

**X-RAY PHOTOELECTRON SPECTROSCOPIC AND IN-SITU
INFRARED INVESTIGATION OF A Ru/SiO₂ CATALYST**

A THESIS

**SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
AND THE INSTITUTE OF ENGINEERING AND SCIENCES
OF BILKENT UNIVERSITY**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE**

By

ŞAFAK SAYAN

September 1997

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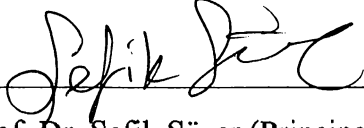
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Prof. Dr. Şefik Süzer (Principal Advisor)

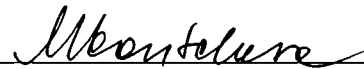
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Asst. Prof. Dr. Deniz Ö. Üner (Co-supervisor)

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis of the degree of Master of Science


Prof. Dr. Hasan N. Erten

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis of the degree of Master of Science


Asst. Prof. Dr. Margarita Kantcheva

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis of the degree of Master of Science



Prof. Dr. Timur Doęu

Approved for the Institute of Engineering and Sciences



Prof. Dr. Mehmet Baray
Director of Institute of Engineering and Science

ABSTRACT

X-RAY PHOTOELECTRON SPECTROSCOPIC AND IN-SITU INFRARED INVESTIGATION OF A Ru/SiO₂ CATALYST

ŞAFAK SAYAN

M.S. in Chemistry

Supervisor: Prof. Dr. Şefik Süzer
September 1997

A 4 wt% Ru/SiO₂ catalyst which was previously prepared via an incipient wetness technique using a ruthenium nitrosyl-nitrate [Ru(NO)(NO₃)₃] solution and a commercially available precursor (ruthenium nitrosyl-nitrate) were used in this study. The activation of the catalyst was investigated by using Infrared (IR) spectroscopy together with X-ray photoelectron spectroscopy (XPS). Special emphasis has been given to the study of formation of active species during annealing of the precursor and the catalyst for comparison purposes. The in-situ IR measurements performed on the catalyst suggested a possible metal and support interaction. XPS experiments revealed mixed oxidation states in the case of annealing of the precursor whereas annealing did not cause any change in the

oxidation state of Ru present in the catalyst which lead to the conclusion that the influence of support and interactions between the metal and support prevented any reduction by annealing only.

Carbon monoxide adsorption on the reduced catalyst followed by IR spectroscopy was performed to investigate the nature of active adsorption sites. The complexity of the spectrum of chemisorbed CO suggested the presence of small metal particles. The presence of Ru^{n+} centers as well as reduced Ru centers showed that the catalyst was not fully reduced under these conditions.

Using this catalyst ammonia synthesis was achieved at 350 °C in a N_2/H_2 gas mixture ($\text{N}_2/\text{H}_2 \approx 3:1$) for different reaction times. In addition to observed NH_3 as reaction product, the results showed that NH_x surface species might represent intermediates in the ammonia synthesis reaction on Ru/SiO_2 .

Carbon monoxide adsorption on the catalyst after NH_3 synthesis was performed to investigate the change in nature of active sites after ammonia production when compared with the reduced sample. Based on the experimental observations, participation of Ru^0 sites in ammonia synthesis was confirmed and a partial oxidation of the reduced Ru sites during synthesis was observed.

Keywords: X-ray photoelectron spectroscopy (XPS), Infrared spectroscopy (IR), catalyst, annealing, chemisorption, precursor, reduction, mixed oxidation states.

ÖZET

BİR Ru/SiO₂ KATALİZÖRÜNÜN X-IŞINI FOTOELEKTRON SPEKTROSKOPİSİ VE YERİNDE İNFRARED YÖNTEMİYLE İNCELENMESİ

ŞAFAK SAYAN

Kimya Bölümü Yüksek Lisans

Tez Yöneticisi : Prof. Dr. Şefik Süzer

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Bu çalışmada, Ru(NO)(NO₃)₃ solüsyonu kullanılarak daha önceden ‘başlayan ıslaklık’ metodu ile hazırlanmış olan yüzde 4 rutenyum içeren Ru/SiO₂ katalizörü ve ticari olarak elde edilen (Johnson Matthey) Ru(NO)(NO₃)₃ kullanılmıştır. Katalizörün aktivasyonu X-ışını fotoelektron spektroskopisi (XPS) ile beraber infrared spektroskopisi (IR) kullanılarak incelenmiştir. Karşılaştırma amacı ile habercinin (precursor) ve katalizörün tavlama sırasında oluşan aktif türlerin formasyonunun çalışılmasına ayrıca özel önem verilmiştir. Katalizör üzerinde gerçekleştirilen yerinde IR ölçümleri, muhtemel bir metal taşıyıcı ilişkisini işaret

etmiştir. XPS deneyleri, habercinin tavlama sırasında karışık oksidasyon hallerini göstermesine karşın katalizörün tavlama sırasında katalizörde bulunan rutenyum metalinin oksidasyon halinde bir değişiklik göstermemiştir. Bunun sonucunda, taşıyıcı etkisi ve metal taşıyıcı ilişkisi sebebiyle sadece tavlama yöntemiyle katalizörün indirgenemeyeceği yargısına varılmıştır.

IR spektroskopisi ile takip edilen indirgenmiş katalizör üzerine karbon monoksit adsorpsiyonu deneyleri, aktif adsorpsiyon bölgelerinin doğasını incelemek için gerçekleştirilmiştir. Adsorbe edilmiş CO spektrumunun karmaşık olması küçük metal parçacıklarının bulunduğunu işaret etmiştir. Bu çalışma, indirgenmiş rutenyum merkezlerinin yanında Ru^{n+} merkezlerini de içermesinden dolayı katalizörün bu şartlar altında tam olarak indirgenemediğini göstermiştir.

Amonyak sentezi, bu katalizör kullanılarak 350 derecede ve N_2/H_2 (1:3) gaz karışımı ile farklı reaksiyon zamanlarında gerçekleştirilmiştir. Sonuçlar, Ru/SiO_2 katalizörü üzerinde yapılan amonyak sentezi reaksiyonunun ürünü olarak gözlemlenen NH_3 ile beraber NH_x türü bileşiklerin ara ürün olabileceğini göstermiştir.

Amonyak sentezinden sonra katalizör üzerine karbon monoksit adsorpsiyonu, amonyak üretimi sonucunda aktif bölgelerin doğasındaki değişimleri incelemek amacı ile yapılmıştır. Bu deneysel gözlemlere dayanarak, Ru^0 bölgelerinin amonyak

sentezinde rol oynadıđı ve indirgenmiř Ru bölgelerinin sentez sırasında kısmen oksitlendiđi yargısına varılmıřtır.

Anahtar kelimeler:X-ıřını fotoelektron spektroskopisi (XPS), İnfrared spektroskopisi (IR), katalizör, tavlamak, adsorpsiyon, haberci, indirgemek, karıřık oksidasyon halleri.

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1. INTRODUCTION

1.1 Catalysts

Catalysis is of primary importance to the global problems related to energy, resources, and environment. Catalysis is the heart of the chemical and petroleum industry. The success of the chemical industry is based largely on catalysis technology. The development of new and improved catalysts and catalytic processes is essentially important to the industry.

According to the transition-state theory, chemical reaction rate is determined by the free energy of formation complex postulated to exist between reactants and products. Catalysis is that process in which the catalytic agent, catalyst, aids the attainment of chemical equilibrium by reducing the free energy of the transition-complex formation in the reaction path [1].

Formally speaking, homogeneous catalysis implies that all reacting species are present in one phase, usually the liquid phase. Today, homogeneous catalysis is often used in a restricted sense to refer to catalysis with organometallic and coordination complexes. A great variety of dissolved homogeneous catalysis are known such as Brønsted and Lewis acids and bases, metal complexes, metal ions, organometallic complexes, organic molecules and enzymes [2].

Heterogeneous catalysts are important for a variety of industrial reactions such as hydrotreating, polymerization, hydrogenation-dehydrogenation, isomerization, reforming and selective oxidation. These reactions play key roles in the synthesis of fuel, fine chemicals, and a wide range of materials and in the area of pollution control [3].

Industrial catalysts consist of a highly dispersed metal or metal oxide phase deposited on a high-surface-area support. The reason for the application of supported catalysts in industry is that they combine a relatively high dispersion, amount of active surface, with a high degree of thermostability of the catalytic component. The support, which, itself, is not usually catalytically active is a thermostable, highly porous material onto which the active component is applied.

Preparation of supported catalysts is much more of an art than a science. After the catalyst for a particular purpose has been identified, its manufacture is

optimized through varying experimentally easily accessible parameters in a previously established basic recipe. The best catalyst-preparation recipes are generally so complicated and precise description of the reactions taking place during manufacturing process can not be given.

Supported catalysts can be prepared basically in three ways: (i) selective removal of a component from a non-porous phase containing (a precursor of) the active component and the support, e.g. a coprecipitate ; (ii) separate application of (a precursor of) the catalytically active material onto a pre-existing support, e.g. by impregnation or precipitation ; (iii) The terms adsorption and ion exchange are used interchangeably to describe the strong adsorption of a metal precursor to the surface of a support, because the ionic interaction do not play as important role as in the case of impregnation. For adsorption, the larger the total surface area of the support, the higher the total uptake of the precursor [4]. The method to be chosen in a particular case depends, on the loading one wants to achieve : when applying cheap metals and oxides one typically strives for maximum active surface area per unit volume, in which case the selective removal strategy may well be advantageous ; however, the very expensive noble metals are employed only at low loadings, where the aim is to prepare very small particles having almost all their atoms at the surface. Therefore the impregnation is the method of choice [2].

Industrial catalysts consist of a highly dispersed metal phase deposited on a high-surface-area support. In impregnation, a solution of a metal salt of sufficient concentration to give the desired loading is added to the support, after which the system is aged usually for a short period of time, dried and calcined. With the preshaped support an incipient wetness, also called dry or pore volume, impregnation is generally used. In this preparation technique, an amount of solution is added which is just sufficient to fill up the pore volume the support particles. With powdered supports a volume of solution substantially larger than the pore volume is applied which is called the wet impregnation.

Transition metals and their compounds are uniquely active as catalysts, and they are used in most surface catalytic processes. The effective-medium theory of the surface chemical bond emphasizes the dominant contribution of d-electrons to bonding of atoms and molecules at surfaces. Other theories also point out that d-electron metals in which the d-bond is mixed with the s and p electronic states provide a large concentration of low-energy electronic states and electron vacancy states. This is ideal for catalysis because of the multiplicity of degenerate electronic states that can readily donate or accept electrons to and from adsorbed species. Those surface sites where the degenerate electronic states have the highest concentrations are most active in breaking and forming chemical bonds. These electronic states have high charge fluctuation probability, configurational and spin

fluctuations, especially when the density of electron vacancy or hole states is high [6].

It is generally accepted that surface coordinative unsaturation is important in surface chemistry. This concept is analogous to that in coordination chemistry and arises from the fact that because of steric and electronic reasons, only a limited number of ligands or nearest neighbors can be within bonding distance of a metal atom or ion.

Metal surfaces can be made to be coordinatively unsaturated by treatment under vacuum to remove adsorbates without loss of their structures. Reactivity of metal surfaces enable them to show catalytic activity for many reactions. The surface can be used with varying degrees of coverage and can be applied as catalysts with feeds providing a wide variety of reactants. One of the important concepts articulated about metal catalysis is that the surfaces are nonuniform and that only a minority of specific surface sites may be active for a particular catalytic reaction under a particular set of conditions. This infers that not all the coordinatively unsaturated sites are active for a specific catalytic reaction. Therefore it is important to specify the active sites for a particular catalytic reaction [5].

The supported metal catalysts used widely in technology consist of aggregates of metals of various sizes and shapes dispersed on a support. Following

preparation and calcination, the catalyst is treated with hydrogen at high temperatures to reduce the metal. During reduction, the metal migrates and forms aggregates dispersed on the support. The metal aggregates may be extremely small clusters, consisting of only a few atoms, but some are particles consisting of hundreds, thousands or more atoms. Since the chemistry of synthesis is imprecise and the support surfaces nonuniform, the metal aggregates are nonuniform in size and shape. The distribution of sizes is strongly dependent on the details of preparation and not easily predicted, since the surface phenomena occurring during the preparation are not well understood. The larger metal particles in supported metal catalysts are three-dimensional and may be considered as small chunks of bulk metal. Their surfaces present a number of different crystal faces. Aggregates smaller than about 1 nm may be most important catalytically because they have a large fraction of the metal exposed at the surface.

Metal-catalyzed reactions are classified as structure insensitive when the reaction rate is almost independent of the average aggregate or particle size of dispersed metal. On the other hand, when there is substantial difference in rate from one average metal aggregate size to another, the reaction is classified as structure sensitive. These definitions reflect the fact that systematic variation of the size of the metal aggregate leads to systematic changes in the surface structure. The catalytic sites for structure sensitive reactions are complicated with the activity being sensitive to the arrangement of the ensemble of metal atoms constituting the site [5].

1.2 Catalytic Ammonia Synthesis

The ammonia synthesis reaction is among the most widely studied reactions in heterogeneous catalysis. Although the reaction is energetically favorable and does not suffer from side reactions, high reactivities of dinitrogen and dihydrogen to ammonia are difficult to achieve because of kinetic limitations. Ammonia synthesis on heterogeneous catalysts require high temperatures (700 K) and pressures (100-300 bar) to achieve desirable reaction kinetics. Because ammonia synthesis is an exothermic reaction, the high temperatures required for kinetic purposes make the reaction thermodynamics less favorable. Ammonia synthesis involves a decrease in the number of moles upon reaction, so an increase in the pressure can compensate for the negative effects of temperature on the equilibrium conversion (0.20 at 700 K). For these reasons, the reaction is carried out at high pressures.

Typical commercial catalysts for ammonia synthesis are based on iron. They include doubly promoted iron ($\text{Fe-Al}_2\text{O}_3\text{-K}_2\text{O}$) and triply promoted iron ($\text{Fe-Al}_2\text{O}_3\text{-CaO-K}_2\text{O}$). The role of Al_2O_3 and CaO is to stabilize a high surface area of metallic iron under reaction conditions, and these oxides are therefore termed structural promoters. In contrast, potassium oxide serves as a chemical promoter by increasing the rate of ammonia synthesis per metallic iron surface area. The role of this promoter probably involves a stabilization of dinitrogen on the iron surface, which

leads to an increase in the rate of dinitrogen dissociation which is known to be rate determining step in ammonia synthesis [7].

There are some drawbacks of utilization of this commercial catalyst for ammonia synthesis. The reactant gases namely, hydrogen and nitrogen should be purified before entering the reactor. Because hydrogen is produced by water-gas shift reaction and carbon monoxide is always present in the effluent gases. The carbon monoxide present in nitrogen forms a complex with the metallic iron particles of the catalyst which is volatile, therefore during the reaction the amount of the catalyst in the reactor decreases if nitrogen is not purified before entering the reactor. Similarly, nitrogen is produced by liquefaction of air therefore there is always oxygen in the nitrogen which can oxidize the reduced iron catalyst. This, in turn, decreases the yield of the ammonia synthesis reaction. Purification makes a significant contribution to operating cost which in turn increase the product cost. The high reaction temperature increases both the operating cost and the fixed cost since the reactor building material should be resistant to higher temperatures.

1.3 Ruthenium Catalysts

Ruthenium based catalysts are expected to be the second generation ammonia synthesis catalysts. The high activity of Ru-based catalysts at low temperatures coupled with their ease of reduction and good tolerance toward common reaction

poisons make them potentially excellent catalysts for use in ammonia synthesis at thermodynamically favored low temperatures. This explains, in part, the amount of research done in recent years on Ru-catalyzed ammonia synthesis [8]. The Ru-based catalysts permit milder operating conditions compared with the magnetite-based systems, such as low synthesis pressure (70-105 bars compared with 150-300 bars) and lower synthesis temperatures, while maintaining higher conversions than a conventional system [9].

