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**Three pathways to Cleaner Platform Chemicals: Conventional, Microwave and Solar Transformation of a By-product from the Orange Juice Manufacturing Process.**

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**ABSTRACT**

For a sustainable development, chemical processes should be designed around the use of renewable raw materials (RRM). The aim of this study is using limonene, chosen as example of an industrial by-product, to prepare limonene oxides, carvone, carveol, carvacrol and terephthalic acid, all of great industrial interest, with values of one to two orders of magnitude greater than limonene and compare the results obtained with conventional, microwave or solar activation in order to decrease the environmental impact of the process. The reactions were carried using catalysts based on materials of low toxicity, i.e. iron, manganese, titania and sepiolite. A number of techniques were used to characterise the compositional, structural and textural properties of the catalysts used. The results of this research indicate that for similar conversions conventional activation requires the highest energy expenditure, related to a negative environmental impact, while the use of microwave heating greatly reduces the reaction times and solar activation proves to be a very competitive and indeed the most environmentally friendly activation method. Furthermore, orange peel oil

(containing 95% limonene), under optimised conditions, achieves similar results to those found with limonene, thus increasing the economy and sustainability of the process.

Keywords: By-product valorization, microwave, solar activation, carvacrol, terphthalic acid

## 1. Introduction

Negative environmental issues are a major challenge for society that has led to increasingly stringent governmental laws that force the need for technological changes to improve chemical processes in order to reduce their negative impacts on human wellbeing (Martinez Serrano et al., 2015). Furthermore, the use of RRM and/or activation methods that lead to a reduction in energy consumption or even the direct use of renewable energies, provides the basis towards the substitution in the use of non-renewable fossil fuel derived energy, substances and materials. (Yates et al., 2017).

In this study, three different reaction activation methods were compared: conventional heating, microwave irradiation and solar irradiation. Microwave activation of reactions was used as it allows a significant reduction in the reaction times, thus leading to huge economic, energy savings and thus reduction in CO<sub>2</sub> emissions, compared to conventional heating (Martin-Luengo, 2010). The shorter reaction times can give high yields under mild conditions, which helps to avoid thermal decomposition of products or sensitive reagents and thus improve the selectivity of the processes (Lucas-Torres, 2016).

The use of solar energy to modify chemical substances was first studied at the beginning of the 20<sup>th</sup> century. In 1943 there was already a technical-scale production of an

anthelmintic drug and later on, influenced by the oil crisis in the 70's, this method of activation was revisited due to the importance of the potential market of heterogeneous photocatalysts. Natural sunlight has been used in several reactions such as the preindustrial production of fine chemicals and intermediates, especially important in countries with high amounts of solar irradiation, leading towards a "low-carbon" economy (Zhang, 2013).

The methods used in this work were designed to be consistent with a sustainable development and cleaner production of chemicals, choosing catalysts, procedures, reactants and solvents of low toxicity. The reaction parameters were chosen so that the three activation techniques could be compared under similar conditions. The catalysts were structured by mixing the active phases (iron or manganese salts) and titania with sepiolite, a clay of low cost, to produce extrudates that on heat treatment lead to stable ceramic structures that support the active oxide species and can transform limonene into oxygen containing fine chemical intermediates, under conventional, microwave or solar activation, in the search for lower impact processes towards a sustainable development (Rodrigues, 2017) and may be easily separated from the reaction medium for their reuse (Blanco, 1995).

The catalytic oxidation of limonene gives added value products (in this work limonene oxides, carvone, carveol, carvacrol and terephthalic acid) that are useful substances in themselves or as intermediates in fine chemical processes for a myriad of industrial uses (cosmetics, pharmaceuticals, monomers, solvents, coolants, insecticides, *etc.*), and given the development carried out here, have the advantage of being more environmentally friendly than conventionally derived compounds (Martin-Luengo, 2011). Carvone and carveol exist in nature, although in many areas their harvest has lead to over exploitation of resources, and laws that protect them from abuse have been developed. The other products are industrially

obtained by expensive and often toxic syntheses and catalysts, for example limonene epoxide is conventionally manufactured by the oxidation of limonene with stoichiometric amount of peracids (Gupta, 2009). Carvacrol is obtained by supercritical (300 bar) CO<sub>2</sub> extraction from oregano essential oils (Ocaña-Fuentes, 2010) or by industrial scale isopropylation of *o*-cresol with propylene at high operating pressures and temperatures (633 K and 50 bar), or by oxidation of xylene (Li, 2008; Partenheimer, 2011). Terephthalic acid is normally produced by oxidation of *p*-xylene in air (Banella, 2016). Given their industrial importance sustainable development is sought for all of these substances and alternatives to these processes should avoid the use of non-renewable and strongly contaminating substances related to the greenhouse effect.

## 2. Materials and methods

### 2.1 Reactants and catalysts

D-limonene (>99 %) from Panreac, orange peel oil (95% limonene, 1% myrcene, 1% alpha pinene (1%), 1% beta pinene, 0,5% linalool, 0,4% decanal, < 0,1% others (hexanal, 1,8-cineol, 1,8 -cineol, borneol, n-octanal and citral) was kindly provided by Frusa (“Frutas y zumos S.A.”). The oxidant used was tert-butyl hydroperoxide (tbHP) (5.5 M in decane on a molecular sieve 0.4 nm) provided by Fluka. Iron nitrate (Fe (NO<sub>3</sub>)<sub>3</sub> • 9 H<sub>2</sub>O, > 98 % purity) and manganese acetate ((CH<sub>3</sub>COO) 2Mn • 4H<sub>2</sub>O, > 98% purity) from Sigma-Aldrich were used to provide the paramagnetic and oxidizing centres in the catalysts. Commercial titanium dioxide DT51 from Millennium, in the form of anatase, was used in this work due to its low toxicity and high stability and wide application as a photocatalyst. Sepiolite Pangel from

Tolsa S.A., a hydrated magnesium silicate abundant in Madrid with valuable textural and rheological properties, was chosen to structure the materials.

