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Propylene epoxidation with in situ generated H_2O_2 in supercritical conditions

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ABSTRACT

Several bi-functional materials based on palladium nanoparticles supported onto nanocrystalline titanium silicalite zeolite (Pd@TS-1) were prepared and used as active and reusable catalysts to direct PO production from hydrogen, oxygen and propylene through one-pot two-step combined process. This type of catalysts was able to carry out the consecutive process where palladium nanoparticles catalyzed the formation of H_2O_2 that was used as intermediate reagent for propylene epoxidation catalyzed by TS-1 nanocrystals, used as supporting active matrix. Influence of supercritical CO_2 conditions in batch reactions was evaluated together with the associated effect due to the presence of platinum promoters (Pd(Pt)@TS-1). Other reaction parameters were also considered, such as palladium loading, use of acidity inhibitors and modification of $H_2/O_2/C_3^{=}$ ratio. Reusability studies showed the high stability of the catalysts in consecutive catalytic cycles, their regeneration being possible.

1. Introduction

Propylene oxide (PO) is an important monomer for production of polyurethane foams, resins and propylene glycol [1]. The PO production is about 7.5 million tons per year, which comes mainly from the chlorohydrins and organic hydroperoxide (Halcon Method) processes. The chlorohydrins method was originally used for the production of ethylene oxide, but in the 1960s was replaced by a direct oxidation method and started to be used for the PO synthesis. In this method, propylene and chlorine react leading to a mixture containing different types of chlorohydrins, which react with an alkali to produce PO with high selectivity. However, this methodology has an important drawback, because chlorine and $Ca(OH)_2$ are necessary as sources, and $CaCl_2$ is produced, together with a large amount of waste water. On the other hand, in the Halcon process, ethylbenzene hydroperoxide or *tert*-butyl hydroperoxide react with propylene to yield PO. But, in this process, methylbenzyl alcohol or *tert*-butanol are obtained, which are dehydrated to form styrene monomer and isobutylene, i.e., two compounds severely affected by market trends [2–5].

Taking this into account, the most convenient solution would be the direct oxidation with O_2 [6], although the high reactivity of the allylic C—H bonds in the propylene precursor makes extremely difficult this reaction [7,8]. In this sense, it is reported that ethylene epoxidations can be carried out employing silver catalysts in the only presence of O_2 [9]. However, when these catalysts have been employed in the case of propylene, results have certainly been poor [10]. So, it would be decisive to avoid the drawbacks associated to chlorohydrins and Halcon processes, being important the development of safe and low contaminating propylene epoxidation routes.

Regarding safety and contamination, the use of catalysts becomes essential in the industry to prevent these problems. Homogeneous catalysts have been widely used in the industry, but their disadvantages, including their difficult and expensive recovery, poor thermal stability, limited applicability and the cost of catalyst losses makes desirable the use of another kind of catalyst. Although heterogeneous catalysts are sometimes less selective than homogeneous have also a wide applicability, and besides, important advantages, including easy and cheap catalyst separation and low costs associated to catalyst losses, factors which are enhanced by the catalyst reusability [11]. For these reasons, the preparation of heterogeneous catalysts which would catalyze the propylene epoxidation with high performances and selectivities would be highly desirable [12].

Besides the chlorohydrins and Halcon processes, the production of PO from propylene has also been carried out through two consecutive steps (Scheme 1): (i) H_2O_2 formation from hydrogen and oxygen and (ii) generation of PO from propylene and previously formed H_2O_2. Even, different industrial prototypes have recently

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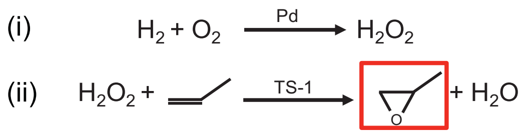


Scheme 1. Individual reaction steps to produce propylene oxide (PO).

been reported based on the combination of two connected reaction systems where the intermediate H_2O_2 is circulated between the reactor vessels, such as the HPPO two-step process based on the direct synthesis of hydrogen peroxide [13–15]. Into this combined reaction route, several types or polymeric resins [16] and/or different transition metals [17,18], such as Pd, Pt and Au, supported onto inorganic oxides have been able to directly produce H_2O_2 [19]. Additionally, titanium-silicalite zeolite (TS-1), firstly synthesized by Taramaso et al. [20], has been an excellent solid catalyst for the propylene epoxidation. Furthermore, in the last years, optimized synthesis methods of nanocrystalline TS-1 zeolites, from different synthesis routes, have allowed the development of highly active and recyclable titanium-catalysts for PO production, using ex situ generated H_2O_2 [21].

The next step to improve the PO production would be to combine the two individual reaction steps in only one process, developing an efficient one-pot two-step system based on the in situ generation of H_2O_2 and the use of bi-functional solid catalysts. Nowadays, the catalytic processes which combine two or more consecutive reactions are being very attractive from sustainability point of view due to the reduction in the number of sub-processes associated to isolation and separation tasks of intermediate products [22]. Into this approach, the use of active and reusable bi-functional catalysts which contain metallic nanoparticles (NPs) embedded into inorganic oxide type-matrixes are currently being profusely considered for different catalytic processes [23–25].

With the discovery by Hayashi et al. [19] of bi-functional materials formed by Au nanoparticles (NPs) supported onto titania matrix and their catalytic performances, a new possibility for the direct epoxidation of propylene trough in situ generated H_2O_2 was opened. Specifically, this type of gold-catalysts were highly selective in the direct vapor-phase oxidation of propylene to PO in the presence of oxygen and hydrogen, being established that Au nanoparticles with sizes between 2 nm and 5 nm were the most active for the PO production when titania was employed as the support [26,27]. However, Au@TiO_2 catalysts suffered deactivation phenomenon, its stability being too low in the profusely studied gaseous phase catalytic conditions [8]. With the purpose of increasing the reactivity and stability of bi-functional gold-materials, Yap et al. [28] concluded that Au@TS-1 catalysts containing Au nanoclusters with sizes between 1 nm and 2 nm were the most active for the epoxidation of propylene when TS-1 is used as a supporting matrix, being its stability also enhanced. Optimization of gold-catalysts was recently achieved by Huang et al. [29] using aqueous alkaline solutions to increase surface defects in TS-1 supports. In this case, the majority of deposited gold nanoclusters exhibited sizes below 2 nm, being homogenously distributed onto the inorganic matrix with reduced metallic agglomeration. The resulting bi-functional Au@TS-1 catalysts improved the performances for PO production using a fixed-bed reactor. Furthermore, due to the broad range of explosion limits of hydrogen and oxygen mixtures, which could be explosive with hydrogen concentrations between 3.8 and 95.5 mol% [30], the use of an inert gas becomes essential in order to dilute the mixture at the same time that equal molar amounts of hydrogen and oxygen are used.

