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Selective continuous flow phenylacetylene hydrogenation over Pd-biogenic calcium carbonate

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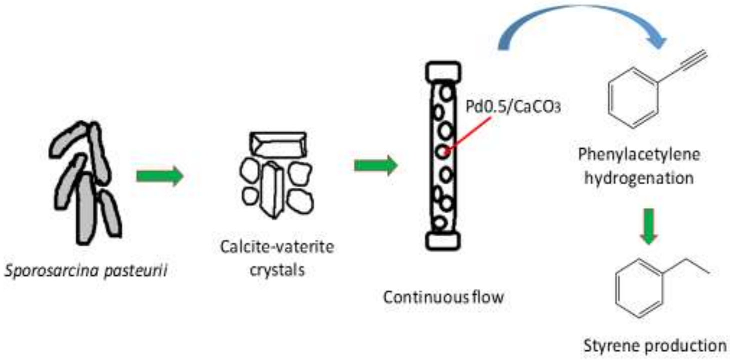
Graphical Abstract



Highlights

- Biogenic $CaCO_3$ was obtained from *Sporosarcina pasteurii* isolated from agricultural soils.
- $CaCO_3$ impregnated with Pd 0.5% was an effective catalyst in the continuous phenylacetylene hydrogenation.
- Under optimized conditions, 30°C, flow rate 1mL/min and 10 bar pressure, a styrene yield of 65% was reached.
- Pd0.5/$CaCO_3$ was stable along twelve hours on stream with any decrease in the catalytic performance.

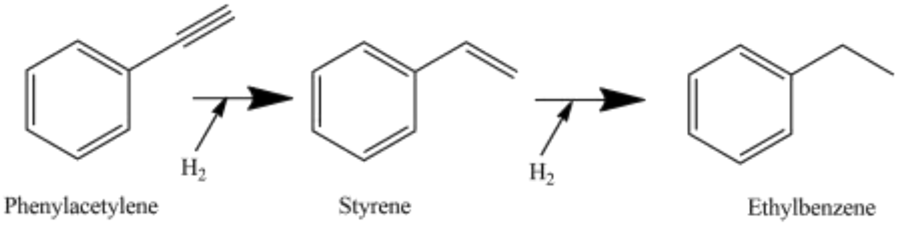
Abstract

$CaCO_3$ obtained from *Sporosarcina pasteurii* isolated from agricultural soils has been employed as catalytic support for Pd that was subsequently loaded on $CaCO_3$ by wet impregnation with a metal loading of 0.5 wt.% using Palladium acetate as precursor. The materials were characterized via nitrogen physisorption measurements, X-ray diffraction, X-ray photoelectronic spectroscopy, TGA Analysis and TEM microscopy. Pd0.5/$CaCO_3$ was able to successfully hydrogenate phenylacetylene into styrene and ethylbenzene as products. Thus, through the proper optimization of the reaction conditions (flow rate, temperature, pressure) it was possible lead the reaction towards the selective production of styrene, a monomer widely used in the polymer industry, from phenylacetylene as starting material in yields up to 65 %.

Keywords: Biomaterials, continuous flow, hydrogenation reactions, *Sporosarcina pasteurii*, Styrene.

1. Introduction

The hydrogenation of carbon-carbon multiple bonds has been widely used in industrial and chemical processes for the production of high added-value chemicals. In this sense, the selective hydrogenation of alkynes to alkenes minimising alkanes production has been widely investigated due to its importance for both agrochemical and petrochemical industry [1,2]. In particular, styrene (ST) is a relevant monomer for the production of polystyrene and other synthetic rubbers such as Acrylonitrile Butadiene Styrene (ABS) resin, commonly used in 3-D printers, and styrene-butadiene that owns good abrasion resistance [3,4]. Industrially, styrene can be obtained by ethylbenzene oxidative dehydrogenation as well as by extractive processes in the gasoline pyrolysis (pygas, byproduct of naphtha cracking process) [5]. In the recent years, research efforts has been focused on this area due to the high styrene production from pygas, since a plant with an annual production capacity of 1 million tons of ethylene can produce about 24-42 kilo tons of ST per year [5]. However, raw material contains small amounts of phenylacetylene (PA) that causes problems in process control and increases production costs. Such difficulties root in the difficult separation of PA from ST because of their similar chemical properties. Therefore, the most effective way to separate them is to carry out a PA selective hydrogenation, process that converts completely PA into styrene avoiding ethylbenzene production (Scheme 1) [6].



Scheme 1. Illustrative representation of the hydrogenation of phenylacetylene towards the different products, styrene and ethylbenzene.

