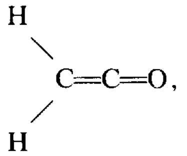
JOURNAL OF CATALYSIS **145**, 246–249 (1994)

NOTE

Decomposition of Ketene over Supported Rhodium

An important concept in catalysis is the direct study of reaction intermediates on the surfaces of the catalyst particles. As pointed out by Ibach and co-workers (1), a clever approach in the study of such intermediates is to decompose a reactive molecule which produces a surface species which is thought to be of importance in some chemical reaction. For example, the fascinating organic molecule ketene,



might be expected to decompose to CO and methylene (CH_2) on a catalytic surface, the latter of which has been proposed to be a prominent intermediate in the Fisher–Tropsch reaction (2). In fact, Blyholder and Emmett used radioactively labelled ketene to investigate the mechanism of chain growth in this reaction (3).

Elegant investigations concerning the decomposition of ketene over metal single crystals have been performed during the past decade. Such studies have included EELS investigations of the process for Fe(110) (1), and HREELS, SIMS, and TPD for ketene decomposition over Pt(111) (4–7) and Ru(001) (8, 9). Also, recently the adsorption and decomposition of ketene over silica (10) and zinc oxide (11) have been monitored using FTIR. The present investigation addresses the decomposition of ketene over supported Rh catalytic films in an infrared-cell reactor with FTIR as the analytical probe.

In this work ketene was prepared on a daily basis by pyrolysis of the vapors of spectroscopic grade acetone with a heated Chromel A filament and passing the decomposition products into a series of four traps held at 273, 195, 158, and 77 K using helium as a carrier gas. The ketene samples collected at 77 K were stored at 77 K until use, but never for more than 30 min. The material was purified on a clean, glass vacuum line by freeze–pump–thaw cycles immediately before introduction into a glass infrared cell reactor similar to that described elsewhere (12). Supported Rh films containing 2.2% weight Rh were prepared by spraying a slurry of $RhCl_3 \cdot 3H_2O$ (Johnson Matthey), a support material (Al_2O_3 (Degussa Aluminumoxid C, 100 m^2g^{-1}), TiO_2 (Degussa titanium dioxide P25, 50 m^2g^{-1}), and SiO_2 (Degussa Aerosil 200, 200 m^2g^{-1})), spectroscopic grade acetone, and distilled–deionized water onto a 25-mm CaF_2 IR window held at 353 K. Evaporation of the volatile components provided IR-transparent supported $RhCl_3 \cdot 3H_2O$ films (4.4 mg cm^{-2}) firmly adhered to the window. The window was mounted in the cell reactor, and the cell was evacuated overnight at ca. 2×10^{-6} Torr. The sample was converted to supported Rh by 100-Torr H_2 reduction cycles of 5, 5, 10, and 20 min at 473 K with evacuation following each cycle. After evacuation overnight, ketene was introduced into the cell reactor at a pressure of 2.3 Torr at 298 K, and its decomposition was followed by FTIR (IBM 32 spectrometer operated at 2 cm^{-1} resolution; 100 scans accumulated over a period of 1.5 min). In some experiments hydrogenation of the surface at 473 K using 99.999% H_2 (Air Products) was performed. All pressure measurements were made with an MKS Baratron capacitance manometer. In some experiments gaseous products were analyzed using mass spectrometry (VG 70EHF) or GCMS (Finnigan 3300).

Figure 1 indicates the purity of the ketene used in these experiments. There were no features in the infrared or the mass spectra of gas-phase ketene attributable to diketene or other decomposition or impurity products. However, upon exposure to the supported Rh films, the ketene began to decompose, as illustrated for Rh/Al_2O_3 in Fig. 2. The IR spectrum labeled (a) in Fig. 2 was accumulated within 0.5–2.0 min after pure ketene was flowed into the cell reactor. Bands at 1897, 1857, 1692, and a portion of the one at 1742 cm^{-1} can be assigned to the species diketene (13). Those at 1829, 1812, and a portion of the one at 1742 cm^{-1} are characteristic of an anhydride species as pointed out by Vikulov *et al.* in their investigation of ketene decomposition over silica (10). The bands at 1709, 1378, and a portion of the 1400–1500 cm^{-1} region can be assigned to surface acetate species (10), and the ones developing at *ca.* 1578 and in the 1400–1500 cm^{-1} region as well are due to surface carboxylate species (14–18).

