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Synthesis of cyclic carbonates from epoxides: Use of reticular oxygen of Al_2O_3 or Al_2O_3-supported CeO_x for the selective epoxidation of propene

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Abstract

Reticular oxygen of Al_2O_3 or CeO_x supported on Al_2O_3 was used for the epoxidation of propene without any double bond cleavage. In batch reaction, Al_2O_3 alone was able to convert propene into propene oxide (PO) with 100% selectivity and 2% conversion of propene with a close to 3:1 ratio with respect to the number of Al(III) reduced to elemental Al. When Ce_2O_3/Al_2O_3 or CeO_2/Al_2O_3 was used, Al remained in its +3 oxidation state, while the Ce oxide was the oxidant as demonstrated by XPS analyses. CeO_x/Al_2O_3 was more active (propene conversion yield of 4–5%) but the selectivity was lower (70%) as PO was isomerized into acetone and propionaldehyde.

Interestingly the use of reticular oxygen very much improves the selectivity with respect to the use of pure O_2. In fact, while propene was more efficiently oxidized (10%) with O_2 in presence of Al_2O_3 or CeO_x/Al_2O_3, the selectivity was as low as 40% because C1 and C2 products were formed. However, the use of reticular oxygen represents a selective two-step technique for the use of molecular oxygen as oxidant of propene. The used oxides can be re-oxidized and the whole process can be further improved towards higher yields.

PO is quantitatively converted into propene carbonate by reaction with CO_2 in presence of Nb_2O_5.

Keywords: Epoxidation of olefins; Propene oxide; Reticular oxygen; Oxides as oxygen source; Selectivity

1. Introduction

The epoxidation of propene is a process of high industrial interest as propene oxide finds a wide utilization in the synthesis of molecular compounds [1] or polymeric [2] materials. In particular, the co-polymerization of PO with carbon dioxide forms propene-poly-carbonate [3]. Current and envisaged industrial production of PO is based on routes (i–vi) categorized below.

(i) Use of propene-chloridrine [4]; (ii) oxidation of propene with organic peroxides (Halcon-ARCO and Shell processes) [5]; (iii) oxidation of propene with hydrogen peroxide [6]; (iv) gas phase oxidation with air [7]; (v) co-oxidation of propene and aldehydes using air [8]; (vi) oxidation with Fe-catalysts using NO as promoter [9].

A drawback in processes (i) and (ii) is the formation of a stoichiometric amount of waste salts, while processes (iii)–(vi) still need improvements. The great research effort done so far has produced some interesting positive results. The method that uses diluted hydrogen peroxide gives a good selectivity with an interesting peroxide conversion. In fact, the Ti-silicalite (TS-1) and hydrophobized Ti substituted molecular sieve catalysts afford 97% PO selectivity with 97 and 90% hydrogen peroxide conversion, respectively [10]. The TS-1 supported Pd or Pt catalysts in presence of hydrogen and oxygen give 99% PO selectivity [11], with a propene conversion that does not exceed

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3.5% and with a difficult separation of the product from methanol, used as reaction medium. Other attempts have been made using Au as catalyst [12–14]. The vapor-phase propene epoxidation over Au-supported on Ti-silicates results in PO selectivity greater than 90% at relatively low temperatures and at atmospheric pressure. The propene conversion yield is 3.7%.

In order to reduce the waste production and implement the atom efficiency principle, the direct propene epoxidation with molecular oxygen or air has also been investigated. The direct oxidation with air is one of the most important and challenging reactions in catalysis, responding to the green chemistry requirements. After the direct ethylene epoxidation on silver catalysts was successfully commercialized, Ag received much attention and has also been used in the propene epoxidation. Various attempts have been made using unsupported silver sponge [7] or NaCl [15], CuCl [16] and $BaCl_2$ [17] modified Ag. In all cases, the PO selectivity was 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 [9].

However, the epoxidation of propene with hydrogen peroxide actually seems to be the most convenient process, considering both the conversion yield and selectivity. Nevertheless, there is a barrier to a large exploitation of such technology, represented by the capacity of production of hydrogen peroxide, that cannot supply the amount required for the desirable volume of PO. The direct epoxidation of propene with air would be highly desirable. New catalysts are needed that have a selectivity as close to 100% as possible, even if at a low propene conversion, since it would be possible to develop a process technology for increasing the propene conversion and, thus, the epoxide yield.

