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Activating Ru nanoparticles on oxide supports for ring-opening metathesis polymerization

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Abstract

Nano-sized particles mounted on heterogeneous oxide supports such as silica have altered reactivity when compared to their homogeneous analogs. In particular, catalyzed olefin metathesis using supported Ru nanoparticles has shown great promise and various methods have been employed to develop functional heterogeneous Ru catalysts. This article reports a method for synthesizing Ru nanoparticles supported on silica and titania. The nanoparticles were characterized using XPS showing Ru(0) dominates when not exposed to air. TEM showed Ru nanoparticle sizes of 3.1 ± 0.8 nm for Ru supported on SiO_2 and 5.6 ± 1.3 nm for Ru supported on TiO_2 . The materials demonstrated modest activity in ring-opening metathesis reactions via diazo activation and nanoparticle-embedded polymers of norbornene and norbornadiene were synthesized using dry box and Schlenk line techniques. The Ru/support/polymer composite materials were characterized using proton NMR, XPS, and SEM/EDS.

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Proposed activation and synthesis of polynorbornene on Ru nanoparticles on metal oxide support particles (SiO_2 shown).

Introduction

Transition metal nanoparticles (NPs) have found applications in a multitude of fields in materials chemistry¹ and catalysis.² Of the transition metals used to produce NPs, Ru has shown considerable promise as a catalyst for many reactions, notably hydrogenolysis^{2, 3} and olefin metathesis.⁴ With hydrogenolysis being a crucial step in the Fischer-Tropsch reaction, many groups have focused efforts on the efficient syntheses of Ru NPs due to their potential application as catalysts. Less attention has been placed on Ru NPs acting as catalysts for

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Conflicts of Interest

There are no conflicts to declare.

olefin metathesis in part because current homogeneous catalysts developed by Grubbs, Hoveyda, and Schrock are highly efficient and readily available. However, Ru NPs still have the potential to act as efficient heterogeneous olefin metathesis catalysts and may lead to the production of unique composite materials with interesting electrical and optical properties if the Ru is embedded inside a conductive organic polymer matrix.⁵

One method of developing Ru NPs for olefin metathesis is the reduction of a Ru precursor, typically RuCl_3 , followed by stabilization and activation of the surface with an alkylidene.⁶ There are several notable examples of this type of NP synthesis in the literature. The first example is the reduction of RuCl_3 in 1,2-propanediol in the presence of sodium acetate generating Ru NPs as described by the Chen group.⁷ An alternate method to produce Ru NPs is via the reduction of RuCl_3 in the presence of Zn and cyclooctadiene to produce $\text{Ru}(\text{cyclooctadiene})(\text{cyclooctatriene})$ ($\text{Ru}(\text{cod})(\text{cot})$). This compound can be reduced under a hydrogen atmosphere at high temperatures to produce ~50 nm diameter $\text{Ru}(0)$ nanoparticle agglomerates as reported by Nuckolls and coworkers.⁴ Both groups reported olefin metathesis activity if the Ru NPs were activated with diazoalkane reagents. Once activated, Chen and coworkers were able to perform olefin metathesis ligand exchange whereas the Nuckolls group were successful in creating polyolefins using ring opening metathesis polymerization (ROMP) on the strained olefins of norbornene (NBE) and norbornadiene (NBD). They could further conjugate the polynorbornadiene (PNBD) by treating it with iodine which led to a change in its optical and electrical properties. Progress made by the Nuckolls and Chen groups can be considered as first steps in generating Ru NPs to act as olefin metathesis catalysts by relatively straightforward syntheses.

Although diazo-activated, unsupported Ru NPs have been shown some reactivity, less is known about their olefin metathesis activity if they are placed on a solid support. There have been several studies of Ru NPs on oxide supports for reactions other than olefin metathesis as the ability to produce a high surface area catalyst using minimal amounts of metal could lead to the development of more cost effective industrial catalysts. With this goal in mind, many groups have advanced the field of nanoparticle chemistry by studying the interactions of Ru NPs with various support structures. Two materials that have garnered considerable attention have been SiO_2 ⁸ and TiO_2 ^{2, 3} as groups seek inexpensive supports that are stable and provide high surface area.

