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REDUCTIVE DEGRADATION OF CHLOROPHENOL IN WATER-BASED SOLVENT USING HETEROGENEOUS CATALYST GRAFTED BY A HYDROPHOBIC REAGENT

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Introduction

As an environmentally benign degradation of persistent organic pollutants (POPs) including chlorine, reductive degradation (hydrodechlorination; HDC) is a desirable method because of preventing additional toxic production as dioxins[1]. A recent trend on the HDC has paid more attention to process in water. For example, some organic chlorinated compounds existing in sewage is of great advantage to direct treatment in water. HDC in water requires that catalyst sufficiently overcomes deactivation caused by water adsorption onto the surface. Hybrid modification of catalyst surface with organic group considers solving this problem. Kopinke et al. promoted reactivity using alumina-supported Pd catalysts coated with hydrophobic silicone polymers[2]. Uozumi and coworker adopted immobilizing Pd nanoparticles in amphiphilic copolymers[3]. Similarly, we also found that organosilanes grafting on surface of catalyst support facilitated HDC of aromatic chlorinated compound in water-based solvents[4-5]. Pentachlorophenol and derivatives were now listed in POPs. Here, we reports that an organosilane-grafted Rh/SiO_2 catalyst easily hydrodechlorinates chlorophenol to reductive products thereof in a water/ ethanol mixture.

Materials and methods:

Materials

A reactant (4-chlorophenol: CLPL) and products (phenol: PL, cyclohexanone: CHNE, and cyclohexanol: CHL) were purified by distillation before reaction. Solvents (water, ethanol), a catalyst precursor (rhodium (III) hexammine trichloride) and a grafting reagent (trichloro-4-tolylsilane: TS) were used without further purification. A Silica gel support removed impurities with hydrochloric acid, washed well with water and dried.

Catalyst preparation

Rh/SiO_2 (bare catalyst) used in the previous report[5] was also utilized to estimate standard catalyst performance in the HDC. The surface of the bare catalyst was silylated using trichloro-4-tolylsilane as a grafting reagent, and named as Rh/SiO_2–TS. Catalyst preparation and organosilylation procedure have been described previously[5].

Reaction procedure

The catalyst (10 mg) in a 77-mL glass tube put in a batch autoclave was reduced under a hydrogen flow of 100 mL/min under 0.5 MPa for 60 min at 473 K. Water (35 mL) was introduced to the grass tube at 373 K. After keeping temperature, CLPL (2 mmol) in ethanol (5 mL) was introduced using 1 MPa hydrogen, and then the HDC reaction was started. The product solutions were periodically extracted from the reaction mixture through a pressure-resistant valve.

Analysis

The products quantitatively analyzed using a gas chromatograph (Shimadzu Co., GC-14A) equipped with a flame ionization detector. Toluene was used as an internal standard. The products were identified by gas chromatography-mass spectroscopy (Shimadzu Co., GCMS5050QA).

Results and discussion:

Optimization of catalyst concentration

Previous to HDC performance, initial reaction rate according to catalyst concentration was investigated in the range 0.125–2.00 g/L (10–80 mg/40 mL) using Rh/SiO_2–TS. Two reaction orders are observed. One is good agreement with a first order below 0.50 g/L, where the slope is 8.83 mol/min/g, coefficient of determination is R^2=0.9970. The other is approximately zero's order over 0.50 g/L. To avoid liquid-solid mass transfer resistance, catalyst concentration of 0.25 g/L (10 mg/40 mL) was adopted here.

HDC reaction over Rh/SiO$_2$

Fig.1 shows the reaction conversion and product yields for the HDC of CLPL over the bare Rh/SiO$_2$ catalyst in 7:1 (v/v) water/ethanol for 60 min at 373 K. The detected products were phenol (PL, 38% yield), cyclohexanone (CHNE, 14% yield), cyclohexanol (CHL, 2% yield). Both the reaction conversion and the dechlorinated product yield amounted to 54% for 60 min because all products have no chlorine. Surprisingly, there was induction period that any product was barely detected in 5 min. This phenomenon means that reactant surrounding water is very difficult to approach active metal sites on catalyst surface. As with the HDC reaction of chloroacetophenone over Pt/SiO$_2$ in water/ethanol[4], water potently interacts with silica and metal surface before injecting the reactant mixture; preventing approach of reactant on the metal active site. Therefore, initial reaction rate was slow (1.08 mol/L/min, coefficient of determination R^2=0.9729), where initial reaction rate was decided by a differential coefficient at 0 min from curve fitting function for 10 min after reaction started.

