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Catalytic selective oxidation of propane

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Abstract

Results on the oxidative conversion of propane on three types of catalysts on which different mechanisms of propane activation prevail are discussed, whereby the reaction conditions and final product distribution are affected. In the case of the redox-mechanism on V_2O_5-based catalysts the degree of catalyst reduction which is affected by the propane-to-oxygen ratio determines the catalyst activity and selectivity. On rare-earth oxide-based catalysts, activation of propane by adsorbed oxygen takes place. As derived from transient experiments under vacuum conditions, adsorbed oxygen species convert propane into C_3H_6, C_2H_4, CH_4, and CO_x. Continuous flow experiments on Na–P/Sm_2O_3 (Na:P:Sm=2:1:700) and Ln_2O_3/SrO (Ln=Sm, La, Nd; Ln:Sr=5:1) catalysts at 1 bar showed that due to high catalyst activity the ignition of the reaction mixture takes place at 420–450°C. The heat produced by the oxidative conversion of propane was sufficient to sustain the reactions after ignition with the preheat of the feed gas under conditions chosen. Higher selectivity to C_2H_4 (ca. 30%) compared to C_3H_6 (ca. 20%) was observed in the whole range of the reaction conditions indicating that C–C splitting prevails when adsorbed oxygen participates in the reaction. Finally, propane activation via redox-mechanism and adsorbed oxygen is ruled out for B_2O_3/Al_2O_3 catalysts. The involvement of Lewis acid sites in the generation of propyl radicals is assumed; olefins and C_1–C_3 oxygenates are formed with high selectivities even in excess of oxygen most probably via secondary reactions of propyl radicals and oxygen in the gas phase. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Partial oxidation; Propane; Reaction mechanism; TAP studies; V_2O_5/TiO_2; Rare-earth oxide-based catalysts; B_2O_3/Al_2O_3

1. Introduction

There are a number of studies describing mechanistic assumptions on the key-reaction steps and on the solid-state properties being responsible for propane activation [1–3]. In our previous work [4], assumptions were made about possible mechanisms prevailing in the oxidative dehydrogenation of alkanes on oxides in general. Three types of mechanisms were considered based on the character of surface species involved in the alkane activation. Along with a redox-mechanism which is widely accepted for transition metal containing catalysts oxygen can participate in propane activation via its adsorbed state. Almost no attention was paid in the literature to the latter case although this type of alkane activation was proposed for the oxidative coupling of methane [5–7] and for the oxidative dehydrogenation of ethane [8]. In the third case it was assumed that propane activation takes place on solids with strongly bound lattice oxygen, which, in addition, exhibit low activity towards dissociative adsorption of oxygen.

Catalysts studied in the present work (V_2O_5/TiO_2, rare-earth oxide-based systems, B_2O_3/Al_2O_3) were

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chosen taking into account the above classification. The aim of the work was to compare the catalytic performance of these systems, which is expected to activate propane in different ways. In each case an attempt has been made to identify the factors determining activity and product distribution.

2. Experimental

2.1. Catalysts

V_2O_5 (1 wt%)/TiO_2 (EL10V1, [9]) catalyst was used as received. Sm_2O_3 was calcined in air at 973 K for 4 h before catalytic testing. Na–P/Sm_2O_3 catalysts were prepared by impregnation of Sm_2O_3 with an aqueous solution of $Na_2HPO_4 \cdot 12\ H_2O$. After drying at 393 K the catalyst was calcined in air at 973 K for 4 h. The Ln_2O_3/SrO (Ln=La, Nd, Sm; Ln:Sr=5:1) and La_2O_3/SrO (La:Sr=50:1) catalysts were prepared by addition of strontium hydroxide solution to the respective lanthanide nitrate solution. The mixture was stirred and heated to evaporate the water. The dried sample was finally calcined in a flow of oxygen at 973 K for 2 h. The B_2O_3 (30 wt%)/Al_2O_3 catalyst was prepared by impregnation of γ-Al_2O_3 with boric acid dissolved in warm water. After stirring for 1 h the excess water was evaporated; the remaining solid was dried at 383 K for 16 h and then calcined at 873 K for 14 h.

