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Oxidative dehydrogenation of propane over monoliths at short contact times

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Abstract

A specially designed tubular microreactor with independent control of feed preheat as well as catalyst temperature and allowing to rapidly quench reaction products was used to test performance of supported Pt-based monolithic catalysts in the reaction of propane oxidative dehydrogenation at short contact times. To minimize the impact of undesired homogeneous reactions capable of decreasing propylene selectivity, proprietary straight-channel thin-wall high cell density corundum micromonoliths were chosen as supports. Catalytic properties of supported platinum were modified by using promoters known as dehydrogenation catalysts (tin, zinc aluminate spinel, transition metal pyrophosphates) as well as by tuning reaction mixture composition (propane/oxygen ratio, water and hydrogen content). In the operation temperature range up to 900°C with contact times ~0.03–0.1 s, ethylene/propylene selectivities were found to strongly depend upon the chemical composition of the active component and type of feed. The results thus obtained demonstrate that for Pt-based catalysts, propylene yield can be substantially improved by suppressing secondary reactions of deep oxidation and cracking. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Propane oxidative dehydrogenation; Propylene; Platinum; Corundum micromonoliths; Promoters

1. Introduction

In the recent years, extensive studies of the oxidative dehydrogenation of saturated hydrocarbons have been carried out. Recently, it has been demonstrated [1,2] that olefins can be efficiently produced by the autothermal oxidative dehydrogenation of paraffins at short contact times over Pt-containing foam monoliths at temperatures in the range of 900–1000°C. Under such reaction conditions, for the case of ethane feed, the ethylene yield was acceptable for the practical application reaching 60%. For more valuable propylene, at all process parameters, yields were much lower not exceeding 20% for the case of propane oxidation. Hence, the task of maximizing the propylene selectivities appears to be quite demanding. The most important side reactions leading to decrease of the propylene yield are cracking and complete combustion. At moderate temperatures, these processes are purely heterogeneous, and they can be regulated by appropriate tuning of the active component, support and reaction mixture composition.

In this work, to change catalytic properties of platinum, its combination with non-metallic promoters active and selective in the dehydrogenation reactions (transition metal pyrophosphates, SnO_2 and zinc aluminate) as well as lower operating temperatures were used. To reduce probability of propylene secondary reactions (oxidation, cracking, steam reforming),

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straight channel thin wall corundum and zinc aluminate monolithic supports were used, and the process was carried out in the excess of hydrocarbon, so that nearly all oxygen was consumed at the short inlet part of the catalytic layer. A special reactor design was developed to ensure rapid quenching of the reaction products thus minimizing secondary gas-phase reactions. For tuning the feed mixture composition, water and hydrogen were added.

2. Experimental

2.1. Catalyst preparation

As supports, proprietary corundum monoliths with specific surface area in the range of 5–10 m^2/g annealed at 1300°C and bulk zinc aluminate monolithic supports (surface area 15–50 m^2/g) of ~20 mm diameter with wall thickness 0.25 mm and channel sizes ca 1 mm were mainly used. To suppress inherent acidity of alumina, a mullite surface layer was formed using impregnation of support with silica sol followed by drying and high-temperature calcination.

Sols of Co and Mn pyrophosphates were prepared by mixing solutions of corresponding nitrates and acid ammonium phosphate in the required ratio. Corundum micromonoliths were impregnated by these sols and then purged by compressed air to remove their excess which is capable of plugging the channels. Catalysts were calcined at 700°C, pyrophosphate content was ~5 wt.%.

Platinum was supported onto monolithic supports via incipient wetness impregnation with aqueous solutions of H_2PtCl_6. Sn was added either to α-Al_2O_3 by impregnation with solution of $[Pt(SnCl)_3Cl_2]^{2-}$ complex in 2 M HCl [3] or to Pt-containing catalysts calcined at 700°C by impregnation with $SnCl_2$ solutions. After impregnation, all samples were dried and calcined at 700°C. Pt and $SnCl_2$ concentration in the solution were chosen in such a way as to ensure 0.5–2.5 wt.% Pt loading and a required Pt:Sn ratio. Usually, samples of micromonoliths with lengths in the range of 2–20 mm were used.

