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Agglomeration of Ti-SBA-15 with clays for liquid phase olefin epoxidation in a continuous fixed bed reactor

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Abstract

Titanium-containing SBA-15 material has been agglomerated with bentonite clay to form macroscopic structured catalyst particles with the purpose of being used in continuous epoxidation processes on a fixed bed reactor. The binding conditions, the mass ratio catalyst to binding agent as well as the calcination temperature of the material were studied to improve as much as possible the catalytic behavior and mechanical strength of the titanium-based catalyst. The binded material has been finally tested in the liquid epoxidation of 1-octene with ethyl benzyl hydroperoxide in a continuous up-flow fixed bed reactor. Reaction results reveal a better catalytic performance of this catalyst, both regarding to the conversion of the olefin and efficient use of the oxidant, than conventional commercially available TiO_2–SiO_2, specially when pellet surface hydrophobization is performed by silylation treatment.

Keywords: Ti-SBA-15; Mesoporous; Epoxidation; Agglomeration; Fixed bed reactor

1. Introduction

Epoxides are very important in the chemical industry due to their application as intermediates for the synthesis of a large variety of products. For example, propylene oxide is employed as starting material in the synthesis of many commercial products, including adhesives, paints, and cosmetics [1]. The major application of propylene oxide is the production of polyether polyols, which are mainly used for the production of polyurethane foams, though other applications include the production of propylene glycol ethers and propylene glycol [2]. Current methods for the production of propylene oxide are the chlorohydrin process and the hydroperoxide process [1]. The first of them involves a great environmental impact due to the production of chlorinated by-products and calcium chloride wastes, which have no commercial value; besides wastewater with high concentration in salts are produced. For many reasons the hydroperoxide process has displaced the chlorohydrin process and now it is the most extended industrial procedure for the production of propylene oxide [1]. This process shows low production of waste and good efficiency in the use of the oxidant. However, a great disadvantage is the production of a by-product, ethylbenzyl alcohol or *tert*-butyl alcohol, depending on which variant of the hydroperoxide process is applied (SMPO/PO–TBA) [1], which has to be commercially valuable to ensure the proficiency of the process. Thus, the use of industrial oxidants like the ethylbenzyl hydroperoxide (EBHP) or *tert*-butyl hydroperoxide (TBHP) leads to two different processes resultant from the valuation of the alcohol by-product. The former leads to ethylbenzyl alcohol which is subsequently transformed into styrene through a dehydration step. The process is known as SMPO because of the name of the two main products—Styrene Monomer Propylene Oxide. On the other hand, the *tert*-butyl alcohol resultant from TBHP is usually valuated through its conversion into methyl *tert*-butyl ether (MTBE) which shows commercial interest as fuel additive. In this case the overall process, including the production of propylene oxide, is known as Propylene Oxide–*tert*-Butyl Alcohol (PO–TBA). Nevertheless, SMPO process is more extended than PO–TBA process because of the higher commercial value of styrene compared to *tert*-butyl alcohol [1]. Besides the valua-

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tion of the alcohol resultant from the conversion of the oxidant, some other difficulties are found for the separation of the residual hydroperoxide from the oxirane. Thus, the hydroperoxides employed in the production of oxiranes have to be highly converted in a very high efficient manner, decreasing in this way the importance of the main disadvantages of the hydroperoxide process. In this sense, the catalyst plays an important role in achieving both objectives. Thus, the development of an efficient catalyst for the production of propylene oxide has been and still it is an important industrial challenge [2]. Different kinds of catalysts can be used to drive the oxidation of olefins by alkyl hydroperoxides but most of the industrial processes are based on molybdenum [3,4] and titanium [5] as catalytic active metal. Moreover, a great part of these epoxidation processes involve the use of molybdenum homogeneous catalysts and therefore the catalyst recovering results difficult as well as the equipment corrosion troubles become frequent. The discoveries of the Shell catalyst [6] and TS-1 zeolitic material [7], as heterogeneous catalysts for olefin epoxidation, partially overcame these troubles and nowadays they are still being used on an industrial scale, although the latter makes use of hydrogen peroxide as oxidant. However, these materials show some inconvenients, such as the high sensitivity of titanium species against water traces in the Shell catalyst or the small pore size of the TS-1 material, which hinders the access of bulky substrates to the catalytic sites, reducing the applicability of the material. The oxidation of bulky substrates requires the synthesis of materials with large pores such as mesoporous xerogels [8] or the recently developed mesostructured materials MCM-41 [9] and SBA-15 [10,11], to be used as catalytic supports [12–15]. The preparation of Ti-substituted SBA-15 materials has received special attention due to several advantages offered by this material like the open porous structure or the high hydrothermal stability, moreover compared to MCM-type materials. Incorporation of titanium species into the matrix of SBA-15-type mesostructured materials can be achieved by post-synthesis grafting treatments, involving the reaction between the silica support and a solution containing the titanium starting material [16,17], and direct synthesis procedures [18]. Latter strategy of synthesis usually leads to more stable and dispersed supported metal species than other methods, however its use involves more difficulties mainly caused by the strong acidic conditions for the synthesis of SBA-15 materials. Recently, we have reported that some of the troubles related to the very low pH value of the synthesis media for the incorporation of the metal species can be partially overcome by a proper selection of the titanium precursor [18]. Titanocene dichloride as titanium source and proper synthesis conditions allow to obtain Ti-SBA-15 samples showing a good metal dispersion, free from anatase domains and displaying a high accessibility to the titanium sites [18]. These materials have shown a very high catalytic activity in the epoxidation of olefins with alkyl hydroperoxides under batch conditions.

Industrial requirements for catalysts usually involve their adaptability to continuous processes and Ti-SBA-15 materials are usually prepared as fine powders, which avoid their use in a continuous flow fixed bed reactor because of the extremely high pressure drop caused by the catalyst. Very few articles deal with the preparation of macroscopically structured particulated catalyst for its use in a continuous process [5,19,20]. These articles have prompted us to prepare an extruded catalyst based on Ti-SBA-15, which might have interest in a prospective industrial application. Herein, we report our studies on the formulation of an extruded Ti-SBA-15/bentonite catalyst prepared from the powdered mesostructured material. This material has been fully developed from the early stages to its application in a packed-bed reactor for the liquid phase epoxidation of 1-octene as model olefin with ethylbenzyl hydroperoxide as oxidant.

