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Oxidative dehydrogenation of propane over molybdenum-containing catalysts

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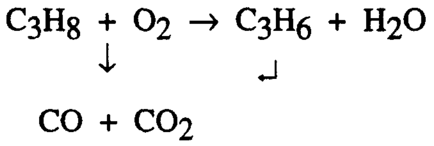
Abstract

Catalysts consisting of molybdena supported on different oxides (niobia, alumina, zirconia, silica, magnesia and titania) have been compared for the oxidative dehydrogenation of propane. Of these, titania-supported molybdena was found to be the most selective at isoconversion. A coverage of the titania support greater than a monolayer was necessary in order to achieve an improved selectivity towards propene, with an optimum at approx. 2.4 monolayers. In addition to giving propene and carbon oxides, the majority of the catalysts also had a low selectivity towards oxygenated compounds, mostly acrolein. Some loss of molybdenum was also found with most of the catalysts. Addition of the oxides of vanadium and niobium to the titania-supported molybdena material gave an increase in the rate of the reaction without any loss in the selectivity to propene. This formulation gave a catalyst whose performance was close to a $NiMoO_4$ catalyst examined under similar experimental conditions.

Keywords: Propane; Oxidative dehydrogenation; Titania-supported molybdena

1. Introduction

Over the last few years, much work has been devoted to investigations of the oxidative dehydrogenation of light hydrocarbons (frequently propane or butane) with the aim of finding a new route to the corresponding olefins. Oxidative dehydrogenation involves the removal of hydrogen from the reactant molecules by oxygen of the feed to form the corresponding olefins without parallel or consecutive oxidation reactions giving carbon monoxide or dioxide as non-selective products. For propane, the reaction network may be represented as follows:



$$\begin{tikzcd} C_3H_8 + O_2 \arrow[r] \arrow[d] & C_3H_6 + H_2O \arrow[dl] \\ CO + CO_2 & \end{tikzcd}$$

The most active and selective catalysts reported in the literature for the oxidative dehydrogenation of propane consist of vanadia supported on magnesia [1] or niobia [2] and nickel molybdate [3]. Recently, it has been claimed that some multicomponent formulations give much improved olefin yields [4] but insufficient details have been given of these materials for these data to be confirmed in this laboratory. Titania-supported vanadia or molybdena, modified by alkalis,

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have also recently been reported as promising propane ODH catalysts [5].

As part of their investigations of niobia as an oxidative dehydrogenation catalyst, Ross et al. [2] showed that niobia-supported molybdena has interesting catalytic properties. This material gave a high selectivity to propene at low conversion; however, the overall activity was not very high. In the work reported here, we have studied the behaviour of a series of samples consisting of molybdena supported on a variety of different oxides with a view to increasing the activity as compared with the MoO_3/Nb_2O_5 material. Results are reported here for materials having a constant molybdena content (5 wt.%) supported on various supports (with a variety of different surface areas). For the best formulation, MoO_3/TiO_2, the effect of molybdenum loading was also examined and related to the theoretical coverage of titania by molybdena. In an attempt to further improving this material, following former work highlighting the synergistic effect existing between Mo, V and Nb for the ODH of ethane to ethene [6,7], vanadium oxide or a mixture of vanadium and niobium oxides were added to MoO_3/TiO_2.

2. Experimental

Ammonium heptamolybdate (Rhone Poulenc, Normapur AR) was dissolved (0.10 g cm^{-3}) in hot, deionised water (343 K) and impregnated onto the different supports using the incipient wetness method. The supports used were as follows: niobia (prepared from hydrated niobia calcined at 900 K according to Ref. [8]), γ alumina (Ketjen), zirconia (monoclinic, Gimex), silica (Spherosil), magnesia (BDH) and titania (anatase, BDH). The impregnated supports were first dried overnight at 343 K and then calcined at 723 K or 923 K under flowing air. The heating rate used to achieve this calcination temperature was 5 K min^{-1}. For a catalyst containing both Mo and V, an aqueous solution of ammonium heptamolybdate (0.20 g cm^{-3}) and ammonium metavanadate (0.058 g cm^{-3}) was used to co-impregnate these salts on the titania. In contrast, for a catalyst containing Mo, V and Nb, oxalic acid solutions (approx. 0.25 g cm^{-3}) of ammonium heptamolybdate (0.20 g cm^{-3}), ammonium metavanadate (0.068 g cm^{-3}) and niobium oxalate (0.10 g cm^{-3}) were used to co-impregnate these compounds on titania; the acidic medium was necessary in this case to avoid any precipitation of niobium compounds. When the volumes of the solutions needed to dissolve the salts were higher than the pore volume of the support, the impregnation was carried out several times. Each step was followed by drying at 343 K. The supports not supplied as extrudates were pressed into pellets and the samples were then crushed to give particle sizes ranging from 0.3 to 0.6 mm for use in the catalytic tests.

