High-Throughput Nanoparticle Catalysis: Partial Oxidation of Propylene

Shici Duan, Michael Kahn and Selim Senkan^{*}

Department of Chemical Engineering, University of California, Los Angeles, CA 90095, USA

Abstract: Partial oxidation of propylene was investigated at 1 atm pressure over Rh/TiO₂ catalysts as a function of reaction temperature, metal loading and particle size using high-throughput methods. Catalysts were prepared by ablating thin sheets of pure rhodium metal using an excimer laser and by collecting the nanoparticles created on the external surfaces of TiO₂ pellets that were placed inside the ablation plume. Rh nanoparticles before the experiments were characterized by transmission electron microscopy (TEM) by collecting them on carbon film. Catalyst evaluations were performed using a high-throughput array channel microreactor system coupled to quadrupole mass spectrometry (MS) and gas chromatography (GC). The reaction conditions were 23% C₃H₆, 20% O₂ and the balance helium in the feed, 20,000 h⁻¹ GHSV and a temperature range of 250-325 °C. The reaction products included primarily acetone (AT) and to a lesser degree propional-dehyde (PaL) as the C₃ products, together with deep oxidation products COx.

Keywords: Combinatorial heterogeneous catalysis, propylene oxidation, pulsed laser ablation, nanoparticle synthesis.

INTRODUCTION

Partial oxidation of propylene is of significant industrial importance due to the possibility of production of a large number of commodity chemicals and intermediates [1]. For example, propylene can be converted into acrolein and acrylic acid by the oxidation of the allylic C-H bonds [2], into propylene oxide by the oxidation of the C=C double bond [3], and into acetone by the oxidation of the 2-carbon [4, 5]. Since the C-H bond dissociation energies of allylic carbons are weaker, propylene readily is oxidized to acrolein and to acrylic acid rather than into propylene oxide or acetone.

Previously Rh was reported to selectively produce acetone from propylene under ultra high vacuum conditions [5]. In that investigation, 111 Rh surface was exposed to O_2 first, followed by propylene addition, resulting in the production of 0.02 acetone molecules per Rh atom per cycle. Although not significant from a commercial point of view, these results clearly demonstrated that Rh selectively activated the C-H bond at the 2-carbon as opposed to the allylic C-H bonds.

In order to further explore this selective C-H bond activation induced by Rh, we undertook a systematic study with rhodium nanoparticles supported on a variety of oxide supports using combinatorial or high throughput techniques developed previously in our laboratories [6]. Initial screening experiments with γ -Al₂O₃, CeO₂, SiO₂, TiO₂ and Y-ZrO₂ supports revealed that TiO₂ was the most suitable support material for Rh for the production of acetone from propylene and oxygen.

EXPERIMENTAL

Catalytic materials were prepared using the highthroughput pulsed laser ablation (HT-PLA) system, the details of which have been described earlier [7]. Briefly, the HT-PLA facility consists of a rotatable Rh target holder and a pulsed laser beam (Lambda Physik Compex 100 Excimer Laser, 300 mJ/pulse, 30 ns pulse duration) which is focused to a spot of ~ 0.1 cm diameter, off axis on the surface of the target, arriving at an angle of approximately 45 degrees. Nanoparticles emanating from the target were deposited on the external surfaces of the TiO₂ support pellets (0.4 cm diameter by 0.1 cm thick cylinders) or on standard transmission electron microscope (TEM) grids that were placed inside the ablation plume at a pre-determined distance from the target surface. Consequently it was possible to characterize the nanoparticles prior to reaction screening using a TEM (JEOL JEM-2000FX TEM). The HT-PLA chamber was maintained at 1 Torr Ar pressure, and a mask was used to prevent the cross contamination of different support pellets and TEM collection surfaces during the ablation process.

