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Ir-Beta zeolite as a heterogeneous catalyst for the one-pot transformation of citronellal to menthol

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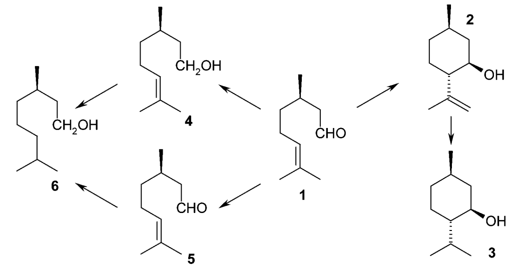
Beta zeolites, impregnated with Ir, catalyze the one-pot full conversion of citronellal to menthol by consecutive acid-catalyzed cyclization and Ir-catalyzed hydrogenation, with 95% selectivity for the menthol isomers, of which 75% is the desired (−)-menthol.

The synthesis of menthol is of a large interest because this molecule is consumed on a massive scale in flavouring and pharmaceutical applications. One of the major routes to menthol is the Takasago process,[1] in which enantiopure (*R*)-citronellal (**1**) is converted to (−)-isopulegol (**2**) with an aqueous $ZnBr_2$ catalyst; isopulegol is then hydrogenated to (−)-menthol (**3**) over a Ni catalyst. The cyclization of citronellal over acid catalysts may produce, besides the desired (−)-isopulegol, three stereoisomers and other side products. Therefore many homogeneous[2–5] and heterogeneous catalysts have been studied,[6–12] *e.g.* Sc-triflate,[3,4] Al-phenoxides,[5] or the recently reported Lewis acid Sn-substituted Beta zeolite.[12]

In order to simplify menthol production, it has been attempted to perform the cyclization of citronellal and the subsequent hydrogenation in a single step, preferably on a heterogeneous catalyst.[13–16] With a SiO_2 support, impregnated with $ZnBr_2$, and loaded with 10 wt.% Ru, an 85% yield of (−)-menthol was obtained.[14] Alternatively, with Cu–SiO_2, 80% stereoselectivity for (−)-menthol has been reached at 90% yield of the menthol stereoisomers.[15] However, in both cases, only one g or less of substrate was converted per g of catalyst. The major parallel and consecutive reactions in the citronellal conversion are represented in Scheme 1.

The present paper reports on a bifunctional Ir/H-Beta zeolite as a new active and selective heterogeneous catalyst for one-step synthesis of menthol **3** from citronellal **1**. Ir/H-Beta zeolites have previously been reported to be useful catalysts, *e.g.* for the chemoselective reduction of α,β-unsaturated carbonyl compounds.[17] For the citronellal reaction, use of truly catalytic amounts of Ir/H-Beta, *e.g.* 0.05 g catalyst per ml of substrate, leads to complete and selective substrate conversion.

Beta zeolites were loaded with Ir *via* impregnation.† FT-IR measurements using pyridine as a probe molecule showed that both Brønsted and Lewis acid sites are present. XPS data indicated that Ir is not only present as metallic Ir^0, with a $4f_{7/2}$ line binding energy of 61.2 eV, but also as ionic Ir, as evidenced by the $4f_{7/2}$ BE of 62.7 eV.[18] The ratio of ionic to metallic Ir decreased monotonously from 1 to 5% Ir. This was also confirmed by TPR, which indicated that for 3% Ir/H-Beta, the reduction degree of the Ir was about 75%. Finally, TEM shows, for the 3% Ir/H-Beta samples, that small metallic particles are present, with sizes between 6 and 10 nm.



