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1 Introduction

Menthol is a fine chemical having the largest global demand among the mint products. It is widely used as a fragrance or flavouring agent in the production of pharmaceuticals, cosmetics, and food products.¹⁻¹¹ From four diastereoisomeric pairs: (±)-menthol, (±)-neomenthol, (±)-isomenthol, and (±)-neoisomenthol, only (–)-menthol has a physiological cooling effect and a characteristic peppermint odor.^{1,3,4,6}

Menthol is produced from natural sources (80%) and by synthetic routes (20%).^{2,4,7} New synthetic routes are constantly explored because the current menthol demand cannot be met by menthol production from only natural sources.⁷ The selective synthesis of menthol from citral in a one-step process may be a tempting option. Citral is an attractive renewable raw material that can be obtained mainly by distillation of essential oils (lemongrass oil contains *ca.* 70–80% citral).^{3,4,6,8} Another advantage of this process is easy separation and reuse of the heterogeneous catalyst in one step.¹² On the other hand, the direct one-pot synthesis of menthol from citral is also a challenging task

Catalytic transformations of citral in a continuous flow over bifunctional Ru-MCM-41 extrudates†

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The three-step reaction of citral to menthol was investigated in an autoclave and a trickle-bed reactor over Ru-MCM-41 catalysts in powder and shaped forms, respectively, with the same composition and controlled metal location. All catalysts were characterized in detail and the results were correlated with catalytic tests. Activity and selectivity were strongly affected by controlling the location of Ru in the powder catalyst applied in the batch experiments. The catalyst with the largest distance between the metal and acid sites, and at the same time, with the highest total acidity, *i.e.* with Ru deposited exclusively on a binder Bindzil, displayed the highest yield of menthols. In contrast, in the trickle-bed reactor with extrudates the Ru location was of almost no importance which is related to mass transfer. Comparison between batch and continuous experiments also revealed significant differences in the product distribution. The highest yield of the desired menthol of 6% with stereoselectivity of 66% was obtained at a residence time of 12.5 min after 3 h of time-on-stream over egg-shell extrudates with Ru distribution at the outermost layer, deposition of Ru on both H-MCM-41 and the binder Bindzil, and the smallest Ru particle size.

requiring bifunctional metal/acid catalysts with the ability to selectively promote several consecutive reaction steps (Fig. 1): citral hydrogenation to citronellal, citronellal cyclization to isopulegol, and finally isopulegol hydrogenation to menthol. Additionally there are four different isopulegol and menthol diastereoisomeric pairs, which can be formed in the reaction. These reaction routes are very complex (Fig. 1) and it is difficult to control side reactions such as defunctionalization, dehydration and hydrogenolysis, which might be the reason for the lower yields of the desired menthol production.^{2,4,7}

Various heterogeneous powder catalysts, such as Pd, Pt, Ir, Os, Ru, Rh, Ni, Co, Cu, and Fe on SiO₂,^{3,4,13,14} Pd, Ni, Ru, Ir, Pt, Rh, and Co on C, Al₂O₃, SiO₂–Al₂O₃, Al-MCM-41, H-MCM-41 or zeolites H–beta, Zr–beta, and H-Y,^{2–4,6,8,15–18} Pd and Ni on heteropoly acid-supported montmorillonite (HPA-MM),⁷ Ir, Pd, and Pt on AlF₃,⁸ Ru(bpy)₃ on saponite materials,¹⁹ bimetallic Pt–Co/C catalyst¹⁵ and supported ionic liquid catalysts²⁰ have been tested for one-pot synthesis in batch reactors.

These studies revealed that the one-pot transformation of citral to menthol is strongly dependent on the selection of the metal and support pair and the solvent nature. It was shown that the narrow *d*-band width of Ru, Ni and Pd compared with those of other metals decreases the electrostatic repulsion between the metal surface and the conjugated C==C bond of citral, thereby favoring citral adsorption *via* its C==C bond and subsequently citronellal formation.^{4,8} In contrast, in ref. 3, 8, and 13 it was stated that



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Fig. 1 Scheme of menthol synthesis from citral with potential side reactions.

Co, Pt, Os, Ru, and Ir were more selective for C=O hydrogenation. Hydrogenolysis was very prominent on Ir, whereas Pd, Ni, and Ru exhibited very low initial hydrogenolysis activity.² The highest selectivity to menthol was obtained in the presence of Ni (65%),^{3,4} Pd (51%),⁸ Ir (44%)⁸ or Ru-based catalysts (9.6%).⁸ The strong acidity of the support (*ca.* >400 μ mol g⁻¹) promoted the undesirable side reactions.^{2,4,6,21}

Nevertheless, according to our knowledge, studies focusing on the one-pot menthol synthesis from citral over shaped catalysts in continuous mode have not been reported yet in the open literature, despite its industrial attractiveness. It is difficult to avoid mass transfer limitations in continuous mode under industrial conditions which leads to significant changes in activity, selectivity, and stability compared to batch operations over powder catalysts.^{1,22–25} Moreover the catalyst scale-up process, typically involving a binder synthesis and shaping into the catalyst body, also often leads to different results compared to a pure powder catalyst.^{22–34}

The current work builds on our recent study of the onepot menthol synthesis from (\pm) -citronellal over Ru-MCM-41 extrudates in a continuous reactor.¹ The main aim is to demonstrate if a Ru-shaped catalyst is a feasible catalyst for producing menthols from combined three-step transformations directly from citral in a trickle-bed reactor. In addition, this work is focused on the comparison between batch and continuous processes and the influence of the controlled metal location on the mechanism, product distribution, and catalyst deactivation.

