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Effects of nanoparticle and porous metal oxide supports on the activity of palladium catalysts in the oxidative coupling of 4-methylpyridine

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ABSTRACT

The oxidative coupling of 4-methylpyridine to 4,4′-dimethyl-2,2′-bipyridine over palladium oxide is a simple, environmentally friendly, one-step process to produce bipyridines, which are commonly used with transition metal ions to form complexes with interesting properties. However, the reaction is slow and the palladium catalyst deactivates during reaction, which means that catalyst improvements are needed for large-scale production of more economically viable bipyridine products. In this study, a number of metal oxides were investigated as catalyst supports and compared to the best performing catalysts to date, i.e. Pd/C and Pd/n-Al_2O_3(+). Catalysts supported on several nanoparticle oxides with varying properties as well as some conventional supports were prepared and characterized in an attempt to determine properties that lead to high catalytic activities in the oxidative coupling of 4-methylpyridine. It was found that two general categories of active catalysts can be prepared; (1) palladium supported on very high surface area materials, such as Pd/n-Al_2O_3(+) and Pd/MgO, and (2) palladium supported on metal oxides known to induce strong palladium-support interactions, e.g. Pd/ZrO_2, Pd/(n-ZrO_2 + n-CeO_2) and Pd/n-ZnO. While there is no simple correlation between the palladium surface area and the catalytic activity, higher palladium dispersions generally gave higher yields compared to lower dispersion catalysts. The results indicate that the reaction is structure sensitive, i.e. not all the palladium on the surface is equivalent and some palladium species are more active than others. The acidic and basic properties of the supports were determined via chemisorption of ammonia and carbon dioxide, respectively. The data indicate that there is no correlation between the acidic or basic sites of the supports and the palladium dispersion or the catalytic activity, although highly acidic or highly basic supports should be avoided as they resulted in lower dispersions than expected from their corresponding surface areas.

In terms of economic viability the porous TiO_2 support was determined to be the most competitive with the nanoparticle alumina support as it results in a catalyst with comparable yields and is less expensive compared with nanoparticle alumina. The palladium supported on nanoparticle ZrO_2 and MgO are also promising catalysts.

1. Introduction

Palladium is a transition metal that has the ability to induce C–H activations in hydrocarbons and aromatic systems [1]. The efficacy with which palladium inserts into the C–H bond of methane, which is the strongest of hydrocarbon C–H bonds, is evident in the large number of publications involving palladium-catalyzed methane oxidation [2–4]. While partial and complete oxidation reactions of hydrocarbons are very important, reactions that can lead to C–C coupling after a C–H activation step are of particular interest [5]. Naturally, C–H activation and C–C coupling of CH_4 would be a highly desirable method to produce chemicals directly from methane. However, C–C coupling of aromatic compounds after a direct C–H activation step is also of significance in the synthesis of fine chemicals and pharmaceuticals. An important example is the oxidative coupling of 4-methylpyridine to 4,4′-dimethyl-2,2′-bipyridine (Scheme 1). This is a simple one-step process in which the bipyridine is formed directly from the pyridine reactant and the only byproducts are water and the terpyridine. Consequently, this is an environmentally friendly reaction since no solvent or halogenated compounds are needed. In addition to reducing halogenated byproduct salts or compounds, avoiding halogenated reactants is also more cost-effective. Halogenated derivatives are usually significantly more expensive, with 2-bromo-4-methylpyridine available through reaction with commercially available 2-amino-4-methylpyridine at ~$200/kg [6], compared to the non-halogenated analogue, 4-methylpyridine, which is relatively inexpensive at less than $40/kg [7], if purchased in small quantities. The disadvantages of this reaction are the slow reaction rate and the deactivation

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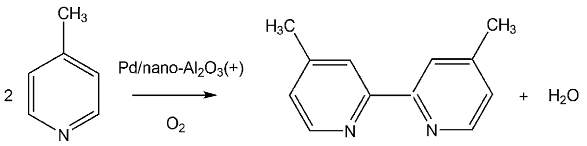

Scheme 1. Oxidative coupling of 4-methylpyridine to 4,4′-dimethyl-2,2′-bipyridine over a palladium on nanoparticle alumina catalyst.

of the catalyst [8]. The low yields of bipyridine product over the palladium (or Raney nickel) catalysts [9–13] and the high prices of halogenated reactants result in prices of 4,4′ dimethyl-2,2′-bipyridine in excess of $4,500/kg [14]. This prohibits large scale use of the 4,4′ dimethyl-2,2′-bipyridine, and its transition metal complexes. This is unfortunate since transition metal complexes with bipyridine ligands have many interesting photo- and electrochemical [15–23] or catalytic [24–28] properties. The oxidative coupling of 4-methylpyridine is thus a useful “probe” reaction on which to test new catalyst formulations to find more efficient catalysts.

