Investigations on the promoting effect of metal oxides on La–V–O catalyst in propane oxidative dehydrogenation

Bao Zhaorigetu [a], Roger Kieffer [b] and Wenzhao Li [a]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PO Box 110, Dalian 116023, PR China*
E-mail: lab807@ms.dicp.ac.cn
[b] *LERCSI ECPM, 25, rue Becquerel, BP, 67087 Strasbourg Cedex 2, France*

Received 2 November 2000; accepted 26 February 2001

The addition of reducible metal oxides as promoters shows a positive effect on the catalytic behavior of lanthanum vanadate ($LaVO_4$). A C_3H_6 yield increase of 6.5% is observed at 500 °C on molybdenum-promoted $LaVO_4$, which can be attributed to the change of the redox properties, the blocking of the strong oxidation sites of the catalysts and to an increase of the accessibility of the labile oxygen toward the reactant. The influence of the catalyst preparation method and of the Mo loading as well as the additional promoting effect of CO_2 in the gas feed was also examined.

KEY WORDS: propane; oxidative dehydrogenation; $LaVO_4$; metal oxide promoters

1. Introduction

Rare earth orthovanadate catalysts show good catalytic properties in oxidative dehydrogenation (ODH) of propane to propene [1–4]. However, the propene selectivity is limited since the reaction is always in competition with the total oxidation of propane or of the formed propene producing CO_2 and CO.

In order to increase C_3H_6 selectivity at a given C_3H_8 conversion, the promoting effect of niobium on rare earth vanadates and the addition of CO_2 in the feed have been investigated [5–7]. An improvement of the selectivity at isoconversion is obtained both by the addition of 1–5% Nb (as Nb_2O_5) to rare earth orthovanadate catalysts and by the presence of 10% CO_2 in the gas feed. Both promoters are able to neutralize the strongly oxidizing sites of the rare earth oxide and then suppress the total oxidation reaction. In addition, a definite compound ($LaNbO_4$) can be formed in the presence of Nb, which reveals even higher activity in propane ODH [8] whereas CO_2 seems to be in competition with C_3H_8 in the chemisorption on the rare earth oxide sites [7]. Au and Zhang [3] working on various rare earth vanadates considered that the oxidizing properties of these systems in ODH are mainly dependent on the nature and the accessibility of the lattice oxygen of the catalysts. Yoon et al. [9] working on magnesium molybdate catalysts, concluded that the excess of molybdenum ions on the surface of the $MgMoO_4$ catalyst induced the formation of catalytic sites able to provide active oxygen ions for the selective oxidation. These authors also suggested that the properties of the lattice oxygen ions of the catalyst surface play a key role in the propane ODH reaction.

The aim of the present work is, in order to increase the selectivity in the ODH reaction on lanthanum vanadate catalysts, to study the promoting effect of different metal oxides on $LaVO_4$. The links between catalytic behavior and the characteristics of the catalyst are discussed.

2. Experimental

2.1. Catalyst preparation

Lanthanum vanadate was prepared from aqueous solutions of lanthanum nitrate and ammonium vanadate. The resulting precipitate was evaporated to dryness and heated at 120 °C for 16 h. The obtained solid was ground into a fine powder and calcined in air at 550 °C for 1 h.

The promoted catalysts were prepared by incipient wetness impregnation of the previous lanthanum vanadate samples by solutions of metal salts. Then, the precursor was dried at 120 °C for 16 h, and calcined in air at 550 °C for 1 h. The promoted catalysts were denoted further in the text by xMe/$LaVO_4$, where x is the percentage of promoted metal (e.g., 1, 3, 6 and 10 at%), Me is Mo, Nb, V, W, Sb and Bi.

10Mo/$LaVO_4$(p) was prepared by coprecipitation from aqueous solutions of lanthanum nitrate, ammonium vanadate and ammonium molybdate, then dried and calcined in the previous conditions.

2.2. Catalyst characterization

The BET surface areas of the catalysts were measured by N_2 adsorption using a Coulter SA3100 equipment.