For this reductive approach palladium based heterogeneous catalysts are quite efficient due to their high dissociation energy for molecular hydrogen [7,8]. With this respect, Lindlar catalyst is the most used in this reaction and it is formed by palladium supported in calcium carbonate doped with lead, which improves the selectivity by catalyst poisoning due to the deactivation of some palladium active sites. However, the high toxicity related to lead limits Lindlar catalyst use [9] boosting the research towards different alternatives. For this reason, different supports and catalysts for selective phenylacetylene hydrogenation have been reported. For instance, Akhmedov et al. [4] investigated the use of metal-free graphite-like carbon nitrides in the selective PA hydrogenation to ST in gas phase, obtaining conversion values up to 85.5% with a styrene selectivity of 76.4% at 250°C and 2 bar of H_2 pressure. However, the main limitation of such approach was the high temperature required, which lead to increased production costs. Another interesting option for PA hydrogenation was the use of titanium oxide as support loaded with Pd by photodeposition, obtaining a conversion and selectivity of 85 and 100%, respectively [7]. In addition, the use of mesoporous materials as support has been studied by Yang et al. [6], who studied PA hydrogenation reaction with several mono- and bimetallic catalysts such as Ni and Ni-M (M = Zn, Ga, Cu, or Fe) over SBA-15 aluminosilicates in a semi-batch reactor at 40°C and 1 bar H_2 pressure. Among them, the results showed that best performance was obtained through the use of $NiZn_3$/AlSBA-15 catalyst with a high selectivity towards the production of styrene (90.3%) and a phenylacetylene conversion of 99.6%, after 16 hours of reaction. In addition, alumina was investigated by Hu et al. [10] that carried out PA hydrogenation reaction using a Pd loading of 0.5 wt.% on the catalyst in a batch reactor at 50°C and 1 bar of H_2; showing a conversion of 98% and 70% of selectivity towards the production of styrene. The effect of Pd particle size was investigated by Markov et al. [11] in a Pd/Al_2O_3 catalysts (with Pd loading of 1 wt.%), varying particle size from 1.5 to 22 nm, with 5 bar H_2 pressure and room temperature (25°C), leading to PA conversion values that ranged from 25 to 100% and selectivity between 83 and 97%. Also, bifunctional Zn-Ti layered-double hydroxides modified with PdAu alloy was used as catalyst in the PA hydrogenation reaction, achieving high styrene selectivity (over 90%) and quantitative phenylacetylene conversion after 6 hours at 45 ºC using molecular hydrogen that was continuously circulated with a 10 mL/min flow [12].

In the context of Green Chemistry, we developed a novel biogenic carbonate to be used as support using a methodology eco-compatible that avoids thermal treatments to obtain supports. The methodology is very simple and involves the microbial induced carbonate precipitation (MICP) which commonly has been employed to

adsorb metals [13-16]. MICP employs a bacterium that secretes metabolic products (CO_3^{-2}) that react with ions (Ca^{2+}). The formation of CO_3^{-2} occurs via enzymatic through urea hydrolysis. To remove all organic matter is employed alcoholic solvents with NaClO. Thus, it is possible to produce large homogenous quantities of $CaCO_3$ with a strict morphology control. However, the use of biogenic calcium carbonate impregnated with metals as catalyst remains unexplored. In this sense, from a practical point of view, biogenic $CaCO_3$ application is attractive in industrial reactions due to advantages such as simple separation, high chemical and thermal stability.

$CaCO_3$ is used as support in the Lindlar catalyst with 1%w/w of Pd, however, lead content is this catalyst makes it toxic, while biogenic calcium carbonate can be an adequate support in PA reaction with high conversion and selectivity. Thus, in this work we report the preparation Pd by wet impregnation supported on biogenic $CaCO_3$. The synthesized material was investigated in the continuous flow hydrogenation of phenylacetylene to styrene. Interestingly, the proper tune of the reaction conditions (flow rate, temperature and hydrogen pressure) helps to improve the reaction control, leading to improved selectivity towards the desired reaction product, styrene in this case.

2. Experimental

2.1 Materials

Palladium (II) acetate (99.8%), phenylacetylene (PA) (98%) and toluene were purchased from Sigma Aldrich (Berlin, Deutschland). They are analytical grade and used without any further purification.

2.2 Catalyst preparation

Biogenic calcium carbonate was produced by *Sporosarcina pasteurii* was isolated from agricultural soils from Boyacá (Colombia) according to protocol previously established by Al-Thawadi and co-workers [17]. The strain was molecularly identified by amplification of the 16 S ribosomal gene (**Fig. A.1**). Bacteria growth in nutrient broth with urea (1M) at 30°C, 200 rpm during 24 h. After fermentation, $CaCl_2$ 1M was added in media and it was mixing during 5 hours to $CaCO_3$ crystal formation. After an hour settling, calcium carbonate was recovered by centrifugation (6000 rpm during 15 min) and washed three times with distilled water. Subsequently, the sample was treated for 12 hours with sodium hypochlorite (30 mL) to reduce organic fraction. Finally, $CaCO_3$ was mixed with ethanol to remove hydrophobic particles in the sample and the final biogenic calcium carbonate was obtained by drying at 80°C along 24 hours.

Supported Pd catalyst was prepared by the wet impregnation method using biogenic $CaCO_3$ synthesized in the preceding step as the support and palladium (II) acetate ($C_4H_6O_4Pd$) as metal precursor. In a typical preparation, the required amount of palladium (II) acetate was adjusted to yield catalysts containing 0.5 wt.% Pd loading, was dissolved in acetone after complete dissolution. Subsequently, $CaCO_3$ was added and impregnation carried on under vigorous stirring at room temperature. Then, the solid obtained was reduced with sodium borohydride solution for 2 h. Finally, solvent was removed using a rotary-evaporator and the material was named as Pd0.5/$CaCO_3$.