2.2. Catalyst characterization

Surface areas were measured by the BET method of nitrogen adsorption at liquid nitrogen temperature. The surface compositions of Na–P/Sm_2O_3 samples were derived from XPS spectra recorded with an ESCALAB 220i-XL (Fisons Instruments) spectrometer using Al K_α radiation (1486.6 eV). NH_3-TPD experiments were performed applying an AMI-1 Altamira Instruments apparatus. The sample was pretreated in a flow of helium at 683 K for 0.5 h. Afterwards a NH_3 (3%)/He flow (50 ml/min) was passed over the catalyst at 100°C for 30 min and then the sample was purged with He (50 ml/min) at 373 K for 90 min. In TPD, the sample was heated to 823 K at a rate of 10 K/min; the final temperature was held for 1 h. The liberation of NH_3 was monitored by a thermal conductivity detector.

2.3. Catalytic studies

For the catalytic experiments, a fixed-bed reactor ($\varnothing_{in}$=6 or 12 mm) made of quartz, operated at ambient pressure and equipped with on-line gas chromatography was used. A reaction mixture consisting of propane, oxygen and nitrogen was passed through undiluted catalyst (0.2–1 g; d_p=250–355 μm) packed between two layers of quartz of the same particle size. Total flow rates from 20 to 220 ml/min were used depending on the type of catalyst partial pressures of propane and oxygen, which were varied from 30 to 60 and 15 to 50 kPa, respectively.

2.4. Transient experiments

Oxygen adsorption and reaction of propane with adsorbed oxygen on the Sm_2O_3 and Na–P/Sm_2O_3 surfaces were studied by means of pulse experiments at 823 K in vacuo ($P=10^{-4}$ Pa) applying the temporal-analysis-of-products (TAP) reactor [10]. The catalyst (m_{cat}=0.3 g) was first exposed to oxygen pulses at reaction temperature and kept under vacuum for 10 min before the pulse experiments. O_2/He (Ne)=1:1 and C_3H_8/Ne=1:1 mixtures were pulsed separately or sequentially over the catalyst with a time interval of 0.05 or 0.2 s. For the sequential pulse experiments, oxygen pulse sizes were varied from 2×10^{14} to 4×10^{15} molecules per pulse to adjust different surface coverages by adsorbed oxygen, while C_3H_8 pulse size was kept constant at 10^{15} molecules/pulse.

3. Results and discussion

3.1. V_2O_5-containing catalysts

As shown in our previous work [11], lattice oxygen of the V_2O_5 (1 wt%)/TiO_2 catalyst consisting of VO_x species attached to the TiO_2 surface reacts with propane as confirmed by transient experiments in vacuum at 766 K using the TAP reactor system. Pulsing propane over the oxidized surface resulted in propane conversion of 36%; propene selectivity amounted to 27%. Selectivity was, however, improved with an increase in the degree of surface reduction. A propene selectivity of 67% ($X_{C_3H_8}$=7%) was achieved at relatively high degree of surface reduction (Θ=0.48,

where Θ is the ratio of catalyst oxygen removed by pulsing propane to the total amount of vanadium atoms). Thus, the degree of surface reduction which is affected in a steady state by the propane-to-oxygen ratio is a key factor determining both propane conversion and propene selectivity in the oxidative dehydrogenation of propane on a V_2O_5/TiO_2 catalyst. This is also valid for other redox systems. For example, Yoon et al. [12] showed that on cobalt molybdates the reduced surface is more selective in the formation of propene. High propene selectivities on redox catalysts can be achieved in general by operating at low oxygen partial pressures and therefore at low propane conversions.

3.2. Rare-earth oxide (REO)-based catalysts

Catalysts containing REO are known for the oxidative dehydrogenation of ethane [13–15]. Only few studies dealt with the oxidative conversion of propane using REO-based catalysts. Zhang et al. [16] studied fluorine promoted oxides of Ce, Sm, Nd and Y. The catalytic performance of pure CeO_2 and Sm_2O_3, on which CH_4, C_2H_4 and CO_2 were the main products at 773 K was given for comparison with CeF_3 promoted samples without discussing the reaction mechanism. Oxidative dehydrogenation of propane over rare-earth orthovanadates was recently reported [17] but the catalytic performance was related to the redox properties of these catalysts.

