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$_2$O$_3$(+). 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$_2$O$_3$(+) 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
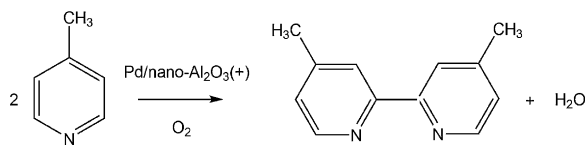
Scheme 1. Oxidative coupling of 4-methylpyridine to 4,4′-dimethyl-2,2′-bipyridine over a palladium on nanoparticle alumina catalyst.

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$_2$O$_3$(+)] 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$_2$O$_3$(+) catalyst gave yields in excess of 2.5 g/g of catalyst [8]. In addition to the excellent n-Al$_2$O$_3$(+)-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$_2$O$_3$(+) catalyst, and 5% Pd precipitated on n-Al$_2$O$_3$(−) [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$_2$O$_3$(+) 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$_2$O$_3$(+)	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$_2$O$_3$(−)	NanoScale	275	NA [e]	70
γ-Al$_2$O$_3$	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$_2$O$_3$(+) (6 samples) and p-TiO$_2$ (5 samples). These were found to have average yields of

2.5 ± 0.15 g/g catalyst for Pd/n-Al$_2$O$_3$(+) and 2.6 ± 0.25 g/g catalyst for Pd/p-TiO$_2$ (from this and previous work [29]). This amounts to standard deviations of approximately ±6.5% and ±%10, respectively. These numbers are typical for the catalysts used in this study, except for the commercial Pd/C catalyst. In the case of the Pd/C catalyst, the variation was closer to 20%, which in this case is attributed to variations in the PdO:Pd ratio on this catalyst. Since the ±6.5% and ±10% are typical values of the standard deviation the more conservative ±10% value was used in the research. The variation in yield is believed to be caused mainly by varying qualities of palladium precursor and reactant distillate, since these have been shown in previous research to have large effects upon the yields [29]. These are very important parameters to control in order to assure reproducible results. However, other parameters such as variations in support and other extraneous variables, e.g. varying chlorine contents, can also influence the catalytic activities of the resulting catalysts and ultimately the product yield.

The regeneration experiments were performed on spent catalysts, which after reaction were washed with hot ethyl acetate and then heat treated at 450 °C in air for 3 h.

2.3. Catalyst characterization

The surface areas of supports as received and the prepared catalysts were characterized by multipoint BET isotherms using a Quantachrome Nova 1200 instrument. Chemisorption measurements to characterize active surface area of the catalysts and the number of acidic and basic sites of the supports were performed on a ChemBET 3000 from Quantachrome Instruments. Reduction in hydrogen followed by CO titration was used to determine the palladium surface area. Since PdO is believed to be the active phase, or a necessary precursor for this reaction [8], measuring the Pd surface area after reduction of the PdO phase is not necessarily a good measure of the active surface area. This is particularly the case when the surface consists of a mixture of Pd and PdO phases. However, in our prepared catalysts the palladium phase after calcination is PdO in all cases and no partially reduced PdO has been observed. Furthermore, reductions are performed using mild conditions (170 °C in a stream of 5% hydrogen) to minimize sintering of the formed Pd phase. A temperature of 170 °C was chosen to be close to the temperatures experienced by the catalyst during reaction.

The Pd particle size was calculated using Eq. (1) [78].

$$\Phi_{av} = \frac{1}{V_g S_{av}} \frac{k V_m C_m}{N_a \rho_m} \tag{1}$$

where: Φ_{av}, average particle size; S_{av}, average stoichiometry: CO/Pd = 1. This value was selected to be conservative and report a lower Pd surface area (or dispersion) rather than one that may be higher than the true value; k, shape factor. A value of 5 was used in the current study. It corresponds to a cube with one side attached to the support. This is reported to be a reasonable approximation for calculating Pd crystals in this size range [78]; V_m, molar volume; N_a Avogadro's number; ρ_m, metal density; V_g, volume of gas adsorbed; C_m, surface density of metal atoms. Values between 1.27×10^{15} and 1.44×10^{15} atoms/cm^2 have been reported in the literature [78]. The value 1.27×10^{15} atoms/cm^2, which assumes roughly equal distribution of 1 0 0, 1 1 0, and 1 1 1 crystal faces, was used in the current study.

