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Valorization of Different Wastes and Their Use for the Design of Multifunctional Eco-catalysts

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Abstract The desire to protect the environment for future generations has led to the reutilization of all recoverable and recyclable wastes. Consequently, different residues from various sources were collected to make mixed compounds to be used as catalyst supports. Such wastes included sand and cement from the building industry, nonreturnable glass bottles, and used tires. The synthesized supports were impregnated with molybdophosphoric acid, a heteropolyacid with Keggin structure, and characterized by potentiometric titration, optical microscopy, SEM–EDS, and textural property analyses. The bifunctional properties of the new catalysts were evaluated in two relevant transformations in green conditions: (i) the selective oxidation of sulfides to sulfoxides using a green oxidant such as *tert*-butyl hydroperoxide, and (ii) the multicomponent synthesis of 3,4-dihydropyrimidinones (Biginelli reaction, catalyzed in acid media).

Graphical Abstract
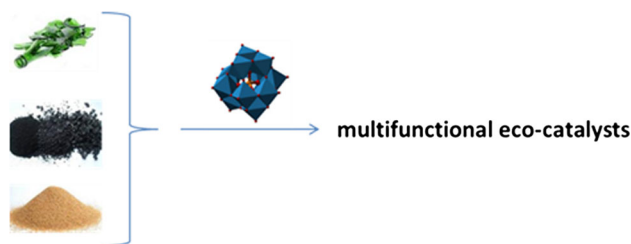
Introduction

Pollution is one of the major problems affecting the planet; it arises when the qualitative and quantitative presence of matter and energy causes an imbalance in the environment. It can be defined as the addition of any substance or energy to the environment in such quantity that may be harmful to human beings, animals, vegetables or materials. Human groups, organized in different ways, interact with, change and use the environment to meet their needs, such as food, clothing, and quality of life, which usually lead to gradual deterioration of their surroundings [1].

For people to be considered within a certain standard of living in most consumer societies, they should consume devices and products that are mostly disposable. The purchase of cheap unreliable devices that break down fast is usually promoted by the media. People can buy better things that last longer or rent items instead. Depending on the items in question, resource depletion is a looming

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concern. As a result, the desire to protect the environment for future generations has led to the reutilization of all recoverable and recyclable wastes, i.e., those materials that can be reintroduced into the production chain of consumer goods. In this way, partial compliance with the principles of Green Chemistry may be sought [1, 2].

Green Chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment [2]. It should be recognized for its ability to address sustainability at the molecular level, and it should be at the heart of tomorrow's chemistry, integrating sustainability into science and its innovations [3, 4].

Taking into account the aforementioned concepts, different wastes from various sources were collected to make mixed compounds to be used as catalyst supports. Such residues included sand and cement from the building industry, nonreturnable glass bottles and used tires.

Tires are an essential element in our motorized society. Their manufacture and disposal once they are used is a serious environmental problem due to first, the large amount of energy used in their production (half a barrel of crude oil to manufacture a truck tire) and second, because they usually end up their useful life in uncontrolled landfills, with the subsequent environmental impact [5]. Regarding recycling and reuse of tire components, there are currently various methods to replace direct burning and stockpiling, which cause harmful gas emissions and proliferation of rodents and insects, respectively. Such methods include thermolysis and pyrolysis, among others [5, 6].

Within the framework of clean technologies, different catalytic systems have been developed in the last years, namely, heteropolyacids (HPAs) [7]. In our research group, the use of these compounds as catalysts can be illustrated by oxidation reactions with hydrogen peroxide, such as the selective oxidation of anilines, alcohols, phenols, naphthols and sulfides [8–12]. Recently, oxidation reactions of sulfide with hydrogen peroxide using catalysts supported on conventional oxides have been studied [13]. The influence of different heteropolycompounds with Keggin-type structure and their pyridine salts on the oxidation of alcohols with hydrogen peroxide has been investigated [14]. There is a large number of examples that illustrate the importance of the use of HPAs in catalytic processes, such as the synthesis of coumarins [15, 16], synthesis of flavones [17, 18], synthesis of imidazoles [19, 20], and C-alkylations [21, 22].

In the application of these catalysts, selective conversion of sulfides to sulfoxides is of great importance both in the industry and in basic research [23, 24]. Due to the aforementioned reasons, there is an urgent need to implement clean technologies in the processes to obtain sulfoxides.

Oxidizing reagents such as hydrogen peroxide can be conveniently used for the oxidation of organic substrates due to its oxygen content and low cost, besides the fact that water is its only reaction by-product [25]. Another oxidizing reagent that has started to be used is *tert*-butyl hydroperoxide, which only gives *tert*-butanol as by-product and is also soluble in organic solvents such as toluene, giving the possibility of working with heterogeneous catalysts [26].

In order to test the suitability of supported HPAs for acid catalysis reactions, the Biginelli reaction was selected. This reaction, which is the simplest procedure for the preparation of 3,4-dihydropyrimidinones, was reported by Pietro Biginelli in 1893 [27]. This synthesis belongs to the field of multicomponent reactions [28]. In this procedure, urea, an aldehyde and a β-ketoester are combined in the presence of the catalyst. Although in the original procedure developed by Biginelli, hydrochloric acid was used as catalyst and the yields were not very good (20–50 %), in the last decade and due to the importance of these compounds, different experiments using different catalysts and methods to soften the conditions and raise the yields of this reaction have been carried out and published. Due to their biological properties, they can be used as calcium channel modulators, α-1a antagonists, anticancer, antiviral, antibacterial and antimicrobial agents, inhibitors of blood platelet aggregation, and as anti-inflammatory, antioxidant and antifungal agents [29–33]. Some of these methods use homogeneous catalysis, such as $ZrCl_4$ [34], $SbCl_3$ [35] and various HPAs such as $H_4PMo_{11}VO_{40}$ [36], $H_3PMo_{12}O_{40}$ [37]. For heterogeneous catalysis, ionic exchange resins [38], different ionic liquids [39], supported heteropolyacids [40] and zeolites [41] have been studied. Finally, several catalysts, in solvent-free conditions, have been investigated: $Y(NO_3)_3 \cdot 6H_2O$ [42], chloroacetic acid [43], $KAl(SO_4)_2 \cdot 12H_2O$ supported on silica gel [44], $TaBr_5$ [45], and alumina-supported MoO_3 [46].

Within this framework, the general goal of this work is to contribute to the knowledge in the field of catalysis, with particular focus on the bifunctional Keggin phase supported on mixed waste, i.e., wastes from various sources, and on the organic synthesis of high-value compounds, applying environmentally friendly synthesis procedures. As specific goal, the efficiency of recyclable materials characterized by particular surface area (S_{BET}), potentiometric titration, optical microscopy, and scanning electron microscopy (SEM–EDS) was analyzed. The synthesized supports, made from recoverable and recyclable wastes, were impregnated with a heteropolyacid with Keggin structure, molybdophosphoric acid (MPA), and tested in the selective oxidation of sulfides to the corresponding sulfoxides using *tert*-butyl peroxide (Scheme 1). These catalysts were also studied in the synthesis of 3,4-
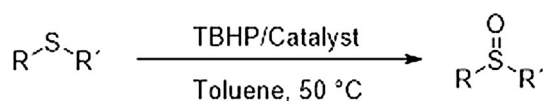
Scheme 1 Selective oxidation of sulfides to sulfoxides using a *tert*-butyl peroxide/catalyst system

dihydropyrimidinones (DHPMs) by the Biginelli reaction under solvent-free conditions (Scheme 2).

