Sustainable p-cymene and hydrogen from limonene

M.A. Martin-Luengo a,∗, M. Yates b, E. Saez Rojo a, b, D. Huerta Arribasa b, D. Aguilar a, b, E. Ruiz Hitzky a

a Institute of Materials Science of Madrid, CSIC, Calle Sor Juana Ines de la Cruz, Campus UAM, Cantoblanco, 28049 Madrid, Spain
b Institute of Catalysis and Petroleochemistry, Campus UAM, CSIC, Calle Marie Curie 2, Cantoblanco, E-28049 Madrid, Spain

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A B S T R A C T

A fine chemical intermediate in a wide range of chemical processes, p-cymene, has been obtained from Limonene, solids based on a natural clay (sepiolite) modified with sodium, nickel, iron or manganese oxides and programmable focalised microwaves. The process has the added bonus of one mol of hydrogen being produced per mol of limonene converted to p-cymene.

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1. Introduction

Environmental problems pose a great challenge, and are being taken into account by ever more stringent legislation, due to the recognition of the need for a sustainable development, particularly in countries where water use, residues and desertic and contaminated soils have become a matter of the utmost concern. Efforts from academia, industry and government are mainly based on technological changes that improve chemical processes to avoid negative environmental consequences for health and environment [1]. To address this point, new renewable and sustainable chemicals are now being obtained from agricultural wastes, reducing in this way the need for non-renewable fossil resources (NRFR) [2]. This work is based on designing a clean process to transform limonene, a renewable raw material (RRM) into p-cymene a value added product usually prepared by alkylation of NRFR (benzene or toluene), in a rapid, simple and economic way. Limonene, a subproduct from citrus fruit processing, is a cyclic terpene with empiric formula C10H16 (Fig. 1), of low toxicity (LD50 5 g kg⁻¹ oral rat) [3], that constitutes ca. 95% of orange peel oil. Having a six membered ring this substance has the potential for use to obtain compounds that are usually produced from non-renewable petroleum derivatives. It is used as a biodegradable solvent (replacing mineral oils, aromatics, CFCs, etc.), as an additive in pigments, inks, adhesives, pharmaceutical and commodity compositions [4]. New uses are being sought to give added value to this subproduct, in this way increasing the income of citrus juice industries, and also with obvious benefits to the environment and society in general. The catalytic supports used in this study were based on sepiolite, a natural clay of high abundance and low cost in Madrid [5,6], (Table 2), in order to decrease the fabrication costs and waste, due to its negligible negative environmental impact. Sepiolite is a hydrated magnesium silicate of the philosilicate type 2:1 with a layer of magnesium between two layers of silica tetrahedra. The octahedral sheet is composed mainly of Mg2+. It has substitution of Si4+ and Mg2+ by small amounts of Al3+ and its specific surface area (S BET) is close to 300 m² g⁻¹, of which 150 m² g⁻¹ is external (pores with diameters >2 nm diameter) and the remainder is related to the volume filling of micropores (<2 nm diameter). It has a density of SiOH groups of ca. 2.2 groups/10 nm² originated at the edges due to breakage of Si–O–Si bonds. Its uses are related to its sorbent and colloidal properties, surface area, mechanical resistance and thermal stability [6,7], as a support for catalysts, absorbent to clean gaseous effluents [8,9], decolouring agent for foods [10,11], support for insecticides [12] and more recently as a component in nanocomposites [13].

A key point in improving chemical processes is decreasing their reaction time, since this lowers energy use. In this sense microwave irradiation has been chosen to activate the reactions, since it allows extraordinary reaction rates to be achieved, in many
cases not comparable to those obtained by classical heating [14]. Coupling microwave irradiation with solvent less processes or with solid supports increases the positive environmental aspect of these systems [3,14], since it avoids the use of costly or toxic organic solvents and can also avoid secondary unwanted reactions leading to higher yields and selectivities in soft conditions \[15,16\]. Thus, careful design of the processes, in many cases, can lead to conversions and selectivities that cannot be achieved with conventional heating.

The activity of the parent sepiolite was modified by adding sodium, iron, manganese or nickel oxides, being of low price compared to Au or Ag \[17\] or low toxicity (except nickel) compared to sodium, iron, manganese or nickel oxides, being of low price compared to Au or Ag \[17\] or low toxicity (except nickel) compared to other metals commonly used as catalysts for this kind of reactions \(i.e\). Pd, Cd, Cr, etc.) (LD50 oral rat 0.3, 2, 3.4 and 0.05 g kg\(^{-1}\) for sodium, iron, manganese and nickel oxides, respectively \[18\]).

