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Additional Information

**Ferric sludge derived from the process of water purification as an efficient catalyst
for the removal of volatile organic compounds**

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Abstract

A ferric sludge obtained from the purification of water for human consumption can be used as an efficient catalyst for the removal of volatile organic compounds (VOCs) by total oxidation. This waste isolated in the purification process has been activated by calcinations in air, characterized by several physicochemical techniques and employed as a catalyst for the removal by total oxidation of two representative VOCs: toluene and propane. This ferric sludge has shown a catalytic activity one order of magnitude higher than that of a commercial iron oxide. This high activity has been related to the composition of the sludge (as it contains active metal oxides such as oxides of iron and manganese) and to the porous structure (leading to a reasonably high surface area). Moreover, it can be used as a support for platinum, showing comparable (or even higher) catalytic activity than a similar platinum catalyst supported on conventional γ -alúmina.

Keywords: VOCs; sludge; platinum; support.

Introduction

During the purification of water for human consumption a series of wastes are generated. Thus, one of the most important stages in this process involves the removal of suspended particles and colloidal matter. Therefore it is necessary to treat the water with coagulants, which destabilize the colloids and form aggregates which are readily settleable. This treatment results in clear water with low levels of turbidity, below 3 NTU. Specifically, in the water purification plant "El Atabal" in Málaga, Spain, a commercial 40% FeCl_3 solution as coagulating agent is used. After the coagulation process, decantation and drying a high amount of dry residue (about 5 tons) is produced on a daily basis. This process generates large amount of sludge, which can be used after treatment together with sludges generated in wastewater treatment plants for producing compost.

Herein an alternative use for this waste is proposed; as a catalyst for the elimination of volatile organic compounds. We consider that this sludge has a good potential as a catalyst due to: i) a promising composition as it presents a high concentration of oxides of transition metals and ii) the amount of catalyst to be used can be high and this can lead to high reaction rates in the VOC elimination.

Waste materials originated by human actions have demonstrated to be useful suppliers of alternative renewable feedstocks. Thus, chemicals as well as good quality fuels can be obtained with reasonably high yields. Interestingly, the anthropogenic wastes can also be resources from which catalysts can be synthesized. In fact they have been tested as catalysts using either the waste material alone or promoted with additional commercial metal or metal oxides. The catalytic activity of these waste derived materials is mainly due to the fact that these wastes usually contain transition metal

oxides which are active for a number of catalytic applications. There are also residues with high concentration of alkaline and alkaline earth oxides which are also useful in catalysis, especially those derived from biomass. Interestingly, silica and alumina the most used supports for active phases are also present in industrial residues.

Although this is not a topic extensively studied, there are quite a few articles that deal about the use of anthropogenic wastes as catalysts. In this way, Balakrishnan et al. conducted a short review about their use for catalysis [[Balakrishnan, M.; Batra, V. S.; Hargreaves, J. S. J.; Pulford, I. D. Waste materials - catalytic opportunities: an overview of the application of large scale waste materials as resources for catalytic applications. *Green Chem.* 2011, 13 \(1\), 16–24](#)]. These waste materials seem to be especially useful for reactions of environmental interest, such as those involving the utilization of biomass [[Catalytic applications of waste derived materials, James A. Bennett,* Karen Wilson and Adam F. Lee, *J. Mater. Chem. A*, 2016, 4, 3617-3637](#)]. Thus, wastes have been used for several reactions such as esterification and transesterification reactions, bio-oil upgrading and waste biomass valorization, which is a double exploitation of the anthropogenic residues.

In the more specific field of the total oxidation of hydrocarbons Klose et al. ([Klose, F.; Scholz, P.; Kreisel, G.; Ondruschka, B.; Kneise, R.; Knopf, U. Catalysts from waste materials. *Appl. Catal., B* 2000, 28 \(3–4\), 209–221](#).) studied the total oxidation of propane using sludges from tannery, sewage and textile dying obtaining high catalytic activity but far from those using noble metal oxides. Industrial wastes were also used as precursors of catalysts for the total oxidation of ethanol and o-xylene [[O.E. Lebedeva, A.G. Sarmurzina, Industrial wastes as catalyst precursors: VOC oxidation, *Applied Catalysis B: Environmental* 26 \(2000\) L1–L3](#)]. In the final catalysts either copper or chromium were added to the waste based material showing almost complete VOC

oxidation at temperatures of 300°C. Unfortunately to reach reasonable activity the incorporation of additional metals was required. Similarly, the total oxidation of propane was studied using catalysts derived from wastes obtained from tannery and electroplating industries [Sushil, S.; Scholz, P.; Pollok, K.; Ondruschka, B.; Batra, V. S., Application of industrial waste based catalysts for total oxidation of propane. Chem. Eng. J. 2011, 166 (2), 568–578.]. The transformation of propane into propene has also been studied using industrial wastes to which vanadium was incorporated. These catalysts showed reasonable results of activity and selectivity to propene although very far from possible industrial application [Ind. Eng. Chem. Res. 2013, 52, 7341–7349].

Synthesis of Industrial Waste Based Metal Catalysts for Oxidative Dehydrogenation of Propane Sandra L. Herrera,* ,† D. Ángela Hoyos,† Luz A. Palacio,† José Luis Pizarro,‡ and Roberto Aguado§].

Amongst some of the most prevalent VOC emissions we can find the release of light alkanes and aromatics to the environment. The use of catalysts has meant a remarkable decrease in both mobile (as the three way car exhaust catalysts) and stationary sources. The main components of these catalysts are noble metals, mainly platinum and palladium, [R.M Heck, R.J. Farrauto, Catalytic Pollution Control, second ed., Wiley-Interscience, New York, 2002.][L.F. Liotta, Catalytic oxidation of volatile organic compounds on supported noble metals, Applied Catalysis B: Environmental 100 (2010) 403–412] as they present high catalytic activity and resistance to deactivation. Unfortunately, they are expensive. The replacement of noble metals for other cheaper oxides of non noble metals as cobalt oxide or manganese oxide [ref][ref] or the decrease in the concentration of the noble metal concentration would be highly interesting.

At the present work ferric sludge submitted to simple calcinations in air will be used as catalysts for the total oxidation of two representative VOCs: propane as a model for short chain alkanes and toluene as a model for an aromatic compound.

As the specific surface area of the sludge is not low (40-70 m²/g) it can also be used as a support for noble metals. Thus, platinum catalysts supported on the ferric sludge will also be studied in the total oxidation of propane and toluene.