One study of note was produced by the Copéret group in 2008.⁸ In this publication, the group produced $\text{Ru}(0)$ NPs on SiO_2 in a manner similar to the work of Nuckolls *et al.* The primary difference in these two papers was the modification of the method⁹ to adsorb $\text{Ru}(\text{cod})(\text{cot})$ onto pretreated SiO_2 by preparing a solution of $\text{Ru}(\text{cod})(\text{cot})$ in pentane and evaporating the solvent while the solution was mixed with SiO_2 . After reduction in H_2 , the Ru NPs formed were characterized by TEM and measured as ~2 nm in diameter as opposed to the ~50 nm agglomerates seen in the work of Nuckolls. Coperét *et al.* expanded on their work with characterization and synthetic improvement to the SiO_2 -supported NPs as well as their activation for Fischer-Tropsch reactions.¹⁰

The results of the Nuckolls and Copéret groups led us to investigate whether Ru NPs on an oxide support are active for olefin metathesis. The relatively stable oxides SiO_2 and TiO_2

were chosen as supports in our work. Supported Ru NPs, activated with a diazoalkane compound, were used to perform ROMP on strained cycloolefins as shown in Figure 1. These supported Ru nanoparticles remained embedded in the polymers producing composite materials. The physical properties of a polyolefin composite material have been shown to have interesting characteristics when embedded with TiO_2 and Ru species.^{1, 5}

Experimental

Preparation of Ru(cod)(cot)

The preparation of the Ru(cod)(cot) was based on a method described by Pertici and Vitulli.¹¹ 12 g of Zn powder (Sigma Aldrich) was added to approximately 10 mL of degassed MeOH and 25 mL of degassed cod (Sigma Aldrich) in a three-necked round bottom flask. This solution was kept under an inert atmosphere and sonicated at 70 °C. Approximately 1 g of RuCl_3 (Sigma Aldrich) was then dissolved in approximately 25 mL degassed MeOH to make a dark black/brown solution. This solution was transferred to the cod-containing solution dropwise over twenty minutes while sonicating. The solution was allowed to sonicate for an additional 2 hours then filtered using Schlenk line techniques to remove the solid and the solvent evaporated overnight. The resulting brown residue was extracted with pentane and filtered in an air-free basic alumina column and the yellow band was collected. The pentane was evaporated under vacuum and the identity of the resulting yellow powder was confirmed to be Ru(cod)(cot) by ^1H NMR spectroscopy.

Preparation of Ru NPs supported on $\text{SiO}_2(700)$ (Ru/ SiO_2)

Preparation of Ru NPs on support structures was adopted by a method described by Copéret *et al.*⁸ Before Ru(cod)(cot) was adsorbed onto the surface of SiO_2 , the silica (AEROSIL 200, Evonik Industries) was pretreated.⁸ SiO_2 was compacted by filtration with deionized water and then placed on a stainless steel sample puck. This puck was calcined in air for 2 hours at 500 °C then placed under high vacuum ($\sim 10^{-6}$ torr) at 500 °C for 12 hours. The temperature was increased to 700 °C for a further 4 hours under high vacuum and then allowed to cool to room temperature in vacuo. The sample was transferred into a nitrogen-filled dry box without air exposure. The pretreated SiO_2 (known as $\text{SiO}_2(700)$) was transferred into a reaction flask, mixed with Ru(cod)(cot), and a small (less than 3 mL) portion of pentane was added to dissolve the Ru(cod)(cot). The resultant yellow heterogeneous suspension was stirred and the pentane was evaporated using a vacuum line. This process was repeated twice more. The resultant yellow powder was sealed in Schlenk flask with a Teflon valve, purged with approximately 1 atm of dry H_2 , and transferred to a 300 °C sand bath. The yellow powder turned black within seconds. The powder was left under a partial atmosphere of H_2 for 2 days with the gas being replenished once at 24 hours. After 2 days, the gas was evacuated, the reaction flask sealed, and the powder was transferred back into the nitrogen dry box.

Preparation of Ru NPs supported on TiO_2 (Ru/ TiO_2)

The preparation of Ru/ TiO_2 was very similar to the process used for SiO_2 with three notable exceptions. First, the TiO_2 was not pretreated in any way to avoid any potential reduction or phase changes in TiO_2 that occur at high temperatures. Second, the hydrogenation of the

cyclic ligands of Ru(cod)(cot) occurred at 200 °C rather than 300 °C to avoid partial reduction of TiO₂ to Ti₂O₃, which has been shown to have a much stronger metal support interaction.² Lastly, the resultant powder typically tended to be a dark grey rather than black, the color depending on the Ru loading.