1.3.1 Supported Ru Catalyst preparation

Aika et al. prepared and characterized the chlorine-free Ruthenium catalysts for ammonia synthesis. It was reported that $\text{Ru}(\text{NO})(\text{NO}_3)_3$ and $\text{Ru}_3(\text{CO})_{12}$ were effective precursors among four compounds, including $\text{Ru}(\text{acac})_3$ and K_2RuO_4 precursors when they were supported on Al_2O_3 . The reason is probably obtaining a higher dispersion. They also investigated the effect of other supports on the efficiency in ammonia synthesis and found MgO to be the most efficient support among several pure oxides under low pressure conditions, but the effect of SiO_2 as a support was not investigated in this study. They reported that the activity was correlated roughly with the basicity of the support [10].

The reason for studying chlorine-free Ruthenium catalysts is that the chlorine originated from the precursor is left on the catalyst after activation and chlorine

retards ammonia synthesis [15]. It is reported that Ru/Al₂O₃ prepared from RuCl₃ gives low dispersion and that the value depends on the reduction temperature.

A chlorine-free precursor was preferred in the preparation of this catalyst because chlorine left on the catalyst after activation inhibits the ammonia synthesis by blocking the active sites for the reaction.

It is essentially important to investigate the activation of the catalyst which is usually accomplished in a reducing hydrogen atmosphere. During the activation, reduced state or states of the metal are produced. The versatility of activated catalysts is associated with their capability of forming intermediate oxidation states, therefore in this study, the activation of the catalyst is investigated and knowledge about the active sites for adsorption are obtained by using IR spectroscopy together with XPS and Mass spectroscopy. Special emphasis has also been given to the study of formation of the active phase during the annealing of both precursor and the catalyst for comparison purposes.

1.4 Characterization of Heterogeneous Catalysis

Surface science is one of the most important branches of modern chemistry and physics, because many important properties of solids such as catalytic activity, selectivity, adsorption ability etc. are determined by the surface state. The most

widely quoted motivation for modern surface studies is the goal of understanding heterogeneous catalysis. The greatly increased rates of certain chemical interactions which occur in the presence of solid catalysis, usually powder, must result from the modification of at least one of the constituent chemicals. This modification occurs when constituent chemicals are adsorbed on the solid surface and interact with other constituents. One would therefore like to understand what these modifications are, whether there are new intermediate species formed, what are the rate limiting steps and activation energies, what kind of sites on the catalyst surface are active, what is the nature of these sites and how these processes depend on the catalytic material. This might lead to development of better and/or cheaper catalysts since many such catalysts are based on precious metals like ruthenium or platinum [11].

Spectroscopic methods like IR and XPS are most commonly used for characterization of catalysts.

1.5 IR Spectroscopy

Vibrational Spectroscopies are certainly among the most promising and most widely used methods for catalyst characterization. This is due to the fact that very detailed information on molecular structure and symmetry can be obtained from vibrational spectra. Most importantly, several vibrational spectroscopies can be applied under in-situ conditions and they can successfully be used for studies of

high-surface area porous materials. Because of its relative simplicity and wide applicability, infrared transmission/absorption spectroscopy and more recently reflectance spectroscopy are most frequently used today [12].

Infrared spectroscopy is the study of the interaction of infrared light (200-6000 cm^{-1} wavenumber which corresponds to a frequency range of 50-2 μ) with matter. The vibrational motions of the chemically bound constituents of matter have frequencies in the infrared regime. The oscillations induced by certain vibrational modes provides a means for matter to couple with an impinging beam of infrared electromagnetic radiation and to exchange energy with it when the frequencies are in resonance. Among the different ways of recording this exchange of energy with the sample, Fourier Transform methods are the most widely spread. The variation of light intensity with optical path difference is measured by the detector as a sinusoidal wave. A plot of light intensity versus optical path difference is called an interferogram. The fundamental measurement obtained by a Fourier Transform Infrared is an interferogram which is Fourier transformed to give a spectrum. This is where the term Fourier Transform Infrared Spectroscopy (FTIR) comes from. The major advance was the invention of Fast Fourier Transform which is an algorithm which quickly performs Fourier transforms on a computer.

The ultimate advantages of FTIR are its capability of high signal-to-noise ratio (SNR), high scan rate, and absence of slits. High SNR absorbance enables a

more accurate measurement and high scan rate allows multiple scans of the same sample to be added together in a short period of time which in turn increases the SNR [13].

In-situ infrared spectroscopy has been one of the most important means of studying IR-observable adsorbates on supported metal catalysts under reactions conditions. In heterogeneous catalysis, reactants adsorb on the catalyst surface to form adsorbates which may undergo various interactions, surface reactions, and desorption to form products. Knowledge of the nature -structure and reactivity- of adsorbates is essential for developing a fundamental understanding of the reaction mechanism. Since the nature of adsorbates is closely related to the surface sites to which adsorbates bind, IR spectra of adsorbates can provide information not only on the structure of the adsorbates but also on the state of the catalyst surface [14].

1.5.1 Infrared Transmission-Absorption Spectroscopy

The principle is well known from conventional infrared spectroscopy of solids in transmission mode via usage of thin pressed self-supporting wafers for surface studies. The applicability of the transmission technique is determined by the properties of the solid powder to be studied. Thus, samples which exhibit only weak bulk absorption, and the average particle size (d) of which is smaller than the wavelength of the infrared radiation in the region of interest will be optimally suited

for the transmission mode. The size condition ($\lambda \gg d$) which determines the wavelength range of suitably low scattering losses, is usually met in the mid and far infrared region in practice, whereas scattering losses become strongly involved in the near infrared region. On the other hand, most samples show strong bulk absorption in the low wavenumber region (roughly 1000 cm^{-1}). As a result, the accessible wavenumber range for transmission infrared spectroscopy will generally be limited for surface studies to the mid-infrared region ($1000\text{-}4000\text{ cm}^{-1}$). However, when less than optimal spectroscopic conditions can be accepted spectra may be obtained also in the near infrared region. A reduction of scattering losses could be achieved by the immersion technique in which the solid is immersed in a solvent having approximately the same refractive index (e.g. SiO_2 immersed in CCl_4).

Infrared transmission spectroscopy is a bulk rather than a surface specific technique. It is therefore necessary to provide an independent proof for any detected species that it is a surface group. This can be realized in many cases by following changes in band position on exposure of the solid adsorbent to a suitable adsorptive or by isotopic exchange experiments.

The sensitivity of the technique is dependent on the extinction coefficients of the surface groups. Since the magnitude of the extinction coefficients is rather small, solid samples with a high surface-to-volume ratio is desirable. The possible increase in sample thickness is limited by the concomitant increasing energy losses by

absorption and scattering. With the application of data acquisition techniques, the sensitivity of the technique can be increased further. Quantitative measurements of surface group densities should be possible, provided the Lambert-Beer law is valid for optically homogeneous materials and deviations may occur for disperse substances [12].

1.5.2 Infrared Diffuse Reflectance Spectroscopy

The transmission technique fails when strongly scattering materials are to be studied. Diffuse reflectance can be used in such cases provided the solid material does not absorb too strongly in the frequency range to be studied.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy is used to obtain the infrared spectra of powders and other solid materials. The advantage of DRIFTS is that it does not require pressing of a pellet. The powder or solid material to be analyzed is simply introduced into the sample holder which is usually made of metal. Therefore the sample preparation is much easier. Filling of the holder is actually important since the intensity of the diffusely reflected light is dependent upon the packing density of particles in the sample. The suggested way of sample introduction into the sample holder is to level the surface of the sample with brim of the holder. The intensity of diffusely reflected light also depends on the particle size

of the sample, therefore after introduction of the sample, the sample holder should not be tapped. Because tapping causes the big particles to rise to the top, presenting an atypical sample surface to the infrared beam.

The sample is placed at the focal point of a diffuse reflectance accessory. The accessory consists of mirrors that direct and focus the incoming radiation on the sample in the holder and collect the diffusely reflected radiation after interaction with the sample. Diffusely reflected radiation is made up of light scattered, absorbed, transmitted, and reflected by the sample, therefore carries information about the sample.

The reflectance technique in general sample the surface rather than the bulk of a sample. DRIFTS is useful for studying the surface of powdered materials. Chambers for in-situ analysis are also available for DRIFTS accessories. This enables the surface of catalysts and adsorbates to be monitored under the real world conditions.

1.6 IR Characterization of Catalyst Surfaces by Probe Molecules

The most common application of infrared spectroscopy in catalysis is to identify adsorbed species and to study the way in which these species are chemisorbed on the surface of the catalyst. The infrared spectra of adsorbed probe

molecules give valuable information on the adsorption sites that are present on catalysts. The probe molecules represent substances that are specifically adsorbed on a given type of surface sites on the catalyst [16-18]. The changes in their spectral features upon adsorption give an information about the nature and strength of the adsorption sites. The following requirements should be taken into consideration for the selection of suitable probe molecules [17,18]:

1. The probe molecule should possess well determined electron accepting or donating ability.

2. The probe molecule should occupy the same type of adsorption sites on different catalyst surfaces and to form adsorption complexes of the same structure.

3. The adsorbed species formed on interaction of a probe molecule with an adsorption or active site must be detectable, that is, concentration and lifetime of adsorbed species must be sufficiently high for the sensitivity and time scale of experimental technique applied.

4. The molecular size of the probe molecule should be as low as possible for following reasons:

- the adsorption site may be located in narrow pores of the catalyst that might be inaccessible for large probe molecules;
- the adsorption site may be a subject of steric hindrance;
- a large molecule may adsorb on a particular adsorption site and may shield another site located nearby.

5. The probe molecule should not undergo chemical reactions with the surface other than the acid-base processes characteristic for the direct interaction with the adsorption site.

6. The adsorption of the probe molecule should not lead to any surface reconstruction.

By application of the probe molecules the following information about [16-18]:

1. the presence of Lewis and/or Bronsted acid sites on the catalyst surface and their nature, strength and concentration;

2. the nature, strength and concentration of Lewis basic sites can be obtained.

The probe molecules used for surface acidity determination are hard and soft bases. The hard bases are employed in the simultaneous determination of Lewis and Bronsted acidity. They may be adsorbed on both strong and weak acid sites. The most used probe molecules of this type are ammonia and pyridine [16-20]. The weak bases are divided into two groups: probe molecules for determination of Lewis acidity (CO, NO) and probe molecules used for quantitative determination of the acidity of surface hydroxyl groups (benzene, CO at low temperatures) [16-18,20,21]. Chloroform and CO₂ are probe molecules which have application for surface basicity determination [22,23].

Carbon monoxide is the most widely used probe molecule for Lewis acidity determination [16,17,24]. The molecule in the gas phase has a rotational freedom, and the vibrational transitions (at 2143 cm^{-1}) are accompanied by rotational excitations. Upon adsorption, the CO loses its rotational freedom and now only the vibrational transition is observed, however, at a different frequency. Three factors contribute to this shift [25]:

- mechanical coupling of the CO molecule to the heavy substrate increases the CO frequency by some $20\text{ to }50\text{ cm}^{-1}$,
- the interaction between C-O dipole and its image in the conducting, polarizable metal weakens the CO frequency by $25\text{-}75\text{ cm}^{-1}$ (physical interaction),
- the formation of a chemisorption bond between CO and the substrate alters the distribution of electrons over the molecular orbitals and weakens or strengthens the CO bond (chemical interaction).

Thus, strictly speaking, it is not correct to interpret the frequency difference between adsorbed and gas phase CO in terms of chemisorption bond strength only (although the contribution of the latter is most significant).

When CO molecule is coordinated to a metal ion in high oxidation state (without filled d orbitals or d^0) the M-C bond is formed at the expense of the lone electron pair of carbon situated on the 3σ orbital. i.e. there is a partial transfer of electrons from CO to the adsorption center. However, the electron donor properties

of CO are weak, so the bond formed is not strong. The coordination of CO in this case leads to increase of the C-O stretching frequency because electron density is removed from the 3σ orbital which is considered to be slightly antibonding. As a result the bond order in CO increases. Support for this assumption is provided by IR data: when one of the lone pair (HOMO) electrons is removed from CO to form CO^+ , the CO stretching frequency is increased from 2143 to 2184 cm^{-1} , showing that the CO bond order also increases. Thus the stronger the $\text{C} \rightarrow \text{M}$ electrodonor bond, the stronger the C-O bond. Hence, the frequency of the adsorbed CO can be used for determination of the bond strength [17,24].

When the adsorption center has filled d orbitals, CO molecule acts as an electron acceptor [17,24]. Electron density is removed from the metal into CO π^* orbitals (π back bonding). As a result the C-O bond order strongly decreases and the CO stretching mode is red shifted. Indeed the promotion of one electron from the lone pair in gaseous CO to π^* level causes the C-O stretching frequency to drop from 2143 to 1489 cm^{-1} . This dramatic change is a strong indication about the sensitivity of this adsorption to the electron population of the CO antibonding orbitals. The following rule is valid: the stronger the π back bond, the lower frequency and its position does not depend on the atomic mass of the adsorption site.

In low oxidation state of the adsorption center, on the other hand, electron density that tends to be built up via the σ system can be dispersed through the π system. The two systems (σ and π) help each other, that is a synergistic effect occurs and each system can augment the bonding abilities of the other [17,26]. In this case both red and blue shifts occur. This hinders, sometimes, the observation of an exact correlation between the strength of the adsorption center and the position of $\nu(\text{CO})$ stretching band. It is possible for strongly adsorbed CO to manifest its absorption band close to this in gas phase due to cancellation of the both effects. However, usually the magnitude of the red shift is higher compared to that of the blue shift and this provides a possibility for identification of different adsorption sites [17,26].

1.7 X-Ray Photoelectron Spectroscopy

The genesis of a catalyst involves multiple steps such as impregnation, drying and calcination. After calcination one has a precursor to a catalyst, often referred to as the oxidic catalyst. The oxidic precursor is then activated; for hydrogenation catalysts this, typically, involves reduction in hydrogen, to produce a reduced state or states of the metal, which can be free metal or an intermediate oxidation state. The reduced catalysts are active for hydrogenation, metathesis, isomerization, and hydrogenolysis reactions. The versatility of these catalysts has long been recognized to be associated with their capability of forming intermediate oxidation states. It was speculated but not proven that different oxidation-state

requirements may be needed for different catalytic functions. This highlights the need to analyze the specific oxidation states present on the surface of the reduced catalyst and to investigate how they relate to the catalytic activity or selectivity [3].

X-ray photoelectron spectroscopy is a technique which yields spectra for all metals of catalytic importance, provides oxidation-state information, is quantitative, and gives information about dispersion of species on a surface. Thus, it is ideal for examining catalysts. It is possible to use XPS to identify single oxidation states and possibly molecular symmetry and to measure mixtures of states and the amounts of the individual components therein.

X-ray photoelectron spectroscopy (XPS) or ESCA (electron spectroscopy for chemical analysis) is a technique for measuring electron-binding energies. Photoelectrons are ejected from the sample by monoenergetic X-ray excitation. The kinetic energy of the ejected electrons is analyzed, and the peaks in the resulting kinetic energy spectrum correspond to electrons of specific binding energies in the sample.

The binding energy of the photoelectron is the core-level energy relative to Fermi level. These binding energies are dependent on the kind of atom, its valence state, its environment, and the penetration depth. The electron spectral lines are

referred to by the symbol of the element and the indication of the atomic energy levels involved in the emission process.

Shifts in the binding energy can be measured and are related to the chemical environment of the atom. When comparing ESCA lines from the same element in different chemical surroundings, shifts in peak positions can be observed. Chemical shifts arise from the fact that an electron being ejected from an inner atomic shell probes the chemical environment as it leaves the molecules or solid. In simplest terms, the more highly oxidized a given species, the lower the electron density in the valence shell, and consequently, the greater the energy needed to remove a core electron.

From the intensity of the peaks, a quantitative composition of the surface layers can be deduced. Methods for quantifying the XPS measurements utilizing peak-area sensitive factors and peak-height sensitivity factors have been developed. Ratios based on peak areas are a more reliable source of information on which to base atomic concentrations [1].

2. EXPERIMENTAL

2.1 IR Measurements

The IR spectra were obtained using a Bomem MB 102 FT-IR spectrometer. IR data were collected at 4 cm^{-1} resolution. The spectral subtractions were done by subtracting data of two spectra obtained in ASCII format.

