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High throughput experiment approach to the oxidation of propene-to-propene oxide with transition-metal oxides as O-donors

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ABSTRACT

The oxidation of propene-to-propene oxide (PO) has been achieved via oxygen-transfer from transition-metal oxides to the olefin. Under the operative conditions, the cleavage of the olefinic double bond is not observed. The only co-products are acetone (AC) and propinoaldehyde (PA), that can be considered as isomerisation products of propene oxide. The "*parameter space*" of the reaction has been investigated using a High Throughput Experiment (HTE) approach. However, it has been shown that the reaction yield and selectivity are sensitive to: temperature, time of the reaction, nature of the metal and its oxidation state and redox potential, lattice energy of the oxide, shape of the oxide (massive or supported), nature of the support, presence of the solvent, and the presence of CO_2. Several metal oxides have been investigated. In this paper, we report the general trend for the tested oxides and discuss in detail the behaviour of PdO_x and V_2O_5, either in the massive form or as supported oxides (on alumina or silica). The oxides have been monitored using UV–vis and XPS and the organic products have been identified and determined by GC–MS.

1. Introduction

Propene oxide finds a wide utilisation in the synthesis of molecular compounds [1] or polymeric [2] materials. Among the latter, the co-polymer with carbon dioxide, i.e., propene-polycarbonate [3] has a great market value for its various applications. The industrial production of PO is based on the use of propene-chlorohydrine [4] or the oxidation of propene with organic peroxides (Halcon-ARCO and Shell processes) [5,6] or else the oxidation of propene with hydrogen peroxide [7]. Gas phase oxidation with air [8] and the co-oxidation of propene and aldehydes using air [9] or else the oxidation with Fe-catalysts using NO as promoter [10] are recent attempts to avoid the use of organic oxidants that produce a large amount of waste, also as solvent for the reaction. Hydrogen peroxide seems to afford interesting results when Ti-silicalite or hydrofobised-Ti substituted molecular sieves (TS-1) catalysts are used: these allow to reach an average selectivity of 97% towards PO with a selectivity of 97 or 90% towards hydrogen peroxide conversion, respectively [11]. The TS-1 supported Pd or Pt catalysts give 99% PO selectivity [7,12], with a propene conversion that does not exceed 3.5%, with a difficult separation of the product from methanol, used as reaction medium. Au catalysts [13–15] also supported on Ti-silicates in presence of hydrogen and oxygen result in PO selectivity greater than 90% at relatively low temperatures and at atmospheric pressure. The propene conversion yield is 3.7%.

The use of H_2O_2, although improves the selectivity and presents the advantages of a gas phase reaction, nevertheless it shows some limitations due to its cost and availability. It is worth noting that the present amount of H_2O_2 on the market would not cover the request for the production of epoxides to be used, as co-monomers with CO_2 for making polycarbonates.

The direct use of dioxygen (air), a most challenging and important reaction in catalysis responding to the green chemistry requirements, is, thus, highly wished. This approach would make it possible to convert propane into PO using the appropriate catalysts in the gas phase. While the conversion of propane into propene can be carried out with an interesting yield and selectivity [16], the following step (epoxidation of propene) has a serious drawback due to the radical reactions that occur between dioxygen and the olefin. In fact, the addition of dioxygen across the double bond takes place that causes its cleavage with the formation of C2 and C1

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moieties. This is a serious limitation to the exploitation of the reaction due to the loss of the olefin (even more than 50%) and waste formation.

Nevertheless, attempts have been made using Ag, a commercial catalyst for the epoxidation of ethene. Unsupported silver sponge [8] or NaCl [17], CuCl [18] or $BaCl_2$ [19] modified Ag affords a PO selectivity not higher than 33.4% at a propene conversion of 18.6%. The epoxidation over iron oxide as catalyst supported on silica with nitrous oxide as promoter gave a selectivity of 40–60% with 6–12% propene conversion [10].

However, new catalysts are needed that have a selectivity as much close to 100%, also if at a low propene conversion as the latter may be improved through a process design.

Following our previous studies on the oxidative carboxylation of olefins [20–22] and the epoxidation of propene using either neat Al_2O_3 nano-powders or Al_2O_3-supported Ce_2O_3 (0.1–2%) or CeO_2 in absence of solvent [23], we have investigated in detail the process of O-transfer from a metal-oxide to propene using a HTE approach. We have defined the influence of the "*parameter space*" on yield and selectivity and shown that they depend on temperature, time of reaction, nature of the metal and its oxidation state and redox potential, lattice energy of the oxide, shape of the oxide (massive or supported), nature of the support, presence of a solvent and CO_2. Such HT study is the pillar for building a robust relationship between the intrinsic physico-chemical properties of the oxides and the reaction conditions that may bring to identify best candidates for the selective epoxidation of propene. An effective O-transfer agent would easily be used in a two-step process using air to re-oxidise the reduced oxide: the net process would then be the epoxidation of propene with air. Of the various oxides tested, we report the general trend in the O-transfer reaction and discuss here in detail the results obtained using PdO_x or V_2O_5. Both oxides have been used either as massive samples or supported on silica or alumina that show a different influence on yield and selectivity. The results demonstrate the role of the various components of the "*parameter space*" on the reaction.