The catalysts were characterized by powder diffraction techniques at room temperature with a Siemens D5000 X-ray diffractometer working with Cu Kα radiation with $\lambda = 1.5406$ Å.

Temperature-programmed reductions (TPR) of the catalysts were performed by using an Ar + H_2 (96/4) gas mix-

1011-372X/01/0500-0133$19.50/0

ture. The flow rate of the carrier gas was 50 ml/min. 50 mg sample was used and heated (rate 15 °C/min) to a final temperature of 900 °C. The H_2 consumption was measured by a thermal conductivity detector connected to a data acquisition computer.

The X-ray photoelectron spectra were recorded with a VG ESCA 3 spectrometer equipped with a Mg Kα X-ray excitation source ($h\nu = 1253.6$ eV) and hemispherical electron analyzer operated at 10 kV and 20 mA. The samples were outgassed at room temperature at 10^{-9} mbar and then moved into the analysis chamber. Surface composition of the catalysts was determined from the peak areas of Mo 3d, La 3d and V $2p_{3/2}$. The binding energies (BE) were calibrated with surface of the C 1 peak at 284.8 eV.

2.3. Catalytic tests

The dehydrogenation reactions were performed in a U tube quartz reactor (inner diameter 6 mm) containing 0.5 g of catalysts. The gas feed was prepared on line using four mass flow regulators (total flow rate 6 $\mathrm{l\,h^{-1}\,g^{-1}}$). The reaction products were analyzed on line by GC. Feed $O_2/C_3H_8/He = 5/5/40$ (ml/min); or $O_2/C_3H_8/CO_2/He = 5/5/5/35$ (ml/min).

3. Results and discussion

3.1. Preparation and characterization of the catalysts

XRD analysis shows only the crystalline phase of $LaVO_4$ (huttonite structure) over all samples prepared here; the oxide promoters are in amorphous form or present in too small amounts to be detected by XRD. The BET surface areas decrease with the metal loading of Mo, Nb, Sb and Bi (table 1), which can be explained by a pore blocking mechanism. A slight increase of BET of $V/LaVO_4$ and $W/LaVO_4$ may be caused by an attack of the catalyst surface during the impregnation process.

Table 1
Characteristics of $LaVO_4$ and the promoted $LaVO_4$ catalysts.

	Catalyst						
	$LaVO_4$	1Bi/ $LaVO_4$	1Nb/ $LaVO_4$	1W/ $LaVO_4$	Sb/ $LaVO_4$	1Mo/ $LaVO_4$	1V/ $LaVO_4$
BET (m^2/g)	11.1	8.9	8.0	13.1	7.3	7.6	13.6
H_2 uptake in TPR (ml/g)	88.0	90.0	90.3	92.8	93.0	93.8	97.2

The H_2 consumption tests in TPR show that the promoted $LaVO_4$ catalysts have more oxygen to the reactant than that of the unpromoted one. Moreover, the amount of the oxygen also depends on the nature of the promoting metal oxides (table 1). According to H_2 consumption, it can be estimated that in TPR reaction conditions, more than 90% $LaVO_4$ was reduced to $LaVO_3$. It was furthermore confirmed by XRD analysis.

As shown in figure 1, comparing with $LaVO_4$, the TPR diagrams of the promoted one were significantly changed. Especially in the presence of transient metal oxides, the curves of the promoted catalysts were shifted to high temperatures. It means that oxygen species in the promoted catalysts was less active because of a strong interaction between the metal oxides and the lanthanum vanadate.

3.2. Catalytic behavior of unpromoted and promoted $LaVO_4$ in propane ODH

The addition of metal oxide promoter results in the enhancement of both the C_3H_8 conversion and the C_3H_6 selectivity, as shown in figure 2, based on the 1% of molybdenum promoted catalyst.

