

Catalytic Epoxidation of Limonene

E. Herrero, S. Casuscelli, J. Fernandez, C. Poncio, M. Rueda and O. Oyola

CITeQ, Universidad Tecnológica Nacional, Facultad Regional Córdoba, C.C.36, 5016 Córdoba, Argentina

Tel: 0351-4690585, E-mail: eherrero@sa.frc.utn.edu.ar

Abstract: The epoxidation of limonene with hydrogen peroxide was studied over zeolite Ti-beta (a large pore material) and heteropoly acids on carbon and alumina supported. PW₁₁/C was catalyst the best tested.

Introduction

In the last years, the increase in environmental restrictions lead to the search for new oxidant systems to replace the traditional ones in order to avoid the generation of polluting effluents.

The terpenes containing oxygen are very important to be used in the fragrances production; in our country we have great quantities of limonene and thus we studied its oxidation to 1,2-epoxilimonene using a heterogeneous catalysts system.

In a previous paper the pillared clays from mixed oligomers of Si-Ti [1] were studied, in this paper the results using supported heteropolyacids (HPA) and zeolites Ti-beta are shown.

Experimental

The HPA were prepared from phosphomolybdic acid (PMA) and tungstophosphoric acid (TPA) and then impregnated on alumina (A) or carbon (C) to fill the pores with solution in ethanol-water [2]. PW₁₁ refers to a lacunar phase supported on C. Ti-beta zeolite (Ti-β) was prepared according to [3].

The reactions were run in a batch type glass reactor with vigorous stirring and at 343°K, the rate limonene/H₂O₂(35%) = 4 and 100 mg of catalysts and acetonitrile as solvent; the reaction was followed by taking samples at different times and analyzing them by GLC, the remanent H₂O₂ was determined by iodometric titration. The reaction products were identified by comparison with chromatographic authentic samples and mass spectroscopy.

Results and Discussion

Limonene and H₂O₂ conversion and products selectivity at time on stream 7 hours, are shown in the next table.

CATALYSTS (mmoles HPA/g)	CONVERSION		SELECTIVITY			
	% max.	H ₂ O ₂	H ₂ O ₂	Epoxide	Cetones	Others
TPA/A (1.120)	33,85	54,93	61,63	31,20	42,88	25,92
TPA/C (0,855)	13,03	33,92	38,41	22,95	41,49	35,56
MPA/A (1.280)	34,62	65,36	52,96	36,89	33,86	29,25
MPA/C (0,649)	22,35	33,46	66,80	24,28	32,78	42,94
PW ₁₁ /C (0,820)	38,22	71,58	53,40	58,74	30,23	11,04
Ti-β (2,6% TiO ₂)	46,21	71,51	63,62	22,94	54,60	23,86

We can observe that supported HPA on A show a higher conversion and selectivity to the epoxide than the supported on C, which are more selective to other products (glycols and acid catalysis products), owing to a lower interaction between HPA and support. The catalyst with higher activity is Ti-β but the more selective is the lacunar phase PW₁₁/C, with high yield of epoxide derivative, because this phase has a vacancy compared with Keggin structure, which is active for oxydation reactions.

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References and Notes

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