2. Experimental

2.1. Materials and methods

All solvents were dried as described in the literature [24] and stored under nitrogen. All reactions and manipulations were carried out under a dinitrogen atmosphere. Either batch or flow reactors were used. For all the reaction tests, nano-powders were used (80–130 nm diameter), that were prepared by High Energy Milling-HEM (6 h, three 2 h cycles at 700 rpm) using a "Planetary Micro Mill pulverisette 7″ by Fritsch. Reflectance UV–vis–NIR spectra were obtained using a Varian Inc. Cary 5000 equipment. γ-Al_2O_3 ($S_{BET} = 250\ m^2/g$ obtained from the Taixing Reagent Plant, Tianjin, China) or SiO_2 ($S_{BET} = 300–350\ m^2/g$, Chemical Engineering Institute, Faculty of Chemical Engineering, University of Tianjin, Tianjin, China) were used as support. Both of them were calcined at 873 K for 4 h prior to use.

GC analyses were carried out with a Hewlett Packard HP 6850 (capillary column: 30 m, Zebron ZB-wax polyethyleneglycol, 0.25 μm film) and GC–MS analyses with a Shimadzu GCMS-QP5050 (capillary column: 60 m, MDN-5S, 0.25 μm film).

2.1.1. Reactions carried out in the parallel reactor 4XR

The reactions in batch were run using a in-house built stainless steel high pressure 4X parallel reactor-4XR. Such 4XR allows to carry out four reactions at the same temperature, but at different gas pressures, using different amounts of the same oxide or different oxides, in presence or absence of solvent.

Each microreactor in the 4XR has a volume of 10 mL. The amount of solid and the pressure of the gas were regulated in such a way to obtain the wanted ratio propene/metal-oxide. In the batch-assays the oxide was dispersed on a synthesised glass disk placed in the middle section of each of the four microreactors to assure the best contact with the gas. Alternatively, single batch tests were carried out in a 100 mL autoclave equipped with the same dispersion support of the solid material.

When the solvent (dimethylformamide, DMF) was used, it was placed in the reactor with the solid oxide suspended in it and the mixture was magnetically stirred.

2.1.2. Reactions in a flow reactor

A 25 cm stainless steel tubular reactor (4 mm i.d., 6 mm o.d.) was used for the continuous flow reactions. The solid material (massive or supported oxide) was mixed with glass-microspheres in order to increase the contact surface and to prevent sticking. The gas leaving the reactor was either analysed by GC–MS or passed through a cool trap in order to condense the formed products and recycled (see below). The inlet and outlet of the tubular reactor were connected to a three-way pressure valve that allowed from one side to set the pressure within the reactor and the flow through the reactor and on the other to admit into the reactor either propene or air or dinitrogen. Air was used for the re-oxidation of the oxide (573 K, 1.5 h) after the reaction. Dinitrogen was used to flush the oxide after re-oxidation in order to avoid the presence of residual molecular dioxygen when propene was admitted. In a typical cycle, propene was passed over the oxide containing the metal in high oxidation state, then air was admitted for re-oxidation of the oxide that was finally flushed with dinitrogen and re-used for the epoxidation of propene. Alternatively, two parallel reactors were used, one for the oxidation of propene, the other for re-oxidation of the metal. During the regeneration of the oxide (back to its high oxidation state), the temperature was kept in the range 450–600 K. The unreacted propene was recycled over the catalyst using a High Pressure Gas Pump-HPGP. The contact time of propene with the oxide in the reactor ranged from a minimum of 30 min to a maximum of 2 h. This general procedure was used with all oxides tested. We report in detail the working procedure with Pd and V.

2.1.3. Determination of the oxidation state of PdO_x and V_2O_5 before and after the reaction with propene

X-ray photoelectron spectroscopy-XPS analyses were performed with a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the non-monochromatised Al Kα source (1486.6 eV) operated at 14 kV and 15 mA. The analyser operated in the constant analyser energy (CAE) mode. Survey spectra were measured at 50 eV pass energy. For the individual peak energy regions a pass energy of 20 eV was used. The sample powders were pelletised and then mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10–8 Torr during data collection. The constant charging of the reference samples, like pure PdO or V_2O_5 and pure gold, was corrected by referencing all the energies to the C 1s peak energy set at 285.1 eV, arising from adventitious carbon. Peaks were fitted by a non-linear least square fitting program using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood [26,27]. The relative atomic concentrations were calculated by a standard quantification routine, with the VG instrument provided programme, from fitted peak areas using appropriate sensitivity factors. The binding energy values are quoted with a precision of ±0.15 eV. The uncertainty on the atomic concentration is of the order of <10% (Fig. 1). UV–vis spectroscopy was used to monitor the changes in the V-sample (Fig. 2).

