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Solvent mediated impurity removal process for a spent hydroprocessing catalyst and its use in alcohol oxidations

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Abstract. Spent catalyst waste derived from a petrochemical refinery was treated to remove oil and other hydroprocessing process impurities aimed to a subsequent reuse. The catalyst recovery was accomplished through an oil removal method which involved a consecutive draining- solvent extraction- calcination process. Some solvents were tested for catalyst solvent extraction step and ethyl acetate showed optimal impurity removal and environmental compatibility. The recovered catalysts were analyzed by diverse techniques and tested in the oxidation of benzylic alcohols. Results demonstrate that conversion to carboxylic acids requires 10 % W/W recovered catalyst together to hydrogen peroxide as co-oxidant.

Keywords. Recovery, spent catalyst, reuse, alcohol oxidation.

1. Introduction

Nowadays, spent catalysts represent a significant environmental problem since its final disposal requires special handling and management. Catalyst life and performance is different from plant to plant, and a variety of deactivation phenomena during the process contribute to the decrease of catalyst performance [1].

In particular, petroleum refining industries use catalysts extensively in many processes. One of the most important processes is the conversion of heavy oil fractions into lighter products due to the increasing demand in the market [2-4]. In this process, the continuous activity causes deposition of contaminants on the catalyst surface (sometimes carbon and sulfur) which origins gradual deactivation of the catalysts [5].

Hydroprocessing catalysts combine metals from group VI (Mo, W) with metals from group VIII (Co, Ni) [2]. At the end of their living cycle, the disposal of these catalysts is complicated by numerous technical, environmental and organizational issues involved [6]. Although leaching is proposed for the treatment of these catalysts [7-9], metal separation is a challenge for this kind of processes.

One of the desired properties of heterogeneous catalysts is their reusability, mainly due to the cost reduction and also to avoid the production of hazardous waste material. There are several ways to regenerate a catalyst for reuse, and the method will depend on the type of catalyst. For chemical synthesis applications, catalyst is used in most of times for the production of organic molecules and a wide surface coverage is necessary. The available methods for catalyst recovery include desorption-filtration [10-12], or calcination [13-14] which were used for alumina and silica-based catalysts.

These elements inspired us to start an investigation about the recovery of spent catalyst waste derived from a petrochemical refinery aiming to reuse as catalysts in benzyl alcohol oxidations which are important in both academic research and industrial manufacturing [15-19]. Herein is summarized our recent endeavors in this area.

2. Experimental

2.1. General remarks

Samples of spent catalyst waste pellets were provided from a Mexican oil refinery and they were used as received. Additional starting materials were purchased from Aldrich Chemical Co. and were used without further purification. Solvents were distilled before use. Silica plates of 0.20 mm thickness were used for thin layer chromatography. Melting points were determined with a Krüss Optronic melting point apparatus and they are uncorrected.

2.2. Analysis methods

Infrared spectra were recorded on a Bruker Tensor 27 instrument with platinum accessory. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE 300; the chemical shifts (δ) are given in ppm relative to TMS as internal standard (0.00). For analytical purposes the mass spectra were recorded on a Shimadzu GCMS-QP2010 Plus in the EI mode, 70 eV, 200 °C via direct inlet probe. Only the molecular and parent ions (m/z) are reported. TGA studies were carried out in a range of 25°C to 560°C (10°C/min. warming up speed) under a 20 mL/min nitrogen atmosphere flow (99.997% purity) and performed on a Jupiter instrument model Netzsch STA 449-F3, equipped with an external Mettler Toledo XP6 microbalance with 1 nanogram of resolution. The used smoothing algorithm was Savitzky-Golay. For SEM and EDS studies, surface topography was evaluated in a JEOL JSM 6510LV at 15 kV, using both secondary and backscattered electron signals. Samples were sputtered with a thin layer of about 15 nm of gold using a Denton Vacuum DESK IV system. In order to determine the elemental composition and distribution of the samples, EDS analysis was performed with an Oxford PentaFetx5 probe on the SEM. The probe was calibrated prior to analysis with a copper standard and the data was analyzed with the INCA software included with the equipment.

2.3 General procedure for catalyst recovery

Spent catalyst (1 g) was added to the appropriate solvent (20 mL) and the resulting mixture was stirred for 3 h at reflux temperature. The mixture was cooled to room temperature and the catalyst was filtered, washed with cold solvent and dried under vacuum. The catalyst was treated at 650 °C in a muffle for 15 min and cooled to room temperature.

