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Short Communication

Efficient clay supported Pd nanoparticles as heterogeneous catalyst for arylation of alkenes

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ABSTRACT

A new pincer-type ligand containing Pd(II) was immobilized on a modified bentonite. The material was evaluated as catalyst in the arylation of iodobenzene and several alkenes under room conditions. The catalyst combines high activity and selectivity, and can be reused three times with no observed deactivation.

1. Introduction

The arylation of alkenes under a palladium catalyst is referred as the Heck reaction. This reaction has become an important tool in organic synthesis [1–3]. The homogeneous palladium-based catalysts suffer from low stability and high costs, which prevent their application in industrial processes. As a metal, palladium is also highly undesirable as a contaminant of pharmaceutical products. In efforts to develop a heterogeneous catalyst for the Heck reaction, palladium salts or its complexes have supported on materials such as active carbon [4,5], mesoporous silica [6], inorganic oxide [7,8], molecular sieves [9], polymers [10], zeolites [11], hydrotalcites [12,13], and clays [14,15].

Our interest is the use of a modified clay material as a catalyst for the arylation of olefins. For that, we report the immobilization of a nonionic surfactant with multiple N groups on a bentonite modified with a cationic surfactant and the use of this material as support for the immobilization of palladium acetate. The amino groups in the surfactant were designed to coordinate with Pd(II) and additional amino groups could be varied in order to improve the performance of the complexes in catalytic reactions and prevention of palladium leaching. The new catalyst reported in this work does not require addition of phosphins, commonly introduced in to palladium catalyzed reactions, and exhibit high activity toward the Heck reaction of iodobenzene with olefins with small amount of palladium.

2. Experimental section

2.1. Preparation of immobilized palladium (II) on a modified bentonite

Synthesis, characterization, and immobilization of 3,3′-(dodecylazanediyl)bis(N-(2-(2-aminoethylamino)ethyl)propanamide) (DAEP) on a modified bentonite have been described in a previous work [16]. The modified bentonite at this stage has a layer of cationic surfactant (cetyl pyridinium) and a layer of DAEP. With the multiple amine groups on the surface of the bentonite, a suitable pincer-type ligand for immobilization of palladium nanoparticles have been designed (see Scheme 1).

In a typical experiment to prepare Pd(II)-bentonite composite, 0.5 g of the modified bentonite (DAEP-bentonite) was dispersed in 100 cm^3 of n-hexane to which 10^{-4} dm^3 of 10^{-2} mol/dm^3 of a aqueous solution of palladium acetate were added in ten steps to the suspension during 72 h, under vigorous stirring in a Morton flask. The resulting product was separated via centrifugation, and washed few times with distilled water. The solid was dried under vacuum at room temperature, before characterization and catalytic activity measurements. The amount of palladium in the catalyst was determined by ICP-AES method. The maximum palladium load achieved was 164 μmol/$g_{catalyst}$.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were recorded by using a Siemens D-500 diffractometer, at 40 kV and 30 mA, and employing filtered Cu Kα radiation over a 2θ range between 5 and 80°.

Scanning electron micrographs were obtained using a Cambridge Oxford 7060 Scanning Electron Microscope (SEM) connected to a

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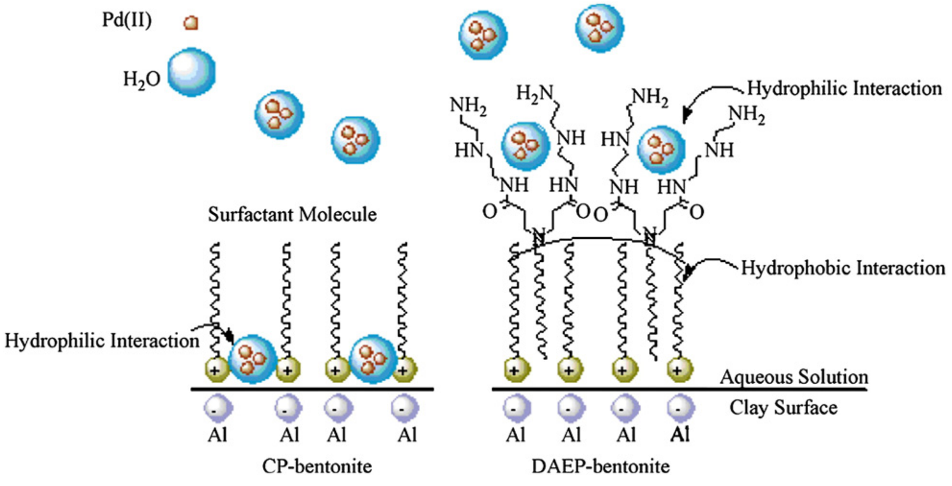

Scheme 1. Modification of the clay surface with a surfactant and impregnation of Pd particles.

four-quadrant backscattered electron detector with resolution of 1.38 eV. The samples were dusted on a double sided carbon tape placed on a metal stub and coated with a layer of gold to minimize charging effects.