Adsorption of nitrogen at 77 K using a Micromeretics system was used to measure the total surface areas of the samples. Prior to these measurements, the samples were outgassed for 2 h at 473 K under dynamic vacuum (residual pressure lower than 20 Pa). X-ray diffraction analyses were carried out using a Philips Diffractometer. Atomic absorption and XRF measurements were performed on the catalysts to determine the molybdenum, vanadium and niobium contents.

A quartz flow microreactor (3 mm internal diameter) was used for the catalytic tests, the catalytic bed being held in place by quartz wool plugs. The temperature of reaction was measured inside the reactor, just after the catalyst bed, by a quartz-shielded thermocouple. A sample of 600 mg of catalyst was used for each experiment; the reactant gas was made up of 29.4% propane (Air Products, 99.9%) and 9.6% oxygen (BOC 99.9%) with a balance of helium (BOC 99.9%), and the total flow rate was 136 cm^3 (stp) min^{-1}. The stainless steel connecting tubing after the reactor was maintained at 393 K to prevent condensation of the water or of any oxygenated product formed by the reaction. On-line injections were made to a Varian 3300 gas chromatograph fitted with TCD detectors. A HayeSep Q column was used to separate carbon dioxide, hydrocarbon products, acrolein and some other oxygenated products, while a molecular sieve column was used to separate oxygen and carbon monoxide. Off-line injections were also made to a Porapak T column to separate water, formaldehyde and carboxylic acids. In all the experiments, propene and carbon oxides were the main products. A complete carbon balance within ±2% was achieved in all cases.

All the experiments were carried out using a standard sequence in which the furnace temperature was increased from 523 K to 923 K in steps of 50 K, each step taking one hour. The effluent mixture was analysed twice at each temperature. In separate experiments, it was found that neither the empty reactor nor the reactor filled with quartz wool had any significant activity at temperatures lower than 923 K.

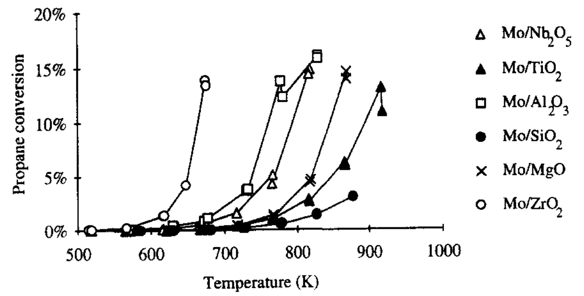

Fig. 1. Propane conversion as a function of temperature for molybdena supported on the different oxide supports (Mo load approx. 5 wt.%, see Table 1).

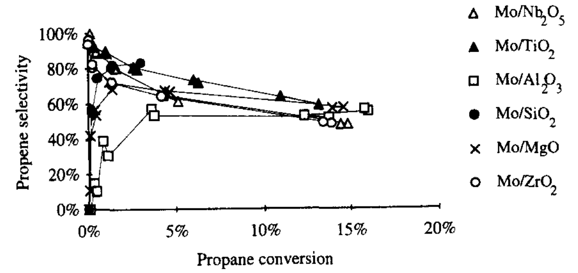

Fig. 2. Propene selectivity as a function of conversion for molybdena supported on the different oxide supports (Mo load approx. 5 wt.%, see Table 1).

