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Microwave-assisted hydroarylation of styrenes catalysed by transition metal oxide nanoparticles supported on mesoporous aluminosilicates

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ABSTRACT

The addition of phenols to styrene to form *ortho* and *para*-(1-phenylethyl) phenols was catalysed by a range of metal oxide nanoparticles supported on mesoporous aluminosilicates (M/Al-SBA-15 catalysts) under microwave irradiation. Moderate to excellent yields to products could be obtained at short times of reaction (typically 10 min). 0.5%Fe/Al-SBA-15 as readily available, environmentally friendly and cheap catalysts exhibited remarkable improvements in yield as compared to the majority of utilized catalysts. The heterogeneous catalyst can be reused at least three times without a significant loss in activity.

1. Introduction

Alkenes are attractive starting materials for organic synthesis as they can be easily functionalized using a plethora of both oxidative and reductive mono- and difunctionalization methods [1]. In general, Friedel–Crafts alkylations and acylations are one of the most powerful methods for Carbon—Carbon bond-forming reactions [2–4]. These reactions have been traditionally performed using strong Lewis acids including $TiCl_4$, $BF_3{\cdot}OEt_2$, and $AlCl_3$ as well as mineral acids such as HF and H_2SO_4. Ongoing investigation programs are currently trying to identify and design catalysts that address typical problems in Friedel–Crafts chemistries including high catalyst loading, low selectivity, over-alkylation, formation of byproducts (salts) and sensitivity toward moisture and strong acid media.

C—H transformations of arenes and heteroarenes have recently attracted a considerable interest in organic synthesis. Protocols have been developed using various transition-metal and acid catalysts [5,6]. The addition of olefins to acetophenones [7,8] and aromatic imines [9,10], alkene additions to arenes [2,4] and heterocyclic compounds [11,12] as well as the addition of aromatics to alkynes [13,14] or alcohols [15] are elegant examples of these types of transformation. In particular, the use of aromatic-derived alkenes has been found to be very useful and practical as the resulting diarylalkane block represents an important part in biologically active compounds and pharmaceuticals substrates that include haplopappin, phenprocoumone, papaverine, or afenopin (Fig. 1).

During the past decade, transition metal nanoparticles supported on mesoporous materials emerged as promising nanoentities to develop readily available, cheaper and more efficient catalysts as alternatives to traditionally employed in several catalytic reactions, especially for their use in heterogeneous catalysis [16–18]. Nanoparticles can offer remarkably different properties as compared to bulk metals based on their degenerated density of energy states and small sizes which often lead to high activities and specificities in chemical reactions [19,20].

Solid acid catalysts are increasingly utilised in organic transformations due to their simple separation from the reaction mixture and possible reuse. Additionally, the catalytic activity of solid acid (e.g. aluminosilicates) can be increased via incorporation of metal ions such as Cu^{II}, Zn^{II}, Fe^{III}, etc., which causes the generation of highly active Lewis acid sites [21]. The combination of such active Lewis acid site along with the available Brönsted acid sites in metal-exchanged Al-SBA-15 together with the high surface area and exceptional textural properties and hydrothermal stability can facilitate reactions by localizing the reactants in

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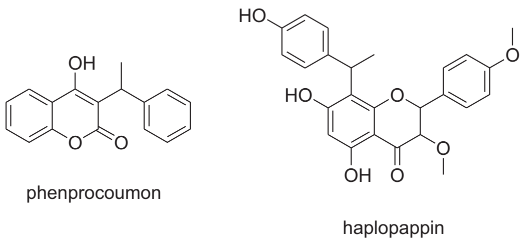

Fig. 1. Biologically and pharmaceutically active compounds.

their pores/external surfaces and providing high local concentration [22,23]. Among these transition metals, iron NPs have attracted a great interest in the design of environmentally friendly and effective catalysts as alternative to traditionally employed noble metal catalysts in several catalytic reactions. Fe-based systems have been proven to be the most effective and green system in modern organic synthesis because of their lower toxicity and easy accessibility [24,25].

In this work, we have aimed to combine the high activities and specificities of supported metal oxide nanoparticles with a simple but important C—H transformation such as the hydroarylation of styrenes with phenol derivatives [26]. A number of catalytic systems were developed and utilised in the proposed reaction under microwave irradiation.

2. Experimental

2.1. Materials synthesis

Al-SBA-15 materials were prepared in a similar way to those reported in our previous work, following the previously reported methodology by Bonardet et al. [22,27] and characterized using available techniques including X-ray diffraction (XRD), nitrogen physisorption, elemental analysis and surface acidity. Al-SBA-15 parent materials possessed a Si/Al ratio of 41 and were selected as catalyst support due to their excellent hydrothermal stabilities and textural properties (high surface area and appropriate mesoporosity) combined with a good balance of Brönsted/Lewis acid sites of moderate acidic strength. Importantly, we also needed a mechanically resistant support to the milling process utilized for the deposition of metal oxide nanoparticles.

