

DRIFTS STUDY OF SELECTIVE CO OXIDATION ON Au/Al₂O₃ CATALYST

by

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ABSTRACT

DRIFTS STUDY OF SELECTIVE CO OXIDATION ON Au/Al₂O₃ CATALYST

The aim of this study was to investigate the surface species formed during the selective CO oxidation over 1 wt. % Au/Al₂O₃ catalyst prepared by homogeneous deposition-precipitation method. The surface analyses were carried out using a DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) system while the CO conversions were measured with MS (Mass Spectroscopy). First, the most appropriate conditions for sampling such as amount of sample, the particle size and KBr dilution were determined. Then the effects of reaction temperature on the formation of surface species were examined at the range of 25°C to 150°C in the presence of CO and O₂ and in balance helium. Afterwards, the concentrations of the feed components (CO, O₂, CO₂, H₂, and H₂O) were changed systematically at 110°C to see the effects of these species on the formation of the surface intermediates. The peaks in the DRIFTS spectra obtained were analyzed with the help of similar studies in the literature. It was found that the carbonates, bicarbonate, carboxyl and hydroxyl like surface species formed with varying amounts depending on the reaction conditions used. Finally the possible contributions of these surface species to the mechanisms suggested in the literature for the CO oxidation over the Au based catalyst were discussed.

ÖZET

Au/Al₂O₃ KATALİZÖRÜ ÜZERİNDE SEÇİMLİ KARBON MONOKSİT OKSİDASYONUNUN DRIFTS İLE İNCELENMESİ

Bu çalışmanın amacı; homojen tortu çöktürmesi yöntemi ile hazırlanılmış ağırlıkça %1 Au/Al₂O₃ katalizörünün seçimli karbon monoksit oksidasyonu esnasında katalizör yüzeyinde oluşan ara bileşenlerin incelenmesidir. CO dönüşümleri kütle spektroskopisiyle ölçülürken, yüzey analizleri, Dağınık Yansımali Kızılötesi Fourier Dönüşüm Spektroskopisi (DRIFTS) sisteminde yürütülmüştür. İlk olarak, numune miktarı, tanecik boyutu ve KBr içeriği gibi örnekleme koşullarından en uygun olanları tayin edilmiştir. Sonra, 25°C'den 150°C'ye değişen tepkime sıcaklığının yüzey bileşenlerinin oluşumuna etkisi helyum içersindeki CO ve O₂ karışımı kullanılarak incelenmiştir. Ardından, besleme bileşenlerinin (CO, O₂, CO₂, H₂ ve H₂O) yüzey ara bileşenleri üzerindeki etkisini görmek için 110°C'de bu bileşenlerin derişimleri sistematik olarak değiştirilmiştir. Elde edilen DRIFTS spektrumlarındaki pikler literatürdeki benzer çalışmaların yardımıyla analiz edilmiş, kullanılan tepkime koşullarına bağlı olarak değişen miktarlarda karbonat, bicarbonat, karboksil ve hidroksil türü yüzey bileşenlerinin varlığı saptanmıştır.. Son olarak, altın tabanlı katalizörler üzerine CO oksidasyonu için önerilmiş mekanizmalara, bu yüzey türlerinin olası katkıları tartışılmıştır.

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LIST OF SYMBOLS

F	Total flow rate
MW	Molecular weight
P	Pressure
R	Universal gas constant
T	Temperature
$\dot{V}$	Volumetric flow rate
W	Weight of the catalyst
X	Conversion
ρ	Density

LIST OF ABBREVIATIONS

AFC	Alkaline Fuel Cell
BOS	Birleşik Oksijen Sanayi
CP	Co-Precipitation
DMFC	Direct Methanol Fuel Cell
DP	Deposition-Precipitation
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
FTIR	Fourier Transform Infrared
GHSV	High Residence Times for The Gas
HPLC	High Performance Liquid Chromatography
HTS	High Temperature Shift
IEA	International Energy Agency
LTS	Low Temperature Shift
MCFC	Molten Carbonate Fuel Cell
MS	Mass spectrometer
MEA	Membrane Electrod Assembly
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
PROX	Preferential Oxidation
PSA	Pressure Swing Adsorption
SOFC	Solid Oxide Fuel Cell
WGS	Water-Gas Shift Reaction
XRD	X-Ray Diffraction

1. INTRODUCTION

The significantly increased demand for the alternative energy sources in the last decades has given rise to a considerable interest in the fuel cell technologies. When it is compared with the fossil fuels or nuclear energy, there is no pollutant or toxic by-product in the fuel cell systems. Moreover, there is a variety of usage area of fuel cells from the small scale devices and automobiles to power plants (Guerrero *et al.*, 2009).

Although a variety of fuel cells are available today, the proton exchange membrane fuel cell (PEMFC) is considered as one the most promising types with its several benefits such as running at low temperatures and having very high power densities (Lewis, 2009).

In the near future, the hydrogen fuel for the PEMFC is expected to be obtained by steam reforming process of hydrocarbons or alcohols followed by the water gas shift (WGS) reaction, where CO occurs as effluent. However, the amount of CO in this feed should be less than 10 ppm, otherwise it poisons the electrode in the PEMFC; therefore, the preferential CO oxidation (PROX) reaction is proposed to be used as a purification method for the remaining CO after WGS process (Gamarra and Martínez-Arias, 2009).

Comparing the Pt group catalyst, which have been studied for this purpose for a long time, Au based catalysts have been attracted more attention in the recent years due to their low cost, high availability and high performance when they are in the form of nanosize particles dispersed over a suitable support. The supports used for this purpose are Fe_2O_3 , MnO_2 , TiO_2 , CeO_2 , Al_2O_3 and SiO_2 (Li *et al.*, 2009).

Fourier transform infrared spectroscopy (FTIR) measurements, which is related the change in vibrational frequency of the molecule, have been widely used to probe the catalyst behavior. Particularly, in recent years, the active state of the catalyst as well as the surface species like carbonates, bicarbonates and formates during the CO oxidation reaction have been examined by many researchers under realistic conditions called operando (Topsøe H., 2003; Gomez-Cortes *et al.*, 2008). However, the kinetics and the rate-determining step, the competition between reactants, and the products for adsorption

sites, and therefore the mechanism of the CO oxidation on supported Au catalysts are still controversial (Chang *et al.*, 2005).

In this study, the surface species formed during the selective CO oxidation on Au/Al₂O₃ catalyst were examined to contribute to the understanding of the reaction pathways valid for this important reaction. For this purpose, the analysis was conducted by a combined DRIFTS-MS system under the reaction conditions. The effect of feed composition as well as the reaction temperature over the formation and consumption of surface species was investigated.

The study mainly consists of five chapters. Chapter 2 involves general literature survey about the topics of fuel cell technology, hydrogen production, catalysts for selective CO oxidation systems (specifically gold based catalysts) and the mechanisms of CO oxidation over the gold catalysts as well as the relevant FTIR studies. In Chapter 3, the experimental set-ups and procedures are given in detail while Chapter 4 covers the results obtained and related discussions. The conclusions drawn from the present study and some recommendations for the future work are summarized in Chapter 5.

2. LITERATURE SURVEY

The significance of the alternative/renewable energy sources has been dramatically increased in the last decades due to the noticeable rises in both energy consumption all over the world and environmental effects of the current fuel emissions. Today, approximately % 80 of the world primary energy is dependent on the fossil fuels. According to the International Energy Association forecasting, the increase of the world population to 8.5 billions will result in the tripled rate of energy demand as well as the 28 percent rise in CO₂ emission (Baniasadi and Alemrajabi, 2010). Therefore, most of the energy policies and the researches, nowadays, have been focusing on the alternative energy sources and the new energy technologies to meet the clean energy demand of the world.

2.1. Fuel Cell Technology

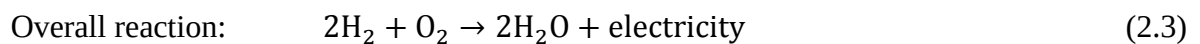
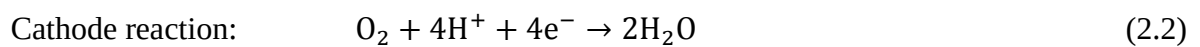
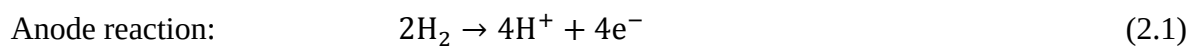
Fuel cells are one of the clean energy technology devices suggested for the sustainable energy demand of the future. These devices are able to convert the chemical energy of the hydrogen (or a hydrogen-rich fuel) and an oxidant (mainly pure oxygen or oxygen from air) directly into electrical energy through an electrochemical process leading water and heat as the by-products (Chen *et al.*, 2011).

The basics of fuel cells were discovered by Swiss scientist Christian Friedrich Schonbein in 1838. Afterwards, it was improved by many other scientists such as Sir William Grove in 1839 and Francis Bacon (in 1950), who was founder of alkaline fuel cell. In principle, a fuel cell consists of an electrolyte membrane layer and two electrodes (anode and cathode) in contact with electrolyte. The hydrogen fuel is continuously fed to the anode layer, where it decomposes into H⁺ and electron, while the oxidant is fed to the cathode side. The electrolyte membrane layer, as a kind of insulator, lets only the positive ions flow to the cathode side. Simultaneously, the free electrons move the cathode side through an external electrical circuit creating electricity and recombining with the positive ions and the oxidant on the cathode to form water (Kirubakaran *et al.*, 2009; Lee *et al.*, 2007; Jayasankar *et al.*, 2009).

The fuel cells can be classified according to the type of the electrolyte and the fuel. The proton-exchange membrane fuel cell (PEMFC), the alkaline fuel cell (AFC), the phosphoric acid fuel cell (PAFC), the molten carbonate fuel cell (MCFC), the solid oxide fuel cell (SOFC) and the direct methanol fuel cell (DMFC) are some major types of fuel cells that are currently used and researched (Alcaide *et al.*, 2006; Gou *et al.*, 2010). The PEMFC, AFC and PAFC can operate in the low temperature range of 50–250°C, while MCFC and SOFC requires higher operating temperatures such as 650–1000°C (Kirubakaran *et al.*, 2009).

Among the all types of fuel cells, PEMFC seems to be the most promising technology for many application areas from the automotive systems, buildings and portable applications to replacement of the rechargeable batteries (Andujar and Segura, 2009). The low-operating temperature, high current density, high potential for low cost and volume, fast start-up ability, and suitability for discontinuous operation are some of the key advantages of the PEMFC compared to the other fuel cell system (Pei *et al.*, 2008).

Today's PEMFC technology depends on the expensive perfluorinated proton-exchange membranes, which effectively operate only in the presence of fully hydrated environments (Peighambardoust *et al.*, 2010). This perfluorinated polymer backbone is able to turn into a protonic conductor under the operational condition of the fuel cell, and it works with sulfonic acid side chains. Structurally, the membrane, two layers of catalysts and two diffusion electrodes are collected together forming a membrane electrode assembly (MEA) between two current collectors working as gas distributors. At the anode side of the MEA, hydrogen rich fuel is divided into its protons and electrons, whereas at the cathode side water forms from the oxygen and those protons and electrons (Yu *et al.*, 2009).



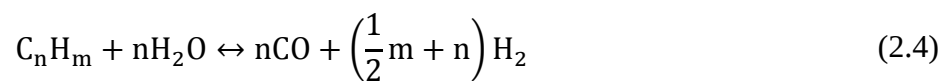
2.2. Hydrogen Production

Hydrogen is considered as one of the most important potential energy supply for the future because it is non-polluting and high-density energy carrier. Moreover, it is also more suitable to the electrochemical and combustion processes compared to the other fuels. According to International Energy Agency (IEA), 50% of total energy consumption is expected to be provided by the hydrogen energy by 2050. Another advantage of the hydrogen is that it can be produced in many ways from water, natural gas, coal, biomass, municipal waste and hydrocarbons. However, the hydrogen production from the fossil fuels seems to be the most feasible (lowest cost) technology today (Chen *et al.*, 2011; Önsan, 2007; Yazıcı, 2010).

Hydrogen from hydrocarbons can be obtained in fuel processing system converting hydrocarbon, which is usually methane, into a hydrogen rich stream, (Holladay *et al.*, 2009). Due to the technical difficulties in its safe and effective storage, on-site hydrogen production tends to be the most proper solution for the mobile and small-medium scale stationary applications in the near future (Chen *et al.*, 2010; Avcı, 2003).

An on-board fuel processor mainly consists of a reformer for the fuel conversion into hydrogen-rich gas stream, a water-gas shift unit to convert excess CO into CO₂ producing additional H₂, and an additional clean-up system for the remaining CO which can poison the catalysts if it is more than 10 ppm in the fuel (Fajardo and Probst, 2006).

In the reforming step of the fuel processor system, the hydrocarbon fuel is catalytically broken down into synthesis gas containing hydrogen and other products as in Reaction (2.4). Typically, a non-precious metal (usually Ni) based catalyst is used for this reaction (Holladay *et al.*, 2009).

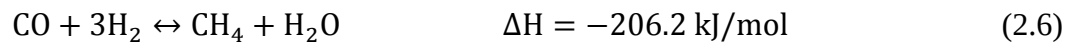


Then the water gas shift process removes most of the CO produced in the first step and produces some additional hydrogen through the following reaction:

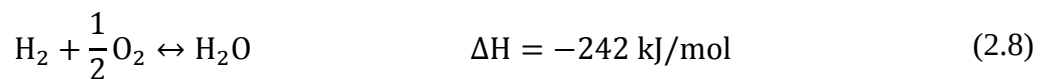
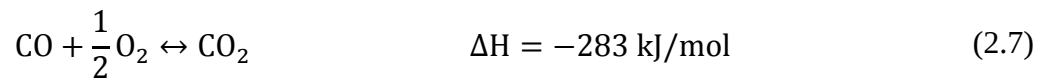


The CO level is reduced from 6-10% to 0.5-1% after this reaction (Siddle *et al.*, 2003). The reaction is usually conducted in two steps: the high temperature shift (HTS) and the low-temperature shift (LTS). The former is carried out by Fe/Cr catalysts in the range of 300°C to 500°C, while the latter requires a temperature range between 200°C and 300°C by using Cu/Zn catalysts (Lima *et al.*, 2009).

0.5-1% levels of CO are still too high for the low temperature PEMFC; therefore, further CO removal methods are required for good performance of the fuel cell. The methanation (Reaction (2.6)), selective H₂-diffusion through membranes necessitating high pressure and temperature, pressure swing adsorption (PSA) and the selective (preferential) CO oxidation (PROX) are the processes that are commonly studied for this purpose (Hessel *et al.*, 2005; Ayastuy *et al.*, 2007).



Among these methods, the preferential CO oxidation (PROX) seems to be the most simple and efficient method reducing the CO in the feed to 10 ppm or less (Yu *et al.*, 2007). Two basic reactions occur in this method when the oxygen is added to the fuel processor: CO oxidation (Reaction (2.6)) and H₂ oxidation (Reaction (2.7)).



The CO oxidation reaction is desired whereas the H₂ oxidation is unfavorable because it consumes the fuel H₂ unintentionally. In addition, water-gas shift (WGS), (Reaction (2.5)) and methanation (Reaction (2.6)) reactions also spontaneously take place in the process. The former reaction contributes to the hydrogen production while the latter reduces the efficiency of the process by consuming some H₂, hence it should be avoided (Hessel *et al.*, 2005; Basar, 2010; Demir, 2009).

2.3. Preferential CO Oxidation Catalysts

The studies on the PROX catalysts have indicated that an effective PROX catalyst should have some specialties such as being suitable not only for CO chemisorptions, but also for dissociative O₂ adsorption (Trimm and Önsan, 2001). In addition, it should exhibit a good activity in a wide range (80–250⁰C) of operating temperature, providing a 99.9% CO conversion in a steam containing, 1 vol. % CO in 60 vol. % H₂, to minimize CO content to 10 ppm. Furthermore, it should have high *GHSV* (*high* residence times for the gas) *values* and great resistance to the deactivation by other products in the steam (Chen *et al.*, 2008; Ayastuy *et al.*, 2007).

In this aspect, a variety of catalysts has been studied for the PROX reactions which can be classified in two main groups; supported noble metals and base-metal oxides. The noble catalysts such as Pt, Ru, Rh and Au exhibit good catalytic activity and selectivity in the temperature range of 150-250⁰C (Kim and Park, 2010). However, there are still some concerns about their high cost and their limited availability as well as their possibility to have sulfur poisoning comparing to the base metal catalysts (such as CuO/CeO₂ and Co₃O₄) having also high activity, but with lower cost and more availability (Moreno *et al.*, 2008; Zou *et al.*, 2009).

