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Oxidative dehydrogenation of propane over vanadium oxide based catalysts Effect of support and alkali promoter

A.A. Lemonidou*, L. Nalbandian, I.A. Vasalos

Department of Chemical Engineering, Aristotle University of Thessaloniki and Chemical Process Engineering Research Institute,
PO Box 1517, University City, 54006 Thessaloniki, Greece

Abstract

The oxidative dehydrogenation of propane was investigated using vanadia type catalysts supported on Al_2O_3, TiO_2, ZrO_2 and MgO. The promotion of V_2O_5/Al_2O_3 catalyst with alkali metals (Li, Na, K) was also attempted. Evaluation of temperature programmed reduction patterns showed that the reducibility of V species is affected by the support acid–base character. The catalytic activity is favored by the V reducibility of the catalyst as it was confirmed from runs conducted at 450–550°C. V_2O_5/TiO_2 catalyst exhibits the highest activity in oxydehydrogenation of propane. The support's nature also affects the selectivity to propene; V_2O_5 supported on Al_2O_3 catalyst exhibits the highest selectivity. Reaction studies showed that addition of alkali metals decreases the catalytic activity in the order non-doped>Li>Na>K. Propene selectivity significantly increases in the presence of doped catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Propane; Oxidative dehydrogenation; Vanadia based catalysts; Alkali promoters; Temperature programmed reduction

1. Introduction

The conversion of light saturated hydrocarbons to unsaturated hydrocarbons is a challenging pursuit in both economic and scientific terms. The development of catalysts, which under low temperature conditions and in the presence of oxygen could activate the light alkanes and promote with high selectivity alkenes formation, is considered to be the key to such an attempt.

Most catalysts described in the literature are based on vanadium oxide as the active component [1,2]. In particular, mixed vanadium magnesium oxide (VMgO) catalysts have been reported to exhibit a promising yield for the production of propene and butenes from the corresponding alkanes via oxidative dehydrogenation (ODH) and have been studied by various groups [3–8].

Catalysts based on vanadium oxide supported on various oxides show promising results for the ODH of C_2–C_4 alkanes, as recently reviewed [1,2]. The catalytic performance of vanadia supported catalysts in the ODH of alkanes depends on the nature of the support, the preparation procedure and the vanadia loading [2]. Acidic and basic nature as well as the redox character are the most important factors that affect the performance of selective oxidation catalysts [9]. Corma et al. [10] found that in ODH of propane the most selective catalysts were obtained with V supported on basic, rather than on acidic metal oxides. Arena et al. [11] reported that the reactivity of V on various supports is much higher with ampho-

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* Corresponding author. Fax: +30-31-996184.
E-mail address: lemonido@eng.auth.gr (A.A. Lemonidou).

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teric oxides (highest reactivity with TiO_2) and that the acid–base character of the support affects the dispersion and reducibility of the active phase. The effect of V loading in catalytic activity and selectivity was investigated by Blasco et al. [12].

Modification of acid–base properties has been attempted not only by using substrates with various acidities but also by incorporating different promoters, usually alkaline ions [13–16]. Doping of V_2O_5/TiO_2 catalysts with alkali metals, was investigated by Martin Aranda et al. [13] and Grzybowska and co-workers [14] and interesting results relating to the catalytic performance in the ODH of propane to the surface characteristics and the preparation were derived. Galli et al. [16] reported that K acts as a promoter in V_2O_5/Al_2O_3 catalysts increasing C_4 alkenes selectivity in the ODH of butane, while the same alkali metal acts as inhibitor decreasing C_2H_4 selectivity in the ODH of ethane compared with the performance of the non-doped catalyst.

The aim of the present work was the preparation of V supported catalysts, their physicochemical characterization, with emphasis on the clarification of the role of the support on reducibility and the evaluation of their catalytic performance in ODH reaction of propane. The promotional effect of alkali addition was also investigated.

2. Catalysts and experimental procedures

The supports used were γ-Al_2O_3 (Engelhard, SA=202.6 m^2/g), ZrO_2 (Norton, SA=102.3 m^2/g), TiO_2 (Norton, SA=50.8 m^2/g) and MgO (Caustflot, SA=32.9 m^2/g). V_2O_5 (4 wt.%) was deposited on the carriers by wet impregnation using NH_4VO_3 as precursor. After drying, the samples were calcined in an air stream at 600°C for 5 h. Alkali promoters were introduced by the addition of appropriate amounts of Li, Na and K nitrates to the NH_4VO_3 solution followed by wet impregnation of γ-Al_2O_3. The samples were dried and calcined in the same way as the non-doped catalysts. The same molar ratio $A_2O/V_2O_5=0.25$ was used in all doped samples (A=Li, Na, K).

