Isomerization of \(\alpha\)-pinene oxide to campholenic aldehyde over modified silica and titania nanoparticles

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Introduction

The synthesis of nanoparticles is an active research area with practical applications in many fields (optics, gas sensors, catalysis, etc.). Metal oxide-based nanoparticles show increasing use as supports for catalytic systems. In this paper we investigated catalytic systems based on Lewis acids (ZnCl\(_2\), FeCl\(_3\) and H\(_3\)BO\(_3\)) supported on SiO\(_2\) and TiO\(_2\) nanoparticles. They are tested in the rearrangement of epoxides, a versatile reaction allowing transformation in a wide variety of functional groups. In this concern, the acid-catalyzed isomerization (see scheme 1) of \(\alpha\)-pinene oxide (1) into campholenic aldehyde (2) is of relevant interests, being this latter product an important intermediate used in the fragrance industry [1].

![Scheme 1. Main reaction products in the acid-catalyzed isomerization of \(\alpha\)-pinene oxide.](image)

On catalytic homogeneous systems, a considerable formation of by-products from (3) to (5) occurs causing an irreversible catalyst deactivation. Heterogeneous systems are highly desirable offering an easy recovery of the catalyst. The present study aim to investigate the characteristics of the Lewis acids supported on metal oxide nanoparticles in order to enhance the catalytic properties towards the target reaction.

Results and Discussion

Silica and titania nanoparticles used as support were synthetized by a sol-gel method. They show a spherical form (Fig. 1) with a high monodispersivity (\(d_{\text{SiO}_2} = 400 \pm 20\) nm); (\(d_{\text{TiO}_2} = 550\pm50\) nm). The catalysts were prepared by wetness impregnation of the Lewis acids on the metal oxide nanoparticles, and calcined in the range 120 – 450 °C before use. The loading of Lewis acids was varied between 5 and 10 wt(%). Also
at the highest loading Lewis acids were found highly dispersed on the surface of these supports. The textural, microstructural and acid-base characteristics were investigated by BET surface area measurements, XRD, SEM-EDX, FT-IR and TPD of probe molecules.

The reaction of isomerization of α-pinene oxide was carried out in cyclohexane as solvent at atmospheric pressure and in the range of temperature between 30 and 70 °C. The progress of the reaction was followed analyzing by GC samples withdrawn from the reaction mixture at different times.

The catalytic performance of the SiO₂- and TiO₂-supported catalysts in the isomerization of pinene oxide has shown that TiO₂-based catalysts are more actives than the analogous SiO₂-based catalysts. The products distribution is instead similar regardless of the support used. For each series, the boric acid-doped catalysts are the most actives, following the ranking: H₃BO₃ > FeCl₃ ≈ ZnCl₂. The reverse situation was found comparing the selectivity to campholenic aldehyde being the Zn-doped catalysts the most selectives (about 68 % at 100 of conversion). The other main reaction products observed were pinocarveol (3), iso-pinocamphone (4) and trans-carveol (5). The selectivity to these reaction products is independent on the conversion level thus indicating that they are formed by parallel reactions.

The effects of some parameters of preparation of the catalysts (calcination temperature, Lewis acid loading) and of reaction conditions were studied in order to increase the selectivity to the desired product. The acid-base characteristics of these catalysts were also investigated and correlated to the catalytic properties.

![Fig.1. Morphology of the silica and titania nanoparticles used as supports.](image)

**References**