The formula can be rearranged and simplified to give the metal surface area (SA_m) (Eq. (2)).

$$SA_m = \frac{V_g S_{av}}{V_m C_m N_a} \tag{2}$$

The basic sites of the supports were probed by titration with CO$_2$, and acidic sites were probed by titration with anhydrous ammonia in a stream of helium. Prior to titration, the support samples were outgassed in a flow of nitrogen at 105 °C for an hour. Although some of the more basic supports may have adsorbed atmospheric CO$_2$ that does not desorb at 105 °C, the possibility of sintering precludes the use of higher temperatures during out-gassing.

3. Results and discussion

3.1. Catalytic activity measurements

All prepared catalysts were subjected to catalytic activity measurements. The results from these experiments are summarized in Table 2. Entries 1 and 2 have been added for comparison. Entry 1 reports a typical yield for the commercial Pd/C catalyst and Entry 2 is the result from a nanoparticle alumina catalyst, and is the best yield reported for this reaction to date [29]. As can be seen in Table 1, the surface areas of the various supports included in this study covers a wide range from ~700 down to 35 m^2/g. If the only function of the support is to provide the surface area onto which the palladium is dispersed, the yields would be expected to decrease with the surface area of the support. This is indeed observed for some of the supports used in this study (see Fig. 1A). In particular, catalysts supported on n-Al$_2$O$_3$(+), n-MgO, n-SiO$_2$, γ-Al$_2$O$_3$ and n-SnO$_2$ give yields that appear to be a linear function of the support surface area. Fitting this data to a straight line gives a regression coefficient of 0.99 (line equation: $Y_x = 7.9 ± 2.2 SA_x + 0.058 ± 0.004$, where Y_x is the yield obtained over the palladium catalyst deposited on support x and SA$_x$ is the surface area of that support). The n-TiO$_2$ support also is also close to this line and including the yields obtained from the Pd/n-TiO$_2$ catalyst gives a linear regression coefficient of 0.98.

Evidently, there are also a number of catalysts that result in higher yields than expected from the support surface areas. This may be expected in cases where there are strong palladium-support interactions, since favorable interactions can induce, for example, higher Pd surface areas, or a more catalytically active Pd species, compared with non-interacting supports. Consequently, strong palladium-support interactions are most likely the reason why the yields obtained from the catalysts supported on n-ZrO$_2$ + CeO$_2$, n-ZrO$_2$, n-ZnO and n-CeO$_2$ are high, or reasonably high, despite their low support surface areas (70 m^2/g and below). These oxides have been shown to exhibit strong interactions with palladium in other catalysts [37,42,43]. In the light of this, it is unexpected that the CuO and SnO$_2$ do not result in catalysts with higher activities, since Cu(II)

Table 2
Catalytic activities for all prepared catalysts (calcination temperature: 350 °C). The table is presented in order of decreasing support surface area, as in Table 1.

Entry	Catalyst: 5% Pd on	Yield (g/g cat)[c]	Yield (g/g Pd)[c]
1	Activated C[a,b]	1.8	36
2	n-Al$_2$O$_3$(+)[b]	2.5	50
3	n-MgO	2.3	46
4	n-TiO$_2$	1.6	31
5	n-SiO$_2$	1.7	35
6	n-Al$_2$O$_3$(−)[b]	0.3	5.8
7	γ-Al$_2$O$_3$[b]	1.2	24
8	p-SiO$_2$	1.6	32
9	p-TiO$_2$	2.6	52
10	n-CaO	0.15	2.8
11	n-ZnO	2.1	44
12	n-CeO$_2$	1.5	29
14	n-ZrO$_2$ + 10%CeO$_2$	2.45	49
15	Al(OH)$_3$	0.8	17
16	n-ZrO$_2$	2.3	47
17	n-SnO$_2$	0.5	10
18	n-CuO	NP[c]	NP