Following our previous studies on the oxidative carboxylation of olefins [18], and the carboxylation of epoxides [19,20] we have investigated the epoxidation of olefins. We report here the results of our studies on the gas phase epoxidation of propene using as catalyst either neat Al_2O_3 nano-powders, or Al_2O_3-supported Ce_2O_3 (0.1–2%), or CeO_2. Ce was selected for its electronic properties and for the catalytic activity of dispersed nano-powders shown in the conversion of CO to CO_2 [21]. In all cases reticular oxygen was used in the conversion of propene to PO. The catalytic activity of the nano-powdered alloys was studied both in batch and in a continuously fed fixed-bed reactor.

2. Experimental

2.1. Materials and methods

All solvents were dried as described in the literature [22] and stored under nitrogen. All reactions and manipulations were carried under dinitrogen atmosphere. A stainless-steel autoclave (0.1 L) was used for the batch experiments. 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).

In the batch-assays the catalyst was dispersed on sintered glass suspended in the middle section of the autoclave in a glass container. In the flow-assays, the catalyst was dispersed on sintered glass or silica in a stainless-steel reactor connected to a peristaltic pump (see Section 2.3).

For the catalytic tests Al_2O_3, Ce_2O_3/Al_2O_3 or CeO_2/Al or Al_2O_3 nano-powders were used. Al nano-powders (20–70 nm) were obtained by explosion in inert gas [21]. The Ce/Al nano-powders containing 0.1% atomic Ce was obtained using the same technique [21]. The 2% CeO_2/Al_2O_3 mixed-oxide was prepared by High Energy Milling (HEM) nano-powdered Al and CeO_2 (6 h, three 2 h cycles at 700 rpm) and subsequent oxidation. HEM apparatus was a "Planetary Micro Mill pulverisette 7" by Fritsch.

2.2. Catalytic runs using Al_2O_3 or Ce_2O_3/Al as catalysts in batch experiments

Both Al_2O_3 or Ce_2O_3/Al_2O_3 were used as catalysts using two different reaction strategies:

(i) Use of O_2 as oxidant;
(ii) Absence of O_2 and use of reticular oxygen from metal oxides for propene oxidation.

In the first case (technique i), the catalyst was charged in a stainless-steel autoclave (V = 0.1 L) with dioxygen and propene (propene/oxygen molar ratio = 2; total pressure 1.2 MPa; propene/catalyst molar ratio varying in the range 18–22) and the system heated at 473 K. After the reaction time was elapsed, DMF (1 mL) was used to extract the product(s) formed from the catalyst and the glass container. The DMF solution was analyzed, using toluene as internal standard, by GC and GC–MS and the products identified and quantified.

Alternatively, (technique ii) oxidized Al or CeO_x/Al_2O_3 nano-powders were used in batch experiments. The Al or CeO_x/Al catalysts were treated with air in a oven at 730 K for 3.5 h. The oxidized catalyst was then cooled to room temperature and pumped in vacuum for 3.5 h in order to eliminate adsorbed humidity and dioxygen. The catalytic run and the isolation of the products were carried out as reported above. The degree of oxidation of the metal surface was determined by XPS before and after the catalytic run. In this way it was possible to estimate the amount of Al_2O_3 reduced to Al that was related to oxidized propene. A ratio propene/oxidized metal centres in the range = 1.27–1.39 was used in each run.

2.3. Catalytic runs in a flow reactor

Flow-experiments were carried out at atmospheric pressure in a 250 mm long tubular stainless-steel reactor with an inner diameter of 4 mm. The catalyst was mixed with silica in order to increase the contact surface and to prevent sticking. The gas leaving the reactor was passed through a cool trap in order to condense the formed products. The inlet and outlet of the reactor system were connected to a two-way valve that allowed feed of air, or nitrogen or propene. Air was used for the oxidation of the Al catalyst (573 K, 1.5 h). Higher temperatures were used for CeO_x. Then the catalyst was de-oxygenated and dried in vacuo at the same temperature for 1 h and purged with dinitrogen at room temperature before feeding propene at 473 K. The unreacted propene was recycled over the catalyst using a Gilson Minipuls-2 peristaltic pump. The residence time of propene in the reactor ranged from 45 min to 1 h.