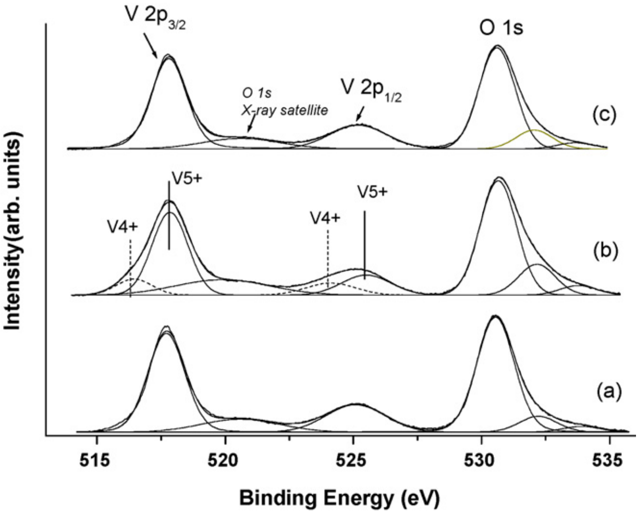


Fig. 1. XPS spectra of V_2O_5 before use (a), after O-transfer (b) and after re-oxidation (c).

2.2. Epoxidation of propene

2.2.1. Use of massive PdO_x

In a typical experiment, PdO_x was placed in each of the microreactors of the 4XR as described above. The microreactors were charged with propene at the pressure of 1 MPa were heated to 473 K for 1 h (or longer, see Table 3) and then heating was switched off. After cooling to room temperature, the gas phase of each microreactor was bubbled through 2 mL of dimethylformamide (DMF) cooled at 250 K. The 4XR was then opened and each microreactor was washed with 2 × 1 mL of DMF. The DMF solutions from the same microreactor were collected and analysed. Each organic product formed was quantitatively determined by comparison with a standard sample.

The reaction was repeated at different temperatures. Per each temperature and pressure two experiments were run: if they did not agree within 10% a third experiment was carried out. The data are summarised in Table 3. Each value reported is affected by an error ranging around 7%.

XPS analyses were recorded on PdO_x before and after the reaction (see Table 2).

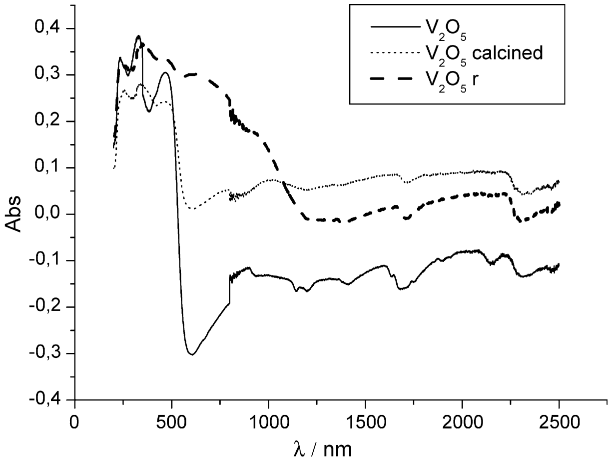


Fig. 2. UV–vis reflectance spectra of the oxide before use (solid), after use (broken) and after calcination of the used sample (dotted).

2.2.2. Preparation of supported Pd(II)O and its use

Pd(II) supported on alumina was prepared by adding alumina (10.0 g) activated as reported in Section 2.1 to a solution of $PdCl_2$ (0.195 g, 1.10 mmol) in water containing an excess of KCl. The original reddish solution turned colourless while alumina become yellowish. After 20 min stirring, the solution was neutralised with KOH 0.1 M. Alumina was filtered, washed with water and calcined for 2 h at 573 K. The Pd-loading was determined by elemental analysis and found to be equal to 0.87% w/w of Pd. XPS analyses were carried out in order to verify the composition of the supported oxide (Table 2). Then this solid was used in a O-transfer reaction (see Table 3).

2.2.3. Use of massive V_2O_5

Commercial V_2O_5 was charged in each of the four microreactors of the 4XR following the procedure described in Section 2.2. The oxide was analysed by XPS and UV–vis before and after the reaction. Either a gas phase (GP in Table 4) reaction was carried out or DMF (LP in Table 4) was used as solvent. Table 4 summarises the results obtained with massive V_2O_5.

2.2.4. Synthesis of supported V_2O_5 and its use

V_2O_5 was also used supported on silica or alumina. The supported oxide was prepared according to one of the procedures reported below.

