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Hydrolysis of silicon–hydride bonds catalyzed by ferromagnetic cobalt nanoparticles

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Ferromagnetic cobalt nanoparticles with average diameter of 9.5 nm, used for the purpose of magnetic catalyst recovery, were shown to catalyze the hydrolysis of silicon–hydride bonds for a range of hydrosilanes. The highest turnover frequencies (220–311 moles silane/moles Co/h) were observed for the dialkylsilanes (R_2SiH_2), which were hydrolyzed to give the corresponding dialkylsilanediols. The monoalkylsilanes ($RSiH_3$) reacted more slowly (2–20 moles silane/moles Co/h) and gave an oligomeric product. Trialkylsilanes (R_3SiH) required elevated temperatures in order to observe trace activity.

KEY WORDS: ferromagnetic; cobalt nanoparticles; catalysis; hydrosilanes; polysiloxane.

1. Introduction

As nanoparticle research continues its rapid evolution, greater emphasis is being placed on exploiting their favorable properties (e.g., high surface to volume ratio) for developing practical applications. These studies are aided greatly by the fact that the vast, ever-increasing library of synthetic methods for transition metal nanoparticles allows for tailoring the particle in a way to fit the specifications of the application [1]. The use of nanoparticulate materials as catalysts for chemical reactions represents an important bridge between homogeneous and heterogeneous processes [2]. Many ligand-stabilized nanoparticle colloidal dispersions form stable suspensions that behave very much like homogeneous mixtures. However, the chemical transformations are taking place on a metal surface analogous to heterogeneous systems. The utility for a nanoparticulate catalyst is intuitive: smaller particle size increases the percentage of surface atoms capable of performing the desired transformation. This advantage would be especially important for industrial catalysts requiring expensive metals such as platinum or rhodium.

Nanoparticles that are highly sensitive to magnetic fields (i.e., superparamagnetic and ferromagnetic) have found a particular niche in applications research. Most important among these are the use of magnetic particles for magnetic resonance image enhancement, drug delivery and hyperthermic cancer treatment [3,4]. Magnetism applied to catalysis might have intriguing potential, especially when dealing with materials on the nanoscale. While ligand-stabilized nanoparticles are technically suspended in the reaction solvent, and therefore considered heterogeneous, their small size and high dispersion usually precludes filtration or conventional centrifugation, thus lacking the key component that makes this method so attractive for practical use: ease of catalyst separation and recovery. However, if these catalysts were magnetic, it would be possible to collect the catalyst with, and subsequent re-dispersion by removal of, a strong magnet. One popular application of this concept is the covalent linkage of iron oxide nanoparticles to an active homogeneous catalyst whereby the particle acts as a magnetic support (in the classical heterogeneous sense), allowing for efficient catalyst recycling [5,6]. Of particular relevance to this work are magnetic particles being the active catalyst (rather than a simple magnetic anchor) such as the catalytic decomposition of a model for organophosphorus nerve agents by a modified magnetite nanoparticle [7].

The toxicity of cobalt has precluded its use from biocatalysis applications, however, its proclivity for carbon–carbon bond formation makes it useful from an industrial standpoint. The utilization of cobalt nanoparticles (CoNP's) as catalysts has been sparse, with the most notable study being the use of stabilized aqueous particles for the intramolecular Pauson-Khand transformation [8]. The colloidal cobalt was relatively stable under the reaction conditions (20 atm CO, 130 °C) and recyclable, although the catalyst separation steps did not utilize magnetic recovery. Despite this success, a follow-up study indicated that a CoNP catalyst on a charcoal support was still preferable from a stability and

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separation perspective [9]. Despite the continuing work in development of dispersed cobalt nanoparticles, there has been little progress toward their utilization in applied catalysis.

