



## Development of reusable palladium catalysts supported on hydrogen titanate nanotubes for the Heck reaction



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### ABSTRACT

Palladium catalysts supported on hydrogen titanate nanotubes were prepared by adsorption of palladium (II) acetate from dichloromethane solutions. At low Pd(OAc)<sub>2</sub> loadings (up to 5 wt.%), the catalysts contained only highly dispersed chemisorbed Pd<sup>0</sup> and Pd<sup>2+</sup>O species (XPS). Characteristic signals of Pd(OAc)<sub>2</sub> were not detected in these catalysts by FT-IR, FT-Raman, or XPS, indicating decomposition of the precursor salt due to the strong metal–support interaction. An increase in the palladium loading resulted in an increase in the proportion of Pd<sup>0</sup> species and the appearance of some supported Pd(AcO)<sub>2</sub> (XPS). In the sample with the highest palladium loading (8.84 wt.% of Pd(OAc)<sub>2</sub>), formation of small (~1.2–2.4 nm) palladium-containing clusters was detected on the support surface by HRTEM. Catalytic activity was tested in the Heck reaction between 4-bromobenzaldehyde or 4-bromostyrene and styrene. Only the E-isomers of the corresponding cross-coupled products were obtained. The activity and TON numbers of the supported Pd catalysts were higher than those of the palladium(II) acetate under homogeneous catalysis conditions. Strong palladium–support interaction resulted in the generation of catalytically active Pd(0) species without additional reduction pretreatment of the catalyst. The possibility of reuse of the same catalysts in several catalytic cycles was tested. It was found that both the Pd loading in the catalysts and the amount of water in the support have a strong influence on the catalyst's deactivation. A catalyst with stable activity, able to be recycled at least five times, was prepared with Pd loading of 5 wt.% of Pd(AcO)<sub>2</sub> using titanate nanotubes calcined at 350 °C for 2 h prior to the preparation of the catalyst.

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## 1. Introduction

Carbon–carbon bond formation is a general aim in organic chemistry synthesis catalyzed by transition metals yielding valuable fine chemicals. The Heck coupling reaction is an effective method for the C–C cross-coupling of aryl halides with aryl or alkenyl compounds, leading to a variety of alkenes with great pharmaceutical and industrial value [1–3]. The growing demand for fine chemicals in the industries and increasingly stringent ecological standards require development of new technologies for cross-coupling reactions catalyzed by transition metal catalysts in order to provide convenient synthetic routes for regio- and stereodefined systems [4,5]. Different palladium catalysts, homogeneous and heterogeneous, have been widely used for the cross-coupling Heck

reaction, giving good results. Nevertheless, homogeneous Heck catalysis has some drawbacks, such as difficulty of catalyst separation and reuse after the reaction, as well as facile deactivation leading to limited catalyst lifetime. Because of this, in the past few years, several attempts have been made to prepare active, stable, and easy-to-handle and -separate palladium catalysts. Palladium catalysts supported on different materials (carbon [5], metal oxides [6], layered clays [7], zeolites [8], mesoporous molecular sieves [9], carbon nanotubes [10], etc.) or encapsulated in large organic structures (dendrimers [11], block copolymer micelles [12], etc.) have attracted much attention. The interest in them is due principally to the fact that immobilization of Pd nanoparticles on the surface of a solid material or inside an organic matrix makes it possible to stabilize catalytically active well-dispersed metal species and prevent their sintering. In [9], Pd-TMS11 catalysts with high Pd dispersion (25–32%) were prepared by the vapor grafting of a volatile organometallic complex [Pd(η-C<sub>5</sub>H<sub>5</sub>)-(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] onto the surface of

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Nb-MCM-41 material previously degassed at 600 °C, followed by the reduction of the catalyst in a stream of hydrogen at 350 °C for 3 h. These catalysts showed high catalytic activity (TON numbers between 1000 and 5000) for the cross-coupling Heck reaction of *n*-butyl acrylate with activated aryl substrate. However, the Pd-TMS11 catalyst, recovered after the catalytic test, showed some agglomeration of palladium and partial structural damage of the Nb-MCM-41 support material [9]. In [10], poly(lactic acid) grafted carbon nanotubes (*f*-CNTs) were used as a platform for in situ deposition of Pd nanoparticles. The obtained catalysts were found to be effective in the promotion of the Heck cross-coupling reaction between aryl halides and *n*-butyl acrylate. The recycled *f*-CNTs-Pd nanocatalyst showed stable activity in another three reaction cycles. However, up to now, the search for new heterogeneous catalysts with well-dispersed and stable supported Pd species remains an incomplete task.

In the present work, palladium catalysts supported on hydrogen titanate nanotubes were prepared and tested in the cross-coupling Heck reaction. Hydrogen titanate nanotubes are a novel and intensively studied material that has attracted much attention in the past decade because of its unique textural and physicochemical properties [13–16]. This material found a variety of applications, including catalysis [17,18] and photocatalysis [19,20]. Titanate nanotubes have high specific surface area (~200–400 m<sup>2</sup>/g), internal tube diameter between 3 and ca. 10 nm, open mesoporous morphology [21,22], and an absence of micropores that facilitate transport of reagents and products during a catalytic reaction. The high cation exchange capacity [14,23] of hydrogen titanate nanotubes should enable high loading of an active catalyst with even distribution and high dispersion. The semiconducting properties of titanate nanotubes [24,25] may result in a strong electronic interaction between the support and a catalyst, which could be beneficial for some catalytic reactions. Palladium catalysts supported on titanate nanotubes have already been prepared by an ion-exchange technique [23,26], incipient wetness impregnation [27], and photodeposition [28] and by hydrothermal synthesis of titanate nanotubes with the simultaneous addition of a PdCl<sub>2</sub> precursor [29]. In all these cases, water was used as a solvent. Palladium catalysts with different characteristics were obtained depending on the preparation method used and the palladium loading. Here we report on the synthesis of palladium catalysts supported on hydrogen titanate nanotubes by adsorption of Pd(II) acetate from a nonaqueous solvent (dichloromethane). We selected this method of preparation because of its simplicity and the possibility of deposition of palladium species only by interaction with the support. Catalysts were characterized and tested in the Heck reactions between activated aryl substrates (4-bromobenzaldehyde or 4-bromostyrene) and styrene.