2 Experimental

2.1 Preparation of the shaped Ru-catalysts

Ru-H-MCM-41-Bindzil catalysts with the same composition but different Ru locations were prepared in both powder and extrudates forms. For all catalysts, the nominal loading of Ru was 2 wt% and the weight ratio of H-MCM-41 as a mesoporous catalytic material to Bindzil-50/80 (50% colloidal silica in water from Akzo Nobel) as a binder was 70/30. MCM-41 was prepared at 100 °C for 72 h from a gel solution (fumed silica, scintran, BDH Laboratory; sodium silicate solution, water glass, Merck; cetyltrimethylammonium bromide, 95%, Aldrich; aluminium isopropoxide, 98+%, Aldrich; tetramethylammonium silicate, 15-20% solution in water, Aldrich). Subsequently, the sodium form of the catalyst was transformed into H-MCM-41 by ion exchange with 0.5 M ammonium chloride solution, dried and calcined in a step calcination procedure: 25 °C-3 °C min⁻¹-250 °C (held for 1 h) and 250 °C-6.6 °C min⁻¹-550 °C (held for 6 h). Ru was introduced onto the catalyst from an aqueous solution of RuCl₃ hydrate by the incipient wetness impregnation method. Ru-Catalysts were reduced under a hydrogen flow at 350 °C for 3 h. The reduction temperature was selected on the Ru catalysts basis of the TPR experiments with unsupported ruthenium (oxide) from RuCl₃ hydrate,³⁵ which revealed complete reduction at 267 °C (with a maximum rate of reduction at 202 °C).

Three powder samples were denoted as Ru/(H-MCM-41+Bindzil) (**P**–**B**), (Ru/Bindzil)+H-MCM-41 (**P**–**C**), and (Ru/H-MCM-41)+Bindzil (**P**–**D**), where **P** stands for the powder catalyst, **B** for Ru deposition on both H-MCM-41 and the Bindzil binder, **C** for Ru deposition exclusively on the Bindzil binder, and **D** for Ru deposition exclusively on the H-MCM-41 mesoporous catalytic material.

The cylindrical-shaped bodies with a diameter of 1.4 mm and a length of ca. 10 mm were prepared by extrusion using a one-screw extrusion device (TBL-2, Tianjin Tianda Beiyang Chemical Co. Ltd., China). The catalytic slurry for extrusion contained 33 wt% of the powder catalyst, 65 wt% of distilled water and 2 wt% of methylcellulose as an organic binder. Selection of the composition for extrusion was discussed previously.1 Methylcellulose was burned out from the final extrudates during calcination at 400 °C for 3 h.1,23,25 Four extrudates were denoted as post-synthesized Ru/(H-MCM-41+Bindzil) (E-A), in situ synthesized Ru/(H-MCM-41+Bindzil) (E-B), (Ru/Bindzil)+H-MCM-41 (E-C), and (Ru/H-MCM-41) +Bindzil (E-D), where E stands for extrudates, A for Ru distribution at the outermost layer of extrudates (i.e. eggshell) with Ru deposition on both H-MCM-41 and the Bindzil binder, B for the uniformly distributed Ru in the entire shaped body with Ru deposition on both H-MCM-41 and the Bindzil binder, C for the uniformly distributed Ru in the entire shaped body with Ru deposition exclusively on the Bindzil binder, and D for the uniformly distributed Ru in the entire shaped body with Ru deposition exclusively on the H-MCM-41 mesoporous catalytic material.

In the current work, the same batch of Ru-catalysts was used as in our previous work focusing on citronellal to menthol transformations,¹ where all details regarding the preparation and characterization of the catalysts are described.

2.2 Characterization of Ru-catalysts

Complete characterization of Ru-extrudates was already reported in the previous study.¹ Exactly the same batch of the shaped catalysts was applied in the current work, therefore, only data for the powder catalysts are presented here. Characterization was performed using the same methods as for extrudates.1 Textural physicochemical properties were measured by nitrogen physisorption (Micrometrics 3Flex-3500) using the Dubinin-Radushkevich and density functional theory (DFT) methods for calculations of the specific surface area and pore size distribution, respectively. The morphology of the surface and the particle size and shape of Ru were analysed by transmission and scanning electron microscopy (TEM, JEOL JEM-1400Plus; SEM-EDX, Zeiss Leo Gemini 1530). The metal concentration in the entire volume of the catalyst was determined by inductively couple plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 5300 DV instrument). Details of the physicochemical characterization methods and equipment are presented in our previous publications.^{1,22-26}

2.3 Catalytic tests

All the Ru-catalysts were tested in one-pot cascade transformations of citral to menthol, using powder catalysts or extrudates with 0.086 M initial citral (*cis-/trans*-isomer ~ 1/1, \geq 95.0%, Sigma-Aldrich) concentration in cyclohexane (\geq 99.9%, Alfa Aesar) at 70 °C and 10 bar in an autoclave and a trickle-bed reactor, respectively.

The cascade transformations of citral to menthol over the powder catalysts were performed in a batch reactor (300 mL) using 0.2 g of the pre-reduced catalyst. Reduction was done *ex situ* in a glass tube under a hydrogen flow of 40 mL min⁻¹ at 350 °C for 3 h with a heating ramp of 2 °C min⁻¹. Before the reaction, the reduced catalyst was kept in 10 mL of cyclohexane to avoid oxidation. The total reaction volume was 90.2 mL, where 50.2 mL of the solvent with the catalyst was added into the autoclave directly, and the rest of the solvent with the reactant was injected into the reactor from the pre-heated vessel after the reaction conditions in the reactor were achieved. A stirring rate of 1000 rpm was selected to avoid external mass transfer limitations, while a catalyst particle size below 63 µm was needed to eliminate internal mass transfer resistance.

The influence of the mass transfer limitations, which are an integral part of almost any industrial process, was investigated with the Ru-shaped catalysts (10×1.4 mm). The experiments were carried out in a trickle-bed reactor (the internal diameter and length of the diluted catalyst bed were 12.5 mm and 102 mm, respectively) in continuous mode.^{1,22,23,25} For a better flow distribution throughout the reactor, the catalyst bed contained 1 g of extrudates and 15 g of inert quartz of the size 0.2–0.8 mm. The liquid residence time was 12.5 min at 0.4 mL min⁻¹ of the feed and 50 mL min⁻¹ of hydrogen. The Ru-shaped catalysts were reduced *in situ* using the same reduction procedure as described above.