In this sense, Laufer et al. [31] reported the use of solid bi-functional Pd@TS-1 catalysts in batch conditions, achieving higher C_3H_6 conversions with medium selectivities, claiming additionally the use of iridium and gold species as palladium promoters, although the better results were obtained when platinum nanoparticles were incorporated as promoters. Further investigations showed that the previous impregnation of the catalyst with the corresponding salts and the use of alcohols or ketones as solvent for the catalyst impregnation with metallic species improved the PO selectivity. Moreover, the autoreduction of Pd@TS-1 catalysts under pure nitrogen reduced the olefins hydrogenation with the reaction conditions, reducing the by-products formation. Similar Pd/Pt@TS-1 bi-functional catalysts were also employed by Jenzer et al. [32] in a tubular flow reactor, achieving also medium PO yields.

Nevertheless, the low yields obtained for the epoxidation of propylene with in situ generated H_2O_2 to direct PO formation, together with the associated difficulty to work with explosive mixtures of hydrogen and oxygen as reaction reagents, make realistically unfeasible the industrial scaled of this catalytic process, being indispensable to find possible alternatives to this one-pot two-step combined reaction in presence of solid bi-functional catalysts. Nowadays, the use of supercritical CO_2 ($scCO_2$) as a solvent in different reactions is receiving considerable attention due to its numerous advantages, including inactivity, low cost, no transfer limitations and high solubility [33]. In the case of direct PO production, the presence of CO_2 could provide a reaction medium capable to solubilize large quantities of gases, being possible to work in a non-flammable and safe environment in which to merge hydrogen and oxygen miscible with propylene and PO [34]. Although the supercritical CO_2 state is reached at 73.8 bar and 31 °C, the properties of $scCO_2$ in the region near the critical point ($Tr = T/Tc = 1.0–1.1$ and $Pr = P/Pc = 1–2$) are specially interesting. In this region, the single phase system has a density which enhances the dissolution power, the diffusivity of solutes is higher than in liquids and the viscosity is lower, enhancing mass transfer. These three properties make the reactants easier to reach the catalyst's active site [35]

In this way, Chen et al. [36] described the use of $scCO_2$ for the epoxidation of propylene with external H_2O_2 in presence of large grains of TS-1 as catalyst. On the other hand, the use of $scCO_2$ has also been reported by Chen et al. [37a] both for the synthesis of H_2O_2 and direct PO production from hydrogen and oxygen with promising results. In their research, it was shown that the addition of small volumes of methanol and water as co-solvents and the use of acidity inhibitors under $scCO_2$ conditions improved the PO selectivity and the yield of the reaction, using bi-functional Pd/Pt@TS-1 catalysts. Taking account the attractive results obtained, further studies would be necessary, using supercritical CO_2 as solvent to analyze its influence on the PO formation and the effect on reactivity of the heterogeneous catalyst that takes part in the reaction.

In the current study, several bi-functional materials based on Pd nanoparticles supported onto TS-1 nanocrystals have been prepared (Pd@TS-1) through different synthesis and deposition methods, followed by the evaluation of their catalytic activity for the PO production from hydrogen and oxygen. The Pd@TS-1 catalysts were able to carry out the one-pot two-step consecutive process where metallic nanoparticles catalyze the formation of H_2O_2 that is used as intermediate for propylene epoxidation catalyzed by TS-1 nanocrystals. The effect of supercritical CO_2 as solvent, during the reaction process, together with the use of additional co-solvents was considered, seeking to enhance and optimize the performances and selectivities to PO direct synthesis. The physico-chemical treatment of the bi-functional catalysts through the incorporation of Pt promoters and surface acidity inhibitors were also considered. The Pd(Pt)@TS-1 catalysts showed high stability, their regeneration and reuse being possible after consecutive catalytic cycles, partly recovering the initial activity.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of nanocrystalline TS-1

The preparation of TS-1 nanocrystals, used as inorganic support, was carried out by combination of micellar and hydrothermal synthesis methodologies [38].

Specifically, 2.0 g of Tween 20 (s.d. FINE CHEM.) were dissolved in 32 g of distilled water. This surfactant solution was added to 19.2 g of tetrapropylammonium hydroxide (TPA-OH, 32% aqueous solution) under mild stirring, resulting in the formation of a clear transparent solution. To the above micellar solution, 36 g of tetraethyl orthosilicate (TEOS, Aldrich) were added in a dropwise fashion under vigorous stirring. The stirring was continued for 1 h more. To this clear solution, 1.808 g of tetra *n*-butyl titanate (TNBT, Aldrich) in 9.12 g of isopropyl alcohol (IPA, s.d. FINE CHEM.) were added dropwise under vigorous stirring that was continued for another 1 h. The resulting mixture still remained clear. The mixture was then crystallized at 160 °C for 18 h under autogeneous pressure. The product was recovered by centrifugation, washed with distilled water and dried (100 °C, 12 h). The starting mixture has a molar composition as follows: 0.03 TiO_2:SiO_2:0.12 TPAOH:0.009 Tween 20:0.88 IPA:14.45 H_2O. The calcination was carried out in a muffle furnace at 550 °C for 3 h with a heating rate of 1.5 °C/min.

2.2. Metallic nanoparticles deposition

(Pd + Pt)@TS-1 catalysts were prepared following the methodology described by Hancu et al. [39] For instance, to prepare bifunctional catalyst containing 0.2% Pd and 0.02% Pt, 1.0 g of previously prepared and calcined TS-1 was placed in a glass flask and 5 mL of deionized water were added, followed by heating the solution up to 80 °C under continuous stirring. To this mixture, 36 μL of $[Pd(NH_3)_4](NO_3)_2$ (Strem Chemicals) 15%wt aqueous solution and 0.34 mg of $[Pt(NH_3)_4]Cl_2$ (Aldrich) were added. These amounts were changed depending on the desired catalyst. The mixture was stirred for 24 h, the solid obtained was filtered and washed with deionized water and it was finally dried at 60 °C overnight. Then, it was calcined at 150 °C for 4 h and reduced by H_2 at room temperature for 4 h. In the case of Pd@TS-1 catalysts, the procedure was the same but Pt complex was not added.

