

Valorization of Citrus Waste: Use in Catalysis for the Oxidation of Sulfides

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ABSTRACT: The utilization and valorization of industrial waste is an effective strategy for environmental protection. Since the juice industry generates a huge amount of citrus waste, we studied the application of thermally treated orange peel in catalysis. On the other hand, Keggin heteropolyacids are excellent oxidant catalysts used as a replacement for conventional oxidants; however, their solubility in polar solvents and the low specific area limit their use as heterogeneous catalysts. The utilization of treated orange peel as heteropolyacid support for the selective oxidation of sulfides is presented here. Firstly, orange peel was thermally treated, and then it was incorporated with heteropolyacids (PMo) during the silica synthesis by the sol-gel method. Therefore, $\text{SiO}_2\text{-PMo}$, $\text{SiO}_2\text{-OP100-PMo}$, and $\text{SiO}_2\text{-OP200-PMo}$ were obtained, characterized by FTIR, S_{BET} , XRD, and potentiometric titration, and were tested as heterogeneous catalysts in the selective oxidation of sulfide to sulfoxide in a greener process: H_2O_2 as oxidant and ethanol as solvent, at 25 °C.

KEYWORDS: Waste valorization, orange peel, heteropolyacids, heterogeneous catalysis, sulfide oxidation

1 INTRODUCTION

One of the main environmental issues is the deposition of solid waste generated by different industries, which causes water, air, and soil pollution. As Green Chemistry teaches, the elimination or reduction of hazardous waste and substances must be considered in every chemical/industrial process [1, 2].

The orange juice industry generates a huge amount of citrus waste, almost half of the fresh fruit used. This residue is composed of peel, seeds, pulp, and leaves, which amounts to 15 million tons per year [3, 4].

Some juice industries remove the liquid from the residue, and the dry solid is sold to cosmetic industries or as cattle feed. However, the treatment of citrus waste can represent a huge additional cost, and the disposal in open dumps is the traditional option chosen by industries. This constitutes a nutrient source and a potential pollution agent because of the high content of organic matter and its humidity [3, 5]. On the other hand, the incineration of solid waste can produce energy through the heat generated, but also

produces a large amount of flue gases, toxic fumes and ash. Therefore, the transformation of this waste into value-added products could allow industries to reduce treatment costs and generate some economic benefits. In addition, by-product processing is essential for sustainable development [6].

The composition of the orange waste is rich in soluble sugars, cellulose, hemicellulose and pectin, which can provide molasses, dietary fiber supplements, essential oils, essences, D-limonene, hydroxymethylfurfural, bioethanol, biofuel, oil seeds, flavonoids, fertilizers, charcoal, biosurfactants, adsorbents, etc. [7–12].

On the other hand, heteropolyacids (HPAs) constitute a field of increasing importance worldwide, especially in catalysis as a replacement for inorganic acid catalysts, such as sulfuric, hydrofluoric or hydrochloric acids, which produce toxic waste and require drastic reaction conditions. HPAs possess a very strong acidity and appropriate redox properties, are noncorrosive, cheap and environmentally friendly [13, 14]. Our research group has vast experience employing HPAs (Keggin, Wells-Dawson and Preyssler) as catalysts for heterocyclic synthesis and selective oxidation reactions [15–17].

With respect to their use as redox catalysts, we used HPAs together with hydrogen peroxide, which

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is an eco-friendly oxidant due to its oxygen content, low cost, and the fact that water is the only reaction by-product, in the selective oxidation of anilines, alcohols, phenols, naphthols, and sulfides [18–20]. Due to the high solubility in polar solvents, such as water and ethanol, and the low specific area of bulk HPAs, these reactions were studied using HPAs supported on conventional oxides [21, 22] or their pyridine salts [23] to convert HPAs to heterogeneous catalysts. The utilization of heterogeneous catalysts is more advantageous than that of homogeneous catalysts, mainly because they can easily be recovered from the reaction mixture by simple filtration procedures and then reused after activation, thereby making the process economically viable.