Analysis of the reaction products was carried out using an Agilent GC 6890 N equipped with an FID and a DB-1 column (30 m × 250 μ m × 0.5 μ m). The temperature program consisted of two steps: 110 °C-0.4 °C min⁻¹-130 °C and 130 °C-13 °C

 $\rm min^{-1}$ -200 °C. The temperature of the FID was 340 °C. The products were confirmed with an Agilent GC/MS 6890 N/5973 using the same temperature program and column. Before analysis, the samples were diluted with cyclohexane (solvent).

Definitions are presented in the ESI.†

3 Results and discussion

3.1 Characterization results of Ru-catalysts

In line with the previous literature,^{1,22,24} the success of the controlled deposition of Ru on both H-MCM-41 and the binder Bindzil (A, B) or exclusively only on the binder (C) or H-MCM-41 (D) was confirmed by TEM analysis (Fig. S1 and S2[†]). At the same time, EDX analysis confirmed that extrudates E-A prepared via the post synthesis is of the eggshell type.1 SEM analysis pointed out the chemical interactions between the catalyst support and the binder leading to physicochemical properties (Table 1) different from the anticipated ones based on the additive contribution of the components.^{1,22-26} Analysis of the Brønsted and Lewis acidity (Table S1[†]) revealed that already shaping H-MCM-41 with the Bindzil binder led to significant changes in acidity. The theoretical value of the total acidity should be ca. 25% higher than the experimentally measured, moreover both amounts of strong Brønsted and Lewis acid sites decreased to almost zero. This also led to a decrease in the ratio of Brønsted to Lewis acidity to 1.2 compared to the theoretical value of 1.48. After introducing Ru, the acidity decreased further depending on the support nature. This is in line with the work of Kubička et al.³⁶ and observations of the authors for Pt-catalysts.^{22,24} The changes in the acid sites (Brønsted and Lewis acid sites, and their ratio) after modification with Ru depend on the structure, SiO₂/Al₂O₃ ratio, hydrophobicity and hydrophilicity of microporous zeolites and the mesoporous material MCM-41. Ru nanoparticles deposited on the H-MCM-41 mesoporous material can substitute the Brønsted acid sites, thereby decreasing acidity.

Different options for controlled deposition of Ru led, besides variations of acidity in the final catalysts (44–69 μmol

Table 1 Characterization results of the powder and shaped Ru-catalysts with a controlled metal location. Data for the spent catalysts in parentheses. Legend: TAS – total acid sites; BAS – Brønsted acid sites; LAS – Lewis acid sites; B/L – ratio of Brønsted and Lewis acid sites; d_{Ru} – Ru particle size; D_{Ru} – metal dispersion (100/ d_{Ru}); c_{Ru_E} – Ru concentration on the top of the extrudates surface; c_{Ru} – Ru concentration in the entire volume; A – specific surface area; V_p – specific pore volume; $V_{\mu p}$ – micropore volume; c_{AS} – concentration of total acid sites

	$c_{\rm Ru}/c_{\rm AS}$	TAS	BAS	LAS	B/L	$d_{\rm Ru}$	$D_{\rm Ru}$	$c_{\rm Ru_E}$	c_{Ru}	Α	$V_{\rm p}$	V_{μ}
Cat.	_	µmol g ⁻¹			— nm		%			$m^2 g^{-1}$	$\mathrm{cm}^3 \mathrm{g}^{-1}$	
P-B	0.26	65	21	44	0.5	8	13	_	1.4	440 (329)	0.62 (0.39)	0.12 (0.09)
P-C	0.09	69	37	32	1.1	20	5	_	1.3	496 (400)	0.54(0.48)	0.13 (0.11)
P-D	0.20	44	28	15	1.9	12	8	_	1.1	528 (458)	0.37 (0.55)	0.14(0.12)
$E-A^1$	0.29	60	37	24	1.5	7	14	8.8	1.2	483 (361)	0.65(0.74)	0.14 (0.08)
$E-B^1$	0.17	51	31	21	1.5	13	8	1.2	1.2	514 (383)	0.72 (0.73)	0.14 (0.09)
E-C ¹	0.14	60	35	25	1.4	11	9	0.3	0.9	502 (365)	0.67 (0.65)	0.14 (0.09)
$E-D^1$	0.23	52	29	22	1.3	10	10	1.6	1.2	520 (399)	0.71 (0.72)	0.14 (0.09)

P - powder catalyst; E - extrudates; P-B - Ru/(H-MCM-41+Bindzil); P-C - (Ru/Bindzil)+H-MCM-41; P-D - (Ru/H-MCM-41)+Bindzil; E-A - Ru/(H-MCM-41+Bindzil) post synthesis; E-B - Ru/(H-MCM-41+Bindzil) in situ synthesis; E-C - (Ru/Bindzil)+H-MCM-41; E-D - (Ru/H-MCM-41)+Bindzil) +Bindzil.

 g^{-1} , Table 1), also to different particle sizes of Ru (7–20 nm, Table 1) and slightly different metal concentrations in the entire catalyst volume (0.9–1.4, Table 1). Related to this, the metal-to-acid site ratio ($c_{Ru}/c_{AS} = 0.09-0.29$, Table 1) was not the same as that for the catalyst with the same composition (70% H-MCM-41 and 30% Bindzil) and the same metal nominal loading (2 wt% of Ru), which is in line with the literature.^{1,22,24} However, it should be noted that the acidity of the final extrudates was similar for all types.

