

Comparing the Pyrophoricity of Palladium Catalysts for Heterogeneous Hydrogenation

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ABSTRACT: We compare the pyrophoricity of two commonly employed hydrogenation and hydrogenolysis palladium solid catalysts, Pd/C and SiliaCat Pd⁰, and the reactivity of SiliaCat Pd⁰ with that of two commercial hydrogenation catalysts (Pt⁰ EnCat and Pd/C) in the hydrogenation of six different nitroarene compounds under optimized reaction conditions.

KEYWORDS: pyrophoric, palladium, heterogeneous, hydrogenation, hydrogenolysis

INTRODUCTION

The hazards of heterogeneous catalytic hydrogenation and hydrogenolysis reactions is renowned.¹ Conventionally carried out in organic solvent over supported metal catalysts, catalytic hydrogenation and hydrogenolysis reactions are inherently hazardous processes because H₂ is in contact with air, and flammable solvents may easily catch fire and even explode, especially during hydrogenation reactions which are highly exothermic.¹ Further increasing risk, conventional Raney-type Ni or Pd/C catalysts are highly pyrophoric because they absorb H₂ at their outer surface. In brief, the latter catalysts can spark spontaneously upon exposure to air, readily causing ignition of flammable solvents such as methanol, especially when filtered to dryness and not handled correctly (removal of the spent catalyst via filtration through a glass filter, cover with wet sand, and disposal of waste in dedicated container containing water).²

In brief, owing to the industrial importance of hydrogenation reactions, finding safe and active catalytic alternatives is highly desirable.¹

As emphasized by Felpin and Fouquet,³ in catalytic hydrogenation over 10% Pd/C or 5% Pd/C, high catalyst loadings are commonly employed (>5 wt %) because commercially available batches have a random distribution and size of Pd⁰ nanoparticles over the charcoal, further increasing risk because the aforementioned catalysts absorb and retain significant amounts of H₂. Finally, highly flammable methanol, once commonly used as solvent of choice in hydrogenation reactions, increases the hazard because MeOH burns with an almost invisible flame.

To decrease risk, one successful approach is to prepare the catalyst *in situ* from homogeneous Pd(OAc)₂ in the presence of charcoal and the reactants.³ This allows the use of exceptionally low palladium loadings (0.025 mol %) under remarkably mild reaction conditions (1 atm H₂, 25 °C), while

the catalyst shows excellent stability with practically no leaching of Pd (<4 ppb), even though conversion of 5 mmol substrate typically requires 12 h.³

Another approach based on risk prevention via inherently safer chemistry (a key principle of green chemistry)⁴ is to switch to nonpyrophoric catalysts. Comprised from highly dispersed Pd nanoparticles (uniformly in the range 2.0–6.0 nm) encapsulated within organically modified silica (ORMOSIL), one such catalyst is SiliaCat Pd⁰.⁵ Available today as powder comprised of spherically shaped regular microparticles, the catalyst can be successfully employed, for example, in the solvent-free hydrogenation of squalene⁶ and in the hydrogenolysis⁷ of aromatic alcohols, aldehydes, and ketones using a low catalyst amount (0.2 mol % and 0.1 mol % Pd, respectively) under mild reaction conditions (70 °C, 3 bar H₂).

We now compare the pyrophoricity of two hydrogenation and hydrogenolysis palladium solid catalysts, Pd/C and SiliaCat Pd⁰, and the reactivity of the latter catalytic material with that of two commercial hydrogenation catalysts (Pt⁰ EnCat and Pd/C) in the hydrogenation of six different nitroarene compounds under optimized reaction conditions. In addition, we investigate the limits of the ORMOSIL catalyst's lack of pyrophoricity.

RESULTS AND DISCUSSION

A two-neck 250 mL round-bottom flask kept under a fume hood was filled with 5 mL MeOH. One of the two necks was uncapped so that air could freely enter the flask. Through the same aperture, an aliquot of SiliaCat Pd⁰ was added with a spatula. No flame or explosion was recorded.

