Latin American Applied Research 35:273-280 (2005)

OXIDATIVE DEHYDROGENATION OF PROPANE OVER (Mo)-Sm-V-O CATALYTIC SYSTEM. ROLE OF THE DIFFERENT PHASES

B. P. BARBERO[1], R. PRADA SILVY[2] and L. E. CADÚS[1].

[1] *Instituto de Investigaciones en Tecnología Química (INTEQUI), UNSL – CONICET, Casilla de correo 290, 5700, San Luis, Argentina.*

E-mail: bbarbero; lcadus@unsl.edu.ar

[2] *Université Catholique de Louvain, Croix du Sud 2, 1348 Louvain-la-Neuve, Belgium.*

Abstract **- The (Mo)-Sm-V-O catalytic system has been exhaustively studied in the propane oxidative dehydrogenation reaction. In order to obtain different surface arrangements, simple oxides (V_2O_5, Sm_2O_3 and MoO_3), SmV mixed oxides with different Sm/V molar ratio and $SmVO_4$ impregnated with vanadium, samarium or molybdenum were prepared. The function that the possible arrangements play has been identified. A slight samarium excess favors total combustion causing a strong drop of selectivity, therefore, it is necessary to avoid it. On the other hand, vanadium excess constituting surface vanadium oxide species (VO_x) notably increases the catalytic activity while a higher vanadium amount leads to crystalline V_2O_5 formation and the catalyst behavior tends to that of bulk V_2O_5. Molybdenum at low concentrations constitutes surface molybdenum oxide species (MoO_x) which showed to be highly selective in propane ODH. High contents of molybdenum favor the formation of crystalline MoO_3, thus, causing an important catalyst deactivation. Finally, a comparison with other known efficient vanadium based catalysts is made and hence, the potentiality of (Mo)-Sm-V-O catalysts is shown.**

Keywords **- oxidative dehydrogenation, propane, vanadium, samarium, molybdenum.**

I. INTRODUCTION

One of the major interests to the refining and petrochemical industry is the upgrading of cheaper feedstock. In this sense, the oxidative dehydrogenation (ODH) reaction of light alkanes so as to obtain the corresponding olefin is an attractive alternative (Kung, 1994; Cavani and Trifiro, 1995; 1997; Albonetti *et al.*, 1996; Baerns and Buyevskaya, 1998). However, the practical application of this type of process still remains an unresolved scientific and technological challenge in spite of the broad research effort devoted to this goal. The main aim is to obtain olefin selectivity and productivity to make the process economically feasible. Thus, the catalyst should be optimized in order to minimize the unselected oxidation pathways which lead to low yields.

Among the large number of catalytic systems essayed in the ODH of light alkanes, vanadium based catalysts are the most efficient whether the vanadium oxide is deposited on an oxide support or combined with other oxides (Mamedov and Cortés Corberán, 1995; Bañares, 1999). The physico-chemical properties of such catalysts, and hence, its catalytic performance, are highly dependent on dispersion, repartition, coordination, and oxidation state of V atoms (Wachs and Weckhuysen, 1997; Kung and Kung, 1997; Blasco and López Nieto, 1997; Grzybowska-Swierkosz, 1997; Khodakov *et al.*, 1998; Burrows *et al.*, 1999; Solsona *et al.*, 2001a, b; Argyle *et al.*, 2002; Keränen *et al.*, 2002).

In previous papers (Barbero and Cadús, 2002a, b, 2003a, b), the (Mo)-Sm-V-O solid system has been exhaustively characterized by studying the possible physico-chemical arrangements. In this work, the performance of (Mo)-Sm-V-O catalytic system in ODH of propane is compiled and the role of the different phases is deduced. A comparison with other known efficient vanadium based catalysts is also made and hence, the potentiality of (Mo)-Sm-V-O catalysts is shown.

II. EXPERIMENTAL SECTION

A. Catalysts preparation

Simple oxides. V_2O_5 was prepared by calcination in air of NH_4VO_3 (Mallinckrodt) at 450°C for 4 h. Sm_2O_3 and MoO_3 from commercial origin were used.

