

P13. Methoxylation of α -pinene over mesoporous carbons and microporous carbons: a comparative study

M. F. Silva¹, I. Matos¹, R. Ruiz-Rosas², A.M. Ramos¹, J. Vital¹, J. Rodríguez-Mirasol², J.E. Castanheiro^{3**} and I.M. Fonseca^{1*}

1. *REQUIMTE, CQFB, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

2. *Chemical Engineering Department, School of Industrial Engineering, University of Málaga, c/Doctor Ortiz Ramos s/n, Campus de Teatinos, 29071 Málaga, Spain*

3. *Centro de Química de Évora, DQ, Universidade de Évora, 7000-671 Évora, Portugal*

**blo@fct.unl.pt; **jefc@uevora.pt*

Introduction

Monoterpenes are renewable resources that are widely used in the pharmaceutical, cosmetic and food industries. α -Pinene is a renewable raw material usually obtained from pine gum or as a waste from the Kraft process. Its acid catalysed methoxylation yields a complex mixture of monoterpene ethers, being α -terpinyl methyl ether the main product. The α -terpinyl methyl ether smells grapefruit-like and might be used as flavour and fragrance for perfume and cosmetic products [1].

Traditionally, mineral acids are used as catalysts, but the effluent disposal leads to environmental problems. One of the areas that can have a great contribution to overcome these problems is the development of catalysts leading to reactions more energetically efficient, more selective and less hazardous.

Activated Carbon with micro and meso porous structure have been employed successfully in several catalytic reactions [2-3]. Mesoporous carbon has the advantage of presenting meso and macro porous which may result in more efficient selectivity towards products. The microporous carbon used in this work has the advantage of being developed by pyrolysis of olive stones, which adds value to a biomass residue. The mesoporous carbon was synthesised by the sol gel method and oxidized with nitric acid.

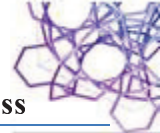
Experimental

Mesoporous carbons were prepared according to sol-gel method according Lin and Ritter [4].

The microporous carbon catalysts were prepared from olive stones, an agricultural waste predominantly produced in the Mediterranean countries. Olive stones were obtained from local olive manufacturers, cleaned with deionized water, dried at 100 °C, and ground with a roller mill to obtain samples of 1–2mm particle size. This olive stone waste was impregnated with 85% (w/w) H₃PO₄ at room temperature and dried for 24 h at 60 °C. The impregnated samples were activated under continuous N₂ flow (150cm³ STP/min) in a conventional tubular furnace. The activation temperature was reached at a heating rate of 10 °C/min and maintained for 2 h at 600 °C after cooling the samples were washed in hot distilled until neutral pH and negative phosphate analysis in the eluate. The resulting activated carbons were dried at 100 °C and grinded and sieved (100–200 m).

The mesoporous xerogel and the microporous carbon were treated with nitric acid. The samples were refluxed with a nitric acid solution (13M) for 6h (1g/20cm³) then washed with deionized water in soxhlet until pH 7 and then dried in oven at 110°C. Catalysts C1 and C2 micro and meso porous respectively were obtained. The materials were characterised by N₂ adsorption and TPD [5].

The catalytic experiments were carried out in a stirred batch reactor, at 60°C. In a typical experiment, the reactor was loaded with 50 mL of methanol and 0.2 g of catalyst. Reactions were started by adding 3 mmol of α -pinene.



Results and discussion

Table 1 shows the physicochemical characterization of the microporous (C1) and mesoporous (C2) activated carbons treated with nitric acid. The C1 catalyst showed higher amount of oxygenated groups and surface area (S_{BET}) than the C2 catalyst.

Table 1. Physicochemical characterization of catalysts

Catalyst	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{p} (cm^3/g)	Total CO^1 ($\mu\text{mol}/\text{g}$)	Total CO_2^1 ($\mu\text{mol}/\text{g}$)
C1	838	0.32	0.38	116.7	171.9
C2	622	0.16	0.34	24.5	25.3

(1) TPD

The activity of C1 is higher than the activity of C2 (Fig. 1). This behavior can be explained due to the higher amount of oxygenated groups present on activated carbon surface of C1.

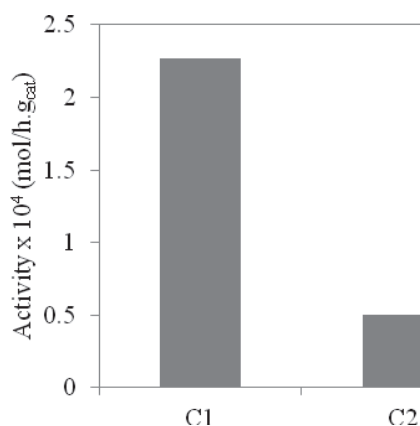


Figure 1. Activity of C1 and C2 catalysts.

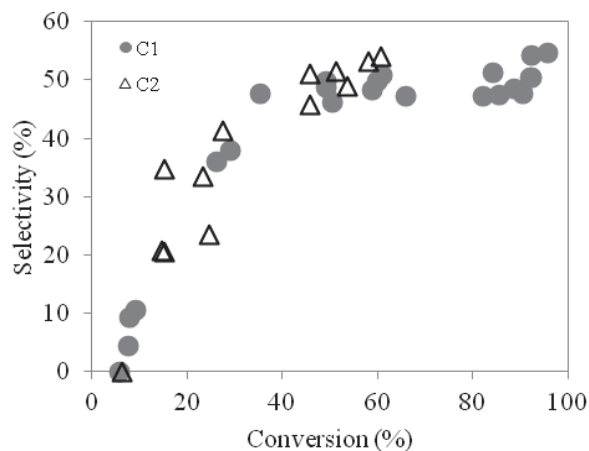


Figure 2. Selectivity to α -terpinyl methyl ether.

C1 and C2 catalyst showed good selectivity to α -terpinyl methyl ether (Figure 2).

Conclusions

Activated carbons showed high catalytic activity in the metoxylation of α -pinene and good selectivity to α -terpinyl methyl ether.

Acknowledgements

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