Air stable ligandless heterogeneous catalyst systems based on Pd and Au supported in SiO2 and MCM-41 for Suzuki–Miyaura cross-coupling in aqueous medium

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ABSTRACT

Palladium and palladium-gold containing siliceous-MCM-41 and sol–gel palladium and palladium-gold silica composites have been prepared. The catalytic performance of incorporated Pd/MCM-41, Au-Pd/MCM-41 and Pd and Au/Pd/SiO2 sol–gel catalysts for the Suzuki–Miyaura cross-coupling reaction was determined and the influence of the matrix and the catalyst composition on the catalytic activity were also studied. The catalysts were characterized by N2 physisorption (BET/BJH methods), X-ray diffraction, temperature programmed reduction analysis, H2 chemisorption, atomic absorption spectrophotometry and Raman spectroscopy. The silica-containing palladium and palladium-gold catalysts prepared using the MCM-41 matrix showed greater catalytic activity than using the conventional sol–gel method; however, gold had a significant influence on this reaction. The catalyst did not undergo metal leaching and could be easily recovered and re-used (reused).

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1. Introduction

The Suzuki reaction [1–3], involving the Pd-catalyzed C–C cross-coupling reaction of aryl boronic acids with aryl halides, has become an attractive process for the synthesis of biaryls, which have a broad and diverse range of applications from pharmaceuticals to science materials [4–6]. Thus, efforts have been directed to achieve improvements in the Suzuki reaction by designing new ligands and/or precursors of palladium, such as phosphine ligands [7–10], N-heterocyclic carbenes [11–16] and palladacycles [13,17], in order to achieve an efficient cross-coupling reaction under mild and environmentally benign conditions, which includes the choice of solvent, low catalyst loading and/or easy separation and recyclability of the catalyst. In this regard, reducing the use of organic solvents in many reactions, including C–C coupling reactions, it is aligned with the development of green chemistry. The use of water as a solvent has several advantages such as its low cost, abundance and easy separation of lipophilic products from the aqueous phase [18–20].

Aiming to promote the development of green chemistry, interest has increased in studying methods for the preparation of heterogeneous catalysts to achieve a catalyst that can be efficient, stable and recyclable for several applications. Silica [21], MCM-41 [22], SBA-15 [23], activated carbon [24] and metallic nanoparticles [25] have been successfully used as supports in Suzuki coupling with several advantages compared to homogeneous systems. However, in several cases, Pd leaching has been observed and the distinction between a homogeneous or heterogeneous catalyst is not an easy task [26]. Palladium is the most commonly used metal catalyst in Suzuki coupling, but gold has recently been studied as a catalyst for these reactions as well [20,27–29].

The sol–gel method has great potential for the preparation of materials, by allowing the structural control of ceramics [30]. The materials obtained with this method have a high surface area that allows the incorporation of different components dispersed in the matrix [31–35]. Another widely known matrix is the ordered (suggested: commercial) mesoporous molecular sieve produced by the company Mobil, denoted with the number 41 (MCM-41 [36]. This
material possesses regular arrays of large uniform channels and a high surface area (above 700 m²). These mesoporous materials are very attractive for the development of new heterogeneous catalysts for many reactions, e.g., the oxidation of hydrocarbons, hydrogenation, etc. [37]. The presence of silanol groups, which are capable of being functionalized, make them useful as supports for organic compounds and metal oxides on which very high dispersion of the active phase may be achieved [38,39]. Mesoporous molecular sieves containing different transition metals have great potential as heterogeneous catalysts in liquid-phase reactions.

In this study, we evaluated the catalytic activity in Suzuki coupling under a normal air atmosphere using water as the solvent and palladium- and/or gold-based catalysts, i.e., Pd and Au-Pd/SiO₂ and Pd and Au-Pd/MCM-41, without any ancillary ligands. The effects of gold on the catalytic properties were also studied. Recycling of the catalysts was also performed and demonstrated the possibility of reusing the catalytic system.

2. Experimental

2.1. Chemicals

All reagents were purchased from commercial sources and used as received.

