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A Fourier Transform Infrared Spectroscopic Study of the Oxidation of Propylene over Supported Silver Catalysts

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Fourier transform infrared spectroscopy has been used to investigate the reaction products and intermediates formed during the oxidation of propylene over Ag/SiO_2 catalysts. Apart from bands caused by gas-phase CO_2 and H_2O an absorption band was found at 1690 cm^{-1}, which can probably be assigned to adsorbed acrolein. These results support an idea described earlier for other systems concerning the possible cause of the low selectivity of supported silver catalysts in the oxidation of propylene to propylene oxide.

I. INTRODUCTION

Silver supported on α-Al_2O_3 is a well-known catalyst for the oxidation of ethylene to ethylene oxide and has fairly high activity and selectivity. However, attempts to produce propylene oxide using the same catalyst in a similar process have failed, owing to a very low selectivity of the catalyst. ir spectroscopy can supply direct information about the state of the adsorbed intermediates at the catalyst surface and thus may shed light on the possible cause of this low selectivity.

Numerous papers on the spectral analysis of the interaction between propylene and oxide catalysts are available, examples of which are described briefly below. No data are known, however, concerning the interaction between propylene and silver.

Kugler and Kokes (*1*), working with ESR and ir spectroscopy, found that, on the surface of zinc oxide at room temperature, a reaction occurs between alkyl and O_2^- species. It is thought that O_2^- species are also present on silver catalysts under ethylene oxidation conditions; the formation of ethylene oxide is in fact attributed to them. ir spectroscopy was used to follow the course of the reaction, and acrolein was found to be the major product adsorbed at the surface. However, the reaction products could not be desorbed without raising the temperature so high that reactions yielding primarily carbon oxides and water were caused.

Further results obtained by Kugler and Gryder (*2*) indicated that a more complex mechanism was involved in which glycidaldehyde, the epoxide of acrolein, reacted with another propylene molecule to give acrolein. Cant and Hall (*3*) found that the diatomic oxygen species played a very important role in the oxidation of propylene to acrolein over Rh and Ru/α-Al_2O_3 catalysts. According to the work of Akimoto *et al.* (*4*), molecularly adsorbed oxygen species on CuO/SiC systems are important in the incorporation of oxygen in propylene to produce acrolein.

Apart from absorption bands of hydrocarbon groups, characteristic bands appear in the 1680–1692 cm^{-1} region of the ir spectra, demonstrating the existence of surface species containing carbonyl groups. It is assumed that these adsorbed species are further converted to unsaturated aldehydes (*5–8*).

We decided to conduct an ir spectroscopic study of the propylene/oxygen/silver system, with the specific object of obtaining information on the interaction between silver and propylene. We hoped thereby to gain a better understanding of

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the deep oxidation of propylene on silver catalyst, and hence to be able to explain the low selectivity in relation to propylene oxide.

II. EXPERIMENTAL

A. Apparatus

The experiments were carried out in a cylindrical Pyrex ir absorption cell of dimensions 10 × 4 cm, similar to one described recently (*9*). A double-walled quartz cylindrical furnace (i.d. 22 mm, tungsten resistance wire) on the axis of the cell made possible the heating of the sample disc, which was placed on a baffle in the center of the furnace. A chromel/alumel thermocouple in the close vicinity of the sample disc, positioned by means of a quartz thermowell, permitted accurate temperature measurement and control. The ends of the cell were sealed with KBr windows, seated on Viton O-rings.

An oil diffusion pump with a rotary prepump was used for evacuation during sample pretreatments and exchange of gases in the cell. Gases were admitted to the cell from the gas manifold through Delmar Pyrex inlet valves equipped with Teflon spindles.

With the valves closed, the cell could be detached from the vacuum/gas handling system, to which it was connected by Pyrex ball joints, and transported to a Digilab FTS 14 ir spectrometer on which the spectra were recorded. Spectral resolution was set at 2 cm^{-1}. The number of scans ranged from 200 to 500.

B. Materials and Pretreatments

The catalyst used in the experiments consisted of 20% by weight (%w) Ag on silica. It was prepared by impregnation of Degussa Aerosil SiO_2 (specific surface area > 200 $m^2\ g^{-1}$) with a solution of $AgNO_3$ followed by drying at 120°C. Subsequently the catalyst was calcined in air at 250°C and reduced in a hydrogen stream at 300°C.

The catalyst was ground thoroughly by means of a vibratory mill equipped with a stainless-steel capsule and ball, and pressed into a thin self-supporting wafer (diameter 20 mm, typical thickness 10–20 mg cm^{-2}). The sample was compressed under pressures up to 200 MPa (2 kbar).