2.3.1. Gold Based Catalysts for Low Temperature Selective CO Oxidation

During the past decade, the studies related to the low temperature CO oxidation has particularly focused on the gold catalysts since Haruta *et al* (1989) showed the remarkable activity of nano-sized supported gold catalysts (Wen *et. al.*, 2008). The gold catalysts, which have a rich coordination and organometallic chemistry, was found to be more active for the CO oxidation at the temperatures as low as 200 K comparing with the other noble (especially Pt based) catalysts (Li *et al.*, 2008). Apart from this, supported gold catalysts exhibit low activity for H₂ oxidation; hence, it is unequivocally suggested that they can be also used in the selective CO oxidation in a H₂-rich system (Illieva *et al.*, 2009).

The activity and the selectivity of supported gold catalyst in low temperature CO oxidation are directly influenced by the size of the Au-particle and the preparation method

of the catalyst. In order to increase the turnover frequency of the CO oxidation reaction, Au particles with the size of less than 5 nm was widely suggested (Chang *et al.*, 2009).

The choice of the preparation method has a major impact on the Au particle size and therefore the catalytic activity. Two techniques are mainly used to prepare the gold catalysts: the deposition–precipitation (DP) technique and the co-precipitation (CP). It was reported that the former technique have superiority in dispersing the active Au nanoparticles on the support surface (Nakman *et al.*, 2009). Liu and Vannice also indicated that the deposition method gave way to a dramatic increase on the catalytic activity for CO oxidation over the TiO₂ supported Au catalysts (Sangeetha *et al.*, 2010). Yang *et al.* (2009) also reported that the activity was remarkably improved by the preparation of smaller Au particle size, which was approximately 1.5 nm, over TiO₂ using PD technique (Yang *et al.*, 2009).

In addition, the choice of the support has a significant effect on the activity of the gold catalyst. It was conceded that bulk gold catalyst showed low activity due to some surface properties such as low chemisorptions strength and electronic configuration. On the other hand, dispersed gold catalysts on a metallic oxide support increased the catalyst activity and selectivity by changing the surface chemistry (Kudo *et al.*, 2010).

Various metal oxides can act as the support for the gold catalysts. These support materials can be classified into two groups as active and inert supports. Active supports, such as TiO₂, ZrO₂, CeO₂, MnO are able to provide extra oxygen for the reaction, while the inert supports, such as Al₂O₃, SiO₂, MgO, have no extra contributions to the reaction (Ribeiro *et al.*, 2008; Steyn *et al.*, 2007) The study of Ivanova *et al.* indicated that gold catalysts supported on reducible kind metal oxides were found to be more active than the other type of support (Ivanova *et al.*, 2006).

2.3.2. Gold catalyst over Al₂O₃ Support

Among the suitable metal oxide supports for Au catalysts, alumina has been widely used due to its practical benefits such as low cost, manageable porosity, high stable surface area as well as inert behavior toward the steam (Moroz *et al.*, 2009).

As it has been mentioned above, Al_2O_3 is considered as a kind of irreducible support. In other words, there are no active oxygen atoms on its surface to interact with the adsorbed CO on gold particles. Therefore, in the alumina supported gold catalyst, it has been well accepted that the oxygen adsorption and dissociation are likely to appear in the surface of the gold particles (Chang *et al.*, 2007).

In order to investigate the influence of the support material in the reaction process, Widmann *et al.* prepared Au particles with various supports such as Al_2O_3 , TiO_2 , ZnO and ZrO_2 , which are prepared at the same size and Au loadings. The study declared that only Au/ Al_2O_3 catalyst showed a ‘gold-only mechanism’, which means reaction appeared only on the Au nanoparticles, whereas the others resulted in ‘metal/oxide boundary mechanism’. The former mechanism was also proposed to be active on all non-supported Au catalysts (Widmann *et al.*, 2010).

Confirming the low metal-support interaction of Au/ Al_2O_3 catalyst further, Liotta *et al.* indicated that around 2.5–3 nm Au particle size were observed over reducible oxides supports (TiO_2 , Co_3O_4 – CeO_2 and Co_3O_4), while Au/ Al_2O_3 has bigger gold particles up to 5nm (Liotta *et al.*, 2010).

According to the study of Georgaka *et al.*, a reductive pre-treatment of Au/ γ - Al_2O_3 within the excess H_2 was more helpful to activate the oxygen molecules (e.g. through HO–O species) than the one in a diluted H_2 surroundings. Moreover, it was reported that Au/ Al_2O_3 was able to show a 42% CO conversion at 80°C with a selectivity of 25% in the presence of hydrogen (Georgaka *et al.*, 2008).

It was shown by the various investigators that the performance of supported metal catalysts may be changed by adding some promoter or modifier (Iwasa *et al.*, 2008). For this purpose, the metal oxide promoters such as Cr, Sn, Mg, Mn, Fe, Co, Ni, Cu, and Zn were used on the supported gold catalysts by various investigators (Grisel *et al.*, 2001a; Grisel *et al.*, 2001b; Grisel *et al.*, 2002; Wang *et al.*, 2003; Szabo *et al.*, 2005; Gluhoi *et al.*, 2006; Lippits *et al.*, 2007).

Although different promoters could have different level of improvement (even some negative effects) and even the effect of the same promoter could be different under different conditions, the promoters can be generally considered as beneficial. Various investigators shown that MgO seems to be the best promoter for Au/Al₂O₃ catalyst; this is commonly attributed to the fact that MgO stabilizes the formation of small gold nanoparticles (Davran-Candan *et al.*, 2011; Tezcanlı, 2008)

2.4. Mechanisms of Low Temperature CO Oxidation

2.4.1. The Active Sites of Au

The nature of the active sites of Au particles for CO oxidation has been a matter of debate and there has been no consensus on it yet. Some authors advocate that metallic gold (Au⁰) is to be active species, whereas the others suggest ionic gold species (Au(I) or Au(III)) as the active sites (Steyn *et al.*, 2007). As to the Kung, for instance, an ensemble of metallic Au and a cationic Au⁺ species with hydroxyl ligands are the active phases of Au similar to the active sites claimed by Haruta and Daté: the metallic Au atoms with a Au cation (Au(I) or Au(III)) at the periphery with a hydroxyl legend as shown in Figure 2.1 (Qian *et al.*, 2008; Ma *et al.*, 2010).

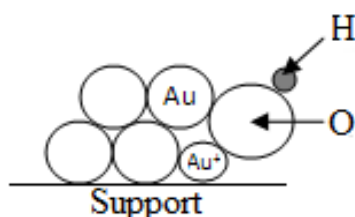


Figure 2.1. Proposed model for active sites of supported Au catalyst (adapted from Kung *et al.* (2007)).

Boccuzzi *et al.* (2001) indicated that Au⁰ sites of the catalyst were active in CO oxidation, and the other parts of the catalyst were unable to adsorb CO even at low temperatures. Li *et al.* (2009) studied the influence of oxidative pretreatments on the active sites of Au/FePO₄ catalyst for CO oxidation reaction. They reported that the cationic Au came out after the oxidative treatment while the metallic Au occurred after reductive treatment in H₂, and it was more active than the oxidatively pretreated catalyst.

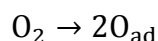
In a study of CO oxidation on Au/TiO₂ catalysts by Casaletto *et al.*, it was indicated that the fresh catalyst prepared by PD technique involved more cationic gold and showed more activity and selectivity toward CO oxidation (Yang *et al.*, 2009). The study conducted by Moroz *et al.* on the Au/Al₂O₃ catalyst showed that Au/Al₂O₃ catalysts prepared by DP method had ionic Au surface species with bridging oxygen as well as metallic Au particles, which should be taken into account in the low-temperature CO oxidation over Au/Al₂O₃ catalysts (Moroz *et al.*, 2009). In addition, Somodi *et al.* indicated that metallic gold species have higher binding energy values than the ionic forms of gold through the XRD analysis of Au/Al₂O₃ catalyst (Somodi *et al.*, 2009).

In the study of CO oxidation over Au/ γ -Al₂O₃, Gavril *et al.* showed that the CO chemisorption took place at both the cationic Au and the alumina support while the mild CO bonding located at the active sites of metallic Au (Gavril *et al.*, 2007).

2.4.2. Suggested Mechanisms for CO Oxidation Over Supported Gold Catalyst

It has been widely accepted in the CO oxidation over gold supported alumina catalysts that both reactants, O₂ and CO, are bounded to the surface of the catalyst where CO gases is fully adsorbed. However, whether the oxygen is activated by adsorption or not is a controversial issue. Therefore, many possible reactions have been asserted for the CO oxidation mechanism over supported Au catalysts so far (Scire *et al.*, 2008).

In general, it is believed that the low temperature CO oxidation on Au depends on the mechanism involving O₂ dissociation on Au surfaces, and oxidation of CO molecule on Au supported inactive-materials such as Au/Al₂O₃ takes places in two steps (Georgaka *et al.*, 2008):



In some cases, it was also possible to observe the O₂ adsorption on the cluster and its reaction with gas phase CO in an Eley–Rideal type mechanism (Chrétien *et al.*, 2007).

Haruta *et al.* studied the catalytic activity of Au/TiO₂ catalysts over the three temperature regions. At the temperature below 200 K, the CO reaction with O₂ occurred only on the Au surface with a virtually 0 kJ/mol for apparent activation energy. It was also found that the carbonate species covered the support surfaces and its perimeter interfaces. When the temperature was above 300 K; however, the reaction tended to proceed at the perimeter interfaces between CO adsorbed on the gold surfaces and molecularly oxygen adsorbed at the support interface. The activation energy of the reaction was also approximately zero, but its rate was much faster than the one at the temperature below 200 K. Finally, in the temperature region between 200 K and 300 K, the reaction came about at partly carbonate species covered perimeter interface. This coverage was directly influenced by the change of temperature, leading to activation energy around 30 kJ/mol (Haruta *et al.*, 2001).

According to Langmuir-Hinshelwood type mechanism proposed in the literature, it was accepted that the oxygen was adsorbed weakly while the carbon monoxide adsorbed more strongly on the gold in the presence of inert supports like alumina and silica (Carabineiro *et al.*, 2010). There are two versions of the mechanisms; one involves the reaction of O₂ and CO over the gold cluster while the other suggests that O₂ adsorbed at the metal support interface (Chrétien *et al.*, 2007).

The mechanism proposed by Bond and Thompson (2000) was dependent on the role of the lattice oxygen of the support in the reaction. This oxygen reacted directly with CO, and additional O₂ was needed to reform the damaged support surface. For this reason, this mechanism was highly dependent on the support properties such as having a good metal-support interaction, like TiO₂ has. The chemisorption of CO molecule occurred on a gold particle whereas an hydroxyl ion (OH⁻) from the support is transferred to a Au (III) ion forming a carboxylate group (-COOH) on the Au-metal oxide interface. The oxygen molecule was negatively charged (O₂⁻) and reacts with the (-COOH) resulting in carbon dioxide and hydro peroxide ion (HO₂⁻), which further oxidizing with another carboxylate group (Carabineiro *et al.*, 2010).

The studies of Daté *et al.* on Au/TiO₂, Au/Al₂O₃, and Au/SiO₂ catalysts also exhibited that OH⁻ groups, such as moisture in the steam, was positively affected the activity in CO oxidation. They proposed that the chemisorbed H₂O on the support surface contributed the oxygen activation as well as the carbonate decomposition on the interface of Au and metal oxide (Qian *et al.*, 2011).

Kung *et al.* have been particularly interested in the reaction mechanism of low-temperature CO oxidation on Au/Al₂O₃ catalyst (Figure 2.2). They proposed that the active sites of the catalysts contain (Au⁺)-(OH⁻) complex and Au (0) atoms. Adsorbed CO on the catalyst, together with (Au⁺)-(OH⁻), leads to hydroxycarbonyl (COOH). The oxidization of hydroxycarbonyl tends to form bicarbonate, which can result in the decarboxylation to CO₂, and to (Au⁺)-(OH⁻) or Au-H, which is also oxidized to (Au⁺)-(OH⁻) (Kung *et al.*, 2007; Qian *et al.*, 2011).

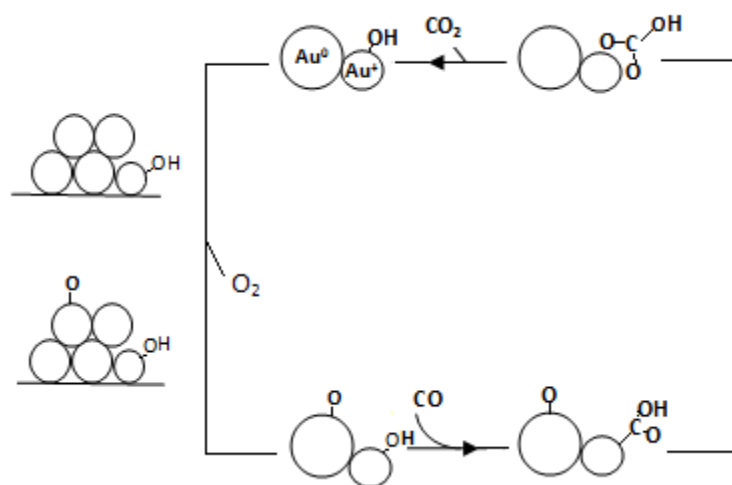


Figure 2.2. Model proposed for the active site and corresponding reaction mechanism (adapted from Kung *et al.* (2007)).

In the study of Moroz *et al.* on catalytic performance of the Au/Al₂O₃, the CO mechanism on supported Au catalysts is showed to be in accordance with the one proposed by Bond and Thompson as well as Kung *et al.* in terms of the active sites as an ensemble of metallic gold atoms with some amount of Au⁺ (or Au³⁺) cations coordinated with the OH groups. Moreover, the argument of Gates and Guzman, related to the dependence of the catalytic activity on both zero-valent (Au⁰) Au and cationic (Au⁺) gold in the Au/MgO catalyst was approved by this study (Moroz *et al.*, 2009).

Molina *et al.* investigated the competition of O₂ and CO for the reactive sites of Au catalyst as well as the simultaneous interaction between O₂ and several co-adsorbed CO molecules. In contrast to the usually proposed mechanisms for surface reactions, three intermediate species were reported to exist in the reaction pathway. First one is an adsorbed OCOO⁻ peroxyformate complex formed from CO and O₂ in a bound superoxo O₂⁻ state. Then it transformed through the interaction with a neighbor CO into a labile OCOOCO complex, which was then immediately separated into two CO₂ molecules. Additionally, it was indicated that pre-adsorbed O₂ was replaced by CO forming the OCOO⁻ intermediate due to the electronegativity of the catalyst (Molina *et al.*, 2009).

It was proposed that, the low temperature CO oxidation in the presence of H₂ followed the mechanism given on the left-hand side of Figure 2.3 (Quinet *et al.*, 2009). The oxygen was molecularly adsorbed on Au through the reaction with H₂, forming OOH* and H* species. In contrast to the mechanisms proposed by Kung, and Haruta and Date *et al.*, this mechanism has no oxygen dissociation on Au, which was stabilized by H*. Afterwards, CO* and OOH* were turned to CO₂ and OH*. Then, OH* was reacted with CO* to produce CO₂ and H*, and cycle was closed with the recombination of H* atoms into H₂ or with the reaction of H* with O₂ molecules forming additional OOH* species.

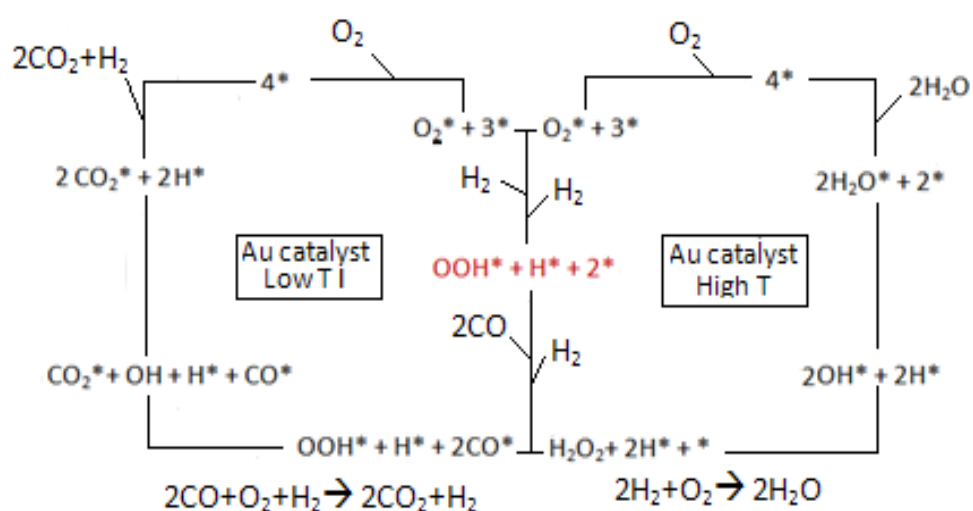


Figure 2.3. Mechanistic scheme for CO oxidation in the presence of H₂, where * denotes the active sites (adapted from Quinet *et al.* (2009)).

