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INFRARED STUDY OF ISOTOPIC EXCHANGE DURING METHANATION OVER SUPPORTED RHODIUM CATALYSTS; AN INVERSE SPILLOVER EFFECT

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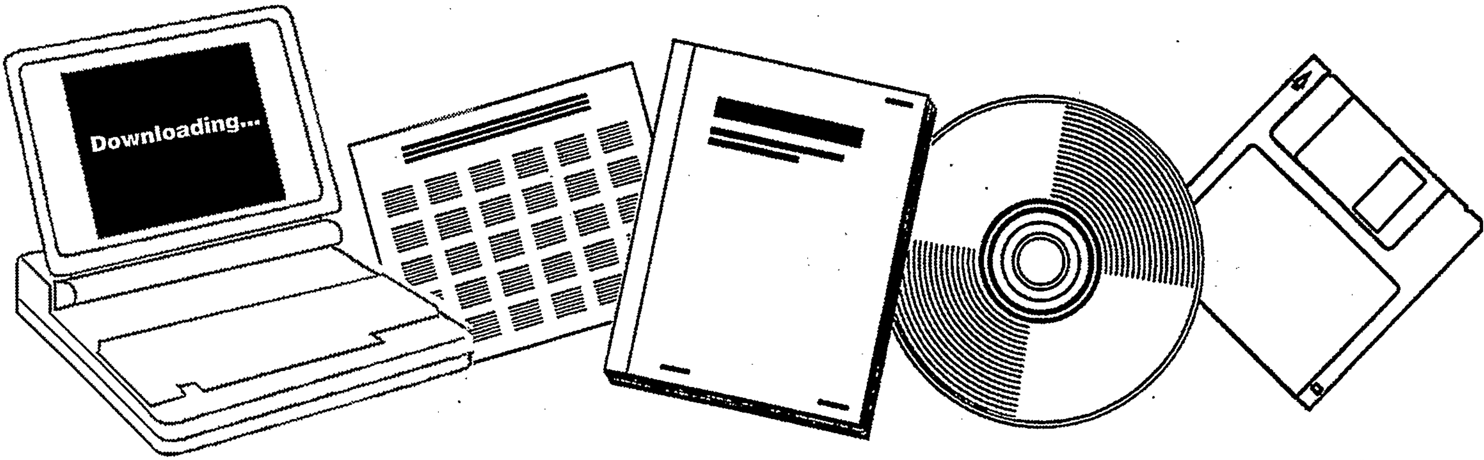

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An Infrared Study of Isotopic Exchange During Methanation Over Supported Rhodium Catalysts; An Inverse Spillover Effect

by

M. A. Henderson and S.D. Worley
Department of Chemistry
Auburn University
Auburn University, AL 36849

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Department of Chemistry (Dr. S. D. Worley)
Auburn University
Auburn University, AL 36849

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Infrared spectroscopy has been employed to study the reduction of carbon dioxide on supported catalyst films. The investigation included isotopic labeling using D_2 as the reduction gas. Isotopic exchange was observed for both CO_2/D_2 and CH_4/D_2 mixtures. The mechanisms of this isotopic exchange involves migration of hydrogen from the support to the Rh sites, an "inverse spillover effect". A key intermediate in the dissociation of CO_2 on the supported Rh films was a carbonyl hydride species.

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AN INFRARED STUDY OF ISOTOPIC EXCHANGE DURING METHANATION OVER SUPPORTED RHODIUM CATALYSTS; AN INVERSE SPILLOVER EFFECT

ABSTRACT

(U) INFRARED SPECTROSCOPY HAS BEEN EMPLOYED TO STUDY THE REDUCTION OF CARBON DIOXIDE ON SUPPORTED CATALYST FILMS. THE INVESTIGATION INCLUDED ISOTOPIC LABELING USING DEUTERIUM AS THE REDUCTION GAS. ISOTOPIC EXCHANGE WAS OBSERVED FOR BOTH CARBON DIOXIDE/D2 AND METHANE/DEUTERIUM MIXTURES. THE MECHANISM OF THIS ISOTOPIC EXCHANGE INVOLVES MIGRATION OF HYDROGEN FROM THE SUPPORT TO THE RHODIUM SITES, AN INVERSE SPILLOVER EFFECT. A KEY INTERMEDIATE IN THE DISSOCIATION OF CARBON DIOXIDE ON THE SUPPORTED RH FILMS WAS A CARBONYL HYDRIDE SPECIES.