In the present work, REO doped with strontium oxide, sodium phosphate and calcium oxide were studied. Oxygen adsorption and the involvement of adsorbed oxygen species in the propane activation on this type of catalysts were investigated by means of pulse experiments in vacuum. Responses on pulsing oxygen at 823 K over Sm_2O_3– and Na–P/Sm_2O_3 catalysts with different loadings of sodium phosphate are presented in Fig. 1.

On Na–P/Sm_2O_3 doped with a very low amount of sodium phosphate (Na:P:Sm=2:1:700), the oxygen response was broader compared to that on the undoped samaria indicating a stronger adsorption. An increase in the amount of the dopant loading resulted in a narrow response on pulsing oxygen which is due to suppression of the oxygen adsorption. Results of the moment analysis for the responses obtained (cf. Fig. 1) along with XPS data on the surface composition are summarized in Table 1.

Na/Sm atomic ratios in the surface layer for Na–P/Sm_2O_3 (P:Na:Sm=1:2:700) and Na–P/Sm_2O_3 (P:Na:Sm=1:2:70) samples amounted to 0.21 and 2.37, respectively. For the latter catalyst with the surface enrichment by sodium, no oxygen adsorption was detected at 823 K; the mean residence time of the measured oxygen response correspond to that of inert molecule with the same molar mass (cf. Table 1). However, strong oxygen adsorption takes place when the amount of sodium does not exceed the concentration of samarium in the surface layer.

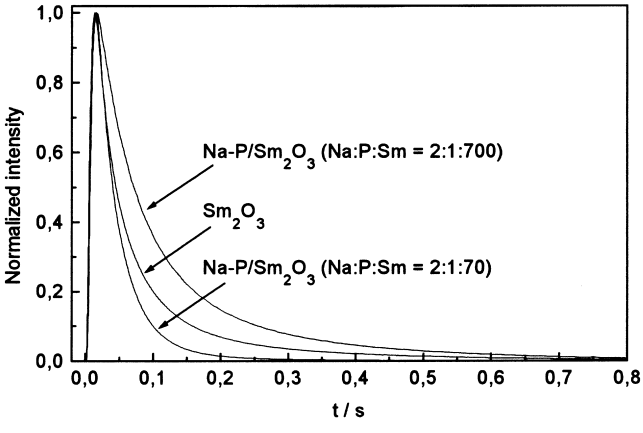

Fig. 1. O_2 response signals on pulsing oxygen over different catalysts at 823 K applying the TAP reactor ($m_{cat.}$=0.3 g, 10^{15} O_2 molecules/pulse).

Table 1
Results of characterization (BET, XPS, TAP) of Sm_2O_3-containing catalysts

Catalyst	S_{BET} (m^2/g)	Atomic ratios in the surface layer (XPS)		Oxygen adsorption at 550°C (TAP)
		Na/Sm	P/Sm	$t(O_2)/t(O_2,I)$*
Sm_2O_3	5.6	—	—	1.8
Na–P/Sm_2O_3 (P:Na:Sm=1:2:700)	4.6	0.21	0.02	2.6
Na–P/Sm_2O_3 (P:Na:Sm=1:2:70)	3.3	2.37	0.12	1.0

*$t(O_2)$ – experimentally observed mean residence time of oxygen response; $t(O_2,I)$ – mean residence time of an inert molecule with AMU 32 estimated from the measured Ne response according to Buyevskaya et al. [18].

The reaction of propane with adsorbed oxygen was studied applying sequential pulsing of the reactants over undoped Sm_2O_3 and Na–P/Sm_2O_3 (P:Na:Sm=1:2:700). The response signals obtained when pulsing oxygen and afterwards propane (Δt=0.1 s) over Na–P/Sm_2O_3 (P:Na:Sm=1:2:700) catalyst are given in Fig. 2.