3. Results

3.1. *The effect of the support on the properties of supported molybdena*

A series of catalysts, all containing approximately 5 wt.% MoO_3 was prepared and tested for the oxidative dehydrogenation of propane. Table 1 gives the total (BET) surface areas of the supports used, the molybdenum contents and the surface areas after impregnation and calcination. It also gives for the data reported in Figs. 1 and 2 and discussed further below the selectivities to propene and to oxygenates at propane conversions of 5%; as the silica-supported material did not give a 5% conversion of the propane under the experimental conditions used here, the corresponding values for 3% conversion are given. The optimum temperatures of calcination for the supports were determined in preliminary experiments and found to be 723 K for niobia and titania, and 923 K for alumina, zirconia, silica and magnesia; these were the values which gave the highest propene selectivity at the highest conversions of propane. The surface areas after the calcination step were in several cases somewhat different to those of the untreated supports; although in most cases the areas of the final catalysts were somewhat lower, the values obtained for the alumina- and magnesia-supported materials were significantly higher, indicating that there must have been some sort of interaction between the molybdenum species and the support to cause this increase.

Fig. 1 shows the propane conversion as a function of reaction temperature for the catalysts of Table 1.

Table 1
Surface areas, molybdena contents and selectivity data for a series of molybdena-containing catalysts (approx. 5 wt.% Mo) supported on various oxides

Catalyst	Surface area of support ($m^2 g^{-1}$)	Mo content (wt.%)	Calcination temperature (K)	Surface area of catalyst ($m^2 g^{-1}$)	Selectivity to propene [a] (%)	Selectivity to oxygenates [a] (%)
Mo/Nb_2O_5	12.9	5.44	723	12	62	6.3
Mo/TiO_2	41	5.04	723	31	75	3.7
Mo/Al_2O_3	211	5.52	923	229	54	0.0
Mo/SiO_2	230	3.64	923	133	82	3.0
Mo/MgO	58	4.70	923	88	68	0.9
Mo/ZrO_2	95	6.33	923	53	64	2.0

[a] The selectivities to propane and oxygenates are given in each case for a propane conversion of 5% except for the silica-supported sample for which the propane conversion was 3%.

For the catalysts using silica, titania and magnesia as supports, the conversion of oxygen was not complete at the highest temperature of reaction examined: this temperature was chosen so that no homogeneous reactions were likely to have occurred. The zirconia-supported catalyst was much more active than the others but gave high proportions of carbon oxides and correspondingly lower selectivities to propene at higher conversions. The activities of the alumina- and niobia-supported materials were roughly equivalent, the next most active were the magnesia- and titania-supported materials and, finally, as noted above, the silica-supported catalyst was much less active than the others.

Fig. 2 shows the values of the selectivity to propene as a function of the propane conversion corresponding to the data of Fig. 1. The propene selectivity at a very low conversion is difficult to analyse accurately and was also strongly affected in our case by the calcination temperature used. For instance, for the Mo/TiO_2 material calcined at 723 K, a 100% selectivity to propene at 0% propane conversion was observed but the value was 0% for the calcination at 923 K. This effect could arise from differences in the Mo dispersion, the degree of hydration of the support or the extent of elimination of the precursor salts. The catalysts based on titania, zirconia and niobia all tended to give 100% selectivity to propene at low conversions for the calcination temperature used for the data of Figs. 1 and 2, whereas the other materials gave low or zero selectivities. However, for all the preparations studied, the difference due to the calcination temperature vanished at conversion levels greater than 1%, the region of greatest interest in this work. However, at yet higher propane conversions, when the conversion of the oxygen was essentially complete, the propene selectivities of the catalysts were also rather irreproducible, one problem being that the surface molybdenum oxide was likely to be reduced to different extents, depending on the temperature and the residual oxygen partial pressure, as well as on the concentrations of the products of the reaction. At intermediate conversions, the titania-supported molybdena catalyst was the most selective of the series examined; in addition to giving propene, this material exhibited a selectivity of up to 3.7% towards oxygenated compounds, mostly acrolein (see Table 1). The magnesia- and zirconia-supported materials gave slightly lower selectivities than did the titania-supported material at all conversions. The alumina-supported catalyst gave relatively poor selectivities at low conversions (see Table 1) but its behaviour was somewhat better at higher conversions. The silica-supported molybdena material also showed good selectivity at low conversions but its activity was very low over the temperature region examined, the highest conversion obtained being approximately 3%.