The hydrolytic polymerization of simple hydrosilanes (R_xSiH_{4-x}, $x = 0-3$) is a convenient test case since the reaction is known to proceed with diamagnetic nanoparticles of gold [10] and rhodium [11]. Through the use of ferromagnetic cobalt nanoparticles, the goal is to find an active catalyst while using its magnetic properties for particle separation and recycling with minimal loss of activity. Additional consideration must be given to the fact that the thermodynamically favored agglomeration of particles will be the primary source of catalyst deactivation. In order to retard agglomeration, cobalt particles covalently bound to oleic acid, a long chain carboxylic acid, will be employed. Previous workers have shown that larger CoNP's (15 nm) of this type may be collected by a small bar magnet and re-dispersed by ultrasonic agitation [12].

2. Experimental

Unless otherwise specified, all syntheses and manipulations were carried out on a double manifold Schlenk vacuum line under an argon atmosphere or in a helium-filled glovebox. Methanol (anhydrous, 99.8%), *o*-dichlorobenzene (anhydrous, 99%), *p*-dioxane (anhydrous, 99.8%), octadecylsilane (97%, mixture of isomers), phenylsilane (97%), diethylsilane (99%), diphenylsilane (97%), and triethylsilane (99%) were purchased from Aldrich and degassed prior to use, either by freeze/pump/thaw three times or bubbling with argon for 1 h. Triphenylsilane was purchased from Aldrich and recrystallized prior to use. Oleic acid (99%) and trioctylphosphine oxide (99%) were purchased from Aldrich and used as received. Octacarbonyldicobalt (stabilized by 1–5% hexane) was purchased from VWR International and was dried by passing a stream of argon gas over the solid immediately prior to use. Cobalt(II) oleate was purchased from City Chemical and used without further purification. ^1H and ^{29}Si NMR spectra were recorded on a Varian 400 MHz superconducting high-resolution spectrometer. The operating frequency for ^{29}Si was 79.5 MHz. Routine infrared spectra were collected using a Mattson Research Series 10000 FTIR spectrometer with DTGS detector. Elemental analyses were carried out by Galbraith Laboratories, Inc. Molecular weight determinations (M_w and M_n) were carried out at the New Jersey Center for Biomaterials, Rutgers University. The GPC system consists of a Perkin Elmer LC 250 binary pump, ISS 200 autosampler and Waters' 410 RI detector. Two PL gel columns (Polymer Laboratories) 1000 and 100,000 angstrom were used in series. The mobile phase used was THF at a flow rate of 1 mL/min. For data collection and molecular weight calculations, Waters' Empower 2 software on an IBM Thinkcenter was used. The molecular weights were computed against polystyrene standards.

Cobalt nanoparticles with an approximate diameter of 9.5 nm were prepared by a previously published method [13]. The particles were precipitated from the reaction mixture using 50 mL of methanol. After decanting the liquid portion, the particles were allowed to dry in the inert atmosphere glove box and then were suspended in 1,2-dichlorobenzene and transferred to a 100 mL volumetric flask. The cobalt concentration was determined by taking a 1 mL aliquot of solution, drying *in vacuo*, followed by acidification with aqueous 1 M HCl. After neutralization with aqueous 1 M NaOH, the cobalt sample was placed in an acetic acid/sodium acetate buffer solution (pH 5.8) and titrated with 9.91×10^{-4} M aqueous EDTA solution with xylenol orange as indicator. Two trials gave an average [Co] of 0.0243 M, giving a yield of 77% with respect to cobalt.

Silane reactions were monitored by observing the decay of the ν(Si–H) stretch observed from 2050 cm^{-1} to 2200 cm^{-1}. This was conveniently done through the utilization of the Mettler-Toledo ® ReactIR 4000 attenuated total reflectance (ATR) infrared spectrometer with a 25 mL stainless steel Parr ® reactor as the reaction cell. The ATR window material is silicon hitran. The reaction mixture is stirred using a stainless steel 4-prong propeller attached to a magnetic drive. The magnet resides a minimum of 4″ above the reaction mixture and should not significantly influence the suspended cobalt nanoparticles. After drying the reactor at 80 °C *in vacuo* overnight, the reactor was loaded with 10 mL of background solvent (containing the nanoparticle catalyst) and then brought to the desired reaction temperature. A single 128-scan background spectrum was collected followed by injection of the silane dissolved in the reaction solvent and water. A single 128-scan spectrum is collected at a regular interval (3 or 5 min) for the entire reaction period. Reaction profiles showing the concentration of silane as a function of time can be generated after baseline correction. The reactor was then cooled to room temperature, and the reaction mixture was transferred to a clean vial for analytical testing.