The conformed catalysts were prepared by mixing titania and sepiolite at a 3:1 ratio, which with the addition of water produced a paste that was subsequently extruded as 1 mm diameter cylinders with a Bonnot single screw extruder, since previous studies have shown that this allows the formation of a strong and porous structure after controlled calcination (Blanco, 1995). The addition of iron or manganese salts was accomplished by previous mixing of all of the components. After conformation, the extrudate was allowed to dry at room temperature for two days, and then calcined at 500 °C or 700 °C in order to decompose the precursor salts and form the stable ceramic materials. The catalytic activity results were determined on these 1 mm diameter extrudates cut to 2 mm lengths.

## 2.2 Characterisation techniques

Thermogravimetric and thermodifferential analyses (TG-DTA) were carried out to determine the necessary conditions to decompose the precursor salts in a SEIKO SSC/5200 analyser (25–900 °C in 50 mL min<sup>-1</sup> air). The compositions of the catalysts were analysed by atomic emission spectroscopy with inductively coupled plasma (ICP) in an Optima 3300 DV from Perkin-Elmer.

Textural analyses by N<sub>2</sub> sorption were carried out at 77 K on samples degassed under vacuum at 300 °C overnight in a Micromeritics Tristar 3000 to study the specific surface areas, and pores up to 50 nm diameter. Mercury intrusion porosimetry was carried out to study pore diameters of 150 µm down to 7.5 nm in a CE Instruments Pascal 140/240.

X-Ray diffraction (XRD) measurements of the catalysts crystallinities were carried out using a Phillips DW 1130 instrument with Cu K $\alpha$  (1.542 Å) radiation (40 kV, 25 mA) over the range  $2\theta = 5\text{--}80^\circ$  at a scan rate of  $1^\circ\text{min}^{-1}$  with  $0.1^\circ$  step size. The study of the crystallite sizes was made by applying Scherrer equation on the oxides main peaks.

The determination of the basic sites was done by coupling thermogravimetric analysis and mass spectrometry (TG-MS) of species formed on the materials by acetic acid adsorption-decomposition, analysing at mass 44 corresponding to CO<sub>2</sub> evolved in a Stanton STA model 781 thermal analysis equipment coupled to a Thermostar QMS200 M3 mass spectrometer.

The diffuse reflectance absorption spectra of the catalysts were recorded with a Varian 2300 UV–Visible apparatus. This technique was used to determine the light absorption of the catalysts.

Scanning electron microscopy was carried out in a Hitachi TM-1000 apparatus in order to study the topography of the calcined catalysts conformed by wet kneeding and extrusion of the pastes, containing all of the precursors.

Preliminary experiments were carried out under microwave irradiation, with reaction temperatures between 100–160 °C, reaction times up to 25 min, and various ratios of limonene:tbHP were considered, giving importance to the selectivity towards highly valuable carvone, carveol, carvacrol and terephthalic acid. The final chosen conditions for the subsequent reactions were 4 mL of limonene, 0.15 g of catalyst and 14 mL of tbHP (5.5 M in decane) at 120 °C, in order to avoid over oxidation to unwanted products.

A Hewlett Packard 5890 series II GC-MS chromatograph coupled to a Hewlett Packard series 5971 mass selective detector, with a 25 meter methylsilicone capillary column, heated from 50 °C to 170 °C at a heating rate of  $6^\circ\text{C min}^{-1}$ , in a flow of helium carrier gas

was used to analyse the progress of the reactions, calibrating with commercial reactants and products. The solvent chosen to carry out chromatographic analyses was diisopropyl ether (>99 %) from Sigma-Aldrich, of low toxicity and price. The best catalyst for each activation method was also studied at the optimised conditions using orange oil as the reactant instead of pure limonene.

### *2.3 Reactions under conventional heating*

Conventional oxidations were carried out for up to 12 hours at temperatures ranging from 100 to 160 °C in order to avoid over oxidation and optimise selectivities. The final chosen conditions for further work were: 120 °C under reflux with reaction times of up to seven hours.

### *2.4 Reactions with microwave activation*

The microwave radiation experiments were carried out in a Synthwave 402, with focused microwaves and a maximum power of 300 Watts, that allows programming of temperature and time. The reactions were undertaken under reflux, at a reaction temperature of 120 °C, leaving the microwave power free and with reaction times up to 70 minutes in order to achieve similar conversions to those obtained by conventional heating and avoid uncontrolled over oxidation.

### *2.5 Reactions under solar activation*

The solar activation experiments were done in glass vials filled with the reaction mixture and exposed to solar irradiation up to four hours, where the amount of radiation was



measured with a TES 133 solar power meter. The average solar radiation was  $1090 \text{ Wm}^{-2}$  and a final temperature of *ca.*  $50 \text{ }^{\circ}\text{C}$  was reached.

### 3. Results and Discussion

The catalytic oxidation of limonene under the conditions used here renders limonene epoxides, carvone, carveol, carvacrol and terephthalic acid (Table 1a, b and c), all value added substances with prices of between 5 to 10 times higher than that of limonene. Limonene oxides have a wide range of uses as fine chemical intermediates (Schmidt, 2005), carvone and carveol (of proven anticarcinogenicity) are derived from limonene epoxides or the double bonds oxidation of limonene, while carvacrol (anticarcinogenic and antibacterial) and terephthalic acid are derived from its allylic oxidation, aromatization and further oxidation of the alkyl chains (Casuscelli, 2004).

The reaction path first shows selectivity to limonene epoxides at low conversions (produced by epoxidation through electrophilic attack). With longer reaction times the selectivity towards carvone and carveol (from allylic oxidation with hydrogen abstraction and/or from limonene oxides) increased and that to epoxide decreased. At even longer reaction times the selectivity to carvone and carveol was reduced to give carvacrol and terephthalic acid, as a result of aromatization and further oxidation of the alkyl chains (Gioia, 2015).

The nomenclature used for the catalysts is the following: Iron (Fe), manganese (Mn), titania (Ti) and sepiolite (Sep)) and the calcination temperatures ( $500$  or  $700 \text{ }^{\circ}\text{C}$ ). The composition of the catalysts used in this work analysed by ICP indicate that they contain 47 %

Ti, 6 % Si, 3.4 % Mg, 3.3 % Fe (FeTiSep) and 3.3 % Mn (MnTiSep). The presence of silicon and magnesium are due to sepiolite, a magnesium silicate clay used as the agglomerating agent for the conformation of the catalysts.

