

ELECTRONIC SUPPORTING INFORMATION (ESI)

One-step microwave-assisted asymmetric cyclisation/hydrogenation of citronellal to menthols using supported nanoparticles on mesoporous materials

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Reaction conditions

Reaction samples were analysed (after reaction completion under microwave irradiation) by GC/GC-MS using an Agilent 6890N GC model fitted with a Rt- γ DEXsaTM cyclodextrin based column (30 m, 0.25 i.d.) and an FID detector. The products analysis was performed in a similar to that reported for the analysis of peppermint oils by Chiral GC/MS [1, 2]. 1 μ L of sample was injected. Injector temperature was set to 230°C. Helium (constant pressure) was employed as carrier gas at a flow rate of 35 cm/s. The oven temperature for the analysis of the natural products was programmed as follows: 40°C initial temperature; 40 to 120°C at a heating rate of 5°C/min; from 120 to 140°C at a heating rate of 2°C/min and finally from 140 to 200°C at 5°C/min.

Products obtained are presented in the GC trace shown in Figure 1 for the particular case of Pd/Ga-MCM-41, that shows the presence of the menthol isomers (peaks between approx. 24 to 26 min, retention time) together with other products found in the reaction including minor quantities of isopulegols, citronellal ethers and related by-products (see manuscript for more details). The GC trace of this catalyst was selected to better appreciate

the menthol isomers as well as the other products. A standard calibration was also performed to ensure no significant differences of products between products and reaction runs.

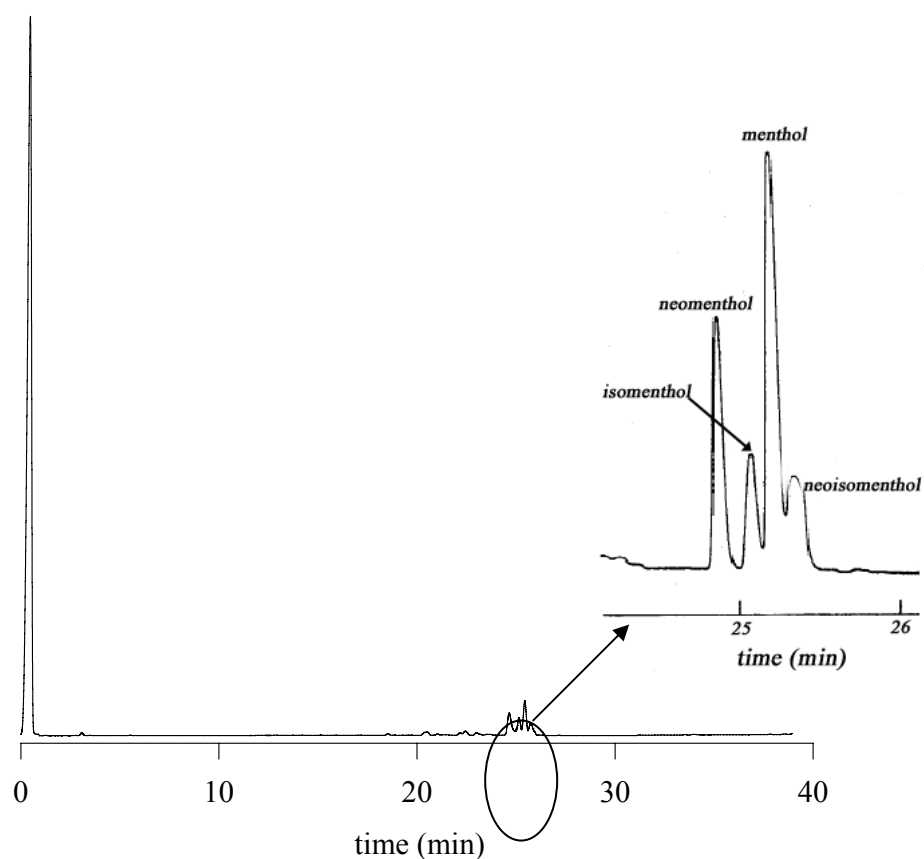


Figure 1. GC trace showing reaction products of the microwave-assisted tandem cyclisation/hydrogenation of (\pm)-citronellal to (\pm)-menthols using Pd/Ga-MCM-41 as catalyst.

Catalyst characterisation

Materials were also characterised by means of porosimetry, Scanning and Transmission Electron Microscopy (SEM and TEM) and XPS (see manuscript for more details and results).

N₂ adsorption measurements were performed in a volumetric adsorption analyser Micromeritics ASAP 2000. Samples were degassed for 24 h at 100°C under vacuum ($p < 10^{-2}$ Pa) and subsequently analysed. An example for 2%Pt-Ga-MCM-41 material is shown in Figure 2.