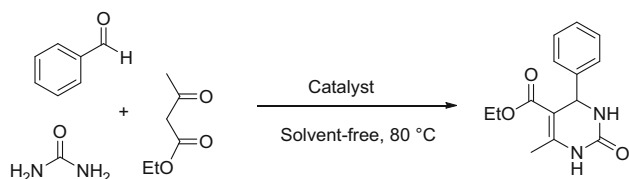## Experimental

Catalyst Preparation

Preparation of the Supports

Samples with different amounts of sand, cement, rubber, glass and water were prepared in order to impart different properties to each of them. The sand was incorporated without physical or chemical changes to the mix. The water used was potable water, not distilled or chemically modified. Brown and green glass bottles were rinsed and dried at room temperature, and then they were ground to powder in an industrial mill. In all cases, the last element to be incorporated was cement, which combines with water to form a paste that provides the basis for the incorporation of all other building components.

The different compositions of each sample are listed in Table 1.

Catalyst Synthesis

The supports were used without further treatment, as mentioned above. One g of the mixed and unmixed materials (*Samples* 1–8) was impregnated with $H_3PMo_{12}O_{40}$ solution with a concentration of 110 mg Mo/mL. The supported catalysts were obtained by equilibrium adsorption technique by dissolution of $H_3PMo_{12}O_{40}$ in 4 mL of absolute ethanol [17.4 % (w/v)]. The solution was contacted with 1 g of support. The impregnated solid was left without stirring for 24 h. After that, the obtained solid was shaken for 3 h and then was kept undisturbed overnight. Then it was shaken for 7 h, and the impregnated solid was

Table 1 Composition (%) of prepared support

Sample	Sand	Cement	Glass	Tires	Water
Sample 1	60	20	–	–	20
Sample 2	40	20	20	–	20
Sample 3	20	20	40	–	20
Sample 4	60	20	–	10	10
Sample 5	40	20	20	10	10
Sample 6	20	20	40	10	10
Sample 7	40	20	10	10	20
Sample 8	20	20	30	10	20

allowed to stand for 24 h [13]. This technique was chosen because both the diffusion process and the contact time between the support and the solution in the active phase would give a better distribution of the heteropolyacid in the different synthesized solids. Then, the solids were dried at room temperature. Finally, the catalysts were thermally treated at 200 °C for 6 h.

Characterization of the Supports and Supported Catalysts

Scanning Electron Microscopy (SEM–EDS)

The solids were characterized by a Philips 505 scanning electron microscope using an accelerating voltage of 20 eV and a magnification range of 2500× to 10,000×. Carbon film was used to enhance image quality.

Optical Microscopy

The optical observations were made with an Axiotech Zeiss microscope with an attached Philips video camera.

Inductively Coupled Plasma Atomic Emission Spectroscopy

The experimental contents of Mo in the bulk $H_3PMo_{12}O_{40}$ as in the impregnated catalysts were determined by means of the inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique using a Shimadzu 1000 III instrument.

Textural Properties

The nitrogen adsorption/desorption isotherms at 77 K were determined using Micromeritics ASAP 2020 equipment. Previous degasification was carried out for 700 min at 100 °C and below 30 μm Hg. From these isotherms, the

Scheme 2 Biginelli synthesis of 3,4-dihydropyrimidinones

specific surface area (S_{BET}), the pore volume, and the mean pore diameter of the samples were determined.

Potentiometric Titration

The titration was carried out by adding 0.05 mL of a solution of *n*-butylamine in acetonitrile (0.05 N) to a certain amount (0.05 g) of the solid of interest that had been previously suspended in acetonitrile (90 mL) with stirring for 3 h. The potential variation (mV) was measured with 794 Basic Titrino Metrohm equipment using a double junction electrode. This technique enables the evaluation of the total number of acid sites and their acid strength. In order to interpret the results, it is suggested that the initial electrode potential (E) indicates the maximum acid strength of the surface sites, and the values (meq/g solid) where the plateau is reached indicate the total number of acid sites. The strength of the acid sites can be classified according to the following scale: $Ei > 100$ mV (very strong sites), $0 < Ei < 100$ mV (strong sites), $-100 < Ei < 0$ mV (weak sites), and $Ei < -100$ mV (very weak sites) [47].

Catalytic Test

General

All chemicals were purchased commercially and used without further purification. The yields were calculated from crystallized products when sulfoxide was solid. All the products were identified by comparison of analytical data, thin layer chromatography (TLC), mass spectra and nuclear magnetic resonance (NMR) data with those reported. ^{13}C NMR and ^{1}H NMR spectra were recorded at room temperature on Bruker AC 400 using tetramethylsilane (TMS) as internal standard.

Reaction Parameters For a given chemical reaction involving balanced reagents A and B and give a target product associated product P and Q, $v_A A + v_B B \rightarrow v_{P-}P + v_Q Q$ with appropriate stoichiometric coefficients v. Assuming that the reagent A is the limiting reagent.

Reaction Yield

$$RY = \left(\frac{moles\,P}{moles\,A}\right)\left(\frac{vA}{vP}\right)$$

Selectivity

$$S = \frac{moles\,P}{moles\,P + moles\,Q}$$

Conversion

$$C = \frac{moles\,A\,(remnants)}{moles\,A}.$$

Sulfide Oxidation

A solution of the corresponding sulfide (1 mmol) was stirred with 50 mg of catalyst in 4 mL of toluene. Then 3 mmol of *tert*-butyl hydroperoxide (TBHP), 5–6 M in decane, at 20 °C, was added. The solution was stirred at 50 °C up to conversion of 100 % of the starting material (controlled by TLC). The catalyst was filtered and washed with 2 mL of toluene. Organic extracts were evaporated, and the residue was purified by recrystallization to obtain pure sulfoxide when sulfoxide was solid.

3,4-Dihydropyrimidinone Synthesis

Aldehyde (1 mmol), ethyl acetoacetate (1 mmol) and urea (1.5 mmol) were intimately mixed with 50 mg of catalyst. The mixture was stirred at 80 °C until disappearance of the aldehyde or when no changes in the composition of the mixture were detected by TLC. Once the reaction was complete, successive washings with toluene at the reaction temperature were performed. The organic extracts were evaporated and then, the solid was purified by recrystallization to obtain the corresponding pure 3,4-dihydropyrimidinone.