[a] Commercial catalyst.
[b] Results from previous work [83].
[c] NP: no Product, i.e. no measurable amount of product could be recovered
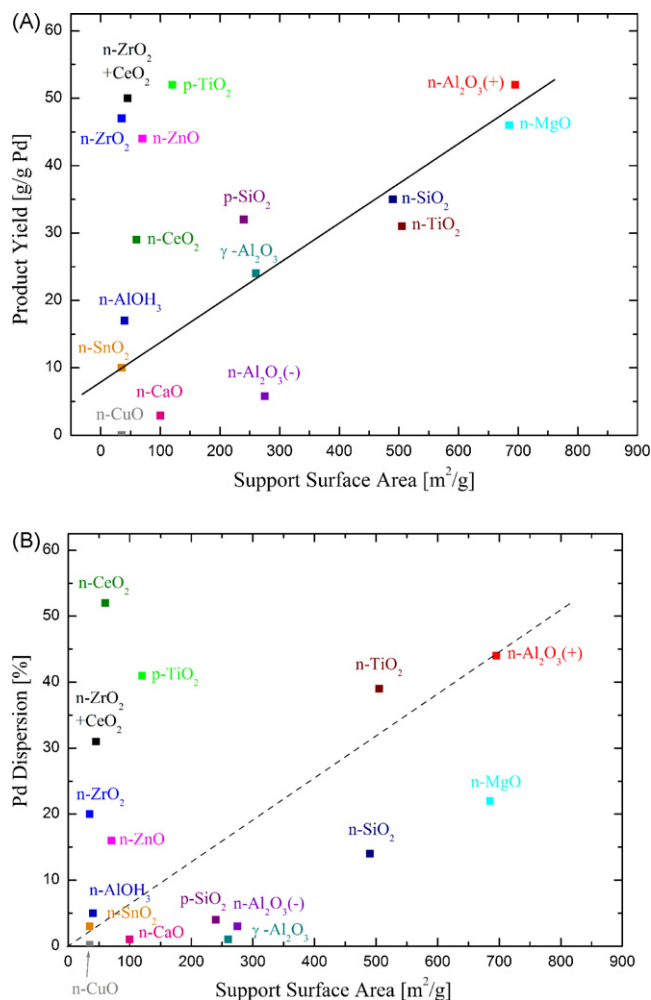
Fig. 1. (A) Product yield versus support surface area for palladium catalysts prepared using various oxide supports. (B) Palladium dispersion versus support surface area for the catalysts in (A).

and Sn(II) are often added as co-catalysts to palladium in homogeneous reaction systems [79–83]. In fact, the Sn(II)/Pd(II) pair has been shown to be effective in homogeneous C–H activation and C–C coupling reactions [84].

The yields obtained from the catalysts supported on n-CaO and the n-Al$_2$O$_3$(−) are also unexpectedly low, which appears to indicate some unfavorable interactions between the palladium and these supports. In contrast, the yields obtained from the catalysts supported on n-Al(OH)$_3$ and the traditional supports p-SiO$_2$ and p-TiO$_2$ are higher than predicted from their corresponding surface areas according to the equation derived above. In this case, it appears that there again are some favorable interactions between the palladium and the support. However, in the case of SiO$_2$ and Al(OH)$_3$ no specific palladium-support interactions have, to our knowledge, been reported previously.

3.2. Catalyst and metal surface area

Since the support surface area does not necessarily correlate with the amount of palladium available at the surface, it is important to determine the palladium surface areas of the catalysts. For reactions that are not structure sensitive, it is expected that there is a linear correlation between the catalytic activity and the palladium surface area. Carbon monoxide adsorption measurements were therefore performed on reduced catalysts to determine the palladium surface areas of all catalysts. The results are presented

in Table 3. From these measurements the dispersions of the catalysts, i.e. the fraction of Pd atoms at the surface (compared to all palladium atoms on the catalyst), were calculated. The palladium dispersions obtained on several of the prepared catalysts are high, ranging from 20 to over 40% (Table 3). By comparison, the dispersion on the commercial 5% Pd/C is 23%. It is noteworthy that such high dispersions (relative to the commercial Pd/C catalyst) can be obtained from a simple precipitation method. This indicates that nanoparticles have strong potential as catalyst supports also in other reaction systems.

When analyzing the data it is important to keep in mind that PdO and not Pd metal is the active site on these catalysts. For this reason, the temperatures were kept low during the reductive pretreatment to avoid palladium particle growth. However, it is possible that different oxide supports could exhibit different amounts of palladium sintering during the reduction process. This together with structure sensitivity can lead to deviations from a linear correlation between the activity and the Pd surface area in this case. Despite these limitations, the experiments are important and very valuable information can be obtained from the measured Pd surface areas, as will be described below.

