How oxide carriers affect the reactivity of V_2O_5 catalysts in the oxidative dehydrogenation of propane

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The catalytic pattern of several oxide carriers (MgO, Al_2O_3, ZrO_2, TiO_2, SiO_2, HY zeolite) and supported V_2O_5 (4.7–5.3 wt%) catalysts in the oxidative dehydrogenation of propane to propylene (PODH) has been comparatively investigated. The fundamental role of the oxide support on both reducibility and reactivity of vanadia catalysts has been assessed. A direct relationship between the specific surface activity of oxide carriers and that of vanadia catalysts is discussed. The inverse relationship between the specific activity and the onset temperature of reduction marks the prevailing redox behaviour of V_2O_5 catalysts in the PODH reaction.

Keywords: oxidative dehydrogenation of propane, oxide carriers, V_2O_5 catalysts, specific activity, redox properties

1. Introduction

The production of light olefins by oxidative dehydrogenation (ODH) of the corresponding paraffins is to date one of the most attractive options for converting natural gas into more valuable products. Indeed, ODH reactions present remarkable advantages over conventional catalytic or thermal dehydrogenation processes, the main of which are the absence of both thermodynamic constraints and coking phenomena along with the fact that the exothermic character of the reaction allows one to run the process under adiabatic conditions [1].

Intensive research efforts have documented that vanadia-based systems are active and selective catalysts for attaining the ODH of light paraffins [1–5]. However, the reactivity of supported V_2O_5 catalysts is greatly affected by the nature of the oxide carrier [1–3,6], extent of loading [2,4] and nature of additives [5]. In particular, oxide supports exert a very crucial effect on the reactivity of vanadia catalysts since they determine the coordination and dispersion as well as the electronic properties of the surface V species [2,3,6–9]. In addition, it has been claimed that the acid–base characteristics of oxide supports can also play a role in determining the activity–selectivity pattern of the title systems in the ODH reactions [1,3,10]. Then, although the fundamental role of the oxide carrier on the physico-chemical properties and reactivity of the active phase has been generally recognised, the own functionality of bare oxides and its relevance to the catalytic behaviour of supported vanadia systems in ODH reactions has been not adequately addressed [1–3,6]. Therefore, in this study an attempt to relate thoroughly the activity of various bare oxide carriers (MgO, Al_2O_3, TiO_2, ZrO_2, SiO_2 and HY zeolite) and supported (4.7–5.3 wt%) V_2O_5 catalysts in the oxidative dehydrogenation of propane to propylene (PODH) is reported. The factor(s) affecting the reactivity of both supports and catalysts are discussed.

2. Experimental

Catalysts. Supported V_2O_5 (4.7–5.3 wt%) catalysts were prepared by incipient wetness of commercial oxides (MgO, γ-Al_2O_3, TiO_2, ZrO_2, SiO_2, HY zeolite) with an aqueous solution (pH $=$ 11) of ammonium metavanadate. All the catalysts were dried at 110 °C and then calcined at 600 °C for 16 h. The list of studied samples is presented in table 1.

Catalytic measurements in PODH were carried out in a linear quartz microreactor (i.d., 4 or 8 mm) connected on line with a GC (TCD, FID) system. Reagents and products have been analysed by a three-column system: (1) Porapak Q (length, 3 m; $\varnothing$, $1/8''$) for the separation of CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8; (2) Molecular Sieve (length, 3 m; $\varnothing$, $1/8''$) for the separation of N_2, O_2, CH_4, CO; and (3) Carbowax 20M (length, 3.5 m; $\varnothing$, $1/8''$) for the separation of oxygenates and C_3H_4. Catalytic tests have been performed at 500 °C under the following experimental conditions: P_R, 1 bar; W_{cat}, 0.01–0.25 g (particle size, 0.3–0.5 mm; diluted (1/1) with SiC). The molar composition of the reaction mixture was $C_3H_8 : O_2 : N_2 : He = 2:1:1:8$, whereas a total flow rate of 100 STP $cm^3\,min^{-1}$ was used for all the experiments. Activity data were taken after 20 min time on stream (t_0).