The general acronym of the synthesized bi-functional catalysts was Pd*xx*@TS-1, being *xx* indicative the palladium amount, percentage in weight, supported onto TS-1 support, i.e., 02, 04, 05 and 10 would correspond to 0.2%wt, 0.4%wt, 0.5%wt and 1.0%wt of Pd, respectively. When platinum promoter was also supported onto inorganic matrix, Pd*xx*(Pt)@TS-1 was the acronym used during the discussion. In these samples, the content of platinum corresponded approximately to 10%wt of palladium content.

2.3. Catalysts characterization

XRD analysis was carried out with a PANalytical X'Pert PRO diffractometer in the Bragg–Brentano geometry using Cu Kα radiation. C, N and H contents were determined with a Carlo Erba 1106 elemental analyzer, while Pd and Pt contents were obtained by means of atomic absorption spectroscopy (Spectra AA 10 Plus, Varian). A Cary 5 spectrometer equipped with a diffuse reflectance accessory was used for UV measurements. Volumetric analyses were performed by nitrogen adsorption isotherms at 77 K with a Micromeritics ASAP2010. Before the measurements, the samples were outgassed for 12 h at 100 °C. The BET specific surface area [40] was calculated from the nitrogen adsorption data in a relative pressure range from 0.04 to 0.2. The total pore volume [41] was obtained from the amount of N_2 adsorbed at a relative pressure of ~0.99. External surface area and micropore volume were estimated with the *t*-plot method in the *t* range from 3.5 to 5. The pore diameter and the pore size distribution were obtained following the Barret–Joyner–Halenda (BJH) method [42] on the adsorption branch of the isotherms. Scanning and transmission electron microscopies (SEM and TEM) characterization were carried out in a JEOL6300 and Philips CM10 (100 kV) microscopes, respectively. Before TEM observation, the samples were prepared by suspending the solid in water, ultrasonicating for 15 min and placing one drop on a carbon-coated copper grid (300 mesh).

2.4. Catalytic tests

The experiments for the synthesis of PO from propylene, employing external H_2O_2 as oxidant, were performed in a 3 mL round bottom glass reactor in which the stirring was driven by a Teflon-coated magnetic stirrer. Known amounts of catalyst (2.5 mg), methanol (1.2 g), and propylene (9 mmol) were added, followed by the addition of the oxidant, 35%wt H_2O_2 in water (0.4 mmol). Then, the mixture was heated at 60 °C, and the reaction was carried out for 5 h. Different samples were taken during the reaction, and were analyzed with a gas chromatographer Fisons GC8000 provided with a flame ionization detector (FID) and a 60 m length 0.25 mm ID, 0.25 μm df. Rtx-Wax column.

The experiments for the direct synthesis of PO with in situ generated H_2O_2 were carried out in a 15 mL stainless steel autoclave coated with a Teflon beaker and with a relief valve, for safety. The stirring was driven by a Teflon-coated magnetic stirrer. Known amounts of catalyst (15 mg), acidity inhibitor (ammonium acetate, 0.01 g) and co-solvent (0.2 g of MeOH or a 50/50 mixture of MeOH/H_2O) were added to the reactor, followed by the addition of propylene (2 mmol) and CO_2. Known amounts of oxygen and finally hydrogen were then added to the reactor, which was then heated up until the desired temperature, the critical point (73.8 bar and 31 °C) being surpassed. The reaction experiments were carried out for 5 h, unless otherwise stated. After that time, the reactor was cooled down using a mixture of acetone and ice, and the pressure was slowly released by venting, recovering the gaseous mixture in an inert gas sampling bag. 3-pentanone was used for recovering any product that could be in the walls of the reactor, avoiding the employment of acetone because could be a possible by-product.

The amount of formed products, i.e., propylene oxide, acetone, propionaldehyde, acrolein, isopropanol, 1-methoxy-2-propanol (MP1), 2-methoxy-1-propanol (MP2), propylene glycol (PG) and propylene carbonate were then analyzed using a Fisons Gas chromatograph GC8000 provided with a FID detector and a 60 m length 0.25 mm ID, 0.25 μm df. Rtx-Wax column. The amounts of propane and un-reacted propylene, oxygen and hydrogen were analyzed using a Bruker 450-GC which contains two different independent channels. The first one is provided with a thermal conductivity detector (TCD) and 3 different columns: Hayesep N (0.5 m length), Hayesep Q (1.5 m length) and a molsieve 13× (1.2 m length), employing argon as carrier. The second one is provided with two different flame ionization detectors (FID) and 3 different columns: a capillary column CP-Wax (1 m length and 0.32 mm ID), a CP-Porabond Q (25 m length and 0.32 mm ID) and other CP-Wax (5 m length and 0.32 mm ID).

Due the extensive list of possible by-products that have been reported in literature for this kind of reaction, all the products have been calibrated using mixtures with known composition. All the products in the liquid phase have been identified by GC–MS and by GC with commercial samples.

Table 1
Chemical analyses and textural properties of Pd(Pt)@TS-1 samples.

Samples[a]	Ti (%wt)	Pd (%wt)	Pt (%wt)	S_{BET} ($m^2 g^{-1}$)	S_{MICRO}[b] ($m^2 g^{-1}$)	V_{TOT} ($cm^3 g^{-1}$)	V_{MICRO} ($cm^3 g^{-1}$)
TS-1	1.99	–	–	416	271	0.298	0.132
Pd02	2.00	0.23	–	391	236	0.315	0.116
Pd02(Pt)	1.85	0.18	0.03	391	242	0.319	0.120
Pd04(Pt)	1.81	0.40	0.10	397	251	0.379	0.123
Pd05(Pt)	2.00	0.50	0.09	396	244	0.376	0.120
Pd10(Pt)	1.98	1.03	0.13	387	240	0.319	0.118

[a] Number after Pd indicates the theoretical Pd loading (0.2%wt, 0.4%wt, 0.5%wt and 1.0%wt). Theoretical Pt loading was approximately 10%wt of Pd content. All samples were supported onto TS-1 zeolite.
[b] From *t*-plots curves.