2.2. Catalyst characterization

The phase composition of catalysts was studied by XRD (URD-63 diffractometer, Cu Kα radiation). Size of Pt particles were estimated from the diffraction lines broadening using the Scherrer equation. The surface composition of catalysts was characterized by XPS. Photoelectron spectra were recorded for samples dusted onto an adhesive tape without any pretreatment using a VG ESCA-3 spectrometer and Al Kα radiation. Some data are presented in Table 1.

2.3. Catalyst testing

Pieces of monolithic catalysts were tested using a specially designed quartz tubular reactor allowing to independently preheat a feeding mixture flow up to desired temperature (usually ca 300°C) and control the monolith temperature. Pieces of monolithic catalysts with diameters ca 16 mm and length in the range of 3–10 mm wrapped in silica–alumina fiber cloth for insulation and preventing reactant bypass were placed into the reactor. To avoid back-heating of the reaction

Table 1
Samples composition

Sample	Support	Pt (wt.%)	Phase composition		Pt particle size (Å)	Sn/Al ratio, before/after reaction
			Before reaction	After reaction		
P-1	α-Al_2O_3	3				
P-2	α-Al_2O_3+SiO_2[a]	2	Pt, SnO_2	Pt_3Sn+PtSn; SnO_2	200	0.1/0.29
P-3	α-Al_2O_3+SiO_2[b]	2	Pt	Pt	360	0.043/0.017
P-4	$ZnAl_2O_4$[b]	0.5		Pt_3Sn	150	0.56/9
P-5	$Co_2P_2O_7$/α-Al_2O_3	0.5				
P-6	$Mn_2P_2O_7$/α-Al_2O_3	0.5				

[a] Atomic ratio Pt/Sn=1:7, tin was added after Pt supporting.

[b] Atomic ratio Pt/Sn=1:3, Pt–Sn complex was used.

mixture, a piece of corundum monolith was usually kept up-stream of the catalyst, with no thermal insulation being placed down-stream. To obtain probes of the gas phase immediately after catalyst, a tube sampler kept at constant temperature to prevent water condensation and stop any homogeneous reactions was used. The temperature of the monolithic catalyst was measured by thermocouple inserted into the plugged up monolith channel. The feed mixture composition was controlled using automatic flow-meters and corresponding gas mixing devices. The feed flow rate was 5–100 l h^{-1} (STP; corresponding contact times were 0.03–0.8 s). The C_3H_6/O_2 ratio was varied from 1 to 3 at a nitrogen dilution of 40–60%. A specially designed saturator was used to add steam into the feed when required. Inlet and outlet compositions were analyzed by GC (columns with alumina, NaX, carbon) using specially designed computer programs. To estimate components concentrations (exception: H_2O), standards were used, while 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 usual limits of the GC uncertainty (±10%), the carbon balance was usually closed. In all experiments, oxygen was shown to be completely consumed at the catalyst.

Before runs, 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. Catalysts were kept at least 1 h in the reaction mixture before starting the outlet reaction mixture analysis.

3. Results

3.1. Phase composition and Pt dispersion

In some samples, metallic Pt phase was not registered by XRD either due to its low content or small particle sizes (Table 1). Due to low content of supported pyrophosphates, their reliable phase identification by XRD was found to be impossible. XPS is not able to detect Pt due to superimposition of its characteristic $3d_{5/2}$ line with the support Al 2p line. When metallic Pt phase was revealed, particle sizes were reasonably small despite low surface area of monolithic support. For tin-promoted samples, after reaction, Pt–Sn alloys were detected. For P-3 sample prepared using Pt-tin chloride complex, too low Sn content as judged by XPS can be explained by a partial sublimation of $SnCl_4$ during air calcination [3]. As a result, in this case, after reaction only Pt phase represented by rather big particles was observed, and aggregation of tin oxide particles was suggested by a decline of the Sn/Al ratio. Such a sublimation appears to be suppressed when more basic support is used (sample P-4) as revealed by higher Sn/Al ratio and formation of Pt–Sn alloy after reaction.