### 2. Experimental

#### 2.1. Raw materials

Sepiolite was kindly supplied by Tolsa S.A. form Vallecas, Madrid. The \(\alpha\)(+)-limonene pro synthesis from Panreac with a purity of 95% was used as the reactant since this is similar to the purity of limonene produced as a subproduct form citrus fruit processing. Nickel and iron nitrates and manganese acetate used as precursor salts were from Panreac (NiNO\(_3\)·6H\(_2\)O 99.7%, FeNO\(_3\)·6H\(_2\)O 99.7%, FeNO\(_3\)_2·4H\(_2\)O 99.5% and Mn(CH\(_3\)COO)_2·4H\(_2\)O 99%).

#### 2.2. Catalyst preparation

The iron, manganese or nickel containing sepiolites were prepared so as to have similar amounts of these elements as the sodium containing material, by mixing iron nitrate (SepFe), manganese acetate (SepMn) or nickel nitrate (SepNi) with distilled water. The solid–liquid mixtures were stirred in a rotary evaporator at 50 °C under vacuum, until dryness.

The preparation of sodium containing sepiolite (SepNa) \[19\] was carried out by mixing the sepiolite Pangel 1N NaOH solution, under continuous stirring, introduced in a hermetically closed reactor and kept in an oven at 100 °C for 16 h, cooled to room temperature and then subsequently the product was thoroughly washed with distilled water and dried at 100 °C overnight.

All the precursors were then calcined at 400 °C in an air flow of 50 mL min\(^{-1}\) (according to TG–DTA analyses, as explained below), the sepiolite was also calcined at 400 °C for comparison purposes.

#### 2.3. Characterisation methods

The precursors of SepFe and SepMn, were analysed by TG–DTA in an Stanton model STA 781 thermogravimetric analyser in an air flow of 50 cm\(^3\) min\(^{-1}\) using 20–30 mg of solid, at a heating rate of 5 °C min\(^{-1}\) from room temperature to 1000 °C. By analysing their thermal and weight loss behaviours, thermal stability and change in composition, the best procedure to achieve the complete decomposition of the impregnated compounds to their corresponding oxides was determined.

The chemical composition of the solids after calcination was analysed in a Thermo Jarrel Ash ICP 300 apparatus after treatment with LiBO\(_2\) at 1000 °C. The amount of sodium was determined by flame spectrophotometry.

The surface areas, micro- and mesopore analyses of the solids were carried out in a Micromeritics ASAP 2010 apparatus using adsorption-desorption of N\(_2\) at \(-196 °C\), outgassing the solids overnight at 150 °C to a vacuum of less than \(10^{-2}\) Pa to ensure clean dry surfaces, free from any loosely bound adsorbed species. The specific surface areas were calculated according to the BET method, taking the area of the nitrogen molecule as 0.162 nm\(^2\).

### Table 1

#### Chemical analyses.

<table>
<thead>
<tr>
<th>Solid</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>MgO</th>
<th>Na(_2)O</th>
<th>Mn(_2)O(_4)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>K(_2)O</th>
<th>NiO</th>
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</thead>
<tbody>
<tr>
<td>Sepiolite</td>
<td>62.5</td>
<td>1.2</td>
<td>25.2</td>
<td>0.1</td>
<td>0.5</td>
<td>0.6</td>
<td>0.4</td>
<td>0.3</td>
<td>0.0</td>
</tr>
<tr>
<td>SepNa</td>
<td>56.8</td>
<td>1.3</td>
<td>23.9</td>
<td>7.3</td>
<td>0.5</td>
<td>0.7</td>
<td>0.3</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>SepNi</td>
<td>55.4</td>
<td>1.3</td>
<td>25.1</td>
<td>0.1</td>
<td>0.5</td>
<td>0.7</td>
<td>0.3</td>
<td>0.2</td>
<td>5.7</td>
</tr>
<tr>
<td>SepFe</td>
<td>56.5</td>
<td>1.3</td>
<td>24.1</td>
<td>0.1</td>
<td>0.5</td>
<td>7.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>SepMn</td>
<td>56.8</td>
<td>1.4</td>
<td>24.8</td>
<td>0.1</td>
<td>7.4</td>
<td>0.9</td>
<td>0.3</td>
<td>0.3</td>
<td>0.0</td>
</tr>
</tbody>
</table>

