

Liquid phase hydrodechlorination of perchloroethylene over 0.8 wt. % Pd/TiO₂ sol-gel

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Introduction

Perchloroethylene (PCE), a suspected human carcinogen, widely used in dry cleaning, metal degreasing and paint stripping industrial processes has become one of the most widely detected chlorinated organic solvents in the environment, especially in ground and waste waters. Therefore, the detoxification of PCE is an important environmental and social concern [1]. Catalytic hydrodechlorination over heterogeneous catalysts is a highly efficient, safe alternative technology for the degradation of organic halides. A number of catalysts have been proposed for the hydrodechlorination of organochlorinated compounds in liquid phase. Among them, palladium-supported catalysts are highly active and selective [2].

Molecular hydrogen has been often used as a hydrogen source. Notwithstanding, studies of catalytic hydrodehalogenation using other hydrogen donors such as alcohols and formates have been performed in combination with heterogeneous catalysts. The hydrogen-transfer process generally proceeds under relatively mild conditions, having advantages not only in reducing energy costs but also suppressing the formation of undesirable by-products [3,4]. In the present study, gaseous hydrogen, formic acid and isopropanol were investigated as reductants for the hydrodechlorination of PCE over 0.8 wt. % Pd/TiO₂ sol-gel catalysts samples in methanolic solutions of NaOH under mild conditions.

Materials and Methods

0.8 wt-% Pd/TiO₂ sol-gel catalyst samples were prepared by incipient wetness impregnation using a palladium (II) acetylacetonate as precursor salt. Catalyst samples were crushed, sieved to particle size between 63-90 μm, calcined in air at 300 °C and pretreated at 300 °C in flowing 5 % H₂/N₂. Fresh and used samples were characterized by a wide range of physicochemical techniques such as N₂ adsorption-desorption, TGA-DTA, TEM, XRD, UV-VIS, AAS, NH₃-TPD-MS, TPR-MS, FTIR, H₂-chemisorption. Liquid-phase catalytic hydrodechlorination was carried out in a 4590 Parr reactor (25 mL) at a constant agitation speed of 1685 rpm. All reactions were conducted with an overall liquid volume of 20 mL, an initial PCE concentration of 3 mM in methanol, and varying amounts of NaOH and catalyst (5-100 mg). The reaction temperature was 20 ± 2°C. The concentration of PCE was determined by GC equipped with a FID and a DB-1 column. Carbon tetrachloride was used as the internal standard. The amount of NaCl produced was determined by titration, using K₂CrO₄ as indicator.

Results and Discussion

Diffusion problems under the operating conditions were checked following the Koros-Nowak criterion. Hydrodechlorination was first order with respect to PCE with all hydrogen sources. The first order degradation rate constants of PCE are shown in table 1. Formic acid was found to be less reactive than H₂ and isopropanol. Isopropanol is effective as H-donor for hydrodechlorination under alkaline conditions; however, the reaction is slower than with H₂.

Table 1 Reaction rate constants of PCE with different hydrogen sources

Reductant Agent	Reaction rate constant min ⁻¹
Hydrogen	0.2617
Isopropanol	0.0003
Formic Acid	0.0006

NaOH addition remarkably increased the degradation rate of PCE with all reductant agents, for NaOH/Cl_{substrate} ratios greater than unit. However, the concentration of NaOH must not be allowed to become too high, since a strong alkali medium can destroy the porous system of the catalyst support and dissolve supported Pd. In addition, NaCl produced by neutralization of HCl, might deposit on Pd/TiO₂ blocking TiO₂ pores thereby inhibiting the adsorption and activation of PCE. Figure 1 shows the effect of NaOH on hydrodechlorination of PCE with hydrogen. BET of used samples was 45.2501 g/m² while that of fresh catalysts 51.0313 g/m². The decrease of the surface area is attributed to occlusion of sol-gel TiO₂ mesopores. Although Pd particles remain in a metallic state after reaction as revealed by UV-Vis DRS, FTIR analyses of used Pd/TiO₂ samples suggest that the surface of both support and metal particles may be partly covered with by-products of the reaction or species from metal precursor.

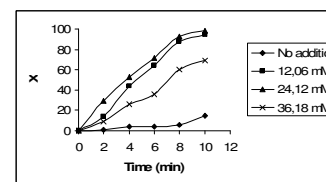


Figure 1 The effect of NaOH on PCE hydrodechlorination with hydrogen; PCE: 3 mM, H₂ pressure: 12.5 psi, temperature: 20 ± 2°C, catalyst: 5 mg of 0.8%Pd/TiO₂.

Significance

Empirical kinetic parameters (reaction order and rate constants) for catalytic hydrodechlorination of PCE over Pd/TiO₂ were determined using different hydrogen sources. Also the most appropriate amount of NaOH was found when molecular hydrogen was used as reductant.

References

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