels plugging by carbon was revealed. Hence, the thickness of the surface carbon layer is determined by a ratio of the carbon deposition rate due to a hydrocarbons cracking and a rate of its removal through gasification reactions. The back heat shield also favors the propylene cracking, and this trend is expected to be more pronounced at higher operation temperatures.

The role of the front heat shield was studied for 2% $Mn_2Zr_4(PO_4)_6/\alpha\text{-}Al_2O_3$catalyst. The data presented in Table 2 show that the front heat shield improves the catalyst performance. In the absence of the front shield the propane and oxygen conversion decreases though the catalyst temperature measured at the end of monolith is somewhat higher (compare data at the same feed rate). At the feed rate of 90 l/h, without the front shield, the outlet gas temperature is higher than the catalyst temperature due to the gas phase propane deep oxidation reaction proceeding in the space after monolith. A high outlet gas temperature and low propane and oxygen conversions suggest that without the front thermal shield the temperature gradient along the monolith changes and its maximum shifts to the end of monolith. It is clearly explained by the incomplete conversion of oxygen, hence, the process of propane deep oxidation proceeds not only at the inlet part of the monolith, but along all its length. Therefore, the front shield helps to locate the high-temperature zone of oxygen consumption within the narrow inlet part of the catalyst, thus, allowing to increase propane conversion and olefins yield. The same effect is achieved under addition heating of the catalyst bed (Table 2).

Thus, it may be concluded that an effective catalyst bed should have a front shield to prevent the heat losses by radiation, and no back shield is required.

3.2. The effect of the heat generation and transfer along the monolith

For the catalytic layer configuration including both front and back thermal shields, in the experiments carried out in the autothermal mode (after the reaction ignition, both heating coils were switched off), the propane conversion increases with the decrease of contact time (Fig. 2A). This feature is certainly not met for any catalytic reaction occurring in the isothermal conditions. In the autothermal mode, the higher is the feed rate (lower contact time), the higher is the amount of heat produced by the catalytic reaction, and, hence, the catalyst temperature (Fig. 2B). As the result, for monoliths of a different length, propane conversion

Table 1
Performance of the monolithic Pt-Sn catalyst with and without the back shield

Type of bed	τ (s)	T_{cat} (C)	X_{pr} (%)	S_{CH_4} (%)	$S_{C_2H_4}$ (%)	$S_{C_3H_6}$ (%)	S_{CO} (%)	S_{CO_2} (%)
1	0.056	690	21	5.8	12.7	24.8	14.3	40.2
1	0.033	760	50	11.4	21.9	23.7	13.8	21.8
1[a]	0.056	770	22	1.4	4.6	18	13	62.6
1[a]	0.034	895	36	7.7	15.1	23	19.6	31
2	0.094	735	59	11	24	22.7	14.6	25
2[a]	0.094	700	58	11.6	25	21	12.9	21.4

Note: 1, the catalyst of 2 mm length; 2, 12.5 mm. The reaction mixture composition, propane:oxygen is equal to 1:1 in 60% N_2.

[a] No back shield.

Table 2
Effect of the front heat shield on performance of 2% $Mn_2Zr_4(PO_4)_6/\alpha\text{-}Al_2O_3$ monolithic catalyst (11 mm length)[a]

V (l/h)	T_{cat} (°C)	T gas outlet (°C)	Conversion (%)		Selectivity (%)					Yield of olefins
			C_3H_8	O_2	CH_4	C_2H_4	C_3H_6	CO	CO_2	
90	810	730	66	99.3	18.2	34	26	8.3	6.2	39.6
70	770	680	62	99.6	15.4	34.4	26	8.9	9.5	37
45	700	610	50	99.5	12.6	32	29	14	8.2	30.5
90[b]	820	870	21	72	13.3	25.3	34	11.8	11.6	12.4
45[b]	720	640	32	98	11.4	30	30	13	12.7	19.3
45[b]	800[c]	765	66	99.7	19.5	32	24	10.6	8.4	36.5

Reaction mixture composition: C_3H_8, 30%; C_3H_8/O_2, 2.2; H_2, 20%; H_2O, 35%.

[a] The inlet gas temperature 500 °C.

[b] No shield.