BET surface area of the samples was measured at an Autosorb-1 Quantachrome apparatus from N_2 adsorption isotherms at 77 K. The crystalline phases of the catalysts were identified by X-ray diffraction (XRD) analysis using a Siemens D500 diffractometer. The reducibility of bulk V_2O_5, supports and catalysts was studied by temperature programmed reduction (TPR) at an AMI-1 (Altamira Instruments) apparatus. Treatment in Ar flow at 750°C for 1 h preceded each TPR experiment. After cooling to 30°C the test was carried out under a flow of 10% H_2/Ar mixture through the micro-reactor, which was heated at a constant rate of 10°C/min up to 750°C. The system was maintained for 1 h at 750°C isothermally under H_2/Ar flow to complete the reduction.

The catalytic experiments were conducted at atmospheric pressure in a conventional fixed bed apparatus using a quartz reactor (ID 9 mm). The products were analyzed on line by a Varian 3400 chromatograph equipped with a TC Detector. Three columns in a series-bypass configuration were used in the analysis: a 20% BEEA–20% DC 200/500, a Porapak N-Chromosorb 106 and an MS 5A. The atomic balances were satisfied at a maximum absolute deviation of less than 2%. The selectivity of the products was calculated on a carbon basis. Catalyst evaluation experiments were carried out at 450–550°C with constant propane to oxygen ratio (1/1) using 0.05–0.5 g of catalyst. The reactant mixture was highly diluted with He (up to 85%). The reaction products were C_3H_6, CO and CO_2, while at runs performed at 550°C very low amounts of C_2H_4 and C_2H_6 were identified. Oxygenates were not detected at the reactor exit.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the composition and the characterization results of the prepared catalysts. Addition of vanadium to the oxidic support results in a decrease of the surface area compared to the bare supports, except for the MgO where a significant increase is observed. Analogous increase, with V–Mg mixed oxide catalysts with low V content, has also been reported [4]. The samples doped with Li, Na and K have approximately the same surface area as the non-doped V_2O_5/Al_2O_3. This may be attributed to the preparation procedure, since dopants and active component

Table 1
Composition and characteristic data of catalysts

Catalyst	SA (m^2/g)	V_2O_5 (wt.%)	A_2O (wt.%)[a]	Θ	VO_x surface density (nm^{-2})	T_{max} (°C)	H_2 uptake (μmol/g)	Average of oxidation state
VMgO	98.2	3.85	–	–	–	660	921	–
$VZrO_2$	70.7	3.96	–	0.26	3.5	544	319	3.54
$VTiO_2$	35.3	3.87	–	0.52	7.1	560	337	3.46
VAl_2O_3	186.8	4.00	–	0.13	1.3	585	402	3.16
$LiVAl_2O_3$	184.2	4.05	0.165	0.13	1.3	604	405	3.15
$NaVAl_2O_3$	182.9	4.13	0.320	0.13	1.3	603	429	3.04
$KVAl_2O_3$	185.1	4.10	0.500	0.13	1.3	600	414	3.11

[a] A=Li, Na, K.

were simultaneously impregnated on support, and/or to the low amount of dopants used.

Powder XRD patterns of the V-containing samples supported on TiO_2, ZrO_2 and Al_2O_3 revealed only the existence of the crystalline phases of the supports, while no peaks of V-containing compounds were detected. No indication of separate phase formation between vanadium and alkali metal was found also in promoted catalysts. The absence of V_2O_5 peaks is due to the very fine dispersion of V on the surface, which corresponds to a less than monolayer coverage (Table 1). There is a general consensus in literature that at low vanadia loading, V-oxide remains as a highly dispersed “monolayer” amorphous phase, while at higher loadings, crystalline V_2O_5 also coexists with the “monolayer” phase [1].

However, on the most basic support, i.e. MgO, where the interaction between V-atoms and support is very strong, characteristic peaks of MgV_2O_6 were observed. This is in agreement with the results of Wachs and Weckhuysen [17], who claimed that the magnesia supported V catalyst cannot form a complete close packed surface vanadia monolayer because of the acid–base reaction between acidic vanadia and basic magnesia. The strong interaction results in the formation of mixed compounds rather than a stable surface vanadia monolayer.