2.4. General procedure for oxidation of benzylic alcohols

Recovered catalyst (0.01 g) was added to a solution of the appropriate benzylic alcohol (0.1 g) in AcOH (10 mL) and H_2O_2 (2 mL). The resulting mixture was heated at reflux temperature for 2 h. The mixture was cooled to room temperature and filtered and the solvent was removed under vacuum. The product was extracted with CH_2Cl_2 (3 × 15 mL), the organic phases were joined and dried over Na_2SO_4 and the solvent was removed under vacuum to yield the corresponding carboxylic acid which was purified by crystallization.

2.4.1 4-Chlorobenzoic acid. White solid; mp 239 °C; IR (ATR, cm^{-1}) 3089, 2054, 1746, 1592; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.06 (d, J= 8.4 Hz, 2H), 7.47 (d, J= 8.4 Hz, 2H), 5.06 (s, broad, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.8 (C), 140.1 (C), 133.7 (C), 131.6 (2 X CH), 120.0 (2 X CH).

2.4.2 2-Chlorobenzoic acid. White solid; mp 137 °C; IR (ATR, cm^{-1}) 3096, 1691, 1619; ^1H NMR ($CDCl_3$, 300 MHz) δ 12.0 (s, broad, 1H), 7.80 (m, 1H), 7.56 (m, 2H), 7.43 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.8 (C), 133.4 (CH), 132.7 (C), 131.7 (C), 131.2 (CH), 130.9 (CH), 129.3 (CH).

2.4.3. 4-methylbenzoic acid. White solid; mp 135 °C; IR (ATR, cm^{-1}) 2963, 2854, 1678, 1612; ^1H NMR ($CDCl_3$, 300 MHz) δ 11.5 (s, broad, 1H), 7.82 (d, J= 8.2 Hz, 2H), 7.37 (d, J= 8.2 Hz, 2H), 2.56 (s, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.6 (C), 141.9 (C), 129.7 (2 X CH), 128.2 (2 X CH), 127.2 (C) 25.0 (CH_3).

3. Results and discussion

3.1 Recovery of spent catalyst waste

The first experiments were carried out with the objective to remove oil and hydroprocessing process impurities. Excess oil was separated by a simple draining through a 1X1 mm sieve for 24 h (Fig. 1). This procedure eliminates to 25 % weight of spent catalyst waste.

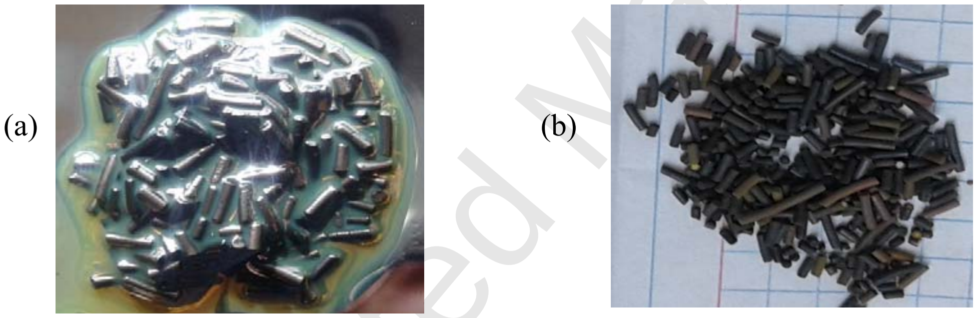

Fig. 1. Spent catalyst waste before (a) and after (b) draining process.

After draining process, we firstly considered catalyst calcination to complete the hydrocarbon removal. However, preliminary experiments proved that temperatures above 800 °C and times around 24 h are required to achieve a total hydrocarbon elimination with pellet destruction. These facts prompted us to propose a combined method which consisted in a consecutive solvent extraction-lower temperature calcination process, according to diagram represented in Fig. 2.