When plotting the Pd dispersion versus the support surface areas (Fig. 1B) and comparing this to the plot of yield versus support surface areas (Fig. 1A), some of the high and low catalyst yields can be explained. For example, the low yields obtained from catalysts supported on CuO, CaO and n-Al$_2$O$_3$(−) are evidently due to very low palladium surface areas on these catalysts. The palladium surface area on the n-SnO$_2$ support is also lower than expected if this support indeed would induce metal-support interactions. As expected, the n-ZrO$_2$ + CeO$_2$, n-ZrO$_2$, n-ZnO and n-CeO$_2$ supports do result in catalysts with high palladium surface areas, compared to the respective support surface area. The palladium surface area as a fraction of the total surface area ranges from 10 to 19% on these catalysts. By comparison the palladium surface areas of the n-Al$_2$O$_3$(+)-supported catalyst and the commercial palladium on carbon catalyst are 10% and 1% of the total surface areas, respectively (see Pd % SA in Table 3). While the reported dispersion on the Pd/n-CeO$_2$ appears abnormally high, this is likely the result of strong metal-support interactions. Since the CeO$_2$ is a reducible oxide, it is possible that some of the CeO$_2$ is reduced in the reduction process due to the Pd–CeO$_2$ interactions. Evidence of oxygen mobility on CeO$_2$ and transfer of oxygen from CeO$_2$ to palladium has been observed in, for example, methane oxidation over Pd/CeO$_2$ [34]. The Pd/CeO$_2$ system could also be similar to CuO/CeO$_2$ catalysts where it has been reported that surface CeO$_2$ can be reduced at low temperatures (less than 200 °C) [85]. It was verified that no CO is adsorbed on a n-CeO$_2$ support after reductive treatment if palladium is not present on the surface. If the Pd does induce low-temperature CeO$_2$ reduction, it is likely that CO adsorbs on these reduced CeO$_x$ sites, in addition to Pd sites during the CO titration process. This would result in very high CO adsorption values, and consequently abnormally high Pd surface areas (or dispersions). A high Pd dispersion on the porous TiO$_2$ support can also explain the high yield obtained from this catalyst. Whilst the high dispersion on this support is likely due to Pd–TiO$_2$ interactions, it is evident that these interactions differ between p-TiO$_2$ and n-TiO$_2$ supports. The Pd dispersions are close to the same on these two supports, while the support surface areas are considerably different, 505 m^2/g (n-TiO$_2$) versus 120 m^2/g (p-TiO$_2$). Since the crystalline phase of TiO$_2$ has been reported to influence palladium-support interactions [68], XRD experiments were performed on the TiO$_2$ supports used in this study to determine the crystal structure of these supports. From the XRD data (not shown) it is evident that the p-TiO$_2$ support consists mainly of anatase and it is much more crystalline than the n-TiO$_2$ support. The n-TiO$_2$ support also contains some anatase, but its crystallinity is poor, and other crystalline and/or amorphous TiO$_2$

Table 3
Measured and calculated catalyst properties, such as surface areas, dispersions and turnover frequencies.

Catalyst 5% Pd	Catalyst SA (m^2)	CO adsorbed (μmol/g cat)	%Dispersion[a]	Pd SA [a] (m^2/g)	Pd % SA	Pd diameter (nm)	Turnover number (mol prod./mol surf. Pd)
C (commercial) [83]	695	110	23	5.2	0.7	4	90
n-Al$_2$O$_3$(+) [83]	180	205	44	9.7	5.5	2	70
n-MgO	85	105	22	5.0	5.9	4	120
n-TiO$_2$	210	185	39	8.8	4.2	2.5	45
n-SiO$_2$	120	65	14	3.1	2.6	7	102
n-Al$_2$O$_3$(−) [83]	155	15	3	0.7	0.5	30	110
γ-Al$_2$O$_3$ [83]	200	6.5	1	0.3	0.2	68	1000
p-SiO$_2$	230	20	4	0.95	0.4	22	435
p-TiO$_2$	115	195	41	9.2	8.0	2	70
n-CaO	30	4.5	1	0.2	0.7	98	180
n-ZnO	35	75	16	3.6	10.2	6	150
n-CeO$_2$	60	245	52	11.6	19.4	2	35
n-ZrO$_2$ + CeO$_2$	40	145	31	6.9	17.2	3	110
Al(OH)$_3$	55	25	5	1.2	2.2	18	175
n-ZrO$_2$	35	95	20	4.50	12.9	4.5	130
SnO$_2$	20	15	3	0.71	3.6	29	180
CuO	30	1	0.2	0.05	0.2	440	0