The supported catalysts were prepared following a previously reported novel dry mechanochemical approach [28]. In a typical synthesis, 0.2 g Al-SBA-15 was ground with the needed quantity of metal precursor (e.g. $FeCl_2{\cdot}4H_2O$ or $AgNO_3$) in a Retsch PM-100 planetary ball mill using a 125 mL reaction chamber and 10 mm stainless steel balls. Milling conditions were 10 min at 350 rpm (previously optimized conditions [28]).

Upon milling, as synthesized materials were conditioned to remove the excess of unreacted and/or physisorbed precursor and directly calcined at 400 °C under air for 4 h. The conditioning step included thorough washing steps with ethanol and then acetone under mild heating (40–50 °C). Prepared catalysts, denoted as Fe0.5%AlSBA, Fe1%AlSBA, Fe2%AlSBA, Fe4%AlSBA, Ag1%AlSBA and Ag10%AlSBA, were characterized by a number of techniques including X-ray diffraction (XRD), N_2 physisorption, TEM and EDX. A similar Co10%AlSBA material was synthesized for comparative purposes.

2.2. Characterization

Structural properties of the materials were determined by XRD on a Siemens D-5000 (40 kV, 30 mA) using Cu Kα ($\lambda = 0.15418$ nm) radiation. Scans were performed over a 2θ range from 10 to 80 at step size of 0.018° with a counting time per step of 20 s.

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2000 volumetric adsorption analyzer from Micromeritics. Samples were degassed for 24 h at 130 °C under vaccum ($p < 10^{-2}$ Pa) prior to adsorption measurements. Surface areas were calculated according to the BET (Brunauer–Emmet–Teller) equation. Pore volumes (V_{BJH}) and pore size distributions (D_{BJH}) were obtained from the N_2 desorption branch.

TEM micrographs were recorded on a JEOL 2010HR instrument operating at 300 kV fitted with a multiscan CCD camera for ease and speed of use as well as with an EDX system. The lattice resolution is around 0.2 nm.

The surface acidity was measured in a dynamic mode by means of a pulse chromatographic technique of gas-phase adsorption of pyridine (PY) at 300 °C (sum of Brönsted and Lewis acid sites) and 2,6-dimethylpyridine (DMPY, Brönsted sites) as probe molecules [29].

DRIFTs characterisation of surface acidity involved the acid sites titration with PY. The basic probe was introduced by bubbling a stream of dehydrated and deoxygenated nitrogen (20 mL min^{-1}) through the liquid and into the sample chamber containing the neat (no KBr diluted) catalyst sample at 100 °C. Samples were equilibrated for at least 1 h at each temperature (100, 150, 200 or 300 °C) and reactant condition prior to collecting the spectra.

2.3. Microwave-assisted reactions

Microwave irradiation was employed as alternative energy source to promote the reactions (as opposed to conventional heating) in view of the possibilities to speed up reactions with often changes in selectivity due to the rapid and homogeneous heating achieved under microwave irradiation, particularly for supported metals [30]. In a typical reaction, 1 mmol (0.115 mL) styrene, 1.5 mmol (0.141 g) phenol, 2 mL solvent (cyclohexane) and 0.050 g catalyst were added to a pyrex vial and microwaved in a pressure-controlled CEM-Discover microwave reactor for a period of time, typically 10 min at 200 W (120 °C, maximum temperature reached) under continuous stirring. Samples were then withdrawn from the reaction mixture and analysed by GC and GC/MS Agilent 6890N fitted with a capillary column HP-5 (30 m × 0.32 mm × 0.25 μm) and a flame ionisation detector (FID).

The identity of the products was confirmed by GC–MS. Bblank reaction showed the thermal effects in the reaction were negligible (less than 5% conversion was obtained after 24 h). Response factors of the reaction products were determined with respect to the substrates from GC analysis using standard compounds in calibration mixtures of specified compositions. The microwave method was generally power controlled (by an infra-red probe) where the samples were irradiated with the required power output (settings at maximum power, 300 W) to achieve different temperatures in the range of 115–120 °C.

3. Results and discussion

Textural and surface properties of the materials have been summarized in Table 1. Surface acidities measured using pyridine (PY) and 2,6-dimethylpyridine (DMPY) as probe molecules pointed to a significant increase of Lewis acidity (difference between PY-DMPY values) upon Fe incorporation in the materials. These findings are in good agreement with previous reports from the group [23,28]. In any case, ball-milling (BM) synthesized nanomaterials possessed similar textural properties (e.g. surface areas, pore size and volumes) as compared to the parent aluminosilicate. Comparatively, the incorporation of Ag into the SBA-15 aluminosilicate material