Among the different ways to convert bulk HPAs to heterogeneous catalysts that have been studied, the inclusion of HPAs in a silica matrix during the sol-gel process has been one of the best strategies [24].

On the other hand, the selective conversion of sulfides to sulfoxides is of great importance both in the industry and in basic research [25, 26], especially due to their therapeutic properties [27].

Our research group has used waste, such as cement and sand from the building industry, used tires and glass bottles, as support for HPAs [28]. Here we present the orange waste as charcoal source, and its incorporation into a silica matrix that can act as support for HPAs. The solids were tested as heterogeneous catalysts in the selective oxidation of diphenyl sulfide to diphenyl sulfoxide in a greener process using aqueous H_2O_2 as oxidant and ethanol as solvent, at room temperature (Scheme 1). We expect that this strategy could be used for the valorization of citrus waste generated by the juice industry.

2 EXPERIMENTAL

2.1 General

Orange peel was obtained from fresh fruit from the local market, and all the chemical reagents were purchased commercially and used without further purification.

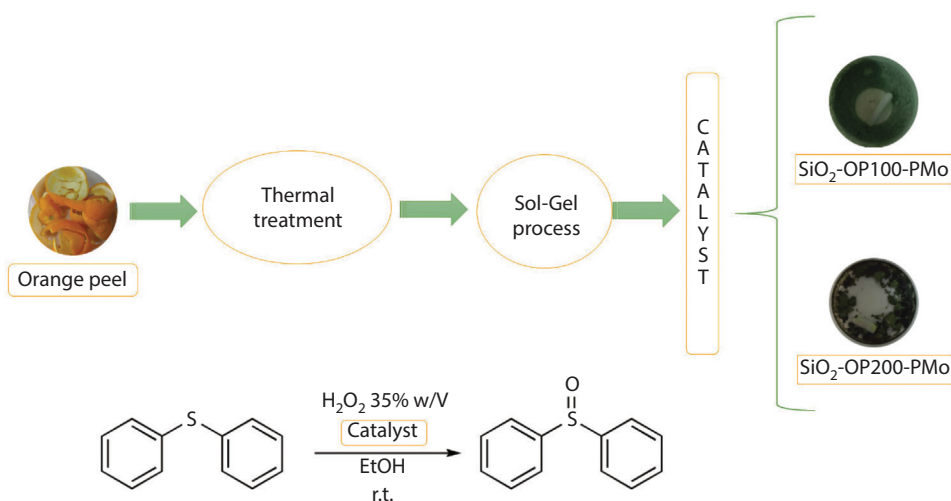
2.2 Catalyst Preparation

Orange peel was cut into small pieces, washed with ethanol and was thermally treated: first it was dried in an oven at 100 °C for 24 h and ground (OP100), then it was carbonized at 200 °C for 2 h under air atmosphere and ground (OP200). Subsequently, OP100 and OP200 were added during the silica synthesis by the sol-gel method, at room temperature: tetraethoxysilane (TEOS, 6.8 mL, 0.03 mol) and absolute ethanol (6 mL, 0.1 mol) were mixed in a glove box under nitrogen atmosphere. Then the mixture was removed from the nitrogen atmosphere and a solution of phosphomolybdic acid (PMo) (300 mg, $1.5 \cdot 10^{-4}$ mol) in absolute ethanol (2.7 mL, 0.03 mol), water (2 mL, 0.1 mol) and OP100 or OP200 (200 mg) were incorporated and stirred until dry sol-gel was obtained. Therefore, SiO_2 -PMo, SiO_2 -OP100-PMo, and SiO_2 -OP200-PMo were obtained.

2.3 Catalyst Characterization

2.3.1 Scanning Electron Microscopy (SEM)

The synthesized solids, fixed on a graphitized band and metalized with Au, were characterized by a Philips 505 scanning electron microscope using an accelerating voltage of 25 eV.



Scheme 1 Selective oxidation of diphenyl sulfide.