[c] With heating of the catalyst bed.

is not a simple function of the contact time. For longer monoliths (length 7.5 and 12.5 mm), propane conversion is nearly independent of the contact time provided the back shield is installed. For the same contact time, the monolith temperature measured at its end tends to be lower for longer monoliths (Fig. 2B). Though for those monoliths propane conversion is nearly independent upon the contact time, some redistribution between the products is observed: at higher catalyst temperatures methane and ethylene selectivities are higher, while those of carbon dioxide and propylene—lower. Hence, for longer monoliths, heterogeneous endothermal reactions appear to be more probable.

For longer monoliths, the reaction mixture preheat was found to enhance the propane conversion and decrease the propylene selectivity, though the catalyst temperature measured at its end is lower than in the case of the autothermal regime. The feed preheat apparently changes the temperature profile along the monolithic piece, shifting the maximum of the temperature to the inlet part. An important role played by the temperature gradient in the oxidative dehydrogenation reactions at short contact times on monolithic catalysts was recently stressed by Schmidt and coworkers [10].

To decrease the catalyst overheating at the reactor outlet, the heat exchanger was found to be very efficient (Fig. 3). However, comparable values of propane conversions and

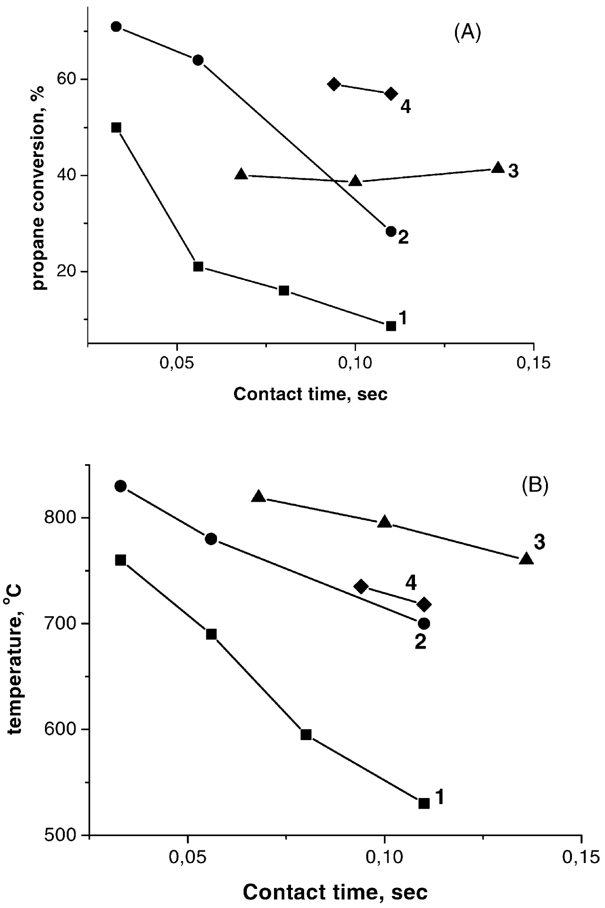

Fig. 2. Dependence of propane conversion (A) and catalyst temperature (B) on the contact time for monoliths 3% Pt + Sn (1:5)/α-Al_2O_3 of different length: 1–2 mm, 2–4 mm, 3–7.5 mm, 4–12.5 mm. Autothermal regime: C_3H_8 20%, O_2 20%, N_2 balance.

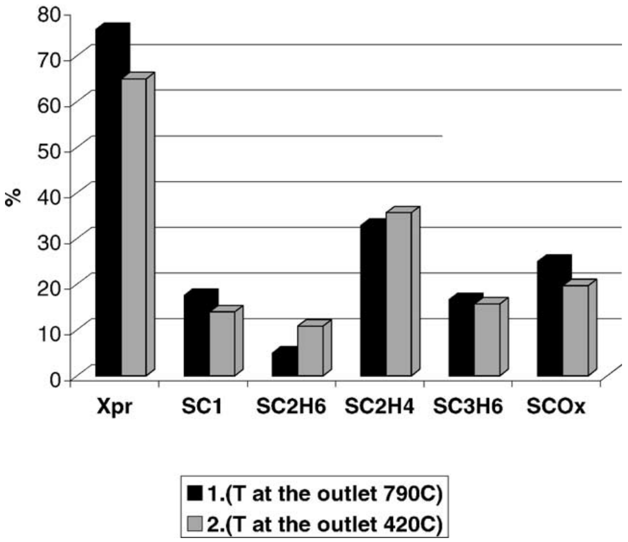

Fig. 3. The influence of the temperature profile along the catalyst layer (Pt + Ce-ZrO_x/α-Al_2O_3) on the propane conversion and product selectivities obtained in reactors without (1) and with (2) the heat exchanger at the catalyst outlet.

