

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

**University
Microfilms
International**

300 N. Zeeb Road
Ann Arbor, MI 48106

8324892

Madden, Michael Preston

**AN INFRARED SPECTROSCOPIC EXAMINATION OF A RHENIUM
OXIDE/ALUMINA OLEFIN METATHESIS CATALYST**

The University of Oklahoma

Ph.D. 1983

**University
Microfilms
International** 300 N. Zeeb Road, Ann Arbor, MI 48106

Copyright 1983

by

Madden, Michael Preston

All Rights Reserved

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark .

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print _____
3. Photographs with dark background _____
4. Illustrations are poor copy _____
5. Pages with black marks, not original copy _____
6. Print shows through as there is text on both sides of page _____
7. Indistinct, broken or small print on several pages
8. Print exceeds margin requirements _____
9. Tightly bound copy with print lost in spine _____
10. Computer printout pages with indistinct print _____
11. Page(s) _____ lacking when material received, and not available from school or author.
12. Page(s) _____ seem to be missing in numbering only as text follows.
13. Two pages numbered _____ . Text follows.
14. Curling and wrinkled pages _____
15. Other _____

University
Microfilms
International



THE UNIVERSITY OF OKLAHOMA
GRADUATE COLLEGE

AN INFRARED SPECTROSCOPIC EXAMINATION OF
A RHENIUM OXIDE/ALUMINA
OLEFIN METATHESIS CATALYST

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

By
Michael Preston Madden

Norman, Oklahoma

1983

AN INFRARED SPECTROSCOPIC INVESTIGATION OF
A RHENIUM OXIDE/ALUMINA
OLEFIN METATHESIS CATALYST

A DISSERTATION APPROVED FOR
THE SCHOOL OF CHEMICAL ENGINEERING
AND MATERIALS SCIENCE

By

A. A. Logan
Roger French
David Martin
Lloyd L. Lee
Robert Clark

ABSTRACT

Alumina and rhenium oxide supported on alumina (Re/Al) were subjected to various treatments and examined using infrared spectroscopy. Lewis acid sites were somewhat stronger on the Re/Al than on alumina. Bronsted acid sites were not detected on either alumina or Re/Al. The rhenium-oxygen stretching vibrational frequency was not appreciably altered by calcination or reduction. Olefin metathesis activity would appear to be more dependent on the properties of the support than on the state of the rhenium.

TABLE OF CONTENTS

	page
Abstract	111
List of Figures	v
List of Tables	x
Acknowledgements	xi
I. Introduction	1
II. Methods	23
III. Results and Discussion	30
IV. Conclusions	74
V. Recommendations	76
VI. References	78
Appendix	
Reactor Construction and sample preparation ...	84

LIST OF FIGURES

	page
Figure I-1 Two possible mechanisms for the olefin metathesis reaction	8
Figure I-2 Comparison of activity with temperature for rhenia and molybdena supported on γ -alumina and θ -alumina	15
Figure II-1. A schematic view of the reactor for powdered catalyst samples	26
Figure II-2. A schematic diagram of the ir cell/ reactor	28
Figure III-1 Spectrum of NH_4ReO_4 in KBr pellet (spectrum No. 75)	31
Figure III-2 Spectrum of KReO_4 in KBr pellet (spectrum No. 64)	32
Figure III-3 Spectrum of ReO_3 in KBr pellet	

	(spectrum No. 65)	33
Figure III-4	Spectrum of $\text{Cd}_2\text{Re}_2\text{O}_7$ in KBr pellet (spectrum No. 70)	34
Figure III-5	Spectra of Al_2O_3 and 5-Re/Al in KBr pellets (spectra 60 and 61)	35
Figure III-6	Difference spectrum: 5-Re/Al minus Al_2O_3 (spectrum 60 minus 61)	36
Figure III-7	Spectrum of unground 5-Re/Al, no treatment, 100-200 mesh, in KBr pellet (spectrum No. 69)	37
Figure III-8	Spectrum of unground 5-Re/Al, 100- 200 mesh, heated in flowing oxygen at 759 K, in KBr pellet (spectrum No. 67)	38
Figure III-9	Spectrum of unground 5-Re/Al, 100- 200 mesh, heated in flowing oxygen followed by flowing hydrogen at 759 K, in KBr pellet (spectrum No. 72)	39

Figure III-10 Spectrum of unground 2-Re/Al, 100- 200 mesh, no treatment, in KBr pellet (spectrum No. 73)	40
Figure III-11 The relationship between the lower and upper peaks in the 910-925 wavenumber band is shown	41
Figure III-12 Four spectra of ReO_3	44
Figure III-13 XPS spectrum of untreated KReO_4	47
Figure III-14 XPS spectrum of ground KReO_4	48
Figure III-15 XPS spectrum of ground KReO_4 mixed with KBr	49
Figure III-16 XPS spectrum of untreated ReO_3	50
Figure III-17 XPS spectrum of ground ReO_3 with two bands used for deconvolution	51
Figure III-18 XPS spectrum of ground ReO_3 with three bands used for deconvolution	52
Figure III-19 XPS spectrum of ground ReO_3 mixed with KBr	53
Figure III-20 Bromine bands in the XPS spectrum of ground ReO_3 mixed with KBr	57

Figure III-21 The effects of hydrogen pretreatment on the adsorption and desorption of pyridine	59
Figure III-22 The effects of carbon monoxide pretreatment on the adsorption and desorption of pyridine	60
Figure III-23 The relationship between peak positions and evacuation temperatures .	61
Figure III-24 In-situ spectra of Al_2O_3 after various treatments	63
Figure III-25 In-situ spectra of Al_2O_3 after various treatments	64
Figure III-26 In-situ spectra of Al_2O_3 after various treatments	65
Figure III-27 In-situ spectra of Al_2O_3 after various treatments	66
Figure III-28 In-situ spectra of 5-Re/Al after various treatments	67
Figure III-29 In-situ spectra of 5-Re/Al after various treatments	68
Figure III-30 In-situ spectra of 5-Re/Al after	

various treatments 69

LIST OF TABLES

	page
Table I-1 Assignments for the infrared spectrum of pyridine adsorbed on silica- alumina	20
Table III-1 Peak locations for the catalyst and model compounds	42
Table III-2 Results of the X-ray Photoelectron Spectroscopic investigation	46

ACKNOWLEDGEMENTS

It would be impossible to mention everyone who helped to make this investigation possible. Many teachers and fellow students provided encouragement and valuable ideas and suggestions. Financial support was provided by Phillips Petroleum Company. The National Science Foundation, the American Chemical Society and the Academy of Sciences of the Soviet Union made it possible to conduct some of the research at the Institute of Chemical Physics in Moscow, USSR.

I particularly want to thank Dr. Arthur Aldag, my principle advisor, and Dr. Roger Frech for their guidance throughout the course of my research. The other members of my committee have also been sources of valuable suggestions and encouragement.

I also want to thank Mr. Ron Stermer for his help in the construction of the glass reactor and reaction system and for teaching me to appreciate the art involved in glassblowing. Mr. K. Hudson was helpful in the construction of the reaction and data collection systems. Special thanks go to Mr. Fred Dillon for keeping the

infrared spectrometer alive long enough to allow me to finish. X-ray photoelectron spectroscopy was performed at Phillips Petroleum Company by Ruth Merryfield.

Last, and certainly not least, I wish to thank my wife, Peggy, my father, and the rest of my family for their support and endurance.

INTRODUCTION

The investigation described here was a continuation of research in the area of olefin metathesis conducted at the University of Oklahoma. Topics examined over the course of the past several years have included adsorption, kinetics, mass transfer effects, catalyst supports, poisoning, and temperature programmed desorption.

Olefin metathesis is an important commercial reaction as evidenced by the large body of literature, much of it generated by industrial laboratories. The reaction is useful for producing feedstocks and intermediates important to the petrochemical industry. Any research which enables the development of catalysts that are more active or active at more moderate conditions will reduce energy requirements, increase productivity, and lower production costs.

Frequent international symposia point the world wide scope of research in the area. Dr. Arthur Aldag and the author were involved in olefin metathesis research at the Institute of Chemical Physics in Moscow, USSR, during the US-USSR exchange in chemical catalysis. Research at the

institute was directed toward heats of adsorption measurements and investigation of support effects. These investigations will be described in more detail in the literature review section of the introduction.

Work by J. C. Hsu (described in more detail later) indicated that various pretreatment conditions had important effects upon reaction kinetics. Pretreatment investigated by Hsu included oxidation, hydrogen reduction and evacuation of catalyst samples at various temperatures. The purpose of the present investigation was to examine the nature of the catalyst with respect to various pretreatment environments, as discussed by Hsu, and probe molecules. Of particular interest was the nature of the interaction of rhenium with the alumina support.

The primary tool used to examine the catalyst was the infrared spectrometer. With this instrument, not only the nature of the rhenium - alumina bonding, but the nature of the bonding between the catalyst and various adsorbed probe molecules can be investigated. The vibrational motion of the rhenium - oxygen bonds in various rhenium oxide model compounds can be compared with the corresponding motion in the catalyst. The nature of acidic sites on the catalyst can be determined when pyridine is used as an adsorbed probe molecule.

A major difficulty in examining an alumina supported catalyst, while it is in a reasonable reaction environment,

is the large infrared absorptivity of alumina in the spectral region of interest, below 1100 wavenumbers. A catalyst sample thin enough to eliminate the problems due to alumina absorption could not be made, and an in-situ examination of the rhenium - oxygen - aluminum vibrational frequencies was impossible.

The problem of alumina absorption was not encountered during the investigation of adsorbed pyridine because the spectral region related to pyridine adsorption is at a frequency higher than 1100 wavenumbers. After design and construction of a suitable in-situ cell/reactor examination of the acid properties of the catalyst without disturbing the integrity of the reaction environment was possible.

A review of the literature concerning olefin metathesis, surface acidity and the use of infrared spectroscopy for catalyst investigations follows. The appendix contains a review of the literature describing the preparation of catalyst samples for infrared examination and construction catalytic reactors that are also infrared cells.

Industrial Applications

The olefin metathesis (OM) reaction has proven to be industrially important since its discovery was reported in 1964 (1). OM, also known as olefin disproportionation, has

been used in the production of long-chain linear olefin precursors of synthetic lubricants, plasticizer alcohols, surfactants, isoamylene, neohexene, terminal olefins and diolefins, and olefins containing functional groups (2). Standard plant design, equipment and operation can be used in commercial applications. Typical reaction temperatures are 300 - 750 K and depend upon the catalyst and reactants. The most active catalysts are oxides of tungsten, molybdenum or rhenium supported on high surface area alumina or silica. Modifiers are often added to the catalyst to improve activity or selectivity. Catalysts are activated and regenerated using air treatment at 750 - 850 K. Moisture and impurities are removed from feedstocks to decrease the extent of catalyst poisoning.

The Triolefin Process, developed by Phillips Petroleum Company (3), was the first commercial application. In this process ethylene, propylene and butenes are interconverted. Near-equilibrium conversions are achieved using tungsten oxide on silica or alumina at 550 - 750 K, pressures of 4 MPa and a weight hourly space velocity (WHSV) of 10 - 100. The Triolefin Process is often used in connection with other refinery processes such as 1-butane alkylation (4) or thermal cracking (5). This process can be operated in reverse, i.e., excess ethylene and 2-butene can be converted to propylene using the same catalyst. Maintaining a high ethylene to butene ratio by

ethylene recycle gives nearly complete conversion of butenes.

Long-chain linear olefins, used for plasticizer alcohols, lubricants, and surfactants, can be produced in multistage units. Processes are similar to the Triolefin Process (6), but as the molecular weight increases in the later stages, milder conditions are used to reduce side reaction production of isoolefins. High surface area magnesia in the same reactor with the metathesis catalyst causes double-bond shift without skeletal isomerization, dimerization or dehydrogenation. $C_{10} - C_{20}$ alpha and internal olefins are produced from ethylene by combining oligomerization, isomerization and metathesis in the Shell High Olefin Process (7).

Isoamylenes, which are precursors for polyisoprene, are produced from metathesis of 1-butylene and propylene or 2-butene at nearly 90% selectivity and equilibrium conversion on tungsten oxide on silica at 700 K, 2 MPa and 100 WHSV (8, 9). Neohexene, used in the production of bicyclic musk fragrances, is produced by the metathesis of a 2:1 ethylene and diisobutene mixture with a dual catalyst system of tungsten oxide on silica and magnesium oxide in a 1:3 weight ratio at 650 K, 3 MPa and 25 WHSV. A commercial unit built in 1980 has a capacity of 1.4 million kg per year (11).

Other potentially commercial applications are the

highly selective production of symmetrical alpha-olefins, alpha-omega diolefins, triolefins and cyclic compounds by the metathesis of single olefins such as 1-octene to yield 7-tetradecene. Self-metathesis of 4-vinylcyclohexene produces 1,2-bis-(3-cyclohexenyl) ethylene for evaluation as a flame retardant (9). Production of isotopically labeled olefinic compounds is another potential industrial application, eg., alpha labeled hydrocarbons can be produced by the metathesis of d_4 -ethylene with an internal olefin. The metathesis of alkynes and substituted alkenes has been demonstrated, but much more research is needed in this area before commercialization. Rhenium oxide/alumina promoted by tetramethyl tin has been shown to be active and selective for the metathesis of unsaturated acid esters (10).

The economics of industrial metathesis is sensitive to the relative costs of feedstocks and products. Integration of a metathesis process with an existing operation, such as an ethylene plant, can reduce the cost by up to 40%.

The Metathesis Reaction

One indication of the commercial usefulness of olefin metathesis is the amount of research undertaken, much of it by industrial research laboratories, since 1964. Annual symposia have been held under the auspices of the

International Symposium on Metathesis (ISOM) and complete issues of journals have been devoted to the proceedings of these international symposia. For example, volume 8 of the Journal of Molecular Catalysis was devoted to the 1979 symposium held at Lyons, France. Several reviews are available (11 - 15) that summarize the "state of the art" of metathesis up to 1979.

Ideas concerning the mechanism have undergone steady evolution since Bradshaw, et al. (16) proposed the "quasi-cyclobutane" four-centered mechanism. The presently accepted theory is a metal carbene propagated chain reaction (12). Evidence indicates that the reaction proceeds by a non-pairwise chain mechanism: a metal carbene interacts with a reactant olefin forming a metallocyclobutane intermediate, and this intermediate rearranges into a different metal carbene and a product olefin (Fig. I-1).

As in all chain reactions, the olefin metathesis reaction has an initiation step. Grubbs (13) discusses formation of the initial metal carbene. For catalysts requiring a metal alkyl co-catalyst, the carbene is formed through a α -hydrogen elimination from the metal alkyl as proposed by Schrock (17). Supporting evidence comes from an investigation of the OM reaction with 2,8-decadiene and a $\text{MoCl}_2(\text{NO}_2)_2(\text{Ph}_3\text{P})_2$ catalyst with methylaluminum sesquichloride, which points to the initial generation of a

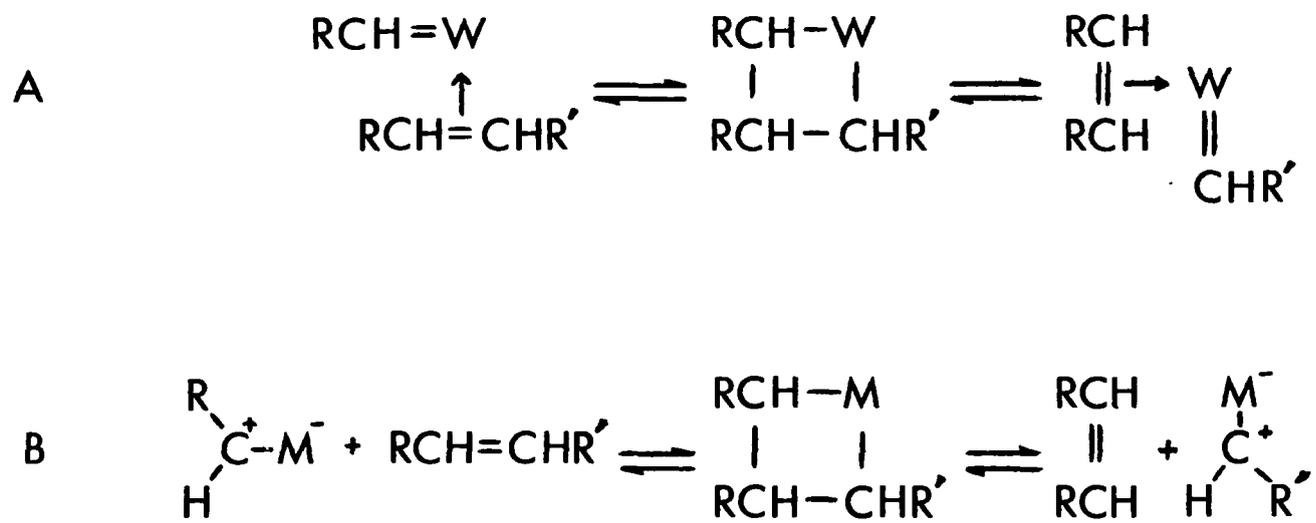


Figure I-1. Two proposed mechanisms for the olefin metathesis reaction are shown. The upper one (A) specifies a π -complexation of the olefin as a precondition to metathesis and an empty coordination site on the metal is required in addition to the complexed carbene. The lower reaction (B) is essentially a dipolar attack of the polarized metal carbene on the olefin (14).

methylene complex that produces propylene and two carbenes during the first turnover with the 2,8-decadiene.

For other catalysts that do not require co-catalysts, the carbene is formed by a β -H addition of a metal hydride to the olefin followed by an α -H elimination (18). Possible sources of the hydride are water or hydroxyl groups on the support, traces of acid from catalyst preparation or siloxyl or aluminium alkoxide groups providing the initial proton.

Casey and Burkhardt (19) presented the first model to describe the chain propagation step for the OM reaction. In their model, a tungsten carbene underwent an alkylidene exchange with the olefin. The question arose as to whether the OM intermediate is a carbene (a complex with a positive carbon) or an alkylidene (a complex with a negative carbon). Gassman and Johnson (20 - 22) proposed alkylidene intermediates while McGinnis et al. (23) showed that a diphenyl carbene will serve as a metathesis catalyst. The actual catalyst may be a species between the extremes of a carbene on the one end and an alkylidene on the other. The actual charge distribution would depend on the oxidation state of the metal, the electronic properties of the ligand, or on the nature of groups attached to the carbon. The metal might be reduced as the complex takes on an alkylidene nature. π -acids favor the formation of an alkylidene complex while σ -donors favor the carbene.

Electrophilic groups attached to the carbon favor the carbene while electron donating groups favor the alkylidene.

In addition to a carbene or an alkylidene, the proposed mechanism calls for a metalocyclobutane intermediate. Three possible reaction pathways from a metalocyclobutane are β -H transfer, β -C-C bond cleavage, and reductive elimination. The first is difficult in small metalocycles while the last is unlikely for metals having low coordination numbers (13).

With the intermediates in mind, the question arises as to how the reaction proceeds. First, it is the double bond that is broken (transalkylidenation) and not a single bond cleavage followed by a transfer of alkyl groups (transalkylation). This was demonstrated by cross metathesis between 2-butene and 2-butene- d_8 giving a product of 2-butene- d_4 (24) and by metathesis of propylene-2- ^{14}C from which the labeled carbons were found only in the butene product (25). Two possible low-energy pathways for the cleavage of the double bonds are: (a) pairwise exchange of alkylidene units between two reactant olefins and (b) cleavage of one double bond at a time and the transfer of individual alkylidene units (nonpairwise).

The quasicyclobutane metal complex mechanism (16) is a pairwise model that accounts for the observed products, but evidence against it is that cyclobutanes have been

shown to be unreactive under metathesis conditions (12, 26) and cyclobutanes have never been reported as OM reaction products. Other pairwise mechanism models include a pairwise concerted scheme in which a tetracarbene metal complex acted as the intermediate (27, 28), and a pairwise, nonconcerted scheme in which a metallocyclopentane complex is formed from two olefins followed by a scrambling of alkyl groups.

The nonpairwise mechanism proposed is one in which a chain reaction is propagated by a metal carbene with the formation of a metallocyclobutane, rearrangement of the alkylidene units and the formation of the product olefin. Some experimental evidence can be explained by the pairwise and the nonpairwise models, but investigations of labeled 1,7-dioctenes suggested that the product mixture supported the carbene mechanism (29 - 32). Detailed discussions of the mechanism models and the verifying experimental results can be found in the reviews of Grubbs (13) and Katz (12).

Chain termination can occur through two possible routes: impurity poisoning and side reactions which destroy the metal carbene or reaction intermediates. Carbene complexes can react destructively with oxygen, removing the chain initiator (33). The metallocycloalkane can undergo a reductive cyclization in the presence of oxygen which results in termination (13). Alkylidene complexes can react with carbon-oxygen double bonds while

carbenes can react with nucleophiles. Carbenes with alkyl substituents are sensitive to bases; impurities with basic functionalities would be expected to decompose OM intermediates. Hsu (34) has shown that water is an effective OM poison, small pulses of oxygen briefly increase the reaction rate and the maximum rate is enhanced by a carbon dioxide impurity of 0.7%. It is thought that water weakens Lewis acid strength while carbon dioxide alters the nature of the Bronsted acidity (37).

Most OM catalyst systems contain molybdenum, tungsten or rhenium. Heterogeneous catalysts are high surface area refractory supports on which one of the transition metal compounds is deposited. Bailey (11) presents a discussion of transition metal carbonyls, oxides and sulfides deposited on oxides of aluminum, silicon, titanium, zirconium, tantalum, tin, nickel and thorium. It is usually necessary to pre-expose these supported catalysts to an olefin to form the required metal carbene initiator. Break-in phenomena have been observed in metathesis activity when fresh catalysts are exposed to propylene (34).

Grinev et al. (35) investigated the heats of adsorption of ethene, propene and 2-butene onto the surface of $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts at various temperatures. The heat of adsorption increased with increasing chain length. The quantity of adsorbed olefin decreased with increasing MoO_3

content and with increasing average oxidation state of the molybdenum.

Calderon, et al. (14) lists such homogeneous catalysts as WCl_6/R_mAlCl_n ($m+n=3$), WCl_6/RLi , WCl_6/R_4Sn , WCl_6/R_2Zn , $MoCl_5/R_3Al$, and $Mo\{(Ph_3P)_2Cl_2(NO)_2\}/R_3Al_2Cl_3$, where R is some organic radical. The homogeneous system of tungsten hexachloride promoted by tetramethyl tin is known to be active for the metathesis of functionalized olefins such as long-chain fatty acids. Secondary amines react to give diamines with a alkylaluminum chloride promoted tungsten carbonyl catalyst system (10).

The catalyst most extensively investigated at the University of Oklahoma has been a 9-10 wt% rhenium oxide on γ -alumina. Lin, et al. (36) determined that the reaction was mass transfer limited when using a 20 wt% Re_2O_7/Al_2O_3 catalyst, but the mass transfer effect was not significant on a 10 wt% catalyst. The catalysts are made using an impregnation technique: a slurry of NH_4ReO_4 and finely ground γ -alumina in distilled water is stirred and slowly evaporated at a temperature below the boiling point of water. Other catalysts that have been investigated in our laboratory are rhenium oxide supported on TiO_2 , SiO_2 and a number of zeolites (37). It was determined that the activity of these catalysts were in the following order: NH_4ReO_4 /alumina, $NH_4ReO_4/3A$ (Ca) zeolite, NH_4ReO_4/TiO_2 , $NH_4ReO_4/13X$ (Ca) zeolite, $NaReO_4$ /alumina, $NH_4ReO_4/13X$ (Na)

zeolite.

Alumina occurs in different modifications. It has been found that metathesis activity is dependent on the type of alumina supporting the rhenium oxide (38). Rhenium oxide supported on the theta modification was more active than when supported on the gamma. Molybdena, on the other hand, was more active when supported on γ -alumina than on θ -alumina (Fig. I-2).

Aldag, et al. (39, 40) reported on the number of active sites on a 10 wt% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. It was found that, although the adsorbate was mobile, the reaction proceeded through an immobile transition state with an active site concentration on the order of 7×10^{11} sites/cm². It was suggested that this reaction path was not dependent on a pairwise or nonpairwise mechanism. El-Sawi, et al. (41) showed that a model based upon the metathesis reaction between two olefin molecules chemisorbed in two successive adsorption steps onto two sites of the same active center is more likely than a model based on a Langmuir-Hinshelwood mechanism and reaction between olefin molecules chemisorbed onto neighboring active centers.