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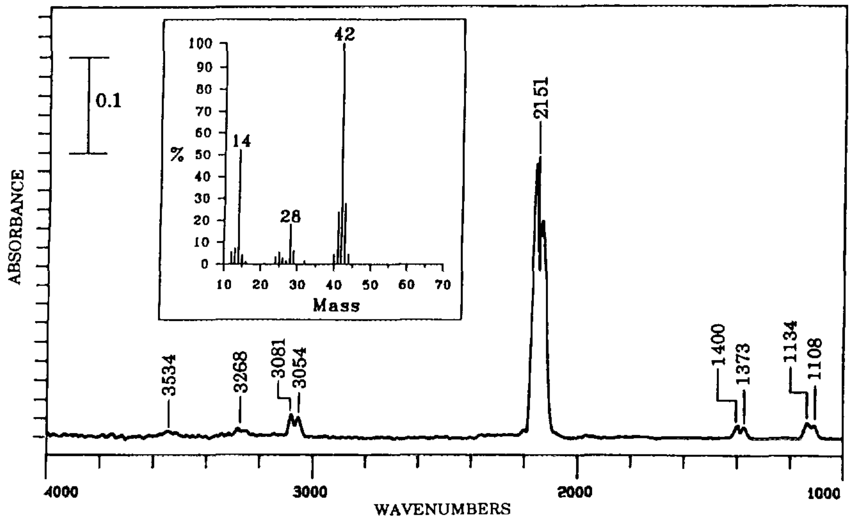

FIG. 1. Infrared and mass spectra for the gas-phase ketene used in these experiments; the pressure was 2.3 Torr at 298 K.

The spectrum in Fig. 2b was accumulated after 180 min of contact of ketene with the Rh/Al_2O_3 surface at 298 K and 5 min of evacuation. The intense band at 2151 cm^{-1} for ketene shown in Fig. 2a, as well as those assigned to diketene and the anhydride species, have vanished, indicating that those species were either gas-phase or weakly bonded surface species. Furthermore, bands at 2080 and 2010 cm^{-1}, and 2030 cm^{-1}, and a weak broad one near 1850 cm^{-1} indicative of the usual gem-dicarbonyl, linear, and bridged CO surface species for supported Rh at low surface coverage (19), respectively, have appeared. Figure 3 shows the results of an analogous ketene decomposition experiment over alumina alone. When Rh was not present, the initial spectrum (a) showed only weak bands attributable to anhydride, acetate, and carboxylate species with none for diketene or CO. After 180 min decomposition and evacuation, the spectrum was characteristic of surface carboxylates and acetates only.

We conclude that Rh catalyzes the dimerization of ketene as well as its decomposition to CO and presumably CH_2, although there is no direct spectroscopic evidence for the latter. Figure 4 illustrates that the diketene further decomposed because its characteristic IR bands at 1897 and 1857 cm^{-1} actually disappeared before evacuation at the end of the experiment. It is notable that the 2151-cm^{-1} ketene band also vanished before evacuation (c)

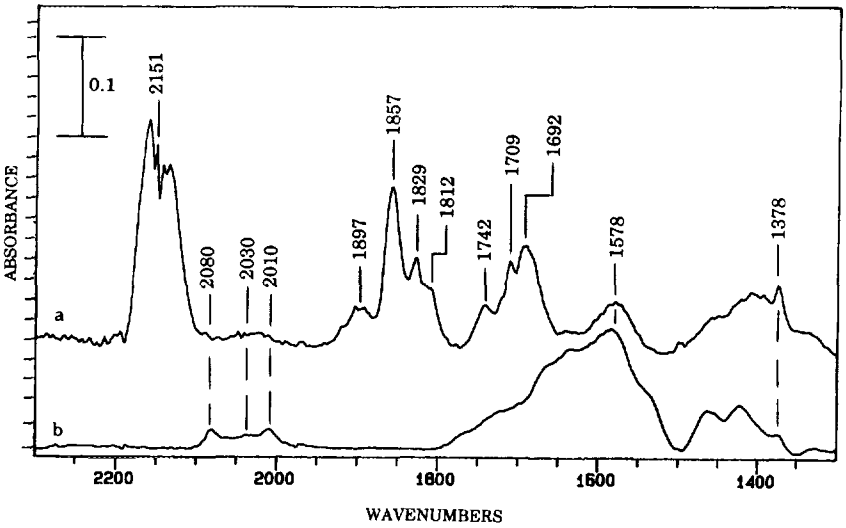

FIG. 2. Infrared spectra for the decomposition of 2.3 Torr of ketene at 298 K over a 2.2% Rh/Al_2O_3 film (4.4 mg cm^{-2}) after (a) 0.5–2.0 min and (b) 180 min followed by evacuation for 5 min.