It is shown in table 2 that the addition of Mo, W, Nb, V and Sb, except Bi, not only increases the C_3H_8 conversion, but also results in an enhancement of C_3H_6 selectivity. The former may be caused by the increase of active oxygen species on the surface of the catalysts, and the latter may be related to a lower activity of oxygen species. This result may be attributed to the fact that the strong oxidation sites of $LaVO_4$ are blocked by the less reducible acidic oxides (e.g., MoO_3, Nb_2O_5, etc.), so that the total oxidation reaction of C_3H_8/C_3H_6 is weakened and C_3H_6 selectivity is then improved. Conversely, the addition of the easily reducible basic oxides (e.g., Bi_2O_3) increases the selectivity to CO_2.

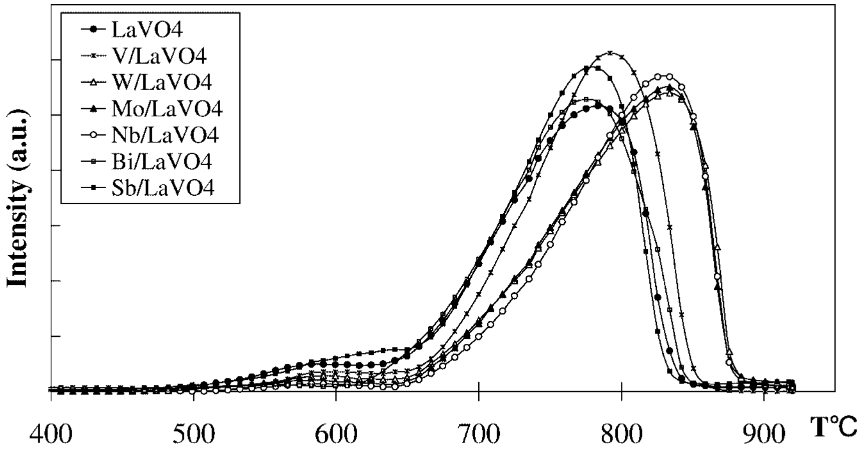

Figure 1. TPR profiles of $LaVO_4$ and $1Me/LaVO_4$.

Table 2
Catalytic behavior of $LaVO_4$ and $1Me/LaVO_4$.

	Catalyst						
	$LaVO_4$	Mo/ $LaVO_4$	W/ $LaVO_4$	V/ $LaVO_4$	Nb/ $LaVO_4$	Sb/ $LaVO_4$	Bi/ $LaVO_4$
C_3H_8 conversion (%)	29.6	36.2	41.1	35.8	34.8	32.0	30.4
C_3H_6 selectivity (%)	19.0	33.5	28.9	28.6	28.6	23.0	13.3
C_3H_6 yield (%)	5.6	12.1	11.9	10.2	10.0	7.4	4.0

Conditions: gas flow 6 $l\,h^{-1}$ g-cat^{-1}, $O_2/C_3H_8/He = 5/5/40$ ml min^{-1}, $T = 500\,°C$.

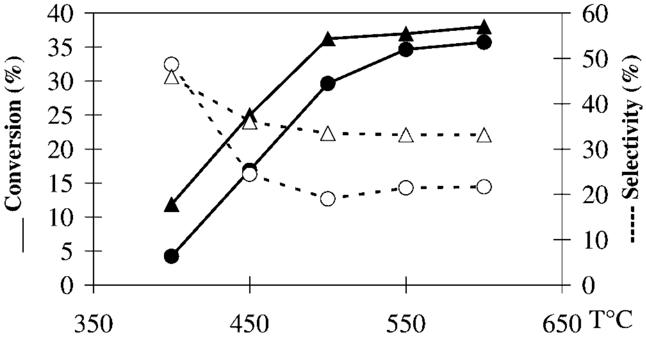

Figure 2. The addition effect of 1% Mo on $LaVO_4$ catalyst: (●) $LaVO_4$, (▲) $1Mo/LaVO_4$, (○) $LaVO_4$ and (△) $1Mo/LaVO_4$. Conditions: gas flow 6 $l\,h^{-1}$ g-cat^{-1}, $O_2/C_3H_8/He = 5/5/40$ ml min^{-1}.