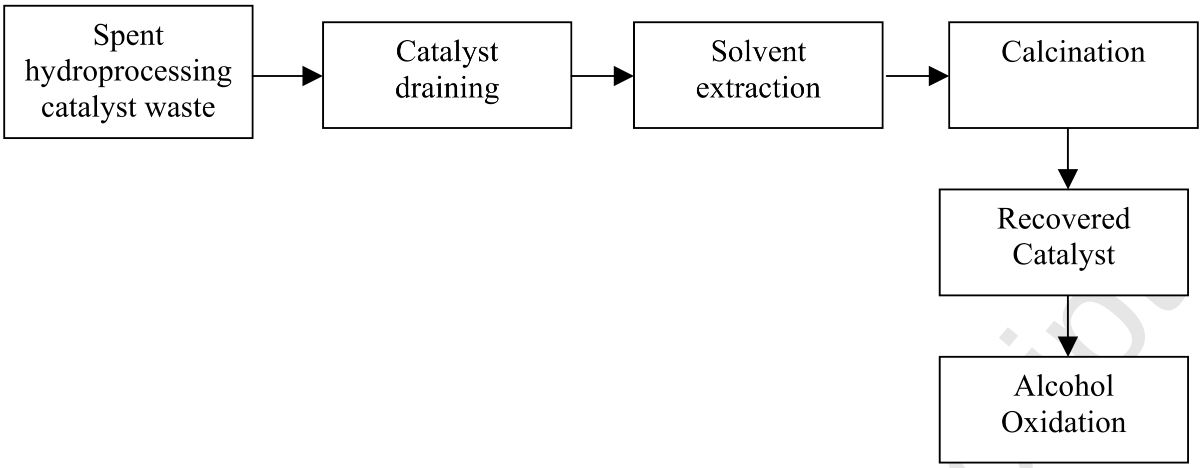

Fig. 2. Diagram of recovery and reuse of spent hydroprocessing catalyst waste.

Following this idea, drained catalysts were treated with several polar and non-polar solvents, including H_2O, at both room and reflux temperatures and best results were observed when a mixture of catalyst and the appropriate solvent was stirred for 3 h at reflux temperature. The results summarized in table 1 show the impurity removal ratio as % loss weight of spent catalyst waste. Although CS_2 and CH_2Cl_2 displayed the best removal ability, we chose AcOEt as impurity removal solvent due to this solvent is relatively as efficient as before mentioned solvents (considering experimental errors), besides AcOEt represents an environmentally friendlier solvent.

Table 1
Impurity Removal using diverse solvents.

Entry	Solvent	% Impurity Removal
1	CS_2	17.3
2	CH_2Cl_2	15.3
3	AcOEt	14.8
4	Hexane	13.3
5	Toluene	13.3
6	Acetone	12.7
7	H_2O	9.0

Analysis by FT-IR (spectrum (a) in Fig 2) and EDS (spectrum (b) in Fig 5) of treated catalysts revealed that solvent treatment was not enough for a total hydrocarbon removal in spent catalyst waste, and a thermal treatment was required. Thus, solvent treated catalysts were calcined using different temperatures. The FT-IR spectra of catalysts after calcination showed an aliphatic C-H bond signal decrease at 2950-2850 cm^{-1} which indicates elimination of hydrocarbon from these catalysts (Fig 2). For practical purposes, treatment at 650 °C for 15 min provides hydrocarbon free catalysts with good catalytic efficiency for subsequent experiments.

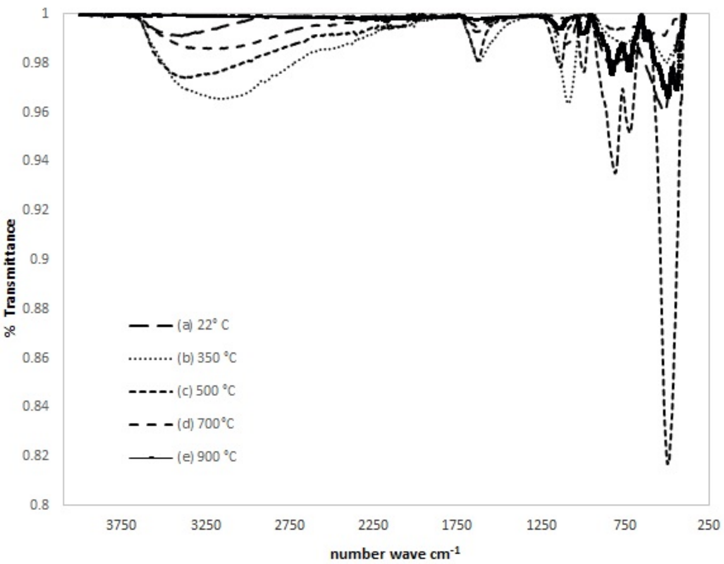

Fig. 2. FT-IR spectra of calcined catalysts at different temperatures.

This information is in agreement with those provided by TGA analysis. Thermograms of catalysts after draining and solvent/calcination process were compared with raw catalyst (namely, fresh catalyst) and showed in Fig 3. An interesting feature is that TG curve for catalyst after draining exhibits a weight loss located at 200-500 °C consistent with the degradation and loss of hydrocarbons. In contrast, the thermal profile of the spent catalyst after solvent/calcination process is closer to raw catalyst TG curve in a range located at 200-300 °C.

