Propane oxidative dehydrogenation on silica based oxide catalysts

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The oxidative dehydrogenation of propane to propylene with molecular O_2 (PPD) has been investigated on commercial bare SiO_2 and medium loaded V_2O_5 and MoO_3 catalysts at 450–525°C. The direct relationship between the density of reduced sites (ρ, 10^{16} s_r g_{cat}^{-1}), evaluated in steady-state conditions by O_2 chemisorption, and the POD reaction rate proves the occurrence of a "concerted" reaction mechanism involving the activation of gas-phase O_2 on the reduced sites of the catalyst surface. A straight-line correlation between the activity of such silica based catalysts in POD and methane partial oxidation to formaldehyde (MPO) at 525°C has been disclosed.

Keywords: silica catalysts; propylene; propane oxidative dehydrogenation; reduced sites; vanadia / silica catalysts

1. Introduction

The oxidative dehydrogenation of propane (POD) is currently attracting a great deal of research interest since it constitutes a potential process for propylene production. Contrary to the conventional non-oxidative catalytic dehydrogenation of propane, this reaction is thermodynamically unlimited by the chemical equilibrium in terms of yield of C_3H_6. A large variety of unsupported and supported oxide catalysts have been claimed as being effective in the POD reaction [1–9]. V–Mg–O systems, owing to their considerable catalytic activity, have been extensively studied in order to identify the active vanadate phase [1–5,9]. Recently, we have reported that a certain 5% V_2O_5/SiO_2 catalyst provides the highest molar yield of C_3H_6 and productivity values with respect to the other oxide catalysts vindicated this finding up to now [10]. Notably, silica supported V_2O_5 catalysts exhibit also an excellent performance in the partial oxidation of methane to formaldehyde (MPO) [11]. On this account, it has been assessed that the activity of silica based oxide catalysts in MPO is controlled by the capability to activate gas-phase oxygen into active species by reduced sites of the catalyst surface [11].

A fundamental issue in the study of partial oxidation reactions of light alkanes is to highlight a generally valid rule which allows to rationalise the catalytic behaviour of a class of catalysts. Then, the aim of this paper is to provide some insights in the understanding of the catalytic action of silica based oxide catalysts in the POD reaction.

2. Experimental

2.1. Catalyst

Two different commercial SiO_2 samples – (i) "precipitated" SiO_2, Si 4-5P Akzo (SA_{BET}, 400 $m^2\ g^{-1}$) and (ii) "fumed" SiO_2, Cab-O-Sil M5, Cabot (SA_{BET}, 200 $m^2\ g^{-1}$) – were used either as catalysts or support. 5.0% $V_2O_5/SiO_{2\,Si4\text{-}5P}$ (SA_{BET}, 281 $m^2\ g^{-1}$), 5.7% $V_2O_5/SiO_{2\,M5}$ (SA_{BET}, 157 $m^2\ g^{-1}$) and 4.0% $MoO_3/SiO_{2\,Si4\text{-}5p}$ (SA_{BET}, 187 $m^2\ g^{-1}$) catalysts were prepared by incipient wetness impregnation of "precipitated" Si 4-5P and "fumed" M5 SiO_2 samples with a basic solution (pH = 11) of ammonium metavanadate or ammonium heptamolybdate, respectively, according to a procedure described elsewhere [11].

2.2. Catalytic testing

Catalytic measurements during the POD reaction were performed by a conventional continuous flow quartz microreactor (∅, 8 mm; *l*, 90 mm) connected on line with a GC system equipped with TCD and FID detectors. The reagents and products were analyzed by a three-column system: (1) Porapak Q (*l*, 3.5 m; ∅, 1/8″) for the separation of CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8; (2) Molecular Sieve (*l*, 3 m; ∅, 1/8″) for the separation of N_2, O_2, CH_4, CO and (3) Carbowax 20M (*l*, 3.5 m; ∅, 1/8″) for the separation of oxygenates and C_3H_4. The catalytic activity of the above catalysts was measured at atmospheric pressure, in the T_R range 450–525°C, by using 0.25 g of catalyst sample (particle size, 0.3–0.5 mm) diluted with similarly sized SiC (1/10, vol/vol). The molar composition of the reaction mixture was

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$C_3H_8 : O_2 : N_2 : He = 2 : 1 : 1 : 8$ while the total flow rate (F_R) was 100 STP cm^3 min^{-1}.