2.3 Catalyst characterization

The textural properties of biogenic calcium carbonate containing Pd as well as the respective support were obtained by N_2 adsorption-desorption measurements at 77K by means of a Micromeritic ASAP 2000 instrument (Micromeritics Instrument Corporation, Norcross, GA, USA). Before the analysis, the samples were outgassed at 623 K for 6 hours with a vacuum of 10^{-3} mmHg. Brunauer-Emmett-Teller (BET) method was used to evaluate the specific surface area of sample. Pore size distribution as well as pore volume were obtained by Barret-Joyner-Halenda (BJH) model in the adsorption branch.

$CaCO_3$ crystalline phases were determined using the X-ray diffraction (XRD) using a Bruker D8 DISCOVER A25 instrument (40 kV, 40 mA; Bruker AXS, Karlsruhe, Germany) employing the Cu_Kα radiation (λ = 1.5418 Å). The diffractograms were acquire using a speed of 1°/min was used in a 2θ range between 10 to 80°. This equipment is provided with the “Diffract.Suite EVA” software (Bruker AXS, Karlsruhe, Germany) that easily permits particle size determination and crystal phase assignment.

Thermogravimetric analysis was performed using a Setaram thermobalance using a heating rate of 10 °C/min under an atmosphere of air flowing at 30 cm^3/min, from 20°C to 1000°C.

TEM micrographs of the solids herein synthesized were acquired using a JEOL JEM 1400 High Resolution Transmission Electron Microscope at the Central Service for Research Support (SCAI) of the University of Córdoba. Prior to the images acquisition, the samples were suspended in ethanol and deposited on a copper grid.

X-ray photoelectronic spectroscopy (XPS) measurements were carried out using an ultrahigh vacuum multipurpose surface analysis instrument, SpecsTM system with a

Phoibos 150-MCD energy detector at SCAI facilities. XPS CASA software was employed to study the obtained spectra. The binding energies (BE) were referenced by setting the adventitious carbon C1s to 285 eV, as has been reported for carbonate samples [18].

2.4 Catalytic tests

The catalytic activity of as-synthesized Pd0.5%/$CaCO_3$ was investigated in continuous phenylacetylene hydrogenation using a X-cube Thalesnano Inc. reactor fitted with pressure regulator. The catalyst (around 0.08 g) was located in a 30 mm metal cartridge, sealed and attached to the reactor. A 0.1 M solution of phenylacetylene in toluene was circulated at different flow rates (0.2, 0.5 and 1.0 mL/min) and system pressures (5, 10, 15 and 20 bar) through the catalyst bed (feed/catalyst contact time: 1 min) at 30°C were investigated. Samples were periodically collected at 0, 15, 30 min and 1 hour after achieving steady state conditions.

All the collected samples were analyzed by gas chromatography in an Agilent-6890 N Series II instrument equipped with FID and a HP-5 column Agilent 19091 J-413 (30 m x 0.32 mm x 0.25µm; phenyl methyl xylosan 5%). Injector and detector temperatures were set as 250°C. Oven temperature was held for 1 min at 80°C, and then increased to 150°C (10°C/ min). Phenylacetylene (PA), styrene (ST), and ethylbenzene (EB) signals (as the reactant, desirable product, and byproduct, respectively) were recorded. **A typical chromatogram is showed in Fig. A.2.** Products identification was done in a GC-MS instrument (Agilent Technologies 7820A GC System coupled with a 5977B MSD mass spectrometer) equipped with a HP-5MS column. **The concentrations of each compound were determined using the equations of calibration curves showed in Table A.1.**

Conversion (PA) and selectivity (ST) were calculated based on areas as a function of concentration:

$$Conversion\ (PA,\%) = \frac{total\ moles - final\ moles\ of\ PA}{total\ moles} \times 100$$

$$Selectivity\ (ST,\%) = \frac{total\ moles\ ST}{total\ moles} \times 100$$

3. Results and discussion

Biogenic $CaCO_3$ has an extraordinary importance for the adsorption of heavy metal ions such as Cd^{2+} and Pb^{2+} [19]. However, the use such Biogenic $CaCO_3$ in the catalysis field has been rarely explored. Regarding to the material characterisation, the textural properties of the Pd0.5/$CaCO_3$ catalyst as well as its respective support were evaluated by nitrogen adsorption/desorption measurements and are listed on Table 1. Firstly, it is important to remark the relatively low surface area in the biogenic $CaCO_3$, which is decreased after Pd incorporation from 25 to 11 m^2/g. In addition, pore volume and pore size were affected by Pd impregnation caused by pore saturation by metal particles. Furthermore, it is important to remark the high pore volume may lead to increased catalytic activity. In contrast, the relatively low surface area, in principle, is disadvantageous and may lead to nanoparticles with larger particle as compared with the use of other supports such as activated charcoal and zeolites among others with higher specific surface. The isotherm plots of the material Pd0.5/$CaCO_3$ is shown on **Fig. A.3**, shows a typical hysteresis type H3 loop at relative pressures between 0.46 and 0.9, similar to other reported for analogous materials [20].