2.4. Synthesis of cyclic carbonates

The DMF solution containing PO was added with Nb_2O_5 (15 mg, 0.056 mmol) and the system heated in an autoclave under 1 MPa of CO_2. After 3 h the gas chromatographic analysis showed that all PO was converted into propene carbonate identified by means of its ^1H, ^{13}C and MS spectra.

2.5. Determination of the oxidation state of the active metals before and after reaction with propene

X-ray photoelectron spectroscopy analyses were performed with a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. Non-monochromatised Al Kα source (1486.6 eV) operated at 14 keV and 15 mA was used for excitation. 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 ceria 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-squares program using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood [23,24]. 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 $<10\%$.

3. Results and discussion

3.1. Propene oxidation: catalytic experiments

The propene oxidation has been studied following two different techniques:

(1) Using Al supported Ce-atoms or neat Al and charging the autoclave with a propene/dioxygen mixture (molar ratio propene/O_2 = 2);
(2) Using the pre-oxidized Al or Ce/Al supported catalyst and charging the autoclave with only propene.

The two techniques gave quite different results. Using dioxygen as oxidant under these conditions a conversion of propene of the order of 5–10% was observed, with a selectivity of ca. 40% with Al (entry 1, Table 1) and ca. 30% with Ce/Al (entry 2, Table 1).

A variety of compounds were identified in the reaction mixture, either C3 moieties (PO, propionaldehyde, acetone) or C2 (methylformate, acetaldehyde, acetic acid) or C1 (formic acid). Propionaldehyde and acetone are PO isomerization products. In fact, they have been observed when pure PO was heated over either catalyst for a time comparable with the reaction time of the oxidation reaction. Their presence increases with time and their abundance depends on the reaction conditions. Conversely, C2 and C1 species are derived from the cleavage of the propene C═C double bond, most probably initiated by addition of dioxygen to C═C. Such behavior is reminiscent of radical processes, that may also be started by the metal-catalysts. We have investigated the direct oxidation of propene with dioxygen in absence of a catalyst under the same operative conditions and found the same product distribution, even if with a much lower conversion yield.

Therefore, it seems that the radical process plays a major role in the oxidation of propene with air. In order to avoid the parasite reaction represented by the double bond cleavage that consumes propene, the two-step process (ii) was developed based on: (a) pre-oxidation of the metal; (b) contact of propene with the oxidized metal. The Al or CeO_x/Al nano-powders were

Table 1
Conversion yield and selectivity in the oxidation of propene using: (i) dioxygen with Al_2O_3, CeO_2–Al_2O_3 as catalysts; (ii) Al_2O_3, Ce_2O_3/Al, CeO_2/Al_2O_3, CeO_2 as oxidant

Entry	Catalyst (reaction time/h)	Propene (mmol)	Oxidant (mmol)	Molar ratio (propene/oxidant)	Propene conversion yield (%)	Selectivity towards propene oxide	Other products
1	Al (1)^B	32	O_2 (16)	2	5–6	40	HCOOH, $HCOOCH_3$, CH_3COOH, CH_3CHO, CH_3CH_2CHO, CH_3COCH_3
2	Ce/Al (1)^B	32	O_2 (16)	2	8–10	30	As above
3	Al_2O_3 (2)^B	32	Al_2O_3 (3)	10.7	2	100	None
4	Ce_2O_3/Al (2)^B	36	Ce_2O_3 (3)	12	4	70	CH_3CH_2CHO, CH_3COCH_3
5	Ce_2O_3/Al (4)^F	100	Ce_2O_3 (3)	33	1.5	98	CH_3CH_2CHO, CH_3COCH_3
6	Al_2O_3 (5)^F	100	Al_2O_3 (3)	33	1.5	99.5	CH_3CH_2CHO, CH_3COCH_3
7	CeO_2/Al_2O_3 (2)^B	33	CeO_2 (3)	11	5	60–70	CH_3CH_2CHO, CH_3COCH_3
8	CeO_2 (2)^B	33	CeO_2 (3)	11	7	<40	CH_3CH_2CHO, CH_3COCH_3