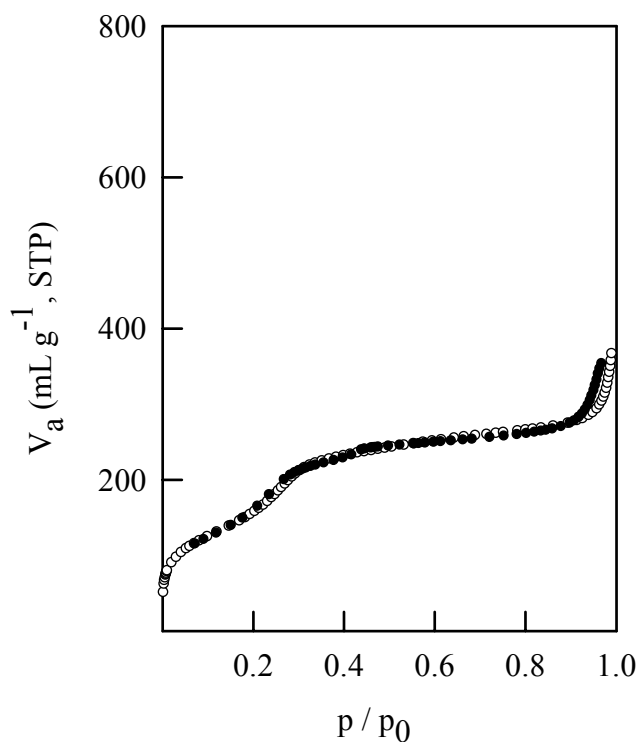


Figure 2. N₂ adsorption isotherm of 2%Pt-Ga-MCM-41

Scanning electron micrographs (SEM) and elemental composition of the calcined samples were recorded using a JEOL JSM-6300 Scanning Microscope with energy-dispersive X-ray analysis (EDX) at 20 kV. Samples were coated with Au/Pd on a high resolution sputtering SC7640 instrument at a sputtering rate of 1.5 kV per minute, up to 7 nm thickness. An example for 2%Pt-Ga-MCM-41 is depicted in Figure 3.

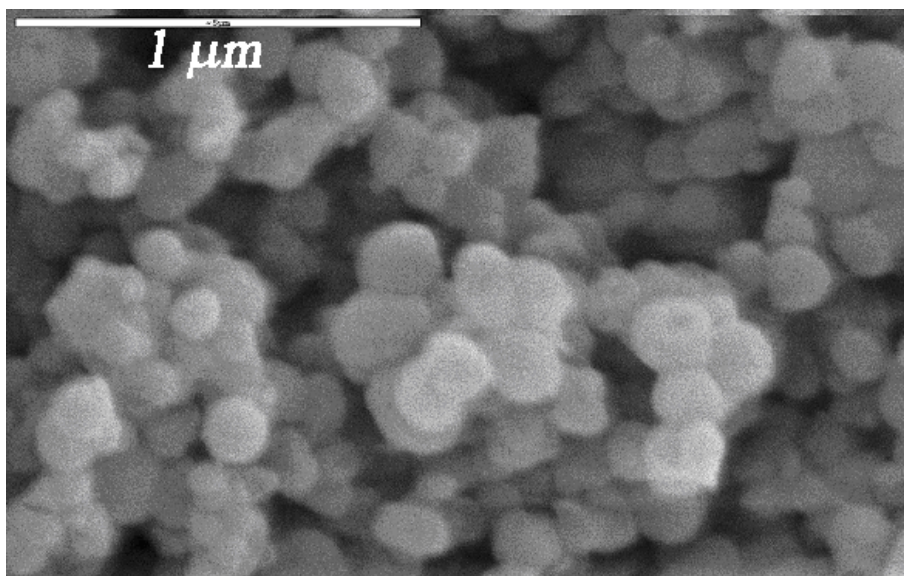


Figure 3. Scanning Electron Microscopy (SEM) micrograph of 2%Pt-Ga-MCM-41.

TEM micrographs were recorded on a FEI Tecnai G2 fitted with a CCD camera for ease and speed of use. The resolution is around 0.4 nm. Samples were suspended in ethanol and deposited straight away on a copper grid prior to analysis. An example for 2%Pt-Ga-MCM-41 is presented in Figure 4.

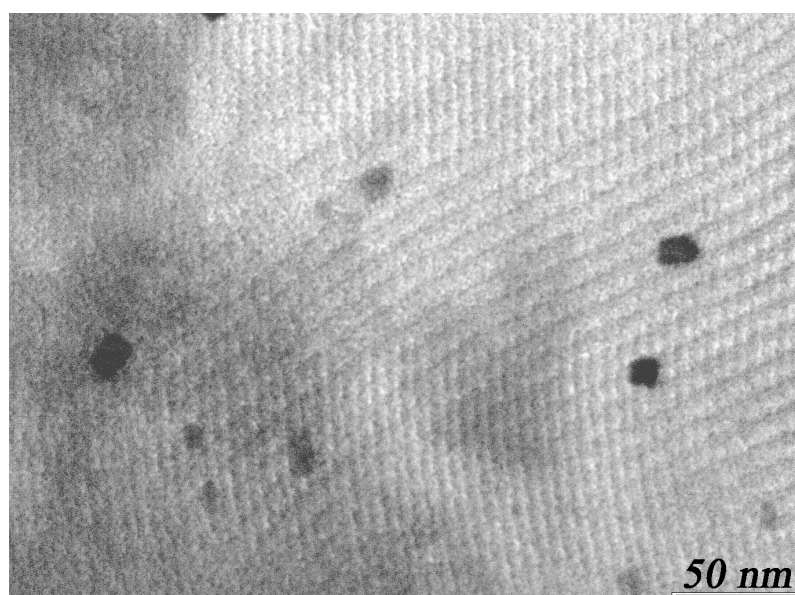


Figure 4. Transmission Electron Microscopy (TEM) micrograph of 2%Pt-Ga-MCM-41 material.

References

- [1] J. Kowalski, Evaluating peppermint oils by Charal GC/MS using a Rt- γ DEXsaTM column, available online: http://www.restek.com/advantage/adv_2005_04_07.pdf.
- [2] S. Alankar, *Asian J. Pharmaceutical Clinical Res.* 2009, **2(2)**, 27-33.