The surface coverage θ was calculated on the basis that complete coverage of support surface with vanadium oxide needs 4.98×10^{14} molecules V_2O_5 cm^{-2} [2]. The theoretical VO_x surface coverage was found to be less than a monolayer for Al_2O_3, TiO_2 and ZrO_2 based catalysts. Another important parameter that was considered for the catalysts is the VO_x surface density. The VO_x surface density is defined as the number of vanadium atoms per square nanometer of the catalyst and provides a convenient parameter for comparing catalysts with a wide range of surface areas [18]. The two parameters θ and VO_x surface density were not considered for the VMgO catalyst, where a solid state reaction between vanadia and magnesia occurs.

The TPR profiles of all V-containing samples are presented in Fig. 1. Negligible amounts of H_2 were

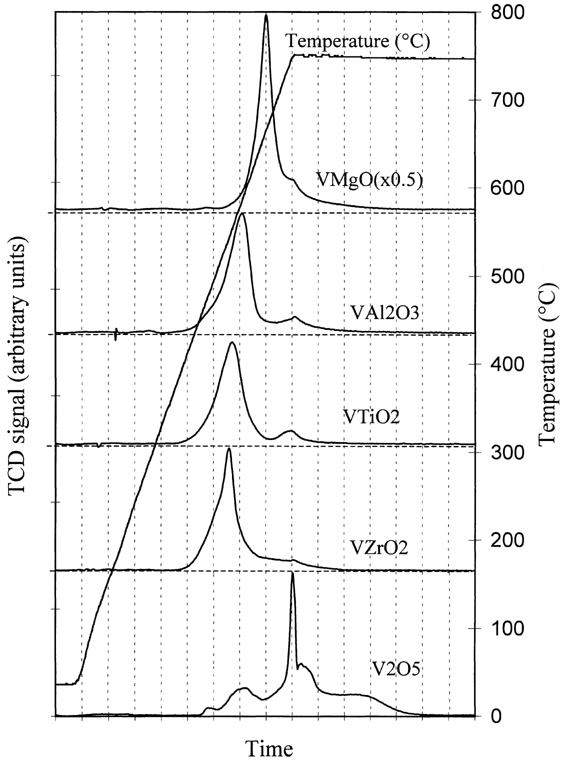

Fig. 1. TPR patterns of vanadia supported catalysts.

consumed in the presence of bare supports confirming that the oxidic carriers used are not reducible. The pattern of bulk V_2O_5 is quite complex indicating that different types of oxygen are present in the bulk V_2O_5. The extent of reduction is very low at temperatures below 750°C, while the major peak is at 750°C. Even though we would not attempt an interpretation of the V^{5+} reduction mechanism, it can be inferred from the TPR multiple peaks that several consecutive steps occur during V^{5+} reduction, in agreement with other reports [19,20].

When V is deposited on various supports, the temperature of maximum H_2 consumption T_{max} shifts to lower values, as it is clearly shown in Fig. 1. This decrease in T_{max} is ascribed to the very good dispersion of V species on the support, which facilitates the reduction [9,21]. The TPR patterns of all catalysts consist of one major peak with maximum in the range of 540–660°C and one much smaller peak centered at 750°C, indicating that the reduction of V dispersed on supports proceeds via fewer steps or that V species present on the surface are of the same type. Furthermore, the promotional effect of the supports on vanadia reducibility strongly depends on the support nature as shown in Table 1, where the T_{max} of VO_x are presented. V is more easily reduced when deposited on ZrO_2 (T_{max}=544°C) while on MgO much higher temperature is required (T_{max}=660°C). The above results show the same trends as those observed by other workers [11,21,22]. The significantly higher temperatures needed for the reduction of V on MgO are due to the high degree of interaction between V and the oxidic support confirmed by the identification of MgV_2O_6 in the VMgO sample.

Aiming to correlate the effect of the acid–base character of the supports in the reducibility of surface V species, a plot of T_{max} versus zero point charge of the supports was drawn. Fig. 2 illustrates a clear linear relation between the temperature of maximum H_2 consumption (T_{max}) and the pH at which the surface possesses zero surface charge. The higher the basicity of the support, within the range 5.5–12, the higher is the temperature needed for V monolayer species to be reduced. Arena et al. [11] also presented a similar correlation, between reduction onset temperature T_{on} and pH at zero point charge of oxidic supports, which shows a hollow trend with a minimum at 6 pH.