Table 3
Comparison between the performance of a catalyst fraction and a piece of a monolithic catalyst[a]

Sample	V (l/h)	τ (s)	T_{cat} (°C)	X_{pr} (%)	X_{O_2}	S_{CH_4}	$S_{C_2H_4}$	$S_{C_3H_6}$	S_{CO}	S_{CO_2}
Piece	20	0.085	730	33	94	8.9	15.9	25.06	14.2	33.1
	50	0.034	820	51.5	97	13.5	25.4	23.2	14.5	16.1
Fraction	28	0.085	730	15	44	8.2	22.5	35.1	7.6	24.1
	70	0.034	820	74	72	16	35	20	16	4.6

[a] Catalyst, 3% Pt + Sn (1:5)/Al_2O_3; catalyst weight, 0.5 g; the reaction mixture composition, C_3H_6:O_2 = 1:1, 60% N_2.

products selectivities in both types of reactors—with the heat exchanger or without it imply that those parameters are mainly determined by high temperatures developed in the inlet part of the monolithic layer.

3.3. *Effect of the catalyst shape (monolith or granulated layer) on its performance*

The data obtained for monolithic catalyst and that crushed into pieces and packed into the layer are compared in Table 3 and in Fig. 4.

As follows from the data presented in Table 3, at the same contact times, at 730 °C propane conversion is higher for a monolith, while the reverse is valid at 820 °C. In all cases, the oxygen conversion is higher for a monolithic piece, thus indicating a much higher oxygen slip for the catalyst fraction. Such a slip can be explained by the non-uniform packing inherent for a catalyst crushed into flat pieces. Because of a higher oxygen slip and because the void fraction of a crushed catalyst is even higher than in the monolith, it is evident that a share of homogeneous reactions is higher in the first case. Due to the oxygen slip, a part of homogeneous/heterogeneous reactions is expected to proceed within the back heat shield thus making the data analysis much more complicated and uncertain. In all cases, a sum of the carbon oxide selectivities is higher for the monolithic piece, hence, carbon oxides appear to be mainly produced via heterogeneous route, which agrees well with the known chemistry of the gas-phase oxidative propane dehydrogenation [11–15]. At lower temperatures and low conversion, the propylene selectivity is higher for the catalyst fraction. At higher temperature and higher propane conversion, propylene selectivity is lower for the fraction layer due to higher methane and ethylene selectivity. Hence, at higher temperatures and propane conversions, undesired thermal cracking in the gas phase or within the back heat shield is certainly more pronounced for the catalyst fraction (granulated catalyst bed in general). The results of Burch and Grabb [13] demonstrated that for non-catalytic oxidative dehydrogenation of propane, propylene selectivity rapidly declines with propane conversion, approaching the value around 2–3% at 70% conversion. This fall is due to propylene cracking into methane and ethylene. Hence, in our case, at high propane conversion within the granulated layer, homogeneous reactions appear to be responsible for this decline in propylene selectivity too, at least, in a degree comparable with that for the back heat shield.

3.4. *Impact of the gas-phase radical reactions*

3.4.1. *Experiments with different distances between the cooled sampler and the monolith exit*

The simplest way to assess the role of homogeneous reactions is to change the distance between the cooled