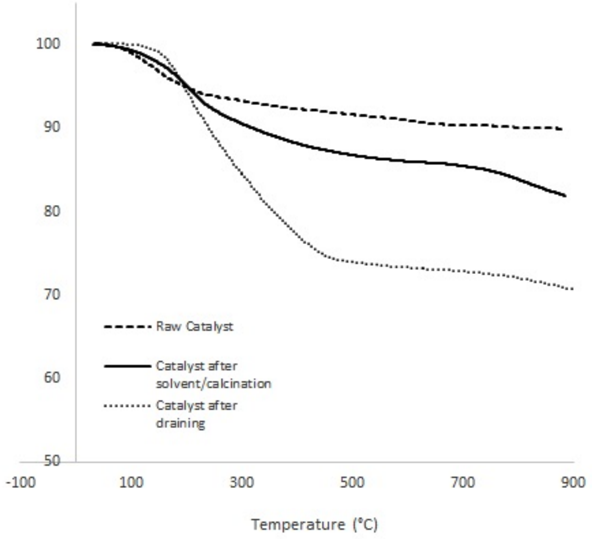

Fig. 3. TG thermograms of raw catalyst, catalyst after draining and catalyst after solvent/calcination process.

In addition, SEM micrographs of samples of raw catalyst (a), catalyst after solvent treatment (b) and catalyst after calcination process (c) are presented in Fig 4, and the corresponding Energy Dispersion Spectra are showed in Fig. 5. EDS experiments demonstrate that catalysts after solvent treatment have a high carbon content (ca 22%) associated to hydrocarbons, while carbon presence was not detected in catalysts after calcination process. The EDS spectrum of spent catalyst after calcination (Fig. 5c) also indicates the presence of intense peaks of S, V and Fe. These results concur with previous studies in which V and S contained in heavy crude oil are deposited on the catalyst during the reaction, causing a decrease in the catalyst life [20]. Moreover, no important modifications in the pellet structure were observed in calcined catalysts in comparison to both raw catalyst and catalyst after solvent treatment.