2.4.3. Possible Surface Species in Selective CO oxidation on Supported Gold Catalyst

Gold based catalysts have a tendency to lose most of their activity on the long periods. The main reason for this short stability was shown to be the formation of carbonate like species on the surfaces. The coordination and speciation of these surface species tend to influence both the activity and the mechanism of reaction (Moreu *et al.*, 2008). In addition, five molecules CO, O₂, H₂, CO₂ and H₂O in CO oxidation process react in various ways at different temperatures and cause various intermediates. Therefore, it is important to understand the role of these species in CO oxidation on supported Au catalysts.

The carbonate-like species such as carbonate (CO₃)⁻², bicarbonate (HCO₃)⁻ and formate/carboxylate/hydroxycarbonyl groups mainly have a CH_xO_y structure as shown in the Figure (2.4) (Bond and Thompson, 2009). These species tend to form during CO adsorption and CO reaction with oxygen through the following step:



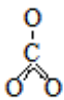
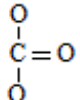
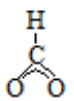
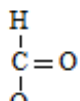
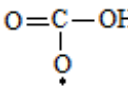
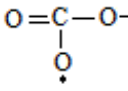
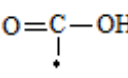
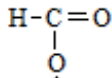
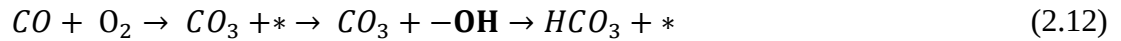
Species	Structures	Species	Structures
Bidentate carbonate		Monodentate carbonate	
Bidentate formate		Monodentate formate	
Bicarbonate		Carbonate	
Carboxyl		Formate	

Figure 2.4. Structures of some possible surface species (adapted from Bond and Thompson (2009)).

These species, in general, are considered as poisons for the particles containing O₂ activation sites. Carbonates, for instance tend to deactivate the catalysts by blocking the

active sites for CO oxidation. However, it is possible to transform the detrimental carbonates species to less stable bicarbonates through the reaction with water forming additional hydroxyl (Raphulu *et al.*, 2010). Also, when a carbonate is reacted with H₂, a hydroxyl and a formate would be produced. Then later would form bicarbonate by reacting with O₂, which was observed through the CO oxidation experiments involving Au/Al₂O₃ catalysts. However, conducting same experiment over Au/TiO₂, the formate or bicarbonate species were not detected on the sample by Piccolo *et al.*, 2009. Although Ntho *et al.* observed the bicarbonates formation as an intermediate during CO oxidation on the titania nanotube (Au/TN) catalyst (Ntho *et al.*, 2009). Through another study by Shi *et al.*, the PROX reaction over a new catalyst FeOx/Pt/TiO₂ was conducted via bicarbonate intermediate in the absence of H₂ and via HCOO intermediate in the presence of H₂ (Shi *et al.*, 2008).

Possible reaction step of a HCO₃ (bicarbonate) group forming on the gold is as in following reaction (Moreno *et al.*, 2008):



And the decomposition steps of poisonous to CO₂ + -OH (Reaction (2.13) and (2.14):



where * is an anionic vacancy, the italic font represents the species adsorbed on the gold site while the bold font is for the species adsorbed on the support or on the ionic vacancy, and Au represents a gold site (Moreno *et al.*, 2008).

Identification of such species contributes to the understanding of the mechanism profoundly. For instance, the formation and decomposition of carbonates are the rate-limiting step on CO oxidation in the mechanism suggested by Haruta *et al.* Later, Daniells *et al.* put forward that the active site was related to the Au⁺³ and Au⁰ with hydroxyls and

bicarbonate participation for the formation of CO_2 . On the other hand, Gupta and Tripathi claimed that carbonates and bicarbonates cannot be the intermediates (Ntho *et al.*, 2009). Jacobs *et al.* also explained the surface mechanism of CO oxidation over ceria supported gold catalyst through formate formation from the reaction of CO and $-\text{OH}$. This intermediate then diffused to the metal–ceria interface and lost its H by metal. Afterwards, monodentate formate formed at the ceria surface and then decomposed to gas phase CO_2 (Jacobs *et al.* 2007).

2.4.4. Effect of the reactants on the surface and reaction of supported gold catalyst

Since the selective low temperature CO oxidation at in fuel cells systems will take places in a realistic atmosphere containing CO_2 , H_2O , the influence of these reactants and H_2 on the mechanism have been also investigating for many years. Although the active metal of Pt based catalysts was protected by a CO adlayer and slightly effected by the other adsorbents such as water and carbon dioxide in the stream, the metal surface of supported gold catalysts exhibits a higher tendency towards those adsorbents (Chrétien *et al.*, 2007)

2.4.4.1. The Effect of CO_2 . The chemisorption of carbon dioxide on the catalysts may lead to adsorbed carbonate species at metal oxides. For example it was shown that even the atmospheric CO_2 played a key role in the formation of bicarbonate species on fresh gold catalyst even during the catalyst preparation phase (Raphulu *et al.*, 2010). In another work, CO_2 was found to deactivate the gold based catalysts in the presence of H_2 as well as to be detrimental on the activity of other catalysts such as CuO/CeO_2 and $\text{Pt/Al}_2\text{O}_3$ catalysts (Liang *et al.*, 2008).

2.4.4.2. The Effect of H_2 . The studies indicated that the presence of hydrogen on CO oxidation over gold catalysts had some positive impact attributed to its prevention of deactivation and helping regeneration (Georgaka *et al.*, 2008). Shumacher *et al.* also observed the inhibition of formate and carbonate formations in the presence of hydrogen over Au/TiO_2 catalysts. Chen *et al.* declared that, under the unconventional PROX conditions, the accumulation of carbonate species and surface hydration slightly affected the deactivation of Au/TiO_2 catalyst (Chen *et al.*, 2007).

On the study of CO oxidation over Au/Al₂O₃ catalyst Quinet *et al.* proposed that Au–O_xH_y species like Au–OOH were more likely to be stabilized when the H₂ was added into the CO+O₂ feed. They also studied the surface species through PROX over Au/TiO₂ catalyst in the presence of H₂ considering the dissociative H₂ adsorption and the formation of OOH* species (Reaction (2.15) and (2.16)):

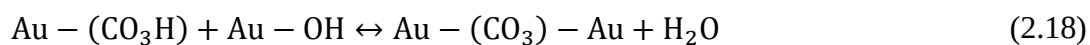
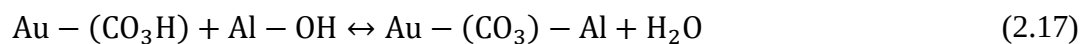


Then these gold–hydroperoxide (Au–OOH) molecules with a gold–carbonyl (Au–CO) can involve a bicarbonate (CO₂OH*), decomposing to a gold–hydroxyl (Au–OH) and a carboxylate CO₂* (Quinet *et al.*, 2009).

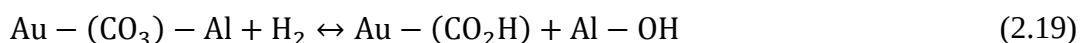
2.4.4.3. The Effect of H₂O. Ntho *et al.* defined the deactivation effect of water as the growth of the metal particles, blockage of the interfacial sites of support (TiO₂) by water, building up of `carbon species` and the depletion of surface hydroxyl groups (Ntho *et al.*, 2009).

Through many studies on the role of water in the CO oxidation, water was found to directly affect the catalytic activity of the catalyst. Boccuzzi *et al.* indicated that the activity of titania supported gold catalyst was promoted by some amount of water. In addition, Bongiorno and Landman stated that the co-adsorption of both water and oxygen led to a decrease in the activation barrier of CO oxidation over gold catalyst. . Romeria *et al.* also found that the adsorbed water on the cerium sites resulted in the generation of the active species for CO oxidation (Au+) (Romero-Sarria *et al.*, 2008). However, Date and Haruta observed that the active sites of the catalysts were started to be blocked by water if its concentration was over 200 ppm.

Through the study on Au/Al₂O₃ catalyst, Costello *et al.* (2003) indicated that the thermal treatment caused the dehydroxylation of the alumina support in the presence of water. The dehydration process of surface bicarbonate intermediate and adjacent hydroxyl led to the inactive carbonates, having an additional hydroxyl group of the support (Reaction (2.17) and (2.18)).



Then carbonates converted into a formate or hydroxycarbonyl and hydroxyl by hydrogenolysis, involving the hydrogen activation (Reaction (2.19)).



2.5. Surface Analysis of Supported Gold Catalysis by DRIFTS

DRIFTS is one of the most preferred IR spectroscopy techniques to probe the molecules and to characterize the supported catalysts. It is possible to gain information about the oxidation and the coordination state of the surface atoms, their status on the surface and their chemical properties like acidity.

Operando spectroscopic analysis is a method to investigate the surfaces under actual reaction condition which can provide information about the reaction pathways by applying sudden perturbation to the reactants (Clark *et al.*, 2006). It is also called “working” referring the simultaneous online activity/selectivity measurements (Banares, 2005).

Traditionally, CO adsorption at low temperature is an ideal technique to characterize the sites on the surface. As Demir (2009) suggested, DRIFTS measurements may be helpful to understand the mechanism of CO on Au/Al₂O₃ through the indication of possible adsorptions of the intermediate species on the catalyst surface and the gas molecules in the feed.

For more clear comprehension of the CO oxidation reactions by DRIFTS methods, a basic spectrum, where the wave number varies from 400 cm⁻¹ to 4000 cm⁻¹, can be analyzed in three main spectral regions as the region between 1200-1800 cm⁻¹, 2000-2500 cm⁻¹ and 3000-3700 cm⁻¹ (Figure 2.5).

The region 1200-1800 cm⁻¹ is mainly considered for the carbonate-like species. For example, the deactivation process on Au/TiO₂ were observed by Denkwitz *et al.* in the

spectral region between 1200 and 1700 cm^{-1} , where the peaks at 1617 cm^{-1} may represent water, or C=C and OCO vibrations of carbonates and carboxylates, while the peaks at 1564 cm^{-1} and 1432 cm^{-1} are for bidentate carbonates (C=O stretch vibration) and monodentate carbonates respectively (Denkwitz et al, 2009). Clark *et al.* also sighted that DRIFTS spectra between 1200 and 1800 cm^{-1} were about carbonate and bicarbonate species not only on the titana (TiO_2) supported gold catalysts, but also on the pure titania (Clark *et al.*, 2007). Similarly, Zou *et al.* (2009), on the analysis of low temperature CO oxidation over $\text{Au}/\text{Al}_2\text{O}_3$ catalysts, observed the adsorption of carbonate like species at 30°C in the region of 1800-1200 cm^{-1} all in the presence of $\text{CO} + \text{Ar}$, $\text{CO} + \text{O}_2 + \text{Ar}$ and $\text{CO}_2 + \text{O}_2 + \text{Ar}$. In addition, the peak at 1620 cm^{-1} observed was related to the molecularly adsorbed water due to the n (O–H) vibration mode of water in the spectral analysis (Piccolo *et al.*, 2009). Therefore, Ntho *et al.* claimed that the identification of C–O stretching region (1450–1600 cm^{-1}) was tended to be difficult in the presence of H_2O as co-reactants/adsorbents. Moreover, they found that the band of unidentate carbonate species at 1329 cm^{-1} were un-influenced in the water environment, whereas bicarbonates at 1290 cm^{-1} were virtually vanished by water (Ntho *et al.*, 2009).

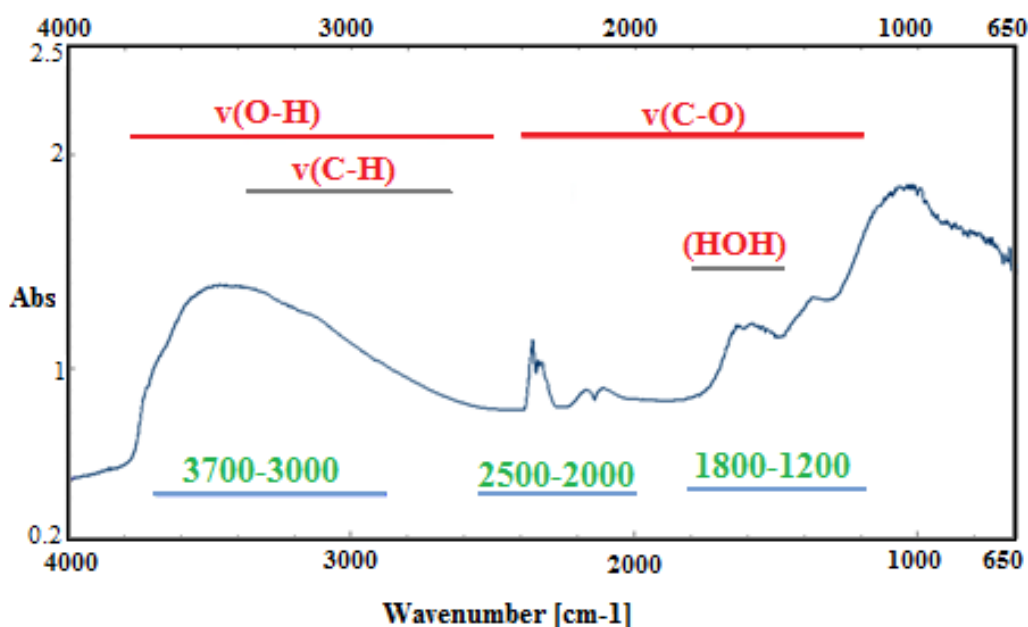


Figure 2.5. An example of DRIFTS spectra for $\text{Au}/\text{Al}_2\text{O}_3$ exposed to $\text{CO} + \text{O}_2 + \text{H}_2$ in He at 110°C.

The 2000 - 2500 cm^{-1} band generally involves the adsorption of CO and CO₂ molecules. On the analysis of low temperature CO oxidation over Au/Al₂O₃ catalysts Zou *et al.* asserted that the peaks at 2100 cm^{-1} was about the CO adsorption on Au⁰ and the ones in 2340 and 2360 cm^{-1} were the CO₂ adsorption on the surfaces which was similarly observed at 2341 and 2360 cm^{-1} band by Centeno *et al.* (Zou *et al.*, 2009; Centeno *et al.*, 2006). In addition, Centeno *et al.* indicated that, at 673 K, CO adsorption on alumina can be seen as a strong band at 2154 cm^{-1} (H-bonded CO) with a shoulder at 2185 cm^{-1} (Al⁺³-CO), where as those peaks were vanished at the low temperatures such as 100 K. Through the study of CO oxidation over Au/TiO₂ catalysts by DRIFT and Mass Spectrometer to analyze the promotional effect of H₂, Piccolo *et al.* illustrated that the band of 2185–2181 cm^{-1} was CO adsorption on Ti⁴⁺ (support) and the band at 2135–2108 cm^{-1} range was for the Au carbonyls in the presence of CO+O₂ in a He flow at 50 °C (Piccolo *et al.*, 2009).

Finally, the region between 3000 and 3700 cm^{-1} are generally defined as the OH group spectral region. Riberio *et al.* (2008) indicated that the physisorbed water appeared in the range of 3100-3600 cm^{-1} , while Piccolo *et al.* (2009) found the OH group in the region of 3500-3200 cm^{-1} in the presence of hydrogen.

As it can be seen from the previous studies, the position of the adsorption peaks may change as to the temperature, reactants, the metal-support interaction and other reaction conditions. Romero-Sarria *et al.*, for instance, concluded that the dependence of the acceptor or the donor feature of the surface sites results in the shifts of stretching mode of gaseous CO molecule (2143 cm^{-1}) to higher or lower wave numbers (Romero-Sarria *et al.*, 2008). Therefore, it seems to be difficult to precisely identify the surface species observed on the catalysts due to the contradictory assignments published in the literature. A variety of the spectra analysis of CO adsorption may help to figure out relations of the surface sites with environments. For this reason, an extensive summary of the FTIR peaks observed during the CO oxidations and the intermediates assigned to these peaks are given in Appendix A.1 to understand the results of this study better.

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

The chemicals used for catalyst preparation and the background spectrum in the DRIFTS measurements are listed in Table (3.1).

Table 3.1. Chemicals used for catalyst preparation and DRIFTS analysis.

Chemicals	Formula	Grade	Source	Molecular Weight (g mole ⁻¹)
Gold(III) chloride trihydrate	HAuCl ₄ .3H ₂ O	Extra Pure	Aldrich	393.83
Aluminium oxide	Al ₂ O ₃	Extra Pure	Zeochm EU	101.96
Urea	CO(NH ₂) ₂	Extra Pure	Merck	60.06
Potassium bromide spectrograde powder	KBr	Pure	Harrick	119.002 g/mol

3.1.2. Gases and Liquids

All of the gases and liquids used in DRIFTS measurements and kinetic analysis are given with their applications and specifications in the Table (3.2) and the Table (3.3). The gases were supplied by Linde Company, except carbondioxide which was from Birleşik Oksijen Sanayi (BOS).