2. Experimental

2.1. Materials and methods

Titanocene dichloride (Cl_2TiCp_2, 97%) was used as titanium source for the synthesis of titanium functionalized mesostructured materials and purchased from ABCR. Non-ionic surfactant (Pluronic 123, $EO_{20}PO_{70}EO_{20}$, M = 5800), tetraethylorthosilicate (TEOS, 98%), hexamethyldisilazane (HMDS, 99%) and 1-octene (99%) were purchased from Aldrich Chemicals. Ethylbenzyl hydroperoxide (EBHP, 50 wt.% in ethylbenzene) was kindly provided by Repsol-YPF to be used as oxidant in epoxidation reactions. The oxidant has been employed as received without previous purification. Commercial TiO_2–SiO_2 catalyst (Shell type catalyst) was also provided by Repsol-YPF as 2 mm spherical pellets as catalyst reference [21]. This reference material has been widely studied in the epoxidation of different olefins using several oxidation agents, from the simplest hydrogen peroxide to the bulky ethylbenzyl hydroperoxide, showing for all of them good performance in epoxidation reactions and efficient use of the oxidant. Chemical analysis of the material revealed titanium content of 0.96% in weight basis.

2.2. Synthesis of powder Ti-SBA-15

The powder Ti-SBA-15 samples have been prepared accordingly to the method previously described in literature [18]. In a typical synthesis, 4 g of tri-block copolymer were dissolved in 125 mL of an aqueous solution of HCl 0.5 M. The resultant mixture was then heated up to 40 °C before adding the Cl_2TiCp_2. The metal species were prehydrolyzed for at least 3 h, followed by the addition, in a unique step of the silicon precursor (TEOS). The resultant gel was then kept under stirring at 40 °C for 20 h and hydrothermally aged at 100 °C for 24 additional hours under static conditions. The solid was recovered by filtration and air-dried. Surfactant was removed by calcination in air at 550 °C for 5 h under static conditions. The solid was then recovered as a white fine powder.

2.3. Macroscopically structured Ti-SBA-15 materials

Agglomeration of powder Ti-SBA-15 catalysts with clays has been performed using different procedures. All of the methods make use of inorganic agglomerant clay (bentonite or sepiolite) and an organic additive (methyl cellulose, 5 wt.%). Mixing all of the components with ultra pure water leads to a homogeneous

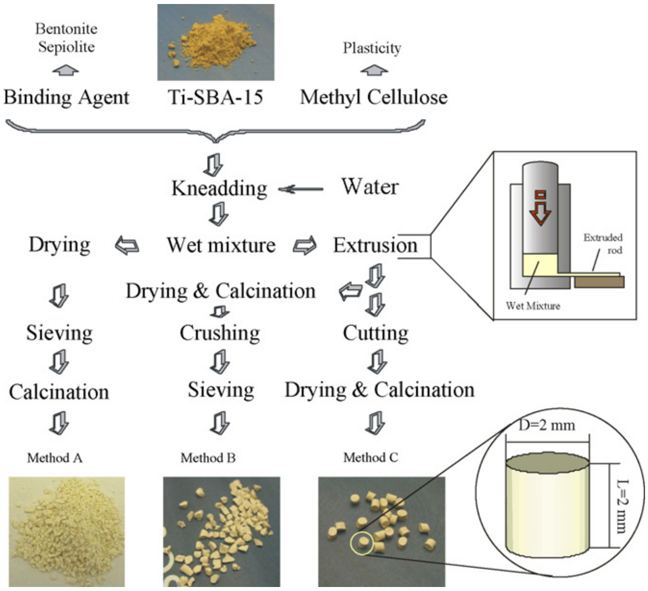

Fig. 1. Agglomeration methods for the preparation of macroscopically structured Ti-SBA-15 materials.

mixture, which is kneaded to achieve an uniform distribution of the liquid. The processing of the resultant composition varies depending on the agglomeration method.

Method A consists on drying the mixture on air at 110 °C during 24 h followed by a crushing step and a final sieving to achieve a material with particle size comprised between 0.7 and 1.0 mm. The resultant particles were then calcined in air under static conditions using a heating ramp of 0.3 °C min^{-1} up to 550 °C during 2 h.

Method B comprises an extrusion step of the raw mixture to form rods. The drying step is carried out in a drying chamber equipped with a humidity controller under the following program: first the extruded rods were subjected to 20 °C and relative humidity of 70% during 24 h. Then, the humidity was reduced down to 35% keeping constant the temperature conditions for 24 h. Final stage comprises 80 °C and relative humidity of 10% during 20 h. The dried rods were then calcined in air at 550 °C for 2 h using a heating ramp of 0.5 °C min^{-1}. The final materials were then crushed and sieved to get particles sized between 0.7 and 1.0 mm.

Method C is derived from method B. In this procedure, instead of crushing the calcined samples, the catalyst particles are formed before the drying step by cutting the extruded rod in 2 mm length particles. The rest of the stages make use of the same conditions to those described for method B although in this case the crushing step is avoided.

Fig. 1 outlines the main steps and final materials obtained through each one of the agglomeration methods.

2.4. *Silylation of agglomerated materials*

The binded Ti-SBA-15/bentonite catalyst was treated with HMDS using a similar procedure to that previously reported in literature [18]. In a typical preparation, a suitable amount of freshly agglomerated material was outgassed at 150 °C during 24 h under vacuum. The material was then reacted for 24 h with a dry mixture of toluene/HMDS in a Soxhlet apparatus under N_2 atmosphere (mass ratio material/HMDS of 1.0). The treatment was carried out under static conditions in order to avoid particle attrition. The silylated material was then washed several times with toluene and dried under nitrogen atmosphere for 4 h at 200 °C.

