

Synthesis of zeotypes with β structure and their activity on R-(+)-Limonene epoxidation with hydrogen peroxide–urea adduct

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Introduction

Zeolite Beta (β) has a pore structure formed by 12-ring interconnected channels with a pore diameter of approximately 7.5 . This zeolite is a highly faulted intergrowth of two polymorphs, A (P4₁22 or P4₃22) and B (C2/c), in a ratio of 40:60 [1]. Since polymorph A is a chiral material, it might potentially be used for enantioselective adsorption or chiral catalytic processes. R-(+)-limonene epoxide is a key raw material for the synthesis of pharmaceuticals, fragrances, perfumes and food additives [2]. Limonene has two olefinic bonds (1,2 and 8,9) whose oxidation give one or two epoxides, with *trans* or *cis* configurations. In this contribution, the chemo-, regio- and stereoselective oxidation of R-(+)-limonene over polymorphic enriched zeotypes with β structure is reported.

Materials and Methods

Zeotypes with β structure were synthesized in fluoride media, using tetraethylammonium hydroxide (TEAOH) as structure directing agent. The gel compositions are listed in table 1. The sources of silica, germanium, titanium and tungsten were tetraethylortosilicate (TEOS), germanium oxide (GeO₂), tetraethylortotitanate (TEOTi), and ammonium tungstate, respectively. After heating in a static oven at 140 C for 6 days, the materials were filtered and washed with deionised water. Then, they were dried at 100 C overnight, and calcined at 560 C for 12 h. The crystallinity and polymorphic composition of calcined materials was determined by XRD using Cu K radiation in the scanning range 2 θ = 3–50. For catalytic epoxidation experiments, 15 mg of β zeotype, 0.3 mmol of R-(+)-limonene, 0.45 mmol of hydrogen peroxide–urea adduct (UHP) and 1.5 mL of CH₃OH, were stirred for 6 h in a glass vial immersed in a heated bath at 70 C. The reaction was quenched by addition of 0.1 mg of MnO₂ and the reaction mixture dried over Na₂SO₄. Reaction products were determined by gas chromatography–mass spectroscopy.

Results and Discussion

The polymorphic composition of synthesized materials was determined by peak deconvolution of XRD profiles, using *OriginPro8*. The first low angle peak was separated in two peaks [3]. The peak centered at 2 θ = 7.34 is assigned to characteristic reflections of polymorph B, and the one at 2 θ = 7.74 to reflections of polymorph A [1]. The polymorph A enrichment as determined by the ratio A/(A + B) varied between 70.2 and 75.6 %. This result confirms that synthesis in fluoride media promotes selective formation of polymorph A [4]. The presence of heteroatoms, such as Ge, Ti and W, does not significantly affect the polymorphic enrichment. Table 2 shows percent conversion, selectivity and diastereomeric excess (*de*) of R-(+)-limonene epoxidation on synthesized β zeotypes. Ti zeotypes showed the highest conversion, the lowest epoxide selectivity, and *de* to *trans* epoxide is favored. It appears to decrease as Ge loading increases. Although low conversions were obtained with the rest of the synthesized materials, limonene conversion increased with germanium loading. The

de toward *cis* epoxide predominates on the latter materials (no Ti) and it is not influenced by the Ge loading.

Table 1 Gel Compositions

Material	Composition
Si- β	1 SiO ₂ : 0.54 TEAOH : 0.54 HF : 7.3 H ₂ O
Ge5- β	0.95 SiO ₂ : 0.05GeO ₂ : 0.54 TEAOH : 0.54 HF : 6 H ₂ O
Ge10- β	0.9 SiO ₂ : 0.1 GeO ₂ : 0.54 TEAOH : 0.54 HF : 6.3 H ₂ O
Ti- β	1 SiO ₂ : 0.017 TEOTi : 0.56 TEAOH : 0.35 H ₂ O ₂ : 0.56 HF : 8.4 H ₂ O
Ti-Ge5- β	0.95SiO ₂ : 0.05GeO ₂ : 0.017TEOTi : 0.54TEAOH : 0.35H ₂ O ₂ : 0.54 HF : 6H ₂ O
Ti-Ge10- β	0.9SiO ₂ : 0.1GeO ₂ : 0.017TEOTi : 0.54TEAOH : 0.35H ₂ O ₂ : 0.54 HF : 6.9 H ₂ O
W- β	1 SiO ₂ : 0.015 WO ₃ : 0.54 TEAOH : 0.54 HF : 7H ₂ O
W-Ge5- β	0.95 SiO ₂ : 0.05GeO ₂ : 0.54 TEAOH : 0.015 WO ₃ : 0.54 HF : 7 H ₂ O
W-Ge10- β	0.90 SiO ₂ : 0.10GeO ₂ : 0.54 TEAOH : 0.015 WO ₃ : 0.54 HF : 7 H ₂ O

Table 2 Epoxidation of R-(+)-limonene with UHP over β zeotypes

Catalyst	Conv. (%) ^a	Selectivity to 1,2-epoxide	de (%) ^b
Si- β	3.5	61.3	8.9
Ge5- β	14.3	55.6	8.6
Ge10- β	11.1	49.9	11.4
Ti- β	48.1	14.3	70.9 ^c
Ti-Ge5 β	33.9	41.2	46.7 ^c
Ti-Ge10 β	18.3	31.8	23.7 ^c
W- β	4.2	61.5	10.8
W-Ge5 β	14.5	56.1	11.4
W-Ge10 β	15.4	50.9	48.9

^a Conversion calculated as percentage of the maximum amount of R-(+) limonene that can be epoxidized. ^b *de* (%), diastereomeric excess percentage, calculated as the ratio (cis-trans)/(cis+trans) x 100. ^c Selectivity to *trans* epoxide.

Significance

Beta structure zeotypes synthesized in fluoride media yield between 70.2-75.6 % polymorph A. Incorporation of catalytic species such as Ti does not affect the polymorphic enrichment of the structure. The addition of Ge to Ti zeotypes appears to improve the selectivity to 1,2 R-(+)-limonene epoxide.

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