Hsu (37) suggested that Lewis and Bronsted acid sites on the catalyst are important to metathesis activity. Pretreatment of the catalyst with CO_2 enhanced the yield by 6% which indicated a role for Bronsted acids. This result is one that the present study was intended to investigate

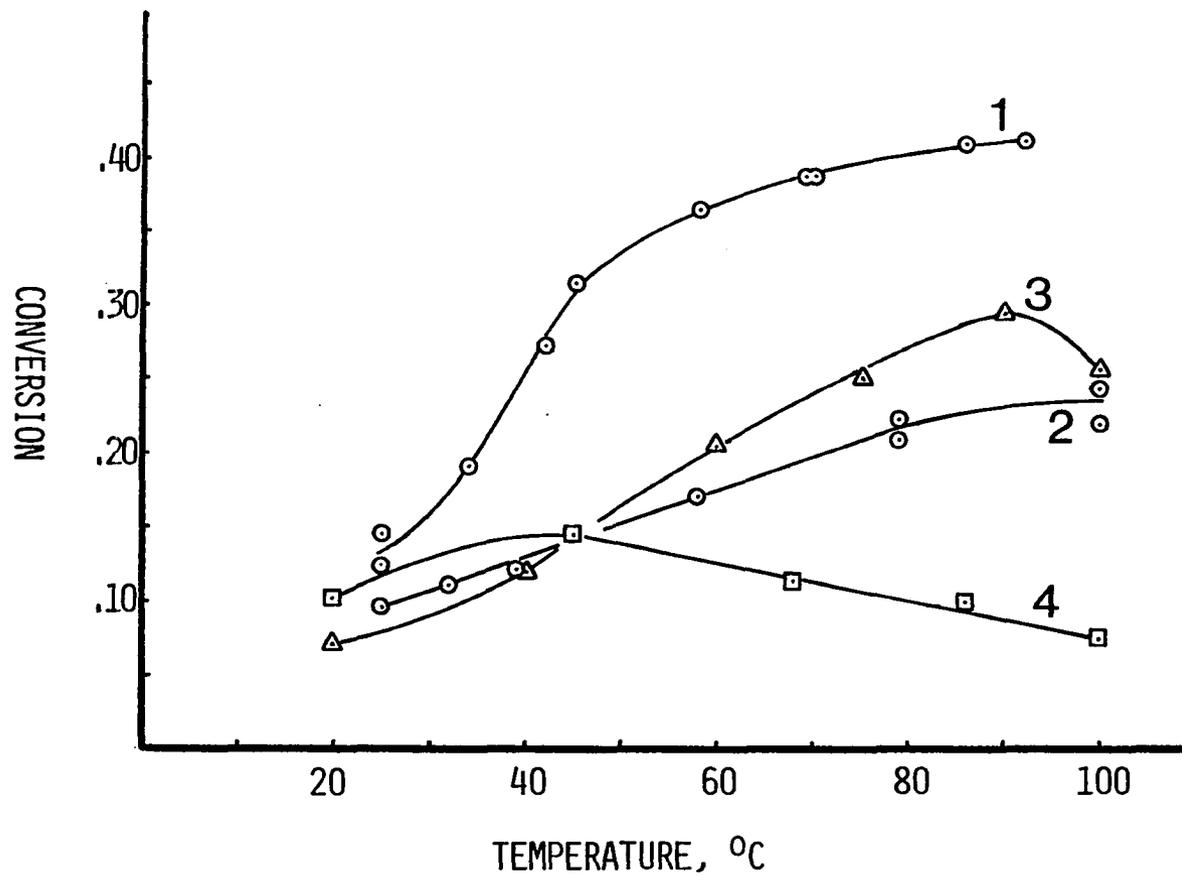


Figure I-1 The relationship between conversion and temperature is shown for: 1. 9 wt % $\text{Re}_2\text{O}_7/\theta\text{-Al}_2\text{O}_3$, 2. 9 wt % $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$, 3. 10 wt % $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$, 4. 10 wt % $\text{MoO}_3/\theta\text{-Al}_2\text{O}_3$.

using ir spectroscopic examination of pyridine adsorption. Water destroyed all metathesis activity, which pointed to the role of Lewis acids. Hsu suggested that the initiation mechanism proposed by Brenner, et al. (42) along with an involvement of a Bronsted acid was reasonable.

Hsu (34) found that initial metathesis activity was decreased if the Re/Al catalyst was reduced in hydrogen. Introduction of oxygen into the reaction mixture caused an increase in activity. Nakamura and Echigoya (43) observed this same phenomenon and reported that metathesis activity was proportional to the amount of a paramagnetic O_2 / Al^{3+} radical. Another interesting result reported by Hsu (34) was the effect of evacuation pretreatment temperature on metathesis activity. As evacuation temperature increased from room temperature to 326 °C, the metathesis activity decreased to almost zero. As the temperature of evacuation was further increased from 326 to 500 °C, the activity increased. The present research was intended to investigate the effect of evacuation temperature on the ir spectra of and pyridine adsorption on the catalyst.

Surface Acidity

Delgass, et al. (44) state that "...infrared spectroscopy is the only technique that can definitively distinguish between proton donor (Bronsted type) and electron acceptor (Lewis type) acid sites". Bronsted

acids, which are thought to be involved in hydrocarbon skeletal rearrangements, consist of protons associated with surface anions. Lewis acids, inactive for skeletal rearrangements unless associated with nearby proton donors, consist of incompletely coordinated surface ions such as aluminum. When nitrogen containing molecules, such as ammonia, pyridine, piperidine, are adsorbed onto the catalyst, the spectra for molecules coordinatively bonded are distinctly different from those of molecules electrostaticly bonded. The frequency shift of the coordinate bonded molecules is proposed as a measure of the strength of the acid sites.

Benesi and Winquist (45) review methods of measuring surface acidity. Aqueous, non-aqueous indicator, adsorption, model reaction, and infrared spectroscopic methods are discussed. It was suggested that the infrared method is the best for complete identification of the number, strength and type of acid sites. However, a large amount of time and sophisticated equipment are required.

The ir spectroscopic method for the investigation of surface acidity was first reported by Mapes and Eischens (46), who demonstrated the existence of Bronsted and Lewis acids on the surface of a silica-alumina cracking catalyst. Parry (47) showed that the spectrum of adsorbed pyridine could be used to distinguish the two acid types. Among the many other reports of the ir spectroscopic technique are

pyridine on silica-alumina (48, 49), Raman studies of pyridine adsorbed on molybdate catalysts (50), pyridine adsorption on 12-molybdophosphoric acid (51), pyridine adsorption on CoO, NiO, MoO supported on alumina (52), adsorbed pyridine, 2,6-Dimethylpyridine and 2,6-di-tert-butylpyridine on boron phosphate (53), pyridine adsorption on Ni and Pt (54), adsorption of pyridine, CO, and carbon dioxide on anatase (55), pyridine adsorption on eta-alumina (56, 57), carbon monoxide adsorption on several oxides (58), pyridine and deuterated pyridine adsorption on amorphous silica, alumina and silica-alumina (59), pyridine, nitric oxide, ammonia, carbon dioxide, acetic acid, and trimethylchlorosilane adsorption on haematite and goethite (60, 61), pyridine and ammonia adsorption on tungsten oxide/silica (62) pyrrole adsorption on alumina and silica-alumina (63), and pyridine adsorption on ZSM-5 type zeolites (64, 65).

It has been shown by ir spectroscopy of pyridine adsorption that pure alumina has Lewis acid sites but not Bronsted acid sites. Alumina promoted with Co and Ni exhibit only Lewis acidity, whereas Mo promoted alumina, with or without associated Ni or Co, exhibits Lewis and Bronsted acidity (66). The sodium content of Co-Mo promoted alumina was found to have a influence on the surface acidity (67). Segawa and Hall (68) report that Lewis and Bronsted acidity occurs on oxidized forms of

alumina supported molybdena, chromia, rhenia and tungsta.

Morterra, et al. (55) adsorbed pyridine on eta-alumina at room temperature. The adsorbed species were described as "...a liquid-like physisorbed species, a species H bonded to surface OH groups through the nitrogen lone pair and three Lewis coordinated species. The latter are assigned to purely octahedral, tetrahedral-octahedral and purely tetrahedral cationic sites, respectively."

Parry (47) makes the following assignments for the frequencies of adsorbed pyridine (see Table I-1). Pyridine bonded to Lewis acid sites (LPy) is represented by a band in the 1440-1465 wavenumber region. The pyridinium ion (BPy) gives a band at 1540 wavenumbers whereas there is not a band for this ion in the 1440-1465 wavenumber region. The bands at 1540 and at 1440-1465 are used to distinguish between LPy and BPy. The frequency increase in the 1440-1465 wavenumber band of coordinately and hydrogen bonded pyridine is related to the stability of the complex. A band at 1583 wavenumbers was shown to shift when the pyridine was coordinately bonded. Proton acidity is indicated by the band at 1540 wavenumbers, a band at 1640 wavenumbers and an intense band at 1485 wavenumbers. Aprotic acidity is indicated by a band in the 1440-1465 wavenumber region. Parry concluded that the strong acid sites on eta-alumina were of the Lewis acid type. No evidence was found for Bronsted acid sites on the alumina.

**Table I-1. Assignments for the Infrared spectrum
of pyridine adsorbed on silica-alumina (60b).**

Assignment	Frequency, wavenumbers			
	Py	LPy	BPy	HPy
7a	-	-	3260	-
7a	-	-	3188	-
20b	3083	3147	3147	-
16	3054	3114	3114	3065
7b	3054	3087	3087	3043
8a	1580	1620	1638	1614
8b	1572	1577	1620	1593
19a	1482	1482	1490	1490
19b	1439	1450	1545	1438

Py = pyridine

LPy = chemisorbed bonded pyridine

BPy = chemisorbed protonated pyridine

HPy = physisorbed pyridine

Infrared Spectroscopy in Catalyst Systems

Several review articles (70 - 74) summarize infrared spectroscopic investigations of adsorbed species. For a review of reactor-ir cell design and sample preparation, see the Appendix. The results of several investigations are applicable to olefin metathesis.

Olsthoorn and Boelhouwer (75, 76) investigated changes in the hydroxyl bands during treatment of 20-30 wt% rhenium oxide/alumina catalysts. Alumina aerogel was saturated with volatile rhenium heptoxide at temperatures between 773 and 873 K. The region between 1300 and 4000 wavenumbers was examined. As a result of the exchange of isotopic oxygen, bands at 1980 and 2000 wavenumbers were assigned to rhenium-oxygen vibration. Similar results were obtained for molybdenum oxide/alumina (76). Using pyridine adsorption, pyridinium ions were detected on reduced samples, but not on oxidized samples.

Nakamura, et al. (77) reported the presence of two different surface rhenium species: ReO_4^- ads and Re_2O_7 ads. It was suggested that the Re_2O_7 ads, present at high rhenium loadings, was responsible for high metathesis activity. Using a catalyst/KBr pressed disc technique, bands were found at 915 and 925 wavenumbers. They proposed that these bands were assignable to $\text{Re}=\text{O}$ stretching in ReO_4^- and ReO_3^+ groups respectively. Using Raman spectroscopy, Kerkhof, et al. (78) found only ReO_4^-

tetrahedra on the surface of 20-26 wt% rhenium oxide/alumina.

Molybdena/alumina catalysts have been investigated using Raman spectroscopy (79) Bands found in the 200 - 1000 wavenumber region were assigned to various vibrational modes of Mo - O: (a) bands in the 310-370 and 900-1000 regions were assigned to normal modes of terminal Mo=O groups and (b) bands in the 200-250 , 400-600 and 700-850 regions were assigned to bridging Mo-O-Mo groups. Cheng and Schrader (80) characterized supported molybdate catalysts during preparation using Raman spectroscopy.

II. METHODS

Materials

Alumina and rhenium supported on alumina at 2.3 and 5.3 Re:Al atomic ratios (2-Re/Al and 5-Re/Al) were prepared in the following manner. Alumina (γ -alumina, Harshaw, lot # 145) was ground using mortar and pestle to less than 60 mesh. The ground alumina was placed in a flask to which 150 ml distilled water was added. The alumina slurry was stirred with a teflon coated magnetic stirring bar and heated to 350 K. For 2-Re/Al and 5-Re/Al, the necessary amount of NH_4ReO_4 (Apache Chemicals, Inc., lot # 08316) was added to the alumina slurry. The slurries were stirred until nearly dry then placed in an oven maintained at 360 K until dry. These powders were sieved and portions less than 200 mesh were used for this investigation.

Gases used for pretreatment were oxygen, hydrogen, carbon monoxide, and nitrogen obtained from Linde. The gases were dried by passing them through molecular sieves. The molecular sieves were dried by heating at 450 K under flowing nitrogen. Pyridine (Baker Analyzed Reagent, lot # 846392) was purified by a method to be described later.

Compounds used in the model compound investigations were: Re_2O_7 (Alfa Products, lot # 062078 and 082378), ReO_3 (Alfa Products, lot # 020178), KReO_4 (Alfa Products, lot # 010478), and Cadmium metal powder (Alfa Products, lot # 042277, <200 mesh). A method described by Donohue et al. (81) was followed to prepare $\text{Cd}_2\text{Re}_2\text{O}_7$. For analysis, the model compounds were finely ground using an agate mortar and pestle and pellets were made by mixing a sample with KBr (Mallinckrodt, Infrared Grade, lot # KMSB).

Apparatus

All spectra of samples made during the pretreatment and pyridine adsorption investigations were made using a Beckman IR-12 spectrometer with a 1 mm slit width at 1000 wavenumbers and a scanning speed of 13 wavenumbers per minute. Frequency calibration was made using polystyrene film having absorption peaks at 906.9, 1028.3, 1154.6, 1601.8 and 1944.5 wavenumbers. This calibration gave a frequency accuracy of 1.5 wavenumbers and transcription of the original spectra introduced an additional 2-3 wavenumber uncertainty.

Spectra of model compounds were made using a Nicolet 200 SX Fourier transform infrared spectrometer with a KBr beam splitter. Background for the model compound spectra was air. The effective resolution was one wavenumber and was set by using 16,128 data points and 32,768 transform

points. One hundred scans were made of each sample and the background. Transform correlation was set at "medium".

Temperatures were measured using chromel-alumel thermocouples. The thermocouple in a reactor was connected in series with a thermocouple in an ice/water slurry. Potential differences were measured using a Leeds-Northrup No. 8667 potentiometer. Temperatures were controlled using thermocouples connected to a temperature regulator (Minneapolis-Honeywell Regulator Co., Type R7086A).

A glove box (Plas-Labs, model XPL-855-AC Anaerobic Chamber) was used when water and oxygen contamination of samples was to be prevented. A nitrogen atmosphere was maintained in the glove box by means of an evacuable air lock and a system which circulated the nitrogen atmosphere through silica gel, molecular sieve, and BASF R3-11, a supported Cu deoxygenation catalyst. The R3-11 catalyst was regenerated by flowing hydrogen at 473 K.

Procedure

During the first phase of the investigation, powdered catalyst samples were treated in a pyrex reactor (Fig. II-1). The samples were calcined in flowing oxygen at the designated temperature (T_{ox}) for 16 - 20 hours. Calcining was followed by evacuation at a designated temperature (T_{ev}) for 2.5 - 3 hours. If $T_{ev} < T_{ox}$, the reactor was sealed and the temperature lowered to T_{ev} at

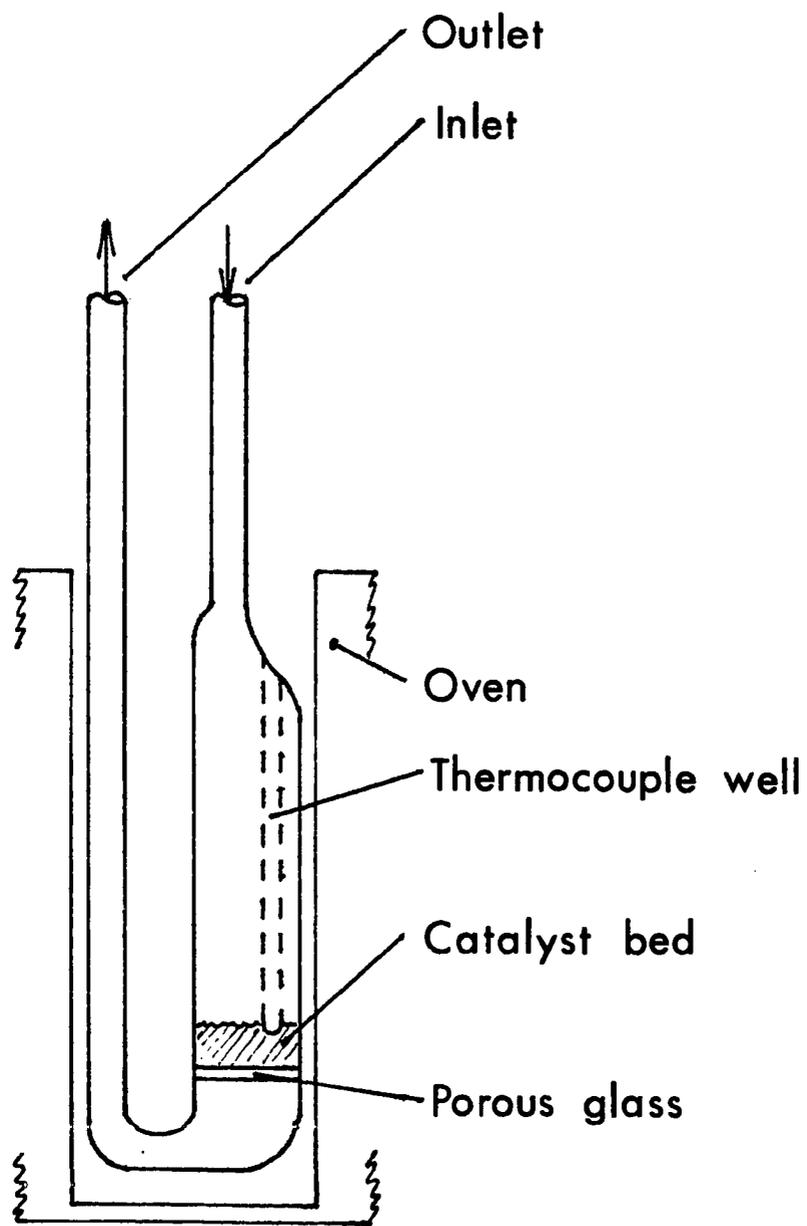


Figure II-1. A schematic view of the reactor for powdered catalyst samples

which time the reactor was opened to the evacuated manifold. After evacuation at T_{ev} , the temperature was lowered to room temperature (RT) and the reactor was sealed. The reactor was then transferred to the glove box in which some of the catalyst was mixed with KBr and put in a pellet press. The press was sealed while inside the glove box to prevent moisture or air contact with the sample. Pellets were made in the press by applying $15,000 \text{ kg/cm}^2$ of pressure. Treatment of the samples with other gases was done in a similar manner.

Two spectra were made of each sample over the range of 750 - 2000 wavenumbers. The spectra for each sample were normalized and averaged to eliminate noise.

The second phase of the investigation involved treatment of catalyst pellets in a reactor/ir cell (see Fig. II-2). A detailed discussion of reactor/ir cells is in the appendix. The samples were pressed, without diluting with KBr, in a pellet press with $15,000 \text{ kg/cm}^2$. Gas treatment was similar to that of the first phase. The samples were treated in an oven section and then moved to the ir beam path using an external magnet.

Pyridine (Py) was introduced into the evacuated reactor at room temperature from an attached vial containing liquid Py. The Py was purified by evacuating the vial and discarding the first ten percent. The last ten percent was also discarded. After introduction of Py

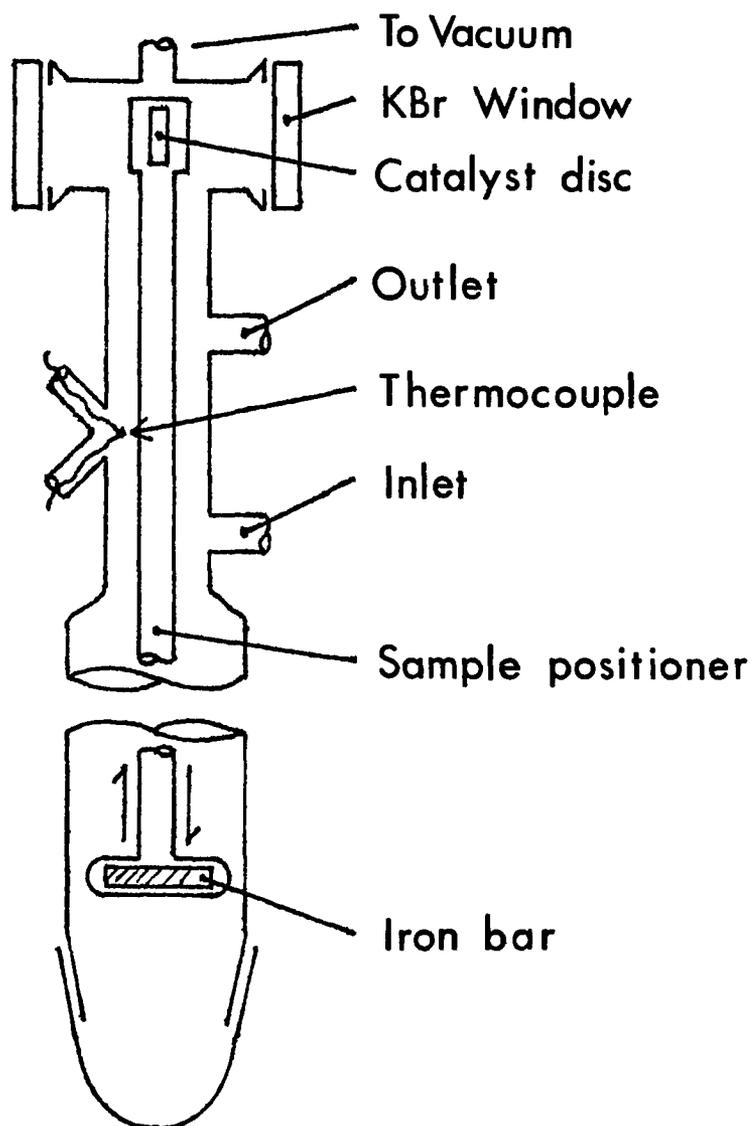


Figure II-2. A schematic view of the ir cell/reactor is shown. The sample is moved between the heating section and the observation section by means of an external magnet acting on the iron bar. The heating section is between the outlet and inlet.

into the reactor, the reactor was evacuated to remove gas phase Py. Spectra were made at RT. The samples were then heated at 430 - 470 K to remove physisorbed Py (48).

III. RESULTS AND DISCUSSION

Model Compound Investigation

Spectra were made of the model compounds KReO_4 , NH_4ReO_4 , ReO_3 , and $\text{Cd}_2\text{Re}_2\text{O}_7$ (Figures III-1 to III-10). In these spectra a band between 910 and 925 wavenumbers appears consistently. This band also appears in the spectra of the 5-Re/Al and 2-Re/Al catalysts. The band is a doublet and has a lower peak at 913.6 ± 1.9 and an upper peak at 923.1 ± 1.0 wavenumbers. The distance between these two peaks remained fairly constant at 9.0 ± 0.7 wavenumbers (see Fig. III-11). This correlated peak shifting indicates that these two peaks are not independent. Many of the spectra indicate a shoulder on the band in the area of 931 wavenumbers and in the spectrum of $\text{Cd}_2\text{Re}_2\text{O}_7$, there is a resolved peak at 932.4 wavenumbers (see Table III-1). Baran et al. (82) recorded spectra of a series of compounds having the general formula $\text{Ba}_{10}(\text{ReO}_5)_6\text{X}_2$ where $\text{X} = \text{F}^-$, Cl^- , I^- , or CO_3^{2-} . Although the authors do not mention it, an examination of their spectra indicates the presence of a doublet band in the 900-925 wavenumber region.