[a] The Pd dispersion, surface area and average particle diameter have been calculated using 1:1 as the CO:Pd stoichiometry and a surface atom density of 1.27×10^{15} atoms/cm^2.

phases may exist. Consistent with the anatase TiO$_2$ phase resulting in stronger palladium-support interactions, compared to other TiO$_2$ phases [68], the Pd/p-TiO$_2$ is located with the catalysts supported on other interacting supports (such as CeO$_2$, ZrO$_2$ and ZrO$_2$ + CeO$_2$) in Fig. 1A and B. In contrast, the results from the palladium supported on the less crystalline n-TiO$_2$ phase appear to correlate reasonably well with the support surface area.

Some unexpected results include the low Pd surface areas on the p-SiO$_2$, n-SiO$_2$, and MgO supports. Considering the reasonably high yields obtained from palladium on these supports, it would be expected that the palladium surface areas are higher than the measured values. Thus, either the palladium sinters more on these supports compared to the other supports, or a greater fraction of the palladium on the surface of these catalysts is active compared to the palladium on the surface of for example the n-Al$_2$O$_3$ (+) support (see Fig. 2 and Table 3). From Fig. 2 it is evident that there is a correlation between the catalytic activity (product yield) and the palladium surface area (dispersion). In general, a higher dispersion results in a higher yield. However, there are some deviations from this relationship and the correlation is definitely not linear (Fig. 2). It appears that several supports interact with the palladium and alter the catalytic properties.

A structure sensitive reaction is also supported by the fact that for the Pd/n-Al$_2$O$_3$(+) catalysts there was no significant difference
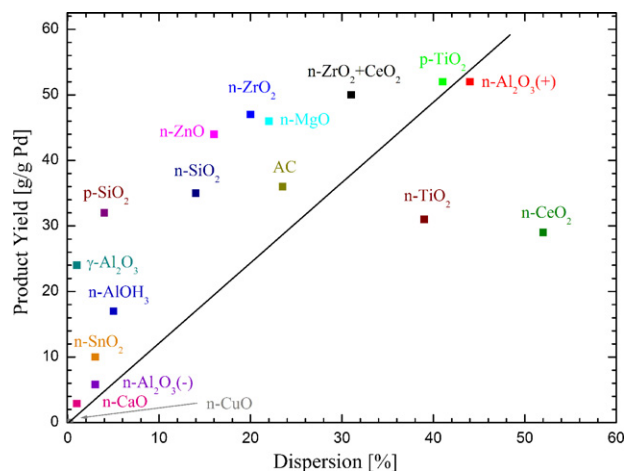
Fig. 2. Product yield versus palladium dispersion for the catalysts on the different oxide supports.

in product yield between palladium loadings of 5% and 10% [29], despite the fact that the palladium surface areas were significantly different. In this case the support is the same, so the extent of Pd sintering during the reduction treatment should be the similar for the two catalysts. These results suggest that there are some species on the surface that are more active than others. Our hypothesis is that the most active palladium species are very small Pd/PdO particles, which may form at corner and edge sites on the supports due to Pd-support interactions. Nanoparticle oxide supports, and, to some extent, more traditional high surface area supports (such as bimodal γ-Al$_2$O$_3$, p-SiO$_2$ and p-TiO$_2$), would have a large number of these corner and edge sites. Once these support sites are saturated with palladium, any additional palladium would be deposited on "non-active" support sites, or on top of the active palladium. The number of corner and edge sites on the support may be more important on "non-interacting" supports, compared to the supports with strong metal support interactions. On reducible oxides there may already be "active" support sites present, which can result in high Pd dispersions and highly active Pd species.

3.3. Acidic and basic sites

In order to further probe how the properties of the supports affect the palladium dispersions and the catalytic activities of the catalysts, the amounts of acidic and basic sites of the supports were investigated. This was done by measuring the adsorption of NH$_3$ and CO$_2$ on the different catalysts (see Table 4).