3. Results and discussion

3.1. Synthesis and characterization of catalysts

The bi-functional Pd@TS-1 catalysts were based on palladium nanoparticles supported onto nanocrystalline titanium silicalite TS-1 which exhibited a double function, as inorganic matrix and epoxidation catalyst of olefins. The modification with metallic promoters, such as platinum species was also considered to improve the catalytic activity of the solids (Pd(Pt)@TS-1).

The preparation of TS-1 nanocrystals was carried out by combination of micellar and hydrothermal routes in presence of surfactants which facilitate the formation of small crystallites during the synthesis process [38]. XRD diffractograms clearly evidenced that the as-synthesized and calcinated phases, removing organic structural directing agents, corresponded to crystalline TS-1 zeolite, showing the characteristic diffraction bands of MFI-type materials (Fig. 1). The alkaline media present in the synthesis gel favored the formation of charged small nuclei which were probably surrounded by surfactant molecules, avoiding crystal growth. In fact, TS-1 nanocrystals with ~600 nm of size and containing very elevated titanium content (Si/Ti = 35, ~2.0%wt) were obtained (Table 1). In these samples, the totality of the titanium was tetrahedrally coordinated into the zeolitic framework, this fact being important to remark because it was reported that when high amounts of titanium are incorporated, significant octahedral extra-framework titanium was obtained, which is not active for epoxidation processes [43,44]. UV–vis analysis and SEM inspection confirmed the coordination state of the titanium on one hand, and the size distribution of the TS-1 crystals on the other, as shown in Fig. 2. The textural properties obtained from nitrogen adsorption showed that the nanocrystalline TS-1 was microporous exhibiting a type I plate isotherm characteristic of conventional 3D microporous zeolites (Fig. 3 and Table 1).

Bi-functional Pd@TS-1 materials were obtained through the deposition of palladium species (from 0.2% to 1.0%wt) by impregnation methodologies onto nanocrystalline TS-1 zeolite, used as supporting matrix. The incorporation of additional metallic promoters was similarly carried out merging palladium and platinum salts. Following this procedure, several Pd@TS-1 and Pd(Pt)@TS-1 materials were prepared with different loading of metallic species in function of metallic salts amount used during the synthesis process. The chemical content of the different samples prepared is shown in Table 1, being observed that the titanium content of TS-1 support (~2%wt) was not modified by the presence of metallic species.

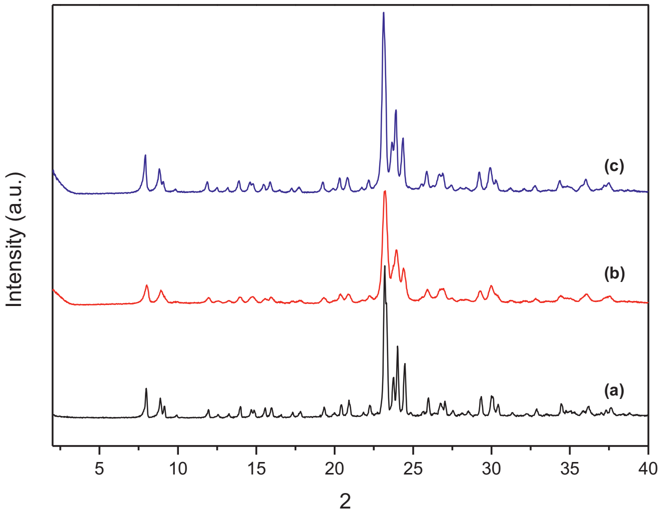


Fig. 1. XRD patterns of (a) purely siliceous MFI-type zeolite, (b) as-synthesized TS-1 and (c) calcinated TS-1.

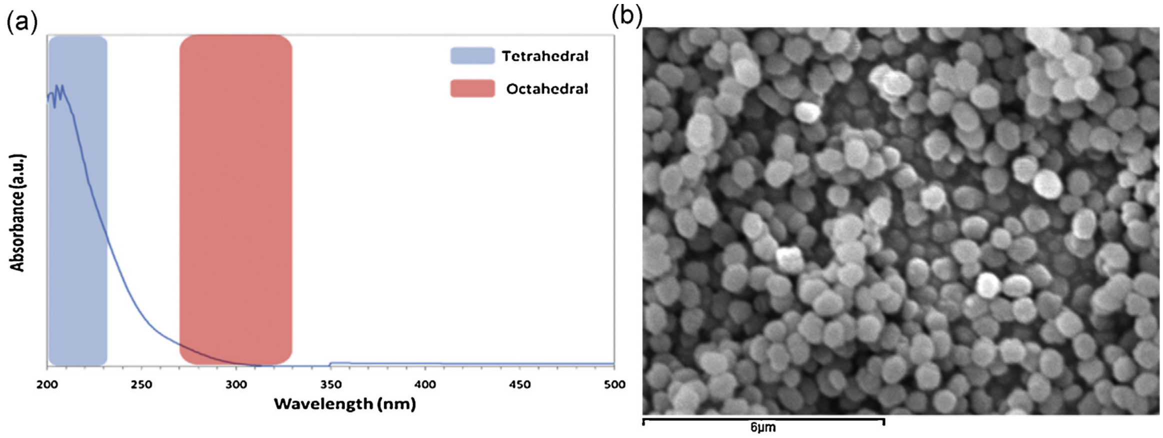


Fig. 2. UV–vis spectrum (a) and SEM micrographs (b) of calcinated TS-1 obtained through combined hydrothermal and micellar routes.

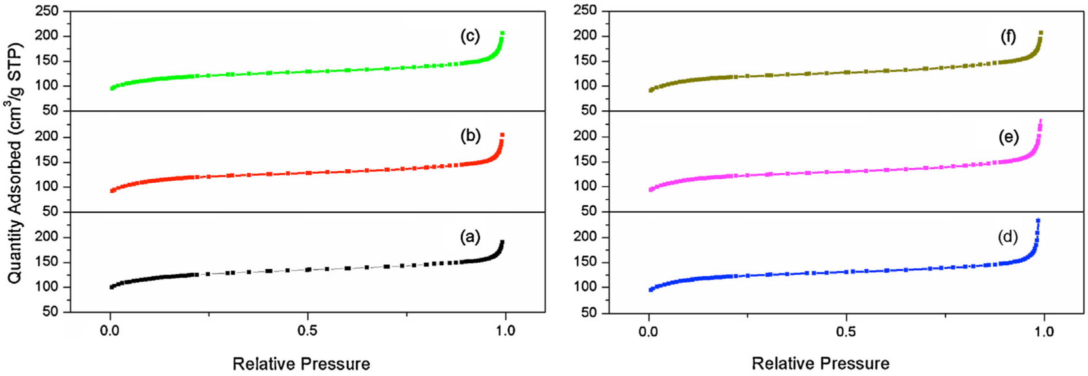


Fig. 3. N_2 isotherms of TS-1 and Pd(Pt)@TS-1 samples: (a) TS-1, (b) Pd02@TS-1, (c) Pd02(Pt)@TS-1, (d) Pd04(Pt)@TS-1, (e) Pd05(Pt)@TS-1 and (f) Pd10(Pt)@TS-1.