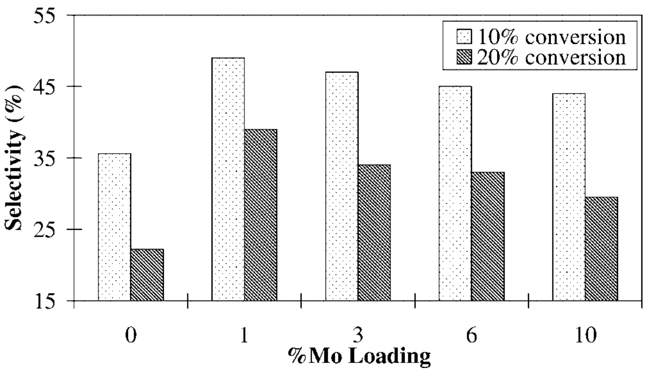

Figure 3. Influence of Mo loading on C_3H_6 selectivity at isoconversion. Conditions: see figure 1.

3.3. Influence of the promoter loading

As shown in figure 3, the best C_3H_6 selectivity at a given conversion is obtained on the 1% Mo loaded catalyst either at 10 or at 20% conversion.

XPS results show an obvious surface enrichment of Mo with the Mo loading (table 3). An important segregation of lanthanum on the catalyst surface is also observed by XPS, although these catalysts have a stoichiometric composition (e.g., V/La = 1) during the preparation. The accumulation of lanthanum is usually considered to promote the total oxidation of the substrate. Anyway, the Mo-surface enrichment is rather higher than that of La can probably be explained that the Mo species will be able to block the total oxidation sites of La.

Table 3
Correlation between Mo loading and Mo surface content on $LaVO_4$.

Catalyst	Mo/La ratio		V/La ratio	
	XPS	Theoretic	XPS	Theoretic
$LaVO_4$	–	0	0.777	1
$1Mo/LaVO_4$	0.079	0.01	0.595	1
$3Mo/LaVO_4$	0.105	0.03	0.926	1
$6Mo/LaVO_4$	0.123	0.06	0.704	1
$10Mo/LaVO_4$	0.252	0.10	0.658	1
$10Mo/LaVO_4$(p)	0.186	0.10	0.722	1

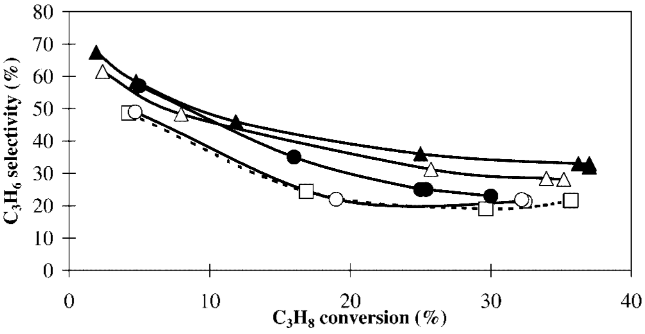

Figure 4. Effect of preparation techniques on $Mo/LaVO_4$ catalytic behaviour: (□) $LaVO_4$, (▲) $1Mo/LaVO_4$, (•) $10Mo/LaVO_4$, (△) $1Mo/LaVO_4$(p) and (○) $10Mo/LaVO_4$(p). Conditions: see figure 1.

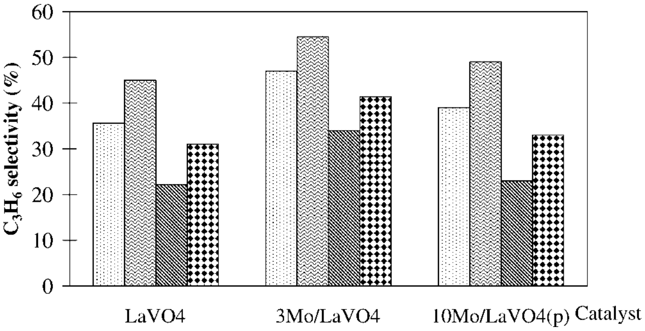

Figure 5. Influence of CO_2 addition on C_3H_6 selectivity at isoconversion: (□) 10 and (▨) 20% conversion; (▨) 10 and (▦) 20% conversion with CO_2. Conditions: gas flow 6 $l\,h^{-1}$ g-cat^{-1}, $O_2/C_3H_8/CO_2/He = 5/5/5/35$ ml min^{-1}.

