

Supplementary Information

Covalently Anchored 2, 4, 6-triallyloxy-1, 3, 5-triazine Pd(II) Complex over Modified Surface of SBA-15 : Catalytic Application in Hydrogenation Reaction

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EXPERIMENTAL

Materials

Tetraethylorthosilicate (TEOS), Pluronic 123 (P₁₂₃, Average Mol. wt. = 5800), 3-Mercaptopropyl trimethoxysilane (3-MPTMS), 2, 4, 6-triallyloxy-1, 3, 5-triazine, Azo-bisisobutyronitrile, Palladium acetate, Olefin, Aromatic olefins, Nitrobenzene were purchased from Aldrich. All solvents used in experiments were obtained from Merck (India) and dried before use according to standard methods [1].

5.2.2. Synthesis Procedure of Catalyst

5.2.2.1. Synthesis of SBA-15 and Surface Modifications

The synthesis of mesoporous SBA-15 was carried out hydrothermally under the autogeneous pressure of an autoclave. The polymer surfactant P₁₂₃ was used as a template and hydrochloric acid served as a mineralizer. The following gel composition was used for the synthesis.

0.043 TEOS: 4.4 g P₁₂₃ M_{avg} = 5800 = [EO₂₀-PO₇₀-EO₂₀]: 8.33 H₂O: 0.24 HCl.

Typically, 4.4 g of tri block co-polymer dispersed in 30 g of distilled water was stirred for 1.5 h. To the resultant solution, 120 g of 2 M HCl was added under stirring and the

stirring was continued for 2 h. Finally, 9 g of TEOS was added drop wise and the mixture was maintained at 40 °C for 24 h with continuous stirring. The mass was submitted to a hydrothermal treatment (100 °C, 48 h) under static condition. The precipitate was filtered, washed with distilled water, dried in an oven (90 °C, 12 h) and then calcined in air (500 °C, 6 h) to remove the template. The calcined SBA-15 was characterized by powder XRD [2].

Surface modification of SBA-15 was achieved by a post grafting method [Scheme 1(A)]. One gram of SBA-15 was suspended in a 100 mL of dry toluene and refluxed with 2.5 mmol of 3-Mercaptopropyl trimethoxysilane (3-MPTMS) for 12 h under N₂ atmosphere. The material was filtered after cooling to ambient temperature, washed with dry toluene and dichloromethane, respectively. Soxhlet extraction was carried out for 24 h in dichloromethane (DCM) to remove occluded organosilane. The sample was dried in vacuum for 10 h. The percentage loading of the 3-mercaptopropyl trimethoxysilane groups anchored on the SBA-15 was estimated from chemical analysis. The obtained material is designated as SBA-15-SH.

Procedure for Hydrogenation Reaction

In a typical liquid-phase Hydrogenation reaction, 1.0 g of olefin, 50 mL of methanol and 0.025 g of the catalyst were placed in a 100 mL Parr autoclave (*Parr Inst. Co. Mod. 3911*), pressurized with hydrogen (150 *psi*) and stirred at 40 °C for a specific time. Samples were periodically withdrawn from the reaction mixture, filtered off, and analyzed. Olefin conversion and selectivity were determined by using gas chromatography (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (5 µm cross-linked methyl silicone gum, 0.2 mm×50 m). Before GC analysis, the samples were centrifuged for 5 min at 4000 rpm. At the end of specified time, the contents were analyzed by GC. Control experiments in the absence of catalyst showed practically no (<1 %) reduction of substrate. Peak positions of various reaction products were compared and matched with the retention times of authentic samples.

All the hydrogenation reactions were carried out under optimized hydrogenation reaction parameters for the reproducibility of the products.

