

Infrared Study of the Decomposition of Polystyrene over Supported Rhodium

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A combined study utilizing infrared spectroscopy and a tubular microreactor on the decomposition of polystyrene over supported rhodium has been performed. The primary product detected by infrared was methane, but only when hydrogen gas was present and only at temperatures higher (523 K) than those necessary (501 K) for hydrogenation of the aromatic rings on polystyrene. Temperatures necessary for production of methane over Rh/SiO₂ (573 K) were higher than those for Rh/Al₂O₃ (523 K). The tubular microreactor studies showed that the yield of methane during sample decomposition was low compared to those of higher hydrocarbons not detected by infrared.

Introduction

For the past 20 years work in these laboratories has focused on infrared studies of the interaction with and decomposition of small molecules over supported rhodium catalyst films. Of particular interest have been investigations of the catalytic hydrogenation reaction of carbon monoxide,¹ carbon dioxide,² ammonia,³ and carbon suboxide,⁴ as several intriguing surface intermediates have been detected by infrared spectroscopy. Recently, the investigations have been extended to the study of polymer decomposition over supported catalytic films; a preliminary report of the hydrogenation of polyethylene over Rh/Al₂O₃ and Rh/TiO₂ to produce methane has appeared.⁵ Such studies are relevant to the problems of recycling waste materials and the conversion of used plastics into fuel. Although it is unlikely that an expensive supported rhodium catalyst could be economically employed for such uses, the in situ transmission infrared techniques and sample-preparation procedures employed in these laboratories for supported rhodium films could be extended to less expensive supported catalysts. Rhodium was chosen for the studies on polystyrene reported in this work because of the extensive experience with infrared investigations of adsorbates on this metal conducted previously in these laboratories.

Experimental Section

Two solutions were prepared in separate atomizer bottles. In one was a slurry containing 0.0265 g RhCl₃·3H₂O, 0.5 g of Al₂O₃ (Degussa aluminoxid C, 100 m² g⁻¹) or 0.5 g of SiO₂ (Degussa Aerosil 200, 200 m² g⁻¹), 90 mL of spectroscopic-grade acetone, and 10 mL of distilled, deionized water. In the other was 0.5 g of polystyrene (Aldrich, average molecular weight 45 000) dissolved in 100 mL of toluene. The two solutions were sprayed separately in an alternating manner onto a 25 mm CaF₂ IR window held at 243 K. Evaporation of the volatile components provided IR-transparent polystyrene/RhCl₃·3H₂O/Al₂O₃ or SiO₂ films (2 mg cm⁻²). The window containing the film was mounted into a high-pressure infrared-cell reactor which has been described previously.⁶ The sample was evacuated overnight at 298 K and then subjected to three

evacuation/reduction cycles with 100 Torr hydrogen at 453–473 K for 5, 10, and 20 min. This pretreatment produced a film containing about 2.0 wt % Rh and about 50 wt % polystyrene.

Following evacuation for 1 h at 298 K, the cell reactor was pressurized with research-grade H₂, D₂, or N₂ and heated rapidly to a temperature near the decomposition point of polystyrene. Then infrared spectra were monitored as a function of temperature or time during the decomposition process. The heating rate was 2.5–3.0 K min⁻¹, and a 2 min equilibration time was allowed at each temperature at which an infrared spectrum was recorded. All spectra were obtained with an IBM 32 FTIR spectrometer operated at 2 cm⁻¹ resolution with 64 scans accumulated over 80 s. Pressure measurements were made with an MKS Baratron capacitance manometer.

Parallel studies on the polystyrene decomposition process in the presence of H₂ under identical temperature and pressure conditions were conducted in a sealed stainless steel tubular microreactor. The contents of the reactor were analyzed following 1 h reaction time in terms of gaseous content, hexane solubles, THF solubles, and THF insolubles.^{7–9}

Results and Discussion

Figure 1 shows a series of infrared spectra obtained for the polystyrene/Rh/Al₂O₃ film before and in the presence of H₂. Spectrum 1a was collected at 298 K before pretreatment of the film with H₂. The infrared bands for unreacted polystyrene are clearly observed; the ones at 3078, 3058, and 3024 cm⁻¹ are characteristic of C–H stretching modes for monosubstituted benzene rings, while those at 2923 and 2850 cm⁻¹ refer to the C–H stretching modes for the CH and CH₂ groups on the alkyl chain of the polymer. The bands in the range 1450–1598 cm⁻¹ are assignable to the ring C–H and alkyl C–H and CH₂ bending modes.