The broken line indicates the oxygen response signal when pulsing oxygen only. When propane is pulsed 0.1 s after the oxygen input, the full-line response was obtained. The amount of surface oxygen consumed in the reaction with propane may be derived from the difference in the areas of these two oxygen responses. Propane left the reactor followed by propene, ethylene and methane. Although not shown in this figure, carbon monoxide was also formed. CO_2 was not detected at the reactor outlet due to its strong adsorption on the catalyst surface; the amount of CO_2 formed can be estimated from the carbon balance. By varying the oxygen pulse size and thereby the surface coverage with adsorbed oxygen, the propane conversion and the selectivities were influenced. Propane conversions of up to 70% due to adsorbed oxygen were obtained in the experiments with sequential pulsing of oxygen followed by propane with time intervals of 0.1–0.2 s. When propane was pulsed 10 min after the oxygen pulse ($O_{ads.}\rightarrow 0$) C_3H_8 conversion amounted to only 4%. Thus, high propane conversions on the REO-based catalyst can be obtained only in the presence of short-lived surface oxygen species formed by the adsorption of the gas-phase oxygen.

Similar results were obtained over undoped samaria. The dependence of propane conversion and product selectivities on the amount of adsorbed oxygen in the sequential pulsing of O_2 and C_3H_8 (Δt=0.2 s) along with results on separate pulsing of C_3H_8 over the Sm_2O_3 surface at 823 K are presented in Fig. 3.

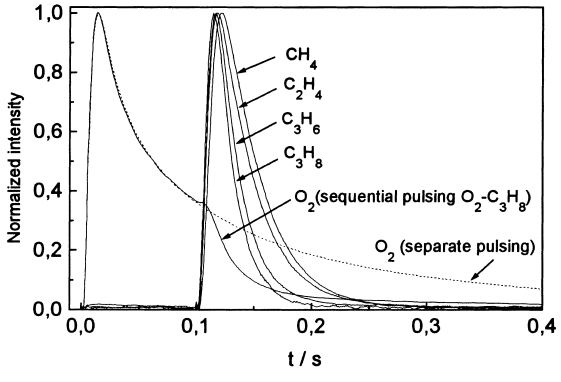

Fig. 2. Responses at the reactor outlet when pulsing oxygen and propane sequentially (Δt=0.1 s) over Na–P/Sm_2O_3 (P:Na:Sm=1:2:700) at 823 K.

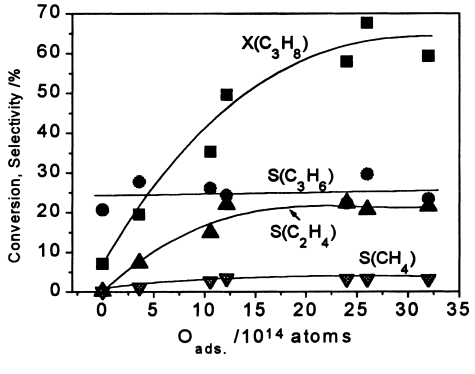

Fig. 3. Propane conversion and product selectivities as a function of the amount of adsorbed oxygen consumed in the reaction with propane in sequential pulsing O_2 and C_3H_8 (Δt=0.2 s) over Sm_2O_3 at 823 K.

A propane conversion of only 7% was observed while pulsing C_3H_8 10 min after oxidation ($O_{ads.} \rightarrow 0$). Propene and CO were observed as products at the reactor outlet. No formation of ethylene or methane was detected. When oxygen was pulsed 0.2 s before propane, ethylene and methane were additionally formed. An increase in propane conversion up to 67% was observed with increase in the surface coverage of adsorbed oxygen. No significant change of selectivities towards propene (S=21–26%) and CO (S=20–25%, not shown in the figure) was detected in the whole range of surface coverages. The formation of C–C bond scission products (C_2H_4, CH_4) was observed only in the presence of adsorbed oxygen. Selectivities to ethylene and methane first increased with increasing surface coverage by adsorbed oxygen and then remained constant.

Thus, activation of propane by adsorbed oxygen on Sm_2O_3-based catalysts was derived from transient experiments. Adsorbed oxygen species of a short lifetime were able to convert propane into propene, ethylene, CO and CH_4 by excluding the involvement of gas-phase reactions due to Knudsen diffusion occurring while pulsing the reactants.