The disc was placed in the cell and secured in the heating device by means of a tight-fitting quartz ring. The cell was sealed with the KBr windows, then connected to the vacuum/gas manifold.

Prior to all adsorption experiments the catalysts were degassed at 300°C for 1 hr at approx. 10^{-2} Pa (10^{-4} Torr). Reduction of the sample was likewise carried out at 300°C, in hydrogen at 1.3×10^4 Pa (100 Torr). During the reduction period of 3 hr the hydrogen was replaced four times to keep the concentration of product water as low as possible.

Cooling to room temperature in hydrogen concluded the pretreatment procedure.

C. Adsorption and Reactions

1. Oxygen adsorption. After the spectrum of the reduced catalyst had been recorded, the catalyst was preoxidized at two different temperatures, 95 and 200°C. The catalyst was first exposed to oxygen at 2.5 kPa for 30 min at 95°C, and a spectrum was recorded at room temperature in oxygen. Subsequently the procedure was repeated with 200°C as the temperature for oxygen chemisorption.

2. Propylene oxidation reaction. The study of propylene oxidation was conducted via two different routes.

a. Adsorption of propylene onto, and reaction with, a preoxidized catalyst in the absence of gas-phase oxygen. This particular experiment was done to study possible intermediate adsorption complexes under conditions where complete oxidation was unlikely to take place owing to the limited amount of oxygen present in the system. The preoxidized catalyst was exposed to propylene at 2.6 kPa (20 Torr) and heated in one case to 95°C and in the other to 200°C. After each treatment a spectrum was recorded at room temperature. One should realize that the possibility of readsorption of gas-phase products cannot be excluded.

b. Adsorption of propylene from an oxygen/propylene (1 :3) gas mixture onto, and reaction with, a preoxidized catalyst. This experiment reflects normal reaction conditions more realistically. The preoxidized catalyst was exposed to a mixture of oxygen (665 Pa = 5 Torr) and propylene (2 kPa = 15 Torr). Spectra were recorded at room temperature after reaction at 95 and 200°C.

In order to make possible compensation of the gas-phase absorption bands of propylene, spectra were recorded of propylene and the propylene/oxygen mixture in the same cell at identical pressures but in the absence of a catalyst.

III. RESULTS AND DISCUSSION

After oxidation, at both 95 and 200°C, the spectrum of the catalyst was virtually identical to that of the reduced catalyst. After 95°C treatment a very weak band was observed at 1630 cm^{-1}; after oxidation at 200°C this band was much stronger. We attribute this band to the formation of bidentate carbonate (*10*), probably via oxidation of traces of contaminant hydrocarbons. The accompanying symmetric stretch vibration at 1260–1270 cm^{-1} cannot be observed due to the strong absorption by the silica lattice vibrations in that region. Unfortunately Ag–O absorption bands are also obscured by absorption bands of the silica carrier. However, in the region where the O–O stretch vibration of molecularly adsorbed oxygen was expected (on the basis of experiments done on a KBr-supported Ag film (*11*)), namely, around 1430 cm^{-1}, an area relatively free of interference from other absorption bands, no changes were detected after oxidation treatments.

Figures 1A–C show the result of the first propylene oxidation experiment, in which the preoxidized catalyst was heated in a 2.6 kPa propylene atmosphere. Figure 1A shows the spectrum of the Ag/SiO_2/propylene system after reaction at 200°C (top), that of the oxidized catalyst (middle), and the difference spectrum (bottom trace). This difference spectrum, containing absorption bands from gas-phase as well as adsorbate species, is subsequently compensated for gas-phase propylene (see Fig. 1B). Finally, Fig. 1C shows detail of the product spectrum after reaction at 200°C. The product spectrum consists of vapor-phase water absorption bands and a single band at 1625 cm^{-1}, possibly due to the formation of bidentate carbonate (*12*). It is possible that this band is (partly) due to the H–O–H deformation vibration of adsorbed water.

There spectra show that basically three product ir bands are formed:

(1) ~2350 cm^{-1}, assigned to gas-phase CO_2;

(2) 1625 cm^{-1}, assigned to bidentate carbonate, with a possible contribution of adsorbed water;

(3) a set of bands between 1850 and 1350 cm^{-1}, indicative of gas-phase water.

It is striking that the H_2O/CO_2 ratio is very high. This leads us to the hypothesis that:

(1) oxidative dehydrogenation of the adsorbed propylene takes place, resulting in the production of adsorbed olefinic materials and vapor-phase H_2O;

(2) the adsorbed olefinic material subsequently polymerizes, which results in the formation of a hydrogen-deficient carbon skeleton on the surface of the catalyst;

(3) partial oxidation of this carbon-rich species leads to the production of some CO_2.