Characterization by XPS

X-ray photoelectron spectroscopy was performed in a Physical Electronics 5200 instrument, using non-monochromated Mg K α radiation ($h\nu = 1253.6$ eV) and an analyzer pass energy of 44.75 eV. The pressure of the chamber was lower than 5.0×10^{-8} torr during analysis and the NP samples were transferred into the spectrometer without air exposure. The powder was pressed into In foil. XPS spectra of the Ru 3d/C 1s, O 1s, Si 2p (if applicable), and Ti 2p (if applicable) regions were measured and corrected for charging effects by assigning a value of 103.5 eV binding energy (BE) for the unresolved Si 2p peak in SiO₂ or by assigning a value of 458.7 eV BE for the Ti 2p_{3/2} peak in TiO₂. The C 1s peak partly overlaps with the Ru 3d doublet therefore peak fitting was performed to separate these components. We estimate that the error in composition determined by XPS is ~0.5 at%.

Determination of particle size by TEM

All samples for TEM analysis were prepared from powder samples suspended in THF dropped onto a copper TEM grid and the solvent allowed to evaporate. The samples were imaged by a T12 Quick CryoEM and CryoET (FEI) transmission electron microscope at the Electron Imaging Center for Nanomachines at UCLA.

Polymerization of NBE and NBD

Inside a nitrogen dry box, 10 mg of silica- or titania-supported NPs was added to a round bottom flask, followed by 8 mL THF, 0.3600 g NBE or 0.40 mL NBD, and finally 0.10 mL of 2.0 M trimethylsilyldiazomethane (TMSDM) in hexanes. Upon addition of TMSDM, effervescence was seen due to N₂ evolution. The flask was sealed with a septum, transferred to an oil bath at 60 °C, and the reaction was mixed with a stir bar at 600 rpm. Once the reaction was complete, the septum was removed and the mixture was placed under vacuum overnight. All solvent and excess olefin were evaporated and only a brown/grey film was left which was composed of the supported NPs and polyolefin. Turnover number (TON) was calculated as moles of monomer converted per mole of Ru. Turnover frequency (TOF) was calculated as moles of monomer per (mole of Ru $\times$ reaction duration in hours).

Characterization of PNBE and PNBD

NBD and NBE polymers were analyzed via proton NMR using CDCl₃ as the solvent (the reaction product was only partially soluble) in a 400 MHz Bruker Avance III spectrometer. Percent composition and morphology of the polymers was determined by an FEI Quanta 600 SEM containing a tungsten hairpin filament electron gun operated at up to 30 keV with E-T and EDS (Oxford Insight) detectors. The surface composition was measured by XPS.

Results and Discussion

Characterization of Ru/SiO₂ and Ru/TiO₂ NPs

As shown in Figure 2, using curve-fitting methods, the location of the Ru 3d_{5/2} peak in the as-synthesized NPs was determined to be at 280.0±0.1 eV, indicative of a metallic Ru(0) component on all supports.¹² In addition, the region shows evidence for Ru(IV) (RuO₂) with a Ru 3d_{5/2} peak at 281.1±0.1 eV and its accompanying satellite feature at 1.9 eV higher BE. The Ru(IV) satellites are an integral feature of the XPS spectra of Ru(IV) species. They are caused by final state effects during the photoionization of this species and are not due to the presence of additional ruthenium species. The Ru 3d region overlaps with the adventitious C 1s region and two C 1s features are required to adequately fit the entire photoemission envelope as shown in Figure 2; a dominant hydrocarbon-type C at 284.7±0.4 eV BE and a minor oxygenated hydrocarbon-type C at 288.5±0.2 eV BE.

The XP envelope in Figure 2(a) shows some Ru oxidation on SiO₂ as synthesized, with 48% of the total Ru being in the metallic Ru(0) form. Once the NPs were exposed to air for an hour, as shown in Figure 2(b), there is a decrease in the amount of metallic Ru on the surface to 22% and a corresponding increase in the amount of Ru(IV). This is in line with the Ru/SiO₂ NPs synthesized by Copéret.⁸

The XP spectrum of the Ru/C region of the Ru NPs supported on TiO₂ is shown in Figure 2(c). Curve fitting was used to discern the contributions of Ru and C as before, the same peak positions and parameters being used as in Figure 2(a) and (b). In this case, there is much less Ru oxidation present on the as-synthesized Ru/TiO₂ NPs. In contrast to the silica supported NPs, on TiO₂ 68% of the total Ru is metallic. Again, after an hour of exposure to air, there was a decrease in the surface concentration of Ru(0) to 60%.