Nakamura, et al. (77) observed only the 915 peak in

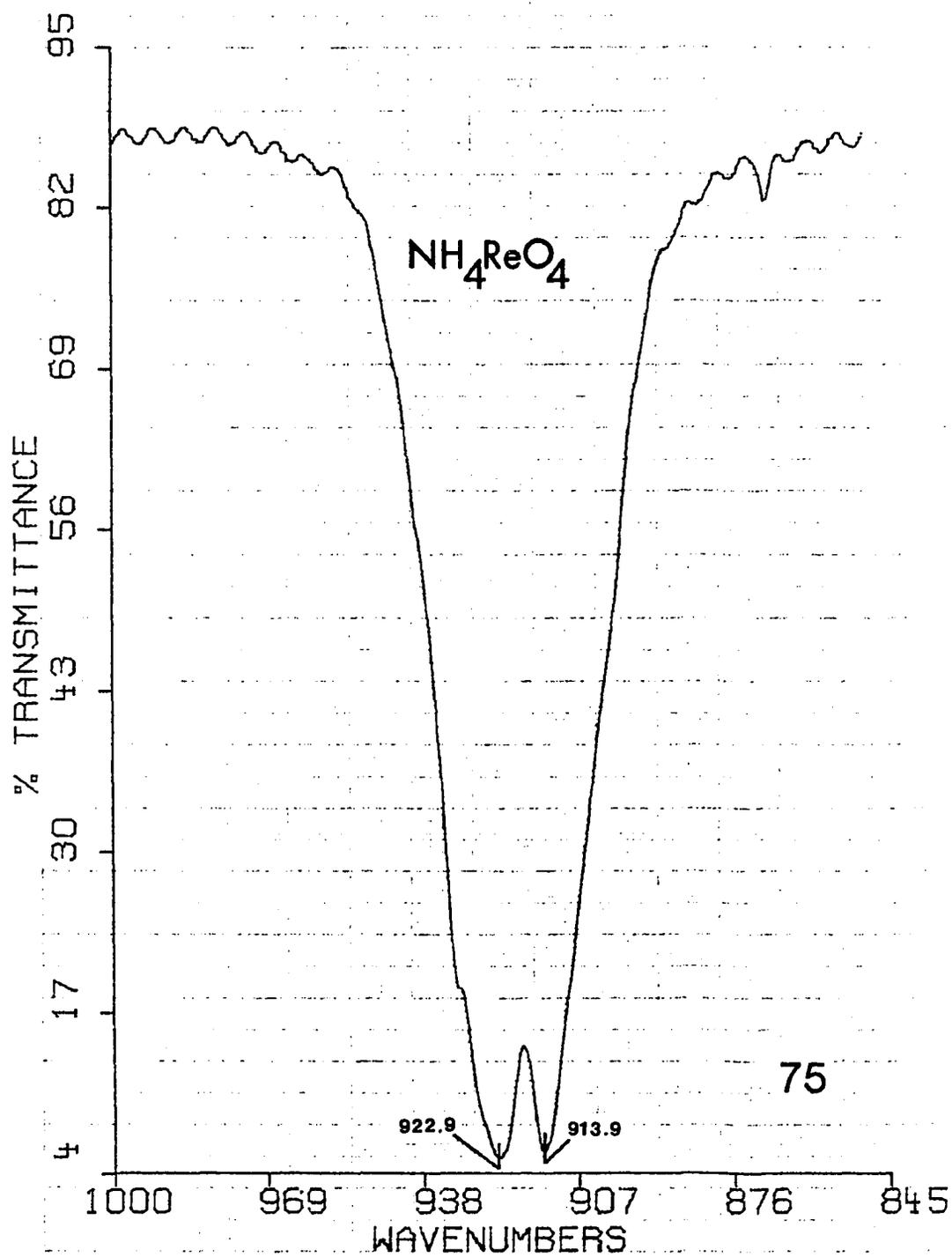
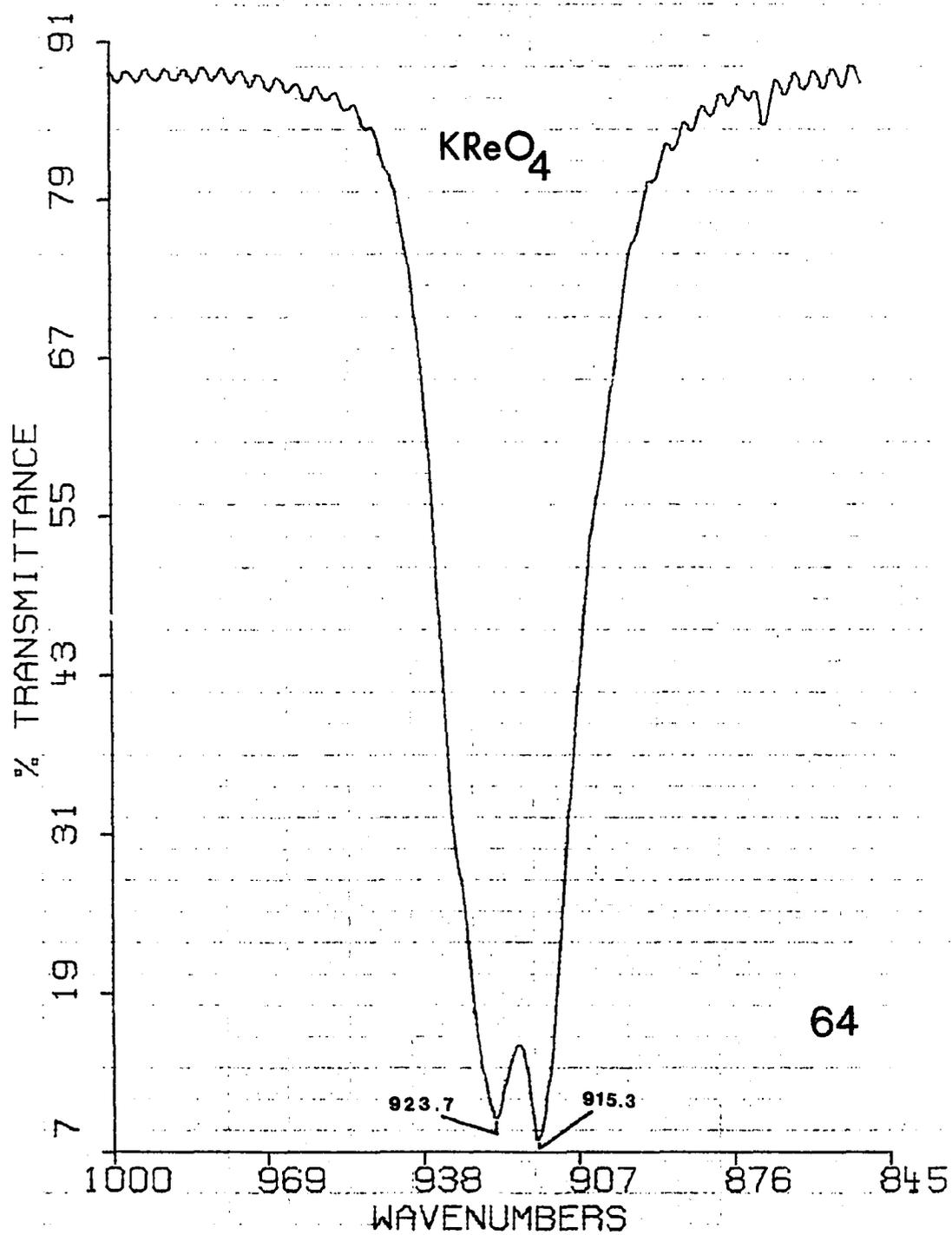


Figure III-1 Spectrum of NH_4ReO_4 in KBr pellet taken
by FT-IR (spectrum No. 75).



FigureIII-2 Spectrum of KReO_4 in KBr pellet taken by FT-IR (spectrum No. 64).

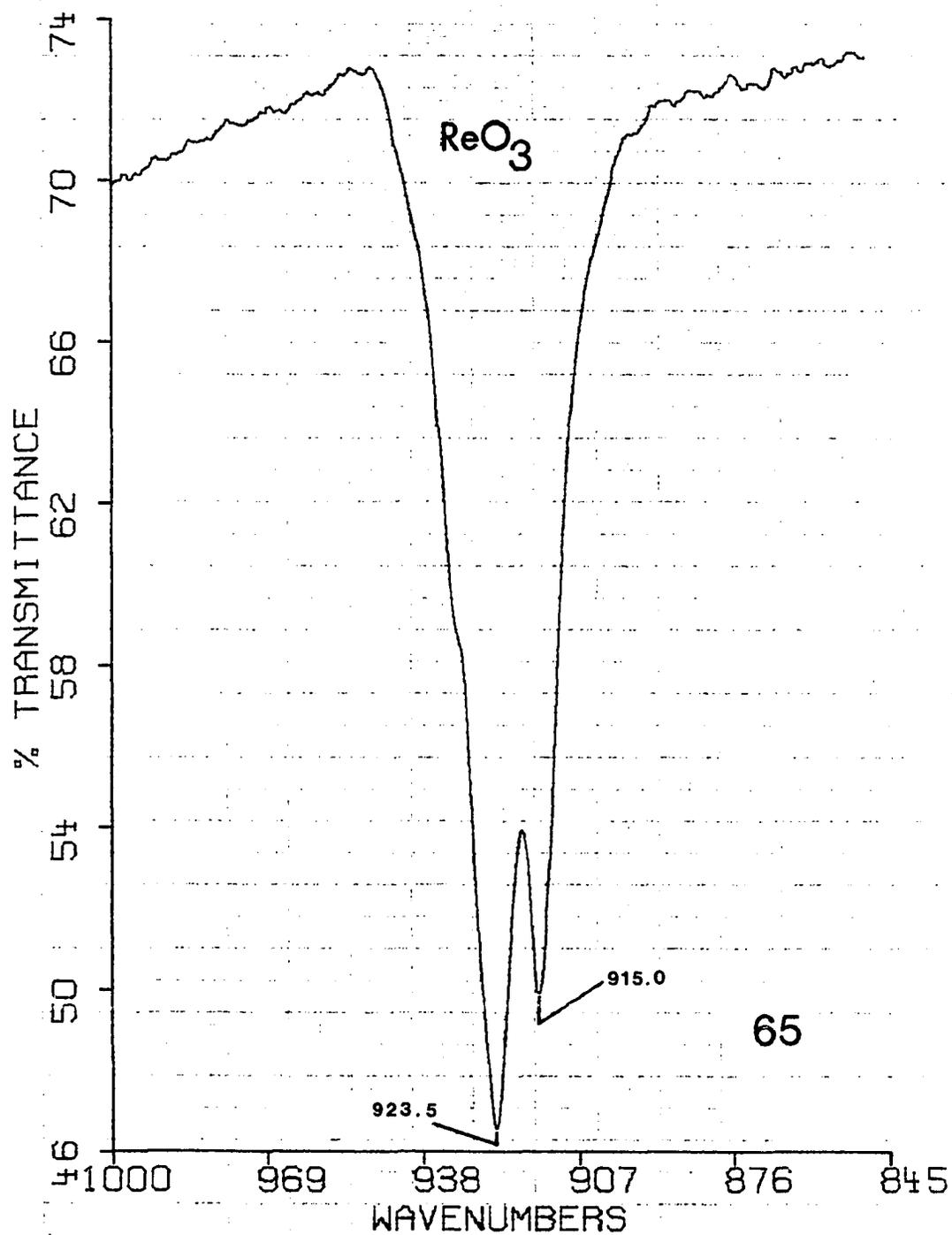


Figure III-3 Spectrum of ReO_3 in KBr pellet taken
by FT-IR (spectrum No. 65).

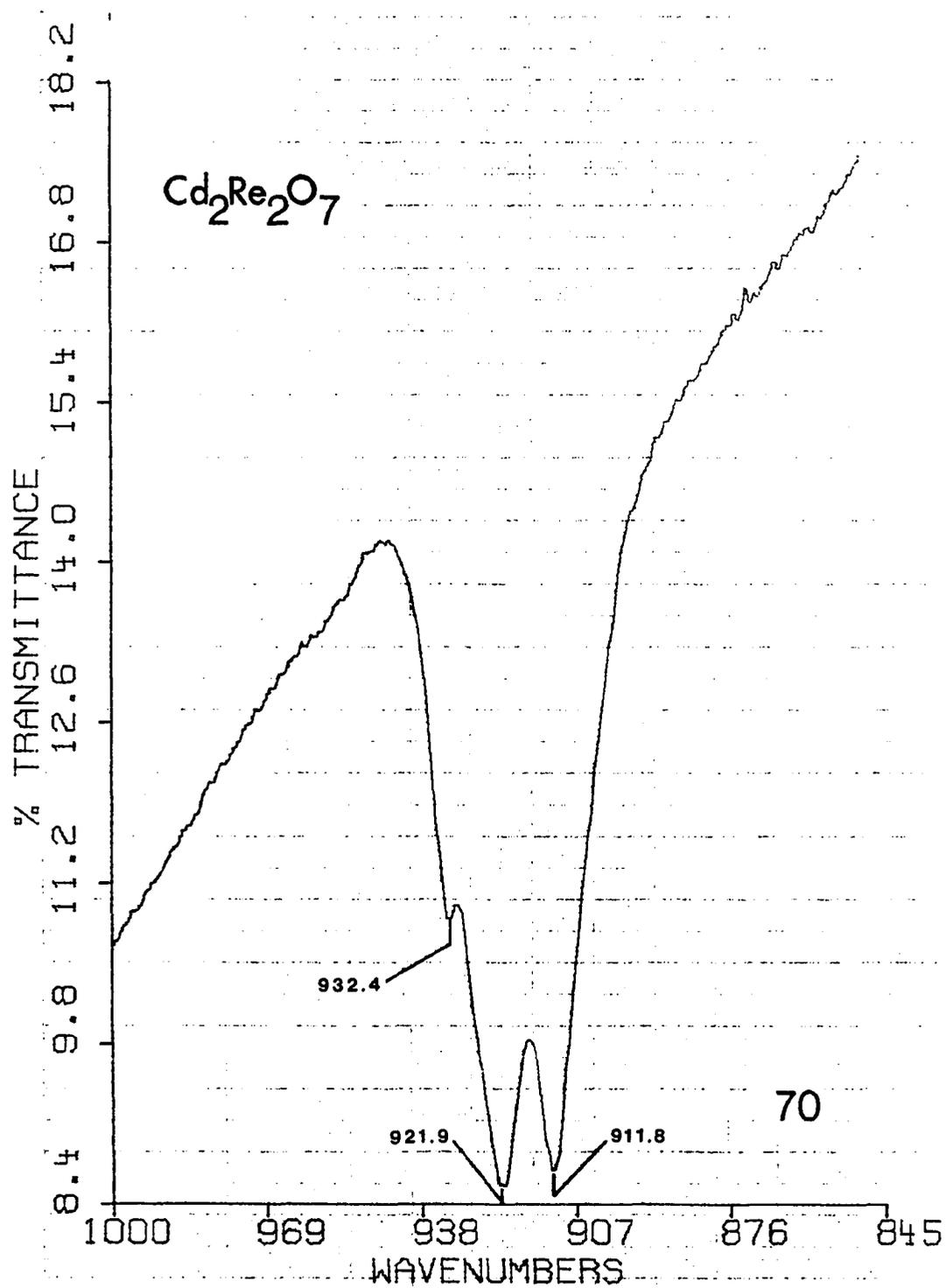


Figure III-4 Spectrum of $\text{Cd}_2\text{Re}_2\text{O}_7$ in KBr pellet taken by FT-IR (spectrum No. 70).

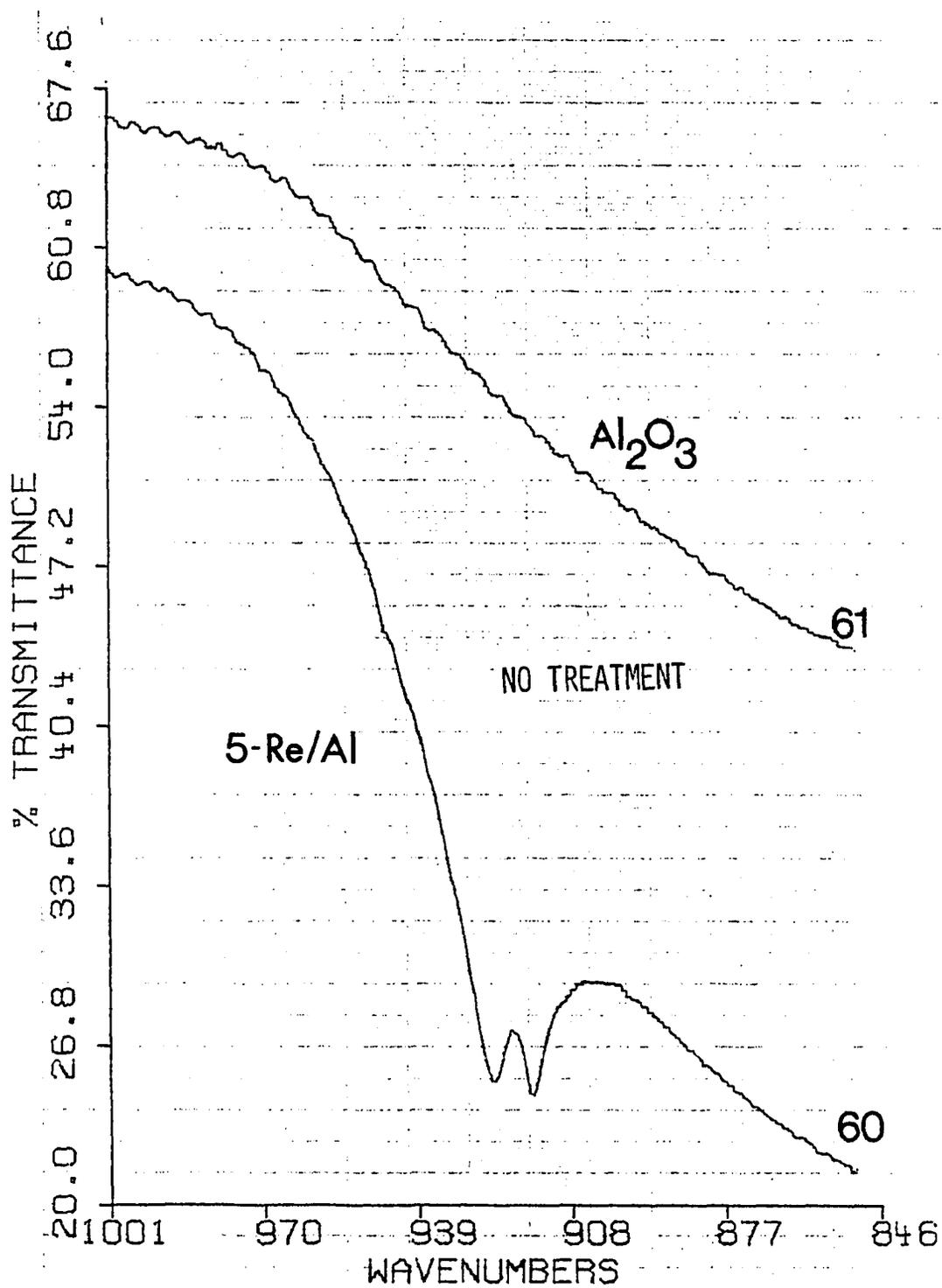


Figure III-5 Spectra of Al_2O_3 and 5-Re/Al in KBr pellets taken by FT-IR (spectra 60 and 61).

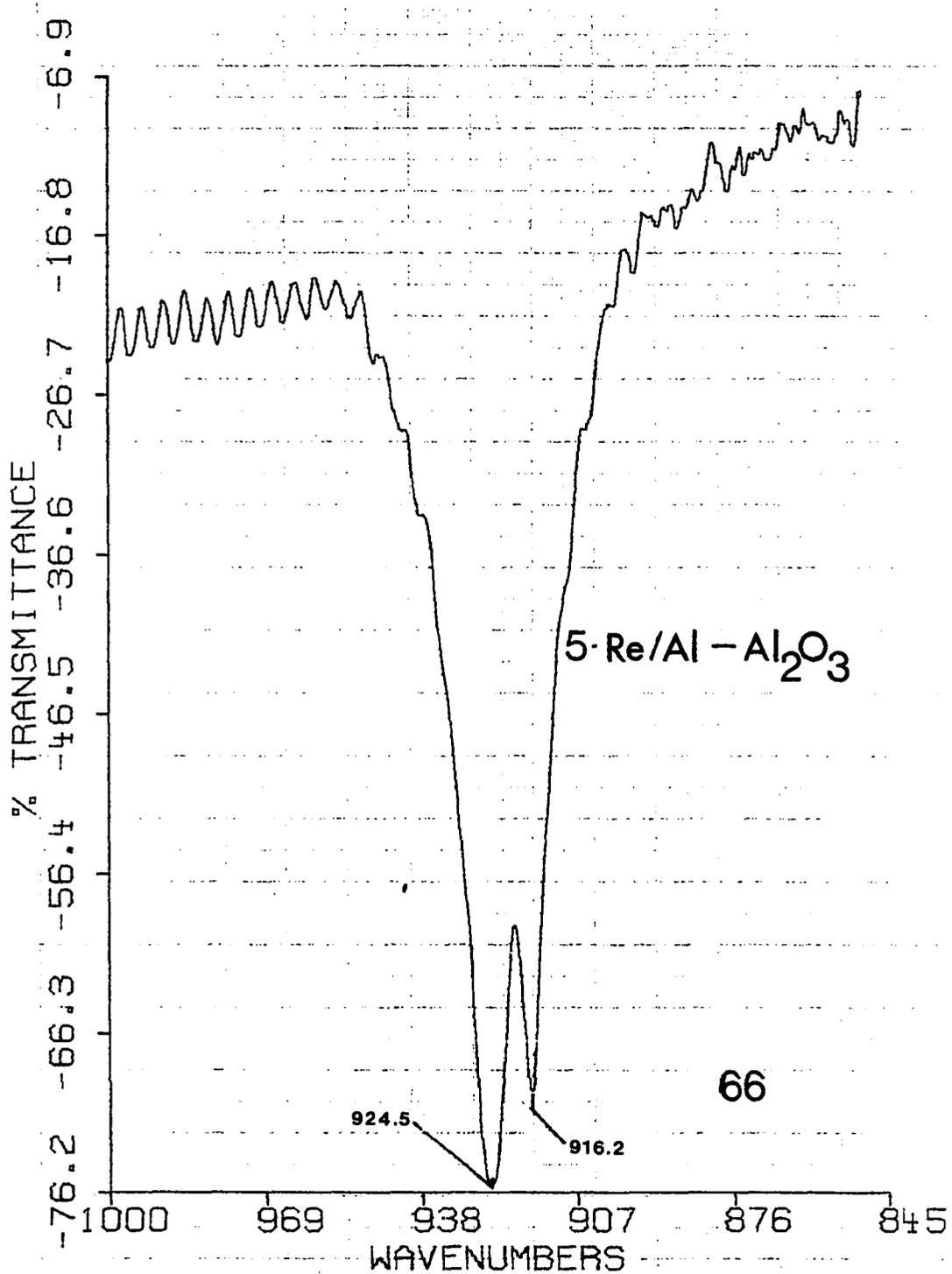


Figure III-6 Difference spectrum: 5-Re/Al minus Al₂O₃
(spectrum 60 minus spectrum 61).