Experimental

Preparation of the catalysts

The starting material for obtaining the catalysts was obtained from a drinking water treatment plant (ETAP El Atabal, Málaga, Spain) after the flocculation step using a commercial 40% FeCl₃ solution. The residue is mainly composed of montmorillonite, iron oxides, humic substances and a minor proportion of Nontronite 5A and calcite. The material was dried at 120 °C for 12 hours and calcined at 350 and 550 °C. They were denoted as sludge(120°C), sludge(350°C) and sludge(550°C), respectively.

A platinum/sludge catalyst was prepared by dissolving H₂Cl₆Pt x H₂O (Aldrich 99.9%) in deionised water at 80°C. The solution was heated to 80°C and stirred continuously. An appropriate quantity of oxalic acid (Aldrich 99+%) was added to the solution (Oxalic acid/Pt = 3 mol). The ferric sludge calcined at 550°C was then added to the heated solution and stirred at 80°C to form a paste. The resulting paste was dried at 110°C for 16 h. The catalyst contained 1 wt% Pt. The final catalyst was prepared by calcination in static air at 550°C for 6 h. The catalyst was named as Pt/sludge.

For a comparative purpose a platinum catalyst with the same preparation method and with the same amount of platinum (1 wt.%) was synthesized using aluminium oxide (Sasol. $S_{\text{BET}} = 179 \text{ m}^2\text{g}^{-1}$) as a support. The catalyst was named as Pt/Al₂O₃.

Characterization techniques

Catalysts were characterized by N₂ adsorption at -196 °C, using a Micromeritics ASAP 2020 apparatus. Samples were degassed at 150 °C prior to analysis. From these data, the following textural parameters were calculated: multipoint Brunauer–Emmet–Teller (BET) surface area (SBET) was estimated from the relative pressure range from 0.05 to 0.25. Pore size distribution and mesopore volumes of these materials were analysed using the Barrett–Joyner–Halenda (BJH) method applied to the adsorption branch of the isotherm.

Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. An Enraf Nonius FR590 sealed tube diffractometer, with a monochromatic CuK α 1 source operated at 40 kV and 30 mA was used. XRD patterns were calibrated against a silicon standard and phases were identified by matching experimental patterns to the JCPDS powder diffraction file.

Temperature programmed reduction was performed using a Micromeritics Autochem 2910 apparatus with a TCD detector. The reducing gas used was 10 % H₂ in argon with a total flow rate of 50 ml min⁻¹ (GHSV ca. 8000 h⁻¹). The temperature range explored was from room temperature to 900 °C with a heating rate of 10 °C min⁻¹.

Morphological and structural characterization of the samples was performed by Transmission Electron Microscopy (TEM), high resolution TEM (HRTEM) and selected Area electron diffraction (SAED) by using a FEI Field Emission Gun (FEG)

TECNAI G2 F20 S-TWIN microscope operated at 200 kV. Energy Dispersive x-rays Spectroscopy (EDS) in TEM nanoprobe mode was achieved to prove the purity of the synthesized iron oxide nanoparticles. The synthesized iron oxide powder samples were treated by sonicating in absolute ethanol for few minutes, and a drop of the resulting suspension were deposited onto a holey-carbon film supported on a copper grid, which was subsequently dried.

The chemical characterization of the surface of the samples was performed by XPS. A Physical Electronics spectrometer (PHI VersaProbe II Scanning XPS Microprobe) was used, with scanning monochromatic X-ray Al K α radiation (100 μm , 100 W, 20 kV, 1,486.6 eV) as the excitation source, and a dual beam charge neutralizer. High-resolution spectra were recorded at a given take-off angle of 45 $^\circ$ by a concentric hemispherical analyzer operating in the constant pass energy mode at 23.5 eV, using a 1400 μm line (with a 100 μm diameter of the x-ray highly focused beam) analysis area. Under a constant pass energy mode at 23.5 eV condition, the Au 4f $_{7/2}$ line was recorded with 0.73 eV FWHM at a binding energy (BE) of 84.0 eV. The spectrometer energy scale was calibrated using Cu 2p $_{3/2}$, Ag 3d $_{5/2}$, and Au 4f $_{7/2}$ photoelectron lines at 932.7, 368.2, and 84.0 eV, respectively. Samples were mounted on a sample holder and kept overnight at high vacuum in the preparation chamber before being transferred to the analysis chamber of the spectrometer for testing. Each spectral region was scanned several sweeps up to a good signal to noise ratio was observed. The pressure in the analysis chamber was maintained lower than 5 $\cdot 10^{-6}$ Pa. PHI SmartSoft-VP 2.6.3.4 software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves. Atomic concentration percentages of the characteristic elements of the surfaces were determined taking into account the corresponding area sensitivity factor

for the different measured spectral regions.

2.4. Catalyst activity determination

Catalytic activity was measured using a fixed bed laboratory micro-reactor. In typical propane oxidation experiments, different amounts of powdered catalyst were placed in 1/2" o.d. quartz reactor tube. The reactor feed contained 8000 vppm propane in air with total flow rate of 25-100 ml min⁻¹ and different catalysts weight to give gas hourly space velocity (GHSV) of 40000 h⁻¹ (standard conditions). For reactions using high contact times/low GHSV a different reactor with a higher diameter (2.5") was employed. Thus GHSV in the 1000 to 40000 h⁻¹ range were used.

In the case of toluene oxidation experiments 1000 vppm of toluene in air with a GHSV=30000 h⁻¹ was used (standard conditions). For reactions using high contact times, gas hourly space velocities in the 750 to 30000 h⁻¹ range were used.

For both oxidations the reactants and products were analysed by an online gas chromatograph with a thermal conductivity and a flame ionisation detector. Two chromatographic columns were employed: i) Porapak Q (for CO₂ and hydrocarbons) and ii) Molecular Sieve 5A (to separate O₂ and N₂). The temperature range 100-500 °C was explored and the reaction temperature was measured by a thermocouple placed in the catalyst bed. The differences between the inlet and outlet concentrations were used to calculate conversion data. In order to corroborate this data the chromatographic area of CO₂ was used as the comparative reference. These two procedures lead us to adjust the carbon balance with an accuracy of ±2% for propane oxidation and ±4% for toluene oxidation. Analyses were made at each temperature until steady state activity was attained (ca. 30 minutes before the first analysis) and the results were averaged. Blank

experiments were conducted in an empty reactor until 500°C, showing negligible conversion.

