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)

2. Experimental

Experimental details were as follows: 100 cm³ 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., Siltion 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 cm³ of toluene or other solvents were placed in a 100 cm³ flask, a reflux condenser was attached, and the mixture was gently heated and refluxed. Every 10 min, a 0.1 cm³ sample of the supernatant was taken and analyzed by HPLC (Waters 600 HPLC, Nova-Pak C18 8 mm i.d. $\times$ 100 mm, wavelength (UV) 254 nm; solvent, acetonitrile: water (0.1% phosphoric acid) = 1 : 1, flow rate 1.5 cm³/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

Scheme 1

Table 1 Solvent effect to *cis*-CA from TCA over Ag-BEA.

Solvent	Yield (%) ^{a)}	
	CA (%)	<i>cis</i> -form (%)
Acetonitrile	0.0	
<i>p</i> -Xylene	0.0	
Acetone	0.7	0.0
Cyclohexane	1.83	0.0
Benzene	3.51	1.4
Ethanol	6.41	0.0
Toluene	6.88	6.88

a) The reaction was carried out at boiling point of solvent for 2 h over Ag-BEA. Solvent: 50 cm³, Ag-BEA: 0.1 g

Si/Al ratio of H-Y, H-MOR and high Si/Al ratio of Ag-BEA, respectively. With the AGZs, isomerization to *cis*-CA to the extent of 2 to 9% was confirmed. The ethyl ester of *trans*-CA was not isomerized with the AGZs. Further, neither of the geometrical isomer, (Z)-2-methyl-2-butenic acid and the (E)-form, were isomerized. The *cis*-isomerization and oxidation of TCA to *cis*-CA over Ag-BEA occurred in aromatic low polar solvent of toluene more efficiently than in nonpolar aromatic solvents such as benzene, but with the polar solvent of ethanol, *cis*-isomerization ceased entirely (Table 1).

In TCA isomerization and oxidation reactions using zeolite-A with different quantities of added silver (Ag-A25, Ag-A50, Ag-A75 and Ag-A) with toluene for 2 h, the conversion of CA (*trans*-form + *cis*-form) from TCA was 5-7%, and a somewhat higher value of the isomerization ratio (*cis*-CA/*trans*-CA), namely 0.9 to 2.0, was obtained with Ag-A and difference in silver ion exchange ratio (Ag wt%; 10, 20, 30 and 40) caused no difference in both isomerization and oxidation ratio. *cis*-CA was obtained from TCA in good yield with Ag-BEA zeolite, most likely because Ag-BEA is a high silica zeolite as compared with the other AGZs.

Further, when solid silver Ag⁰ and solid silver nitrate were used, *cis*-CA was not formed. In view of these facts, and the fact that the molecular diameter of *trans*-CA is approximately 0.5 nm × 1.0 nm, and is larger than the pore diameters of zeolite-A (ca. 0.4 nm), it is inferred that the isomerization from *trans*-CA to *cis*-CA takes place on the surface or pore inlets of the AGZ. As is shown in Figure 1, the percentage of *cis*-CA produced increased as the weight of

Figure 1 The effect of added reagents on yield of *cis*-CA. ■: Ag-BEA (1 g) + 30% H₂O₂ (0.5 cm³), TCA was not oxidized to *cis*-CA with H₂O₂ reagent. ▲: Ag-BEA (5 g), ○: Ag-BEA (1 g), ●: Ag-BEA (1 g) + H₂O (0.023 mg), □: Ag-BEA (1 g) + O₂ (72 cm³/min, 373 K).

Ag-BEA gradually increased from 1 to 5 g. The yield of *cis*-CA increased not with the passage of oxygen gas in toluene or the addition of water. And TCA was oxidized to *cis*-CA with hydrogen peroxide in toluene that presence of Ag-BEA. It was judged from these observations that the oxygen supply source in this reaction system is provided by the Ag-BEA.

In other words, it was concluded that the valence of silver changed from Ag⁺ to Ag⁰ owing to the reaction with AGZ as the oxidizing agent. In fact, after the reaction a silver mirror was observed on the inside wall of the glass vessel. Figure 2 shows XPS spectra of the Ag 3d peaks of Ag (metal). The valence change of the Ag-BEA silver atoms after the reaction was also supported by XPS spectrum. The valence change of the Ag-BEA silver atoms after the reaction was also supported in the XPS spectrum As is shown by the thermogravimetric analysis (TG) profiles of Ag-BEA and pre-ion-exchange zeolite (H-BEA) in Figure 3, the Ag⁺ ion-exchange treatment increased the amount of hydration water for Ag⁺ ion taken up by zeolite skeleton.

Under heating, the water of hydration and some of the water

Figure 2 XPS Ag 3d spectra for the ion-exchanged BEA (Ag-BEA), Ag₂O and Ag (metal).

Figure 3 Weight change of Ag-BEA with rising temperature. ■: H-BEA, □: Ag-BEA.

departed at 318-473 K. Consequently, TCA was not oxidized when zeolites heated over 473 K were used.

Figure 4 shows the temperature dependency of CA formation from TCA. The yield of *cis*-CA gradually increased from 318 K, without concurrent decrease of *trans*-CA. In fact, it is suggested that TCA firstly isomerized to *cis*-form and secondly oxidized to CA with rise of temperature.

Figure 4 Temperature dependency of CA yield. Catalyst: Ag-BEA, ●: *cis*-CA, ○: *trans*-CA.

Scheme 2

From the above, as regards the oxygen supply source to the AGZ, as is shown in **Scheme 2**, it was inferred that the water of hydration around the Ag⁺ ion dissociates, and the oxygen is released from the resulting partial structure shown by the wavy lines.

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