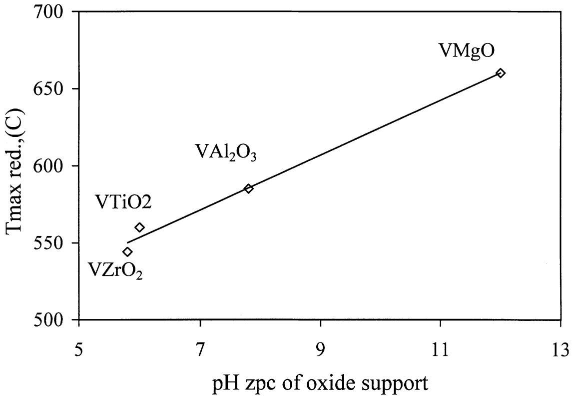

Fig. 2. Relationship between the T_{max} of reduction of V species and the point of zero charge of supports.

TPR patterns of the doped catalysts are presented in Fig. 3. Temperature of maximum H_2 consumption is higher for promoted VAl_2O_3 than for the non-promoted catalysts. T_{max} is 585°C for VAl_2O_3, while for the doped catalysts shifts to 600–604°C.

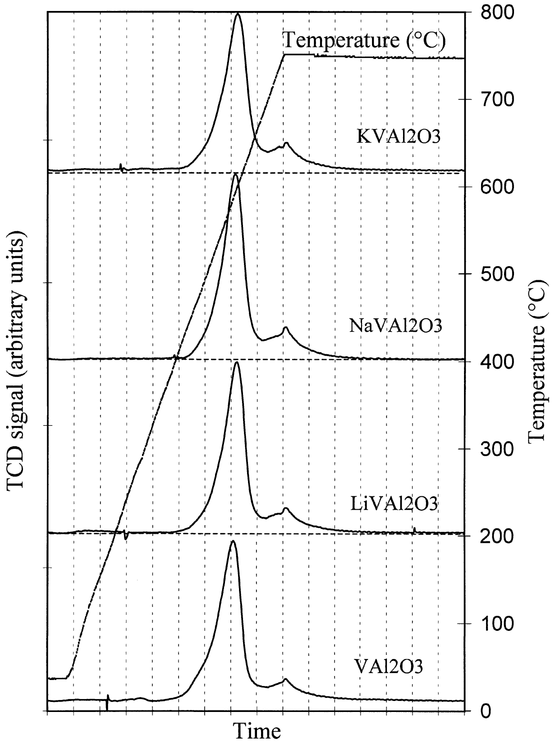

Fig. 3. TPR patterns of alkali promoted V_2O_5/Al_2O_3 catalysts.

The shift to higher temperatures could be due to stronger interaction between V and basic alkalies. Valenzuela et al. [23] reported that doping of VMgO catalyst with K results in higher $T_{\max}$ and analogous results for K doped VAl_2O_3 were observed by Galli et al. [16]. While the presence of alkali metal affects the reducibility of V species no difference was observed in $T_{\max}$ among the alkali metals used.

Even though quantification of TPR profiles does not give direct information about the V oxidation states, it provides some useful indications. Exposure of surface V^{5+} species to reducing H_2, results in the formation of V^{4+} and/or V^{3+} [9,22,24]. Total H_2 consumption and the average oxidation state (AOS) were calculated and included in Table 1. Tested catalysts exhibit different AOS indicating that the extent of reduction is affected by the support. The AOS of V supported on TiO_2 and ZrO_2 is approximately the same, AOS=3.5. The higher H_2 uptake observed with VMgO catalyst cannot be ascribed totally to the reduction of V^{5+}. The XRD pattern of the reduced sample showed characteristic peaks of Mg and MgH_2 with low intensity, thus part of H_2 uptake is most probably due to the partial reduction of Mg in the MgV_2O_6. V supported on Al_2O_3 is almost completely reduced reaching an average oxidation state, AOS=3.16. Doping of VAl_2O_3 catalyst with alkalies does not differentiate significantly the extent of the V species reduction, which was calculated in the range 3.05–3.15. In agreement with the above, Lopez Nieto et al. [25] claimed that AOS after TPR is the same for unpromoted and metal promoted V_2O_5/Al_2O_3 catalysts. On the contrary, Sloczynski [26] reported that the addition of alkalies in $VTiO_2$ catalyst reduces the rate of reduction of V in C_3H_8 flow and the extent of reduction depends on the alkali used. Concluding, there currently appears to be a lack of consensus among various publications as to the extent of reduction of V on various supports. It seems that the valence state of V in supported catalysts is influenced by the reducing environment, surface vanadia coverage and support nature.