Results

Characterization of the ferric sludges

X-ray diffractograms (Figure 1) were recorded for the uncalcined sludge (just dried at 120°C) and the two thermally treated materials (**sludge(350°C)** and **sludge(550°C)**). In addition to weak reflections due to montmorillonite, the crystalline phases identified were calcite (CaCO₃, PDF # 01-072-1214), Nontronite 5A (PDF # 00-029-1497), quartz (SiO₂, PDF # 01-075-0443) and hematite (Fe₂O₃, PDF # 01-089-8104).

The textural properties of the thermally treated sludges were obtained from N₂ adsorption-desorption isotherms at -196 °C (not shown). All isotherms are Type II according to IUPAC classification (Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **87(9-10)**, 1051-1069 (2015)) showing H3 hysteresis loop, characteristic of materials formed by parallel plates. The textural properties are summarized in Table 1. As the calcination temperature increases, there is a decrease in the surface area followed by an increase in average pore diameter.

Transmission microscopy study was undertaken with the ferric sludge calcined at 550°C which is the one that will be comprehensively studied in catalysis. The sample does not present homogeneous aspect and three different morphologies can be clearly observed (Figure 2). The first type consists of agglomerations of thin filaments with different lengths (25-300 nm). The filaments are usually narrow with typical diameter between 1

and 10 nm and cross each other in a random way. In many cases there is space between the different filaments. The second type of units presents more dense and larger particles with a cotton-like aspect. Finally, the third type presents big blocks consisting of overlapping sheets. This agglomeration of sheets mostly leads to units with rectangular shape and, over them, some tinier particles.

It is noteworthy that each structure presents distinct chemical composition. In all cases silicon is present with high proportion (Table 2 and Figure S2). However, in the first morphology the most abundant element detected is iron (40 at.%); with Si, Al and Ca also exceeding 10 at.%. Interestingly manganese was also detected (6.9 at.%) in an important manner. In the second morphology silicon and calcium were the most abundant (more than 30 at.% each), with Fe and Al exceeding 10 at.%. Finally Si and Al are the predominant elements identified in the third morphology.

Interestingly, regardless of the area focused with the microscope only these three morphologies or combinations of them could be observed. The quality of the spatial distribution of the different elements of the sludge was studied by XEDS mapping (Figure 3) over a particle with an aspect which can be considered as a mixture of the former three morphologies. It can be seen that the elements analyzed are rather homogeneously distributed over the sludge although there are zones with predominant elements (Mg, Al and Si) with iron especially present in filament-like areas.

Ferric sludge has been tested in the total oxidation of propane and toluene to check its catalytic potential in the removal of VOCs. The only reaction product detected in toluene oxidation was CO₂. In the case of propane CO₂ was also the main reaction product although small amounts of propene and CO were also observed.

Experiments were conducted with the ferric sludge calcined at different temperatures (see supplementary info). The catalyst heat treated at 350°C was shown to be more active than that at 550°C. We want to note that this sludge is more reactive than a commercial Fe₂O₃ (see details in the Experimental Section). Thus, the temperature required in these conditions to achieve 20% propane conversion (T₂₀) was 370 and 395°C for the sludge calcined at 350 and 550°C, respectively, whereas for the pure iron oxide was 420°C. Similar results were observed for toluene oxidation with values of T₂₀ of 240 and 255°C for the sludge calcined at 350 and 550°C, respectively, lower than that for pure iron oxide (270°C).

Unfortunately, the sludge calcined at 350°C deactivates during the propane oxidation tests (Figure S1); in fact it is observed that the conversion achieved in the second catalytic cycle is considerably lower than that of the first cycle. This is due to the fact that temperatures over 350°C were required to complete the catalytic run to get total propane conversion and at these temperatures the catalyst sinters, leading to a decrease in the catalytic activity. In contrast, the catalyst calcined at 550°C is highly stable, obtaining similar conversions in both first and second cycles. For this reason we have selected for the comprehensive catalytic study the sludge calcined at 550°C.

The effect of the space velocity on the conversion of hydrocarbons was studied using the ferric sludge calcined at 550°C. As can be seen in Figure 4 the light-off curves shift towards lower reaction temperatures when the contact time increases. Thus, for the standard test 20% conversion is achieved at 395 °C and when the space velocity is 40 times lower than that of the standard test is at 265 °C. It is noteworthy that by using the shortest space velocity the total conversion of propane (100%) is obtained at a temperature that is not high, 375° C, despite the sigmoidal form of the conversion-temperature curve which implies a high contribution at high temperatures of mass

transfer in detriment of the catalysis role. Although by increasing the catalyst weight the hydrocarbon conversion, must increase with all (almost all) the catalysts, in these experiments using the sludge a very significant increase has been obtained. The oxidation of propane and toluene on metal oxides has been related to reduction-oxidation mechanisms and for the reaction to take place, reducible metal centers are needed. Therefore, there is a temperature below which, if the active centers are not reduced, the hydrocarbon cannot be activated even using high catalyst mass. However, with the ferric sludge it is observed that (using the lowest space velocity) the propane can be activated and transformed at only 200°C, and in the case of toluene at 125°C.

The role of the ferric sludge as a support was also studied. Typical catalysts for the total oxidation of VOCs are based on noble metals, especially platinum. Accordingly we have prepared one catalyst with platinum (1 wt.%) supported on the ferric sludge. To corroborate that this ferric sludge can be used as a suitable support, a platinum catalyst with the same Pt loading but supported on γ -Al₂O₃ was prepared and tested.

In the propane oxidation an important increase in catalytic activity has been observed by the addition of platinum compared to the bare sludge (Figure 5), shifting the light-off curve ca. 50°C to lower temperatures (T₂₀=335°C). Unfortunately, the catalytic activity obtained was considerably lower than that of the platinum catalyst supported on alumina. However, we must mention that similar performance can be obtained using a catalyst of choice for this reaction (Pt/ γ -Al₂O₃) and with the bare ferric sludge but using higher contact times (40 times higher).

In the toluene oxidation the catalytic activity of the Pt/sludge sample was remarkably better than those of the bare sludge. Interestingly, and in contrast with what happened

with propane, Pt/sludge showed a higher activity in toluene oxidation than the Pt/ γ - Al_2O_3 catalyst. Stability of the sludge and of Pt/sludge was also studied for toluene oxidation showing stability for, at least, 25 h on line (Fig 6).