Temperature-programmed reduction (TPR) measurements in the range 200–1000 °C have been performed in a flow apparatus using a 6% H_2/Ar mixture flowing at 60 STP $cm^3\,min^{-1}$, a heating rate of 20 °C min^{-1} and a mass sample of 0.05 g [7].

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Table 1
List of the studied samples.

Carriers			Catalysts			
Code	Sample	SA_{BET} ($m^2 g^{-1}$)	Code	Sample	V_2O_5 loading (wt%)	SA_{BET} ($m^2 g^{-1}$)
M	MgO	24	VM-5	V_2O_5/MgO	4.7	101
A	Al_2O_3	195	VA-5	V_2O_5/Al_2O_3	4.8	209
T	TiO_2	51	VT-5	V_2O_5/TiO_2	5.0	41
Z	ZrO_2	37	VZ-5	V_2O_5/ZrO_2	5.3	34
S	SiO_2	381	VS-5	V_2O_5/SiO_2	5.0	286
H	HY zeolite	632	VH-5	V_2O_5/HY zeolite	5.3	350

Table 2
PODH on oxide carriers and supported V_2O_5 catalysts at 500 °C.

Sample	W/F ($g\,s\,ml^{-1}$)	C_3H_8 conv. (%)	SA ($\mu mol_{C_3H_8}\,g^{-1}\,s^{-1}$)	SSA ($nmol_{C_3H_8}\,m^{-2}\,s^{-1}$)	$S_{C_3H_6}$ (%)	S_{CO_x} (%)
M	1.5	1.2	0.6	27.1	–	100
VM-5	0.075	4.3	4.7	46.4	31	68
A	1.5	6.2	3.4	18.2	35	62
VA-5	0.012	3.2	21.8	104	73	26
T	0.3	3.7	10.1	197	54	44
VT-5	0.006	5.1	69.5	1,690	30	67
Z	1.5	4.7	2.5	69.2	19	79
VZ-5	0.006	2.5	34.1	1,000	46	53
S	1.5	1.0	0.5	1.4	38	33
VS-5	0.075	3.0	3.3	11.4	72	19
H	0.3	3.3	8.9	14.2	44	55
VH-5	0.03	4.4	11.9	34.2	38	60

3. Results and discussion

The activity data of oxide carriers and supported V_2O_5 catalysts are summarised in table 2 in terms of C_3H_8 conversion (%), reaction rate expressed as both specific activity (SA, $\mu mol_{C_3H_8}\,g^{-1}\,s^{-1}$) and specific surface activity (SSA, $nmol_{C_3H_8}\,m^{-2}\,s^{-1}$), C_3H_6 and CO_x selectivity (%). C_3H_8 conversion never exceeds 6% while the O_2 conversion was quite larger, however keeping always less than 40%. All the systems produce essentially C_3H_6, CO_x and minor amounts of C_2 hydrocarbons (1–3%) and oxyproducts (1–7%), while only silica shows a marked functionality towards the formation of oxygenates (22%) and C_2 products (7%).

It is known that the selectivity to propylene in the PODH reaction decreases with propane conversion, while the specific trend of such an inverse relationship generally accounts for the peculiar catalytic action of a class of catalysts [1,3,4,11]. Then, the activity–selectivity data of all the studied systems (table 2) have been reported in figure 1. The wide (0–75%) and random distribution of selectivity data in a comparatively very small range of C_3H_8 conversion (1–6%) [1,11] leads to ascertain that the specific functionality of supports and catalysts is the predominant factor affecting the catalytic pattern of the studied systems.