As is evident in Fig. 3A and B there is no simple correlation between the catalyst dispersion and the acidic or basic sites on the supports. As expected the n-CaO had a large uptake of CO$_2$ (due to facile CaCO$_3$ formation). The amount of CO$_2$ adsorbed by the calcium (4.4 ml/g) is more consistent with surface adsorption rather than bulk carbonate formation ($\sim$400 ml/g). While moderately basic supports (such as γ-Al$_2$O$_3$ and MgO) evidently can give reasonable product yields (Fig. 1A), it appears that the Pd dispersions are lower on these compared to less basic or neutral supports (Fig. 1B). Considering that the Pd dispersion on the CaO support is very low, avoiding moderately to highly basic supports when preparing well-dispersed Pd catalysts using the base precipitation method may be advisable. It also appears that avoiding highly acidic supports is recommended when preparing well-dispersed palladium catalysts. The support with the highest ammonia adsorption (n-SiO$_2$) resulted in a catalyst with a palladium surface area below that expected for its support surface area (Fig. 1B). However, despite

Table 4
Adsorption of NH_3 and CO_2 on the different catalyst supports.

Support	NH_3 (S cm^3/g)	CO_2 (S cm^3/g)
n-Al$_2$O$_3$(+)	9.0	0.75
n-MgO	3.4	2.0
n-TiO$_2$	4.0	0.6
n-SiO$_2$	52.8	0.0
n-Al$_2$O$_3$(−)	8.3	0.6
γ-Al$_2$O$_3$	1.6	1.75
p-SiO$_2$	5.7	0.0
p-TiO$_2$	9.9	1.0
n-CaO	2.8	4.4
n-ZnO	14.3	0.2
n-CeO$_2$	7.3	0.8
n-ZrO$_2$ + 10%CeO$_2$	2.6	1.1
Al(OH)$_3$	25.0	0.1
n-ZrO$_2$	4.7	0.3
n-SnO$_2$	2.3	0.02
n-CuO	3.3	0.4

Table 5
Economics of catalysts.

Support	Support cost contribution ($/g product)[a]	Cost of product ($/g product)[b]
n-Al$_2$O$_3$(+)	0.29	0.57
n-MgO(+)	0.18	0.49
n-TiO$_2$	0.16	0.62
γ-Al$_2$O$_3$	0.09	0.69
p-TiO$_2$	0.04	0.32
n-ZnO	0.04	0.37
n-CeO$_2$	0.11	0.54
n-ZrO$_2$ + 10% CeO$_2$	0.20	0.53
n-ZrO$_2$	0.16	0.48

[a] Price FOB for 1 kg quantities 3/13/2008.
[b] At a price of palladium at $450/oz. Calculation excludes cost of derivation to a nitrate precursor.

a lower palladium surface area on the n-SiO$_2$ support, the yield obtained from this catalyst is in the range expected for this catalyst considering its support surface area (Fig. 1A). Consequently, the average activity of the palladium on the surface of this catalyst is higher than the activity of for example the palladium on the n-Al$_2$O$_3$(+) support (see the turnover numbers in Table 3). The second most acidic support, the n-Al(OH)$_3$, also results in a cata-

lyst with higher turnover number than the Pd/n-Al$_2$O$_3$(+) catalyst, and the same is true for the most basic supports (Table 3). Consequently, highly acidic or basic supports appear to result in lower Pd dispersions, but the palladium that is on the surface is more active than the palladium on our reference Pd/n-Al$_2$O$_3$(+) catalyst. It is easier to see how an acidic support (electron acceptor) can lead to more electrophilic, and thus more reactive, palladium, than how the basic support leads to more active Pd species. For example, a density functional calculation study of Pd atoms on γ-Al$_2$O$_3$ [1 1 0] found that single Pd atoms interact strongly with tetragonal Lewis acid sites [86]. Evidently, there are some complex interactions between palladium and the supports on the catalysts included in this investigation. Considering the turnover numbers reported in Table 3, more active catalysts should result if the dispersion on the γ-Al$_2$O$_3$ support can be increased.