HDC reaction over Rh/SiO$_2$–TS

On the other hand, Fig.2 depicts the conversion and product yields for the HDC over the organosilane-grafted Rh/SiO$_2$–TS catalyst in the same condition. The conversion and the dechlorinated product yield amounted to 94% in 60 min. The detected products consist of PL (44% yield), CHNE (44% yield), and CHL (7% yield). CLPL was smoothly hydrodechlorinated to PL in initial period, wherein no induction period occurred and PL was successively converted to carbonyl compound. CHNE yield was equal to PL in 60 min whereas PL decreased after reaching maximum yield (49%). Initial reaction rate at 0 min was twice faster than that of the bare catalyst (2.13 mol/L/min, R^2=0.9984). This improvement stems from hydrophobic zone composed of the water-repellant organosilyl substituent[4-5]. Furthermore, as the similar case of chloroacetophenone[5], the advanced HDC reactivity is attributed to aromatic-aromatic interaction between tolyl position of organosilyl substituent and CLPL, thereby indicating much retention of reactant and products in the vicinity of the metal active site on the catalytic surface. Therefore, to modify the silica-support surface on the Rh/SiO$_2$ catalyst using organosilane reagent extremely contributes to the HDC reactivity in water-based solvent.

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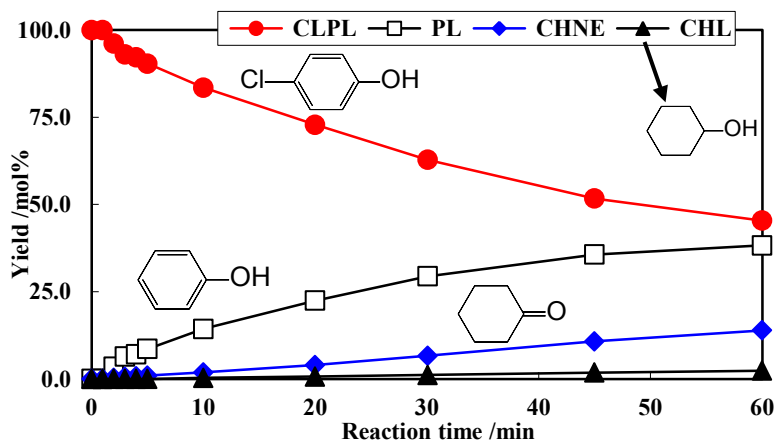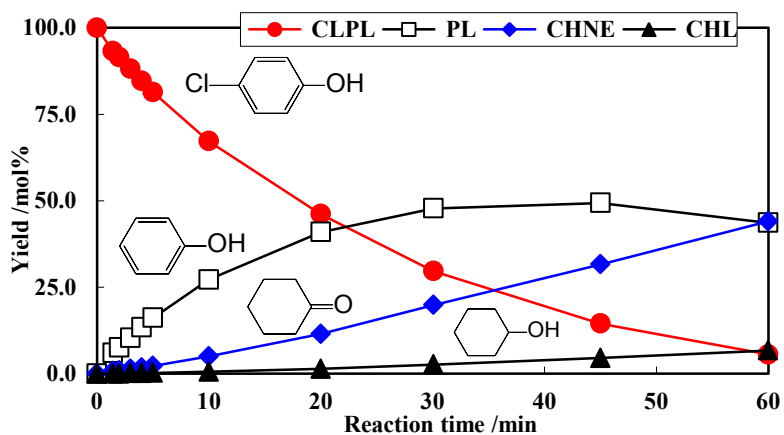5. Yoneda, T., Aoyama, T., Koizumi K., and Takido, T. (2014) Chemistry Letters, 142-143, 344-353

Fig.1 Product yields for the HDC reaction of CLAP over Rh/SiO$_2$ catalyst in 7:1 (v/v) water/ethanol using 1 MPa hydrogen for 60min at 373 K.

Fig.2 Product yields for the HDC reaction of CLAP over Rh/SiO$_2$ –TS catalyst in 7:1 (v/v) water/ethanol using 1 MPa hydrogen for 60min at 373 K.