Effect of vanadia loading in propane oxidative dehydrogenation on V_2O_5/SiO_2 catalysts

M. Puglisi [a], F. Arena [a], F. Frusteri [b], V. Sokolovskii [c] and A. Parmaliana [a,b,1]

[a] *Dipartimento di Chimica Industriale, Università degli Studi di Messina, Salita Sperone c.p. 29, I-98166 S. Agata (Messina), Italy*
[b] *Istituto CNR-TAE, Salita S. Lucia 39, I-98126 S. Lucia (Messina), Italy*
[c] *Department of Chemistry, University of the Witwatersrand, PO Wits 2050, Johannesburg, South Africa*

Received 9 April 1996; accepted 5 June 1996

The influence of V_2O_5 loading on the catalytic behaviour of V_2O_5/SiO_2 catalysts in the oxidative dehydrogenation of propane to propylene (POD) has been investigated. The different activity–selectivity pattern of low (5 wt%) and highly (> 10 wt%) loaded V_2O_5/SiO_2 catalysts is explained in terms of different surface vanadia species.

Keywords: propane oxidative dehydrogenation; vanadia/silica catalysts; propylene; vanadia loading; oxide dispersion

1. Introduction

The oxidative dehydrogenation of propane (POD) is a potential route for making propylene since it does not present either the thermodynamic limitations or the catalyst deactivation problems of the conventional dehydrogenation process. Amongst the various oxide systems vindicated as effective in the POD reaction, we have recently disclosed that a certain 5% V_2O_5/SiO_2 catalyst possesses a superior performance providing the highest molar yield as well as C_3H_6 productivity values [1]. Such catalyst denotes a similar excellent performance in the partial oxidation of methane to formaldehyde (MPO) [2]. It has been also pointed out that the 5% V_2O_5/SiO_2 drives both MPO and POD reactions according to a concerted reaction pathway involving the activation of gas phase O_2 on the reduced sites of the catalyst surface [3].

Silica supported vanadia catalysts are largely used in the selective oxidation of hydrocarbons. However, only a few studies have been devoted to rationalise thoroughly the effects of V_2O_5 loading and surface structure on their catalytic behaviour [4–7]. Recently, Mamedov and Cortés Corberán [8], in reviewing the oxidative dehydrogenation of lower alkanes on V_2O_5 based catalysts, concluded that no clear interpretation regarding either the reaction mechanism or the structure–activity relationship can be derived from a survey of the literature.

This paper aims to point out the influence of V_2O_5 loading on the catalytic behaviour of the V_2O_5/SiO_2 system in the POD reaction, providing also a preliminary analysis of the different reactivity of the surface vanadia species.

2. Experimental

Catalyst. 5% V_2O_5/SiO_2 (SA_{BET}, 281 $m^2\,g^{-1}$), 10% V_2O_5/SiO_2 (SA_{BET}, 198 $m^2\,g^{-1}$), 20% V_2O_5/SiO_2 (SA_{BET}, 193 $m^2\,g^{-1}$) and 50% V_2O_5/SiO_2 (SA_{BET}, 168 $m^2\,g^{-1}$) samples were prepared by incipient wetness impregnation of a precipitated SiO_2 carrier ($Si_{4\text{-}5P}$ grade, AKZO Product, SA_{BET}, 400 $m^2\,g^{-1}$) with a basic solution (pH = 11) of ammonium metavanadate, according to the procedure described elsewhere [5]. For the sake of comparison, a commercial bulk V_2O_5 (SA_{BET}, 6 $m^2\,g^{-1}$) sample was used.

Catalyst testing. Catalytic measurements in POD reaction were performed at atmospheric pressure in the range 425–525°C by a conventional continuous flow quartz microreactor (ϕ, 8 mm, *l*, 90 mm) described elsewhere [1]. The molar composition of the reaction mixture was $C_3H_8 : O_2 : N_2 : He = 2 : 1 : 1 : 6$. All the tests were carried out at GHSV of propane of 1 700 h^{-1} using 0.25 g of catalyst sample (particle size, 0.3–0.5 mm), diluted with similarly sized SiC (1/5 vol/vol), and a total flow rate (F_R) of 100 STP $cm^3\,min^{-1}$.

Catalyst characterisation. The V_2O_5 dispersion of V_2O_5/SiO_2 catalysts has been evaluated by low temperature oxygen chemisorption (LTOC) measurements, according to the procedure described elsewhere [9]. The LTOC dispersion values (V_s/V, where V_s and V refer to surface and total V atoms respectively) were calculated assuming a chemisorption stoichiometry O_2/V_s of 1/2 [10].

