Gold Catalysis

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One-Pot Synthesis of Menthol Catalyzed by a Highly Diastereoselective Au/MgF_2 Catalyst**

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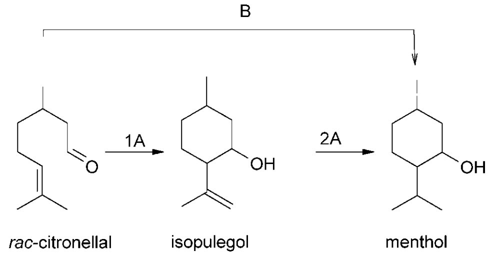
During the last two decades gold has attracted much attention on account of its unique catalytic properties for numerous reactions.[1,2] It is generally accepted that the catalytic activity of gold-based catalysts critically depends on the size of the gold particles, the nature of the support material, the preparation method, and the activation procedure.[3–6] Several preparation methods have been developed that yield active nanosized gold catalysts.[7] Surprisingly, only little attention has been paid to cationic gold species and their application in catalytic reactions. Recently, it has been shown that isolated and heterogenized Au^{n+} ions ($n = 1$ or 3) are highly active in reactions such as the selective hydrogenation of 1,3-butadienes to butenes,[8] the homocoupling of phenylboronic acids,[9] and the selective isomerization of epoxides to allylic alcohols.[10]

More recently, we have showed that nanosized hydroxylated fluoride materials (e.g., $MgF_{2-x}(OH)_x$), which are synthesized by a novel sol–gel synthesis[11] and exhibit interesting bi-acidic properties, can catalyze the cyclization of citronellal to (±)-isopulegol (an intermediate in the synthesis of (±)-menthol, Scheme 1, route 1A); the diastereoselectivity of 91.7% is superior to that of most conventional catalysts used for this reaction.[12] This is a result of the controlled introduction of defined amounts of OH groups on the surface of nanoscopic metal fluorides; owing to the strong electron-withdrawing effect of the dominating fluoride environment, these Mg-OH groups are Brønsted acidic. By fine-tuning the OH/F ratio, the catalytic properties can be optimized for different catalytic syntheses.[11–13] These new nanoscopic metal fluorides are not only superior bi-acidic catalysts, they also exhibit excellent support properties (high surface area, mesoporosity, high proportion of undercoordinated sites[11]).



Scheme 1. The synthesis of menthol from citronellal in two steps (route 1A + 2A) and in one pot (route B).

The synthesis of (±)-menthol in a single-step one-pot reaction (Scheme 1, route B) would be an attractive alternative, both from economic and environmental point of view, to the industrial Takasago process, which involves the isomerization of (+)-citronellal to (−)-isopulegol in the presence of $ZnBr_2$ dissolved in organic solvents, such as CH_2Cl_2 and benzene, or in an aqueous $ZnBr_2$ solution, followed by its hydrogenation to menthol in a separate second step on Raney Ni (Scheme 1, steps 1A and 2A).[14]

Even though several active and selective heterogeneous catalysts for the cyclization of citronellal to isopulegols and the one-pot synthesis of menthols from citronellal have been reported, the diastereoselectivity in the synthesis of (±)-isopulegol and (±)-menthol was generally lower than that with homogeneous catalysts (52–76%).[15–17] There are only a few exceptions. Corma and Renz[18] showed that Sn-β-zeolite catalyzes the cyclization of citronellal to (±)-isopulegol with a diastereoselectivity of 85%. Chuah et al.[19] also showed that over a Zr-β-zeolite catalyst, the cyclization of citronellal occurs with 93% diastereoselectivity.

Therefore, we focused our attention on a simple synthesis of a bifunctionalized metal fluoride catalyst that provides high diastereoselectivity for the cyclization of citronellal to (±)-isopulegol[12] and also catalyzes the hydrogenation of (±)-isopulegol to (±)-menthol. We report herein the preparation of a new gold/hydroxylated magnesium fluoride catalyst (for simplicity the hydroxylated fluoride $MgF_{2-x}(OH)_x$ will be referred to as simple fluoride, MgF_2) by an "incipient wetness impregnation" method. This catalyst provides unexpectedly active ionic gold species for the selective hydrogenation of isopulegols to menthols. At the same time, the catalytic features of fluoride responsible for the diastereoselective isomerization of citronellal to

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(±)-isopulegol are preserved. In this way, the new bifunctional catalyst can serve in the highly diastereoselective one-pot synthesis of (±)-menthol from citronellal.