Table 3.2. Specifications and applications of the gases used.

Gas	Application	Specification
Carbon dioxide	Reactant, MS calibration	99.99% BOS
Carbon monoxide	Reactant, MS calibration	99.0% Linde
Oxygen	Reactant, MS calibration	99.99% Linde
Hydrogen	Reactant, Reducing agent, MS calibration	99.99% Linde
Helium	Reactant (Inert), MS calibration	99.99% Linde

Table 3.3. Specifications and applications of the liquids used.

Liquid	Specification	Application
Water	De-ionized	Aqueous solutions, Reactant
Nitrogen	Cryogenic	Cooling MCT detector

3.2. Experimental Systems

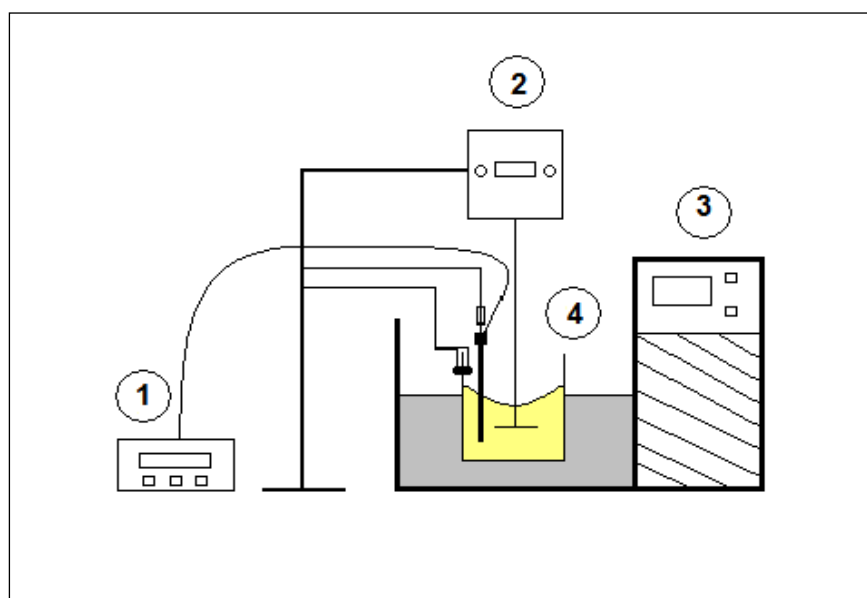
3.2.1. Catalyst Preparation

The catalyst was prepared using the following procedure by homogeneous deposition precipitation (HDP) method, which results nanosized gold particles over Al_2O_3 support.

3.3.1.1. Support Preparation. The alumina support particles were crushed and sieved to obtain a powder with 45-60 mesh size (344-255 μm). Then, a certain amount of support was calcined in a flow of air at 400°C for 2 hours using a heating rate of 5°C/min for the increase of the surface and mechanical properties of the catalysts.

3.3.1.2. Preparation of Au/ Al₂O₃ Catalyst. Au loaded over Al₂O₃ catalysts were synthesized by HDP method using urea as precipitating agent by following the procedure described by Grisel and Nieuwenhuys (2001).

The preparation system used for the deposition of Au on the Al₂O₃ supports by HDP method mainly contains a stirrer to achieve homogeneous mixing, a heater circulation bath for controlling the temperature of the HDP method, a pH meter for determination of the alkalinity of the solution and a beaker as schematically presented in Figure (3.1).



1. pH meter, 2. Stirrer, 3. Heater circulation bath, 4. Beaker

Figure 3.1. The catalyst preparation system (Tezcanlı, 2008).

The H₂AuCl₄.3H₂O was used as the Au precursor; its amount corresponding 1 wt. % Au was firstly dissolved in 25 ml dionized water and then it was added to the Al₂O₃ calcinated support suspending in 80 ml dionized water. The pH of aqueous H₂AuCl₄.3H₂O solution was controlled by addition of 100 ml solution of a 0.84 M excess urea until it reached the desired point. Afterwards, whole solution was heated to 70°C under vigorous stirring in order to gradually ensure decomposition of the urea; the temperature was kept constant under this value for 4 hours. When the pH of the solution reached to 7-8, the procedure was stopped. Then, the slurry was cooled down, and suction filtered. The catalyst was then washed several times with demineralized water in order to remove the remaining Cl⁻ ions. After the filtration process, the catalyst was dried overnight at 100 °C.

The precursor was stored in the dark, and a minimal light was allowed during the catalyst preparations to avoid possible discoloration of the surface caused by photochemical reactions of the Au precursor.

3.2.2. Reaction Analysis System

The schematic representation of the reaction system is given in Figure 3.2. The reactant gases CO, CO₂, He, H₂, O₂ were sent to the reaction system from gas cylinders with the optimum pressure of 30 psia. In this flow system, mainly 1/4", 1/8", and 1/16" OD stainless steel and copper tubing with brass and stainless steel fittings were used. The reactant gases were separately delivered to the system with two Brooks 5850E mass flow controllers coupled with 4-Channel Brooks 0154 control panel.

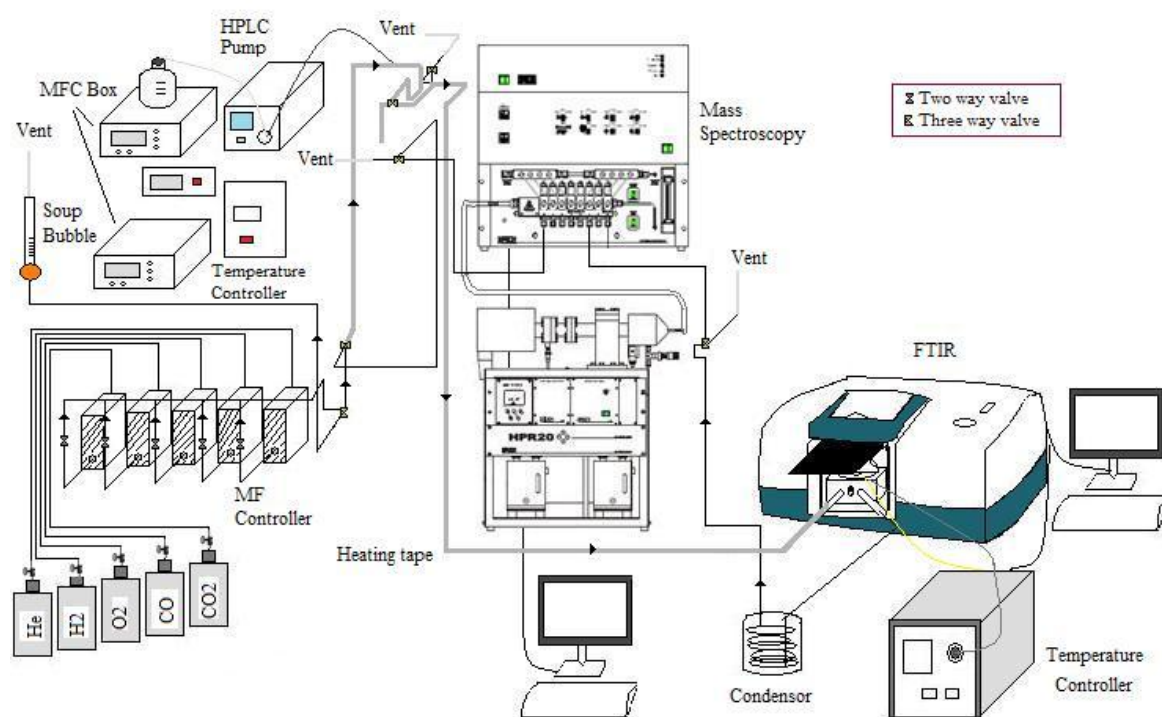
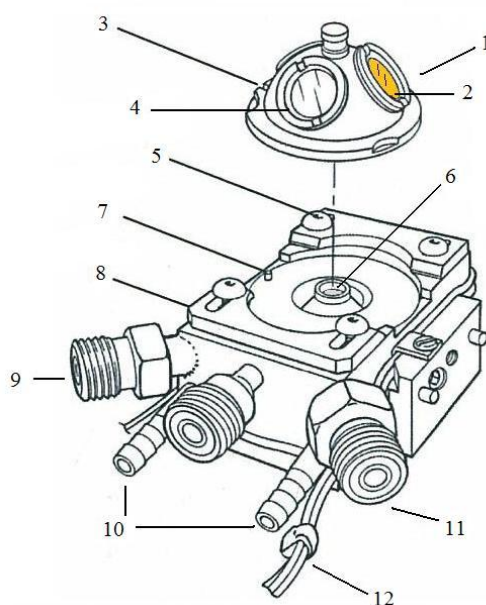


Figure 3.2. Combined FTIR-MS reaction analysis system.

In the water analysis, the whole water entrance system to the reaction chamber was heated up to 140°C by two Dixell XT 110 C temperature controllers with K-type thermocouples.. For the water delivery to the heated gas mixture, a Jasco PU-2080 Plus

HPLC pump was used at a constant flow rate. The reaction mixture from the exit of the reaction chamber of FTIR was passed through a cold trap in order to separate water in the feed and produced during the reaction from the product gases.

The DRIFTS experiments were carried out in a special stainless steel IR reaction cell (Figure 3.3) equipped with ZnSe windows and a praying mantis optical geometry (Harrick, HVC) placed in a Jasco 6100 FTIR Spectrometer fitted with an MCT detector working at liquid nitrogen. The cell contains a heating element and a thermocouple providing the feedback to a temperature controller to maintain constant temperature. Also, a water cooling jacket controls the temperature of the outer surface of the chamber and windows during high or low temperature operation. There are three gas ports equipped with 1/4" VCO fittings in the reaction chamber for evacuating, pressurizing or flowing gas through the sample. Since there was no vacuum on these experiments, only two gas ports near the sides of chamber were used to gas input-output process. The gases flowed upwards through a bed of catalyst reaching the dome and flowing out near its base.



1) HVC Dome 2) ZnSe window 3) Orientation slot 4) Quartz observation window 5) Retaining plate screws 6) sample cup 7) Orientation pin 8) Retaining plate 9) Gas inlet 10) Cooling parts 11) Gas outlet 12) Heater connector

Figure 3.3. High temperaturer reaction chamber and its installing parts.

In addition to DRIFTS analysis, the feed gases and product gases were analyzed by Hidden Hal 210 mass spectrometer after the cold trap separation of water.

3.3. Reaction Test by FTIR

A total of 16 scans were recorded per spectrum, which was displayed in absorbance units, over the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} . Approximately 65 mg sample were placed in the sample holder.

3.3.1. Background Spectrum

Prior to sample test, the background spectrum for each analysis were recorded against a pure KBr at 25°C. The material was filled into the sample cup using the provided packing tool. Then, the dome on the HVC was installed, and the micrometer was adjusted to maximize the signal on the detector. Finally, the background spectrum was collected.

3.3.2. Sample Spectrum

KBr sample was restored to ambient conditions. Then, the sample cup was cleaned and refilled with the samples following the same procedure as in the collection of background spectrum. Samples were powdered and diluted with 2 wt. % KBr in order to improve the reflectivity.. Then, they were pretreated under 50 ml/ min H_2 flow for 1 hr at 300°C and 50 ml/min He flow for 1 hr at 150°C to increase the catalytic activity by cleaning the catalyst surface from oxygen. After reduction, He was flowed for 30 minutes to cool down the samples to the reaction temperature then the first sample spectrum was taken under pure He flow as a reference for the comparison with the sample spectra.

After reduction program, reaction tests were performed under a total flow of 100 ml/min using reaction temperature in the 25-150°C range under atmospheric pressure. Then the sample spectrum was recorded for each test.

Table 3.4. Reduction program for Au/Al₂O₃ catalyst.

Segments	Starting and End Temperatures	Segment Gas
First Segment (Reduction)	Heating from 25°C to 300°C and keeping constant at 300°C	H ₂ with flow rate of 50 ml/min
Second Segment	Cooling down to reaction temperature	He with flow rate of 50 ml/min

Table 3.5. The reaction conditions for Au/Al₂O₃ catalyst at 25-150°C.

Feed Composition (%) with He as Balance					Total Flow (ml / min)
CO	O ₂	CO ₂	H ₂	H ₂ O	
2	-	-	-	-	100
2	1	-	-	-	100
4	-	-	-	-	100
4	2	-	-	-	100
8	-	-	-	-	100
8	4	4	-	-	100
8	4	8	-	-	100
8	4	-	60	-	100
-	-	4	-	-	100
-	-	8	-	-	100
8	4	4	60	-	100
8	4	8	60	-	100
8	4	-	60	8	100
8	4	8	60	8	100

4. RESULTS AND DISCUSSION

The results of the DRIFTS study performed for the selective CO oxidation over 1 wt. % Au/Al₂O₃ are presented and discussed in this section. The effects of temperature and feed composition were studied in the ranges given in Table 4.1 while the pressure was assumed to be atmospheric. The amount of steam introduced during the analysis of water effects was calculated from the amount of liquid water injected using the equation below (4.1).

$$V_{\text{Steam}(H_2O)} = \frac{V_{\text{Liquid}(H_2O)} \times \rho_{H_2O} \times R \times T}{MW_{H_2O} \times P} \quad (4.1)$$

where $\rho=1000 \text{ g.L}^{-1}$; $P=1 \text{ atm}$; $R=0.082 \text{ L.atm.mol}^{-1}.\text{K}^{-1}$; $T=298 \text{ K}$ and $MW_{H_2O}=18 \text{ g.mol}^{-1}$.

The outlet stream from the DRIFTS system was introduced to the Mass Spectrometer to measure the conversion, which is calculated using equation (4.2), and the results were tabulated in the Table 4.1.

$$\text{CO conversion (\%)} = \frac{[CO]_{\text{in}} - [CO]_{\text{out}}}{[CO]_{\text{in}}} \times 100 \quad (4.2)$$

Shubert *et al.* (2004) indicated that the observed peak can be changed a little as to the type of catalysts, reaction and reaction conditions, but take place in a similar range due to the frequencies of atom. For instance, C–H vibrations in formates and O–H vibrations (3000-2700), COO vibrations in formates and carbonates (1700-1350) were obtained through DRIFTS study of CO oxidation over Au/TiO₂ at 80°C (Schumacher et al., 2004). The peak positions given in Figure 4.1 as well as the positions reported in various published papers were used as the guide during the analysis of the DRIFTS spectra.

Table 4.1. CO conversion results of Au/Al₂O₃ for different temperature and reactant concentrations.

CO (mol %)	O ₂ (mol %)	CO ₂ (mol %)	H ₂ (mol %)	H ₂ O (mol %)	T (°C)	^a W _{CAT} / ^b F _{CO} (g.h.mol ⁻¹)	^c X _{CO} (fractional)
8	4	-	-	-	110	3.31	0.03
2	1	-	-	-	110	13.24	0.04
8	8	-	-	-	110	3.31	0.02
8	4	-	-	-	25	3.31	0.01
8	4	8	-	-	110	3.31	-
8	4	-	60	-	110	3.31	0.07
8	4	8	60	-	110	3.31	0.03
8	4	-	60	8	110	3.31	0.06
8	4	8	60	8	110	3.31	0.04

^aCatalyst weight, ^bCO flow rate, ^cCO conversion

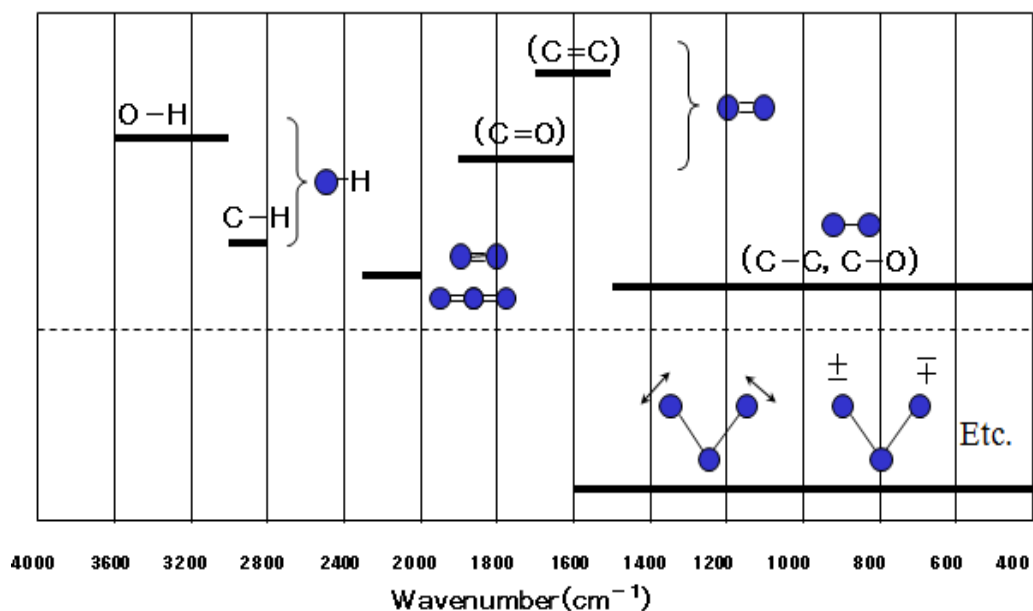


Figure 4.1. Adsorption position of the some molecules (Jasco, 2010).

