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Influence of preparation procedure on catalytic activity of PdBEA zeolites in aqueous phase hydrodechlorination of 1,1,2-trichloroethene

Izabela I. Kamińska [a], [**], Dmytro Lisovytskiy [a], Sandra Casale [b], Anna Śrębowata [a], Stanislaw Dzwigaj [b], [*]

[a] Institute of Physical Chemistry, PAS, Kasprzaka 44/52, PL-01224 Warsaw, Poland
[b] Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 7197, Laboratoire de Réactivité de Surface, 4 Place Jussieu, Case 178, 75252 Paris, France

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ABSTRACT

Pd-loaded BEA zeolites containing 1 wt % of Pd were prepared by a two-step postsynthesis method (PdSiBEA and PdSiAlBEA) and a conventional wet impregnation (PdHAlBEA). Modification of BEA zeolite resulted in the introduction of Pd ions into zeolite framework as pseudo-tetrahedral Pd(II) and extra-framework octahedral Pd(II) evidenced by XRD, DR UV–vis and TPR measurements. Calcination of as prepared zeolites in air at 773 K for 3 h and then reduction in 10% H_2/Ar flow at 873 K for 3 h led to obtain red-C-PdSiBEA, red-C-PdSiAlBEA and red-C-PdHAlBEA zeolites with different Pd nanoparticles size distributions showed by TEM. These zeolite materials were found to be active catalysts in aqueous-phase hydrodechlorination of 1,1,2-trichloroethene (TCE). The conducted catalytic reactions have demonstrated that the rate and course of TCE hydrodechlorination depend on the catalysts preparation method and Pd nanoparticles size.

1. Introduction

Palladium as noble metal has a wide application in catalytic reactions. It accelerates many hydrogenation and dehydrogenation reactions due to its excellent properties [1–4]. Palladium is also the most extensively used metal in purification of air and water containing toxic substances such as volatile organic compounds (VOCs) [5,6]. Particular attention should be focused on the removal of chlorinated hydrocarbons like 1,2-dichloroethane (DCA), 1,1,2-trichloroethene (TCE) and 1,1,2,2-tetrachloroethene (PCE), because of their potential carcinogenic and mutagenic effects on living organisms [7–9]. The application of Pd in the hydrodechlorination (HDC) processes allows to easily, cheaply and without damage of environment transforming harmful chemicals into less toxic products like ethane or ethene [10–12].

High hydrodechlorination efficiency of Pd could be affected by a number of factors such as the metallic nanoparticle size, its shape, oxidation state and interaction with the support, among others [13,14]. A number of authors have deduced that Pd nanoparticle size is crucial for the performance of HDC reactions [15–20]. One of their hypothesis is that bigger Pd nanoparticles are more active and resistant for reaction conditions [15–17]. However, the others have proved the superiority of small nanoparticles, because of its higher surface-to-volume ratio [18–20]. One of the first reports pertains to research carried out by Juszczyk et al. [15]. They noticed that catalytic activity of Pd/γ-Al_2O_3 in gas-phase hydrodechlorination of CCl_2F_2 was strongly related to Pd dispersion: the samples with the lowest metal dispersion exhibited the highest turnover frequencies. Aramendía et al. [16] observed similar effect in liquid-phase hydrodechlorination of chlorobenzene over Pd-supported catalysts. In this case, the change of dispersion from 54 to 7% corresponded to an increase in catalytic activity by a factor of 20. In addition, they noticed a better resistance to chlorine, when the size of Pd nanoparticles increased.

On the other hand, several authors present a different view [18–20]. Gómez-Quero et al. [18] analyzed the effect of metal dispersion on the liquid-phase hydrodechlorination of 2,4-dichlorophenol over Pd/Al_2O_3. They observed a significant decrease in reaction rate with a decrease in palladium dispersion from 67% to 25%, with only residual activity in case of the catalyst with 8% dispersion. Dong et al. [19] also reported that magnetic

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: iikaminska@ichf.edu.pl (I.I. Kamińska), stanislaw.dzwigaj@upmc.fr (S. Dzwigaj).

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porous carbon composite supported palladium nanoparticles (5 nm) displayed high efficiency in HDC of chlorophenols.

Moreover, the appropriate support has also a significant influence on catalytic activity and stability of Pd catalysts [17]. The most popular Pd supports are activated carbons, silica, titania and alumina [15–19,21]. Recently, the significant surge of interest in zeolite materials has been observed due to their specific properties (cation exchange, shape selectivity and acidity) [20,22,23]. Śrębowata et al. [20] have found a beneficial effect of desilication of HZSM-5 zeolite on PdHZSM-5 activity in aqueous-phase hydrodechlorination of TCE. It seems to us to be very interesting to investigate the influence of dealumination process on the activity of Pd-loaded zeolites in TCE removal from water. Therefore, we decided to synthetize Pd-loaded BEA zeolites with different dealumination stage and checked their properties by characterization using different techniques and investigated catalytic reaction with TCE in aqueous-phase.

Very interesting results obtained for transition metals-loaded BEA zeolites used in gas-phase HDC [24–27] were the motivation to investigate the effect of preparation procedure on the catalytic properties of Pd-loaded BEA zeolites in aqueous phase hydrodechlorination of 1,1,2-trichloroethene.