Preliminary experiments were carried out under microwave irradiation to assess the reaction conditions to avoid over oxidation that causes a diminution of selectivity towards the desired compounds (carvone, carveol, carvacrol and terephthalic acid). All the catalysts were studied heating up to 140 °C for up to 50 minutes with a ratio limonene/tbHP sol = 0.2 (mL/mL) and limonene/catalyst = 26.66 (mL/g). Under these conditions the best results were obtained with catalyst FeTiSep500. Using this catalyst, the reaction temperature was varied from 100 to 160 °C and the reaction times from 50 to 100 minutes, to determine the optimum temperature and reaction time to achieve the highest conversion and avoid over oxidation of the products. These experiments lead to 70 minutes at 120 °C being chosen as the optimum reaction conditions. Finally the limonene/tbHP ratio was varied from 1 to 0.2, where it was found that the best ratio to achieve the highest conversion was 0.28.

Having determined the optimum reaction conditions, all of the catalysts were tested. The oxidation experiments were repeated up to four times with no loss of catalytic activity, nor leaching of iron or manganese cations and differences of <1 % in conversion values. Blank experiments showed that the oxidant employed tert-butyl hydroperoxide (tbHP) did not oxidize limonene in the absence of a catalyst.

### *3.1 Oxidations under conventional heating*

The reaction conditions chosen for limonene oxidation under conventional heating were equivalent to those employed under microwave heating with regards to reaction temperature, ratio limonene/amount of catalyst and limonene/tbHP. Under these conditions the optimum conversions were obtained after 7 hours of reaction. Longer times lead to secondary reactions that reduced the selectivities to the desired products.

The conversions under conventional heating (Table 1a) followed the sequence:

$\text{FeTiSep500} > \text{FeTiSep700} > \text{MnTiSep500} > \text{MnTiSep700} > \text{TiSep500} > \text{TiSep700}$

The lower activities for the TiSep catalysts were to be expected since they lack the more active iron or manganese oxide species.

A summary of the textural and crystallographic characteristics of the precursors and catalysts is included in collated in Tables 2 and 3. In Table 3 it may be seen that titania was always in its anatase form (JCPDS File No. 21-1272) (Blanco, 1995). On forming an intimate mixture of titania and sepiolite before extrusion, drying and calcining at 500 or 700 °C, the surface areas were greater than those calculated from the results obtained with the two materials treated separately. This indicated that mixing of these two components stabilised the materials (TiSep) leading to lower losses in surface area on heating, in agreement with the XRD results (Figure 1 and Table 3) which also showed lower crystallinities (peaks of lower intensities) of the catalysts compared with their component materials. When iron was also incorporated in the mixture (FeTiSep) the measured and calculated surface areas were practically the same, indicating that the stabilisation effect of mixing titania and sepiolite disappeared in the presence of iron. For the catalysts incorporating manganese (MnTiSep) at 500 °C the measured surface area was similar to the calculated one, but heat treatment at 700 °C led to a significant reduction in the surface area and pore volume in accordance with the

greater crystallinity of this material, shown by the higher intensity of the XRD peaks, which corresponds with an increase in the size of the oxides due to sintering of the material with heat treatment.

However, as seen from the results in Tables 1a and 2, the surface area alone was not the controlling factor for the catalytic behaviour, since these have a very different order:

$$\text{TiSep500} > \text{FeTiSep500} = \text{MnTiSep500} > \text{TiSep700} > \text{FeTiSep700} > \text{MnTiSep700}$$

Higher surface areas were found for the catalysts that presented smaller titania particle sizes (see Figure 1 and Table 3), with iron oxide species being better dispersed than the manganese oxides and in general, the catalysts that had better iron or manganese dispersion were more active. Due to the good dispersion of the active phases, no peaks could be found in XRD or particles observed in the scanning electron microscope (SEM) results (Figure 2), although SEM show intimate interaction between the sepiolite fibers and titania particles.

Characterisation of the porosity of the conformed catalysts by mercury intrusion porosimetry (MIP) showed that TiSep had a bimodal pore size distribution at both calcination temperatures. The porosity in pores between 50 to 200 nm was due to the titania and below 50 nm to the sepiolite. The threshold diameters, at which the internal structure of the conformed materials is accessed indicated by the sudden upswing in the cumulative pore volume curves, was 176 nm at both calcination temperatures (Figure 3). The incorporation of iron gave rise to a displacement in the threshold diameters to 225 and 253 nm at 500 and 700 °C respectively, indicating that the iron species were associated with the titania and not located within the mesopores of the sepiolite. Similarly in the case of manganese incorporation, there was a displacement of the threshold diameter to 211 and 220 nm at 500 and 700 °C respectively, indicating the association of the manganese species with the titania.

The importance of basic sites in catalytic oxidation reactions is well known (Młodzik, 2016; Li, 2015). Thus, in order to clarify the reasons for the catalytic activities found in this work, the strengths and amounts of basic sites were determined by acetic acid adsorption/decomposition. Acetic acid interacts with basic centres producing carbonates and acetates that decompose to CO<sub>2</sub> on heating, where higher temperatures are necessary to cause the decomposition from the stronger basic sites (Mandal, 2013).

Basic strengths of the catalysts was indicated by the decomposition of acetic acid, where desorption below 250°C was due to low strength, between 250 and 350 °C to medium strength and above 350 indicated the presence of high strength basic sites. TiSep700 only had a small amount of weak basic sites, whereas TiSep500 showed both weak and medium strength basic sites. The incorporation of iron gave rise to weak, medium and strong basic sites, where FeTiSep500 has medium basic sites and the highest amount of strong basic sites. With regards to the manganese containing catalysts, they both showed basic sites of weak and medium strength but only a small proportion of strong basic sites. Comparing the results in Table 1a and Figure 4 it may be appreciated that the catalysts with greater number of centres of strong basicity were those with higher catalytic activities. Furthermore, the textural characterisation indicated wider threshold diameters for FeTiSep catalysts that would improve the access of the reactants to the active sites compared with the MnTiSep. At higher conversions production of greater fractions of the more oxidized compounds was witnessed, *i.e.* carvacrol and terephthalic acid *vs* epoxide, carvone and carveol, in agreement with bibliographic data (Martin, 1992).