After 1 min, the same mixture kept under the fume hood was added to an aliquot of commercial Pd/C (10 wt % Pd loading on activated carbon support, Aldrich, St. Louis, MO). It was enough to agitate the mixture with the spatula to observe a small explosion with flame formation. (Caution! Keep the glass flask under the closed fume hood and wear eyeglasses, a lab coat, and gloves.)

In another experiment aimed to test the flammability limits of SiliaCat Pd⁰, we dried the ORMOSIL catalyst after having soaked it in methanol. The catalyst kept in a Büchner funnel was first vacuum-dried using a water aspirator. Under special conditions which took us several hours to identify via trial and error, the Pd nanobeads inside the ORMOSIL porosity did turn incandescent (over the limit of 350 °C of our laser

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Figure 1. SiliaCat Pd⁰ kept in a Büchner funnel by filter paper during vacuum drying of added MeOH using a water aspirator under optimized conditions.

Table 1. Hydrogenation Yield for Six Different Substrates under Recommended Conditions over Three Different Heterogeneous Metal Catalysts^a

| Nitroaryl Substrates | SiliaCat Pd ^{0b} Conversion ^e (%) | EnCat Pt ^{0c} Conversion ^e (%) | Pd/C (5%) ^d Conversion ^e (%) |
|----------------------|---|--|--|
| | 100 | 15 | 99 |
| | 98 | 0 | 100 |
| | 100 | 45 | 100 |
| | 100 | 12 | 100 |
| | 100 | 22 | 100 |
| | 100 | 46 | 100 |

^aReaction conditions: 2 mmol nitroaryl substrate in 5 mL of MeOH HPLC grade under hydrogen balloon room temperature conditions. ^b1 mol % SiliaCat Pd⁰; 30 min. ^c5 mol % Pt⁰ EnCat; 30 min. ^d1 mol % Pd/C; 30 min. ^eYields were evaluated by GC-MS analysis.

thermometer) due to the exothermic reaction between MeOH vapors and O₂ in the air (Figure 1). However, no flames from the catalyst structure were ever spotted under any applied conditions (rate of solvent removal via the water aspirator). Only the color of the white filter paper used to hold the material in the Büchner funnel turned brown.

The sole drying of the ORMOSIL catalyst did *not* turn it incandescent. The addition of several aliquots of fresh MeOH to the dried catalyst was required prior to achieve the required balance between MeOH vapors and air and observe incandescence. Incandescence required optimally selected conditions. If the air flow through the Büchner filter was too low, there was not enough O₂ intake for the reaction with MeOH vapors. If the flow was too high, the temperature rapidly dropped, and no incandescence was observed.

In brief, even when using methanol, a solvent that was routinely used to carry out hydrogenation reactions, the risk of generating and spreading fire when using the SiliaCat Pd⁰ catalyst is prevented.

The reactivity of SiliaCat Pd⁰ was thus compared with that of two commercial hydrogenation catalysts, namely Pt⁰ EnCat (cross-linked polyurea beads microencapsulating Pt nanoparticles) and Pd/C (5 wt %), in the hydrogenation of six different nitroarene compounds under optimized reaction conditions.⁸

Results in Table 1 show that for all substrates, Pt⁰ EnCat afforded significantly lower yields compared to those of the other catalysts. On the other hand, SiliaCat Pd⁰ and Pd/C afforded comparable conversions in the hydrogenation of each nitroaryl compound, the only difference residing in the easier handling of the nonpyrophoric ORMOSIL material.

To explain the lack of pyrophoricity of the ORMOSIL-encapsulated palladium catalyst, we remind that ORMOSILs are nonflammable silica-based functional materials⁹ in which the organic moieties bound to silicon atoms (R-Si pendant groups) subjected to calcination start to decompose via oxidation to carbon dioxide at temperatures around 350–400 °C.