3.4. Estimated cost of selected catalyst

In the search for a more effective catalyst the economics must also be considered, i.e. cost of the catalyst compared to the yield obtained. For example, this reaction does proceed over Raney nickel, which is a considerably less expensive catalyst. However, the yields over the Raney nickel catalyst are also low per gram of catalyst and the reaction is more involved since the catalyst must be activated and is highly flammable [87]. Consequently, palladium would be the active metal of choice if higher yields and economically viable catalysts can be developed. Although the main cost of the catalysts is due to palladium, the cost of nanoparticle oxide supports can be significant, as can be seen in Table 1. Since the n-Al$_2$O$_3$(+) support is the most expensive of the oxide supports used in this study, it is possible that other supports can be competitive with the Pd/n-Al$_2$O$_3$(+) catalyst if the cost of the catalyst per g of product formed is considered. To allow for variations in the price of palladium, as well as the cost of preparing palladium nitrate, a more expensive palladium cost basis ($450/oz) was used for calculating the cost of catalyst per unit weight of product (Table 5), even though the price of palladium has recently been as low as $250/oz [88]. At these prices the Pd/p-TiO$_2$, Pd/n-ZrO$_2$, and Pd/n-ZnO are catalysts competitive with the Pd/n-Al$_2$O$_3$(+) catalyst. At a commercial scale the amount of catalyst used and the conversion of starting material also comes into the economic analysis, since a larger amount of catalyst and a lower conversion would result in larger reactor sizes (higher capital costs) for the same production rate. This naturally favors the most active catalyst by minimizing reactor size in addition to palladium usage. Consequently, the lower yields of the Pd/ZrO$_2$ and Pd/n-ZnO catalysts likely offset any cost savings from the support compared to the Pd/n-Al$_2$O$_3$(+) catalyst. Consequently, the Pd/p-TiO$_2$ is likely the only support that has potential to exhibit better economics than the Pd/n-Al$_2$O$_3$(+) catalyst. This said, some of the other support oxides with moderate price and relatively
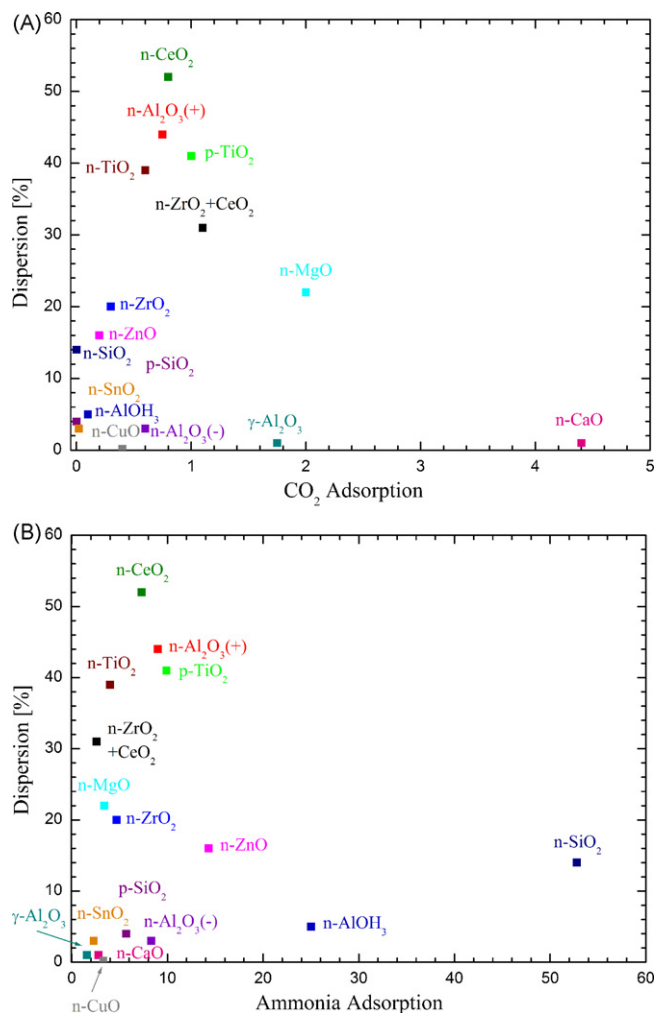
Fig. 3. (A) Palladium dispersion versus CO_2 adsorption for palladium catalysts prepared using various oxide supports. (B) Palladium dispersion versus NH_3 adsorption for palladium catalysts prepared using the same oxide supports as in (A).

high activities, such as the n-MgO, n-TiO$_2$, n-CeO$_2$, n-ZrO$_2$ and n-ZrO$_2$ + CeO$_2$ may make their corresponding catalysts competitive with the n-Al$_2$O$_3$(+) support through optimization and, perhaps, promoter use.