Scheme 1

In order to understand the first step in the citronellal to menthol reaction, the citronellal isomerization was first studied in the absence of H_2.‡ The following activity order was found: H-Mor < 3%Ir/H-Mor < H-Beta < 3%Ir/H-Beta. Remarkably, for both zeolites, the isomerization activity clearly increases upon loading with Ir, calcination and reduction. This indicates that not only the Brønsted acidity of the zeolites contributes to the isomerization; Lewis acidity of non-reduced Ir might also play a role in the isomerization. In all cases, the only products observed were isopulegol (**2**) and its stereoisomers. On 3% Ir/H-Beta, the selectivity for the desired isopulegol was 75%, with 20% neo-isopulegol and 4% iso-isopulegol. This selectivity is even slightly better than the best result reported hitherto with zeolite H-Beta (73%).[9] With Ir on a weakly acid support such as MCM-41, citronellal conversion is very small.

Initial experiments on the reaction of citronellal under H_2 showed that over Ir/H-Beta, menthol is one of the principal products.‡ Hence, by selecting Ir as the reducing metal, one avoids the initial fast reduction of the C=C bond or C=O bonds. Effects of metal loading, solvent, temperature and H_2 pressure are shown in Table 1. Non-polar solvents such as cyclohexane are effective, with 75% menthol yield (entry 2) while polar solvents such 2-propanol lead to inferior yields (47%; entry 1). The poor selectivity in 2-propanol is largely due to the more pronounced formation of citronellol (**4**), which is a product of C=O reduction. Indeed, as previously reported, alcohol solvents favor the hydrogenation of C=O bonds over Ir/H-Beta.[17]

When the reaction is performed at 25 °C, the reduction of the C=C bond or particularly the C=O bond predominates over the cyclization, with a combined selectivity for citronellol (**4**) and 3,7-dimethyloctanol (**6**) of almost 60% (entry 3). With increasing temperature, more cyclization products are formed (compare entries 2–4). This suggests that the cyclization has a higher apparent E_A than the reduction to citronellol.

Also the initial hydrogen pressure is important. When the H_2 pressure is low, *e.g.* 0.5 MPa H_2, the conversion of the isopulegol isomers to menthols was slow or incomplete within reasonable time (entry 5). At 1.5 MPa H_2, the initial hydrogenation of citronellal to

Table 1 Influence of the reaction conditions on the reaction of citronellal with 5% Ir/H-Beta catalyst (X = conversion, S = selectivity)

	p/MPa	T/°C	t/h	X (%)	S**2** (%)	S**3** (%)	S**4** (%)	S**6** (%)
1	1.5	80	10	100	14	47	25	14
2	1.5	80	10	100	0	75	0	25
3	1.5	25	20	92	10	30	39	20
4	1.5	60	16	95	7	54	16	23
5	0.5	80	16	100	52	34	7	6
6	0.8	80	16	100	1	84	0	15

Reaction conditions: 1 ml citronellal, 7 ml cyclohexane (except entry 1: iPrOH), 50 mg catalyst, H_2 atmosphere.

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open chain products is still appreciable. Thus, an intermediate pressure of 0.8 MPa H_2 can be used in order to maximize menthol yields (entry 6).

Finally, Fig. 1 shows the effect of the catalyst metal loading on the menthol yield obtained after 10 h in the two-step reaction. As can be seen, the menthol yield goes through a maximum for 3 wt.% Ir/H-Beta. Metal loadings higher than 3 wt.% Ir favor the formation of 3,7-dimethyloctanol (**6**) and thus decrease the eventual menthol yield; at low Ir contents, the citronellal is almost fully converted, but the subsequent hydrogenation of the pulegols to the menthols is slow. 3 wt.% Ir seems an ideal choice; when this catalyst is used under 0.8 MPa H_2, a full citronellal conversion with 93% menthol yield can be obtained, as illustrated in Fig. 2. The 3 %/Ir-HBeta catalyst can be recycled by simple cyclohexane washing and retains its full activity.