While early research indicated that palladium on alumina exhibits poor activity [9], more recent results have demonstrated that palladium precipitated onto alumina nanoparticles [n-Al_2O_3(+)] is not only active, but one of the best catalysts found for this reaction [29]. The maximum isolated yield reported for commercial 5% Pd/C is ~2 g of product per g of catalyst [30], with yields of 1.5–2 g/g for 10% Pd/C catalysts being more common [8,31,32]. In contrast, the 5% Pd/n-Al_2O_3(+) catalyst gave yields in excess of 2.5 g/g of catalyst [8]. In addition to the excellent n-Al_2O_3(+)-supported catalyst, previous work revealed that 5% Pd precipitated onto a traditional porous alumina support is an active catalyst but with only half the yield compared to the n-Al_2O_3(+) catalyst, and 5% Pd precipitated on n-Al_2O_3(−) [a lower surface area nanoparticle alumina] was a very poor catalyst. Since the earlier study showed that there is not a simple correlation between the measured palladium surface area and the catalytic activity (product yield) of the reaction, it was decided to extend the study and include other supports with varying properties in an attempt to determine the properties that are of importance for a high catalytic activity of the corresponding supported palladium catalysts. Considering that the nanoparticle alumina is a relatively expensive support at a price of nearly $700/kg on a kg purchase basis (NanoScale NanoActive Alumina Plus), it is also important to search for a less expensive support that can give comparable yields to find an economically viable catalyst.

A number of metal oxides have been used to prepare efficient palladium catalysts, either as sole supports or as promoters or additives to other supports. These include for example, CeO_2 [33–37], ZrO_2 and ZrO_2–CeO_2 [38–43], CuO [44,45], ZnO [46–53], SnO_2 [2,54–58], MgO [59–62], SiO_2 [63–66], TiO_2 [67–71], and CaO [72,73]. Since the reaction under investigation is believed to be limited by the reoxidation of the reduced palladium oxide, supports such as CeO_2 and ZrO_2 are of particular interest, as they have been shown to assist in the reoxidation of palladium [34,35,38,39]. More traditional supports, such as SiO_2 and TiO_2 and their nanoparticle analogues were also included to determine if there is an advantage to use nanoparticle supports compared to other high surface area, porous supports.

The main objectives in this work are to (1) determine the effects of the support on the catalytic activity of palladium supported on porous and nanoparticle oxides in the oxidative coupling of 4-methylpyridine; (2) determine if the acidic or basic properties of the supports are important for the preparation of an active catalyst; and (3) identify any catalyst supports competitive with the n-Al_2O_3(+) support in terms of cost and/or activity in the mentioned reaction system.

Table 1
Suppliers, properties and price of the supports used in the study. Listed in order of decreasing surface area.

Oxide	Supplier [a]	SA (m^2/g) [b]	Crystallite diameter [c] (nm)	Cost [d] (kg)
n-Al_2O_3(+)	NanoScale	695	NA [e]	695
n-MgO	NanoScale	685	4	425
n-TiO_2	NanoScale	505	NA [e]	280
n-SiO_2	NanoAmor	490	15	180
n-Al_2O_3(−)	NanoScale	275	NA [e]	70
γ-Al_2O_3	Alfa Aesar	260	NA	115
p-SiO_2	Alfa Aesar	240	NA [e]	115
p-TiO_2	Alfa Aesar	120	NA	110
n-CaO	NanoScale	100	20	65
n-ZnO	NanoScale	70	10	90
n-CeO_2	NanoScale	60	7	200
n-ZrO_2 + 10% CeO_2	NanoAmor	45	20–30	450
n-Al$(OH)_3$	NanoAmor	40	15	320
n-ZrO_2	NanoAmor	35	29–68	395
n-SnO_2	NanoAmor	35	55	270
n-CuO	NanoScale	35	8	Unavailable[f]

[a] Suppliers: *NanoScale*, NanoScale Corporation. NanoActive compounds: http://www.nanoscalecorp.com/content.php/chemicals/powders/. *NanoAmor*, Nanostructured and Amorphous Materials Inc.: http://www.nanoamor.com/. *Alfa Aesar*: https://www.alfa.com.

[b] Determined by BET (Nova 1200).

[c] As specified by supplier (determined from XRD). NA = not available from supplier.

[d] Price FOB for 1 kg quantities 3/13/08.

[e] Amorphous compound.

[f] Discontinued product.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared using commercially available nanoparticle oxides supplied by NanoScale Materials Inc. [74] and Nanostructured & Amorphous Materials, Inc (NanoAmor) [75] as well as some commercially available traditional supports [76]. The properties of these support oxides and their origins are given in Table 1.

The catalysts where prepared by precipitation. In this method, the support was dispersed into a solution of palladium nitrate. Porous oxide pellets were ground before dispersion. The mixture was then titrated with a NaOH solution, which formed $Pd(OH)_2$ on the support [77]. The amount of NaOH used in these experiments corresponds to 50% stoichiometric excess based on the amount of palladium nitrate used. The resulting mixture was aged overnight at room temperature before it was filtered. The recovered catalyst was rinsed by stirring in water overnight, followed by another filtration. The catalyst was then dried overnight at 105 °C and calcined at 350 °C or 450 °C for 3 h.

2.2. Reaction conditions

The 4-methylpyridine (Aldrich or Acros) was doubly distilled over KOH prior to use. In a typical reaction run 0.7 g of catalyst was placed in a round bottom flask along with 7 g of the distilled 4-methylpyridine. The reaction mixture was evacuated and an oxygen atmosphere introduced before it was heated to the boiling point (145 °C). The reaction proceeded under reflux for 72 h. After a complete reaction the flask contents were filtered using a glass micro-fiber filter and washed with chloroform to dissolve the product. The product was recovered by removing the chloroform, the water byproduct and unreacted 4-methylpyridine from the filtrate using a rotary evaporator.

The standard deviation of the reported product yields was estimated from 5% Pd precipitated onto n-Al_2O_3(+) (6 samples) and p-TiO_2 (5 samples). These were found to have average yields of