Furthermore, the crystallinity of the zeolitic phase remained unmodified after the palladium and/or platinum deposition, such as it is confirmed by XRD patterns of the different Pd(Pt)@TS-1 samples which maintain the diffraction bands characteristics of MFI-type zeolites without formation of silica amorphous phases (Fig. 4). It is important to point out that the deposition methodology followed to incorporate metallic species did not imply the generation of extra-framework titanium species because all spectra of the bifunctional samples showed only one band focused at ~200 nm, indicating the majority presence of titanium inserted into the TS-1 network (Fig. 5). Only a slight reduction in the total surface area and microporous volume was detected in the samples when palladium and/or platinum species were finally supported onto inorganic zeolitic matrix (Table 1), probably due to the partial blockage of more accessible pores due to the presence of metallic nanoparticles, exhibiting in all cases type I isotherms characteristic of microporous zeolitic materials (Fig. 3). This fact confirmed that the textural properties were not substantially modified due to the presence of supported metallic nanoparticles. From SEM micrographs, it was observed that the TS-1 morphology of the samples was preserved although palladium or platinum nanoparticles were deposited onto the zeolitic support, the TS-1 nanocrystals being in all cases observed around 600 nm of size. The TEM micrographs clearly evidenced the formation of palladium nanoparticles homogeneously dispersed along the inorganic matrix, exhibiting diameters focused at ~10–20 nm, without observing agglomeration phenomenon between metallic nanoparticles although the metallic content was increased (Fig. 6).

3.2. Catalytic activity

Preliminary batch catalytic tests, using nanocrystalline TS-1 zeolite as catalyst from external H_2O_2 and propylene, were performed to produce PO. The results obtained clearly confirmed the high reactivity of the titanium silicalite TS-1 zeolite support to catalyze the epoxidation of propylene catalysts and the high efficiency of the process to obtain elevated PO yields (~80–85%) with high selectivity (~95–98%). This fact evidenced the validity of nanocrystalline TS-1 materials to be used as active supports to generate effective bi-functional catalysts after the incorporation of palladium and/or platinum nanoparticles. Moreover, the hydrothermal stability of the nanocrystalline TS-1 zeolite support was additionally studied through several catalytic runs carried out with the same sample. Specifically, in Fig. 7, it was observed that the PO

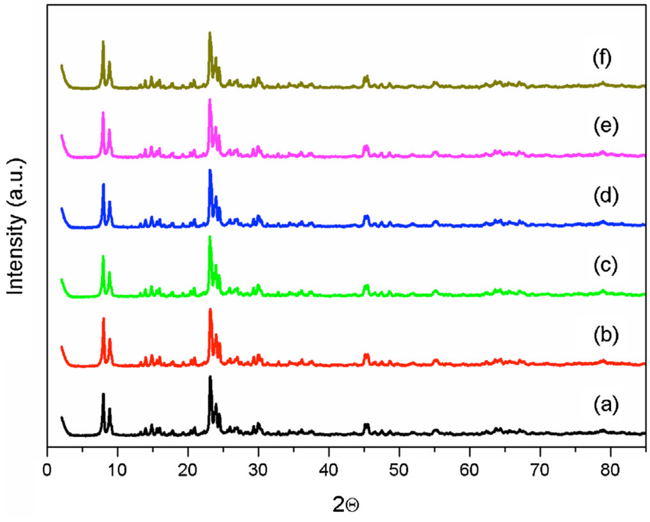


Fig. 4. XRD of different samples: (a) TS-1, (b) Pd02@TS-1, (c) Pd02(Pt)@TS-1, (d) Pd04(Pt)@TS-1, (e) Pd05(Pt) and (f) Pd10(Pt)@TS-1 samples.

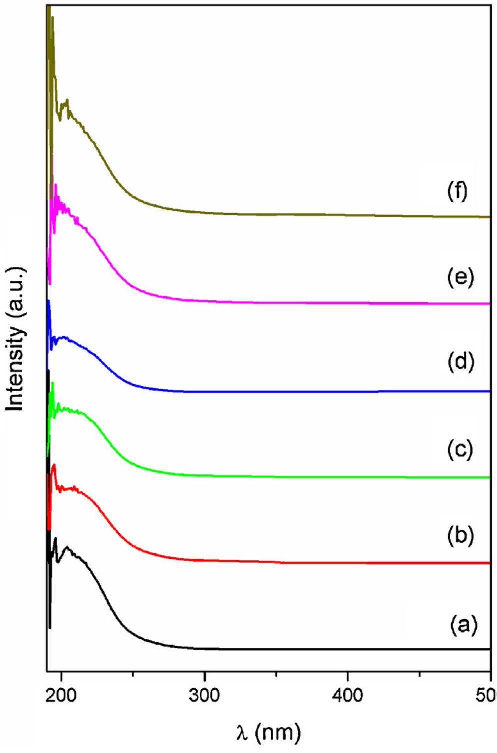


Fig. 5. UV of Pd(Pt)@TS-1 samples: (a) TS-1, (b) Pd02@TS-1, (c) Pd02(Pt)@TS-1, (d) Pd04(Pt)@TS-1, (e) Pd05(Pt)@TS-1 and (f) Pd10(Pt)@TS-1.

