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Hydration of α-pinene over zeolites and activated carbons dispersed in polymeric membranes

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Abstract

The acid catalysed hydration of α-pinene yields a complex mixture of monoterpenes, alcohols and hydrocarbons. By controlling the reaction variables is possible to make it selective to the terpenic alcohols, namely α-terpineol. In this paper the results of the hydration reaction of α-pinene catalysed by polydimethylsiloxane (PDMS) membranes filled with zeolite USY, zeolite beta or a surface modified activated carbon, are reported. The reaction is carried out at 50°C, using aqueous acetone as solvent. The activity and selectivity towards α-terpineol of the composite membranes are compared with those of the free catalysts. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: PDMS membranes; Zeolite USY; Zeolite beta; Activated carbon; α-pinene hydration

1. Introduction

When subjecting α-pinene to aqueous mineral acids, complex mixtures of monoterpenes, alcohols and hydrocarbons are obtained resulting from isomerization and hydration reactions [1]. It is generally accepted that the reactions proceed according to Scheme 1. The terpenic alcohols produced by acid catalysed hydration are valuable products with many applications in the pharmaceutical industry, namely α-terpineol [2,3]. By controlling the reaction variables it is possible to make it highly selective towards the desired products, and much effort has been put on research to develop clean processes to afford it. Zeolites and chemical surface modified activated carbons may have potential in improving the selectivity in these α-pinene reactions.

In previous works, it was shown that USY and beta zeolites exhibit high activities and selectivities towards the α-pinene and camphene hydrations [2,3].

Apart from their use as catalyst supports, carbons can be used as catalysts, owing to the presence of acidic and/or basic surface oxides [4–10]. They are known to catalyse many reactions, such as the decomposition of primary alcohols to produce acetals [4–6].

They also bear activity for a number of reactions, including oxydehydrogenation, dehydration, chlorination, gas phase oxidation and reductive NO removal [4–10]. Functionalized activated carbons have been proved to be efficient catalyst supports for the non-oxidative dehydrogenation of light alcohols, as well [4–6].

When immiscible reactants are involved in a reaction, a problem of product separation may arise. The use of membrane reactors can be a solution for those problems [11,12], and polydimethylsiloxane (PDMS) membranes filled with zeolites are frequently mentioned in the literature [11,13].

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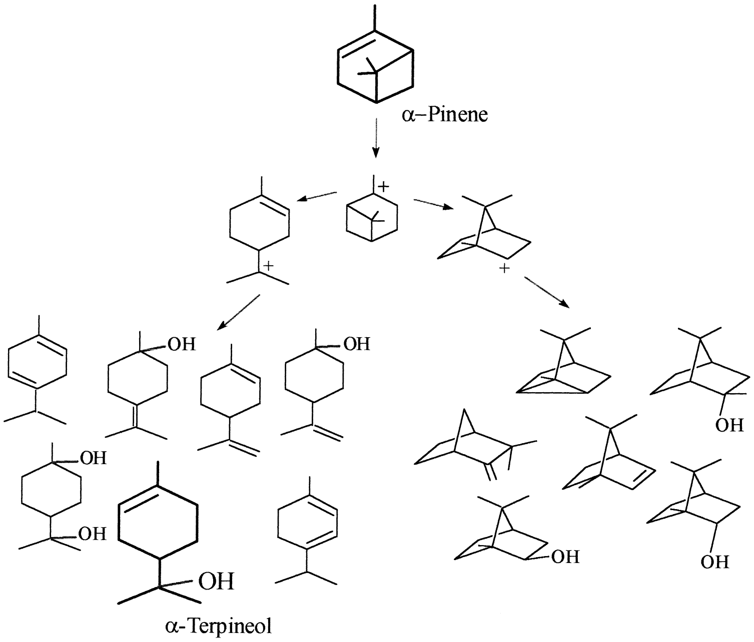

Scheme 1.

The main purpose of this work is to compare the selectivities and activities of the α-pinene hydration reaction, using zeolites (USY and Beta) or a surface modified activated carbon, with the performance of a PDMS membrane filled with these catalysts.

2. Experimental

2.1. Catalysts

The USY 750 zeolite was prepared by hydrothermal treatment from Y zeolites (Aldrich). The dealumination was carried out at 750°C for 3 h in 100% steam, under atmospheric pressure. Catalyst preparation and characterisation were reported in a previous work [2].

Zeolite beta (Si/Al = 30) was synthesised according to the Wadlingler and Kerr procedure [14].

The parent carbon (Norit GCW) was treated during 24 h at 90°C, using fumic H_2SO_4. After the treatment the samples were washed until a neutral effluent and dried at 110°C.