2.1.1 Experimental Set-up for in-situ Diffuse Reflectance IR

Measurements

The IR spectra were obtained using a Bomem MB 102 FT-IR spectrometer equipped with a Harrick DRA-B03 diffuse reflectance attachment (Fig.1). IR data were collected at 4 cm^{-1} resolution and 1024 scans were acquired for each spectrum using an MCT detector. An in-situ cell equipped with ZnSe windows capable of operating in the temperature range of $300 < T < 800\text{ K}$ and a pressure range of

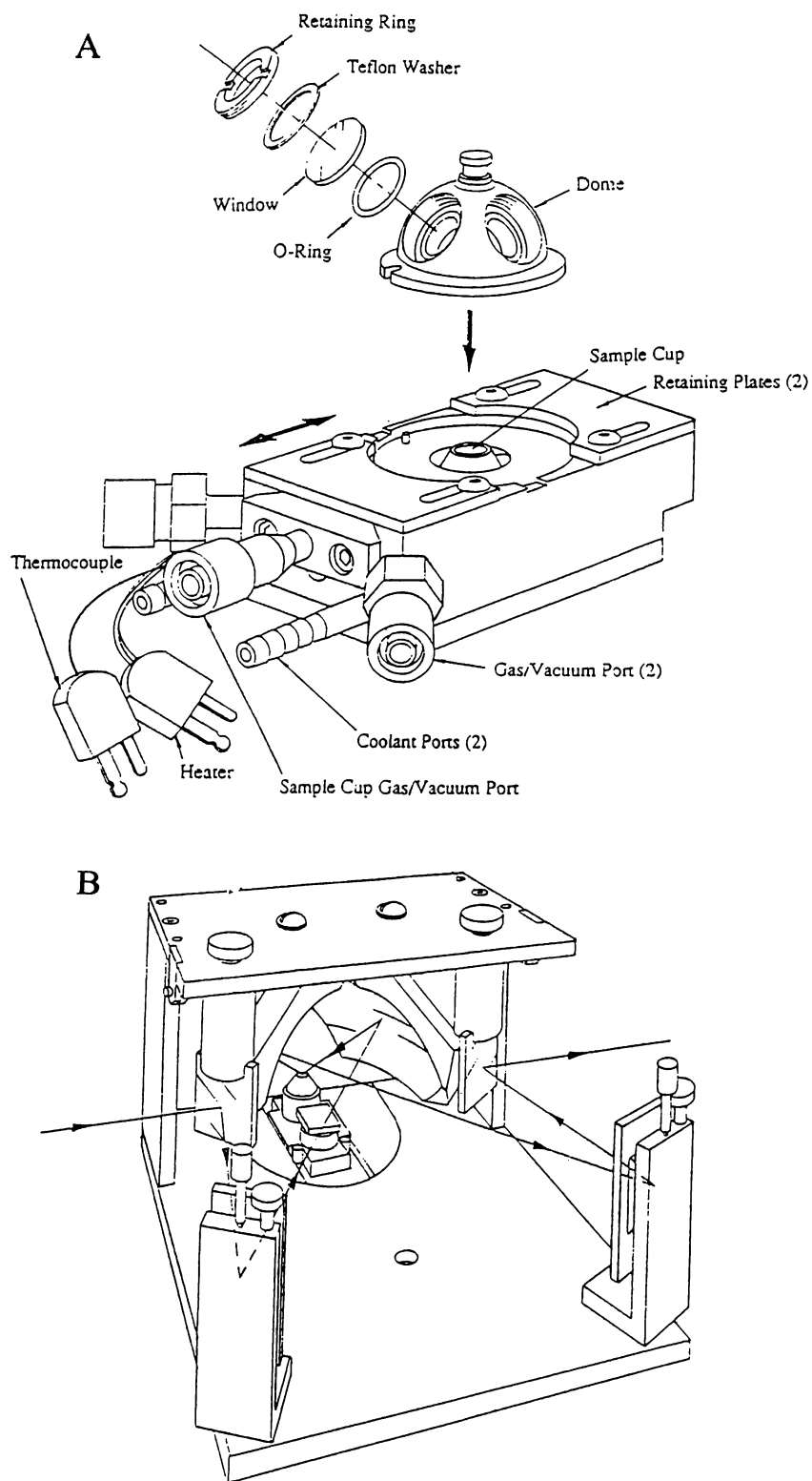


Fig.1 (A) Schematic diagram of in-situ IR cell equipped with ZnSe windows
 (B) Schematic diagram of Harrick DRA-B03 diffuse reflectance attachment

$10^{-4} < P < 1000$ torrs was used for reduction studies. The details of the in-situ IR cell are shown in Fig.1.

2.1.1.1 Reduction Studies

A 4 wt% Ru/SiO₂ catalyst was used in this study which was previously prepared via an incipient wetness technique using ruthenium nitrosyl-nitrate solution (Strem Chemicals, 1.5 wt% Ru) and SiO₂ (Degussa) [37]. Powdered samples were introduced into a copper sample holder, placed in the reactor cell and reduced by successive hydrogen exposure/evacuation cycles at 100, 200, 300, and 350 °C and at a pressure of 1.5 atm for one hour. IR data were collected after treatment of the sample at the corresponding temperature.

The spectrum of the sample is shown in Fig.2. ZnSe windows of the in-situ infrared cell has a cut-off at 500 cm⁻¹ due to the absorption of infrared radiation by ZnSe in the region 200-500 cm⁻¹.

2.1.2 Experimental Set-up for Transmission IR Measurements

Specially designed Pyrex glass IR cell equipped with NaCl windows was used in transmission IR measurements (Fig.3). The cell was 400 mm long with a diameter of 25 mm and is connected to a vacuum/adsorption manifold. The cell has

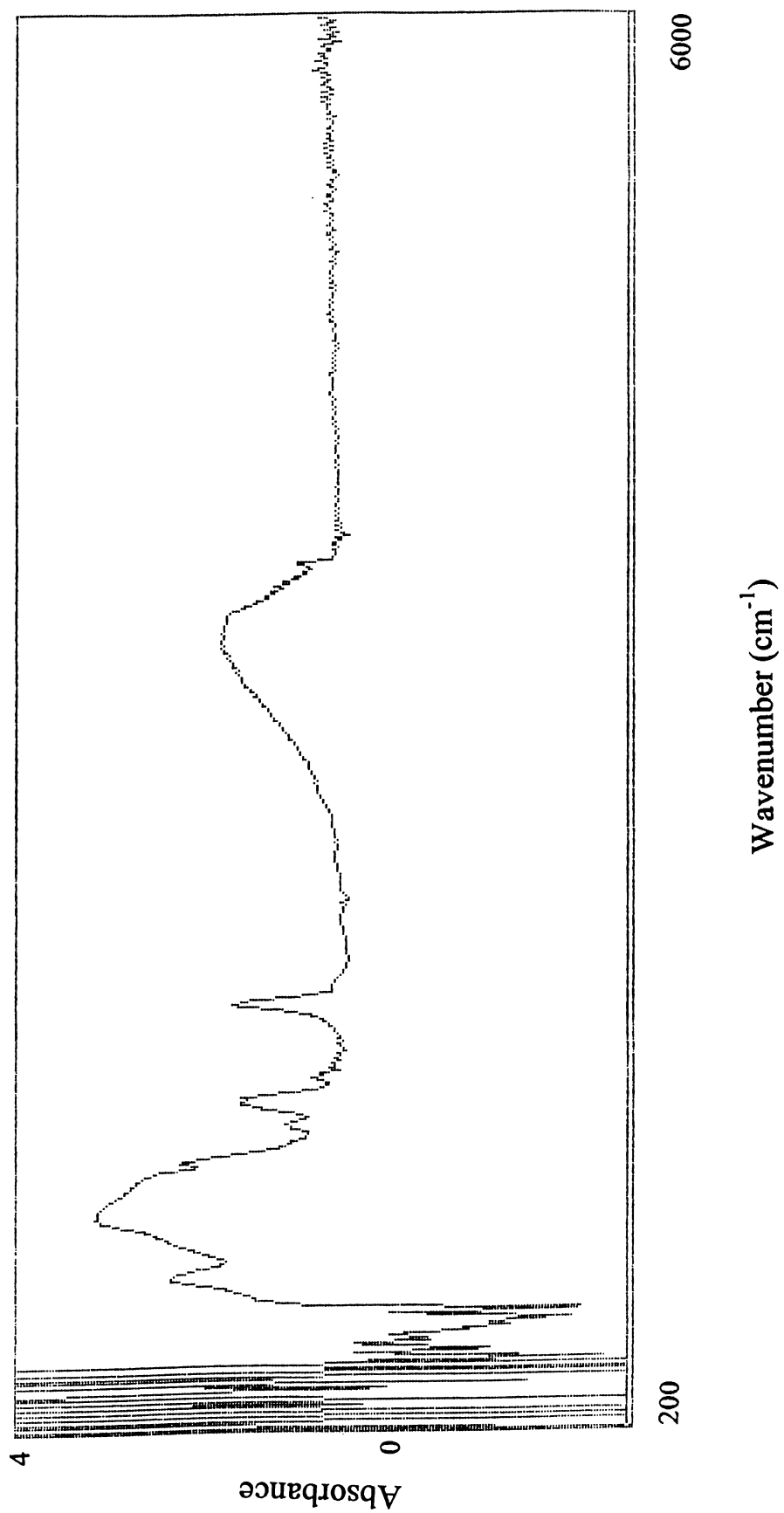


Fig.2 A typical DRIFTS spectrum showing the cut-off of ZnSe windows at 500 cm^{-1}

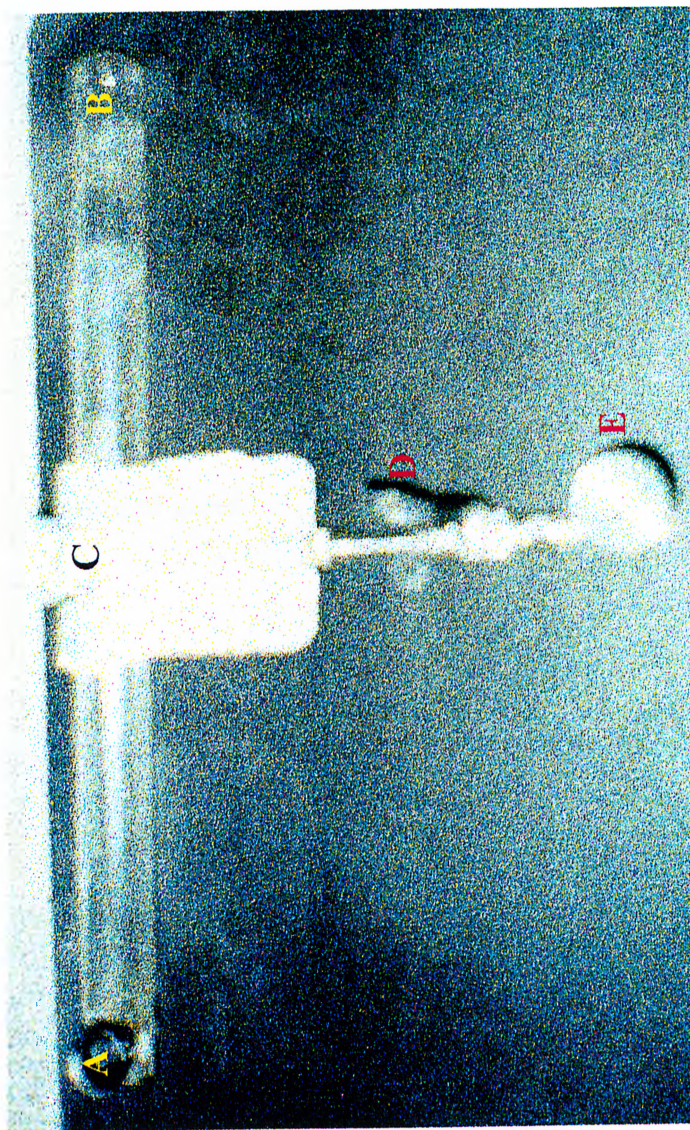


Fig.3 Pyrex glass IR cell equipped with NaCl windows used in transmission IR experiments

- (A) NaCl windows (Analysis-end)
- (B) Reaction-end
- (C) Sample introduction compartment
- (D) On-off valve
- (E) Connection to the manifold

a sample introduction compartment in the middle which was closed after the introduction of the sample into the cell. One end of the glass cell (analysis-end) is specially designed allowing installation of NaCl windows and ensuring a short path length of IR beam. The other end of the cell (reaction-end) was used for performing reactions which could be placed in a small home-made furnace for heating of the sample to desired temperature. The furnace was heated by using a constant - voltage supplier and controlled manually. The temperature was determined by using a Thermocax Chromel-Alumel thermocouple. Transfer of the sample from one end of the cell to the other end was accomplished by tilting the glass cell and allowing the glass sample holder to slide along. Pyrex cell was connected to the manifold through a tubing, equipped with an on-off valve, which allows application of vacuum and exposing of gases.

The vacuum/adsorption manifold (Fig.4) which was designed for vacuum application ($P \approx 2.0 \times 10^{-3}$ mbar) and exposure of different gases or mixture of gases ($P = 2.0 \times 10^3$ mbar), consists of three gas inlets. A diffusion pump backed up with a rotary pump was connected to the manifold for evacuation purposes. The pumps were isolated from the adsorption system by a home made liquid nitrogen trap which also serves for the enhancement of vacuum and prevention of oil leakage from the pumps into the manifold.

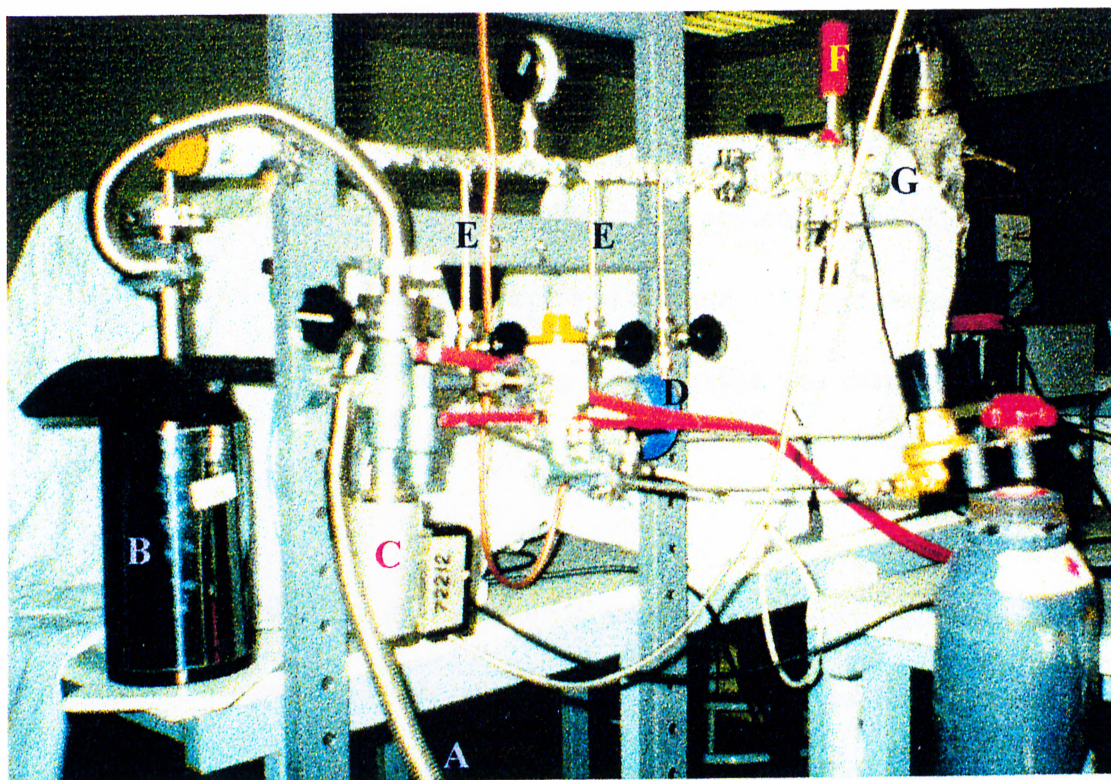


Fig.4 Vacuum/adsorption manifold

- (A) To the rotary pump
- (B) Liquid nitrogen trap
- (C) Diffusion pump
- (D) Alltech oxy-trap
- (E) Gas inlets
- (F) Pirani gauge
- (G) Connection to Pyrex glass IR cell

A typical transmission IR spectrum is shown in Fig.5. NaCl windows of the Pyrex glass cell has a cut-off at 650 cm^{-1} due to the absorption of infrared radiation by NaCl in the region $200\text{--}650\text{ cm}^{-1}$.