B: batch reactor, $P_{propene}$: 0.8 MPa, temperature: 470 and 430 K; F: flow reactor, $P_{propene}$: 0.1 MPa.

oxidized with air as reported in Section 2.2. The oxidized catalysts were heated with only propene at 473 K for a time of 1–3 h and propene oxide was formed. Obviously, the yield of the oxidation was lower than in experiment (i), depending on the number of oxidized Al- or Ce-centers present in the catalyst, their availability to interact with propene and the total mass of catalyst used, but the selectivity was much improved. A first interesting finding was that C2 and C1 molecules were not present among reaction products, confirming that the oxidized catalyst behaves as a one-oxygen transfer catalyst, while radical reactions that cause the cleavage of the double bond as in case I are excluded. The selectivity towards PO ranges from 70 to 100% depending on the reaction conditions and the metal used, the only other observed products being propionaldehyde and acetone which are isomerization products of PO (see above). A short reaction time may prevent their formation: 100% propene oxide is obtained using Al_2O_3 under controlled conditions (2–3 h of reaction at 473 K) in the two-step process with a 7% yield or 2% conversion of propene with respect to the total number of oxidized Al atoms (Table 1, entry 3). Under the same conditions, oxidized Ce/Al (mainly Ce_2O_3/Al_2O_3, Table 1, entry 4) afforded a 14.31% yield or 4% conversion of propene with a lower selectivity (70%). Interestingly, CeO_2/Al_2O_3 affords similar results as Ce_2O_3/Al_2O_3 (Table 1, entry 7). CeO_2 alone is able to oxidize propene but the main products are acetone and propionaldehyde, (Table 1, entry 8). Still, the total absence of C2 species makes this synthetic strategy much more interesting than the use of the mixture of propene and dioxygen. In order to better control the contact of PO with the catalyst and reduce the isomerization of the epoxide, we have used a flow reactor. The yield of the reaction was depleted with respect to the batch technique because of the shorter contact time per step, but the selectivity was again very close to 100%. A maximum propene conversion yield of 1.5% (entries 5–6, Table 1) was observed by running the oxidation reaction for 3 h.

3.2. XPS spectra of Al_2O_3 samples used for propene oxidation

In Table 2 the XPS data of the samples of Al_2O_3 after different treatments are given. In Fig. 1 the Al 2p spectra of the samples are shown.

The experimental spectra were fitted with two component curves one at 71.8 ± 0.2 eV attributed to Al^0 and the other at 74.7 ± 0.1 attributed to Al^{3+} [25]. The O 1s binding energy and quantitative analyses show that ionic aluminum is present as Al_2O_3. In order to determine the relative in depth distribution of the aluminum species, the XPs analyses were also performed at a take off angle $\theta = 45^\circ$, which is more surface sensitive. A 10% increase of the metal aluminum component is observed with the uncalcined sample with respect to the calcined and used samples. Such results would suggest the presence of an external layer of aluminum (0) over aluminum oxide in the untreated sample. Upon calcination the elemental aluminum is oxidized forming an outer layer of Al_2O_3.

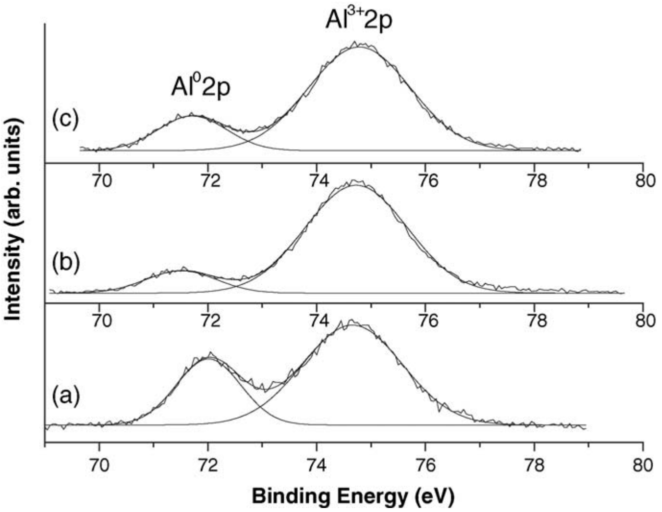

Fig. 1. Al 2p XPS spectra for the (a) untreated; (b) calcined; (c) sample Al_2O_3 after use as oxidant.