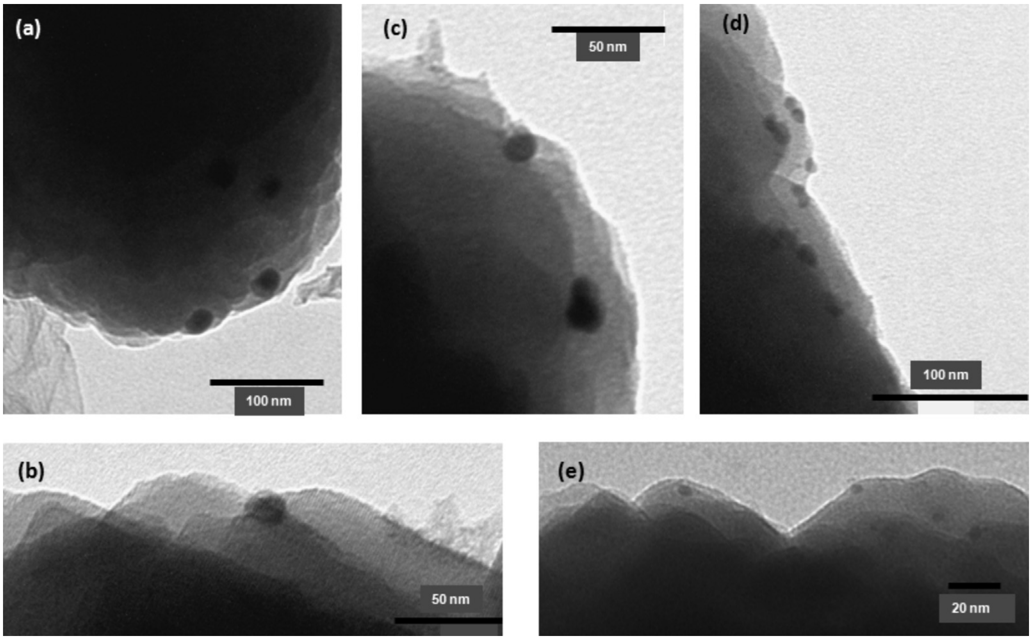


Fig. 6. TEM micrographs of (a) Pd02(Pt)@TS-1, (b) Pd02@TS-1, (c) Pd04(Pt)@TS-1, (d) Pd04(Pt)@TS-1 and (e) Pd10(Pt)@TS-1 samples.

yield obtained after the first reuse of catalyst is similar compared with the results led by the activated fresh TS-1 catalyst. During the different reuses, it was observed that PO selectivity remained stable, although the catalytic activity at short times decreased. However, even if its activity slightly decreased, longer reaction times led to complete conversion of H_2O_2 in the presence of propylene to produce PO. In general, these results corroborated that the TS-1 zeolite, used as active supporting matrix in the following two-step reactions, was catalytically effective, stable and active after several catalytic runs, without observing a substantial activity loss.

Considering these previous results, the next step was the study of the catalytic processes for the direct epoxidation of propylene with in situ generated H_2O_2, during one-pot two-step reaction process (Scheme 1). With this purpose, batch catalytic tests were carried out for the direct PO production from directly hydrogen, oxygen and propylene, using before characterized bi-functional Pd(Pt)@TS-1 nanocrystalline materials as catalysts. It is important to point out that it is characteristic of this type of consecutive process that when high yields to PO are obtained, also an increase in the amount of by-products formed during the reaction is observed, and high selectivities are only obtained at low propylene conversions, especially when gold is employed as metal for the H_2O_2 synthesis from H_2 and O_2, in gaseous phase [28,45]. When Pd catalysts have been tested under gaseous phase, no PO production has been observed [19] or very low yields have been obtained [46]. Specifically, in Scheme 2, the most typical by-products formed are shown, indicating the reaction pathway followed in each case. In this scheme are marked, the by-products detected in the catalytic tests carried out in this work, this information being necessary to correctly estimate the associated yield and selectivity to PO generation.

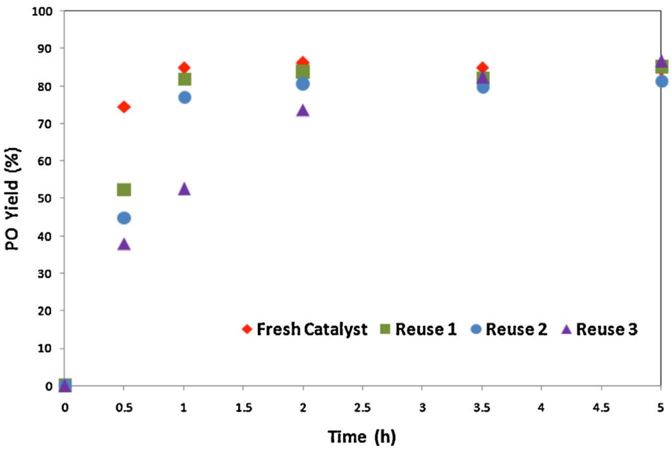
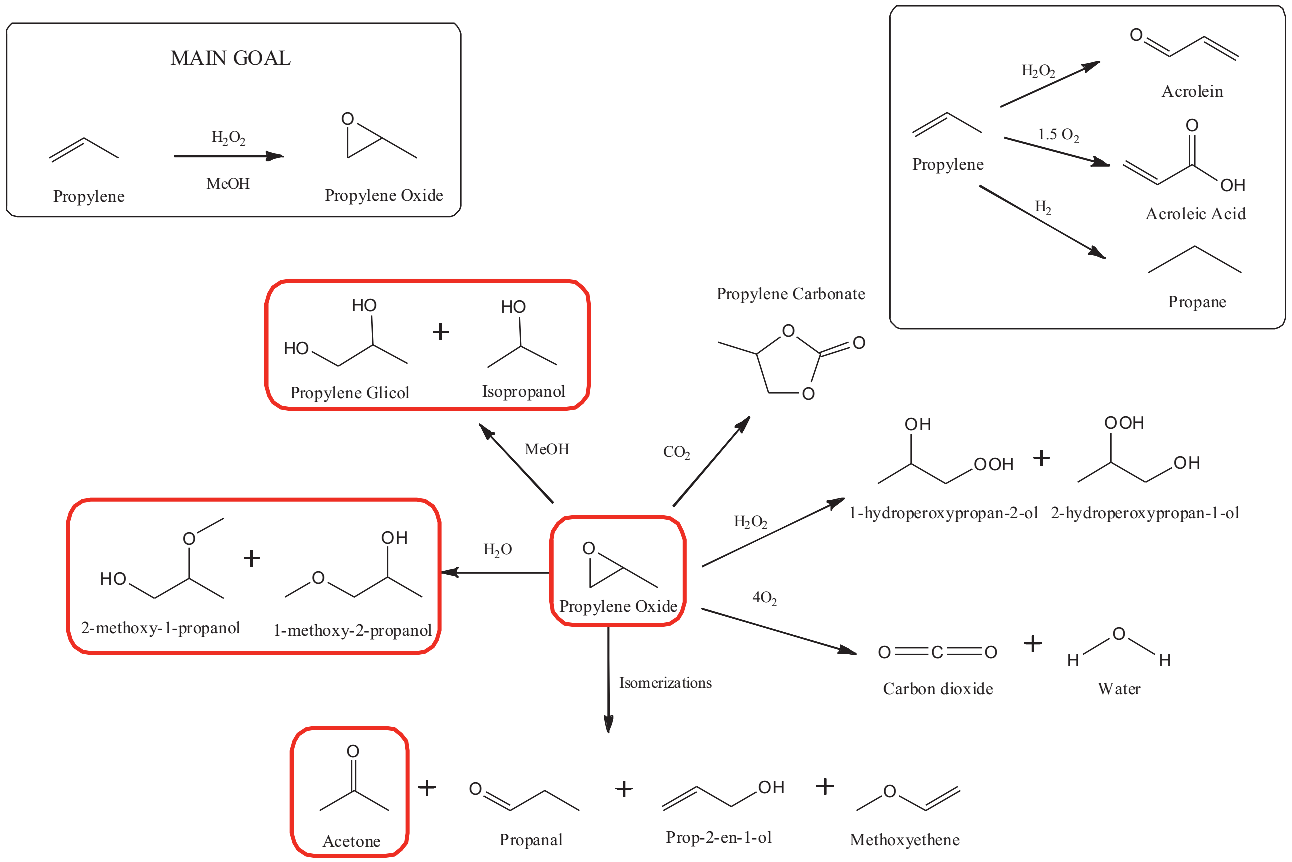