3.2. *Catalytic results*

The catalytic performance of the supports in the propane oxidative dehydrogenation (ODH) reaction was tested at 500°C. The results obtained are shown in Table 2. Apart from propane conversion and product selectivity the specific surface activity (SSAc) expressed as $\mu mol_{C_3H_8}\ m^{-2}\ s^{-1}$ is also presented to account for the different surface areas of the supports used. The carriers exhibit quite different performances in the ODH of propane in terms of activity and selectivity. The maximum SSAc is observed with TiO_2 while the other supports exhibit lower activities. Concerning the selectivities in propene, Al_2O_3 and TiO_2 are quite selective (40–45%) while MgO and ZrO_2 are totally unselective (10%). These results are in agreement with the work of Arena et al. [11].

The deposition of 4 wt.% V_2O_5 on these supports results in a much higher activity in the oxydehydrogenation of propane at 450–550°C as shown in Table 3. To compensate the effect of the different VO_x surface densities of the catalysts on the propane consumption rate, activity was normalized for the VO_x surface densities. Comparison of the catalyst activities based on surface areas (SSAc) and on VO_x surface densities (intrinsic activity) leads to the order:

$$VTiO_2 \gg VZrO_2 > VAl_2O_3 > VMgO$$

The intrinsic activity of $VTiO_2$ catalyst is much higher than the others. The high activity of V_2O_5/TiO_2 catalyst in *o*-xylene oxidation [27], was also confirmed

Table 2
Catalytic performance of supports at 500°C[a]

Support	Conversion C_3H_8 (%)	Selectivity		SSAc ($\mu mol_{C_3H_8}\ m^{-2}\ s^{-1}$)
		C_3H_6 (%)	CO_x (%)	
MgO	1.5	11.4	88.6	0.003
Al_2O_3	2.5	41.2	58.8	0.002
TiO_2	6.9	45.4	54.6	0.020
ZrO_2	4.5	10.1	89.9	0.007

[a] W=0.2 g except for MgO (W=0.4 g).

Table 3
Catalytic performance of V based catalysts in ODH of propane

Catalyst	Tr (°C)	*W* (g)	Conversion C_3H_8 (%)	Selectivity		SSAc ($\mu mol_{C_3H_8}$ m^{-2} s^{-1})	Intrinsic activity (s^{-1})	Propene productivity ($kg_{C_3H_6}$ kg_{cat}^{-1} h^{-1})
				C_3H_6 (%)	CO_x (%)			
VMgO	500	0.40	12.9	33.2	66.2	0.020	–	0.11
	550	0.40	25.6	24.8	74.2	0.042	–	0.15
VAl_2O_3	450	0.20	7.97	59.5	40.5	0.014	0.006	0.23
	500	0.20	20.3	39.8	60.2	0.035	0.016	0.40
$VTiO_2$	450	0.05	16.9	35.0	65.0	0.670	0.057	1.17
	500	0.05	30.4	22.8	77.0	1.200	0.101	1.43
$VZrO_2$	450	0.20	26.2	20.3	79.6	0.122	0.021	0.26
	500	0.20	33.1	17.1	82.5	0.150	0.026	0.28

recently in the ODH of propane [1,13]. The activities of $VZrO_2$ and VAl_2O_3 are lower compared to that of $VTiO_2$ catalyst. Even though VMgO type catalysts have been reported as active catalysts in ODH [1,2], the present catalyst containing 4 wt.% V_2O_5 exhibits very low activity even at higher temperatures compared to the other catalysts. It is worth mentioning that the propylene productivity of the tested $VTiO_2$ catalyst is 1.43 $kg_{C_3H_6}$ kg_{cat}^{-1} h^{-1} at 500°C, and hence much higher than the maximum productivity (0.7 at 550°C for $NiMoO_4$) reported up today [28].