The crystallinity of the samples was evaluated by X-ray diffraction and the results are shown on Fig. 1, where it can be observed that the support $CaCO_3$ it is a mixture of two phases, calcite and vaterite. The presence of Pd particles could not be detected due to either a good particle distribution over the catalyst surface or to the low Pd loading on the material. The crystal size corresponding to vaterite in the Pd0.5/$CaCO_3$ catalyst was measured using Scherrer equation at 2θ ~ 27º was 3.5 nm, which corresponds to the most important phase in the investigated materials. In contrast, this value before of impregnation with palladium was 3.1 nm, slightly smaller. Interestingly, it is observed that vaterite phase proportion increased with respect to the most stable phase calcite, indicating that some spherical crystals evolve [21] while phenylacetylene hydrogenation reaction is taking place. Thermogravimetric analyses were performed to understand the change in the phases of $CaCO_3$ after of reaction. **Fig. A.4**. shown thermograms of Pd0.5/$CaCO_3$ obtained before and after of phenylacetylene hydrogenation. Although, typical loss weight of carbonates is evidenced, a minor weight loss of water was observed after of reaction; because of physisorbed water was removed from solid with continuous flow, which probably changes the polymorphism of calcite to vaterite [22].

The morphology of biogenic calcium carbonate loaded with 0.5 % wt. palladium sample was investigated by Transmission Electron Microscopy (Fig. 2). In TEM micrograph there are three regions that could be observed; firstly, it was possible to differentiate the two $CaCO_3$ phases present in the material. While calcite phase can be observed as elongated hexagonal shape crystals, in the lower part of the image (region 1), other spherical/ovoid shape crystals can be appreciated corresponding to vaterite phase in the upper part of the image (region 2). Likewise, a particle of palladium adhered to crystal surface (3) can be evidenced.

Additional structural analysis corresponding to the sample Pd0.5/$CaCO_3$ was performed by X-ray photoelectron spectroscopy (XPS). Fig. 3a shows the deconvoluted XPS spectra of Pd0.5/$CaCO_3$ in the 3d region, where two contributions of Pd $3d_{5/2}$ are assigned to Pd^0 and Pd^{2+}[23]. The proportion of these two species is 60:40, respectively. Although, reduced particles Me^0 are obtained with $NaBH_4$, it seems be that CO_3^{2-} species inhibits complete reduction of palladium. Ca2p core levels at 347.2 and 350.7 eV (Fig. 3b) are assigned to vaterite phase [18], which is in agreement with results of XRD. Commonly, carbonates are associated in the region C1s at 289.7 eV (**Fig. A.5a**) [18,24]. The peaks at 286.4 and 285 eV are ascribed at C=O groups and adventitious carbon. In the XPS O1s core level appears two peaks in low BE at 531 and 532.6 eV assigned to oxygen in lattices and oxygen in OH groups probably as adsorbed water [25], respectively (see **Fig. A.5b**). The values corresponding to O1s region at low BE could be associated with some interaction Pd-CO_3^{2-}.

The catalytic activity of the catalyst was investigated in the continuous flow hydrogenation of phenylacetylene for the selective production of styrene (ST), which is an important monomer that participates in the production of plastics and rubbers. Therefore, the main aim of this study was focused on finding out the optimized conditions for conversion of phenylacetylene (PA) achieving the maximum selectivity towards the production of styrene using Pd0.5/$CaCO_3$ catalyst. The use of continuous flow reactors entails several advantages as compared to batch reactors such as improved contact between reagents and catalyst, better reaction parameters optimization and improved matter and energy transference that promote the catalytic processes. In addition, with comparative purposes a commercial Pd/C with a metal loading was investigated with comparative purposes at the preliminary stages of the studies performed at 30 ºC, 20 bar and a flow rate of 0.2 mL/min leading to almost the complete conversion of PA but with a low selectivity towards styrene (**Table A.2).** Under analogous conditions, Pd0.5/$CaCO_3$ catalyst achieved lower PA conversion but higher ST selectivity (15 %). Thus, considering the higher selectivity that could be achieved by Pd0.5/$CaCO_3$ catalyst, despite of its lower Pd loading, the optimization of the reaction conditions was carried out using this catalyst.

Firstly, three different reaction temperatures, a relevant parameter in any chemical reaction, 30, 50 and 100°C were evaluated using Pd0.5/$CaCO_3$ catalyst. A conversion of 100% was evidenced in the three tests performed at the different investigated temperatures. **At 30 ºC, it was shown on Table A.2 that PA was converted at this temperature independently of the flow (from 0.2 to 1.0 mL/min) and system pressure (from 5 to 20 bar).** For instance, conversion was complete when flow is 0.2 mL/min and at 10 bar pressure as well as at 0.5 mL/min flow rate regardless the pressure. However, ST selectivity was low obtaining mainly the hydrogenated product, ethylbenzene. Though, when flow is 1.0 mL/min and pressure is 10 bar, ST selectivity and yield showed the highest values. Considering the reduction of energy costs, it was decided to carry out the experiments at a fixed temperature of 30°C as well as phenylacetylene concentration (0.1 M in toluene) in the feeding solution. Therefore, system pressure as well as flow rate would require optimization in other to achieve the maximum styrene yield.