The results of textural properties revealed that lower measured values of the specific surface area and micropore volume by *ca.* 18% and 32%, respectively, were obtained, compared to the theoretical values for the mechanical mixture ($A = 605 \text{ m}^2 \text{ g}^{-1}$, $V_{\mu} = 0.2 \text{ cm}^3 \text{ g}^{-1}$). Similar results were observed in the literature.^{1,23–26} After the reaction, the specific surface area and micropore volume decreased again by *ca.* 23% and 30%, respectively. By comparison of the pore size distribution of the fresh and spent catalysts (Fig. 2), it can be concluded that during the reaction the pores of the catalyst are blocked. The distribution of the mesopores was shifted from a larger pore size to smaller ones, which could be related to coke formation.^{1,2}

The colloidal silica (Bindzil-50/80) was used as a nonacidic inorganic binder without impurities in order to avoid any potential interference of the binder with the catalytic reactions influencing the reaction network.^{1,22,23} However, in line with the literature,^{26,28–31} the characterization results confirmed binder–catalyst interactions inducing the catalytic performance through both physical and chemical means. The binder presence can thus lead to a marked influence on the activity, selectivity, and stability of the catalyst.

3.2 Activity and selectivity of powder Ru-catalysts in the batch experiments

Fig. 3–7 show the catalytic results of citral transformations over the Ru powder catalysts in the batch reactor. For all the

powder catalysts with a controlled Ru location, the initial concentration profiles with normalized time (ESI†), taking into account the catalyst mass, concentration and the particle size of ruthenium, are almost the same (Fig. 3). However, after the first hour, significant deactivation was observed with the catalyst **P–D** with a medium particle size of ruthenium (12 nm, Table 1). In the case of the *Z*-citral isomer, the concentration decreased in the fastest way for the catalyst **P–C** with the largest Ru particle size (20 nm, Table 1). The concentration profile of the *E*-citral isomer was the same for the **P–B** and **P–C** catalysts. Overall, it can be concluded that the structure sensitivity in citral hydrogenation is independent of the particle size of ruthenium. The primary data of the citral concentration profiles are reported in the ESI† (Fig. S3).

Such concentration profiles clearly indicate that the rates and thus turn-over-frequencies (TOFs) depend on the reaction time (Table S2, Fig. S3d† and 4a). After 3 h, the highest values of instantaneous (TOF_{inst} = 0.07 s⁻¹) and cumulative TOFs (TOF_{cum} = 0.25 s⁻¹) were determined for the catalyst **P–C**. Cumulative TOF is calculated as reacted moles per time interval (time t – time zero) divided by moles of exposed measured metal. In the case of instantaneous TOF, the time interval was from time t-1 to time t. Definitions are presented in the ESI.†

The conversion of citral as a function of normalized time revealed a significant difference between the catalysts with a controlled Ru location (Fig. 4b). These differences clearly correlate with the total acidity (Fig. S4a†) and can be also attributed to the proximity between the metal and acid sites (Fig. S5†). In other words, the highest conversion of citral (58% after 5 h, *i.e.* 7×10^{-6} h mol_{Ru(surface)}) was achieved for the catalyst **P**–**C** with Ru deposited on the binder Bindzil, *i.e.* with the largest distance between the metal and acid sites, and at the same time, with the highest total acidity. The liquid phase mass balance closure (MB, Fig. 4c) was similar for all the powder catalysts being *ca.* 80%. The same MB was



Fig. 2 Pore size distribution of (Ru/Bindzil)+H-MCM-41 catalysts. Legend: fresh powder catalyst (P-C_fresh), spent powder catalyst (P-C_spent), fresh extrudates (E-C_fresh), and spent extrudates (E-C_spent).



Fig. 3 Concentration profiles as a function of normalized time: a) racemic mixture of citral, b) *Z*-citral, and c) *E*-citral. Legend: Ru/(H-MCM-41+Bindzil) (**P**-**B**, dark blue diamond), Ru/(Bindzil)+H-MCM-41 (**P**-**C**, red triangle), Ru/(H-MCM-41)+Bindzil (**P**-**D**, green circle). Conditions: 70 °C, 10 bar of H_2 , 0.086 M initial concentration of citral in cyclohexane, 0.2 g of catalyst.



Fig. 4 Citral transformations over Ru powder catalysts in the batch reactor: a) cumulative turn-over-frequency as a function of reaction time, b) conversion of citral, c) liquid phase mass balance (MB) closure, and d) total yield as a function of normalized time. Legend: Ru/(H-MCM-41+Bindzil) (P–B, dark blue diamond), Ru/(Bindzil)+H-MCM-41 (P–C, red triangle), Ru/(H-MCM-41)+Bindzil (P–D, green circle). Conditions: 70 °C, 10 bar of H₂, 0.086 M initial concentration of citral in cyclohexane, 0.2 g of catalyst.



Fig. 5 Product distribution in citral transformations over Ru/(H-MCM-41+Bindzil-50/80) powder catalysts in the batch reactor: a) yield of acyclic hydrogenation products, b) yield of defunctionalization products, c) yield of isopulegols, and d) yield of menthols as a function of normalized time. Legend: Ru/(H-MCM-41+Bindzil) (P-B, dark blue diamond), Ru/(Bindzil)+H-MCM-41 (P-C, red triangle), and Ru/(H-MCM-41)+Bindzil (P-D, green circle). Conditions: 70 °C, 10 bar of H₂, 0.086 M initial concentration of citral in cyclohexane, 0.2 g of catalyst.



Fig. 6 Isopulegol isomers as a function of normalized time in citral transformations over Ru/(H-MCM-41+Bindzil-50/80) powder catalysts in the batch reactor: a) Ru/(H-MCM-41+Bindzil) (P-B), b) Ru/(Bindzil)+H-MCM-41 (P-C), and c) Ru/(H-MCM-41)+Bindzil (P-D). Conditions: 70 °C, 10 bar of H₂, 0.086 M initial concentration of citral in cyclohexane, 0.2 g of catalyst. Legend: isopulegol (red, filled square), neoisopulegol (orange, filled diamond), isoisopulegol (red, empty triangle), and neoisoisopulegol (orange, empty circle).