2. Experimental

2.1. Catalysts preparation

TEABEA zeolite (Si/Al = 19) provided by RIPP (China) was divided into three portions. First portion was treated by a 13 mol L^{-1} HNO_3 solution for 4 h at 343 K to obtain completely dealuminated SiBEA zeolite (Si/Al = 1300). Second portion was treated by a 13 mol L^{-1} HNO_3 solution for 3.5 h at 343 K to obtain partially dealuminated SiAlBEA zeolite (Si/Al = 940). The resulting zeolites with vacant T-sites were recovered by centrifugation, washed with distilled water and dried overnight at 353 K. Third portion of TEABEA was calcined in air at 823 K for 15 h under static conditions to remove organic template, then treated two times with 0.1 mol L^{-1} NH_4NO_3 solution (400 mL) during 3 h at 343 K. Resulted NH_4AlBEA was washed with distilled water and dried overnight at 363 K and next calcined in air at 773 K for 3 h under static conditions to remove NH_3 and obtain HAlBEA zeolite (Si/Al = 17).

Palladium-loaded BEA zeolites were prepared by impregnation of SiBEA, SiAlBEA and HAlBEA under ambient conditions by a 9.4×10^{-4} mol dm^{-3} aqueous solution of $PdCl_2$ (pH in the range of 3.0–3.4). First, 2 g of each zeolite materials were stirred at room temperature for 24 h in excess solvent using 200 mL of the palladium chloride solution (pH in the range of 2.9–3.3) and then the suspensions were stirred in a rotary vacuum evaporator at 333 K for 2 h until complete evaporation of water. The resulting light-brown solids containing 1 wt % of Pd were labelled as PdSiBEA, PdSiAlBEA and PdHAlBEA. Next, all these materials were calcined in air flow at 773 K for 3 h and labelled C-PdSiBEA, C-PdSiAlBEA and C-PdHAlBEA, respectively. Then, small portions of these materials were reduced at 873 K for 3 h in 10% H_2/Ar flow to obtain red-C-PdSiBEA, red-C-PdSiAlBEA and red-C-PdHAlBEA.

2.2. Catalysts characterization and catalytic tests

2.2.1. Diffuse reflectance UV-vis spectroscopy

Diffuse Reflectance (DR) UV-vis spectra of as prepared samples were recorded at ambient atmosphere on a Cary 5000 Varian spectrometer (DR UV–Vis scan rate 10 nm s^{-1}, data interval 1 nm) equipped with a double integrator with polytetrafluoroethylene as reference.

2.2.2. Physisorption

Surface areas and porosities of calcined samples were measured with an ASAP 2020 instrument from Micromeritics, employing the BET (Brunauer-Emmett-Teller) and HK (Horwath-Kawazoe) methods using nitrogen as adsorbate. Before measuring the adsorption isotherm at 77 K, the samples were kept at 473 K for 4 h in vacuum remove adsorbed water and gases.

2.2.3. Temperature-programmed reduction

Temperature-Programmed Reduction (TPR) of calcined samples was carried out using glass flow system equipped with a Gow-Mac thermal conductivity detector. TPR runs were performed in 10% H_2/Ar flow (25 cm^3 min^{-1}), ramping the temperature at 10 K min^{-1}, started from 260 K to 973 K. Injections of known amounts of hydrogen into the H_2/Ar flow were provided for calibration (before and after each TPR run).

2.2.4. Chemisorption

Chemisorption measurements of CO using a conventional static method were carried out with an ASAP 2020 Chem. instrument from Micromeritics. Prior to chemisorption measurement 0.1 g of calcined Pd-loaded BEA zeolite was reduced in 10% H_2/Ar flow (25 cm^3 min^{-1}), ramping the temperature from room to 873 K (at 10 K min^{-1}) and kept at 873 K for 3 h. Then the catalysts were cooled down to the room temperature and connected with the ASAP 2020 Chem. instrument. Chemisorption measurements were carried out according to the procedure described previously [24].

2.2.5. TCE hydrodechlorination

Hydrodechlorination of TCE in aqueous-phase were performed in a 500 mL round bottomed flask equipped with a pH-meter, magnetic stirring bar and temperature controller, using 350 mL of MiliPore water and 20 μL of TCE and 0.1 g of reduced catalyst (at 873 K for 3 h in 10% H_2/Ar flow). Each reaction was carried out at 303 K with continuous stirring (1000 rpm). Before adding the substrate, the water had been saturated with hydrogen for 30 min and then the catalyst was added to reaction mixture. Reaction samples were taken at 0, 2, 5, 10, 15, 20, 60, 90, 120 and 150 min of reaction. The substrate concentration and product distributions were monitored using a gas chromatographic set-up (Bruker 456-GC with ECD and FID detectors, Headspace SHS-40) at it was reported earlier [25]. Samples after hydrodechlorination of TCE were labelled as spent-red-C-PdSiBEA, spent-red-C-PdSiAlBEA and spent-red-C-PdHAlBEA, respectively.

2.2.6. X-Ray diffraction

X-Ray Diffractograms (XRD) of as prepared samples were recorded at ambient atmosphere on a BRUKER D8 Advance diffractometer using the Cu Kα radiation (λ = 154.05 p.m.) in the 2θ range of 5–90°. XRD profiles of samples after reduction and reaction were recorded on a Siemens D5000 diffractometer using Ni-filtered Cu Kα radiation in the 2θ range of 5–90°.

2.2.7. Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) studies for the catalysts after reduction step and after catalytic reaction were carried out using JEOL JEM-100CXII electron microscope operated at an acceleration voltage of 100 keV. The samples before TEM investigations were dispersed in pure alcohol using ultrasonic cleaner and putting a drop of this suspension on carbon films on copper grids.