XRD of the platinum catalysts either fresh or spent in reaction (not shown here) do not present appreciable differences with those of the bare supports, with no apparent detection of platinum containing crystalline phases. In order to check the surface characteristics of these Pt-containing catalysts a study by XPS was conducted. The samples Pt/Sludge and Pt/ Al_2O_3 were studied before and after catalysis in the catalytic combustion of toluene. Table 3 includes the surface chemical composition (in atomic concentration %) determined by XPS, and Table 4 the binding energy values (in eV) of the core level signals studied. In the case of Pt, the typical Pt 4f signal cannot be studied due to its overlapping with the Al 2p signal and therefore the Pt 4d core level signal was studied. The ferric sludge presents the typical elements of a clay mineral plus Pt. It can be observed that there are subtle differences in composition between the fresh and spent sample. For instance, the amount of carbon suffers a slight increase from 8.30 to 10.40%, which is due to the formation of coke (although this coke formation is very limited). In fact, the % of contribution at 284.8 eV of the C 1s signal, assigned to adventitious and graphitic carbon increases from 45 to 58% after catalysis. The percentage of O decreases from 61.30 to 57.29% due to the oxidation of oxygen containing functional groups such a C-O-H and C-O-C and the relative intensity of the contribution at 286.1-286.3 eV decreases from 30 to 14%. The percentages of Mg, Al, Si, Cl, K and Pt increase after catalysis. However, the percentages of Fe and Ca decrease. In the case of the commercial catalysts Pt/ Al_2O_3 the surface content of C, as expected, is very low and similar before and after catalysis (see Table 3). The Pt 4d_{5/2} signal for all studied samples shows a single value at about 315.1 eV which can be

assigned to Pt(II) [J.C. Serrano-Ruiz a , G.W. Huber b , M.A. Sánchez-Castillo b , J.A. Dumesic b , F. Rodríguez-Reinoso a , A. Sepúlveda-Escribano. *J. Catalysis* 241 (2006) 378-388]. The binding energy values of the other elements (Table 4) indicated that Mg is as Mg(II), Al as Al(III), Si as Si(IV), Cl as Cl⁻, K as K(I), Ca as Ca(II) and Fe mainly as Fe(III) although the presence of Fe(II) cannot be ruled out. Overall, the XPS data indicate that the ferric sludge and the commercial catalyst are very stable after reaction. An important difference observed between the Pt/Sludge and Pt/Al₂O₃ is the different amount of platinum detected, being 2-3 times higher in the sample with alumina.

General remarks

Ferric sludge obtained from the purification of water for human consumption has shown a good catalytic activity in the elimination by total oxidation of two representative volatile organic compounds: propane and toluene. In fact, this ferric sludge presents a catalytic activity one order of magnitude higher than that of a commercial iron oxide. This high catalytic activity observed is likely due to two different effects. In one hand, the sludge contains oxides of elements with high potential as combustion catalysts such as iron and manganese oxides. On the other hand, the surface area of the ferric sludge is reasonably high, this way increasing the number of available metallic active sites. In spite of the fact that the activity per mass of catalyst of the ferric sludge is not comparable to commercial catalysts based on noble metals, its low price can allow the use of much higher amounts of catalysts, thus leading to comparable catalytic performance.

Moreover, the ferric sludge presents a high catalytic stability, maintaining the same catalytic performance for at least 30 h. Accordingly, the XPS data indicates that the

outer layers of the ferric sludge are very stable after reaction as well as the crystalline structure observed by XRD.

The sludge has also demonstrated to be a good support for platinum, showing higher catalytic activity in the toluene oxidation than a Pt/alumina catalyst, with the same platinum loading and prepared in the same way. The higher activity of Pt/sludge compared to Pt/alumina can be due to the presence of different metals on the sludge. In fact the promotion of Pt/support catalysts by the addition of several metal oxides has been reported in the past [D. Andreeva, R. Nedyalkova, L. Ilieva, M.V. Abrashev, *Appl. Catal. A: Gen.* 246(2003) 29.][C. Neyertz, M. Volpe, C. Gigola, *Appl. Catal. A: Gen.* 277 (2004) 137.][12] L.S. Escandón, S. Ordóñez, F.V. Diez, H. Sastre, *Catal. Today* 78 (2003) 191.] [C. Neyertz, M. Volpe, C. Gigola, *Appl. Catal. A: Gen.* 277 (2004) 137.][T. Garcia, W. Weng, B. Solsona, E. Carter, A.F. Carley, C.J. Kiely, S.H. Taylor, *Catal.Sci. Technol.* 1 (2011) 1367.] This improvement has been reported in terms of both catalytic activity and resistance to poisoning. A close contact between platinum particles and metal species usually modifies redox properties, platinum oxidation states and platinum crystallite size; these three factors have been proposed to enhance the catalytic activity [Tomas Garcia, Said Agouram, Stuart H. Taylor, David Morgan, Ana Dejoz, Isabel Vázquez, Benjamin Solsona, *Catal. Today* 254 (2015) 12-20][R.S.G. Ferreira, P.G.P. de Oliveira, F.B. Noronha, *Appl. Catal. B: Environ.* 50 (2004)243]. In the present work the same oxidation state has been observed for platinum (Pt(II)) employing alumina and the sludge as supports. However, a higher Pt surface concentration has been observed in the catalyst with alumina, likely showing a higher dispersion on the surface, which can affect the reactivity [Garetto, T. F. and Apesteguia, C.R. (2001). Structure sensitivity and in situ activation of benzene combustion on Pt/Al₂O₃ catalysts. *Appl. Catal. B: Environ.*, 32, pp. 83–94.] .

Pt supported on the ferric sludge has also shown a high stability in catalysis (at least 30 h on line). Accordingly XPS results suggest a reasonable stability, although after reaction a slight increase in the amount of carbon deposited and platinum was observed. No apparent changes in the crystalline structure were observed by XRD.

Conclusions

Ferric sludge obtained from the purification of water can be used as an efficient catalyst for the removal of volatile organic compounds (VOCs) either bare or as a support for platinum. Although the activity per mass of catalyst of the ferric sludge is not comparable to commercial catalysts based on noble metals, its low price can allow the use of much higher amounts of catalysts, thus leading to comparable conversions. This ferric sludge was also studied as a support for platinum and its catalytic performance was compared to a Pt/ γ -alumina catalyst showing higher conversion in the toluene oxidation, thus demonstrating that could also be used as an efficient support. Both the bare sludge and the platinum catalysts supported on the sludge have demonstrated an excellent catalytic stability.