When orange peel oil was used, similar results to those obtained with limonene were obtained. The reactants present in orange peel oil, other than limonene were recovered

unreacted. These results are important; since orange peel oil is *ca.* an order of magnitude cheaper than limonene and therefore its use makes the process more economically and environmentally sound.

### 3.2 Oxidations activated with microwave heating

Microwave heating as an activation method was chosen in order to obtain similar conversions in shorter reaction times to those of conventional heating and avoid over oxidation. After 70 minutes under microwave irradiation, catalyst FeTiSep500 gave the highest conversion, as with conventional heating (Table 1b). The order of activities was the same as that found with conventional heating but the selectivities at similar conversions displayed higher amounts of the more oxidized compounds, *i.e.* carvacrol and terephthalic acid. Previous results obtained with silica supported iron oxide catalysts, showed lower oxidation activities at similar conversion values. The better oxidation activity found here was due to both the greater amounts of basic sites and their higher strengths. As in conventional heating, when orange peel oil was used, similar results to those obtained with limonene were observed.

Bibliographic studies of the oxidation of limonene, show the difficulty of uncontrolled over oxidation at high conversion values, mainly due to polymerisation, when limonene was converted over a 30 hours reaction time (Oliveira, 2006). In this study the reaction conditions allowed a better control of selectivity, by using only up to seven hours of reaction under conventional heating or 70 minutes under microwave irradiation, with lower amounts of oxidant (limonene/tbHP 0.28 in this work vs 0.125 in Oliveiras's work), also the iron or

manganese oxides used here are less toxic than vanadium pentoxide, in the search for modifying processes to achieve lower toxicities.

Other workers using mixed oxides of iron, cobalt and manganese required seven hours of reaction with 1 atmosphere of oxygen and 60 °C (Menini, 2008), whereas here limonene was converted with tbHP, which on oxidation produces OH\* reactive species and low toxicity tbOH, with similar reactivities, without the need of toxic cobalt, an important aspect from an environmental stand point.

### 3.3 Reactions with solar activation

The field of fine chemicals syntheses with solar activated photocatalysis is rapidly growing in interest and this approach favours regions with higher amounts of sunlight, which interestingly are mainly located in less industrialized countries (Preethi, 2016).

A recent review summarizes several solar photo induced reactions to produce fine chemicals that are being carried out worldwide with enormous energy savings (production of  $\epsilon$ -caprolactam, or the photo-oxygenation of citronellol sensitized by Rose-Bengal in isopropanol to Rose Oxide (a fragrance of which over 100 t are produced per annum), acylation of quinones and naphthoquinones to intermediates for the synthesis of tetracyclines, or transformation of aromatic alcohols to the corresponding aldehydes) and therefore subsequent reductions in CO<sub>2</sub> emissions (Spasiano, 2015).

The catalysts prepared in this work show similar conversions compared to the reactions carried out under conventional and microwave heating (Table 1c), although under solar irradiation the maximum temperatures achieved were only about 50 °C and at this temperature neither conventional nor microwave heating activated the reactions. There was no

conversion when tbHP was used in the absence of catalyst. Furthermore, the order of activities was different to those achieved by conventional thermal or microwave activated reactions:



The most active catalyst studied in this work was FeTiSep500, followed by MnTiSep500. These catalysts show selectivity mainly to epoxides and carvone, with small amounts of carveol, carvacrol and terephthalic acid. The activities were directly related to the light absorption of the catalysts as studied by UV-Vis (Figure 5). TiSep catalysts display a steep increase of absorption at wavelength  $< 390$  nm, due to the intrinsic band gap of titania in its anatase form, in agreement with XRD results. The iron or manganese containing catalysts have additional absorptions in the visible region at wavelength *ca.* 400 nm, due to the excitation of 3d electrons of iron or manganese ions to the titania conduction band (charge transfer transition) and at *ca.* 500 nm, that can be ascribed to the d-d transition of the ions ( ${}^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$ ) or the charge transfer transition between interacting iron species (Tada, 2011) or manganese species (Lu, 2015).

The use of orange peel oil with the best catalyst (FeTiSep500) led to similar results to those obtained with limonene as observed with the other activation techniques.

#### 4. Conclusions

Environmentally friendly catalysts and processes were employed to produce value added oxygen containing substances from limonene. The compositions of the catalysts were iron or manganese, titania and sepiolite, all of them of low toxicity, with basic sites active in oxidation reactions, paramagnetic iron or manganese oxide centres making them active for



microwave activation and the presence of iron or manganese to improve their absorption in the visible region, improving their photocatalytic activities under solar radiation.

Interactions between the different components of the catalysts affect their structures and catalytic behaviour, *i.e.* the presence of sepiolite or iron oxide (but not of manganese oxide) decreases the crystallinity of titania, higher calcination temperature leads to greater titania particle sizes and lower surface areas and pore volumes. The catalysts containing iron alone show the presence of crystalline iron oxide (hematite) when calcined at 700 °C but not on calcination at 500 °C, while those containing manganese have peaks of this oxide both at 500 and at 700 °C, indicating that the manganese oxide species were less dispersed than those of iron.

Regarding catalytic activities, conversions of about 35 % were reached under conventional, microwave heating or solar irradiation, competitive with results found in the literature. The main products found are limonene oxides, carvone, carveol, carvacrol and terephthalic acid. Increased activity was observed for the catalysts calcined at lower temperatures and generally lower conversions were associated with a higher selectivity to the epoxides, indicating these to be intermediates of more highly oxidized products. Solar irradiation affords similar conversions to those of conventional and microwave heating and is indeed the most sustainable and economical activation option. The results obtained when orange peel oil was used were similar to those found with pure limonene, improving the economy and sustainability of the process.