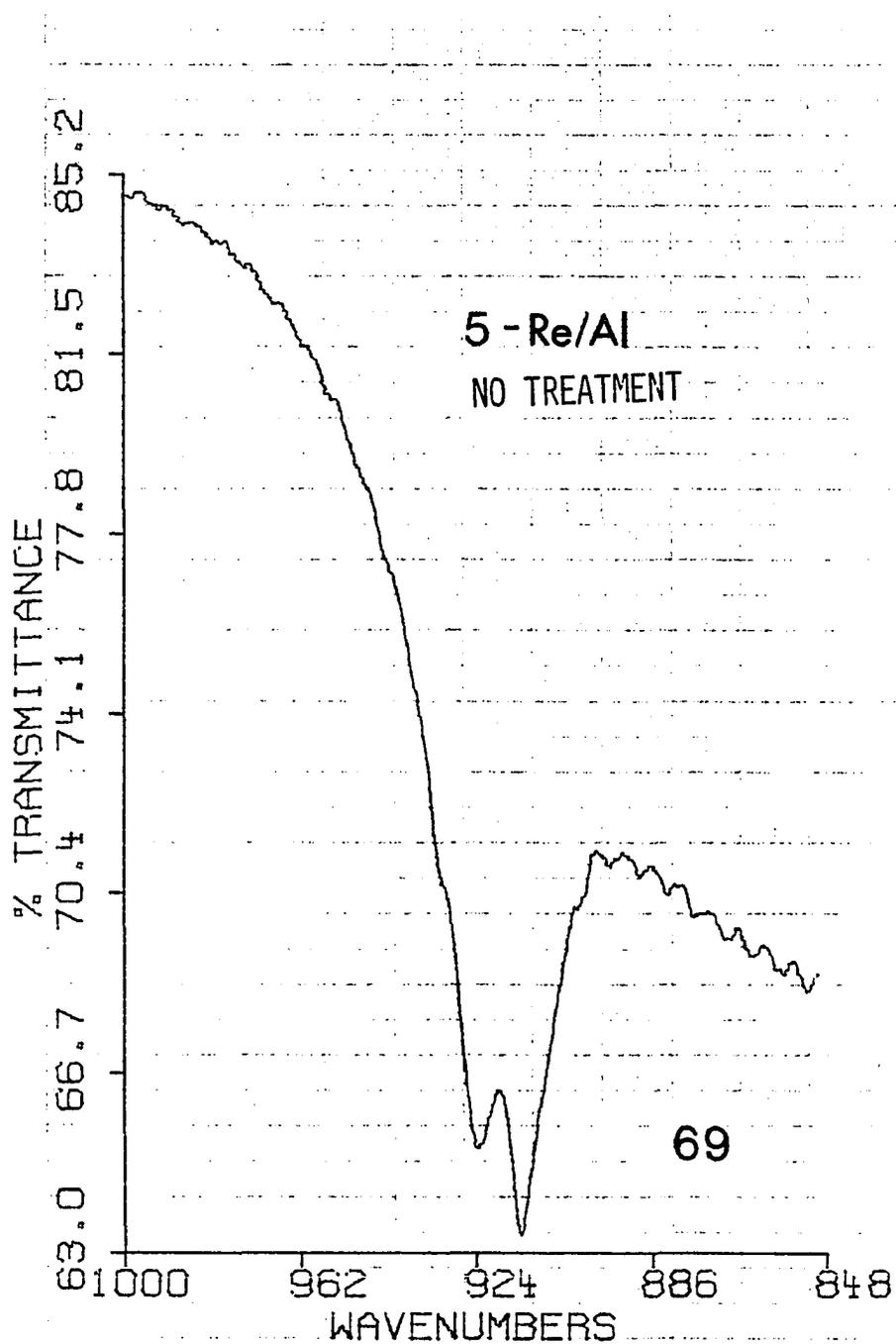


Figure III-7 Spectrum of unground 5-Re/Al, no treatment, 100-200 mesh, in KBr pellet taken by FT-IR (spectrum 69).

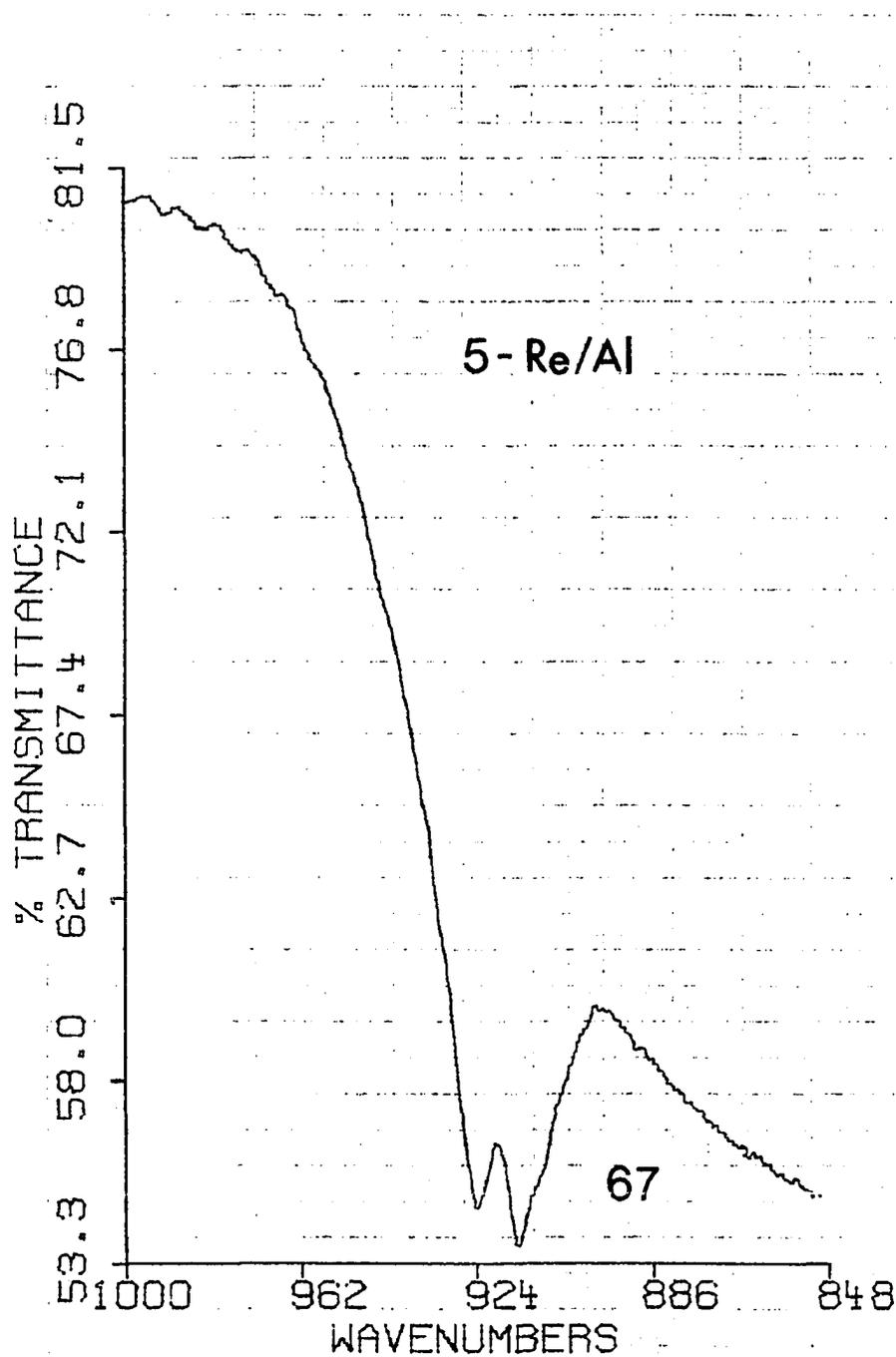


Figure III-8. Spectrum of unground 5-Re/Al, 100-200 mesh, heated in flowing O_2 at 759 K, in KBr pellet taken by FT-IR (spectrum No. 67).

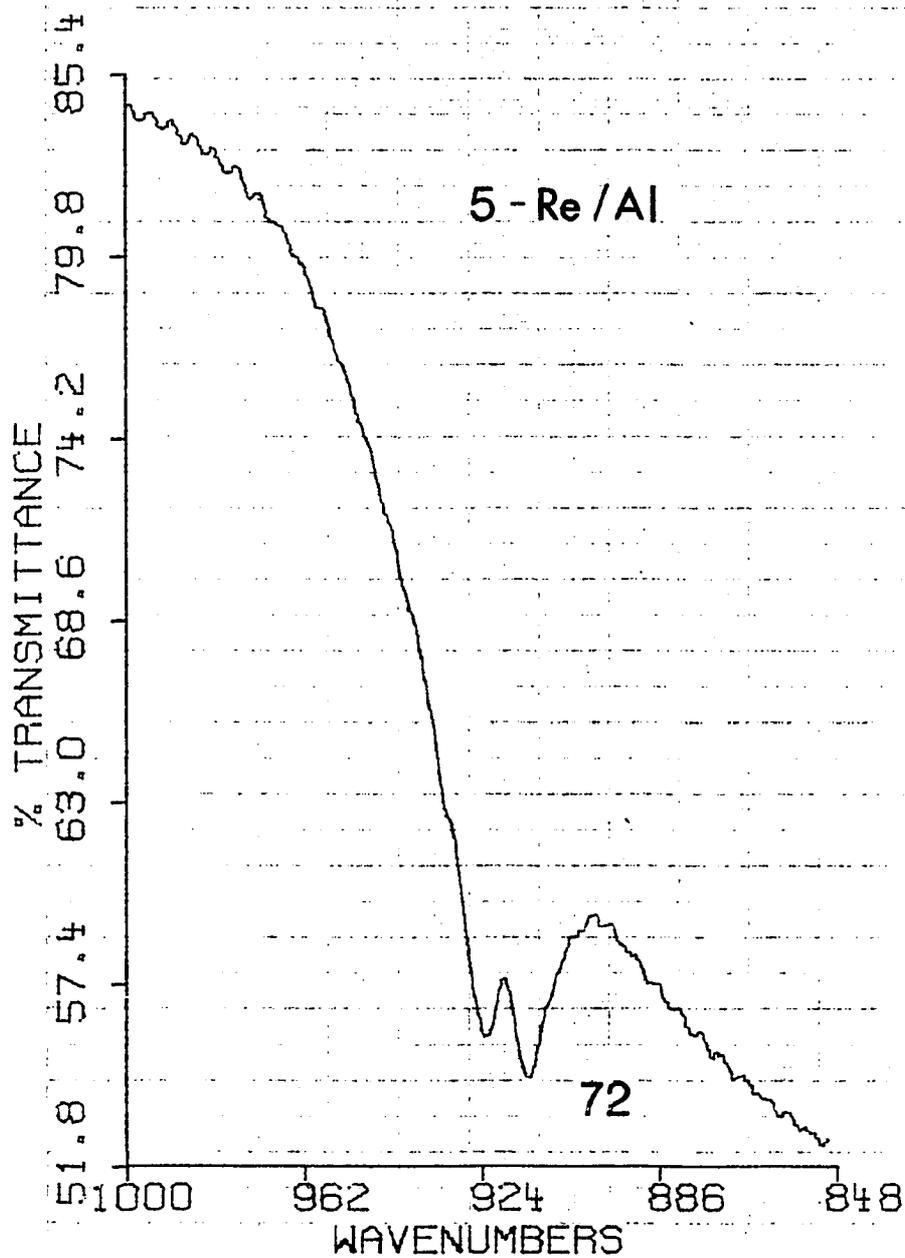


Figure III-9. Spectrum of unground 5-Re/Al, 100-200 mesh, heated in flowing O_2 followed by flowing H_2 at 759 K, in KBr pellet taken by FT-IR (spectrum No. 72).

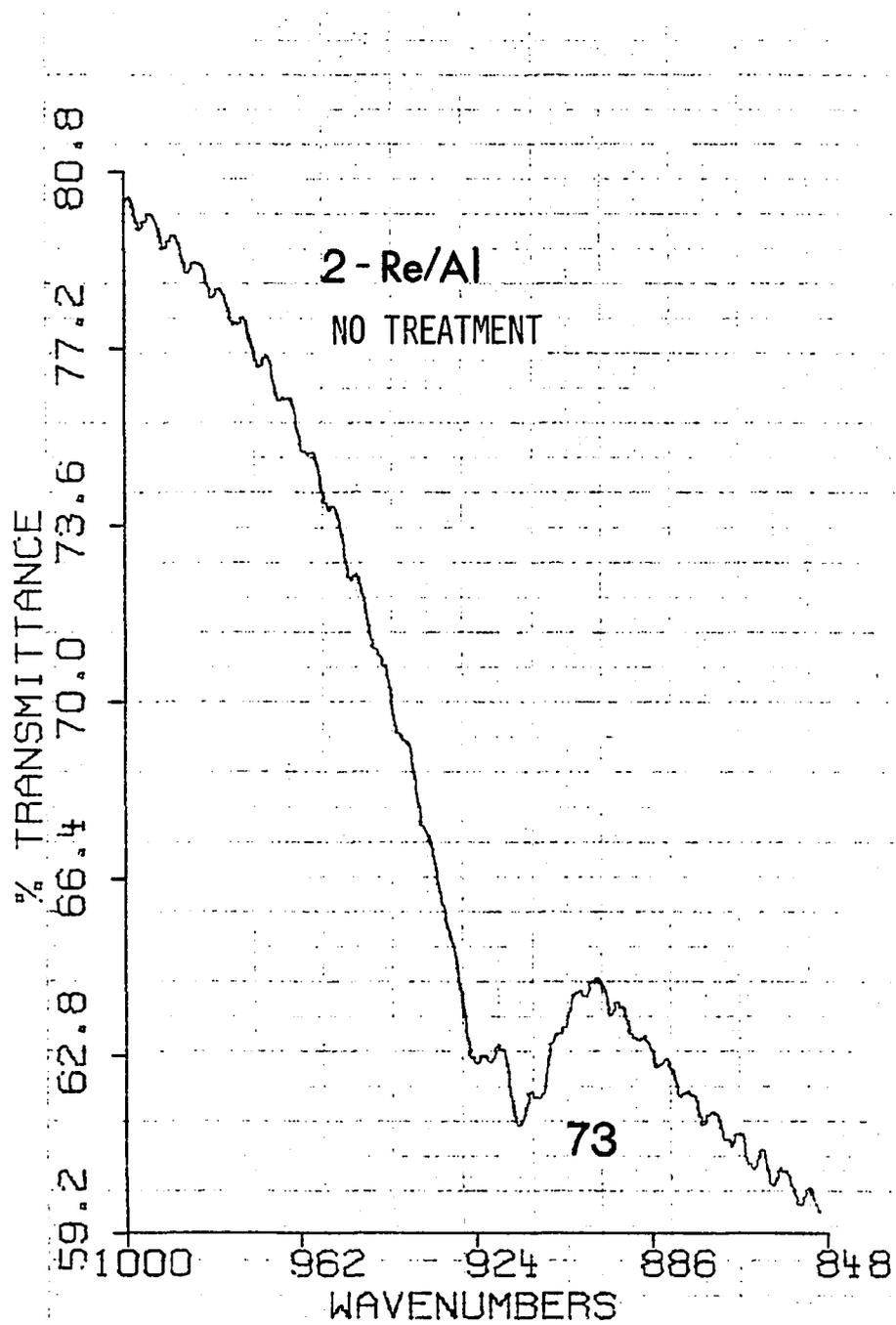


Figure III-10 Spectrum of unground 2-Re/Al, 100-200 mesh
in KBr pellet taken by FT-IR (spectrum No. 73).

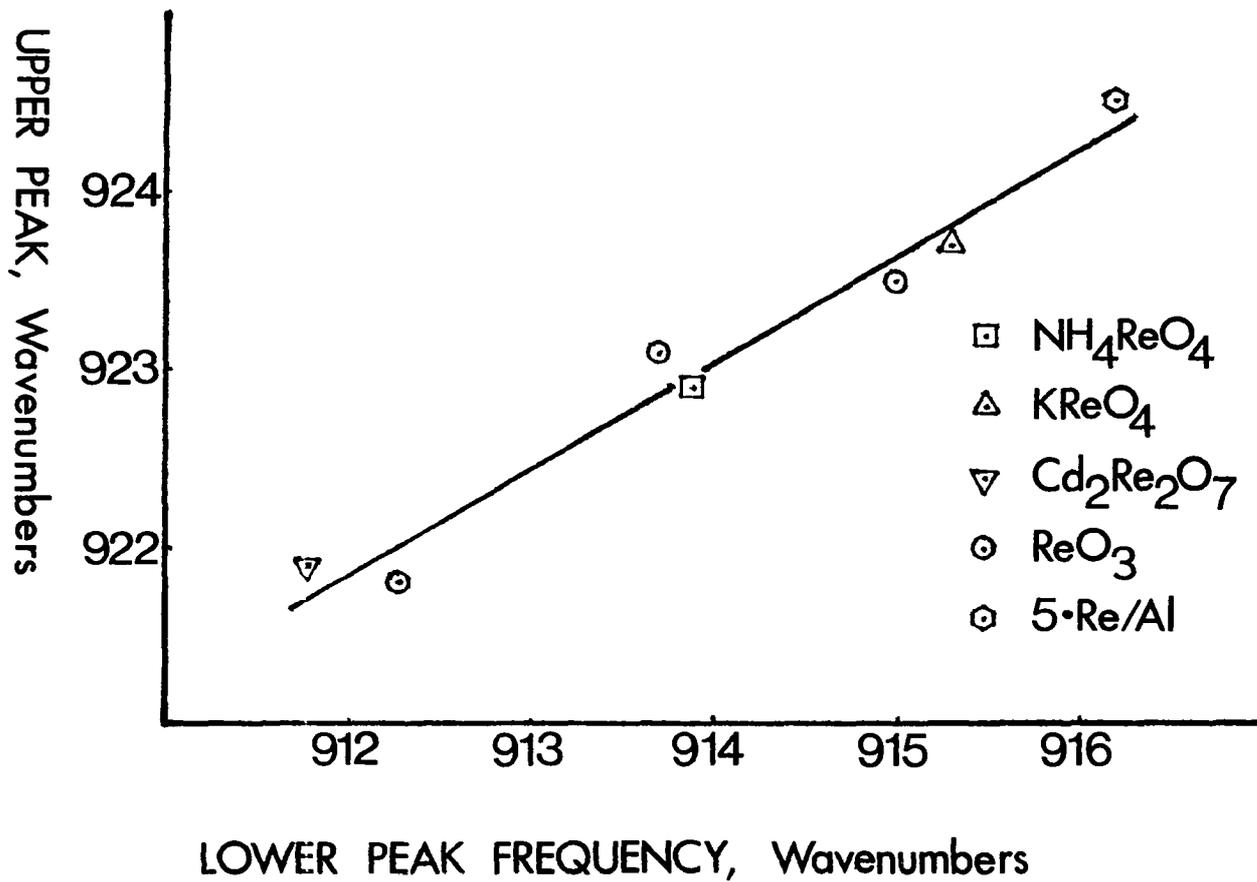


Figure III-11. The relationship between the lower and upper peaks in the 910-925 wavenumber region

Table III-1. Peak locations for the catalyst
and model compounds.

Compound	Peak Location wavenumbers	Band Width wavenumbers	Spectrum Number
5-Re/Al*	916.0, 924.2	22	66
NH ₄ ReO ₄	914.0, 922.8	35	75
KReO ₄	915.3, 923.7	29	64
ReO ₃	915.0, 923.5	24	65
Cd ₂ Re ₂ O ₇	911.8, 921.9, 932.4	31	70

*From the difference spectrum 5-Re/Al minus alumina.

NH_4ReO_4 , but observed peaks at 915 and 925 in Re_2O_7 . The 915 peak was attributed to the Re=O stretching vibration of the ReO_4^- ion. The 925 peak in Re_2O_7 was attributed to Re=O stretch in the ReO_3^+ ion. In his spectra of a 2-Re/Al catalyst, Nakamura observed only the 915 peak, while the 915 and 925 peaks were seen in spectra of his 5-Re/Al. It was concluded that only ReO_4^- was adsorbed onto the 2-Re/Al, but that Re_2O_7 was adsorbed onto the 5-Re/Al.

In the present research, the 915 and the 925 peaks were observed in all rhenium compounds, including the 2-Re/Al and the NH_4ReO_4 . Either all of these compounds contain ReO_4^- and ReO_3^+ ions or some other phenomenon accounts for the appearance of these two peaks. In further contradiction of Nakamura et al. (77), Coverdale et al. (83), using mass spectrometry, found evidence of the presence of Re_2O_7 on Re/Al catalysts with loadings of less than two atomic percent rhenium.

Ishii, et al. (84) observed a singlet band at 905 wavenumbers in a film of ReO_3 deposited on a silicon plate. Some fine structure was observed in the 905 band in the spectrum of a KBr pellet of ReO_3 . The fine structure was attributed to the presence of traces of other forms of rhenium oxide.

Particle size had an effect on the location and appearance of the 910-925 band. This effect is illustrated by four spectra of ReO_3 shown in Figure III-12. Band shape

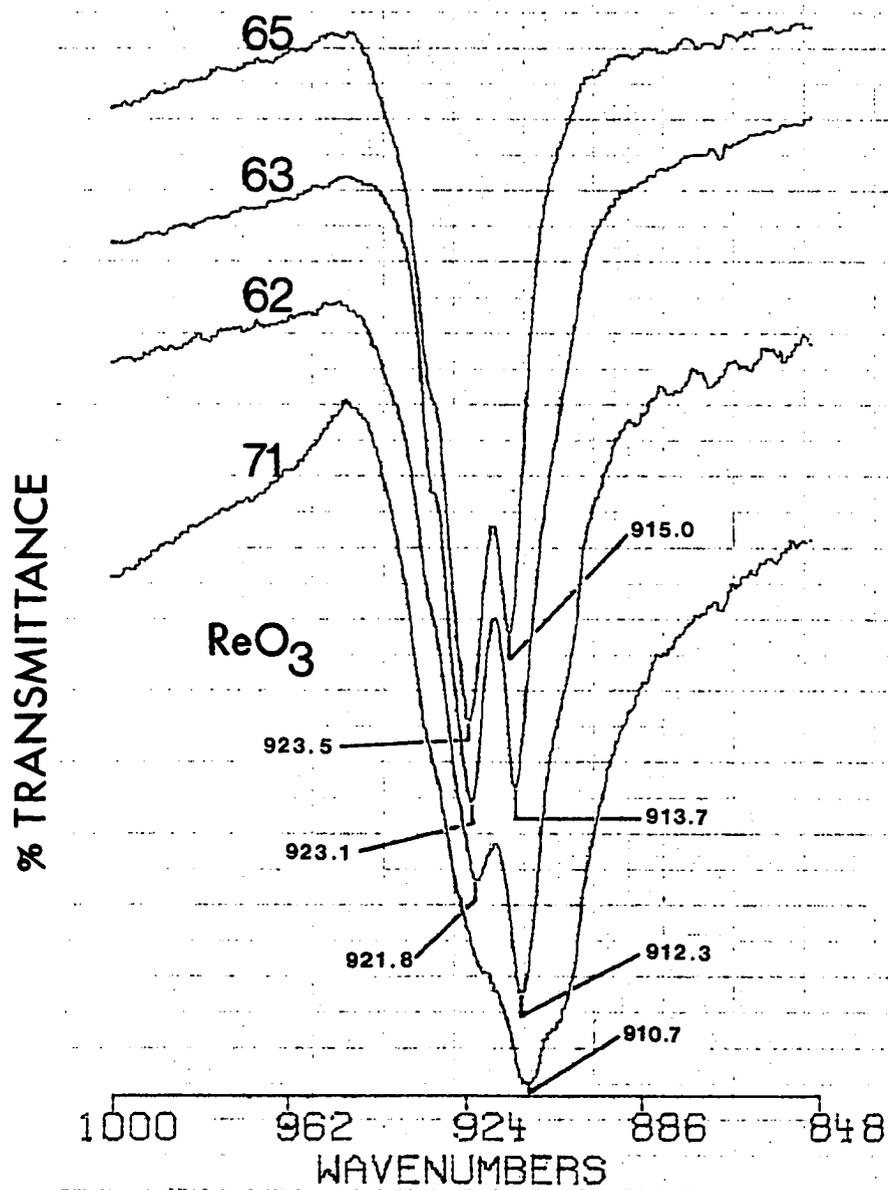


Figure III-12 Four spectra of ReO_3 are shown.

can be effected by particle size, a phenomenon known as the Christiansen effect. At the higher frequency edge of the band there is a greater transmittance than at the lower frequency edge. This distortion, a qualitative measure of particle size, can be minimized by a reduction of the particle size (85). Spectrum No. 71 of ReO_3 shows a great deal of distortion indicating a relatively larger particle size than does spectrum No. 65, which shows very little distortion. In these spectra of ReO_3 , the location of the peak maxima tended to increase in frequency as the Christiansen effect decreased. The higher frequency peak of the doublet increased in size relative to the lower frequency peak as the frequency increased. Examination of spectra of the other model compounds and catalysts show little evidence of band distortion.

In an attempt to better understand the nature of the rhenium compounds, samples of ReO_3 and KReO_4 were examined using x-ray photoelectron spectroscopy (XPS). Three types of samples were studied: untreated from the reagent bottles, ground with mortar and pestle, and ground and mixed with KBr. ReO_3 , normally in the form of small, red crystals, remained red after grinding, but it turned blue when mixed with KBr.

Results of the XPS investigation are summarized in Table III-2. XPS spectra of the $\text{Re}4f$ electrons in ReO_3 and KReO_4 are shown in Figures III-16 through III-21. Shpiro

 Table III-2. Results of the x-ray photoelectron
 spectroscopic investigation.

Sample Description	Binding ^a Energy, eV	Oxidation ^b State	Relative Surface Coverage
1. ReO ₃ - untreated	45.4	6	68.4
	43.2	4	31.6
2. ReO ₃ - ground ^c	47.1	7	16.7
	45.5	6	30.1 (48.2)
	43.1	4	53.2 (51.8)
3. ReO ₃ - ground and mixed with KBr	45.9	6	47.2
	43.1	4	52.8
4. KReO ₄ - untreated	46.7	7	100.
5. KReO ₄ - ground	46.3	7	100.
6. KReO ₄ - ground and mixed with KBr	46.3	7	100.