2.1.2.1 Ammonia synthesis

Self-supporting discs were obtained by pressing the powdered catalyst under a pressure of 6 tons. The disc was cut to a $9\text{ mm} \times 15\text{ mm}$ rectangle and placed in the Pyrex glass sample holder along with the disc was introduced into the Pyrex glass cell.

The reduction of the catalyst was performed with successive hydrogen exposure/evacuation cycles at $350\text{ }^{\circ}\text{C}$ for two hours. Following the complete reduction, the sample was evacuated at that temperature for one hour. After cooling down to room temperature, the sample is transferred to the analysis-end of the glass cell for IR measurements. Data were collected at a resolution of 4 cm^{-1} and 256 scans were acquired with DTGS 2mm detector.

After collection of data, the sample was transferred to the reaction-end of the cell for further treatment. The sample was heated to the reaction temperature of $350\text{ }^{\circ}\text{C}$. The manifold was purged with nitrogen, which was passed through an Alltech Oxy-trap for the removal of oxygen present in the nitrogen cylinder (obtained from

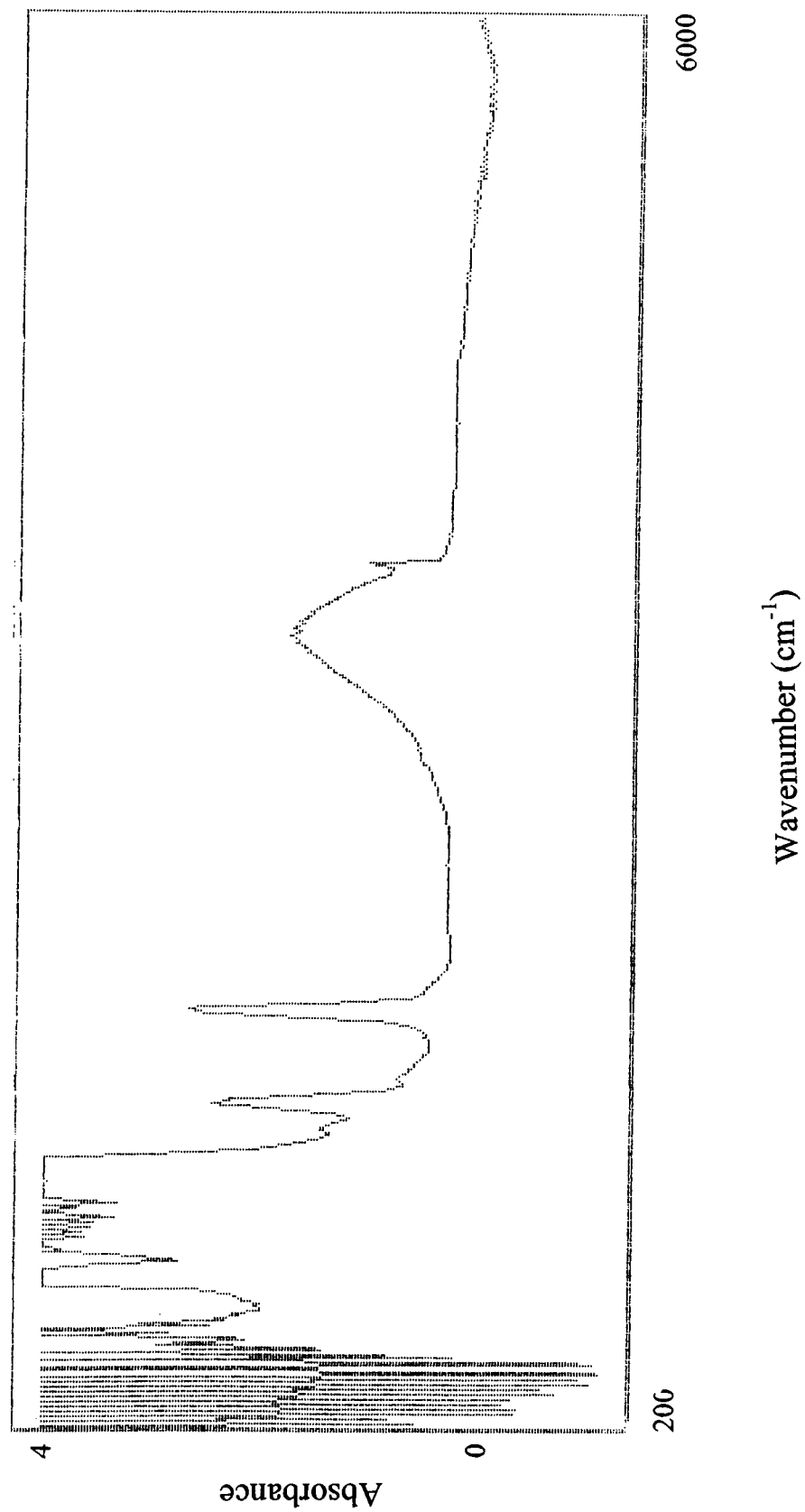


Fig.5 A typical transmission IR spectrum showing the cut-off of NaCl windows at 650 cm^{-1}

Habaş), before entering the manifold. Following nitrogen exposure, the manifold was purged with hydrogen (obtained from Habaş) consequently, hydrogen exposure was accomplished. The ratio of $H_2:N_2$ was approximately 3:1 but this value was not exact due to variable sensitivity of Pirani gauge to hydrogen gas. Ammonia synthesis was performed under these conditions for different reaction times (30, 60, 120, 240, 480, and 720 minutes).

2.1.2.2 Carbon Monoxide Adsorption on Reduced Catalyst

The reduction of the catalyst was performed with successive hydrogen exposure/evacuation cycles at 350 °C for two hours. Following the complete reduction, the sample was evacuated at that temperature for one hour. After cooling down to room temperature, the sample is transferred to the analysis-end of the glass cell for IR measurements. Data were collected at a resolution of 4 cm^{-1} and 256 scans were acquired with DTGS 2mm detector.

Carbon monoxide adsorption was accomplished by pulsing CO onto the reduced catalyst and IR measurements were performed after each pulsing.

2.1.2.3 Carbon Monoxide Adsorption on the Catalyst after Ammonia

Synthesis

The complete reduction of the catalyst was performed as explained previously. Following the completion of activation of the catalyst, the sample was evacuated at that temperature for one hour and cooled down to room temperature. The sample is transferred to analysis-end for collection of data. Carbon monoxide is adsorbed on the reduced sample in pulses at room temperature and acquisition of spectrum is performed after each pulsing. Following the CO adsorption, the sample is evacuated for one hour. The sample is transferred to reaction-end and heated to 350 °C and evacuated for the removal of CO species if any left on the surface of the sample. Data is collected after this treatment to ensure the removal of CO species.

The ammonia synthesis is accomplished at 350 °C in a N₂/H₂ gas mixture (N₂/H₂ ≈ 3:1) for twelve hours. The sample is cooled down to room temperature and acquisition of spectrum is accomplished after the transfer of the sample to analysis-end.

Prior to CO adsorption, the sample is evacuated for one hour (for removal reaction intermediates and products. The sample is exposed to CO (P_{CO}=32 torr) and data is collected following CO adsorption.

2.2 XPS measurements

XPS measurements were performed on a Kratos ES300 spectrometer using Mg K α excitation ($h\nu = 1253.6$ eV). The C1s line (B.E.=285.0 eV) from residual hydrocarbons deposited on the surface of the sample was used as a reference. The Si 2p line (B.E.=103.3 eV) was considered as an internal reference in the study of the supported catalyst (Ru/SiO₂). The pressure in the UHV chamber of the spectrometer was kept below 1.0×10^{-8} torr.

A typical wide spectrum of 4% Ru/SiO₂ is shown in Fig.6 presenting the general features. Hydrocarbon residue on the sample surface is originated from the atmosphere. N 1s line is not visible due to both its small cross-section and its small amount present on the sample surface. O 1s line is mainly composed of oxygen in silica and to a small extent to H₂O from atmosphere. Ru 3d doublet and C 1s lines overlaps giving a single complex peak due to their close binding energies. Particular attention was devoted to the fitting of the peaks in the region including Ru 3d and C 1s. A number of contrivances were used such as fixing the ratio between the 3d doublet area, the relative intensities of the doublet peaks due to their respective degenerations ($2j+1$), hence the intensity ratio of $j=3/2$ and $j=5/2$ components of the Ru 3d doublet is (3:2). The energy spacing of the spin-orbit doublet was also fixed which 4.17 eV for Ru doublet. A perfect symmetry of the peaks was hypothesized (Fig.7) [38].

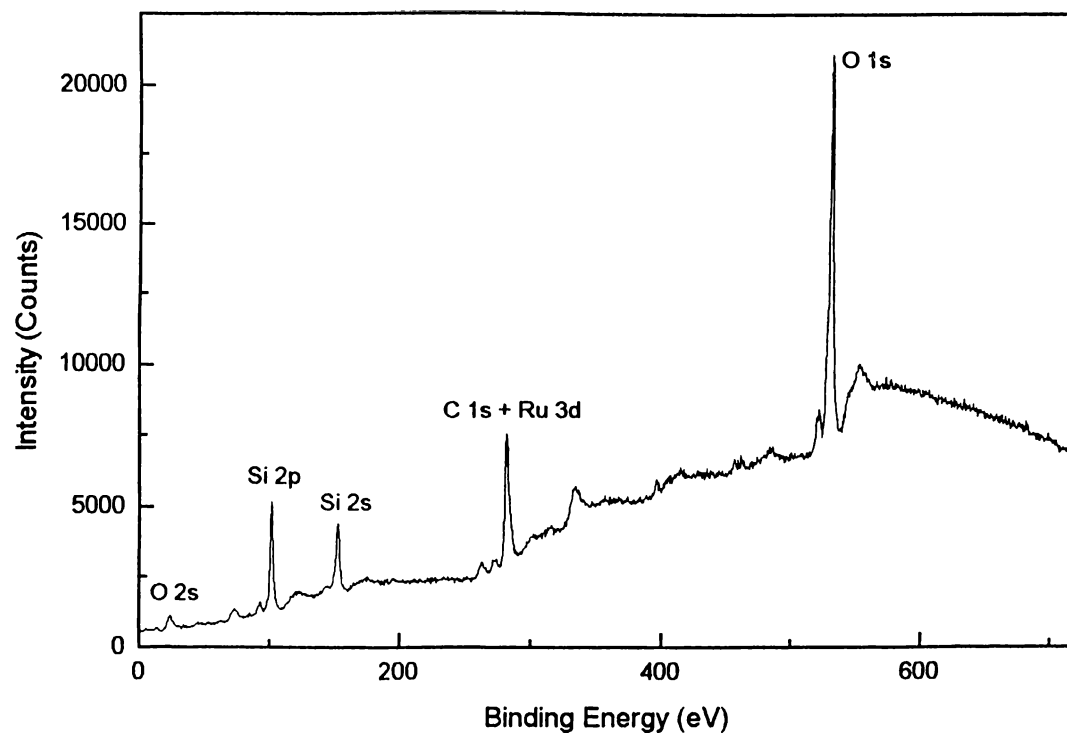


Fig.6 Wide spectrum of 4% Ru/SiO₂

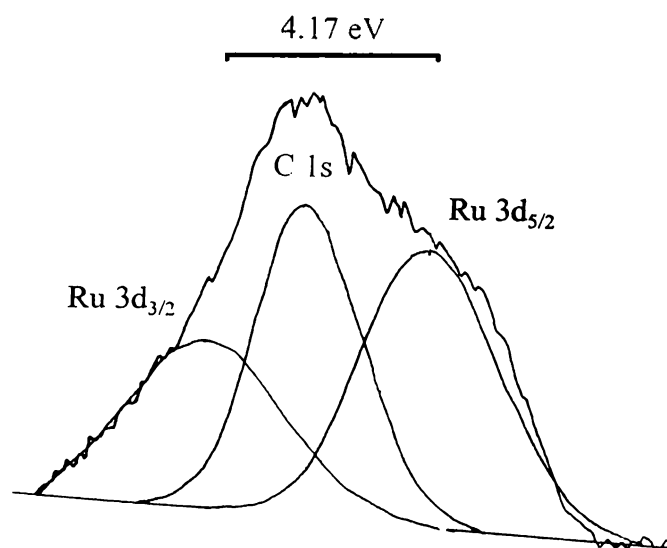


Fig.7 Deconvolution of Ru 3d and C 1s region

2.2.1 Sample preparation and loading

The powdered catalyst was introduced into copper holder and pressed which was then attached to the probe of the spectrometer. The probe together with sample attachment was introduced into the UHV chamber of the spectrometer for analysis.

The pelletized catalyst used for annealing studies was cut to a 4 mm $\times$ 12 mm rectangle and placed in the copper holder which was attached to the probe of the spectrometer.

In the case of the precursor, the precursor was pasted on a stainless steel attachment. The attachment was then connected to the probe of the spectrometer and placed in UHV chamber.

2.2.3 Annealing studies

The thermal treatment of the samples were carried out in the UHV chamber of the spectrometer by gradual heating of the sample to 170 °C in-situ. XPS data were recorded after each step.

3. RESULTS AND DISCUSSION

3.1 DRIFTS Measurements Performed on the Catalyst During the Course of Reduction

Fig.8 displays the diffuse-reflectance IR spectra of the 4% Ru/SiO₂ catalyst at room temperature and after 60 minutes reduction under H₂ atmosphere at the corresponding temperatures. The bands at 1427 and 1925 cm⁻¹ are attributed to bent NO group and terminal NO group respectively. The band at 1521 cm⁻¹ together with the band at 1275 cm⁻¹ (the shoulder at the higher wavenumber region of $\nu(\text{SiO})$) can be assigned to the split ν_3 vibration of monodentate nitrate anion [43]. The separation of the two highest frequency bands, $\Delta\nu_3$ is 246 cm⁻¹. The bands at 1980 and 1880 cm⁻¹ are assigned to SiO overtones. The diffuse band in the region 3500-3700 cm⁻¹ corresponds to hydrogen bonded hydroxyl groups and the band at 3747 cm⁻¹ is attributed to single hydroxyl groups.

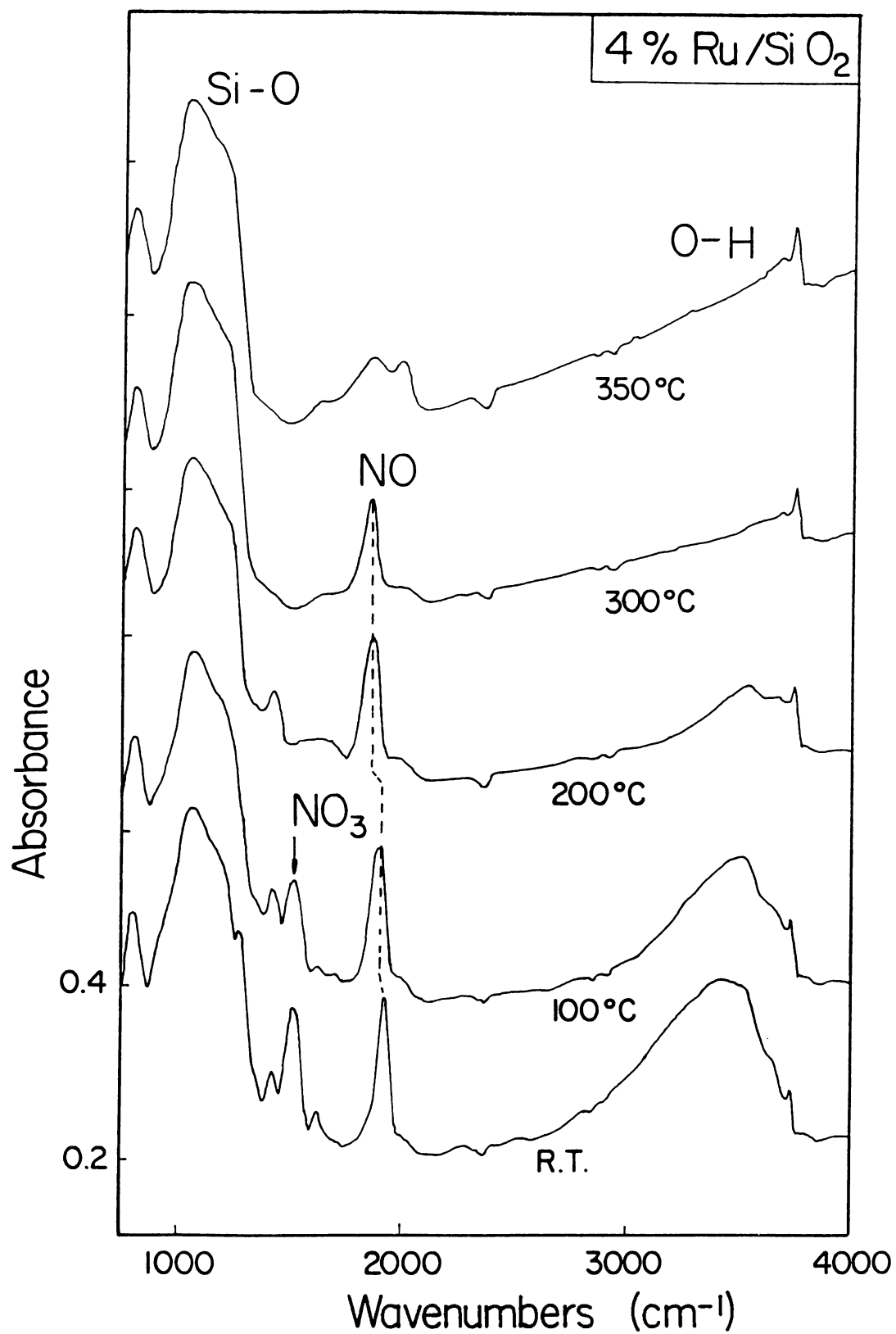


Fig.8 Diffuse-reflectance IR spectra of 4% Ru/SiO₂ catalyst before, during, and after reduction at corresponding temperatures

This nitrosyl complex is accounted for on the basis of the simple three-body (M-N-O) model since the complex does not contain two or more nitrosyl groups that attached to the metal [44] . Bent NO group showed an unusually low vibrational frequency. However, the vibrational frequency of NO is governed by several factors such as electronic effect of other ligands, nature of the metal, structure and charge of the whole complex.