Fig. 7. Catalytic activity and reuses of a TS-1 zeolite support prepared by micellar route. The amount of the H_2O_2 was externally added according to the amount of the weight of catalyst used in each reuse. On average, $R_{H_2O_2}/\mathrm{Ti} = 120$. Propylene is added in excess, using H_2O_2 as limiting reactant. Reaction conditions: 14 bar of pressure, 55 °C, 5 h reaction time.

Due to the high number of possible products that could be obtained in the reaction, it is decisive to find the most favorable reaction conditions, using bi-functional solid catalysts, for both the in situ generation of H_2O_2 and the consecutive epoxidation of propylene, in order to obtain high PO yield and selectivity, avoiding the by-products formation. Supercritical CO_2 ($scCO_2$) has been claimed to be a good solvent for the direct production of PO, enhancing also the H_2O_2 efficiency for the epoxidation reaction [36]. For this reason, $scCO_2$ conditions were used in presence of bi-functional Pd(Pt)@TS-1 catalysts. The reactions were carried out up to 80 bar and 60 °C, in supercritical conditions, according the best results described at literature [37b].

The catalytic results showed that the bi-functional Pd(Pt)@TS-1 catalysts were able to produce H_2O_2 from H_2 and O_2 that reacted with the propylene to generate PO, using CO_2 as solvent and in absence of another co-solvents (entry 1, Table 2). Specifically, when the reaction process was carried out with Pd(Pt)@TS-1 catalyst, the conversion of propylene was high (~52%), although the PO selectivity was low (~6%), propane being the main reaction product, although methoxypropanols and propylene glycol were also detected. However, the formation of high amounts of undesirable by-products was not avoided which implied reduced PO productivities (entry 1). With the objective to improve these results, different reaction parameters were considered such as the incorporation of additional co-solvents together with the presence of metallic promoters.



Scheme 2. Possible by-products formed during the direct PO formation through the in situ generated H_2O_2. In red, the by-products detected in this work. Some products could be generated from more than one reaction pathway. (For interpretation of the references to color in this scheme legend, the reader is referred to the web version of the article.)

It is described into the literature that the addition of small amounts of promoters in the catalyst increased the production of PO [32]. For this, some TS-1 catalysts, containing Pd and Pt as metallic species, were prepared and tested on different conditions, using MeOH as co-solvent in the reaction medium. The results obtained showed that better performances were obtained with the Pd02(Pt)@TS-1 catalyst in presence of MeOH, achieving PO selectivities and yields of ~19% and ~10%, respectively (entry 2). However, the formation of high amounts of undesirable by-products (methoxypropanols and propylene glycol) was not avoided which implied reduced PO productivities. In general, these data clearly confirmed the benefits of the use of metallic promoters and co-solvents for the PO production with in situ generated H_2O_2 in supercritical CO_2 conditions, being detected that the use of water as additional co-solvent substantially worsened the catalytic results (entry 3).

Despite the fact that the use of MeOH as co-solvent effectively enhanced the formation of PO, propane still was the main product. Moreover, it is known that the acidity of the TS-1 surface promoted the decomposition of the produced PO, leading to by-products [31]. Additional water was also formed during the one-pot reaction and, consequently, H_2CO_3 formation is favored in presence of CO_2 which increases the medium acidity, facilitating the decomposition of PO, especially if MeOH was used as co-solvent and favoring the production of ring-opening products, such as methoxypropanols, dropping the PO selectivity. Taking in account all these considerations, the reaction was carried out in the presence of acidity inhibitors such as ammonium acetate, which is a well-known pH-controller buffer.

Table 2
Catalytic tests carried out with in situ generated H_2O_2 using supercritical CO_2 conditions in presence of Pd(Pt)@TS-1 catalysts[a].

Entry	Catalyst @TS-1	Solvent	$C_3^{=}/H_2/O_2$ [b]	$X_{C3^{=}}$ [c]	S_{PO} [d]	S_{MP} [d]	S_{PG} [d]	S_{C3} [d]	Y_{PO} [e]
1	Pd02(Pt)	–	1/1.5/1.3	52.5	6.1	–	1.0	92.7	3.2
2	Pd02(Pt)	MeOH	1/1/1.5	53.0	19.1	10.3	1.4	68.8	10.1
3	Pd02(Pt)	MeOH + H_2O	1/1.8/1.1	47.0	7.0	19.0	7.0	67.0	3.3
4	Pd02(Pt)	MeOH + H_2O + AI[f]	1/1.5/1	24.3	40.1	0.5	1.1	56.3	9.7
5	Pd02(Pt)	MeOH + H_2O + AI	1/1.3/1.2	14.5	70.7	3.5	2.0	21.2	10.3
6	Pd02	MeOH + H_2O + AI	1/1.3/1.1	11.4	72.3	3.9	1.8	22.0	8.2
7	Pd05(Pt)	MeOH + H_2O + AI	1/1.3/1.2	13.7	70.0	3.5	1.8	24.2	9.6
8	Pd10(Pt)	MeOH + H_2O + AI	1/1/1.2	10.1	74.7	3.7	3.5	17.7	7.5

[a] Reactions were carried out for 5 h with pressures around 80 bar and 60 °C, feeding 2 mmol of propylene and 15 mg catalyst.
[b] Gaseous molar ratios.
[c] Propylene conversion.
[d] Propylene oxide, methyl propanols, propylene glycol and propane selectivities.
[e] Propylene oxide yield.
[f] Acidity Inhibitor (CH_3COONH_4).