 Notes:

a. Binding energies are given in electron volts (eV) and are referenced to Au4f as 84.0 eV.

b. Oxidation state determinations based upon the work of Shpiro et al. (86) and on material supplied by the manufacturer of the spectrometer.

c. Numbers in parantheses are relative surface coverages Re(VI) and Re(IV) if Re(VII) was not present.

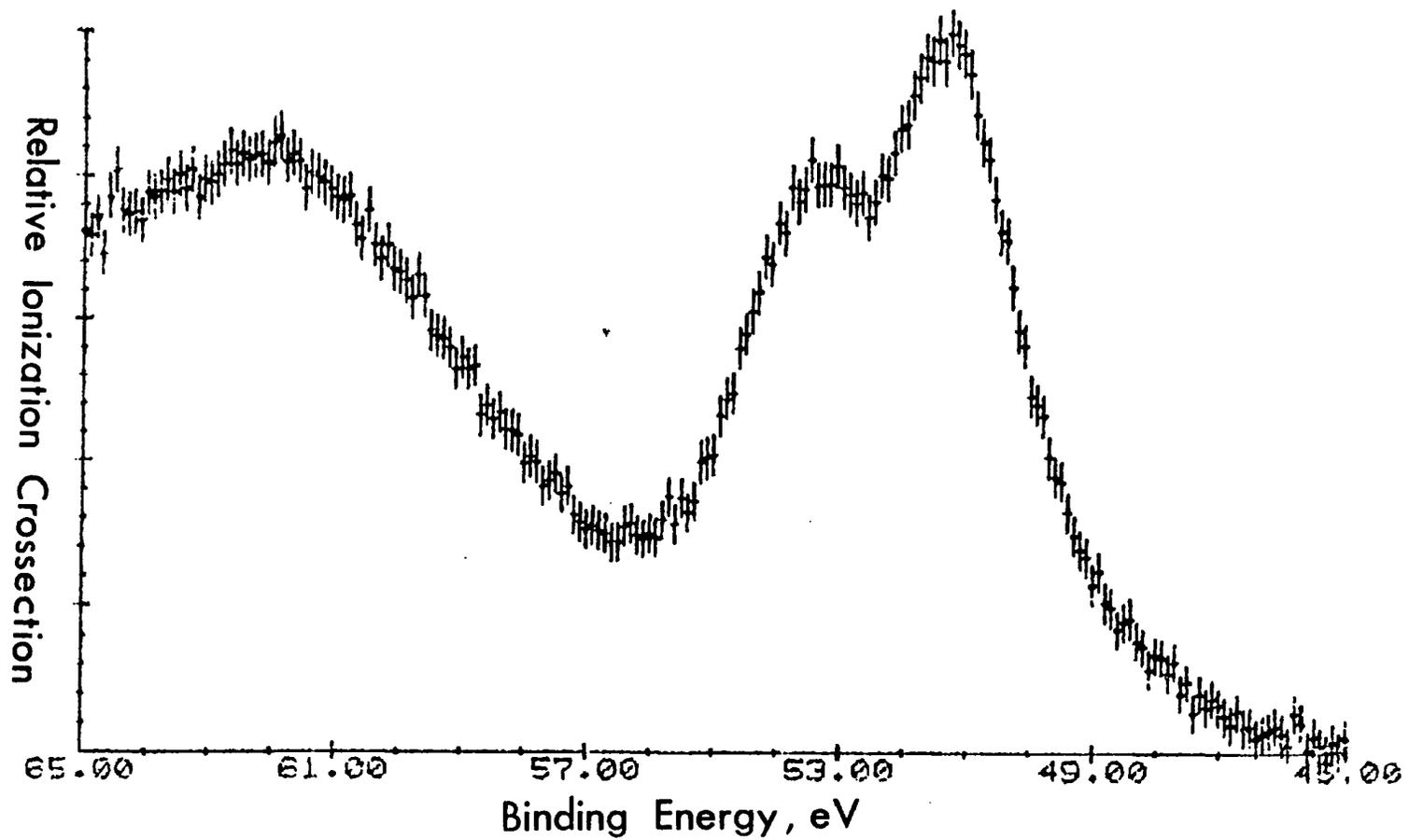


Figure III-13. The Re4f band in the XPS spectrum of untreated KReO_4 is shown. When referenced to the Au4f binding energy of 84.0 eV, the binding energies shown above must be reduced by 4.72 eV.

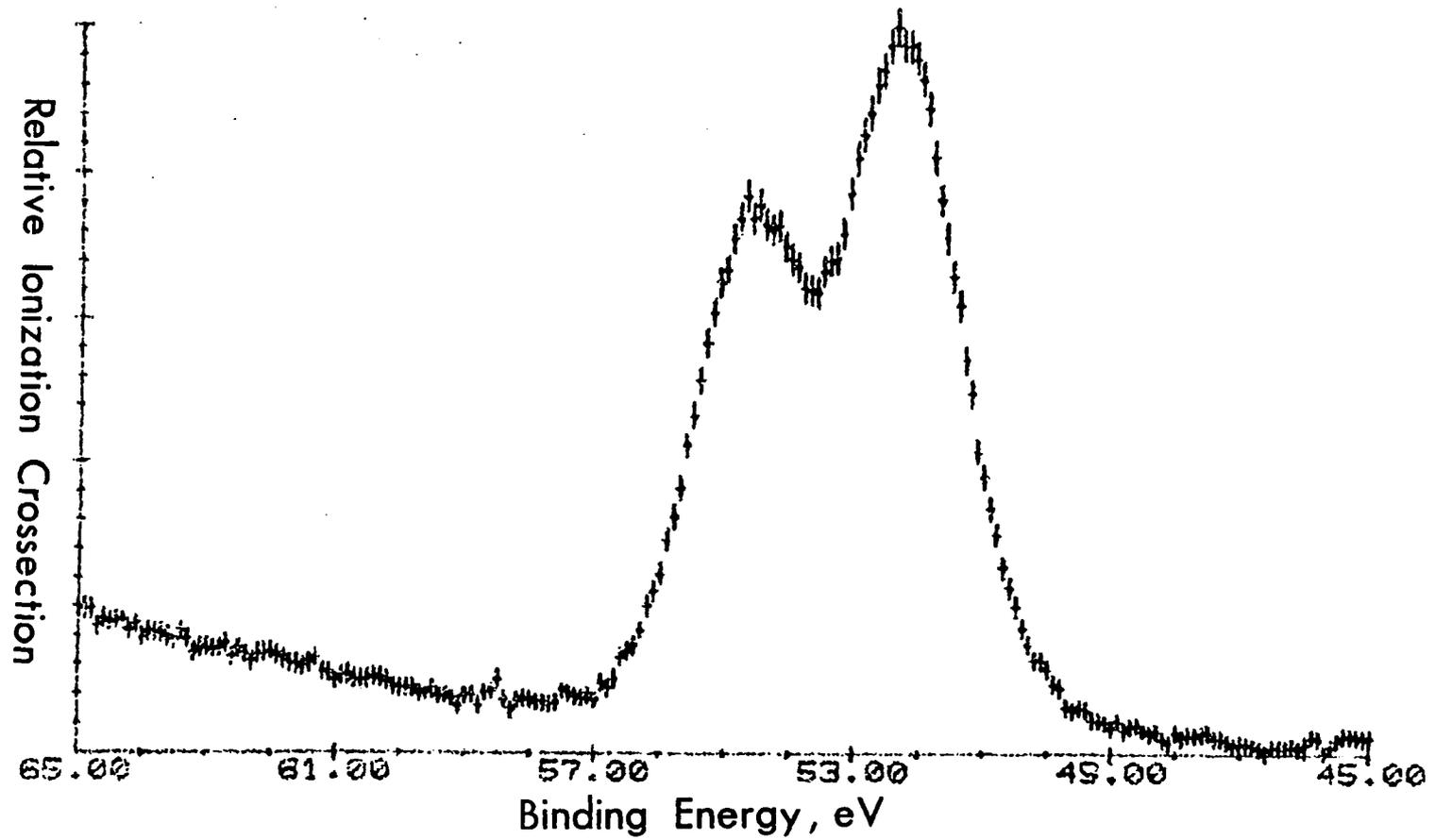


Figure III-14. The Re4f band in the XPS spectrum of ground KReO₄ is shown. When referenced to the Au4f binding energy of 84.0 eV, the binding energies shown above must be reduced by 5.82 eV.

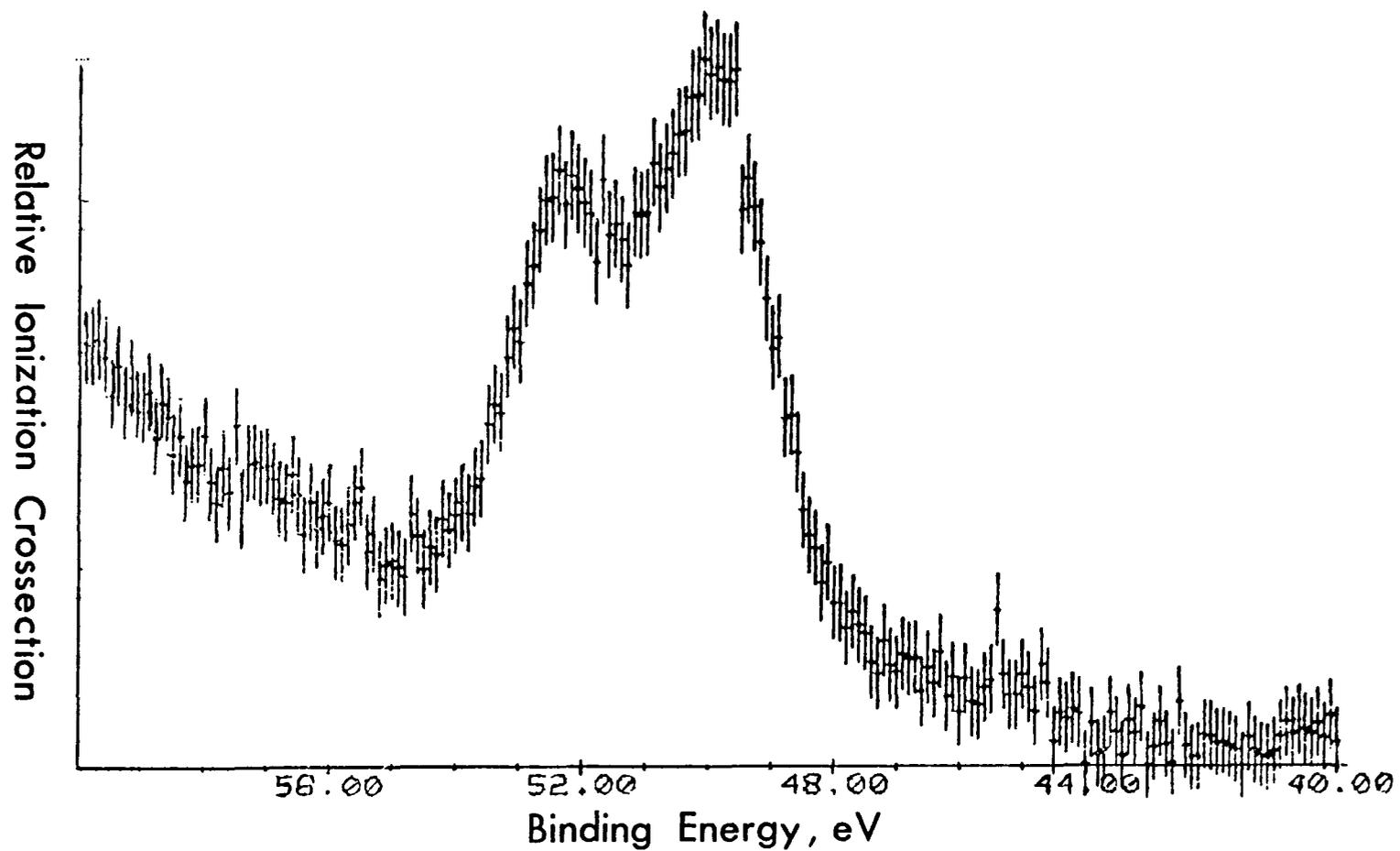


Figure III-15. The Re4f band in the XPS spectrum of ground KReO_4 mixed with KBr is shown. When reference to the Au4f binding energy of 84.0 eV, the binding energies shown above must be reduced by 3.63 eV.

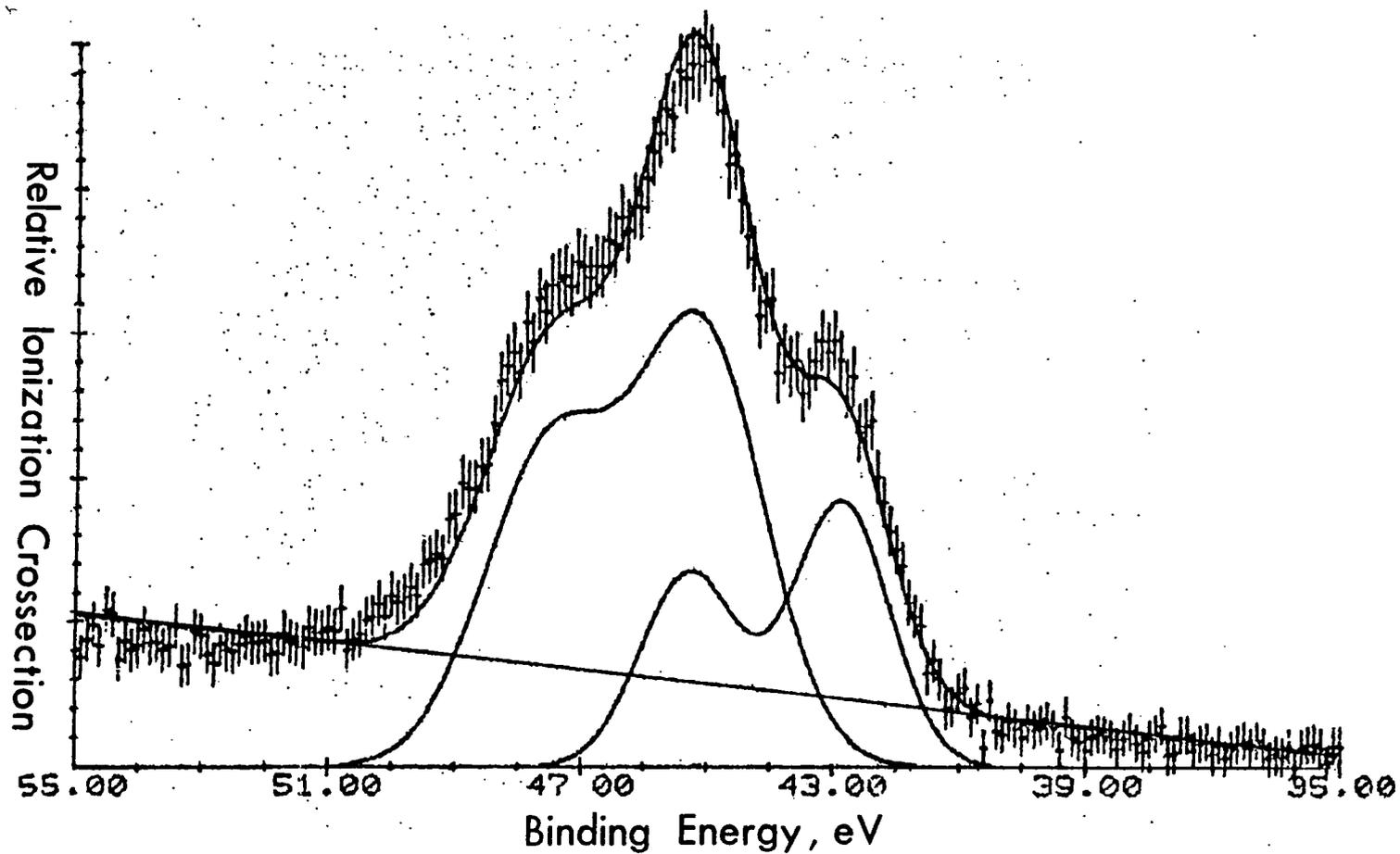


Figure III-16. The $\text{Re}4f$ band in the XPS spectrum of untreated ReO_3 is shown with spectral deconvolution. The binding energies shown must be increased by 0.31 eV with reference to $\text{Au}4f$.

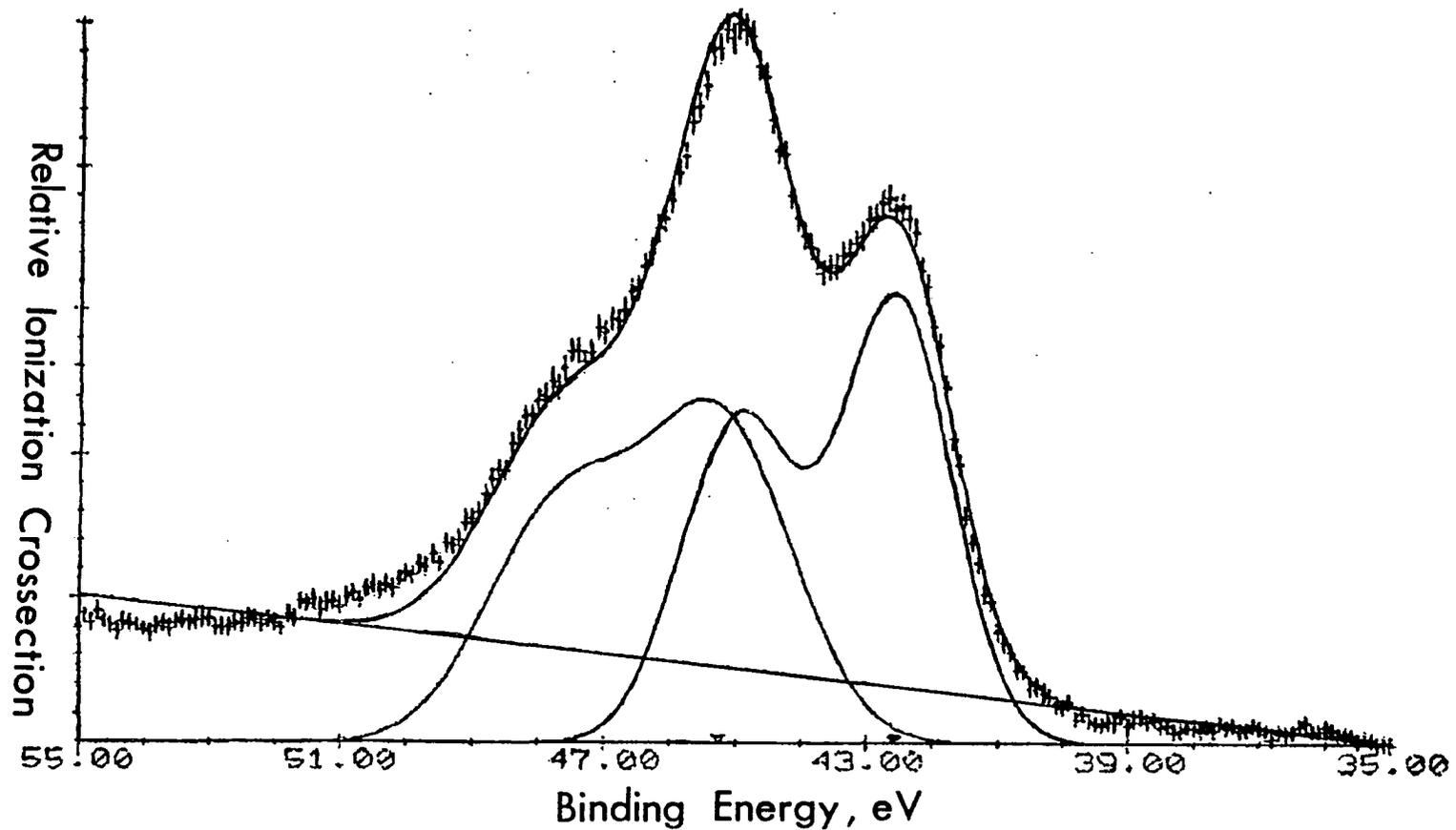


Figure III-17. The Re4f band in the XPS spectrum of ground ReO₃ is shown with a two band spectral deconvolution. The binding energies shown must be increased by 0.45 eV with reference to Au4f.

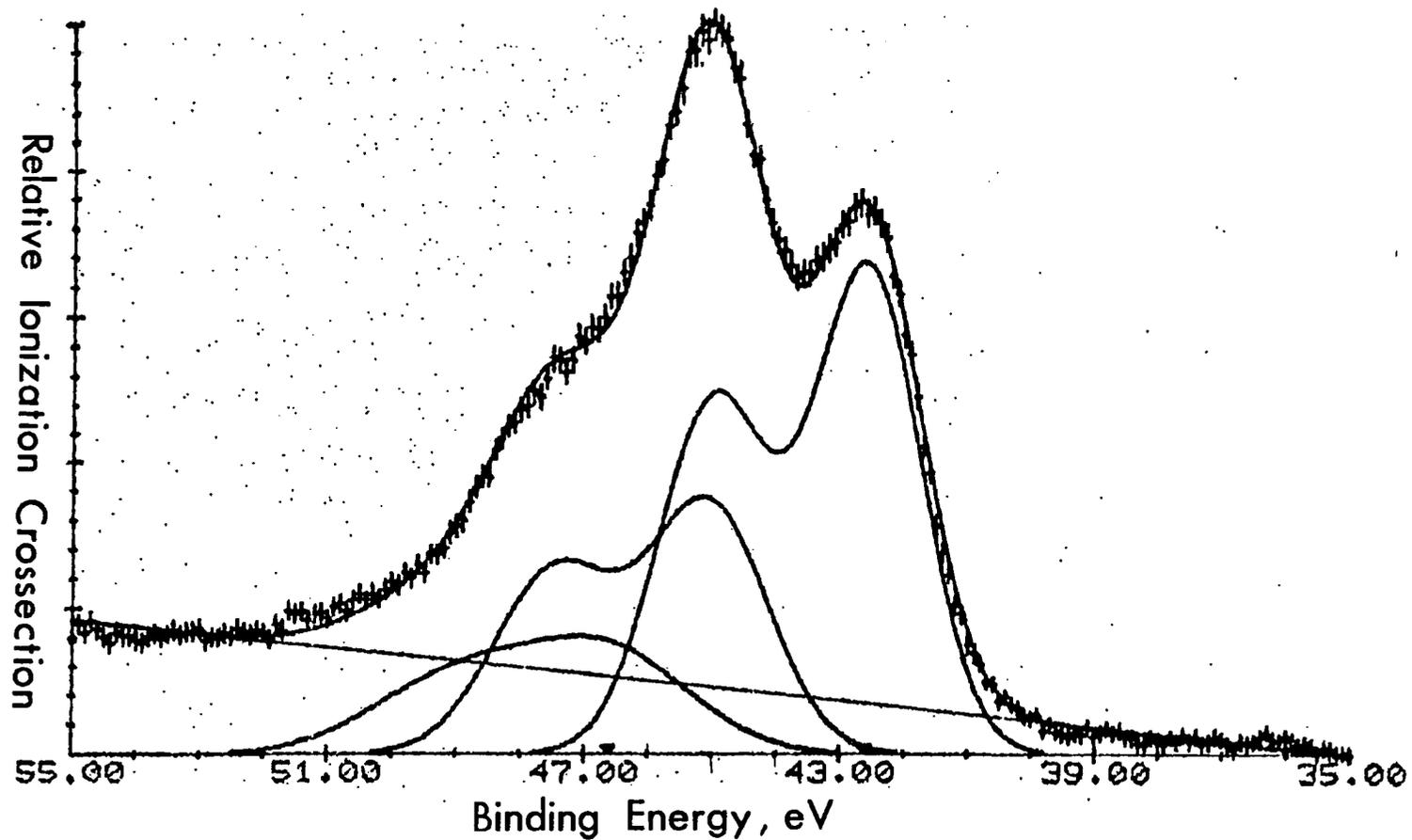


Figure III-18. The Re4f band in the XPS spectrum of ground ReO_3 is shown with a three band spectral deconvolution. The binding energies shown must be increased by 0.45 eV with reference to Au4f.