3. Results and discussion

The reaction of octadecylsilane and water catalyzed by oleate-capped CoNP's was found to be relatively slow in 1,2-dichlorobenzene at ambient temperature. Upon increasing to 60 °C, the activity increased dramatically. However, the ν(Si–H) stretch consistent with the starting silane (2150 cm^{-1}) did not decay to an absorbance of zero, but rather shifted to a higher wavenumber (2156 cm^{-1}) with an absorbance roughly one-third that of the starting silane (figure 1), indicating that not all the silicon hydride bonds are reactive toward hydrolysis. The decrease in absorbance to approximately one-third its original value suggests that each silicon atom retains a single hydride substituent, with the formed Si–O bonds causing the shift in wavenumber to slightly higher energy. Such behavior is distinct from the same reaction catalyzed by gold and rhodium nanoparticles, whereby complete consumption of the silicon–hydride bonds is observed without a perceptible shift in the *v*(Si–H) signal. In order to exclude oleic acid as the catalyst for this reaction, a control reaction utilizing a 1,2-dichlorobenzene solution containing oleic acid, triphenylphosphine oxide, octadecylsilane and water was monitored at 60 °C with no consumption of silane observed. After 1 day, cobalt nanoparticles were added, and the reaction began immediately.

The choice of solvent played an important role in the hydrolysis reactions due to the differences in the solubility of water in various organic solvents. In this study, water is always used in excess on a molar basis. While 1,2-dichlorobenzene is the solvent used to synthesize the catalyst, its poor miscibility with water could limit the catalytic activity, particularly if water is included in the rate-limiting step. This factor necessitated exploration of an organic solvent with a relatively high boiling point and improved miscibility with water, leading to the use of 1,4-dioxane. When comparing the two solvents (figure 2), the miscible dioxane/water mixture shows a longer reaction time of approximately 3 days, in contrast to the 17 h in 1,2-dichlorobenzene, along with a substantial induction period (5 h). While it was expected that a higher [H_2O] would enhance the reaction rate, other factors such as competition between dioxane and/or water for the silane binding sites on cobalt may be important.

Table 1 summarizes the activities and major products (reaction diagram shown in figure 3) using cobalt nanoparticles to catalyze the hydrolysis of a series of hydrosilanes in 1,4-dioxane. Gel permeation chromatography was used to determine the M_w and M_n for the octadecylsilane- and phenylsilane-derived polysiloxanes, which indicates that the chain lengths are fairly short and better described as being oligomeric. NMR spectroscopy (^{1}H and ^{29}Si) is convenient for characterizing the products of these reactions and distinguishing the polymeric materials from the discrete silanediols. The polysiloxane oligomer originating from phenylsilane in 1,4-dioxane was observed to have several silicon-29 resonances (−79.4, −69.8, −60.6, −49.2 and −46.3 ppm; $CDCl_3$) and broad ^{1}H signals consistent with a polymeric material. The products originating from diphenylsilane and diethylsilane displayed only single ^{29}Si chemical shifts at −31.3 and −4.5 ppm, respectively, in $CDCl_3$.

The activity trend ($R_2SiH_2 > RSiH_3 > R_3SiH$) shows that it is likely that steric and electronic effects both play a role in the hydrolysis of the silicon–hydride bond. When using silanes with only two hydridic protons (i.e., dialkylsilanes), it was found that hydrolysis activities increased substantially compared to the trihydride (figure 4). Since the dialkylsilanes would be considerably more sterically hindered, the increase in rate is likely due to increased stability of the resulting secondary silyl anion formed upon oxidative addition to cobalt. While the trialkylsilanes would form an even more stable silyl anion, the increased steric bulk of the third alkyl substituent results in no silane consumption being observed at 60 °C for Et_3SiH and Ph_3SiH. When placed in 1,2-dichlorobenzene and heated to 120 °C, triphenylsilane reacted at a very slow rate. Triethylsilane showed no