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Fig. 7 Menthol isomers as a function of normalized time in citral transformations over Ru/(H-MCM-41+Bindzil-50/80) powder catalysts in the batch reactor: a) Ru/(H-MCM-41+Bindzil) (P–B), b) Ru/(Bindzil)+H-MCM-41 (P–C), and c) Ru/(H-MCM-41)+Bindzil (P–D). Conditions: 70 °C, 10 bar of H₂, 0.086 M initial concentration of citral in cyclohexane, 0.2 g of catalyst. Legend: menthol (light green, filled square), neomenthol (dark green, filled diamond), isomenthol (light green, empty triangle), and neoisomenthol (dark green, empty circle).

also observed for citronellal transformations to menthol over Ru-catalysts.¹ The total yield (Fig. 4d) was the lowest for the catalyst **P–D** with the highest B/L ratio (Fig. S4b†), rather large Ru particle size and Ru deposited on H-MCM-41, which may be related to the shortest distance between the metal and acid sites. The observed deactivation of the **P–D** catalyst and the low MB (*ca.* 75%) could be attributed to the large amount of oligomers because of slow hydrogenation and isomerization in the presence of the catalyst with a high B/L ratio.

In comparison with the literature, a similar conversion of citral (55%) was achieved over 0.05 g of 3 wt% Ru/beta powder catalyst after a longer reaction time of 24 h at 100 °C and 10 bar of H_2 .⁸ In contrast, after a similar time (5.5 h), a significantly higher citral conversion of 95% was observed over 0.3 g of 5 wt% Ru/H-MCM-41 with a higher metal loading and without the presence of the binder Bindzil at the same temperature (70 °C) and pressure (10 bar H_2) compared to the current work.²

For all the powder catalysts, low total yields of acyclic hydrogenation products (0.5% to 4.5%, Fig. 5a) including citronellal (CLAL) were observed. For catalysts P-B and P-C, products 3,7-dimethyloctan-1-ol (DMOL), geraniol (GRL) and citronellol (CLOL) were also detected. The distribution of acyclic products is in line with the literature^{3,4,8,14} where it was stated that Ru with a narrow d-band of 4.9 eV favors C = Cbond hydrogenation forming citronellal and subsequent hydrogenation citronellol to or 3,7-dimethyloctan-1-ol. In contrast, over the 0.75% Ru/SiO₂ powder catalyst mainly geraniol + nerol with 56% selectivity along with citronellal (27%) and isopulegol (17%) at a citral conversion of 5% after 2.8 h at 27 °C and atmospheric pressure13 were obtained.

Overall, in the current work, in all cases, the main products of the reaction were defunctionalization products (*ca.* 8–20% Fig. 5b and S6†), namely *p*-mentha-1,3,8-triene ($Y_{\text{PM138E}} = 5-11\%$) and *p*-mentha-1,5,8-triene ($Y_{\text{PM158E}} = 1.5-4.5\%$). A similar result was observed in the literature² over a 5 wt% Ni/H-MCM-41 powder catalyst without a binder, where 40% of hydrogenolysis products were formed after

5.5 h with menthatrienes as the main hydrogenolysis products.

The highest yield of isopulegols (13%) was observed for the catalyst **P**–**B** with random Ru distribution on both H-MCM-41 and the Bindzil binder (Fig. 5c). On the other hand, the highest yield of menthols (2.8%) was detected for the catalyst **P**–**C** with Ru deposited exclusively on the binder Bindzil with the longest distance between the metal and acid sites and with the highest total acidity (Fig. 5d). This led to a different ratio of isopulegols to menthols: **P**–**B** (7.2) > **P**–**D** (3.9) > **P**–**C** (1.9). As a comparison with the literature,² a selectivity to isopulegol of 13% and an IP/ME ratio of 3.3 were obtained at 50% citral conversion with 5 wt% Ru/H-MCM-41.

The detailed analysis of isopulegols (Fig. 6, Table S3[†]) revealed significantly differences of isomer distribution as was already shown in citronellal transformations over Rucatalysts with a controlled metal location.¹ In general, in citronellal transformations, significantly higher (±)-isopulegol stereoselectivity was achieved with Lewis acid catalysts (ca. 90-94%, ZnBr₂ or Zr-beta)^{10,37,38} while stereoselectivity close to the thermodynamic equilibrium (ca. 70-75% for (±)isopulegol) was observed over an acid solid zeolitic catalyst.^{5,10-12,36,38} In the current work, isopulegol (IP) as the major isomer ($Y_{IP} = 7\%$) was observed only over the catalyst P-B with the highest amount of Lewis acid sites and random Ru deposition on both H-MCM-41 and the Bindzil binder (Fig. S4c[†]). The isopulegol stereoselectivity split was 54%: isopulegol (IP): neoisopulegol 33%:14% for (NIP): isoisopulegol (IIP), while for catalysts with controlled deposition of Ru (catalysts P-C and P-D), the major isopulegol isomer was neoisopulegol (Y_{NIP} = 3.6% and 1.8%, respectively). It could be related to a high ratio of Brønsted to Lewis acid sites (B/L > 1, Table 1, Fig. S4d[†]).

It is noteworthy that also the distribution of menthol isomers was not the same for all the powder catalysts (Fig. 7, Table S4†). Among the isomers isomenthol was the main one $(Y_{IME}/Y_{MES} = 44-100\%)$. The desired menthol was formed only over **P-B** ($Y_{ME} = 0.4\%$, the highest amount of Lewis acid sites) after 2 h and **P-C** ($Y_{ME} = 0.6\%$) after 5 h. Formation of

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isomenthol as the main isomer is contrary to the literature^{2-4,6} where only menthol was reported as the dominant product. This result could be related to the different distributions of the four isopulegol diastereomers formed in the previous step and the different rates of the isopulegol isomer hydrogenation to menthol isomers. The stereoselectivity of menthol:neomenthol:isomenthol: neoisomenthol was (70-72):(20-25):(4-8):(0-4) for Ni on beta, Al-MCM-41, H-MCM-41, and SiO₂-Al₂O₃ catalysts^{2-4,6} and 47:16:37 for Pd on beta catalyst.³ The difference between the ratios of menthol isomers over Pd- and Ni/beta catalysts was explained by formation of DMOL on Pd.³

3.3 Activity and selectivity of shaped Ru-catalysts in the continuous experiments

Experiments with the shaped Ru-catalysts in the trickle-bed reactor revealed significantly different behavior in citral transformations to menthol compared to the batch experiment with the powder Ru-catalysts. This is attributed to the presence of the diffusion regime confirmed by comparison of cumulative TOF and reaction rates over the powder and shaped catalysts (Table S2†). The effectiveness factor for the extrudates was calculated to be 0.18–0.29 (Table S2,† $\eta = r_{\text{extrudates}}/r_{\text{powder_catalyst}}$).