After reaction with propene, the surface layer of oxide is partly reduced confirming that reticular oxygen is used as oxidant towards propene. The amount of PO formed was compared with the amount of surface Al_2O_3 reduced, considering the surface area of the powder and the percent of reduced Al_2O_3 on the surface. It comes out that the number of mol of PO isolated is 2.9 times the number of Al(III) reduced to Al during the reaction with propene. Accordingly, the reaction takes place essentially on the surface of the catalysts, causing a reticular oxygen abstraction and transfer to the olefin. The reaction is very selective when run over less than 3 h. Increasing the reaction time, increases the percent of isomerization of PO to acetone or propionaldehyde, the only two other products found in the reaction medium. These figures suggest that the two-step process based on air oxidation of the metal and use of the oxide in olefin epoxidation is much more selective than the direct oxidation of the olefin, as the radical reaction is cut-off.

In order to check whether better oxidants than Al_2O_3 may improve the reaction yield and rate, we have investigated the

Table 2
Al 2p, O 1s binding energies (eV), atomic percentage of aluminum and atomic ratio O/Al for the different samples Al/Al_2O_3

Sample	Al 2p	O 1s	At.% Al	O/Al
A (untreated)	74.7 (2.2) 71%, 72.0 (1.4) 29%	531.3 (2.8)	42	1.3
B (calcined at 723 K)	74.7 (2.2) 90%, 71.7 (1.4) 10%	531.2 (2.7)	40	1.5
C (sample B after use in propene oxidation to PO)	74.8 (2.1) 82%, 71.7 (1.5) 18%	531.4 (2.8)	42	1.4

The Full Width Half Maximum (FWHM) are given in parentheses. The percentage of each aluminum species is also reported.

Table 3
Al 2p, O 1s and Ce $3d_{5/2}$ binding energies (eV) and atomic percentage for the different Al/Ce samples

Sample	Al 2p	O 1s	Ce $3d_{5/2}$	At.% Al	At.% Ce	At.%O
Al/Ce (untreated)	74.7 (2.5) 84% Al^{3+}, 71.9 (1.5) 16% Al^0	532.3 (3.0)	880.3 (3.8) (V_0), 884.3 (3.8) (V′)	42.8	0.2	57.0
Calcined at 723 K	75.2 (2.8) 100% Al^{3+}	531.9 (3.1)	–	44.3	0.1	55.6
Calcined and then tested	74.9 (2.7) 100%	531.6 (3.1)	–	41.5	0.1	58.3

The Full Width Half Maximum (FWHM) is given in parentheses. The percentages of each aluminum component is also reported.

behavior of CeO_2 and CeO_x/Al_2O_3. The former is a commercial product, the latter material has been obtained as described in Section 2.

3.3. XPS spectra of Al/Ce (0.1%) samples used for propene oxidation

In Table 3 the binding energies of Al 2p, O 1s and Ce 3d are listed along with the XPS derived atomic percentage.

According to the Al 2p binding energy, the Al/Ce nanopowder sample obtained by explosion in inert gas, before any treatment contains aluminum in the form of Al^0 characterized by the energy 71.9 (±0.3) and Al^{3+} at 74.7 eV. After calcination at 723 K the metallic component disappears as shown in Fig. 2b.

The Ce 3d spectrum of the untreated sample is typical of Ce^{3+} [26]. As shown in Fig. 3 the experimental curve of the Ce 3d spectrum was fitted with several components arising from the multiplicity of final states reached during the Ce 3d photoionization process of a Ce^{3+} species [26,28].

The labeling of the peaks follows the convention adopted by Burrough et al. [27]. Letters U and V refer to the $3d_{5/2}$ and $3d_{3/2}$ spin–orbit components, respectively.