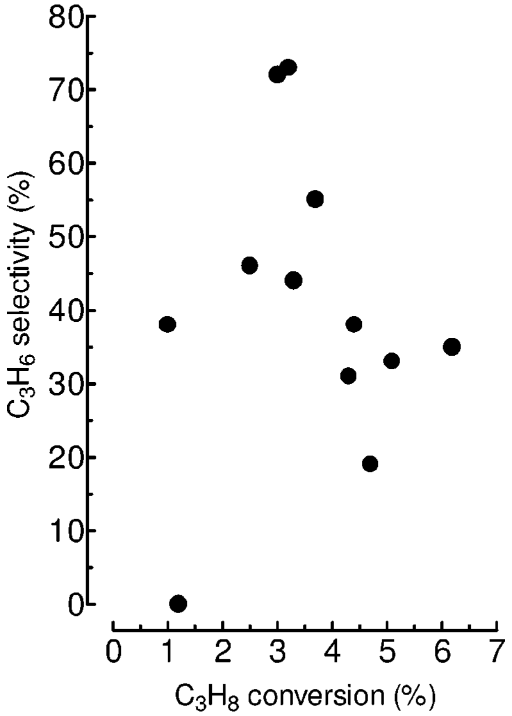

Figure 1. Oxidative dehydrogenation of propane at 500 °C. Selectivity to propylene vs. propane conversion (data from table 2).

Amongst bare oxide supports, titania exhibits the best functionality in PODH bearing the highest values of SA (10.1 $\mu mol_{C_3H_8}\,g^{-1}\,s^{-1}$), SSA (197 $nmol\,m^{-2}\,s^{-1}$) and $S_{C_3H_6}$ (55%). HY zeolite is also a very active system (SA, 8.9 $\mu mol_{C_3H_8}\,g^{-1}\,s^{-1}$), though in terms of SSA (14 $nmol\,m^{-2}\,s^{-1}$) it results more than one order of magnitude less reactive than titania. The $S_{C_3H_6}$ (44%) is also lower than that of titania and, in addition, a progressive loss in activity, likely diagnostic of marked coking phenomena, has been recorded for this system. Zirconia and alumina show comparable SA (2.4–3.5 $\mu\text{mol}_{\text{C}_3\text{H}_8}\,\text{g}^{-1}\,\text{s}^{-1}$) levels, with ZrO_2 being much more reactive than both alumina and zeolite on a surface area unit basis (SSA, 69 $\text{nmol}\,\text{m}^{-2}\,\text{s}^{-1}$). Magnesia and silica are the least active systems with SA values of 0.6 and 0.4 $\mu\text{mol}_{\text{C}_3\text{H}_8}\,\text{g}^{-1}\,\text{s}^{-1}$, respectively; even if in terms of SSA the former (SSA, 27 $\text{nmol}\,\text{m}^{-2}\,\text{s}^{-1}$) is quite more reactive than the latter one (SSA, 2 $\text{nmol}\,\text{m}^{-2}\,\text{s}^{-1}$). Silica displays a $S_{\text{C}_3\text{H}_6}$ (38%) comparable with that of other oxides, while no propylene formation is detected on magnesia. Taking into account that the above oxides are characterized by rather different surface area values, a reliable comparison of their catalytic activity, made on the basis of the SSA, provides the following reactivity scale:

$$\text{T} > \text{Z} > \text{M} > \text{A} > \text{H} > \text{S}$$

Vanadia strongly promotes the functionality of all the oxide carriers enabling a general enhancement in SA, SSA and C_3H_6 selectivity (table 2). VT-5 is the most active catalyst both in terms of SA (69.5 $\mu\text{mol}_{\text{C}_3\text{H}_8}\,\text{g}^{-1}\,\text{s}^{-1}$) and SSA (1,690 $\text{nmol}\,\text{m}^{-2}\,\text{s}^{-1}$), while its lower $S_{\text{C}_3\text{H}_6}$ (30%) with respect to the bare titania support looks mainly a consequence of its high oxidising strength. The VZ-5 sample displays SA (34.1 $\mu\text{mol}_{\text{C}_3\text{H}_8}\,\text{g}^{-1}\,\text{s}^{-1}$) and SSA (1,000 $\text{nmol}\,\text{m}^{-2}\,\text{s}^{-1}$) values comparable with those of the VT-5 catalyst and an enhanced selectivity to propylene (46%) also with respect to the relative carrier. VA-5 exhibits a SA (21.8 $\mu\text{mol}_{\text{C}_3\text{H}_8}\,\text{g}^{-1}\,\text{s}^{-1}$) slightly lower than that of VZ-5 sample and the highest $S_{\text{C}_3\text{H}_6}$ (73%), though it results much less reactive in terms of SSA (104 $\text{nmol}\,\text{m}^{-2}\,\text{s}^{-1}$) of both VT-5 and VZ-5 systems. VH-5 and VM-5 samples are characterised by comparable lower SSA (34.2–46.4 $\mu\text{mol}_{\text{C}_3\text{H}_8}\,\text{g}^{-1}\,\text{s}^{-1}$) and also by similar $S_{\text{C}_3\text{H}_6}$ values (31–38%). Likewise to the relative support, a progressive deactivation of the VH-5 catalyst has been recorded. Finally, the VS-5 is the least reactive system both in terms of SA and SSA even if it enables a high $S_{\text{C}_3\text{H}_6}$ (72%). Then, from the above results, the following SSA scale of vanadia catalysts is obtained:

$$\text{VT-5} > \text{VZ-5} > \text{VA-5} > \text{VM-5} > \text{VH-5} > \text{VS-5}.$$

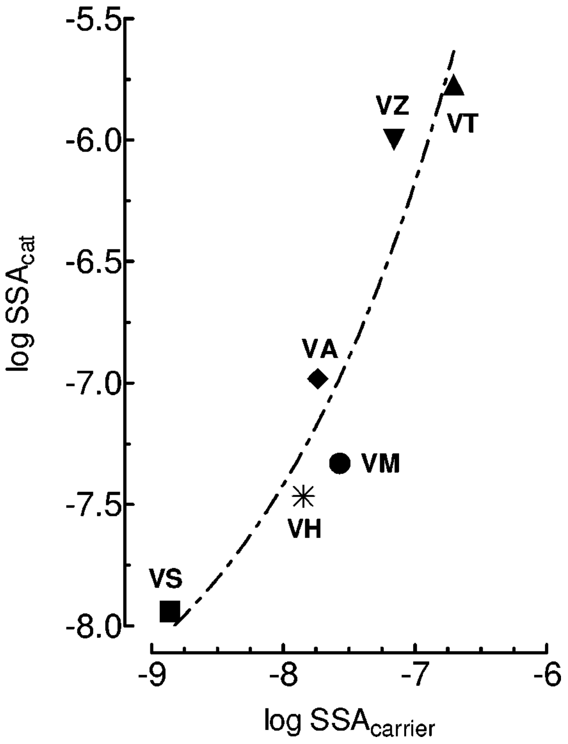

Figure 2. Oxidative dehydrogenation of propane at 500 °C. Relationship between the specific surface activity of catalysts (SSA_{cat}) and that of related oxide carriers ($\text{SSA}_{\text{carrier}}$).

From a comparison of this activity scale with that of the bare oxide carriers (T $>$ Z $>$ M $>$ A $>$ H $>$ S) it immediately emerges that the activity of supported V_2O_5 catalysts practically parallels the own functionality of the corresponding support. In fact, plotting the specific surface activity values of V catalysts (SSA_{cat}) vs. those of the corresponding carriers ($\text{SSA}_{\text{carrier}}$) an unambiguously direct relationship is obtained, as shown in figure 2. Further, the promoting action of V_2O_5 results to be more effective for the oxide carriers (T and Z) denoting a superior reactivity. This implies that a comparative testing of bare carriers can be taken as a time-saving approach to shed light into the reactivity of different supported vanadia catalysts in PODH. Notably, this finding also proves that a same surface property could be the *key-factor* controlling the reactivity of both bare oxides and that of supported vanadia systems. On this account, it is generally accepted that the activity–selectivity pattern of vanadia catalysts in selective oxidation reactions is mostly determined by their reducibility since the strength of the vanadium–oxygen bond controls the activation of the reactant molecule generally acting as rate-determining step of the catalytic surface reaction [1–3,5,9–11]. In order to rationalise the catalytic pattern of our oxide carriers and vanadia catalysts, their reduction features have been comparatively probed by TPR measurements. The reduction profiles of carriers and catalysts are shown in figure 3, while the onset temperature of reduction ($T_{\text{o,red}}$), the temperature of peak maximum (T_{M_i}) and the integral H_2 consumption are summarised in table 3. H_2 consumption data account for the stoichiometric reduction of V^{5+} to V^{3+} in all the catalysts with the exception of the VM-5 sample for which the formation of bulk Mg vanadates hinders a full reduction of vanadia [1,2,7]. In this respect, the unconventional increase in surface area of such catalyst with respect to the bare support (table 1), induced by hydration–dissolution and re-precipitation phenomena during preparation, likely accounts for the partial occlusion of the active phase in the bulk [7]. Moreover, the TPR spectra of vanadia catalysts consist of a complex profile featuring various reduction peaks which can be attributed to surface V species having a different dispersion and coordination symmetry [7]. In particular, peaks at $T < 600\,^{\circ}\text{C}$ arise from the reduction of isolated and oligomeric species in p-tetrahedral and square-pyramidal coordination, whilst peaks at $T > 600\,^\circ\mathrm{C}$ signal the presence of V ions in an octahedral coordination [7].

