

OXIDATION OF OREGANO ESSENTIAL OIL USING ZEOLITE-ENCAPSULATED Cr(SALPN) COMPLEX

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ABSTRACT

Flexible ligand (H₂salpn, N,N'-bis(salicylidene)propane-1,3-diamine) was used to form complex with Cr(III) metal ion inside the cages of NaY-zeolite. The encapsulation of Cr(salpn) complex was confirmed with Fourier transform infrared (FT-IR). The encapsulated Cr(salpn) complex catalysed the liquid-phase oxidation of both carvacrol and thymol in the presence of hydrogen peroxide. The conversion range was found be between 35–39% for the oxidation of both carvacrol and thymol. A high yield of thymoquinone (TQ) was obtained along with other side-products such as, thymohydroquinone (THQ) and benzoquinones (BQ). Oxidation of carvacrol and thymol provided a TQ yield of 31.2 and 34.5%, respectively. Oxidation reaction did not occur in the absence of a catalyst. The Cr(salpn)-NaY catalyst was catalytically active with an acceptable leaching performance. Oxidation of oregano essential oil having carvacrol as major compound caused the formation of an essential oil rich in TQ. The carvacrol present in the oregano essential oil was converted into mainly TQ with 33.6% yield and 70% total conversion as a result of the side-products namely BQ, THQ, and several undefined products.

Keywords: oxidation, thymoquinone, carvacrol, thymol, oregano essential oil.

AIMS AND BACKGROUND

A method known as ship in a bottle^{1,2} can effectively be used for the preparation of heterogeneous catalysts. This method is based on the formation and entrapment of a large metal complex inside the cages of zeolite. Recently, effective oxidation catalysts have been developed by preparing and entrapping the metal complexes of porphyrins,

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salen, salpn and phthalocyanines inside the cages of zeolites^{1,3-6}. The utilisation of hydrogen peroxide as a clean oxidant for the catalytic oxidation of aromatic monoterpenes has an industrial importance^{3,7,8}. Both carvacrol and thymol are examples of *p*-menthane type aromatic monoterpenes, which are the constituents of essential oils obtained from several aromatic plants. Thymoquinone having a commercial importance can be formed as a result of the oxidation of these compounds.

Oregano essential oil rich in carvacrol (47.6%) and thymol (25.1%) was easily oxidised by hydrogen peroxide to oil containing thymoquinone (19.1–63.3%) in the presence of Fe(III) meso-tetraphenylporphyrin or Fe(III) phthalocyanines⁹. The carvacrol was also oxidised catalytically with hydrogen peroxide in the presence of Mn(III) porphyrin complexes⁷, keggin-type tungstoborates¹⁰ and zeolite encapsulated metal (salpn) catalysts¹¹. Mn(III) tetra (4-N-benzylpyridyl)porphyrin encapsulated in Y-zeolite was also active for the oxidation of carvacrol and thymol³. Irreversible deactivation as a result of the partial destruction and variations of the zeolite crystalline structure was a significant problem along with the removal of metal complex from the zeolite cages in the presence of H₂O₂.

In this study, zeolite encapsulated Cr(salpn) complex was successfully prepared by general flexible H₂salpn ligand method as described in literature¹. The prepared catalyst was characterised by using FTIR to confirm the metal complex encapsulation. Activities of the catalyst for the oxidation of carvacrol, thymol and oregano essential oil to form thymoquinone were evaluated. Leaching test or heterogeneity test was also carried out. To the best of our knowledge no previous studies on the oxidation of oregano essential oil using zeolite encapsulated Cr (salpn) complex in the presence of hydrogen peroxide as the oxidant have been reported before.

EXPERIMENTAL

Materials. Chromium(III) nitrate nonahydrate, carvacrol, thymoquinone salicylaldehyde, 1,3-diamino-propane, hydrogen peroxide (30%), all other reagents and HPLC grade solvents were supplied by Sigma-Aldrich. Oregano essential oil was bought from a local company. Zeolite-NaY (CBV100, SiO₂/Al₂O₃, 13.0 wt.% Na₂O) from Zeolyst International Company was used as catalyst support.

Catalyst preparation. Methods reported in the literature¹ were used for the preparation of H₂salpn, metal exchanged zeolite Y, and encapsulated complexes. Flexible ligand, H₂salpn, was prepared by mixing both methanol solution (75 ml) of salicylaldehyde (12.2 g, 0.1 mol) and methanol solution (25 ml) of 1,3-diamino-propane (3.75 g, 0.05 mol). Then ligand was recrystallised in methanol for further purification. Suspension of NaY-zeolite (5 g) in aqueous solution of metal Cr(III) nitrate (300 ml, 0.01 M) was used to form Cr-exchanged zeolite Y. After filtering and washing the solid Cr-exchanged zeolite Y was dried. While stirring Cr-exchanged Y zeolite (5 g) and ligand (10 g) were mixed together at 100°C for 19 h. The resulting material was subjected to Soxhlet extraction with methanol for 72 h in order to remove the unre-

acted excess ligand. The coloured solid was first washed with hot distilled water and dried at 90°C for 24 h.