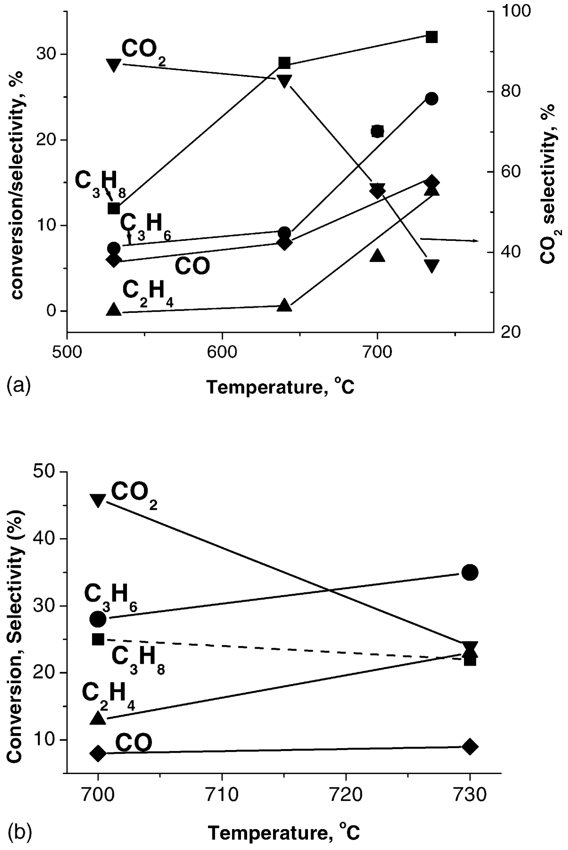

Fig. 4. (a) Temperature dependence of propane conversion and product selectivities for 2.5 mm monolith piece of the catalyst 3% Pt + Sn (1:5)/α-Al_2O_3 at 20 l/h feed velocity of 1:1 reaction mixture of propane and oxygen diluted by 80% of nitrogen: (■) propane conversion; selectivity, (●) propylene; (▲) ethylene; (◆) CO; (▼) CO_2. (b) Temperature dependence of propane conversion and product selectivities for the same monolithic piece crashed into fraction at 28 l/h feed velocity of 1:1 reaction mixture of propane and oxygen diluted by 80% of nitrogen: (■), propane conversion; selectivity: (●), propylene; (▲), ethylene; (◆), CO; (▼), CO_2.

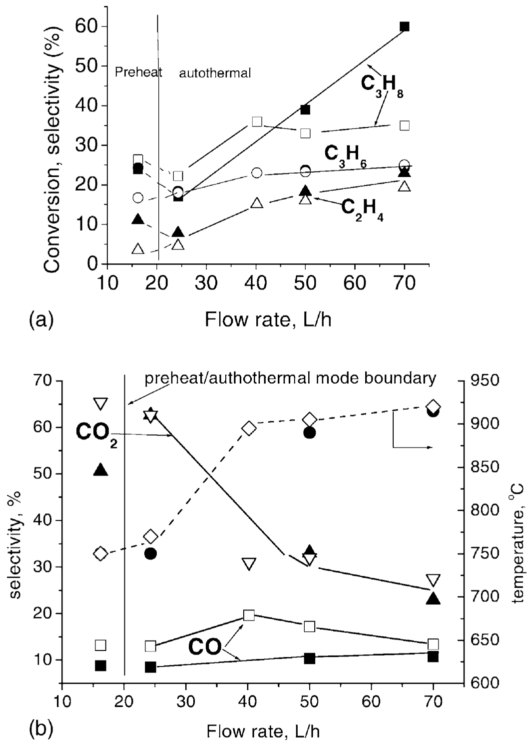

Fig. 5. (a) Propane conversion (■, □), propylene (●, ○) and ethylene (▲, △) selectivities vs. flow rate for experiments with 18 mm (solid) and 2 mm (open) distance between the monolith end and cooled sampler. Back heat shield is absent. Catalyst 3% Pt + Sn (1:5)/α-Al_2O_3, the reaction mixture composition—C_3H_6:O_2 = 1:1, 60% N_2. (b) Catalyst temperature (●, ◇), CO (■, □) and CO_2 (▲, ▽) selectivities for experiments with distances between the monolithic catalyst and cooled sampler equal to 2 mm (open) and 18 mm (solid).

sampler and the catalytic monolith provided back heat shield is absent. The results of these experiments are presented in Fig. 5. The catalyst containing 3% Pt + Sn (1:5)/α-Al_2O_3 with a length of 2 mm was used. Here, a cooled sampler was thermally insulated by the ceramic fiber cloth. As follows from these data, at a high flow rate, the propane conversion is certainly higher when the distance between the catalyst and the sampler is bigger. Hence, at gas temperatures in the range of 600–700 °C homogeneous reactions indeed proceed with the rates comparable to those of the heterogeneous ones. Somewhat lower propane conversion for experiments with 18 mm distance between the sampler and the catalytic monolith when the flow rates were low can be assigned to a lower gas temperature, while the catalyst temperatures were nearly identical. The most interesting fact is that for all products except CO selectivities were identical in both sets of experiments.