Mixed oxides. Samples with atomic ratios Sm/V = 0.8, 1 and 1.2 were prepared by the citrate method (Courty, 1973). $Sm(NO_3)_3.6H_2O$ (Fluka), NH_4VO_3 (Merck) and citric acid (Aldrich) were used as reagents. A citric acid solution with a 10% excess over the number of ionic equivalents of cations was prepared. Transparent solutions of samarium nitrate and ammonium metavanadate were prepared and added to the citric acid solution in such concentration that the Sm/V atomic ratio was equal to that in the resulting catalysts. The resulting solution was concentrated in a Rotavapor at 70°C under reduce pressure until the solution became viscous. Then, it was dried to obtain amorphous organic precursor. The solid obtained was decomposed in air at 400°C for 4 h and finally calcined at 600°C for 3 h. These catalysts were denoted as SmV*x*, where x = 0.8, 1 or 1.2 indicates the Sm/V atomic ratio.

Impregnated catalysts. $SmVO_4$, obtained by the citrate method as described above, was impregnated with:

a) An aqueous solution of $Sm(NO_3)_3.6H_2O$ by the dry impregnation method. The resulting solid was dried in vacuum at 70°C for 2.5 h and then, calcined at 400°C for 3 h and at 600°C for 3 h.

b) An aqueous solution of NH_4VO_3 (Merck) by incipient wetness impregnation in multiple steps. After each impregnation step, samples were dried at 100°C and then, dried solids were calcined at 600°C for 12 h.

c) An aqueous solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ by dry impregnation. Impregnated samples were dried in vacuum at 50°C for 1 h and then, calcined in air at 450°C for 3 h and at 550°C for 3 h.

The resulting catalysts were denoted as $xM/SmVO_4$, being x = 3 or 12 mol% and M = Sm, V or Mo.

B. Catalytic activity

The catalysts were tested in a fixed – bed, U-type quartz microreactor operated at atmospheric pressure. In each test, 500 mg of sample were used. The temperature was varied between 350 and 550ºC. The feed was a mixture of 4 vol.% propane and 4 vol.% oxygen balanced with helium. The total flow rate was 50 ml min^{-1} measured at room temperature. The reaction products were analyzed by a Delsi Di 200 on-line gas chromatograph equipped with a thermal conductivity detector. Helium was the carrier gas. Two columns were used: a Hayesep Q column to separate hydrocarbons and CO_2, and a Carbosieve SII column to separate oxygen, carbon monoxide and methane. The homogeneous contribution was tested in the empty reactor. These runs showed no activity below 550ºC. Results were similar with and without the use of quartz particles. The measurements was made after at least 30 min time-on-stream, which has been verified it is sufficient time to achieve the steady state. The conversion of propane, X (%), is defined as the percentage of propane feed which has reacted. The selectivities, S (%), are defined as the percentage of propane that reacts to a specific product.

III. RESULTS

The catalytic behavior of all the catalysts in the propane oxidative dehydrogenation was studied. The results are shown in Table 1. Propylene, CO_2 and CO were the main products. At high reaction temperatures, cracking products (C_2H_4 and CH_4) were also detected. No other oxygenated products were found.

Simple oxides. V_2O_5 was an active catalyst in the propane oxidative dehydrogenation but its selectivity to propylene rapidly decreases with the increase of propane conversion (S_{C3H6} decreases from 81% to 14% as X_{C3H8} increases from 1.5% to 35%). Thus, the yield to propylene was lower than 5% although the reaction temperature was above 500°C. Sm_2O_3 was very active but its selectivity to propylene was practically negligible, being CO_2 the main product obtained. The selectivity to cracking products was also high. MoO_3 was not very active under the conditions used in this study. The conversion was only 0.5% at 550ºC.