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were obtained in the 400–4000 cm^{-1} wavenumber range using pellets of KBr in a Thermo Bruker IFS 66 spectrometer.

2.3.3 X-ray Diffraction (XRD)

The XRD patterns of the solids were collected in Philips PW-1730 equipment, using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with 40 kV and 20 mA. A nickel filter and scanning angle between 5° and 60° of 2θ at a scanning rate of $2^\circ (2\theta)$ per minute were used.

2.3.4 Textural Properties

The nitrogen adsorption/desorption isotherms at -196°C were determined using Micromeritics ASAP 2020 equipment. The previous degasification was carried out for 700 min at 100°C and below $30 \mu\text{m Hg}$. From these isotherms, it was possible to determine the specific surface area (S_{BET}) of the samples.

2.3.5 Potentiometric Titration

The titration was carried out by adding 0.05 mL of a solution of *n*-butylamine in acetonitrile (0.05 N) to 0.05 g of the solid suspended in acetonitrile (90 mL). The potential variation (mV) was measured with Metrohm 794 Basic Titrino 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.

2.4 Catalytic Test

A mixture of diphenyl sulfide (1 mmol), ethanol (8 mL), aqueous H_2O_2 35% (w/v) (0.15 mL), and catalyst (250 mg) was stirred at room temperature. Samples (0.1 mL) were withdrawn at fixed intervals, extracted with dichloromethane (0.5 mL) and water (0.5 mL), dried on anhydrous Na_2SO_4 and analyzed by gas chromatography in a Shimadzu 2014 equipment with a Supelco capillary column ($0.32 \text{ mm} \times 30 \text{ m}$).

After 24 h of reaction, the catalyst was filtered, washed with ethanol ($2 \times 1 \text{ mL}$), dried, and reused following the procedure described above.

3 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy

Figure 1 shows the SEM micrographs of the solids. OP100 presents a regular and undulating surface, while OP200 shows pores due to carbon formation in the thermal treatment. On the other hand, the siliceous solids, SiO_2 -PMo, SiO_2 -OP100-PMo, and SiO_2 -OP200-PMo, present the typical morphology of pure silica (SiO_2). However, evidence of carbonaceous material can be seen in SiO_2 -OP200-PMo.

3.2 Fourier Transform Infrared Spectroscopy

The FTIR spectra of SiO_2 -PMo, SiO_2 -OP100-PMo, and SiO_2 -OP200-PMo (Figure 2) are similar to the pure silica spectrum. However, there are signs of characteristic bands of Keggin structure (gray lines in the figure), which means that PMo is inside the solid and retains its structure. The PMo spectrum showed bands at 1064 (P-Oa), 960 (Mo=Od), 872 (Mo-Ob-Mo), and 779 (Mo-Oc-Mo) cm^{-1} , where Oa surrounds the central tetrahedral P; Ob connects MoO_6 octahedra by the