(a) *V_2O_5 supported on silica or alumina by impregnation*: 4 g of γ-Al_2O_3 (or SiO_2) were contacted for 3 h with 30 mL of 0.1 or 0.05 M ammonium metavanadate (Fangzheng, Tianjin, China) aqueous solution. Then the solid material was filtered, dried overnight at 383 K and calcinated at 673 K in the air for 4 h. The catalysts prepared in this way are labeled V-A (for V_2O_5 supported on γ-Al_2O_3) and V-S (for V_2O_5 supported on silica). The actual content of V was determined by elemental analysis and shown to be 3.0% V for the catalysts obtained via impregnation with the 1M solution and 1.8% for the system obtained from the 0.05 M metavanadate solution. Table 5 summarises the results obtained when the samples were used in the O-transfer reaction.

(b) *V_2O_5 supported on γ-Al_2O_3 or SiO_2 with the use of a "glow discharge plasma"*: These samples are labeled V-A-P and V-S-P for V supported on γ-Al_2O_3 or SiO_2, respectively. The "glow discharge plasma" equipment was previously described in detail in the literature [25]. 0.5 g of the humid sample (V_2O_5 over γ-Al_2O_3 or SiO_2) separated from the metavanadate solution, after drying at 383 K as reported above, was loaded on a quartz boat that was placed in the glow discharge cell. The gas (>99.999% pure Ar) pressure was adjusted at 100 Pa and the glow discharge was generated by applying 900 V to the electrodes by means of a TREK 20/20B High Voltage Amplifier connected to a function/arbitrary waveform generator (Hewlett Packard 33120A) with a 100 MHz square wave. The duration of each treatment was 10 min and each sample was submitted to five consecutive treatments. The V-loading on the support was determined by elemental analysis and resulted to be 2.3% for the sample originated from the 1 M metavanadate solution and 1.2% for the sample isolated from the 0.05 M solution. The results obtained by using these materials are reported in Table 5.

2.3. Freezing the epoxide by converting it into propene carbonate

In a typical run, propene (1 MPa) and CO_2 (3.5 MPa) were charged with the metal-oxide in the reactor and the reaction stopped after 1 h. The formation of cyclic carbonate was revealed by GC–MS.

Table 1
The “parameter space” for the conversion of propene into propene oxide using metal oxides

Influence on the	Parameters	Notes
Conversion of propene	Temperature; reaction time; metal with its oxidation state, redox potential, and lattice energy; number of active centres implied in the O-transfer reaction.	The conversion of propene increases with the temperature and time, with the number of active centers, the oxidation state of the metal and the redox potential. It decreases with increasing the lattice energy.
Selectivity towards PO	Temperature, reaction time	The selectivity decreases with the increase of the temperature and the reaction time.
	Metal	Different metals give different results: the higher is the H-mobilisation ability, the higher is the isomerisation by H-shift.
	Solvent	In DMF the selectivity towards PO is higher than in the gas phase. Nevertheless, the solvent can be converted on the solid support and may give N-nitride, as shown by the XPS analysis.
	Presence of CO_2	The use of carbon dioxide allows to “freeze” the kinetic product (PO) with a consequent decrease of the isomerisation and increase of the selectivity towards PO derivatives (propene carbonate, PC).

3. Results and discussion

3.1. Propene oxidation with transition-metal oxides: the “parameter space”

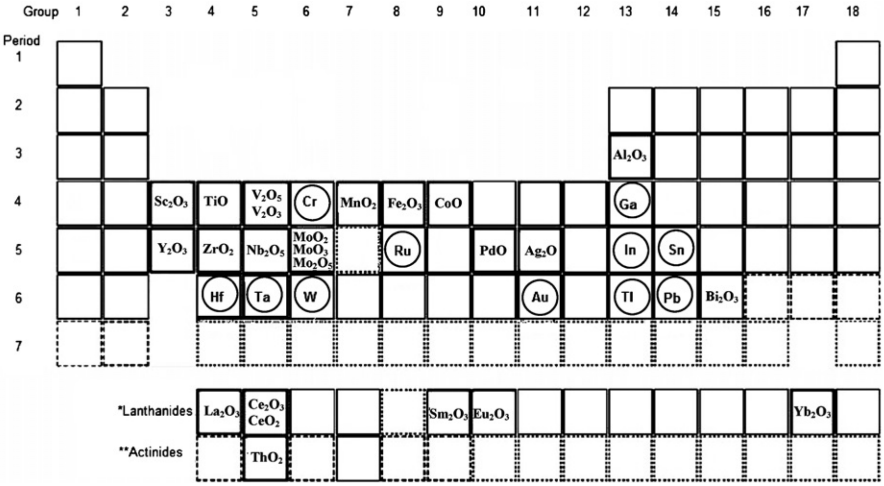
The main advantage of using a metal-oxide as “oxygen-transfer” agent to propene is that the cleavage of the double bond is completely repressed and C2 and C1 moieties are not formed. From propene, the only products formed are PO, AC and PA, all of them being C3 species [23]. The two latter can be considered as isomerisation products of PO. Looking at the formation free energy values for the three compounds ($\Delta G^\circ = -122.6$ for PO, -215.3 for PA and $-248.1\ \mathrm{kJ\,mol^{-1}}$ for AC), one can infer that PO may be the kinetic product of the reaction, while AC is the thermodynamic product, with AP sitting in the middle. Therefore, as PO is isomerised to AC upon heating in presence of a transition-metal compound [23] and the isomerisation reaction is favoured by the ability of the metal to produce a H-shift, by a high temperature and a long reaction time, the selectivity towards PO must be driven by such parameters. If the yield of conversion of the olefin is considered, one can foresee that it depends on the facility of the oxygen transfer from the metal. Even if the overall process is thermodynamically favoured, such transfer may present high kinetic barriers and will require high temperatures. Such kinetic barriers may depend on a number of parameters characteristic of the metal-oxide, such as: the oxidation state of the metal, the redox potential relevant to the involved oxidation states of the metal, the lattice energy and the state of the oxygen (accessibility and co-ordination number) in the lattice, the presence of solvent. Therefore, our first aim was to clearly define the “*parameter space*” that influences the yield and selectivity and we choose the High Throughput Experiment (HTE) approach. The role of the several parameters that drive the reaction was defined and their trend is illustrated in Table 1.

