



Suzuki-Miyaura cross-coupling of phenylboronic acid with aryl halides catalyzed by palladium and nickel species supported on alumina-based oxides



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ABSTRACT

Two different kinds of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ have been prepared by the alkoxide sol-gel process: bulky-shaped and formed into spherical granules with the diameter of 2–3 mm. The catalysts have been obtained either by impregnating the support with the metal precursor (Pd or Ni salt solution) or by simultaneous addition of the precursor during synthesis of the support (the co-precipitation technique). The catalysts have been characterized structurally with scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption studies and successfully applied in the Suzuki-Miyaura cross-coupling of phenylboronic acid with different kinds of aryl halides (2-bromotoluene, 4-bromotoluene, 4-bromoanisole or 4-iodoanisole). Our experiments have shown that nickel species supported on $\text{Al}_2\text{O}_3\text{-ZrO}_2$ can be successfully employed as the catalyst in the Suzuki-Miyaura process.

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1. Introduction

Carbon-carbon bond-forming processes are known as versatile tools in organic synthesis [1–4]. Among them, a special place is occupied by the Suzuki-Miyaura reaction, which is an efficient method of asymmetric biaryls preparation from an aryl halide and boronic acid, with high tolerance to the presence of functional groups as the substituents [5,6]. The biaryl compounds are important substrates in the synthesis of pharmaceuticals and herbicides [7].

The Suzuki-Miyaura cross-coupling is commonly known as a palladium-catalyzed process [8,9]. However, the application of much cheaper nickel species is a very attractive alternative. Only few examples of the Ni-catalyzed Suzuki-Miyaura cross-couplings of aryl halides have been published until now [10–19].

In the present work we report preparation of nanostructured binary $\text{Al}_2\text{O}_3\text{-ZrO}_2$ oxides in a form of bulky-shaped pieces or molded into spherical granules. These mixed metal oxides, used as the supports for the catalytically active metal species, might exhibit several advantages over the usually employed Al_2O_3 . Alumina-zirconia mixed oxides might be prepared by several methods, but only the sol-gel process offers the possibility of making structures

of high surface area, in which the oxide particles and the pores are of nanometric size. Alumina-based mixed oxides are also characterized by good thermal and mechanical stability. All these aspects are especially attractive from the catalytic point of view [20,21]. Additionally, such materials are characterized by advantageous acid-base and redox properties. Their phase composition and the surface hydroxylation degree make them optimal support for catalytically active metal species [22,23].

The catalysts have been prepared either by impregnating the support with the metal precursor (Pd or Ni salt solution) or by simultaneous addition of the precursor during synthesis of the support (the so-called co-precipitation method). The obtained nanostructural catalysts have been characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption studies and applied in the Suzuki-Miyaura cross-coupling of phenylboronic acid with various aryl halides.

2. Experimental

2.1. Materials

All the chemical reagents were purchased as conforming to the

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analytical grade standards and used as received without further purification.

2.2. Characterizations

Textural properties of the samples (surface area, pore volume and average pore size) were determined by nitrogen adsorption-desorption isotherms at liquid nitrogen temperature by using an automatic volumetric apparatus (Micromeritics ASAP 2020). Prior to measurements, the samples were degassed for 4 h at 350 °C and 10^{-3} Torr vacuum. Adsorption of nitrogen was followed until near saturation, then desorption was followed until the closure of the hysteresis loop. The adsorption data were interpreted by the application of a conventional BET method for determination of the surface area. The total pore volume adsorbed near the saturation was read from the adsorption isotherm. The pore size distribution was analyzed with the Dollimore-Heal method [24], which was applied to the desorption branch of each of the isotherms. The mean pore size for each of the samples was read from the corresponding pore size distribution curve.

TEM measurements were carried out using a FEI Tecnai G² 20 X-TWIN electron microscope operating at 200 kV. The SEM images were acquired using a Hitachi S-3400N scanning electron microscope.

Catalytic reaction products were identified and analyzed with a HP 5890 Series II gas chromatograph connected to HP 5971A mass selective detector. Separation was achieved on a capillary HP-5 column coated with a diphenyl (5%) dimethylsiloxane (95%) copolymer film. Helium was used as the carrier gas.

2.3. Alumina-based supports preparation

The nanostructured Al₂O₃-ZrO₂ matrix containing 10% of zirconia was prepared in the following way [25]: 10 g of solid aluminium isopropoxide was hydrolyzed for 15 min in 60 cm³ of distilled water at 90 °C with continuous stirring. The obtained aluminium hydroxide AlO(OH) was then peptized by slow addition of an aqueous solution of zirconyl nitrate hydrate (0.42 g in 5 cm³ of water) containing additionally 0.2 cm³ of 65% HNO₃ (zirconium to nitrate ions ratio 1:4). The resulting homogeneous mixture was heated at 90 °C for 72 h with continuous stirring. Thus obtained transparent sol was then condensed by evaporation to form gel.