Tables

Table 1. Textural properties determined from N₂ adsorption-desorption isotherms at -196 °C

Sample	S_{BET} (m²g⁻¹)	D_p (nm)	V_p (cm³g⁻¹)
Sludge (120°C)	66	7.1	0.11
Sludge (350°C)	65	7.9	0.13
Sludge (550°C)	43	9.5	0.11

V_p: total pore volume was calculated from adsorbed N₂ at P/P₀ =0.996

Table 2. Chemical composition (in at.%) of the different morphologies of the ferric sludge calcined at 550°C observed by EDX.^a

Element	Morphology 1	Morphology 2	Morphology 3
Mg	1.6	3.4	3.0
Al	10.3	14.1	32.8
Si	30.4	32.0	50.3
S	ca. 0	0.7	ca. 0
K	1.7	2.9	8.6
Ca	8.8	32.7	1.0
Mn	6.9	<0.5	<0.5
Fe	40.3	13.9	4.2

^a normalized at 100% without considering the oxygen and carbon of the sample. Carbon has not been quantified as the grids used for microscopy are made of holey carbon.

Table 3. Surface composition (in atomic concentration %) of the studied samples; fresh and spent in the catalytic oxidation of toluene

Sample	C	O	Mg	Al	Si	Cl	K	Ca	Fe	Pt
Pt/Sludge	8.30	61.30	1.79	5.41	11.04	1.98	0.35	4.70	5.04	0.10
Pt/Sludge Spent	10.40	57.29	2.24	6.17	12.12	2.58	0.49	4.10	4.48	0.14
Pt/Al₂O₃	3.52	62.37		33.41						0.34
Pt/Al₂O₃ Spent	3.60	64.04		32.12						0.24

Table 3.- Binding energy values (in eV) of the constituent elements of the catalysts; fresh and spent in the catalytic oxidation of toluene

Sample	C 1s	O 1s	Mg 1s	Al 2p	Si 2p	Cl 2p _{3/2}	K 2p _{3/2}	Ca 2p _{3/2}	Fe 2p _{3/2}	Pt 4d _{5/2}
Pt/Sludge	284.8 (45)	530.3 (20)	1304.3	74.4	102.4	198.7	293.2	347.6	711.8	315.0
	286.1 (30)	531.7 (57)								
	288.1 (7)	532.8 (23)								
	289.8 (18)									
Pt/Sludge Spent	284.8 (58)	530.0 (20)	1304.1	74.0	102.2	198.3	292.9	347.3	710.9	315.2
	286.3 (14)	531.3 (56)								
	288.2 (9)	532.5 (24)								
	289.4 (19)									
Pt/Al₂O₃	284.8 (69)	531.1 (78)		74.1						315.1
	286.9 (17)	533.3 (22)								
	288.3 (14)									
Pt/Al₂O₃ Spent	284.8 (49)	531.2 (79)		74.6						315.1
	286.2 (40)	532.8 (21)								
	288.8 (11)									

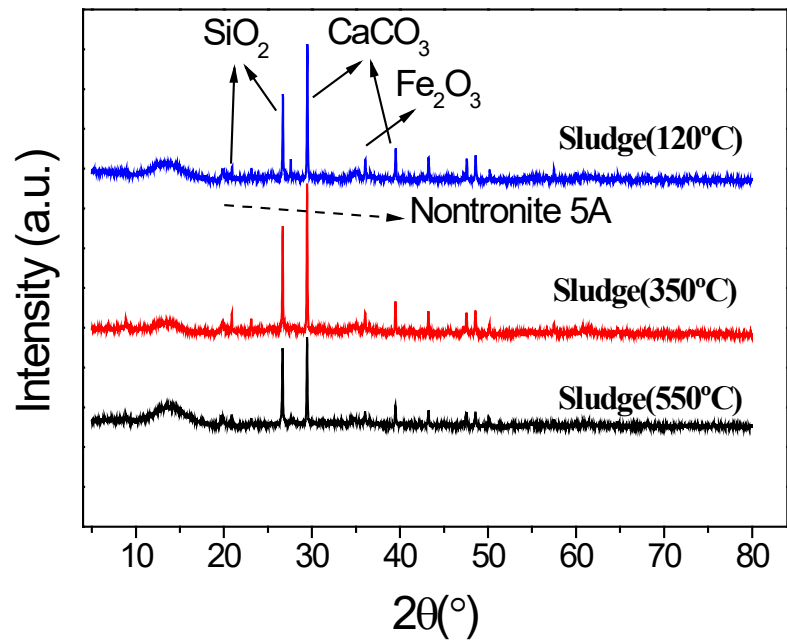


Figure 1. X-ray diffractograms of the dry sludge (sludge(120°C) and the two thermally treated materials (sludge(350°C) and sludge(550°C)).