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Table 1a. Conventional heating (120 °C, 0.15g catalyst, 4 mL lim, 14 mL tbHP)

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Catalyst	Reaction time/h	Conversion %	S <sub>limox</sub> %	S <sub>col</sub> %	S <sub>cone</sub> %	S <sub>cröl</sub> %
<b>TiSep500</b>	0.5	0	0	0	0	0
	1	0	0	0	0	0
	2	2	95	5	0	0
	5	5	95	5	0	0
	7	7	90	7	3	0
<b>TiSep700</b>	0.5	0	0	0	0	0
	1	0	0	0	0	0
	2	2	95	5	0	0
	5	5	95	5	0	0
	7	5	95	5	0	0
<b>FeTiSep500</b>	0.5	7	89	8	3	0
	1	19	72	16	12	0
	2	27	67	5	23	5
	5	32	53	13	24	10
	7	34	34	14	15	37
<b>FeTiSep700</b>	0.5	2	97	3	0	0
	1	5	91	5	4	0
	2	19	50	12	15	23
	5	24	45	10	12	33
	7	25	41	9	10	40
<b>MnTiSep500</b>	0.5	5	97	3	0	0
	1	10	75	19	6	0
	2	16	67	16	10	7
	5	20	51	12	11	26
	7	22	43	11	11	35
<b>MnTiSep700</b>	0.5	5	93	5	2	0
	1	8	85	10	5	0
	2	10	75	15	5	5
	5	17	61	16	7	16
	7	19	58	12	7	23
<b>FeTiSep500*</b>	0.5	6	89	9	2	0
	1	18	73	14	13	0
	2	28	65	7	24	4
	5	31	54	14	22	10
	7	33	33	14	16	37

Table 1b. Microwave activation (120 °C, 0.15g catalyst, 4 mL lim, 14 mL tbHP)

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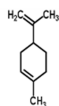
Catalyst	Reaction time/min	Conversion %	S <sub>limox</sub> %	S <sub>col</sub> %	S <sub>scone</sub> %	S <sub>scrol</sub> %	S <sub>terac</sub> %
<b>TiSep500</b>	15	0	0	0	0	0	0
	25	2	98	2	0	0	0
	50	5	93	7	0	0	0
	70	8	93	7	0	0	0
<b>TiSep700</b>	15	0	0	0	0	0	0
	25	0	0	0	0	0	0
	50	2	97	3	0	0	0
	70	5	95	5	0	0	0
<b>FeTiSep500</b>	15	20	68	17	15	0	0
	25	27	43	25	25	5	2
	50	34	39	17	28	11	5
	70	35	37	14	18	20	11
<b>FeTiSep700</b>	15	16	75	20	5	0	0
	25	20	70	18	12	0	0
	50	26	68	16	14	2	0
	70	27	68	8	13	10	1
<b>MnTiSep500</b>	15	14	80	15	5	0	0
	25	17	70	13	17	0	0
	50	25	64	11	20	5	0
	70	25	61	12	27	10	0
<b>MnTiSep700</b>	15	11	75	20	5	0	0
	25	14	73	20	7	0	0
	50	20	70	14	11	5	0
	70	21	69	6	11	14	0
<b>FeTiSep500*</b>	15	19	68	18	14	0	0
	25	25	45	25	21	7	2
	50	33	37	16	30	12	5
	70	34	35	16	17	22	10

Table 1c. Solar activation (0.15g catalyst, 4 mL lim, 14 mL tbHP)

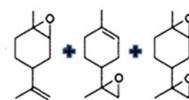
Catalyst	Reaction time/h	Conversion %	S <sub>limox</sub> %	S <sub>col</sub> %	S <sub>cone</sub> %	S <sub>col</sub> %	S <sub>terepac</sub> %
TiSep500	1	5	90	9	1	0	0
	2	10	70	12	18	0	0
	3	12	60	14	24	0	0
	4	14	58	7	35	0	0
TiSep700	1	2	95	5	0	0	0
	2	4	93	5	2	0	0
	3	10	75	15	10	0	0
	4	12	73	15	12	0	0
FeTiSep500	1	17	70	17	13	0	0
	2	25	61	19	20	0	0
	3	34	52	20	25	2	1
	4	36	50	8	32	7	3
FeTiSep700	1	11	75	20	5	0	0
	2	17	72	19	10	0	0
	3	22	62	19	19	0	0
	4	25	57	20	23	0	0
MnTiSep500	1	11	70	20	10	0	0
	2	14	61	30	9	0	0
	3	29	57	18	25	0	0
	4	31	55	7	36	2	0
MnTiSep700	1	5	91	7	2	0	0
	2	7	89	7	4	0	0
	3	20	62	20	18	0	0
	4	22	59	23	18	0	0
FeTiSep500*	1	16	68	18	14	0	0
	2	26	60	19	21	0	0
	3	33	54	21	22	2	1
	4	35	50	9	31	8	2

Orange peel oil \*

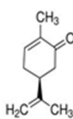
Limonene:



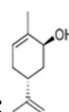
Limonene oxides (Limox):



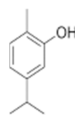
Carvone (CONE):



Carveol (COL):



Carvacrol (CROL):



Terephthalic acid (TEREPAC):

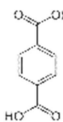




Table 2. Textural characteristics of precursors and catalysts.

Catalyst	Heat Treatment °C	Surface Area $S_{\text{BET}}$ $\text{m}^2\text{g}^{-1}$	Calculated Surface Area $\text{m}^2\text{g}^{-1}$	Difference %	Total Pore Volume $\text{cm}^3\text{g}^{-1}$	Threshold
						Diameter nm
Sep	500	149	-	-	-	-
	700	126	-	-	-	-
Ti	500	78	-	-	-	-
	700	31	-	-	-	-
TiSep	500	103	96	7	0.659	176
	700	70	55	28	0.634	176
FeTiSep	500	97	91	6	0.665	225
	700	50	52	-4	0.598	253
MnTiSep	500	96	91	5	0.600	211
	700	39	52	-25	0.530	220

Table 3. XRD analysis of precursors and catalysts.