Iridium-based zeolites have been previously reported as active catalysts for the one-pot synthesis of (±)-menthol.[17] However, when metal fluorides were used as supports, neither the deposition of iridium as a metal salt nor its reduction generated active catalysts for the cyclization of citronellal to (±)-isopulegol (cf. Table 2S in the Supporting Information). The reduction of the iridium salt is accompanied by extensive damage to the active acidic sites of the metal fluoride support as a result of crystallization at the temperature required for the reduction of Ir^{3+} (450 °C). Even at lower temperatures (200 °C) the amorphous fluorides partially crystallize leading to a substantial decrease in surface area and pore diameters. This is evidenced by XRD and BET measurements (not shown here). Consequently, for the synthesis of (±)-menthol the loss of acidic sites in combination with the decrease in pore diameter resulted in a drastic drop in catalytic activity and lowered diastereoselectivity for
(±)-isopulegol.

In order to preserve the high diastereoselectivity and acidity of nanoscopic fluorides, it is necessary to either optimize the reduction step in order to prevent crystallization or to synthesize bifunctional catalysts that do not require thermal activation. Consequently, we developed the synthesis of gold-based nanoscopic fluoride catalysts.

The magnesium fluoride phases were prepared by the reaction of magnesium methoxide with a methanolic hydrogen fluoride solution. By employing HF solutions with different water content, it is possible to control the introduction of OH groups. If the OH content in the $MgF_{2-x}(OH)_x$ phases is very low ($x < 0.1$), these OH groups are Brønsted acidic in nature.[20] As a result, the bi-acidic catalysts obtained exhibited both Lewis (Mg^{2+}) and Brønsted (OH) sites.

This material was treated with the incipient wetness impregnation method using hydrogen tetrachloroaurate as the gold precursor. The catalyst precursors were calcined at 100 °C and 150 °C, and the resulting materials were denoted Au-100 and Au-150. As evidenced by inductively coupled plasma/atom emission spectrometry (ICP-AES), complete impregnation of the mesoporous MgF_2 co-catalyst with the gold compound was achieved without any loss of gold during the preparation procedure; the final concentration was 4.0 % Au. Furthermore, partial hydrolysis of the tetrachloroauric acid (evidenced by a blueshift in UV/Vis spectrum) results in negatively charged gold complexes that are strongly absorbed onto the positively charged MgF_2 surface (see also the Supporting Information).

The k^2-weighted EXAFS spectra of the Au catalysts and Au foil, together with their Fourier transforms (FT) are shown in Figure 1. For the Au foil, the main split maximum of FT corresponds to the nearest neighbors (12 atoms at 2.884 Å) in the *fcc* structure of the metal. The FT of the sample Au-100 shows a main maximum at 1.87 Å, in line with closer neighbors of Au. The same maximum is visible for the sample Au-150, together with the split maximum characteristic of metallic gold. As indicated by XPS, both samples contain chlorine, evinced by faint, but still visible, Cl 2p photoemission peaks in the survey spectra (not shown here). This prompted us to assign the maximum at 1.87 Å to Cl neighbors in preserved fragments of the precursor structure. Further details regarding the fitting of the EXAFS spectra can be found in the Supporting Information.

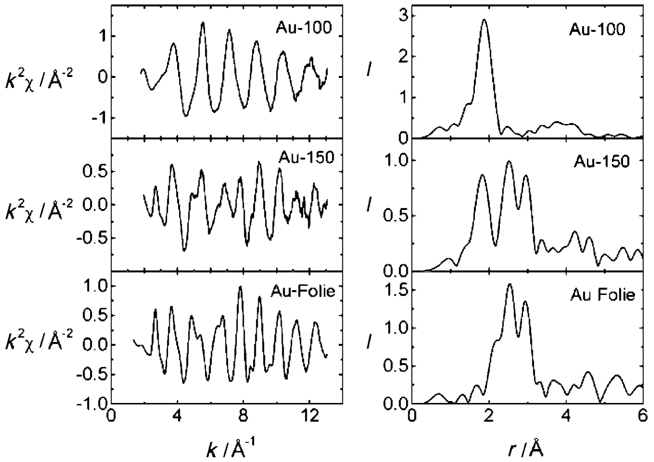


Figure 1. k^2-weighted EXAFS spectra of the Au catalysts and Au foil and the magnitude I (in Å^{-3}) of the corresponding Fourier transforms.