Mixed oxides. SmV*x* catalysts showed a great activity in propane ODH. Propane conversion was similar on all the catalysts (x = 0.8, 1 and 1.2) in the range of tested reaction temperatures. However, selectivity depended strongly on the Sm/V atomic ratio. SmV0.8 presented high selectivity to propylene at low conversion levels but selectivity decreased quickly as conversion increased. This behavior was similar to that observed on pure V_2O_5. SmV1 showed relatively good selectivity at low conversion (S_{C3H6} = 54% at X_{C3H8} = 1.9%) and it decreased slightly as conversion increased. The selectivity to propylene on SmV1.2 drastically dropped being CO_2 the major reaction product. At reaction temperatures higher than 450ºC, the selectivity to cracking products was also important (>1.5%).

Comparing the yield to C_3H_6 as a function of the Sm/V atomic ratio at different reaction temperatures, it has been observed that the curve presents a maximum at a ratio Sm/V = 1/1.

Impregnated catalysts. $SmVO_4$ used as support of the impregnated catalysts resulted slightly different to SmV1. At low reaction temperatures, both propane conversion and selectivity to propylene on $SmVO_4$ were lower than on SmV1. The results on impregnated catalysts indicate that the $SmVO_4$ catalytic behavior is significantly modified by the addition of Sm, V or Mo.

The $3Sm/SmVO_4$ catalyst was less active that $SmVO_4$ and the selectivity to C_3H_6 dropped drastically. High levels of CO were obtained, however, the main product of reaction was CO_2. Considering the variation of S_{C3H6} as a function of X_{C3H8}, the behavior was similar to that of SmV1.2 catalyst.

The addition of 3% vanadium over $SmVO_4$ increased notably the activity at low reaction temperatures (7% conversion at 350ºC) and the level of selectivity to propylene was relatively good (57%). At low conversion levels, catalysts impregnated with vanadium exhibited better selectivity and propylene yield than $SmVO_4$. Selectivity decreased as conversion increased. This decrease was more marked when vanadium loading increased becoming similar to the behavior of pure V_2O_5. Below certain reaction temperature, the selectivity to propylene improved significantly due to vanadium impregnation.

$SmVO_4$ with 3% molybdenum was almost as active as pure $SmVO_4$ but it showed a much higher selectivity to propylene (S_{C3H6} = 84% at 1.5% conversion and 350ºC reaction temperature). Selectivity to propylene decreased with the increase of conversion and this decrease was more rapid as molybdenum loading increased. Propane conversion also decreased with the increase of molybdenum loading. The highest yield to propylene was obtained with $3Mo/SmVO_4$.

IV. DISCUSSION

The nature of (Mo)-Sm-V-O catalytic system has been thoroughly studied in previous works. The results indicate that this system presents promissory alternatives for the propane oxidative dehydrogenation.

Table 1. Results of catalytic test.