### Table 2

#### Textural characteristics of the solids.

<table>
<thead>
<tr>
<th>Solid</th>
<th>(S_{BET})</th>
<th>(S_{EXT})</th>
<th>(V_{mes})</th>
<th>(V_{mic})</th>
<th>(V_{tot})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sepiolite</td>
<td>298</td>
<td>149</td>
<td>0.03</td>
<td>0.417</td>
<td></td>
</tr>
<tr>
<td>Sep400</td>
<td>153</td>
<td>153</td>
<td>0.000</td>
<td>0.455</td>
<td></td>
</tr>
<tr>
<td>SepNa</td>
<td>100</td>
<td>93</td>
<td>0.002</td>
<td>0.376</td>
<td></td>
</tr>
<tr>
<td>SepNi</td>
<td>219</td>
<td>149</td>
<td>0.030</td>
<td>0.439</td>
<td></td>
</tr>
<tr>
<td>SepFe</td>
<td>155</td>
<td>149</td>
<td>0.002</td>
<td>0.416</td>
<td></td>
</tr>
<tr>
<td>SepMn</td>
<td>153</td>
<td>138</td>
<td>0.008</td>
<td>0.431</td>
<td></td>
</tr>
</tbody>
</table>

\(S_{BET}\) = specific surface area (m\(^2\) g\(^{-1}\)).

\(S_{EXT}\) = external surface area (m\(^2\) g\(^{-1}\)).

\(V_{mes}\) = mesopore volume (2–50 nm pore diameters, cm\(^3\) g\(^{-1}\)).

\(V_{mic}\) = micropore volume (0–2 nm pore diameters, cm\(^3\) g\(^{-1}\)).

\(V_{tot}\) = total pore volume (cm\(^3\) g\(^{-1}\)).

### Fig. 1

Chemical structure of reactant, intermediates and products.

### Fig. 2

Nitrogen isotherm for SepFe.
Table 3
Conversions and selectivities under dry media conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time (min)</th>
<th>Conversion (%)</th>
<th>α-terpinene</th>
<th>γ-terpinene</th>
<th>α-terpinolene</th>
<th>p-cymene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sepiolite</td>
<td>5</td>
<td>15</td>
<td>26</td>
<td>17</td>
<td>31</td>
<td>26</td>
</tr>
<tr>
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<td>23</td>
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<td>20</td>
<td>31</td>
<td>10</td>
<td>10</td>
<td>38</td>
<td>32</td>
</tr>
<tr>
<td>SepNa</td>
<td>5</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SepNi</td>
<td>5</td>
<td>70</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>86</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>SepFe</td>
<td>5</td>
<td>75</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td></td>
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<td>89</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
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<tr>
<td></td>
<td>20</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>SepMn</td>
<td>5</td>
<td>63</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>71</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

active pressure of 0.96 on the desorption branch of the isotherms, equivalent to the filling of all pores less than 50 nm diameter. The pore size distributions were analysed from the desorption branch of the isotherms using the Kelvin equation, with the thickness of the adsorbed layer of nitrogen calculated at each relative pressure from the Harkins–Jura equation. The pore size distributions were obtained, applying the Barrer Joyner Halender (BJH) method. A t-plot analysis was used to assess the presence of microporosity in the solids, and the external surface areas, i.e. that not involved in the micropore filling mechanism.

Transmission electron microscopy was carried out in a JEOL model FXII electron microscope operating at 200 kV. Ethanolic suspensions of the solids were deposited on carbon covered copper grids and left to dry for analysis.

To analyse the acidity of the solids they were first thoroughly mixed with pyridine, then introduced into a Stanton model STA 781 TG-MS apparatus and flushed with nitrogen until constant weight. The temperature was then increased under a nitrogen flow from 80 °C to 700 °C at 10 °C min⁻¹ and the evolution of pyridine analysed by means of a mass spectrometer coupled to the thermogravimetric analyser.

The catalytic reactions were carried out in Prolabo Synthewave 402 monomode programmable focalised microwave oven which allows reproducible results when compared with conventional microwave ovens, where heterogeneous distribution of microwave radiation makes reproducibility difficult. Also this oven can be programmed, by choosing time, power and temperature, with reproducibility when compared with conventional ovens.

Under dry media, 200 mg of solid were thoroughly mixed with 0.057 cm² of limonene and introduced in the reactor, being the microwave oven programmed as designed. In the solvent less reactions a maximum temperature of 165 °C was chosen to transform limonene, based on the results obtained under dry media conditions. In this case 5 cm³ of limonene and a maximum of 500 mg of solid were used with a reflux attachment included in the microwave oven. At the end of the reactions, the system was allowed to cool and the solid eluted with 2 cm³ ethanol (dry media) or 0.057 cm³ of liquid were dissolved in 2 cm³ of ethanol (liquid) to extract the reactants and products. The liquid was then filtered and analysed in a Hewlett Packard 5890 Series II chromatograph, coupled to a Hewlett Packard Series 5971 mass spectrometer with a 25 m capillary column of methyl silicone, (50–170 °C at a heating rate of 6 °C min⁻¹).