In general, propane/propylene cracking probability is determined by the relative abundance of *n*-propyl and secondary propyl radicals [16]. While the latter is rapidly converted into propylene by the hydrogen atom abstraction, the former is splitted into methyl radical and ethylene. Heterogeneous route favors formation of secondary propyl radicals due to lower C–H bond strength for central carbon atom, while homogeneous route mainly generates *n*-propyl radicals due to statistical reasons. The results obtained here suggest that for this catalyst, the relative selectivity of propane transformation into *n*-propyl and isopropyl radicals is nearly the same as for the gas-phase reaction. A lower CO selectivity is certainly explained by the absence of carbon gasification reactions for the homogeneous process.

Hence, the impact of homogeneous reactions on the process of propane oxidative dehydrogenation at short contact times is clearly demonstrated.

3.4.2. Experiments with an empty space between two parts of a monolithic catalyst

The results of experiments with separated into two pieces catalytic monoliths are presented in Fig. 6. At low feed rates, the process could not be kept in the autothermal mode, so the feed was preheated. For all feed rates, when the distance between the monolithic pieces is reasonably long (8 mm), propane conversion is higher than for the one piece configuration, thus suggesting an essential impact of the gas-phase reactions occurring in the void between two monolithic parts. As for experiments with a big distance between the cooled sampler and a monolith, a contribution of the homogeneous reactions is certainly higher for higher feed rates. When the distance between monolithic pieces is small (4 mm), at low feed rates, the value of propane conversion is lower as compared with the case of a whole monolith. This feature can be explained by a lower temperature at the rear part of a second piece. Indeed, when the monolithic pieces are separated, the heat transfer from the inlet part to the rear part of monolith is much less efficient, hence, conjugation between the exothermic and endothermic reactions disappears.

Some specificity of this set of experiments as compared with the previous one is reflected in the product selectivities. CO_x selectivity decreases with increasing feed rate whereas propene selectivity is constant and ethene and methane selectivities increase. Though propene selectivities are nearly the same for all configurations of the catalytic bed, higher selectivities for ethene and methane and lower selectivities for carbon dioxide are observed for catalytic bed with a space between two parts of monolith, and this difference increases with the distance between them. The independence of propene selectivity upon the share of a free volume implies the heterogeneous route of this product formation from the secondary propyl radicals more easily generated at the catalyst surface [16]. In a similar way, the increase of the ethene selectivity with the distance between the monolithic pieces can be assigned to gas-phase cracking of *n*-propyl radicals in the free space within the catalyst bed. Decline of carbon oxides selectivity with the flow rate accompanied by the increase of ethene selectivity at a nearly constant propene selectivity can in this case be explained only by the heterogeneous oxidation of *n*-propyl radicals into deep oxidation products. This suggestion is supported by results of the previous set of experiments (vide supra) where the gas-phase