After the use as oxidant, the Ce_2O_3 surface concentration decreased to a such low level that it was not possible to apply any fitting procedure. Interestingly, no signal due to Al(0) was detected. The fact that Al^{3+} was not reduced to Al(0), while propene was oxidized to propene oxide infers that Ce_2O_3 instead of Al_2O_3 is the oxidant. In order to confirm such finding, we have prepared new samples of Ce/Al by reacting by High Energy Milling Al and CeO_2 samples, at 2% (w/w) of CeO_2 in Al nano-powders.

3.4. XPS spectra of CeO_2/Al at 2% (w/w) CeO_2

The results of the XPS analyses of the oxide mixtures prepared by mixing Al with 2% (w/w) CeO_2 are given in Table 4.

For comparison, the data relevant to a sample of pure CeO_2 used under the same conditions are also reported. Table 4 shows that the metallic component of aluminum disappears after calcinations of the oxide mixtures and does not re-appear after use of the catalyst as oxidant towards propene. Ce is present in the starting material as Ce(III), characterized by the component V_0 at 880.7 eV (±0.2), and Ce(IV) characterized by the component V at 882.7 eV (±0.7). In Fig. 4 the Ce 3d spectra of the Al/Ce mixture after different treatments are shown: the experimental patterns have been fitted with several curves due to the peaks corresponding to several pairs of spin–orbit doublets. As compared to the spectrum of Fig. 3, containing only Ce(III) species components (V_0, V′ and U_0, U′), the spectra of Fig. 4 contains also components arising from Ce(IV) (V, V″, V‴ and corresponding U, U″, U‴).

After calcination the Ce(IV) species increases with respect to the Ce(III). Thereafter, after the catalyst has been used in

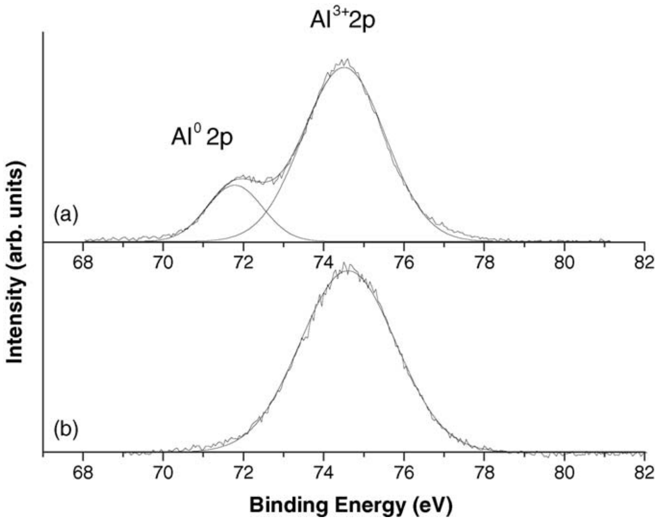

Fig. 2. Al 2p XPS spectra of the (a) untreated and calcined (b) Al/Ce (0.1%) sample.

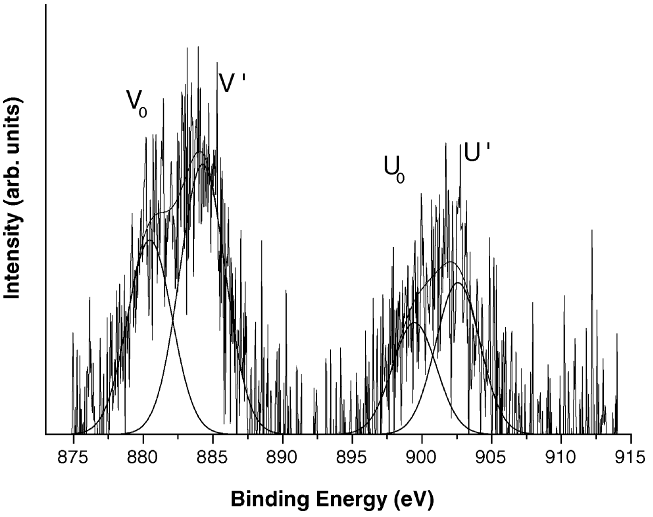

Fig. 3. Ce 3d of untreated Al/Ce (0.1%) sample. The fitted V_0 and V′components of the Ce $3d_{5/2}$ and the U_0 and U′ components of Ce $3d_{3/2}$ in Ce(III) are shown.