Continuous flow experiments were performed using 0.2 g catalysts (d_p=250–355 μm) and 150–200 ml/min total flow rate of the feed gas (C_3H_8/O_2=2–4). It was found that REO-based catalysts, e.g. Ln_2O_3/SrO (Ln=Sm, La, Nd) and Na–P/Sm_2O_3 (P:Na:Sm=1:2:700), ignite the reaction mixture at 693–723 K when using undiluted catalyst particles and fuel rich conditions. After ignition a sharp temperature increase occurred which was mostly well above 873 K being the border line between catalytic and homogeneous gas-phase oxidation. A characteristic temperature profile in the reactor after ignition is shown in Fig. 4.

Huff and Schmidt [19] published results on the conversion of propane in the presence of oxygen over noble metal coated ceramic foam monoliths at T>1173 K and contact times of about 5–10 ms. The reactor was operated autothermally and the heat generated by the reaction was sufficient to sustain reactions after ignition. The propene selectivities obtained did not exceed 30%; ethylene was formed with selectivities up to ca. 40%. Total olefin (C_2H_4, C_3H_6, C_4H_8) selectivities between 55% and 60% were reported for propane conversion >90% at 1283 K. In the present work, it was shown that mixed oxide catalysts based

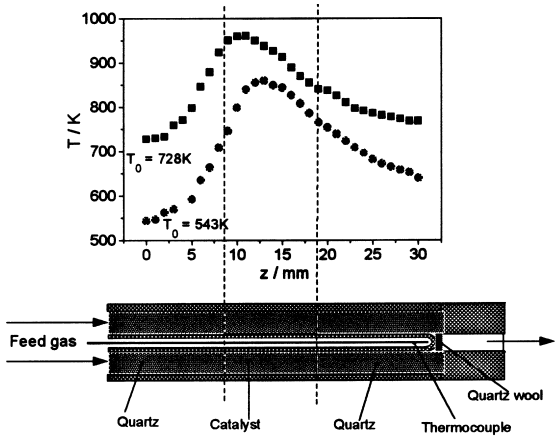

Fig. 4. Temperature profiles after ignition of the reaction mixture in a tubular fixed-bed reactor charged with a Nd_2O_3/SrO catalyst ($C_3H_8/O_2/N_2$=4.5/2/1, τ=0.08 g s/ml).

on REOs are also able to ignite the reaction and sustain the reactions at contact times of the order of 60–80 ms. Results of catalytic experiments on rare oxide-based catalysts using a non-isothermal mode of operation as exemplified by Fig. 4 are given in Table 2.

To sustain the reaction after ignition at the desired maximal temperature (T_{max}), the feed gas was preheated up to a certain temperature T_0 (cf. Fig. 4 and Table 2). Under these circumstances oxygen conversion >90% was achieved in most cases. The products of the reaction were ethylene, propene, methane, CO and CO_2. Traces of C_4-hydrocarbons but no oxygenates were also observed. On undoped samaria, selectivities to propene and ethylene were 13.5% and 18.3%, respectively. Catalytic performance was improved by doping Sm_2O_3 with Na–phosphate or SrO (compare olefin selectivities at T_{max}=823–833 K in Table 2).

It should be noted that in the case of Na–P doping only the addition of a low amount of 0.28 mol% (Na:P:Sm=2:1:700) had a positive effect, in particular, on selectivity. With increasing amount of Na–phosphate (Na:P:Sm=2:1:70), the activity decreased drastically ($X(C_3H_8)$=1.1% at 833 K, τ=0.06 g s/ml) and no ignition was observed by heating the reactor up to 973 K.

The results obtained indicate that high catalyst activity towards oxygen adsorption caused the ignition of the reaction mixture in the oxidative conversion of propane on REO-based catalysts. Oxygen adsorption