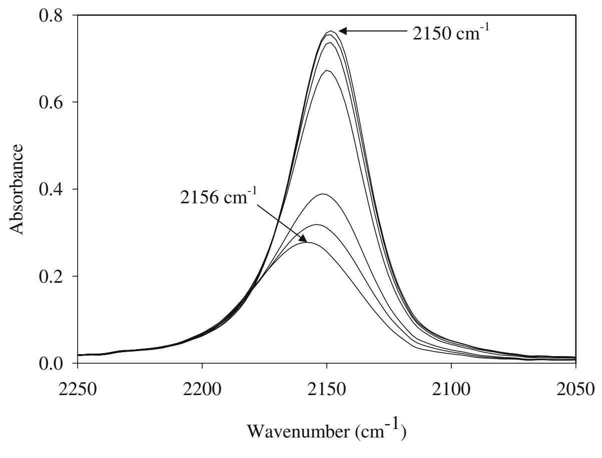

Figure 1. Shift of *v*(Si–H) signal during octadecylsilane hydrolysis catalyzed by CoNP. Reaction conditions: 0.0122 mmol Co, 288 equiv. octadecylsilane, 10 mL 1,2-dichlorobenzene, 0.5 mL water and 60 °C [1 h time lapse between spectra].

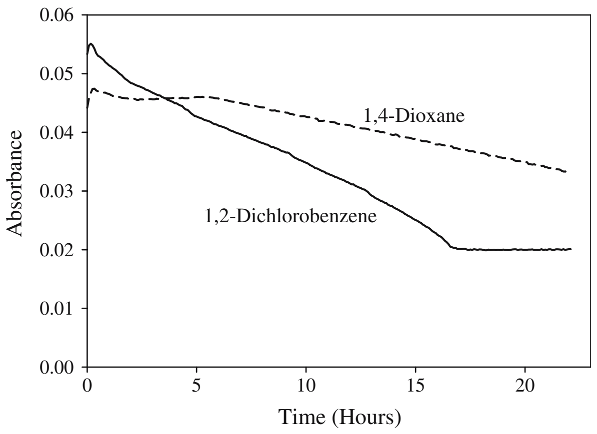

Figure 2. Profile of octadecylsilane consumption, monitored by *v*(Si–H) decay, catalyzed by cobalt nanoparticles in 1,2-dichlorobenzene (solid line) and 1,4-dioxane (dashed line) at 60 °C. Reaction conditions: 0.0486 mmol Co, 72 equiv. octadecylsilane, 1 mL water, and 15 mL total solvent volume.

Table 1
Turnover frequencies and major products of organosilane consumption by hydrolysis using cobalt nanoparticle catalysts[a]

Silane (equiv.)	TOF[b]	Major product	Molecular weight analysis		
			M_w (g/mol)	M_n (g/mol)	PDI
$PhSiH_3$ (167)	20	Polysiloxane	4145	2923	1.4
$C_{18}H_{37}SiH_3$ (57)	2	Polysiloxane	4754	2222	2.1
Ph_2SiH_2 (111)	222	Diphenylsilanediol	N/A	N/A	N/A
Et_2SiH_2 (159)	311	Diethylsilanediol	N/A	N/A	N/A
Ph_3SiH (69)	None[c]	N/A	N/A	N/A	N/A
Et_3SiH (129)	None	N/A	N/A	N/A	N/A

[a] Reaction conditions: 0.0486 mmol Co, 60 °C, dioxane/1,2-dichlorobenzene/water (12:2:1) as solvent.

[b] Units of moles of Si–H consumed/moles Co/h.

[c] Trace activity at 100 °C.