It appears quite clear from Table 1 that the same parameter (e.g., the temperature) may have an opposite influence on the conversion of propene and on the selectivity. The careful definition of the role of each parameter is essential for the optimisation of the yield and selectivity of the process and for defining the best operative conditions.

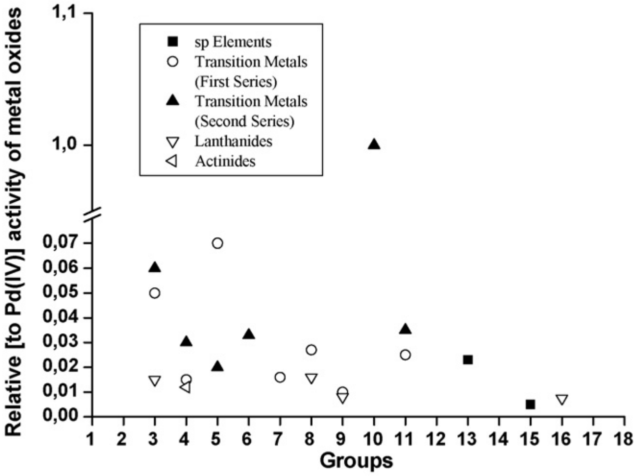
A large number of metal oxides were used in the tests carried out so far (Scheme 1) [28–29].

Scheme 2 shows the trend of the activity of oxides of metals in their highest oxidation state (for Ru only RuO_2 was used) referred to Pd(IV). With the exception of Group 5 elements, the oxides of the elements of the Second Series are more active than those of the first Series. This may be due to the energy of the M–O bond. Such trend has also been encountered in the direct carboxylation of alcohols [31]. In general, the activity of Pd is close to one order of magnitude higher than that of other oxides.

However, it is difficult to foresee the behaviour of each single metal: general conclusions can be drawn for the metals belonging for example to a Series. Moreover, there is not a single property that may be used for comparison of the oxides, but the ensemble of



Scheme 1. Metals whose oxides were tested in this work. The oxides of the circled elements are under test.



Scheme 2. Comparison of the activity of various metal oxides tested according to the position of the metal in the Periodic Table. The oxides in the highest oxidation state of the metal are compared.

properties must be taken into consideration. We are still working on such aspect in order to find out an algorithm that may be useful for the prevision of the behaviour of the oxides. What is clear is that the H-extraction and mobilisation ability of a metal causes a different selectivity towards PO, PA or AC. Also, metals of the second Series are more active than those of the first Series. For what mentioned so far, in our work we have selected oxides of Pd and V (the most active) and investigated in detail their behaviour and the selectivity towards oxidation of propene-to-propene oxide.

3.1.1. *Utilisation of massive PdO_x or supported Pd(II)O*

The XPS spectrum of commercial PdO_x shows that the binding energies of Pd $3d_{5/2}$ are typical of Pd(IV) as in PdO_2 (337.8) and $PdCl_6^{2-}$ (339.2) in agreement with the presence of Cl 2p signals. After the reaction in the gas phase with propene, the signals of Pd(IV) decrease and those of Pd(II) appear as in PdO (336.2) (Table 2).