Table 2
Catalytic performance of rare-earth oxide-based catalysts

Catalyst	S_{BET} (m^2/g)	T_0 (K)	T_{max} (K)	Conversion (%)		Selectivity (%)			Y (Olefins) (%)
				C_3H_8	O_2	C_3H_6	C_2H_4	CH_4	
Sm_2O_3	5.6	573	823	18.1	90.1	13.5	18.3	3.5	5.8
Na–P/Sm_2O_3	4.6	539	833	30.5	93.9	18.9	30.0	5.3	14.9
(Na:P:Sm=2:1:700)		670	933	40.6	96.2	20.9	33.6	5.1	22.1
Na–P/Sm_2O_3	3.3	838	827	1.1	6.8	26.1	10.2	—	0.4
(Na:P:Sm=2:1:70)									
SrO/Sm_2O_3	8.0	500	831	30.3	97.8	17.3	29.3	5.4	14.1
(Sr:Sm=1:5)		803	983	49.7	99.4	20.4	36.0	10.9	28.0
SrO/La_2O_3	4.1	692	933	39.7	94.7	19.3	34.0	8.3	21.1
(Sr:Ln=1:50)									
SrO/La_2O_3	4.1	573	833	32.3	90.7	17.4	31.1	6.5	15.7
(Sr:La=1:5)		828	953	53.5	99.7	20.3	36.7	11.0	30.5
SrO/Nd_2O_3	7.2	693	949	45.1	100	19.9	35.5	8.4	25.0
(Sr:Nd=1:5)									
Quartz		876	873	0.1	<0.1	87.0	13.0	—	0.1
		978	973	21.7	22.5	48.9	31.6	12.6	17.5

$C_3H_8/O_2/N_2$=2/1/2; m_{cat}=0.2 g, F=200 ml/min, quartz reactor ($ø_{in}$=6 mm).

which determines catalyst activity and ignition temperature on REO-based catalysts is significantly suppressed by high alkali doping.

Although high olefin yield of 17.5% was obtained at 973 K using a reactor filled with quartz due to non-catalytic oxidation, it was not possible to ignite the reaction mixture in this case. From the results obtained it follows that an important catalyst function is the ignition of the reaction, which is most probably due to high activity of REO-based catalysts towards oxygen adsorption. After ignition, reaction temperatures of 833–983 K could be achieved without significant external heat input.

On SrO/Ln_2O_3 (Ln=Sm, Nd, La; Sr:Ln=1:5) catalysts olefin yields of 21–30.5% (S=53.3–57.0%) were obtained at a short contact time of 0.06 g s/ml and at C_3H_8/O_2=2 and T_{max}=933–983 K. A higher selectivity towards ethylene (ca. 30%) as compared to propene (ca. 20%) was observed when applying a reaction mixture with C_3H_8/O_2=2 (cf. Table 2). The influence of the propane-to-oxygen ratio on propane conversion and product selectivities is illustrated by Fig. 5 for a SrO/Nd_2O_3 catalyst. An increase in the propane-to-oxygen ratio resulted in a decrease of propane conversion but had no effect on propene selectivity. Small rise in ethylene selectivity from 29% to 33% was observed with decreasing C_3H_8/O_2 ratio from 4 to 2.

Contrary to redox-systems there is no significant influence of the oxygen partial pressure on olefin selectivity on REO-based catalysts. Thus, the selectivity could not be significantly improved by varying the C_3H_8-to-O_2 ratio. On the other hand, an increase of oxygen content in the feed gas had no detrimental

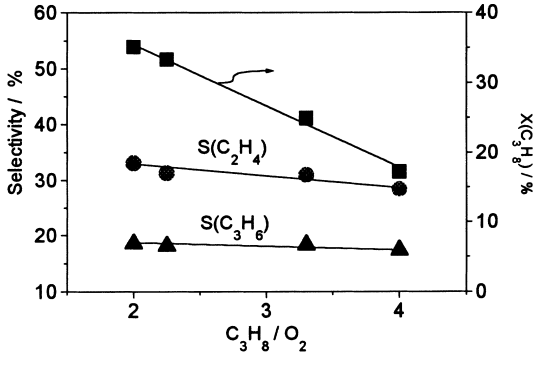

Fig. 5. Dependencies of propane conversion and of propene and ethylene selectivities on the propane-to-oxygen ratios on Nd_2O_3/SrO (Nd:Sr=5:1) catalyst ($P(C_3H_8)$=60 kPa, T_{max}=580–590 K; τ=0.08 g s/ml, $X(O_2)$>98%).

effect on selectivity, this allows to reach olefins' selectivities of ca. 50–56% at high propane conversions (X=45–53%).

