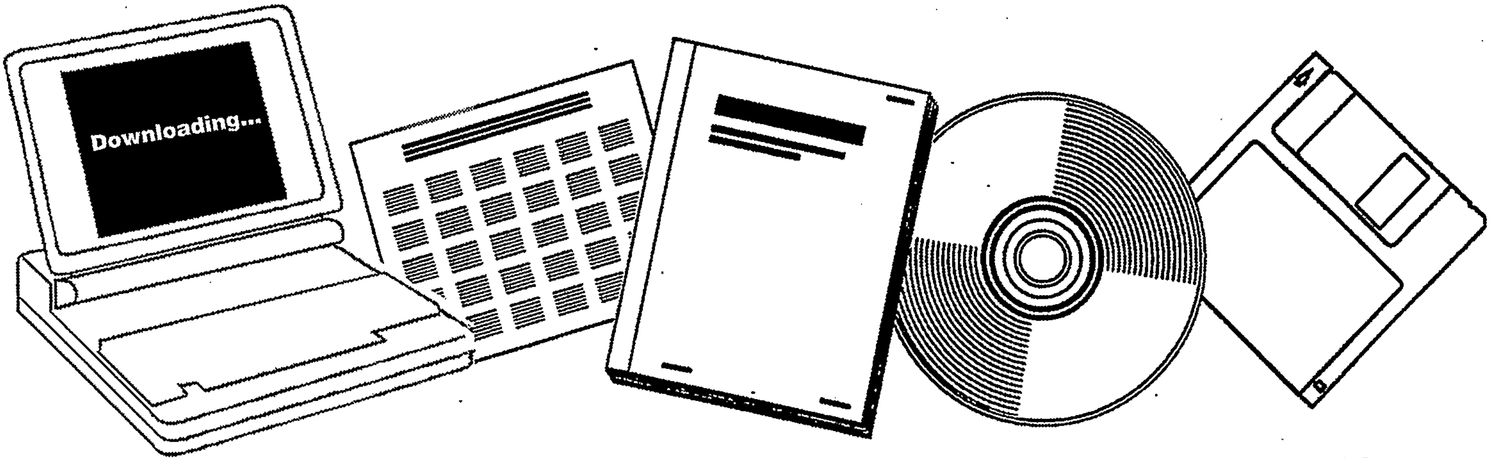
DE91006633

EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL. TECHNICAL PROGRESS REPORT NO. 12, JUNE 16, 1990-SEPTEMBER 15, 1990

AKRON UNIV., OH. DEPT. OF CHEMICAL
ENGINEERING

NOV 1990



U.S. Department of Commerce
National Technical Information Service

One Source. One Search. One Solution.

NTIS

Providing Permanent, Easy Access to U.S. Government Information

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on **www.ntis.gov.** You now have access to information on more than 600,000 government research information products from this web site.

Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

Download Publications (1997 - Present)

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

www.ntis.gov

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

DOE/PC/79923--T4

THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

DOE/PC/79923--T4
DE91 006633

Technical Progress Report 12
Grant No. DE-FG22-87PC79923

June 16, 1990 - Sept 15, 1990

by

Steven S.C. Chuang

Department of Chemical Engineering
University of Akron
Akron, OH 44325 U.S.A.

Date of Submission: November 1990

US/DOE Patent Clearance is not require prior to the publication of this document.

SUMMARY

The objective of this research is to elucidate the role of additives on the methanol synthesis over Rh- and Ni-based catalysts. Chemical additives used for this study will include S, P, Ag, Cu, Mn, and Na which have different electronegativities. The effect of additives on the surface state of the catalysts, heat of adsorption of reactant molecules, reaction intermediates, reaction pathways, reaction kinetics, and product distributions is/will be investigated by a series of experimental studies of NO adsorption, reaction probing, study state rate measurement, and transient kinetic study.

A better understanding of the role of additive on the synthesis reaction may allow us to use chemical additives to manipulate the catalytic properties of Rh- and Ni-based catalysts for producing high yields of ethanol from syngas.

RESULT TO DATE

During the third quarter of 1990, the activity of silica-supported Ru catalysts for the high oxygenate synthesis has been studied by in situ infrared spectroscopy.

DISCLAIMER

Summary

Ethylene hydroformylation, CO hydrogenation, and CO adsorption on Ru/SiO_2 and sulfided Ru/SiO_2 were studied by *in situ* infrared spectroscopy. Ethylene hydroformylation has been shown to occur on the surface of Ru/SiO_2 and sulfided Ru/SiO_2 catalysts. Increasing reaction pressure slightly increased the infrared absorbance of linear CO and greatly enhanced selectivities and activities for the formation of acetaldehyde and propionaldehyde in CO hydrogenation and ethylene hydroformylation, respectively. No relation between the infrared spectra of adsorbed CO and the hydroformylation activity was observed. Sulfidation of Ru/SiO_2 led to the decrease in the wavenumber and absorbance of linearly adsorbed CO; the inhibition of CO hydrogenation, ethylene hydrogenation, and ethylene hydroformylation. The transient and temperature-programmed reaction studies revealed that sulfur poisoning of Ru/SiO_2 catalyst for ethylene hydroformylation was due primarily to the inhibition of desorption of propionaldehyde from the sulfided Ru/SiO_2.

Introduction

Syngas (CO/H_2) and related reactions constitute important pathways for the conversion of coal to chemical feedstocks and liquid fuel [1-5]. One of the most important syngas related reactions is the hydroformylation of olefins that represents the largest volume use of syngas in homogeneously catalyzed reactions [5]. Extensive mechanistic studies have shown that the homogeneous hydroformylation reaction proceeds via (i) the insertion of CO into alkyl-metal complexes leading to the formation of acyl-complex intermediates and then followed by (ii) the hydrogenolysis to give aldehydes [1,3,5-7]. The hydroformylation mechanism has often been used as a model to explain the formation of C_{2+} aldehydes and alcohols in the Fischer-Tropsch (F-T) synthesis (heterogeneous CO hydrogenation) [3-6,8-16]. Probing the mechanism of CO hydrogenation by olefin additions has shown that the reaction of added olefins with syngas on the supported Group VIII metals leads to the formation of aldehydes [12,13,16-19]. It has been suggested that the reaction for the formation of aldehydes on the supported Rh catalyst may be considered as the heterogeneous hydroformylation that resembles the homogeneous hydroformylation catalyzed by metal complexes [12,13].

Ru metal has long been known to be active for the F-T synthesis [4,14,15,20-24]. Increasing reaction pressure shifted the product selectivity from hydrocarbons to aldehydes and alcohols. Oxide-supported Ru catalysts have also been found to exhibit activities for the formation of aldehydes from reactions of syngas and olefins [13,17,18]. Although the reaction leading to aldehyde has been considered as hydroformylation, the nature of the reaction remains unclear.

Sulfur is known to be a severe poison to the heterogeneous metal catalysts that catalyze CO hydrogenation, olefin hydrogenation, paraffin hydrogenolysis, and hydrocarbon related reactions [25-27]. The poisoning effect of sulfur compounds on the metal surface has been attributed to the blockage of active sites as well as the modification of surface states of the catalyst by adsorbed sulfur. Interestingly, several recent studies have shown that sulfur compounds such as H_2S slightly enhanced ethylene hydroformylation over Rh/SiO_2 and Ni/SiO_2 catalysts [28-31] but inhibited the reaction on Ru/SiO_2 [32]. The failure of sulfur to poison the hydroformylation reaction on the Ni and Rh catalysts has been ascribed to the inability of adsorbed sulfur to deactivate the single atom site that is responsible for the reaction. However, the mechanism for sulfur poisoning of Ru catalysts in the hydroformylation is still not understood. Because syngas, produced from coal, usually contaminates with a significant amount of sulfur compounds such as H_2S, developing a better understanding of the role of sulfur in syngas reaction and hydroformylation is of great technological importance.

The objective of this study was to investigate the nature of ethylene hydroformylation over Ru/SiO_2 and the role of sulfur in the reaction. An *in situ* infrared spectroscopic (IR) technique was employed to study CO adsorption, CO hydrogenation, and ethylene hydroformylation on Ru/SiO_2 and sulfided Ru/SiO_2 catalysts. Results of CO adsorption and CO hydrogenation were compared with those of hydroformylation to clarify the IR bands of various adsorbed species. The dynamic behavior of all adsorbed species during the hydroformylation was examined by a transient experiment in which a steady-state $CO/H_2/C_2H_4$ flow was switched to a steady-state CO/H_2 flow. The reactivity of the adsorbed species with H_2 was studied by temperature-programmed reaction (TPR) with H_2.