POSTING TERMS ASSIGNED

CARBON DIOXIDE
  USE ~~CARBON DIOXIDE~~) — co,

DISSOCIATION OF CARBON DIOXIDE
  USE ~~CARBON DIOXIDE~~
    DISSOCIATION

INVERSE SPILLOVER EFFECT
  USE INVERSION
    SPILLING

METHANE DEUTERIUM MIXTURES
  USE ~~DEUTERIUM~~) — co,
    ~~METHANE~~) — co,
    MIXTURES) — co,

REDUCTION GAS
  USE GASES
    REDUCTION

SUPPORTED CATALYST FILMS
  USE CATALYSTS) — co,
    FILMS) — co,

DEUTERIUM
  USE DEUTERIUM

INFRARED SPECTROSCOPY
  USE ~~INFRARED SPECTROSCOPY~~) — co,

ISOTOPIC EXCHANGE
  USE EXCHANGE
    ISOTOPES

MIGRATION OF HYDROGEN
  USE HYDROGEN) — co,
    MIGRATION) — co,

RHODIUM SITES
  USE RHODIUM) — co,
    SITES

SUPPORTED RHODIUM CATALYSTS
  USE CATALYSTS
    RHODIUM

* Isotope exchange) — co,
Reduction (Chemistry)) — co,
Chemical dissociation) — co,
Carbonyl compounds) — co,
Hydrides) — co,

PHRASES NOT FOUND DURING LEXICAL DICTIONARY MATCH PROCESS

CARBON DIOXIDE D2

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An Infrared Study Of Isotopic Exchange During Methanation Over Supported Rhodium Catalysts; An Inverse Spillover Effect

M.A. Henderson and S.D. Worley*

Department of Chemistry, Auburn University, Auburn University, AL 36849

Abstract

Infrared spectroscopy has been employed to study the reduction of carbon dioxide on supported catalyst films. The investigation included isotopic labeling using D_2 as the reduction gas. Isotopic exchange was observed for both CO_2/D_2 and CH_4/D_2 mixtures. The mechanism of this isotopic exchange involves migration of hydrogen from the support to the Rh sites, an "inverse spillover effect". A key intermediate in the dissociation of CO_2 on the supported Rh films was a carbonyl hydride species.

*Author to whom correspondence should be addressed.

Introduction

A substantial amount of effort in these laboratories has been devoted recently to the study of the hydrogenation of carbon dioxide over supported rhodium catalysts. Of considerable interest and importance in this reaction is its likely first step, the dissociation of CO_2 on the supported Rh. The dissociation of CO_2 on Rh, or lack thereof, is a controversial topic at this time, with Somorjai and coworkers favoring a high dissociation probability (10^{-1}) at 300 K,[1] while Weinberg[2] and Goodman and coworkers[3] suggest a low probability (10^{-15} and 10^{-11} at 300 K, respectively). Very recently Solymosi and Kiss[4] have concluded that the dissociation probability at 300 K is low on clean Rh (111), but enhanced by the presence of small amounts of hydrogen gas or boron impurity. Henderson and Worley have reached a similar conclusion for supported Rh catalyst films.[5] Part of the preliminary evidence concerning CO_2 dissociation on Rh/TiO_2 and Rh/Al_2O_3 obtained in these laboratories[5] was derived from isotopic labeling studies. The purpose of this letter is to present those data in more detail and to examine the hydrogen spillover phenomena for supported Rh catalyst films using infrared spectroscopy as a probe.