2.2. Membranes

The PDMS was delivered by General Electric, a pre-polymer (RTV-615A, linear PDMS chains with terminal vinyl groups) and a crosslinker (RTV-615B, linear PDMS chains carrying several hydride groups). The membranes were prepared according to Vankelecom et al. [13]. For the membranes filled with zeolites (denoted M1–M5) it was used a 20 vol.% solution in methylethylketone of a 10/1 weight ratio of pre-polymer and crosslinker. In the membranes M6 and M7, where sulphonated carbons were incorporated, the ratio was 10/2 and 10/4, respectively. The amount of crosslinker was increased due to the fact that with the ratio 10/1 the expected crosslinking did not occur. Probably a reaction between the carbon functional groups and the active polymer took place. The characteristics of the membranes prepared are presented in Table 1.

2.3. Reaction conditions

The membrane reactor, operating at total recycle, is composed of two Teflon slabs, each one having an inlet and outlet. Two metal grids at both sides of the membrane avoid membrane movements under changing pressures caused by pumping. Teflon tubes connect the membrane reactor, the pump and the reagent reservoir. The reagents are pumped at a flow rate of

Table 1
Membrane characteristics

Membrane	Catalyst	Catalyst loading (wt.%)	Thickness (mm)
M1	USY 750	21.9	0.110
M2	USY 750	35.9	0.078
M3	USY 750	52.8	0.139
M4	Beta	35.9	0.181
M5	Beta	52.8	0.265
M6	Sulphonated carbon	33.8	0.207
M7	Sulphonated carbon	46.5	0.220

37 ml/min. The reactor is heated using an oil bath and a thermocouple is inserted in the reactor. The membrane is mounted in a pre-swollen condition (using acetone/H_2O) to prevent wrinkling during the reaction.

The experiments (denoted as M1–M7) were carried out at 50°C, using aqueous acetone as solvent, and a relation acetone/water 1:1 (v/v). The relation α-pinene/catalyst = 2.1 (wt) was kept constant. A typical reaction was conducted using 28.5 ml acetone and 0.6 ml α-pinene.

Free catalyst experiments (F1–F3) with the different catalysts not supported on the polymeric matrix, were carried out under similar conditions. It was used a 250 ml jacketed reactor, stirred at 1000 rpm. A typical reaction was performed using 57 ml acetone and 1.2 ml α-pinene. The reaction products were analysed by GC using a Konic HRGC-3000C, equipped with a 30 m × 0.25 mm DB-1column.

3. Results and discussion

For the three catalysts studied, the incorporation in the PDMS membrane leads to a marked decrease in the catalyst initial activity, being that decrease stronger in the cases of beta zeolite and sulphonated activated carbon than in the case of zeolite USY (Fig. 1). That decrease in activity can be explained not only because the PDMS membrane works as a barrier against mass transfer, but also the Brönsted acid sites on the catalyst particle outer surface may react with the SiH functions of the polymer crosslinker or with the vinyl groups of the pre-polymer [11].

As reported by Vankelecom et al. [11], in the case of zeolite Y the pores are invaded by the PDMS chains. This effect prevents the access of the reagent to the acid sites within the catalyst pore structure.

The increase of the catalyst loading leads to an increase on the membrane activity (Fig. 1). This effect may be ascribed to an increase of the membrane channelling as reported by Süer et al. [15]. At low zeolite loadings the pores created by zeolite particles cannot form a continuous channel network and the reagent molecules must cross polymer void interfaces.

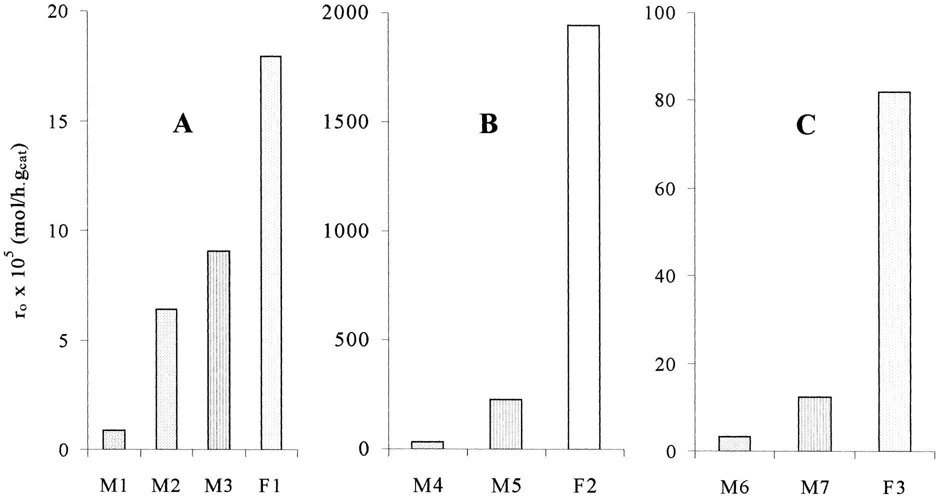

Fig. 1. Initial activities of membranes (M) filled with increasing amounts of catalyst, compared to those of the free catalysts (F). (A) zeolite USY; (B) zeolite beta; (C) sulphonated active carbon.