2.5. *Catalyst characterization*

The titanium content of the prepared materials was determined by ICP-atomic emission spectroscopy. In a typical analysis 100 mg were treated with aqueous hydrofluoric acid and diluted to 250 mL in a calibrated flask. Standard solution of Ti (1000 $\mu\text{g L}^{-1}$) was used for the calibration of the apparatus. Solid state ^{29}Si MAS-NMR analyses were recorded in a Varian Infinity 400 spectrometer operating at 79.4 MHz under the following conditions: MAS at 6 kHz; $\pi/2$ pulse, 4.5 μs; repetition delay, 15 s; 3000 scans. Spectra were referred to tetramethylsilane. The ordering of the mesostructured materials was evaluated by means of XRD analysis performed in a Philips X'pert diffractometer using the Cu Kα line. The diffraction patterns were collected in the range from 0.6° to 5.0° (2θ) using a step size of 0.02° for low angle analysis and in the range from 5.0° to 50° with a step size of 0.04° for high angle analysis. N_2 adsorption–desorption isotherms were recorded at 77 K in a Micromeritics Tristar manometric porosimeter. The specific surface areas were calculated using the B.E.T. method whereas the pore size distributions were determined by the application of the B.J.H. method to the adsorption branch of the isotherm using a Harkins–Jura equation for the adsorbed multilayer thickness specially obtained for SBA-15-type materials [22]. Thermogravimetric analyses were carried out on a SDT simultaneous 2960 microscale analyzer from TA Instruments. The different contributions to the weight lost have been distinguished through the deconvolution of the DTA signal using Lorentz curves and subsequent integration. Diffuse reflectance ultraviolet spectra (DR-UV–vis) were collected in a VARIAN CARY-500 spectrophotometer equipped with an integration sphere accessory in the wavelength range from 200 to 600 nm. FTIR analysis were performed using a Mattson infinity series spectrophotometer using the KBr buffer technique and recording the spectra in the wavenumber range from 4000 to 400 cm^{-1}. XRF analyses were performed on a Philips MagiX spectrometer. The mechanical resistance of agglomerated materials was measured by two different methods, using a standard assay for determining the bulk crushing strength (BCS) [23] and measuring the individual particle resistance. The latter one was carried out as follows: a single particle is subjected to increasing pressure until particle breaks. This procedure is repeated 10 times to obtain the mean value.

2.6. *Catalytic epoxidation of 1-octene with ethyl benzyl hydroperoxide*

The catalytic activity of the titanium-functionalized materials has been evaluated in the liquid phase epoxidation of 1-octene

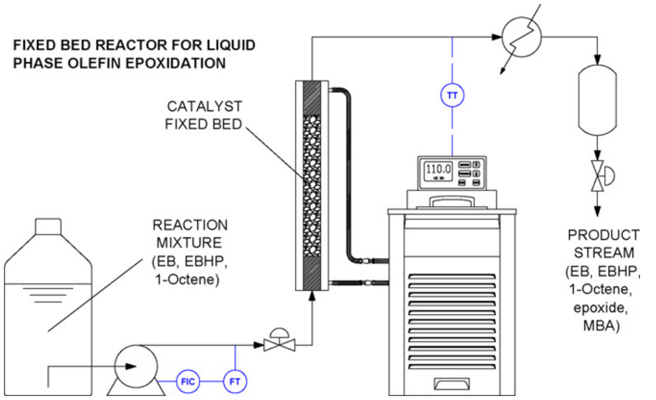

Fig. 2. Scheme of the up-flow fixed bed reactor for the epoxidation of 1-octene in liquid phase under continuous flow.

with EBHP, using both stirred batch and continuous up-flow fixed bed reactors. The batch catalytic assays were carried out in a two-necked round bottom flask magnetically stirred and immersed in a temperature-controlled bath. All reactions were performed at 110 °C for 2 h. In a typical test both the catalyst and 1-octene (1-octene:catalyst mass ratio of 50.0; mass catalyst of 1.0 g) are loaded into the flask and the system is then heated up to 110 °C. Once the temperature is reached, the oxidant is added in a unique step by means of a syringe (EBHP:1-octene molar ratio of 0.12) and all the conditions are then kept constant for 2 h. The epoxidation reactions performed under continuous flow were carried out in a glass-made fixed bed reactor like that shown in Fig. 2. The catalytic fixed bed, 1.2 cm of inner diameter and 15 cm length (catalyst loading of 3.0 g), is located in a jacketed glassware tube between two beds of spherical glass inert particles. The temperature of the system is controlled (110/120 °C) on top of the bed by using an external heating bath recycling a stream of silicone oil through the jacket of the reactor. Typically, the feed solution mixture, containing both 1-octene and oxidant, was loaded into the fixed bed reactor in up-flow operation by means of a Gilson 10SC HPLC pump operating at 1.0 mL min^{-1} (calculated spatial time as the weight of catalyst to mass feed flow was of 3.6 min). EBHP composition was varied in order to determine the influence of the molar ratio oxidant to substrate in the catalytic behavior of agglomerated Ti-SBA-15 materials. Under the reaction conditions, epoxide and methyl benzyl alcohol (MBA) as oxidant by-product were the reaction products. In both cases, either using the batch reactor or the fixed bed, the hydroperoxide conversion was calculated by iodometric titration whereas the rest of the reaction products were quantified by gas chromatography analysis.

3. Results and discussion

The present contribution is focused on the development of a particulated Ti-SBA-15 catalyst to be used in the liquid phase epoxidation of 1-octene in an up-flow fixed bed reactor. The current research comprises the choice of the binding agent among two clays conventionally employed for the preparation of catalysts, due to their excellent plastic properties: bentonite and sepiolite. Likewise, some parameters such as the calcination temperature, the mass ratio binding agent to powder catalyst and the agglomeration procedure have also been investigated. Finally the macroscopically casted catalyst has been tested in the epoxidation of 1-octene in liquid phase in a continuous up-flow fixed bed reactor.