3.4. Influence of the preparation techniques

Although various preparation technique can change the migration of the lanthanum species on the catalyst surface but in any case the surface V/La ratio remains lower than 1, as mentioned above, such a promotion of the total oxidation caused by the surface enrichment of lanthanum, appears in all the experiments.

For the coprecipitated catalysts the Mo/La ratio on the surface is still higher as expected but the ratio is always lower than that for the catalysts prepared by impregnation. The catalytic performance also indicates that for both 1 and 10% Mo loading samples the impregnated catalysts lead always to higher selectivities at a given conversion (figure 4).

3.5. Effect of the addition of CO_2 in the gas feed

CO_2, as a mild oxidant, was used in the dehydrogenation of propane on Cr_2O_3 and Ga_2O_3 containing catalysts [10,11]. In addition, the acidic character of CO_2 is therefore able to neutralize some basic sites of rare earth oxides.

Figure 5 shows the effect of CO_2 addition in the gas feed on C_3H_6 selectivity at isoconversion (e.g., 10 and 20%). The addition of CO_2 in the gas feed leads to an enhancement of C_3H_6 selectivity on $LaVO_4$ and Mo promoted $LaVO_4$ catalysts. Since, in our reaction conditions, CO_2 itself never shows (in the absence of O_2) any oxidation abilities toward C_3H_8 [7], the blocking of the basic combustion sites seems to be the major effect of CO_2.

4. Conclusions

The addition of molybdenum oxide promoters increased both the C_3H_8 conversion and C_3H_6 selectivity. The former can be attributed to an enhancement of the total amount of oxygen species toward the reactant.

The latter may be resulted from the blocking of the total oxidation sites and the formation of less active oxygen species by Mo addition.

The addition of CO_2 in the feed gives an additional increase of the C_3H_6 selectivity at C_3H_8 isoconversion.

References

[1] J. Castiglioni, P. Poix and R. Kieffer, New Frontiers Catal. (1992) 2309.
[2] C.T. Au, W.D. Zhang and H.L. Wan, Catal. Lett. 37 (1996) 241.
[3] C.T. Au and W.D. Zhang, J. Chem. Soc. Faraday Trans. 93 (1997) 1195.
[4] Z.M. Fang, Q. Hong, Z.H. Zhou, S.J. Dai, W.D. Zhang and H.L. Wan, Catal. Lett. 61 (1999) 39.
[5] B. Zhaorigetu, R. Kieffer and J. Castiglioni, in: *Proc. XV Simposio Iberoamericano de Catalisis*, Vol. 2, eds. E. Herrero, O. Anunziata and C. Perez, Cordoba, Argentina, 1996, p. 879.
[6] B. Zhaorigetu, R. Kieffer and J.P. Hindermann, in: *11th Int. Congr. on Catalysis*, Baltimore USA, 30 June–5 July 1996, Po228.
[7] B. Zhaorigetu, R. Kieffer and J.P. Hindermann, Stud. Surf. Sci. Catal. 101 (1996) 1049.
[8] J. Castiglioni, J.M. Curbelo, E.A. Zhilinskaya, A. Aboukais and R. Kieffer, in: *Proc. XVI Simposio Iberoamericano de Catalisis*, Vol. 2, eds. A. Centeno, S.A. Giraldo and E.A. Paez Mozo, Cartagena, Colombia, 1998, p. 655.
[9] Y.S. Yoon, W. Ueda and Y. Moro-oka, Catal. Lett. 35 (1995) 57.
[10] T. Hattori and J. Nurakami, Nikon Kagakukashi (1991) 648.
[11] M. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga and T. Suzuki, Appl. Catal. A 121 (1995) 125.