Prior to the main experiments, some preliminary tests were conducted in order to determine the most appropriate sample conditions for DRIFTS analysis. For this aim, approximately 65 mg crushed and uncrushed samples containing none 2% and 10% KBr were studied at the room temperature through insertion of CO in balance He as well as the CO+O₂ mixture in He. The corresponding spectra are shown in Figure 4.2 and Figure 4.3 as wavenumber (cm⁻¹) versus absorbance value.

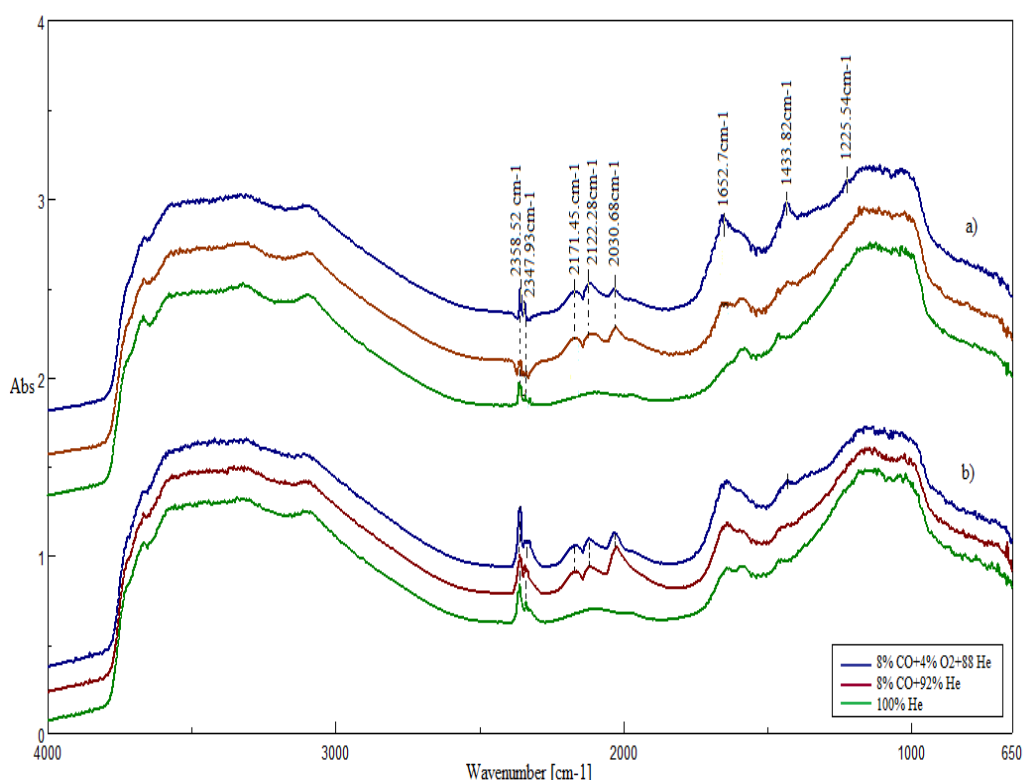


Figure 4.2. The spectra of uncrushed samples 25°C: a) Diluted with 10% KBr; b) Diluted with 2% KBr.

The band observed around 2360, 2340, 2170, 2125, 1600 and 1400 cm⁻¹ were nearly in the same position for each sample as it is seen in Figure 4.2 and Figure 4.3. However, the spectrum of the samples which was crushed and diluted with 2% KBr were found to be smoother and the changes with oxidation was observed more clearly. For instance, the peak at 1225.54 cm⁻¹ was hardly observed in the spectra of Figure 4.2 for both KBr dilutions while it was more apparent in Figure 4.3. Then the crushed samples with 2% KBr were decided as the most proper sample conditions, and used in the remaining part of the study.

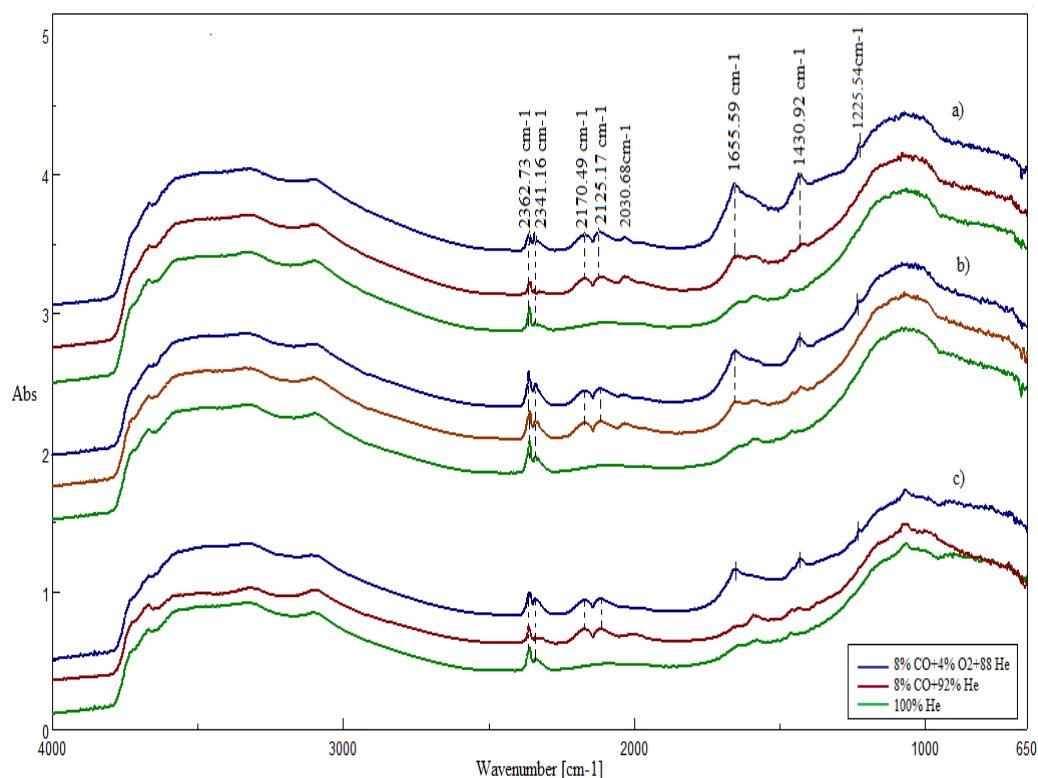


Figure 4.3. The spectra of crushed samples at 25°C: a) No dilution ; b) Dilution with 10% KBr; c) Dilution with 2% KBr.

Then, the effects of temperature as well as the feed composition on the formation of surface species and therefore reaction mechanism were investigated as presented in the following sections.

4.1. Temperature Effect

The spectra of three different gas compositions (pure He gas, 8% CO in balance He, and 8% CO+ and 4% O₂ in balance He) were taken and analyzed at temperatures ranging 25°C to 150°C in order to examine temperature effect on the surface species of CO oxidation Au/Al₂O₃ catalyst. The results are presented in Figure 4.4.

The bands at 2362.37 cm⁻¹ and 2337.3 cm⁻¹ in the Figure 4.4 can be indicated as gaseous CO₂ as the asymmetric O-C-O stretching was defined at 2349 cm⁻¹ (Jasko, 2010). Also, 2167.6 cm⁻¹ and 2122.28 cm⁻¹ bands can be assigned to the gaseous CO since they were also observed during CO flow through the empty DRIFTS cell (no catalysis). The

former peak was nearly the same in all temperatures while the second peak shifted to 2107.81 cm^{-1} over 110°C temperature in the presence of CO and O_2 . The clear peak observed at 2033.46 cm^{-1} at 25°C can be assigned to CO adsorbed on ultrafine gold particles dispersed on Al_2O_3 support with on-top structure (Jia *et al.*, 2001). Conteno *et al.* (2006) assumed that the third peak at 2101 cm^{-1} observed in CO adsorption study over reduced $\text{Au}/\text{Al}_2\text{O}_3$ samples at 100 K was related to $\text{Au}^0\text{-CO}$ band. Similarly, Zou *et al.* (2010) has found the peak at 2100 cm^{-1} caused by CO adsorbed to Au^0 at 30°C . Moreover, Smit *et al.* (2007), through the low temperature CO oxidation over $\text{Au}/\text{Fe}_2\text{O}_3$ catalyst, indicated that the visible peaks at 2155, 2108 and 2070 cm^{-1} could be attributed to adsorbed CO on gold-isolated site; CO adsorbed on metallic gold and irreversibly adsorbed CO at different sites of metallic gold particles, respectively.

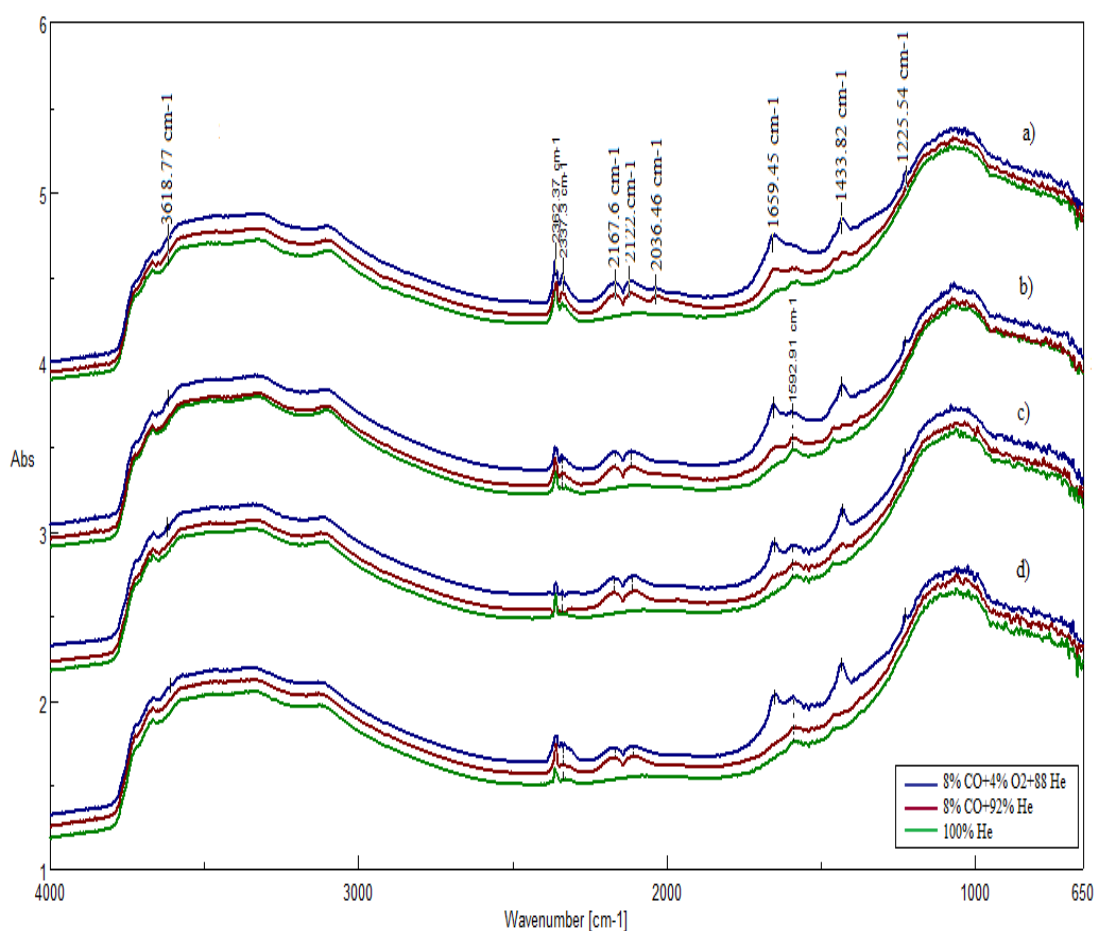


Figure 4.4. Temperature effect on CO oxidation spectra over $\text{Au}/\text{Al}_2\text{O}_3$: a) 25°C ; b) 50°C ; c) 110°C ; d) 150°C .

The spectra of all temperatures studied were similar at first sight, but have some differences in detail. To capture this fine details, the spectra taken at each temperature were examined by subtracting the one belonging to pure He from the spectrum obtained with CO as well as subtracting the last one from the spectrum of CO+O₂ mixture. The results are presented in Figure 4.5 through Figure 4.8.

Through the comparison of all these subtracted figures, it can be observed that the peak at 2033.46 cm⁻¹ seen at 25°C was shifted to 2034.53 cm⁻¹, and 1962.22 cm⁻¹ at 50°C and 110°C, respectively, and it was completely vanished at 150°C.

The common peak around 3622.63 cm⁻¹ which was visible at all temperatures in the presence of CO and O₂ can be referred to the presence of OH region as claimed in the study of Smit *et al.* (2006) for the CO oxidation on Au/Fe₂O₃. Also, a little amount of -OH species on catalyst can lead the formation of bicarbonates during oxidation; therefore, Schubert *et al.* (2004) defined the peak at 3620 cm⁻¹ as the O-H stretching vibration in bicarbonates. The negative peak around 3757 cm⁻¹ in the subtracted spectrum can be illustrated with the continuous consumption of OH species as Smit *et al.* (2007) predicted a similar peak at 3677 cm⁻¹. Schumacher *et al.* also claimed that peaks at 2833, 2873, 2931, and 2955 cm⁻¹ on Au/TiO₂ catalyst assigned to C-H stretch vibrations in formates adsorbed on the anatase support, as well as the carboxylate species, were the result of the consumption of the OH groups. However, those peaks were not observed in our study.

The bands between 1800 and 1200 cm⁻¹ were accepted by many studies as the region of carbonate like species. As seen in Figure 4.4, the presence of CO slightly changed the catalyst surface while the presence of both CO and O₂ together resulted in sharp peaks within 1800-1200 cm⁻¹ at all temperatures indicating that indeed the reaction may be proceeded through carbonate like species.

In Figure 4.5, the band at 1656.55, 1428.99-1434.78 and 1229.4 cm⁻¹ were clearly observed in the presence of CO and O₂ together. The first three were also visible in CO spectrum with small intensities while the one around 1200 was not visible at all. Figure 4.6, 4.7 and 4.8 resulted in the similar band spectrum in the reaction conditions. However, in the presence of only CO, these bands exhibited lower absorbance. In Figure 4.6, the

subtracted spectra of CO absorbance gave way to the formation a additional small peaks at 1739.48, 1563.15 and 1366.32 cm^{-1} . These peaks may be also the carbonate like species, which were under the larger peaks at small temperature and not observed at higher temperatures

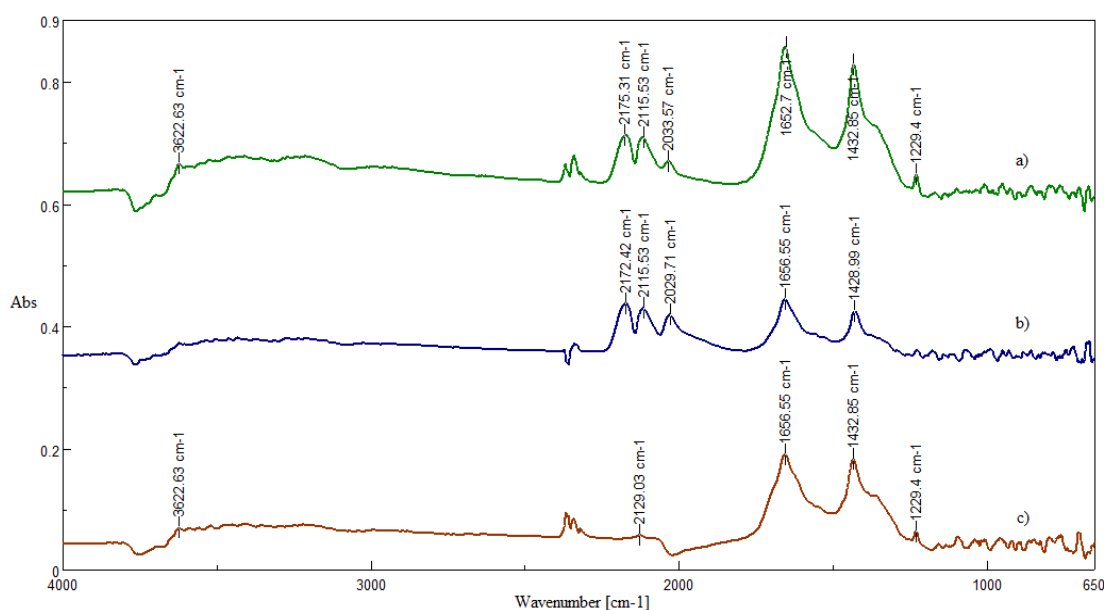


Figure 4.5. Subtracted spectra at 25°C: a) He from CO + O₂ b) He from CO; c) CO from CO + O₂.