Two different pathways of ethylene formation may be discussed. As follows from the transient studies, ethylene can be formed via a surface induced C–C splitting in the propane molecule due to adsorbed oxygen. On the other hand, the results of continuous experiments in the absence of catalyst showed that thermal oxidative dehydrogenation of propane leads to the formation of ethylene with selectivities of about 31.6% ($X_{C_3H_6}$=21.7%) at high temperatures due to homogeneous gas-phase reactions. As a result, propene selectivities did not exceed 20–26%. Although high olefin (propene+ethylene) yields can be obtained using REO-based catalysts at low contact time in the order of 60–80 ms (STP), the propene selectivity still has to be improved.

3.3. B_2O_3-containing catalysts

As reported earlier [20], the dissociative adsorption of both oxygen and propane is suppressed on B_2O_3 (30 wt%)/γ-Al_2O_3 catalyst as confirmed by H–D and oxygen isotopic exchange reactions. Also no reaction of propane with lattice oxygen was detected by pulsing C_3H_8 over boria–alumina catalyst in the TAP reactor in the temperature range from 783 to 853 K. Therefore, propane activation via redox mechanism or by adsorbed oxygen can be excluded on this type of catalyst. A propyl radical is assumed to be the reactive intermediate; olefines and oxygenates are formed with high selectivities by secondary reactions of propyl radicals after their release into the gas phase due to diminished surface oxidation [20].

Oxidation of alkanes via radical chain reactions was assumed for the air oxidation of butane to acetic acid and cyclohexane to adipic acid [21] in the presence of Co compounds. The initiation involves the formation of an alkyl radical which reacts with oxygen forming a peroxy radical. The reaction between the peroxy radical and alkane ($C_nH_{2n+1}O_2^{\bullet} + C_nH_{2n+2} \rightarrow C_nH_{2n+1}O_2H + C_nH_{2n+1}^{\bullet}$) is proposed to be the main propagation step. The decomposition of hydroperoxide results in the formation of olefins and oxygenates. A similar mechanism was proposed by Otsuka et al. [22] for the oxidation of propane on B–P mixed oxides. No correlation of catalytic performance with solid properties was, however, made. Partial oxidation of ethane on alumina–boria catalyst was studied by Colorio et al. [23,24]. The activity was mainly related to the number of acid sites which were determined by adsorption microcalorimetry of pyridine [23] but no definite correlation between the catalytic properties and the acidity was derived. It was assumed that boron oxide species with their particular acidity and electron attractive characteristics are responsible for the formation of ethylhydroperoxide leading to ethylene formation [24].

Thus, the mechanism of the oxidative conversion of propane which takes place on boria-containing catalysts differs from those on V- or REO-based catalysts. In this case acidity seems to play a decisive role in the propane activation. A question about the type of acidity arises. No conventional method of IR spectroscopy of adsorbed NH_3 or pyridine can be used for B_2O_3-containing catalyst to distinguish between Lewis and Brønsted acidity because of strong absorption of boria in the range from 1100 to 1700 cm^{-1} masking any adsorbate peaks. Results of the H–D exchange reaction in C_3D_8 with surface hydrogen showed that addition of boria to alumina resulted in the elimination of mobile hydrogen. Thus, a decrease in Brønsted acidity was assumed for B_2O_3/Al_2O_3 compared to Al_2O_3 [20]. As estimated from NH_3-TPD measurements, the total number of acid sites, however, increased with boria doping and amounted to 1.8 and 8.3 μmol NH_3/m^2 for Al_2O_3 and B_2O_3 (30 wt%)/Al_2O_3, respectively. The values do not differ much from those reported in [23]. Thus, the boria/alumina catalyst possesses most likely a Lewis acidity which determines the activation of propane.

For oxidation of butane to acetic [21], the initiation via the reaction

$$C_4H_{10} + Co^{3+} \rightarrow H_3C - CH^{\bullet} - C_2H_5 + H^+ + Co^{2+}$$

was proposed. If the same initiation takes place in the oxidative conversion of propane on B–Al–O systems, the catalyst should be able to produce the propyl radicals due to its Lewis acidity via the reaction

$$C_3H_8 + L^{n+} \rightarrow C_3H_7^{\bullet} + H^+_{(s)} + L^{(n-1)+}$$

where L^{n+} is the Lewis site.