In view of the low hydrogen content of the assumed deposited species direct spectral verification seems unlikely. No C–H vibrations of adsorbed hydrocarbon species could be detected.

The presence of a carbon-rich deposit on the catalyst could be verified, however, by

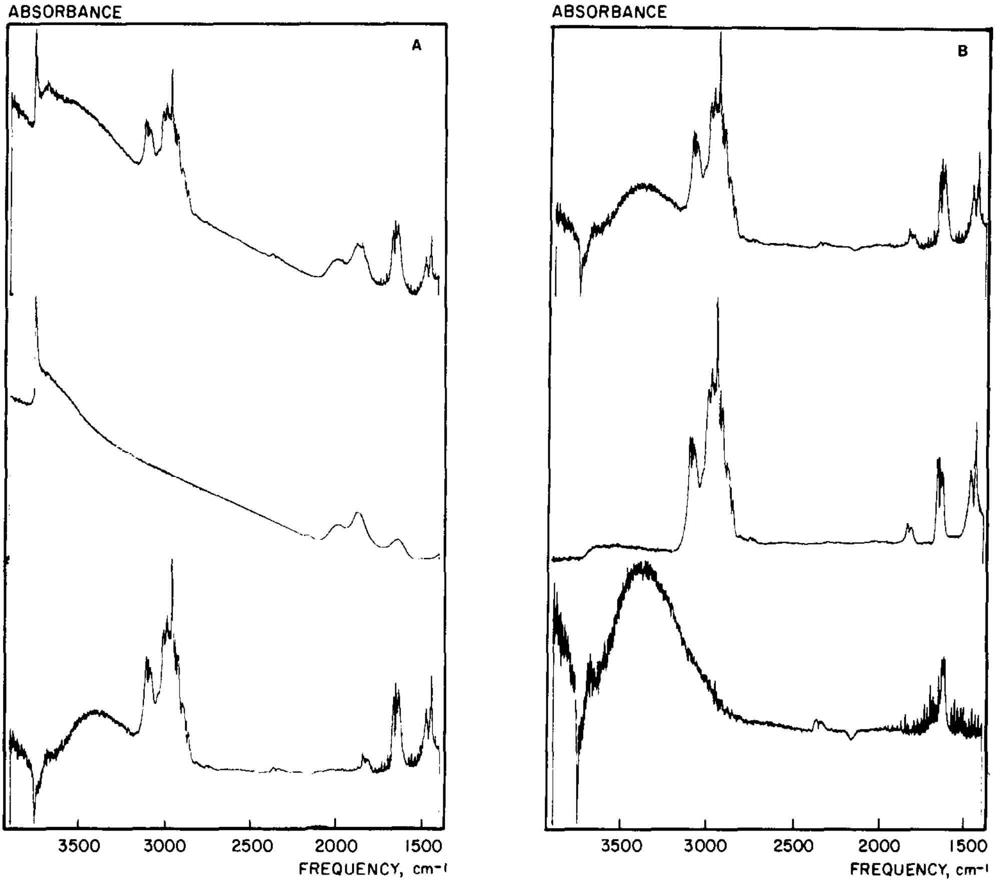


FIG. 1. Infrared spectra of propylene on preoxidized Ag/SiO_2 after 1 hr at 200°C. (A) Top: catalyst + vapor phase + adsorbates; center: preoxidized catalyst; bottom: vapor phase + adsorbates (= top minus center). (B) Top: vapor phase + adsorbates; center: propylene; bottom: product spectrum (adsorbates + vapor phase) (= top minus center). (C) Top: adsorbate + product water (vapor phase); bottom: same spectrum after compensation for water.

subsequent treatment of this sample at 300°C in pure oxygen at 2.6 kPa with the aim of converting the carbon skeleton into CO_2. Production of CO_2 and H_2O in a ratio 10 times that found during propylene oxidation (see Fig. 2) proved that such a deposit is indeed present.

In the series of spectra shown in Fig. 1 one other feature needs explanation. The spectrum of the fresh, preoxidized catalyst (Fig. 1A, middle trace) shows a small band at approx. 2160 cm^{-1}, which has disappeared from the spectra recorded after subsequent treatments in propylene. All spectra recorded after reactions under the different sets of conditions were compensated with this preoxidized catalyst spectrum and hence show a negative band at 2160 cm^{-1}. We are inclined to believe that this band originates from a small amount of cyanate (*13*) formed during oxidation of the incompletely decomposed $AgNO_3$ used in the catalyst preparation.