Table 4
Al 2p, O 1s and Ce $3d_{5/2}$ binding energies (eV) and atomic percentage for the different Al/Ce samples obtained by HEM Al and 2% (w/w) of CeO_2

Sample	Al 2p	O 1s	Ce 3d $_{5/2}$ (V_0), (V)	At.% Al	At.% Ce	At.% O
(a) Untreated	75.0 (2.4) 75% Al^{3+}, 72.0 (1.3) 14% Al^0	531.8 (3.1)	880.9 (2.5) 55% Ce^{3+}, 882.9 (2.5) 45% Ce^{4+}	39	0.4	60.6
(b) Calcined at 500 K and then 723 K	75.3 (2.3) 96% Al^{3+}, 72.1 (1.6) 4% Al^0	531.8 (3.0)	880.6 (3.1) 42% Ce^{3+}, 882.2 (3.1) 58% Ce^{4+}	38.3	0.4	61.3
(c) Sample (b) used in propene oxidation	75.1 (2.3) 97.5% Al^{3+}, 72.0 (1.3) 2.5% Al^0	531.6 (2.9)	880.8 (2.8) 57% Ce^{3+}, 883.0 (2.8) 43% Ce^{4+}	36.6	0.4	63
(d) CeO_2 untreated		529.2 (2.2) 84%, 531.8 (2.2) 16%	881.5 (3.1) 94% Ce^{3+}, 884.3 (2.3) 6% Ce^{4+}		32.8	67.1
(e) CeO_2 oxidation		529.2 (2.4) 81%, 531.9 (2.4) 19%	881.7 (3.4) 96% Ce^{3+}, 884.7 (2.3) 4% Ce^{4+}		32.7	67.3
(g) Sample (e) after use in the oxidation of propene		528.9 (2.3) 83%, 531.5 (2.3) 17%	881.5 (3.3) 94% Ce^{3+}, 884.3 (2.3) 6% Ce^{4+}		33.8	66.2

The Full Widths at Half Maximum (FWHM) are given in parentheses. The percent of each aluminum, oxygen and cerium component is also reported.

propene oxidation, the Ce(IV) concentration decreases again. Under these conditions Al_2O_3 is not acting as oxidant of propene. CeO_2 is the oxidant with a 5% conversion yield of propene (entry 7, Table 1) and a selectivity higher than 50%: acetone and propionaldehyde are again the co-products.

We have also used CeO_2 alone as oxidant, and the results are presented below. In Fig. 5 the Ce 3d spectrum of a pure CeO_2 sample is shown.

The spectrum is typical of Ce(IV) with a small component of Ce(III) characterized by V_0 and V′. It is worth noting that under X-ray exposure a certain reduction of Ce(IV) occurs [28]. In agreement with the literature, a modification of the Ce 3d spectrum was observed after 30 min of X-ray exposure. Therefore, the spectra were collected right after turning on the X-ray source to avoid any X-ray induced artifact. When CeO_2 alone was used, propene was oxidized, but essentially acetone and propionaldehyde were formed (90%), while PO represented only 10% of the oxidized products. Therefore, Ce is a better isomerization catalyst than Al, but still only C3 units are found as products, without C=C double bond cleavage.