Catalyst	$T_{reaction}$ (ºC)	X_{C3H8} (%)	S_{C3H6} (%)	S_{CO2} (%)	S_{CO} (%)	S_{C2H4} (%)	S_{CH4} (%)	Y_{C3H6} (%)
MoO_3	400	0	0	0	0	0	0	0
	450	0	0	0	0	0	0	0
	500	0	0	0	0	0	0	0
	550	0.5	82.1	5.8	0	12.0	t	0.4
Sm_2O_3	400	4.8	0	100	0	0	0	0
	450	20.0	0	72.8	24.6	2.58	0	0
	500	35.0	8.2	56.1	22.2	12.79	0.73	2.9
V_2O_5	350	1.5	81.3	8.6	10.1	0	0	1.2
	400	3.2	67.2	11.8	21.0	0	0	2.1
	450	8.0	43.4	14.2	42.5	0	0	3.5
	500	15.1	27.4	17.5	55.1	0	0	4.2
	550	35.1	13.9	46.5	38.1	0.33	1.19	4.9
SmV0.8	350	1.29	77.47	18.27	4.26	0	0	1.0
	400	4.08	56.62	26.84	16.54	0	0	2.3
	450	13.79	32.27	44.51	44.51	0	0	4.5
	500	29.51	16.21	56.14	56.14	0	0	4.8
	550	31.01	19.79	49.71	49.71	0.37	0	6.1
SmV1	350	1.92	54.24	45.76	0	0	0	1.0
	400	9.27	46.61	33.44	19.96	0	0	4.3
	450	22.99	36.16	35.93	27.90	0	0	8.3
	500	33.99	27.69	38.42	33.89	t	0	9.4
	550	34.08	23.66	41.01	34.49	0.83	0	8.1
SmV1.2	350	1.28	0.00	100.00	0.00	0	0	0
	400	4.66	3.80	80.13	16.07	0	0	0.2
	450	16.20	7.54	49.37	41.62	1.47	0	1.2
	500	29.69	7.86	40.38	46.29	4.14	1.33	2.3
	550	32.49	6.31	45.81	38.69	7.70	1.48	2.1
$SmVO_4$	350	1.1	36.2	57.0	6.8	0	0	0.4
	400	4.5	36.8	47.5	15.8	0	0	1.6
	450	15.6	34.0	41.2	23.9	0.83	0	5.3
	500	33.8	27.6	34.9	35.8	1.66	t	9.3
	550	35.8	24.1	34.4	35.8	4.57	1.18	8.6
$3Sm/SmVO_4$	350	0.41	0	100		0	0	0
	400	1.67	t	100		0	0	0
	450	9.39	7.35	46.9	45.7	0	0	0.7
	500	20.22	9.34	43.7	46.9	t	0	1.9
	550	33.44	9.11	39.3	48.1	3.46	t	3.0
$3V/SmVO_4$	350	6.9	56.7	20.7	22.6	0	0	3.9
	400	19.9	34.0	27.7	38.3	0	0	6.8
	450	29.8	24.8	31.6	43.6	0	0	7.4
	500	31.0	26.1	33.0	40.5	0.36	0	8.1
	550	32.9	26.6	37.2	34.1	0.87	1.19	8.8
$12V/SmVO_4$	350	1.3	87.0	8.1	4.9	0	0	1.1
	400	4.4	64.7	12.0	23.3	0	0	2.8
	450	11.7	41.0	19.2	39.8	0	0	4.8
	500	29.4	18.5	23.4	58.0	0.23	0	5.4
	550	31.3	22.1	28.1	47.9	0.70	1.25	6.9
$3Mo/SmVO_4$	350	1.5	84.4	12.6	2.9	0	0	1.2
	400	4.9	75.7	14.3	9.9	0	0	3.7
	450	12.7	63.2	20.5	16.3	0	0	8.0
	500	28.8	42.8	29.7	26.7	0.83	0	12.3
	550	35.2	37.3	28.8	31.8	1.33	0.76	13.1
$12Mo/SmVO_4$	350	0.5	87.4	12.6	0.0	0	0	0.4
	400	1.5	86.9	13.1	0.0	0	0	1.3
	450	4.5	69.8	16.3	13.9	0	0	3.1
	500	12.3	41.0	21.0	38.0	0	0	5.0
	550	29.9	19.2	23.0	57.5	0.28	0	5.7

t = traces

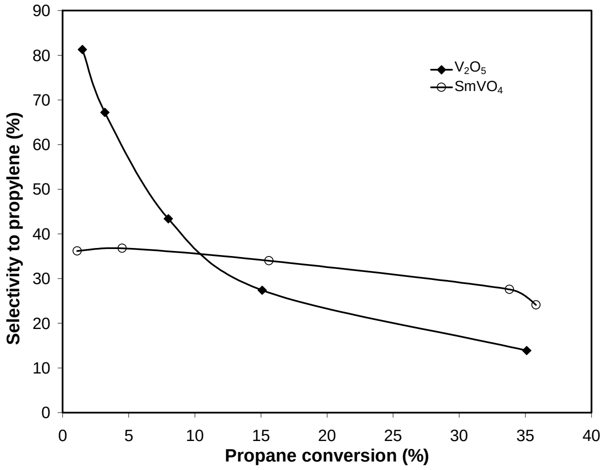
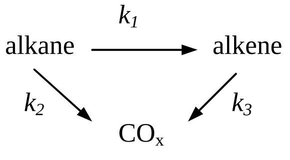


Figure 1. Selectivity to propylene as a function of the propane conversion on V_2O_5 and $SmVO_4$.