Figure 1b was recorded following prereduction of the film at 453 K; there was slight decomposition of the film noted during this pretreatment as evidenced by slight loss of intensity of all of the polystyrene infrared bands but no new bands were observed. However, when the film was held at 501 K for 10 min in the presence of 5000 Torr of H₂, interesting infrared band structure changes began to occur (Figure 1c). The benzene ring bands all declined in intensity, while the bands at 2923

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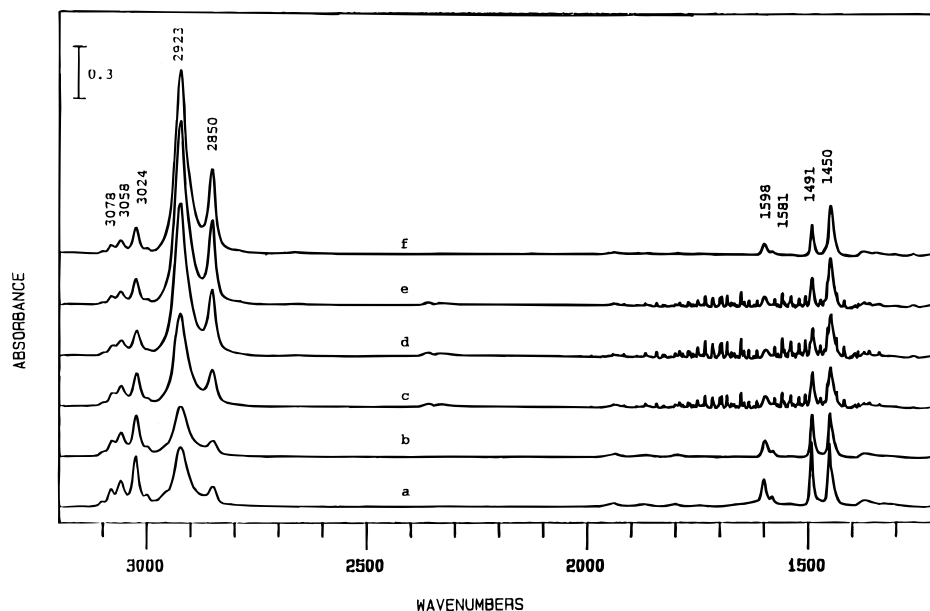


Figure 1. Infrared spectra for polystyrene decomposition over 2.0% Rh/Al₂O₃ (a) at 298 K before sample reduction, (b) after reduction cycles at 453 K, (c) after 10 min at 501 K in the presence of 5000 Torr H₂, (d) after 26 min at 501 K, (e) at 363 K before evacuation, and (f) at 363 K following evacuation.

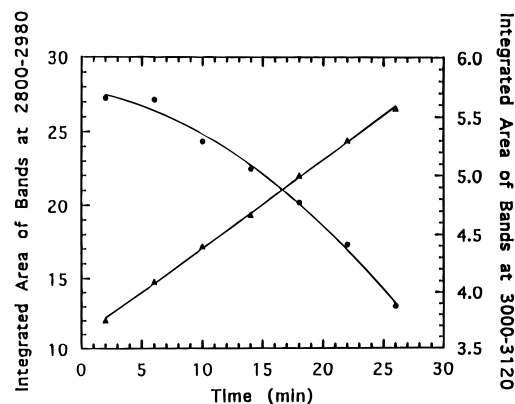


Figure 2. Relative total integrated areas for infrared bands in the range 2800–2980 cm⁻¹ (triangles) and in the range 3000–3120 cm⁻¹ (circles) as a function of reaction time at 501 K in the presence of 5000 Torr H₂.

and 2850 cm⁻¹ due to alkyl C–H stretching modes were enhanced in intensity. This phenomenon continued to become more dramatic as the time of heating was increased (spectra 1d and 1e). Structure near 1600 cm⁻¹ attributable to water on the support and in the gas phase (see fine structure) and a weak band at 2349 cm⁻¹ due to the production of CO₂ gas were also observed. The water was undoubtedly produced from reaction of H₂ with hydroxyl groups on the support, and the small amount of CO₂ was probably the result of reaction of the hydroxyl groups on the support with low concentrations of surface carbon produced early in the decomposition process. Upon evacuation at 363 K, the bands due to CO₂ and H₂O vanished, but the other spectral changes (loss of intensity of all bands except a gain for the 2923 and 2850 cm⁻¹ ones) remained.