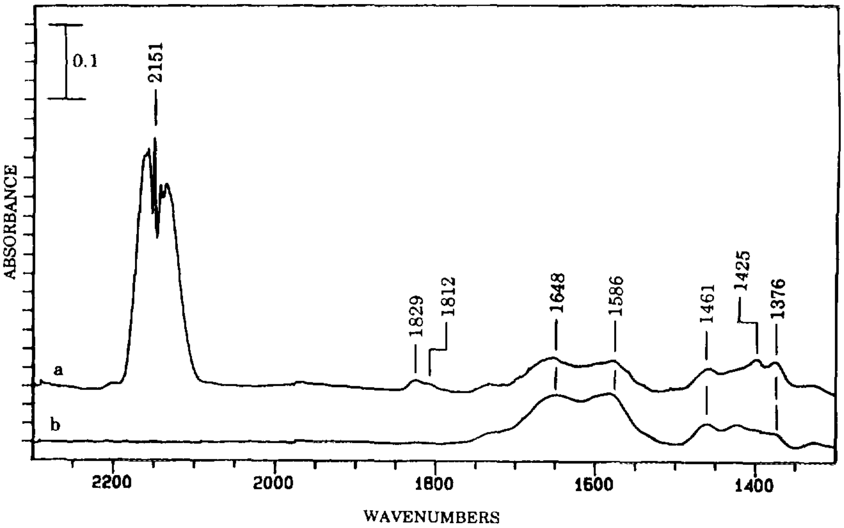

FIG. 3. Infrared spectra for the decomposition of 2.3 Torr of ketene at 298 K over an Al_2O_3 film (4.4 mg cm^{-2}) after (a) 0.5–2.0 min and (b) 180 min followed by evacuation for 5 min.

indicating that the decomposition reaction for ketene was complete within 3 h. A GC mass spectrum of the gaseous products having masses above 20 after 3 h of decomposition indicated the presence of ethylene, higher C_xH_y compounds, acetone, and acetic acid. The ethylene and higher C_xH_y compounds likely resulted from the combination of Rh surface CH_2 species. Acetic acid would be expected from hydrolysis of ketene by the hydrated surface of alumina and decomposition of surface acetate species. The origin of acetone as a gas-phase product is less obvious, but we and others have observed it previously (20, 21) as a product during the hydrogenation of CO over supported Rh doped with potassium, so it may result from the CO surface species, as well as from the anhydrides and acetates.

