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Effect of titania structure on palladium oxide catalysts in the oxidative coupling of 4-methylpyridine

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ABSTRACT

The effects of anatase and rutile titania on PdO/TiO_2 catalysts and how these phases influence the activity in the oxidative coupling of 4-methylpyridine to 4,4′-dimethyl-2,2′-bipyridine were investigated. The anatase and rutile concentrations were systematically varied by heat treating a nearly amorphous nanoparticle titania at temperatures between 105 and 800 °C. X-ray diffraction (XRD) measurements confirmed that the anatase concentration increased with heat treatment temperature until rutile began to form at 600 °C, and at 800 °C rutile TiO_2 was the only phase observed. X-ray photoelectron spectroscopy (XPS) analysis of the catalysts revealed strong $PdO\text{-}TiO_2$ interactions which increased with support treatment temperature. According to XPS, the interactions yielded electron-deficient PdO species ($Pd^{\delta+}$ with $\delta > 2$) and Ti^{3+} species (likely TiO_2 with oxygen vacancies) on the surface of the catalysts, as a result of electron transfer from palladium to titania. These $PdO\text{-}TiO_2$ interactions increased with increasing anatase phase in the TiO_2 support and the turnover number (TON: number of product molecules formed per surface palladium site) followed the same trend. The strongest interactions (the largest amounts of $Pd^{\delta+}$ with $\delta > 2$ and Ti^{3+} species) were observed for the catalysts supported on rutile TiO_2, which is also the catalyst with the highest TON, revealing the importance of electron transfer from palladium to titania in this reaction. Despite the high TON for PdO on rutile TiO_2, the anatase-supported PdO gave a significantly higher product yield due to the very low surface area of rutile TiO_2.

1. Introduction

Palladium catalysts supported on titanium dioxide (Pd/TiO_2) are very versatile and have been used in a number of reactions, ranging from complete oxidations [1–3] to selective hydrogenations [4–13], hydrodechlorination [14], NO_x reduction [15,16], and even Heck reactions [17]. Pd/TiO_2 catalysts have also been used in the acetoxylation of toluene [18,19], and are commonly used in photocatalytic oxidation reactions due to the properties of the TiO_2 support [20,21]. It is well known that high-temperature reduction of Pd/TiO_2 catalysts can induce strong metal support interactions (SMSI) [22,23]. These metal-support interactions can lead to a partially reduced titania support (i.e. oxygen vacancies and the presence of Ti^{3+} due to hydrogen spillover from palladium) and titania migration over the active palladium sites [24]. While this can potentially lead to more stable catalysts (as palladium particle growth, i.e. sintering, is hindered by the titania) and also more selective catalysts (a reduction in coking), the titania is also covering active palladium species which can result in lower catalytic activities [24]. Most studies of Pd/TiO_2 catalysts involve reduction to induce strong metal support interactions [6–9,22–24]. However, there are indications that strong interactions are present even for PdO/TiO_2 catalysts, i.e. between the palladium oxide and the titania support on non-reduced catalysts [21], and oxygen spillover from palladium to titania has also been observed [25,26]. Strong interactions between PdO and TiO_2 can be manifested in PdO decomposition at lower temperatures compared with PdO supported on, for example, Al_2O_3 [27–30]. Furthermore, $Pd\text{-}TiO_2$ interactions are dependent on the structure of the titania support. Titania has two main crystal structures of importance in catalysis, namely anatase and rutile [31], although brookite has also been identified in catalysts [12,13]. The anatase phase is widely used as catalyst support because of its large specific surface area, but this phase has a low thermal stability. At higher temperatures the anatase phase is converted into the more stable rutile phase [31,32]. Unfortunately, this phase transition to rutile is associated with a significant loss in surface area [31], which is typically highly undesirable in catalysis. However, rutile can have

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favorable catalytic properties in some reactions despite the low surface area [18,20,33]. Reduction of titania-supported catalysts, at temperatures as low as 200 °C, leads to strong favorable interactions between palladium and the anatase TiO_2 support [15,31]. In contrast, rutile TiO_2 requires higher reduction temperatures than anatase to induce SMSI [15,23]. The higher temperature needed for SMSI on rutile TiO_2 may be because the less stable anatase TiO_2 is easier to reduce than rutile TiO_2 [7]. Due to the differences in metal-support interactions between the TiO_2 phases, the catalytic activity and selectivity of palladium supported on anatase versus rutile TiO_2 can be markedly different [18].

