The selective oxidative dehydrogenation of propane on vanadium aluminophosphate catalysts

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VAPO-5 and V/ALPO-5 catalysts have been tested for the oxidative dehydrogenation of propane. Depending on the vanadium contents and the preparation procedure, different vanadium species and different catalytic behavior are observed. The catalyst containing V^{5+} species with a tetrahedral coordination presents the higher yield of propene in the oxidative dehydrogenation of propane. The same yields of CO_2 are observed on all vanadium aluminophosphate catalysts, while the higher the yield of propene the lower the yield of CO is.

Keywords: Vanadium aluminophosphate; vanadium based catalysts; oxidative dehydrogenation; propane

1. Introduction

The oxidative dehydrogenation (ODH) of low molecular weight paraffins is an important process from both industrial and fundamental point of view. V–Mg–O based catalysts present a greater selectivity in the oxidative dehydrogenation (ODH) of alkanes [1–3]. However, in the ODH of propane, a low yield of propene (about 10–12%) is obtained [1,2].

Vanadium containing microporous structures could be interesting catalysts for the oxidative dehydrogenation of alkanes. Thus, V-silicalite is highly selective in the ODH of propane [4,5]. In this case [5], as well as on V–Mg–O [2,6] or on V/sepiolite [7] catalysts, isolated VO_4 tetrahedron structures have been proposed as active and selective sites for the ODH of propane.

VAPO-5 catalysts show V^{4+}/V^{5+} redox properties [8,9] and allow a greater incorporation of vanadium than V-silicalite [10]. However, little information on their catalytic properties has been presented up to now. Thus, a low selectivity in the ammoxidation of propane [10] and high selectivity in the dehydrogenation of ethylbenzene (in absence of molecular oxygen) [11] on both VAPO-5 and V_2O_5/

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ALPO-5 catalysts have been reported. In the present paper we present results on VAPO-5 materials which are very active and selective for the oxidative dehydrogenation of propane.

2. Experimental

ALPO-5 and VAPO-5 samples were synthesized hydrothermally from gels of molar composition: $Al_2O_3/P_2O_5/V_2O_5/H_2O/Et_3N = 0.8/1/x/47/1.76$ (the values of x are reported in table 1). The gel was heated in teflon lined stainless-steel autoclaves at 473 K for 16 h and then centrifugated, washed and dried at 353 K. The vanadium was incorporated as V^{4+}, using an aqueous solution of V_2O_5/oxalic acid (sample A) or V_2O_5/hydrazine (sample B) with the stoichiometric ratios of V_2O_5/reductor agent necessary to obtain a total reduction of V^{5+} species to V^{4+}.

For comparison purpose, the V/ALPO-5 and V/MgO samples were prepared by impregnation of ALPO-5 and MgO with a vanadyl oxalate and an ammonium metavanadate aqueous solution, respectively. After impregnation, the samples were dried at 343 K and 27 kPa and then kept at 383 K for 16 h. The samples were finally calcined at 823 K for 8 h in a forced flow of air.

Characterization of the catalysts was carried out as follows: X-ray diffraction (XRD) patterns were recorded in a Phillips 1060 diffractometer using nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm); infrared spectra were recorded with a Nicolet 205xB: diffuse reflectance (DR) spectra in the UV–visible region were taken with a Shimadzu UV-2101PC spectrophotometer equipped with a reflectance attachment.

Catalytic reactions were performed in an isothermal flow reactor at atmospheric pressure [6]. Under the reaction conditions used here, the presence of homo-

Table 1
Physico-chemical characterization of calcined samples

Sample	Vanadium in gel (x)[a]	Vanadium content (wt%)[b]	Crystallinity[c] as-made	Crystallinity[c] calcined	Vanadium species[d]
ALPO-5	0	0	100	88	–
A	0.03	0.38	100	105	VT (VO)
B	0.12	1.59	87	62	VT, VO
V/ALPO-5	–	2.22	82	15 + A[e]	VT, VO, V_2O_5
V/MgO	–	10.6	–	–	$Mg_3V_2O_8$

[a] Vanadium contents in gel, x, in $Al_2O_3/P_2O_5/V_2O_5/H_2O/Et_3N = 0.8/1/x/47/1.76$.

[b] Vanadium contents of calcined samples, given in wt% of V-atoms, obtained from atomic absorption spectrometry.

[c] Crystallinity (%) is referred to as-synthesized ALPO-5.

[d] VT = isolated VO_4 tetrahedron; VO = V=O double bond containing isolated species.

[e] A = dense ALPO with a trydimite-type structure.

geneous reaction has not been observed. Experiments were carried out at different contact times in order to be able to compare catalyst selectivities at the same level of conversion. After almost 30 h of stream, catalyst deactivation was not observed.

3. Results and discussion

The nature and crystallinity of the different samples and their chemical composition are given in table 1. Highly crystalline samples of VAPO-5 are obtained, although the crystallinity decreases slightly with increasing vanadium content (sample B). The crystallinity of this sample decreases after calcination. On the other hand, calcination in air of the ALPO-5 impregnated with a vanadium salt leads to a mixture of ALPO-5 and a trydimite-type ALPO phase. The vanadium content of the VAPO-5 increases by increasing the vanadium content of the synthesis gel.