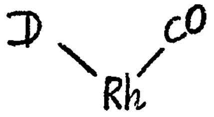
Experimental

The supported Rh catalysts used in this study were prepared as thin films on CaF_2 infrared windows by spraying slurries of $RhCl_3 \cdot 3H_2O$, support material, water, and acetone onto the windows under mild heating to remove the solvents. Complete details concerning this method of sample preparation and subsequent reduction procedures have been presented previously concerning infrared studies of CO adsorbed on supported Rh[6] and the hydrogenation of CO over supported Rh.[7] The support materials were alumina (Degussa Aluminum Oxide C, 100 m^2g^{-1}) and titania (Degussa Titanium Dioxide P25, 50 m^2g^{-1}). The gases employed (H_2, D_2, CO_2, CH_4) were of the highest purity obtainable from Matheson; the H_2, D_2 and CH_4 were passed through liquid nitrogen traps before use. The Pyrex infrared cell used in this investigation was similar to those employed in our earlier studies[6,7] except that it was designed such that it could be heated to ca. 523 K in situ in a Perkin-Elmer model 983 infrared spectrometer. The spectrometer was operated at a resolution of 4.5 cm^{-1} in the 2000 cm^{-1} region, with a Perkin-Elmer infrared data station being employed to facilitate data processing and storage. All experiments were run several times with the results obtained being entirely reproducible.

Results and Discussion

Figure 1 illustrates the effects of heating a mixture of CO_2 and D_2 over a 10% by weight Rh/TiO_2 catalyst film. The film produced by the slurry-deposition technique mentioned in the Experimental Section was heated for 12 hr at 523 K at $2x10^{-6}$ Torr to remove as much hydrogen (from adsorbed H_2O and OH moieties) from the support as possible. However, it is well-established that this treatment at only 523 K is not sufficient to remove all hydrogen from the support. Then the film was reduced at 470 K by four successive doses of D_2 at 70 Torr for time intervals of 5,5,10, and 20 min, each reduction cycle being followed by evacuation to 10^{-5} Torr. Following evacuation to $2x10^{-6}$ Torr at 298 K, a 66 torr 1:4 mixture of $CO_2:D_2$ was introduced into the cell at 298 K, and spectrum 1a and Fig. 1 was recorded. The primary infrared bands observed in 1a (with the exception of the CO_2 gas-phase band at 2349 cm^{-1}) at 2704, 2626, and 2527 cm^{-1} can be attributed to the deuterated support (OD groups); any remaining

OH on the support was not of sufficient concentration to give observable OH infrared bands near 3600 or 1600 cm^{-1}. A weak band in spectrum 1a at ca. 2020 cm^{-1} is also evident, even at 298 K. This band can be assigned to a carbonyl deuteride species formed



as a result of CO_2 dissociation. The corresponding carbonyl hydride band at low coverage for CO_2 dissociation enhanced by H_2 appears at ca. 2030 cm^{-1}.[5] The reproducible 10 cm^{-1} shift to lower frequency caused by the deuterium isotope effect is consistent with isotopic substitution two bonds removed from the CO moiety. It should be noted that Solymosi and coworkers first suggested the existence of such a carbonyl hydride species during CO_2 dissociation.[8] We believe that the isotope effect observed in this study confirms the suggestion of Solymosi and coworkers, and thus negates the arguments of Iizuka and Tanaka[9] which essentially stated that bands observed in the 2020-2040 cm^{-1} region of the infrared spectra of dissociated CO_2 over supported Rh were due to a linear CO species at low coverage rather than a carbonyl hydride.

Following heating the sample at 503 K for 1 hr, spectrum 1b was recorded. The sharp band at 2258 cm^{-1} can be assigned to a C-D stretching mode of gas-phase CD_4,[10] the expected methanation product. A band at 996 cm^{-1} could also be resolved using data substraction which can be attributed to CD_4. The carbonyl deuteride band is shifted to higher frequency (2029 cm^{-1}) due to higher coverage of this species; the corresponding carbonyl hydride band for a sample treated identically, except using H_2 instead of D_2, appears at 2039 cm^{-1}. Bands at 2778 and 2720 cm^{-1} can be assigned to vibrational modes for gas-phase D_2O and HDO, respectively.[10] Also present were small sharp bands at 2988 cm^{-1} and 2141 cm^{-1}. The 2988 cm^{-1} band is indicative of the presence of a small amount of CHD_3. The 2141 cm^{-1} band does not grow in intensity upon further heating and is removed upon evacuation. At this time we can not propose an assignment for this band.

Spectra 1c and 1d show the further development of the bands mentioned above upon further heating at 503 K. New bands at 3010, 1234, 1089, and 1035 cm^{-1} can be assigned to vibrational modes for gas-phase CH_2D_2. Upon evacuation at 298 K, spectrum 1e was obtained showing only the carbonyl deuteride surface species and broad bands indicative of a deuterated support. It should be noted that an analogous series of experiments for 10% Rh/Al_2O_3 gave the CD_4, CHD_3, and CH_2D_2 products, but at a slower rate. Also a 0.5% Rh/Al_2O_3 catalyst film gave qualitatively the same results, although the 0.5% sample actually produced the isotopically labeled methanes at a slightly greater rate than did the 10% sample indicating that small Rh ensembles can be important in the methanation of CO_2.