3.1. Thermal treatment of binding agent

The choice of the binding agent has been carried out attending to its activity in the decomposition rate of the oxidant after different thermal treatments. Clays are known to show a high concentration of hydroxyl groups responsible for the Brönsted acidity of these materials [24–26]. These acid centers are responsible for the non-oxidative consumption of alkyl hydroperoxides [27–29]. Thus, the selection of the proper binding agent includes also an additional study on the removal of their hydroxyl groups.

Fig. 3 shows the TGA analysis carried out for bentonite and sepiolite materials. The detected weight losses have been correlated with different types of hydroxyl groups removed during calcination. Thus, in the case of the bentonite clay (Fig. 3A), the mass change detected in the first and second regions, which comprise up to 300 °C, is attributed to the removal of adsorbed water and water molecules located at narrow pores strongly adsorbed onto the surface of the clay. The third region, comprising the range from 300 to 550 °C includes the removal of the water molecules located between the bentonite plates. Finally, weight loss detected above 550 °C is assigned to the dehydroxylation of the material by condensation of silanol groups evolving water molecules and leading to a collapse of the clay structure.

On the other hand, sepiolite materials show a different distribution of the weight loss (Fig. 3B). TG analysis shows up to three different contributions to the total weight loss. The following processes have been assigned to each mass loss [30]: the weight change detected up to 110 °C corresponds to the removal of the moisture adsorbed on the sepiolite surface, the weight loss at 250–275 °C matches with the water molecules strongly adsorbed filling the micropores of the clay structure and finally the rest of the weight loss is attributed to the removal of the solvating water molecules around magnesium ions. Thus, in the temperature range used for this study, no dehydroxylation processes corresponding to the removal of silanol groups has been detected, which is in accordance with previously reported results [30]. Higher temperature values were not assayed because the damage of the porous structure of the mesoporous material might be caused in the binded Ti-SBA-15/clay materials [10].

Table 1 shows the weight loss calculated from thermogravimetric analyses carried out on samples of both clays (bentonite and sepiolite), after calcination at different temperatures. For the bentonite material, the contribution of physisorbed water and moisture (regions I and II) to the total weight loss becomes less important insofar the calcination temperature increases. This could be related to the lower affinity of the surface of the clay for water molecules because of a decrease in their hydrophylicity. The lower hydrophilic behavior is caused by the lower amount of surface silanol groups being removed by the calcination treatment. Anyway, the contribution to the weight loss never decreases down to zero because there are

Table 1
Weight loss contributions in TG analysis performed on bentonite and sepiolite clays calcined at different temperatures

Bentonite					Sepiolite			
T (°C)	Reg I	Reg II	Reg III	Reg IV	*T* (°C)	Reg I	Reg II	Reg III
r.t.	1.51	1.53	2.13	1.67	r.t.	1.43	3.69	3.07
300	0.69	1.40	2.07	1.69	300	1.11	2.53	2.82
400	0.60	1.17	2.08	1.69	400	0.99	1.20	2.32
550	0.40	1.07	0.10	1.53	550	1.02	1.93	0.64
650	0.30	1.14	0.19	0.48	650	1.09	1.51	0.06

Values in wt.%.

some water molecules coming from the environment, which remain physisorbed onto the surface of these materials. On the other hand, weight loss detected in region III, becomes non-significative for samples calcined beyond 550 °C. Unlike water physisorption, this weight loss, as well as that detected for region IV, is not reversible, since the sample does not show any contribution on both regions to the total mass change after rehydration by contact with the atmosphere. Sepiolite has a rather different behavior regarding the thermogravimetric analysis. Thus, increasing the calcination temperature causes the contribution of the physisorbed water to the total mass loss, especially that located at micropores (region II), became less important. Anyway, the decrease of physisorbed water molecules is not as marked as that detected for bentonite because, for sepiolite materials, the calcination of the different samples is not strong enough to remove the silanol groups and thus, the hydrophilic nature of the clay is not greatly modified. On the other hand, rehydration of magnesium ions seems not to be easy once the water molecules have been removed from its coordination sphere, since the contribution of this region (region III) to the total weight loss is not significative after rehydration by contact with atmosphere.

Having in mind, as previously noticed, the quantity of silanol and hydroxyl functionalities located at the surface of the clays is an indirect measurement of their Brönsted acidity; materials calcined at such a high temperature to cause the dehydroxylation of the material by condensation of silanol groups should lead to a lower decomposition extent of alkyl hydroperoxides. In this sense, if the assumed conclusion is right, only the bentonite samples calcined at temperatures above 550 °C, should lead to poor hydroperoxide conversion. Fig. 4 shows the results achieved in the EBHP decomposition tests carried out in the presence of bentonite and sepiolite samples treated at different temperatures. These tests were developed in presence of a 7 wt.% solution of ethylbenzyl hydroperoxide in ethylbenzene for 2 h at 80 °C.

For both clays, increasing the calcination temperature leads to a gradual decrease of the oxidant consumption, which is in fairly good correlation with the lower quantity of hydroxyl functionalities detected by thermogravimetric and FTIR analyses. In other words, the decrease of the hydroxyl group population onto the surface of the clays causes lower hydroperoxide degradation. Additionally, it is noteworthy for bentonite materials how the hydroperoxide conversion values are rather similar for sam-