The Au environment in the sample Au-100 (3.6 Cl atoms at 2.281 Å) closely resembles that in the tetrachloroauric acid structure (6 Cl atoms at 2.286 Å).[21] This indicates that the structure of the precursor is preserved after thermal treatment at 100 °C. The reduced number of Cl neighbors in the structure of the sample Au-100 indicates a Cl-defective structure of the precursor, and/or also small precursor particles, which effectively lower the coordination number derived from EXAFS.[22]

Upon increasing the treatment temperature to 150 °C, a large fraction of gold is reduced to the metallic state. This was already shown by the FT of the sample Au-150, which is a combination of the FTs corresponding to the sample Au-100 and the metallic Au (Figure 1). EXAFS fitting indicates Cl and Au around the Au atoms, corresponding to the remaining precursor and the developing metallic phase, respectively. For a phase mixture, the coordination numbers (CNs) specific to each component are weighted in the EXAFS analysis by the fraction of that component in the phase composition. In this case, $CN_{Au} = 6$ corresponds to about one-half of the Au atoms in metallic state, while the decrease of CN_{Cl} from 3.6 to 1.3 would indicate about one-third of Au still belonging to the precursor. It is very probable that this discrepancy results from a greater underestimation of CN_{Cl} for the sample Au-150, with smaller particles of the precursor remnants, than the sample Au-100. The change of the chemical state of gold with the treatment temperature is also shown by the "white line" (WL) of the Au L_3-edge absorption spectra (Figure 2S in the Supporting Information).

The formation of high agglomerations of gold particles was also observed in XRD diffraction spectra for the Au-150 sample. The same XRD technique showed that the amorphous state of the pure nanoscopic fluoride was successfully preserved. However, the formation of agglomerations of gold particles was expected, since chloride ions promote the mobility and agglomeration of gold species during thermal treatment.[23] In accordance with the literature, such agglomerations of the metallic gold particles lead to low-index gold surfaces which are known to be inert[24] and inactive towards most molecules. Such behavior is also confirmed in the one-pot synthesis of menthol from citronellal (Table 1).

Table 1: Comparison of MgF_2 and the gold-based catalysts in terms of conversion (*X*), overall selectivity (*S*), and diastereoselectivity (ds).[a]

Sample	*X* [%]	$S_{\text{isopulegols}}$ [%]	$\text{ds}_{\text{menthols}}$ [%]
MgF_2[b]	95.0	87.0	–
Au-100	99.0	57.0	43.0
Au-150	0.5	0	0
Au-100[c]	99.0	39.2	60.8
Au-100[d]	99.0	7.5	92.5

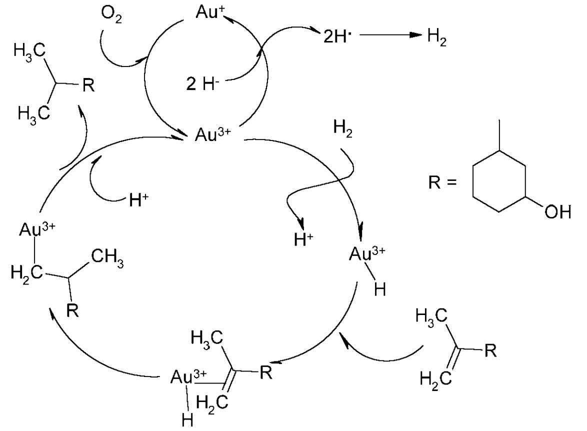
[a] Reaction conditions: 100 mg catalyst, 1.0 mL (860 mg) citronellal, 5 mL toluene, 80 °C, 15 atm H_2, 22 h. [b] The cyclization of citronellal to isopulegol: 100 mg catalyst, 1.0 mL citronellal, 5 mL toluene, 80 °C, 6 h. [c] The second catalytic charge. [d] The third catalytic charge.