In a similar set of experiments a 10% Rh/TiO_2 film reduced with D_2, heated at 523 K in the presence of 70 Torr D_2 for 21 hr, and then evacuated at 298 K to $1x10^{-6}$ Torr, was exposed to a 66 torr 1:4 mixture of CO_2:H_2 at 298 K. At 298 K the infrared spectrum revealed no measurable OD bands, yet a broad band at 1610 cm^{-1} characteristic of a hydrated (H) support appeared. Nevertheless, upon heating to 503 K for 3 hr, infrared bands at 2199 and 1156 cm^{-1} characteristic of CH_3D, as well as those (3014 and 1304 cm^{-1}) for CH_4, were observed.

Figure 2 shows the infrared spectra for a series of experiments involving a CH_4/D_2 mixture over a 10% Rh/TiO_2 film. For these experiments the film was heated and reduced in D_2. Then 100 Torr of a 1:1 mixture of

CH_4:D_2 was added at 298 K, and spectrum 2a was recorded. At 298 K only the 3014 and 1304 cm^{-1} bands for CH_4 are evident. However, after heating to 503 K for 30 min (2b) and 6 hr (2c), bands at 2986, 2258, 2199, 1234, 1156, 1089, 1034, and 994 cm^{-1} clearly indicate the presence of CH_3D, CH_2D_2, CHD_3, and CD_4, in addition to CH_4. Evacuation at 298 K led to the removal of all of these bands (2d). Similar results were obtained for a 0.5% Rh/TiO_2 film.

All of these experiments suggest that isotopic scrambling is occurring on the supported Rh films. To discover whether this scrambling was related to the Rh, or just the support materials, the CO_2 reduction experiments and the CH_4/D_2 mixture experiments were repeated for TiO_2 and Al_2O_3 films containing no Rh. The resulting infrared spectra show <u>no</u> infrared bands characteristic of any of the methanes other than the CH_4 when a CH_4/D_2 mixture was used at the temperatures employed in these experiments. Utiyama and coworkers[11] have reported that isotopic exchange in a CH_4/D_2 mixture does not occur over TiO_2 until temperatures greater that 773 K. However, other workers have observed CH_4/D_2 exchange over Al_2O_3 at low temperature (near ambient).[12-14] The sample pretreatment procedures in these experiments all involved heating to temperatures in excess of 750 K in O_2 or air before the exchange was attempted. Evidently our mild pretreatment procedure did not activate either TiO_2 or Al_2O_3 for isotopic exchange. Thus, it is apparent that all isotopic exchange in these experiments was induced by the presence of the Rh on the supports.

We believe that isotopic exchange in these experiments is a direct result of H or D migration from the support material to the Rh atoms or clusters. Otherwise, CHD_3 and CH_2D_2 could not be formed from a gaseous mixture of D_2 and CO_2 over the supported Rh films as in Fig. 1. There has been much interest recently in hydrogen and deuterium "spillover" from metals to supports.[15] There have also been suggestions of "reverse spillover" of D_2 onto Pt from TiO_2[16] and "back spillover" of protons onto Pt from TiO_2,[17] among other similar observations.[18-21] We prefer to term the phenomenon as an "inverse spillover effect", and to our knowledge, this is the first documented example of such an effect for supported Rh catalysts. Furthermore, we believe that the "inverse spillover effect" significantly enhances the dissociation of CO_2 on supported Rh catalysts in the absence of H_2 gas.[5,22]