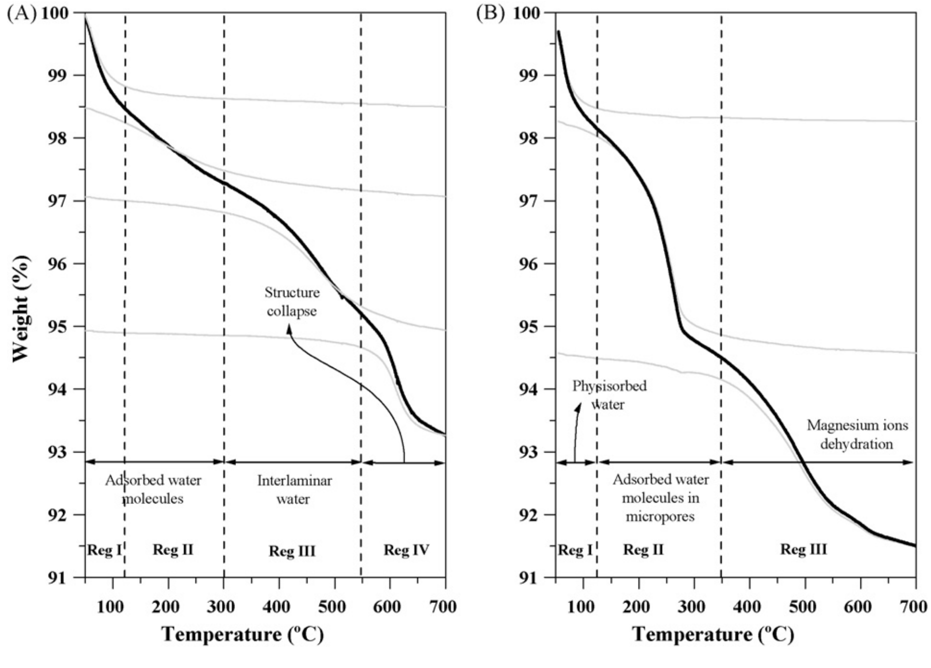

Fig. 3. Thermogravimetric analysis and weight losses assignation for (A) bentonite and (B) sepiolite clays.

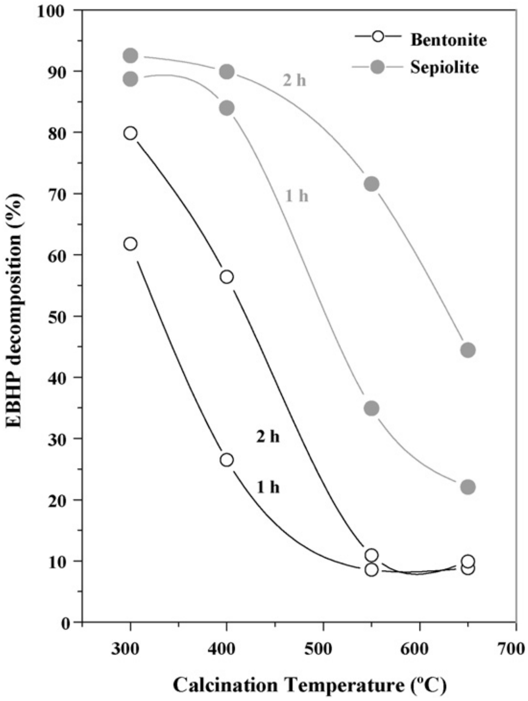

Fig. 4. EBHP decomposition over bentonite and sepiolite clays after different thermal treatments.

Table 2
Physico-chemical properties of Ti-SBA-15/bentonite materials

Sample	Bentonite[a] (%)	$S_{\mathrm{B.E.T.}}$[b] ($m^2\ g^{-1}$)	Vp[c] ($cm^3\ g^{-1}$)	Dp[d] (Å)
Ti-SBA-15	0	809	0.95	92
S-1	10	620	0.81	85
S-2	20	546	0.72	85
S-3	30	447	0.64	88
S-4	40	403	0.59	90

[a] Bentonite composition in weight.

[b] Specific surface area calculated by the B.E.T. method.

[c] Total pore volume measured by N_2 adsorption at $P/P_0 = 0.985$.

[d] Pore size calculated by the B.J.H. method using the K.J.S. correction.

ples calcined above 550 °C, even for long reaction times. Thus, bentonite samples calcined at 550 and 650 °C promote EBHP degradation in a similar extention. This is because the silanol groups, which are removed at 600 °C are located in the interlaminar microporous spacing of the bentonite clay, being not accessible by the bulky EBHP and thus they do not catalyze the hydroperoxide decomposition. Thus, although samples calcined at 550 and 650 °C show different content of surface hydroxyl groups, they promote almost the same hydroperoxide consumption.

On the other hand, sepiolite samples cause higher decomposition degrees of the hydroperoxide than those achieved with bentonite materials, whatever the calcination temperature used in the preparation of the samples. Since the elemental analysis by XRF do not provide meaningful differences related to the presence of transition metals able to catalyze the decomposition of hydroperoxides, differences between sepiolite and bentonite in the decomposition of hydroperoxide have been ascribed to the differences in the population of surface hydroxyl groups. Unlike bentonite, sepiolite samples have not been highly dehydroxylated even at temperatures as high as 650 °C. In this sense, all the sepiolite materials tested in this study show some fraction of their original hydroxyl groups content, and thus the clay is still able to catalyze the degradation of EBHP. Therefore, it can be concluded that there is a direct correlation between the decomposition degree of EBHP and the concentration of hydroxyl groups located onto the surface of the clays used in this study. Anyway, increasing the calcination temperature causes a gradual lowering of hydroperoxide conversion, being this effect more accentuated for bentonite materials than for sepiolite samples. Since calcination at 550 °C is enough to achieve the minimum hydroperoxide conversion with bentonite, this clay, as well as 550 °C have been selected as binding agent and calcination temperature, respectively for the preparation of the agglomerated Ti-SBA-15 materials described in the rest of this research.

3.2. *Composition of the agglomeration raw mixture*

The next variable studied in this research was the proportion of binding agent to catalyst to be employed in the preparation of agglomerated Ti-SBA-15 catalysts. This parameter is essential for the preparation of a catalyst, since it is responsible for two factors: the mechanical strength of the final particles and the concentration of catalytic sites in the final material. Thus, a high proportion of binding agent provides high mechanical resistance but the catalytic behavior of the final material may be greatly reduced because of an excessively low amount of active catalyst. Thus, this study pursues compromising the mass ratio of binding agent to achieve agglomerated materials with high catalytic activity and mechanical resistance. The amount of binding agent has been varied between 10 and 40 wt.% in the agglomeration raw mixture. The materials were prepared by the agglomeration method A (see Section 2) to achieve a particle size between 0.75 and 1.0 mm.