This strongly indicates that Pd(IV) is the active O-transfer agent. If, after Pd(IV) is consumed, the residual oxide is calcined and re-used, no O-transfer is observed (Entry 5 in Table 3) as Pd(IV) is not formed under our operative conditions (450–600 K). When Pd(II) is supported on Al_2O_3 (0.2% loading, as confirmed by XPS) and the solid is used in DMF as solvent, the metal is released in the solvent (as demonstrated by the fact that the XPS of the used material does not contain any signal attributable to Pd in either of the oxidation states +2 or +4), while a signal due to the presence of a nitride-N is found, most likely derived from the decomposition of DMF at the reaction temperature. Consequently, the amount of carbon and oxygen present on alumina increases. The calcinations of Pd/Al_2O_3 again does not cause any rising of Pd(IV) signals and, thus, the calcined material is not active at all in the oxidation of the olefin.

Data reported in Table 3 show that Pd(IV) is the oxidizing agent: a conversion of propene close to 10% is observed (Entry 1). AC or AP, in dependence of the reaction conditions, may be the major products in the reaction. This is attributable to the ability of Pd of mobilizing hydrogen atoms (most likely by β-H shift) within the organic substrate. Noteworthy, shortening the contact time, the selectivity towards PO increases (compare Entries 1–3 in Table 3), but the conversion yield decreases. As it is shown in Table 3, the temperature plays an important role as with its increase a higher conversion yield is observed which is coupled to a reduction of selectivity towards PO. Similarly, increasing the reaction time at a given temperature, causes an improvement of the conversion but reduces the selectivity. Therefore, the H-mobilisation ability does not make Pd a good candidate for a selective epoxidation, unless a very active species is found that may operate at low temperature.

The use of massive oxides does not allow to estimate the number of active centres nor, consequently, to evaluate a correct value for the molar ratio (*converted propene*)/(*metal-oxide*). In order to be able to determine the exact extent at which the oxide transfers oxygen to the olefin, we have prepared nano-materials formed by PdO_x supported on either Al_2O_3 or SiO_2. In this way the total concentration of the active metal was determined by analytical methods and XPS allowed to quantify the surface content of the active species.

The deposition of Pd on alumina or silica does not improve the performance of the catalyst in terms of its re-usability. Also, the isomerisation to AC and AP is not suppressed. Therefore, PdO_2, for the H-mobilisation properties of Pd, is not the ideal species for the selective oxidation of propene to PO by O-transfer from the oxide.

3.1.2. *Utilisation of V_2O_5*

Commercial V_2O_5 shows a good capacity of propene oxidation, as it is shown in Table 4.

Table 2
XPS Spectrum of PdO_x before and after the reaction

Entry	Sample	Pd $3d_{5/2}$	Al 2p	Cl 2p	O 1s	N 1s	At %Pd
1	PdO_x (commercial)	337.8 (77%)		199.3	530.8		
2	PdO_x (after reaction)	336.2 (75%) 338 (25%)			532.6		
3	Al_2O_3		75.0		531.3		
4	Pd/Al_2O_3	336.6	74.9		531.0		0.2
5	Pd/Al_2O_3 calcined	336.8	75.1		531.0		0.2
6	Pd/Al_2O_3 (after reaction)	–	74.9		531.8	397.0	0.0

Table 3
Oxidation of propene with PdO_x in a solid–gas phase system.

Entry	Oxide	$n_{propene}/n_{oxide}$	*T* (K)	*P* (MPa) propene	*t* (h)	Degree of propene conversion (%)	Selectivity %		
							PO	AC	PA
1	PdO_x	1.7	473	1	1	9.63	1.6	98	0
2	PdO_x	17.8	473	1	2	1.2	1.9	92	6.1
3	PdO_x	12.1	473	1	0.5	0.4	29	38	33
4	PdO_x-re-used	12	473	1	1	0.01	1	98	1
5	PdO_x	12.7	575	1	1	3.5	0	98	2
6	PdO/Al_2O_3 (0.87% Pd)	5.64	473	1	1	0.01	0	33	66

Table 4
Use of commercial V_2O_5 as oxidant of propene (473 K, 1 MPa of propene).

Entry	$n_{propene}/n_{oxide}$	$P(CO_2)$ (MPa)	$P(N_2)$ (MPa)	Solvent (mL)	*t* (h)	Conversion yield (%)		Selectivity %			
						GP[a]	LP[b]	PO	AC	PA	PC
1	5.66	–	–	–	15	0.11		–	100	–	–
2	5.18	3.5	–	DMF(5)	5		0.076	10	–	–	90
3	12.30	–	–	–	5	0.027		100	–	–	–
4	11.12	–	–	–	24	0.35		–	100	–	–
5	11.36	–	3	–	15	0.003		–	100	–	–
6	4.87	–	3.5	DMF(5)	5		0.013	100	–	–	–

[a] GP: reaction in gas phase.
[b] LP: reaction in liquid phase (DMF as solvent).

