Recent Advances in the Development of Magnetic Catalysts for the Suzuki Reaction

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Received January 10, 2017; in final form, March 28, 2017

Abstract—Suzuki reactions are one of the most important carbon-carbon bond forming reactions found in organic chemistry, with current methodologies offering excellent yields for a wide range of substrates. Further optimisation of such reactions involves incorporation of iron oxide nanoparticles into the catalytic system leading to the formation of highly efficient, recyclable catalysts. This review will focus on the recent development of magnetic palladium catalysts (palladium on magnetite with carbon-based supports and silicon coatings, and palladium on maghemite). Their application and recyclability in Suzuki coupling reactions will also be presented.

Keywords: magnetic catalysis, recyclable catalysts, iron oxide, Suzuki reaction, nanoparticles

DOI: 10.1134/S2079978017030037

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1. INTRODUCTION

The two major classes of catalysts used both on small laboratory as well as industrial scale are homogenous and heterogeneous catalysts. The distinction between the two lies in whether the catalyst is found in the same phase as in which the reaction occurs (homogenous) or in a different phase (heterogeneous). The potential to recover and reuse catalysts is one of their most desirable features [1–4]. In this regard, homogenous catalysts are at a disadvantage as they are more difficult to separate from reaction mixtures and often have limited reusability due to contamination with the product and/or by-products. They also tend to be more expensive and more difficult to handle. However, this problem of recyclability and reusability can be overcome through a process of heterogenisation [5–7]. Binding the catalyst to a solid support is seen as an efficient method of improving recovery and recyclability of catalyst as the heterogeneous catalyst can be isolated from the reaction medium through a number of ways including centrifugation and filtration. Industrially these methods are inefficient, time-consuming and uneconomical. Therefore, other strategies have been explored that utilise the physical properties of these solid supports.

One of the most widely used methods includes using catalyst supports that are responsive to magnets. These magnetic catalysts are mainly prepared in the form of alloys (SmCo₅, AlNiCo, NdFeB, FePt) [8–11] or iron oxides (FeO, Fe₂O₃, Fe₃O₄) [12–15] with the most efficient of these being iron oxide: magnetite (Fe₃O₄), which has a saturation magnetisation (Mₛ) rating of 92–100 emu/g. The addition of magnetic properties to catalysts means that they can be removed easily from solution by utilising an external magnet.

1 The article is published in the original.
This review will focus on the recent development of magnetic palladium catalysts and their application in Suzuki coupling reactions.

2. PALLADIUM ON MAGNETITE (Fe$_3$O$_4$) NANOPARTICLES

Carbon–carbon bonds are one of the most important bonds found in organic chemistry and are the substantive component in many well-known reactions. One of the most important C–C bond forming reactions is the Suzuki reaction catalysed by palladium (Scheme 1). Standard, non-magnetic catalysts in Suzuki reactions face two major problems. The first is the tendency for the palladium to lose its catalytic activity due to aggregation. The second is the difficulty in separation of the expensive active catalyst which is inevitably lost in standard separating procedures such as filtration and centrifugation. In recent years there have been many incorporations of magnetic nanoparticles in heterogeneous palladium catalysed Suzuki reactions with the aim of producing a magnetically active catalyst that can be easily recovered and reused.

![Scheme 1. General reaction scheme for the Suzuki reaction.](image)

3. CARBON BASED SUPPORTS

There have been many reports highlighting how magnetic nanocomposites which incorporate palladium (Pd) nanoparticles can be used as very effective reusable catalysts for many organic transformations. Carbon based supports, such as graphene can provide an excellent backbone onto which Fe$_3$O$_4$ and Pd nanoparticles can be immobilized. Sun et al. [16], prepared a highly active magnetic catalyst for the Suzuki reaction made up of Fe$_3$O$_4$ on sulphonated graphene (Fe$_3$O$_4$/s-G) that incorporated a homogenous distribution of Pd nanoparticles (Fig. 1). This efficient catalyst required no ligands or surfactants under aerobic conditions and could be efficiently recycled with minimum loss in activity after several cycles.

A range of Suzuki reactions were carried out using a variety of aryl bromides and arylboronic acids using 0.003 mmol Pd in the Pd/Fe$_3$O$_4$/s-G catalyst. Yields were reported to be between 79 to 95%. When reacting 1-bromo-4-methylbenzene (1.0 mmol) with phenylboronic acid (1.2 mmol), the catalyst was recycled eight times, with only a small decrease in yield from 95% to 89% (Table 1) when the reaction time was extended to 2 h.

A reduced graphene oxide incorporated onto the surface of iron oxide nanoparticles was used by Nasrabad et al. [17] as a support for palladium nanoparticles. The formation of spherical Pd/Fe$_3$O$_4$/r-G particles with a mean particle diameter of 2.6 nm according to TEM imaging was reported (Fig. 2). The nanohybrid catalyst was screened under a variety of conditions finding its best performance in a H$_2$O/EtOH (1 : 1) solvent system. The initial yield in the reaction of bromobenzene with phenyl boronic acid was 97%. Subsequent uses of the catalyst for eight consecutive cycles showed no noticeable loss in catalytic activity.

Pd/Fe$_3$O$_4$ supported on graphene nanosheets (Pd/Fe$_3$O$_4$/G) was recently reported by El-Shall et al. [18]. This report is built on previous work where catalysts were prepared for cross-coupling reactions from palladium nitrate and graphene oxide with hydrazine hydrate as a reducing agent under (MW) heating [19]. However, despite its success, it was often quite difficult and time consuming to remove from reaction mixtures using the standard filtration methods. By incorporating Fe$_3$O$_4$ into the synthetic methodology previously developed, a highly effective and easily reusable bimetallic nanocatalyst was produced. In this

<table>
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<th>Cycle</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
<th>5th</th>
<th>6th</th>
<th>7th</th>
<th>8th</th>
<th>9th</th>
<th>10th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)</td>
<td>95</td>
<td>96</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>90</td>
<td>86</td>
<td>89</td>
<td>73</td>
<td>84$^a$</td>
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</table>

Table 1. Recycling experiments of Suzuki reaction of 1-bromo-4-methylbenzene with phenylboronic acid using Pd/Fe$_3$O$_4$/s-G catalyst

Reaction conditions: 1-bromo-4-methylbenzene (1.0 mmol), Phenylboronic acid (1.5 mmol), Pd/Fe$_3$O$_4$/s-G catalyst containing 0.012 mmol Pd, K$_2$CO$_3$ (3.0 mmol), in 7 mL H$_2$O/EtOH at 80°C for 45 min.

$^a$Reaction time extended to 2 h.