The effect of pressure on phenylacetylene reaction was studied in a range of 3 to 20 bar at 30 °C and the flow rate was fixed at 0.5 mL/min of 0.1 M PA solution in toluene using Pd0.5/$CaCO_3$ (Fig. 4). When pressure increases, styrene selectivity and yield decrease, although conversion increases possibly because ethylbenzene production is promoted by increasing hydrogen amount injected into reaction. Besides, it is possible that PdO can be reduced fully to Pd^0 modifying the selectivity obtained when the pressure is highest than 10 bar, this effect is more pronounced at high temperatures (**Table A.2**). Thus, at 15 bar, conversion is 100%, but ST production is 36% and ethylbenzene is the main reaction product with a yield of 64%. The most convenient system pressure investigated was 10 bar when the maximum ST yield was achieved. Therefore, this pressure value (10 bar) was selected to evaluate flow rate effect on the reaction.

Fig. 5 shows the flow rate effect on PA hydrogenation with Pd0.5/$CaCO_3$ that is going to strongly influence ST yield and selectivity, whose highest investigated value was 1.5 mL/min. According to the displayed results, the most adequate flow rate was 1.0 mL/min, where also EB yield is the lowest (about 15%) among all the investigated conditions. This fact suggests that rapid diffusion of the reagents through the catalyst that partially hydrogenates phenylacetylene to styrene with high effectiveness. The best results were obtained using a flow rate of a 0.1 M PA solution of 1.0 mL/min at 30 ºC and 10 bar hydrogen pressure obtaining a yield of 65.8% and a selectivity of 83.3% towards styrene.

Yang et al. [6] studied commercially available catalysts, Pd/Al_2O_3 and Lindlar catalyst, which have selectivity to styrene of 47.8% and 90.2%, with conversions of 99.5 and 99.3%, respectively. Firstly, it is important to note that Lindlar catalyst has a reaction time 20 times higher (2000 min) than Pd/Al_2O_3 (100 min). The differences in selectivity found in Pd/Al_2O_3 and Lindlar catalyst could be related with the proportion of metallic species present in these solids. The formation of ethylbenzene is favored on Pd^0 species which occurs on Pd/Al_2O_3, while the partial hydrogenation favored is related with a minor proportion of hydrogenated species as is the case in Lindlar catalyst. Although Pd0.5/$CaCO_3$ has a selectivity of 83% and a conversion of 78%, this occurs only in shorter reaction times, below one hour on stream, which are good results as compared to previous studies and can be attributed to the ratio Pd^{2+}/Pd^0 present in the catalyst. Interestingly, if reaction conditions change, pressure and flow rate, solid catalytic activity increase due to change in the proportion of such species and, consequently, the selectivity and yield to styrene or ethylbenzene are modified. Finally, it is also important to notice that the low reaction temperature herein used, 30°C, to perform the hydrogenation reaction helps to the process economy. **Although, Lindlar catalyst is the most used solid in phenylacetylene hydrogenation, longer times of reaction (more than 33 hours) are required to obtain these high values under batch conditions.**

In summary, the catalytic activity of Pd0.5/$CaCO_3$ was compared with literature values, which are summarized in Table 2. Different catalysts have been used but some of them need drastic preparation conditions i.e. high temperatures that increase costs in a scalable process. Batch or semi batch reaction limits industrial production of styrene. Conversion and selectivity of PA hydrogenation using biogenic Pd0.5/$CaCO_3$ were low compared with other catalysts, but with biogenic materials this process is short (1 h) and the catalyst did not require high temperatures and complex procedures for synthesis.

Finally, a long-term experiment was carried out to investigate a possible deactivation the Pd0.5/$CaCO_3$ catalyst. The results are depicted on Fig. 6 where it can be seen that Pd0.5/$CaCO_3$ has a stable performance under continuous flow conditions after 12 hours on stream, since during the evaluation period conversion PA, selectivity and yield of styrene remained unchanged, i.e the species of palladium responsible of the activity did not undergo further modification. However, the continuous flow conditions may help to remove physisorbed water and change slightly the polymorphism in $CaCO_3$ used as catalytic support.