2.2. Catalyst preparation Pd/SiO₂ and Au-Pd/SiO₂

The 5.0 wt.% Pd/SiO₂ and 3.0–3.0 wt.% Au-Pd/SiO₂ (3.0 wt.% for each metal) catalysts were prepared by the sol–gel method using tetraethoxysilane (15.1 g, TEOS, 98%, Sigma–Aldrich), PdCl₂ (Sigma–Aldrich) and HAuCl₄ (Sigma–Aldrich) as precursors. The sol was obtained from a TEOS/ethanol/water mixture in a 1/3/10 molar ratio with the addition of HCl and HF (up to pH 2.0) as the catalysts. The sample was dried at 110 °C for 24 h and thermally treated for 2 h at 500 °C in air.

2.3. Catalyst preparation Pd/MCM-41 and Au-Pd/MCM-41

The 5.0 wt.% Pd/MCM-41 and 3.0–3.0 wt.% Au-Pd/MCM-41 (3.0 wt.% for each metal) catalysts were prepared by the direct incorporation of Pd and Au into the MCM-41 [40] framework, aiming for the isomorphous substitution of Si by Pd and Au-Pd ions. TEOS, PdCl₂ (Sigma–Aldrich) and HAuCl₄ (Sigma–Aldrich) were used as the precursors and hexadecyltrimethylammonium bromide (C₁₆-TAB, Sigma–Aldrich) as the structural template. A C₁₆-TAB solution in water was added to the solution of TEOS (2.5 g) in aqueous tetramethyammonium hydroxide (TMAOH, 25 wt.%, Sigma–Aldrich), and the mixture was stirred for 30 min. Then, PdCl₂, HAuCl₄ and the remaining TEOS (21.0 g) were added. After additional mixing (stirring) at 40 °C for 24 h, the mixture was placed in the autoclave at 100 °C for 24 h and then cooled to room temperature. The obtained solid was separated by filtration, washed with deionized water and ethanol and dried at 40 °C. Then, the solid was heated from room temperature to 550 °C under a nitrogen flow and calcined for 3 h at 550 °C under an air flow to remove the residual organics. The TEOS/C₁₆-TAB/TMAOH/water molar ratio was 1.0/0.12/0.3/22.0.

2.4. Catalyst characterization

The powder X-ray diffractometry (XRD) measurements were performed on a Rigaku model Geigerflex-3034 equipment using a CuKa radiation (40 kV, 40 mA, λ = 0.15418 nm). The diffraction pattern was measured between 12 and 50°2θ with a step size of 0.05°2θ and a step time of 4.0 s. Samples were previously dried at 110 °C overnight and pulverized.

The reducibility of the catalyst surfaces was determined by Temperature-Programmed Reduction (TPR) in a Quantachrome equipment ChemBET-300 equipped with a thermal conductivity detector. Prior to analysis ca. 150 mg was packed into a quartz cell, heated for 2 h at 200 °C under a He stream and then it was cooled to room temperature. The experiments were performed between 30 and 900 °C in flow 5%H₂/N₂, increasing the temperature linearly at a rate of 10 °C min⁻¹.

Textural characteristics of the matrices were determined from nitrogen adsorption isotherms at -196 °C using an Autosorb IQ-Quantachrome Instrument. The samples (ca. 200 mg) were degassed for 2 h at 300 °C before analysis. Specific surface areas were determined by the Brunauer–Emmett–Teller equation (BET method) from adsorption isotherm in a relative pressure range 0.05 < P/P₀ < 0.3. The total pore volume was obtained of the amount of N₂ adsorbed at a relative pressure close to unity. The average pore diameter was determined by Barrett–Joyner–Halenda (BJH) from the N₂ desorption isotherms.

The palladium dispersion of catalysts was determined from combined isotherm measured for hydrogen using the extrapolation method in an Autosorb-Quantachrome-IQ-C. Before analysis, the catalysts were dried at 200 °C for 2 h under vacuum. Then, the catalysts were reduced at 500 °C (10 °C min⁻¹) in flowing H₂ (40 cm³/min). Following reduction, the samples were evacuated for 1 h at reduction temperature adsorption temperature under vacuum.