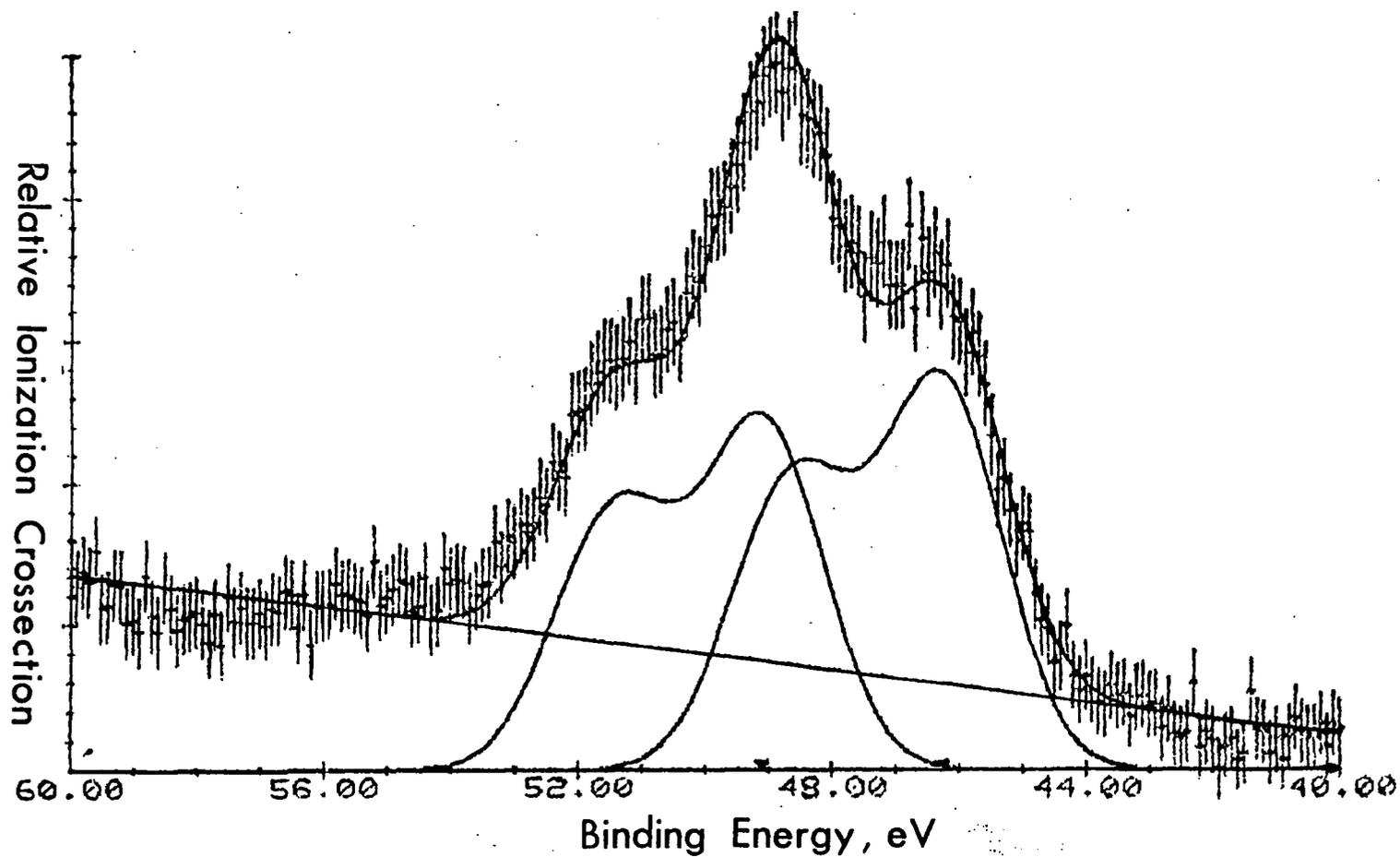


Figure III-19. The Re4f band in the XPS spectrum of ground ReO_3 mixed with KBr is shown with spectral deconvolution. The binding energies shown must be decreased by 3.2 eV with reference to Au4f.

et al (86) reports the binding energy for the Re4f electron in ReO_3 as 44.3 eV, but this investigation found it to be near 45.5 eV. Shpiro says that his ReO_3 was partially oxidized, but it is possible that he meant it had been partially reduced (87). It must be noted that during this investigation, duplicate samples were not examined. The interpretation of the XPS spectra is therefore tentative and not totally unambiguous. Much more work needs to be done to verify the XPS results. More than one oxygen species was identified in the ReO_3 spectra but no attempt was made to further identify them.

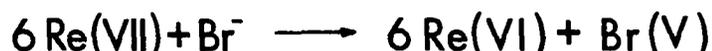
Only one form of rhenium, Re(VII), was found in the KReO_4 samples, but at least two forms, Re(VI) and Re(IV), and possibly a third, Re(VII), were found in the various samples of ReO_3 . It appeared that some degradation of the ReO_3 had occurred over time while it was in the bottle, since approximately 32% of the rhenium was in the 4+ state rather than in the expected 6+ state (Table III-2).

In the sample of ground ReO_3 it is possible that Re(VII) was also present depending on whether two or three bands were used to deconvolute the ground ReO_3 spectrum. There was a reasonably good fit whether two or three bands were used in the deconvolution (Figs III-17 and III-18). If Re(VII) was not present, it appears that the grinding merely increased the extent of degradation of the ReO_3 . The amount of Re(IV) increased from 31.6% in the unground

sample to 51.8% in the ground ReO_3 and mixing the ground ReO_3 with KBr had little effect on the relative amounts of Re(VI) and Re(IV).

If, however, Re(VII) was present in the sample of ground ReO_3 , it is possible that some kind of disproportionation occurred with 24.4% of the original Re(VI) becoming Re(VII) and 31.6% of the original Re(VI) becoming Re(IV). It should be noted that these numbers do not yield an overall charge balance. The deconvolution process might have introduced some uncertainty in the relative magnitude of the three bands. When the ground ReO_3 was then mixed with KBr, the Re(VII) formed during the grinding process was no longer present and the amount of Re(VI) had increased proportionately.

It seems possible that some solid state reaction could have taken place between the Re(VII) and the bromide ions. Wells (88) points out that such solid state reactions are possible between surface atoms. XPS is a technique that examines only the surface species. One possible reaction on the surface could have been:



The reaction as written is possible based on a Gibbs free energy change, $\Delta G = -2.25$ kcal, calculated using electrochemical tables (89). If this reaction took place, there should be evidence of Br(V) in the XPS spectra. An

examination of the bromine spectra shows two species: Br^- and a possible BrO_3^- (Fig III-20).

In-situ Investigation

First, the results from pyridine adsorption will be discussed. Bands (90 - 93) observed after Py adsorption were: 1050-1070 (18a mode), 1140-1150 (15 mode), 1220 (9a mode), 1440-1450 (19b mode), 1490 (19a mode), and 1580-1625 (8a and 8b modes). The band in the 1580-1625 region was complex and the instrument resolution did not allow individual modes to be distinguished.

Pyridine was adsorbed onto alumina and 5-Re/Al samples that had been calcined in oxygen at 693 K. Spectra of these samples show that the 19b mode on the 5-Re/Al is at a slightly higher frequency than on the alumina. Peaks were seen in the spectra of alumina at 1580 wavenumbers whereas the corresponding peaks were not seen in the spectra of 5-Re/Al. The band in the region of 1600 wavenumbers ranged from 1570 to 1620 wavenumbers in the alumina spectra and from 1588 to 1630 wavenumbers in the 5-Re/Al spectra. These higher frequencies may indicate higher Lewis acid strength on the calcined 5-Re/Al samples.

Calcined alumina samples were pretreated with hydrogen in experimental series 10C and with carbon monoxide in series 10D. The calcined 5-Re/Al catalyst was pretreated with hydrogen in series 9H and with carbon

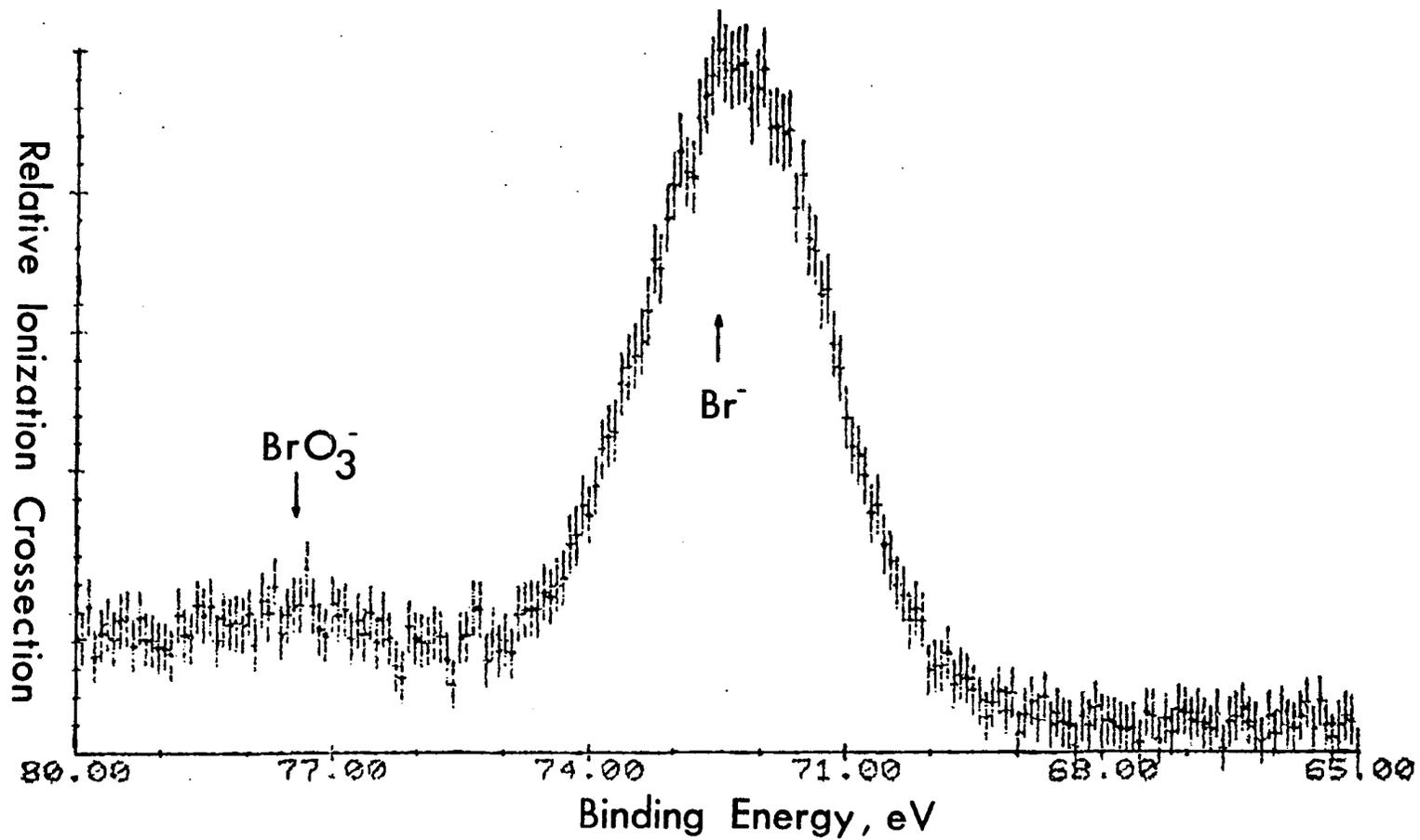


Figure III-20 The Br3d band in the XPS spectrum of ground ReO_3 mixed with KBr is shown.

monoxide in series 9I. The 5-Re/Al catalyst turned black after high temperature reduction whereas the alumina remained white. A summary of the spectra from these four series of experiments is in Figures III-21 and III-22. The appearance of peaks in the regions of 1440 and 1490 wavenumbers (LPy) indicate the presence of Lewis acidity on the alumina and on the 5-Re/Al. Evidence was not found in any of the spectra of a band in the region of 1550 wavenumbers indicative of Bronsted acidity.

When evacuated up to 523 K, the 19b peaks (1450 wavenumber region) in the spectra of alumina after hydrogen pretreatment increased in frequency by two wavenumbers and by four wavenumbers with carbon monoxide pretreatment. The corresponding peak in the spectra of 5-Re/Al increased by 12 wavenumbers with hydrogen pretreatment and by six wavenumbers with carbon monoxide pretreatment. According to Knozinger (93), increasing band frequency can be an indication of increasing bond strength. The previous numbers were obtained through some interpolation and might be subject to experimental error (Fig. III-23). As stated in the methods section, there was a possible 4.5 wavenumber uncertainty in the determination of frequency when using the grating spectrometer. The changes in the 19b peak of 5-Re/Al were larger than the frequency uncertainty while those of alumina were less than the 4.5 wavenumber uncertainty.

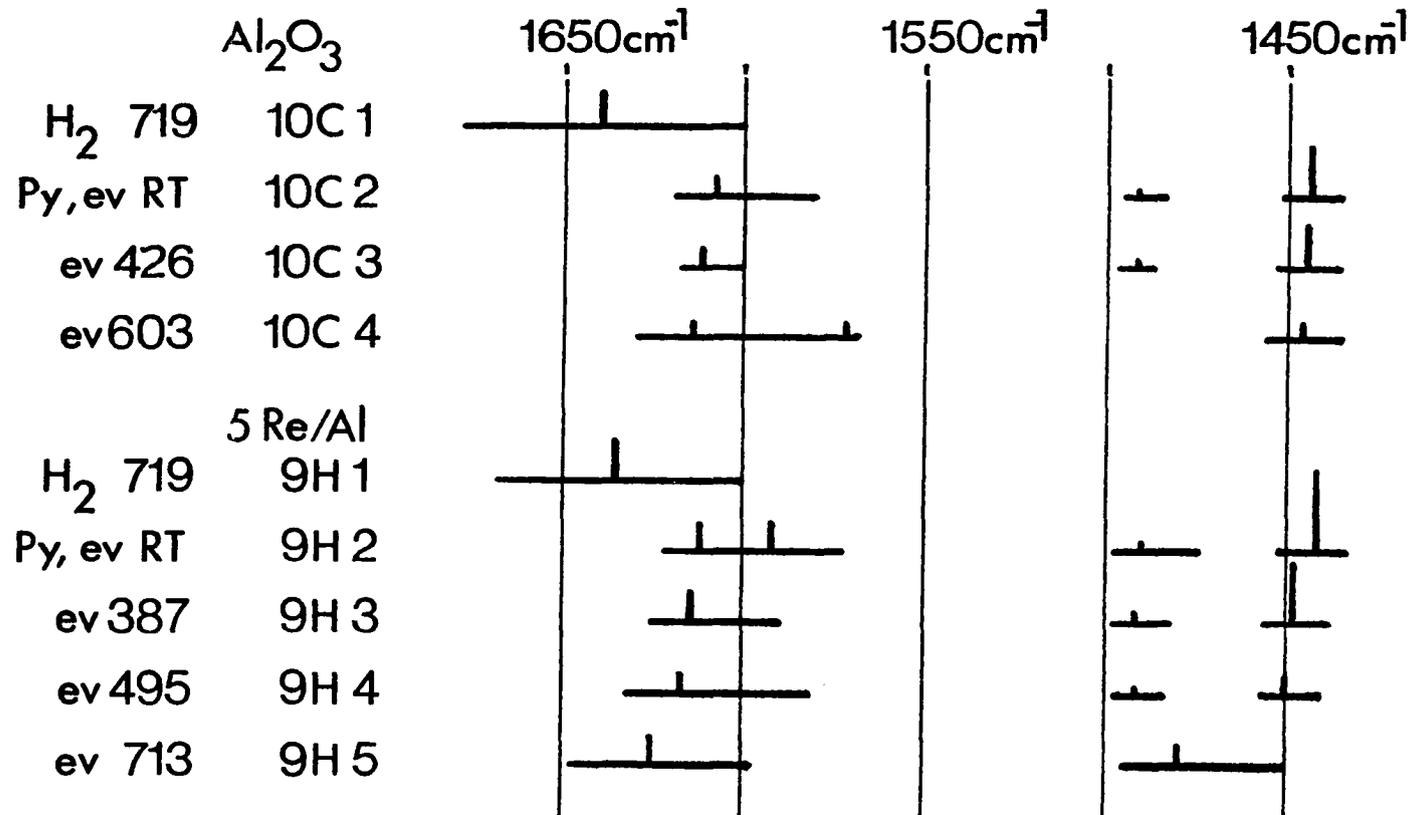


Figure III-21. The effects of hydrogen pretreatment on the adsorption and desorption of pyridine are shown. The verticle lines indicate peak locations and relative transmittance and the horizontal lines indicate bandwidth at half peak height.

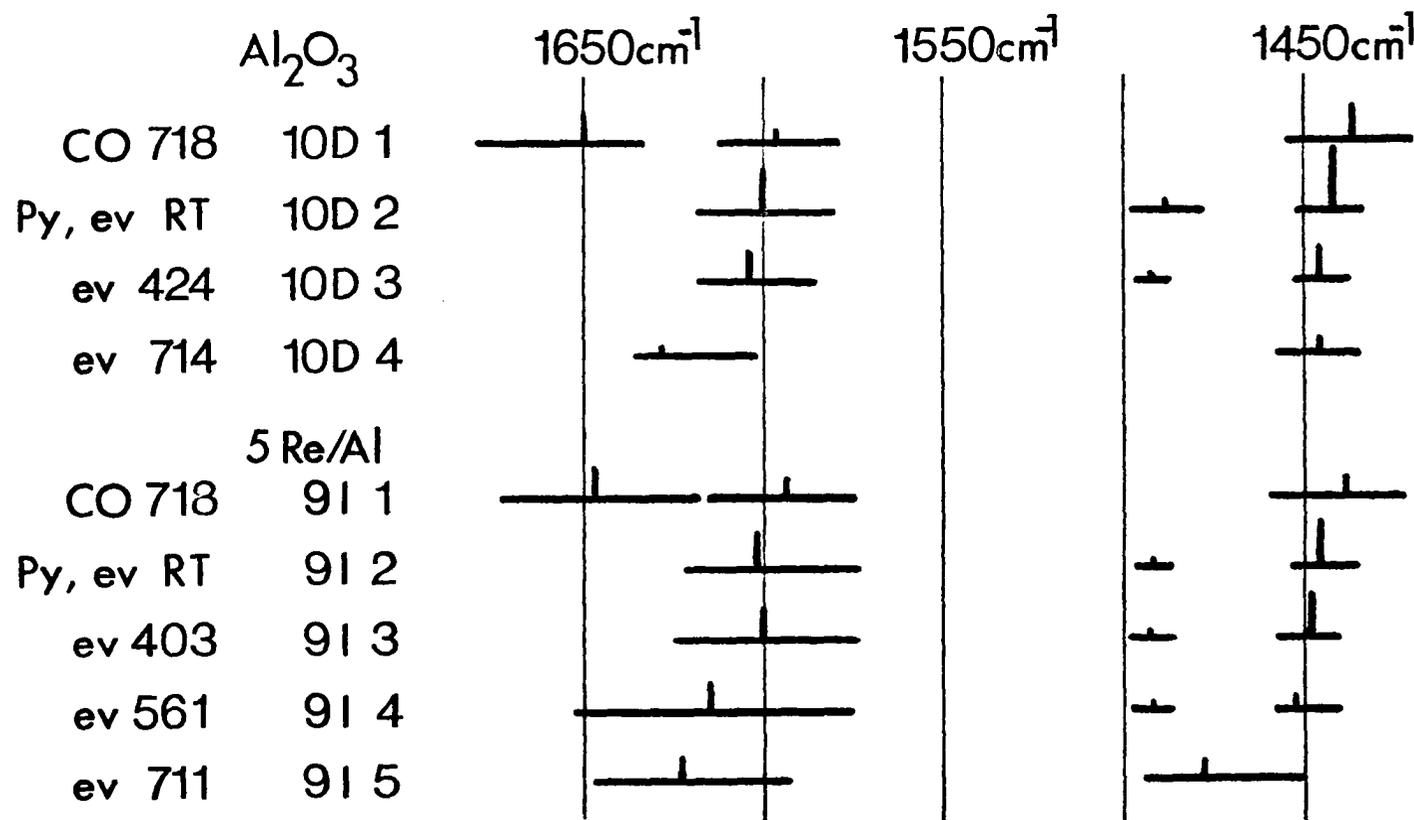


Figure III-22. The effects of carbon monoxide pretreatment on the adsorption and desorption of pyridine are shown. The vertical lines indicate peak locations and relative transmittance and the horizontal lines indicate bandwidth at half peak height.

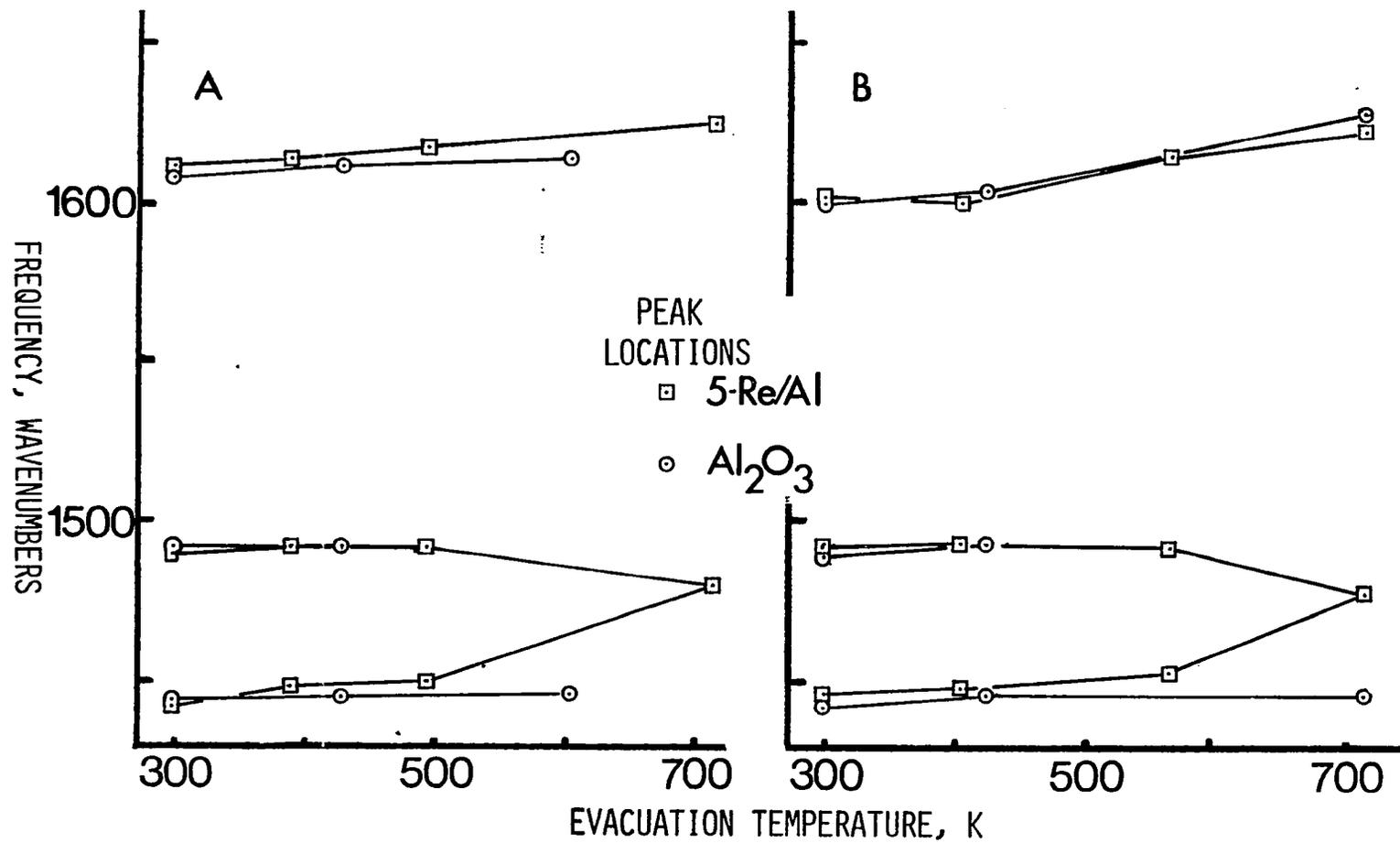


Figure III-23. The relationship between peak positions and evacuation temperatures is shown: A. hydrogen pretreatment, B. carbon monoxide pretreatment.

Upon heating from 523 K to 713 K, the 19a and 19b LPy peaks of the alumina spectra diminished in intensity, but did not appreciably increase further in frequency. In the 5-Re/Al spectra, these peaks not only diminished in intensity, but also seemed to coalesce at 1480 wavenumbers (Fig. III-23). This effect was seen with either hydrogen and carbon monoxide pretreatment.

