Catalysis Communications 32 (2013) 62–66

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Synthesis of menthols from citral on Ni/SiO_2–Al_2O_3 catalysts

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A R T I C L E   I N F O

Article history:
Received 17 October 2012
Received in revised form 14 November 2012
Accepted 30 November 2012
Available online 7 December 2012

Keywords:
Menthol synthesis
Ni catalysts
Citral
Fine chemistry

A B S T R A C T

The one-pot synthesis of menthols from citral was studied on Ni/SiO_2–AlO_3 catalysts containing 3.6%, 8.8% and 11.4% Ni. The yield of menthols increased with the amount of Ni up to 94% on Ni(11.4%)/SiO_2–AlO_3, reflecting the diminution of byproducts formation via acid-catalyzed reactions. The sample deactivation was studied by performing two consecutive catalytic tests. Results showed that Ni(11.4%)/SiO_2–AlO_3 was a stable, active, and highly selective catalyst because it contained the appropriate density and strength of bifunctional acid/Ni^0 active sites to efficiently promote the hydrogenation/isomerization pathway involved in the reaction network while avoiding coke formation.

1. Introduction

Menthol is used extensively in pharmaceuticals, cosmetics and toothpastes, as well as in cigarettes. Of the four pairs of optical menthol isomers, (±)-menthol, (±)-isomenthol, (±)-neomenthol, and (±)-neoisomenthol, only (−)-menthol has the characteristic peppermint odor and exerts a unique cooling sensation on the skin and mucous membranes. Most of the menthol used worldwide is obtained by separation of *Mentha* piperita essential oil, but it is also produced synthetically. Symrise and Takasago are currently the only major producers of synthetic (−)-menthol. In the Symrise process [1], thymol is hydrogenated to racemic (±)-menthols which are separated by a crystallization process to obtain (−)-menthol. The Takasago process [2] produces (−)-menthol from myrcene using an asymmetric synthesis technology.

Other synthetic routes to produce menthols from more readily reliable raw materials have been lately investigated. In particular, we reported for the first time in 2004 the one-pot synthesis of menthols from citral [3]. Citral is an attractive renewable raw material that may be obtained by distillation of essential oils, such as lemongrass oil, which contains ca. 70–80% citral. One-pot synthesis of menthols directly from citral is not easily achieved because it requires to develop bifunctional metal/acid catalysts with the ability to selectively promote the following consecutive reaction steps (Scheme 1): (i) hydrogenation of citral to citronellal; (ii) cyclization of citronellal to isopulegols; and (iii) hydrogenation of isopulegols to menthols. The individual reactions involved in the citral-to-menthols reaction network showed in Scheme 1 have been extensively studied, but often the objectives of these studies were not directed to the synthesis of menthols. For example, the selective hydrogenation of citral was investigated for producing either nerol/geraniol [4] or citronelol [5]; few papers have studied the citral hydrogenation to citronellal [6]. The citronellal cyclization to isopulegol has been carried out by using liquid [7] and solid [8] acid catalysts while the direct synthesis of menthols from citronellal was investigated on Ru [9], Pt [10] and Cu [11] catalysts. In contrast, few papers have investigated the direct synthesis of menthols from citral [12–15]. In previous works [3,13] we studied this later reaction on noble (Pt, Pd, Ir) and nonnoble (Ni, Co, Cu) metals supported over different solid acids (ZnO/SiO_2, CsHPA, zeolites, Al-MCM-41). The best catalyst was Ni(8%)/Al-MCM-41 that yielded more than 90% menthols at 2026 kPa. In this work we have extended these studies to investigate the synthesis of menthols from citral on Ni/SiO_2–Al_2O_3 catalysts containing different amounts of Ni. The goal was to explore the development of Ni/SiO_2–Al_2O_3 catalysts showing at least similar catalytic performance than Ni(8%)/Al-MCM-41, taken into account that Ni/SiO_2–Al_2O_3 catalysts are more economic and easier to prepare. To achieve this objective we need to optimize the catalyst performance by tuning the density and strength of bifunctional Ni^0/acid surface sites that selectively promote the hydrogenation/isomerization/hydrogenation pathway involved in the reaction network depicted in Scheme 1.

2. Experimental

2.1. Catalyst preparation

Silica–alumina supported catalysts were prepared by incipient-wetness impregnation at 303 K. Aqueous Ni nitrate solutions ($Ni(NO_3)_2.6H_2O$ Anedra ACS) were used for impregnating Ni on a commercial SiO_2–Al_2O_3 powder (Sigma-Aldrich 135 grade, Si/Al =