Propylene oxidation tests were also carried out in the temperature range 500–550°C adopting the experimental conditions described above for the POD reaction (W_{cat}, F_R) and using three different reaction mixture compositions $C_3H_6 : O_2 : N_2 :$ He, (A) 1 : 1 : 1 : 17; (B) 1 : 3 : 1 : 15 and (C) 1 : 5 : 1 : 13.

The blank tests with empty reactor show no C_3H_8 or C_3H_6 conversion under the conditions studied.

The activity of the catalysts in the partial oxidation of methane to formaldehyde (MPO) at 525°C was evaluated in a batch reactor according to the procedure described elsewhere [12].

2.3. *Catalyst characterization*

Reaction temperature oxygen chemisorption (RTOC) measurements in the temperature range 450–525°C were performed in a pulse mode using He as carrier gas. After treatment in the C_3H_8/O_2/He reaction mixture flow, the sample was purged in the carrier flow and then O_2 pulses (V_{pulse}, 4×10^{-8} mol O_2) were injected into the carrier gas until saturation of the sample was attained. The density of reduced sites (ρ) was calculated from the O_2 uptakes by assuming a chemisorption stoichiometry O_2/"reduced site" of 1 : 2 [11].

3. Results and discussion

The predominant products in the oxidative dehydrogenation of propane over the silica based oxide catalysts in the T_R range 450–575°C were propylene and carbon oxides (COx). Ethylene and acetaldehyde along with a considerable amount of acrolein and traces of propionaldehyde are formed on the "precipitated" $SiO_{2\,Si4\text{-}5P}$ sample. The addition of MoO_3 and V_2O_5 to the SiO_2 supports implies a higher selectivity to propylene and correspondingly a lower production of COx, a slight cracking activity and a significant decrease in the amount of oxygenates. Table 1 shows a detailed comparison of the activity of bare and MoO_3 or V_2O_5 promoted SiO_2 samples in terms of propane and oxygen conversion, product distribution, reaction rate and C_3H_6 productivity values ($STY_{C_3H_6}$, in $g_{C_3H_6}\,kg_{cat}^{-1}\,h^{-1}$).

The "precipitated" Si 4-5P silica sample bears (exhibits) a catalytic activity essentially higher than that of the fumed M5 silica. Most notably, the activation energy value of the overall reaction in the T_R range 500–550°C is much higher in the case of the $SiO_{2\,Si4\text{-}5P}$ than for the $SiO_{2\,M5}$ sample. Even the product distribution obtained with two such different SiO_2 catalysts is rather different. In fact, the major product on the "fumed" M5 silica is CO_2 with a small amount of C_3H_6, while on "precipitated" Si 4-5P silica only a small amount of CO_2 has been found, the main products being olefins (C_3H_6, C_2H_4) and acrolein. The catalytic functionality of the SiO_2 surface is dramatically modified by the addition of V_2O_5. Indeed, the activity of both 5.0% $V_2O_5/SiO_{2\,Si4\text{-}5P}$ and 5.7% $V_2O_5/SiO_{2\,M5}$ catalysts is one order of magnitude higher than that of the corresponding SiO_2 carrier. Such an enhancing effect exerted by the V_2O_5 is accompanied by a higher selectivity to C_3H_6 for both

Table 1
Activity of bare and MoO_3 and V_2O_5 promoted silica catalysts in the oxidative dehydrogenation of propane