Interesting is the fine line between a highly active and diastereoselective catalyst (Au-100) and a totally catalytically inactive material (Au-150), imposed by a difference of only 50 °C in the calcination temperature (Table 1). Therefore, as Table 1 lines 1 and 2 show, the ds of the fluoride support was preserved after its impregnation with gold salt. The Au-100 catalyst is as active as the MgF_2 sample in the isomerization of citronellal to (±)-isopulegol;[12] high conversion (99.0 %) is also reached after 6–7 h, but the hydrogenation of the formed (±)-isopulegols to (±)-menthol is much slower.

After a reaction time of 22 h the selectivity to (±)-menthol reaches 43 %, and the diastereoselectivity in the formation of the isopulegols in the first step is preserved (Table 1, entry 2). The (±)-isopulegol/(±)-neo-isopulegol ratio is 87.8:12.2, according to GC and ^1H NMR analysis (Figures 4S and 5S in the Supporting Information). The ^1H NMR data are in perfect agreement with the literature data.[25] When the catalyst was removed by filration, dried in air at room temperature, and reintroduced for another 16 h, the selectivity to menthol improved by another 17.8 %, reaching a level of 60.8 %. This can be explained by the re-oxidation of the gold particles to the Au^{3+} oxidation state upon contact with air; this has been confirmed by XPS and is in agreement with previous results.[26] Based on this observation, the reaction was stopped after 15 h and the catalyst was exposed to air. As a consequence of re-oxidation the selectivity to (±)-menthol increased to 92.5 %. This procedure was repeated and the selectivity to (±)-menthol was maintained in the range of 91–93 %.

The pure MgF_2 support catalyzed only the cyclization of citronellal to isopulegol with a conversion of 95 % and a selectivity of 87 % (Table 1). Several dehydration products ($C_{10}H_{16}$) of isopulegol were identified. In addition, the etherification of isopulegol to various isomeric isopulegol ethers also occurred, and these underwent further dehydration and cracking (see the Supporting Information). However, the presence of stronger acidic sites than those in our catalysts generated higher amounts of these by-products.[27] An important effect of Au-100 catalyst is the complete suppression of these by-products. This behavior probably corresponds to the blockage of the strongly acidic sites during the impregnation with the gold precursor. By comparing the Au-100 gold catalyst with Ir-based catalysts,[17] it was found that the former is totally selective to menthols (no by-products such as citronellol, 3,7-dimethyloctanol, and 3,7-dimethyloctanal were observed) suggesting a different reaction mechanism.

The hydrogenation of the C=C bond of isopulegol requires the activation of molecular hydrogen by the supported gold species (Scheme 2). In principle, this activation may occur by two routes: the homolytic activation or the heterolytic cleavage of molecular hydrogen. Homolytic activation is highly improbable because it is difficult for the metallic species to reach the oxidation state Au^V. Therefore, the heterolytic cleavage of H_2 is more probable and in agreement with the previous work of Comas-Vives et al.[28] These authors proved that the heterolytic cleavage of hydrogen requires a polar environment provided by the solvent.



Scheme 2. Proposed catalytic cycle.

We have found that a highly polar heterogeneous catalyst can be used instead of homogeneous catalysis in a polar solvent. In the presence of the Au-100 catalyst, the hydrolytic activation of hydrogen is favored by the MgF_2 support; the proton remains on the polar surface whereas the hydride is bonded to the metal center. Thus this novel catalyst can be used to perform such reactions in nonpolar solvents like toluene. However, the reduction of Au^{III} to Au^I accompanies the hydrogenation cycle. This reduction to the in active Au^I species occurs through electron donation from the hydride with the formation of hydrogen radical, which recombines to form the molecular hydrogen (Scheme 2).

In order to regenerate the active Au^{III} species, Au^I must be reoxidized. This oxidation can occur either through the generation of H^+ in the media or more effectively by air. This mechanism is less probable when the Au-150 catalyst; the Au^0 sites present are not active since they cannot participate in a spontaneous electron-transfer process.

To compare the above results we used the same procedure to prepare bifunctional catalysts with different loadings of gold and with β-zeolite as the support. The catalysts obtained displayed high activity (conversions higher than 91 %) for the cyclization of citronellal to (±)-isopulegol, which indicates that the acidic properties of the β zeolite are conserved. However, when these catalysts were used under conditions similar to those applied with the Au/fluoride catalysts, the selectivity to menthol was very low (maximum 31.0 % for the 4.0 % Au/β-zeolitecatalyst).

Such results support the unique behavior of nanoscopic hydroxylated fluorides, not only as potential catalytic materials, but also as potential supports for active catalytic functions.