Catalyst Reuse

Both sulfide oxidation as 3,4-dihydropyrimidin-2-ones the catalyst was separated by filtration, washed whit toluene (2 × 1 mL), dried under vacuum at room temperature, and then reused. The catalyst reuse was tested in both syntheses for three consecutive experiments (Table 3 entries 1, 6 and 7; Table 5 entries 1, 6 and 7) under the same reaction conditions.

Characterization of Synthetized Representative Compounds

Sulfoxides The structure of the products was confirmed by mass spectra.

Dibutyl sulfoxide colorless oil [48] EM, m/z (relative intensity): 162 (M+, 5 %), 145 (11 %), 106 (32 %), 89 (45 %), 57 (58 %), 41 (98 %), 29 (100 %).

Dibenzyl sulfoxide colorless solid. M.p.: 129–130 °C [49]. EM, m/z (relative intensity): 230 (M+, 5 %), 181 (2 %), 180 (3 %), 91 (100 %), 65 (9 %), 39 (3 %).

Benzyl phenyl sulfoxide colorless solid. M.p.: 121–123 °C [50]. EM, m/z (relative intensity): 216 (M+, 10 %), 182 (16 %), 165 (2 %), 125 (5 %), 91 (100 %), 77 (11 %), 65 (18 %).

Diphenyl sulfoxide colorless solid. M.p.: 69–71 °C [51]. EM, m/z (relative intensity): 202 (M+, 83 %), 185

(18 %), 154 (73 %), 109 (90 %), 97 (48 %), 77 (78 %), 65 (59 %), 51 (100 %), 39 (32 %).

3,4-Dihydropyrimidin-2-Ones The structure of the products was confirmed by ^{1}H-and ^{13}C-NMR spectra.

5-Ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyrimidin-2-one M.p.: 202–204 °C. lit. 206–207 °C [52] ^{1}H-RMN (d6-DMSO, 400 MHz): δ (ppm) 1.12 (t, J = 7.0 Hz, 3H); 2.28 (s, 3H); 4.03 (q, J = 7.0 Hz, 2H); 5.17 (d, J = 2.5 Hz, 1H); 7.22–7.41 (m, 5H); 7.78 (s, 1H); 9.22 (s, 1H). ^{13}C-NMR (d6-DMSO, 400 MHz): δ (ppm) 14.9; 18.6; 54.7; 60.1; 100.2; 127.1; 128.1; 129.3; 145.7; 149.2; 153.0; 166.2.

5-Ethoxycarbonyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2-one M.p.: 211–212 °C. lit. 214–215 °C [53] ^{1}H-RMN (d6-DMSO, 400 MHz): δ (ppm) 1.12 (t, J = 7.5 Hz, 3H); 2.25 (s, 3H); 2.32 (s, 3H); 4.00 (q, J = 7.5 Hz, 2H); 5.11 (d, J = 3.0 Hz, 1H); 7.12 (s, 4H), 7.70 (s, 1H); 9.19 (s, 1H). ^{13}C-RMN (d6-DMSO): δ (ppm) 14.1; 17.7; 20.6; 53.7; 59.1; 99.5; 126.1; 128.8; 136.3; 141.9; 148.1; 152.2; 165.3.

4-(4-Clorophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2-one M.p.: 212–213 °C. lit. 210–212 °C [53] ^{1}H-RMN (d6-DMSO, 400 MHz): δ (ppm) 1.07 (t, J = 7.0 Hz, 3H); 2.24 (s, 3H); 3.95 (q, J = 7.0 Hz, 2H); 5.13 (s, J = 2.5 Hz, 1H); 7.22–7.40 (m, 4H); 7.77 (s, 1H); 9.24 (s, 1H). ^{13}C-NMR (d6-DMSO, 400 MHz): δ (ppm) 14.0; 17.7; 53.3; 59.2; 98.8; 128.1; 128.3; 131.7; 143.7; 148.5; 151.8; 165.1.

5-Ethoxicarbonyl-4-(4-hidroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2-one M.p.: 229–230 °C. lit. 228–230 °C [54] ^{1}H-RMN (d6-DMSO, 400 MHz): δ (ppm) 1.01 (t, J = 7.0 Hz, 3H); 2.23 (s, 3H); 3.97 (q, J = 7.0 Hz, 2H); 5.03 (d, J = 3.3 Hz, 1H); 6.69 (d, J = 8.8 Hz, 2H); 7.02 (d, J = 8.8 Hz, 2H); 7.62 (s, 1H); 9.11 (s, 1H); 9.34 (s, 1H). ^{13}C-RMN (d6-DMSO, 400 MHz): δ (ppm) 12.7; 16.3; 52.0; 60.6; 98.3; 113.5; 126.0; 134.0; 146.3; 150.7; 155.1; 164.0.

Results and Discussion

Optical and Scanning Electron Microscopies (SEM–EDS)

According to optical microscopy characterization, Fig. 1 shows an optical micrograph of Sample 1 depicting the different components.

Sand particles are rounded and larger, and are contained in a very fine-grained material that forms the cementitious matrix; the degree of compaction is good and no pores are visible. Sample 2 (Fig. 2), where two parts of sand have been replaced by two parts of ground waste glass, has a similar appearance to Sample 1, with glass particles being perfectly integrated with the cementitious matrix.

The glasses in these samples are similar in size to sand particles and are discriminated from them due to their more elongated shape. Sample 3 (Fig. 3), with a higher percentage of replacement of sand by glass, shows areas with a higher proportion of glass and others with greater accumulation of sand particles.

Sample 4 (Fig. 4) has the same proportional quantity of cement and sand as Sample 1, but with an additional part of rubber. Microscopically, these solids are darker and at microscopic level, rubber particles are easily detected due to their bright black color in a great variety of shapes.

This material is integrated into the cementitious matrix, but significant porosity is observed around it. Figure 5, the SEM–EDS pattern of Sample 4, shows large rounded particles of sand, which is incorporated into the cementitious matrix.

Figure 6 shows a mapping of Sample 4 for Si and Ca elements that are representative of sand and cement phases. The porous morphology of the sample, which may be due to the different interactions among the solid components or to the formation of the cementitious matrix, with all its component materials can be seen. The remaining samples exhibit a similar morphological behavior.

Figure 7 shows a comparison, by Mo mapping, between impregnated unmixed materials (sand, cement and glass) and Samples 4–8.