3. Results and discussion

The catalytic activity data of differently loaded V_2O_5/SiO_2, bulk V_2O_5 and bare SiO_2 samples in the

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[1] To whom correspondence should be addressed.

range 425–525°C, in terms of reaction rate (r_0, $mol_{C_3H_8}\ g_{cat}^{-1}\ s^{-1}$), specific reaction rate (r_1, $mol_{C_3H_8}\ g_{ox}^{-1}\ s^{-1}$) and product selectivity are presented in table 1.

The V_2O_5 exerts a significant promoting effect on the activity of the SiO_2 surface enhancing on the whole the formation of propylene and depressing the selectivity to oxygenates.

The reaction rate ($mol_{C_3H_8}\ s^{-1}\ g_{cat}^{-1}$) is slightly affected by the V_2O_5 loading, rising by less than one order of magnitude upon T_R increases from 450 to 500°C. However, on an oxide weight unit ($mol_{C_3H_8}\ g_{ox}^{-1}\ s^{-1}$) a regular decrease in activity with the loading level is observable. The increase in the V_2O_5 loading implies a lowering in the selectivity to propylene along with a corresponding increase in CO_x ($CO + CO_2$) selectivity. Namely, on the low loaded 5% V_2O_5/SiO_2 catalyst the selectivity to propylene stays almost unchanged (ca. 55–65%) in the whole range of T_R, whilst at loadings higher than 10% it drops at $T_R > 450$°C. Bulk V_2O_5 exhibits a low selectivity to C_3H_6 (ca. 15%), even at 475°C. As a result, the propylene productivity at 475°C expressed in terms of space time yield ($STY_{C_3H_6}$, $g_{C_3H_6}\ kg_{cat}^{-1}\ h^{-1}$) as a function of the loading, shown in fig. 1, reaches its maximum value on 5% V_2O_5/SiO_2 catalyst, thereafter it decreases dropping at loadings higher than 10%. The reason of such remarkable differences in reactivity of ($V_2O_5 < 10\%$) low and ($V_2O_5 > 10\%$) highly loaded V_2O_5/SiO_2 catalyst likely reflects a different catalytic action attributable to the difference of low and highly loaded systems.

In a comparative study of differently loaded V_2O_5/SiO_2 catalysts in the MPO reaction [9] we pointed out that low loaded ($\leqslant 5$ wt%) catalysts possess the peculiar capability to stabilise surface "reduced sites" able to provide "activated" oxygen species which effectively react with CH_4 leading to the formation of partial oxidation products [2,9], while highly loaded (> 5 wt%) systems, as well as bulk V_2O_5 sample, enable a different and less effective reaction pathway involving mainly lattice oxygen species which results in a lower reaction rate and HCHO selectivity [9]. Likewise, a similar catalytic pattern could be invoked on V_2O_5/SiO_2 catalysts in the POD reaction. In particular, the low loaded ($\leqslant 5$ wt%) catalysts, providing large amounts of active oxygen species, are very active and selective towards the formation of partial oxidation product. Whilst, highly loaded V_2O_5/SiO_2 catalysts as well as bulk V_2O_5, stabilising lower amounts of surface activated oxygen species [2,9], are on the whole less effective in the POD reaction as a consequence of a drop in activity and selectivity. In order to shed light on the influence of the surface properties on the reactivity of the V_2O_5/SiO_2 system in the POD reaction, the trends of the specific reaction rate and C_3H_6

Table 1
Activity of SiO_2, V_2O_5 and V_2O_5/SiO_2 catalysts in the oxidative dehydrogenation of propane

Catalyst	T_R (°C)	Reaction rate [a]		Selectivity (%)							
		r_0	r_1	CO_2	C_2H_4	CO	C_3H_6	C_2H_4O	C_3H_6O	C_2H_6CO	C_3H_4O
Si 4-5P	475	0.25	0.25	25.0	4.0	12.0	47.0	4.0	1.0		17.0
	500	0.49	0.49	20.0	5.2	20.0	37.0	2.0	0.7		15.0
	525	1.04	1.04	16.0	5.3	25.0	36.8	1.4	0.6		14.9
5.3% V_2O_5/SiO_2	450	1.52	30.4	21.6		9.2	66.0	0.8		0.4	2.0
	475	2.50	50.0	20.0		13.0	63.1	0.9	0.1	0.5	2.5
	500	4.25	85.0	16.6	1	17.0	60.0	1.0	0.2	0.5	3.7
	525	7.25	145.0	14.6	1	22.9	54.9	1.3	0.1	0.4	4.8
10.1% V_2O_5/SiO_2	450	1.04	10.4	10.5		15.3	72.0			0.2	2.0
	475	2.46	24.6	13.0		21.6	62.5	0.3		0.3	2.3
	500	5.34	53.4	16.1	0.3	29.4	50.6	0.3		0.2	3.0
	525	9.65	96.5	18.3	0.4	37.5	40.7	0.3		0.1	2.7
20.8% V_2O_5/SiO_2	450	1.26	6.3	15.0		22.9	60.0			0.1	2.0
	475	3.16	15.8	21.0		46.7	31.0	0.2		0.1	1.0
	500	4.25	21.3	21.7		50.0	26.7	0.2		0.1	1.3
50.8% V_2O_5/SiO_2	425	1.42	2.73	14.3		37.0	47.3				1.4
	450	2.72	5.23	17.2		54.0	27.3	0.1		0.1	1.3
	475	8.17	15.71	18.1		67.5	14.4				
V_2O_5	450	1.37	1.37	16.0		36.5	46.4				0.2
	475	8.17	8.17	20.9		63.8	15.1				0.1
	500	8.72	8.72	21.7		62.0	16.2				