Fig. 5 shows the N_2 adsorption isotherms recorded for the different binded Ti-SBA-15/bentonite catalysts after calcination at 550 °C. The so-prepared materials display type IV isotherms featured with H1 hysteresis loops, accordingly to the I.U.P.A.C. classification, typical from mesostructured materials with pore sizes larger than 40 Å. Increasing the amount of the clay in the agglomeration mixture leads to a clear decrease of the adsorbed nitrogen volume on every partial pressure measurement points. These differences between samples are related to a decrease in the total pore volume and specific surface area when increasing the amount of bentonite in the final materials (Table 2). The explanation for this behavior is simply dilution of the mesostructured material with the bentonite clay, which acts as a dispersant and, since the surface area and pore volume of this mineral is quite low, its contribution to the resultant textural properties is negligible. A clear evidence of this fact is the high coincidence of the relative isotherms of all the materials depicted in Fig. 5B. Regarding the mesoscopic ordering of the final agglomerated materials, XRD analysis provides diffraction patterns typical from a *P6mm* structure regardless of the clay content (see supplementary data). Textural properties and

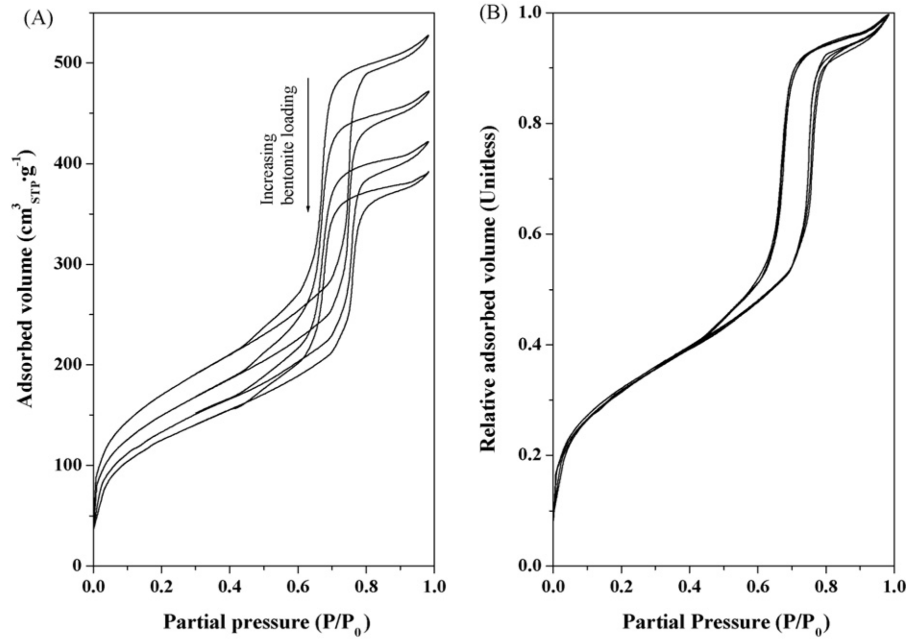

Fig. 5. Nitrogen adsorption–desorption isotherms recorded at 77 K for agglomerated Ti-SBA-15 materials with different loadings of bentonite. (A) Recorded scale and (B) normalized scale.

XRD patterns indicate that the mesostructure has been well preserved during the agglomeration and thermal treatment of the Ti-SBA-15/bentonite bindings.

Fig. 6A depicts the trend of the titanium loading as well as the particle resistance versus the amount of bentonite in the final materials. The use of increasing amounts of binding agent causes a decrease of the final metal content in the materials because of an expected dilution effect. In contrast, the higher the loading of bentonite the more resistant is the agglomerated particles. In this sense, it seems to be an inflection point of the trend in the particle resistance around a mass composition in bentonite of 25–30 wt.%. Higher clay loadings do not provide increasing particle resistance but, on the contrary, causes an unnecessary dilution of the active catalyst reducing in this way the proportion of titanium species. This dilution can exert negative influence on the catalytic behavior of the agglomerated materials in catalytic epoxidation of olefins. Thus, in order to evaluate properly which is the true influence of the binding between bentonite and Ti-SBA-15 materials, some catalytic assays have been performed using agglomerated materials as catalysts in a stirred batch reactor in presence of EBHP as oxygen source. Fig. 6B shows the correlation between the bentonite loading and the titanium content with the conversion of the substrate. It is noticeable that all the materials displayed similar values for the efficiency in the use of the oxidant towards the epoxide (∼70–75%) and moderate oxidant conversion (60–80%). These results indicate that the non-oxidative consumption of EBHP has been cut down because of the removal of surface hydroxyl functionalities during post-synthesis calcination. Thus, when increasing the bentonite loading on the final particles of binded Ti-SBA-15/bentonite, the conversion of 1-octene is reduced because of the lower quantity of catalytic sites present in the material. In

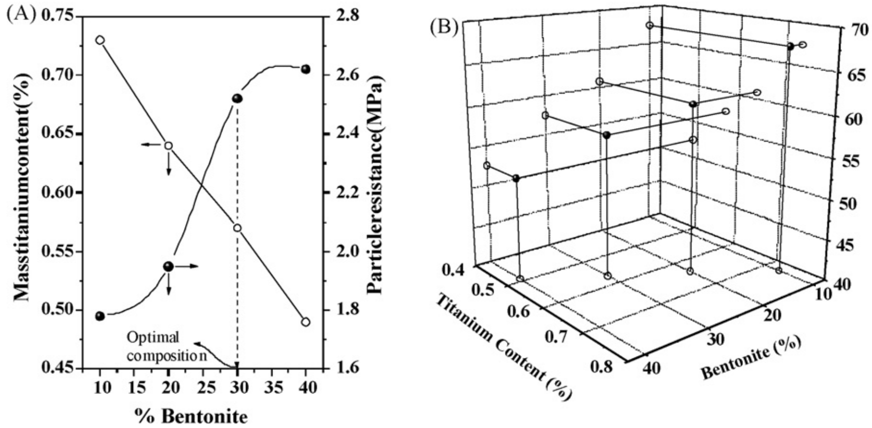

Fig. 6. (A) Correlation between the bentonite loading, particle mechanical resistance and titanium loading. (B) Catalytic activity in the liquid phase epoxidation of 1-octene for different clay loadings. (1) Conversion of 1-octene referred to the maximum stoichiometric value.

this sense, it is noteworthy the dependency of the substrate conversion with the titanium loading follows a linear relationship indicating the catalytic activity per titanium site is almost the same for all the materials. This result means that the intrinsic catalytic activity per titanium site of the Ti-SBA-15 materials has not been changed during the agglomeration process and it is independent on the clay content.