Since the economics of the reaction is very dependent on whether or not the catalysts can be reused, a few regeneration experiments were attempted. From previous studies it is known that the catalysts after reaction are reduced (palladium is present as Pd^0), while the fresh catalysts consist of supported PdO. It is also known that some carbon- and nitrogen-containing species are present on the catalysts after reaction. Consequently, to reoxidize the Pd metal and remove the carbon containing species, a few spent catalysts [Pd/C, Pd/n-Al$_2$O$_3$(+) and Pd/(ZrO$_2$ + n-CeO$_2$)] were washed with hot ethyl acetate and then subjected to an oxidative heat treatment (air at 450 °C for 3 h). No product was recovered for any of the treated catalysts. In the case of the Pd/C a significant mass loss indicated oxidation of the carbon support and thus destruction of the catalyst. In the case of the Pd/(n-ZrO$_2$ + CeO$_2$) a color change after the oxidative treatment indicated reoxidation of the palladium. However, the Pd surface area of this catalyst was low indicating inefficient removal of the carbon-containing species, sintering of the palladium, or loss of palladium due to leaching into the solution during the reaction. More extensive experiments on catalyst regeneration with concomitant catalyst characterizations are necessary and will be performed in a future study.

4. Conclusions

Palladium supported on n-ZrO$_2$, (n-ZrO$_2$ + 10% CeO$_2$), n-CeO$_2$, n-ZnO, n-MgO, n-TiO$_2$ and p-TiO$_2$ all demonstrated high catalytic activities. While none of the catalysts significantly outperformed the activity of the precipitated 5% Pd/n-Al$_2$O$_3$(+) catalyst developed in previous research, several of the catalysts outperformed the highest yields reported for commercial Pd/C catalysts (2 g product/g catalyst, Table 2).

In general there appeared to be two groups of supports giving highly active catalysts; (1) supports with high surface areas and (2) support oxides known to result in strong Pd-support interactions. For example, supports with very high initial surface areas (more than 450 m^2/g), such as n-TiO$_2$, n-SiO$_2$, n-MgO and n-Al$_2$O$_3$(+), were generally quite active (>35 g product/g Pd) and high surface area supports (450 > SA > 200 m^2/g), such as porous SiO$_2$ and γ-Al$_2$O$_3$ gave moderate yields (32 and 24 g/g Pd, respectively). The other group of active catalysts includes, for example, palladium supported on n-ZrO$_2$, (n-ZrO$_2$ + CeO$_2$), n-CeO$_2$, and n-ZnO, which all have relatively low surface areas. As a result of strong metal-support interactions these supports resulted in relatively high Pd surface areas compared to the surface area of the support (10–19% of the total SA), which in turn gave higher yields than expected from the support surface areas (Fig. 1A). It is also possible that these supports can result in Pd-support electronic interactions which positively affect the catalytic activity. This would explain why the activities for some of the catalysts are higher than what would be expected from the Pd dispersion on these catalysts.

No simple correlation between the catalytic activity and the support surface area or the palladium dispersion could be identified, which indicates that the reaction is structure sensitive, i.e. some palladium species are more active than others. It is also evident that there is no correlation between the acidic or basic sites of the supports and the palladium dispersion or the catalytic activity. However, highly acidic and highly basic supports appear to result in lower dispersions compared to more neutral supports. Despite the fact that the palladium surface areas are lower on the highly acidic and basic supports, it appears that the small amount of surface palladium present on these supports is more activity compared to the less acidic or basic supports, i.e. the turnover numbers are higher.

In summary, the search for more active and economically competitive catalysts, identified a few promising supports. In particular, the n-ZnO and p-TiO$_2$ result in catalysts that are significantly less expensive but with comparable activity to Pd/n-Al$_2$O$_3$(+) catalysts. The high surface area n-MgO support also results in a catalyst with reasonably high activity. This support may, thus, prove useful in future catalyst development where the effects of promoters or additives are investigated. This is particularly important in cases where the additives are known to form inactive aluminates with alumina supports.

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