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Synthesis of *cis*-Cinnamic Acid from *trans*-Cinnamaldehyde over Ag^+-Exchanged Beta-Zeolite in Toluene

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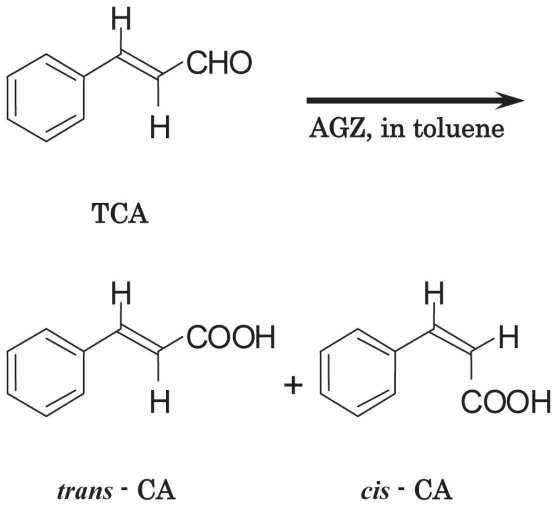
Synthesis of *cis*-cinnamic acid (*cis*-CA) was carried out by isomerization and oxidation of *trans*-cinnamaldehyde (TCA) over Ag^+-exchanged beta-zeolite in toluene. This novel method for synthesis of *cis*-CA was efficient in toluene, whereas synthesis in other solvents was inefficient.

Key Words : *cis*-cinnamic acid, one pot synthesis, silver ion-exchanged zeolite catalyst, solvent effect

1. Introduction

With a view to promoting green chemistry, *cis*-cinnamic acid (*cis*-CA) has been synthesized by using Ag^+-exchanged zeolites (AGZ). *cis*-CA [(Z)-3-phenyl-2-propenoic acid] and derivatives are physiologically active substances having plant growth regulatory activity, and have recently been isolated from plants[1,2]. Methods of synthesizing *cis*-CA reported up to now include photoisomerization of *trans*-cinnamic acid [the (E)-form, *trans*-CA], the method of reacting (Z)-2-bromostyrene with carbon monoxide in the presence of a palladium triphenylphosphine phase-transfer catalyst[3], and the method of electrolytic carboxylation of 2-bromostyrene using a nickel catalyst[4]. On the other hand, silver ion (Ag^+) -exchanged zeolite, silver ion supported on porous material[5] and complex membranes made up of amino acids and silver polymers[6] and the like have been utilized as olefin separation agents. In the present study, *cis*-CA was prepared in one pot synthesis using AGZ in toluene by novel methods of isomerization and oxidation of *trans*-cinnamaldehyde (TCA) to *cis*-CA exploiting the fact that Ag^+ soft Lewis acid on AGZ forms a π-complex with the olefin double bond of TCA and reacts as the oxidant. **(Scheme 1)**



Scheme 1

2. Experimental

Experimental details were as follows: 100 cm^3 of 1 mol dm^{-3} aqueous silver nitrate solution was added to 20 g of each of zeolite (H-Y: JRC-Z-HY, Si/Al 5.6; Ag 11.3 wt%, H-MOR: JRC-Z-HMOR, Si/Al 20; Ag 11.3 wt%, and H-BEA: JRC-Z-HB25 (1), Si/Al 25; Ag 7.7 wt%) and Na-A (Mizusawa Industrial Chemicals Ltd., Silton B, Si/Al 1.0; Ag 40 wt%) and after stirring for 1 week, the resultants were suction-filtered, washed with pure water until Ag^+ was no longer detected, washed with a small quantity of methanol, and stored in desiccators protected from light (these were labeled Ag-Y, Ag-MOR, Ag-BEA and Ag-A). In the same way, Ag^+-exchanged zeolites-A were prepared in mobilized 10, 20 and 30 silver (Ag) wt% of zeolites, and respectively labeled Ag-A25, Ag-A50 and Ag-A75. 0.1 g of TCA, reactant sample, 0.1 g of AGZ, and 50 cm^3 of toluene or other solvents were placed in a 100 cm^3 flask, a reflux condenser was attached, and the mixture was gently heated and refluxed. Every 10 min, a 0.1 cm^3 sample of the supernatant was taken and analyzed by HPLC (Waters 600 HPLC, Nova-Pak C18 8 mm i.d. ×100 mm, wavelength (UV) 254 nm; solvent, acetonitrile: water (0.1% phosphoric acid) = 1 : 1, flow rate 1.5 cm^3/min). The thermogravimetry (TG) was done by using a Rigaku Thermo plus 2 apparatus with heating rate of 10 K/min. The X-ray photoelectron spectra (XPS) of Ag 3d were acquired by JPS-9000SX (JEOL, Japan) using Mg K_α radiation (1253.6 eV).

3. Results and Discussion

trans-CA was heated under reflux for 1 h in toluene in the presence of low Si/Al ratio of various Ag-A zeolites, intermediate