After air exposure, the Ru:O ratios were seen to remain approximately constant within estimated error on both substrates. The partial oxidation of the small concentration of Ru NPs observed in Figure 2(a) and (b) was too small to detect as an overall composition change. Regardless, the increasing Ru(IV) contribution as well as inactivity of the NPs when exposed to TMSDM (see below) lead to the conclusion that Ru(0) oxidizes irreversibly upon exposure to air. Attempts to re-reduce the Ru under H₂ and treatment with TMSDM did not lead to active particles.

Surface elemental analysis performed by XPS also showed good control of Ru loading on both SiO₂ and TiO₂. For example, in one experiment, the stoichiometrically predicted Ru:Si ratio was calculated to be 1:38 (2.6% Ru) while the measured value was 1:41 (2.4% Ru), identical within experimental error. As both ratios were in good agreement with the predicted values, it is a good assumption that this method gives relative control over Ru loading. The Ru loading on the silica and titania supports was typically 1.2±0.3 wt% as determined from both starting reagent masses and XPS quantitation. Ruthenium loading was not specifically varied to explore its effect on activity.

The TEM micrographs of the Ru/SiO₂ show relatively homogeneously dispersed NPs on the surface of the pretreated silica (Figure 3a). The size distribution was 3.1±0.8 nm, a size

comparable to the literature value reported.⁸ The TEM micrographs of Ru/TiO₂ showed NPs with a size distribution of 5.6±1.3 nm (Figure 3b). The larger size in Ru/TiO₂ could be due several factors. The most probable is due to a possible metal-support interaction as such an interaction could cause Ru to aggregate during the reduction process and lead to larger sizes of nanoparticles. Additionally, the difference in reduction temperatures could have had a role in size formation; however, no temperature dependent studies were performed for these NPs.

Activation of NPs and Polymerization of NBE and NBD

When the NPs were exposed to a diazo compound (TMSDM), mild effervescence was observed. This was likely due to the evolution of N₂(g) and may be consistent with the formation of surface alkylidene moieties. Indeed, gas release concomitant with the formation of a surface alkylidene (or alkylidene-like species) was observed by Nuckolls during the preparation of their Ru NPs.⁴ Once TMSDM was added, ROMP took place as indicated by ¹H NMR spectroscopy. Based on mass loss, less than 10% of the polymer was soluble in CDCl₃ solvent. *Cis* and *trans*-olefinic protons peaks were observed in the ¹H NMR spectrum at 5.23/5.36 ppm for PNBE, as shown in Figure 4, while the monomer proton peak was absent. The catalyst did not show any significant stereoselectivity.

The polymers' appearance varied depending on the support structure and Ru loading. Polymers grown from Ru/SiO₂ or Ru/TiO₂ tended to be brown, grey, and black (Figure 5a) but in the case of PNBD on Ru/TiO₂ there were some hints of orange (Figure 5b). While many polymers (such as the PNBE produced by Nuckolls)⁴ are known to have an innate brownish coloring, it is believed the appearance of grey and black in the polymer is due to the embedding of the supported Ru species. Ru loading on the support affected the coloring, with higher loadings (<5%) leading to the black coloring from the Ru/oxide support, becoming greyer at lower loadings. This is most likely due to a combination of the white oxide support and the black NPs. The grey could have also been due to reduction of TiO₂ during NP synthesis (Ti³⁺ is grey or violet); however, XPS ruled out significant amounts of Ti³⁺ as only Ti(IV) species were seen in both the NPs and the composite polymers. Previous studies have shown that bulk TiO₂ is not reduced under H₂ atmospheres below 400 °C; small amounts of reduction can occur at the TiO₂ *surface* at a noticeable amount at 250 °C however our TiO₂ samples were not heated above 200 °C.¹⁴

Analysis of the polymers by SEM/EDS gave interesting qualitative data. First, EDS elemental maps showed relatively even distribution of elements throughout the composite material (Figure 6). Minor clustering of both Ru and oxide support was noted; however, it did not appear that the clustering was correlated suggesting Ru may have been migrating off the surface of the support during the polymerization process. This migration may have helped lead to a more even distribution of Ru throughout the composite. The composition of the polymers determined by XPS was highly variable due to the burial of some NPs inside the polymer, but ranged up to 0.5 at% Ru and 32–51 at% support, the balance being C (polymer).

SEM micrographs of all composites showed charging effects characteristic of insulating materials except for PNBD-Ru/TiO₂ composites (Figure 7). Charging effects result from a buildup of charge as the sample is bombarded with electrons which cause bright areas, shifts

in the image, and lower resolution in the micrograph. The lack of charging effects seen in PNBD-Ru/TiO₂ composites, imaged under identical conditions, suggests that qualitatively the PNBD-Ru/TiO₂ composite is at least a moderate conductor or semi-conductor. At this time the conductivity of this composite has not been fully explored and will require further investigation.