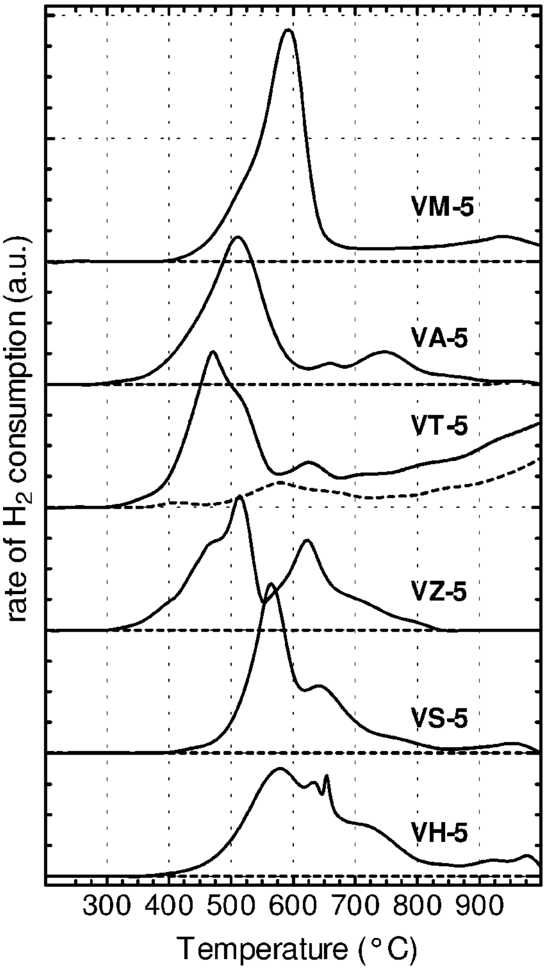

Figure 3. TPR profiles of vanadia catalysts (—) and relative oxide supports (- - -).

Amongst the bare oxide supports, only TiO_2 displays a peculiar reduction profile accounting for a relatively enhanced reducibility both at the surface and in the bulk, whilst the flat profiles of HY zeolite, SiO_2, ZrO_2, Al_2O_3 and MgO indicate that such systems are essentially not reducible [7,9]. However, further qualitative insights into the *surface reduction characteristics* of the bare oxide carriers can be indirectly achieved from the TPR analysis of the related vanadia catalysts monitoring the reactivity of the "V–O support" *bridging functionalities* [7,9]. In fact, the reducibility scale of V_2O_5 catalysts:

$$\text{VT-5} > \text{VZ-5} > \text{VA-5} > \text{VS-5} > \text{VH-5} > \text{VM-5},$$

the same either based on $T_{\mathrm{o,red}}$ or $T_{\mathrm{M_1}}$ values (table 3), is in a very good agreement with the literature data accounting for a quite different reactivity of the surface oxygen layer in the various oxide carriers [7–9]. Moreover, the similar trend of the SSA and reducibility scales matches a more general pattern for the catalytic behaviour of vanadia systems relating an easier reduction (i.e., VT-5, VZ-5, VA-5) with a higher reactivity in various oxidation reactions [2,3,6,8,9]. Indeed, plotting the values of SSA and SA of vanadia catalysts (table 2) vs. the relative $T_{\mathrm{o,red}}$ (table 3), two analogous inverse relationships are obtained, as shown in figure 4. Evidently, such correlations account for the prevailing redox behaviour of vanadia systems in PODH likely occurring through the cyclic activation of propane and gas-phase oxygen molecules, respectively, over the same surface site according to a *concerted* mechanism [2,4,5,10,11]. Then, it must be stressed that for the above systems, likely bearing quite different surface functionality in terms of acid–base properties, the catalytic action in PODH is clearly decided by the redox character. Further, the fact that *surface reducibility* and reactivity of oxide carriers and V_2O_5 catalysts are strictly related each other can be taken as a proof of the surface catalytic activation of gas-phase oxygen also on some specific sites of solids (i.e., MgO, Al_2O_3, SiO_2, HY zeolite)