As regards unmixed materials, the percentage of Mo is higher in sand, Mo distribution is very homogeneous in cement, and in waste glass the Mo content is very low. It could be assumed that there is a low content of impurity components in sand, as shown in Fig. 5, so that MPA interacts directly with silica, its major component, but its distribution is not homogeneous. In regard to cement, the EDS analysis (Fig. 5) shows the presence of a set of elements and, assuming that some of them are in the form of cations (Na, Mg, Al, among others), an interaction between the $[PMo_{12}O_{40}]^{-3}$ anion and these cement cations may be expected. In glass, the interaction is very low and may be attributed to the polished surface of waste glass and hence, the smoothness or different topology prevents an interaction between the support and the impregnating solution. Please note that rubber from used tires (as unmixed material) could not be impregnated with MPA, because when ethanol was used as solvent during the impregnation, tires partially dissolved and this ruled out the possibility of reproducing the solids obtained. Impregnated Samples 4
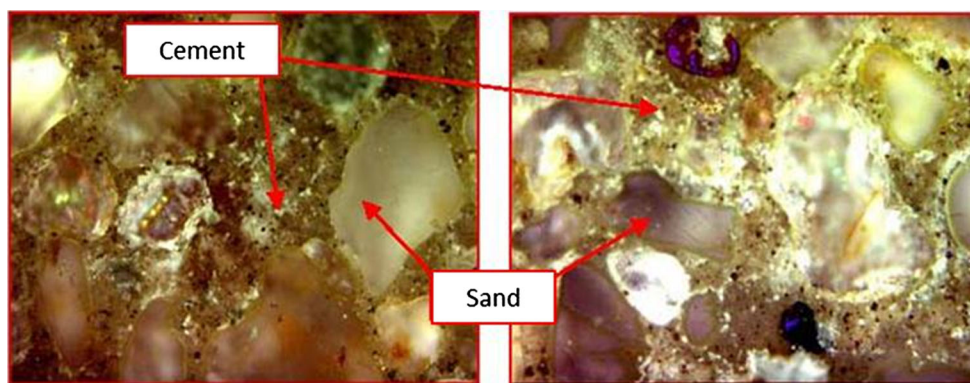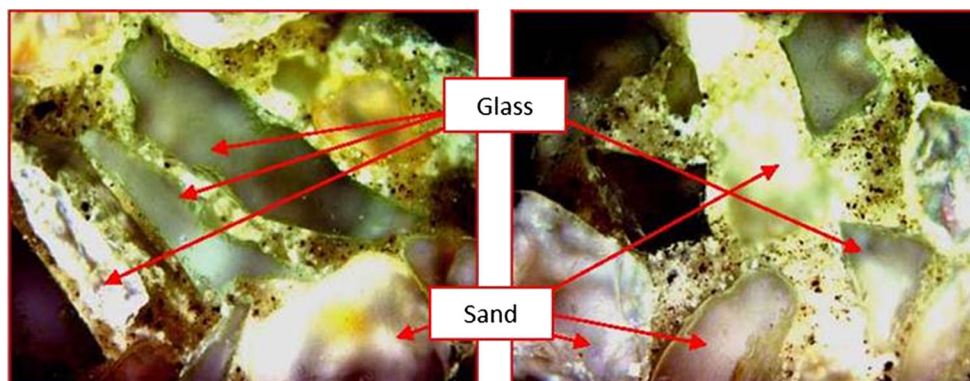
Fig. 1 Optical micrographs of Sample 1 (magnification ×500)
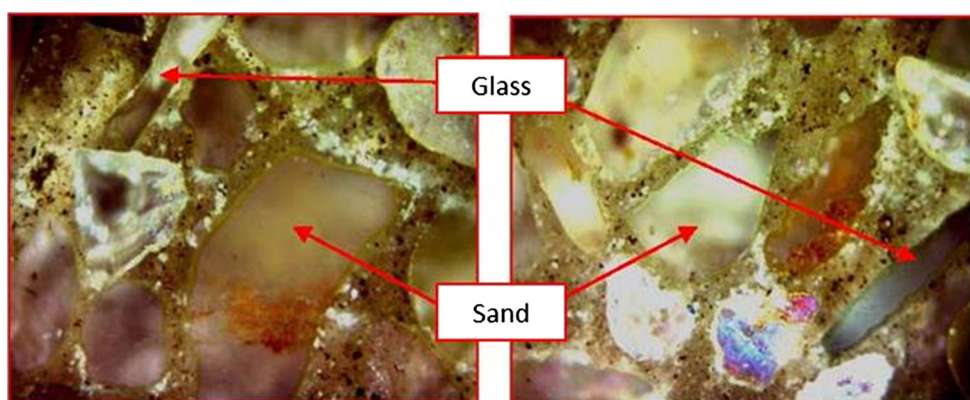
Fig. 2 Optical micrographs of Sample 2 (magnification ×500)

Fig. 3 Optical micrographs of Sample 3 (magnification ×500)

and 6 have similar Mo content and distribution, with impregnated Sample 5 having the highest Mo content, although its distribution is not homogeneous. These three samples contain 10 % of tires, as mentioned above. Sample 5 is composed of four parts of sand, two parts of cement, two parts of glass and one part of tire, which would match the results found in unmixed samples as sand has the

highest Mo content. Sample 7 has four parts of sand and Sample 8, only two parts of sand and 3 parts of glass. Sample 7 has a homogeneous distribution and higher Mo content than Sample 8, which has very little Mo and a heterogeneous distribution that may be attributed to the high glass content, in agreement with the aforementioned results when unmixed glass was used.
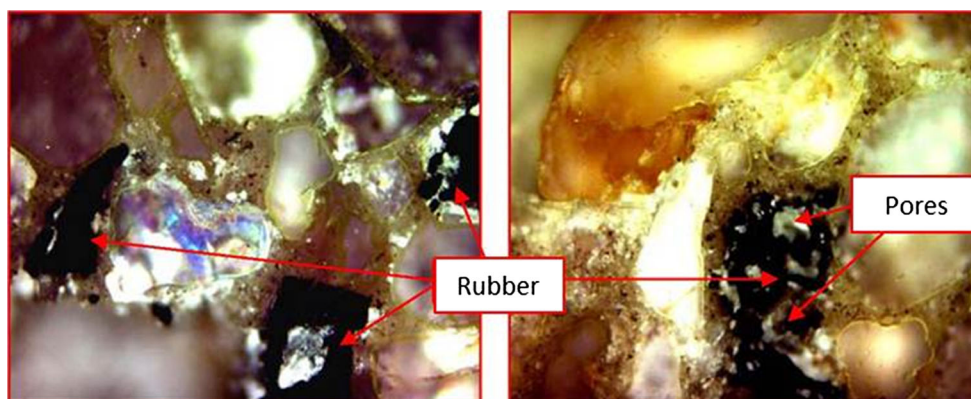
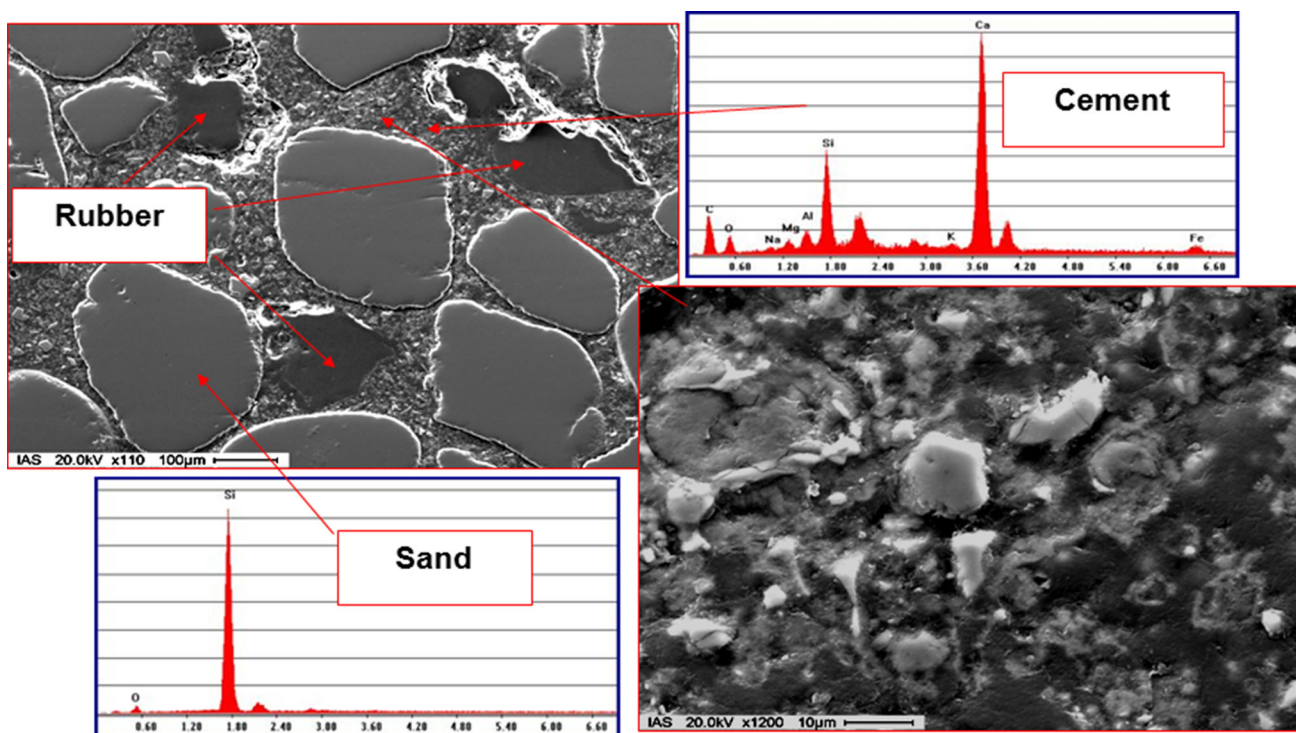**Fig. 4** Optical micrographs of Sample 4 (magnification ×500)