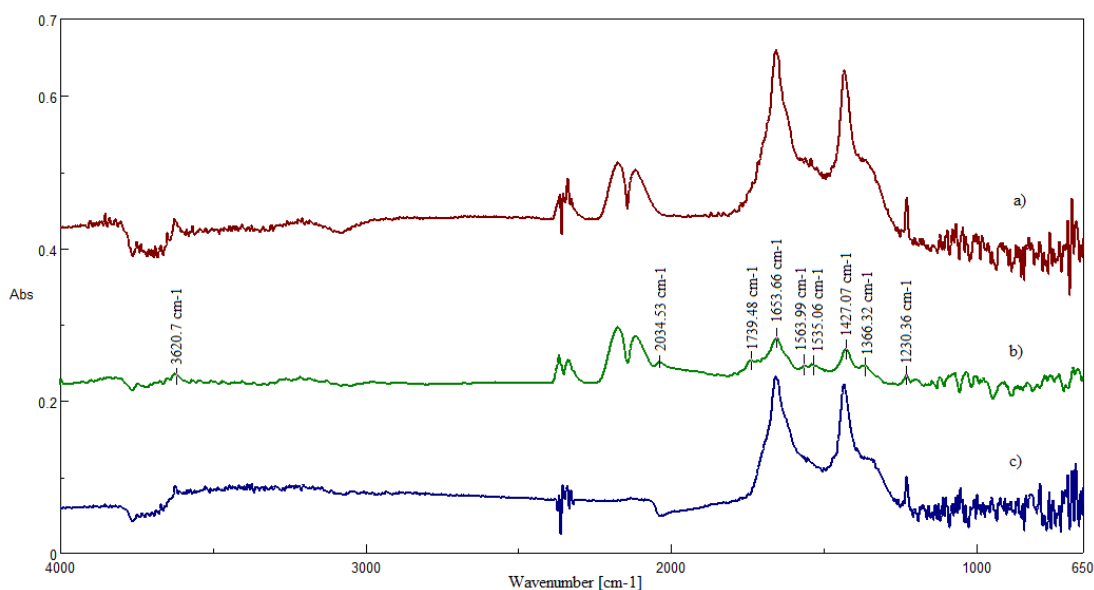


Figure 4.6. Subtracted spectra at 50°C: a) He from CO + O₂ b) He from CO; c) CO from CO + O₂.

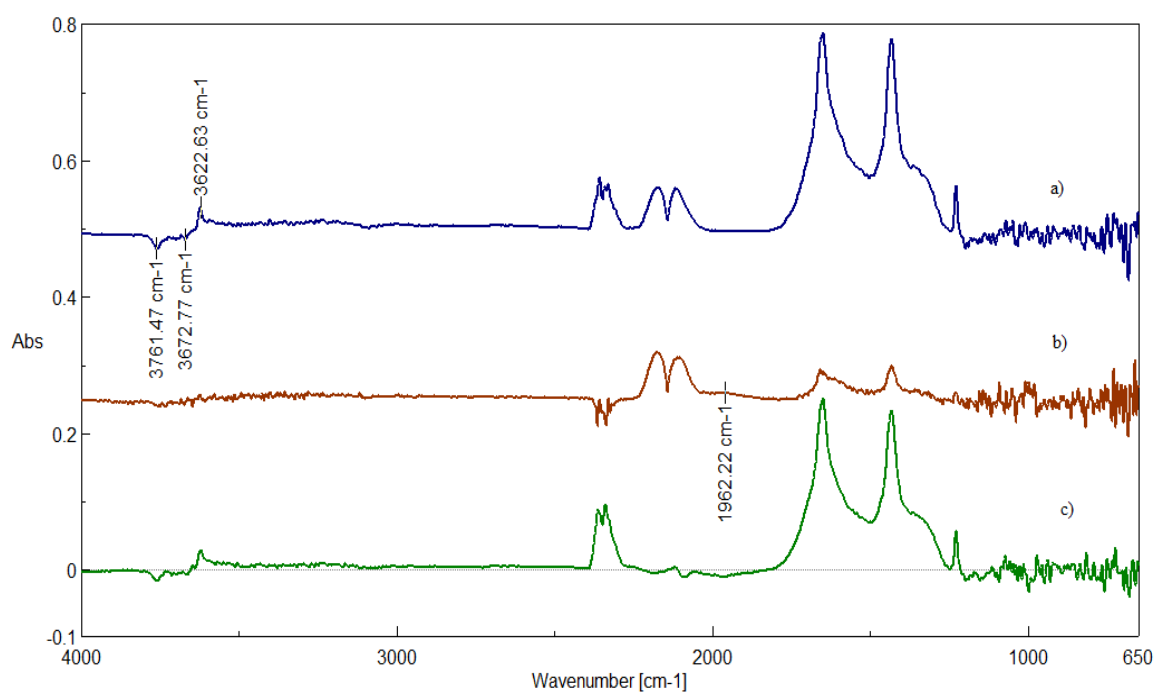


Figure 4.7. Subtracted spectra at 110°C: a) He from CO + O₂ b) He from CO; c) CO from CO + O₂.

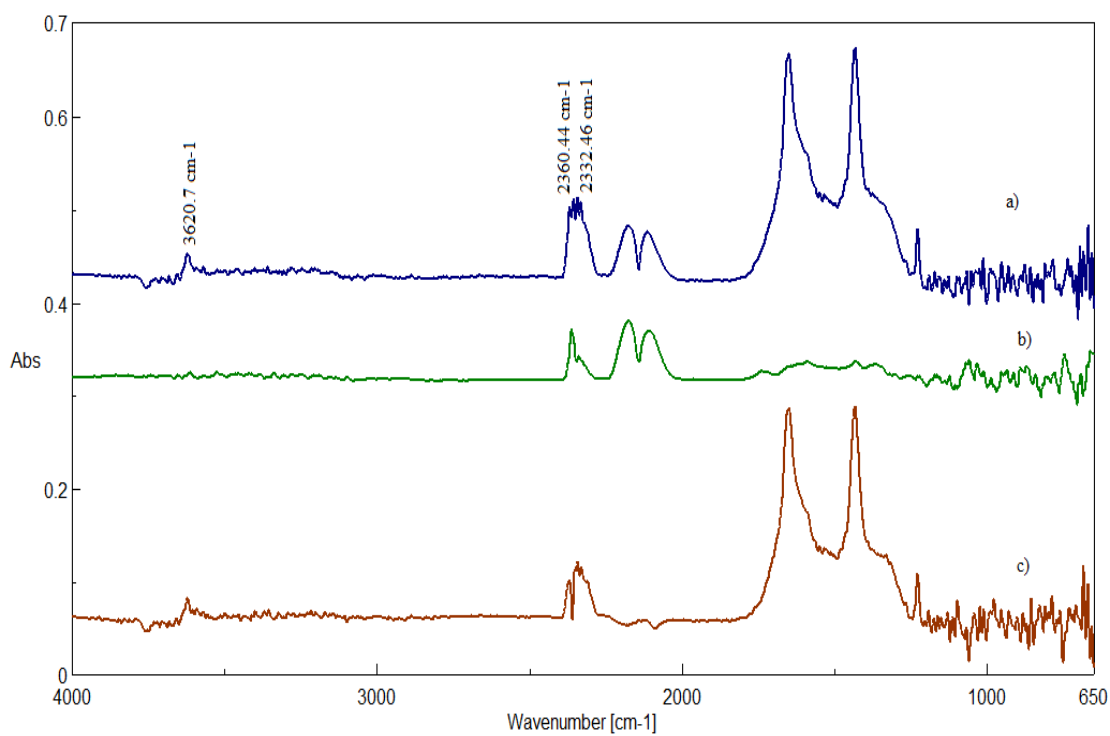


Figure 4.8. Subtracted spectra at 150°C: a) He from CO + O₂ b) He from CO; c) CO from CO + O₂.

In Figure 4.5, the band at 1656.55, 1428.99-1434.78 and 1229.4 cm^{-1} were clearly observed in the presence of CO and O₂ together. The first three were also visible in CO spectrum with small intensities while the one around 1200 was not visible at all. Figure 4.6, 4.7 and 4.8 resulted in the similar band spectrum in the reaction conditions. However, in the presence of only CO, these bands exhibited lower absorbance. In Figure 4.6, the subtracted spectra of CO absorbance gave way to the formation a additional small peaks at 1739.48, 1563.15 and 1366.32 cm^{-1} . These peaks may be also the carbonate like species, which were under the larger peaks at small temperature and not observed at higher temperatures

Since the studies related to the formation of carbonate like species over Au/Al₂O₃ catalyst are limited, the peaks found in this study can be analyzed using the results obtained over other supports in the literature. Raphulu *et al.* (2010), on their study over Au/TiO₂, defined the peak at 1645 cm^{-1} as hydroxycarbonyl (COOH) and the peak at 1420 cm^{-1} as carbonate species (COO) in the presence of O₂, while Rasko and Kiss (2006) assumed that the peak at 1620 cm^{-1} belonged to the bidentate carbonate species in anatase. Costello *et al.*, (2003) explained the presence of hydroxycarbonyl species, which were oxidized to bicarbonates, as the CO addition into (Au⁺) - (OH⁻) lattice species. The peak at 1445 cm^{-1} was indicated as the monodenate carbonate. The peaks at 1229.4 - 1226.5 cm^{-1} found in this study can be assumed as bicarbonate species considering Tseng *et al.* (2009) found the bicarbonate peak at 1220 cm^{-1} band in their study of CO oxidation over Au/Fe₂O₃. Although it is a controversial issue, the presence of bicarbonates (HCO₃⁻), can also be explained by the study of Kung *et al.* (2007). It was indicated that the formation of Au-OH species as an initiating step at the gold atom through the support hydroxide atom in selective CO oxidation mechanism, then their reaction with CO molecule forming carboxyl group (Au-CO₂.OH) which tends to be oxidized to bicarbonate.

In addition, in the presence of CO and O₂ together, Piccolo *et al.* (2009) defined a distinct peak at 1576 cm^{-1} on the surface of Au/TiO₂ catalyst as the bidentate carbonate or carboxylate, which did not appear clearly in this study. However, Figure 4.6 for subtracted spectra for CO at 50°C exhibits some additional peaks around 1700, 1500 and 1300 cm^{-1} , which are, in general, considered as the carbonate like species. Raphulu *et al.* (2010) assigned the peak around 1587 cm^{-1} as the formates in the case of pure CO adsorption. The

monodentate carbonates were observed at 1354 cm^{-1} in the presence of reactant gases. The peaks between 1330 and 1370 cm^{-1} were generally assigned to COO symmetric stretch frequencies in the absence of O_2 . The peak at 1725 cm^{-1} was also assumed as carbonate on TiO_2 , while the one at 1560 cm^{-1} was decided as bidentate carbonates. The close and sometimes varying positions of the peaks assigned to different surface species make the interpretation of the DRIFTS spectra for CO oxidation over gold catalyst quite difficult.

The formation of carbonate like species on the surface of catalyst has been observed in several studies; however, their role in the CO oxidation reaction mechanism has been still unclear. Some believe that they were crucial part of the CO oxidation mechanism, while the others claim that they are passive on CO oxidation or deactivate the catalyst. Smit *et al.* (2007) explained the CO oxidation at low temperature on $\text{Au/Fe}_2\text{O}_3$ through the formation of formates as intermediates from the reaction of CO and a hydroxyl ($-\text{OH}$) than its reaction with O_2 forming CO_2 and H_2O , where the dissociation of water molecules maintained the amount of $-\text{OH}$ groups on the surface.

The peak observed at about 1430 cm^{-1} , especially apperant in the presence of CO and O_2 together (see Figure 4.6, 4.7 and 4.8) and assigned as the carbonate species (CO-OO) in above discussion may be the indicator of the validity of the CO oxidation mechanism proposed through these species. For example a two step Eley-Rideal-type mechanism may result in this peak since O_2 adsorption on Au and reaction with CO formed an O-O-CO complex. This complex was dissociated to CO_2 and adsorbed O atom which then reacted with another CO to form the second CO_2 (Liu *et al.*, 2002). Similarly, Molina *et al.* (2009) pointed out that O_2 was adsorbed on the surface through CO.OO reaction intermediate on the study of reaction mechanisms for CO oxidation on Au catalysts. On the other hand, the pure CO_2 , which is the product in all the mechanisms, has also some similar peaks at about 1430 cm^{-1} (as discussed below) making the discrimination of the mechanism difficult.

When the CO conversion was evaluated, it was found as in Table 4.1 that conversion values seemed to be very low in general comparing with the previous kinetic studies on CO oxidation over the same $\text{Au/Al}_2\text{O}_3$ catalyst. For example, Demir (2009) reported a 43% CO conversion for 10 mg %1 wt $\text{Au/Al}_2\text{O}_3$ catalyst at 110°C in the presence 2% CO, 1% O_2 , 60% H_2 ; while the conversion was about 7% in this work for the feed composition

of 8% CO, 4% O₂, 60% H₂ at the same temperature even though 65 mg %1 wt Au/Al₂O₃ catalyst was used. The conversion was also quite low for the other temperatures and feed composition compared to the previous works in fixed bed reactor. Apparently the reactants and the catalyst are not in a full contact in the DRIFTS cell as much as they are in the fixed bed micro flow reactor.

4.2. Concentration Effect

The study of selective CO oxidation over Au/Al₂O₃ catalyst by Demir (2009) indicated that the increase in CO concentration resulted in the reduction of the active sites for O₂ adsorption, hence decreasing conversion. The rise in O₂ concentrations, on the other hand, caused to an increase in H₂ oxidation decreasing the CO₂ selectivity. This result indicates that there is an optimum CO/O₂ ratio; hence the effects of CO and the O₂ as well as the other species in the feed must be also investigated.

4.2.1. CO Concentration Effect

The CO concentration in the feed was changed from 2% to 8%, and its effects on the DRIFTS spectra were evaluated for both in the absence and presence of stoichiometric O₂ concentration. According to the results shown in Figure 4.9, the peaks are nearly the same in all concentrations, as OH species are at 3618.77, CO and CO₂ gaseous are at around 2300 and 2100 cm⁻¹ respectively, and proposed carbonate like species are at 1657, 1430.93 and 1226.5 cm⁻¹ band. Schumacher *et al.* (2004) observed a shift of 2111 cm⁻¹ band to 2104 cm⁻¹ upon a CO partial pressure increase from 0.05 to 1.0 kPa in the case of CO oxidation on Au/Fe₂O₃. They attributed this due to the fact that increased CO partial pressure led to C-O absorption intensity. This trend was not observed in this study. Furthermore, the MS analysis of the outlet stream showed that the CO conversions did not change much either as the the presence of 8% CO and 2% CO resulted 3% and 4% CO conversion respectively (Table 4.1). It should be noted that, however, the the spectrum of 8% CO in balance He was clearer than that of 2% CO.