Experimental

The 3 wt% Ru/SiO_2 catalyst was prepared by impregnation of SiO_2 (Strem Chemicals, #14-7420, SA:350 m^2/g) using $RuCl_3 \cdot 3H_2O$ (Johnson Matthey Chemicals). The catalyst was dried overnight in air at 301 K, then reduced in flowing hydrogen at 673 K for 16 hr. Details of sulfidation, catalyst characterization, IR cell, and sample preparation for IR studies have been described elsewhere [31,32]. Briefly, sulfidation was conducted by exposure of Ru/SiO_2 to flowing H_2S flow (1000 ppm H_2S in H_2) at 513 K for 1 hr. The bulk ratio of sulfur to ruthenium was determined by energy-dispersive spectroscopy. Ru crystallite size before and after sulfidation was determined to be 80 A^0 by X-ray diffraction (XRD) line-broadening technique. No significant difference in XRD spectra for the sulfided and unsulfided Ru indicates that sulfidation at 513 K could reach to the surface of the particle rather than the entire particle of Ru. Hydrogen uptake for the Ru/SiO_2 and the $S\text{-}Ru/SiO_2$ was measured by hydrogen temperature-programmed desorption. The catalyst was pressed into a form of a self-supported disk (20 mg, 10 mm in diameter and 1 mm in thickness) and then placed in the IR cell which is made of stainless steal with CaF_2 windows.

CO hydrogenation ($CO:H_2 = 1:1$) and ethylene hydroformylation ($CO:H_2:C_2H_4 = 1:1:1$) were studied in steady-state flow conditions of 513 K and 0.10 - 3.0 MPa in the IR cell which can be considered as a differential reactor. IR spectra of adsorbed species were recorded by a Nicolet 5SXC FTIR spectrometer with a DTGS detector at a resolution of 4 cm^{-1}. Gas phase CO bands were eliminated by subtracting the adsorbance of gas phase CO with a SiO_2 disk in the cell from the spectra of gaseous reactants and products as well as absorbed species on the Ru/SiO_2 and S-Ru/SiO_2 catalysts. Subsequent to recording each IR spectrum, the effluent of the IR cell was sampled and analyzed by an on-line HP-5890A gas chromatography with a Porapak PS column.

The transient infrared study was conducted by switching a steady-state $C_2H_4/CO/H_2$ flow to a steady-state CO/H_2 flow and maintaining at constant pressure. The change in the IR intensity of adsorbed species during the switch was closely monitored by infrared spectromeyer.

Following the steady-state ethylene hydroformylation, reactor temperatures and pressures were decreased to 303 K and 0.10 MPa. The temperature-programmed reaction (TPR) was then carried out by introducing a flow of H_2 to the IR cell at 10 cm^3/min and heating the reactor at a rate of 5 K/min to 513 K. IR spectra were taken during the entire course of the TPR study.

Results and Discussion

CO Adsorption

Figure 1 shows the infrared spectra of CO adsorption on the Ru/SiO_2 and the S-Ru/SiO_2 catalysts at 513 K. Two bands were observed for CO adsorption on the Ru/SiO_2 catalyst at 1.0 MPa: a linear CO band at 2040 cm^{-1} and a weak bridge-CO band at about 1787 cm^{-1}. The observed wavenumbers of adsorbed CO are in good agreement with those reported for Ru/SiO_2 [22,32,33,35-38]. Decreasing the pressure of CO from 1.0 to 0.10 MPa caused a slightly downward shift of the linear CO wavenumber. Admission of H_2 to the reactor at 513 K resulted in a decrease in the intensity of the linear CO and in a downward shift of its wavenumber. Such a downward shift can be attributed to the reduction in dipole-dipole coupling [37,38] as a result of the removal of the adsorbed CO by reaction with hydrogen.

The influence of sulfur on the infrared spectra for adsorbed CO is also shown in Figure 1. Sulfidation of the catalyst resulted in (i) a reduction in the intensity of the linear CO band, (ii) a downward shift of the linear CO wavenumber, and (iii) a suppression of the weak bridge-CO band. Adsorbed sulfur appeared to disrupt the adjacent pairs of Ru metal atoms, and therefore suppressing bridge-CO sites. The inhibition of CO adsorption in the bridge form brought about by adsorbed sulfur has also been reported for Ni and Rh [25,27,28,30-32]. The results of (i) and (ii) may be due to a lower concentration of adsorbed CO on the surface of sulfided Ru (S-Ru) rather than a ligand effect of adsorbed sulfur [26]. The effect of sulfur on the CO adsorbed on Ru has been found to differ from the effect on Ni and Pt [39,40]. An upward shift of the wavenumber for the linear CO has been observed on the sulfided Ni and Rh [27,28,32]. The sulfided Ni and Rh catalysts showed a lower bonding energy for the CO than the unsulfided catalysts.

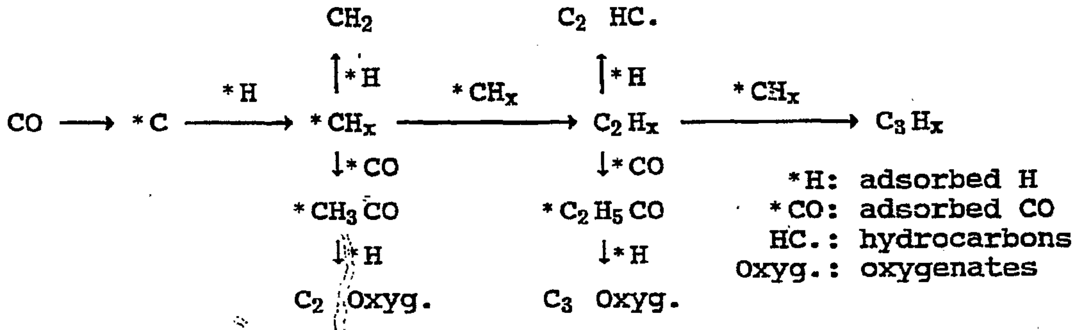
The decrease in CO pressures from 1.0 to 0.10 MPa resulted in a slight modification of the intensity and wavenumber of linear CO on the Ru/SiO_2, but a marked decrease in the intensity and a downward shift of the wavenumber for linear CO on the S-Ru/SiO_2. The greater dependence of the intensity of the linear CO on the CO pressure reflects a smaller equilibrium constant for the adsorption of CO on the S-Ru/SiO_2.

CO Hydrogenation on Ru/SiO_2

The effect of reaction pressure on the infrared spectra for Ru/SiO_2 and S-Ru/SiO_2 are shown in Figure 2. Table 1 presents results of the rates of product formation from CO hydrogenation corresponding to IR spectra taken under steady-state conditions. The TOFs for CO conversion on the Ru/SiO_2 catalyst are lower than those reported in the literature [8]. This may due to the use of higher ratio of CO/H_2. The major bands observed for the CO hydrogenation at 513 K and 0.10 MPa were the linear-CO band at 2003 cm^{-1} and bands corresponding to hydrocarbon species in the region of 2860-2970 cm^{-1} and 1461 cm^{-1} [41]. Methane was identified to be the major product while no oxygenates were observed under this reaction condition.

As reaction pressure increased from 0.10 to 1.0 MPa, the linear CO shifted from 2003 cm^{-1} to 2020 cm^{-1} and its intensity increased; the intensity of hydrocarbon bands and the rate of hydrocarbon formation also increased (shown in Table 1). Further increases in reaction pressure increased the intensity of hydrocarbon bands, but did not affect the intensity and wavenumber of the linear CO at pressures above 1.0 MPa. The stability of these adsorbed CO and Hydrocarbons were examined by treating the catalyst in flowing H_2 (10 cm^3/min) at 513 K and 0.1 MPa. As shown in Figure 2(A)-e, a decrease in the intensity of the linear-CO band was accompanied by a downward shift of the band. In contrast, the intensity of the hydrocarbon bands were not affected by flowing hydrogen indicating that these hydrocarbons may be inert spectator species [34] and adsorbed on the silica support. Unreactive surface hydrocarbons have also been observed on the CO hydrogenation on alumina-supported Ru catalysts. It has been suggested that these hydrocarbon species were formed on the Ru metal surface and then migrated onto the alumina support [24,42].

Table 1 shows that the rate of acetaldehyde formation increased with reaction pressure. It has been suggested that C_2 oxygenate such as acetaldehyde and ethanol is formed via the insertion of CO into CH_x which is produced from carbon monoxide dissociation followed by hydrogenation as shown in the following reaction pathway [9-15].