There is, however, another possibility of propane activation involving homolytic C–H-bond splitting with the formation of propyl and hydrogen radicals

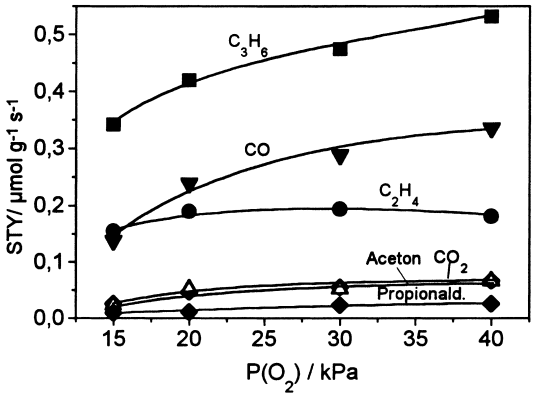

Fig. 6. Dependence of product space–time-yield on oxygen partial pressure on B_2O_3 (30 wt%)/Al_2O_3 at 823 K, $P(C_3H_8)$=40 kPa, τ=2 g s/ml.

which both release in the gas phase due to suppressed surface oxidation.

The effect of oxygen partial pressure on product formation over a B_2O_3 (30 wt%)/Al_2O_3 catalyst is illustrated in Fig. 6. An increase of oxygen partial pressure resulted in a significant increase of propene and CO space time yields. No predominant formation of CO is, however, observed with increasing oxygen concentration. The effect of oxygen partial pressure on the space time yields of ethylene and CO_2 was less pronounced (cf. Fig. 6).

Propene yields amounted to 14–20% at 550°C. CO_x selectivities did not exceed 20% even when using a reaction mixture with an excess of oxygen (C_3H_8/O_2=0.8). Ethylene, methane, methanol, formaldehyde, methylformate, formic acid, ethanol, acetaldehyde, acetic acid, propionaldehyde, acetone, propanol, propylene glycol, acrolein were also formed depending on reaction conditions. When using a reaction mixture with $p(C_3H_8)$=40 kPa and $p(O_2)$=20 kPa propane conversion was 28.4% after 10 h on stream at T=823 K and τ=2 g s/ml; selectivities to olefins and oxygenates amounted to 67.4 and 18.1%, respectively ($Y_{C_3H_6}$=14.9%; $Y_{C_2H_4}$=4.2%; $Y_{acr.}$=2.3%; Y_{CH_3OH}=0.5%; Y_{CH_3CHO}=0.3%; $Y_{C_2H_5OH}$=0.3%; Y_{HCOOH}=1.3%; $Y_{CH_3COCH_3}$=0.2%).

Boria–alumina catalysts show high propene and oxygenates selectivities even at degrees of propane conversions higher than 20%. The unique performance of this catalyst is most probably due to B_2O_3 being, however, melted under reaction conditions ($T_{melt.}$=450°C [25]). Formation of borates cannot be considered as an active phase [20]. Catalyst stability is an important issue for this type of catalyst. Additional studies regarding the stabilisation of boria, which plays a key role in the propane activation and formation of the selective products are required.

4. Conclusions

From the results described one can conclude that there are at least three different ways of propane activation in its oxidative conversion which are summarized below:

1. Redox systems operating at temperatures <773 K can produce propylene selectively, especially at a high degree of catalyst reduction at which, however, only low propane conversion levels can be achieved.
2. On REO-containing catalysts, adsorbed oxygen is involved in propane activation. Surface reaction of propane with adsorbed oxygen leads to the formation not only of propylene and CO_x but also cause significant formation of ethylene, methane and C_4-hydrocarbons due to C–C cleavage. No oxygenates are formed. Also ignition of the reaction mixture takes place due to the high activity of these catalysts towards oxygen adsorption. Although this type of catalysts is promising for the oxidative dehydrogenation of ethane, their use in the case of propane is limited due to significant formation of ethylene besides propene.
3. On B_2O_3/Al_2O_3 catalysts, propane activation on Lewis acid sites with the formation of propyl radicals which desorb in the gas-phase is assumed. Oxygen participates in the product formation not via its surface-bound form but in the gas phase forming propylhydroperoxide as a key-reaction intermediate. As a result, olefins and oxygenates are formed with significant selectivities.

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