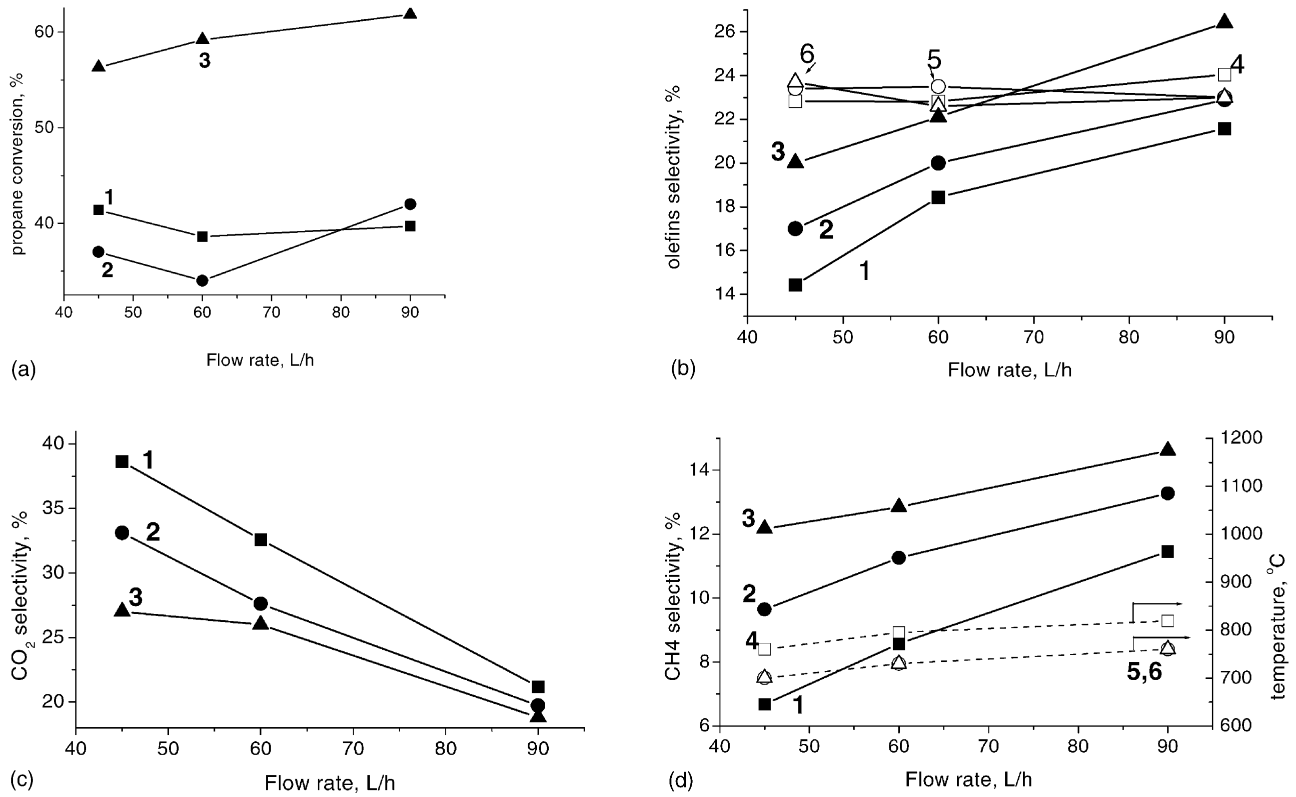

Fig. 6. (a) Propane conversion vs. flow rate for various configurations of the catalyst bed with 7.5 mm integral length and various distances between the catalyst parts of monolith 3% Pt + Sn (1:5)/Al_2O_3, the reaction mixture composition, $C_3H_6:O_2 = 1:1$, 60% N_2. One piece (1) or two piece configurations at a distance of 4 mm (2) and 8 mm (3) apart. (b) Ethylene (1–3) and propylene (4–6) selectivity vs. flow rate for catalytic layer configurations with various distances between the catalyst parts. 1, 4: One piece; 2: 5–4 mm apart; 3: 6–8 mm apart. (c) CO_2 selectivity vs. flow rate for various configurations of the catalyst bed with the same integral length of monolith. 1, One piece; 2, 4 mm apart; 3, 8 mm apart. (d) Methane selectivity (1–3) and temperature of catalyst (4–6) vs. flow rate for one piece (1, 4) and two pieces (2, 3, 5, 6) catalysts configurations. Distance between the pieces is equal to 4 mm (2, 5) and 8 mm (3, 6).

process was not affected by the catalyst post-effect. In that case, at high flow rates, selectivities for ethylene were identical for all distances between the monolith end and cooled sampler. Hence, cracking and/or deep oxidation appears to be enhanced when some intermediates (first of all, *n*-propyl radicals) generated by gas-phase homogeneous reactions are then transformed at the surface of a catalyst.

Hence, from the point of view of the most efficient combination of heterogeneous and homogeneous reactions, dividing the catalytic monolith in two pieces separated by the void volume is certainly not the most promising approach for the given catalyst. However, this approach might work if the second piece contains less active and more selective oxidation catalyst such as V-Mg-O, etc. Indeed, for the latter system, very promising results were obtained when *n*-butane and oxygen were fed over a catalytic bed combined in series with a post-catalytic void volume [17].