Figure 2 shows a plot of the integrated band intensities for the two groups of C–H stretching modes over a period of 30 min at 501 K in the presence of H₂. Clearly the alkyl C–H mode intensities are inversely related to the benzene ring C–H mode intensities. We believe that the most likely explanation for these observations is that the initial stage of polystyrene decomposition involves hydrogenation of the benzene ring to produce a cyclohexyl derivative of polyethylene.

Figure 3 shows the spectral changes which result when the

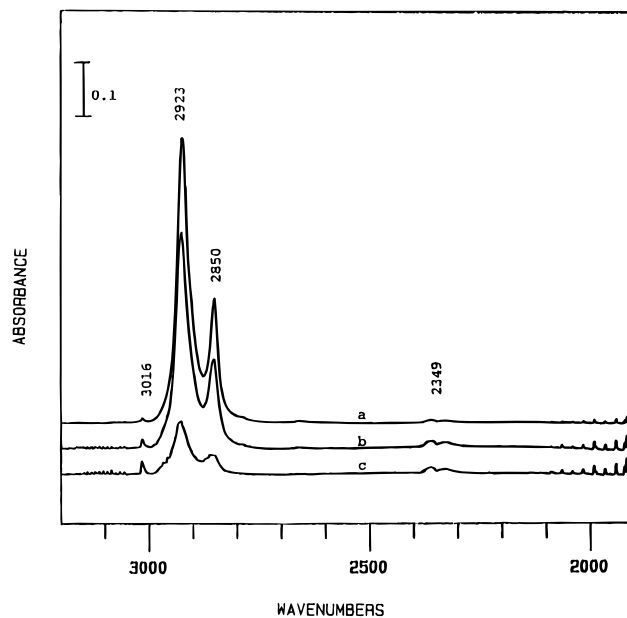


Figure 3. Infrared spectra for polystyrene decomposition over 2.0% Rh/Al₂O₃ (a) after 90 min at 523 K in the presence of 5000 Torr H₂, (b) after 125 min at 523 K, and (c) after 180 min at 523 K.

temperature is raised to 523 K and held for 90, 125, and 180 min. The bands due to the C–H stretching modes for the saturated cyclohexyl ring decline markedly during this time with the concomitant production of CO₂, water, and methane (the new band centered at 3016 cm⁻¹). This is illustrated more dramatically in Figure 4, which pertains to a similar experiment conducted at higher temperature (553 K). At 553 K the methane production is observed after only 1 min; bands due to the intermediate cyclohexyl polyethylene are not observed. Evidently the hydrogenation of the benzene ring proceeds too rapidly at 553 K for infrared observation. Furthermore, it is evident that the methane production proceeds primarily after the ring hydrogenation is complete, for the methane band did not appear until the cyclohexyl bands began to decline in intensity.

It has been observed that polymers decompose at high temperatures in the presence of N₂ as well as H₂ to form similar