The size of the nanoparticles formed in PLA is primarily determined by the laser power density (i.e. fluence, energy of the photons and pulse duration), the number of pulses, the nature and density of the ambient gas in the ablation chamber, and the distance from the target surface [7]. In the present experiments the number of laser pulses and the distance from the target surface were used to control the Rh nanoparticle size.

It is important to note that with PLA a new class of supported heterogeneous catalysts can be prepared. First, since the nanoparticles created by PLA are narrowly sized, a better control of reaction selectivities should be achievable. Second, as a consequence of the placement of metal nanoparticles on the external surfaces of the support pellets, labile products are readily removed from catalytic sites without undergoing subsequent destruction reactions. This is in stark contrast with porous catalysts prepared by impregnation or co-precipitation, in which the fragile reaction products can be destroyed within the same pores they were created in, on their journey to the outside. It is also significant to note that because catalytic materials prepared by PLA never exhibit pore diffusion limitations, they can be compared to one an-

^{*}Address correspondence to this author at the Department of Chemical Engineering, University of California, Los Angeles, CA 90095, USA; Fax: 310-267-0177; E-mail: ssenkan@gmail.com

other under intrinsic reaction rate limited conditions, without being disguised by internal transport phenomena.

Catalyst evaluations were performed using a computer controlled array channel microreactor system described previously [6]. In array microreactors, reaction gases flow over the flat nanoparticle coated surfaces of the pellets which are individually placed into wells along each reactor channel. Consequently, the gases are not forced through the pellets, and the resulting flow regime is similar to that of a monolithic reactor. The experiments were performed under atmospheric pressure and at temperatures of 250, 275, 300 and 325 °C using a gas feed stream of 23% propylene and 20% oxygen, with the balance being helium. The gas hourly space velocity (GHSV) was 20,000 h⁻¹. The partial oxidation of propylene can form a variety of products such as acetone (AT, molecular weight, MW 58), propylene oxide (PO, MW 58), acrolein (AL, MW 56), propionaldehyde (PaL, MW 58), acrylic acid (ACA, MW 72), together with deep oxidation products of CO and CO₂. Consequently, in addition to mass spectrometry (MS, SRS RGA-200, Sunnyvale, CA) which was used for rapid initial screening, gas chromatography (Varian CP4900/ Mini-GC with thermal conductivity detector and Porapak Q (10 m) and Molecular sieve 13X (10 m) columns) was also used for the unambiguous quantification of reaction products.

RESULTS AND DISCUSSION

In Fig. 1, the TEM images of Rh nanoparticles collected on carbon film are presented as a function of distance from the target in the range 1.0 to 1.3 cm (y-direction) and as a function of the number of laser pulses from 50 to 200 (xdirection). These images correspond to the Rh nanoparticles that are expected to exist on the TiO₂ supports prior to the reactions, which will be discussed further below. An examination of Fig. 1 reveals several important features. First, the Rh particles were larger in diameter with a lower number density early in the plume and become progressively smaller with higher number densities further away from the target. The breakup of larger energetic particles with distance from the target provides a reasonable explanation for these results. In addition, the evaporative shrinkage of large particles followed by the nucleation and growth of new nanoparticles along the plume cannot be ruled out. It is likely that both mechanisms exist in an actual PLA plume. Attempts to acquire TEM images below 1.0 cm were not successful because of carbon film destruction by the high energy Rh particles. Consequently, stronger single crystal silicon wafers were used to collect particles below 1.0 cm from the target. The atomic force microscopy (AFM) analysis of a sample collected at 0.9 cm indicated the presence of Rh nanoparticles with a mean diameter of about 10 nm, which is consistent with the TEM images shown in Fig. 1.

Second, as also evident from Fig. 1, Rh nanoparticles progressively became larger with increasing number of pulses, suggesting the collision and fusion of new particles with those already present on the surface. Thus, both the distance to target and the number of pulses can be used to control the sizes of the nanoparticles created by PLA. The TEM images shown in Fig. 1 can also be used to establish metal loadings using the sizes and number densities of the particles. It is important to note that the spherical expansion

of the ablation plume and the concomitant decrease in metal flux with distance from target must also be considered in making reaction rate comparisons between catalytic materials prepared at different plume heights.