Acknowledgements

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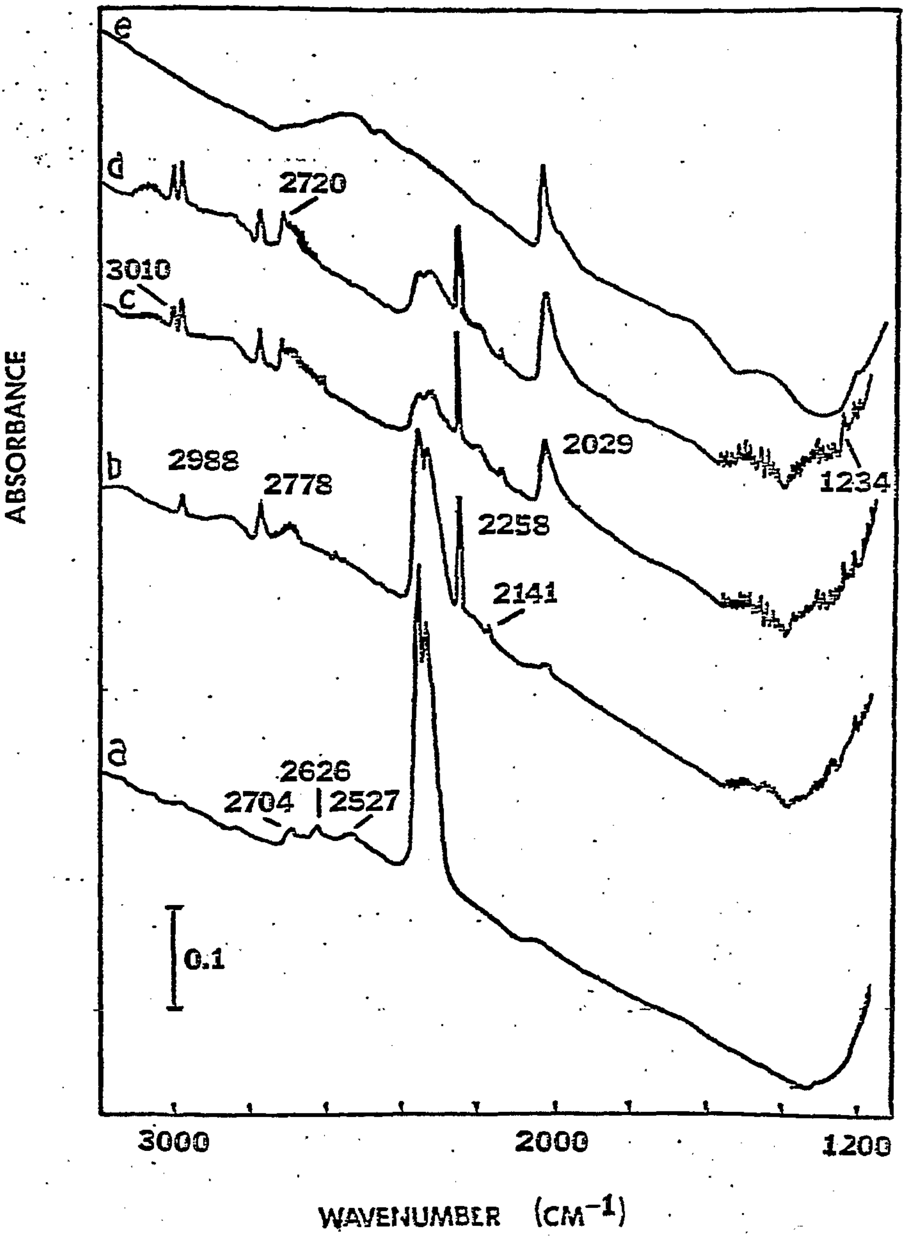
(22) A referee has suggested that an alternative explanation for our observations is a water gas shift sequence in which D_2O produced from deuteration of CO_2 exchanges with the support to produce HDO which then reacts with CO to give CO_2 and HD. The resulting HD would then react with CO_2 on Rh to produce the CHD_3 and CH_2D_2 observed. While this explanation is possible, we believe that an inverse spillover effect is more plausible because of the substantial amount of the deuterated products observed in a reactor in which D_2 would be in tremendous excess relative to any HD produced. Also, we observe infrared bands for CHD_3 *before* those for HDO appear.

Figure Captions

Figure 1. Infrared spectra of a 10% Rh/TiO_2 film (4.8 mg cm^{-2}) following heating at 523 K for 12 hr at $2x10^{-6}$ Torr, reduction in D_2 at 470 K, evacuation at 298 K to $2x10^{-6}$ Torr, and then: (a) introduction of 66 Torr of a 1:4 mixture of CO_2:D_2 at 298 K, (b) heating at 503 K for 1 hr, (c) heating at 503 K for 3 hr, (d) heating at 503 K for 4.5 hr, (e) following evacuation at 298 K.