3. Results

3.1. Catalyst characterisation

After preparation, the solid precursors of SepNi, SepFe and SepMn were analysed by TG–DTA in order to assess the best conditions to achieve the thermal decomposition of the precursor salts, leading to the corresponding impregnated oxides. The thermograms obtained (not shown) indicate a total weight loss of ca. 20% due to decomposition of the precursor salt anions, divided in ca. 8% in the interval 20–120 °C (loss of adsorbed water), 5% between 120 and 250 °C (loss of zeolitic water, also found in the parent sepiolite) and decomposition of the anions at ca. 400 °C for nickel or iron nitrate and at ca. 300 °C for manganese acetate, with weight losses of ca. 8%. In accordance with these findings all the precursor solids were calcined at 400 °C for 4 h in an air flow of 50 mL min⁻¹. FTIR analyses, were in agreement with the disappearance of the anions.

The compositions of the catalysts are included in Table 1, the main differences between the samples being due to the introduction of sodium or nickel, iron and manganese oxides, as expected. XRD analyses showed that the structure of sepiolite is maintained after impregnation and calcination to produce the supported oxides, as shown by the (1 1 0) reflection at 7.42° (2θ), but did not show peaks corresponding to the oxides, due to the high dispersion of their particles, in agreement with the TEM results showing sizes of ca. 3–4 nm [Fig. 3], whose XRD peaks would have very low intensities and would thus be occluded inside the background noise of the XRD patterns [6].

The nitrogen adsorption isotherms for the parent sepiolite gave a mixed type I/II form, due to the presence of both micropores (0–2 nm) and mesopores (2–50 nm) that extend into the macropore region (>50 nm). The textural characteristics of the solids are included in Table 2. The original sepiolite had a surface area of 300 m² g⁻¹ as expected. On calcination the surface areas of the solids decreased to ca. 150 m² g⁻¹ mainly due to the rotation and folding of the clay structure which causes the collapse of the microporous channels, giving type II adsorption branches, as shown in Fig. 2.

For all the samples the hysteresis loops were of type H3, typical for solids with slit-shaped pores, commonly found with clay materials [7,20,21]. The pore size distributions of the solids show the presence of mesopores with maxima at ca. 30 nm, extending into the macropore region at pore diameters >50 nm. The external surface areas corresponding to pores...
Transmission electron microscopy was used to obtain information about the morphology and particle size of the oxide containing solids. Selected electron micrographs are presented in Fig. 3. The solids present no observable alteration of the sepiolite microtubules (0.2–2 μm in length) and the oxide particles have sizes of 3–4 nm. More homogeneous distributions of the oxide particles were observed for SepNi and SepFe compared to SepMn, the latter displaying agglomerates of particles. Homogeneous particle sizes have been claimed to be a positive effect for the reactivity in this kind of reactions [22]. However, there are researchers that claim different effects of the oxide particle sizes on the reactivity and selectivity for dehydrogenations, for example White et al. found that changes in the particle size did not alter the overall activity, although larger particles gave lower selectivities for C₆ products than smaller ones in the oxidative dehydrogenation over bismuth oxide (475–625 °C) [23], Chen et al. claimed the same effect on oxidative dehydrogenation on zirconia-supported molybdenum oxide catalysts [24] and Frank et al. found that propene selectivity in the oxidative dehydrogenation of propane decreased with an increase in the size of the catalyst particles [25].
The amount and strength of acid sites, determined by the TPD of pyridine, are shown in Fig. 4. From these results it was observed that pyridine desorbs from sepiolite in the temperature range of 200–260 °C, while temperatures in excess of 400 °C were required to clean the surfaces of the oxide doped sepiolites. The increase in the amount and strength of acid sites by addition of oxides to these supports is mainly related to the presence of Me⁺⁺ ions [26] (Lewis acidity) and to surface OH groups (Brönsted acidity) [27–30] and followed the order: SepFe > SepNi > SepMn > Sep. As expected no pyridine adsorption was found for the sodium containing sample (SepNa). Furthermore, due to the strong relationship between OH- and water, the presence of Brönsted acidity is usually difficult to demonstrate and relate to catalytic activities [30].