Of the catalysts which have been examined above, the most promising were those based on zirconia, alumina and particularly titania. In what follows, we report results with higher molybdena loading for the zirconia and alumina supports aimed at examining the possibility that if these supports were more fully covered by molybdena, the selectivities might be higher. We also examine in detail the effect of molybdena content for the titania support with a view to optimising this combination. All the data are reported at propane conversions of 5% since none of the irreproducibilities associated with low and high conversions referred to above apply at that conversion.

3.2. *The effect of molybdena loading using zirconia and γ-alumina as supports*

The theoretical monolayer coverage by molybdena of the zirconia and alumina supports, these having surface areas of 95 $m^2 g^{-1}$ and 211 $m^2 g^{-1}$, respectively, are about 8.9 and 18 wt.% Mo, respectively; these values have been calculated using the assumption that the density of the molybdenum atoms on the surface of these two supports was equal to that which has been reported for titania, 6.5 Mo ions per nm^2 [5]. One sample with a loading greater than a monolayer was made using the zirconia support, while a number of samples with loading just below as well as above monolayer coverage were made using the alumina support; the temperature of calcination of all the samples was 923 K. The results obtained for these materials are summarised in Table 2 where the data reported above for approximately 5 wt.% Mo are also shown for comparison. For molybdenum supported on zirconia, no improvement of the propene selectivity was observed when the molybdenum loading was increased above that of the theoretical monolayer coverage (8.9 wt.%) and the activity of the catalyst was also reduced. In contrast, the selectivities of the

Table 2
Catalytic data for catalysts with different Mo loading on zirconia and alumina compared with data for a sample prepared on titania

Sample	Molybdenum content (wt.%)	*T* for 5% propane conversion (K)	At 5% propane conversion: Propene selectivity (%)	At 5% propane conversion: Oxygenates selectivity (%)
Mo/ZrO_2	6.33	675	63	n.m.
Mo/ZrO_2	12.9	724	64	n.m.
Mo/Al_2O_3	5.52	738	54	0.00
Mo/Al_2O_3	14.2	684	68	2.00
Mo/Al_2O_3	19.3	674	72	1.50
Mo/Al_2O_3	25.5	695	72	2.00
Mo/Al_2O_3	44.0	725	72	4.00
5% Mo/TiO_2	4.27	878	77	3.92

n.m.: not measured.

materials prepared with the alumina support were increased significantly using a molybdenum loading equal to or greater than about 20 wt.%. The activities of these samples were also increased compared to that for the 5 wt.% Mo material. The alumina-supported catalysts were much more active but slightly less selective than the Mo/TiO_2 material described above, the results of which are also shown in Table 2 for comparison purposes.

3.3. *The effect of molybdena loading using titania as support*

As molybdena supported on titania gave the highest selectivities of the samples examined (Fig. 2), equivalent experiments to those reported in the last section on the effect of molybdena loading were carried out using titania as support and the results are summarised in Table 3. All the samples, ranging from unpromoted titania up to the 10 wt.% Mo/TiO_2 material, required approximately the same temperature to give 5% conversion. However, the unsupported molybdena and 15 wt.% Mo/TiO_2 samples were less active. The selectivity to propene and also to oxygenates (made up of between 60 and 100% acrolein, 0–20% acetaldehyde and 0–20% formaldehyde) also increased with Mo loading up to 10 wt.% Mo. It is interesting to note that the first analyses at any temperature showed the presence of ethanol and propanol, as well as of acetone and propanone but that acrolein and acetaldehyde were the main products in the second analyses; the latter were used to calculate the results cited above. Table 3 also shows for comparison results for pure titania and unsupported molybdena. In the former case, the results are similar to those with low Mo loading, indicating that the samples with lower load-

Table 3
The temperature for 5% conversion of propane and the selectivities to propene and oxygenates as a function of Mo loading for a series of catalysts supported on titania; results for unsupported molybdena are also shown for comparison (catalyst calcination temperature=923 K)