Table 5
O-Transfer to propene by using supported V_2O_5 and the selectivity towards PO (1 h, 473 K)

Entry	Oxide	mmol of V_2O_5	Molar ratio Propene/V_2O_5	Conversion of propene %	Molar ratio Converted propene/V_2O_5	Molar ratio PO/V_2O_5	Selectivity towards PO%
1	V-A	58	297	0.168	0.87	0.47	54
2	V-A-P	45	251	0.154	0.86	0.58	68
3	V-A-P-R	61	210	0.274	0.95	0.38	40
4	V-S	48	329	0.137	0.93	0.65	70
5	V-S-P	70	497	0.136	0.97	0.68	70
6	V-S-P-R	47	397	0.115	0.96	0.66	69

V-A: V_2O_5 on γ-alumina; V-A-P: sample prepared by plasma treatment (see below); V-A-P-R: V-A-P recovered, regenerated and re-used; V-S: V_2O_5 on silica; V-S-P: sample prepared by plasma treatment; V-S-P-R: V-S-P recovered, regenerated and re-used.

In general, there is a large difference between massive and supported V_2O_5. The latter (Table 5) performs much better than the former (or Pd) and the theoretical limit of 1 mol of propene converted per mol of V_2O_5 is almost reached.

Comparison of data in Tables 4 and 5 with those in Table 3 shows that V_2O_5 is much better than PdO_x also from the point of view of the selectivity: this is most likely due to the lower H-mobilisation ability of V with respect to Pd.

We have observed that, as Fig. 1 shows, the XPS of the starting material contains only V(V) signals (Fig. 1a). After the reaction the signals of V(IV) appear (Fig. 1b), that disappear after regeneration of the oxide via calcination (Fig. 1c).

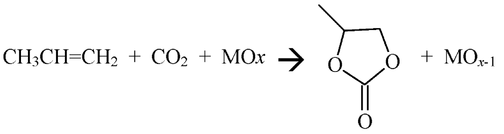
Similarly, the UV-reflectance spectrum of vanadium oxide run on the sample before and at the end of the reaction (Fig. 2 - solid and broken line, respectively) shows the reduction of V(V) to V(IV) (appearance of the band at 630 nm [30]). Moreover, when the used oxide is calcinated at 750 K, V(IV) is re-converted into V(V) (Fig. 2 - dotted line).

As said before, the molar ratio PO/V cannot be easily evaluated when massive samples of vanadium(V)oxide are used as counting the active sites is impossible: more likely only the most external V-centres will act as oxidant. Consequently, the apparent conversion yield will be quite low (Tables 3 and 4). Therefore, we have used V(V) supported (on silica or alumina) for better exploring the possibility of "measuring" the O-transfer per atom of V by "counting" the number of molecules of propene oxidised per atom of vanadium. As a matter of facts, 93–98% of the loaded V stays on the surface of the support also for the fact that nano-particles are used, as demonstrated by XPS. Table 5 shows the molar ratio of PO to V(V) for the supported materials. This makes possible to estimate the real percent of V(V) reduced to V(IV). This fact is important as higher is the number of active sites, lower will be the amount of metal-oxide used for the practical oxidation of propene.

The data in Table 5 (Entries 1–3 vs. 4–6) show that V/alumina is in general less active than V/silica. This demonstrates that the acidity/basicity of the support may influence the yield of the reaction. Vanadium gives a better selectivity towards PO than Pd, most probably for the lower H-mobilisation ability. In our previous work [23] we have shown that Al can give 100% selectivity in PO, also if at a very low conversion yield. In the present case, V(V) is the oxidizing species and Al(III) does not play a role in the O-transfer reaction. These and other results in our hands [29] seem to support that the nature of the metal drives the selectivity.

Assuming that the metal-oxide interacts with the olefin giving an intermediate that may originate either of the products PO, AC, PA (Fig. 3) we have also investigated the use of CO_2 as a "freezing agent" of the adduct between the oxide and the olefin for avoiding the isomerisation to AC and PA.

Fig. 4 shows the influence of time, temperature and presence of CO_2 on the conversion yield and the selectivity towards PO and its H-shift products, namely AC and PA. Under pressure of CO_2 the epoxide was converted into the cyclic carbonate (Eq. (1)) (see data A Fig. 4) that did not show any further reaction with the metal-oxide. Consequently, the formation of AC and PA was prevented. In principle, CO_2 can either interact with the oxide to afford the carbonate anion that then interacts with the olefin bonded to the oxide, or CO_2 can insert into the C–O bond formed by the olefin that is bonded to the oxide [23]. Which one is the operating mechanism is still under investigation.



(1)

As Fig. 4 shows increasing the time (20 h) and temperature (573 K) in absence of CO_2 causes the preferential formation of AC

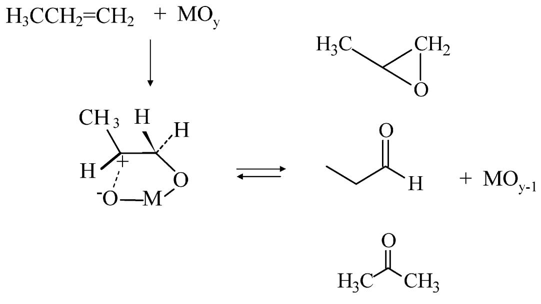


Fig. 3. Interaction of the metal-oxide with the olefin and formation of PO, AC, PA.