The highest values of cumulative turn-over-frequency (TOF) were observed for the **E–B** and **E–C** catalysts while for the egg-shell extrudates **E–A** the lowest TOF was observed (Table S2,† Fig. 8). A lower liquid phase mass balance closure (MB, by *ca.* 17%) and total yield (by *ca.* 18%) were observed for extrudates **E–C** compared to the other extrudates. The profiles of these parameters as a function of time-on-stream were similar for all the extrudates (Fig. 8).

The results showed that the catalysts were not stable and continuous deactivation has occurred at about the same rate. A comparable conversion of citral was observed after 3 h of TOS (64–70%). A significantly different deactivation pattern was obtained when (\pm) -citronellal was used as a substrate.¹ In the literature¹ it was observed that the citronellal conversion was *ca.* 86% and 95% after 3 h of TOS for random (E–A, E–B) and selective Ru deposition on extrudates (E–C, E–D),

respectively. The significantly higher deactivation rate in citral hydrogenation could be related to the formation of a higher amount of terpenic compounds (Fig. S7†), which can deactivate the catalyst in comparison to the citronellal case.

In both cases, the experiments confirmed a complicated reactor dynamics showing stable behaviour of the total yield after *ca.* 1.5-2 h (Fig. 8d).¹

Fig. 9 clearly shows that the effect of the controlled Ru location on selectivity in citral transformations to menthol is negligible compared to the effect of internal mass transfer resistance for consecutive reactions. In the case of the powder catalysts, the highest yield of menthols was achieved over the catalyst P-C with Ru deposited exclusively on the Bindzil binder, *i.e.* with a longer distance between acid and metal sites (Fig. 5). For extrudates with uniformly distributed Ru in the entire shaped body and controlled Ru deposition (E-B, E-C, E-D), the selectivities were very similar. In contrast, significant differences in selectivity were observed for the egg-shell type extrudates E-A with Ru distribution at the outermost laver of extrudates, random Ru deposition on both H-MCM-41 and the Bindzil binder and the smallest Ru particle size (7 nm, Table 1). Over shaped catalyst E-A, ca. 4-fold, 20-fold and 1.5fold higher yields of menthols, acyclic hydrogenation products and isopulegols, respectively, (Fig. 9) and at the same time, ca. 2.5-fold lower yield of p-menthatrienes (Fig. S7[†]) were obtained compared to the other extrudates (Tables S5 and S6[†]). This catalyst exhibits the highest Ru dispersion (Table 1) among all the studied extrudates, while acidity was comparable.

As in the case of the powder catalysts, the defunctionalization products constituted the major part of the reaction mixture (*ca.* 25–35%). However, the highest initial concentration was detected not for *p*-mentha-1,3,8-triene and *p*-mentha-1,5,8-triene, but for *p*-menthane in a continuous reactor (Fig. S7†). *p*-Menthane is formed on a catalyst active in hydrogenation (Fig. 1). The concentration of *p*-menthane decreased with TOS to zero (from *ca.* $Y_{pMA} = 20-25\%$) while the concentration of *p*-menthatrienes increased (from $Y_{TE} = 0-2\%$ to $Y_{TE} = 18-20\%$ in 3 h of TOS) for extrudates with uniformly distributed Ru in the entire shaped body (**E–B, E–C, E–D**). Changes in the product composition and selectivity are clearly related to catalyst deactivation and



Fig. 8 Citral transformations over Ru/(H-MCM-41+Bindzil-50/80) extrudates in the trickle-bed reactor: a) cumulative turn-over-frequency, b) conversion of citral, c) liquid phase mass balance closure, and d) total yield as a function of time-on-stream (TOS). Legend: Ru/(H-MCM-41+Bindzil), post synthesis (E–A, light blue square), Ru/(H-MCM-41+Bindzil), *in situ* synthesis (E–B, dark blue diamond), Ru/(Bindzil)+H-MCM-41 (E–C, red triangle), and Ru/(H-MCM-41)+Bindzil (E–D, green circle). Conditions: 70 °C, 10 bar of H₂, 0.086 M initial concentration of citral in cyclohexane, 1 g of catalyst, residence time of 12.5 min.

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Fig. 9 Product distribution in citral transformations over Ru/(H-MCM-41+Bindzil-50/80) extrudates in the trickle-bed reactor: a) yield of acyclic hydrogenation products, b) yield of defunctionalization products, c) yield of isopulegols, and d) yield of menthols as a function of time-on-stream. Legend: Ru/(H-MCM-41+Bindzil), post synthesis (E–A, light blue square), Ru/(H-MCM-41+Bindzil), *in situ* synthesis (E–B, dark blue diamond), Ru/ (Bindzil)+H-MCM-41 (E–C, red triangle), and Ru/(H-MCM-41)+Bindzil (E–D, green circle). Conditions: 70 °C, 10 bar of H₂, 0.086 M initial concentration of citral in cyclohexane, 1 g of catalyst, residence time of 12.5 min.

subsequently lower conversion. The results also indicate that mass transfer limitations have a higher effect on the acidbase catalysed reaction than on hydrogenation.