Figure 3 shows the results of the second experiment, interaction of propylene with preoxidized silver in the presence of gas-phase oxygen at elevated temperatures. At low temperatures ($T <$ 100°C) only H_2O and CO_2 are formed (not shown in Fig. 3). At higher temperatures (200°C, reaction time 2 hr) more H_2O and CO_2 are produced, but only to the same extent and in the same

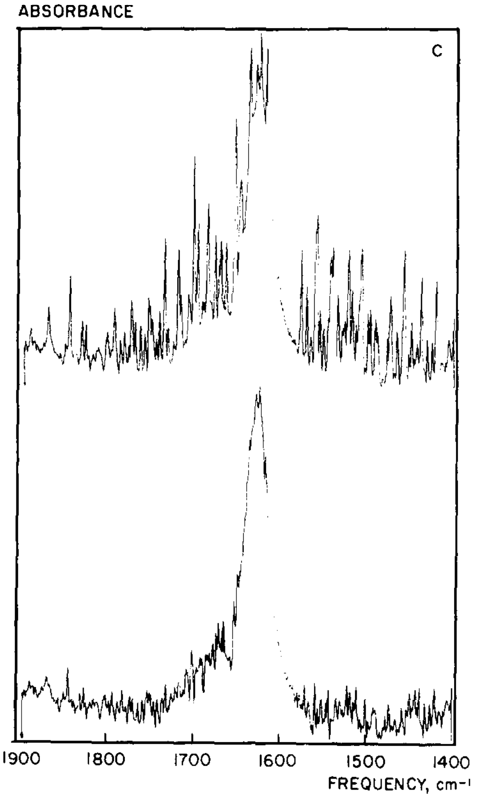
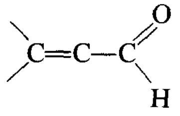


FIG. 1.—*Continued*

ratio as in the first experiment. In addition, the 1625 cm^{-1} band observed in the first experiment is again present.

A fresh observation is that a band has formed at 1690 cm^{-1}. This detail can be seen the most clearly in Fig. 3B. An additional 2 hr treatment at 210°C caused the 1690 cm^{-1} band as well as the gas-phase H_2O and CO_2 absorption bands to increase by almost 50% in intensity. The spectra showing this are presented in Figs. 3A and B.

The 1690 cm^{-1} band is a strong one in the second experiment. Close inspection of Fig. 1C (first experiment) also reveals some intensity between 1700 and 1650 cm^{-1}. At present we are inclined to attribute this to the formation of acrolein, a  $>C{=}C{-}C(=O)H$ species (*12*), in the adsorbed state. Due to the high extinction coefficient of the carbonyl group relative to all other vibrations in the species the 1690 cm^{-1} band is the only one which is shown clearly in the spectrum.

Independently, recent ir and temperature-programmed desorption experiments by Davydov *et al.* (*14*) with propylene oxidation on gallium molybdate catalysts led to the same conclusion, viz. that an acrolein-type intermediate was formed.

The low intensity of this band in experiment 1 (Fig. 1C) can therefore probably be explained by secondary reactions (polymerization and subsequent oxidation to CO_2 and H_2O) reducing the amount of adsorbed acrolein present.

The presence of gas-phase oxygen in the second experiment makes possible reoxidation of the silver, and subsequent formation of newly adsorbed acrolein, so that a higher

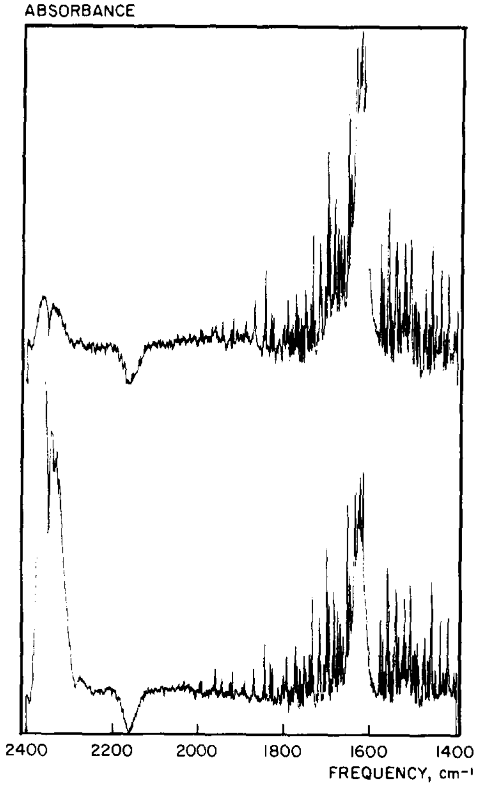


FIG. 2. Propylene on preoxidized Ag/SiO_2: vapor phase and adsorbed product spectra. Top: after reaction with propylene at 200°C; bottom: subsequent reaction with oxygen at 300°C.