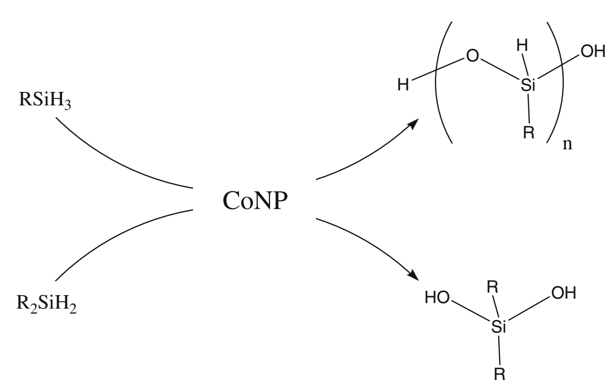

Figure 3. Reaction diagram for silicon hydride hydrolysis catalyzed by cobalt nanoparticles in 1,4-dioxane in the presence of excess water.

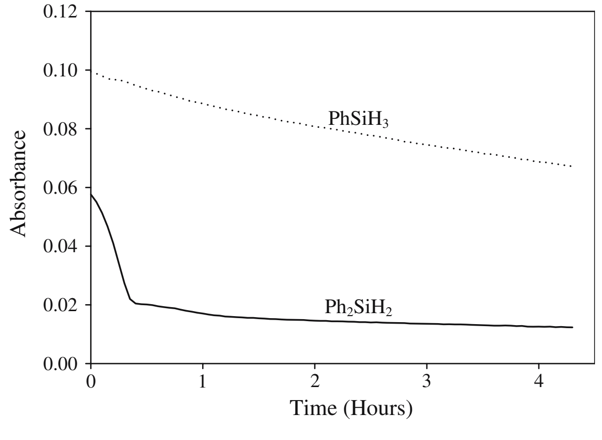

Figure 4. Consumption of diphenylsilane (solid) and phenylsilane (dotted) catalyzed by CoNP monitored by infrared spectroscopy via ν(Si–H) absorbance. Reaction conditions: 0.0486 mmol Co, 1.0 mL silane, 60 °C, dioxane/1,2-dichlorobenzene/water (12:2:1) as solvent.

reactivity even at elevated temperatures. The bigger question as to why the monoalkylsilanes form polymeric materials while the dialkyl analogues yield discrete molecules has not yet been answered.

The identity of the active cobalt is a topic that merits further examination. While it is known that the cobalt precursor, $Co_2(CO)_8$, is active for oxidative addition of a variety of Si–H bonds [14] (and potentially active for hydrolytic polymerization), the compound is unlikely to survive the high reaction temperatures employed in the nanoparticle synthesis due to its low thermal stability. The methanol wash step would also remove any remaining dicobalt octacarbonyl. When dealing with nanoparticulate catalysts, it is important to ensure that the nanoparticles are not a precursor for the actual active species (i.e., generation of discrete metal complexes or bulk metal). While the vast majority of cobalt atoms are beneath the surface and in the zero oxidation state, the surface atoms covalently bound to oleate will be in a higher oxidation state. It therefore became important to test a monomeric cobalt complex for activity under these conditions. Cobalt(II) oleate (60 mg, 96 μmol) was used as a catalyst for hydrolysis of Et_2SiH_2 in dioxane and was found to be active (figure 5). Although the discrete cobalt(II) salt has significant activity toward hydrolysis, it is far less active than the nanoparticles. More than half of the starting silane was consumed before the first scan was collected

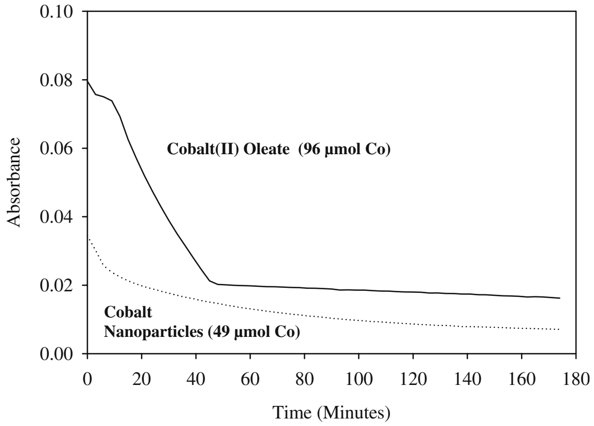

Figure 5. Disappearance of diethylsilane in the presence of cobalt nanoparticles (dotted line) and cobalt(II) oleate (solid line) monitored by infrared spectroscopy via ν(Si–H) absorbance. Reaction conditions: 7.7 mmol diethylsilane, 60 °C, dioxane/1,2-dichlorobenzene/water (12:2:1) as solvent.