It has been recognized that the acidic and basic nature as well as redox character are important properties of the catalysts, which affect the catalytic performance in oxidation reactions. As it was confirmed by the TPR patterns, the reducibility characteristics of V species are strongly related to the support nature and more specifically are in linear relation with the isoelectric point of the supports. From the results obtained here it could be inferred that generally the activity scale of the catalysts is in analogy with the reducibility of the supports, e.g. the higher the reducibility of V species, the higher is the activity of the catalyst in the ODH of propane. Recent investigations on the effect of support on the activity of V based catalysts in ODH reactions showed that oxidative reaction rates depend on support composition and on VO_x surface density [18]. According to Khodakov et al. [18] reaction rates increase as the VO_x surface density increases for all supports suggesting that polyvanadate domains, which have been identified at VO_x surface density higher than 1 nm^{-2} are more active than monovanadates. Even though the present $VTiO_2$ catalyst was not structurally characterized, the very high activity of this catalyst could be attributed to the unique dispersion of VO_x species in polyvanadate domains on the TiO_2 surface that permit the easy reduction–oxidation cycles of V^{+5} centers.

Runs were conducted at 500°C using variable *W*/*F* ratios to attain propane conversions up to 35%, in order to investigate in more detail the selectivity of the catalysts. The influence of the conversion on product distribution is depicted in Fig. 4. First, the detrimental effect of secondary reactions in propene selectivity as the conversion increases is confirmed. However, it is clear that the rate of the secondary reactions that mainly contribute to the formation of CO_x is different among the V-containing catalysts. Although it was not possible, due to experimental limitations, to obtain very low conversions at 500°C the dramatic lowering of selectivity to the desirable product shows that the rate of secondary reactions is much higher with the $VTiO_2$.

In the whole range of propane conversions measured (10–35%), the propylene selectivity in the presence of vanadia supported on alumina is significantly higher than with the other tested catalysts. VMgO is the catalyst with the lowest selectivity, which remains relatively constant at different conversions. Mixed V–Mg catalysts with V_2O_5 content higher than 20 wt.%, are known to be selective catalysts in the ODH of propane [1–8]. However, the low selectivity of this sample is attributed to low vanadium content as was also observed in the literature [4,8] with 5 wt.% V_2O_5/MgO catalyst and to the presence of the mixed phase compound, magnesium metavanadate, that is known to be a non-selective phase in ODH reactions [4,6].

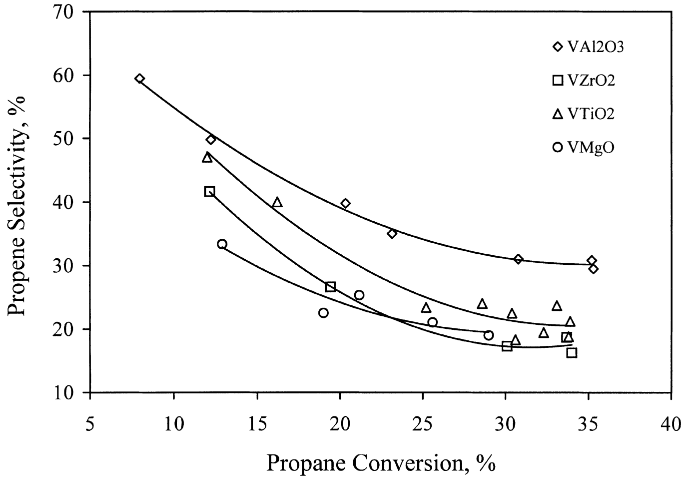

Fig. 4. Propene selectivity as a function of propane conversion at 500°C in the presence of vanadia supported catalysts.

The results analyzed above lead to the conclusion that the propene selectivity in the presence of supported vanadia catalysts varies and depends on the support nature. At the same degree of conversion the selectivity decreases according to the scale:

$$VAl_2O_3 > VTiO_2 > VZrO_2 > VMgO$$

While the reducibility of V_2O_5 on various supports plays an important role in activity, it fails to explain the dehydrogenation selectivity. It appears that other factors also play important role in determining the dehydrogenation selectivity. It has been proposed that the differences in selectivity to dehydrogenation reactions, apart from the acid–base character and the reducibility of the catalysts, could be controlled by the type of V species and the distance between the active sites [2].