For instance, fully methylated silica xerogels release heat and lose CO₂ at a temperature of 450 °C due to oxidation of the methyl groups but do not catch fire.¹⁰ Furthermore, the sol-gel entrapment stabilizes the catalytic species (Pd⁰ nanoparticles, in this case) within the 3D inner porosity of the organosilica matrix which, as first demonstrated by Avnir,¹¹ is a completely different phenomenon than 2D surface derivatization in which the active species are deposited at the outer surface of a supporting material. Sol-gel encapsulation, for example, enables one-pot sequences of reactions with mutually destructive reagents encapsulated in different sol-gel matrices.¹²

As a result, the ORMOSIL-entrapped palladium catalyst SiliaCat Pd⁰ shows a better stability in hydrogenation and hydrogenolysis reactions than Pd/C. The material offers a safer alternative to pyrophoric metal catalysts such as Pd/C or Raney Ni for reactions involving flammable H₂ and flammable organic solvent. As shown by Figure 1, caution will in any case be exercised also when working with sol-gel entrapped palladium nanoparticles in reactions involving hydrogen.

CONCLUSION

The comparison of the pyrophoricity of two commonly employed hydrogenation and hydrogenolysis palladium-based catalysts, Pd/C and SiliaCat Pd⁰, demonstrates that the latter can be a safer replacement for the presently most active but pyrophoric catalyst, namely palladium on charcoal.

Furthermore, the reactivity of SiliaCat Pd⁰ in the hydrogenation of six different nitroarene compounds under optimized reaction conditions was compared with that of two commercial hydrogenation catalysts, Pt⁰ EnCat and the aforementioned Pd/C. SiliaCat Pd⁰ displays the same high activity as that of the Pd/C catalyst in terms of conversion but is easier to handle due to lack of pyrophoricity.

The ORMOSIL catalyst is not the only nonpyrophoric hydrogenation catalytic material. Polyurea beads are also nonpyrophoric. The polyurea support of Pt⁰ EnCat, for example, is considerably less flammable than carbon, while the encapsulation of the metal improves handling, showing no evidence of pyrophoricity on a small scale even when solvent wet catalyst is left to dry in air on a filter cloth following a hydrogenation reaction.¹³

These findings are relevant also in view of potential large-scale applications as well as of use of the spherical SiliaCat Pd⁰ in catalytic hydrogenation reactions under flow, wherein H₂, the substrate in liquid phase, and the solid catalyst interact in a much more efficient way than under batch.¹⁴

Finally, these outcomes may also be useful as instructional materials for undergraduate chemistry educators seeking to foster student creativity relying on recent research outcomes.¹⁵

EXPERIMENTAL SECTION

Catalytic Reactions. In a typical hydrogenation reaction, the catalyst (1 mol % Pd/C, 1 mol % SiliaCat Pd⁰, and 5 mol % Pt⁰ EnCat) was mixed with the substrate (2 mmol) dissolved in MeOH HPLC grade (5 mL). The reaction mixture, connected to a balloon of hydrogen, was vigorously stirred at room temperature for 30 min. The catalyst was then filtered off and rinsed with THF, whereas the filtrate was concentrated to give a crude product. Yields were evaluated by GC-MS analysis.

The GC-MS analyses were performed using a 7890B GC System (Agilent Technologies) equipped with an HP-5MS 30 m capillary column (comprised of (5%-phenyl)-methylpolysiloxane, 0.25 mm inner diameter, and 0.25 μm film thickness) equipped with a mass spectrometer of 5977B with selective detector operated in electron impact ionization mode (70 eV). The analyses were carried out in split mode, using helium as carrier gas (1 mL/min flow rate). The injection temperature was 250 °C; the interface was set at 325 °C, and the ion source was adjusted to 230 °C. The column was maintained at an initial temperature of 50 °C for 4.5 min, then ramped to 325 °C at 100 °C/min heating rate, and maintained at 325 °C for 5 min. Mass spectra were recorded at 5.5 scans/s (*m/z* 50–550). Identification of the compounds was based on the comparison of their retention times with those of authentic samples and on the comparison of their EI-mass spectra with the NIST/NBS, Wiley library spectra, and literature.

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Notes

The authors declare no competing financial interest.

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