4. Conclusions

Pd0.5/$CaCO_3$ catalyst was prepared using biogenic carbonate obtained by microbiological precipitation with *Sporosarcina pasteurii* to be used as support for Pd nanoparticles. The adequate ratio Pd^0/Pd^{2+} in this material allows to obtain good yields to styrene in phenylacetylene hydrogenation under continuous flow conditions. Once optimized the reaction conditions, the best results were obtained when a temperature of 30°C, flow rate 1 mL/min of a 0.1 M PA solution in toluene and 10 bar of pressure were used to obtain a yield and selectivity towards styrene of 65% 83%, respectively. Remarkably, after 12 hours on stream, catalytic activity of Pd0.5/$CaCO_3$ remained unchanged keep constant PA conversion and selectivity to styrene as indicative of catalyst stability under investigated condition. Thus biogenic Pd0.5/$CaCO_3$ has been proved to be a robust catalyst in continuous flow phenylacetylene hydrogenation to produce selectively styrene.

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Author contributions

SC performed all experiments and wrote the first draft of the manuscript. AP-S supported the experimental work and revised the manuscript draft. JM and HR review the paper. RL provided the lab for all experiments, planned the experimental work, and finalized and submitted the manuscript.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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LIST OF FIGURES

Fig. 1. X-ray diffractograms corresponding to Pd0.5/$CaCO_3$ used in the phenylacetylene hydrogenation.

Fig. 2. TEM image corresponding to the material Pd0.5/$CaCO_3$.

Fig. 3. High-resolution XPS spectra corresponding to the Pd0.5/$CaCO_3$ sample in the regions: a) Pd3d and b) Ca2p

Fig. 4. Effect of system pressure in phenylacetylene hydrogenation with Pd0.5/$CaCO_3$. Reaction conditions: 30 °C and flow rate of 0.5 mL/min of 0.1 M PA solution in toluene.

Fig. 5. Effect of flow in phenylacetylene hydrogenation with Pd0.5/$CaCO_3$. Reaction conditions: 30 °C and system pressure of 10 bar, 0.1 M PA solution in toluene.

Fig. 6. Catalytic activity of Pd0.5/$CaCO_3$ in phenylacetylene hydrogenation along 12 hours on stream. Reaction conditions: 30 °C, system pressure of 10 bar, flow rate of 1.0 mL/min and 0.1 M PA solution in toluene.

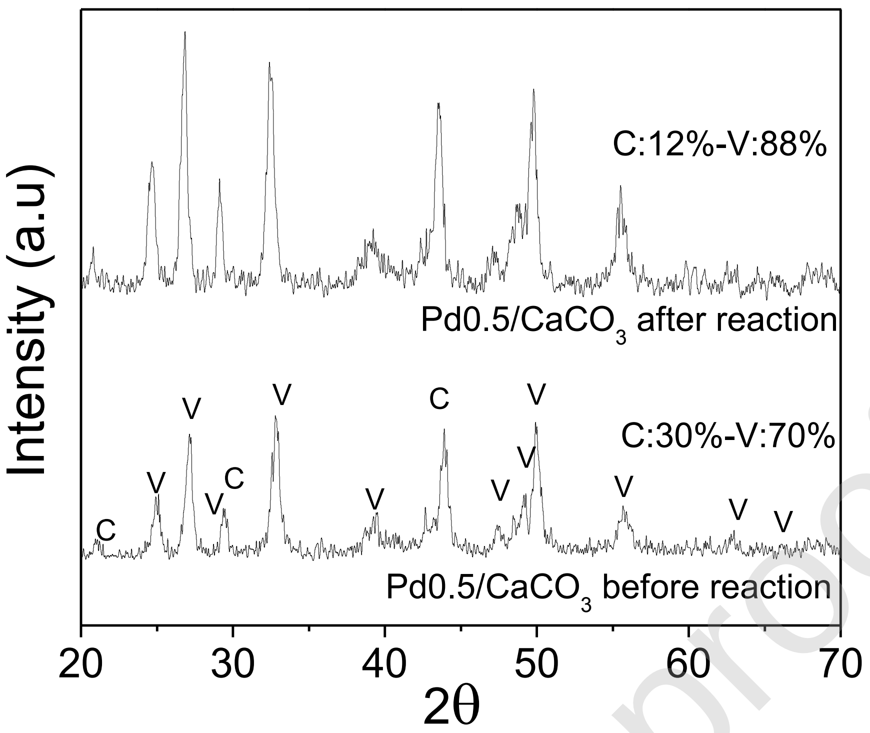

C:12%-V:88%
Pd0.5/$CaCO_3$ after reaction
C:30%-V:70%
Pd0.5/$CaCO_3$ before reaction
C
V
V
V
C
V
V
C
V
V
V
V
V
V
Intensity (a.u)
2θ
20
30
40
50
60
70

Fig. 1.