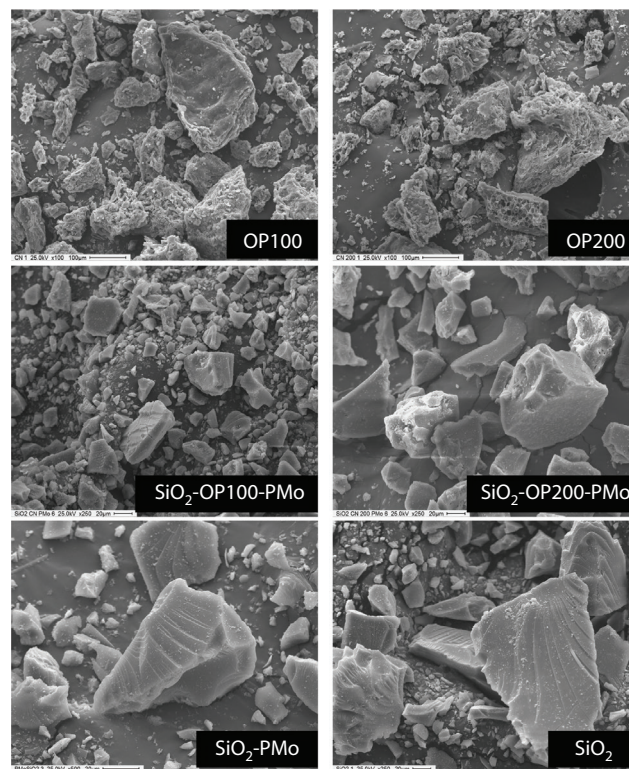


Figure 1 SEM micrograph of OP100, OP200 (magnification 100x), SiO_2 -OP100-PMo, SiO_2 -OP200-PMo, SiO_2 -PMo, and SiO_2 (magnification 250x).

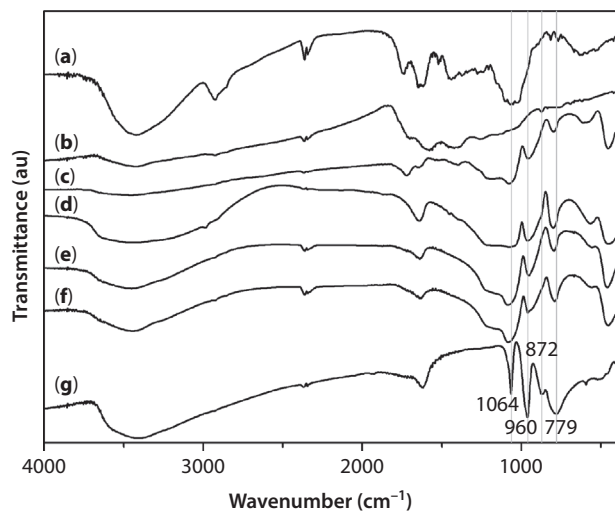


Figure 2 FTIR spectra of (a) OP100, (b) OP200, (c) SiO₂, (d) SiO₂-PMo, (e) SiO₂-OP100-PMo, (f) SiO₂-OP200-PMo, and (g) PMo.

corners; Oc shares the octahedra edges; and terminal oxygen Od is bonded to only one Mo atom.

The OP100 spectrum presents the characteristic signals of organic material, while the ones observed in OP200 are from carbonized organic material [5].

3.3 X-ray Diffraction

Figure 3 shows the XRD patterns of the solids. The thermally treated orange peel shows an amorphous pattern, as well as pure silica. The synthesized catalysts present a pattern similar to that of pure silica, which indicates a high dispersion of citrus waste and PMo inside the silica matrix. However, peaks of bulk PMo (Figure 3g) are present in SiO₂-OP200-PMo (Figure 3f).

3.4 Textural Properties

Nitrogen adsorption/desorption isotherms of SiO₂ and SiO₂-PMo are of type I, indicating a microporous material. The isotherms of SiO₂-OP100-PMo and SiO₂-OP200-PMo are similar to type II isotherms, characteristic of materials with large pores or that are non-porous. The surface area S_{BET} (Table 1) of the included silica is lower than that of pure silica, possibly due to pore blocking for the HPA and citrus waste remaining inside the silica structure.

3.5 Potentiometric Titration

PMo heteropolyacid is a strong acid ($E = 826$ mV) with a large number of acid sites. However, the acid