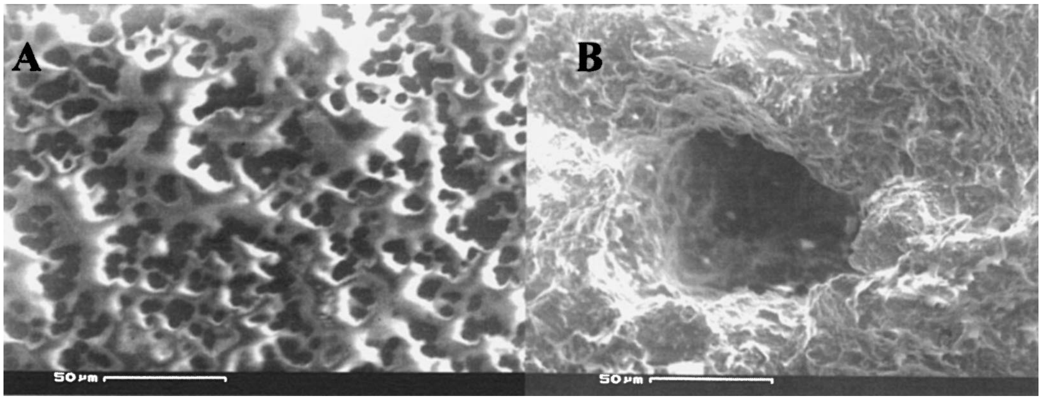

Fig. 2. SEM pictures of PDMS membranes illustrating the influence of the catalyst loading on the membrane porosity. Membranes loaded with sulphonated carbon: (A) membrane M6; (B) membrane M7.

As the percentage of zeolite in the matrix increases the channel network may mature and connect the separate voids providing an alternative path for terpene and water molecules. In fact, the increase in the membrane channelling with the increase of catalyst loading is clearly illustrated in Fig. 2. The increase of carbon loading leads to an increase of the channels diameter from an average of about 20 µm observed for membrane M6, to more than 50 µm in the case of membrane M7.

The increase in the membrane channelling leads to an increase of the reagent permeation and therefore higher diffusion rates to the catalyst particles.

The effect of membrane selectivity to α-terpineol is shown in Fig. 3. Depending on the catalyst a different behaviour is observed. For USY zeolite the maximum selectivity increases from 30%, observed with the free catalyst, to 55% for the composite membrane (Fig. 3A).

In the case of zeolite beta the opposite effect is observed. The maximum selectivity, 70%, observed for the free catalyst, decreases to around 58% in the presence of the membrane (Fig. 3B).

For the activated carbon catalyst, the PDMS membrane allows only a slightly improve in the selectivity comparatively to the free catalyst (Fig. 3C). In all cases the different catalyst loadings seems to have no effect on selectivity.

The somewhat contradictory results observed for the selectivity to terpineol may be due to the different

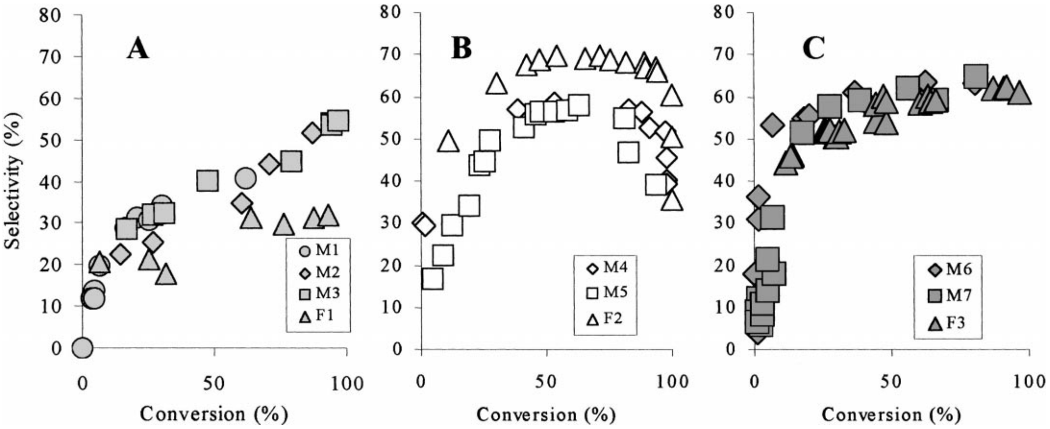

Fig. 3. Selectivity towards α-terpineol versus conversion, for the membranes (M) loaded with increasing amounts of catalyst, compared to the free catalysts (F). (A) zeolite USY; (B) zeolite beta; (C) sulphonated active carbon.