The small angle X-ray scattering (SAXS) measurements were obtained using synchrotron radiation with λ = 1.488 nm. Synchrotron radiation measurements were carried out at the D11A-SAXS beamline of the LNLS (Campinas, Brazil) using a Huber-423 3-circle diffractometer. The SAXS setup was equipped with a Si (1 1 1) monochromator, giving a horizontally focused X-ray beam. The incident X-ray wavelength λ was 1.488 nm and the scattering angle 2θ was approximately 0–10° (Table 1).

2.5. General procedure for Suzuki cross-coupling

In a typical experiment of the Suzuki cross-coupling reaction, an aqueous suspension (20 mL of deionized water) containing the corresponding aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), KOH (4 mmol), catalyst (130 mg) and tetradecane (internal standard; ~120 mg) was stirred for an appropriate period of time in a glass reactor with magnetic stirring at 80 °C. After the desired time (2 or 4 h, cf. Tables 2 and 3), the reaction mixture was

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal content</th>
<th>Dispersion D (%)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/SiO₂</td>
<td>–</td>
<td>4.9</td>
<td>–</td>
<td>0.90</td>
<td>33</td>
</tr>
<tr>
<td>Au-Pd/SiO₂</td>
<td>2.9</td>
<td>2.8</td>
<td>none</td>
<td>0.92</td>
<td>47</td>
</tr>
<tr>
<td>Pd/MCM</td>
<td>–</td>
<td>4.8</td>
<td>–</td>
<td>1.35</td>
<td>19</td>
</tr>
<tr>
<td>Au-Pd/MCM</td>
<td>2.9</td>
<td>2.7</td>
<td>none</td>
<td>1.58</td>
<td>20</td>
</tr>
</tbody>
</table>
Table 2
Suzuki–Miyaura reactions catalyzed by Pd/SiO2 and Au-Pd/SiO2 (sol–gel).a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl halide</th>
<th>Product</th>
<th>Catalyst (M/SiO2)</th>
<th>Yield (%b,c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 h</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>Pd</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>Pd</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>Pd</td>
<td>41</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>44</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>Pd</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>Pd</td>
<td>34</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>39</td>
</tr>
</tbody>
</table>

a Reaction conditions: [aryl boronic acid] = 1.2 mmol, [aryl halide] = 1.0 mmol, catalyst = 0.130 g (%mol), H2O (20 mL), T = 80 °C.
b Yields were determined by GC using tetradecane as the internal standard and based on the amount of aryl halide consumed.
c By-products were detected as the minimum amount of homocoupling products and reduced aryl halide.
d 3rd recycling of the catalyst.

cooled to room temperature and extracted with dichloromethane (3 × 20 mL). The organic phases were uncolored and clear and no visible particles of catalyst could be observed. The organic phases were mixed and the products were identified and quantified by gas chromatography using a Shimadzu GC-2014 apparatus (using tetradecane as internal standard with a respective calibration curve). The products were also analyzed by GC-MS on a 17B Shimadzu GCMS-QP5000. The fragmentation patterns were compared with standards and library data.

For the recycling experiments, after extraction of the organic products, the reagents were added to the liquid phase containing the catalyst [aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), KOH (2 mmol), tetradecane (~120 mg)]. Thus, the mixture was allowed to react further and the analysis was performed as described above.