Sample	Molybdenum content (wt.%)	BET surface area ($m^2 g^{-1}$)	*T* for 5% propane conversion (K)	At 5% propane conversion: Propene selectivity (%)	At 5% propane conversion: Oxygenates selectivity (%)
TiO_2	—	31.8	863	46	0.58
1% Mo/TiO_2	0.81	32.5	876	56	1.34
2.5% Mo/TiO_2	2.14	33.6	878	67	2.42
5% Mo/TiO_2	4.27	29.9	878	77	3.92
10% Mo/TiO_2	9.38	18.6	870	80	5.40
15% Mo/TiO_2	14.8	8.6	906	78	4.34
MoO_3	66.0	0.7	902 [a]	64	0.20

[a] At 1% propane conversion.

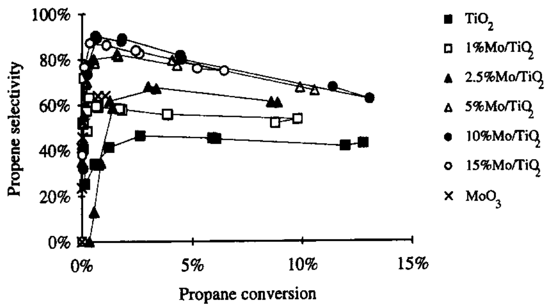

Fig. 3. Propene selectivity as a function of propane conversion for a series of catalysts with different loads of molybdenum supported on titania; results for titania and unsupported molybdena are shown for comparison.

ing may be influenced to a certain extent by some activity from the uncovered titania. On the other hand, the sample with the highest Mo loading is much more selective than unsupported molybdena, indicating that the properties of the supported sample are still influenced by the nature of the underlying support.

Fig. 3 shows the selectivity to propene as a function of propane conversion for these catalysts. The optimal selectivities to propene were obtained for a loading of molybdenum of 9.4 wt.%; the samples with 5 and 15 wt.% also gave good results. The theoretical monolayer coverage on this 41 $m^2 g^{-1}$ titania is 3.9 wt.% Mo and so we conclude that at least a monolayer of molybdena is necessary to give most selective preparations. The optimum corresponds to approx. 2.4 monolayers. It is interesting to note the significant decrease of the specific surface area of the catalysts with increasing metal loading above the monolayer coverage (Table 3). Table 4 gives the rates of formation of propene and CO_x (in parentheses) per unit surface area of each of the catalysts with theoretical coverages greater than a monolayer at three different temperatures; for these the selectivities to propene ranged from 90% to 78% and the propane conversions from 0.60% to 5.70%. The specific rates of propene formation for the 5% Mo sample, for which the loading was just above the monolayer coverage, were about half the values of those with higher loading.

Table 4
Comparison of propene and CO_x (in parentheses) formation rates per unit surface area of the catalyst at different temperatures (see Table 3 for catalyst surface areas and exact Mo loadings)

Catalyst temperature (K)	Rates of propene and CO_x formation per unit surface area of catalyst (10^{-10} mol s^{-1} m^{-2})		
	5% Mo/TiO_2	10% Mo/TiO_2	15% Mo/TiO_2
773	79 (20)	188 (21)	184 (28)
823	223 (35)	506 (46)	560 (72)
873	570 (121)	1185 (197)	1245 (180)

When three temperature cycles were performed using the 5 wt.% Mo/TiO_2 catalyst, some deactivation was observed between the first and second cycle but not between the second and third. The decrease of propane conversion was about 25%. This change was not due to sintering of the support since the values of the total surface area before and after the experiments were 30.5 and 29.3 $m^2 g^{-1}$, respectively. Further, the plots of propene selectivity against propane conversion were unchanged by the temperature cycles. After experiments with the samples with the higher loads of molybdena (10–15 wt%), many small crystallites were observed following reaction in the volume after the catalyst bed. The appearance of these was very similar to those of pure molybdena – very thin shining platelets. Atomic absorption analysis also showed a small decrease in the molybdenum content after the series of cycles, from 9.38 to 9.11 wt.%. A change of the colour of the catalyst particles was also visible along the length of the catalytic bed, from the pale yellow of the fresh material to black. This colour change could be accounted for either by some reduction of the molybdenum species or by coke deposition, since the reaction atmosphere became reductive as the oxygen was converted.