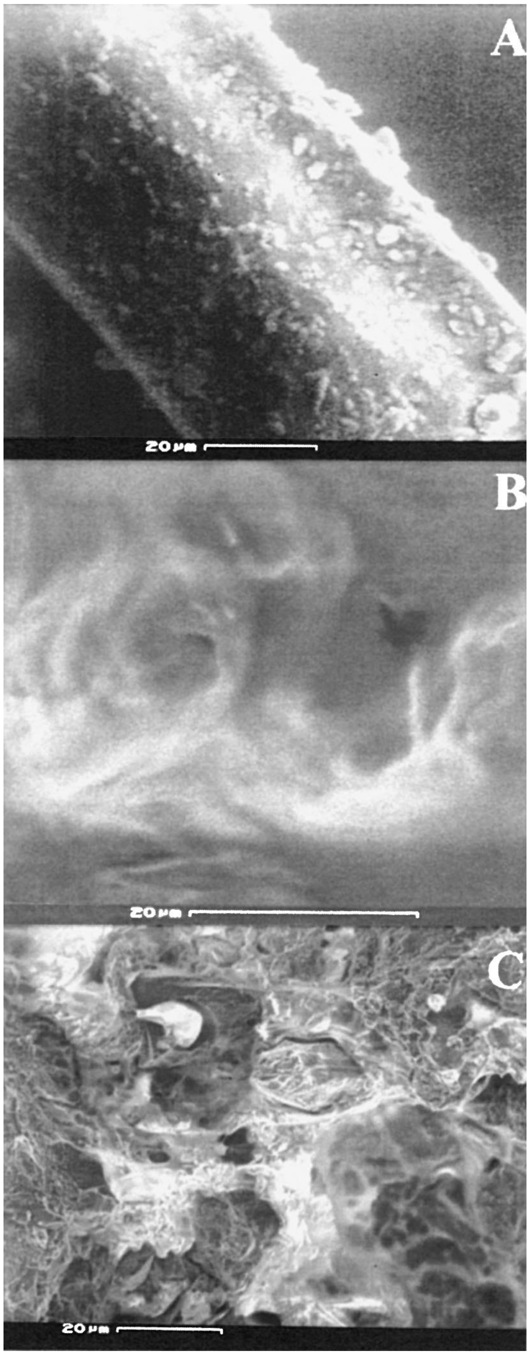

Fig. 4. SEM pictures of the cross section of PDMS membranes loaded with different catalysts. (A) membrane M1 (loaded with zeolite USY); (B) membrane M4 (loaded with zeolite beta); (C) membrane M7 (loaded with sulphonated carbon).

catalyst particle sizes. In fact, the different catalyst particles exhibit average diameters ranging from 20 to 0.1 μm.

As reported by Vankelecom et al. [11], for heterogeneous particle distributions in the polymeric matrix, the membranes obtained with small catalyst particles sorb more hydrocarbon than those prepared with bigger particles. In these circumstances, an increase of the membrane hydrophobicity should be expected when decreases the particle size: the water content in the membrane should decrease, decreasing therefore the selectivity to terpineol. Although the PDMS membrane exhibits hydrophobic properties, sorption of water should be favoured by bigger catalyst particles.

Fig. 4 shows SEM pictures for the cross section of membranes M1, M4 and M7. While membranes M1 and M7 bear relatively big particles with sizes ranging from 2 to 20 μm, in membrane M4 the particles are so small that cannot be distinguished individually. In agreement with what was said above, the selectivity to α-terpineol increases for membranes M1 and M7 in relation to that observed with the free catalysts, while for membrane M4 is just the opposite effect what is observed (Fig. 3). All these effects may explain the increase in selectivity observed for the PDMS-USY and PDMS-carbon composite membranes.

4. Conclusions

For all the catalysts tested, the composite membranes exhibit lower activities than the free catalysts. When the catalyst loading is increased the membrane activity increases, probably due to the increase of the membrane channel system.

The PDMS membrane seems to have complex effects on the selectivity to α-terpineol. It increases for the USY zeolite, decreases for the beta and shows only a slight increase for the activated carbon. The effect of the solvent water content on the selectivity as well as the effect of the particle size on the membrane sorption properties may explain those different behaviours.

Acknowledgements

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