Material	TiO <sub>2</sub> <sup>*</sup>	d <sub>TiO<sub>2</sub></sub> <sup>**</sup> / d <sub>Fe</sub> or d <sub>Mn</sub>
<b>Ti500</b>	25.38	30/-
<b>Ti700</b>	25.38	39/-
<b>TiSep500</b>	25.38	25/-
<b>TiSep700</b>	25.38	27/-
<b>FeTiSep500</b>	25.54	23/-
<b>FeTiSep700</b>	25.44	25/5 <sup>a</sup>
<b>MnTiSep500</b>	25.36	25/(7,7) <sup>b</sup>
<b>MnTiSep700</b>	25.39	27/(7,8) <sup>c</sup>

\* 2 $\theta$  position Plane 101 TiO<sub>2</sub> (°)

\*\* nm TiO<sub>2</sub> (101 reflection)

<sup>a</sup>: Fe<sub>2</sub>TiO<sub>5</sub> (5 nm)

<sup>b</sup>:  $\beta$ -MnO<sub>2</sub> (7 nm),  $\alpha$ -MnO<sub>2</sub> (7 nm)

<sup>c</sup>:  $\beta$ -MnO<sub>2</sub> (7 nm),  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> (8 nm)

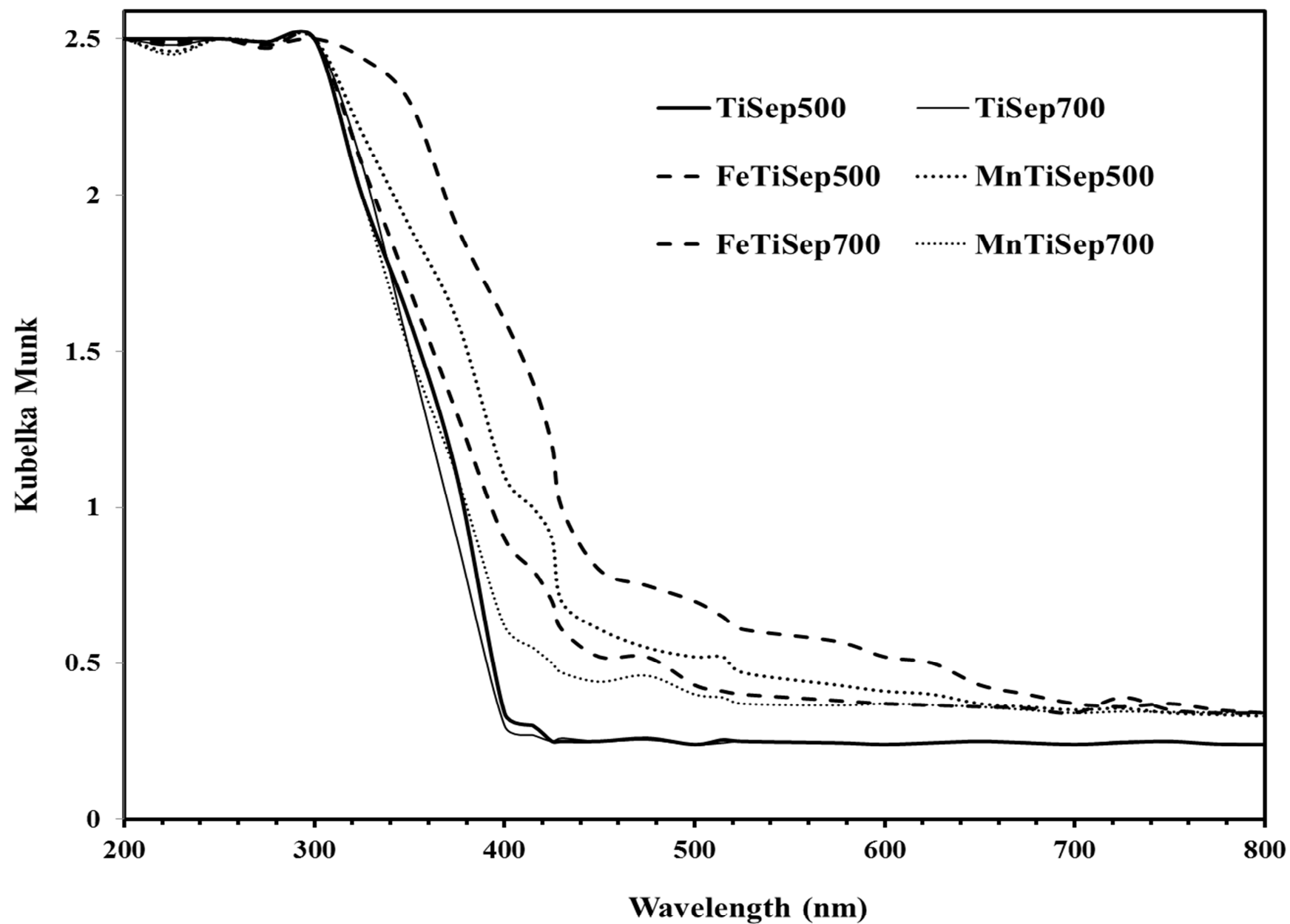


Figure 5. UV-VIS analysis of catalysts

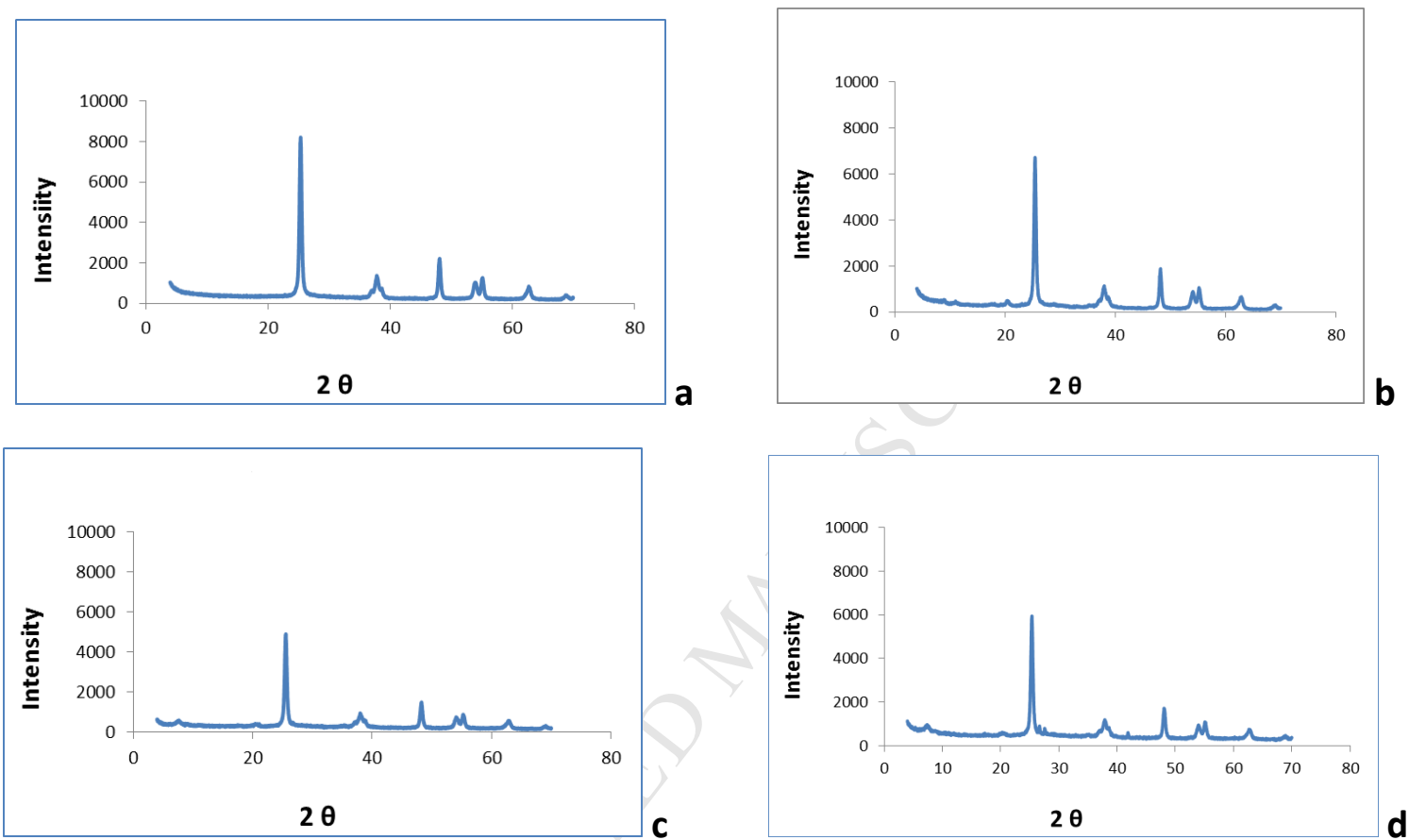


Figure 1. X-Ray diffractograms of precursors and catalysts calcined at 500 °C (a: Ti500, b: TiSep500, c: FeTiSep500, D: MnTiSep500)

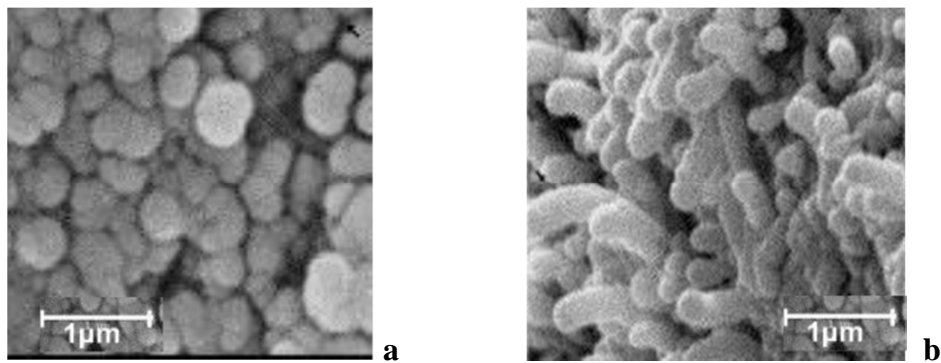


Figure 2. a. Ti500 particles b. FeTiSep500 (Sepiolite fibres and titania particles)

