



Transformations of monoterpene hydrocarbons on ferrierite type zeolites

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ABSTRACT

Transformations of α -pinene and limonene over hydrogen forms of commercial ferrierite type zeolites of different origin (Tosoh Corp. and Zeolyst Intern.) have been studied in the liquid phase at 313–363 K. The catalysts were characterized by XRD, sorption of nitrogen, scanning electron microscopy, FTIR and ²⁷Al & ¹H MAS NMR. The concentration of Brønsted acid sites has been determined by ¹H MAS NMR and FTIR quantitative measurements, while their strength was estimated by adsorption of CO. The liquid-phase isomerization of α -pinene proceeds smoothly on the two zeolite catalysts, and the initial reaction rates have been compared. Camphene and limonene were the main products, while the selectivity to these hydrocarbons differed. Isomerization of pure limonene was also studied, showing large difference in activity over the two ferrierite catalysts. The selectivity of α -pinene transformations has been rationalized in terms of retarded consecutive isomerization of limonene over the zeolite from Zeolyst.

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1. Introduction

Monoterpenes constitute a sub-group of terpenes, various compounds occurring in nature as components of essential oils (mainly in plants). They consist of two isoprene units (2-methyl-1,3-butadiene, corresponding to C₁₀H₁₆) and can be classified into three main arbitrary categories: acyclic, monocyclic and bicyclic [1]. Monoterpenes are particularly interesting from a fine chemical synthesis standpoint. The chief sources of the monoterpenes and their derivatives are the essential oils obtained by distillation or extraction under pressure of various plant parts: flowers, leaves, roots, rhizome, wood, bark, fruit and seeds [2,3]. The major industrial source of monoterpene hydrocarbons is crude sulphate turpentine obtained from wood pulp as a waste product in the manufacture of cellulose via the sulphate process. A minor source of bicyclic terpene hydrocarbons is wood turpentine that is obtained by the steam distillation of chopped tree trunks and dead wood. The crude sulphate turpentine is a complex mixture of C₁₀ hydrocarbons composed mostly of α -pinene (60–65%), β -pinene (25–35%) and other monocyclic terpenes, such as limonene. α -Pinene and β -pinene are distilled off from the crude sulphate turpentine and used to produce a variety of flavour and fragrance materials [1,2]. Transformation of α -pinene over solid acids by two routes yields:

(i) bicyclic products of the camphene series; and (ii) monocyclic products like limonene, *p*-cymene and other (cf. Scheme 1) [4,5].

Isomerization of α -pinene is of industrial significance because camphene is an intermediate compound for commercial chemicals, such as synthetic camphor, toxaphene and isobornyl acetate. Camphor is applied, inter alia, as a counterirritant, anaesthetic, expectorant, and antipruritic agent. It is also used as a substrate in manufacturing terpene phenolic resins, as a plasticizer for paints, resins and also in the synthesis of acrylates and methacrylates [6,7].

Generally, the main method for manufacture of camphene is based on the isomerization of α -pinene in the presence of a weakly acidic TiO₂ catalyst in the hydrated state (titania modified by sulphuric acid). The process is carried out in the liquid phase using stirred tank reactors at 403–418 K [8,9], resulting in considerable waste streams and corrosion problems. Therefore, all works concern to design highly active and selective solid acid catalysts suitable for the replacement of the currently applied material. Solid catalysts offer several advantages: facility of the easy catalysts separation from the reaction mixture makes neutralization superfluous, while corrosion is minimized, and the catalysts can be applied several times. Isomerization of α -pinene has been tested over various acidic catalysts: modified zeolites [10–16], oxides treated with acids [17–19], activated clays [20,21] and heteropolyacids [22–24].

The aim of this work was to study catalytic transformations of monoterpene hydrocarbons, α -pinene and limonene, over two ferrierite type zeolites of different origin. The samples were obtained from Tosoh Corp. and Zeolyst Intern. companies, respectively. All

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