3. Results and discussion

3.1. Characterization of the catalysts

The XRD patterns of sol–gel silica and MCM-41 doped with Pd and Au-Pd are shown in Fig. 1. The diffractogram of the sample Pd/SiO2 indicated the presence of a low intensity peak at 2θ = 33.7° corresponding to crystalline phase of palladinite PdO(1 0 1) [41], formed by the thermal decomposition of the precursor PdCl2 under air atmosphere. The XRD pattern of Pd/MCM-41 indicated the presence of two peaks at 2θ = 33.7° and 42.0° corresponding
Table 3
Suzuki–Miyaura reactions catalyzed by Pd/MCM-41 and Au-Pd/MCM-41.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl halide</th>
<th>Product</th>
<th>Catalyst (M/MCM-41)</th>
<th>Yield (%)&lt;sup&gt;a,c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 h</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>Pd</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>Pd</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>Pd</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>58</td>
</tr>
<tr>
<td>7</td>
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<td></td>
<td>Pd</td>
<td>36</td>
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<tr>
<td>8</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>Pd</td>
<td>55</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>62</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: [aryl boronic acid] = 1.2 mmol, [aryl halide] = 1.0 mmol, catalyst = 0.130 g, H₂O (20 mL), T = 80 °C.

<sup>b</sup> Yields were determined by GC using tetradecane as the internal standard and based on the amount of aryl halide consumed.

<sup>c</sup> By-products were detected as the minimum amount of homocoupling products and reduced aryl halide.

<sup>d</sup> 3rd recycling of the catalyst.

to Palladinite phases PdO(1 0 1) and PdO(1 1 0), respectively. The lower intensity of the palladinite in Pd/SiO₂ catalyst than Pd/MCM-41 indicates a greater reduction of PdCl₂ precursor during the preparation of the composite and it was not reoxidized after the calcination step. The XRD patterns of the Au-Pd/MCM-41 and Au-Pd/SiO₂ catalysts indicated two diffraction peaks at 2θ = 37.9° and 44.6° attributed to metallic gold Au(1 1 1) and Au(2 0 0) [42] and a peak corresponding to Palladinite (PdO) coinciding with the angles described in the XRD patterns of palladium catalysts. The band observed at 2θ = 18° is related to amorphous SiO₂ that was formed during calcination of catalysts [43].

The profiles of temperature programmed reduction analysis (TPR) of catalysts are shown in Fig. 2. The TPR analysis results revealed that Pd/SiO₂ and Au-Pd/SiO₂ showed no reducible phases of palladium and gold oxides. The TPR profiles of Pd/MCM-41 and Au-Pd/MCM-41 indicated reduction of palladium oxide phases to metallic palladium (100–240 °C and 120–225 °C respectively). These results are consistent with the observations obtained by XRD which indicated predominance of Au(0) for all samples. For the Pd phases, it was observed that there are the predominance of Pd(0) for the samples prepared by sol–gel method and Pd (II) for MCM-41 catalysts. For the Pd-containing catalysts, it was observed in the TPR profiles a strong and negative peak near 100 °C characteristic of the β-hydride palladium decomposition (β-H-Pd) formed during TPR analysis [44,45]. This indicates that the PdO species previously observed by XRD were reduced at low temperature, followed by hydrogen sorption, forming hydrides over metallic Pd particle surfaces [46,47]. The temperature range to palladium
Fig. 3. \( \text{N}_2 \)-Adsorption–desorption isotherms of \( \text{Pd/SiO}_2 \), \( \text{Au-Pd/SiO}_2 \), \( \text{Pd/MCM}-41 \) and \( \text{Au-Pd/MCM}-41 \) and their pore size distribution curves using the BJH method.

Hydride decomposition has been reported between 323 and 373 K [48,49] and is in agreement with those observed for the composites prepared.

Table 1 shows the values of the textural characteristics of the catalysts measured by \( \text{N}_2 \) physisorption and \( \text{H}_2 \) chemisorption techniques. Fig. 4 shows the \( \text{N}_2 \)-adsorption–desorption isotherms and their respective BJH distribution of pore sizes graphs. The catalysts showed values of specific surface area between 259 and 580 \( \text{m}^2\text{g}^{-1} \) that are within the expected range for the composite preparation of silica sol–gel and MCM-41.