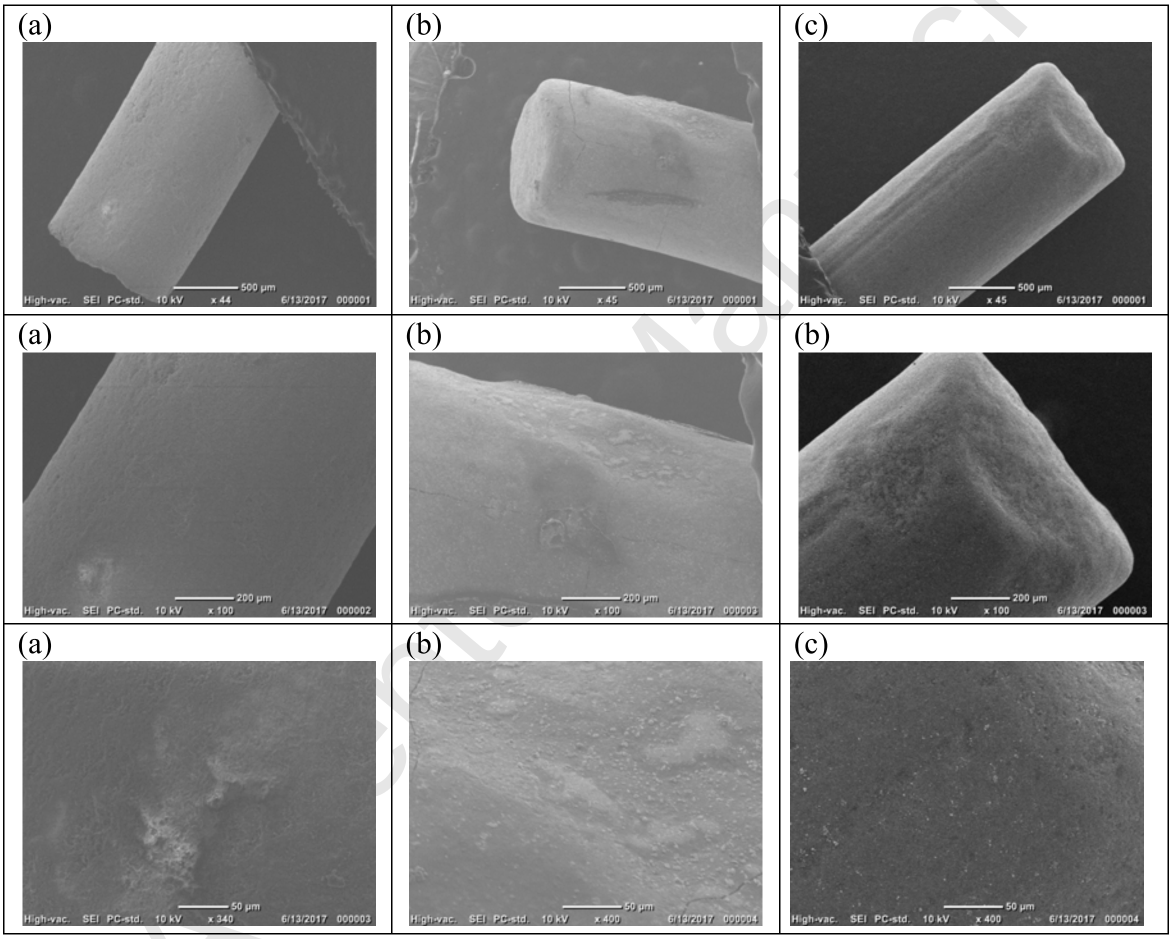

Fig. 4. Top line: SEM Micrographs of (a) raw catalyst, (b) catalyst after solvent treatment, (c) catalyst after calcination process, scale bar: 500 µm. Middle line: SEM Micrographs of (a) raw catalyst, (b) catalyst after solvent treatment, (c) catalyst after calcination process, scale bar: 200 µm. Bottom line: SEM Micrographs of (a) raw catalyst, (b) catalyst after solvent treatment, (c) catalyst after calcination process, scale bar: 50 µm.

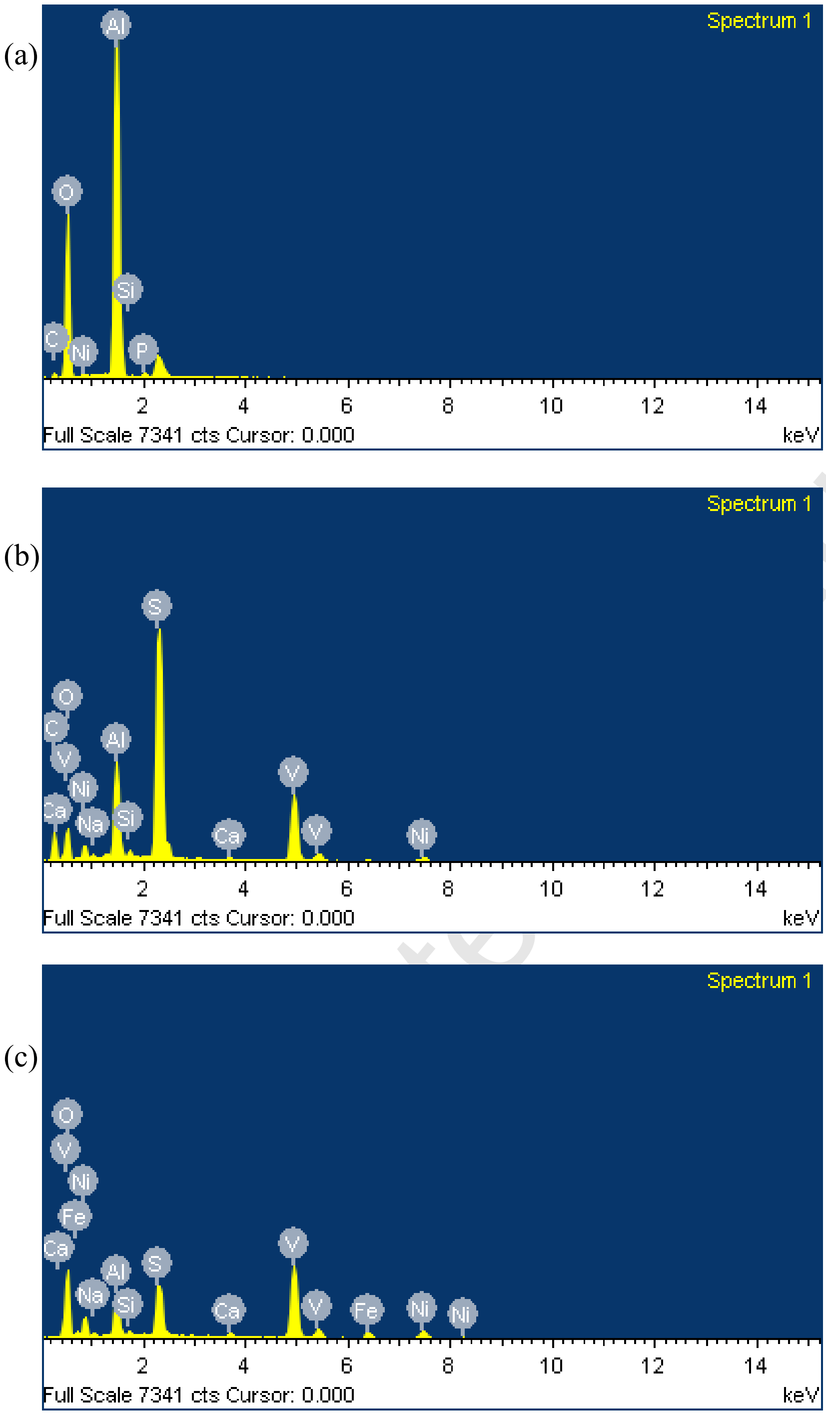

Fig. 5. EDS spectra of (a) raw catalyst, (b) catalyst after solvent treatment, (c) catalyst after calcination process.

