Investigation of Nano-Particle Metal Oxide Supports for the Oxidative Coupling of 4-Methylpyridine Over Palladium

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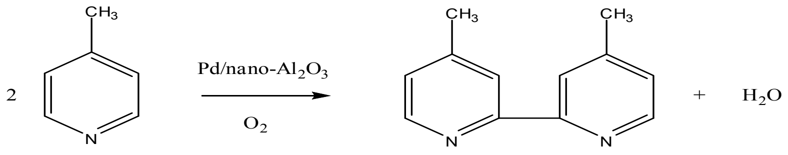
Bypyridines are important due to their ability to coordinate to transition metal ions and form complexes with interesting electronic properties. For example, these organometallic complexes can be utilized in numerous catalyst systems. However, due to the difficulty of synthesizing bipyridines, they are prohibitively expensive for large scale processes, which limit their wide-range application. The oxidative coupling of 4-methylpyridine to 4,4'-dimethyl-2,2'-bipyridine over palladium is a one-step process in which the bipyridine is formed directly from the pyridine reactant via C-H activation and C-C coupling. The only by-products of this reaction are water and the terpyridine. No solvent or halogenated compounds are needed, which make this an environmentally friendly pathway to bipyridine compared with synthesis methods using halogenated precursors.



In our previous research it was demonstrated that 5% palladium deposited onto alumina nanoparticles by precipitation was the most active palladium catalyst reported to date for this reaction. Our hypothesis is that the high activity of this catalyst is due to the high number of low coordination sites, such as corners and edges that many nanoparticles and some traditional porous supports have. These sites could interact with the palladium and result in higher dispersions compared to more traditional supports. Alumina is a commonly used support due to its thermal stability and high surface area and was thus a good prospective nanoparticle-support. However, it is not expected that there are any alumina-specific metal support interactions in Pd/Al_2O_3 catalysts. The main objective of this work was to determine if palladium supported on other nanoparticle or porous oxides are active in this reaction, and determine which support properties are important for a high catalytic activity. Therefore, 5% loadings of Pd were precipitated onto a variety of nanoparticle and porous supports. The Pd dispersion on these catalysts was determined by CO adsorption and CO_2 and NH_3 titrations were used to determine the acidity and basicity of the various supports. Some of the nanoparticle supports, such as nanoparticle CaO, $Al(OH)_3$, SnO and CuO, formed catalyst with little or no activity. The low actives of these supports could in part be explained by low Pd dispersions. Nanoparticles of ZrO_2 (with and without CeO_2 doping), CeO_2, ZnO, TiO_2, MgO and SiO_2, as well as porous TiO_2 and SiO_2 exhibited activities at or above what would be expected considering their surface areas. In fact, the Pd dispersions on the nanoparticle ZnO, CeO_2, ZrO_2, and CeO_2 doped ZrO_2 supports were high relative to their surface areas. This indicates strong Pd-support interactions on these catalysts. The porous SiO_2 catalyst had a similar behavior to a porous alumina catalyst from previous research. The Pd dispersions on these catalysts were low but some activity was observed. The porous TiO_2 catalyst had high yields and high dispersions. As for the lower surface area nanoparticles, the higher dispersion on this support likely indicates strong Pd-support interactions. The nanoparticle MgO and SiO_2 catalyst, while not as good as the nanoparticle Al_2O_3 catalyst previously develops, had high dispersions and reasonable activities. No direct correlation between CO_2 and NH_3 uptake and activities was found. However, catalysts with high NH_3 uptake usually exhibited moderate to high activities, indicating that acidic support sites are important in the preparation of an active catalyst.

Only the CeO_2 doped ZrO_2 support was shown to give yields comparable to the best performing nanoparticle alumina catalyst. Other supports that have potential are the porous TiO_2 and nano-particle MgO. Consequently, it appears that active catalysts can be prepared using high surface area nanoparticle supports (with potentially a high number of corner and edge sites to interact with palladium), highly acidic supports, or supports with known strong palladium-support interactions.