Table 3.1 Assignment of Observed IR Bands

Absorption Bands (cm^{-1})	Compound	Interpretation
1000-1200	SiO_2	$\nu(\text{SiO})$
1275	NO_3^- (monodentate)	$\nu_3(\text{split})$
1427	NO (bent)	$\nu(\text{NO})$
1521	NO_3^- (monodentate)	$\nu_3(\text{split})$
1627	H_2O	$\nu_2(\text{H}_2\text{O})$
1925	NO (terminal)	$\nu(\text{NO})$
1864	SiO_2	$\nu(\text{SiO})$ overtone
1980	SiO_2	$\nu(\text{SiO})$ overtone
3500-3700	OH (hydrogen bonded)	$\nu(\text{OH})$
3747	OH (single)	$\nu(\text{OH})$

Loss of hydrogen bonded OH bands, stepwise removal of NO_3^- bands followed by those of NO, and the growth of single hydroxyl band are the general features, and complete removal of species is achieved only after heating to 350°C in hydrogen atmosphere. In addition, the NO band originally centered at 1925 cm^{-1} is

red-shifted and broadened during the course of reduction. This change can be attributed to a partial loss of NO_3 groups and/or to change in valence state of the metal possibly due to reduction and/or to electron transfer from the support to antibonding orbital of NO which resulted in weakening of the NO bond. The terminal NO groups presented a certain stability during reduction when compared with the bent NO groups. It was possible to remove the bent NO species at a reduction temperature of $200\text{ }^{\circ}\text{C}$ whereas the terminal NO groups were removed only at a temperature of $300\text{ }^{\circ}\text{C}$.

Fig.9 shows the behaviour of the precursor and the catalyst during reduction under identical conditions. The mentioned red-shift and broadening is observed for the catalyst whereas in the case of precursor, the NO band remained in the same position (1925 cm^{-1}) and a shoulder appeared on the high-frequency side of this band. This suggested that a possible metal and support interaction can be pronounced for the former case.

3.2 CO Adsorption on the Catalyst After Reduction :

Carbon monoxide adsorption on the reduced catalyst was performed in order to investigate the nature of active adsorption sites.

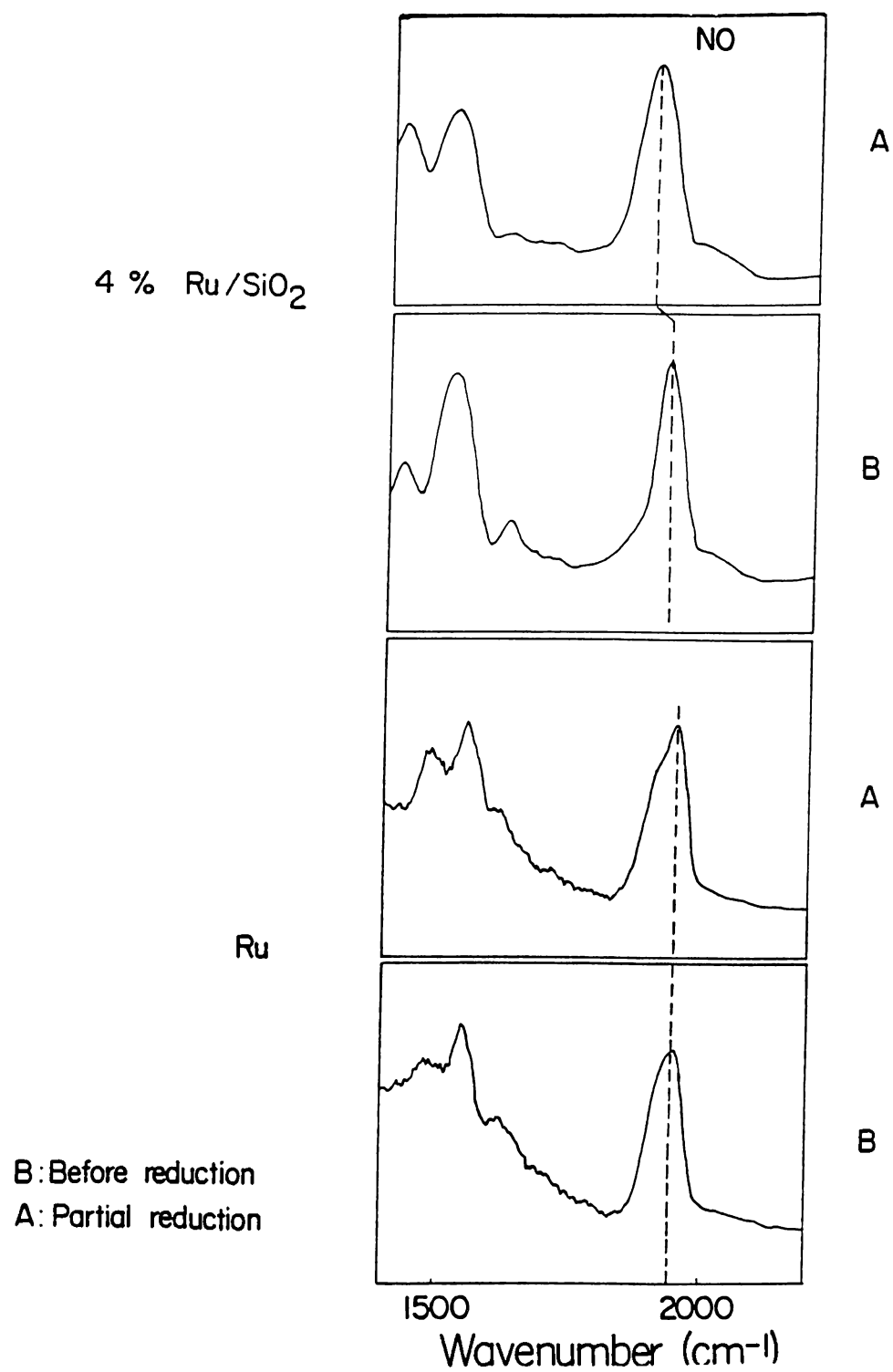


Fig.9 Diffuse-reflectance IR spectra of precursor and catalyst before and during reduction under identical conditions

The chemisorption of CO on silica-supported Ru has been studied extensively by infrared spectroscopy. The complexity of spectrum of chemisorbed CO depending on the Ru particle size has been discussed by Dalla Betta [32]. He studied the adsorption of CO on supported and unsupported Ru catalysts (Ru/Al₂O₃) of varying Ru metal particle sizes. The author inferred that samples with very large metal particles exhibited only one infrared band while three bands were observed for smaller particles. Adsorption measurements indicated the presence of multiple CO adsorption on samples containing small metal particles. This lead to the conclusion that as the particle size decreases, the fraction of surface atoms of low coordination number increases causing a multiple adsorption of CO to occur.

In general, the adsorption of CO on various supported Ru catalysts leads to the appearance of three groups of bands : HF (high-frequency) bands at 2156-2133 cm⁻¹ , MF (medium-frequency) bands at 2100-2060 cm⁻¹ and LF (low-frequency) 2080-1995 cm⁻¹. This classification is conventionally used in literature. Some authors denoted HF and MF bands as (HF₁) and (HF₂) respectively. Further throughout the text, this convention will also be used.

There is consensus on the assignment of the low-frequency band (LF) at $2040 \pm 10 \text{ cm}^{-1}$ to linearly adsorbed CO on metallic Ru but, there is disagreement over the assignment of the two high-frequency bands at (HF₁) $2140 \pm 10 \text{ cm}^{-1}$ and (HF₂) $2080 \pm 10 \text{ cm}^{-1}$. The observations of a constant ratio of the intensities of these

bands with changing CO coverage has led several investigators to attribute the pair of HF bands to dicarbonyl species [27,28,29]. By contrast, other investigators have noted a change in the ratio of intensities of the HF bands and have assigned them to linear or multicarbonyl species [30,31]. The increase in intensity of the HF bands with oxidation of the catalyst has led several authors to conclude that the adsorption sites associated with these bands are partially or completely oxidized [27,30,31].

Bell et.al [33] studied the nature of the sites involved in CO chemisorption on reduced and oxidized Ru surfaces. In their study, three peaks were observed upon CO exposure on the fully reduced sample; 2144 (HF₁), 2082 (HF₂), and 2047 cm⁻¹ (LF). By exposing ¹³CO-¹²CO mixture on the sample and observing the changes in the intensity and position of the bands, the former two bands were assigned to tricarbonyl species on metallic Ru centers, Ru(CO)₃. Whereas the band at 2047 cm⁻¹ corresponded to monocarbonyl species of the type Ru⁰-CO. The LF band intensity decreased significantly upon passage of He over the catalyst and the intensity ratio HF₁/HF₂ was approximately 0.5. To complement the studies performed on fully reduced samples, CO chemisorption was also performed on intentionally oxidized catalyst. In this case, three bands were observed, namely at 2136 (HF₁), 2080 (HF₂), and 2032 (LF) cm⁻¹. The intensities of the HF bands were greater than those for the reduced sample, but the intensity of the LF band is significantly smaller. It was also noted that the ratio of the intensities of HF₁ / HF₂ was less than 0.5. Upon flushing with He, the LF (2032 cm⁻¹) band decreases significantly in intensity. This band was

assigned to monocarbonyl species adsorbed on the sites not extensively affected by adsorbed oxygen. The band at 2136 cm^{-1} together with the band at 2080 cm^{-1} corresponded to tricarbonyl species of the type $\text{Ru}^{+8}(\text{CO})_3$.

By some authors, the bands in the region $1950\text{--}2000\text{ cm}^{-1}$ are attributed to bridged carbonyl species. It is reported that these species are very stable surface species upon evacuation [34,35].

The spectra of CO adsorbed at 298 K on reduced Ru/SiO₂ with increasing and decreasing CO pressure are given in figures 10a and 10b respectively. CO bands and their behaviour are found to be in good agreement with those reported in previous investigations [33,34,35]. Seven peaks are found after deconvolution of the spectrum, at 1909, 1957, 1997, 2035 (LF), 2066 (HF₂), 2112 (HF₁¹), and 2131 (HF₁) cm^{-1} upon 32 torrs of CO exposure (Fig. 11a). With increasing CO pressure, the band at 2112 cm^{-1} grew in intensity together with the band at 2131 cm^{-1} . The former band decreased in intensity upon evacuation. The intensity of the band at 2035 cm^{-1} disappeared after evacuation. Whereas the bands at 1909, 1957, 1997 are not affected by evacuation suggesting a certain stability. The bands at 2131 (HF₁) and a component of the band at 2066 (HF₂), are attributed to tricarbonyl species on metallic Ru centers [Ru(CO)₃]. Whereas the band at 2035 cm^{-1} (LF) corresponds to monocarbonyl of the type Ru-CO in accordance with the observations done by Bell et.al [33]. In our study, the bands at 2112 (HF₁¹) together with the band at 2066

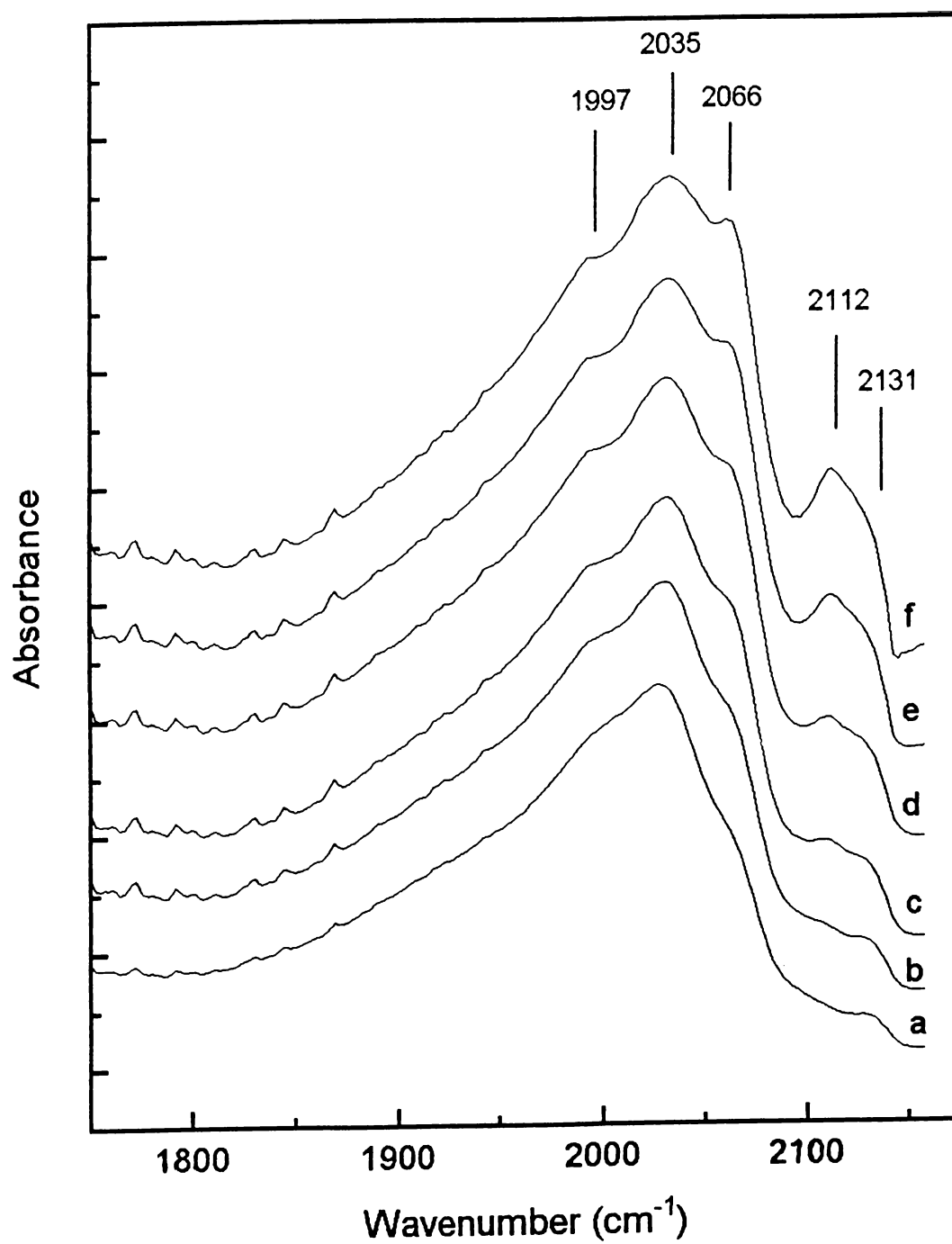


Fig.10a The difference spectra of CO adsorption on reduced Ru/SiO₂ with increasing CO pressure (a)0.2 torr (b)1 torr (c)5 torr (d)10 torr (e)20 torr (f)32 torr