Because the formation of C_2 oxygenates, methane and C_{2+} hydrocarbons involves a common intermediate, CH_x, a higher ratio of CH_3CHO/CH_4 represents a higher CO insertion selectivity. The increase in the ratio of CH_3CHO/CH_4 and $CH_3CHO/C_{2+}HC$ with increasing pressures (see Table 1) indicates that CO insertion competed favorably with hydrogenation and chain growth at higher reaction pressures. However, the intensity and the wavenumber of the linear CO band are relatively insensitive to the overall reaction pressure in the range from 1.0 to 3.0 MPa. No obvious relation between IR spectra of the adsorbed CO and the activity for CO insertion can be discerned.

Comparison of IR spectra of adsorbed CO in the CO hydrogenation (Figure 2) with those in the CO adsorption study on Ru/SiO_2 (Figure 1) reveals that the linear CO in the CO/H_2 atmosphere exhibited a lower wavenumber and a lower absorbance compared to that observed in the pure CO atmosphere. Coadsorption of CO and H_2 has been found to result in a downward shift of linear CO wavenumber on Ru [24,34,42]. The downward shift accompanied by the decreases in the absorbance for the adsorbed CO may be attributed to the decrease in dipole-dipole interactions a result of dilution by adsorbed hydrogen [42,43] rather than the ligand effect of adsorbed hydrogen [6].

CO Hydrogenation on Sulfided Ru/SiO_2

As shown in Table 1, the addition of sulfur inhibited the formation of both C_{2+} hydrocarbons and oxygenates. Methane was the only product observed on the sulfided catalyst. Increasing the pressure from 0.10 to 3.0 MPa enhanced the rate of the methane formation by a factor of 2.8. Comparison of the rate of methane formation on Ru/SiO_2 and $S-Ru/SiO_2$ shows that sulfur slightly inhibited the rate of methane formation at 0.10 MPa. A more pronounced suppression of the rate of methane formation by sulfur was observed at higher pressures. Sulfur appeared to have a small effect on the methane formation but a greater inhibition effect on the production of C_{2+} hydrocarbons and oxygenates. Energy-dispersive spectroscopic studies of the S-Ru/SiO_2 showed that the bulk ratio of S to Ru was 0.12. Hydrogen TPD studies showed that sulfidation led to complete loss of hydrogen chemisorption capacity [44]. Studies on S-Ru(III) indicated a sulfur coverage of 0.33 could result in the complete suppression of hydrogen chemisorption [45]. The presence of sulfur on Ru has also been found to poison the methanation [46]. The lack of poisoning effect of sulfur on the methanation in this study could be due to the low sulfur coverage of the S-Ru/SiO_2.

The infrared spectra corresponding to the rate data shown in Table 1 are presented in Figure 2(B). The spectrum 2(B)-a is the background spectrum recorded for the used Ru/SiO_2 that had been exposed to $CO/H_2/C_2H_4$ reactant mixture and then followed by reduction in flowing hydrogen for 10 hr and sulfidation for 1 hr at 513 K. A certain amount of hydrocarbon species on the catalyst was observed by infrared spectroscopy. It is important to note that those hydrocarbon bands in the IR background have no effect on the performance of the sulfided Ru. Sulfidation of the used Ru/SiO_2 catalysts and the fresh Ru/SiO_2 resulted in the same activity and selectivity. The major spectral feature for CO hydrogenation on the sulfided catalyst is the linear CO at 2009-2013 cm^{-1}. The hydrocarbon bands at 2860-2960 cm^{-1} exhibiting the same intensity at various conditions appear to be spectator species.

Comparison of the IR spectra for Ru/SiO_2 and S-Ru/SiO_2 (see Figure 2) shows the major effect of adsorbed sulfur on the adsorbed CO during CO hydrogenation is to decrease its intensity and wavenumber. Flowing hydrogen over the catalysts at 513 K (see spectra 2(A)-e and 2(B)-e) caused a downward shift of the linearly adsorbed CO by 59 cm^{-1} on Ru/SiO_2 and by 10 cm^{-1} on S-Ru/SiO_2 and a more decrease in the CO intensity for Ru/SiO_2 than for S-Ru/SiO_2. Such a less shift and decrease of the adsorbed CO on the S-Ru/SiO_2 catalyst may be due to the fact that adsorbed sulfur inhibits hydrogen chemisorption [25-27,45]. As a result, less adsorbed hydrogen was available to react with CO and to remove CO from the surface of sulfided Ru/SiO_2 catalyst. The observed inhibition effects of sulfur on CO adsorption and CO hydrogenation in this study are, in some respect, consistent with those reported in the literature [25-27,46]. Adsorbed sulfur has been found to block the bridge-CO sites, weaken the metal-CO bond, and inhibit CO hydrogenation.

Ethylene Hydroformylation on Ru/SiO_2

Table 2 shows the influence of reaction pressure on the rate of product formation for $CO/H_2/C_2H_4$ reaction (hydroformylation) over Ru/SiO_2. The formation of CH_4, C_{3+} hydrocarbons, C_2 oxygenates, ethane, and propionaldehyde indicates that CO hydrogenation, ethylene hydrogenation, and ethylene hydroformylation take place at the same time. Higher rates of C_4 hydrocarbon formation than C_3 hydrocarbon formation suggest that dimerization of ethylene occurred to a significant extent. Although the rate of formation of all the products increased with increasing pressure, there was significant variation in the pressure effect on the rate of product formation. As reaction pressure increased from 0.10 to 3.0 MPa, the rate of methane formation increased by a factor of 2; the rate of ethane formation increased by a factor of 7.7; and the rate of propionaldehyde formation increased by a factor of 65. The extent of pressure effect on the rate of product formation decreased in the order: $C_2H_5CHO > C_2H_4 > CH_4$, suggesting that CO insertion is highly favorable at high pressures.

Figure 3 shows the infrared spectra taken under steady-state $CO/H_2/C_2H_4$ reaction conditions corresponding to the reaction results listed in Table 2. At 0.10 MPa, the linear CO was observed at 1983 cm^{-1}. The lower wavenumber of the linear CO under the hydroformylation condition compared with that of linear CO under the CO hydrogenation condition (see Figure 2) is primarily due to the dilution of adsorbed CO by the adsorbed ethylene and hydrogen species [37]. Increasing in the total pressure resulted in increases in the intensity of the linear CO and an upward shift of the linear CO wavenumber. No obvious relation between CO insertion selectivity and the wavenumber of adsorbed CO was observed. The gaseous ethylene was observed at 1921, 1888, 1861 cm^{-1}, 1400-1500 cm^{-1} and in the vicinity of 3100 cm^{-1}. One band at 1738 cm^{-1} with a shoulder at 1681 cm^{-1} began to emerge as reaction pressure increased. The former corresponds to adsorbed propionaldehyde, which was identified by the injection of the propionaldehyde to the Ru/SiO_2 catalyst. The intensity of this band paralleled the rate of formation of the propionaldehyde. The shoulder at 1681 cm^{-1} may be assigned to be an acyl species [47,48]. The band has also been detected on Rh derived catalysts which exhibit high selectivity for C_2 oxygenate formation [9,47,48].

Admission of flowing H_2 to the reactor at 513 K removed the gas phase ethylene and ethane bands and gradually attenuated the intensity of the adsorbed CO band and propionaldehyde band. However, the hydrocarbon bands that resemble those observed in CO hydrogenation study did not readily desorb under the this reduction condition. This observation further supports the proposition that these species are situated on the support rather than on the metal surface.

Ethylene Hydroformylation on Sulfided Ru/SiO$_2$

Table 3 shows the effect of reaction pressure on the rate of product formation for $CO/H_2/C_2H_4$ on S-Ru/SiO$_2$. Ethane was the major product; methane and propionaldehyde were the minor products. A trace amount of C_{3+} hydrocarbons and acetaldehyde were also observed. Increasing reaction pressure led to increases in the rates of formation of all products. Increases in the ratio of C_2H_5CHO to C_2H_6 with increasing reaction pressures indicates that the formation of propionaldehyde is favorable at high pressures. Comparison of ratios of the formation rates of propionaldehyde and ethane before sulfidation to those after sulfidation shows that sulfur had a greater inhibition effect on the rate of the propionaldehyde formation than that of the ethane formation.