The specific surface area of the catalysts decreases in the following order: \( \text{Au-Pd/MCM}-41 > \text{Pd/MCM}-41 > \text{Au-Pd/SiO}_2 > \text{Pd/SiO}_2 \). It was observed that the bimetallic catalysts show a small increase in area as compared to the monometallic catalysts for both methods (correct, Table 1). The presence of gold can have influenced the increase in surface area of bimetallic composites. The high surface area of the oxide support normally can lead to increased dispersion of the metal and this tendency was observed between the sol–gel and MCM-41 samples (Table 1, \( D (%)\) = 73 vs. 86, \( \text{Pd/SiO}_2 \) and \( \text{Pd/MCM}-41 \) respectively). However, Au–Pd catalysts showed lower dispersion of palladium than Pd catalysts (Table 1, \( D (%)\) = 73 for \( \text{Pd/SiO}_2 \) and \( D (%)\) = 57 for \( \text{Au-Pd/SiO}_2 \) and \( D (%)\) 86 vs. 78 for \( \text{MCM}-41 \) catalysts).

The isotherms of \( \text{Pd/SiO}_2 \) and \( \text{Au-Pd/SiO}_2 \) catalysts are corresponding to type IV (in the IUPAC classification), which is typical of mesoporous materials (Fig. 3) [50,51]. The appearance of the hysteresis loop type H1 is presented at high relative pressures \( (P/P_0 \approx 0.7 \text{ to } 0.9) \) and can be related to the formation of textural mesoporosity. Pore size distribution curves (Fig. 4) for the catalysts exhibited unimodal profile with a narrow range of variation of pore size, ranging from 2 to 6 nm for \( \text{Au-Pd/SiO}_2 \) and \( \text{Au-Pd/SiO}_2 \).

\( \text{Pd/MCM}-41 \) and \( \text{Au-Pd/MCM}-41 \) catalysts exhibit a type IV isotherm (in the IUPAC classification) with a well-defined H3 loops that do not level off at relative pressures close to the saturation vapor pressure were reported for aggregates of plate-like particles giving rise to slit-shaped pores (Fig. 3) [50,51]. However, the average pore diameter in sol–gel materials nm are larger than that in MCM-41 materials, as a peak width at half-maximum is 1.9 nm for both MCM-41 materials vs 2.6 and 4.6 nm for \( \text{Pd/SiO}_2 \) and \( \text{Au-Pd/SiO}_2 \) respectively.

The SAXS pattern of \( \text{Au-Pd/MCM}-41 \) (Fig. 4(a)) showed \( (100), (110) \) and \( (200) \) reflections at \( 2\theta = 1.67, 2.91 \text{ and } 3.33^\circ \), respectively. The synchrotron radiation small-angle pattern for the \( \text{Pd/MCM}-41 \) catalyst showed \( (100) \) and \( (110) \) reflections at \( 2\theta = 1.62 \) and \( 2.85^\circ \), respectively (Fig. 4(b)). The peaks can be attributed to 2-D hexagonal symmetry, indicating a highly ordered hexagonal structure [40]. This confirms that the silica-containing Pd and Au–Pd catalysts have the typical structure of the MCM-41 silica, which is in agreement with the pore size distribution curves.

3.2. Catalytic tests: Suzuki cross-coupling

Having obtained and characterized the Pd and Au–Pd/SiO2 and Pd and Au–Pd/MCM-41, we evaluated them for the Suzuki cross-coupling reaction. The performance of metal–MCM-41 (metal = Pd or Au–Pd) was compared with that of a silica-included metal material prepared by a conventional sol–gel method without the surfactant. We also evaluated the influence of gold in the performance of catalysts. However, this study aims to apply the heterogeneous catalysts of Pd and Au–Pd under an air atmosphere, without any ancillary ligands and using water as the solvent in the Suzuki cross-coupling reaction. We chose as a reaction model the reaction of electron-rich p-bromoanisole with phenylboronic acid.