[a] r_0 (reaction rate), $10^{-6}\ mol_{C_3H_8}\ g_{cat}^{-1}\ s^{-1}$; r_1 (specific oxide rate), $10^{-6}\ mol_{C_3H_8}\ g_{V_2O_5}^{-1}\ s^{-1}$.

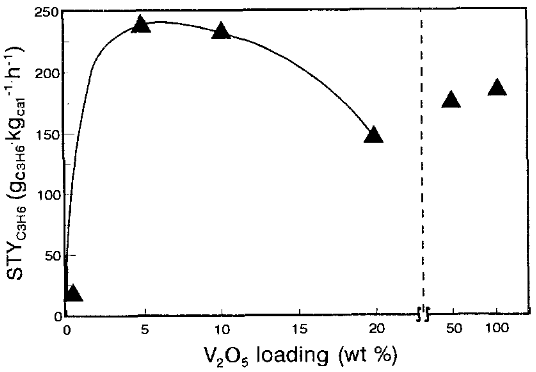

Fig. 1. Propane oxidative dehydrogenation. Effect of V_2O_5 loading on the space time yield to C_3H_6 ($STY_{C_3H_6}$) of V_2O_5/SiO_2 catalysts at 475°C.

selectivity at 450 and 475°C against the oxide dispersion, as evaluated by LTOC measurements [9] are reported in fig. 2. Both at 450 and 475°C a remarkable straight-line increasing relationship for the specific reaction rate with the oxide dispersion has been found. Even C_3H_6 selectivity is enhanced by the V_2O_5 dispersion. Since oxygen chemisorption mostly monitors the concentration of coordinatively unsaturated (CUS) V ions in tetrahedral (T_d) coordination [11], the above findings clearly prove the main role of such surface V moieties in providing active oxygen species under reaction conditions able to activate light alkanes forming mainly partial oxidation products. By contrast, the extensive formation of octahedral (O_h) V_2O_5 clusters in highly loaded V_2O_5/SiO_2 catalyst does not exert any beneficial influence on the activity level owing to the inability of lattice oxygen ions to assist the selective oxidation of light alkanes. Indeed, V_2O_5 clusters, having a great availability of "extractable" lattice oxygen ions, quickly react with less stable partial oxidation products enabling their further oxidation via a "redox-type" reaction mechanism according to the fact that CO_2 formation involves a number of oxygen atoms larger than that required for the formation of partial oxidation products [7]. Thus, it can be concluded that both POD [3] and MPO [2,9] reactions on low loaded V_2O_5/SiO_2 catalysts effectively proceed with the participation of activated oxygen species (surface mechanism), while on highly loaded systems the reaction mainly occurs via the less effective redox mechanism involving a direct participation of lattice oxygen ions. Then, the bulk of previous [2,3,9] and present experimental results point to the process of oxygen activation as the key-step in both the POD and MPO reactions.

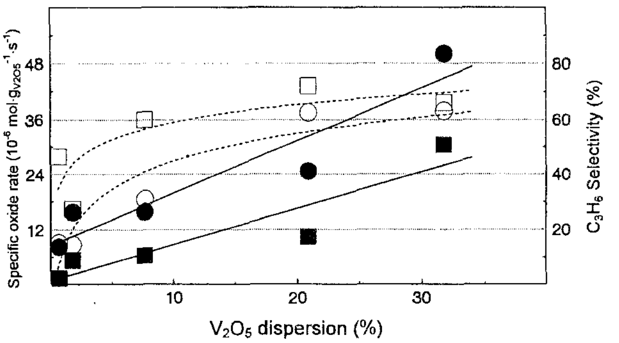

Fig. 2. Propane oxidative dehydrogenation. Influence of the oxide dispersion on the specific oxide rate (■, ●) and C_3H_6 selectivity (□, ○) of V_2O_5/SiO_2 catalysts at 450 (■, □) and 475°C (●, ○). (Oxide dispersion data as determined by LTOC measurements from ref. [9]: 5% V_2O_5/SiO_2, 31.8%; 10% V_2O_5/SiO_2, 20.9%; 20% V_2O_5/SiO_2, 7.7%; 50% V_2O_5/SiO_2, 1.9%; bulk V_2O_5, 0.8%).

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