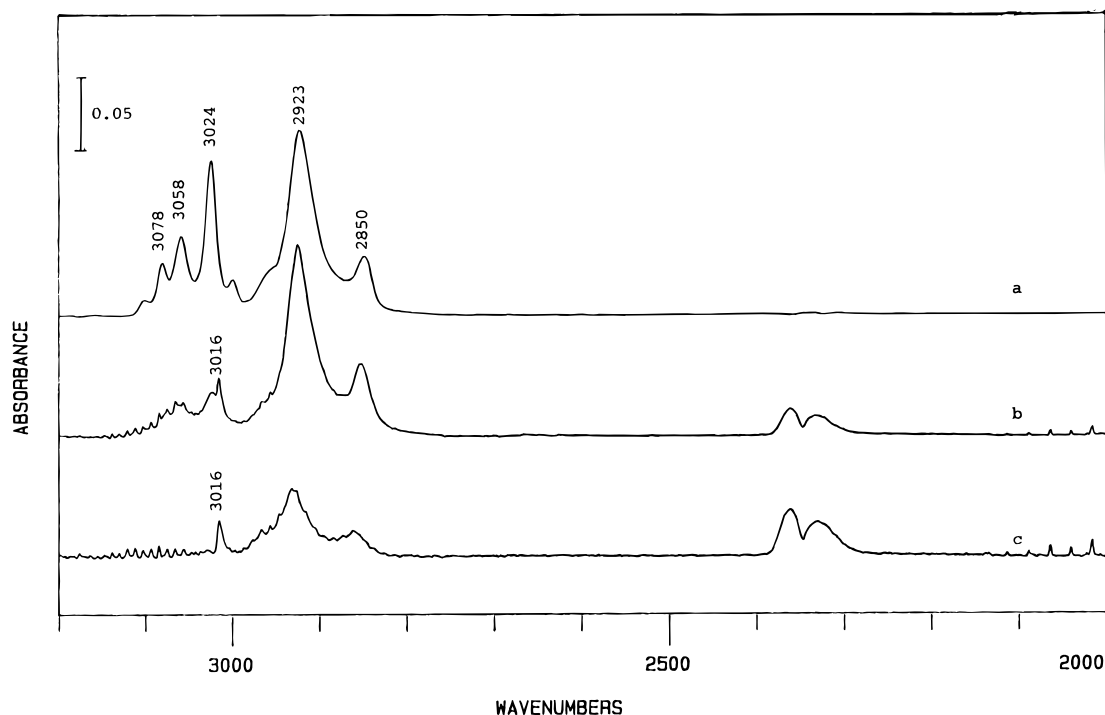


Figure 4. Infrared spectra for polystyrene decomposition over 2.0% Rh/Al₂O₃ (a) at 298 K before sample reduction, (b) after 1 min at 553 K in the presence of 5000 Torr H₂, and (c) after 48 min at 553 K.

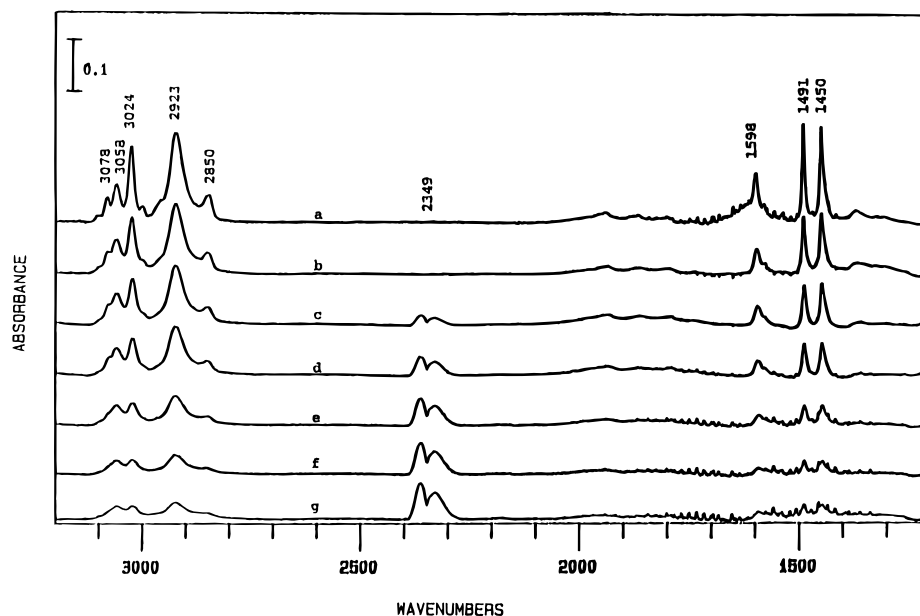


Figure 5. Infrared spectra for polystyrene decomposition over 2.0% Rh/Al₂O₃ (a) at 298 K before sample reduction, (b) after reduction cycles at 453 K, (c) after 20 min at 538 K in the presence of 5050 Torr N₂, (d) after 35 min at 563 K, (e) after 10 min at 613 K, (f) after 20 min at 613 K, and (g) after 30 min at 613 K.

products, although not in the same distribution ratios. Thus we performed an experiment similar to those discussed above using high-pressure N₂ (5050 Torr) instead of H₂. The results are shown in Figure 5. In this case high temperatures were required to cause significant decomposition (about 573 K), the intermediate cyclohexyl polyethylene was not observed, there was band structure due to CO₂(g) and H₂O on the support, and there was no evidence for the formation of CH₄(g). Thus it would appear that H₂ gas is necessary for the production of CH₄, presumably via hydrogenation of carbon formed on the catalytic film during the decomposition of the polystyrene. In other words, the hydrogen present in polystyrene is not sufficient to yield CH₄ gas during the decomposition process.