Fig. 5 SEM–EDS analysis of Sample 4

Inductively Coupled Plasma Atomic Emission Spectroscopy

ICP-AES analysis were performed for the $H_3PMo_{12}O_{40}$ bulk and, sample 3 and sample 5, which were the most active catalysts for the oxidation of sulfides and the Biginelli synthesis respectively.

$H_3PMo_{12}O_{40}$. Calculated (theoretical): Mo, 63.08. Found: Mo, 62.95

Sample 3. Calculated (theoretical): Mo, 25.90. Found: Mo, 22.25

Sample 5. Calculated (theoretical): Mo, 25.90. Found: Mo, 24.63

Comparing the EDS analysis, mapping and ICP-AES analysis, we can see that for sample 3 and sample 5 most of the heteropolyacid is deposited on the surface. This is consistent with leaching tests.

Textural Properties

In relation to textural properties, S_{BET} data (m²/g) of unmixed materials are listed in Table 2.

In these MPA impregnated samples, impregnated cement has the highest specific surface area (14 m²/g) and impregnated glass, the lowest (lower than 1 m²/g). This matches data obtained by mapping Mo incorporation into
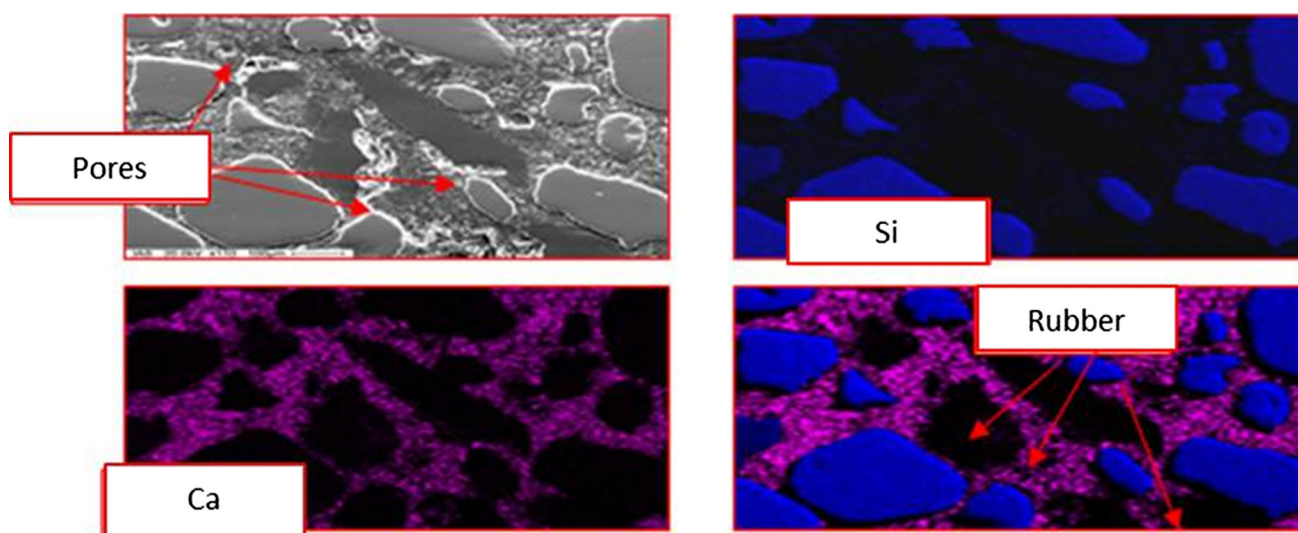
Fig. 6 Mapping of Si and Ca on Sample 4

the structure of waste glass (very low) as opposed to the very homogeneous distribution of Mo when unmixed cement was used (Fig. 7). However, the S_{BET} of impregnated sand is 1 m^2/g; it is very close to that of impregnated glass but with a macroporous structure formed by different particles, which makes it more effective at the impregnation stage. The S_{BET} of impregnated rubber is a bit low (3 m^2/g), but porosity is relatively lower than in impregnated sand. S_{BET} results for synthesized samples (Table 2) are not above 6 m^2/g, which is a very low value to synthesize a heterogeneous catalyst, although it is an average value of the materials used (sand, glass, cement and tire). The lowest value corresponds to Sample 7 (S_{BET}: 2 m^2/g) with a ratio of 4:2:1:1 as required (sand:glass:cement:tire), and the highest value, to Sample 3 (S_{BET}: 5.49 m^2/g) with a ratio of 2:2:4:0:2 (sand:glass:cement:tire:water, respectively). The difference between both samples is the absence of rubber in Sample 3, and it is evident that the quantity of water used causes a better distribution of materials in the cementitious matrix forming larger intraparticle pores. Moreover, it should be noted that the S_{BET} of impregnated Samples 5 and 7 is 3 and 2 m^2/g, respectively, with the greatest Mo content (Fig. 7). This result may be due to the sand/MPA surface interaction together with an HPA diffusion process in the support used when the support contains a high proportion of silica.