The influence of reaction pressure on infrared spectra for the ethylene hydroformylation on S-Ru/SiO$_2$ are shown in Figure 3(B). The infrared bands for S-Ru/SiO$_2$ were similar to those observed for the Ru/SiO$_2$ catalyst. The hydrocarbon bands on the Ru/SiO$_2$ and the S-Ru/SiO$_2$ were identical in wavenumber and intensity. The intensity of the linear CO band was smaller on the sulfided catalyst. A relatively strong IR intensity of adsorbed propionaldehyde was also observed on the sulfided catalyst. Admission of flowing H_2 to the reactor led to a gradual decrease in the intensity of linear CO and a very slow reduction in the intensity of propionaldehyde. As compared to the Ru/SiO_2 catalyst, the propionaldehyde appeared to be strongly bonded on the $S-Ru/SiO_2$. As a result, the desorption of the adsorbed propionaldehyde from $S-Ru/SiO_2$ was greatly inhibited.

A careful comparison of the infrared spectra and rate data for the Ru/SiO_2 and the $S-Ru/SiO_2$ shows that adsorbed sulfur (i) slightly decreased the intensity and wavenumber of the linear CO band; (ii) inhibited desorption/reaction of linear CO in flowing hydrogen at 513 K; (iii) caused an emergence of the shoulder band of an unknown species at 1880 -1890 cm^{-1}; (iv) increased the intensity of the propionaldehyde band; (v) suppressed the formation of CO hydrogenation products such as C_{3+} hydrocarbon and acetaldehyde; (vi) exhibited a more severe inhibition effect on the formation of propionaldehyde than the formation of ethane. The most interesting part of the above observations is the increase in the intensity of the propionaldehyde band and the decrease in the rate of formation of propionaldehyde with the addition of sulfur. The result suggests that sulfur appears to promote CO insertion but inhibit the desorption of propionaldehyde; therefore making desorption of propionaldehyde the rate-limiting step on the $S-Ru/SiO_2$.

Dynamic Behavior of Adsorbed Propionaldehyde

In order to determine the effect of adsorbed sulfur on the dynamic behavior of adsorbed propionaldehyde, a transient FTIR study was conducted by the following procedure. Following the steady-state hydroformylation at 1.0 MPa and 513 K, the feed was switched from a steady-state flow of $CO/H_2/C_2H_4$ to a steady-state flow of CO/H_2. Figure 4-A shows a series of infrared spectra taken during the switch on the Ru/SiO_2. As CO/H_2 displaced $CO/H_2/C_2H_4$, the intensity of gaseous ethylene, adsorbed propionaldehyde, and acyl bands gradually decreased while the intensity and wavenumber of adsorbed CO increased. The displacement process for the gaseous ethylene is slow due to the condition of high pressure and the low flow rate even though the volume of the IR cell is less than 120 mm^3.

Infrared spectra for the $S-Ru/SiO_2$ similar to those for the Ru/SiO_2 during the transient condition were also obtained as shown in Figure 4-B. The major difference in the spectra of adsorbed species on the Ru/SiO_2 and the $S-Ru/SiO_2$ during the switch is that the intensity of adsorbed propionaldehyde on the Ru/SiO_2 decreased much more rapidly than that of adsorbed propionaldehyde on the $S-Ru/SiO_2$. These results indicate that adsorbed propionaldehyde is more strongly bonded on the $S-Ru/SiO_2$ than on the Ru/SiO_2. As a result, the desorption of adsorbed propionaldehyde from $S-Ru/SiO_2$ is strongly inhibited, thus leading to the inhibition of the formation of gaseous propionaldehyde product from the hydroformylation.

Temperature Programmed Reaction (TPR) with H_2

The reactivity of all the adsorbed species toward hydrogen was examined by temperature-programmed reaction with hydrogen. Prior to the TPR study, the $CO/H_2/C_2H_4$ reaction was carried out at 513 K and 1.0 MPa for 1 hr to reach the steady state and then the reactor pressure and temperature were decreased to 0.10 MPa and 298 K. Hydrogen was then passed through the reactor at a flow rate of 10 cm^3/min; the reactor temperature was increased at a rate of 5 K/min.

Figure 5 shows a series of IR spectra taken during the TPR study. The initial spectrum at 298 K included the adsorbed linear-CO, hydrocarbons, and propionaldehyde bands which are similar to those under reaction conditions. Band at 1672 cm^{-1} that has been assigned to an acyl group were also observed.

In order to discriminate the change of intensity for various bands with respect to temperature, a relative change in intensity of the adsorbed bands was plotted as a function of temperature. The area of the integrated absorbance is related to the concentration of the adsorbed species if the extinction coefficient is assumed to be independent of the surface coverage of the adsorbed species [42,49]. As shown in Figure 6, the intensity of linear CO band on the Ru/SiO_2 showed a small decline from room temperature to 473 K and then followed by a rapid decrease as temperature increased above 473 K, while the intensity of the propionaldehyde band exhibited a rapid decrease to 423 K and then slowly depleted. In contrast, the intensity of the linear CO on the S-Ru/SiO_2 decreased linearly with increasing temperature, while the intensity of the propionaldehyde band showed an initial decline and then level off. These observations provide evidence that linear CO is more strongly bonded on the Ru/SiO_2 than the S-Ru/SiO_2 at 303-480 K under flowing H_2 while the adsorbed propionaldehyde showed the reverse trend. By contrast, the more rapid diminishing of the liner CO on the

Ru/SiO_2 than on the $S\text{-}Ru/SiO_2$ catalyst at 513 K under flowing H_2 (see Figure 2) may be explained by the easier of hydrogenation of adsorbed CO on the Ru/SiO_2 than on the $S\text{-}Ru/SiO_2$.

Conclusions

Although olefin hydroformylation has been well recognized as homogeneously catalyzed reaction, the presence of linearly adsorbed CO and adsorbed propionaldehyde and the absence of Ru carbonyl species on the surface of the Ru catalysts suggest that the ethylene hydroformylation can also occur on the surface of the Ru/SiO_2 catalyst. Increases in reaction pressure enhance the selectivity to propionaldehyde on both Ru/SiO_2 and $S\text{-}Ru/SiO_2$ catalysts. The effect of sulfur on the reaction on Ru/SiO_2 can be summarized as follows:

(i) Sulfur blocked bridge-CO sites and inhibited the desorption of adsorbed propionaldehyde.

(ii) Sulfur poisoned the formation of higher hydrocarbons and oxygenates in CO hydrogenation.

(iii) Sulfur poisoned ethylene hydrogenation and hydroformylation.

This is in contrast to our previous observations that adsorbed sulfur is ineffective in poisoning ethylene hydroformylation on the Rh/SiO_2 catalyst [29,30]; adsorbed sulfur promotes hydroformylation on the Ni/SiO_2 [31,32]. While sulfur poisons indiscriminately Group VIII metals for CO hydrogenation, it exhibits different poison and promotion effects on the Ru, Rh, and Ni metals for hydroformylation. The poisoning effect of sulfur on hydroformylation on the Ru/SiO_2 has been ascribed to an inhibition of desorption of the adsorbed propionaldehyde brought about by adsorbed sulfur.

Acknowledgment

Funding for this research was provided by the U.S. Department of Energy under Grant DE-FG-22-87PC79923.

References

1 B. Cornils, in J. Falbe (ed.), *New Syntheses with Carbon Monoxide*, Springer-Verlag, New York, 1980, P. 1.

2 E. E. Euklund and G. A. Mills, *Chemtech*, (1989) 549.

3 R. A. Sheldon, *Chemicals from Synthesis Gas*, D. Riedel., Co., Boston, 1983.

4 R. B. Anderson, *Fischer Tropsch and Related Syntheses*, Acadamic Press, New York, 1983.

5 G. W. Parshall, *Homogeneous Catalysis - The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, Wiley, New York, 1980.

6 G. Henrici-Olive and S. Olive, *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*, Springer-Verlag, New York, 1984.

7 P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (eds.), *Organic Syntheses via Metal Carbonyls*, Vol. 2, Wiley, New York, 1976, P. 43.