3.2. Effect of the catalytic layer design

To check performance of our experimental set-up, experiments with 2.5 wt.% Pt/corundum micromonolith catalyst were carried out. At a constant preheat of feed containing 20% C_3H_6, 20% O_2, balance N_2, the increase of GHSV from 50 000 to 115 000 h^{-1} was accompanied by increase of temperature from 610 to 780°C, though remaining lower than temperatures attained in the autothermal regimes [1,2]. This feature is explained by the balance of heat generation within monolith due to catalytic reaction and heat loss through radiation exchange with a cooled sampler. With the temperature rise, propane conversion was increased from 26 to 53%, while the sum of olefin selectivities was found to be close to that reported by Schmidt et al. [1,2] for Pt/corundum foam catalysts (ca 55–56%) with somewhat higher propylene selectivity in our case (up to 30%). Hence, straight-channel catalytic monoliths and rapid quenching of the reaction products due to absence of the outlet thermal shield appear to enhance the propylene selectivity.

3.3. Effect of platinum modification by tin dioxide

Table 2 demonstrates the effect of SnO_2 on performance of Pt-based monolithic catalyst. It follows from these results that at temperature ca 850°C and 1:1 reaction mixture composition, SnO_2 has a promoting effect as regards propylene selectivity. This result agrees with the data of Schmidt et al. [4] for the reaction of ethane oxidative dehydrogenation. As judged by decreased methane selectivity, tin promotion helps to decrease propylene cracking. However, promotion by tin has a drawback of decreasing ethylene yield mainly due to a higher carbon dioxide selectivity. This situation is the most pronounced for P-2 catalyst with

Table 2
Effect of tin on performance of Pt-supported catalysts

Sample	T_{cat} (°C)	Contact time (s)	Propane conversion (%)	Selectivity (%)[a]				
				CH_4	C_2H_4	C_3H_6	CO	CO_2
P-1	835	0.03	63	18	34	17.5	21	2.7
P-2	850	0.1	47	11.7	23.5	26.4	2.5	28.5
P-3	840	0.1	61.5	14.5	29.5	20.6	15.2	11.5
P-4[b]	880	0.1	32.6	5.2	12.4	25.3	10	45

[a] Support specific surface 50 m^2/g.

[b] Small amounts of ethane and C_4–C_6 hydrocarbons with a sum of carbon selectivity up to 10% are also present.

a higher tin content and P-4 catalyst supported onto zinc aluminate (Tables 1 and 2). Hence, tin dioxide addition increases surface oxidation potential provided substantial amount of oxygen is present in the feed. More specifically, the excess of tin is accompanied by appearance of tin dioxide phase, which remains even in catalysts discharged after reaction, though probably partially reduced. As the result, oxygen vacancies at the oxide surface can act as stabilization centers for oxygen radicals known for their high reactivity with respect to olefins [5]. In the case of P-4 sample, very low methane selectivity suggests basic support suppresses propylene cracking catalyzed by the surface acidic centers [6]. The highest yield of CO_2 for this sample can be explained by too high specific area of this support. As a result, some intra-pore oxidation of olefins can occur.

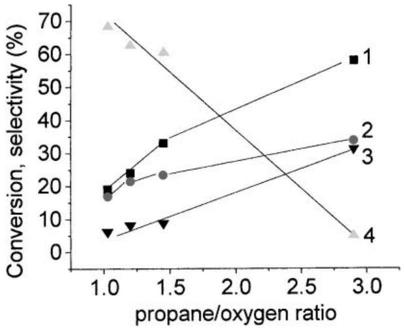

Fig. 1. Dependence of propane conversion (1), and selectivities of propylene (2), ethylene (3) and carbon dioxide (4) on the propane/oxygen ratio in the feed. GHSV=21 000 h^{-1}, 700°C, 22 vol.% C_3H_8.

3.4. *Effect of the feed composition (propane concentration, propane/oxygen ratio, addition of water and hydrogen)*

Figs. 1 and 2 demonstrate the effect of these parameters for P-2 catalyst. A substantial gain in propylene selectivity was achieved by tuning propane/oxygen ratio (Fig. 1). For the richest mixture used here, the carbon dioxide formation was suppressed, while no carbon build-up or performance deterioration with time were observed. Simultaneous increase in concentration of both reagents provided their ratio was kept constant was found to increase further propane conversion and ethylene selectivity, while propylene selectivity improved only slightly.