Hence, for the first time, the role of gas-phase reactions for propane oxidative dehydrogenation on monolithic catalysts at short contact times was clearly demonstrated. Though propane conversion is increased due to gas-phase reactions, no gain in propylene selectivity is found.

3.5. The new types of active component

The samples of Co- and Mn-substituted Zr phosphates supported on α-Al_2O_3 were found to demonstrate good performance and olefins yield at low CO_x selectivity in the autothermal mode at short contact time without any Pt. Moreover, addition of Pt deteriorates performance due to increase of CO_x selectivity (Fig. 7). Up to date, such systems able to ignite the process and keep it at high GHSV without Pt were unknown. In contrary to samples of Mn- and Co-pyrophosphates [9], the primary CO_x selectivities for Co(Mn)-zirconium phosphates are quite low decreasing further with the increase of temperature. Hence, zirconium phosphate matrix appears to be very efficient in site isolation function favorable for selective oxidation. The increase of ethylene selectivity with temperature implies too high acidity favoring propylene cracking. Samples acidity also increases oxidation ability of added Pt.

Therefore, catalysts based on Co- and Mn-substituted Zr phosphates are promising with respect to propane conversion and selectivity and their ability to keep process in the autothermal mode at high gas flow rates. Tremendously

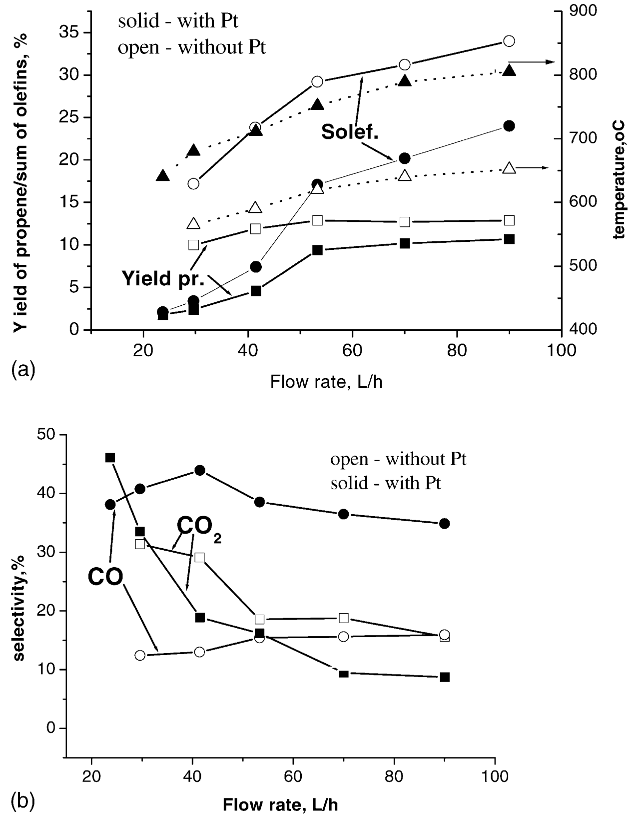

Fig. 7. (a) The flow rate dependence of the outlet catalyst temperature (▲, △), the yield of propene (■, ☐) and the sum of olefins (●, ○) for Co-Zr phosphate supported honeycomb catalysts without Pt (open) and with Pt (solid). The feed composition: C_3H_8 20%; O_2 20%; N_2 balance. Autothermal mode. (b) The dependence of CO (●, ○) and CO_2 (■, ☐) selectivity on the flow rate for Co-Zr phosphate/α-Al_2O_3 (open) and Pt-Co-Zr phosphate/α-Al_2O_3 (solid).

important is the fact that micromonoliths with this active component are not subjected to coking even for feeds with the excess of propane, and their performance is stable.

4. Conclusions

In the reaction of the autothermal propane oxidative dehydrogenation at short contact times on monolithic supported catalysts, a substantial impact of the homogeneous gas-phase reactions on the propane conversion and product selectivities is demonstrated. A share of those reactions is shown to strongly depend upon the longitudinal temperature gradient within the monolithic layer which is determined by its design, operation parameters (feed rate and composition) and a nature of the active component. The yield of propylene is improved when the temperature maximum is shifted to the monolith inlet, and undesired endothermal reactions of cracking or steam reforming are suppressed.

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