8 C. S. Kellner and A. T. Bell, *J. Catal.*, 71 (1981) 288.

9 M. Ichikawa, *Chemtech*, (1982) 674.

10 P. R. Watson and G. A. Somorjai, *J. Catal.*, 74 (1982) 282.

11 V. Ponec, in G. C. Bond and G. Webb (eds.), *Catalysis*, The Royal Society of Chemistry, London, 5, 1982, P. 48.

12 W. M. H. Sachtler and M. Ichikawa, *J. Phys. Chem.*, 90 (1986) 4752.

13 S. C. Chuang, Y. H. Tian, J. G. Goodwin Jr. and I. Wender, *J. Catal.*, 96 (1985) 396.

14 P. Biloen and W. M. H. Sachtler, *Adv. Catal.*, 30 (1981) 165.

15 A. T. Bell, *Catal. Rev. Sci. Eng.*, 23 (1981) 203.

16 F. G. A. Van der Berg, Ph.D. Thesis. University of Leiden. The Netherlands, 1984.

17 D. S. Jordan and A. T. Bell, *J. Phys. Chem.*, 90 (1986) 4797.

18 D. S. Jordan and A. T. Bell, *J. Catal.*, 108 (1987) 63.

19 A. Kiennemann, C. Diagne, J. P. Hindermannn, P. Chaumentte and P. Courty, *Appl. Catal.*, 53 (1989) 197.

20 M. A. Vannice, *J. Catal.*, 37 (1975) 449, 462.

21 R. Oukaci, A. Sayari and J. G. Goodwin, Jr., *J. Catal.*, 102 (1985) 126.

22 J. G. Ekerdt and A. T. Bell, *J. Catal.*, 58 (1979) 170.

23 H. Yamasaki, Y. Kobori, S. Naito, T. Onishi and K. Tamaru, *Chem. Soc. Faraday Trans* 1 77 (1981) 2913.

24 R. A. Dalla Betta and M. Shelef, *J. Catal.*, 48 (1977) 111.

25 C. H. Bartholomew, P. K. Agrawal and J. R. Katzer, in D.D. Eley, H. Pines and P. B. Weisz (eds.), *Advanced in Catalysis*, vol. 31, Acadamic Press, New York, 1982, P. 315.

26 D. W. Goodman, in B. L. Shapiro (ed.), *Heterogeneous Catalysis*, Texas A&M Univ. Press, College Station, 1984, P. 231.

27 J. Oudar, in J. Oudar and H. Wise (eds.), *Deactivation and Poisoning of Catalysts*, Marcel Dekker, Inc., New York and Basel, 1985, P. 51.

28 Y. Konishi, M. Ichikawa and W. M. H. Sachtler, *J. Phys. Chem.*, 91 (1987) 6286.

29 S. C. Chuang and C. Sze, in J. W. Ward (ed.), *Catalysis 1987*, P. 125. Elsevier, Amsterdam, 1988.

30 S. C. Chuang and S. I. Pien, *J. Mol. Catal.*, 55 (1989) 12.

31 S. C. Chuang and S. I. Pien, Catal. Lett., 6 (1990) 389.

32 S. C. Chuang, S. I. Pien and C. Sze, *J. Catal.*, 126 (1990) 187.

33 M. M. McClory and R. D. Gonzalez, *J. Catal.*, 89 (1984) 392.

34 D. L. King, *J. Catal.*, 61 (1980) 77.

35 G. H. Yokomizo, C. Louis and A. T. Bell, *J. Catal.*, 120 (1989) 15.

36 P. Winslow and A. T. Bell, *J. Catal.*, 86 (1984) 158.

37 F. Stoop, F. J. C. M. Toolenaar and V. Ponec, *J. Catal.*, 73 (1982) 50.

38 A. Crossley and D. A. King, *Surf. Sci.*, 68 (1977) 528.

39 J. A. Schwarz and S. R. Kelemen, *Surf. Sci.*, 87 (1979) 510.

40 H. P. Bonzel and R. Ku, *J. Chem. Phys.*, 58 (1973) 4617.

41 L. H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, New York, 1966.

42 C. S. Kellner and A. T. Bell, *J. Catal.*, 71 (1981) 296.

43 H. M. Miura, M. L. Mclaughlin and R. D. Gonzalez, *J. Catal.*, 79 (1983) 227.

44 C. Sze, M.S. Thesis, University of Akron, 1989.

45 G. Q. Xu and J. A. Hrbek, Catal. Lett., 2 (1989) 35.

46 P. K. Agrawaal, W. D. Fitzharris and J. R. Kaatzer, in B. Delmon and G. F. Froment (eds.), *Catalyst Deactivation*, Elsevier Scientific, Amsterdam, 1980, P. 179.

47 T. Fukushima, H. Arakawa and M. Ichikawa, *J. Chem. Soc. Chem. Commun.*, (1985) 729.

48 R. P. Underwood and A. T. Bell, *J. Catal.*, 111 (1988) 325.

49 A. T. Bell, in J. T. Yates and T. E. Maney (eds.), *Vibrational Spectroscopy of Molecules on Surfaces*, Plenum Press, New york, 1987, P. 105.

Table 1
Rate of Formation under CO Hydrogenation over Ru/SiO$_2$ and Sulfided Ru/SiO$_2$

	Pressure (MPa)			
	0.10	1.0	2.0	3.0
Ru/SiO$_2$ Catalyst				
10^{-3} × TOF (sec^{-1})	0.13	0.76	0.73	1.2
Product Formation (gmol/kg-hr)				
CH_4	0.011	0.041	0.037	0.041
C_2H_4	0.0	0.005	0.004	0.004
C_2H_6	0.001	0.0007	0.0006	0.0006
C_3 HC [a]	0.0005	0.006	0.005	0.005
CH_3CHO	0.0	0.005	0.008	0.031
CH_3CHO/CH_4 [b]	0.0	0.12	0.22	0.75
CH_3CHO/C_{2+}HC	0.0	0.42	0.83	3.2
S-Ru/SiO$_2$ Catalyst [c]				
Product Formation (gmol/kg-hr)				
CH_4	0.01	0.023	-	0.028

Temperature: 513 K
CO:H$_2$ = 1:1

a: HC: Hydrocarbon
b: CH_3CHO/CH_4 is the ratio of the CH_3CHO formation rate to the CH_4 formation rate.
c: The ratio of S to Ru for S-Ru/SiO$_2$ is determined to be 0.2 by EDS [32].

Table 2
Rate of Formation under $CO/H_2/C_2H_4$ Reaction over Ru/SiO_4

Pressure (MPa)	0.10	1.0	2.0	3.0
Product Formation (gmol/kg-hr)				
CH_4	0.023	0.037	0.042	0.046
C_2H_6	0.214	1.23	1.19	1.65
C_3HC	0.004	0.013	0.016	0.02
C_4HC	0.01	0.034	0.034	0.04
CH_3CHO	0.0	0.0	0.006	0.006
C_2H_5CHO	0.01	0.29	0.46	0.65
C_2H_5CHO/C_2H_6	0.05	0.24	0.38	0.39

Temperature: 513 K
$CO:H_2:C_2H_4$ = 1:1:1

Table 3
Rate of Formation under $CO/H_2/C_2H_4$ Reaction over Sulfided Ru/SiO_2

Pressure (MPa)	0.10	1.0	2.0	3.0
Product Formation (gmol/kg-hr)				
CH_4	0.02	0.037	0.038	0.040
C_2H_6	0.062	0.33	0.39	0.42
C_3HC	0.0006	0.002	0.003	0.005
CH_3CHO	0.0	0.008	0.005	0.009
C_4HC	0.0	0.005	0.018	0.021
C_2H_5CHO	0.0	0.04	0.08	0.11
C_2H_5CHO/C_2H_6	0.0	0.12	0.2	0.26
$C_2H_5CHO(S)/C_2H_5CHO$ [a]	0.0	0.14	0.17	0.17
$C_2H_6(S)/C_2H_6$	0.29	0.27	0.33	0.25

Temperature: 315 K
$CO:H_2:C_2H_4 = 1:1:1$

[a] Ratio of the rate of the product formed on the sulfided Ru/SiO_2 to the rate of the product formed on the Ru/SiO_2

LIST OF FIGURES

Figure 1. Infrared spectra of CO adsorption at 513 K : (a) on Ru/SiO_2 at 1.0 MPa for 20 min, (b) at 0.10 MPa for 20 min, (c) after reduction in flowing H_2 at a rate of 5 cm^3/min at 0.10 MPa for 20 min, (d) on $S-Ru/SiO_2$ at 1.0 MPa for 20 min, (e) at 0.10 MPa for 20 min.