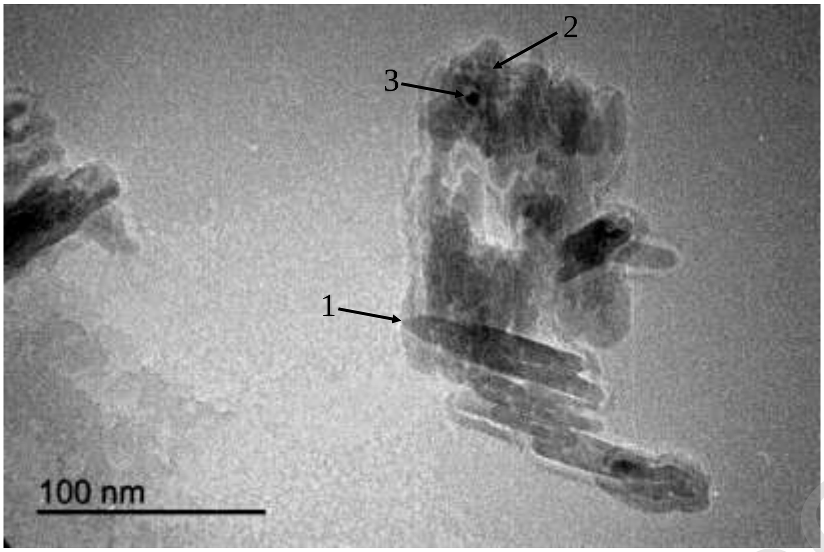


Fig. 2.

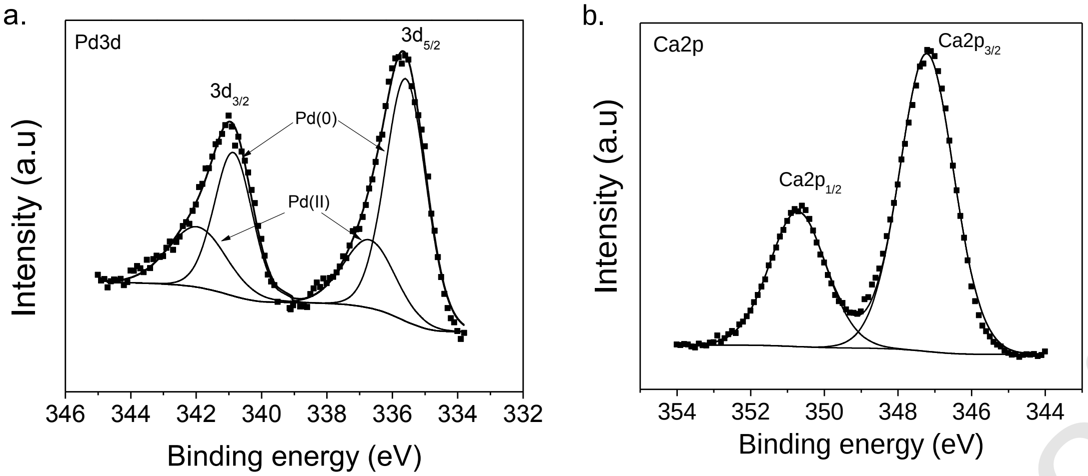

a.
Pd3d
3d$_{5/2}$
3d$_{3/2}$
Pd(0)
Pd(II)
Intensity (a.u)
346
344
342
340
338
336
334
332
Binding energy (eV)
b.
Ca2p
Ca2p$_{3/2}$
Ca2p$_{1/2}$
Intensity (a.u)
354
352
350
348
346
344
Binding energy (eV)

Fig. 3.

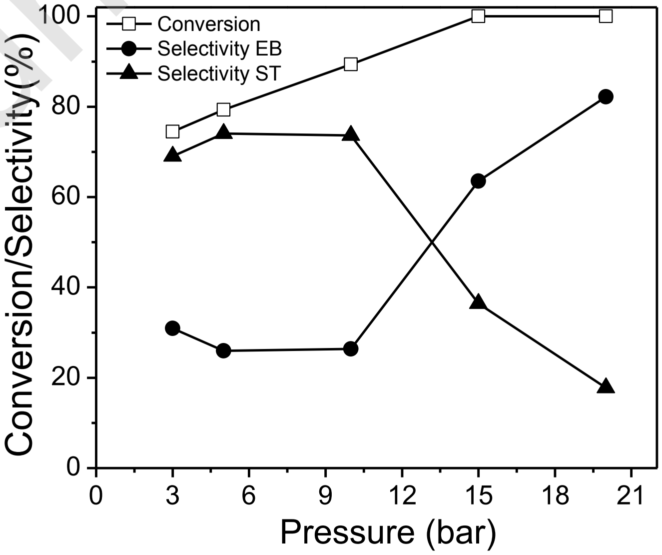

Conversion
Selectivity EB
Selectivity ST
Conversion/Selectivity(%)
0
20
40
60
80
100
0
3
6
9
12
15
18
21
Pressure (bar)

Fig. 4.