Among the simple oxides studied in this work (V_2O_5, Sm_2O_3 and MoO_3), only V_2O_5 showed a relevant activity but the yield to propylene was lower than 5%. The formulation of a more complex catalytic system, as it is the case of SmV*x* mixed oxides, could yield a best performance. In fact, yield to propylene on $SmVO_4$ pure phase resulted more than the double that on V_2O_5.

The active centers on V_2O_5 as well as on $SmVO_4$ are constituted by vanadium ions. However, its catalytic behavior in propane ODH is noticeably different (Fig. 1). This indicates that the type of coordination that the vanadium presents in each oxide determines its performance as catalyst. This observation is coherent with the different V-O bonds existing. The vanadium ions present octahedral coordination in V_2O_5 (Haber *et al.*, 1997) and there are terminal oxygen atoms (V=O) while in $SmVO_4$, vanadium ions are in tetrahedral coordination and there are only bridging oxygen atoms (V-O-V).

In order to explain the function each oxygen atom type (or the coordination type of the vanadium ions) plays in the oxidative dehydrogenation, it is convenient to consider the scheme of parallel and consecutive reactions proposed by several research teams (Kung, 1994; Blasco and López Nieto, 1997) and that can be represented as follows:



where k_1, k_2 and k_3 are the kinetic constants. In agreement with this scheme, the selectivity at low conversion levels will be related to the k_1/k_2 ratio, while at high conversion levels the selectivity will be associated to the $k_1/(k_2+k_3)$ ratio.

Blasco and López Nieto (1997) have obtained theoretical curves of selectivity to propylene as a function of the conversion of propane varying the k_2/k_1 and k_3/k_1 ratios. Comparing these curves with the results obtained experimentally on our catalysts, it can be observed that the behavior of $SmVO_4$ corresponds to a k_2/k_1 ratio greater than 1, *i.e.* there is an important contribution of the reaction of direct combustion of propane. On the other hand, the k_3/k_1 ratio would be very small, indicating that propylene consecutive combustion is almost negligible. The curve of selectivity to propylene as a function of propane conversion obtained on V_2O_5 (Fig. 1) is comparable to that theoretically obtained with k_2/k_1 ratio ca. 0 and k_3/k_1 ratio approx. 10. This indicates that propane direct combustion is negligible but propylene consecutive combustion is relevant.

Consequently, either terminal oxygen atoms or octahedrally coordinated vanadium ions would be responsible for propylene combustion, while tetrahedrally coordinated vanadium ions would be more selective.

From these observations, with regard to a catalyst design it can be suggested that the challenge is to find a host matrix in which the cation constituting the active site is in a desirable coordination. Then, the way to increase the amount of these sites would be found. Likewise, samarium showed to be an appropriate element, since V_2O_5 (octahedrally coordinated vanadium ions) easily reacts with samarium to constitute $SmVO_4$ (tetrahedrally coordinated vanadium ions) (Barbero and Cadús, 2002a). Other advantageous feature of $SmVO_4$ is its high thermal stability with respect to V_2O_5.

With the aim of optimizing the oxide structure holding the catalytically active vanadium iones, the effect of Sm-V-O system non-stoichiometry was studied. It has been found that when the composition of SmV*x* mixed oxides is different from the stoichiometry corresponding to $SmVO_4$, the catalytic behavior varies notably. The selectivity to propylene on the sample with samarium excess (SmV1.2) drops drastically. It has been reported (Zhang *et al.*, 1999) that an excess of Y_2O_3 in nYVO catalysts prepared by the citrate method is responsible for total oxidation. Unlike what happens with MgO in MgVO catalysts, Y_2O_3 does not promote the propylene desorption. This would be due to the strong basic sites existing on Y_2O_3 which are very active in the total oxidation (Zhaorigetu *et al.*, 1996). Thus it could be suggested that free samarium present in $SmVO_4$ favors the direct combustion of propane causing the decrease of the selectivity to propylene. To confirm this, a probable arrangement including $SmVO_4$ and Sm_2O_3 was synthesized artificially by impregnating $SmVO_4$ with samarium ($3Sm/SmVO_4$). As a matter of fact, a similar behavior to SmV1.2 was obtained on this catalyst.