For the egg-shell type extrudates **E**–**A**, after 3 h of TOS the concentration of *p*-menthane was still higher than the concentration of *p*-menthatrienes, which, in contrast, increased with TOS (Fig. S7, Table S6†). It is worth noting that *p*-menthane was the main compound among the defunctionalization products in (\pm) -citronellal transformations over the Ru-containing extrudates.¹ However, the yield of *p*-menthane was *ca*. 5-fold lower and the maximum was observed at a longer time (*ca*. 1 h of TOS) compared to the citral case. Overall, *p*-menthatrienes were formed more rapidly from citral than from citronellal.¹

As mentioned above, a significant amount of acyclic hydrogenation products (ACP) was observed only with extrudates **E**–**A** with the highest dispersion (Fig. 9a, Tables S5 and S6†). The major component was 3,7-dimethyloctan-1-ol ($Y_{\text{DMOL}} = 3.1\%$ at 3 h of TOS) which was the only ACP product obtained over extrudates **E**–**C** with Ru located exclusively on the Bindzil binder ($Y_{\text{DMOL}} < 1.5\%$ with a maximum at 2 h of TOS) indicating the efficient hydrogenation activity of Ru on a mildly acid support and with the longest distance between the metal and acid sites (Fig. S7†). In contrast, in the case of the **E**–**B** and **E**–**D** extrudates, only a dehydration product of DMOL, 2,6-dimethyloctane ($Y_{\text{DME}} < 1.2$), with a maximum at 0.3 h of TOS was detected among ACP (Fig. S7†).

Citronellal ($Y_{CLAL} = 0.5-3\%$, Fig. S6†) obtained with the powder catalysts was detected only over extrudates **E**–**A** after 3 h of TOS with a very low yield ($Y_{CLAL} = 0.6\%$, Fig. S7, Table S6†). It should be also pointed out that dimeric ethers and heavy components were observed only over extrudates **E**–**B** ($Y_{DM} = 9.4\%$) and **E**–**D** ($Y_{DM} = 4.4\%$) (Table S6†). Since the Ru distribution, Ru particle size and acidity of the catalysts were comparable with those of extrudates **E**–**C**, it can be assumed that the short distance between the metal and acid sites in combination with the diffusion regime had a strong effect on the formation of ethers.

Overall, the largest differences in the product distribution caused by the scale-up of the catalysts (1 g of extrudates from a powder catalyst) were observed for citronellal (CLAL) formation occurring in higher concentrations only in the presence of the powder catalysts contrary to 3,7-dimethyloctan-1-ol (DMOL) and *p*-menthane (pMA), which were detected in higher concentrations only over the extrudates. The formation of other acyclic hydrogenation and defunctionalization products was only marginally affected by mass transfer (Table S6, Fig. S5 and S6†).

As already mentioned above for the powder catalysts and in the literature¹ for extrudates with a controlled Ru location significantly different isopulegol stereoselectivity was observed in citronellal transformations. The same was noticed for citral transformations over the extrudates even though the acidity of the extrudates was quite similar to each other (Table 1, Fig. 10, Table S3[†]). Similar stereoselectivity (ca. 55%:35%:10% for IP:NIP:IIP) was observed only for the P-B, E-A and E-B catalysts with random Ru deposition on both H-MCM-41 and Bindzil in citral transformations. The highest yield of isopulegol ($Y_{\rm IP}$ = 3.7%) as the major isopulegol isomer was achieved over extrudates E-A with the highest dispersion. In the case of extrudates E-C with Ru deposited exclusively on the Bindzil binder, neoisopulegol $(Y_{\text{NIP}} = 1.9\%)$ was detected as the major isopulegol isomer with low interactions between Ru and acid sites. In the case of the E-D extrudates with Ru deposited exclusively on H-MCM-41 and the shortest distance between the metal to acid sites, the stereoselectivity of isopulegol and neoisopulegol was the same (42%).

The absolutely highest yield of the desired menthol of 6% with stereoselectivity of 66% was obtained in the current work over the egg-shell extrudates E-A with the highest dispersion after 3 h of TOS. It was ca. 3-7.5-fold higher compared to extrudates with uniformly distributed Ru in the entire shaped body (E-B, E-C, E-D). Although the major isomer obtained in citral transformations over extrudates was menthol as in the citronellal case,¹ the stereoselectivity of menthol isomers was significantly different (Fig. 11, Table S4[†]). In the citronellal case, the stereoselectivity was the same for all extrudates (70%:20:1%:9% for ME:NME:IME: NIME),¹ while in the citral case, a similar result (*ca.* 66%:20: 0%:14% for ME:NME:IME:NIME) was obtained only over extrudates E-A and E-B with random Ru deposition. In the case of the E-C and E-D extrudates with selective Ru deposition, some amounts of isomenthol ($Y_{\text{IME}} = 0.5\%$) were



Fig. 10 Isopulegol isomers as a function of time-on-stream in citral transformations over Ru/(H-MCM-41+Bindzil-50/80) extrudates in the tricklebed reactor: a) Ru/(H-MCM-41+Bindzil), post synthesis (E–A), b) Ru/(H-MCM-41+Bindzil), *in situ* synthesis (E–B), c) Ru/(Bindzil)+H-MCM-41 (E–C), and d) Ru/(H-MCM-41)+Bindzil (E–D). Conditions: 70 °C, 10 bar of H₂, 0.086 M initial concentration of citral in cyclohexane, 1 g of catalyst, residence time of 12.5 min. Legend: isopulegol (red, filled square), neoisopulegol (orange, filled diamond), isoisopulegol (red, empty triangle), and neoisoisopulegol (orange, empty circle).



Fig. 11 Menthol isomers as a function of time-on-stream in citral transformations over Ru/(H-MCM-41+Bindzil-50/80) extrudates in the tricklebed reactor: a) Ru/(H-MCM-41+Bindzil), post synthesis (E–A), b) Ru/(H-MCM-41+Bindzil), *in situ* synthesis (E–B), c) Ru/(Bindzil)+H-MCM-41 (E–C), and d) Ru/(H-MCM-41)+Bindzil (E–D). Conditions: 70 °C, 10 bar of H_2 , 0.086 M initial concentration of citral in cyclohexane, 1 g of catalyst, residence time of 12.5 min. Legend: menthol (light green, filled square), neomenthol (dark green, filled diamond), isomenthol (light green, empty triangle), and neoisomenthol (dark green, empty circle).

also observed with a stereoselectivity of 38% and 22% for extrudates with Ru deposited exclusively on the Bindzil binder and on H-MCM-41, respectively (Table S4†). This is different from a batch experiment over a powder catalyst in citral transformations where isomenthol was observed as the major isomer with a stereoselectivity of 44–100% (Fig. 7, Table S4†).