In Fig. 2, the array microreactor exit mole percentages of the reactants C_3H_6 and O_2 as well as those for the major products are presented at 250 °C as a function of number of laser pulses (i.e. metal loading and particle size) for Rh nanoparticles collected at a fixed location along the ablation plume which is indicated above each graph. The graphs are ordered in an increasing distance from the target from 1.0 cm (top) to 1.3 cm (bottom), in 0.1 cm increments.

These plots were chosen to directly illustrate the effects of metal loading and particle size on rates and selectivity, without the need to evaluate changes in metal flux along the ablation plume.

The TEM images presented in Fig. 1 correspond to the Rh nanoparticles for each of the different catalytic materials prepared, screened and presented in Fig. 2. Similar mole percentage *vs* number of laser pulse plots are presented in Figs. **3-5** for temperatures 275, 300 and 325 °C, respectively.

An examination of the top graph at Fig. 2 (i.e. Rh nanoparticles collected at 1.0 cm from the target) clearly shows the increased production of acetone (AT) together with propionaldehyde (PaL) with increased pulse number or Rh loading, both reaching levels of about 0.04% at 200 pulses. However, these levels steadily decreased with increasing distance from the target as shown by the lower graphs. As noted before, this is due to decreases in Rh nanoparticle loading on TiO_2 surfaces as a consequence of the spherical expansion of the ablation plume or decreases in particle diameter, or both.

The conversion of propylene and production of AT and PaL significantly increased with increasing temperature, as shown in Figs. **3,4**. For example, maximum propylene conversions were about 7 and 20% at 200 pulses, at 275 and 300°C, respectively. Highest AT levels were 0.15% and 0.25%, and highest PaL levels were at 0.08% and 0.12%, respectively at the same conditions. From these figures, it is also clear that the formation of CO₂ was substantial at higher temperatures under all conditions investigated. In fact, at 300 and 325 °C (Figs. **4,5**), CO₂ levels dominated the product mix at higher Rh loadings. These results clearly suggest the need to use temperatures below 300 °C for the synthesis of acetone and propionaldehyde using TiO₂ supported Rh nanoparticles.

As seen in Fig. 3, at 275 °C, acetone levels exhibited a steady increase with increased Rh loading or number of pulses, while those for PaL leveled off. However, similar results at 300 °C (Fig. 4) exhibited several intriguing features. First, both acetone and propionaldehyde concentrations exhibited maxima at about 150 laser pulses, suggesting the existence of an *optimal Rh loading* and/or *optimal particle size* (Fig. 1). In contrast, CO₂ formation exhibited no such behavior, with its concentration steadily increasing with increasing pulse number over the entire set of conditions investigated. A close examination of Figs. 2-5 also clearly shows that *all* product levels consistently decreased over catalysts prepared at increasing distance from the target due to decreased metal flux (loading) and/or particle size.

TEM Characterization of Rhodium Nanoparticles



Fig. (1). The TEM images and nanoparticle size distributions as a function of distance from the target and number of laser pulses. Histogram scale is shown at the top.



Fig. (2). Species mole percent profiles as a function of number of laser pulses (50, 100, 150 and 200 pulses) at different target to substrate distances (1.0, 1.1, 1.2 and 1.3 cm) at 250 °C. Propylene (C_3H_6), Oxygen (O_2), and Carbon dioxide (CO_2) right scale. Acetone (AT), Propionaldehyde (PaL) left scale.