A detailed analysis of SEM micrographs allows observing that some hydroprocessing impurities still remain adhered on the catalyst surface after solvent treatment and they are removed with the calcination. Therefore, both solvent treatment and calcination steps are necessary for an efficient impurity removal.

3.3 Oxidations of benzylic alcohols with recovered catalysts

The success of the catalyst recovery process motivated us to reuse the recovered catalysts in the oxidation of benzylic alcohols. In a model reaction, 4-chlorobenzyl alcohol was treated with the recovered catalyst using diverse solvents at reflux temperature. The results in Table 2 show that in all cases, 4- chlorobenzoic acid was obtained after a 48-72 h period.

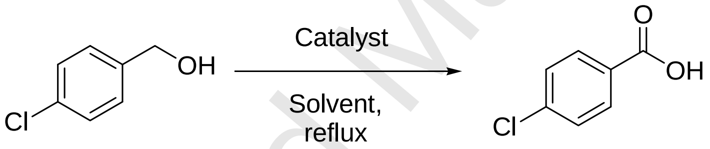

Table 2
Oxidation of 4-chlorobenzyl alcohol using recovered catalyst.

Entry	Solvent	Reaction Time (h)	% Coversion[a]	% Yield
1	hexane	72	45	25
2	AcOEt	72	53	30
3	Toluene	48	75	51
4	Xylene	48	75	55

[a]Determined by ^{1}H RMN

However, we observed that the use of hydrogen peroxide as co-oxidant and acetic acid as solvent increased the reaction yield affording the corresponding acid in 80% yield. These reaction conditions were extended to other benzylic alcohols giving good yields reported in table 3. The use of H_2O_2-AcOH oxidizing system produced additional advantages as lower reaction times and an easy work up.

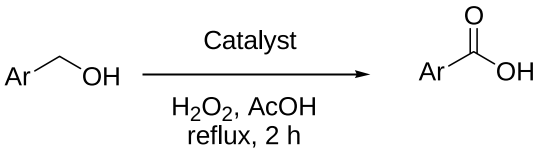

Table 3

Oxidation of 4-chlorobenzyl alcohol using recovered catalyst.

Entry	R	Reaction Time (h)	% Coversion[a]	% Yield
1	4-ClC_6H_4	2	95	80
2	2-ClC_6H_4	2	87	75
3	4-$CH_3C_6H_4$	2	95	82

[a]Determined by ^{1}H RMN

The formation of carboxylic acid in the process was confirmed through the melting point of final products, as well as some relevant spectroscopic signals. For example, the FT-IR spectrum (Fig. 6) of 4-chlorobenzoic acid showed an intense band at 1682 cm^{-1} due to the stretching vibration of the C=O bond. On the other hand, the characteristic aldehyde signal at δ 10 ppm was not observed in the ^{1}H NMR spectrum (Fig. 7), whereas the corresponding ^{13}C NMR spectrum displayed a carbon signal at δ 169.8 ppm assigned to the carboxylic acid carbon (Fig. 8).

