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

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Received: 29 January 2016/Accepted: 15 July 2016
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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

Keywords Waste valorization · Catalysts · Heteropolyacids · 3,4-Dihydropyrimidinones · Sulfide oxidation · Green Chemistry

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...
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 ZrCl4 [34], SbCl3 [35] and various HPAs such as H4PMo11VO40 [36], H3PMo12O40[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(NO3)3·6H2O [42], chloroacetic acid [43], KAl(SO4)2·12H2O supported on silica gel [44], TaBr5 [45], and alumina-supported MoO3 [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-
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 $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ solution with a concentration of 110 mg Mo/mL. The supported catalysts were obtained by equilibrium adsorption technique by dissolution of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ 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 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 $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ 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 1](image1)

**Scheme 1** Selective oxidation of sulfides to sulfoxides using a tert-butyl peroxide/catalyst system

![Scheme 2](image2)

**Scheme 2** Biginelli synthesis of 3,4-dihydropyrimidinones

| 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    |
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 Titriino 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. 13C NMR and 1H 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**

\[
R_Y = \left( \frac{\text{moles } P}{\text{moles } A} \right) \left( \frac{v_A}{v_P} \right)
\]

**Selectivity**

\[
S = \frac{\text{moles } P}{\text{moles } P + \text{moles } Q}
\]

**Conversion**

\[
C = \frac{\text{moles } A(\text{remnants})}{\text{moles } A}
\]

**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 with 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 Synthesized 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...
3,4-Dihydropyrimidin-2-Ones  The structure of the products was confirmed by 1H- and 13C-NMR spectra.

5-Ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyrimidin-2-one  M.p.: 211–212 °C  lit. 206–207 °C [52] 1H-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). 13C-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.: 202–204 °C lit. 206–207 °C [53] 1H-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). 13C-NMR (d6-DMSO): δ (ppm) 14.0; 17.6; 53.7; 59.1; 99.5; 113.5; 126.1; 128.8; 136.3; 141.9; 149.2; 152.2; 165.3.

4-(4-Chlorophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2-one  M.p.: 212–213 °C lit. 210–212 °C [53] 1H-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). 13C-NMR (d6-DMSO): 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-Ethoxycarbonyl-4-(4-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2-one  M.p.: 229–230 °C lit. 228–230 °C [54] 1H-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). 13C-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.
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.
Inductively Coupled Plasma Atomic Emission Spectroscopy

ICP-AES analysis were performed for the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ bulk and, sample 3 and sample 5, which were the most active catalysts for the oxidation of sulfides and the Biginelli synthesis respectively.

$\text{H}_3\text{PMo}_{12}\text{O}_{40}$. 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, $S_{\text{BET}}$ data (m$^2$/g) of unmixed materials are listed in Table 2.

In these MPA impregnated samples, impregnated cement has the highest specific surface area (14 m$^2$/g) and impregnated glass, the lowest (lower than 1 m$^2$/g). This matches data obtained by mapping Mo incorporation into
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 $S_{\text{BET}}$ 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 $S_{\text{BET}}$ of impregnated rubber is a bit low (3 m$^2$/g), but porosity is relatively lower than in impregnated sand. $S_{\text{BET}}$ 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 ($S_{\text{BET}}$: 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 ($S_{\text{BET}}$: 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 $S_{\text{BET}}$ 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 (E_i) of pure and synthesized samples impregnated with H₃PMo₁₂O₄₀

| Entry | Sample              | S_BET (m²/g) | Pore volume (cm³/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      |
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 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.

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*Fig. 8* Potentiometric titration with \( n \)-butylamine
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

| Entry | Substrate | Product | Time (min) | Yields (%) |
|-------|-----------|---------|------------|------------|
| 1     | ![Structure](structure1) | ![Structure](structure2) | 45         | 85         |
| 2     | ![Structure](structure3) | ![Structure](structure4) | 60         | 91         |
| 3     | ![Structure](structure5) | ![Structure](structure6) | 60         | 89         |
| 4     | ![Structure](structure7) | ![Structure](structure8) | 60         | 88         |
| 5     | ![Structure](structure9) | ![Structure](structure10) | 45         | 89         |
| 6     | ![Structure](structure11) | ![Structure](structure12) | 120        | 92         |
| 7     | ![Structure](structure13) | ![Structure](structure14) | 180        | 79         |

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

| 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        |

*Parentheses indicate the yields of first and second reuse*

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

| Entry | Time (min) | Product | Yield (%) |
|-------|------------|---------|-----------|
| 1     | 120        | ![Chemical structure] | 60        |
| 2     | 120        | ![Chemical structure] | 58        |
| 3     | 150        | ![Chemical structure] | 55        |
| 4     | 120        | ![Chemical structure] | 57        |
| 5     | 120        | ![Chemical structure] | 53        |
| 6     | 120        | ![Chemical structure] | 57        |
| 7     | 150        | ![Chemical structure] | 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 acetooacetate 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 conditions, 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-dihydropyrimidinones 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 acetooacetate 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 molyb- dophosphoric 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.

Acknowledgments We thank Universidad Nacional de La Plata (UNLP), CONICET (PIP 003) and ANPCyT (PICT 0409) for financial support. V. P., A. S., P. V., and G. R. are members of CONICET. N. Q. is member of CIC. We also recognize Lilian Osiglio’s technical contributions to this work.

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