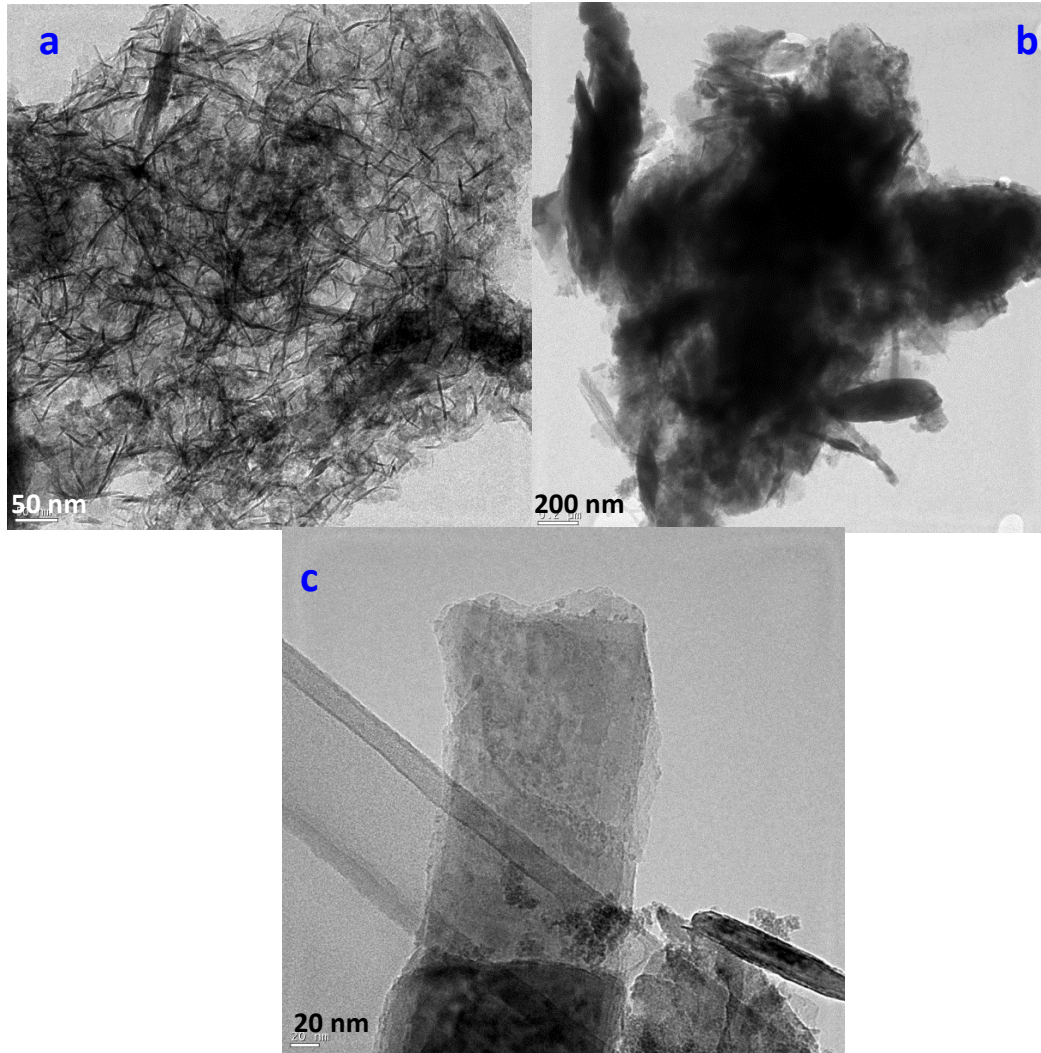


Figure 2. TEM images of the ferric sludge calcined at 550°C showing different morphologies.

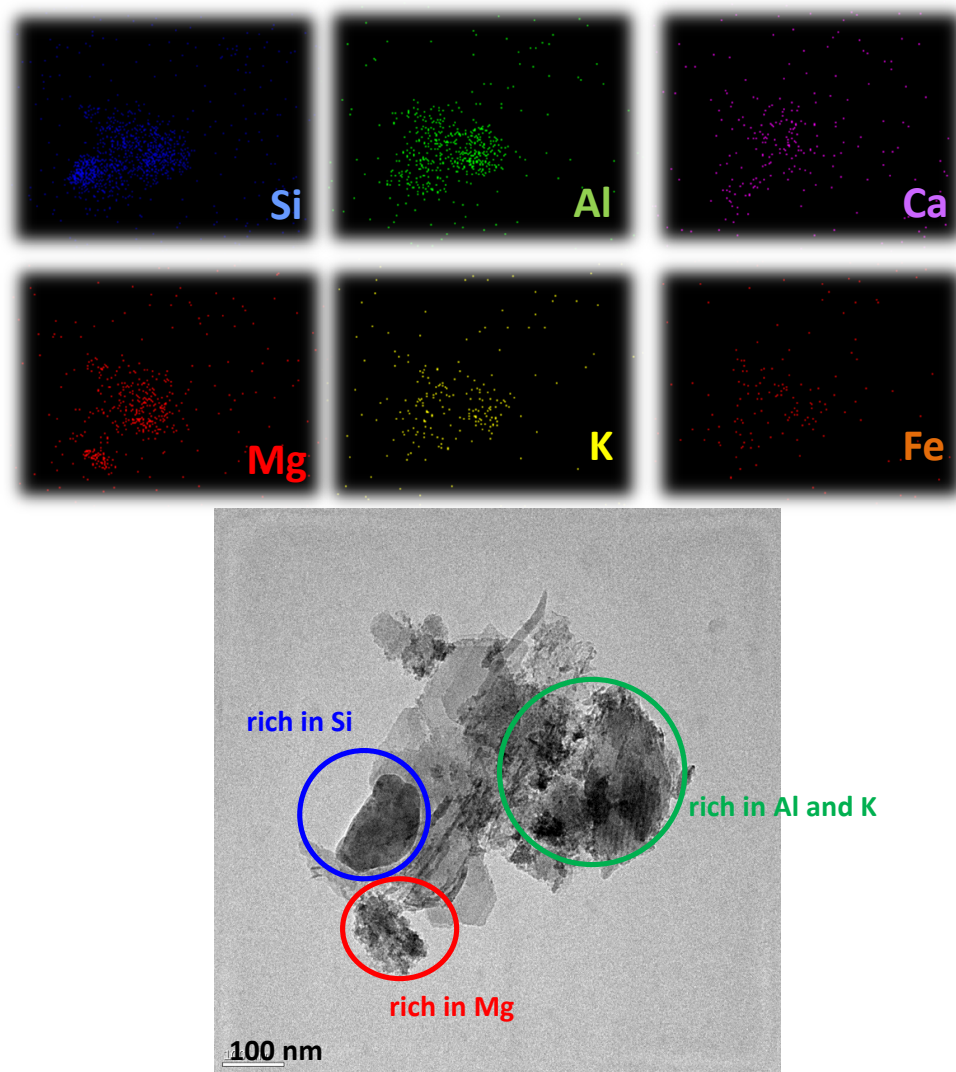


Figure 3. TEM image with its corresponding XEDS analysis for Si, Al, Ca, Mg, K and Fe of the ferric sludge calcined at 550°C.