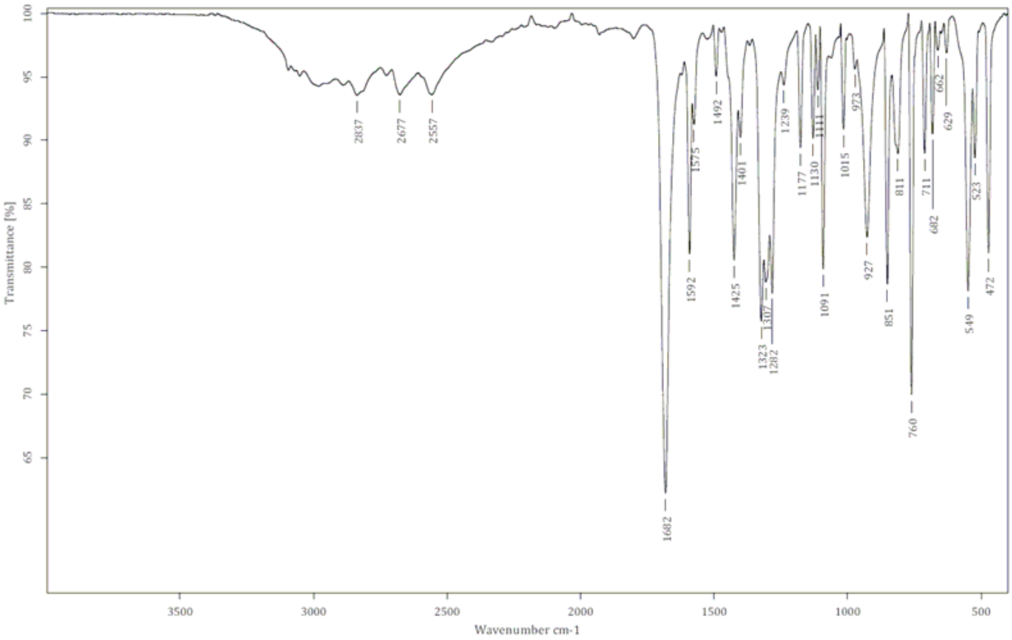

Fig. 6. IR spectrum of 4-chlorobenzoic acid obtained from catalyzed oxidation of 4-chlorobenzyl alcohol.

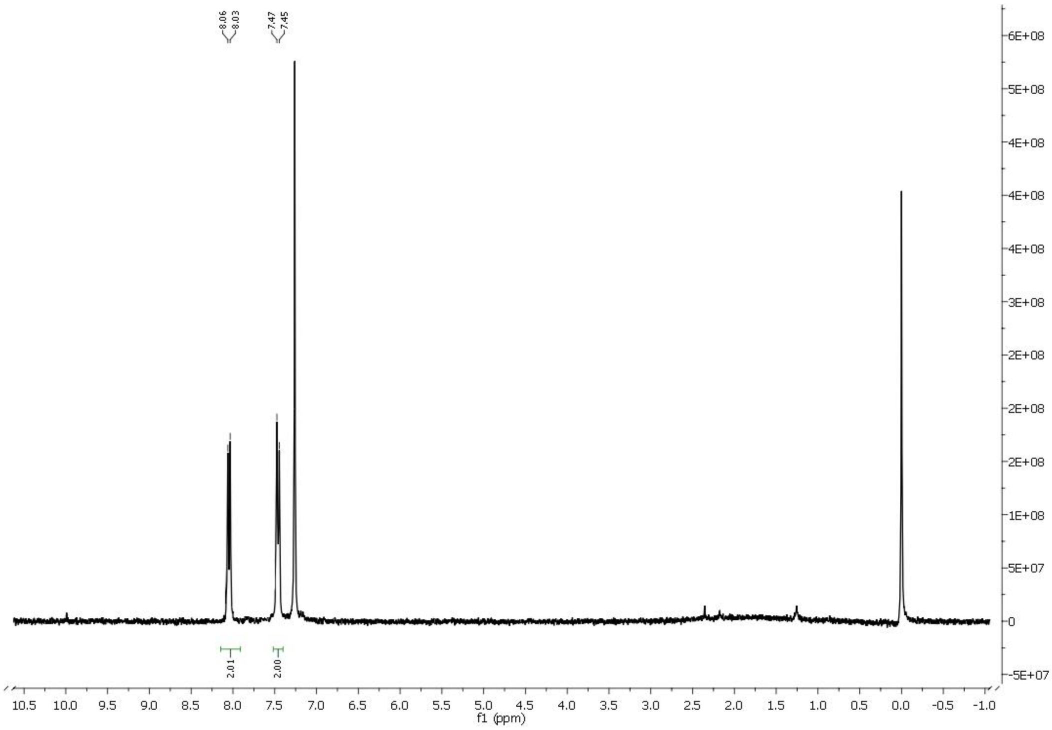

Fig. 6. ^{1}H NMR spectrum of 4-chlorobenzoic acid obtained from catalyzed oxidation of 4-chlorobenzyl alcohol.