After the initial screening, we chose to run the coupling reactions using KOH at 80 °C. The Pd and Au–Pd/SiO2 and Pd and Au–Pd/MCM-41 catalysts were evaluated for the coupling reaction of different aryl halides with phenylboronic acid (Scheme 1), affording the corresponding coupling products in good to excellent yields (Tables 2 and 3). As shown in Table 2, for both the
Pd and Au-Pd/SiO2 catalysts, the Suzuki–Miyaura cross-coupling reaction of p-bromotoluene gave the corresponding coupled products in almost quantitative yield (Table 2, entries 3 and 4). Up to 80% yield of the coupling product was obtained for the p-bromoanisole and the catalyst was recycled three times without a noticeable change in the yield (Table 2, entries 1 and 2). The presence of a strong electron-donating group such as methoxy would decrease the oxidative addition rate and the overall activity if the oxidative addition is the rate-determining step [52]. In this context, the lower yields obtained for the coupling with p-bromonitrobenzene or p-bromobenzaldehyde were unexpected (Table 2, entries 5–8). Further studies are required to explain these results, which could be associated with surface effects on the rate-determining step. Benzylic chloride was coupled only in moderate yields (Table 2, entries 9 and 10). Since benzylic chlorides are active substrates for the Suzuki coupling reaction in homogeneous systems such as Pd(OAc)2/PPPh3 [53], the results also indicate the presence of surface effects and, as a consequence, that our catalytic system actually operates as a heterogeneous catalyst.

In terms of the different aryl halides evaluated, a similar trend was observed for the Pd and Au-Pd/MCM-41 catalysts (Table 3). However, under the same conditions, the catalysts supported in MCM-41 gave higher yields than the silica sol–gel catalysts. The XRD and TPR analysis indicated a predominance of Pd(0) and Au(0) in the silica sol–gel materials over MCM-41. Since the zero valent species are the active site for the catalytic cycle, higher activity would be expected for the silica sol–gel materials. MCM-41 was a better support than silica for the catalytic activity of Pd and Au-Pd catalysts, probably due to the larger surface area and pore volume, which may improve the dispersion of the metals and the accessibility of organic substrates to the metal centers.

The beneficial effect of gold can be verified in every entry. In both supports, the relative increase in the yields was verified through experiments; it did not matter if the substituent group in the aryl halide was electron-donating or withdrawing (Tables 2 and 3). Some reports in the literature have shown increased efficiency of a catalyst by adding gold to palladium–doped materials. This increase has been attributed to changes in the electronic structure of the catalytically active metals, formation of gold nanoparticles below 10 nm and structural changes in catalyst by adding gold [54,55].

The possibility of reusing the catalyst was evaluated using the deactivated aryl bromide p-bromoanisole. The reaction mixture was cooled to room temperature after 4 h and the organic products were extracted with an organic solvent. Then, a new batch of reagents was added to the water phase containing the catalyst. All the catalysts, including Pd and Au–Pd in silica (Table 2, entries 1 and 2) or in MCM-41 (Table 3, entries 1 and 2), were reused (reused) without any significant change in the yield of the coupling product. Assuming that some catalyst is lost each cycle, no major yield deterioration would be noted for several cycles if the reaction time of each cycle were overestimated (or the loading of catalyst is higher than the necessary). However, the turnover frequency (TOF) would decrease markedly from cycle to cycle [56,57] which it does not observed in the recycling tests. It is important to note that for the tested catalyst the yield of the third was the same, considering the experimental error of the CG analysis (±5%) showing that there is no noticeable decrease in the Pd catalyst concentration.

4. Conclusions

We have developed a ligand-free, air-resistant practical and efficient catalyst system that allowed us to perform the Suzuki–Miyaura cross-coupling reaction of aryl bromides with arylboronic acids in water using Pd or Au-Pd immobilized in silica or MCM-41 as the catalyst. MCM-41 was a better support than silica sol–gel for the catalytic activity of the Pd and Au-Pd catalysts, and the bimetallic catalyst gave higher yields, demonstrating the beneficial effect of gold. Furthermore, the reactions proceeded under mild conditions using an aqueous and recoverable medium. The ligand-less system, mild conditions, air stability and recyclability as well as the use of water as the solvent are consistent with the principles of green chemistry for the production of cleaner chemicals.

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