At constant feed mixture preheat, water addition up to 40% was found to decrease the monolith temperature by about 100°C without changing propane conversion. For propane/oxygen 1:1 mixture and P-2 catalyst at 21 000 GHSV (propane conversion around 27%), water addition increased propylene selectivity from 20 to 30%, while ethylene selectivity remained unchanged. Concomitant decline of methane and

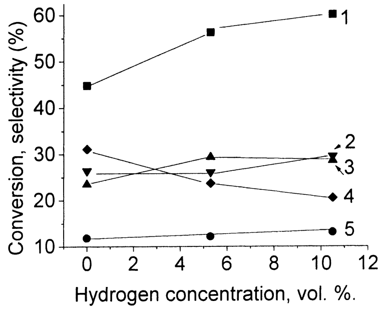

Fig. 2. Effect of H_2 content in the feed with 21% C_3H_8 and 18% O_2 in N_2 on propane conversion (1), and selectivities of propylene (2), ethylene (3), CO+CO_2 (4) and methane (5). GHSV=34 000 h^{-1}, 850°C.

Table 3
Performance of catalysts 0.5% Pt+$M_2P_2O_7$/α-Al_2O_3(M=Co, Mn) for the feed composition 30% C_3H_6, 10% O_2, 60% N_2 and GHSV=13 600 h^{-1}

Catalyst	Catalyst temperature (°C)	Propane conversion (%)	Selectivity (%)[a]				
			CH_4	C_2H_4	C_3H_6	CO	CO_2
P-5	590	9.3	0.8	0.8	21.7	17.3	59.4
P-6	525	19.4	0.8	2.9	23.4	36	37
P-1	678	58	14	31.3	33.9	6.1	4.9

[a] Small amounts of ethane and C_4–C_6 hydrocarbons with a sum of carbon selectivity up to 10% are also present.

carbon dioxide selectivities (from 6.8 to 4.6% for the former and from 53 to 45% for the latter) was observed evidencing suppression of cracking and deep oxidation reactions as the reason for improving propylene yield. Hydrogen addition (Fig. 2) is also beneficial for olefins production. In this case, ethylene selectivity is more strongly raised, though propylene selectivity is also improved.

3.5. *Transition metal pyrophosphates as secondary supports*

For these systems (Table 3), without water and hydrogen added, even in the fuel-rich feed, deep oxidation dominates. Hence, platinum performance is strongly affected by such support modification (cf. P-1 sample, Table 3). Very low methane and ethylene selectivities for pyrophosphate-containing samples imply suppression of cracking reactions. At least in part, it is explained by the fact that pyrophosphate surface is mainly covered by weakly acidic P–OH groups not capable to activate olefins [7].

3.6. *Feed tuning to maximize propylene selectivity*

For the most promising systems, to maximize propylene selectivity, water and hydrogen were added simultaneously to propane-rich feed. Table 4 shows the results of these experiments. As seen from these results, very high integral olefins selectivity (ca 90%) was obtained, not to mention high propylene selectivity. Further, for most systems, in these conditions carbon dioxide production was completely suppressed, which is very important from the point of view of the process economy. Moreover, low methane selectivity indicates suppression of cracking. Note that chemical composition of catalysts remains to be an important factor in determining their selectivity and performance. To increase further propylene yield, operational temperatures are to be increased.

4. Discussion

4.1. *Effect of reactor design and products quenching*

According to earlier results of Schmidt et al. [1,2,8], propane oxidative dehydrogenation can be satisfactorily described by a heterogeneous β-elimination mechanism based purely on surface Pt chemistry. This conclusion was in part supported by the fact that for their reactor design (catalytic monolith was placed between two pieces of uncoated corundum foam support) cooling by N_2 introduced into the reactor 5 mm

Table 4
Performance of catalysts in propane-rich mixtures ($C_3H_8/O_2\sim3$) in the presence of H_2 (20 vol.%) and H_2O

Catalyst	H_2O (vol.%)	GHSV (10^3 h^{-1})	T_{cat} (°C)	Propane conversion (%)	Selectivities (%)			
					CH_4	C_2H_4	C_3H_6	CO/CO_2
P-2	–	34	660	32	5.4	18	53	1.6/22
P-4[a]	38	26	598	20	5.6	20	72	2.4
P-5	40	14	560	18	2	18	69	11
P-6	38	14	560	13	3	19	71	7

[a] Specific surface of zinc aluminate support 16 m^2/g.

downstream of the catalyst bed showed no difference between quenched and unquenched experiments [8]. However, higher propylene selectivity obtained in our experiments with non-promoted supported Pt catalyst, sum of olefins selectivity being close to earlier reported value (vide supra) suggests that a part of secondary cracking reactions proceeds within downstream thermal shield. Due to tortuous paths in foam, gas residence time and mass transfer rates are sufficient for these side reactions to diminish the yield of propylene. Hence, rapid quenching of products is useful here, as is the case for oxidative dehydrogenation of C_4+ hydrocarbons [8] or HCN synthesis [9].

