Novelties of eclectically engineered sulfated zirconia and carbon molecular sieve catalysts in cyclisation of citronellal to isopulegol

G. D. Yadav* and J. J. Nair

Chemical Engineering Division, University Department of Chemical Technology, University of Mumbai (formerly Bombay), Matunga, Mumbai - 400 019, India. E-mail: gdy@udct.ernet.in

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Sulfated zirconia (S-ZrO_2) is a well-known solid superacid catalyst used in various reactions of commercial importance such as isomerisation, alkylation and acylation, nitration, *etc.* The selectivity towards the formation of isopulegol, a potential intermediate in the synthesis of menthol, can be drastically increased by using carbon molecular sieve (CMS) with S-ZrO_2.

Isopulegol is an important intermediate for the manufacture of menthol, used extensively in pharmaceuticals, cosmetics, toothpastes, chewing gum, and other toilet goods as well as in cigarettes.[1] Isopulegol is manufactured from the cyclisation of citronellal. Bogert and Hasselstrom[2] have reported the use of UV in the cyclisation reaction. Activities and selectivities of acid clinoptilolite, mordenite, and faujasite zeolites in the isomerisation of citronellal in n-hexane, chloroform and dichloromethane as solvents have been investigated.[3] The activities of the acidic zeolites for the isomerisation of citronellal were found to be in the following order: HY(max.) > HCC > (clinoptilolite) > HMCP (clinoptilolite + mordenite) > HX at 84 °C in dichloroethane, and the selectivities to isopulegol were HCC (90%) > HMCP (85%) > HY (80%) > HMP (72%) at 80% conversion level. The activity in these studies is related to the total amount of Brønsted acid sites of the catalysts and only a fraction of these sites, located mainly on the external surface of the crystal, were accessible to the reactants due to the diffusional resistance. It was found that the selectivity increases to the isopulegol ether as the accessibility to the acidic centres increases. There are several reports whereby Cu–Cr and Cu–Cr–Mn,[4] tris(triphenylphosphine)rhodium chloride[5] and micellar[6] catalysts have been employed to catalyse the cyclisation reaction. Several Lewis acids as catalyst for the preparation of L-isopulegol from D-citronellal have been used.[7] Dean and Whittaker[8] have studied this reaction with superacids (*e.g.* FSO_3H/SO_2) to observe that the cyclisation follows the same path as the normal acids, yielding isopulegol and neoisopulegol.

We present here the efficacy of a novel shape selective catalyst synergistically produced from sulfated zirconia (S-ZrO_2) and carbon molecular sieve (CMS) in the cyclisation of citronellal to isopulegol. S-ZrO_2 is a very well-known solid superacidic catalyst used in various reactions. The activity of this catalyst is superior to many other solid acid catalysts. But one of the major drawbacks of S-ZrO_2 is that it is not a shape selective catalyst. Hence it cannot be employed in reactions where selectivity is of utmost importance. However, S-ZrO_2 when combined with other materials can produce the desired shape selective catalyst. In this respect, carbon molecular sieve (CMS) can be used in combination with S-ZrO_2 to get a composite shape selective catalyst. The selectivity engineering aspects of catalysts are embodied in this CMS–S-ZrO_2 composite media where one acts as a siever and the inside core as the true catalyst. The isomerisation of citronellal was considered to be interesting in view of the fact that the reaction has been studied by others using zeolites and there are several products generated depending on the type of carbocation and hence on the type and strength of acidic sites.

Zirconium oxychloride, 25% ammonia solution, polyvinyl alcohol, toluene and 98% sulfuric acid were obtained from S.D. Fine Chemicals Ltd. Citronellal containing about 14% isopulegol was obtained from Arofine Industries Ltd.

The catalyst was prepared using the conventional precipitation method.[9] 100 g of zirconium oxychloride were dissolved in distilled water. The solution was then filtered. This solution and 25% aqueous ammonia were added dropwise simultaneously in a beaker with constant stirring while a white precipitate of zirconium hydroxide was obtained at pH 9–10. After complete precipitation it was digested in the vessel for 6 h. The precipitate was filtered through a Buchner funnel and washed thoroughly with distilled water until free of ammonia and chloride ions. The filtered precipitate was dried in an oven at 120 °C for 24 h. The dried catalyst was then crushed to make a fine powder, which was treated with 0.5 M H_2SO_4. 15 ml of 0.5 M H_2SO_4 was required for 1 g of the catalyst. The catalyst so prepared was dried in an oven at 120 °C for 24 h followed by calcination at 230 to 650 °C.

To 10 g of the above prepared catalyst 7.2 ml polyvinyl alcohol (PVA) solution (2 g PVA dissolved in 25 ml distilled water) was added dropwise until it was just wet. It was mixed well to get a uniform coating. It was dried at 100 °C for 1 h and calcined at different temperatures. This catalyst is referred to as S-ZrO_2/CMS catalyst.

In another method, S-ZrO_2 was initially soaked with different solvents such as benzene, cyclohexane, carbon tetrachloride, hexane till wetness. This was coated with the same amount of PVA solution as was done without wetting the catalyst with solvent. These were calcined at different temperatures. Eight different catalysts were prepared as shown in Table 1 where the nomenclature S-ZrO_2/Benzene/CMS refers to S-ZrO_2 soaked with benzene followed by coating with CMS.