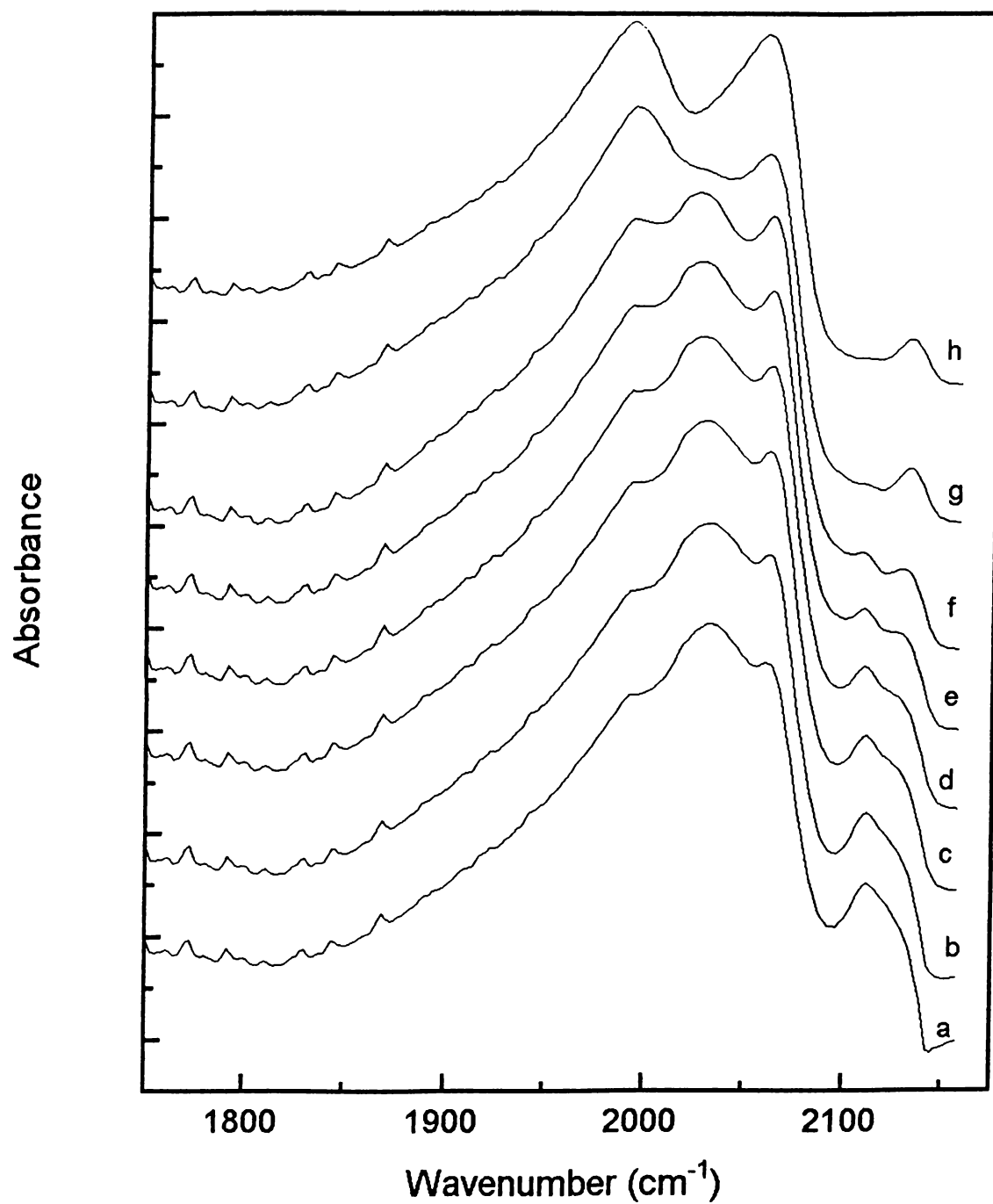


Fig.10b The difference spectra of CO adsorption on reduced Ru/SiO₂ with decreasing CO pressure (a)32 torr (b)20 torr (c)10 torr (d)5 torr (e)1 torr (f)0.2 torr (g) after 10 min.evacuation (h) after 30 min. evacuation

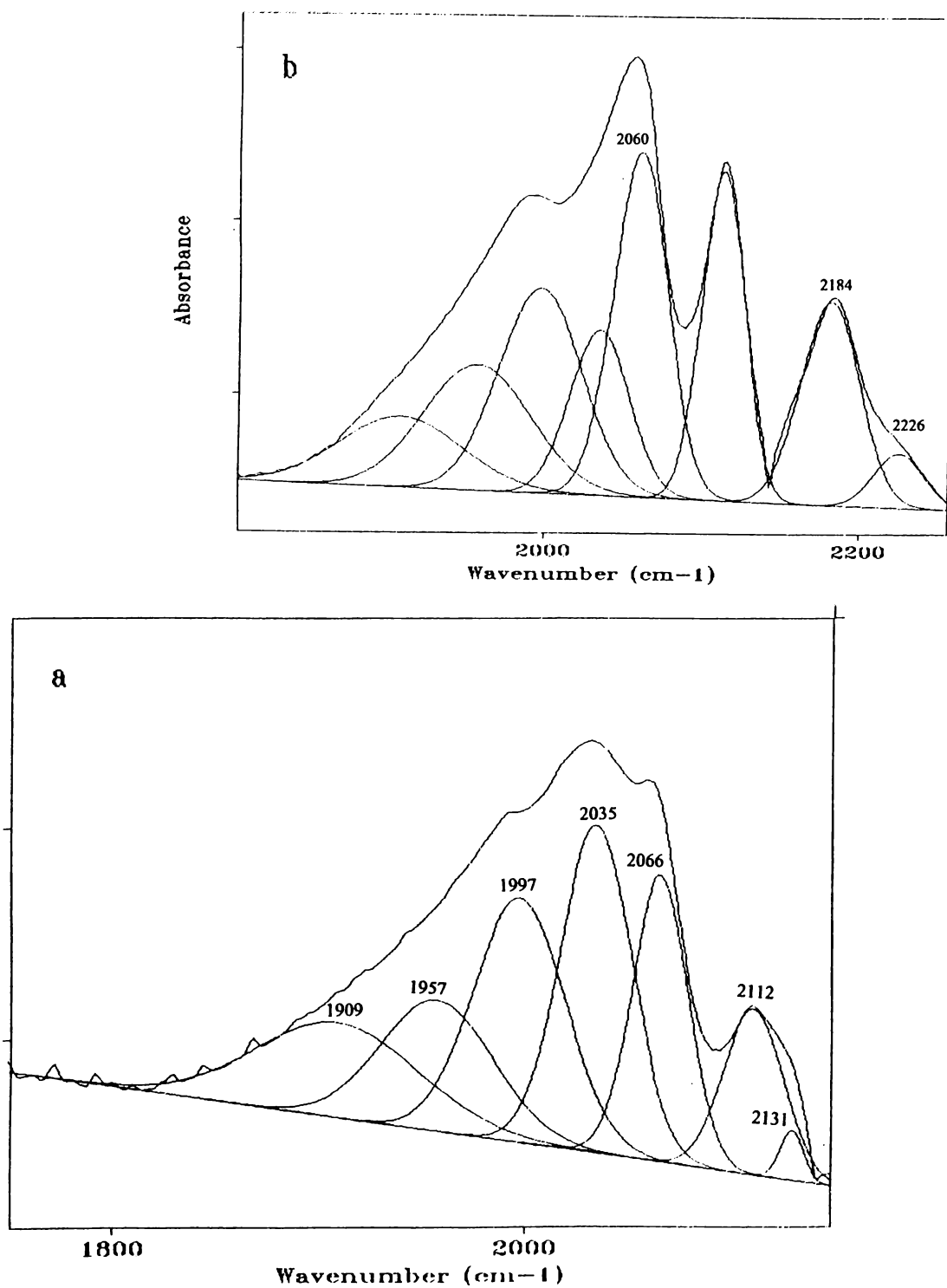


Fig.11 (a) Deconvolution spectrum of 32 torrs CO adsorption on reduced Ru/SiO₂
(b) Deconvolution spectrum of 32 torrs CO adsorption on catalyst after NH₃ synthesis

(HF₂) are attributed to CO adsorbed on oxidized centers in the form of tricarbonyl [Ru^{+δ}(CO)₃]. The ratio of the intensities of HF₁/HF₂ was found to be approximately 0.2. This is due to the fact that HF₂ band is composed of two overlapping bands namely, the HF₂ band of tricarbonyl on reduced and oxidized Ru surfaces.

The bands 1909, 1957, and 1997 cm⁻¹ are attributed to bridged carbonyl species due to their stability and position [34,35].

Table 3.2 Infrared Assignments for ¹²CO Adsorbed on Ru/SiO₂

Frequency (cm ⁻¹)	Assignment	Adsorption site
1909	Bridged CO	
1957	Bridged CO	
1997	Bridged CO	
2035	Linear	Ru
2066	Tricarbonyl	Ru , Ru ^{δ+}
2112	Tricarbonyl	Ru ^{δ+}
2131	Tricarbonyl	Ru
2184	Linear	Ru ⁿ⁺
2226	Linear	Ru ⁿ⁺

3.3 CO Adsorption on the Catalyst After NH₃ Synthesis

CO adsorption on the catalyst after NH₃ synthesis was performed in order to investigate the change in nature of active sites after ammonia production.

The band at 2112 cm^{-1} disappeared after evacuation whereas the bands at 2184 and 2226 cm^{-1} were not essentially affected suggesting a certain stability due to strong Lewis acidity of the that center. Upon evacuation the band at 2060 cm^{-1} grew in intensity (Fig.12).

When compared with the CO adsorption spectrum of the reduced sample, it was seen that the band originally at 2066 cm^{-1} decreased significantly in intensity and shifted to 2060 cm^{-1} . The band at 2035 cm^{-1} is not visible. The band at 2131 cm^{-1} and a component of the band at 2066 cm^{-1} were previously assigned to tricarbonyl species on metallic Ru centers whereas the band at 2035 cm^{-1} corresponded to monocarbonyl of the type Ru-CO in accordance with the literature data [33]. The absence of the band corresponding to Ru-CO species (2035 cm^{-1}) and the decrease in intensity of these bands at 2057 and 2131 cm^{-1} is due to $\text{Ru}(\text{CO})_3$ on the reduced catalyst evidences the participation of the Ru^0 sites in the ammonia synthesis. Here it should be noted that after evacuation of the reaction mixture at room temperature, no adsorbed NH_x ($x=1-3$) were observed, i.e, that the active sites are liberated from the reaction product and intermediates and they were available for CO adsorption.

In our study, the bands at 2112 (HF_1^1) together with the component of the band at 2066 (HF_2) are attributed to CO adsorbed on oxidized centers as a tricarbonyl $[\text{Ru}^{+\delta}(\text{CO})_3]$. In comparison with CO adsorption spectrum of the reduced

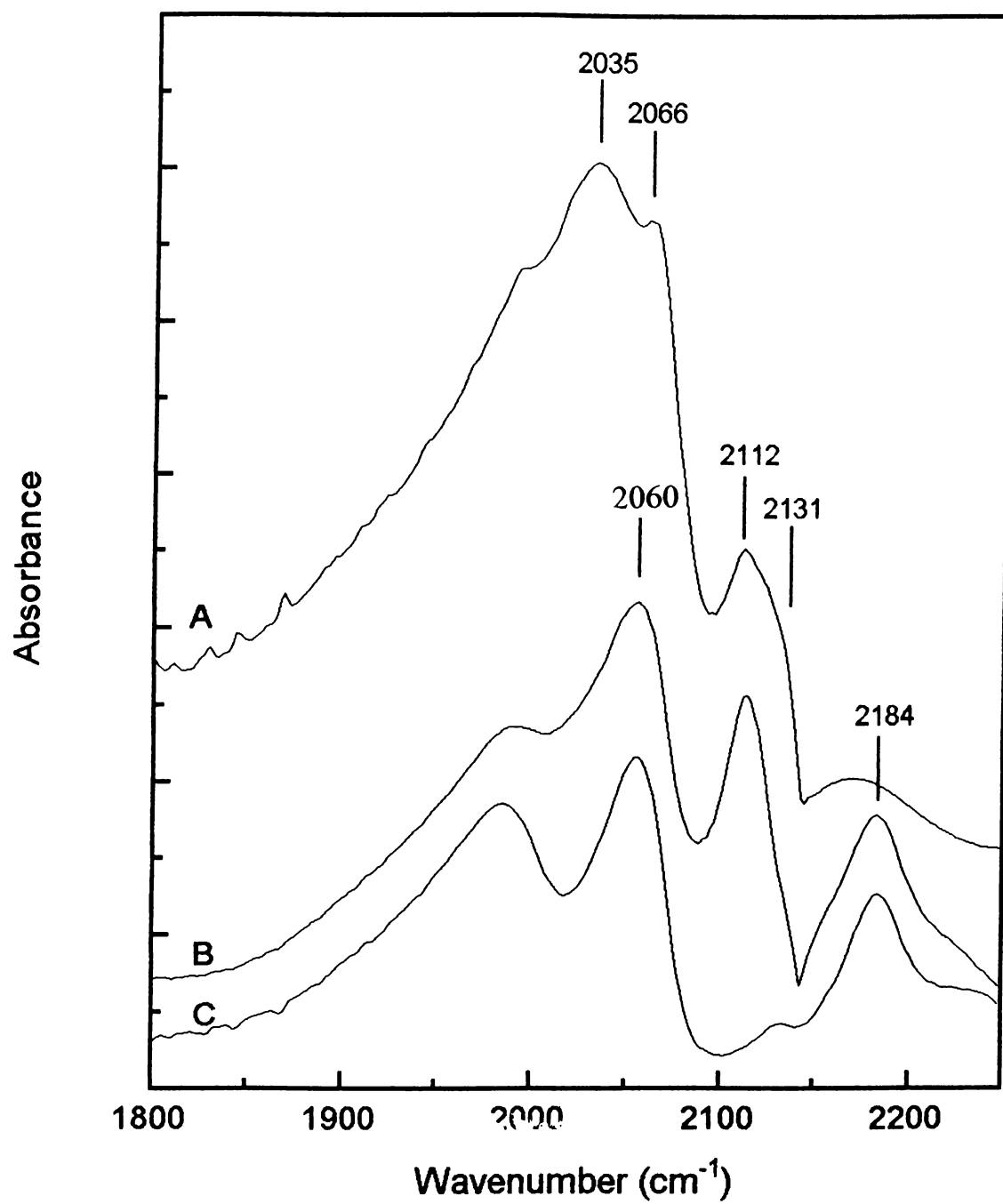


Fig.12 (a) 32 torrs CO adsorption on reduced Ru/SiO₂
(b) 32 torrs CO adsorption on catalyst after NH₃ synthesis
(c) evacuation after (b)

sample, these two bands are more intense suggesting an increase in the number of oxidized Ru sites. The disappearance of 2112 (HF_1^1) cm^{-1} band upon evacuation was accompanied by an increase in the intensity of the band at 2057 cm^{-1} . This result suggested the transformation of tricarbonyl species into monocarbonyl species present on oxidized Ru surfaces.

The origin of the bands at 2184 and 2226 cm^{-1} observed upon CO adsorption on the catalyst used in ammonia synthesis (the reaction mixture was evacuated prior to CO adsorption) is not clear. But it is possible to assign them to $\text{Ru}^{n+}\text{-CO}$ where $n > 2$. The reason for this is the band position. These species show a stability upon evacuation suggesting the presence of strong Lewis acid sites.

Eight peaks are seen in the deconvoluted spectrum at 1909, 1957, 1997, 2035 (LF), 2060 (HF_2), 2112 (HF_1^1), 2184, and 2226 cm^{-1} upon 32 torrs of CO exposure (Fig.11b). The absence of the band at 2131 cm^{-1} in the deconvoluted spectrum is probably due to overlapping of this band with the intense band at 2112 cm^{-1} .