Table 3

TPR of oxide carriers and V_2O_5 catalysts. Onset temperature of reduction ($T_{\mathrm{o,red}}$), temperature of peak maximum (T_{M_i}) and integral H_2 consumption.

Catalyst	$T_{\mathrm{o,red}}$ (°C)	$T_{\mathrm{M_1}}$ [a] (°C)	$T_{\mathrm{M_2}}$ [b] (°C)	$T_{\mathrm{M_3}}$ [c] (°C)	H_2 consumption (μmol/g_{cat})	($\mathrm{mol_{H_2}}$/g $\mathrm{at_V}$)
M	–	–	–	–	–	
VM-5	400	587	–	930	435.4	0.84
A	–	–	–	–	–	
VA-5	315	517	649	752	512.9	0.98
T	400	579	–	–	234.1	
VT-5	285	479	620	–	846.2	1.53
Z	–	–	–	–	–	
VZ-5	300	510	625	–	595.8	1.02
S	–	–	–	–	–	
VS-5	370	558	642	955	548.7	0.99
H	–	–	–	–	–	
VH-5	385	581	652	978	587.5	1.01

[a] $T_{\mathrm{M_1}} < 600\,^\circ\mathrm{C}$.
[b] $600 < T_{\mathrm{M_2}} < 750\,^\circ\mathrm{C}$.
[c] $T_{\mathrm{M_3}} > 750\,^\circ\mathrm{C}$.

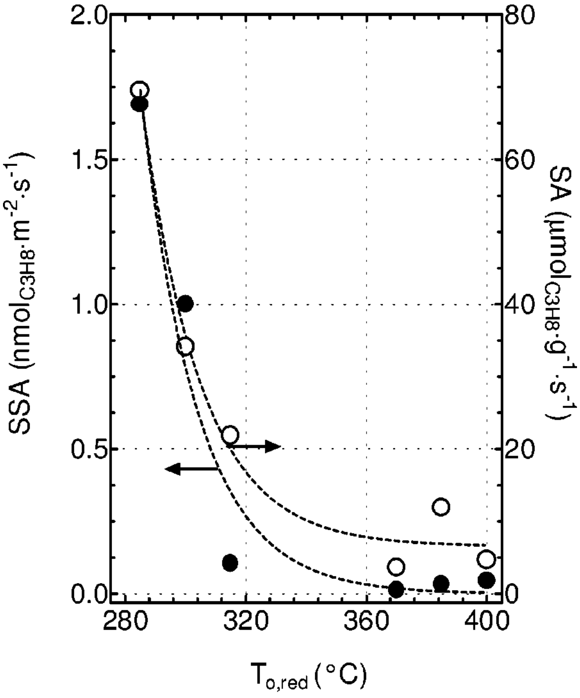

Figure 4. Oxidative dehydrogenation of propane on supported vanadia catalysts at 500 °C. Specific surface activity (SSA, $\mathrm{nmol_{C_3H_8}\,m^{-2}\,s^{-1}}$) and specific activity (SA, $\mu\mathrm{mol_{C_3H_8}\,g^{-1}\,s^{-1}}$) vs. the onset temperature of reduction ($T_{\mathrm{o,red}}$).

bearing a prevailing ionic character [1,4,6,10]. This is in agreement with our previous findings outlining the occurrence of a direct relationship between *density of reduced sites*, evaluated under steady-state reaction conditions, and activity of various silica catalysts in the partial oxidation of methane to formaldehyde [12,13].

4. Conclusion

The catalytic behaviour of several oxide carriers and supported vanadia catalysts in the PODH has been investigated. A direct relationship between the activity of bare supports and catalysts has been outlined.

Redox properties play a prevailing role in determining the activity–selectivity pattern of supported vanadia catalysts in PODH.

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