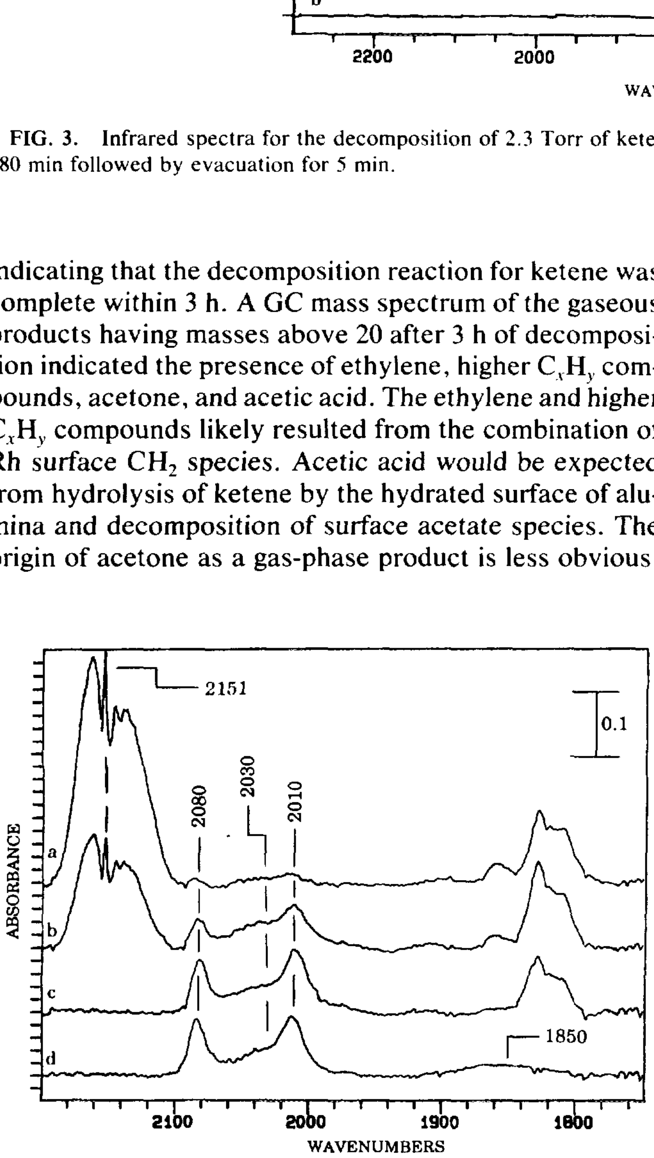

FIG. 4. Infrared spectra for the decomposition of 2.3 Torr of ketene at 298 K over a 2.2% Rh/Al_2O_3 film (4.4 mg cm^{-2}) after (a) 0.5–2.0 min, (b) 60 min, (c) 180 min but before evacuation, and (d) following evacuation for 5 min.

Figure 5 shows the IR spectrum at 298 K resulting from hydrogenation of the species on the Rh/Al_2O_3 surface at 473 K following complete decomposition of ketene and evacuation. The new band at 1304 cm^{-1} which vanished upon evacuation is indicative of the production of methane. The intense bands at 1574 and 1464 cm^{-1} may be assigned to surface carboxylate species on the alumina support. When D_2 was employed in the reduction, CD_4 was produced, as evidenced by a sharp IR band at 2258 cm^{-1}. It is notable that the 1235-cm^{-1} band for CH_2D_2 (20) was not detected in most deuteration experiments, indicating that methane was produced primarily from the CO/Rh species rather than from any CH_2/Rh species. It would appear that the methylene species were depleted in forming ethylene and C_xH_y products before the hydrogenation reaction was performed.

Analogous experiments were performed using Rh/TiO_2 and Rh/SiO_2 films. The results were very similar to those obtained for Rh/Al_2O_3 except that methane was not detected by IR following hydrogenation of the species on the Rh/SiO_2 surface.

In conclusion, the decomposition of ketene over supported Rh most probably occurs through dissociation of the carbon–carbon double bond to form surface Rh methylene and CO species with accompanying anhydride, acetate, and carboxylate species on the support. Diketene also forms during the process, but it decomposes within 3 h. Such surface species as vinylidene (1) and ethylidyne

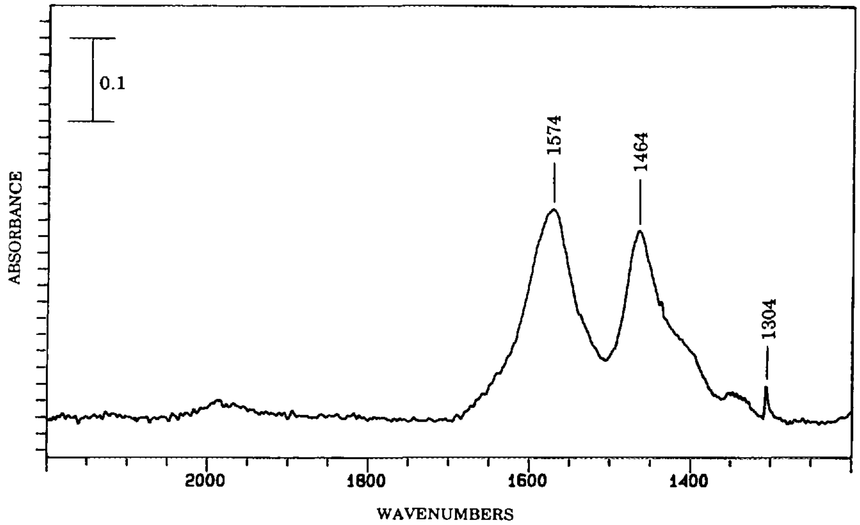

FIG. 5. Infrared spectrum of the Rh/Al_2O_3 film from Fig. 4d following exposure to 10 Torr H_2 at 473 K for 2 h and subsequent cooling to 298 K.

(4, 8) observed during decomposition of ketene over metal single crystals were not detected in these experiments for supported Rh.

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Received June 9, 1993; revised August 9, 1993

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