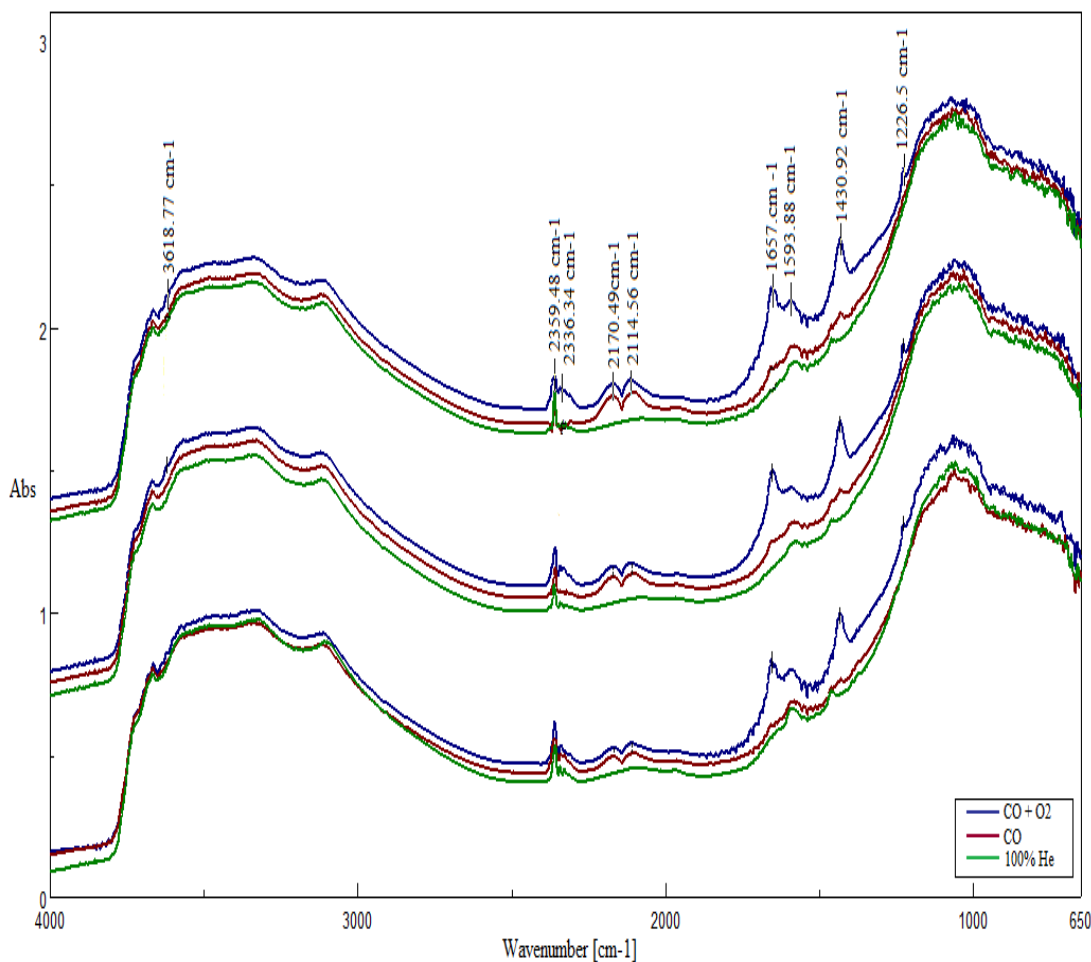


Figure 4.9. The effects of CO concentration on DRIFTS spectra at 110 °C a) 8% CO and 4% O₂ in balance He; b) 4% CO and 2% O₂ in balance He; c) 2% CO and 1% O₂ in balance He.

4.2.2. O₂ Concentration Effect

Next, the effect of O₂ concentration was tested by changing it from 2% to 8% at 110 °C and at the constant CO concentration of 8%. The results are presented in Figure 4.10. It can be seen from Figure 4.10 that the peaks previously assigned as the carbonate like species at 1652.7, 1593.88, 1430.92 and 1226.5 cm⁻¹ dramatically decreased in 2% O₂ and the peak at 1226.5 cm⁻¹ was completely vanished. Surprisingly the results were the same at 8% O₂ concentration. Apparently the excess amount of O₂ blockaded the active sites preventing CO adsorption and therefore the reaction the opposite was also true for the low O₂ concentrations.

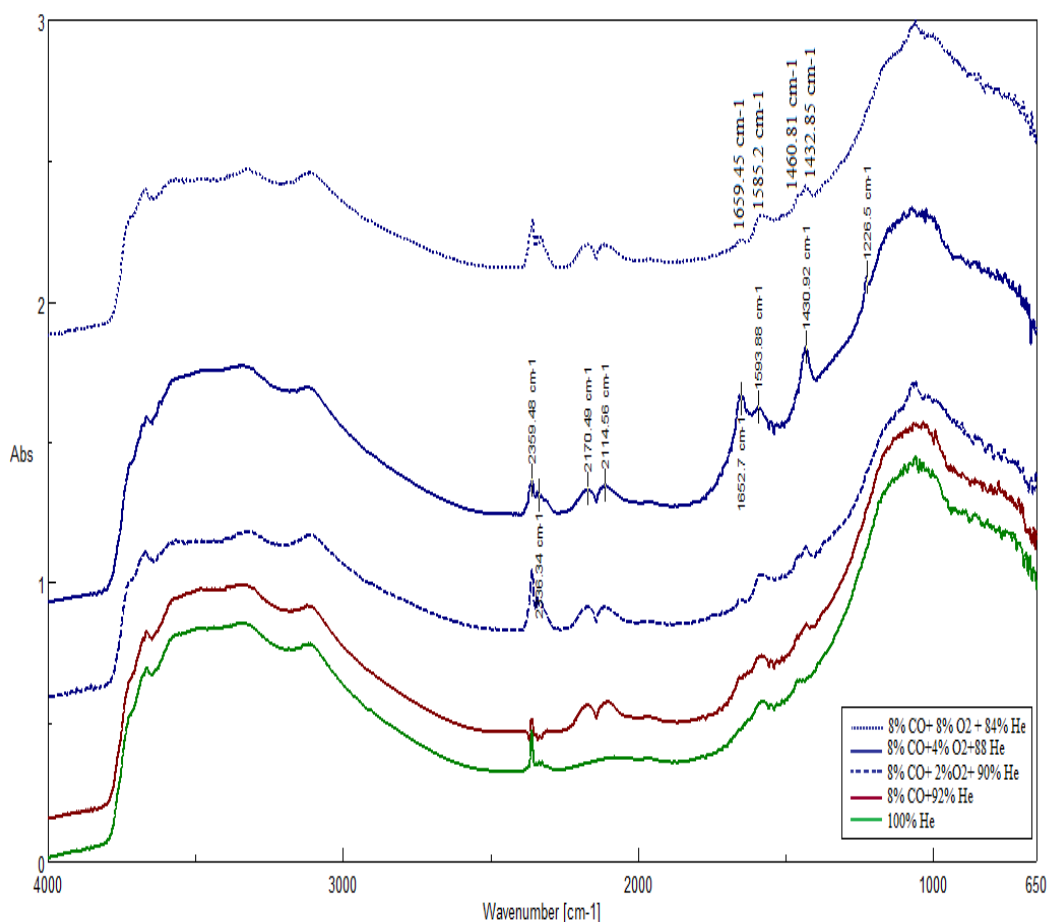


Figure 4.10. The effects of O₂ concentration on DRIFTS spectra at 110 °C in the presence of 8% CO.

4.2.3. CO₂ Concentration Effect

In order to investigate the effect of CO₂ on the catalyst surface during CO oxidation, the spectra of 4% CO₂ and 8% CO₂ in balance He were compared first at 110°C. The results are shown in Figure 4.11. As CO₂ was introduced to the He gaseous at 110°C, the sharp and clean peaks at 1651.3, 1432.85 and 1227.47 cm⁻¹, which were previously attributed to carbonate like species, were observed. Similarly, the peak at 3620.7 cm⁻¹ was also seen even though it was attributed to the OH containing groups by various investigators as discussed in the Section 4.1. Peaks at 2356.59 cm⁻¹ and 2335.37 cm⁻¹ corresponding to the gaseous CO₂ were increased with the increasing CO₂ in the feed as expected. Raphulu *et al.* (2010) also observed bicarbonate and/or hydroxycarbonyl at 1680 cm⁻¹ which is then shifted to 1650 and formate species at 1587 cm⁻¹ upon the exposure of CO₂ on the Au/TiO₂ catalyst.

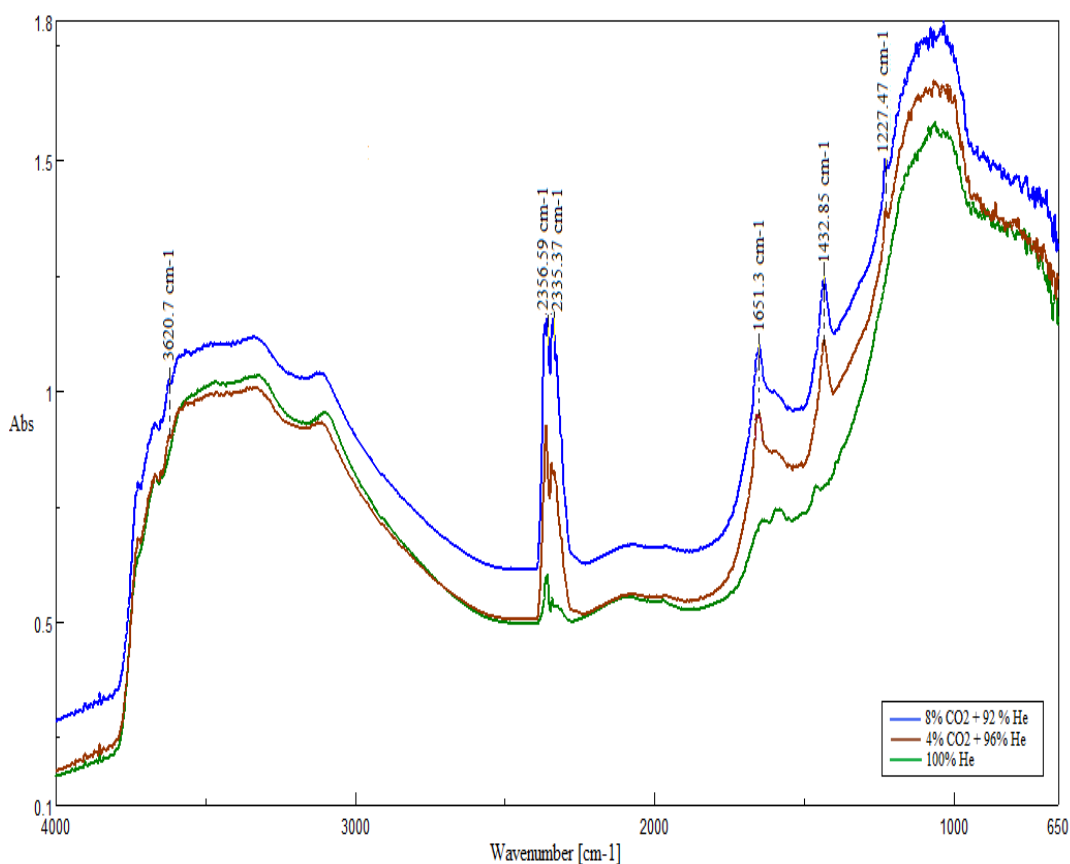


Figure 4.11. The effects of CO₂ on the Au/Al₂O₃ spectra in the absence of CO and O₂.

Figure 4.12 mainly compares the effect of CO₂ in the presence of CO and O₂ reaction mixture. As it is seen, the band at 1648.84, 1433.82 and 1230.36 cm⁻¹ was observed in all cases with some small shifts.

4.2.4 H₂ Concentration Effect

CO oxidation reaction was also conducted on the presence of excess H₂ at 50°C and 110°C reaction temperature (Figure 4.13). As it is seen, all peaks around 1620, 1430, 1225 cm⁻¹ assumed as the carbonate like species as well as the one illustrated OH regions were disappeared, but a new sharp peak occurred at 1643.05 cm⁻¹. This new peak can be related to the ν(HOH) vibration mode of adsorbed water as Piccolo et al. (2009) observed at 1620 cm⁻¹ for CO oxidation over Au/TiO₂ catalyst in presence of H₂. This HO-O species were proposed to be highly oxidizing intermediates making H₂ positively contributes to the CO oxidation (Gavril *et al.*, 2007).

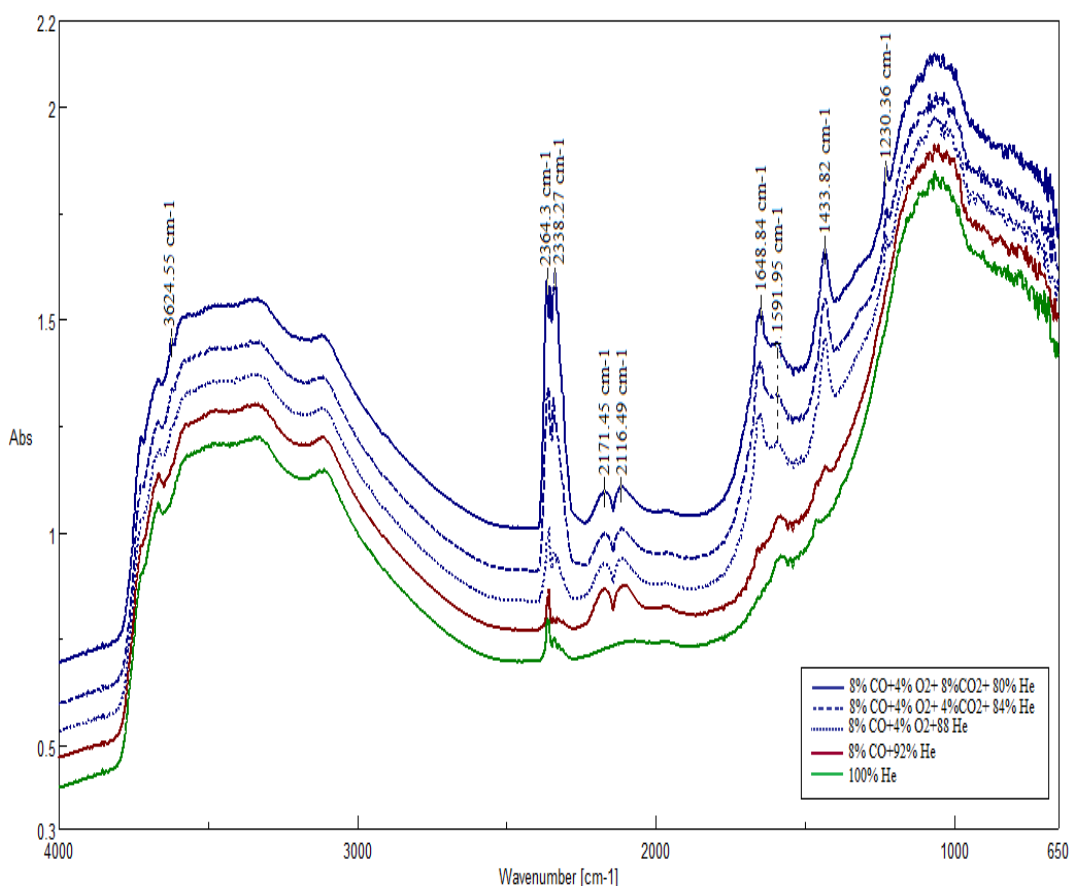


Figure 4.12. The effects of CO₂ on the Au/Al₂O₃ spectra in the presence of CO and O₂.

Furthermore, Piccolo *et al.* (2009) indicated that the feature above 3600 cm⁻¹ decreased when H₂ introduced the CO and O₂ feed, but a wide band between 3500 and 3200cm⁻¹ came out due to the ν(O-H) vibrational modes in hydrogen-bonded hydroxyl groups and water adsorbed at the catalyst surface on the study of water effect on CO oxidation over Au/TiO₂. A similar change can be seen in the left sight of the spectra in Figure 4.13 comparing the one without H₂.

In addition, as it is seen in the Figure 4.13 at 110°C, neither formates nor carbonate/carboxylate species were formed in the presence of H₂. The other small peaks at 1560.13, 1456.96 and 1372.1 cm⁻¹ were observed when the excess H₂ inserted into the CO and O₂ mixture as seen in Figure 4.13. Figure 4.14 indicates surface change of sample from 50°C to 110°C in the presence of excess H₂. The intensity of the peak at 1643.05 cm⁻¹ was higher at 50°C, while the peak at 1456.96 and 1372.1 cm⁻¹ became more apparent and wider at the same temperature.

The effects of CO₂ in the presence of H₂ were also evaluated in two concentrations (4% and 8%) at 110°C, and the results were collected in Figure 4.15. The effects of both concentrations were quite similar except the intensity of the peaks corresponding to the gaseous CO₂. When the excess H₂ was introduced, it was observed that a sharp band peak were observed at 1638.23 cm⁻¹ together with a small but wide 1437.67 and 1366.32 cm⁻¹ peaks. The peak observed at 1220 cm⁻¹ for the reaction mixture in the absence of H₂ was not seen in this case. Moreover, the surface changes observed in the reaction mixture containing H₂ (but not CO₂) on the left sight of the spectrum was also observed in the presence of CO₂ as long as the H₂ is present indicating that the region of 3700 -3600 cm⁻¹ may be related to the O-H vibrational modes as discussed above.