Another fact to highlight is that the selectivity to cracking products on SmV1.2 increases significantly. This would be due to the presence of samarium excess since pure Sm_2O_3 also showed a high selectivity to cracking products.

On the other hand, the sample with vanadium excess (SmV0.8) exhibits a great increase of selectivity to propylene at low conversion levels (around 20% at 3% conversion) with respect to SmV1. However, the selectivity decreases with increasing conversion similarly to that on pure V_2O_5. The preparation method of SmV0.8 catalysts does not assure about how vanadium excess is distributed. Vanadium could have remained dispersed in a matrix of $SmVO_4$ or it could have segregated to the surface during the preparation, resulting in a $SmVO_4$ recovered by vanadium. In an attemp to study in detail the behavior of this last arrangement, catalysts were prepared by impregnating $SmVO_4$ with vanadium.

$SmVO_4$ used as support of impregnated catalysts was prepared by the citrate method in the same way as SmV*x* catalysts. Although this synthesis method confers high purity and good reproducibility, this $SmVO_4$ resulted slightly different to SmV1. By an enlarged physico-chemical characterization that has been reported (Barbero and Cadús, 2003a), it was found that $SmVO_4$ contains a slight excess of samarium on the surface and this explains the differences on the propylene selectivity at initial levels of conversion (X_{C3H8}~0%) between the $SmVO_4$ used as support of impregnated catalysts (S_{C3H6}~36%) and SmV1 (S_{C3H6}~ 55%).

The impregnation of $SmVO_4$ with vanadium increases notably the selectivity to propylene at low conversion levels. This indicates that propane direct combustion would be controlled. Probably, the impregnated vanadium blocks the active sites responsible for direct combustion. An important increase of conversion on $3V/SmVO_4$ at low reaction temperatures was also observed. The differences found in the catalytic behavior of $3V/SmVO_4$ and $12V/SmVO_4$ make us think that different vanadium species exist on the surface as a function of vanadium loading. The characterization of these catalysts has been made by several techniques and reported (Barbero and Cadús, 2003a). Briefly, it has been determined that the vanadium surface coverage in $3V/SmVO_4$ catalyst is lower than the theoretical monolayer (approx. 50 %) and that vanadium is found as surface vanadium oxide species (VO_x) characterized by a reduction signal at about 500ºC in the temperature programmed reduction profile and the appearance of bands at 980-1010, 680-720 and 505-540 cm^{-1} in Raman spectrum. In the case of $12V/SmVO_4$ catalyst, the surface coverage is higher than two theoretical monolayers. The formation of V_2O_5 crystals was observed by XRD and confirmed by the results of temperature programmed reduction studies, the appearance of a band at 1020 cm^{-1} in the FT-IR spectra and the characteristic bands of bulk V_2O_5 in Raman spectra. Consequently, the increase of the activity at low reaction temperature could be attributed to surface VO_x species while V_2O_5 crystals on the surface of $12V/SmVO_4$ catalyst would be the reason why the catalytic behavior of the latter is similar to that of pure V_2O_5.

Taking into account that the behavior of SmV0.8 catalyst is also similar to that of bulk V_2O_5, it can be suggested that the vanadium excess has segregated during the preparation forming V_2O_5 crystals. This would indicate that $SmVO_4$ cannot include a higher amount of vanadium ions than that corresponding to stoichiometry. Consequently, one of the optimal structures of Sm-V-O system in which vanadium ions would exist in tetrahedral coordination, would be pure $SmVO_4$. Then, the addition of one or more cations could improve $SmVO_4$ performance. As it has been discussed above, surface vanadium species increase $SmVO_4$ catalytic activity. The addition of another appropriately chosen element which helps to design a surface architecture similar to that observed with vanadium could be of interest.