Based on the experimental observations it is concluded that during the ammonia synthesis partial oxidation of the reduced Ru sites also takes place.

3.4 Interaction with H₂/N₂ Gas Mixture and NH₃ Synthesis

The introduction of gas mixture (H₂:N₂≈1:3) in the IR cell at 350°C causes the appearance of broad and strong absorption centered at about 3004 and 3020 cm⁻¹ for reaction times of 8 and 12 h, respectively (Fig.13c). The shift observed at different reaction times could be explained by different degree of hydrogen bonding. At the same time, sharp and less intensive bands at 3324 and 3405 cm⁻¹ are observed. In the low-frequency region an asymmetric band with a maximum at 1624 cm⁻¹ (Fig.13b) and a complex band in the region 1260-1300 cm⁻¹ (Fig.13a) are detected. All these bands increase in intensity or broaden with the increase of the reaction time. The bands in the 3000 - 2800 cm⁻¹ region present in the background spectrum (Fig.13c) are due to hydrocarbon residue on the sample surface. The bands at 3405 and 3324 cm⁻¹ correspond to stretching modes $\nu_{as}(\text{NH}_3)$ whereas, the bands in the low-frequency region are due to $\delta_{as}(\text{NH}_3)$ (1624 cm⁻¹) and $\delta_s(\text{NH}_3)$ (the complex band in the region 1300-1260 cm⁻¹) vibrations of coordinated ammonia [17]. Since the position of the latter band is sensitive to the strength of the coordination centers [17], it could be assumed that there are two types of adsorption sites differing in their coordinative unsaturation. These sites are characterized by $\delta_s(\text{NH}_3)$ of coordinated ammonia at 1291-1280 cm⁻¹ and 1278-1267 cm⁻¹, respectively (Fig.13a).

Table 3.4 Assignment of IR Bands Observed After
NH₃ Synthesis

Absorption Bands (cm ⁻¹)	Compound	Interpretation
1260-1300	NH ₃	δ_s (NH ₃)
1624	NH ₃	δ_{as} (NH ₃)
2800-3000	Hydrocarbon residue	
3004,3020	NH _x (x=1-3)	ν_{as} (NH _x), ν_s (NH _x)
3324	NH ₃	ν_{as} (NH ₃)
3405	NH ₃	ν_{as} (NH ₃)

It is known [17] that SiO₂ does not possess Lewis acidity, i.e. it cannot form coordination complexes with ammonia. On this oxide only NH₄⁺ ion is observed upon ammonia adsorption due to the present of Bronsted acid sites. For that reason it could be concluded that the ammonia produced on Ru/SiO₂ catalyst is located on Ru sites [17]. The ν_s (NH₃) stretching modes and ($\nu_s+2\delta_{as}$) combination band of coordinated ammonia which are expected to be at about 3250 and 3150 cm⁻¹ respectively, are overlapped by the strong absorption at about 3000 cm⁻¹. This strong and broad band could reveal the presence of amide groups (NH). Indeed, the associated secondary organic amides manifests their stretching vibration in the region 3100-3070 cm⁻¹ [35,36]. These bands are intense and diffuse due to hydrogen bonding.

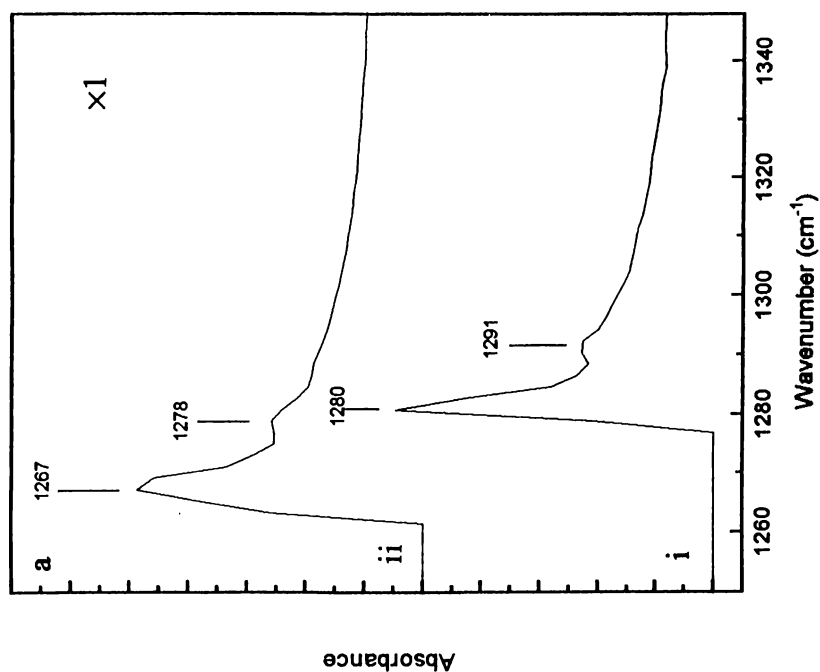


Fig. 13a IR spectra in the region 1250-1350 cm⁻¹
after NH₃ synthesis on Ru/SiO₂
(i) after 8 hr. (ii) after 12 hr. of reaction time

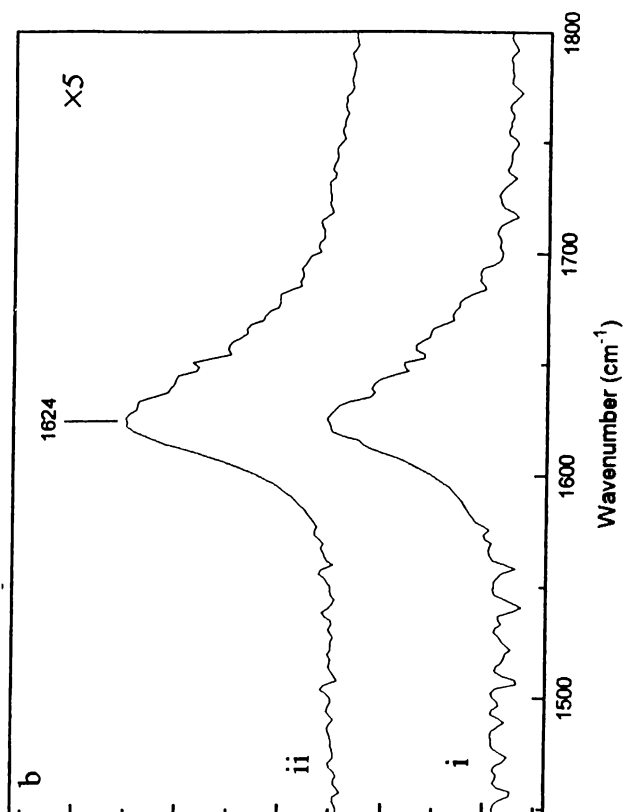


Fig. 13b IR spectra in the region 1450-1800 cm⁻¹
after NH₃ synthesis on Ru/SiO₂
(i) after 8 hr. (ii) after 12 hr. of reaction time

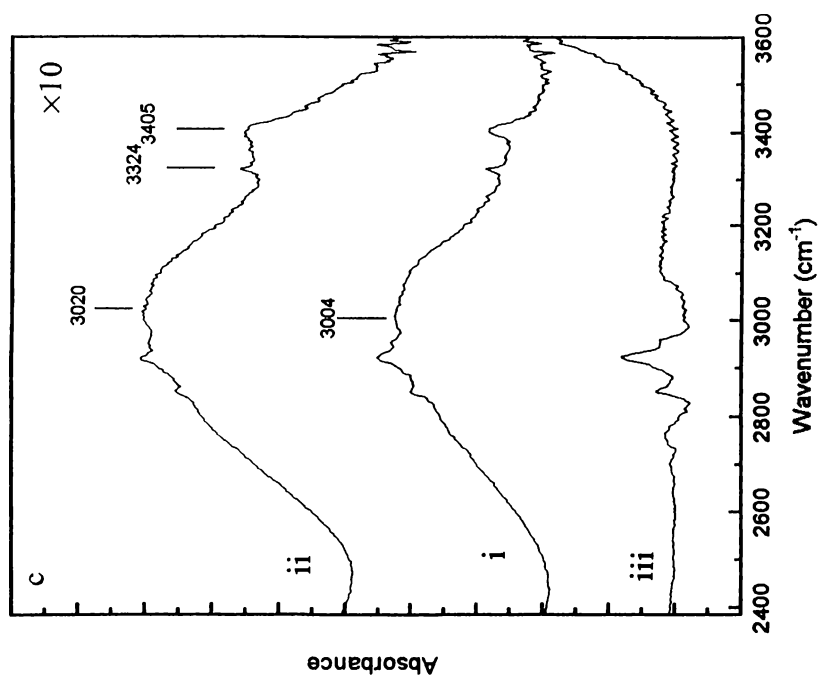


Fig. 13c IR spectra in the region 2400-3600 cm⁻¹
after NH₃ synthesis on Ru/SiO₂
(i) after 8 hr. (ii) after 12 hr. of reaction time
(iii) background spectrum

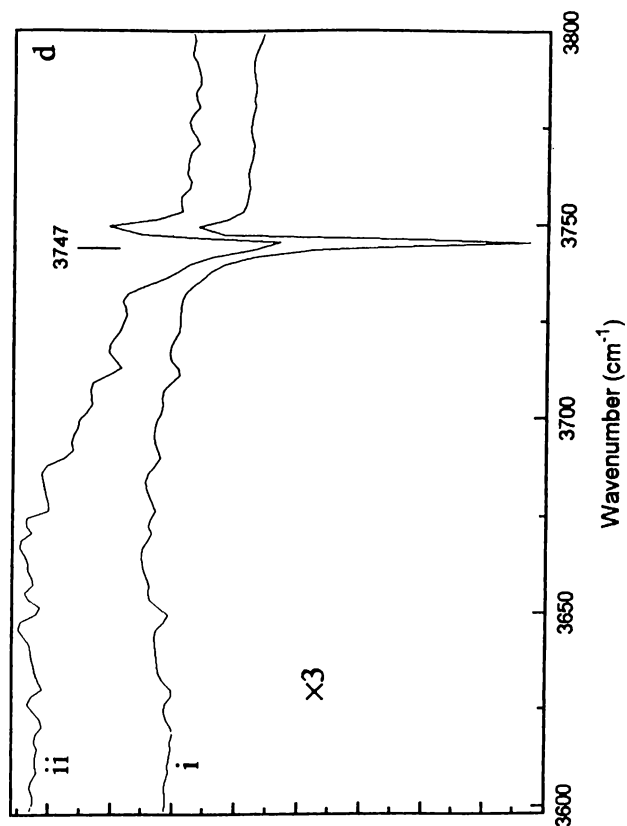
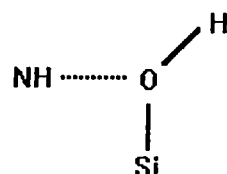


Fig. 13d IR spectra in the region 3600-3800 cm⁻¹
after NH₃ synthesis on Ru/SiO₂
(i) after 8 hr. (ii) after 12 hr. of reaction time

In general, the formation of ionic nitrogen-hydrogen groups of the type -NH_x ($x=1-3$) can not be excluded. Organic amine salts containing these groups are characterized by very strong absorption in the region $3200\text{-}1800\text{ cm}^{-1}$ due to $\nu_{\text{as}}(\text{NH}_x)$ and $\nu_{\text{s}}(\text{NH}_x)$ modes. The bending modes (symmetric and asymmetric) are observed in the region $1640\text{-}1480\text{ cm}^{-1}$ [35,36].

The decrease in isolated OH groups and appearance of OH hydrogen bonded groups may be due to the following reaction (Fig.13d):



Based on these considerations it could be concluded that NH_x surface species may represent intermediates in the ammonia synthesis on Ru/SiO₂ catalyst.

3.5 XPS measurements performed on the catalyst and the precursor

A series of catalysts with varying amounts of ruthenium supported on alumina and prepared from different precursors were analyzed via XPS by Bianchi et.al [42]. In this study, metal Ru, RuO₂, RuCl₃·3H₂O, Ru(acac)₃, and (NH₄)₃RuCl₆ were the analyzed precursors. The binding energy of the 3d_{5/2} level of ruthenium in the samples were found to be in the range 279.91-282.88 eV.

It is reported that on non-supported samples, it is also possible to obtain the metallic species by heating at about 250 °C without hydrogen. The same treatment on supported samples did not cause any reduction, it is concluded that the influence of the support and the possible interactions between the metal and the support itself prevent reduction without a reducing gas.

XPS spectra of Ru 3d-C 1s region of the precursor, catalyst and the catalyst after reduction are given in Fig.14. After the deconvolution of spectra, there is only one Ru 3d spin-orbit doublet with the 5/2 component at 283.1 eV found which can be assigned to the +4 state [39] for the precursor. When the supported ruthenium compound (catalyst) was studied, the Ru 3d doublet was found to be broad with a binding energy of 282.3 eV corresponding to the +3 state. The broadening can be attributed to dispersion of metal particles and the reduction Ru from +4 of the precursor compound to +3 of the supported one can either be attributed to a partial loss of NO_3^- groups and/or to electron transfer from the support and/or NO groups. In fact, the main features for the changes in spectra of the valence levels for dispersed metal particles on supports are the shift and broadening of the density of states [41]. XPS spectrum of the catalyst after reduction with hydrogen again revealed a single, broad Ru 3d doublet at a binding energy of 281.3 eV corresponding to Ru^{2+} . The failure to observe the zero-valent state is most probably due to exposure to air during transfer of the sample for XPS measurement. It is

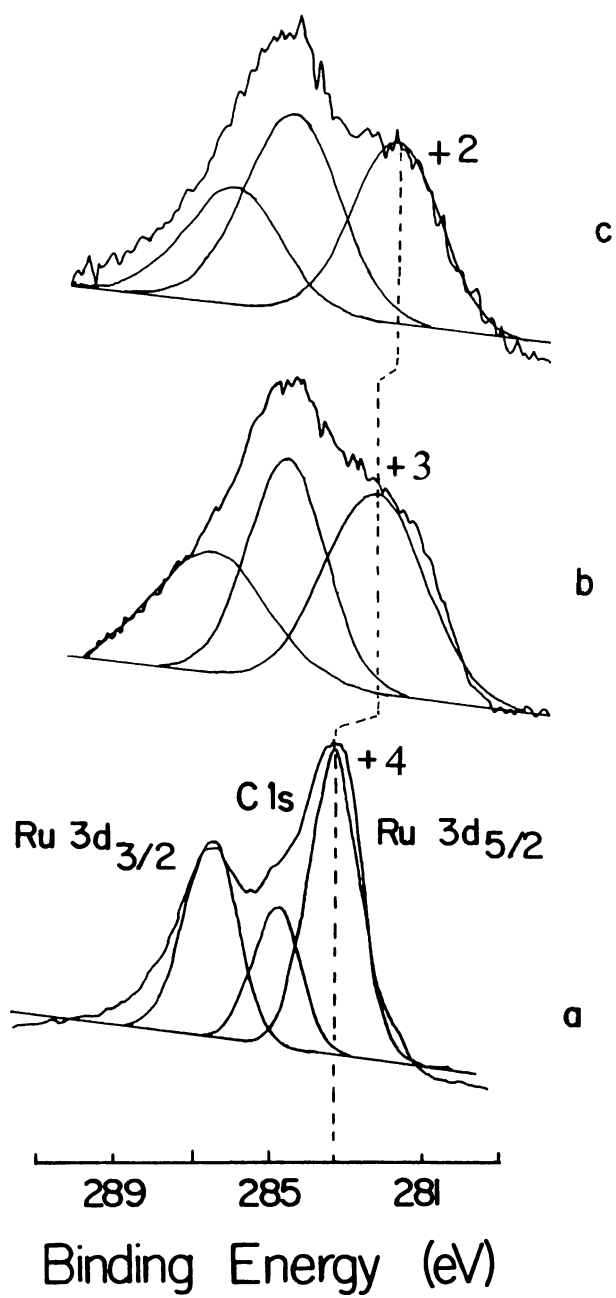


Fig.14 XPS spectra of Ru 3d-C 1s region of (a) precursor (b) catalyst (c) catalyst after reduction

known that metallic ruthenium is very easily oxidized in air even at room temperature [40].

