

Epoxidation of allyl alcohol over mesoporous Ti-MCM-41 catalyst

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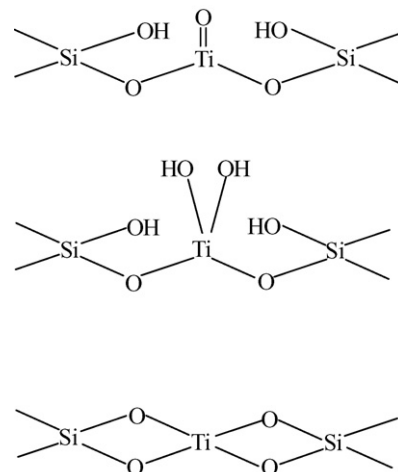
ABSTRACT

Epoxidation of allyl alcohol with 30 wt% hydrogen peroxide over Ti-MCM-41 catalyst under atmospheric pressure and in the presence of methanol as a solvent has been studied. The influence of the following parameters: temperature (20–60 °C), the molar ratio of AA/H₂O₂ (0.5–5), methanol concentration (5–90 wt%), catalyst concentration (0.1–5.0 wt%) and reaction time (5–180 min) has been investigated. The process has been described by the following functions: the selectivity of transformation to glycidol in relation to allyl alcohol consumed, conversions of the substrates and selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed. The technological parameters, at which the functions describing the process take the optimum values, have been established.

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1. Introduction

One of the main challenges in contemporary chemical technology is development of new alternative technologies exerting lower pressure on the natural environment, i.e. cleaner, safer and environmentally friendly. New processes should be more efficient, use less energy, raw products and have a minimum effect on the natural environment. Much helpful in realization of these goals proved to be heterogeneous catalysts, e.g. molecular sieves of the redox type, e.g. zeolites, in which oxygen is bonded with metal in an inorganic matrix (TS-1 [1–3], TS-2 [4–6], Ti-Beta [7–9], Ti-MCM-41 [10,11] and Ti-MCM-48 [12]). The structure of titanium-silicalite catalysts is presented below [1–3]:



Development of such catalysts belongs to the area of nanotechnologies currently of great interest.

The titanium-silicalite catalysts such as TS-1, TS-2, Ti-Beta, Ti-MCM-41 and Ti-MCM-48 have been applied in the processes of hydroxylation of aromatic compounds, epoxidation of unsaturated compounds by hydrogen peroxide, oxidation of alkenes, alcohols and ketones [13]. They have been tested in the processes of epoxidation by hydrogen peroxide because they show high selectivity (including stereoselectivity) and permit performing the processes in mild temperatures and under atmospheric pressure. Moreover, very often the reactions lead to high conversion of hydrogen peroxide and the unsaturated compound [14]. Because of their beneficial

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properties they have been tested in new – satisfying the green chemistry demands – technologies of production of the known or new chemical compounds. The mesoporous sieves can act as a catalyst or a support. They have been successfully used in production of fine chemicals and pharmaceutical products, in petrochemical industry and in oxidation of organic compounds in the liquid phase [15,16].

The Ti-MCM-41 catalyst has a hexagonal structure with regularly arranged groups of mesopores. The mesopores are distributed in the form of long, unbranched and one-dimensional channels of the same diameters. The average MCM-41 pore diameter is 4.9 nm \times 7.6 nm, the surface area of this catalyst is 1200 m²/g and the thickness of the pore walls varies in the range of 0.8–1.2 nm. Because of larger size of pores in Ti-MCM-41 relative to those in TS-1, TS-2, Ti-Beta, during the organic compound oxidation can have easier access to the active sites of titanium [17]. The MCM-41 catalyst has been used in the following processes: hydrodesulfurization, hydrocarbon cracking, polyethylene conversion, naphthalene and anthracene alkylation by alcohols, naphthalene hydrogenation, polymerisation of propene, styrene and aniline, dimerization of ethylene, decomposition of cumene into phenol and acetone [17]. Moreover, the Ti-MCM-41 catalyst has been used in the processes of oxidation and epoxidation of various organic compounds, e.g. oxidation of D-glucose, propylamine, propylene, epoxidation of crotyl alcohol, α -terpineol and terpinen-4-ol [17]. In these processes this catalyst shows high selectivity. From among the other catalysts of this type, TS-1, TS-2, Ti-Beta, the Ti-MCM-41 catalyst is distinguished by having channels of greater diameter, showing smaller diffusion effects of the reagents and products, and offering the possibility of oxidation of large volume molecules of organic compounds. The best catalytic performance of this catalyst was observed in the oxidation of branched and cyclic alcohols. An interesting catalyst was obtained by introducing Ti-MCM-41 into polydimethylsiloxane polymer. The spaces between the polymer and the catalyst particles formed an additional channels system.