Molybdenum has been reported as a highly selective element in dehydrogenation reactions forming Mg-Mo-O (Yoon *et al*., 1996; Abello *et al*., 1996; Cadús *et al*., 1996, 1997) and Mo-Mn-O (Cadús and Ferretti, 2000, 2002) systems. The promotive effect of molybdenum on V-Mg-O (Oganowski *et al*., 1996; Dejoz *et al*., 1999) has been studied as well. Moreover, $SmVO_4$ was impregnated with different molybdenum loadings. As with vanadium, the object here was to discriminate different species that may be formed on the surface and to determine the role that these species play in propane ODH.

The results of catalytic activity show that the impregnation of $SmVO_4$ with 3% Mo does not modify significantly propane conversion but brings about a marked increase of yield to propylene (12.3% at 500ºC). As in the case of impregnated catalysts with vanadium, it has been calculated that the surface coverage is lower that 50% of the theoretical monolayer. From Raman spectroscopy results reported in elsewhere (Barbero and Cadús, 2003b), the existence of surface molybdenum oxide species (MoO_x) was detected. These species would be very selective to propylene and, consequently, they are responsible for a higher yield. With higher molybdenum loadings (12% Mo), a remarkable decrease of conversion as well as of yield and selectivity to propylene is observed. The surface coverage of this catalyst was about two theoretical monolayers. Both Raman spectroscopy and TPR studies show that molybdenum is present on $12Mo/SmVO_4$ catalyst as surface polymolybdate species and MoO_3 crystals. The formation of MoO_3 crystals on the surface would explain of the catalytic behavior since pure MoO_3 is practically inactive in propane oxidative dehydrogenation under the experimental conditions used in this study. Propane conversion was only 0.5% at 550ºC.

It has been reported that propane direct combustion step brings about CO_2 mainly, while propylene consecutive combustion produces both CO and CO_2. Taking this into account and also the scheme of parallel and consecutive reactions presented above, a way to

Table 2. Results of catalytic activity reported in the literature.

Catalyst	$T_{reaction}$ (ºC)	C_3H_8:O_2 ratio	W/F (g_{cat} h/mol_{C3})	Y_{C3H6} (%)	Reference
19V-Mg-O	540	2:1	30	15.2	Chaar *et al.*, 1988.
24V-Mg-O	540	2:1	10	12.3	
40V-Mg-O	540	2:1	20	14.0	
(1/2)MgVO	540	1:2	60	10.0	Gao *et al.*, 1994.
(3/4)MgVO	540	1:2	60	11.3	
(1/1)MgVO	540	1:2	60	14.4	
(5/4)MgVO	540	1:2	60	15.3	
(4/1)MgVO	540	1:2	60	16.4	
20VO/MgX	550	1:2	2.7	7.1	Corma *et al.*, 1993.
34VO/MgX	550	1:2	8.9	11.0	
18VO/Mg	550	1:2	8.9	9.9	
V/MgO	400	1:2	30	6.0	Corma *et al.*, 1992.
V/Bi_2O_3	400	2:1	120	8.3	
VO_x/AlNbO	500	2:19.6	80	6	Eon *et al.*, 1993.
	500	2:19.6	140	6.4	
VO_x/γ-Al_2O_3	400	2:19.6	40	7.3	Eon *et al.*, 1994.
	450	2:19.6	40	8.3	
VAPO-5	475	1:2	90	11.1	Concepción *et al.*, 1995
	500	1:2	90	14.6	
	525	1:2	90	16.7	
	550	1:2	90	17.6	
2V/AP	475	1:2	80	8.4	
	500	1:2	80	10	
	525	1:2	80	11	
	550	1:2	80	11	
V/MgO	525	1:2	23	10.3	
	550	1:2	23	14.5	
0.6V/MCM	550	1:2	26	9.0	Solsona *et al.*, 2001a.
0.6V-MCM-41	550	1:2	26	8.1	