Catalyst characterisation. FT-IR spectra of catalyst samples in KBr pellets were taken using a Shimadzu 8101 FT-IR spectrophotometer. An inductively coupled plasma spectrometer (ICP, Varian 8410) was used to determine the Cr content in the prepared catalyst.

Oxidation of carvacrol, thymol and oregano essential oil. Reactants such as carvacrol, thymol and oregano essential oil were subjected to oxidation reactions at 60°C in a three-necked flask (250 ml) connected to a reflux condenser. The predetermined amounts of reactant and acetonitrile were used along with appropriate amount of 30 wt.% aqueous H₂O₂ (0.029 mol) corresponding to the required reactant-to-hydrogen peroxide molar ratio. The oxidation reaction was started after heating the reaction mixture to 60°C and adding certain amount of catalyst to the reaction mixture. Samples from the reaction mixtures at different times were analysed using a high performance liquid chromatography (HPLC) method described in literature^{11,12}. The wavelength of 254 nm was used for the detection of carvacrol, thymoquinone, and dithymoquinone. The wavelength of 294 nm was used for thymohydroquinone, which has a low absorptivity at 254 nm. Percentage of each compound in the reaction mixtures was estimated directly from the corresponding peak area.

Heterogeneity tests. After hot filtration of the reaction mixture, the organic solvent in filtrate was completely evaporated to form a residue. In leaching tests, this residue digested with HNO₃ in a Teflon beaker was used to determine the Cr content using inductively coupled plasma (ICP) technique.

RESULTS AND DISCUSSION

Catalyst characterisation. H₂ salpn, flexible ligand, was used as described by several researchers in the literature to encapsulate its Cr(III) complex in NaY-zeolite^{1,11,13}. The colour of Cr(salpn)-NaY catalyst was pale blue-green. Cr content was determined with ICP technique as 1.74 wt.%. As seen in Fig. 1, the bands belonging to the zeolite lattice in the range 450–1200 cm⁻¹ were observed in the IR spectrum of Cr-exchanged zeolites. The broad band around 1000 cm⁻¹ could be attributed to the asymmetric stretching vibrations of (Si/Al)O₄ units of the zeolite. The broad bands observed at the region 1650 and 3500 cm⁻¹ in the IR spectrum were due to the lattice water molecules and surface hydroxylic groups. The zeolite bands were dominant in the IR spectrum of encapsulated complexes. Based on the FTIR results, dealumination or structural changes of zeolite did not occur during the encapsulation process. This was an indication of good fit of structure of metal complexes within the zeolite cavities.

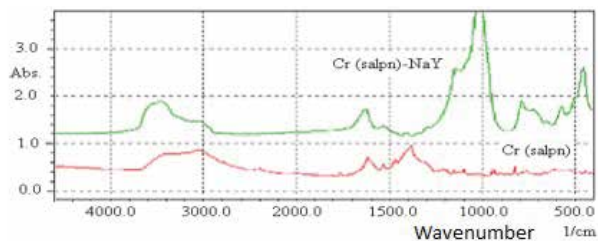


Fig. 1. IR spectra of Cr(salpn)-NaY, and Cr (salpn)

The average size of Cr (salpn) complex was about 12.7 Å which was determined from Spartan program (Wavefunction, Inc. 1996–1997, trial version) as shown in Fig. 2. Before complexation, the size of ligand was about 7 Å. It shows clearly that this complex was too large to diffuse out from the zeolite cage.

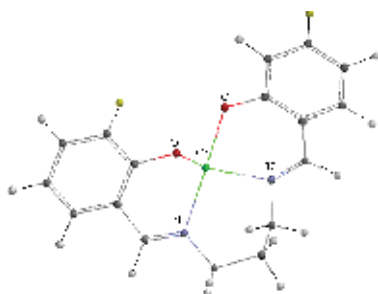


Fig. 2. Cr(salpn) complex

Oxidation of carvacrol and thymol. Catalytic activities of prepared Cr(salpn)-NaY catalyst were evaluated for the oxidation of carvacrol and thymol in the presence of hydrogen peroxide which has an advantage of being a smaller size molecule and having a high mobility in the pores of zeolite. Moreover, hydrogen peroxide is cheaper and sufficiently environment-friendly. With NaY zeolite alone, no significant carvacrol or thymol oxidation reactions were observed under the reaction conditions, indicating that Y zeolite was inactive. Oxidation of both carvacrol and thymol can only take place in the presence of an active catalyst. Similar observations were made by several other researchers^{3,11,14}. As seen from Fig. 3 Cr(salpn)-NaY catalyst has shown activity for the oxidation of both carvacrol and thymol. Carvacrol and thymol, geometrical isomers having very similar chemical structures, are aromatic monoterpenes found in the essential oils of many aromatic plants⁹.