To obtain bulky-shaped supports, denoted in this paper as Al₂O₃-ZrO₂ (*bulk*), the gel was directly calcined at 500 °C for 4 h. To prepare the supports as small (2–3 mm) spherical granules, denoted as Al₂O₃-ZrO₂ (*gran*), an additional oil-drop procedure was involved [26]. The drops of gel were slowly added to a 20 cm layer of paraffin oil (density: 0.860 g/cm³, kinematic viscosity: 215 cSt at 40 °C) placed over a 5 cm layer of 8% ammonia solution. The liquids were slowly stirred (18–40 rpm) at the phase interface by a mechanical stirrer. The spherical granules were formed while passing through the oil layer. After aging for at least 45 min in ammonia solution phase, they were carefully washed with cold water, warm water and finally with ethyl alcohol. Next, they were left to dry at room temperature for 48 h and then calcined at 500 °C for 4 h.

2.4. Catalysts preparation

Catalysts containing Pd and Ni were prepared either by impregnating the supports with an aqueous solution of the metal salt, or by adding this solution during the Al₂O₃-ZrO₂ mixed oxide synthesis, the so called co-precipitation method.

Pd and Ni catalysts obtained by impregnation, denoted as Pd(*impr*) and Ni(*impr*), were prepared by the following procedure: 0.8 g of the support was impregnated, respectively, in 10 cm³ of an

aqueous acidic solution ($C_{\text{HCl}} = 0.09 \text{ mol/dm}^3$) of PdCl₂ containing 25 mg of Pd, or in 10 cm³ of an aqueous solution of NiCl₂ containing 25 mg of Ni. After 48 h, the solution was decanted and the catalyst was washed with water and dried in vacuum.

Pd and Ni catalysts obtained by co-precipitation, denoted as Pd(*copr*) and Ni(*copr*), were prepared by the following procedure: during the Al₂O₃-ZrO₂ support synthesis, introduction of zirconyl nitrate was followed by addition of, respectively, 0.9 cm³ of an aqueous acidic solution ($C_{\text{HCl}} = 0.09 \text{ mol/dm}^3$) of PdCl₂ containing 22.5 mg of Pd, or 0.9 cm³ of an aqueous solution of NiCl₂ containing 22.5 mg of Ni (the same solutions concentration as in case of the impregnated catalysts). Then, the standard support synthesis procedure was continued: the sol was condensed to obtain gel and finally calcined. During calcination metal nanoparticles were formed on the Al₂O₃-ZrO₂ support.

Metal content on the support was estimated by the ICP method, after mineralization of a weighted sample with *aqua regia*. The obtained metal loading was ranging from 1.25 to 1.65% in the final catalysts.

2.5. Suzuki-Miyaura reaction

The catalytic tests were carried out in a 40 cm³ Schlenk tube with magnetic stirring. The reagents: aryl halide (2-bromotoluene, 4-bromotoluene, 4-bromoanisole or 4-iodoanisole) 1 mmol, phenylboronic acid 1.1 mmol (0.135 g), base 2 mmol: KOH (0.112 g) or K₃PO₄ (0.424 g) were first introduced, then the reaction medium: 1,4-dioxane 10 cm³ or 2-propanol mixture with water 5 + 5 cm³ and n-dodecane 0.100 cm³ (the internal standard). Finally, the Al₂O₃-ZrO₂ supported catalyst (1.0×10^{-2} mmol Pd or Ni) was added. The reactor was sealed and placed in a thermostated oil bath (at 40 or 130 °C). In case of Pd catalysts, the reactions were carried out for 15 min or 1 h and in case of Ni catalysts for 24 h. Afterwards, the reactor was cooled down to the ambient temperature and the organic components were extracted by intensive shaking for 5 min with two portions of 5 cm³ of n-hexane. After the extraction, a small amount of water was added, in case of reactions carried out in 1,4-dioxane, to facilitate separation of the liquid phases. A colorless n-hexane phase was transferred to a 10 cm³ volumetric flask and analyzed with GC-MS.

3. Results and discussion

3.1. Structure of supported catalysts

Palladium and nickel catalysts supported on alumina-zirconia mixed oxides have been obtained: 3 of them have been prepared by impregnation of the supports with metal salt solutions and 3 by the co-precipitation method (Table 1). Two different kinds of Al₂O₃-ZrO₂ supports, synthesized by the sol-gel technique, have been used for that purpose: bulky-shaped and formed into spherical granules with the diameter of 2–3 mm.

A TEM micrograph (Fig. 1a) showing the sol precursor of Pd(*copr*)/Al₂O₃-ZrO₂ (*bulk*) demonstrates a characteristic nanocrystalline structure of this material. The image shows an aggregate that is composed of the rod-shaped particles with a fairly uniform size distribution: their average width is approximately 1 nm and the length is about ten times larger. The nanostructure and the morphology of the material are preserved while the heat treatment at 500 °C. After the calcination, Pd(0) nanoparticles are observed on the surface of the alumina-based support (Fig. 1b). They are spherical and none of them show typical crystal outlines that are frequently observed for palladium particles protected by polymers [27–30]. They have similar sizes, do not indicate any agglomeration, and are nearly uniformly dispersed on the surface of the

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