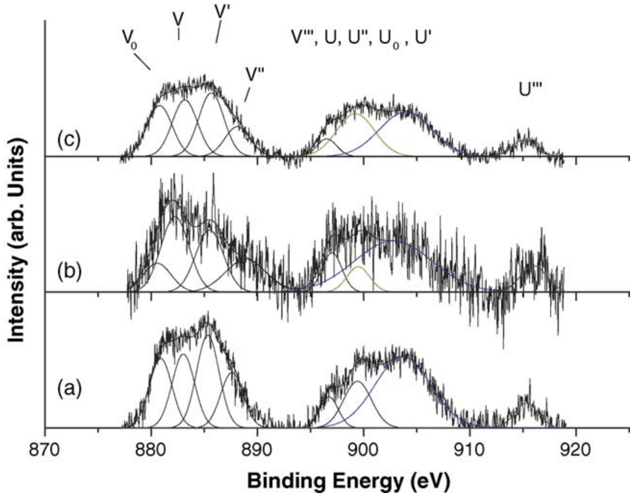

Fig. 4. Ce 3d Photoelectron spectra of 2% (w/w) CeO_2 mixed with Al (a) as prepared; (b) after calcination at 500 K and then 723 K; (c) after use in the catalytic test of propene oxidation to PO.

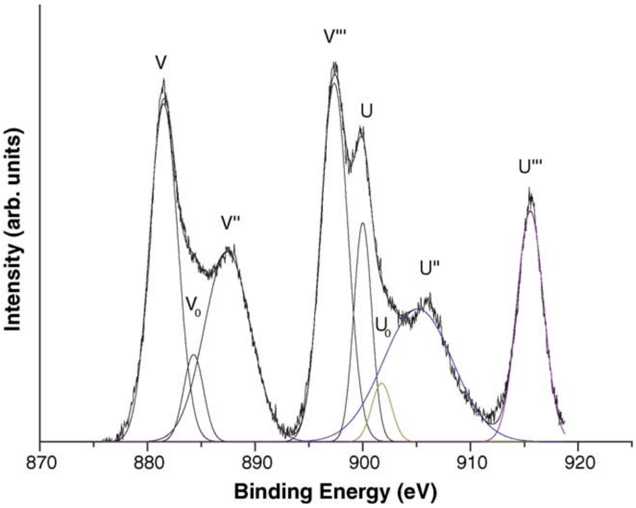

Fig. 5. Ce 3d XPS spectrum of the pure untreated CeO_2 powder.

3.5. Use of PO in the synthesis of propene carbonate

The propene oxide extracted with DMF is easily and quantitatively converted into the relevant carbonate by direct exposure of the DMF solution to CO_2 under the conditions we have already reported [18–20] using Nb_2O_5 as catalyst. The conversion is very selective (100%). Therefore, the oxidation of propene with Al_2O_3 or Ce_2O_3/Al and the subsequent carboxylation of PO with Nb_2O_5 represent a methodology for the selective (close to 100%) conversion of propene into propene carbonate even if the overall yield is low at the moment with respect to propene.

4. Conclusion

We have shown that Al or CeO_x–Al nano-powders are good catalysts for the epoxidation of propene at 473 K using O_2 as oxidant. A radical reaction is implied in the epoxidation with the formation of C3, C2 and C1 species. The selectivity in PO is equal to 30 (Ce) or 40% (Al). Conversely, if the Al or CeO_x–Al catalyst is first reacted with O_2 at 750 K and the oxidized form of the catalyst is allowed to react with propene in absence of O_2, PO is formed with a selectivity ranging from 70 to 100%, depending on the reaction time and the catalyst used. C2 and C1 species are not formed at all and the only compounds that accompany PO are propionaldehyde or acetone formed upon isomerization of PO.

According to the XPS analyses after the catalytic test using the calcined Al_2O_3/CeO_2 sample, the aluminum stays in its +3 oxidation state. Cerium, which is present as 0.1% Ce(III)/Al in samples prepared via the plasma technique, almost disappears after calcination (probably it migrates into the particle). The amount left after the test is so low that it was not possible to do any fitting of the curve to establish the chemical state of cerium. Therefore, we have used CeO_2 (2%) mixed with Al. The calcined material was used and in this case aluminum does not change its oxidation state (+3) during the propene oxidation reaction, whereas it is possible to analyse the cerium spectrum which contains both Ce(III) and Ce(IV) signals. We have clearly shown that there is a decrease of the signals of Al(III) or Ce(III) or Ce(IV) after running the catalytic reaction, that suggests a direct involvement of Al_2O_3 or Ce_2O_3/CeO_2 in the formation of PO using reticular oxygen with high selectivity towards PO. This reactions recalls the Mars-van Krevelen mechanism [29].

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