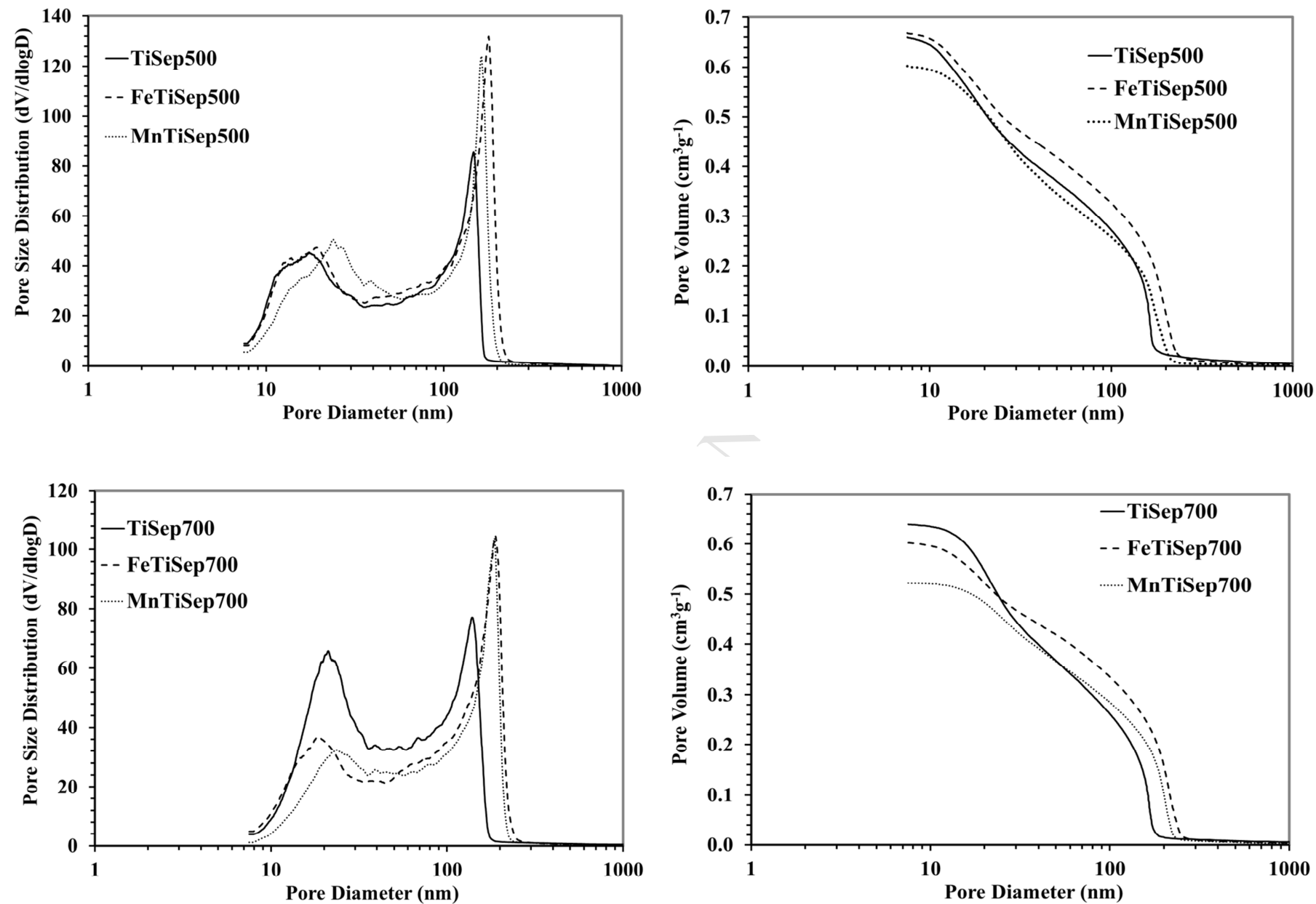


Figure 3. MIP of catalysts

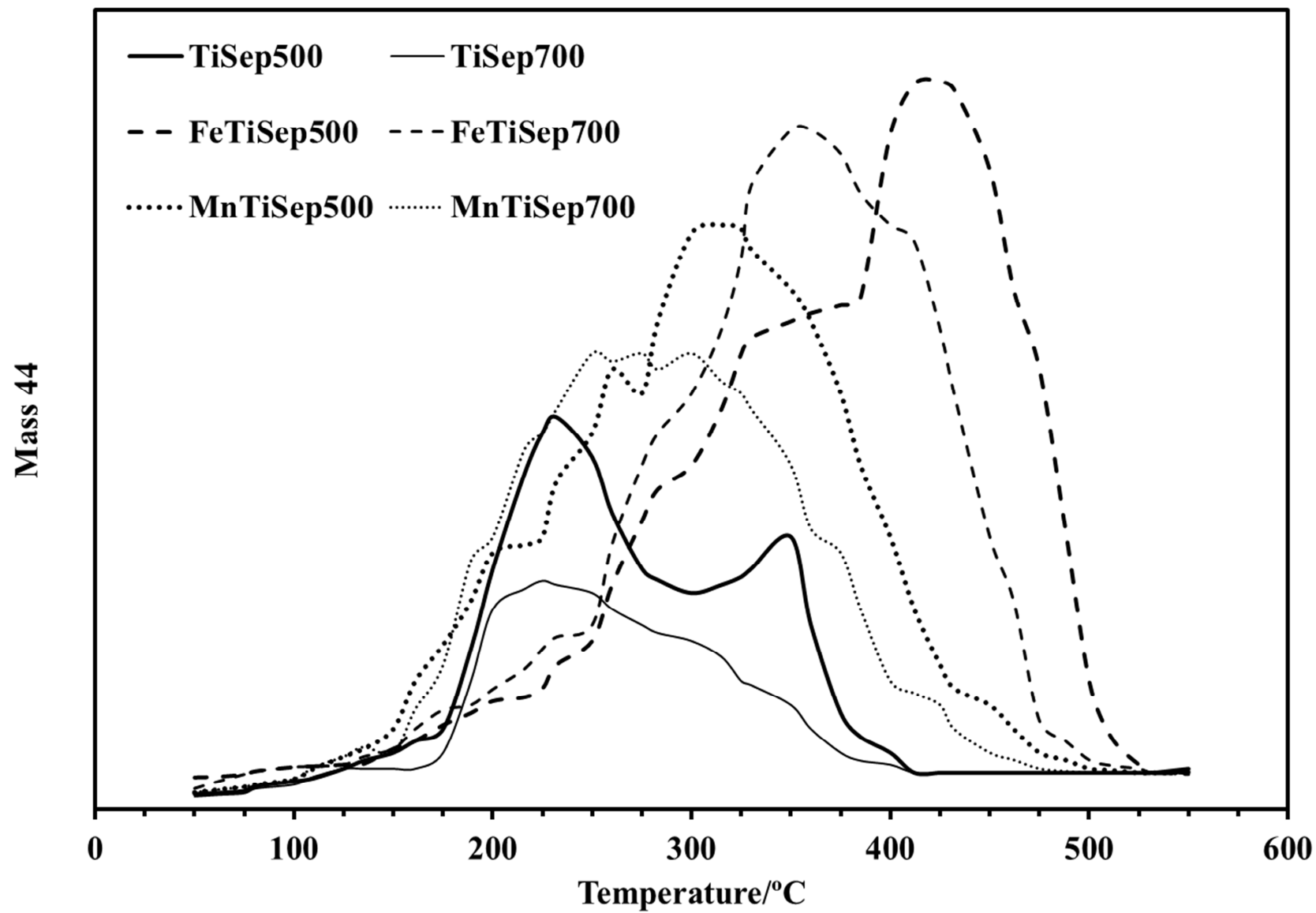


Figure 4. Basicity analysis of catalysts

**Highlights**

- Cleaner production of platform chemicals from limonene a by-product of orange juice industry.
- Design of economic low toxicity catalysts.
- Comparison of conventional, microwave and solar activations.
- Solar activation favours countries with high amounts of sunlight.
- Using orange peel oil versus purified limonene improves the economy and sustainability of the process.

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