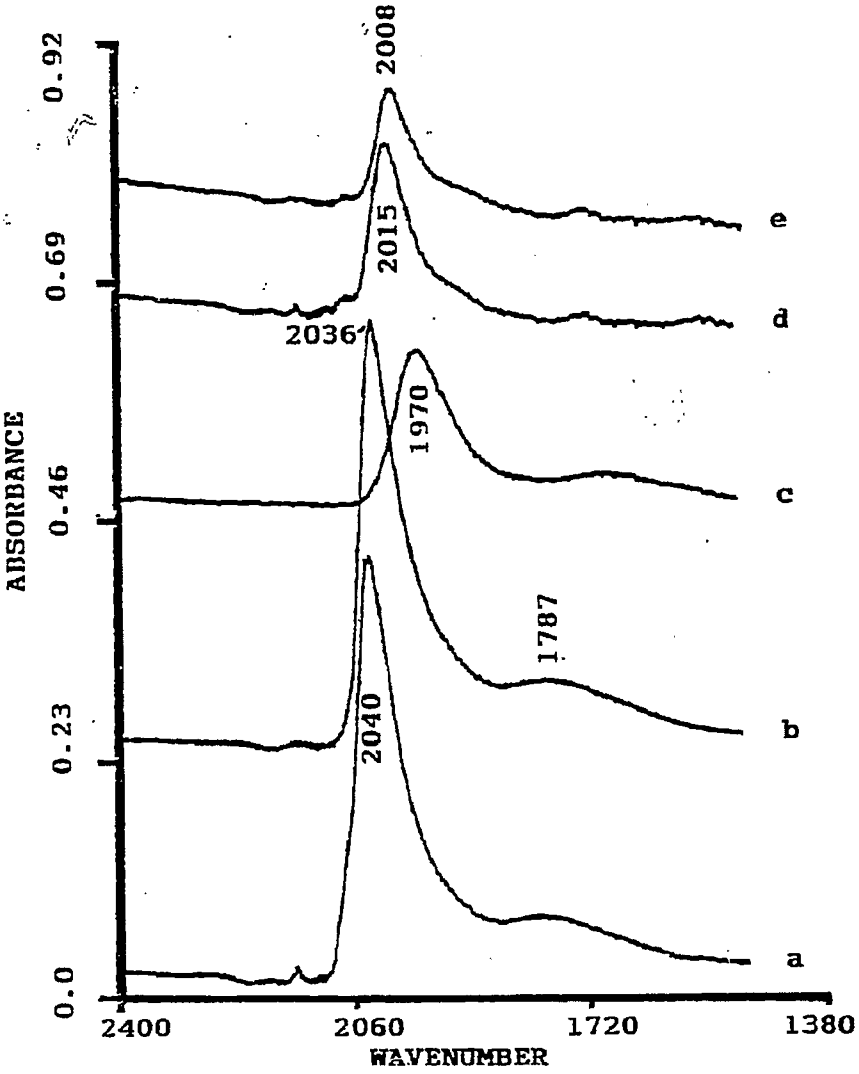
Figure 2. Infrared spectra of CO/H_2 reaction at 513 K : (A)-(a) on Ru/SiO_2 at 0.10 MPa, (b) at 1.0 MPa, (c) at 2.0 MPa, (d) at 3.0 MPa, (e) reduction in flowing H_2 at a rate of 5 cm^3/min at 0.10 MPa for 20 min; (B)-(a) background : reduction in flowing H_2 5 cm^3/min for 10 hr after the $CO/H_2/C_2H_4$ reaction, (b) CO/H_2 reaction on $S-Ru/SiO_2$ at 0.10 MPa, (c) at 1.0 MPa, (d) at 3.0 MPa, (e) reduction in flowing H_2 at a rate of 5 cm^3/min at 0.10 MPa of 20 min.

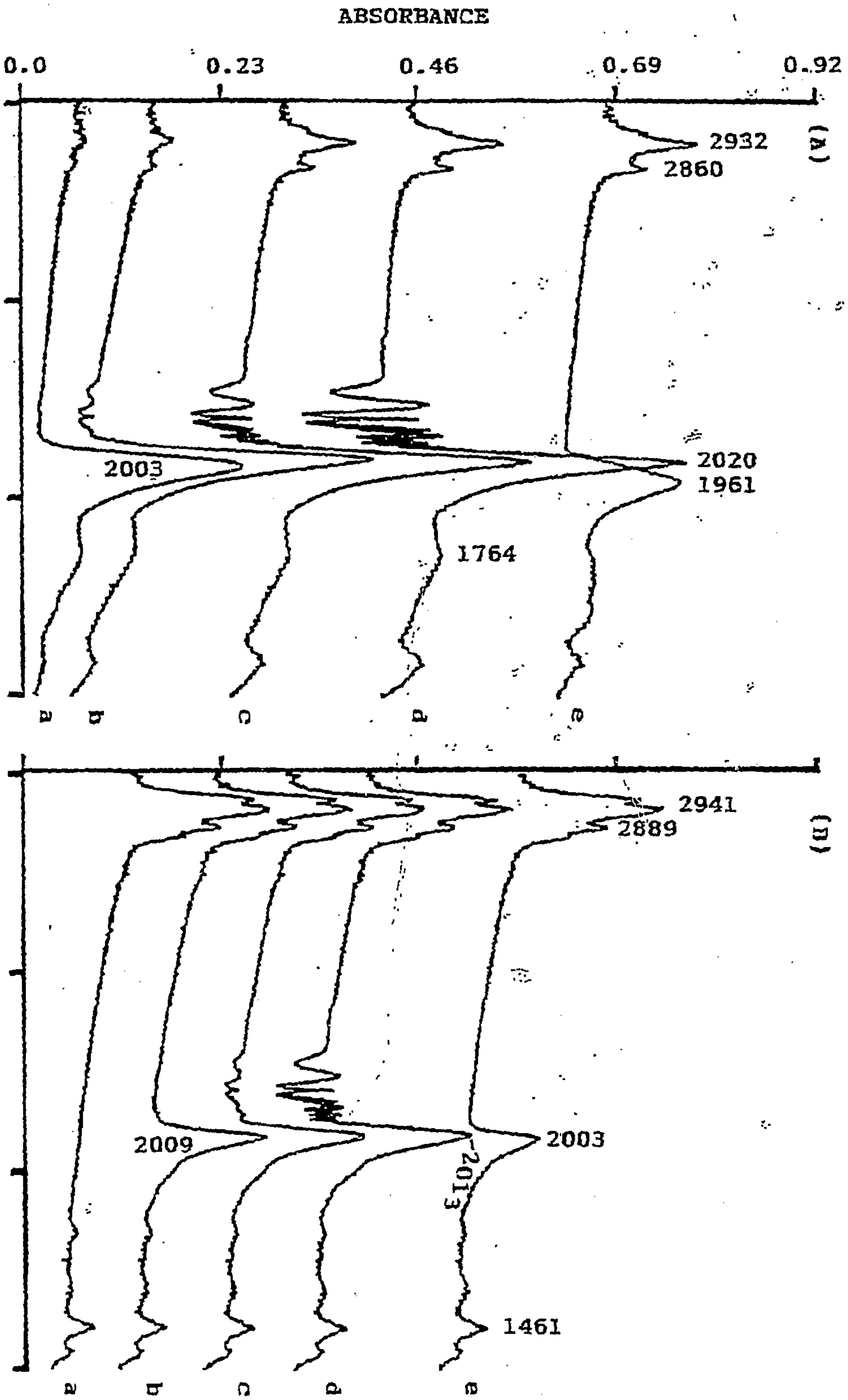
Figure 3. Infrared spectra of $CO/H_2/C_2H_4$ reaction at 513 K on (A) Ru/SiO_2 and (B) sulfided Ru/SiO_2: (a) at 0.10 MPa, (b) at 1.0 MPa, (c) at 2.0 MPa, (d) at 3.0 MPa, (e) reduction in flowing H_2 at a rate of 5 cm^3/min at 0.10 MPa for 20 min, (f) for 10 hr.