Figure 2. Infrared spectra of a 10% Rh/TiO_2 film (5.1 mg cm^{-2}) following reduction in D_2 at 470 K and evacuation at 298 K to $2x10^{-6}$ Torr, and then: (a) introduction of 100 Torr of a 1:1 mixture of CH_4:D_2 at 298 K, (b) heating at 503 K for 30 min, (c) heating at 503 K for 6 hr, (d) following evacuation at 298 K.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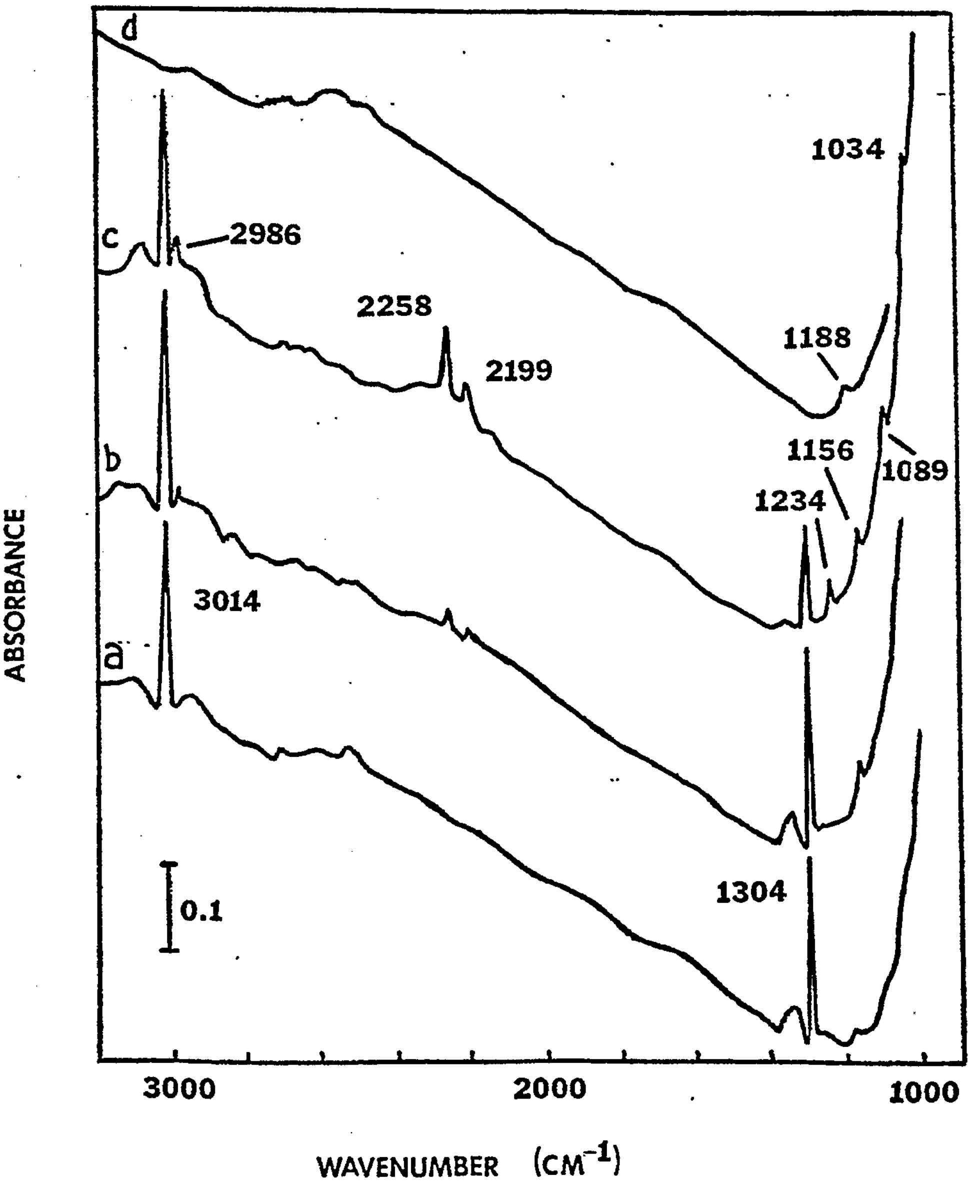
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