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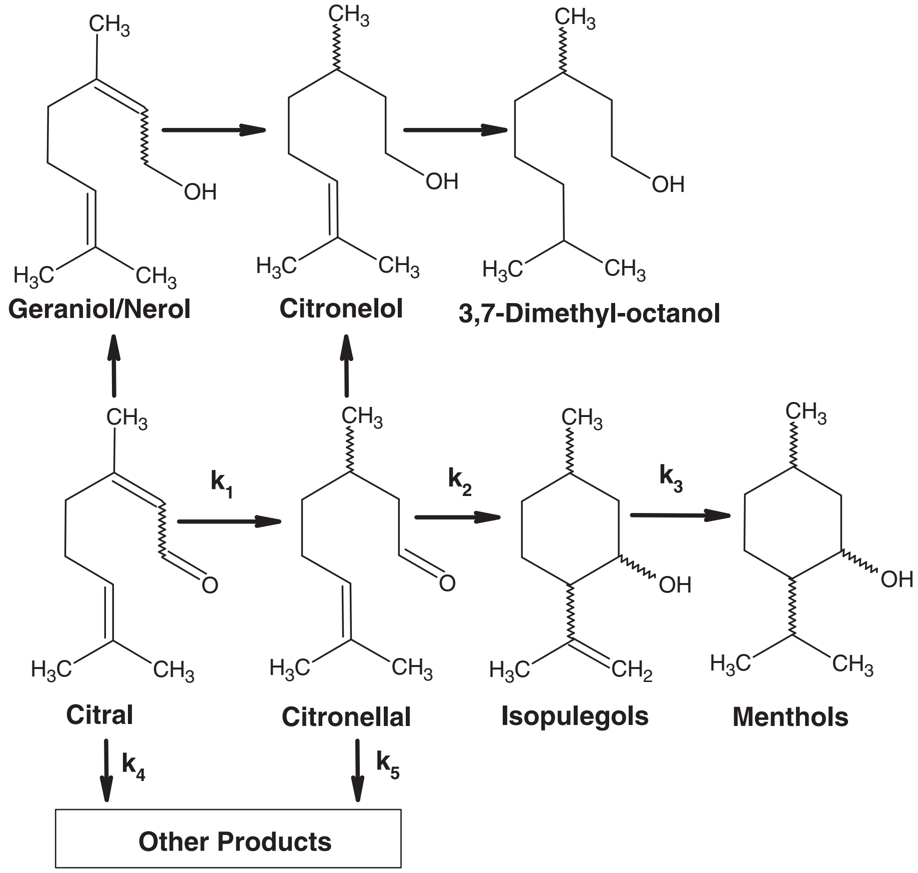
http://dx.doi.org/10.1016/j.catcom.2012.11.030



Scheme 1. Synthesis of menthols from citral.

16). The impregnated samples were dried overnight at 363 K, then heated in air (60 cm^3/min STP) at 10 K/min to 673 K and kept at this temperature for 2 h. Three samples containing 3.6, 8.8 and 11.4 % Ni were prepared and are identified here as Ni/SA-I, Ni/SA-II and Ni/SA-III, respectively.

2.2. Catalyst characterization

BET surface areas (S_g), mean pore diameter (dp), and pore-size distribution were measured by N_2 physisorption at 77 K using the BET method and Barret–Joyner–Halender (BJH) calculations in a Micromeritics Accusorb 2100E sorptometer. Elemental compositions were measured by atomic absorption spectroscopy (AAS) in a Perkin-Elmer 3110 espectrometer. Powder X-ray diffraction (XRD) patterns were collected in the range of $2\theta = 5$–80° using a Shimadzu XD-D1 diffractometer and Ni-filtered Cu Kα radiation. Oxide crystallite sizes were calculated using the Debye–Scherrer equation.

The accessible Ni fraction was determined by chemisorption of hydrogen. Volumetric adsorption experiments were performed at 298 K in a conventional vacuum unit. Catalysts were reduced in H_2 at 673 K for 2 h and then outgassed 2 h at 773 K prior to performing gas chemisorption experiments. Strong hydrogen uptake was determined using the double isotherm method as detailed previously [16].

The temperature programmed reduction (TPR) experiments were performed in a Micromeritics AutoChem II 2920, using 5% H_2/Ar gaseous mixture at 60 cm^3/min STP. The sample size was 150 mg. Samples were heated from 298 to 1050 K at 10 K/min. Since water is formed during sample reduction, the gas exiting from the reactor was passed through a cold trap before entering the thermal conductivity detector.

Sample acidity was determined by temperature-programmed desorption (TPD) of NH_3 preadsorbed at 373 K. Samples (150 mg) were treated in He (60 cm^3/min STP) at 773 K for 0.5 h and then exposed to a 1% NH_3/He stream for 40 min at 373 K. Weakly adsorbed NH_3 was removed by flushing with He at 373 K during 2 h. Temperature was then increased at 10 K/min and the NH_3 concentration in the effluent was measured by mass spectrometry in a Baltzers Omnistar unit.

2.3. Catalytic activity

The liquid-phase hydrogenation of citral (Aldrich, 98%) was studied in a Parr 4843 reactor at 343 K, using toluene (Cicarelli, p.a.) as solvent. The autoclave was loaded with 150 ml of solvent, 2 ml of citral and 1 g of catalyst. Prior to catalytic tests, samples were activated ex-situ in hydrogen (50 ml/min) for 1 h at 723 K and loaded immediately to the reactor under inert atmosphere. The reaction system was heated to 343 K at 2 K/min, and the pressure was then rapidly increased to 2026 kPa with H_2. Product concentrations were determined by ex-situ gas chromatography using a Agilent 6850 GC chromatograph equipped with flame ionization detector and a 30 m Supelco α-DEX capillary column. The product analysis and carbon balance were performed using n-dodecane as an external standard. Data were collected every 20–30 min for 130–220 min. Interparticle and intraparticle diffusional limitations were verified as negligible. Conversion of citral was calculated as $X_{Cit} = (C^0_{Cit} - C_{Cit})/C^0_{Cit}$, where C^0_{Cit} is the initial concentration of citral and C_{Cit} is the citral concentration at time t. Selectivities (S_j, mol of product j/mol of citral reacted) were calculated as $S_j = C_j/(C^0_{Cit} - C_{Cit})$. Yields ($\eta_j$, mol of product j/mol of citral fed) were calculated as $\eta_j = S_j X_{Cit}$. The main reaction products detected were citronellal, isopulegols, (±)-menthols, (±)-neomenthols, (±)-isomenthols and (±)-neoisomenthols. The yield of other products not detected by gas chromatography was calculated as $\eta_{Others} = 1 - \Sigma_j \eta_j$.