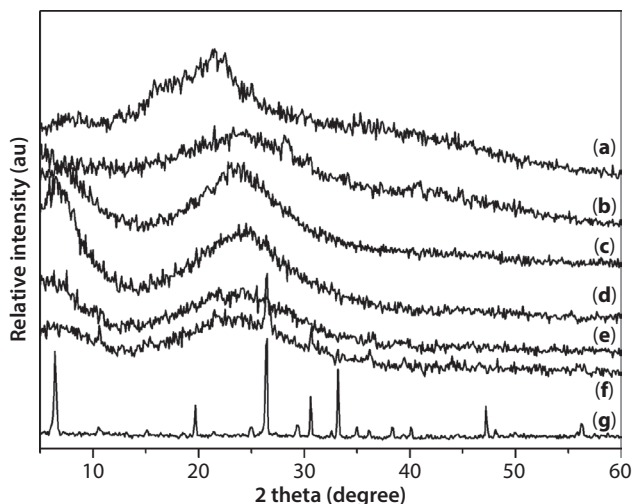


Figure 3 XRD patterns of (a) OP100, (b) OP200, (c) SiO₂, (d) SiO₂-PMo, (e) SiO₂-OP100-PMo, (f) SiO₂-OP200-PMo, and (g) PMo.

Table 1 Textural properties of catalysts.

Sample	S_{BET} (m ² /g)	Sample	S_{BET} (m ² /g)
SiO ₂	760	SiO ₂ -OP200-PMo	19
SiO ₂ -PMo	545	OP100 ^a	–
SiO ₂ -OP100-PMo	324	OP200	2.3

^aVery low values, in the range of experimental error

strength and the number of acid sites decrease when it is included in the different silica supports (Figure 4). This fact could be related to the proton mobility of the PMo into the silica framework.

3.6 Catalytic Test

The results of the catalytic test (Figure 5) show that the conversion was complete at 6 h for SiO₂-OP100-PMo, 12 h for SiO₂-PMo, and 24 h for SiO₂-OP200-PMo. Diphenyl sulfoxide was obtained with more than 98% selectivity for the selected time. In a blank experiment using the pure support, diphenyl sulfide conversion was not observed after 24 h.

The activity of SiO₂-PMo and SiO₂-OP100-PMo slightly decreases in the second and third uses (Figures 6 and 7). However, in the reuses of SiO₂-OP200-PMo, a small increase was observed (Figure 8). For the three catalysts, the selectivity toward diphenyl sulfoxide was excellent.

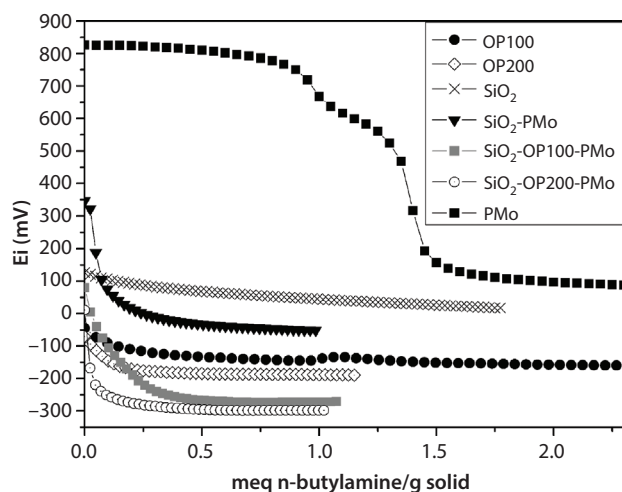


Figure 4 Potentiometric titration curves of PMo and synthesized catalysts.

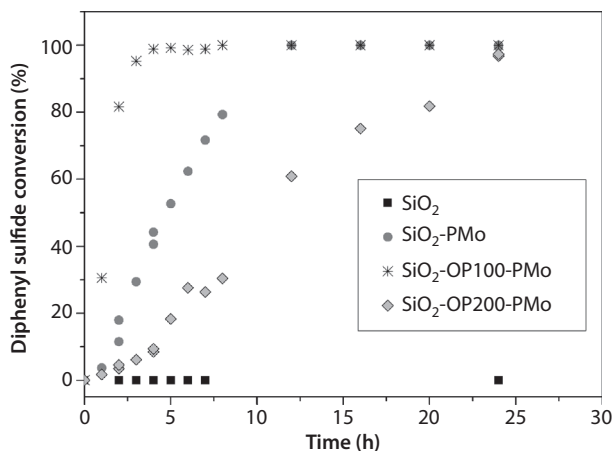


Figure 5 Diphenyl sulfide conversion using the synthesized catalysts.