Figure 6 shows that the results for decomposition of

polystyrene over Rh/SiO₂ in the presence of H₂ were similar to those for Rh/Al₂O₃ except that a higher temperature of 573 K was required for the production of CH₄(g) for the Rh/SiO₂ than for Rh/Al₂O₃ (523 K). Again, the polystyrene aromatic rings were hydrogenated at lower temperatures before decomposition to CH₄ began; the first observed accentuation of bands at 2930 and 2850 cm⁻¹ occurred at 433 K during the sample pretreatment reduction process (not shown in this figure). A similar run was made using a lower pressure of D₂ (1600 Torr) than for H₂ (5000 Torr). The results are shown in Figure 7. After exposure to 1600 Torr D₂ for 2 min at 513 K (Figure 7c), the aromatic band structure near 3025 cm⁻¹ has almost vanished with the appearance of new bands centered at 2098, 2195, and 2778 cm⁻¹. The band at 2778 cm⁻¹ can be attributed to D₂O

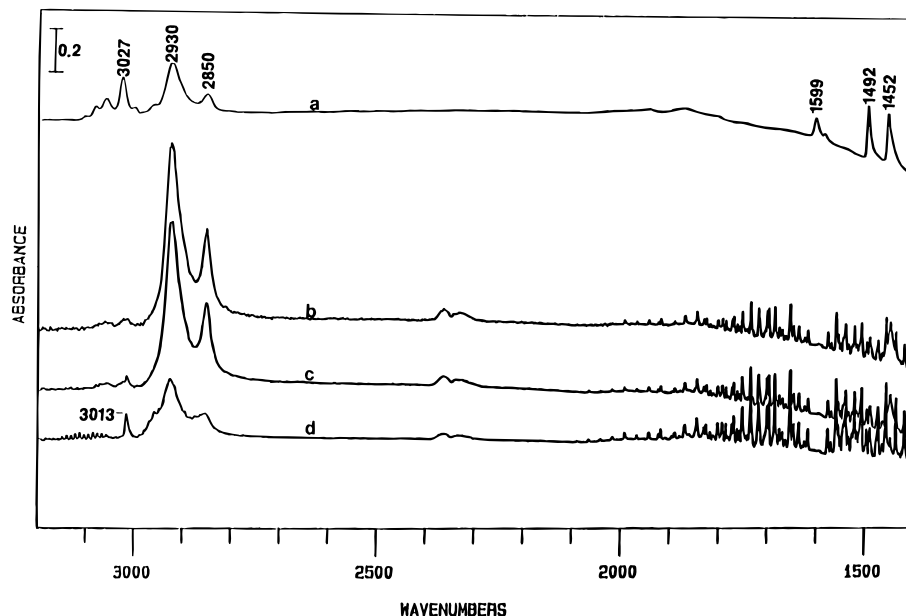


Figure 6. Infrared spectra for polystyrene decomposition over 2.0% Rh/SiO₂ (a) at 298 K after reduction cycles, (b) after 2 min at 553 K in the presence of 5000 Torr H₂, (c) after 2 min at 573 K, and (d) after 180 min at 573 K.