Potentiometric Titration

Afterwards, the acid properties of the solids were characterized by potentiometric titration with *n*-butylamine; the Ei values for each MPA-impregnated unmixed material and samples are listed in Table 2. Additionally, as an example, Fig. 8 shows the potentiometric curves of some catalysts.

The curves for sand, glass and cement with and without MPA confirm that MPA behaves alike in all of them, i.e., with a single type of proton in which the environment changes when Ei varies, and the area under the curve, which represents the number of acid sites in the catalyst, is similar in the three of them. MPA-impregnated sand has the highest Ei (964 mV), impregnated unmixed glass has an Ei of 530 mV and finally, the Ei of the impregnated cement is 127 mV. The forth box of Fig. 8 shows the potentiometric curves of Samples 4, 5 and 6, respectively, with the following Ei values: 174, 335 and 138 mV. Sample 5 has the highest Ei (335 mV) of all the impregnated catalysts and is the support with the intermediate sand content; Sample 4 has the highest proportion of sand and Sample 6, the lowest among the three selected catalysts. Based on the contents of unmixed materials (Table 1), sand is the component that most influences catalyst acidity due to the interaction with MPA. But it is clear that the acidity values are also affected by the homogeneous or heterogeneous composition of the support used. The presence of different areas on the surface and inside the materials affects the values of Ei and the number of acid sites.

Catalytic Test

In order to observe the efficiency of the synthesized materials, exploratory tests for the selective oxidation of sulfides to sulfoxides and the synthesis of dihydropyrimidinones (a reaction sensitive to acid conditions) were carried out.
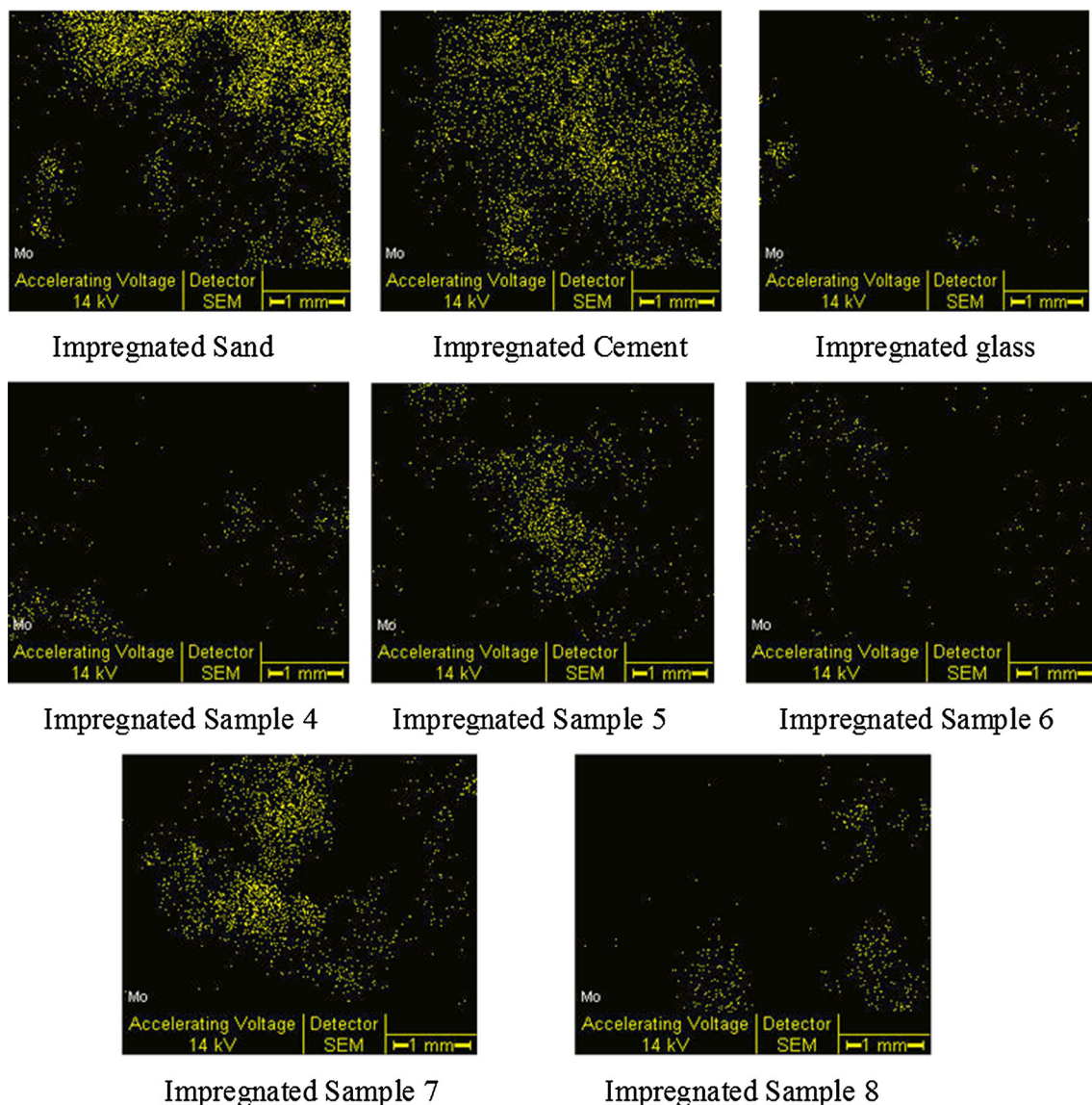
Fig. 7 Mapping of Mo on different MPA-impregnated solids

Table 2 Textural properties and acidity (Ei) of pure and synthesized samples impregnated with $H_3PMo_{12}O_{40}$