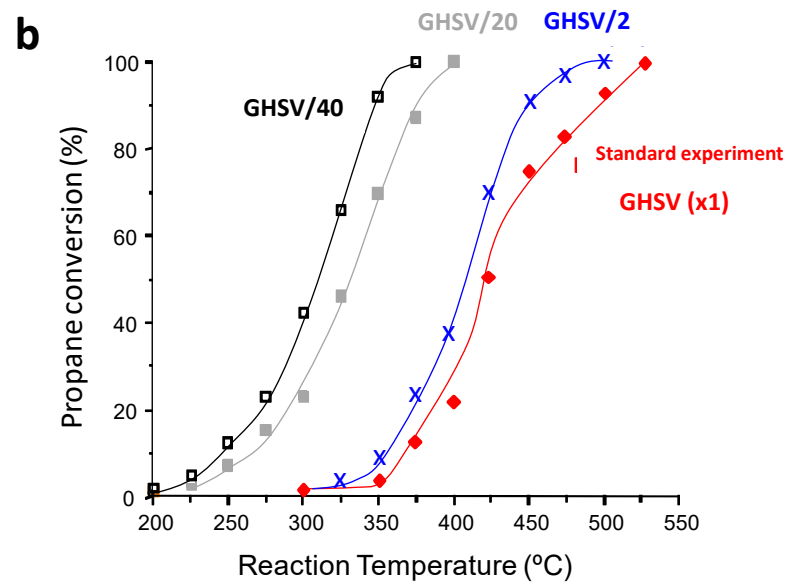
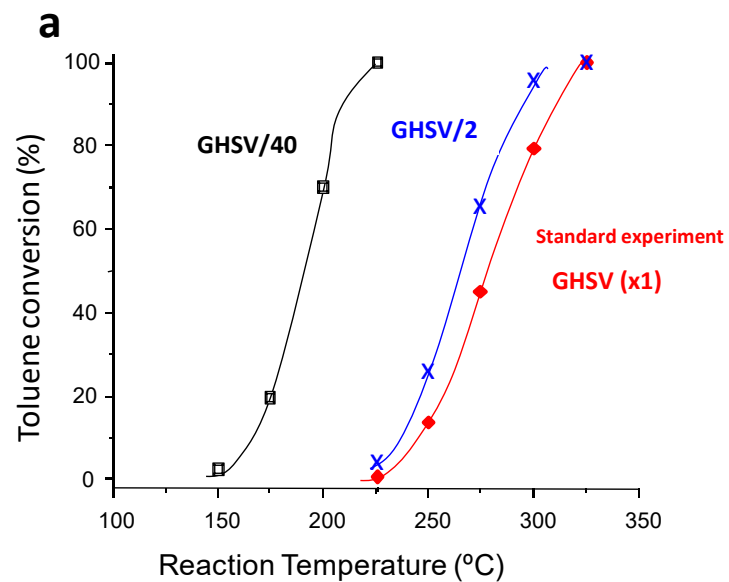


Figure 4. Variation of the toluene conversion (a) and propane conversion (b) with the reaction temperature for the ferric sludge calcined at 550°C. Effect of the space velocity. Reaction conditions in text.

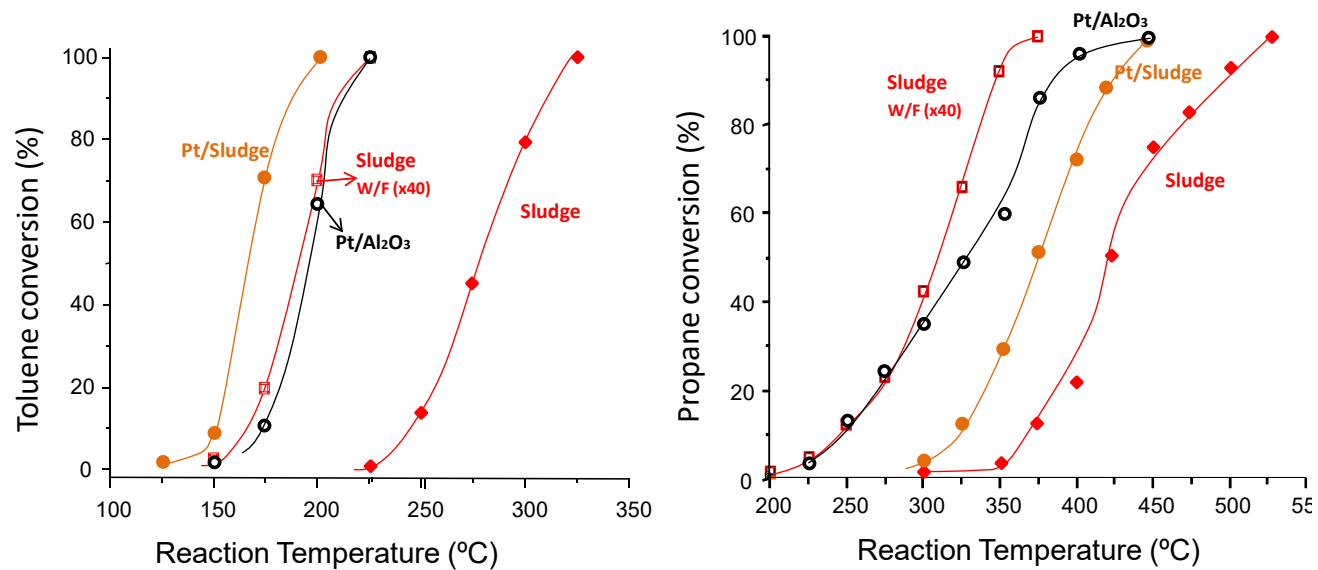


Figure 5. Variation of the toluene conversion (a) and propane conversion (b) with the reaction temperature for the ferric sludge calcined at 550°C (♦), Pt/Sludge (●), Pt/Al₂O₃ (○). The symbol □ corresponds to the results obtained with the sludge but with a space velocity 40 times lower. Reaction conditions in text.