All experiments were conducted in a 100 ml fully baffled glass reactor of 5 cm internal diameter. The reactant and solvent were charged to the reactor and the temperature was raised to 95 °C. 0.5 g (2.13×10^{-2} g cm^{-3}) of the desired catalyst was then added to the reactor under constant stirring.

Table 1 Activities of catalysts for cyclisation of citronellal

Catalyst	Time/min	Conversion of citronellal (%)	Selectivity for isopulegol (%)
ZrO_2[230–350]	90	0	—
S-ZrO_2[230–350]	10	96	46
S-ZrO_2[650]	05	95	35
S-ZrO_2[230–350]/CMS	30	91	65
S-ZrO_2[230–350]/Benzene/CMS	20	95	52
S-ZrO_2[230–350]/Cyclohexane/CMS	20	96	61
S-ZrO_2[230–350]/CCl_4/CMS	30	88	53
S-ZrO_2[230–350]/Hexane/CMS	20	95	58

Solvent: toluene = 15 g, reactant: citronellal = 5 g, temperature: 95 °C. Values inside square brackets indicate the calcination temperature.

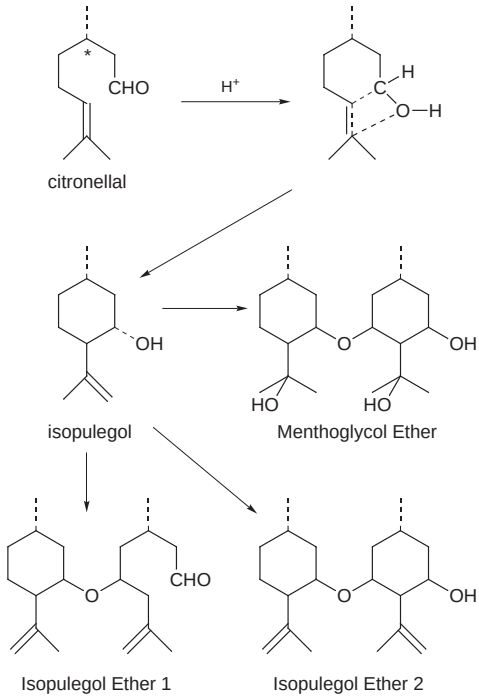

Fig. 1 *trans* addition and cyclisation mechanism.

An initial sample was drawn and the progress of the reaction was monitored on a Perkin Elmer (Model 8500) Gas Chromatograph using an FID detector and coupled with an integrator/plotter. A 2 m × 1/8′ S.S. column of Carbowax with Chromosorb W and 10% C-20M + 2% KOH washed, 80–100 mesh was used. The by-products obtained were predicted, from GC-MS, to be an ether of citronellal–isopulegol (isopulegol ether 1), diisopulegol (isopulegol ether 2) and dimenthoglycol ether (Fig. 1). The mechanism given in Fig. 1 shows the cyclisation of citronellal to isopulegol and the different ethers obtained from isopulegol.[10] There are different stereoisomers of isopulegol.

Table 1 lists the results of the experiments conducted under otherwise similar conditions of mole ratio of reactant and solvent, catalyst loading, speed of agitation and temperature.

It is well established that the formation of isopulegol ether takes place if citronellal is easily accessible to the Brønsted acid sites of the catalyst. Hence, in the case of S-ZrO_2[650] as catalyst, where the calcination temperature is high, the average pore size was found to be 41 Å by nitrogen adsorption isotherm using a Micromeritics surface area analyser (ASAP 2010 Model). When S-ZrO_2[650] was compared with S-ZrO_2[230–350] the selectivity towards the formation of isopulegol was found to increase in the latter. The pore size of S-ZrO_2[230–350] was found to be 28 Å. Hence, even though the Brønsted acidity is expected to be more in case of S-ZrO_2[230–350] as compared to S-ZrO_2[650], which is a Lewis acid catalyst, the pore size is smaller than the latter. This leads to the diffusion controlled formation of isopulegol ether which is kinetically much bulkier than isopulegol and hence the subsequent increase in the formation of the latter. The same reason is true for the decrease in the rate of the reaction. Further, when S-ZrO_2[230–350] is coated with CMS a uniform barrier of pore size 27 Å is obtained. This marginal drop in pore size provides further resistance to the formation of isopulegol ether and hence favour the formation of isopulegol. Also, the external surface of the catalyst which may consist of Brønsted acid sites becomes inaccessible to citronellal which further decreases the formation of isopulegol ether.

In other catalysts used S-ZrO_2[230–350] was initially soaked with different solvents which were immiscible with polyvinyl alcohol solution, before coating with CMS, to prevent the diffusion of polymers into the pores of the catalyst, if any. The initial soaking was not found to be very effective though there was a slight increase in the formation of isopulegol.

S-ZrO_2 modified carbon molecular sieve can be prepared using different polymers as precursors and hence the catalysts can be tailor-made by fine-tuning the pore size according to the requirements. Thus eclectically engineered S-ZrO_2/CMS catalysts lead to much greater selectivity to isopulegol in the cyclisation of citronellal.

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Notes and references

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