2. Experimental

2.1. Raw materials used in the epoxidation of allyl alcohol

In the epoxidation of allyl alcohol (AA) the following materials were used: allyl alcohol (98 wt%, Fluka), titanium-silicalite catalyst Ti-MCM-41 (prepared at the Institute of Organic Chemical Technology, Szczecin University of Technology), hydrogen peroxide (30 wt% water solution, P.O.Ch. Gliwice, Poland), methanol (analytical grade, P.O.Ch. Gliwice, Poland).

2.2. Preparation of Ti-MCM-41 catalyst and its characteristics

Ti-MCM-41 catalyst was prepared by the method described by Schumacher et al. [18]. A glass reactor was charged with hexadecyltrimethylammonium bromide, deionised water, ammonia solution (33 wt%) and ethanol. The content of the reactor was vigorously stirred for 15 min and subsequently tetrabutyl o-titanate and tetraethyl o-silicate were dropped very slowly. The mixture was stirred for 2 h before being heated at 70 °C for 4 h. The solid product was washed with deionised water and methanol, and next dried at 60 °C for 5 h. The product was calcined in air at 550 °C for 5 h.

The catalyst was characterised by the techniques: XRD (the X-ray diffraction spectroscopy), XRF (the X-ray fluorescence spectroscopy), IR (the spectroscopy in infrared radiation), UV–vis (the spectroscopy in ultra-violet and blank space visible) and SEM (the scanning electron microscopy). The X-ray diffractions pattern of the obtained Ti-MCM-41 catalyst (Fig. 1) was the same as in literature [18,19].

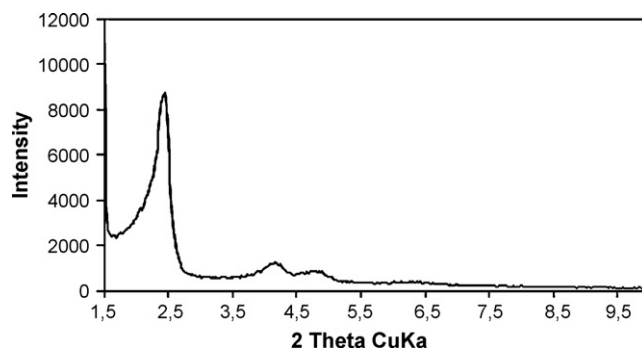


Fig. 1. XRD pattern of the obtained Ti-MCM-41 catalyst.

The SEM micrograph of the Ti-MCM-41 is typical of MCM-41 mesoporous metallosilicalites and is shown in Fig. 2.

The FT-IR spectra of Ti-MCM-41 catalyst revealed a band at around 960 cm⁻¹ and the UV–vis spectrum shows a band at 210 nm. The bands confirm that titanium is incorporated in silica structure (presence of titanium species with tetrahedral oxygen coordination).

2.3. Epoxidation procedure, apparatus and analytical methods

The process of allyl alcohol epoxidation was carried out under atmospheric pressure in a glass reactor equipped with a reflux condenser, thermometer, mechanical stirrer and a dropping funnel. The substrates, in proper amounts, were introduced into the reactor in the following sequence: titanium-silicalite catalyst Ti-MCM-41, allyl alcohol and methanol as a solvent. When temperature reached a target value 30 wt% water solution of hydrogen peroxide was dropped in. The process was performed for a certain time, then the reactor content was weighted and the product was subjected to analyses.

In order to make mass balances of the syntheses performed, the following analyses were made: unreacted hydrogen peroxide was iodometrically determined [19], glycerine formed in the process was potentiometrically determined [20], the other products and the unreacted allyl alcohol were determined by a gas chromatography. The chromatographic analyses were performed on a FOCUS GC instrument (Thermo, Poland) equipped with a flame-ionization detector (FID), using a capillary column Quadrex 30 m \times 250 μ m \times 0.25 μ m packed with methylsiloxane modified with phenyl groups. The parameters of chromatographic separation were as follows: helium pressure 50 kPa, sensitivity 10, sample chamber temperature 150 °C, detector temperature 250 °C. The thermostat temperature was programmed in the following way: isothermally 40 °C for 3 min, followed by an increase at the rate

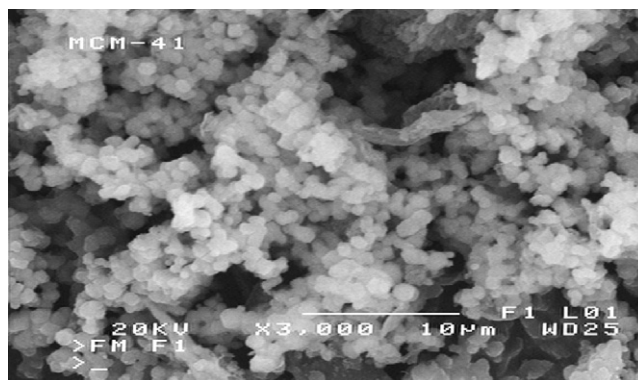


Fig. 2. SEM micrograph of Ti-MCM-41 catalyst obtained.

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