The existence of an optimal Rh nanoparticle size for the title reaction is also supported by the fact that reactor exit concentrations were similar for catalysts that had similar particle sizes but different metal loadings. For example, catalysts prepared at 1.0 cm and at 100 pulses and those prepared at 1.1 cm and at 200 pulses exhibited similar Rh particle

sizes of about 5 nm (Fig. 1), yet their metal loadings were clearly different. Nevertheless, as seen in Figs. 3,4 reactor exit concentrations for these two catalysts were quite similar. These results support the important role the Rh particle size plays, as opposed to loading, in influencing propylene conversion and product selectivity.



Fig. (3). Species mole percent profiles as a function of number of laser pulses (50, 100, 150 and 200 pulses) at different target to substrate distances (1.0, 1.1, 1.2 and 1.3 cm) at 275 $^{\circ}$ C. Propylene (C₃H₆), Oxygen (O₂), and Carbon dioxide (CO₂) right scale. Acetone (AT), Propionaldehyde (PaL) left scale.



Fig. (4). Species mole percent profiles as a function of number of laser pulses (50, 100, 150 and 200 pulses) at different target to substrate distances (1.0, 1.1, 1.2 and 1.3 cm) at 300 $^{\circ}$ C. Propylene (C₃H₆), Oxygen (O₂), and Carbon dioxide (CO₂) right scale. Acetone (AT), Propionaldehyde (PaL) left scale.



Fig. (5). Species mole percent profiles as a function of number of laser pulses (50, 100, 150 and 200 pulses) at different target to substrate distances (1.0, 1.1, 1.2 and 1.3 cm) at 325 °C. Propylene (C_3H_6), Oxygen (O_2), and Carbon dioxide (CO_2) right scale. Acetone (AT), Propionaldehyde (PaL) left scale.

Mass transfer limitations can mask the intrinsic kinetics of highly exothermic catalytic reactions, and prevent the undertaking of comparisons between different catalysts. Partial oxidation of propylene would be particularly prone to such effects because of its exothermicity. In order to evaluate the existence of such transport effects, the results presented in Figs. 2-5 were replotted in Arrhenius diagrams, and one set of such plots is shown in Fig. 6 for acetone. The results shown in Fig. 6 indicate mild transport limitations at the higher temperatures. This is most apparent with catalysts prepared at 1.0 and 1.1 cm from the target.

In Fig. 7, the calculated activation energies (i.e. the slopes of the lines in Fig. 6) are plotted as a function of number of pulses, with distance to target being the parameter. An examination of this figure clearly suggests that smaller Rh nanoparticles (i.e. catalysts prepared at lower pulse numbers and particles collected farther away from the target) are more prone to transport limitations. For example, the catalysts prepared by collecting nanoparticles at 1.2 and 1.3 cm from the target and at 50 laser pulses exhibited activation energies of ~10 kcal/mole. On the other hand, catalysts prepared at other conditions exhibited higher activation energies of about 20-25 kcal/mole. These results clearly support the notion that the Rh/TiO₂ catalysts prepared within 1.1 cm of the ablation plume exhibit intrinsic reaction kinetics, thus can safely be compared to one another without being disguised by transport phenomena.

A detailed consideration of the TEM images shown in Fig. 1 together with the data presented in Fig. 4 (i.e. top plot at 300 °C) indicates extremely high site time yields (STY) or turnover frequencies (TOF) for the Rh nanoparticle catalysts reported [8]. For example, the 10.0% conversion of propyl-

ene as observed for the best performing 150 pulse Rh/TiO₂ catalyst suggest a STY *in excess* of 100 s⁻¹, using an average particle diameter of 10 nm and a surface particle number density of about 10^{12} cm⁻² (Fig. 1). For a mean particle diameter of 20 nm, the STY would be ~10 s⁻¹, still representing an excellent activity. The STY of 100 s⁻¹ is well below the calculated film diffusion limited STY of ~10³ s⁻¹, a result which is consistent with the experimental data that exhibited activation energies of 20-25 kcal/mol (Fig. 7).