Analysis of TON as well as TOF for the polymerization showed that the supported Ru NPs were not robust catalysts. The growth of the polymer slowed down (but did not stop entirely) as the reaction was allowed to proceed with reactivity seen up to 41 hours (Figure 8). This trend was seen on both support structures and for both monomers. This slowdown was likely caused by the congestion created by the polymer around the active site as the polymer grows. This growth of polymer led to a smaller chance of monomer reaching the active site of the NPs due to the steric hindrance provided by the support structure and the growing polymer. This steric congestion and subsequent reduction in activity is also the most likely reason for observation of poor overall polymer yields, even after extended reactions. The yield of polymer was determined based on mass change, comparing the mass of the starting reagents and products. Excess monomer was removed from the product by extended evacuation, until the NMR data showed no presence of monomer or solvent. The highest percent yield based on monomer conversion for PNBD on Ru/TiO₂ was 14% while the highest TON was 45 after 41 hours.

Similar reactivities were seen for both polymers on both support structures which suggests that the higher degree of oxidation observed for the Ru/SiO₂ compared with the Ru/TiO₂ NPs does not seem to hinder the activity significantly. Lower Ru loading seemed to have a small negative impact on overall turnovers; however, it did not seem to scale linearly i.e. a threefold decrease in Ru loading did not lead to a threefold decrease in TON. Further investigation will be needed to understand the factors involved in this heterogeneous polymerization.

Conclusions

In conclusion, XPS and TEM have shown that the creation of Ru NPs free of strong ligands can be attained from perhydrocarbyl complexes on typical oxide supports such as SiO₂, which had been previously reported,⁸ as well as TiO₂, which we believe is the first reported case of such a synthesis in this manner. Additionally, these oxide-supported NPs could be activated for ring-opening metathesis polymerization on strained cycloolefins by exposing them to a diazo compound allowing for the production of nanoparticle-embedded polymers. This new synthesis of composite materials in this manner allows a relatively homogeneous dispersion of Ru NPs and oxide support as shown by SEM/EDS. Additionally, the use of a semiconducting support structure (TiO₂) as well as a polyolefin with multiple pi bonds (PNBD) allowed the production of a material that acted as a poor conductor as it qualitatively resists charging effects typically seen in insulating materials when taking XPS spectra or SEM micrographs.

This synthesis offers the potential to tailor the reaction in a variety of ways, from changing the metal NP to another metal known to catalyze olefin metathesis (such as Mo or W),

activation with a different carbene-precursor, or replacing the oxide support. Additionally, the polymers themselves are open to modification from traditional methods such as plasma modification¹⁵ allowing for even more variability in preparing these composite polymers. Further studies in tailoring the catalytic system for olefin metathesis as well as studying the properties of the composite materials will be required to get a complete understanding of the work accomplished in this publication.

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Figure 1.
Proposed activation and synthesis of polynorbornene on Ru nanoparticles supported on SiO₂.

Figure 2.

Ru 3d and C 1s peaks show as overlapping features on (a) Ru/SiO₂ nanoparticles (b) Ru/SiO₂ nanoparticles exposed to air for 1 hour (c) Ru/TiO₂ nanoparticles and (d) Ru/TiO₂ nanoparticles exposed to air for 1 hour. Curve fitting was used to separate the components and, in all cases (a)–(d), the same set of peaks was used with only the intensity of each allowed to vary.

Figure 3.

(a) TEM micrograph of Ru/SiO₂ NPs (b) TEM micrograph of Ru/TiO₂ NPs with a fraction of the NPs highlighted on the surface of the oxide supports

Figure 4.
¹H NMR of CDCl₃-soluble fraction of PNBE produced on Ru/silica.

Figure 5.
(a) PNBE embedded with Ru NPs/SiO₂ and (b) PNBD embedded with on Ru NPs/TiO₂

Figure 6.
EDS elemental distribution maps of a PNBE-Ru/SiO₂ composite. Shown from top left to bottom right are carbon (red), oxygen (green), ruthenium (orange), and silicon (blue)

Figure 7.

(a) SEM micrograph of PNBE-Ru/SiO₂ showing characteristic charging effects in the form of bright areas as well as shifts in the image. (b) SEM micrograph of PNBD-Ru/TiO₂ composite, showing no significant charging as well as a magnified inset

Figure 8.
TOF for the polymerization of PNBD on Ru/TiO₂