In our previous research, we have shown that palladium oxide supported on a porous anatase titania (p-TiO_2) is more active in the oxidative coupling of 4-methylpyridine to 4,4′-dimethyl-2,2′-bipyridine than PdO on a nearly amorphous nanoparticle TiO_2 (n-TiO_2), despite the significantly larger surface area (505 m^2/g) of n-TiO_2 compared with p-TiO_2 (120 m^2/g) [34]. Strong PdO_x-TiO_2 interactions were identified on the TiO_2-supported catalysts resulting in slightly more electron-deficient PdO species compared with PdO on the surface of a non-interacting support, such as Al_2O_3 [35]. However, except for varying anatase concentrations no other difference was observed over the TiO_2-supported catalysts to explain the catalytic behavior [34]. Therefore, the objectives of this study were to investigate the metal-support interactions of PdO/TiO_2 catalysts in detail, and determine how they vary with TiO_2 structure, as well as how these interactions influence the oxidative coupling of 4-methylpyridine. A series of PdO catalysts supported on TiO_2 with different structures (ranging from nearly amorphous to anatase and rutile) were prepared and carefully characterized using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared using commercially available titanium dioxide nanoparticles (n-TiO_2, NanoScale Corporation), porous titania pellets (p-TiO_2, Alfa Aesar), and rutile titania powder (r-TiO_2, Sigma–Aldrich). The titania pellets were crushed before catalyst preparation, and the nanoparticle TiO_2 was pretreated in air at 105 °C, 350 °C, 450 °C, 600 °C, or 800 °C for 3 h in a muffle furnace. A precipitation method was used to deposit palladium onto the supports. For this method, an aqueous solution of palladium nitrate ($Pd(NO_3)_2{\cdot}2H_2O$, Sigma–Aldrich) was added to an aqueous dispersion of the titania support. The mixture was titrated with an aqueous solution of sodium hydroxide (Sigma–Aldrich) to form palladium hydroxide(s) on the support (using 50% stoichiometric excess of hydroxide based on the amount of palladium nitrate) [36]. The resulting mixture was aged overnight at room temperature before being filtered. The filtered material was rinsed in deionized water overnight and filtered again. The recovered material was then dried at 105 °C overnight and calcined in air at 350 °C for 3 h, unless otherwise noted. In two cases, higher calcination temperatures, 600 °C and 800 °C, were used. In all cases, the palladium loading was 5% by weight on a metal basis.

2.2. Reaction conditions

The reactant, 4-methylpyridine (Acros), was doubly distilled over KOH prior to use. In a typical reaction, 0.7 g of catalyst was placed in a round bottom flask with 7 g of distilled 4-methylpyridine. The reaction mixture was evacuated before introducing an oxygen atmosphere. The mixture was then heated to the boiling point (145 °C) under continuous agitation. After refluxing for 72 h, the flask contents were washed with chloroform to dissolve the product and filtered using a glass micro-fiber filter. The product was obtained by removing the chloroform, water, and unreacted 4-methylpyridine using a rotary evaporator. The yields are reported as the amount of product formed per unit weight of catalyst or palladium. A turnover number was defined as the number of moles of product formed per mole of surface palladium calculated based on the CO titration measurements.

2.3. Catalyst characterization

The as-received support surface areas (after drying over night at 105 °C), the pretreated support surface areas, and the surface areas of the prepared catalysts were determined by multipoint Brunauer–Emmett–Teller (BET) isotherms on a Quantachrome Nova 1200 instrument as described in previous work [37].

Chemisorption measurements were performed in a Quantachrome ChemBET 3000 instrument and used to characterize the active metal surface area. The catalysts were first reduced with 5% hydrogen in nitrogen at 170 °C for 1 h, and then outgassed in nitrogen at 170 °C for another hour. The mild conditions were used to limit sintering of the Pd particles on the surface. This was followed by pulse titrating carbon monoxide over the reduced catalysts to measure the CO adsorbed and determine the palladium surface area and dispersion of the catalysts. Detailed descriptions of the procedure and calculations are given in previous work [34]. While PdO is believed to be the active phase, or at least a necessary precursor, the CO chemisorption measurements on reduced catalysts are important since the PdO surface cannot be measured directly. It is assumed that there is a correlation between the original PdO surface area and the Pd surface area of the reduced catalyst. Previous XRD and TEM data support this assumption [35]. The turnover number (TON), i.e. the number of moles of product formed per mole of surface palladium, was calculated from the product yield and the CO adsorbed on the catalyst using a Pd:CO stoichiometry of 1:1.

The XRD data were gathered on a PANalytical X′Pert Powder X-ray diffractometer using Bragg-Brentano geometry with Cu Kα radiation ($\lambda = 1.54$ Å). The supports and catalyst powders were secured onto a glass slide with double-sided sticky tape prior to the measurements.

XPS was performed on selected fresh catalysts using a custom built instrument equipped with a double-pass cylindrical mirror analyzer (PHI model 25-270 AR). The catalyst powders were pressed into aluminum cups prior to insertion into the ultra-high vacuum (UHV) chamber (base pressure 1×10^{-10} Torr). Spectra were taken in retarding mode with a pass energy of 50 eV for survey spectra and 25 eV for high-resolution spectra using a Mg Kα X-ray source (PHI04-151). Data were collected using a computer interface and then digitally smoothed. A value for the C 1s binding energy of 284.6 eV was assigned to correct for static charging and work function differences [38].

3. Results and discussion

Several PdO/TiO_2 catalysts were prepared using different titania supports: a porous anatase support (p-TiO_2), a commercially available rutile TiO_2, (r-TiO_2), and a nearly amorphous n-TiO_2 support. The latter was heat treated at increasing temperatures between 105 °C and 800 °C to systematically increase the contribution from the anatase phase until the temperature was sufficiently high for rutile formation. All of the PdO/TiO_2 catalysts were tested for activity in the oxidative coupling of 4-methylpyridine and characterized using a number of analytical techniques.