In this context, the optimal amount of bentonite for the preparation of agglomerated Ti-SBA-15 materials seems to be ca. 30 wt.% because it leads to an important increase in the particle resistance whereas the amount of titanium present in the resulting material is not largely reduced. Larger amounts of bentonite do not provide increasing particle mechanical resistance whereas it reduces the activity of the final material because of dilution of the Ti-SBA-15 catalyst.

3.3. Enhancement of mechanical resistance and hydrophobicity of catalyst particles

The method for producing particulated solids exerts an important influence on the final properties of the casted solid. Thus, several steps are crucial in the final mechanical resistance, for instance the drying method [31]. During the drying step, particles trend to shrink and become distorted and cracked reducing the mechanical resistance of the particle. In order to avoid these problems, water has to be slowly removed from extruded particles. Additionally, any procedure involving transmission of mechanical stress to the solid can dramatically reduce the mechanical resistance of the particles because of the creation of micro-fissures inside the particles. With the purpose to increase as much as possible the mechanical resistance of the Ti-SBA-15/bentonite materials, different agglomeration methods were used (Fig. 1). Thus, the general procedure to obtain particulated Ti-SBA-15/bentonite materials (method A) has been modified through the use of an extrusion step as well as an intermediate controlled drying procedure (method B). Additionally, the extruded rods have been reduced to discrete particulated solids by using a crushing step (method B) or by cutting the moist rods (method C) into particles before drying and calcination step. Table 3 shows the physico-chemical properties of the materials obtained with the different agglomeration methods as well as the results achieved in the catalytic epoxidation of 1-octene in presence of EBHP in a stirred batch reactor. The characterization of the materials has been completed by determining the mechanical particle resistance of the prepared samples. The materials obtained through the different agglomeration methods do not show significant differences regarding their textural and structural parameters. In the same sense, all the agglomeration procedures lead to materials showing almost the same catalytic behavior, both regarding the conversion of the substrate and the efficiency in the use of the hydroperoxide, indicating the modifications introduced on each agglomeration method do not cause differences on the catalytic activity of the final materials. However, differences regarding the particle resistance are quite noteworthy since controlling the drying step as well as using an extrusion procedure leads particles with increasing mechanical resistance, probably as a consequence of the lower stress caused

Table 3
Physico-chemical properties and catalytic activity of materials agglomerated by different methods

Synthesis treatments		Physico-chemical properties					Catalytic activity[a]			
Agglomeration method	Post-synthesis treatment	Ti[b] (%)	$S_{\text{B.E.T.}}$[c] ($m^2\,g^{-1}$)	Vp[d] ($cm^3\,g^{-1}$)	Dp[e] (Å)	Rp[f] (MPa)	X_{OCT}[g] (%)	X'_{OCT}[h] (%)	X_{EBHP}[i] (%)	η_{EBHP}[j] (%)
Method A	–	0.57	407	0.64	88	2.52	3.45	63.9	91.1	70.1
Method B	–	0.52	407	0.62	87	3.13	3.52	65.1	90.4	72.0
Method C	–	0.59	403	0.62	86	5.94 (0.74)	3.42	63.3	91.5	69.2
Commercial TiO_2–SiO_2	–	0.96	334	0.87	160	5.90 (0.72)	3.44	63.7	85.6	74.4
Method C	Silylation	0.53	365	0.55	80	5.94	3.24	60.0	70.4	85.2
Commercial TiO_2–SiO_2	Silylation	0.86	294	0.85	154	5.90	3.41	63.1	78.7	80.2

[a] Reaction runs carried out in a batch reactor at 110 °C for 4 h. Mass of catalyst 1.0 g. EBHP to 1-octene molar ratio of 0.12.
[b] Mass titanium loading in final materials.
[c] Surface area calculated by the B.E.T. method.
[d] Total pore volume measured at $P/P_0 = 0.985$.
[e] Pore size calculated by the B.J.H. method.
[f] Individual mechanical particle resistance, BCS in brackets.
[g] Conversion of 1-octene.
[h] Relative conversion of 1-octene referred to the maximum stoichiometric value.
[i] Absolute conversion of ethyl benzyl hydroperoxide.
[j] Efficiency in the use of the oxidant.

Table 4
Steady state results for the epoxidation of 1-octene in a fixed bed reactor under continuous flow

Run	Catalyst	EBHP[a] (%)	X_{OCT}[b] (%)	X'_{OCT}[c] (%)	X_{EBHP}[d] (%)	η_{EBHP}[e] (%)	A[f] (mmol g_{cat}^{-1} h^{-1})	A_{Ti}[g] (mmol g_{Ti}^{-1} h^{-1})
1	Ti-SBA-15/bentonite silylated	1.5	1.5	56.5	57.8	97.8	1.02	192
2		3.0	3.0	54.3	62.0	87.6	1.97	372
3		6.0	3.2	28.6	33.0	86.8	2.08	392
4		12.0	2.5	11.7	19.0	61.5	1.69	319
5	Commercial TiO_2–SiO_2 silylated	3.0	2.5	47.3	96.4	49.1	1.71	199

[a] Amount of ethyl benzyl hydroperoxide in the feed stream in weight basis.
[b] Conversion of 1-octene.
[c] Relative conversion of 1-octene referred to the maximum stoichiometric value.
[d] Absolute conversion of ethyl benzyl hydroperoxide.
[e] Efficiency in the use of the oxidant.
[f] Catalytic activity in mmol of epoxide per gram of catalyst per hour of reaction.
[g] Catalytic activity in mmol of epoxide per gram of titanium per hour of reaction.

by the mild conditions used during the controlled drying procedure. The slow removal of water from extruded rods avoids the formation of microscopic cracks in the solid, jeopardizing the particle resistance. Additionally, it is noticeable the significant increase achieved in the mechanical strength when casting the particles by cutting before drying and calcination (method C) instead of crushing calcined rods (method B). This better behavior is assigned to the lower mechanical stress suffered by particles when applying this method which leads to materials as resistant as the commercial catalysts used as reference material (SiO_2/TiO_2), as it is inferred from almost the same BCS index achieved for both materials (Table 3).