FTIR spectra of the catalyst were recorded on a JASCO FTIR 680 plus spectrometer with the KBr pellet method.

2.3. Arylation of alkenes with iodobenzene

The reactions were carried at 130 °C in a sealed reactor immersed in a thermo-stated bath. A typical reaction run was as follows: 0.05 g of catalyst, 1 mmol of iodobenzene, 2 mmol of alkene, 2 mmol of base (NaOAc or triethylamine) and 3 cm^3 of DMF. The reaction mixture was heated to the desired temperature and stirred for 20–24 h. When the reaction was completed, the reaction mixture was centrifuged and the reaction products were analyzed by gas chromatography (Agilent, model 6890, equipped with a wide bone OV-17 capillary column and a FID detector). The products were identified by GC–MS (Fisons Instruments, model 8060).

3. Results and discussion

3.1. Synthesis of the catalyst

DAEP-dendrite was immobilized on a modified bentonite starting from bentonite with monolayer cetyl pyridinium cation coverage. This process was monitored by the adsorption isotherm of DAEP on modified bentonite. The FTIR spectrum of the catalyst contains peaks corresponding to the primary amino groups of the dendrite which appear at 3390 cm^{-1} and 3344 cm^{-1}, and shifted to 3358 cm^{-1} and 3300 cm^{-1} after complexation with metal [16]. The electronic spectrum of the complex showed a broad band at 450 nm, which may be due to charge transfer transition, and a band at 650 nm due to first excited transition [16].

3.2. X-ray diffraction analysis

The interlayer spacing of the original bentonite (Na-bentonite) is 12.3 Å [17], which has changed to 12.95 Å after adsorption of cationic surfactant, cetyl pyridinium bromide. However, by adsorption of the pincer-type surfactant (DAEP) onto the monolayer modified bentonite, the interlamellar distances did not change to a meaningful value (13.0 Å). Therefore, it was presumed that DAEP molecules adsorbed on the external surface of the monolayer modified bentonite and edges of the layers, and could not penetrate into the interlamellar spaces of the bentonite. Also it should be mentioned that by loading the support with palladium, the interlayer space increased to 13.21 Å, which probably means that some of the palladium ions with their water shells penetrated into the bentonite layers.

3.3. SEM

The SEM images of the modified bentonites with or without palladium nanoparticles are shown in Fig. 1. Palladium nanoparticles had a strong influence on the morphology of the support. The Na-bentonite after modification with cetyl pyridinium bromide has found a pack type aggregation of the particles [18]. This packed structure completely changed when it was modified with DAEP in the next step (Fig. 1B). The hydrophilic nature of the head of DAEP seems to

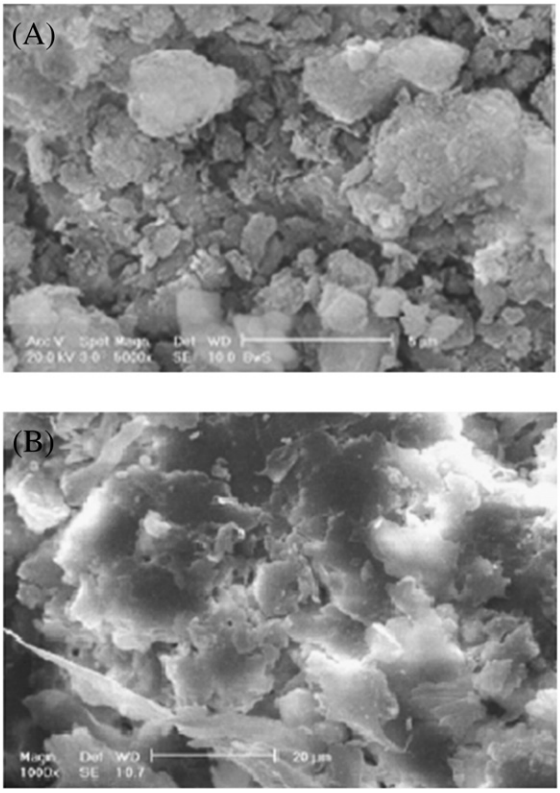

Fig. 1. SEM images of (A) Na-bentonite; (B) DAEP-bentonite with Pd(II).