A further small improvement in menthol yield can be realized by conducting the reaction with 3%Ir/H-Beta in a N_2 atmosphere for the first 4 hours; during this period, citronellal is almost completely transformed to the pulegol isomers. After 4 h, H_2 is supplied. In this way, the menthol selectivity amounts to 95% at 30 h and complete citronellal conversion. The menthol (**3**) : neomenthol : isomenthol isomer distribution typically is 75 : 20 : 5. When other metals are used instead of Ir in similar conditions, undesired reaction products are formed. 3% Ru/H-Beta forms citronellol in a 70% yield, in analogy with reported results;[16] with 3% Pd/H-Beta, 3,7-dimethyloctanal is the dominant product (69%). Considerable menthol yields are only obtained with 3% Pt/H-beta (56% yield) and 3% Rh/H-Beta (55% yield). While a pursued optimization of metal content, acidity and reaction conditions may also in these cases lead to higher menthol yields, it is clear that Ir is the best metal for the present conditions.

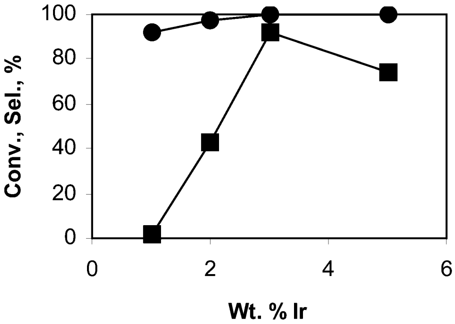

Fig. 1 Citronellal conversion (●) and menthols selectivity (■) *vs.* metal loading (1 ml **1**, 50 mg catalyst, 80 °C, 1.5 MPa H_2, 10 h).

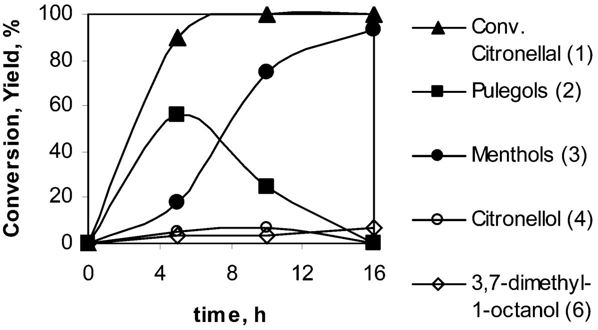

Fig. 2 Citronellal hydrogenation on 3%Ir/H-Beta (0.8 MPa H_2, 80 °C, cyclohexane).

In conclusion, Ir/H-Beta is a very efficient bifunctional catalyst able to selectively transform citronellal to menthol in a one-pot reaction. In contrast with earlier studies, where high catalyst/substrate ratios were used, as much as 17 g menthol can be produced per g of catalyst in a single run.

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Notes and references

† The Ir/zeolite catalysts were prepared by incipient wetness impregnation of H-Beta zeolite (Si/Al = 12 from PQ-Valfor) or H-mordenite (Si/Al = 10 from PQ, CBV 20A). The zeolite Beta precursor was used in the as-synthesized form or after calcination. The Ir precursor used was $Ir(acac)_3$, as 2 ml of a 26, 53, 81 or 134 mM solution in toluene per g of zeolite. After the impregnation with the Ir solution, the zeolites were dried at 60 °C, calcined at 300 °C for 4 h and reduced. For the reduction, samples were heated at a rate of 1 °C min^{-1} under a 30 ml h^{-1} flow of hydrogen to 450 °C; this temperature was maintained for at least 6 h. Following this procedure, samples with 1, 2, 3, and 5 wt% Ir were prepared. For catalysts containing 3 wt.% of other noble metals, an analogous procedure was followed, using the acetylacetonate complexes of the metals as precursors.

‡ The catalytic tests were performed at 80 °C in a stirred stainless steel autoclave using H_2 pressures in the range 0.5–1.5 MPa, 50 mg catalyst, 1 ml citronellal and 7 ml solvent (cyclohexane or 2-propanol). In order to separately study the isomerization, the reaction was carried out in absence of hydrogen at 80 °C using 50 mg of catalyst, 1 ml citronellal and 7 ml cyclohexane. Samples were analyzed by GC (CP-Wax 58) and retention times were compared with those of commercial standards

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