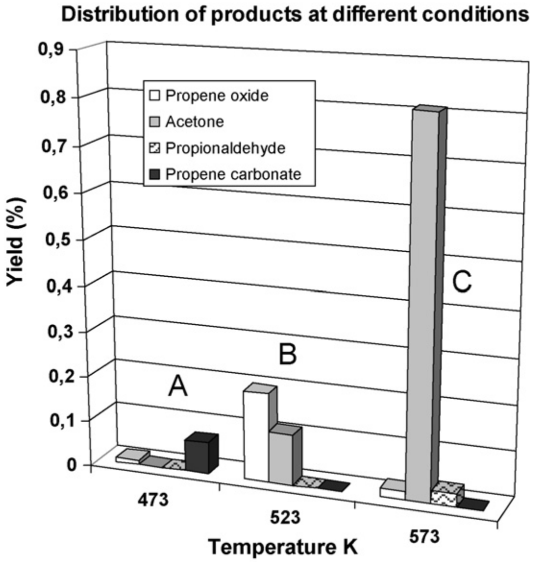


Fig. 4. Influence on the yield and selectivity of some drivers of the O-transfer reaction (V_2O_5 is used as O-transfer). (A) Reaction under CO_2 in DMF (5 h); (B) reaction with only propene in absence of CO_2 (5 h); (C) reaction with only propene in absence of CO_2 (20 h).

(data C). At intermediate conditions (data B) it is possible to increase the selectivity towards PO, but at a lower conversion yield.

When V/silica is considered (Table 5), the conversion of propene is in the range 0.9–1.0 mol propene per V_2O_5 (1 represents the theoretical limit). Also, the recovered catalyst can be re-oxidised and re-used. Table 5 also shows that recycled catalysts are as active as the parent compounds that is not the case with Pd. This is important for the exploitation of the technology.

Supported catalysts are, thus, much more active than massive oxides and can be easily recovered, regenerated and re-used. This allows saving metals lowering the cost of the process. Among the tested metals, nevertheless, V is not yet the most active [29].

V-S-P shows an average selectivity close to 70% with a molar ratio propene oxide/V_2O_5 close to 1 (0.93–0.96). Such results are quite interesting also because the supported oxide can be easily regenerated and re-used (using a two-reactors technology) maintaining the original activity and selectivity (Entries 4–6, Table 5). The temperature at which the re-oxidation of the catalyst occurs is another key parameter in this technology as the regeneration should be carried out in such conditions that there is no modification of the structural features of the oxide. Reducing the temperature of regeneration is, thus, an important issue for maintaining for long time the activity of the oxide.

Interestingly, the samples obtained by plasma treatment show in general a higher activity than those obtained by impregnation (Table 5). This may be linked to structural features of the supported oxide, an issue that is still under investigation in our laboratory.

Another interesting feature of this work is that controlling the temperature makes possible the propene oxidation instead of allylic-hydrogen extraction that would afford products like acroleine ($CH_2{=}CH{-}CHO$) a reaction that is typical of V_2O_5 and other metal oxides at higher temperatures [32]. Acroleine was never observed in our work most probably also for the absence of free oxygen. It is also worth to note that the reduced form of V_2O_5 (i.e., V_2O_4) is not able to oxidise propene under our reaction conditions, but can be easily re-oxidised with air to V_2O_5 and re-used so that the net reaction is the oxidation of propene with air.

4. Conclusions

The utilisation of transition-metal oxides as oxygen-transfer agents results to be a quite convenient method for the conversion of propene into PO. The epoxidation reaction, which ultimately uses air as oxidant of the olefin, carried out using transition-metal oxides allows to avoid radical reactions and eliminates the olefinic double bond splitting that occurs when free oxygen is used as direct oxidant of the olefin. Therefore, the loss of olefin and the production of waste is cut at the source. The O-transfer reaction is driven by several parameters that must be optimised in order to get high yield and selectivity. Massive metal oxides are less active and less selective than supported oxides. The latter may reach the stoichiometric value of the molar ratio oxidised metal/olefin per propene oxide. The selectivity towards the epoxide can be as high as 70% with the oxides used in the present work: nevertheless, it is strongly dependent on the metal: Pd mobilises the hydrogens of the formed intermediate and causes the isomerisation of propene-oxide into acetone or propionaldehyde at a much higher extent than vanadium. The efficiency and selectivity of the supported catalysts depends on the support: silica is a better support than alumina. In both cases the materials can be easily recovered and, in the case of V_2O_5, re-used, after regeneration.

The plasma treatment of the supported oxides seems to increase their efficiency and the oxygen-transfer occurs under milder conditions. Such aspect is still under investigation in our laboratory.

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