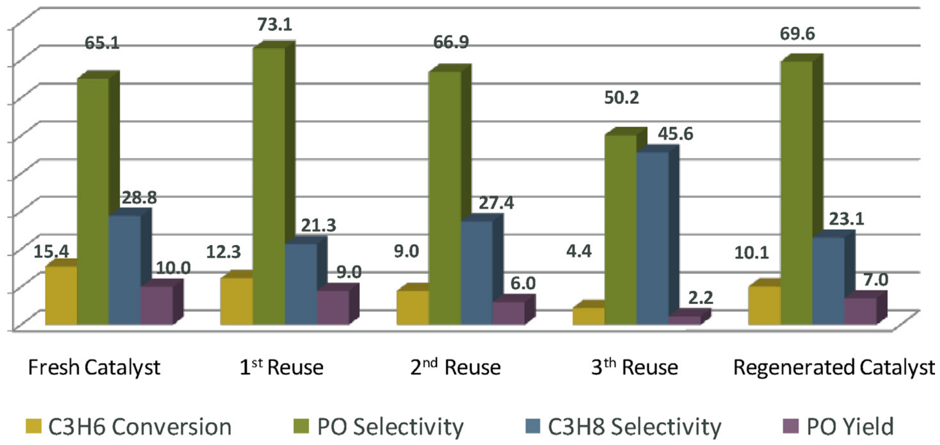


Fig. 8. Catalytic reuses for PO direct production through in situ generated H_2O_2, using Pd04(Pt)@TS-1 catalyst.

In this case, the acidity was effectively controlled during the reaction process, decreasing the formation of methoxypropanols and propane which were promoted in acidic medium. In fact, the results in Table 2 showed that the use of this acidity inhibitor enhanced the formation of PO (yields of ~10%), achieving selectivities up to 40% due to the minimization of PO ring opening phenomenon, using Pd02(Pt)@TS-1 catalyst (entry 4).

On the other hand, the $C_3^{=}/H_2/O_2$ ratios used during the catalytic tests were also analyzed, being observed that when higher amounts of O_2 than H_2 were used in the reactor batch, and in presence of MeOH, H_2O and acidity inhibitor, propane formation, i.e., the main hydrogenation product, was markedly reduced (entries 4 and 5). Particularly, improved results were obtained when $C_3^{=}/H_2/O_2$ molar ratios of approximately 1/1/1 were used during the combined catalytic process, achieving PO selectivities close to 70% with PO yields maintained around of 10% (entry 5). Moreover, the benefits of the metallic promoters was corroborated because the catalytic activity of Pd02@TS-1 sample, without platinum nanoparticles, tested in the most suitable reaction conditions, implied a slight reduction in the total propylene conversion that worsened the final PO yield (entry 6).

Taking into account that the presence of metal nanoparticles was necessary for the generation of H_2O_2 from H_2 and O_2, the amount of metals deposited onto the TS-1 support was also studied in order to obtain as much H_2O_2 as possible, at the same time that selectivity to PO in the epoxidation of propylene remained high. For this, several bi-functional catalysts with different Pd loading (0.5% and 1.0%wt of Pd) were checked, being observed that the PO selectivity was maintained (~70%) but associated to progressive propylene conversion decrease (entries 5 and 7). This phenomenon was more marked when the palladium loading was higher, decreasing the PO yield up to 7%, approximately (entry 8). These results showed that it was more convenient the use of catalysts with palladium content lower than 0.5%wt which exhibiting metallic nanoparticles with diameters around 15–20 nm (Fig. 6).

Finally, the stability of the bi-functional Pd(Pt)@TS-1 catalysts was evaluated through three consecutive catalytic cycles. After each reuse, the catalyst solid was recovered and exhaustively washed with methanol. The results obtained showed that, overall after the third reuse, an appreciable decrease in the PO selectivity and propylene conversion were observed, confirming a partial deactivation of bimetallic supported catalysts (Fig. 8). This fact could be associated to incorporation of organic compounds, from reaction media, during the catalytic process which blocked several active sites. When these surface organic species were removed through thermal treatments the regenerated and reactivated bi-functional catalyst recovered, at least partially, its initial activity (Fig. 8).

4. Conclusions

Promising results were obtained to direct propylene oxide (PO) production through one-pot two-step consecutive process from hydrogen, oxygen and propylene, using supercritical CO_2 conditions in batch reactors in presence of optimal bi-functional catalysts, based on palladium nanoparticles supported onto nanocrystalline titanium silicalite zeolite (Pd@TS-1). These catalysts were prepared and characterized, being active and reusable to carry out the two-step process in which metallic nanoparticles catalyzed the generation of in situ hydrogen peroxide as intermediate product for propylene epoxidation catalyzed by TS-1 active matrix. The combined process was performed in presence of only one solid and recyclable catalyst without necessity to use separated catalytic processes, avoiding additional steps related with the removing or separation of sub-products and/or intermediate substrates. All these facts would imply a higher efficiency of global catalytic route inside of more sustainable and environmental combined process. Further improvements were achieved through the modification of different reaction parameters, being concluded that use of methanol as co-solvent, presence of acidity inhibitors, incorporation of platinum nanoparticles as promoters (Pd(Pt)@TS-1) and employ of high amounts of oxygen in the reaction media increased the PO yields (~10%) and selectivities (~70%), always working in supercritical CO_2 conditions. Partial deactivation of the catalysts was observed during successive catalytic cycles probably due to adsorbed organic compounds during the catalytic process, being possible their regeneration after thermal treatments.

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