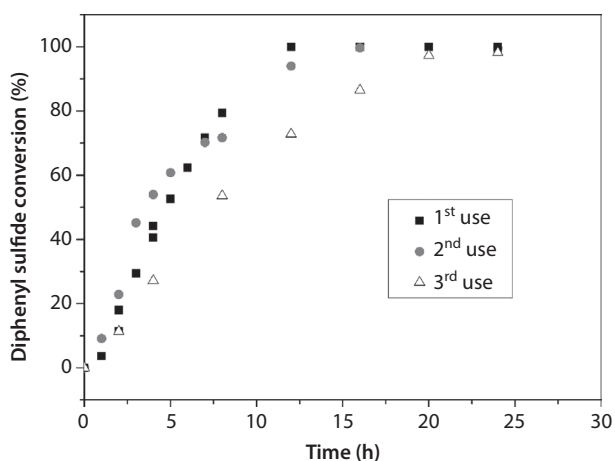


Figure 6 Diphenyl sulfide conversion in the reuses of $\text{SiO}_2\text{-PMo}$.

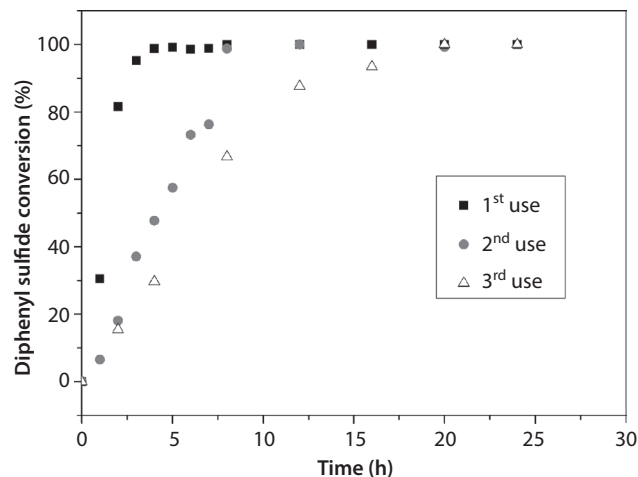


Figure 7 Diphenyl sulfide conversion in the reuses of $\text{SiO}_2\text{-OP100-PMo}$.

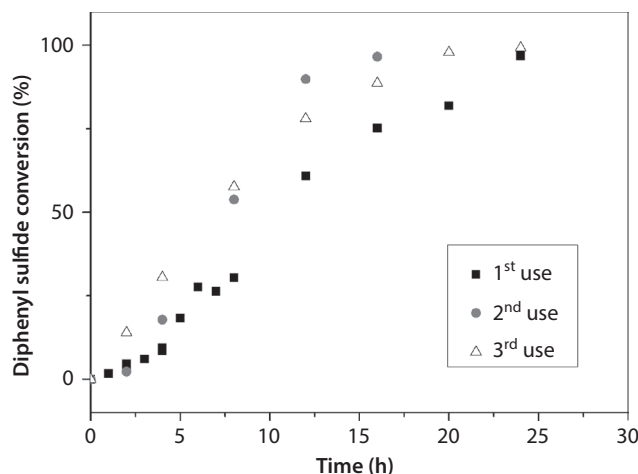


Figure 8 Diphenyl sulfide conversion in the reuses of $\text{SiO}_2\text{-OP200-PMo}$.

4 CONCLUSION

The valorization of citrus waste was achieved by the incorporation of orange peel into catalysts containing a Keggin heteropolyacid in a silica matrix. The catalysts were satisfactorily tested in the selective oxidation of diphenyl sulfide to diphenyl sulfoxide in an eco-friendly process: heterogeneous catalysts, room temperature, ethanol as solvent, and hydrogen peroxide as oxidant. The catalytic activity was maintained after three reaction cycles.

The obtained results have encouraged us to extend the reaction using more complex sulfides for the synthesis of bioactive sulfoxides.

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