All the materials display catalytic activity in the epoxidation of 1-octene. The low values achieved for substrate conversion are due to the employed reaction conditions since the substrate is also used as solvent and thus it is present in large excess regarding the oxidant. For this reason, the conversion of 1-octene has been referred to the maximum stoichiometric value. On the other hand, as negative feature, all the prepared materials, regardless the agglomeration method employed for their preparation, show a rather low efficiency in the use of the oxidant (ca. 70%). It is well known that the removal of surface hydroxyl functionalities reduces hydroperoxide by-reactions like the non-oxidative consumption, improving in this way the efficiency in the use of the oxidant [18]. For this reason, post-synthesis silylation has been performed on the material prepared through the agglomeration method C, that shows the higher particle resistance, as well as the commercial catalyst based on SiO_2–TiO_2. The physicochemical properties, as well as their behavior in catalytic tests have also been included in Table 3. Although some textural properties, like the surface area and pore volume are partially modified by the silylation process, because of the grafting of trimethyl silyl functionalities onto the inner porosity, the particle resistance is not altered at all, probably as a consequence of the gentle conditions employed for the silylation treatment of agglomerated particles. On the contrary, the efficiency in the use of the oxidant is enhanced when using silylated materials as catalysts. In this case this parameter reaches an acceptable value of ca. 85% for the silylated Ti-SBA-15/bentonite material.

3.4. Liquid phase epoxidation of 1-octene with EBHP in an up-flow fixed bed reactor

Once the catalyst has been fully developed and characterized, the final agglomerated and silylated materials have been used as catalysts in the catalytic epoxidation of 1-octene with EBHP under liquid phase in a fixed bed reactor. Table 4 summarizes the catalytic results obtained in the epoxidation of 1-octene in a fixed bed reactor under different amounts of the oxidant in the feedstock solution and using the silylated Ti-SBA-15/bentonite material as catalyst. Since the conversion of the oxidant, as well as the efficiency on its use, are critical parameters in the epoxidation of olefins with alkyl hydroperoxides, maximizing the conversion of this reagent in an efficient way can improve the proficiency of the process. In this way, results indicate that increasing the amount of the oxidant in the reaction mixture largely decreases the activity of the catalysts, since the relative conversion achieved for the olefinic substrate decreases from almost 60% to less than 12%. Nevertheless when considering the real substrate conversion, the reduction of the catalytic activity insofar the oxidant content is increased turns opposite to lead the expected trend. Anyway, when using a 12% mole of oxidant in the feedstock solution, the catalytic activity decreases compared to catalytic assays with a less concentrated oxidant. This fact seems to be related with the observed trend for the efficiency in the use of the oxidant, which is dramatically reduced from 100 to 60% when increasing the concentration of EBHP. These results suggest that the secondary reactions involving hydroperoxide, like the non-oxidative consumption, are enhanced when increasing the concentration of this reagent in the reactants stream, becoming as important as the epoxidation reaction.

The catalyst developed in this study has been compared with a commercial Shell-type SiO_2–TiO_2 catalyst. Results reveal the SBA-based catalyst display a better catalytic behavior than the commercial one since the olefinic substrate is converted in a higher extension, even containing much lower titanium loading than TiO_2–SiO_2 commercial catalyst does. This fact is easily observed when comparing the catalytic activity of both catalysts per gram of catalyst and per gram of titanium (Table 4). The first one indicates a similar catalytic behavior of both materials per mass of catalysts but differences are clearly evident when comparing the catalytic activity per titanium site. In this way the catalytic activity of the agglomerated Ti-SBA-15 material is almost twice that calculated for the commercial TiO_2–SiO_2-based catalyst. In the same sense, the oxidant is largely converted, almost total conversion in the steady state, when using the commercial catalyst. This behavior involves a much lower efficiency in the use of the oxidant than that achieved with the mesostructured catalyst. This fact is related to the amount of surface hydroxyl functionalities at the commercial catalyst. A deeper insight to the population of hydroxyl functionalities onto both catalysts, performed by means of solid state MAS-NMR and FTIR analysis (see supplementary data), reveals a much higher amount of these groups located onto the commercial catalysts than inside the pores of the SBA-based material. In this way, the non-oxidative consumption of the hydroperoxide is enhanced when using the commercial catalyst. This different behavior between both materials can be explained because of the different composition of both solids. Thus, the commercial catalyst is based on 99 wt.% silica and thus, the amount of hydroxyl functionalities is much higher than that located at the agglomerated material before silylation. Hydrophobization treatment is not so effective in the removal of hydroxyl groups for the commercial catalyst than for the mesostructured material and thus, the behavior of both treated materials regarding the efficient use of the hydroperoxide becomes different.

4. Conclusions

Mesostructured Ti-SBA-15 material has been agglomerated with bentonite clay to lead macroscopically structured catalyst particles displaying good catalytic activity in the epoxidation of 1-octene with ethylbenzyl hydroperoxide under liquid phase conditions. The calcination temperature of the Ti-SBA-15/bentonite binding as well as the surface hydrophobization of the calcined material by silylation treatment exert a dramatic effect in the improvement of the effective use of the hydroperoxide, minimizing the effect of the non-oxidative consumption of the oxidant because of catalytic decomposition. The comparison between this novel structured material with conventional Shell-type SiO_2–TiO_2-based catalyst in the epoxidation of 1-octene with ethyl benzyl hydroperoxide in a continuous up-flow fixed bed reactor reveals a much better catalytic behavior of the mesostructured material, not only because of driving higher conversions of the olefin but also because of a more efficient use of the oxidant. This new extruded Ti-SBA-15-based material might have true industrial potential as an alternative to the conventional homogeneous catalysts used for the liquid phase epoxidation of olefins under continuous flow conditions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2008.01.013.

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