3.2. Transformation of limonene to p-cymene

3.2.1. Dry media conditions

The results for dry media conditions are presented in Table 3. The SepNa material was chosen for comparison purposes, but due to its lack of acid sites and since it showed no activity it has been omitted from the table. A bibliographic search indicated that for basic sites to react in isomerisation and dehydrogenation of terpenes, temperatures close to 400 °C are required [31]. Since with mw irradiation the temperatures were not higher than 210 °C, the inactivity of this material was to be expected. From Table 3 it may also be seen that for the solids studied 100% selectivity to p-cymene was found after only 5 min of reaction. The increase of activity, compared to the parent sepiolite, can be related to the metal oxide contents, since they are microwave-adsorbing centres, but not to the final temperature attained, since they did not follow the same trend (Fig. 5a).

3.2.2. Liquid phase reaction

Only the solids that presented activity under dry media conditions were tested in the liquid phase reactions, designed to allow higher liquid to solid ratios. Chosen sets of conditions were repeated three times and the differences found were less than 3% in conversions and selectivities. It may be observed (Fig. 6) that the selectivity to p-cymene increased with longer reaction times and higher temperatures, in accordance with the formation of this product being an endothermic reaction. For SepFe, SepNi and SepMn, 100% conversion was reached after 20 min of reaction with high selectivities to p-cymene (88, 82 and 77%, respectively). The temperatures reached by the systems were in the order Sep > SepNi > SepMn > SepFe (Fig. 5b). Although similar reactivities and selectivities are found for these oxide containing solids, it should not be forgotten the higher toxicity of SepNi, compared to SepMn and SepFe, which makes these last two easier to dispose of after use. The higher microporosity of the SepNi catalyst appears to have little effect on the overall reactivity. This suggests that the active sites on the more accessible external area,
which are similar for all three samples, are where the reaction takes place.

The characterisation by pyridine desorption (Fig. 4) indicated that the amount of acid sites followed the order: SepFe > SepNi > SepMn > Sep and no acid sites were found for SepNa. Previous work has shown that the acid sites of a series of silica–aluminas could dehydrogenate limonene towards \( p \)-cymene, with higher activities found for the solids that contained more acid sites \([3]\), in agreement with the results found here, where the order of activity (and selectivity to \( p \)-cymene) was also the order of acidity of the solids, as found with pyridine desorption.

When SepFe was reacted using conventional heating (Fig. 6e), much lower activities and selectivities to \( p \)-cymene were found in agreement with literature data \([32,33]\). We believe the short reaction times required using dielectric heating were responsible for the higher conversions and selectivities found, due to the presence of paramagnetic absorbing centres, thus avoiding unwanted products, that are formed during the longer reaction times necessary with conventional heating.

Although similar conversions and selectivities to those found in this study have recently been reported for the transformation of limonene, toxic catalysts (i.e. \( \mathrm{Cr} \)) or hydrogen pressures, greater than atmospheric and the use of toxic and expensive palladium catalysts were required \([34,35]\).

Regarding the mechanism of reaction, according to the work of Catrinescu \([33]\), limonene can react in the pores of acid solids in two main ways: isomerise to terpinenes and terpinolences, with further dehydrogenation of these, or disproportionate to \( p \)-cymene and menthene. The presence of isomerisation compounds (terpinenes and terpinolences) in the products would support the first mechanism, while the presence of menthene or menthanes would support the second mechanism. Since only terpinenes, terpinolences and \( p \)-cymene were found, the results agree with the first mechanism (isomerisation and dehydrogenation, but not disproportionation).

From an environmental point of view, it is important to note that this method does not need hydrogen \([34]\) and every mol of limonene that produces \( p \)-cymene leads to the production of a mol of hydrogen \([36]\).

4. Conclusions

The transformation of limonene, an inexpensive subproduct from citrus fruit processing, to \( p \)-cymene, a fine chemical intermediate, by means of a cheaper, simpler and lower toxicity method than the catalytic dehydrogenation presently used in industry, has been demonstrated. In this reaction for each mol of limonene converted to \( p \)-cymene a mol of hydrogen is produced.

Under microwave irradiation the reaction is activated by the microwave-adsorbing paramagnetic centres. Solids with both acid and paramagnetic sites lead to increased reaction rates and selectivities, compared to conventional heating. SepFe and SepNi had more highly dispersed oxide particles and greater acidity than SepMn, (although the latter had stronger basic sites), and showed also higher activities and selectivities towards \( p \)-cymene.

Acknowledgements

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