3.5.1 XPS Measurements Performed on Precursor During Annealing

Fig.15 shows the XPS spectra of the N 1s and Ru 3d-C 1s regions before, during, and after annealing of the precursor $[\text{Ru}(\text{NO})(\text{NO}_3)_3]$ compound. Before annealing, two N 1s peaks at 405.6 eV and 401.8 eV, corresponding to NO_3 and NO nitrogens and with correct stoichiometry of 3:1, are present. Ru 3d doublet with 5/2 component at 283.1 eV is found which can be attributed to +4 state. During annealing, a stepwise removal of NO_3 followed by NO can be observed. In spite of the gradual decrease in the intensity of the N 1s peaks, the binding energies remain constant in contrast with the case of Ru 3d. Starting with the initial loss of NO_3 , a Ru $3d_{5/2}$ peak at 282.3 eV assigned to +3 oxidation state appears, followed by another one at 281.3 eV (+2) all the way to metallic Ru at 279.4 eV. After the loss of all the NO_3 and NO species, the deconvolution of Ru 3d region revealed the presence of not only metallic Ru but Ru with an oxidation state of +4 as well.

Bianchi et.al. [42] reported that all samples showed more than one species of ruthenium, on the surface where the analysis was performed in-situ. Similarly, in-situ experiments revealed two different species of ruthenium corresponding to different oxidation states.

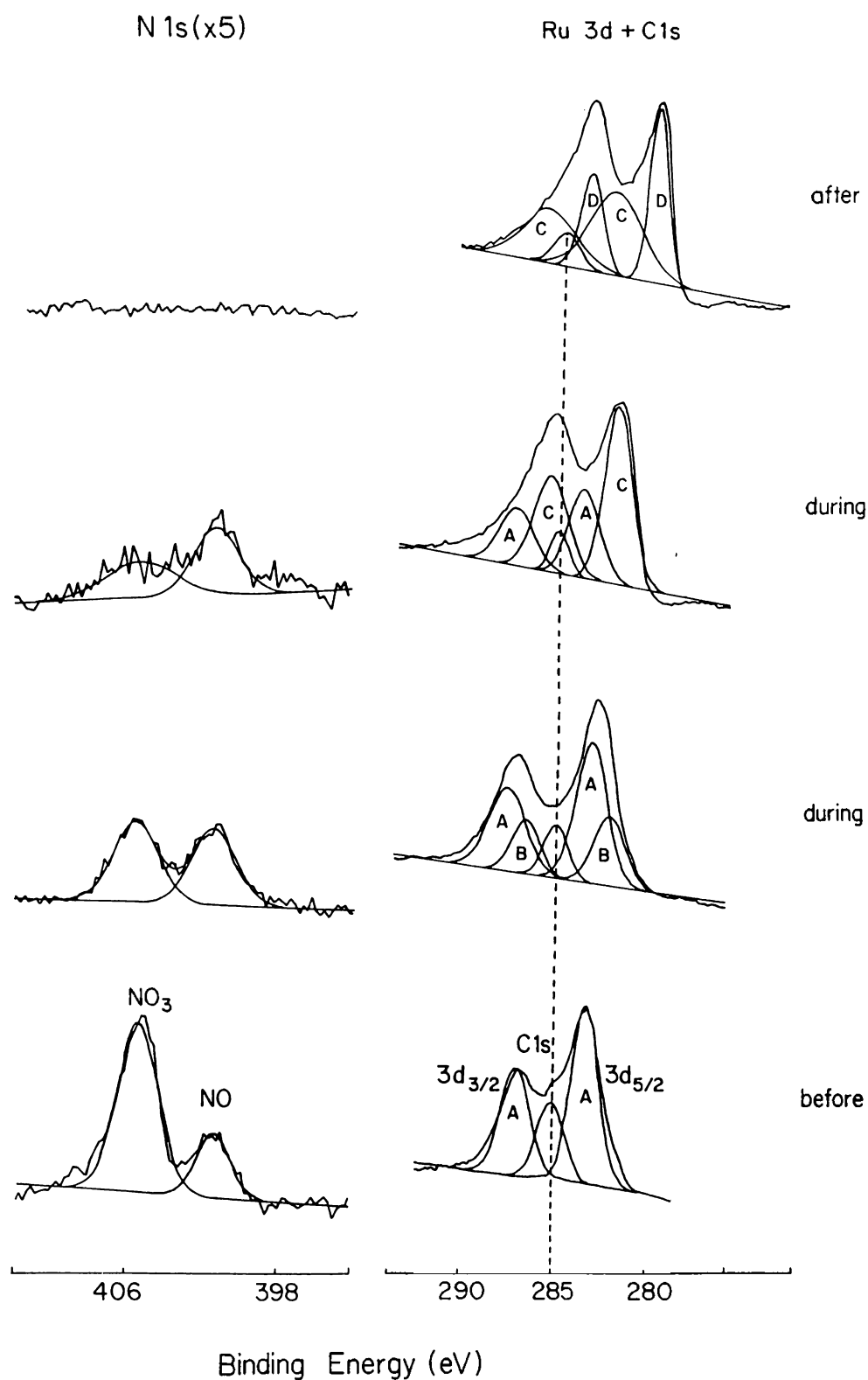


Fig.15 XPS spectra of N 1s and Ru3d-C1s regions before, during, and after annealing of the precursor $[\text{Ru}(\text{NO})(\text{NO}_3)_3]$. A, B, C, and D refer to the +4, +3, +2, and 0 oxidation states of Ru respectively

Table 3.5.1 List of the Binding Energies

Ru sample	(a) BE (eV)	(b) BE (eV)
Ru	279.4	279.9
RuO ₂	281.3	280.7
RuO ₃	282.3	282.4
RuO ₄	283.1	283.3

(a) Calculated values in this study

(b) Literature values [39,42]

It was possible to obtain the metallic ruthenium species by heating at about 170 °C without hydrogen in UHV conditions in the absence of SiO₂ support.

3.5.2 XPS Measurements Performed on Catalyst During Annealing

Ru 3d-C 1s and N 1s regions before, during, and after annealing of the catalyst are given in Fig.16a and 16b. Owing to the small cross-section of the N 1s level in comparison with Ru 3d level, the signal-to-noise ratio was not very high and the baseline was inclined. Before annealing, two nitrogen peaks corresponding to NO₃ and NO nitrogens revealed the correct stoichiometry (3:1). During and after annealing this ratio decreased to 2.25:1 and 1.97:1 respectively. But it was not possible to remove these species even after 60 minutes of annealing at 170 °C in UHV conditions. Consequently, the binding energies of Ru 3d levels remained essentially constant and corresponded to +3 oxidation state.

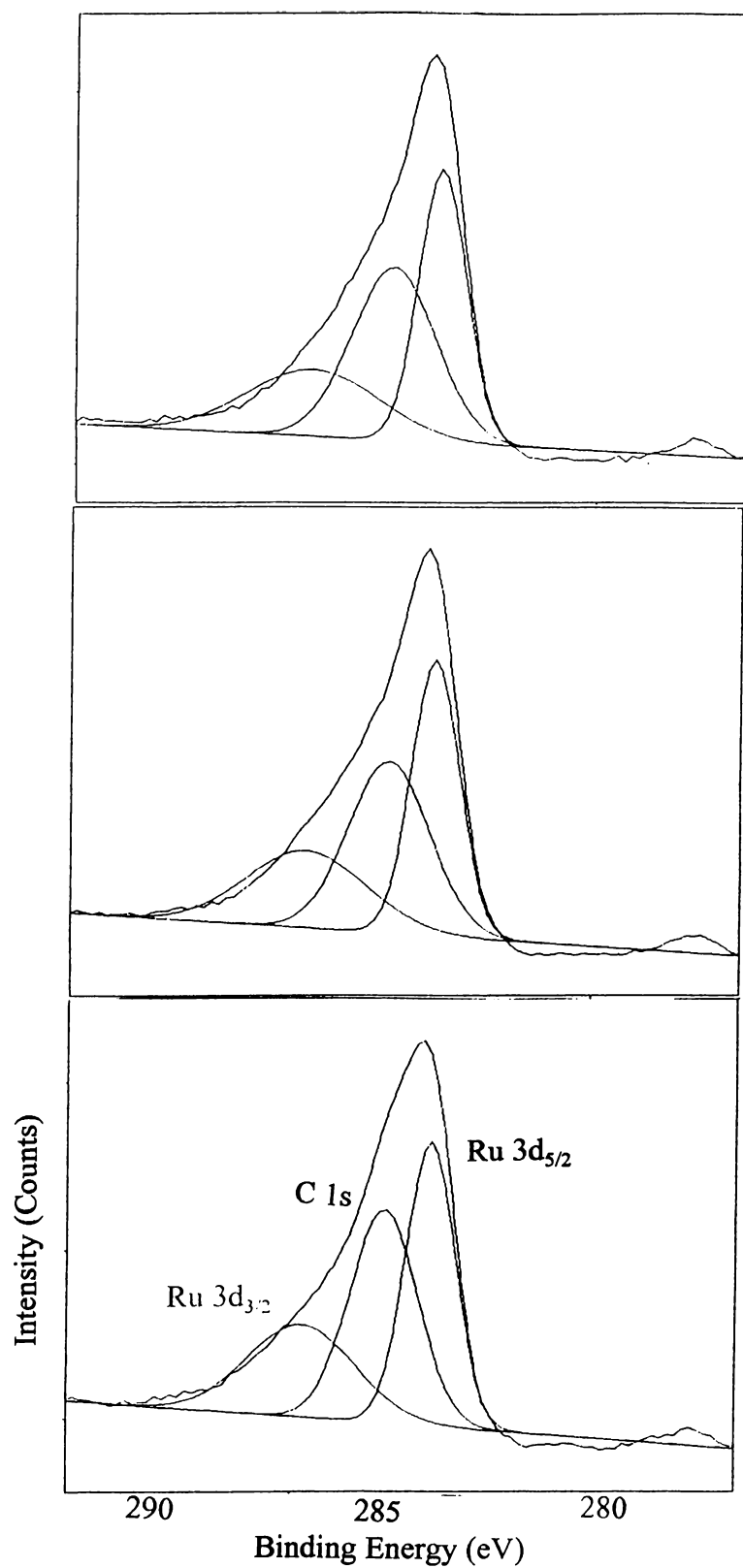


Fig.16a XPS spectra of Ru3d-C1s region before, during, and after annealing of the catalyst

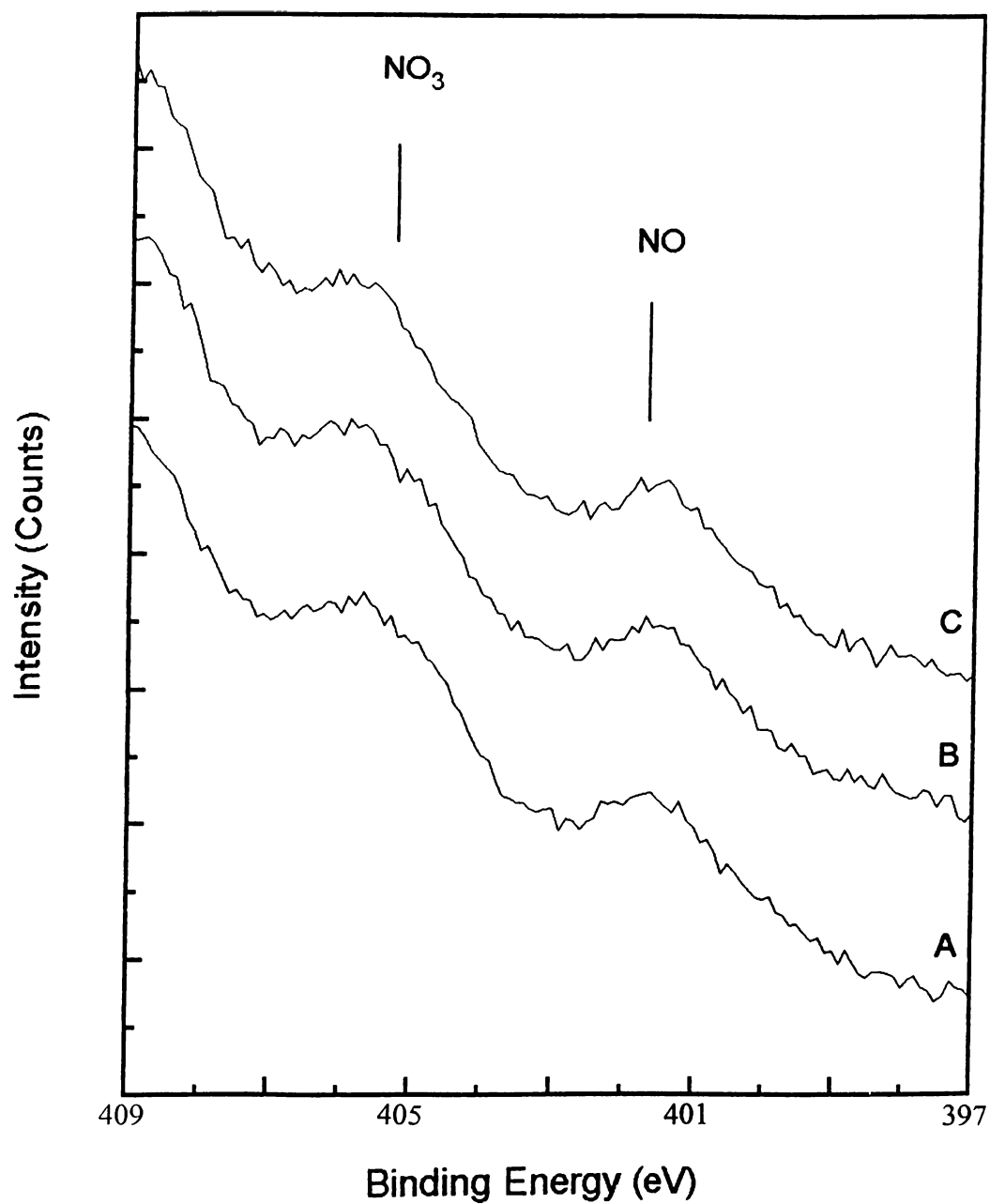


Fig.16b XPS spectra of N 1s region (A)before, (B)during, and (C) after annealing of the catalyst

Upon these observations, it is concluded that due to possible influence of the support and interactions between the metal and the support itself, reduction is prevented. Therefore, reduction is not possible without a reducing gas. This conclusion is in good agreement with the results of Bianchi et.al. [42] where they studied Ru/Al₂O₃ catalysts prepared from different precursors.

4.CONCLUSION

$\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{SiO}_2$ catalyst and its precursor were characterized via XPS and in-situ diffuse-reflectance IR spectroscopy before, during, and after reduction by hydrogen over the temperature change 300-800 K. IR results indicated that the catalyst and the precursor lost NO_3 groups first, with subsequent loss of NO both in reducing atmosphere and during thermal annealing. XPS characterization of the precursor and the catalyst revealed that the ruthenium is at an oxidation state of +4 and +3 respectively. After reduction of the catalyst, Ru^{2+} was observed which is due to brief exposure of the sample to air during the transfer of the sample to XPS instrument. During thermal annealing of the precursor in vacuum, a stepwise removal of NO_3 followed by NO can be observed. Accompanying the loss of these groups, ruthenium is reduced from +4 to metallic state, but complete reduction of ruthenium could not be achieved. Thermal treatment of the catalyst did not cause any reduction ruthenium due to possible influence of the support and interactions between the metal and the support.

The reason for the incomplete reduction of the catalyst may be due to the interaction of Ru with NO. The red-shift observed during the course of reduction of the catalyst is probably due to weakening of NO bond as a result of electron transfer to the antibonding orbital of NO from ruthenium upon reduction.

CO adsorption on reduced catalyst is followed by FTIR and results showed that the catalyst was not fully reduced under these conditions which was evidenced by the presence of Ru^{n+} centers as well as the completely reduced Ru centers. The complexity of the spectrum of chemisorbed CO suggested the presence of small dispersed metal particles.

Ammonia synthesis on Ru/SiO_2 catalyst was accomplished at 350°C in a N_2/H_2 gas mixture ($\text{N}_2/\text{H}_2 \approx 3:1$) for different reaction times. NH_3 is observed as a reaction product and NH_x surface species as intermediates of the reaction.

Carbon monoxide adsorption on the catalyst after NH_3 synthesis followed by IR spectroscopy revealed the participation of Ru^0 sites in ammonia synthesis and a partial oxidation of the reduced Ru sites during synthesis.

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