Catalyst	T_R (°C)	C_3H_8 conv. (%)	O_2 conv. (%)	Rate (10^{-6} $mol_{C_3H_8}$ g_{cat}^{-1} s^{-1})	Selectivity (%)								$STY_{C_3H_6}$ ($g_{C_3H_6}$ kg_{cat}^{-1} h^{-1})
					C_2H_4	C_3H_6	C_2H_4O	C_3H_6O	$(CH_3)_2CO$	C_3H_4O	CO	CO_2	
$SiO_{2\,Si4\text{-}5P}$	500	0.90	3	0.49	5.2	37.0	2.0	0.7		15.0	20.0	20.1	27.50
	525	1.90	9	1.04	5.3	36.8	1.4	0.6		14.9	25.0	16.0	57.70
	550	3.10	15	1.69	7.4	33.0	1.4	0.6		16.6	27.5	13.5	84.46
	575	4.60	23	2.52	8.7	30.9	1.1	0.5		15.0	29.0	14.8	117.35
$SiO_{2\,M5}$	500	0.51	2	0.27		15.0						85.0	6.19
	525	0.57	2	0.32		20.0						80.0	9.41
	550	0.60	2	0.33		23.0						77.0	11.39
4.0% $MoO_3/SiO_{2\,Si4\text{-}5P}$	500	0.73	3	0.39		69.0	1.0			6.0		24.0	41.58
	525	1.38	5	0.75	3.5	59.0	1.1	0.4		7.0	15.0	14.0	67.22
	550	2.20	9	1.20	4.0	60.3	1.2	0.4	0.1	8.0	15.0	11.0	109.52
5.0% $V_2O_5/SiO_{2\,Si4\text{-}5P}$	450	2.80	11	1.52		66.0	0.8		0.4	2.0	9.2	21.6	152.57
	475	4.60	14	2.50		63.0	0.9	0.1	0.5	2.5	13.0	20.0	239.63
	500	7.80	28	4.25	1.0	60.0	1.0	0.2	0.5	3.7	17.0	16.6	386.37
	525	13.30	54	7.25	1.0	54.9	1.3	0.1	0.4	4.8	22.9	14.6	602.81
5.7% $V_2O_5/SiO_{2\,M5}$	475	3.90	17	2.13	0.5	65.6	1.0	0.6	0.4	1.8	17.1	13.0	211.21
	500	7.10	35	3.80	0.7	56.0	1.0	0.5	0.2	2.4	24.8	14.5	328.25
	525	13.10	77	7.10	0.9	42.0	0.5	0.1	0.2	2.0	38.8	15.5	454.23

V_2O_5/SiO_2 catalysts along with the formation of some amounts of acrolein, cracking products and oxygenates for the 5.7% $V_2O_5/SiO_{2\,M5}$ sample. However, the selectivity to acrolein of the 5.0% $V_2O_5/SiO_{2\,Si4\text{-}5P}$ sample is much lower than that observed with the bare "precipitated" $SiO_{2\,Si4\text{-}5P}$. The addition of MoO_3 to the $SiO_{2\,Si4\text{-}5P}$ causes a slight decrease in the overall activity of the SiO_2 support and a modification in the product distribution similar to that exerted by the V_2O_5.

Despite the promoting effect exerted by the V_2O_5 on the reactivity of the silica the origin of the different product distributions found with bare and V_2O_5 promoted SiO_2 catalysts is intriguing. Such different functionality could arise from a catalytic pattern of SiO_2 and V_2O_5/SiO_2 systems in the transformation of C_3H_6 which is generally considered the primary product of the POD on oxide catalysts [1]. In order to elucidate such issue, a series of comparative tests in propylene oxidation in the T_R range 500–575°C on bare and V_2O_5 promoted $SiO_{2\,Si4\text{-}5P}$ catalysts has been performed. Several reaction mixture (C_3H_6/O_2/diluent) compositions have been used in order to face with a reaction mixture having C_3H_6 and O_2 concentrations similar to those of the POD stream in the adopted operating conditions. The results listed in table 2, in terms of C_3H_6 and O_2 conversion, product distribution and reaction rate values, indicate that the propylene oxidation on the bare $SiO_{2\,Si4\text{-}5P}$ sample proceeds with a lower reaction rate along with a much higher selectivity towards acrolein formation with respect to the 5.0% $V_2O_5/SiO_{2\,Si4\text{-}5P}$ catalyst: namely, the selectivity to acrolein on the bare SiO_2 is 4–10 times higher than that of the V_2O_5/SiO_2 catalyst. Then, the observed difference in acrolein selectivity could be attributed to the different behavior of unpromoted and V_2O_5 promoted SiO_2 catalysts in the consecutive transformation of C_3H_6 to C_3H_4O. In fact, from the data presented in tables 1 and 2, it can be deduced that the ratio ($R = r''/r'$) between the rates of C_3H_6 (r'') and C_3H_8 (r') transformation of the SiO_2 surface ($R = 5.1$ and 4.3 at 500 and 525°C respectively) is higher than that of the V_2O_5/SiO_2 catalyst ($R = 2.97$ and 1.89 at 500 and 525°C respectively). This finding definitely proves that the consecutive conversion of C_3H_6 towards the formation of C_3H_4O is essentially more favoured on the bare SiO_2 surface.