Pyridine bands in the region of 1600-1630 wavenumbers, generally assigned to the 8a and 8b ring vibrational mode, are also attributable to Lewis acidity (93). This feature was present in the 10C and 10D series of alumina and the 9H and 9I series of 5-Re/Al. The peak maxima were lower in frequency at room temperature when the samples were pretreated with carbon monoxide (series 10D and 9I) than when pretreated with hydrogen. With hydrogen and carbon monoxide pretreatment, the peak maxima increased in frequency with an increase in evacuation temperature. As for the 19b mode, an increasing wavenumber of these modes indicates increasing coordination bond strength (93). In the 1600 region, the differences between the spectra of alumina and 5-Re/Al are probably within the range of experimental error, but the differences between the spectra after hydrogen or carbon monoxide pretreatment are greater than experimental error.

The spectral summaries that appear in Figures III-24 to III-30, as well as Figures III-21 and III-22, are from

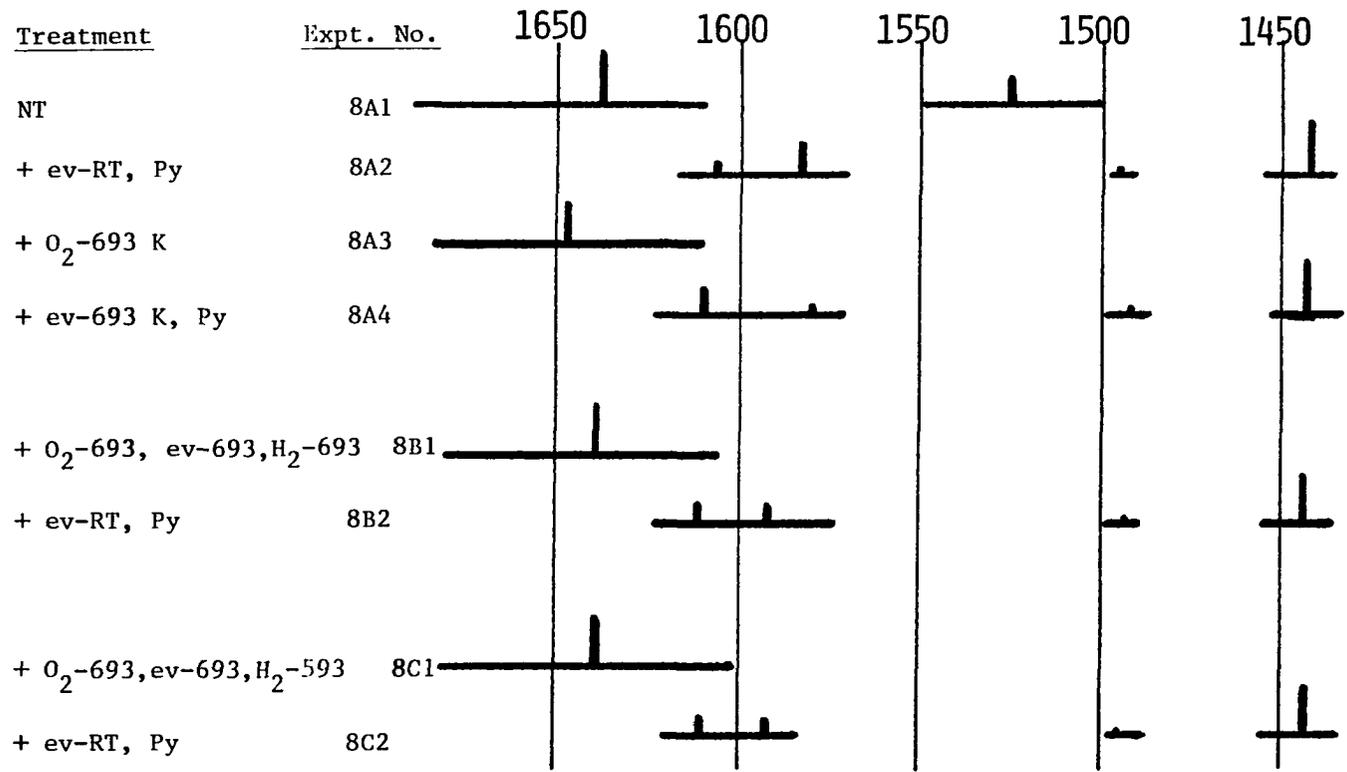


Figure III-24. In-situ spectra of Al₂O₃ after various treatments are shown. The treatments are in sequential order from top to bottom.

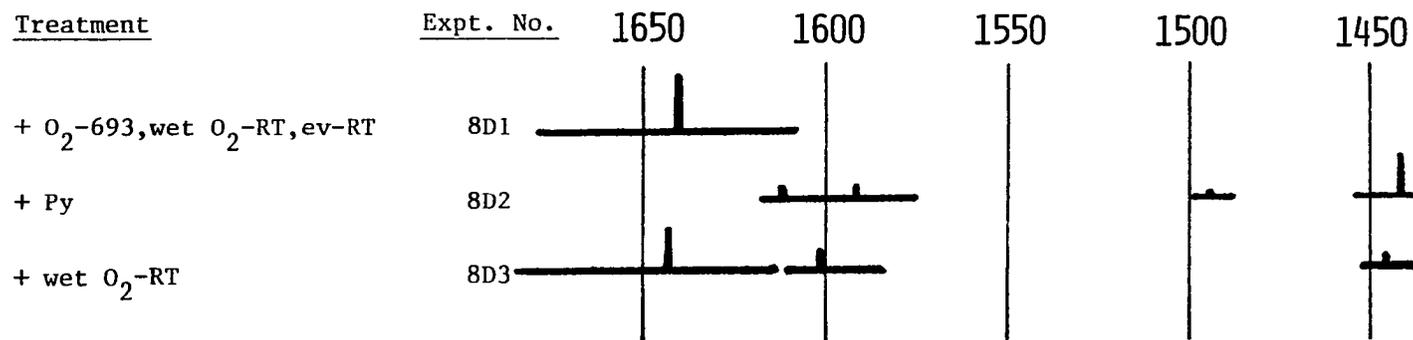


Figure III-25. In-situ spectra of Al₂O₃ after various treatments are shown. These spectra follow sequentially from those shown in Fig. S1.

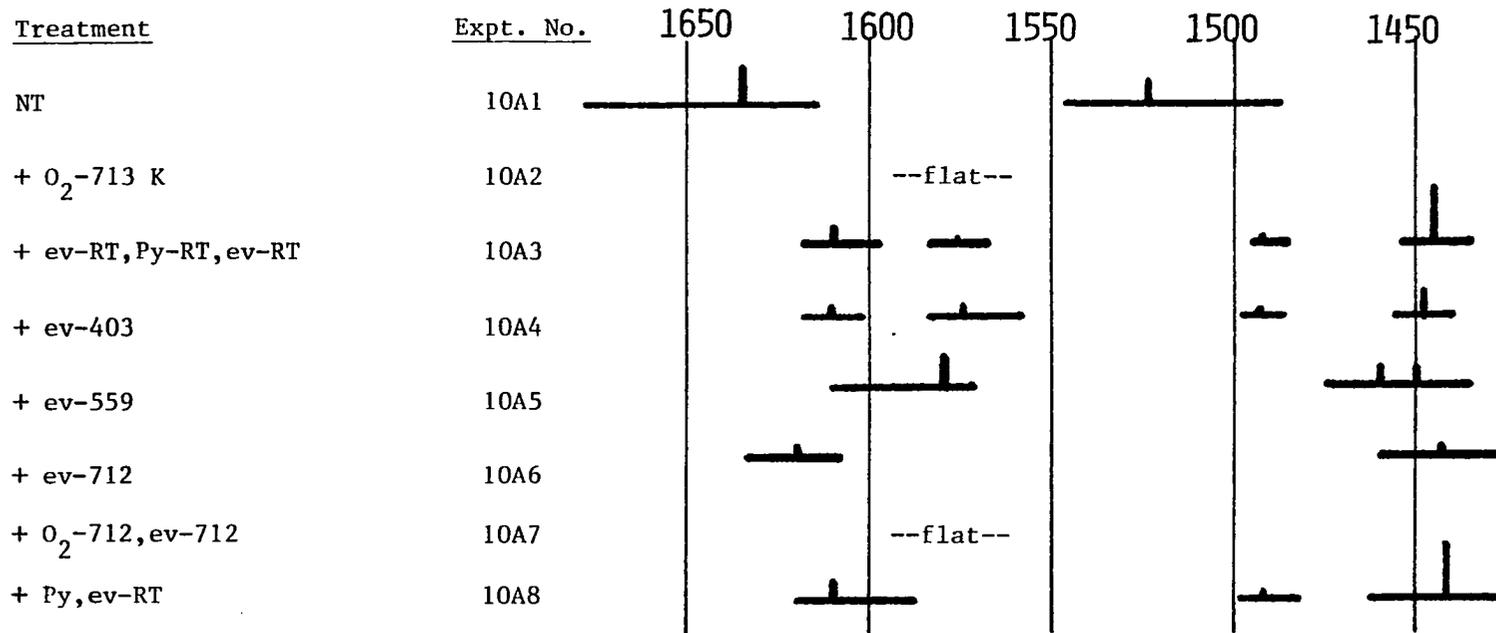


Figure III-26. In-situ spectra of Al₂O₃ after various treatments are shown. The treatments are sequential from top to bottom.

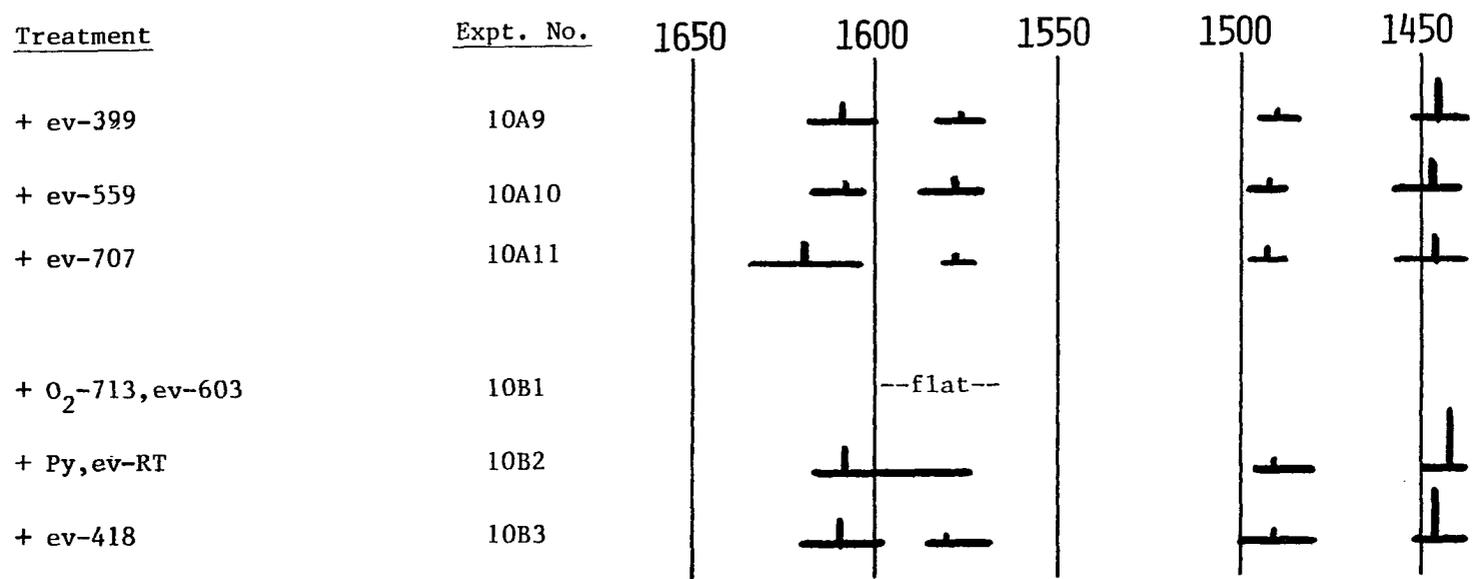


Figure III-27. In-situ spectra of Al₂O₃ after various treatments are shown. These spectra follow sequentially from those shown in Figure S3.

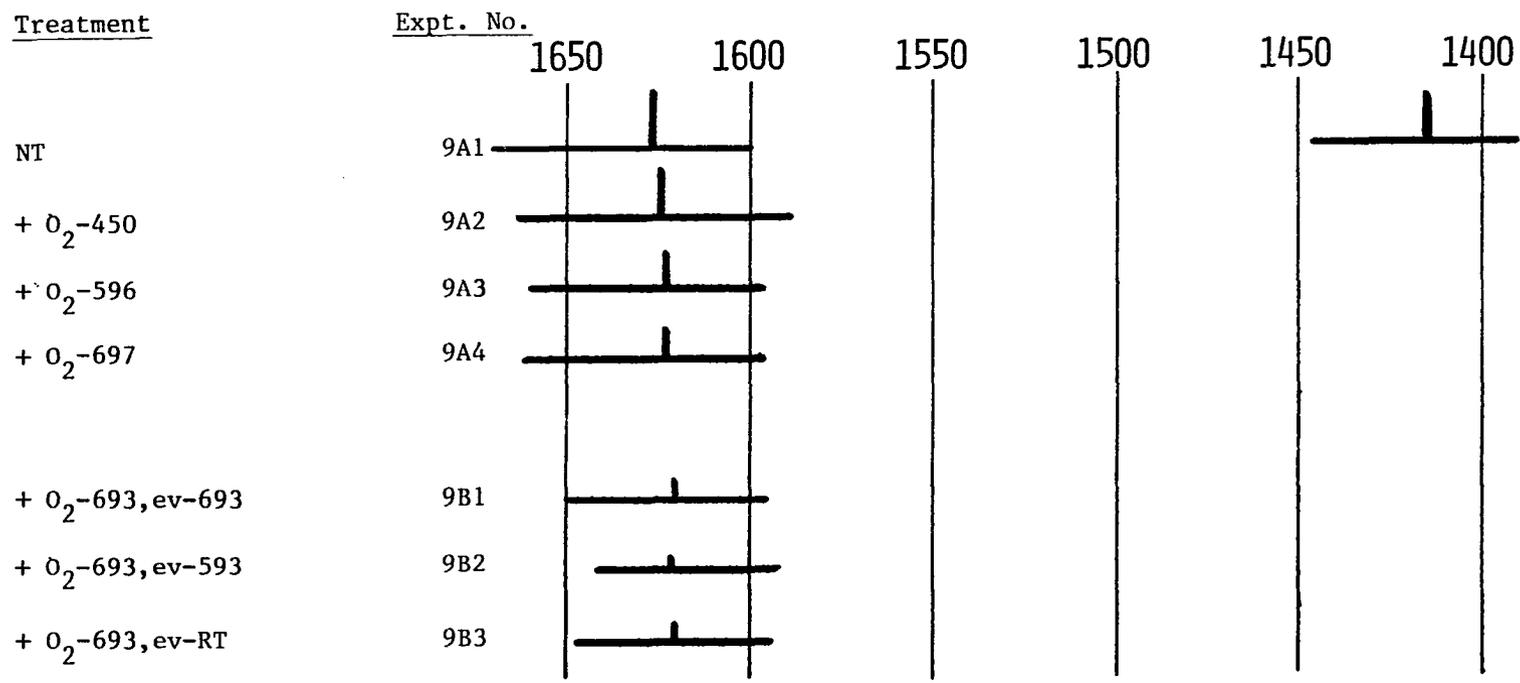


Figure III-28. In-situ spectra of 5-Re/Al after various treatments are shown. These spectra are sequential from top to bottom.

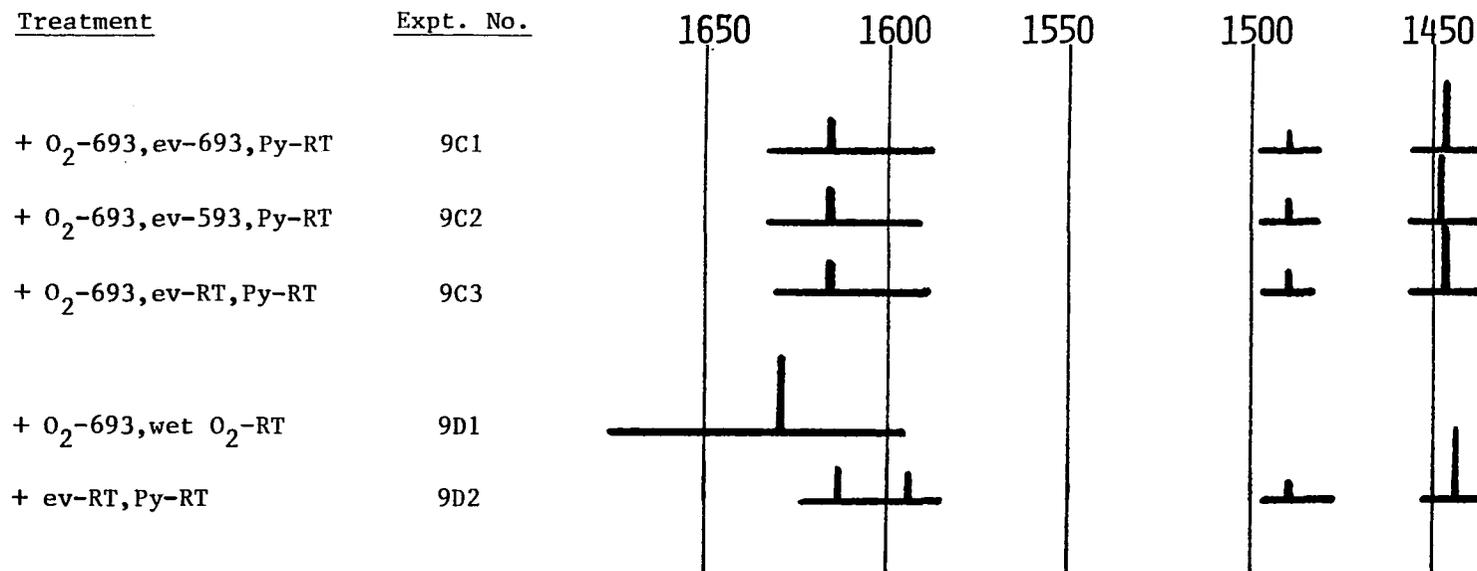


Figure III-29. In-situ spectra of 5-Re/Al after various treatments are shown. These spectra follow sequentially from those in Figure S5.

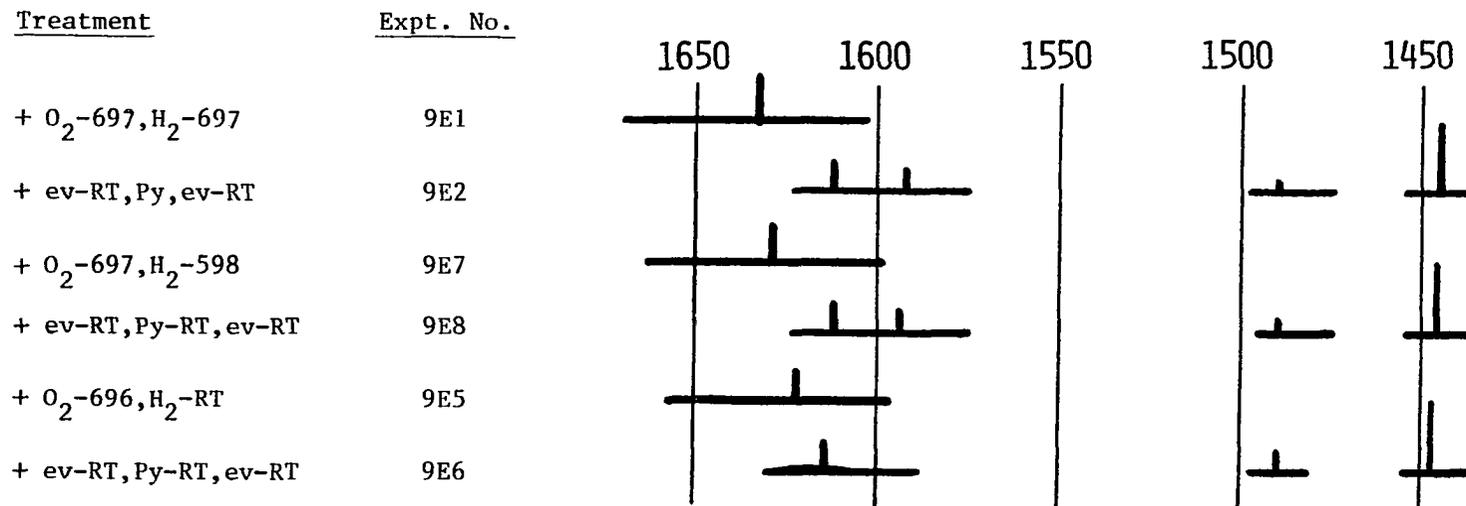


Figure III-30. In-situ spectra of 5-Re/Al after various treatments are shown. These spectra follow sequentially those in Figure S6.

spectra of in-situ catalyst discs, and were made to reduce the amount of noise present in the original spectra and to enable the analysis. Figures III-24 to III-27 contain summaries of Al_2O_3 spectra and Figures III-28 to III-30 contain summaries of 5-Re/Al spectra. Horizontal lines in the figures represent the bandwidth at one half the peak height. Vertical lines indicate the peak locations. Where two peaks are shown within the boundaries of a single band, their bandwidths overlapped in the original spectra. Band edges were sometimes difficult to define because of noise. Frequencies are given in wavenumbers, temperature in Kelvin and abbreviations present in the figures are: NT = no treatment, RT = room temperature (293-300 K), ev = evacuation, and Py = pyridine.

An additional peak between 1590-1600 wavenumbers was seen in the spectra of hydrogen pretreated 5-Re/Al (9E2, 9E8 and 9H2) which was not seen in the carbon monoxide pretreated 5-Re/Al. A similar peak was seen in the spectra of 5-Re/Al which had been pretreated with wet oxygen. This indicates that carbon monoxide could have blocked a potential pyridine adsorption site, or that water formed during the hydrogen reduction made a pyridine adsorption site available. The peak was not seen when the hydrogen treatment occurred at room temperature. The peak disappeared when the evacuation temperature was increased to 400 K. This is further evidence that this peak may be

due to an interaction of water, formed during reduction of the catalyst by hydrogen, and the adsorbed pyridine.

When the 5-Re/Al was pretreated with oxygen alone (series 9C), the 8a band was at a higher frequency, 1616 wavenumbers, than when pretreated with hydrogen or carbon monoxide. This frequency is very close to that reported by Knozinger (93). This reduction in Lewis acidity with hydrogen reduction corresponds to a reduced metathesis activity as reported by Hsu (34).

Pretreatment with wet oxygen resulted in an 8a band of lower frequency, 1594 and 1612 wavenumbers. This would indicate that water reduced the strength of the Lewis acidity. This loss of Lewis acidity on the catalyst corresponds to a loss of metathesis activity after introduction of water (34). Although some researchers have reported that the addition of water caused the appearance of bands indicative of Bronsted acidity, Knozinger (93) reports that there is little agreement on this point. In the present research, the addition of water did not result in detectable Bronsted acidity. This research cannot confirm the proposal that Bronsted acid sites participate in the metathesis reaction (37).

It appears that the effects of hydrogen and carbon monoxide reduction, as well as water adsorption, on the Lewis acidity of 5-Re/Al are different in degree, but not in kind, from the effects of corresponding treatments on

the properties of alumina. Although in-situ spectra of the rhenium - oxygen bands in the 910 - 925 wavenumber region were not obtained, it seems from the model compound investigation that the reduction had little effect on this band (Fig. III-9).

It may be that the effects of the treatments are directed more toward the properties of alumina support than toward the state of rhenium on the catalyst. The activity of the catalyst for olefin metathesis might be altered more by changes in the electron transferring and olefin adsorbing ability of the support than on the condition of the rhenium. This confirms the results of previous investigations (37, 38) which indicated a wide variance in olefin metathesis activity of rhenium when supported on different materials.

Powdered Catalyst Investigation

The investigation involving treatment of powdered catalyst samples followed by preparation of KBr pellets was not as useful as the in-situ investigation. First, the act of removing the samples from the reactor and preparing KBr pellets introduced variables not connected to the pretreatment process: contact with the KBr itself, pressure in the pellet press, and contact with the atmosphere. The sensitivity to handling has been demonstrated in the above discussion of XPS results.

Actual grinding of the catalyst after treatment did not occur because of possible physical changes. The catalyst was merely mixed as thoroughly as possible with the KBr prior to pressing. This technique typically does not result in an even distribution of sample throughout the pellet. Therefore, the quality of the spectra was not as high as with normal pellets.