3.4. *Promotion of titania-supported molybdena*

In an attempt to increase the activity of the titania-supported molybdena, other promoters were co-impregnated with the molybdena. A vanadia sample with a Mo/V atomic ratio of 4:1 was first prepared in which the molybdena content was kept at 10 wt.%, since this loading gave the optimal propene selectivity on this titania. The results of Table 5 and of Figs. 4 and 5 show that this gave a much more active catalyst; the temperature required for 5% conversion was lowered by more than 100 K (Table 5). However, the selectivity to propene was somewhat lower at higher conversions (Fig. 5). As it had been reported earlier [6,7] that the addition of niobium to Mo–V systems can improve their catalytic properties, a sample con-

Table 5
The effect of adding vanadia or vanadia plus niobia to a titania-supported molybdena catalyst on the temperature for 5% conversion and the corresponding selectivities to propene and oxygenates (catalyst calcination temperature=923 K)

Sample	Mo (wt.%)	V (wt.%)	Nb (wt.%)	Surface area ($m^2 g^{-1}$)	*T* for 5% propane conversion (K)	Propene selectivity (%)	Oxygenates selectivity (%)
TiO_2	—	—	—	31.8	860	46	0.60
Mo/TiO_2	9.38	—	—	18.6	870	80	5.40
$(Mo+V)/TiO_2$	9.02	1.21	—	28.6	757	74	2.60
$(Mo+V+Nb)/TiO_2$	9.30	1.36	1.0	21.8	777	81	1.80

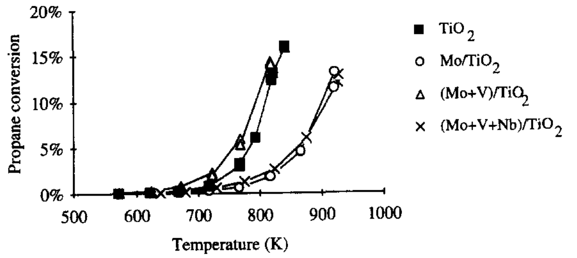

Fig. 4. Propane conversion as a function of temperature for a molybdena–titania catalysts, showing the effect of adding vanadia or vanadia plus niobia.

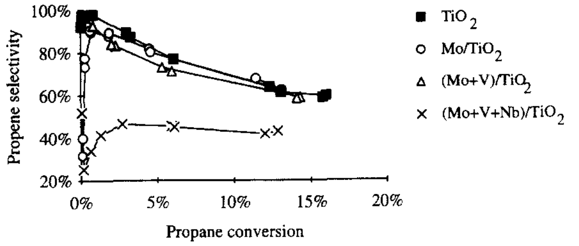

Fig. 5. Plots of propene selectivity versus propane conversion for the data shown in Fig. 4.

taining Mo, V and Nb with the atomic ratio 7.2:2.0:0.8 was then made and tested, and the results are also given in Table 5 and Figs. 4 and 5. The addition of niobia to the formulation caused the rate of reaction to be slightly lowered; however, the good selectivity found with the unpromoted titania-supported molybdena was recovered and the temperature to give 5% propane conversion was now 93 K lower compared with molybdena alone. The addition of vanadium and niobium also decreased somewhat the selectivity to oxygenated compounds.

4. Discussion

Molybdena-containing catalysts have already been widely used for the oxidation reactions of the hydrocarbons, mostly for the selective oxidation of propene to acrolein [11,12]. Molybdena supported on different carriers has also been used for other types of oxidation reactions: e.g., silica-supported molybdena has been used for the transformation of the methane to formaldehyde [13] and titania-supported molybdena for the oxidation of olefins and alcohols [9]. More recently, the use of molybdena-containing catalysts has also been investigated for the oxidative dehydrogenation of propane [3,5,8,10,14]; for example, the modification of titania-supported molybdenum by the addition of bismuth [14] or by doping by alkali [5,10] have been studied. However, no systematic study of the molybdenum loading effect has been reported. A systematic survey of the promotion of niobia by many different dopants showed that molybdena was one of the best promoter to achieve an active and selective catalyst [15]. However, molybdena-promoted niobia had a lower activity than vanadia- or chromia-promoted niobia. In order to find formulations which are selective and active for the oxidative dehydrogenation of propane, we have investigated a variety of catalyst formulations using molybdenum.