Furthermore, in line with the literature,² Z-citral (neral) was transformed always faster than *E*-citral (geranial) over all the catalysts but with a different rate depending on the catalyst type (Table S5, Fig. S8†). The initial *Z-/E*-citral ratio decreased from 1 to 0.22-0.60 and to 0.28-0.64 for the powder catalysts and extrudates, respectively (Table S5†).

Fig. S8a and b,[†] related to the powder catalyst, clearly show that the changes in the *Z*-/*E*-citral ratio strongly depend

on the Ru location and that the yield of menthols increased with decreasing *Z*-/*E*-citral ratio. The opposite result was obtained for extrudates in the presence of mass transfer limitations (Fig. S8c and d†), *i.e.* the yield of menthols decreased with decreasing *Z*-/*E*-citral ratio and changes in the *Z*-/*E*-citral ratio (Fig. S8c†) were significantly different for eggshell extrudates **E**-**A** compared to those for other materials with uniformly distributed Ru in the entire shaped body (**E**-**B**, **E**-**C**, **E**-**D**).

The simplified scheme of menthol synthesis from citral (Fig. 12) displays rationalization of data obtained in threestep transformations of citral over a Ru/H-MCM-41 catalyst containing the Bindzil binder. The first step shows that hydrogenation of citral to citronellal requires a small particle size of Ru (d_{Ru}), *i.e.* a high dispersion (D_{Ru}) and a high ratio of metal-acid sites ($c_{\text{Ru}}/c_{\text{AS}}$) (Fig. S9†). The next step,



Fig. 12 A simplified scheme of menthol synthesis from citral.

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citronellal cyclization to isopulegols, is favored by Lewis acid sites (LAS), i.e. a low ratio of Brønsted to Lewis sites (B/L) (Fig. S4 and S10[†]), while Brønsted acid sites (BAS), a high B/ L, a low $c_{\rm Ru}/c_{\rm AS}$ and the presence of mass transfer limitations are favourable for side reactions (Fig. S10⁺). Preferential citronellal cyclization to isopulegols over Lewis acid sites is in line with the studies available in the literature^{10,39} when utilization of non-supported Lewis acids such as ZnBr₂ and ZnCl₂ afforded >95% selectivity to isopulegols with stereoselectivity to the desired (±)-isopulegol exceeding 90%. The mechanism proposed for cyclization of citronellal over $ZnCl_2$, a Lewis acid,^{40,41} includes coordination of citronellal through oxygen in the carbonyl group and the electron-rich double bond onto the Zr ion bringing citronellal into an orientation favourable for the ring closure. Undesired sideproducts can be obtained from each step of citral to menthol transformations.^{2,4,6,15,22} In the final step, isopulegol hydrogenation to menthols depends on the particle size of Ru (dispersion) as in the case of the first step. However, the highest yield of menthol over a powder catalyst was obtained over the catalyst with the highest particle size of Ru, but with Ru deposited exclusively on the Bindzil binder, i.e. the longest distance between the active sites of the catalyst (Ru-AS distance) (Fig. 5), which turns out to be a key parameter under the kinetic regime. Overall, the relatively low yield of menthol over Ru-catalysts (4.5-18.6%) compared to that over powder Ni catalysts $(54-94\%)^{2-4,6}$ could be related to the 2.6fold lower initial hydrogenation rate observed over Ru/H-MCM-41 compared to the Ni/H-MCM-41 catalyst in the literature.²

4 Conclusions

Ru–H-MCM-41–Bindzil catalysts with the same composition but different Ru locations were prepared in both powder and extrudates forms and tested in one-pot cascade transformations of citral to menthol. For all catalysts, the nominal loading of Ru was 2 wt% and the weight ratio of H-MCM-41 as a mesoporous acidic material to Bindzil-50/80 as a binder was 70/30. Experiments with the powder catalysts and extrudates were performed with 0.086 M initial citral concentration in cyclohexane at 70 °C and 10 bar in an autoclave and a trickle-bed reactor, respectively.

Detailed physicochemical characterization results confirmed the success of the controlled deposition of Ru giving a real Ru loading of 0.9–1.4 wt% with Ru particle sizes ranging between 7 and 20 nm. The total acidity of the catalysts was 44–69 μ mol g⁻¹. After the reaction the surface area and microporosity of the catalysts decreased by *ca.* 23% and 30%, respectively, which can be attributed to coke formation.

In the kinetic regime, the Ru location in the powder catalyst affected both activity and selectivity. The best results in terms of citral conversion (58%) and the menthol yield (2.8%) were achieved over the catalyst where Ru was deposited on the Bindzil binder, *i.e.* with the largest distance

between the metal and acid sites, and at the same time, with the highest total acidity.

In contrast, data in the trickle-bed reactor over extrudates showed that the location of Ru is of minor importance compared to the effect of mass transfer. The best results in terms of citral conversion (70%) and the menthol yield (9.1%) were achieved over egg-shell extrudates with Ru distribution at the outermost layer of extrudates and random Ru deposition on both H-MCM-41 and the Bindzil binder, exhibiting the highest Ru dispersion among the studied extrudates. The same catalyst displayed the absolutely highest yield of the desired menthol of 6% with stereoselectivity of 66% at a residence time of 12.5 min after 3 h of time-on-stream.

Comparison between batch and continuous experiments confirmed the presence of mass transfer limitations in the case of the extrudates. The effectiveness factor for the extrudates was calculated to be 0.18–0.29. Moreover, significant differences in the product distribution were observed. For the powder catalysts the presence of citronellal and isomenthol isomers was characteristic, while for the extrudates 3,7-dimethyloctan-1-ol, *p*-menthane and menthol isomers were formed in significant amounts.

Conflicts of interest

There are no conflicts to declare.

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