The superior performance of the supported Rh nanoparticle catalysts can be attributed to several factors. First, the number density and dispersion of nanoparticles, as demonstrated by TEM images in Fig. 1, were high and this enabled the excellent utilization of the expensive Rh metal. This also is an important issue for scale up because extremely small quantities of Rh were sufficient to achieve high propylene conversions. For example, 150 pulses of Rh nanoparticles deposited are equivalent to about 10⁻⁷ g of Rh loading per pellet. Second, because the Rh nanoparticles are deposited on the exterior surfaces of the support materials (pellets in the present experiments), highly reactive and metastable products, such as acetone, are rapidly transported away from the active catalytic sites thereby avoiding subsequent destruction. Clearly, this advantage can be realized only at high GHSV values, which indeed was the case in the present experiments. In contrast, metastable products would be destroyed inside the pores of the catalytic materials prepared by impregnation or co-precipitation methods. Indeed, the acetone yields were substantially poorer over 1%Rh/TiO2 catalysts prepared by impregnation [9]. As a consequence of these advantages, the new classes of catalytic materials prepared by PLA appear particularly suitable to carry out reactions in which the products are less stable than the reactants.



Fig. (6). Arrhenius plots of acetone (AT) production as a function of distance from target (1.0, 1.1, 1.2 and 1.3 cm).



Fig. (7). Activation energies for acetone (AT) production as a function of laser pulses (50, 100, 150 and 200 pulses) and distance from target (1.0, 1.1, 1.2 and 1.3 cm).

ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation and the US Environmental Protection Agency.

REFERENCES

- [1] Gellings, P.J.; Bouweester, H.J.M. Catal. Today, 2000, 58, 1.
- [2] Nojiri, N.; Sakai, Y.; Watanabe, Y. Catal. Rev. Sci. Eng., 1995, 37, 145.
- [3] (a) Takahashi, A.; Hamakawa, N.; Nakamura, I.; Fujitani, T. App. Catal. A. Gen., 2005, 294, 34. (b) Orzesek, H.; Schultz, R.P.; Dingerdissen, U.; Maier, W.F. Chem. Eng. Tech., 1999, 22, 691. (c) Liu, Y.; Murata, K.; Inaba, M.; Mimura, N. Catal. Lett., 2003, 89, 49. (d) Hayashi, T.; Han, L.B.; Tsubota, S.; Haruta, M. Ind. Eng. Chem. Res., 1995, 34, 2298. (e) Hayashi, T.; Tanaka, K.; Haruta,

Received: September 6, 2006

Revised: December 4, 2006

Accepted: December 5, 2006

M. J. Catal., **1998**, *178*, 566. (f) Uphade, B.S.; Okumura, M.; Hayashi, T.; Haruta, M. App. Catal. A. Gen., **2000**, *190*, 43. (g) Sinha, A.K.; Seelan, S.; Tsubota, S.; Haruta, M. Angew. Chem. Int. Ed., **2004**, *43*, 1546.

- [4] Liu, Y.; Murata, K.; Inaba, M.; Mimura, N. Catal. Comm., 2003, 4, 281.
- [5] Xu, X.; Friend, C.M. J. Am. Chem. Soc., 1991, 113, 6779.
- [6] (b) Senkan, S. Angew. Chem. Int. Ed., 2001, 40, 312. (b) Senkan, S.; Ozturk, S. Angew. Chem. Int. Ed., 1999, 38, 791. (c) Senkan, S.; Krantz, K.; Ozturk, S.; Zengin, V.; Onal, I. Angew. Chem. Int. Ed., 1999, 38, 2794.
- [7] Senkan, S.M.; Duan, S.; Kahn, M.; Ly, A.; Leidholm, C. <u>Catal.</u> Today, **2006**, 117, 291.
- [8] Boudart, M. Chem. Rev., **1995**, 95, 661.
- [9] Miyazaki, T.; Ozturk, S.; Onal, I.; Senkan, S. <u>Catal. Today</u>, 2003, 81, 473.