## 2. Experimental

### 2.1. Support and catalyst preparation

Sodium titanate nanotubes were synthesized by an alkali hydrothermal treatment following a procedure reported by Kasuga et al. [13,30]. Commercial titanium dioxide (anatase, Aldrich, 54 m<sup>2</sup>/g) was used as the TiO<sub>2</sub> source. In each synthesis, 10 g of TiO<sub>2</sub> was mixed with 150 ml of a 10 M alkali solution, followed by hydrothermal treatment in a Teflon-lined autoclave at 140 °C for 20 h under constant magnetic stirring. After the hydrothermal reaction, the white powder of sodium titanate nanotubes (NaNT) was filtered in vacuum, thoroughly washed with deionized water to eliminate the excess of nonreacted NaOH, and dried at 120 °C for 12 h. To decrease the sodium content, the dry NaNT was slurried into a 0.1 M HCl solution for 2 h (100 mL of solution per 2 g

of NaNT), filtered, washed with deionized water, and dried again at 120 °C for 12 h. This procedure resulted in the formation of hydrogen titanate nanotubes with low content of residual sodium (below 0.1 wt.%), which will be denoted hereafter as NT. Part of the synthesized NT material was calcined at 350 °C for 2 h (NTc sample). Palladium catalysts supported on the synthesized NT or NTc were prepared by adsorption of Pd(II) acetate (Pd(OAc)<sub>2</sub>) from dichloromethane solutions. Briefly, 1 g of the support was slurried in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> solution of Pd(OAc)<sub>2</sub> for 8 h at room temperature. After the first hour of this treatment, the white powder of the support changed color to light brown, whose intensity depended on the initial concentration of Pd(OAc)<sub>2</sub>. The catalysts were filtered, washed with a small amount of CH<sub>2</sub>Cl<sub>2</sub>, and dried at room temperature and then at 120 °C for 12 h. The remaining solutions were analyzed by atomic absorption spectroscopy (Perkin–Elmer) to determine the quantity of adsorbed palladium. In addition, palladium loading in the dried catalysts was determined by SEM-EDX, giving good correlation between both techniques. Four catalysts with nominal Pd(OAc)<sub>2</sub> loadings between 2.5 and 10 wt.% were prepared using the NT support and two catalysts using the NTc material. Hereinafter, the prepared catalysts are designated as Pd(*x*)/NT or Pd(*x*)/NTc, where *x* is the theoretical wt.% of Pd(OAc)<sub>2</sub> in the catalyst.

### 2.2. Catalyst characterization

Obtained hydrogen titanate nanotubes (NT and NTc) and catalysts were characterized by N<sub>2</sub> physisorption, X-ray powder diffraction (XRD), scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and FT-IR, FT-Raman, and X-ray photoelectron spectroscopy (XPS). Nitrogen adsorption–desorption isotherms were measured with a Micromeritics ASAP 2020 automatic analyzer at liquid N<sub>2</sub> temperature. Prior to the experiments, the samples were degassed (*p* < 10<sup>−1</sup> Pa) at 250 °C for 6 h. Specific surface areas (*S*<sub>BET</sub>) were calculated by the BET method, the total pore volume (*V*<sub>p</sub>) was determined by nitrogen adsorption at a relative pressure of 0.98, and pore diameters (*D*<sub>p</sub>) and pore size distributions were obtained from the adsorption isotherms by the BJH method. The X-ray powder diffraction patterns of the synthesized samples were recorded at room temperature from 3 to 80° (2θ) on a Bruker D8 Advance diffractometer, using Cu Kα radiation (λ = 1.5406 Å) and a goniometer speed of 1° (2θ) min<sup>−1</sup>. The chemical composition of the synthesized materials was determined by SEM-EDX using a JEOL 5900 LV microscope with OXFORD ISIS equipment. High-resolution transmission electron microscopy (HRTEM) images were recorded with a JEOL 2010 microscope operating at 200 kV (resolving power 1.9 Å). The solids were ultrasonically dispersed in heptane and the suspension was collected on carbon-coated grids. HRTEM pictures were taken from different parts of the same sample dispersed on the microscope grid. TGA analysis was used to determine the amount of chemisorbed water in the synthesized materials. TGA experiments were performed on a Mettler-Toledo TGA/SDTA 851<sup>e</sup> in dry air flow (50 ml/min) in the temperature range between 25 and 1000 °C with a heating rate of 10 °C/min. FT-IR spectra were recorded on a Varian 640-IR spectrometer equipped with a PIKE accessory. Micro-Raman spectra of the catalysts were obtained using an HR LabRam 800 system equipped with an Olympus BX40 confocal microscope. A Nd:YAG laser beam (532 nm) was focused by a 50× microscope objective onto an ≈1 μm diameter on the sample surface. The laser power at the sample was regulated by a neutral density filter (OD = 1) to prevent sample heating and structural changes induced in the sample. A cooled CCD camera was used to record the spectra, usually averaged for 100 accumulations in order to improve the signal-to-noise ratio. All spectra were calibrated using the 521 cm<sup>−1</sup> line of

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