The results of the present paper obtained with different supports with loadings of 5 wt.% molybdenum showed that titania-supported molybdena was the most selective material at isoconversion. By increasing the molybdenum loading on zirconia or alumina, whose surface areas are higher than titania, no better selectivity could be found than with the titania support and so the effect of the loading of molybdena on the titania sample (anatase, 41 $m^2 g^{-1}$) was studied. It was shown that a coverage higher than the theoretical monolayer value (3.9 wt.% Mo) was required to achieve a good selectivity to propene; such full coverage is likely to prevent total oxidation arising from the bare support. The optimum load to give high activity and selectivity was found to be approx. 9.5 wt.% Mo, i.e., approx. 2.4 monolayers. This coverage gives a material with a lower surface area than that of the sample with approximately one monolayer (Table 3) but results in a higher rate of propene formation per unit surface area with little change in the rate of formation of total oxidation products at temperature below 823 K (Table 4). Increasing further the loading resulted in a further significant decrease of the surface area but this had little effect on the rates of product formation.

As titania-supported molybdenum has previously been used for other oxidation reactions, its preparation and structure have already been thoroughly worked out. The preparation according to a variety of different methods has been studied [16]; these methods include incipient wetness impregnation or equilibrium adsorption of molybdenum species using aqueous solutions, grafting of $MoCl_5$ and thermal spreading of MoO_3. It has been concluded that these methods all lead to the same surface molybdenum oxide structure after the final thermal treatment. The spreading of molybdenum species over titania has been reported to be easy and to be favoured thermodynamically [16]. It has even been found to be possible to carry out thermal spreading of molybdenum compounds at 723 K over titania starting from a mechanical mixture of titania and molybdena. Raman and FTIR spectroscopic studies have shown that the surface oxide species formed after calcination at 773 K depend on the coverage [17,18]. Below the monolayer coverage, only surface molybdate species were observed; a molybdate with a tetrahedral symmetry MoO_4^{2-} was reported at very low content. A significant Raman shift indicated that there was a strong interaction between these surface compounds and the support. As coverage approached the monolayer, more molybdate species of octahedral symmetry such as polymeric surface $Mo_7O_{24}^{6-}$ were observed. Above the monolayer coverage, distorted molybdena crystallites appeared in addition to the previous species and these became more and more regular in shape with increasing loading [19]. The most selective catalysts in the present study were obtained with Mo loadings from one to three times the theoretical monolayer coverage. This shows that total coverage of the titania is required to prevent any total oxidation reaction occurring on the support. As the rate of propene formation per surface unit increases by a factor of two on varying the coverage from one to two or three layers, we conclude that the reaction of propane is structure sensitive, being faster on the molybdena-like crystallites than on monolayer molybdate species.

The proportion of oxygenated products found on the titania-supported molybdenum varies significantly and this is probably related to the experimental feed. Using a feed of 7% propane in air, Grzybowska et al. observed very few oxygenates, less than 1% [5,10]. In this work, using 30% propane and 10% oxygen in helium, a selectivity to oxygenates, mostly acrolein, up to 6% was observed. At higher propane pressures, with 60% propane and 20% oxygen in helium, Barrault et al. observed a selectivity up to 39% (acetic acid and acrolein being the main products) [14]. This trend can be explained by the homogeneous and/or successive reactions of reactants and products that are favoured with increasing partial pressure. This stresses the need of using comparable experimental conditions of feed to get comparable data for the ODH of propane. The relatively low amounts of oxygenated products formed throughout this study (<6%) indicates that there is no major influence of homogeneous reactions, triggered by surface initiated radicals.