The effect of alkali metals (Li, Na and K) addition on VAl_2O_3 catalyst was also investigated. The catalytic activity was measured at 450 and 500°C and the results, in terms of propane conversion and product selectivity, are depicted in Table 4. Given that the surface area of the undoped and doped catalysts is almost the same, the comparison was made in terms of propane conversion. In agreement with relevant work [25] on doped V_2O_5/Al_2O_3 catalysts, a decrease in the propane conversion is observed at 450 and at 500°C. It is also clear that the nature of the alkali metal affects the activity. The K promoted catalyst exhibits the most drastic decrease in activity. The increase in the temperature of maximum H_2 uptake (T_{max}) of promoted catalysts during TPR compared to that of non-promoted (Fig. 3) could explain the lower activity of these samples. The strong basic alkali metals decrease the reducibility of V species and the number of acid sites. According to Sloczynski [26], a certain amount of propane adsorption centers is blocked by the alkali metal ions. This effect becomes more pronounced as the ionic radius of the promoter increases, e.g. from Li to Na and K. Consequently, more active sites are blocked with K present than with Li, explaining the differentiation among the activities of the doped catalysts.

Table 4
Propane conversion and product selectivity in the presence of alkali promoted V_2O_5/Al_2O_3 catalysts

Catalyst	Temperature (°C)	Conversion C_3H_8 (%)	Selectivity	
			C_3H_6 (%)	CO_x (%)
VAl_2O_3	450	13.7	49.7	50.3
	500	30.8	28.8	71.2
$LiVAl_2O_3$	450	7.5	73.7	26.3
	500	23.9	49.6	50.4
$NaVAl_2O_3$	450	6.2	77.3	22.7
	500	20.2	50.7	49.3
$KVAl_2O_3$	450	5.7	80.2	19.8
	500	16.9	57.2	42.8

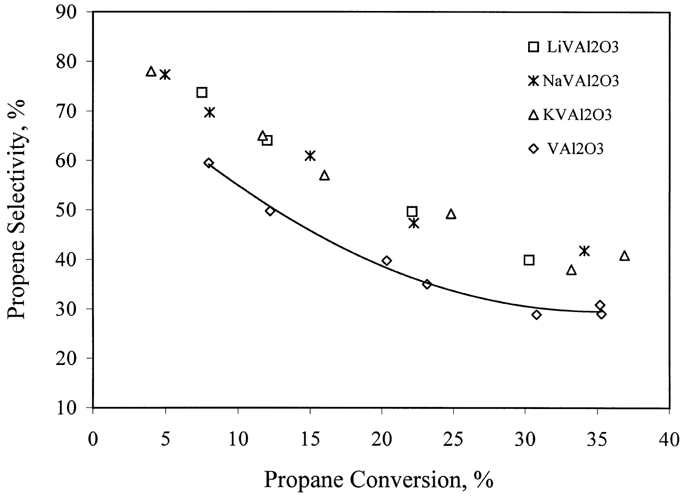

Fig. 5. Propene selectivity as a function of propane conversion at 500°C in the presence of alkali promoted V_2O_5/Al_2O_3 catalysts.

The beneficial effect of the alkali addition in propylene selectivity is shown in Fig. 5 where the propene selectivity is plotted against conversion at 500°C. Over the whole range of conversions, an increase in propene selectivity is observed. However, no remarkable difference in selectivity is exhibited among the alkali metal doped catalysts. It is not been clarified yet how the alkali metals affect the alkene selectivity; either by blocking unselective strong acid sites that favor the formation of CO_x and/or by facilitating the quick desorption of propene from the surface thus prohibiting secondary reactions. Further investigations are required to elucidate the role of the alkali metal promoters in the mechanism of ODH.

4. Conclusions

Highly dispersed monolayer V species are formed with deposition of 4 wt.% V_2O_5 on Al_2O_3, ZrO_2 and TiO_2, while on MgO the mixed magnesium metavanadate phase is formed. The support nature affects the reducibility of V species and the extent of reduction. The temperature at maximum H_2 uptake (T_{max}) is higher in the case of more basic support oxides. The catalytic activity in propane oxidative dehydrogenation is influenced by the reducibility and the structure of V species on the surface. V_2O_5/TiO_2 is the most active catalyst while V_2O_5/Al_2O_3 is the most selective in propene.

Addition of alkali metals (Li, Na and K) to V_2O_5/Al_2O_3 catalyst hinders the reducibility thus decreasing the catalytic activity. The extent of this effect depends on the nature of the promoting alkali and is more pronounced in alkali metals with higher ionic radius. The promoting effect of the alkali metals in propene selectivity is significant, irrespective of the alkali used.

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