at 3 min (a result that was seen in several diethylsilane experiments utilizing cobalt nanoparticles). It should be noted that while all of the metal centers of the cobalt(II) oleate can participate in the reaction, only the surface atoms of the cobalt nanoparticle (~15% of the total number of atoms) can operate. Taking this into account, the effective ratio of "active" cobalt centers in nanoparticulate cobalt and cobalt oleate is approximately 1:12, emphasizing that the nanoparticles still have superior activity despite a disparity in active sites compared to cobalt oleate. These results argue favorably for the nanoparticles being the actual catalyst rather than merely a source for discrete, homogeneous cobalt(II) complexes.

Since the particles are ferromagnetic, the use of a magnetic stir bar for mixing might cause problems due to their mutual attraction. This was tested by running the reaction in a glass round bottom flask. In both 1,2-dichlorobenzene and dioxane, the particles remain suspended in the initial stages of the reaction, ideally as the original nanoparticles rather than larger agglomerated colloids. In the case of Ph_2SiH_2 and Et_2SiH_2, the reaction mixtures remain dark brown for approximately 1 h, after which the cobalt quickly collects onto the stir bar, coinciding with the end of the reaction, leaving a completely clear solution. From a catalyst removal perspective, this is very convenient as the organic phase can simply be decanted. However, attempts to re-suspend the nanoparticles in fresh dichlorobenzene by ultrasonication and/or heating were unsuccessful, implying that catalyst deactivation occurs, possibly from agglomeration of the particles to form larger cobalt particles that can no longer overcome the magnetic forces of the stirring bar in order to remain in solution.

4. Conclusion

This work was conducted to test if a magnetically separable nanoparticle could serve as the active catalyst phase instead of just being used as a magnetically separable support, as has been previously demonstrated [5,6]. The hydrolysis of hydrosilanes was chosen as the test reaction because this is a catalytic process that proceeds smoothly using other diamagnetic metal nanoparticles such as gold and rhodium [10,11]. Morphologically well-characterized oleate stabilized cobalt nanoparticles, CoNP, that are actively investigated for their magnetic properties, were chosen because previous workers have shown that CoNPs can be isolated from a solution phase using a 0.05 Tesla magnet and reversibly re-dispersed using ultrasound [12].

The hydrolysis of hydrosilanes proceeds smoothly, in the absence of external magnetic fields, using CoNP to yield dialkylsilanediols in the case of R_2SiH_2 reactants and oligomeric products in the case of $RSiH_3$ reactants. The products were characterized by NMR, ^1H and ^{29}Si, and FTIR spectroscopy as well as gel permeation chromatography for the polymeric products. In the absence of magnetic fields, the CoNP remains dispersed within the solution phase even after the hydrosilane reactant has been consumed. Alternatively, when the reaction is conducted in the presence of a magnetic stirring bar, the CoNP remains dispersed during the bulk of the reaction. However, when the hydrosilane is nearly consumed, the cobalt material collects on the surface of the magnet resulting in a colorless solution phase. This observation is somewhat unusual because the original nanoparticles are synthesized in the presence of a magnetic stirring bar [13].

In contrast to the reported work using unaltered CoNP [12], our attempts to re-disperse the resulting cobalt material after the catalytic reaction process using heat and or ultrasound have been unsuccessful. These results suggest that changes occur to the surface of the nanoparticles during the course of the silane hydrolysis reaction and oleate is no longer bound with sufficient strength to the altered nanoparticle surface to prevent irreversible agglomeration under the influence of a magnetic field.

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