Catalytic Hydrodechlorination of PCBs by Pd/SBA-15 under Mild Condition

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Introduction

Polychlorinated biphenyls (PCBs) are mainly destroyed by incineration and thermal destruction methods. However, incomplete oxidation of PCBs results in forming more high toxic pollutants such as dioxins. Hydrodechlorination (HDC) of PCBs can convert these toxic pollutants into safer compounds or useful chemicals [1]. Catalytic hydrodechlorination proceeds in liquid and vapor phases mainly using supported metals of Group III like Pd, Pt, Ni, Fe etc. The metal of Pd is considered as the best catalyst among all metals of the VIII group because HDC reaction can progress efficiently under mild conditions [2,3]. Pd catalysts are stabilized on variable supports with high surface area, which leads to high proportion of Pd atoms on surface and high reactivity of catalytic HDC. Several substrates such as activated carbon [4], nanosized silica and alumina [5] have been used as Pd supports. A family of mesoporous silica molecular sieves with high surface area and controllable pore size with an ordered structured designated as M41S and SBA families, is of considerable interest for heterogeneous catalysis and material science [6].
As our best knowledge, few HDC catalysts use Pd/MCM or Pd/SBA. Takehira et al. have carried on the HDC reaction over Pd/AlMCM-41 via template-ion exchange method showing high activity for the hydrodehalogenation of aryl halide compounds [7]. The mesoporous SBA-15 materials possess much larger pore size and numerous micropore channels to interconnect mesopores to permit organic compound entrance into the channel easily [8]. Herein Pd/SBA-15 catalyst was preparing and its activity tendency for HDC was studied.

Material and Method

Synthesis of Pd supported catalyst

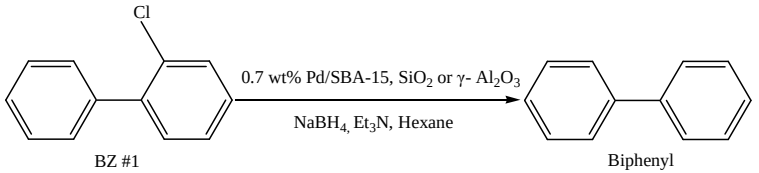
The SBA-15 silica materials were prepared by hydrothermal synthesis method. Pluronic P123, and tetraethyl orthosilcate were used as the sources of the template and silica, respectively. In typical synthesis, block copolymer P123 was dispersed in 2 M HCl(aq) and then this solution was mixed with tetraethyl orthosilicate under stirring. The mixture gel was stirred at room temperature for 24 h and then crystallized at 90 °C for 24 h. The resulting solid was isolated by filtration and washing, and dried in oven at 100℃, then calcined at 550°C for 6h. Typically, 0.7 wt% Pd supported catalysts were prepared by the wet impregnation of SBA-15, γ -Al_2O_3 (220 m2/g) and fumed silica (390 m2/g) with the appropriate amounts of H_2O and palladium nitrate and vigorous stirring at room temperature for 4h. The resultant solid was recovered by filtration and washed by DI water, thereupon dried at 70 °C for 24h. The dried sample was calcined at 500 °C for 2h and white powder was obtained.

Hydrodechlorination

The liquid-phase HDC reaction was performed under atmospheric pressure at room temperature. Typically, 0.1 g of the catalyst was suspended with 30 ml of hexane containing 10 ppm of PCBs in a 50ml flask , then 0.16 g of fresh $NaBH_4$ was added under stirring for 4 h. The reaction products were analyzed by GC-MS.

Result and Discussion

2-monochlorobiphenyl (BZ #1) was chosen as the model compound for the catalytic investigation of HDC of PCBs. The catalytic properties of Pd/SBA-15, Pd/fumed silica and Pd/γ-Al_2O_3 were studied at room temperature for variable reaction time in Scheme 1 and Figure 1. The reaction conditions were shown in scheme 1. The HDC of PCBs using 0.7 % Pd/SBA-15 was completed within 1 h for 100% conversion of BZ #1. However, two and four hours of reaction time were needed for 100% conversion of BZ #1 using the catalysts of Pd/γ-Al_2O_3 and Pd/fumed silica respectively. The activity of studied catalysts varied in the order Pd/SBA-15 > Pd/α Al_2O_3 > Pd/fumed silica. The oxidation states and dispersion will be further investigated by temperature programmed reduction, ESCA, TEM and N_2 adsorption/desorption isotherms.



Scheme 1. Hydrodechlorination of BZ #1 using Pd/SBA-15, Pd/SiO_2 and Pd/γ- Al_2O_3.

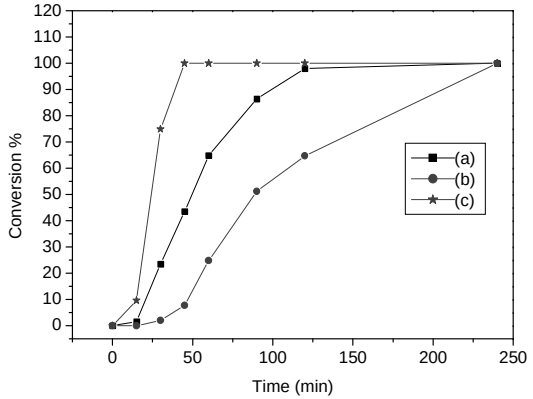


Figure 1. The catalytic activity of various substrates. (a) Pd/ γ -Al2O3, (b) Pd/SiO_2, (c) Pd/SBA-15

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