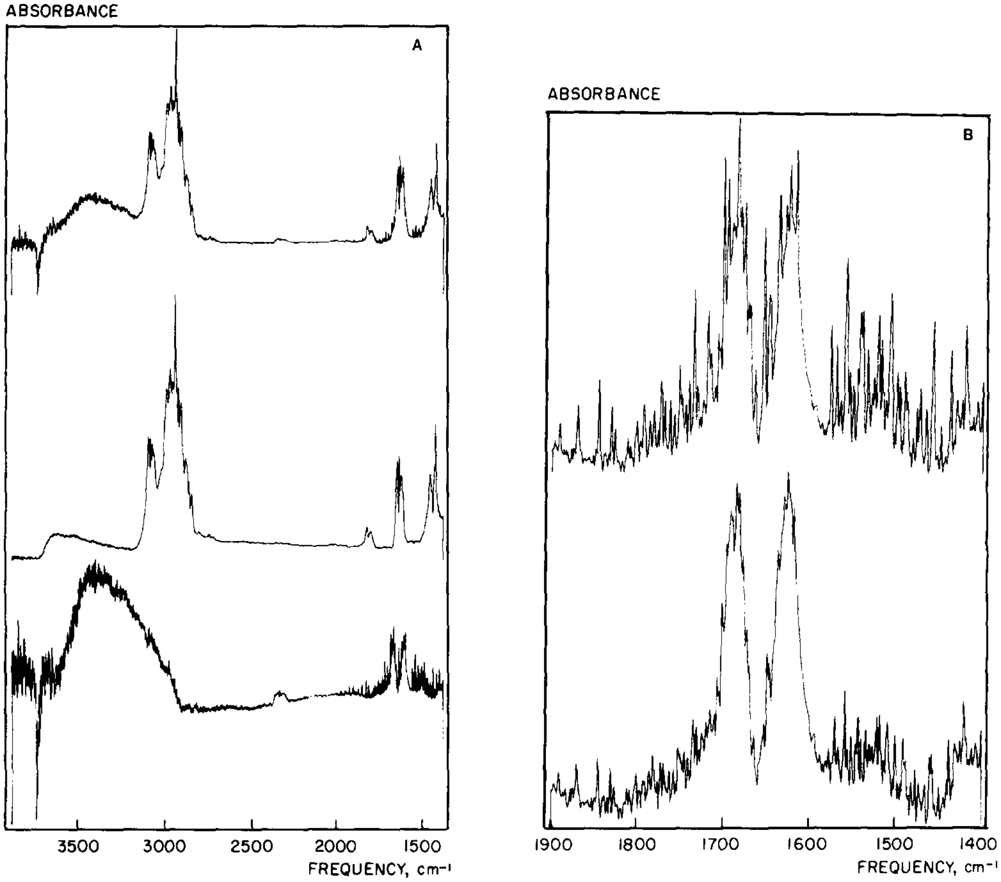


FIG. 3. Infrared spectra of oxygen/propylene (1 : 3) on Ag/SiO_2 after 4 hr at 200–210°C. (A) Top: gas phase + adsorbates; center: mixture O_2/propylene (1 : 3); bottom: spectrum corrected for the oxygen/propylene gas phase. (B) Top: spectrum corrected for catalyst and gas-phase propylene; bottom: same spectrum after subtraction of product water.

(steady state) concentration is obtained than in experiment 1.

IV. CONCLUSIONS

Under conditions where oxygen is present only in the adsorbed state, the major reaction is oxidative dehydrogenation of the adsorbed propylene followed by polymerization. The presence of a carbon-rich deposit has been established. Possible acrolein-type intermediates have probably been almost completely removed by secondary reactions.

Under more realistic conditions, with oxygen and propylene in the gas phase in a 1 : 3 ratio, a similar reaction occurs but, probably owing to the higher steady-state concentration, the presence of the intermediate adsorbed acrolein can be established.

These results lend support to the idea described earlier for other systems (*14*) that the low selectivity of the oxidation of propylene to propylene oxide is caused by the formation of acrolein, which polymerizes and is deeply oxidized by gaseous oxygen at CO_2 and H_2O.

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