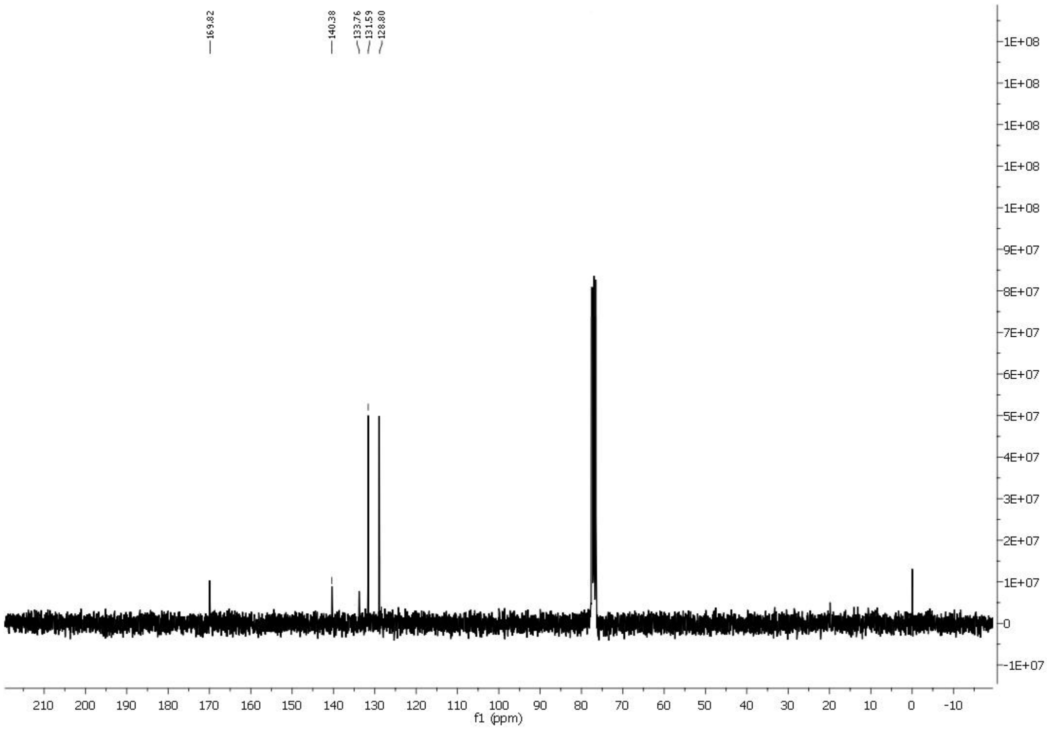

Fig. 6. ^{13}H NMR spectrum of 4-chlorobenzoic acid obtained from catalyzed oxidation of 4-chlorobenzyl alcohol.

Moreover, an additional benefit of this methodology is that heterogeneous recovered catalyst is removed by simple filtration, leaving only the product with traces of raw material in the reaction mixture. Another outstanding feature is that these reactions proceed with the addition of a simple co-oxidant as hydrogen peroxide, making this process environmental friendly, in contrast to other protocols which use classical transition metal oxidizers such as $KMnO_4$ [21] or PCC [19]. Hence, recovered catalyst reutilization in alcohol oxidations results an attractive solution to the problem derived from spent catalyst waste taking advantage of the transition metals contained in recovered catalysts, avoiding leaching and a difficult metal separation.

Conclusion

This work shows that the recovery of spent hydroprocessing catalysts is possible through consecutive draining- solvent extraction- calcination process which represents a suitable alternative for an environmentally safe disposal of the waste spent catalyst. Based on thermogravimetric analysis, the scanning electron microscopy and energy dispersion spectra, carbon and sulphur can be removed from the catalyst surface, making it able to reuse it in benzyl alcohol oxidations. These characteristics suggest a wide application of the present procedure for oxidation catalysis.

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Highlights

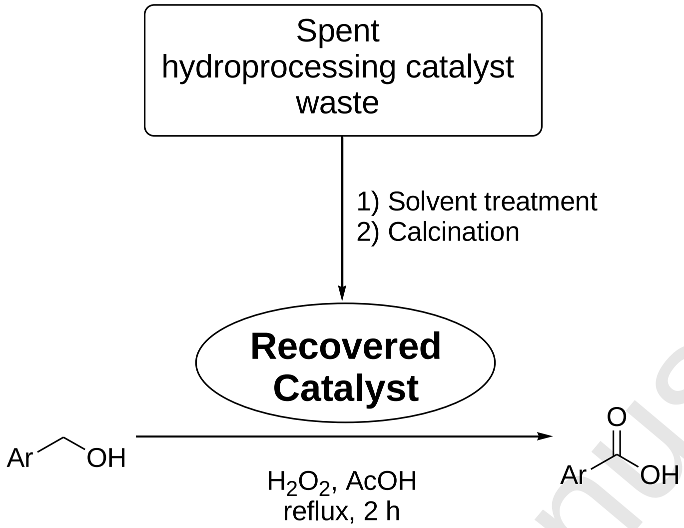
“Solvent mediated impurity removal process for a spent hydroprocessing catalyst and its use in alcohol oxidations”

- Spent catalyst waste from refinery underwent sequential solvent-treatment- calcination process

- Recovered catalysts were analyzed and tested in the oxidation of benzylic alcohols

- Benzylic alcohols were efficiently converted to carboxylic acids with H_2O_2 as co-oxidant

- This method is a suitable alternative to an environmentally safe disposal of waste spent catalyst


Spent hydroprocessing catalyst waste
1) Solvent treatment
2) Calcination
Recovered Catalyst
Ar
OH
H_2O_2, AcOH
reflux, 2 h
O
Ar
OH