compare the performance of several catalysts could be based on the values of CO/CO_2 ratio. Thus, it can be observed that the impregnation of $SmVO_4$ with vanadium causes an increase of the average CO/CO_2 ratio from 0.6 to the range of 1.2-1.7. This ratio grows with the increase of vanadium loading, approaching the average value of 2.0 obtained with the V_2O_5. In the case of catalysts impregnated with molybdenum, the average CO/CO_2 ratio is also higher than that obtained on $SmVO_4$ but lower than that resulting on catalysts with vanadium (0.7-1.0 range). Therefore, it can be inferred that vanadium impregnation favors the consecutive combustion of propylene and simultaneously controls the propane combustion. The same conclusion was reached comparing the shape of curves of selectivity to propylene as a function of the conversion of propane with the theoretical curves reported by Blasco and López Nieto (1997). Molybdenum produces a similar effect, *i.e.* it decreases the rate of propane combustion causing an increase of selectivity at low conversion levels and favors the consecutive combustion of propylene but to a smaller extent than vanadium. Thus, it can be explained why it is possible to obtain the highest yield (13%) on the catalyst with low molybdenum loading.

Finally, the high yield showed by (Mo)-Sm-V-O catalysts led us to compare their performance with the other vanadium based catalysts. Although a direct comparison of propylene yields is difficult since the results reported in literature have been obtained under very different conditions (reaction temperature, C_3H_8:O_2 ratio, W/F, etc.), it can give an idea about the potentiality of our system. Among vanadium based catalysts, V-Mg-O catalysts are known for exhibiting high efficiency in ODH of propane (Chaar *et al.*, 1988; Gao *et al.*, 1994, Corma *et al.*, 1992, 1993). Good results have been also obtained with supported vanadium oxide catalysts (Corma *et al.*, 1992; Eon *et al.*, 1993, 1994; Concepción *et al.*, 1995; Solsona *et al.*, 2001a) and different rare earth vanadate (Au *et al.*, 1996; Fang *et al.*, 1999). Table 2 shows the higher yields presented by several research teams. It is observed that propylene yield levels obtained with our (Mo)-Sm-V-O catalysts are among the best ones reported in literature. In consequence, we think that this catalytic system has a great potentiality for being employed in propane ODH. Further studies tending to optimize both the catalyst and the operative conditions could lead to enhance propylene yield and productivity.

V. CONCLUSIONS

The (Mo)-Sm-V-O catalytic system has been evaluated in propane ODH and the function that each of the possible arrangements plays has been identified. Briefly, vanadium ions into $SmVO_4$ structure are catalytically more convenient than in V_2O_5 when these oxides are used as catalysts of propane oxidative dehydrogenation. A slight samarium excess favors the total combustion causing a strong drop of selectivity, therefore it is necessary to avoid it. On the other hand, vanadium excess constituting surface vanadium species (VO_x) increases notably the catalytic activity while at higher vanadium loadings, crystalline V_2O_5 is formed and catalyst behavior tends to that of bulk V_2O_5. Molybdenum is an appropriate element to improve $SmVO_4$ performance when it is at low concentrations constituting surface molybdenum species (MoO_x) which showed to be highly selective in propane ODH. High contents of molybdenum favor the crystalline MoO_3 formation, which causes an important catalyst deactivation.

The ways to attain a higher increase of propylene yield in order to make this reaction type competitive, would be:

- To optimize the catalyst design including elements in a host matrix able to stabilize the cations constituting the catalytic sites in a suitable coordination.

- To optimize the reactor design and the selection of the operative conditions.

ACKNOWLEDGEMENTS

Financial support from CONICET and from Universidad Nacional de San Luis are gratefully acknowledged.

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Received: June 27, 2004
Accepted for publication: December 3, 2004
Recommended by Subject Editor J. Pinto