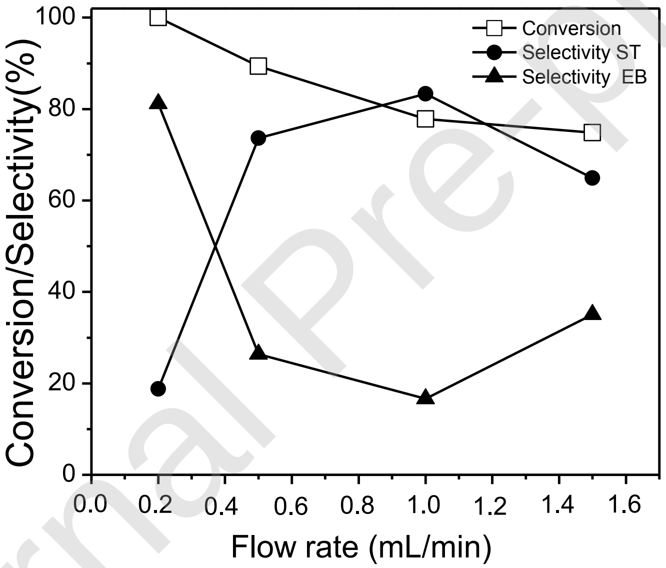
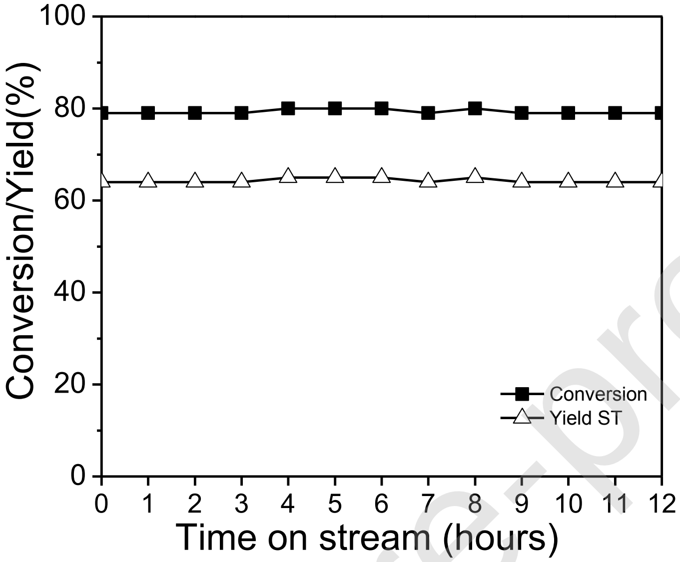

Conversion/Selectivity(%)
0
20
40
60
80
100
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Flow rate (mL/min)
Conversion
Selectivity ST
Selectivity EB

Fig. 5.



Conversion/Yield(%)
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
10
11
12
Time on stream (hours)
Conversion
Yield ST

Fig. 6.

TABLES

Table 1. Textural properties of the investigated materials in this work measured by nitrogen adsorption/desorption measurements.

Catalyst	**Specific Surface BET (m^2/g)**	**C_{BET}**	**Pore volume BJH (cm^3/g)**	**Pore size BJH (nm)**
$CaCO_3$	25	67	0.11	28.0
Pd0.5/$CaCO_3$	11	59	0.04	26.6

Table 2. Comparison of catalytic performance between Pd0.5/$CaCO_3$ and the literature

Catalyst	***Conditions***	***Conv*.(%)***	***Y_{ST}* (%)***	***S_{ST}* (%)***	***S_{EB}* (%)***	***Ref***
Pd0.5/$CaCO_3$	0.08 g of catalyst, 0.1 M PA in toluene, 10 bar of H_2 pressure, flow: 1 mL/min 30°C, t= 1 h	78	65	83	17	This work
mpg-C_3N_4	0.4 g of catalyst, 0.0135 mol/h of PA in hexane, 0.027 mol/h of H_2, 250°C, t= 1 h	86	76.4	89	10.6	[4]
Pd @mpg-C_3N_4	0.010 g of catalyst, 5.85 mmol PA in ethanol, atmospheric H2 bubbling, 30°C, t= 1.5 h (batch reaction)	>99	-	94	-	[8]
Pd/TiO_2	0.05 g of catalyst, 0.4 M PA in ethanol, 0.5 MPa in H_2 pressure, 25°C (Batch reaction) t= 40 min	100	-	95	-	[7]
$NiZn_3$/AlSBA-15	0.15 g of catalyst, 0.4 M PA in methanol, 0.1 MPa in H_2 40°C (Semibatch reaction), t= 13 h	100	-	90	-	[6]
nano-Pd/α-Al_2O_3	0.3 g of catalyst, 0.72 M PA in ethanol, 0.1 MPa in H_2 50°C (Semibatch reaction), t= 30 min	98	-	70	-	[10]
1% Pd/ND@G	0.005 g of catalyst, 0.18 M PA in ethanol, 1 bar of H_2, 30°C, t= 1 h (batch reaction)	100	85	85	-	[26]
PdAu/ZnTi	0.005 g of catalyst, 0.3 M PA in ethanol, 10 mL/min of H_2, 45°C, t= 1.5 h (batch reaction)	100	-	90	-	[12]

Cu/PNDs	0.01 g of catalyst, 0.02 M PA in ethanol, 12 mL/min of H_2 , flow: 0.6 mL/min 20°C, t= 1 h	68	-	90	-	[27]
Ni_2Si	0.10 g of catalyst, 1 M PA in ethanol, 1 MPa of H_2 , flow: 0.6 mL/min 80°C, t= 4 h	79	-	88	12	[28]

**Conv: conversion, Y_{ST}: yield to styrene, S_{ST}:selectivity to styrene, S_{EB}:selectivity to ethylbenzene*