According to the literature, the formation of quinones is possible as a result of the oxidation of hydroquinone intermediate^{7,9–11,14}. Therefore, the mixture of quinones such as thymoquinone (TQ), thymohydroquinone (THQ) and several benzoquinones (BQ) can be expected to form due to the catalytic oxidation of carvacrol⁹. Among these benzoquinones TQ was predominant. The benzoquinones (BQ) were not individu-

ally attempted to be identified. The catalytic conversion of carvacrol and thymol was determined to be in the range of 35–39%. The variations of the conversion with time given in Fig. 3 were very similar for both carvacrol and thymol due to the structural similarities of these molecules. Oxidation of carvacrol and thymol resulted mainly in TQ with a yield of 31.2%, 34.5% TQ, respectively. The reaction mixture contained TQ, THQ and BQ. The TQ yields observed for the oxidation of thymol and carvacrol were found to be very close to each other. In literature, small amount of TQ was produced by the catalytic oxidation reaction of carvacrol and thymol¹⁰. However, in the present study, a relatively higher yield of TQ formation was observed for both thymol and carvacrol oxidation reactions. ICP analyses revealed the presence of Cr ions in the reaction mixture, indicating that the heterogeneity of Cr-based catalyst was good enough, but catalyst was not completely heterogeneous. The leaching of Cr ions can be attributed to the destructive effect of hydrogen peroxide on the stability of Cr complexes. Similar observations were made by Skrobot et al. and their results suggested that hydrogen peroxide rather than the solvent causes the leaching phenomenon⁴. The Cr(salpn)-NaY catalyst was subjected to a recycling study as well. Catalyst was reused at least 3 times successively without a significant change in the catalytic activity. This result was in accordance with the comparable IR spectral patterns of fresh and used encapsulated chromium-based catalysts suggesting the reusability of this catalyst in further catalytic reactions.

Oxidation of oregano essential oil. The chemical composition of oregano essential oil was reported in many studies available in literature. Monoterpenes such as thymol or carvacrol were determined to be the major components in the essential oil⁹. In HPLC analyses of oregano essential oil performed at three different wavelengths (254, 280 and 295 nm) only carvacrol and thymoquinone were observed and no other components (thymol, *p*-cymene, α -terpinene) were identified.

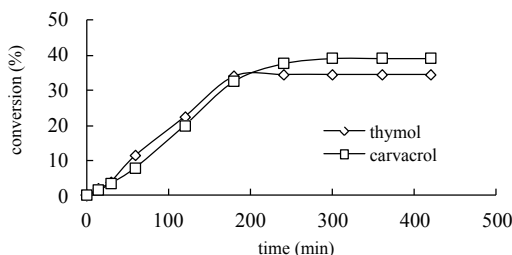


Fig. 3. Percentage of thymol and carvacrol conversion (thymol or carvacrol/ H_2O_2 molar ratio = 1, 0.2 g Cr(salpn)-NaY catalyst, 60°C)

HPLC can be considered as the method of choice due to the absence of further oxidation with residual H_2O_2 at elevated temperature experienced in the GC system¹⁶. As shown in Fig. 4 carvacrol was the major component of oregano essential oil converted to BQ, THQ, TQ (with 33.6% yield), unknown products with a total

conversion of 70% at 60°C. The catalytic oxidation reaction significantly increased the thymoquinone amount in the essential oil.

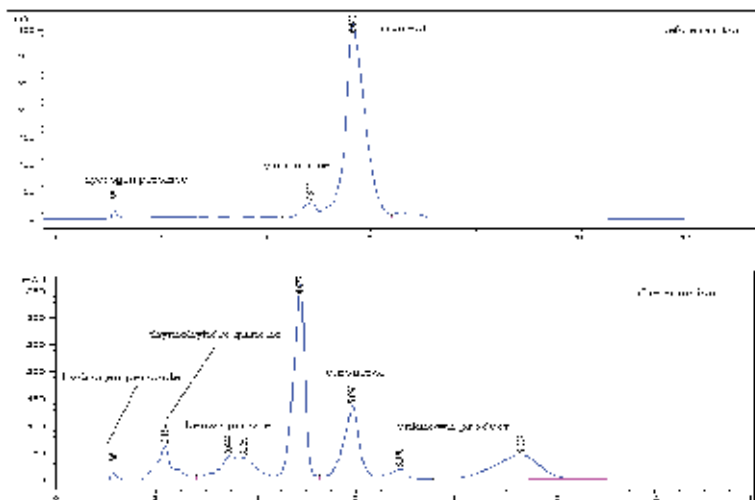


Fig. 4. HPLC chromatograms of oregano essential oil before and after catalytic oxidation reaction (0.2 g Cr(salpn)-NaY catalyst, 60°C)

CONCLUSIONS

The complex of H_2salpn ligand and Cr(III) has been successfully encapsulated in NaY zeolite and characterised with FTIR to confirm its encapsulation in the supercages of NaY zeolite. Thymoquinone, having a considerably higher commercial value than those of its precursors, can be obtained in carvacrol oxidation reactions catalysed by Cr(salpn)-NaY catalysts. Chromium complex did not leach completely from the catalysts during oxidation reactions. The chromium complex when immobilised seemed to be more stable in the oxidising medium, probably due to the electrostatic interactions between Cr and the anionic aluminosilicate framework. Comparable IR spectral patterns of fresh and used encapsulated chromium-based catalysts suggested that this catalyst could be used further for catalytic study.

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