Instruments for Characterization

Powder X-ray diffractograms (XRD) of the materials were recorded using a PAN analytical X'pert Pro dual goniometer diffractometer. A proportional counter detector was used for low angle experiments. The radiation used was Cu K α (1.5418 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg-Brentano geometry (0.5–5 °; 0.2 °/min). Care was taken to avoid sample displacement effects. N₂ adsorption–desorption isotherms, pore size distributions as well as the textural properties of the hybrid materials were determined by using a Micromeritics ASAP 2020 instrument and Autosorb 1C Quantachrome USA. The program consisting of both an adsorption and desorption branch and typically ran at –196 °C after samples were degassed at 250 °C for 2 h. Specific surface areas were calculated via the BET model at relative pressures of P/P₀ = 0.06–0.3. The total pore volume was estimated from the uptake of adsorbate at a relative pressure of P/P₀ = 0.99. A JEOL JEM-3010 and Tecnai (Model F30) both operating at 300 KV were used for HRTEM samples observation. Samples were crushed and dispersed in isopropanol with low power sonication before putting a drop over carbon coated Cu grid for observation. Chemical analysis was carried out in a Lab Tam 8440 Plasma lab sequential mode ICP–OES Spectrometer and a Spectro Arcos ICP-OES instrument. Standard solution was used for calibration purpose. The scanning electron micrographs of the samples were obtained in dual beam scanning electron microscope (FEI company, model Quanta 200 3D) operating at 30 kV. The samples were loaded on stubs and sputtered with thin gold film to prevent surface charging and also to protect from thermal damage due to electron beam. ¹H NMR spectra were recorded on Bruker AC–200 instruments using deuteriated solvent. Liquid ¹³C NMR spectra were recorded on Bruker AC–200 instruments operating at 50 MHz. ¹³C NMR chemical shifts are reported in ppm relative to the central line of CDCl₃ (d 77.0). Solid-state ¹³C CP MAS NMR and ²⁹Si MAS NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer with a resonance frequency of 75.5 MHz and 59.6 MHz, respectively for ¹³C and ²⁹Si, and the chemical shifts were referenced to glycine and TMS respectively. Infrared spectra were recorded using a Perkin Elmer Spectrum one FTIR spectrophotometer. IR spectra were recorded in the range of 4000–400 cm⁻¹. Thermal analysis (TG-DTA) of the samples was conducted using a Pyris Diamond

TGA analyzer with a heating rate of 10 °C min⁻¹ under air atmosphere. Palladium core levels were studied using an ambient pressure photoelectron spectrometer and more details of the instrument are available in reference [3].

REFERENCES

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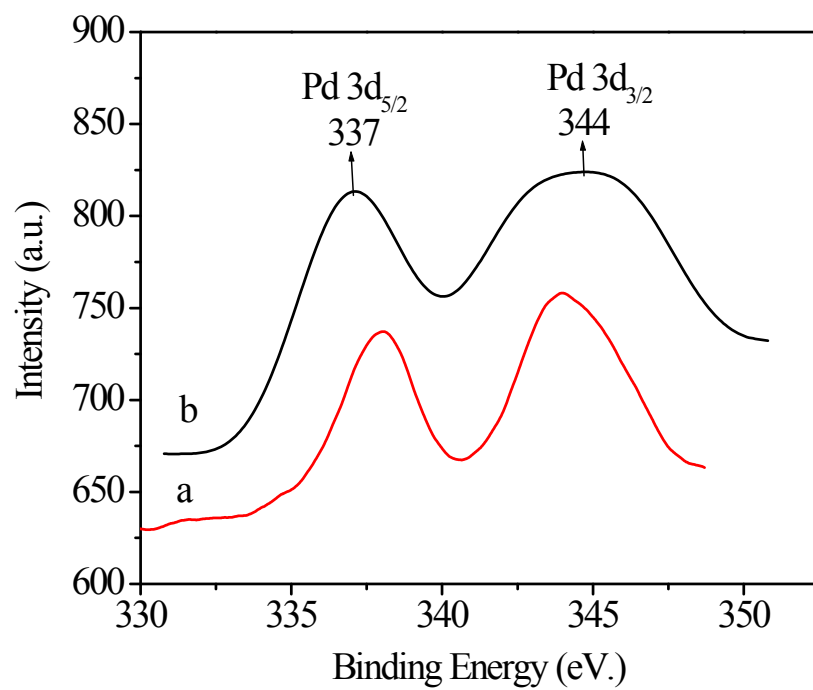


Figure S1. XPS spectra of SBA-15-TAT-Pd(II) (a) Fresh catalyst, (b) spent catalyst.