The similarity in the promoting and poisoning effect exerted by V_2O_5 and MoO_3 respectively in the activity of the "precipitated" $SiO_{2\,Si4\text{-}5P}$ in MPO [1] and POD led us to compare the activity of the studied silica based oxide catalysts in POD and MPO reactions. In fig. 1, the results of such comparison are presented in terms of MPO reaction rate vs. POD reaction rate at 525°C. The straight-line relationship between the reaction rates in POD and MPO allows one to infer that similar reaction pathways make it possible to rationalize the catalytic action of the silica based oxide catalysts in both MPO and POD reactions. Remarkably, the absolute value of the POD reaction rate on silica based oxide catalysts is about one order of magnitude higher than the corresponding value for the MPO reaction (fig. 1).

In our previous paper, the MPO reaction is shown to be controlled by the process of O_2 activation which occurs on the reduced sites of the catalyst surface [11]. The above correlation (fig. 1) leads to infer that the process of O_2 activation is also crucial for the POD reaction on the studied silica based catalysts. To prove the validity of such hypothesis the densities of reduced sites of the studied catalyst under POD steady-state conditions have

Table 2
Activity of bare V_2O_5 promoted silica catalysts in the oxidation of propylene

Reaction mixture composition $C_3H_6 : O_2 : N_2 : He$	T_R (°C)	C_3H_6 conv. (%)	O_2 conv. (%)	Rate (10^{-6} $mol_{C_3H_6}$ g_{cat}^{-1} s^{-1})	Selectivity (%)							
					CH_4	C_2H_4	C_3H_4	CH_3CHO	C_2H_3CHO	$(CH_3)_2CO$	CO	CO_2
5% $V_2O_5/SiO_{2\,Si4\text{-}5P}$												
1 : 1 : 1 : 17	500	34.0	100.0	5.1		1.7	1.2	2.0	10.8	0.4	55.0	29.0
	525	37.5	100.0	5.6	2.1	2.3	1.9	1.8	8.0	1.0	55.4	27.5
	550	36.0	100.0	5.4	2.0	3.0	2.4	2.0	8.6	2.0	54.0	26.0
1 : 3 : 1 : 15	500	82.0	87.0	12.2		1.5	0.2	1.3	5.0	0.2	60.0	31.8
	525	85.0	99.0	12.6		1.5	0.2	1.2	4.2	0.1	62.0	30.8
	550	86.0	100.0	12.8	0.7	2.0	0.4	1.0	4.0	0.2	64.4	27.4
1 : 5 : 1 : 13	500	85.0	60.0	12.6	1.0	1.6	0.2	1.4	4.8	0.2	59.8	31.0
	525	92.0	65.0	13.7	0.9	1.6	0.1	0.9	3.0	0.1	63.7	29.7
	550	96.0	75.0	14.3	0.8	1.5	0.1	0.4	1.7		67.0	28.5
$SiO_{2\,Si4\text{-}5P}$												
1 : 5 : 1 : 13	500	17.0	9.0	2.5		2.5	3.0	3.0	18.0	0.5	42.5	30.5
	525	30.0	18.0	4.5		3.0	2.5	2.5	18.0	0.2	44.8	31.0
	550	49.0	34.0	7.3		3.4	2.0	2.0	18.0	0.1	46.5	28.0

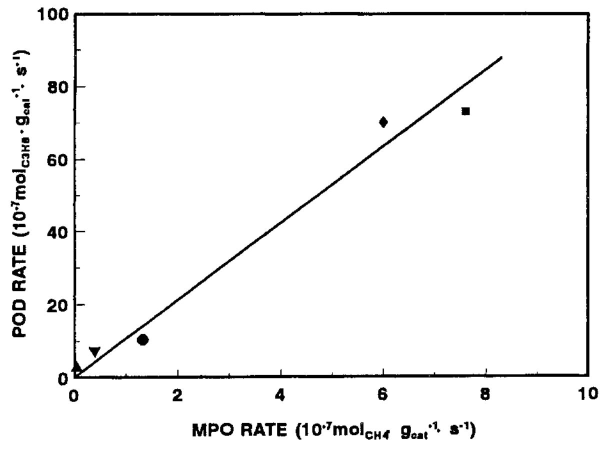

Fig. 1. Relationship between the rate of POD and MPO reactions on (▲) $SiO_{2\,M5}$, (▼) 4.0% $MoO_3/SiO_{2\,Si4\text{-}5P}$, (●) $SiO_{2\,Si4\text{-}5P}$, (◆) 5.7% $V_2O_5/SiO_{2\,M5}$ and (■) 5.0% $V_2O_5/SiO_{2\,Si4\text{-}5P}$ catalysts at 525°C.