Entry	Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)	E_i (mV)
1	Impregnated sand	1	0.001	52	964
2	Impregnated glass	<1	0.001	60	530
3	Impregnated cement	14	0.033	93	127
4	Impregnated rubber	3	0.002	34	–
5	Impregnated Sample 1	4	0.015	134	91
6	Impregnated Sample 2	5	0.019	136	187
7	Impregnated Sample 3	5	0.021	152	145
8	Impregnated Sample 4	3	0.017	199	174
9	Impregnated Sample 5	3	0.021	266	335
10	Impregnated Sample 6	3	0.016	182	138
11	Impregnated Sample 7	2	0.009	174	201
12	Impregnated Sample 8	3	0.013	165	135
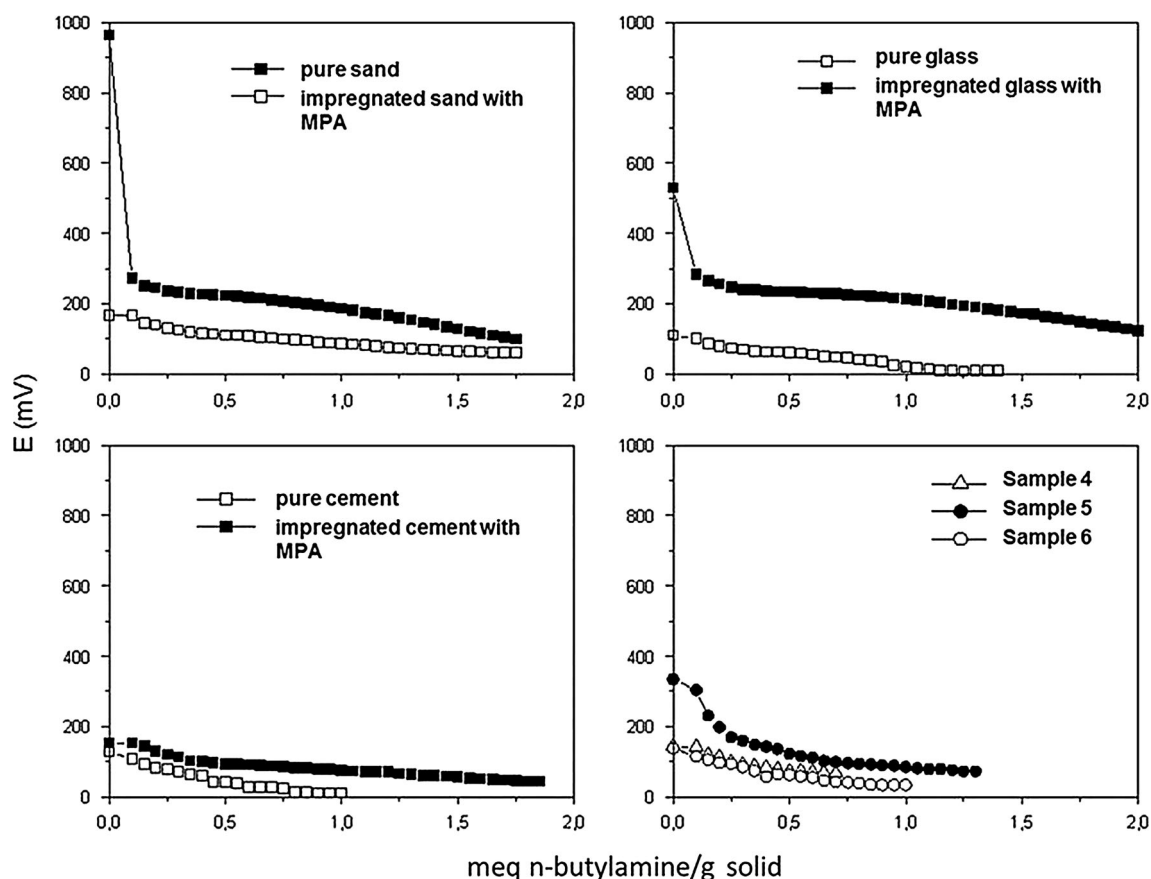
Fig. 8 Potentiometric titration with *n*-butylamine

Selective Oxidation of Sulfides to Sulfoxides

First, we studied the influence of the synthesized materials on the selective oxidation of methyl *p*-tolyl sulfide, with *tert*-butyl hydroperoxide (TBHP) as green oxidant. In these conditions, the corresponding sulfoxide was obtained with a high selectivity (90–95 %). In some cases, minor amounts of secondary products were detected by TLC. Very low conversion was detected in the absence of the catalyst (5 % in 240 min), but when the sample containing HPAs was added, the times decreased considerably, and the conversion increased to values close to 100 %. The complete conversion of methyl *p*-tolyl sulfide was obtained in 60 min using impregnated sand (95 % yield, Table 3, entry 1). Impregnated glass and cement needed/required a reaction time of 90 and 250 min to gives similar yields (Table 3, entries 2 and 3). In relation to the samples prepared by mixing original materials (sand, glass, cement and tire) the most effective were those not containing rubber). Impregnated Samples 1, 2 and 3 give a yield of 89, 90 and 91 % of the corresponding sulfoxide (Table 3, entries 4, 5 and 6, respectively). The samples containing rubber give lower yields in the same time period (60 min.). The

corresponding yields were: impregnated Sample 4 (51 %), 5 (55 %), 6 (72 %), 7 (75 %), and 8 (88 %), respectively (Table 3, entries 7–11).

We also investigated the reuse of the catalysts. For this purpose, after completion of the reaction, the catalyst was separated by simple filtration and dried under vacuum (20 °C). The two most active catalysts (impregnated sand and Sample 3) were recycled, and the product yields for the first and second reuse were 92 and 90 % for impregnated sand (Table 3, entry 1) and 90 and 90 % (Table 3, entry 6) using impregnated Sample 3 as catalyst. Similarly, samples containing rubber were investigated, and leaching was observed for these materials. For example, the obtained yields for impregnated Sample 4 were: 51, 48, and 44 %, respectively (Table 3, entry 7), indicating that toluene, the solvent used in the reaction, dissolves the rubber present in the material.

It is important to note that although it is an oxidation reaction, the acid properties determined in previous studies using hydrogen peroxide [10, 11] indicate that a certain number of acid sites are required so that the heteropolyacid redox properties may be effective during the oxidation process, which is due to the redox reaction Mo (V) to Mo (VI) that occurs in the HPA structure.
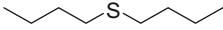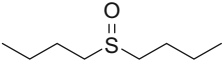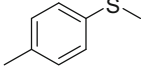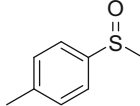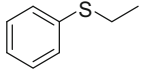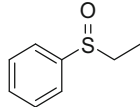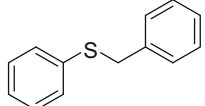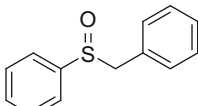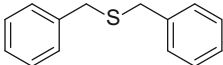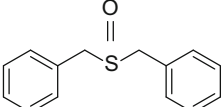
Table 3 Selective oxidation of methyl *p*-tolyl sulfide to methyl *p*-tolylsulfoxide

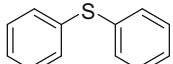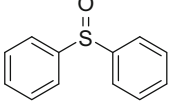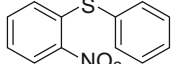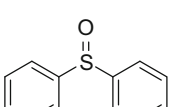| Entry	Sample	Time (min)	Yield (%)	Entry	Sample	Time (min)	Yield (%)
1	Impregnated sand	60	95 (92, 90)[a]	7	Impregnated Sample 4	60	51 (44, 38)[a]
						230	78
2	Impregnated glass	60	70	8	Impregnated Sample 5	60	55
		90	94			240	79
3	Impregnated cement	60	55	9	Impregnated Sample 6	60	72
		250	92			105	82
4	Impregnated Sample 1	60	89	10	Impregnated Sample 7	60	75
						90	85
5	Impregnated Sample 2	60	90	11	Impregnated Sample 8	60	88
6	Impregnated Sample 3	60	91 (90, 90)[a]				