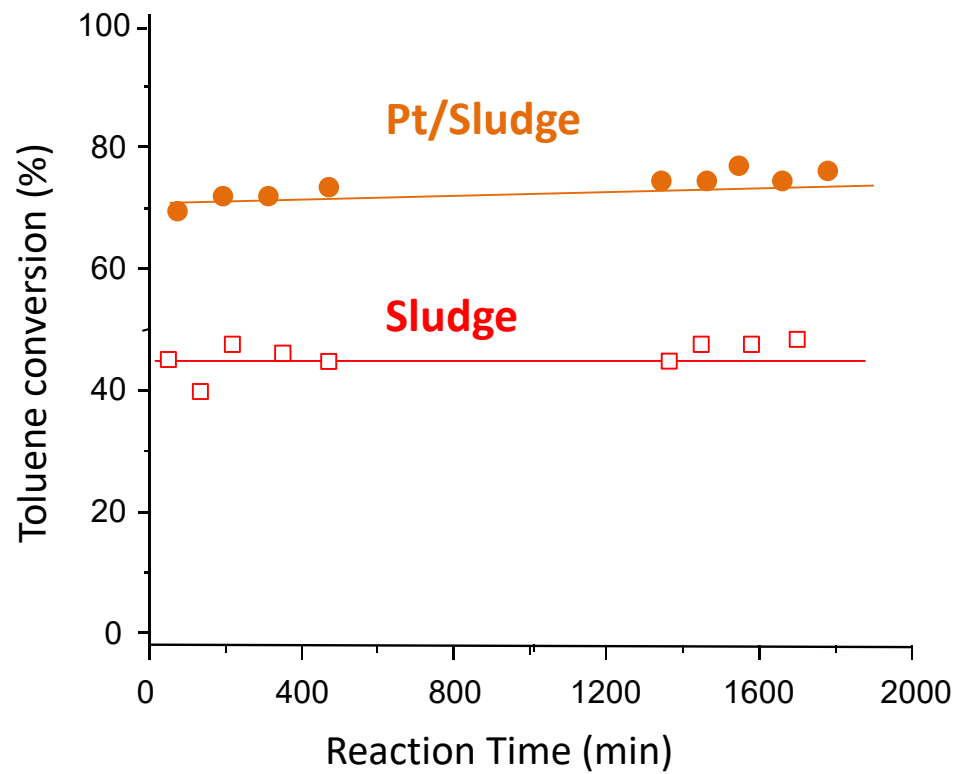


Figure 6. Evolution of the toluene conversion with the time on line for the sludge calcined at 550°C (♦) and for Pt/sludge (●). Reaction Temperature for the ferric sludge = 275°C; Reaction Temperature for Pt/Sludge = 175°C. GHSV = 30000 h⁻¹. Remaining reaction conditions in text.

Supplementary information

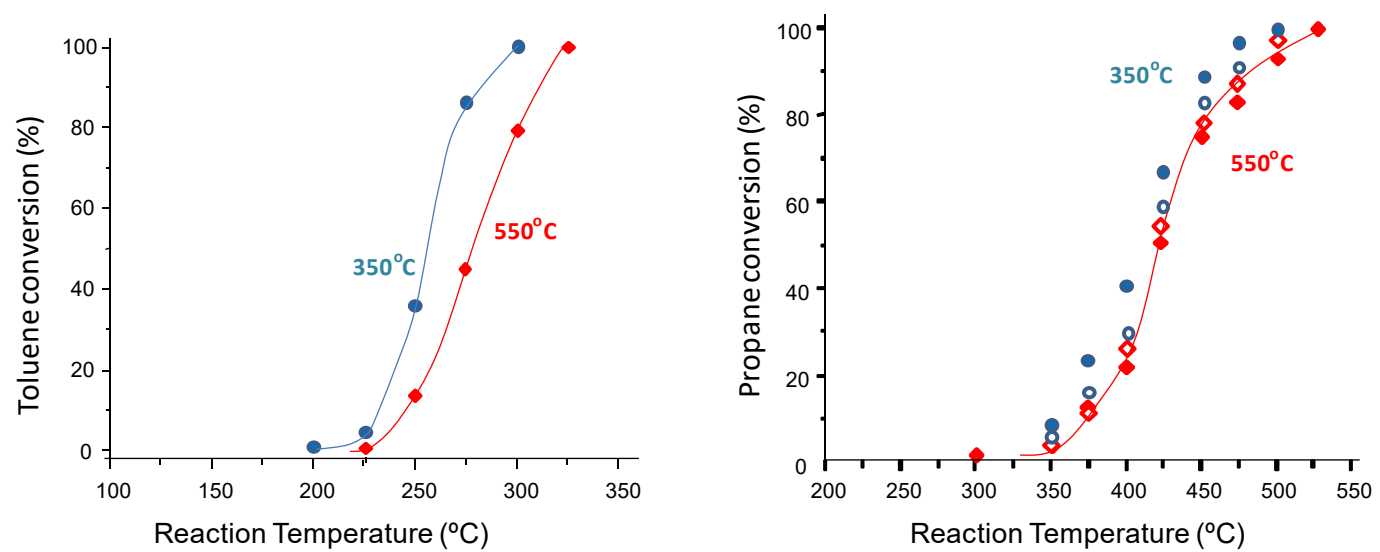
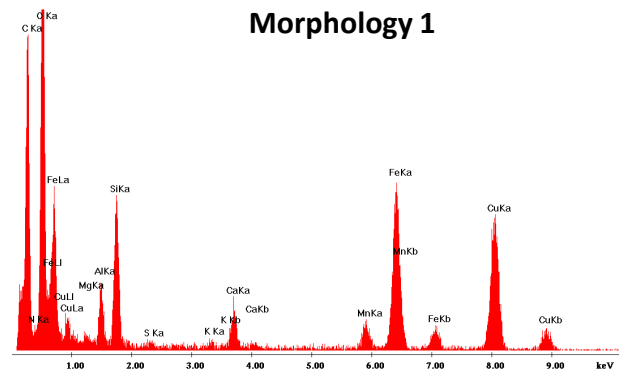


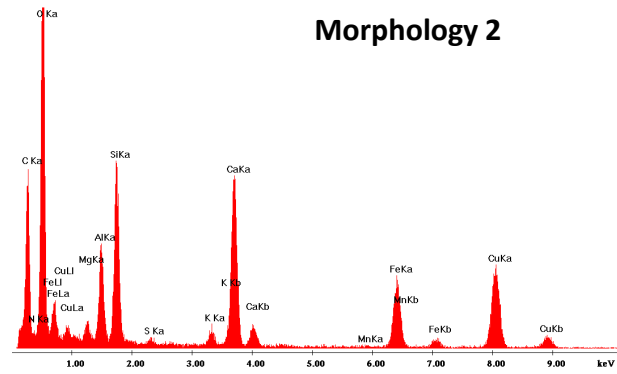
Figure S1

Supplementary information

Label A: Chlorite (Nm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)



Label A: Chlorite (Nm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)



Label A: Chlorite (Nm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)

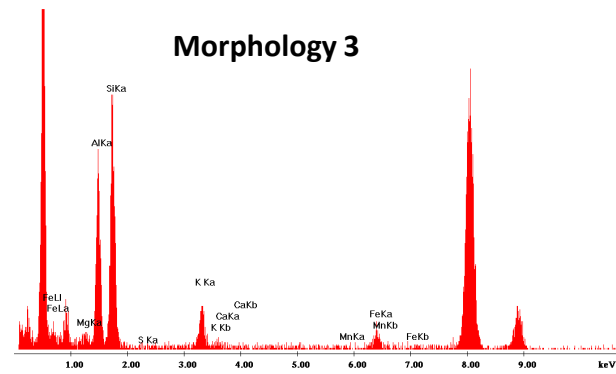


Figure S2