The FT-IR spectrometer produced much higher quality spectra than the grating spectrometer. The two peaks in the 910-925 wavenumber region were resolvable even without grinding a catalyst sample of between 100 and 200 mesh (Figs. III-10 to III-13). Pellets of catalyst undiluted with KBr could not be made thin enough to observe catalyst spectra below 1100 wavenumbers with either the FT-IR or the grating spectrometers.

IV. CONCLUSIONS

- 1 The model compounds and the Re/Al exhibited nearly the same frequency for the rhenium-oxygen stretching vibration, namely a doublet band between 910 and 925 wavenumbers.
- 2 The 910-925 band was not appreciably shifted by oxidation or reduction of Re/Al.
- 3 Based on the XPS investigation, the 6+ state of rhenium in ReO_3 is subject to modification in the process of preparing KBr pellets for subsequent ir examination.
- 4 Lewis acid sites were somewhat stronger on the Re/Al than on the alumina.
- 5 Bronsted acidity was not detected on either alumina or Re/Al.

- 6 The effects of pretreatment on olefin metathesis activity appear to be directed more toward the properties of the alumina support than on the state of the rhenium.

V. RECOMMENDATIONS

- 1 Time resolved ir spectroscopy using an FT-IR would be useful in conjunction with temperature programmed desorption to determine the strength of various surface sites. Acidic sites could be investigated by desorbing pyridine. Olefin adsorption sites could be investigated by desorbing olefins.
- 2 The break-in phenomenon could be investigated by observing the time resolved FT-IR spectrum of the catalyst during olefin adsorption.
- 3 Continued work needs to be done to develop a method of observing the 910 - 925 wavenumber band in-situ. At present, the rhenium - oxygen - aluminum bond vibrations have not been directly observed during pretreatment or the metathesis reaction itself.
- 4 Further investigation of the effects of various modifications of alumina on the activity of the rhenium/alumina and molybdenum/alumina catalysts would enable the development of more active catalysts.

- 5 More work needs to be done using x-ray photoelectron spectroscopy on the rhenium model compounds to determine the changes in oxidation state of rhenium when ground, mixed with KBr and adsorbed onto the alumina support.

VI. REFERENCES

- 1 R. L. Banks and G. C. Bailey, I & E. C. Prod. Res. Devel., 3 (3), 170 (1964)
- 2 R. L. Banks, J. Mol. Cat., 8, 269 (1980)
- 3 Phillips Petroleum Company, Hydr. Proc., 46 (11), 232 (1967)
- 4 R. S. Logan and R. L. Banks, Oil & Gas J., 66 (21), 131 (1968)
- 5 R. E. Dixon, et al., Oil & Gas J., 65 (4), 98 (1967)
- 6 K. L. Anderson and T. D. Brown, Hydr. Proc., 55 (8), 119 (1976)
- 7 E. R. Freitas and C. R. Gum, C. E. P., 73, Jan. (1979)
- 8 R. L. Banks and R. B. Regier, I. & E. C. Prod. Res. Devel., 10 (1), 46 (1971)
- 9 R. L. Banks, et al., J. Mol. Cat., 15, 21 (1982)
- 10 J. C. Mol, J. Mol. Cat., 15, 35 (1982)
- 11 G. C. Bailey, Cat. Rev., 3 (1), 37 (1969)
- 12 T. J. Katz, Adv. Organomet. Chem., 16, 283 (1977)
- 13 R. H. Grubbs, Prog. Inorg. Chem., 24, 1 (1978)
- 14 N. Calderon, J. P. Lawrence and E. A. Ofstead, Adv. Organomet. Chem., 17, 449 (1979)
- 15 J. C. Mol and J. A. Moulijn, Adv. Cat., 24, 131 (1975)
- 16 C. P. C. Bradshaw, E. J. Howman and L. Turner, J. Cat., 7, 269 (1967)
- 17 R. R. Schrock, J. A. C. S., 96 (21), 6796 (1974)

- 18 D. T. Lavery, J. J. Rooney and A. Stewart, J. Cat., 45, 110 (1976)
- 19 C. P. Casey and T. J. Burkhardt, J. A. C. S., 96 (25), 7809 (1974)
- 20 P. G. Gassman and T. H. Johnson, J. A. C. S., 98 (19), 6055 (1976)
- 21 P. G. Gassman and T. H. Johnson, J. A. C. S., 98 (19), 6057 (1976)
- 22 P. G. Gassman and T. H. Johnson, J. A. C. S., 98 (19), 6058 (1976)
- 23 J. McGinnis, T. J. Katz and S Hurwitz, J. A. C. S., 98 (2), 605 (1976)
- 24 N. Calderon, et al., J. A. C. S., 90 (15), 4133 (1968)
- 25 J. C. Mol, J. A. Moulijn and C. Boelhouwer, Chem. Commun., 1968, 633
- 26 G. S. Lewandos and R. Pettit, J. A. C. S., 93 (25), 7087 (1971)
- 27 G. S. Lewandos and R. Pettit, Tetr. Lett., 780 (1971)
- 28 J. L. Wang and H. R. Menapace, J. Org. Chem., 33, 3794 (1968)
- 29 W. B. Hughes, J. A. C. S., 92 (3), 532 (1970)
- 30 R. H. Grubbs, P. L. Burk and D. D. Carr, J. A. C. S., 97 (11), 3265 (1975)
- 31 R. H. Grubbs, et al., J. A. C. S., 98 (12), 3478 (1976)
- 32 N. Calderon, H. Y. Chen and K. W. Scott, Tetr. Lett., 34, 3327 (1967)
- 33 E. O. Fischer and S Riedmuller, Chem. Ber., 107, 915 (1974)
- 34 J. C. Hsu, PhD Dissertation, University of Oklahoma (1979)
- 35 V. Ye. Grinev, M. Madden, V. A. Khalif, E. L. Aptekar, A. Aldag and O. V. Krylov, Kinetika i Kataliz, 24 (2), 429 (1983)

- 36 C. J. Lin, A. W. Aldag, and A. Clark, J. Cat., 45, 287 (1976)
- 37 C. C. Hsu, PhD Dissertation, University of Oklahoma (1980)
- 38 M. P. Madden, I. L. Tsitovskaya, A. A. Kadushin, O. V. Krylov and A. W. Aldag, work conducted in the Institute of Chemical Physics, Moscow, paper in progress: "Diffuse Reflectance Spectra and Activity of the Propylene Metathesis Reaction catalyzed by Molybdena and Rhenia Supported on γ - and θ - Alumina".
- 39 A. W. Aldag, C. J. Lin and A. Clark, J. Cat., 51, 278 (1978)
- 40 A. W. Aldag, C. J. Lin and A. Clark, J. Roy. Neth. Chem. Soc., 96, 279-292/M27 (1977)
- 41 M. El-Sawi, et al., J. Chem. Tech. Biotechnol., 31, 388 (1981)
- 42 A. Brenner and R. L. Burwell, J. Cat., 52, 364 (1978)
- 43 R. Nakamura and E. Echigoya, J. Mol. Cat., 15, 147, (1982)
- 44 W. N. Delgass, et al., Spectroscopy in Heterogeneous Catalysis, Academic Press (1979)
- 45 H. A. Benesi and B. H. C. Winquist, Adv. Cat., 27, 97 (1978)
- 46 J. E. Mapes and R. P. Eischens, J. Phys. Chem., 58, 1059 (1954)
- 47 E. P. Parry, J. Cat., 2, 371 (1963)
- 48 M. R. Basila, T. R. Kanter and K. H. Rhee, J. Phys. Chem., 68 (11), 3197 (1964)
- 49 M. R. Basila and T. R. Kanter, J. Phys. Chem., 70 (5), 1681 (1966)
- 50 C. P. Cheng and G. L. Schrader, Spec. Lett., 12 (11 & 12), 857 (1979)
- 51 M. Furuta, et al., Chem. Lett., 31 (1979)
- 52 F. J. Gil, J. L. G. Fierro and A. L. Agudo, Zeit. Phys. Chem. N. F., Bd. 123, S. 115 (1980)

- 53 H. Miyata and J. B. Moffat, J. Cat., 62, 357 (1980)
- 54 B. A. Morrow, et al., J. Cat., 44, 467 (1976)
- 55 C. Morterra, et al., J. Chem. Soc. Farad. I, 75, 271 (1979)
- 56 C. Morterra, et. al., J. Chem. Soc. Farad. I, 75, 289 (1979)
- 57 C. Morterra, et al., J. Chem. Soc. Farad. I, 76, 2102 (1980)
- 58 E. A. Paukshtis, R. I. Soltanov and E. N. Yurchenko, React. Kin. Cat. Lett., 16 (1), 93 (1981)
- 59 P. Pichat, M. Mathieu and B. Imelik, Bul. Soc. Chim. Fr., 8, 2611 (1969)
- 60 C. H. Rochester and S. A. Topham, J. Chem. Soc. Farad. I, 75, 872 (1979)
- 61 C. H. Rochester and S. A. Topham, J. Chem. Soc. Farad. I, 75, 1259 (1979)
- 62 A. J. van Roosmalen, D. Koster and J. C. Mol, J. Phys. Chem., 84 (23), 3075 (1980)
- 63 P. O. Scokart and P. G. Rouxhet, J. Chem. Soc. Farad. I, 76, 1476 (1980)
- 64 N. Topsoe, K. Pedersen and E. G. Derouane, J. Cat., 70, 41 (1981)
- 65 J. C. Vedrine, et al., J. Cat., 59, 248 (1979)
- 66 F. E. Kiviat and L. Petrakis, J. Phys. Chem., 77, 1232 (1973)
- 67 P. Ratnasamy, D. K. Sharma and L. D. Sharma, J. Phys. Chem., 78, 2069 (1974).
- 68 K. Segawa and K. Hall, J. Cat., 76, 133 (1982)
- 69 M. R. Basila, Appl. Spec. Rev., 1 (2), 289 (1968).
- 70 G. Blyholder, "Spectra of Adsorbed Species", in R. B. Anderson, ed., Experimental Methods in Catalytic Research, vol. 1, Academic Press, N. Y. (1968)

- 71 R. P. Eischens and W. A. Pliskin, Adv. Cat., 10, 1 (1958)
- 72 M. L. Hair, Infrared Spectroscopy in Surface Chemistry, Marcel Dekker, Inc., N. Y. (1967)
- 73 F. Pritchard and T. Catterick, "Infrared Spectroscopy", in R. B. Anderson and P. T. Dawson, eds., Experimental Methods in Catalytic Research, vol. 3, Academic Press, N. Y. (1976)
- 74 A. A. Olsthoorn and C. Boelhouwer, J. Cat., 44, 197 (1976)
- 75 A. A. Olsthoorn and C. Boelhouwer, J. Cat., 44, 207 (1976)
- 76 A. A. Olsthoorn and J. A. Moulijn, J. Mol. Cat., 8, 147 (1980)
- 77 R. Nakamura, F. Abe and E. Echigoya, Chem. Lett., 51 (1981)
- 78 F. P. J. M. Kerkhof, J. A. Moulijn and R. Thomas, J. Cat., 56, 279 (1979)
- 79 H. Jerziorowski and H. Knozinger, J. Phys. Chem., 83 (9), 1166 (1979)
- 80 C. P. Cheng and G. L. Schrader, J. Cat., 60, 276 (1979)
- 81 Donohue, et al., Inorg. Chem., 4 (8), 1152 (1965)
- 82 E. J. Baran, G. Baud and J. Besse, Spec. Acta, 39A (5), 383 (1983)
- 83 A. K. Coverdale, P. F. Dearing and A. Ellison, JCS Chem. Commun., 1983 (10), 567
- 84 M. Ishii, et al., J. Phys. Soc. Japan, 41 (3), 908 (1976)
- 85 W. J. Potts, Jr., Chemical Infrared Spectroscopy, Volume I: Techniques, John Wiley and Sons, Inc., NY (1963)
- 86 E. S. Shpiro, et al., J. Cat., 55, 402 (1978)
- 87 Private communication with Ruth Merryfield of Phillips Petroleum Company

- 88 A. F. Wells, Structural Inorganic Chemistry, 3rd edition, Oxford University Press (1962)
- 89 R. C. Weast, ed. CRC Handbook of Chemistry and Physics, 61st edition, Chemical Rubber Company (1980)
- 90 H. Knozinger, et al., in G. C. Bond, et al., eds., Proc. Sixth Intl. Cong. Catal., 183 (1976)
- 91 C. H. Kline and J. Turkevich, J. Chem. Phys., 12 (7), 300 (1944)
- 92 D. Cook, Can. J. Chem., 39 (10), 2009 (1961)
- 93 H. Knozinger, Adv. Cat., 25, 184 (1976).

APPENDIX

REACTOR CONSTRUCTION AND SAMPLE PREPARATION

The experimental objective of this investigation was to observe the infrared spectrum of an Re/Al₂O₃ catalyst during catalyst pretreatment. These observations provided information concerning the interaction between the Re atoms and the Al₂O₃ support and the effects of pretreatment on the Re - Al₂O₃ interaction.

For these objectives to be realized, a catalyst sample had to be prepared that was active and suitable for observation at appropriate ir frequencies. Furthermore, a suitable reactor had to be constructed which enabled reproducible spectra to be made while maintaining the desired environment within the reactor.

A major obstacle to the investigation was the high absorptivity of Al₂O₃ in the frequency range of interest: 500 - 1200 wavenumbers. A partial solution was to make a very thin sample. Thin samples present new problems: (a) self-supporting wafers thin enough to transmit adequate ir

radiation are difficult to prepare, (b) powder samples scatter radiation, and (c) thin samples contain small amounts of catalyst and therefore adsorb small amounts of material. A particular problem with the $\text{Re}/\text{Al}_2\text{O}_3$ catalyst is that physical manipulation might alter its character. For example, the shape of the bands at 915 and 925 wavenumbers seemed to be dependent on the severity of grinding.

Many researchers have used a self supporting wafer (or disc) in their catalyst investigations (1, 3-6, 8, 9, 12-16, 18, 20-22, 25-28). Amenomiya (1) investigated the water gas shift reaction using an alumina catalyst in the form of a pressed disc of 19mm diameter having a density of 42 mg/cm^2 . He was not able to observe spectra below 1200 wavenumbers due to the strong absorption of alumina. Dalla Betta and Shelef (8) investigated the hydrogenation of CO over a $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst in the form of self-supporting wafers of 12 - 30 mg/cm^2 and were able to measure adsorption isotherms and observe spectra in the 1000 - 4000 wavenumber region. Gregg and Ramsay (12) investigated the adsorption of CO_2 in the 1200 - 5000 wavenumber region using alumina catalyst discs 32 mm in diameter and 12.5 mg/cm^2 made from powder <100 mesh. Oh-Kita, et al. (21) observed N_2 adsorption on transition metal/alumina discs, including 1% $\text{Re}/\text{Al}_2\text{O}_3$, in the form of pressed discs 60 mg/cm^2 . Peri and Hannan (22) used aerogel plates to

investigate surface OH- groups on γ -alumina. Vannice, et al. (28) formed a catalyst disc inside their reactor so that gases had to flow through the disc, thus allowing transmission of ir radiation and accurate kinetic measurements. Their arrangement allowed a maximum temperature of 700 K.

Blyholder (7) discusses self-supporting disc samples. The major advantage of a disc is reduced light scattering. One disadvantage is a limited operating range of 1200 - 4000 wavenumbers for a reasonably thin disc. Pritchard and Catterick (24) suggest that the main advantage of the pressed disc is the large surface area within the infrared beam which results in a large concentration of adsorbed molecules. Hair (14) discusses disc techniques. He suggests that the catalyst particle size should be on the order of one micron before pressing and that the thickness of the disc should be on the order of .01 cm. Many disc dies are equipped for pressing under a vacuum, but it is suggested that this facility not be used because the disc could adhere to the die. It is also suggested that a completely dry powder be avoided for pressing and that the die be heated slightly before pressing. Methods of pressing between sheets of teflon, saran wrap, or tissue paper are discussed, however these methods could introduce contamination. Another drawback to the disc technique is that alterations in the nature of the

surfaces could be induced by pressing. The lowest pressure that yields a satisfactory disc should be used.

Techniques using powdered catalysts have been reported (2, 7, 10, 11). Blyholder (7) indicates that scattering is not prohibitive if the particle size is considerably less than the wavelength of the radiation. Eischens, et al. (10, 11) have used a technique in which the powder is sprinkled on a horizontal window with the ir beam traveling vertically. This method requires extensive equipment modification. Ahmed and Gallei (2) "dusted" catalyst particles between two windows held vertically in the ir path. One disadvantage with these methods is the difficulty in measuring the amount of sample in the beam path.

Other researchers have employed a spray technique for sample preparation (6, 7, 29, 30). Benesi and Jones (6) used a method of spraying a suspension of fine particle silica gel in i-propanol onto a salt window held at a temperature of 333-363 K. They obtained films of 4 mg/cm², much thinner than is possible with the pressed disc technique. Yates, et al. (30) made an aqueous solution of RhCl₂, diluted it 10:1 in acetone and added a high area alumina. While being mixed, this slurry was sprayed onto a CaF₂ window maintained at 350 K. They obtained deposits of 11 mg/cm². The window onto which the slurry is sprayed can act as the reactor window or can be positioned in the

center of the reactor as described by Yates, et al. (29).

Another method of sample preparation is to support the catalyst on a wire screen (7, 19). Lynds (19) used a small-mesh nickel screen to support Ru/Al₂O₃ and Ir/Al₂O₃ catalysts. This method has the advantage of allowing the sample to be heated directly by passing electricity through the screen or to be cooled by direct contact of the screen with liquid nitrogen. Good gas - solid contact is enabled by this method.

Of the preparation techniques mentioned, the pressed disc method has the advantages of handling ease and reduced light scattering. The disadvantage of the disc method is the possible irreversible effect of grinding and pressing on the structure of the catalyst. The powder technique has the disadvantage of light scattering, but overcomes the problems due to grinding and pressing if these processes occur prior to impregnation. In the spray technique, the sample is applied to a window while in slurry form thereby depositing very fine particles and partially avoiding light scattering and grinding problems. The effect of the solvent on the structure and activity of the catalyst must be determined. In addition, the support window itself might affect the catalyst activity or be altered by the reaction environment.

Just as there are many techniques for sample preparation, many types of reactor/ir cell are described in

the literature. These reactors fall into two major categories. The first is a reactor in which the sample is pretreated or activated in one region and then moved to another region through which the ir beam passes. In the second, the sample is mounted in a fixed position. Blyholder (7) gives a general review of reactor designs.

Of the many investigations using movable sample reactors (3, 4, 12, 20-22, 25, 26), two representative designs will be discussed here. Peri and Hannan (22) proposed one of the most widely used reactor/cell designs. Their reactor allowed for reproducible positioning of the sample, in the form of an aerogel plate (23), in the furnace section and in the observation section. The sample was moved horizontally by means of an external magnet. Ramamoorthy, et al. (25, 26) presented the design of a vertically mounted reactor/cell. The sample is moved from the oven section to the ir beam by suspending a stainless steel sample holder from a crank using stainless steel wire. The short optical path length in their reactor allowed increased transmittance and reduced the magnitude of gas phase absorption.

Many investigators have used fixed sample reactors (1, 5, 6, 8, 9, 11, 13, 15-19, 27-30). Many of these reactors require a cooling system to maintain low temperatures near the windows to insure a good seal between the reactor body and the window. Vannice, et al. (28)

constructed a cell in which reactant gases are forced to flow through a pressed disc. The disc acts as a single-pass differential reactor. The design of Heal, et al. (13) is more typical of reactors described in the literature. This type of reactor has a long beam path which is offset by a similar cell placed in the reference beam of the spectrometer. Yates, et al. (29) used a cell in which the catalyst was sprayed onto a CaF₂ plate held vertically in the beam path by a metal holder that can be connected directly by liquid nitrogen for low temperature adsorption experiments. King (17) constructed a reactor that consists entirely of two NaCl windows separated by a graphite gasket and inlet and outlet tubing. The catalyst is in the form of a pressed disc placed between the windows. Although this reactor has the advantage of a short beam path, it is not suitable for low pressure operation. Seanor and Amberg (27) combined a reactor with a null-reading microbalance for adsorption studies, but their reactor had no facilities for heating the sample. Lynds (19), who supported the catalyst on nickel screens, constructed a reactor which allows direct electrical heating or cryogenic cooling of the catalyst. The effect of oxygen at high temperatures on the metal screen were not discussed.

All investigations reported discussed surface adsorbed species. The spectral region of interest was usually 2000 - 4000 wavenumbers and never lower than 1200

wavenumbers. None of the investigators examined catalyst molecules or the interaction of the catalyst with the support.

References

- 1 Y. Amenomiya, Appl. Spec., 32, 484 (78)
- 2 A. Ahmed and E. Gallei, Appl. Spec., 28, 430 (74)
- 3 M. F. Brown and R. P. Gonzalez, J. Phys. Chem., 80, (15), 1731 (76)
- 4 A. Buckland, et al., J. Phys., E, 4, 146 (71)
- 5 G. Blyholder and L. D. Neff, J. Phys. Chem., 66, 1464 (62)
- 6 H. A. Benesi and A. C. Jones, J. Phys. Chem., 63, 179 (59)
- 7 G. Blyholder, "Spectra of Adsorbed Species", in R. B. Anderson, ed., Experimental Methods in Catalytic Research, Vol. 1, Academic Press, N. Y. (68)
- 8 R. A. Dalla Betta and M. Shelef, J. Cat., 48, 111 (77)
- 9 J. G. Ekerdt and A. T. Bell, J. Cat., 58, 170 (79)
- 10 R. P. Eischens and W. A. Pliskin, Adv. Cat., 10, 1 (58)
- 11 R. P. Eischens, et al., J. Phys. Chem., 60, 194 (56)
- 12 S. J. Gregg and J. D. F. Ramsay, J. Phys. Chem., 73, 1243 (69)
- 13 M. J. Heal, et al., J. Phys., E, 7, 352 (74)
- 14 M. L. Hair, Infrared Spectroscopy in Surface Chemistry, Marcel Dekker, N. Y. (67)
- 15 T. R. Hughes and H. M. White, J. Phys. Chem., 71, 2193 (67)

- 16 A. Igarashi, et al., Rev. Sci. Instr., 44, 321 (73)
- 17 S. T. King, Appl. Spec., 34 (6), 632 (80)
- 18 J. W. London and A. T. Bell, J. Cat., 31, 32 (73)
- 19 L. Lynds, Spec. Acta, 20, 1369 (64)
- 20 M. J. D. Low, et al., Env. Sci. Technol., 5 (12), 1191 (71)
- 21 M. Oh-Kita, et al., J. Cat., 44, 460 (76)
- 22 J. B. Peri and R. B. Hannan, J. Phys. Chem., 64, 1526 (60)
- 23 J. B. Peri, J. Phys. Chem., 69, 231 (65)
- 24 F. Pritchard and T. Catterick, "Infrared Spectroscopy", in R. B. Anderson and P. T. Dawson, eds., Experimental Methods in Catalytic Research, Vol 3, Academic Press, N. Y. (76)
- 25 P. Ramamoorthy and R. D. Gonzalez, J. Cat., 58, 188 (79)
- 26 P. Ramamoorthy, Appl. Spec., 33, 310 (79)
- 27 D. A. Seanor and C. H. Amberg, Rev. Sci. Instr., 34, 917 (63)
- 28 M. A. Vannice, et al., J. Phys., E, 12, 849 (79)
- 29 J. T. Yates, et al., J. Chem. Phys., 71, 3908 (79)
- 30 J. T. Yates, et al., J. Chem. Phys., 70, 1219 (79).

	(spectrum No. 65)	33
Figure III-4	Spectrum of $\text{Cd}_2\text{Re}_2\text{O}_7$ in KBr pellet (spectrum No. 70)	34
Figure III-5	Spectra of Al_2O_3 and 5-Re/Al in KBr pellets (spectra 60 and 61)	35
Figure III-6	Difference spectrum: 5-Re/Al minus Al_2O_3 (spectrum 60 minus 61)	36
Figure III-7	Spectrum of unground 5-Re/Al, no treatment, 100-200 mesh, in KBr pellet (spectrum No. 69)	37
Figure III-8	Spectrum of unground 5-Re/Al, 100- 200 mesh, heated in flowing oxygen at 759 K, in KBr pellet (spectrum No. 67)	38
Figure III-9	Spectrum of unground 5-Re/Al, 100- 200 mesh, heated in flowing oxygen followed by flowing hydrogen at 759 K, in KBr pellet (spectrum No. 72)	39