Experimental conditions: substrate: methyl *p*-tolyl sulfide (1 mmol); catalyst: 50 mg; oxidant: *tert*-butyl hydroperoxide (TBHP) 5–6 M, in decane (3 mmol); solvent: toluene (4 mL); temperature: 50 °C, stirring

[a] Parentheses indicate the yields of first and second reuse

Table 4 Selective oxidation of sulfides to sulfoxides using impregnated Sample 3 as catalyst

Entry	Substrate	Product	Time (min)	Yields (%)
1			45	85
2			60	91
3			60	89
4			60	88
5			45	89
6			120	92
7			180	79

Experimental conditions: substrate: methyl *p*-tolyl sulfide (1 mmol); catalyst: 50 mg; oxidant: *tert*-butyl hydroperoxide (TBHP) 5–6 M, in decane (3 mmol); solvent: toluene (4 mL); temperature: 50 °C, stirring

Encouraged by the remarkable results obtained with the above reaction and in order to show the generality and scope of this catalytic method, the selective oxidation of seven sulfides to sulfoxides was studied, using the most active sample (impregnated Sample 3) under similar conditions. The results are summarized in Table 4. All the

Table 5 Biginelli reaction between benzaldehyde, ethyl acetoacetate and urea

Entry	Sample	Time (min)	Yield (%)
1	Impregnated sand	90	85 (82, 80)[a]
2	Impregnated glass	150	55
3	Impregnated cement	130	80
4	Impregnated Sample 1	120	53
5	Impregnated Sample 3	120	54
6	Impregnated Sample 5	120	60 (58, 57)[a]
7	Impregnated Sample 7	120	52 (44, 38)[a]
8	None	240	21

Experimental conditions: substrates: benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1 mmol), catalyst: 50 mg, solvent-free, temperature: 80 °C, stirring
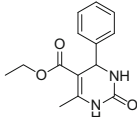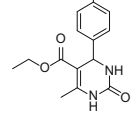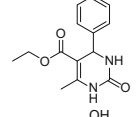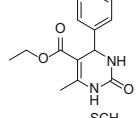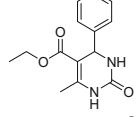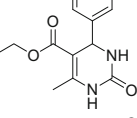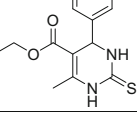
[a] Parentheses indicate the yields of first and second reuse

reactions were run within a very short time, and the sulfoxides were obtained in excellent yields at 50 °C. No important amount of secondary products, such as sulfone, was detected by TLC. The present methodology is appropriate to synthesize 2-nitrodiphenyl sulfoxide, an active anti-HIV drug [55] (Table 4, entry 7).

Synthesis of 3,4-Dihydro-2-(1H)-Pyrimidinones

Due to the results obtained for the selective oxidation of sulfides, the catalyst performance was tested in an acid catalyzed reaction. Consequently, some samples were tested in the Biginelli reaction to obtain 3,4-dihydro-2-(1H)-pyrimidinones under solvent-free conditions (Table 5). Reactions were optimized by varying reaction temperature, reaction time, reagent molar ratio, and solvent. First, we

Table 6 Synthesis of 3,4-dihydropyrimidinones using impregnated Sample 5

Entry	Time (min)	Product	Yield (%)
1	120		60
2	120		58
3	150		55
4	120		57
5	120		53
6	120		57
7	150		55

Experimental conditions: substrates: aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea or thiourea (1 mmol), catalyst: 50 mg, solvent-free, temperature: 80 °C, stirring

performed a blank experiment, the reaction in the absence of catalyst, between benzaldehyde, ethyl acetoacetate and urea (1:1:1.5), at 80 °C, for 240 min, in solvent-free conditions. Under these conditions, only 21 % of the desired product was achieved. However, when 50 mg of catalyst was added, the reaction times decreased considerably, and the yields of 3,4-dihydropyrimidinones increased. For example, the reaction using impregnated sand is complete in 90 min (85 % yields, Table 5, entry 1). Then, we performed the reaction using selected impregnated samples (Sample 1, 3, 5, and 7), and the yields were 53, 54, 60, and 52 %, respectively (Table 5, entries 2, 3, 4, and 5). It is important to note that the two most active catalysts are those with higher acidity (impregnated sand: Ei: 964 mV and Sample 5: Ei: 335 mV, respectively) determined by potentiometric titration.

Similarly to the experiment performed by the selective oxidation of sulfide, we also investigated the reuse of the catalyst in the synthesis of 3,4-dihydropyrimidinones. For this purpose, after completion of the reaction, in order to separate the catalyst from the reaction product, 4 mL toluene was added, the catalyst was filtered in hot condition, and was finally dried under vacuum (20 °C). The two most active catalysts (impregnated sand and Sample 5) were recycled, and the product yields for the first and second reuse were 82 and 80 % for impregnated sand (Table 5, entry 1), and 58 and 57 % for impregnated sample 5 (Table 5, entry 6). A sample containing rubber was investigated and leaching of these materials was observed. For example, the obtained yields for sample 7 were 52, 44, and 38 %, respectively (Table 5, entry 7), indicating that toluene, the solvent used in the extraction of the product, dissolved the rubber present in the material.

Due to the remarkable results obtained with the above reaction and in order to show the generality and scope of this catalytic method, the synthesis of seven 3,4-dihydropyrimidinones was studied, using impregnated Sample 5, under similar conditions. The results are summarized in Table 6. All the reactions were run within a very short time and the 3,4-dihydropyirimidinones were obtained in good yields at 80 °C. No important amount of secondary products was detected by TLC. The present methodology is appropriate to synthesize monastrol, a potential drug for cancer therapy [30]. This compound was obtained by reaction of 3-hydroxybenzaldehyde, ethyl acetoacetate and thiourea instead of urea (Table 6, entry 7, yield 55 %).

Conclusions

In this paper, we report the valorization of residues from various sources to prepare catalyst supports. The waste included sand and cement from the building industry,

nonreturnable glass bottles and used tires. These wastes were mixed to obtain materials of different composition. The synthesized supports were impregnated with molybdophosphoric acid, a heteropolyacid with Keggin structure, and the new materials were characterized by potentiometric titration, textural properties, and SEM–EDS analyses. The samples were tested in the selective oxidation of sulfides to the corresponding sulfoxides, using TBHP as green oxidant. The conversion and selectivity were excellent, and no appreciable formation of secondary products was detected. The catalysts were reused without appreciable loss of the catalytic activity. Similarly, 3,4-dihydropyrimidinones were obtained in good yields in solvent free conditions. Two bioactive compounds, monastrol and 2-nitrodiphenyl sulfoxide, were synthesized by these methodologies. This work represents an important contribution to the synthesis of these compounds and a relevant innovation in the field of catalysis for the design of recyclable solid materials from wastes.

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