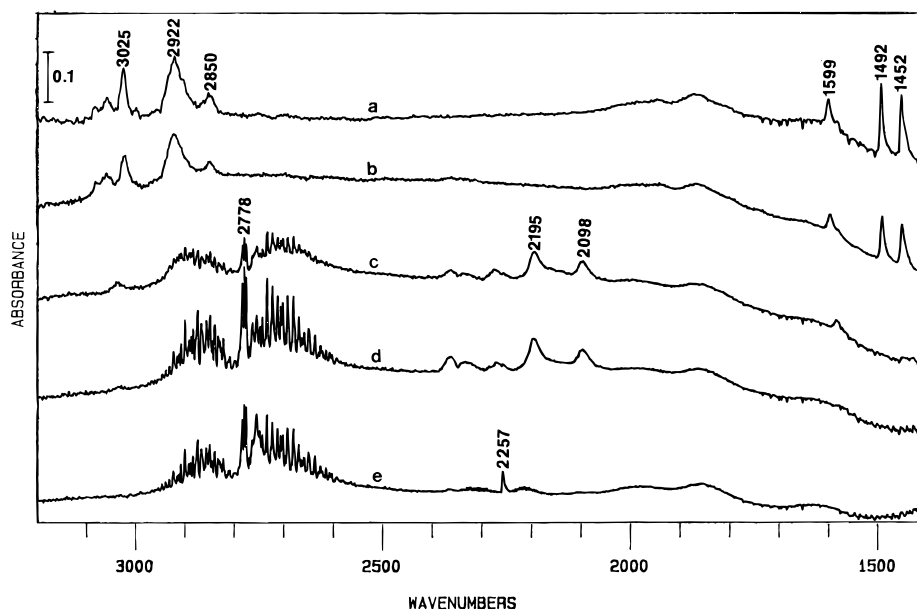


Figure 7. Infrared spectra for polystyrene decomposition over 2.0% Rh/SiO₂ (a) at 298 K before sample reduction, (b) at 473 K after reduction cycles, (c) after 2 min at 513 K in the presence of 1600 Torr of D₂, (d) after 2 min at 553 K, and (e) after 180 min at 573 K.

on the support and in the gas phase; the bands at 2098 and 2195 cm⁻¹ correspond to the C–D stretching modes for the deuterated cyclohexyl moieties on the polyethylene chain. These two bands vanish following extended exposure to D₂ at 573 K (Figure 7e) with the concomitant appearance of a band at 2257 cm⁻¹, which can be assigned to the production of CD₄(g). Bands for partially deuterated methane were not observed. This experiment supports our earlier conclusion that H₂ (or D₂) gas is necessary for the decomposition of polystyrene to methane. Had the hydrogen moieties on polystyrene been involved in producing the CH₄ decomposition product, surely CH₃D, CH₂D₂, and CHD₃ infrared bands would have been observed during the experiment.

Although methane was the only product which was detected by infrared spectroscopy in these experiments, it was likely that higher hydrocarbons were also produced. For this reason the decomposition of polystyrene in the presence of H₂ and Rh/Al₂O₃ was also studied in a tubular microreactor. In these

experiments 0.7–0.8 g of sample containing 50 wt % polystyrene and 50 wt % Rh/Al₂O₃ was prepared and loaded into the reactor as a dried powder. The reactor was evacuated, and 5170 Torr of H₂ gas plus 10 340 Torr of inert He gas were added. The helium was necessary to increase the total pressure for later gas sampling for gas chromatography analyses. The reactor was held at 553 K for 1 h, at which time a product analysis was performed using procedures employed previously in these laboratories.^{8,9} The total conversion of polystyrene was 98.9 ± 0.2%, the H₂ consumption during the reaction being 25.6 ± 0.1%. The product distribution was gas 1.7 ± 0.6%, hexane solubles (lower hydrocarbons C₇–C₃₆) 38.2 ± 0.9%, THF solubles (higher hydrocarbons >C₃₆) 9.8 ± 0.6%, and THF insolubles (primarily Rh/Al₂O₃) 50.4 ± 0.2%. The gas analysis showed H₂ at 99.4 ± 0.1%, CH₄ at 0.5 ± 0.1%, and C₂H₆ at 0.1%. Thus the amount of CH₄ produced in the decomposition of polystyrene over Rh/Al₂O₃ is low relative to other higher hydrocarbons (>C₅); yet it is the only detectable product by

infrared. This implies that the utility of infrared analyses during catalytic polymer decomposition will probably be confined to answering mechanistic questions such as the one answered here, namely that the aromatic ring is hydrogenated before sample decomposition to produce methane (and probably other decomposition products as well) begins.

Conclusions

Infrared spectroscopy has shown that during the decomposition of polystyrene over Rh/Al₂O₃ films hydrogenation of the aromatic rings occurs at temperatures lower (ca. 500 K) than those necessary for decomposition to CH₄ (ca. 523 K). Temperatures necessary for production of CH₄ over Rh/SiO₂ are higher (ca. 573 K). The presence of H₂ gas is a necessary condition for the production of CH₄ during the decomposition of polystyrene over supported Rh. However, the yield of CH₄ relative to those of higher hydrocarbons is low.

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