Diffuse reflectance spectra of the as-synthesized sample show the presence of absorption bands at 250 and 500–800 nm, which are associated to the presence of vanadyl VO^{2+} species [12]. However, different V^{5+} species were observed on calcined samples according to the literature data [13]: (i) isolated VO_4 tetrahedron (at 280 nm); (ii) isolated V=O species (in the 350–450 nm region) and V_2O_5 (at 500 nm). The nature of V-species detected on calcined samples is presented in table 1. Both tetrahedral VO_4 and V=O species are observed in the two samples of VAPO-5, but the relative intensity of the V=O bond is much higher in sample B. However, the coordination geometry of the V=O species cannot be assessed. Besides these two bands, V_2O_5 is also detected in the V-impregnated ALPO-5. On the other hand, on the V/MgO sample only the presence of $Mg_3V_2O_8$ is detected.

Table 2 shows the catalytic properties of VAPO-5 and V/ALPO-5 catalysts for

Table 2
Catalytic properties for the oxidative dehydrogenation of propane of VAPO-5 and V/ALPO-5 catalysts

Sample	W/F [a]	T (°C)	Conversion (%)	Selectivity (%)			Yield
				C_3H_6	CO	CO_2	C_3H_6 (%)
ALPO-5	175	500	0.09	100	0	0	0.09
		540	4.22	96.6	0	3.4	0.13
A	175	500	14.5	74.3	17.1	8.6	10.8
		540	30.7	52.8	32.8	14.4	16.2
B	87	500	19.1	52.0	38.5	4.5	9.9
		540	25.7	37.7	49.8	12.4	9.7
V/ALPO-5	87	500	19.1	54.2	34.6	11.1	10.4
		540	37.2	33.8	49.9	16.3	12.6
V/MgO	25	500	14.5	55.1	13.2	31.7	8.0
		550	30.0	42.3	24.8	32.9	12.7

[a] Contact time, W/F, in g_{cat} h (mol C_3H_8)$^{-1}$; $C_3H_8/O_2/He$ molar ratio of 4/8/88.

the oxidative dehydrogenation of propane, together with those of a calcined ALPO-5 sample. It can be seen that only the structures containing vanadium are catalytically active, and therefore the active sites must be associated with V species. However, great differences in activity exist in different V-containing samples. These differences cannot be explained only on the base of vanadium content, since sample B and V/ALPO-5 have similar vanadium content but different catalytic activity. Indeed, catalyst A shows higher activity than B, despite of its lower vanadium content. Then other factors such as accessibility of propane to the active sites and/or differences in the activity of V species present on the catalyst, can be responsible for the differences observed in the catalytic properties, and its influence will be discussed here.

Beside their differences in activity, great differences in selectivity to propene can also be observed between the V-containing samples, when compared at the same conversion level of propane (fig. 1). It can be seen that VAPO-5 with the lowest vanadium content (sample A) has the highest selectivity to propene, the yield of propene decreasing in the order: A > V/ALPO-5 > B. In addition to this, the formation of CO shows an inverse trend, while the formation of CO_2 is similar on all catalysts (fig. 1). Moreover, catalyst A also shows the highest activity per mol of vanadium.

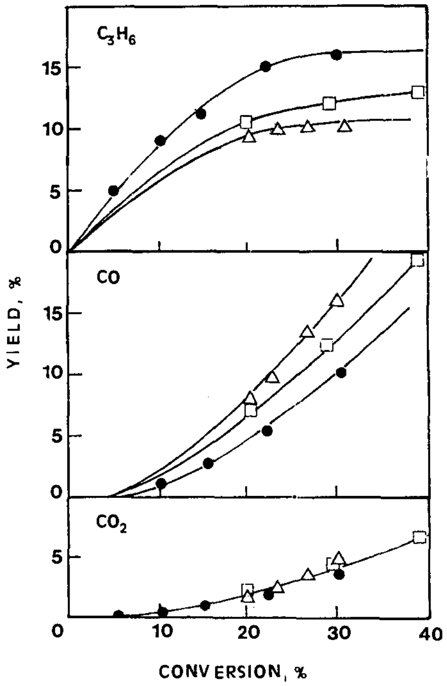

Fig. 1. Influence of the propane conversion level on the yields of propene, CO and CO_2, obtained on: A (●); B (△); and V/ALPO-5 (□) catalysts. Experimental conditions: temperature 540°C; $C_3H_6/O_2/He$ molar ratio of 4/8/88.

In order to explain these results, it has to be taken into account that the DR-spectrum of sample A shows that the vanadium atoms are preferably forming part of isolated VO_4 tetrahedra, whereas in sample B a higher relative intensity of the V=O bonds is observed, and finally, even V_2O_5 is observed in V/ALPO-5 (table 1).

On the other hand, isolated VO_4 tetrahedra have also been claimed to be the active and selective sites in the oxidative dehydrogenation of propane on V-based catalysts, such as VMgO [2,6], V-silicalite [5] or V/sepiolite [7]. We must indicate that on the sample A, the same yield of propene as with V-silicalite [5], and a greater yield of propene than with V/MgO catalyst (table 2) are obtained.

In conclusion, it can be proposed that isolated vanadium species with a tetrahedral coordination present in VAPO-5 are also the more active and selective species in the selective oxidative dehydrogenation of propane. The higher the vanadium content in VAPO catalysts the higher the activity is. Nevertheless, the amount of vanadium should be balanced in order to maximize not only activity but also selectivity to propene.

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