Grzybowska et al. have recently reported studies over Mo/TiO_2 based catalysts for the ODH of propane [5]. Preparations consisting of 1 or 5 monolayers of Mo over the titania were investigated. By adding different alkali promoters to those, they observed an increase of selectivity into propene with increasing basicity of the catalysts. The authors proposed that the reduction of the acidity of the surface facilitates the desorption of propene (nucleophile) before further oxidation. Better yields to propene at isoconversion were then obtained. In parallel works, the promoting effect of molybdenum and vanadium were compared on niobia [15] and titania [5,10]. Vanadia-based catalysts always showed a much higher activity than the corresponding molybdenum-based material. In order to enhance the activity of the selective Mo/TiO_2 catalyst, supported mixed oxides were prepared in the present work. A much more active catalyst was observed by adding vanadium to the Mo/TiO_2 for-

Table 6
Comparison of the Mo+V+Nb/TiO_2 (this work) and $NiMoO_4$ [3]

Catalyst	Mo+V+Nb/TiO_2 [a]		$NiMoO_4$ [b]
Temperature (K)	767	793	773
Propane conversion (%)	3.23	6.06	7.20
Propene selectivity (%)	87.3	76.8	78.1
Propene yield (%)	2.82	4.65	5.62
Activity (mmol C_3H_6/h per g) (%)	5.03	8.30	11.3

[a] 600 mg of catalyst with a total feed of 136 sccm, propane 29.4%+oxygen 9.6%+helium.
[b] 500 mg of catalyst with a total feed of 250 sccm, propane 15%+oxygen 15%+nitrogen.

mulation (Fig. 4). Nevertheless, the selectivity of the catalyst was lowered. Other works showed the benefit of adding niobium to MoV system [6,7,20]. A mixture of these three elements showed indeed a good behaviour in the oxydehydrogenation of ethane. For the conversion of ethane to ethene, addition of niobium allowed to increase both the activity and selectivity [7]. The respective atomic ratio used were Mo/V=6/3 and Mo/V/Nb=6/3/1. It is still not clear what is or are the active phases, as many mixed oxides do exist in this system. In the present work, the ratio of oxide Mo/V=8/2 is reported. Lower ratios (higher vanadium proportion) were prepared but turned out to be much less selective at isoconversion. One has to underline that the amount of oxidic promoter is between two and three monolayers on titania. Thus, the supported mixed oxides obtained are furthermore likely to be different both for the structure and the catalytic behaviour from the bulk material having the same average formulation. By adding niobium to the (Mo+V)/TiO_2, we observed a small decrease of the activity as compared to the niobium-free catalyst. However, the good selectivity of Mo/TiO_2 is recovered and even improved. Comparison to the reported activity of a $NiMoO_4$ catalyst shows that the (Mo+V+Nb)/TiO_2 catalyst is nevertheless still less efficient (Table 6). The activity of the latter is lower by about two times, but the selectivity at isoconversion is close.

The lower experimental partial pressure of oxygen in our case lowers yet the yield to propene (results not shown). More, the formulation of the catalyst needs to be optimised, varying the atomic ratio Mo/V/Nb or adding alkalies might still improve the activity [21]. As highlighted by other authors, these molybdena and vanadia on titania systems are promising catalysts for the oxydehydrogenation of propane [5,10]

5. Conclusions

TiO_2 anatase (41 $m^2 g^{-1}$) provides an effective support to disperse molybdenum species to give a selective catalyst for the oxydehydrogenation of propane. The coverage of titania must be higher than the monolayer coverage to prevent any side reaction due to the bare support. An optimal load is found at an equivalent of approx. 2.4 monolayers coverage. The activity of the catalyst can be enhanced by the addition of vanadium, but a worse selectivity is then achieved. A mixture of molybdenum, vanadium and niobium oxides supported on titania then provides a more selective formulation for which the catalytic activity is close to that of best reported ones. Further improvement by means of a modification of the elemental composition and/or the addition of other dopants (e.g., alkalies) is likely and will be pursued.

Of the other supports tested, γ-Al_2O_3 proved to be one of the most effective. Loading above the theoretical monolayer coverage was required to obtain selective formulations. These materials were less selective than the titania-based samples; however, it will be shown elsewhere that alumina materials with lower areas can be used to give much improved Mo-containing catalysts [22].

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