Another important question concerns physical properties of monolithic support. While too high surface area and developed pore structure of support are certainly undesirable here leading to decline of olefins yield (vide supra), moderate surface area does not appear to be harmful in this respect. In general, mass transfer rates in straight-channel monoliths are usually lower as compared with those in foams. Hence, oxygen concentration profile along the channel is to be more flat, thus affecting surface- and gas-phase reactions. According to Schmidt and Dietz [10], for foams, all oxygen is usually consumed within approximately 1 mm of the catalyst, and remaining part of catalyst is covered by the carbon monolayer thus preventing olefins secondary reactions. However, estimations of the gas flow hydrodynamics not shown here for brevity, revealed that for our catalytic bed real configuration, provided boundary conditions are taken into account, the mass transfer rates are high enough to ensure complete oxygen consumption in the diffusion-controlled regime within 1–2 mm of catalyst. Hence, in our as well as in earlier experiments, predominant part of catalyst appears to act in a dehydrogenating mode in the presence of such mild oxidants as carbon dioxide and water.

4.2. *Effect of catalyst chemical composition*

Catalysts tested for oxidative dehydrogenation of paraffins can be broadly divided into two group. Catalyst formulations claimed to give good results in propane oxidative dehydrogenation at moderate temperatures include typical catalysts of olefins partial oxidation such as Nb based systems, bulk or supported vanadates, molybdates, complex systems consisting of bismuth, alkali, alkali earth, chlorine and oxygen, transition metal pyrophosphates, supported boria [7,11–14], etc. In all these studies, fixed-bed reactors with granulated catalysts were used. Reasonable conversions were achieved at GHSV not exceeding 2000–4000 h^{-1}, and yields of propylene were not higher than 10–20%. Propylene selectivity usually declines with conversion, which is a typical feature of selective oxidation processes, thus limiting yield of the desired product with inherent reactivity exceeding that of the feedstock. Hence, for these systems, high yields of propylene sufficient for process commercialization appear to be not achievable.

Another group of catalysts based upon supported Pt operates at high (up to 900–1000°C) temperatures [1,2,8,10]. At such temperatures, cracking and gas phase oxidation are likely to assume increasing importance.

In the approach used in this work, typical oxide dehydrogenation catalysts were combined with platinum in an attempt to obtain a system with improved performance. This idea was based upon the fact that a predominant part of the catalyst monolith operates in oxygen-free conditions, and hence, some conjugation between functions played by metallic and oxidic components could be expected. Very high propylene selectivities obtained for modified catalysts (vide supra) at reasonable conversions not observed earlier for non-promoted Pt systems, evidence that such conjugation indeed takes place. Though detailed studies are needed to find out the nature of this effect, some preliminary ideas can be speculated. First, suppression of the propylene secondary cracking due to promoters can be assigned either to decrease of the surface acidity or to modification of the platinum particle surface properties (formation of alloys and/or decoration). Probably, cracking of olefins is less probable for isolated Pt atoms, while they are still able to abstract hydrogen from propane molecule. Second, since for all modified systems water addition was accompanied by the increase of olefins yield, steam reforming of olefins is certainly not accelerated by promoters. Third, due to oxygen spill-over, oxidic components are expected to help reoxidation of Pt atoms by water and carbon dioxide molecules, which are the only available oxidants in the predominant part of catalyst monolith (vide supra). Such an effect appears to be responsible for the increase of carbon oxides selectivity in lean mixtures as well as for the increase of propylene selectivity with steam addition.

Finally, it is worth noting that olefins yield obtained for tin-promoted catalyst (ca 40%) is sufficiently good to encourage further efforts in this direction.

5. Conclusions

For the reactions of propane oxidative dehydrogenation at short contact times on Pt supported monolithic catalysts, propylene yield was shown to improve due to quenching of the reaction products, minimization of the homogeneous reactions impact, Pt modification by typical dehydrogenation compounds and feed tuning.

Acknowledgements

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