In conclusion, we have described the synthesis of a bifunctional ionic gold/magnesium fluoride catalyst using an easy and facile incipient wetness impregnation method. Moreover, this procedure did not require additional treatment with highly toxic compounds such as KCN or high-temperature activation steps, as usually needed for the generation of isolated cationic gold sites. The obtained material is able to catalyze both steps of the synthesis of (±)-menthol—cyclization of citronellal to (±)-isopulegol and hydrogenation of (±)-isopulegol—resulting for the first time, in a diastereoselective one-pot heterogeneous synthesis of (±)-menthol. Our results may have important implications for the synthesis of other gold/porous material catalysts and their application as bifunctionalized catalysts. In addition, the presented Au/MgF_2 catalyst may also be applied to other reactions requiring both acid and hydrogenation activity.

Experimental Section

The nanoscopic fluoridew were synthesized as reported elsewhere[11,29,30] using aqueous 71 wt % HF solution. XRD, MAS NMR spectroscopy, TEM, thermal analysis, and elemental analysis were applied to study the structure, composition, and thermal behavior of the bulk material. XPS measurements, FTIR with probe molecules, and the determination of N_2 and Ar adsorption–desorption isotherms were carried out to investigate the surface properties.[11]

Ir-based catalysts were prepared by incipient wetness impregnation using [Ir(acac)$_3$] as the metal precursor, and H-β-zeolite (Südchemie, $SiO_2/Al_2O_3 = 21.6$, BET-surface area = 739 m^2 g^{-1}) as the support. Further details regarding the catalysts' preparation can be found in the Supporting Information.

The gold-based MgF_2 samples were prepared by incipient wetness impregnation. The amount of solid $HAuCl_4$ needed for 4.0 wt % Au in the final material was dissolved in a volume of pure water corresponding to the pore volume of the support. The impregnation solution was added dropwise to the support during intensive stirring. After the addition of the solution was complete, the support was slightly damp.

The resulting catalyst precursor was divided in two parts and dried for 4 h at either 100 °C or 150 °C under vacuum (Au-100 and Au-150). The same procedure was applied using H-β-zeolite as the support and the amount of $HAuCl_4$ needed for a finding loading of 0.5, 1.0, 3.0, 4.0, and 5.0 wt % Au.

The catalysts were characterized by numerous conventional techniques such as ICP-AES, XRD, XPS, EXAFS, TG-DTA, and UV/Vis spectroscopy. X-ray diffraction was recorded by using a Siemens D5000 X-ray diffractometer with nickel-filtered $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) at a scanning rate of 0.1 min^{-1} in the 2θ range of 10–80°. The local Au environment was investigated by EXAFS spectroscopy at the Au L_3 edge. The absorption spectra of the catalysts and a Au foil standard were recorded in transmission mode at the CEMO beamline of the HASYLAB synchrotron radiation facility (Hamburg, Germany). Further details regarding calculation of the EXAFS spectra can be found in the Supporting Information. The thermogravimetric analysis was conducted with a SDT Q600 instrument supplied by TA Instruments. The samples were placed in an aluminum sample holder and heated at a rate of 10 °C min^{-1} from room temperature to 300 °C under a N_2 flow with a rate of 100 mL min^{-1}. UV/Vis spectra were recorded using the diffuse reflectance technique. The spectrometer was a Specord 250 (Analytik Jena).

Activity tests were carried out in pressurized reactors as described in the following procedure: Racemic citronellal (d=0.855 g mL^{-1}, 1.0 mL, 5.6 mmol, 860 mg) was dissolved in 5 mL of toluene. The catalyst (100 mg) was added to this mixture. After the reactor was closed, it was pressurized with H_2 (15 bar), and heated up to 80 °C, and the reaction mixture was stirred for 22 h. After the reaction the catalyst was filtered off and the reaction mixture was analyzed by GC chromatography and ^{1}H and ^{13}C NMR spectroscopy. The diastereoselectivity (ds) is the selectivity for (±)-isopulegol with respect to the other isopulegol isomers.

The separated catalyst was kept in air at room temperature until dried. The dried powder was transferred into the pressurized reactor with the reaction product from the first charge and kept under the same reaction conditions for another 22 h. After the second reaction the product was separated, analyzed, and used in a third charge with the same catalyst.

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