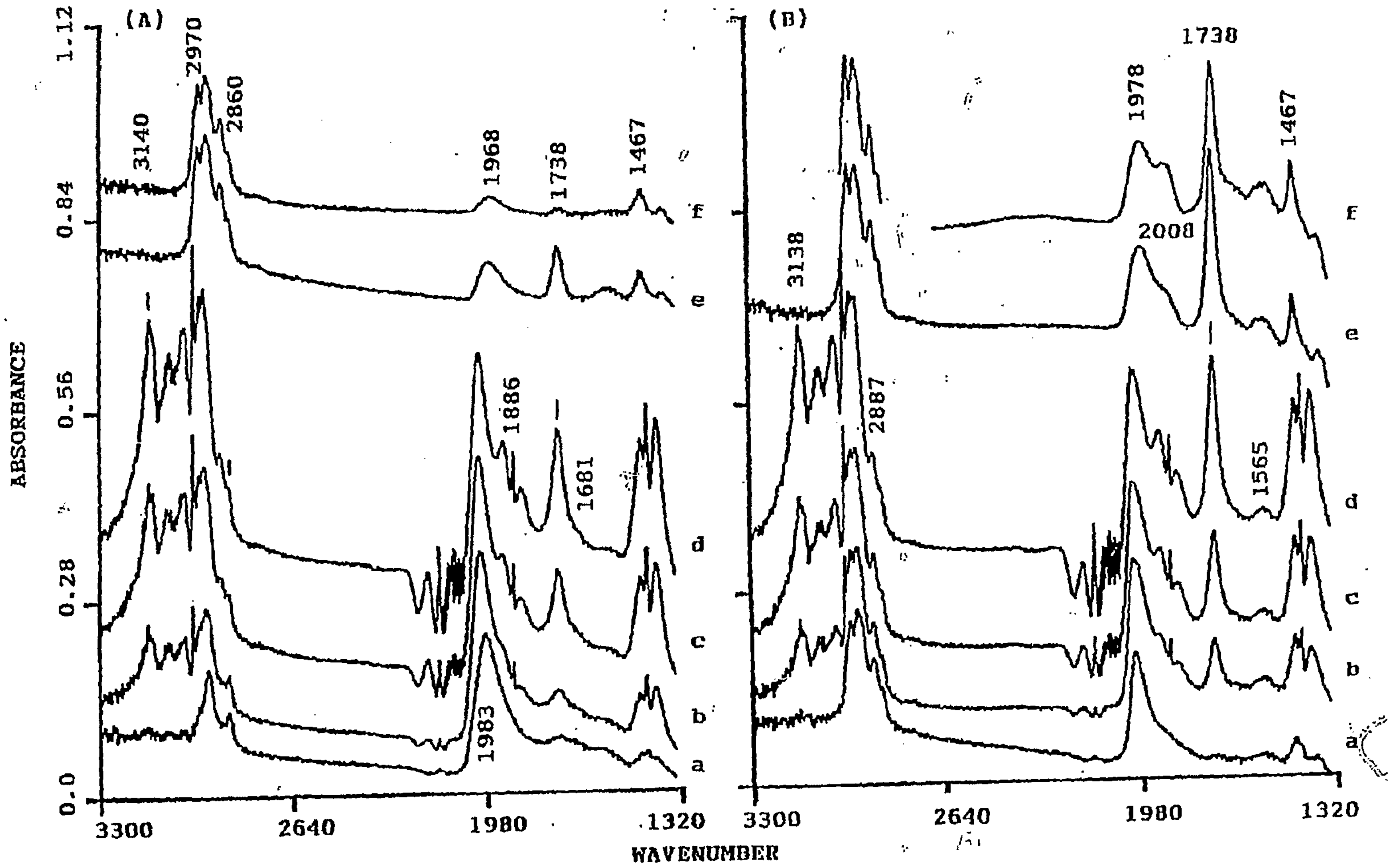
Figure 4. Transient observation by switching $CO/H_2/C_2H_4$ flow to CO/H_2 flow at 0.10 Mpa, 513 K on (A) Ru/SiO_2 and (B) sulfided Ru/SiO_2: (a) steady state of $CO/H_2/C_2H_4$ reaction, (b) right after cut off C_2H_4 flow, (c) for 2 min, (d) for 4 min, (e) for 6 min, (f) for 15 min, (g) for 50 min.

Figure 5. Temperature programmed-desorption of adsorbed species with hydrogen (10 cc/min) on (A) Ru/SiO_2 and (B) sulfided Ru/SiO_2: (a) at 298 K, (b) at 323 K, (c) at 343 K, (d) at 373 K, (e) at 425 K, (f) at 473 K, (g) at 493 K, (h) at 513 K, (i) at 513 K for 10 hr.

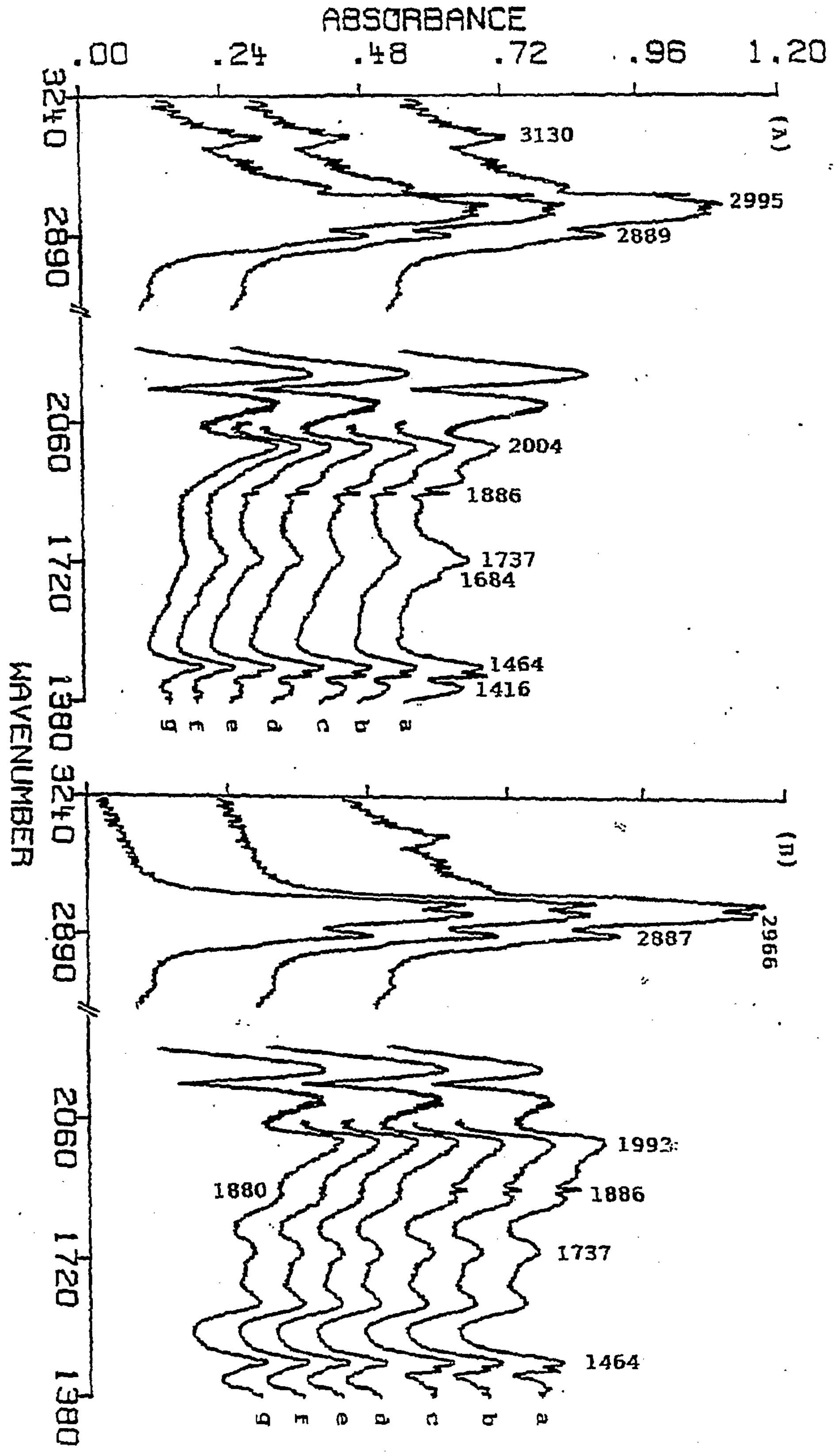
Figure 6. Relative intensity versus temperature for the TPR of the adsorbed CO and propionaldehyde on Ru/SiO_2 and sulfided Ru/SiO_2. Relative intensity is the ratio of the intensity of adsorbed species during TPR to the initial intensity of adsorbed species. (Δ) linear CO on Ru/SiO_2, (□) propionaldehyde on Ru/SiO_2, (Δ) linear CO on $S-Ru/SiO_2$, (□) propionaldehyde on $S-Ru/SiO_2$.