been measured. In fig. 2, the catalytic activity of all studied catalysts is plotted against the densities of reduced sites. The direct relationship between catalytic activity and density of reduced sites conforms that the process of O_2 activation governs the catalytic activity of the silica based oxide catalysts in the POD reaction. Additionally, the observed relationship between reaction rate and density of reduced sites (fig. 2) allows one to generalize the following reaction pathway for the POD on silica based oxide catalysts, based on the occurrence of a surface reaction mechanism, from that already proposed for MPO reaction [11]:

$$R + \mathcal{L} \rightarrow (R)_s^* \qquad (1)$$

$$O_{2(g)} \text{ or } O_{2(s)} + \mathcal{RS} \rightarrow (O)_s^* \qquad (2)$$

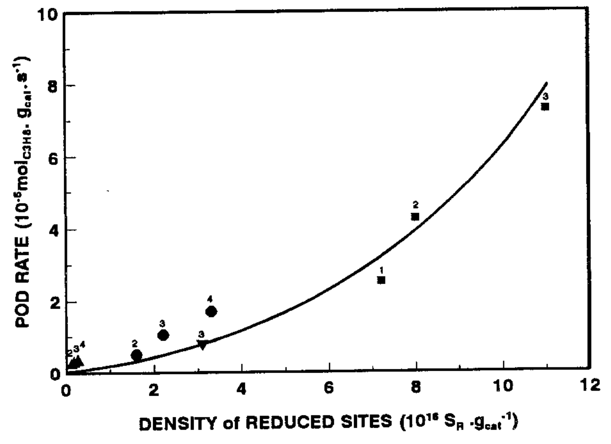

Fig. 2. Relationship between density of reduced sites (ρ) and POD reaction rate on (▲) $SiO_{2\,M5}$, (▼) 4.0% $MoO_3/SiO_{2\,Si4\text{-}5P}$, (●) $SiO_{2\,Si4\text{-}5P}$ and (■) 5% $V_2O_5/SiO_{2\,Si4\text{-}5P}$ catalysts at (1) 475°C, (2) 500°C, (3) 525°C and (4) 550°C.

$$(R)_s^* + (O)_s^* \rightarrow P + \mathcal{L} + \mathcal{RS} \qquad (3)$$

where $(R)_s^*$ and $(O)_s^*$ indicate light alkane (CH_4 or C_3H_8) and O_2 surface activated species respectively, P refers to primary reaction products (i.e., HCHO and CO_2 for MPO and C_3H_6 and CO_2 for POD), $\mathcal{L}$ and $\mathcal{RS}$ represent specific surface sites enabling alkane or molecular oxygen activation from gas-phase ($O_{2(g)}$) or adsorbed form ($O_{2(s)}$), respectively.

Further studies are in progress in order to elucidate whether one or two different kinds of sites, $\mathcal{L}$ and $\mathcal{RS}$, providing specific activation of hydrocarbon and oxygen molecule, respectively, are present originally on the catalyst surface. In fact, it can be inferred that the site on which the hydrocarbon molecule is activated undergoes a transformation into a reduced site becoming able to activate also oxygen molecule.

Step (3) of the above reaction pathway must include the C–H bond cleavage. Evidently, the C–H bond energy should affect the reaction rate constant of this step. The higher rate of POD in comparison with MPO reaction reflects probably a higher rate of interaction of active oxygen species with propane than with methane due to stronger C–H bonds of the latter.

Thus, 5% V_2O_5/SiO_2 catalyst, being one of the most effective oxide catalysts in the MPO reaction [13], is a very active catalytic system also for the POD reaction [10]. Then, it can be concluded that the catalytic action of silica based oxide catalyst in both MPO and POD reaction lies in the peculiar ability to create active oxygen species on the catalyst surface [11].

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