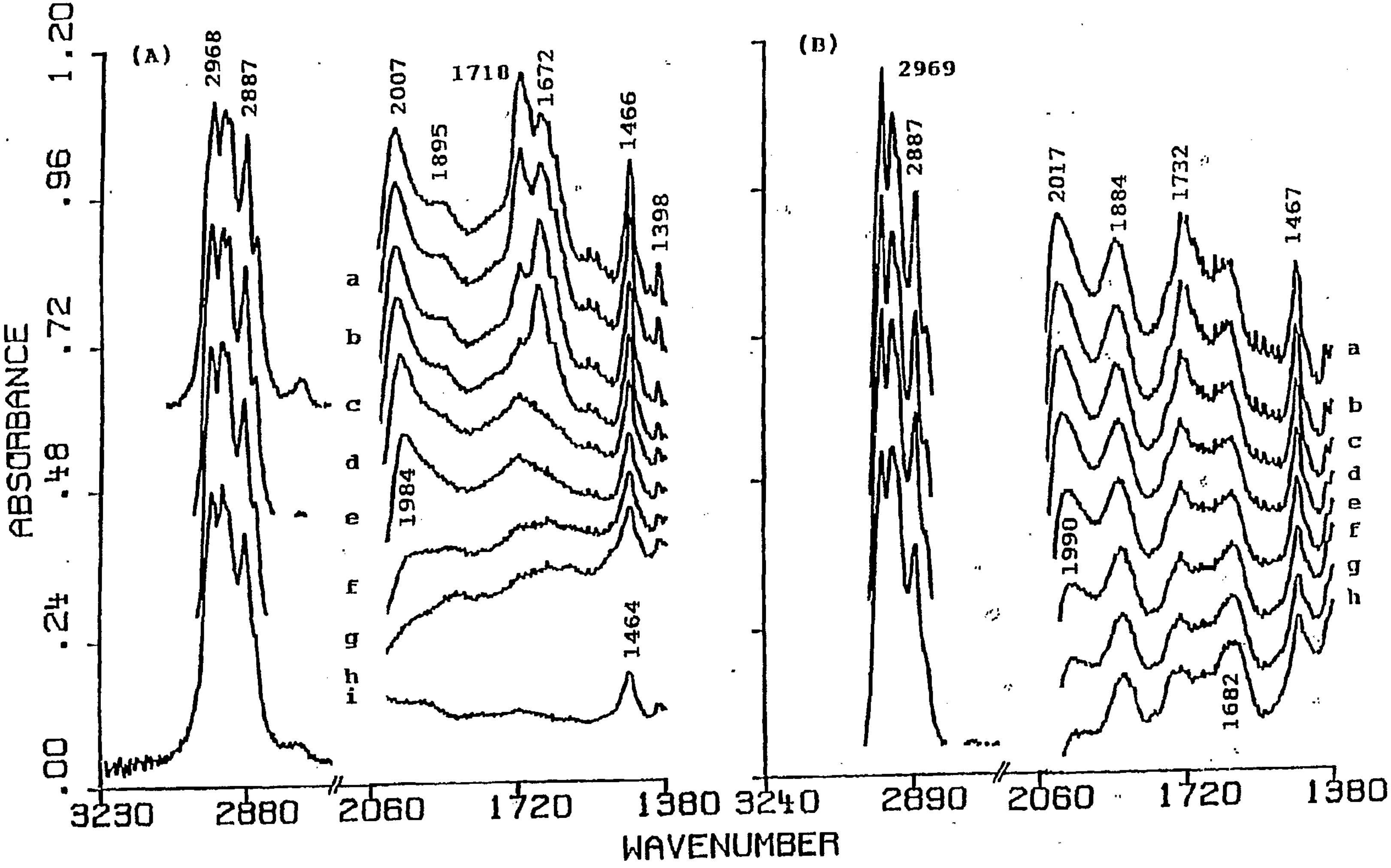

ABSORBANCE
0.92
0.69
0.46
0.23
0.0
2400
2060
1720
1380
WAVENUMBER
2008
2015
2036
1970
1787
2040
e
d
c
b
a

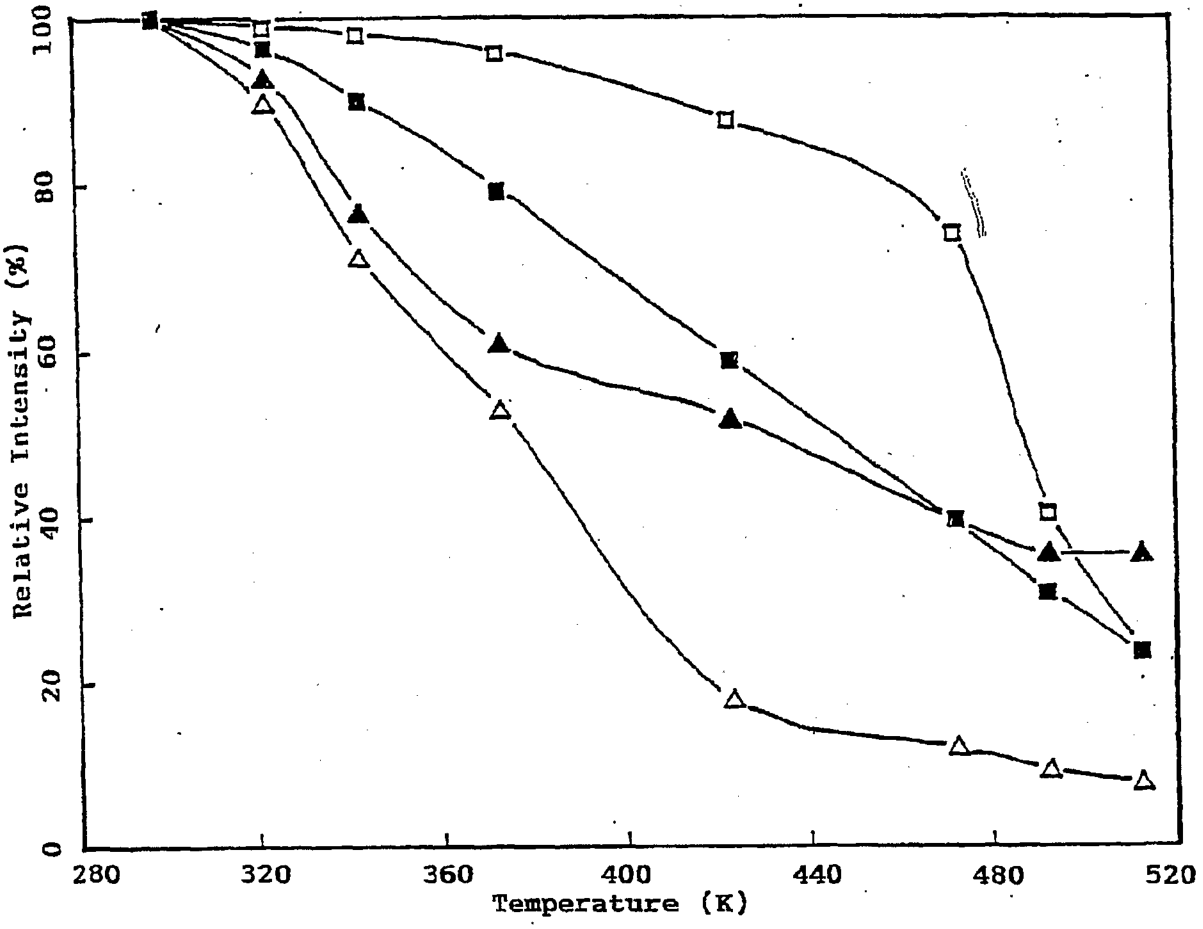

ABSORBANCE
0.0
0.23
0.46
0.69
0.92
(A)
2932
2860
2020
1961
2003
1764
a
b
c
d
e
(B)
2941
2889
2003
2013
2009
1461
a
b
c
d
e



(A)
(B)
ABSORBANCE
0.0
0.28
0.56
0.84
1.12
WAVENUMBER
3300
2640
1980
1320
3140
2970
2860
1968
1738
1467
1886
1681
1983
3138
2887
1978
2008
1565
a
b
c
d
e
f


ABSORBANCE
.00
.24
.48
.72
.96
1.20
(A)
3130
2995
2889
2004
1886
1737
1684
1464
1416
a
b
c
d
e
f
g
(B)
2966
2887
1993
1886
1880
1737
1464
a
b
c
d
e
f
g
3240
2890
2060
1720
1380
WAVENUMBER


(A)
(B)
ABSORBANCE
.00
.24
.48
.72
.96
1.20
3230
2880
2060
1720
1380
3240
2890
2060
1720
1380
WAVENUMBER
2968
2887
2007
1895
1718
1672
1466
1398
1984
1464
a
b
c
d
e
f
g
h
i
2969
2887
2017
1884
1732
1467
1990
1682
a
b
c
d
e
f
g
h


Relative Intensity (%)
0
20
40
60
80
100
280
320
360
400
440
480
520
Temperature (K)

Reproduced by NTIS

National Technical Information Service
Springfield, VA 22161

This report was printed specifically for your order from nearly 3 million titles available in our collection.

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

About NTIS

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at **http://www.ntis.gov**.

NTIS

Ensuring Permanent, Easy Access to U.S. Government Information Assets

SATISFACTION GUARANTEED

NTIS strives to provide quality products, reliable service, and fast delivery. Please contact us for a replacement within 30 days if the item you receive is defective or if we have made an error in filling your order.

▶E-mail: info@ntis.gov
▶Phone: 1-888-584-8332 or (703)605-6050

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000