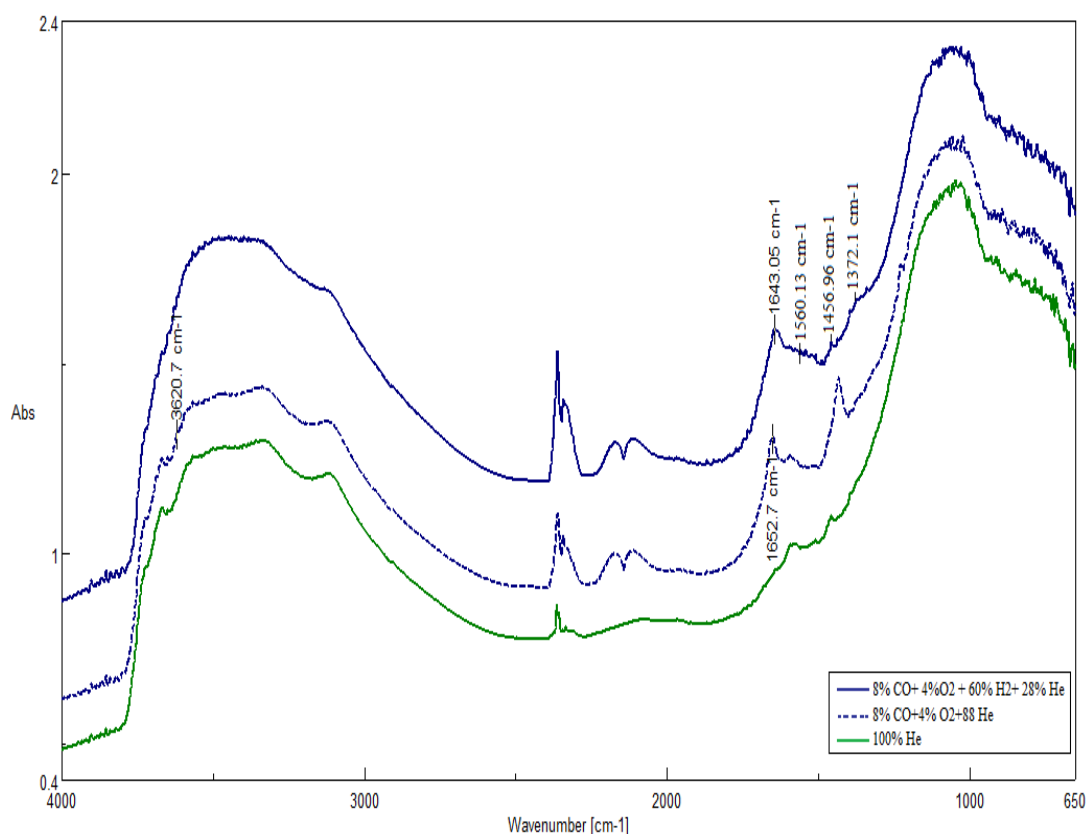


Figure 4.13. The effect of H₂ on the spectra of CO oxidation at 110°C.

In the presence of H₂ together with CO and O₂, Shi *et al.* (2008) observed the C-H vibration bands at 2870-2960 cm⁻¹ on their study over FeO_x/Pt/TiO₂ at 333 K; however, no such peaks were observed in this study.

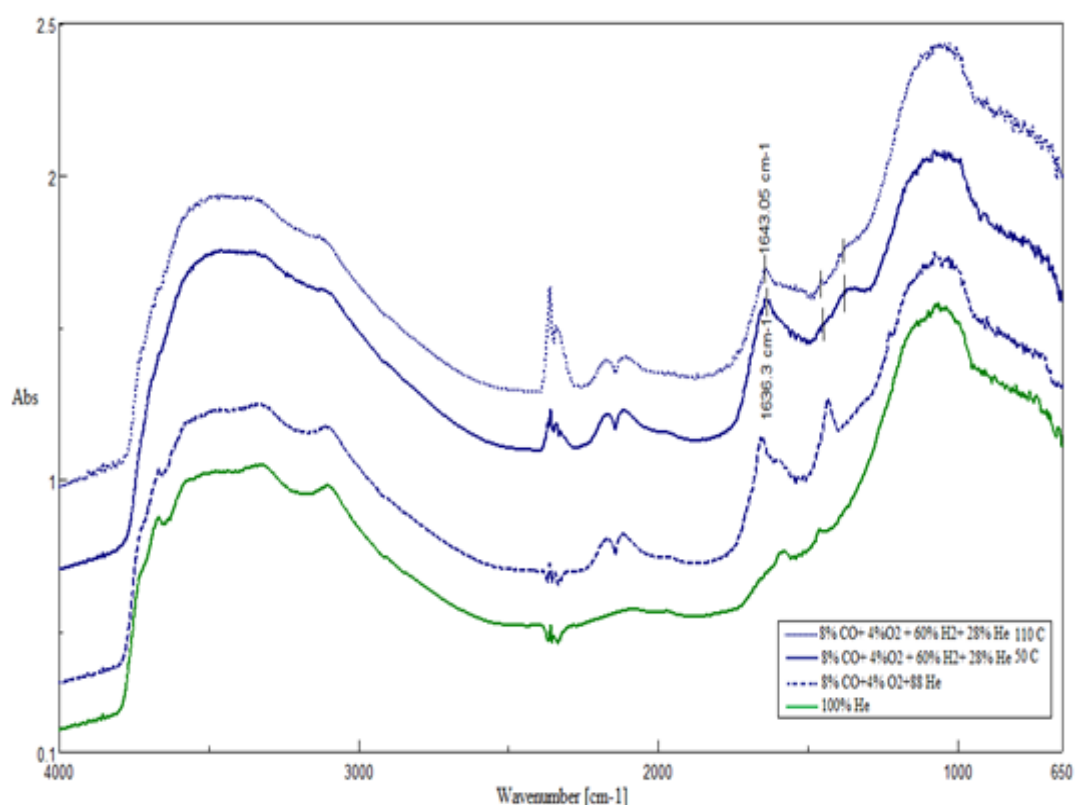


Figure 4.14. The effect of H_2 on on the spectra of CO oxidation at 50°C compared with the one at 110°C .

Schumacher *et al.* also investigated the effect of H_2 on CO oxidation over Au/TiO_2 catalyst. They indicated that carbonate and formate species were decomposed due the presence of H_2 ; these species were significantly visible in a H_2 free atmosphere and deactivated the catalyst although they did not influence the mechanism of CO oxidation.

Quinet *et al.* (2009) declared the mechanism in the presence of H_2 as molecularly adsorbed oxygen on Au reacted with H_2 , forming OOH^* and H^* species, where $*$ donated the adsorption on catalyst surface. Then the reaction between CO^* and OOH^* led CO_2 and OH^* , which was then reacted with CO^* producing CO_2 and H^* . Finally, OOH^* species can reformed by this H^* reacting with another O_2 molecules. This may explain the increased O-H vibrational modes; and the vanishing other carbonate species.

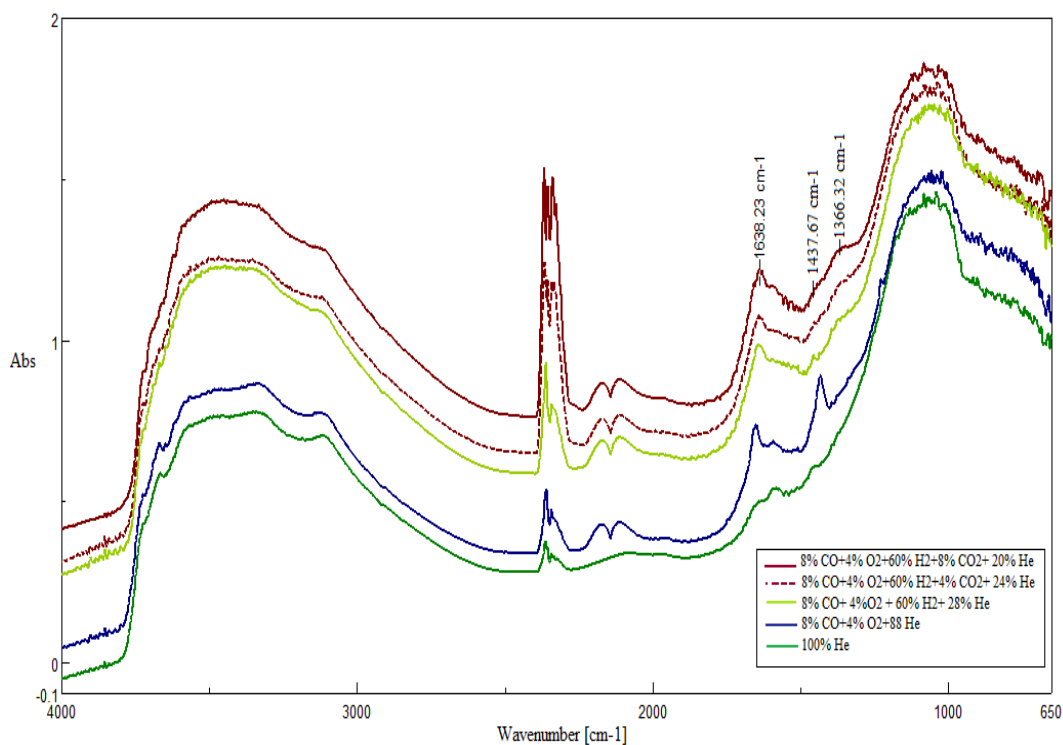


Figure 4.15. The effect of excess H_2 on on the spectra of CO oxidation in the presence of CO_2 at $110^\circ C$.

4.3.3. H_2O Concentration Effect:

The effect of water vapor was studied in the presence of excess H_2 containing reactant gases (CO and O_2) with and without CO_2 . The results for this test were collected in Figure 4.16.

The water vapor was firstly introduced at 8% CO and 4% O_2 in the excess of H_2 (60%) and balance He as shown in Figure 4.16. When the spectrum of this mixture was compared with the one obtained without water, the peak at 1634.38 cm^{-1} remained the same while some new peaks appeared at 1585.2 and 1386 cm^{-1} . The region between 3000 and 3700 cm^{-1} seemed to be smoother. Ntho and co-workers reported that the $C-O$ stretching region ($1450-1600\text{ cm}^{-1}$) was difficult to be observed clearly in the presence of H_2O , and the band at 1329 cm^{-1} (described as unidentate carbonate species) and the peak at 1290 cm^{-1} (assigned as bicarbonates) were disappeared (Ntho *et al.*,2009). A similar change was observed in this case even with the addition of H_2 only as well as with $H_2 + H_2O$. On the other hand H_2O addition caused to another peak at 1366 cm^{-1} which was

slightly seen in the presence of CO only at 50°C. This peak decreased with the addition of CO₂ while the peaks at 1634 cm⁻¹ become more apparent in the CO₂ presence. Considering that those peaks are both associated with some form of carbonate like species, the effects of H₂O and CO₂ on the surface species are not conclusive at this stage.

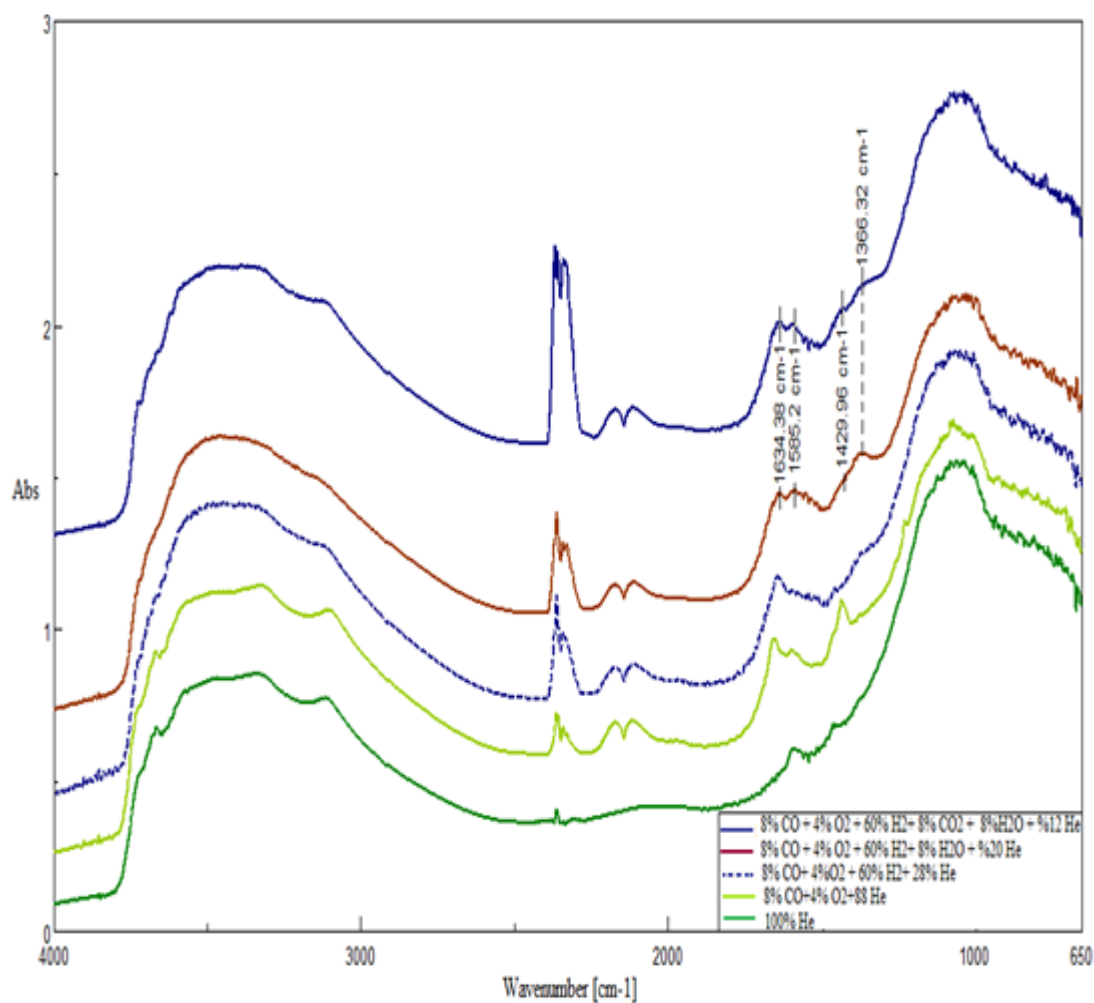


Figure 4.16. The effect of H₂O on the spectra of CO oxidation in the presence of H₂ at 110°C.

It was declared that the presence of water and hydroxyl groups prevented the formation of inhibitors such as CO₃²⁻ and HCO₃⁻ or eradicating them when once formed (Bond and Thompson, 2009). As it was known, OH⁻ groups in Al₂O₃ are more stable and less reactive compared to the supports like TiO₂. Therefore, chemisorbed water molecules on gold particles over alumina were found as more beneficial compared to the other catalysts such as Au/TiO₂. It was also accepted that the reaction of H₂ with a carbonate

would lead a hydroxyl and a formate then forming bicarbonate with O_2 on the catalyst of Au/Al_2O_3 (Piccolo *et al.*, 2009).

Costello and co-workers predicted that surface bicarbonate intermediates (HCO_3^-) and adjacent hydroxyl ($-OH$) led to the inactive carbonates. Those carbonates were proposed to be change to a formate or a hydroxycarbonyl ($COOH$) and hydroxyl by hydrogenolysis process in which the hydrogen activation occurred. These results of Costello and co-workers may be related to the mechanism of Kung *et al.* proposed for the low-temperature CO oxidation mechanism on Au/Al_2O_3 catalyst. It was assumed that adsorbed CO on the catalyst, together with Au^+-OH^- , resulted in hydroxycarbonyl, and the oxidization of hydroxycarbonyl formed the bicarbonate ($COOOH$) which can lead the decarboxylation of CO_2 with Au^+-OH^- or Au^+-H (Kung *et al.*, 2007; Qian *et al.*, 2011).

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

This study focused on the formation of the intermediate species during the selective CO oxidation over Au/Al₂O₃ catalyst surface. The analysis was conducted by a combined DRIFTS-MS system using various concentrations of CO, O₂, H₂, H₂O and CO₂ at a temperature range of 25°C and 110°C. The conclusions from this study were summarized as follows:

- The comparison of the spectra of the reactant gases in the presence and absence of reaction indicates that there are some changes on the surface species with the reaction (even with adsorption) as evident from the sharp peaks which were regarded as the presence of carbonate-like surface species.
- The temperature change from 25°C to 50°C resulted in some small changes in the spectra while the further increase of temperature to 150°C did not make any significant changes. This may be an indicator of the mechanism changes with the temperature as suggested by some investigators.
- The change of CO concentration in the feed did not make significant change in the spectra when the stoichiometric ratio of O₂ is used while the lower and the higher values of O₂ made some peaks in the spectra disappeared. This may be attributed to the competition between CO and O₂ for the active site of the catalyst; increase of one blocked the adsorption of other.
- The CO₂ in the balance helium was generated peaks that are similar to the ones obtained during the CO oxidation and attributed to the carbonate like species. The presence of CO and O₂ (i.e. reaction) did not make much difference in the CO₂ spectrum.
- The introduction of H₂ decreased the intensity of carbonate like species. The similar effects were observed in the presence of H₂O as well.

5.2. Recommendations

Considering the results of the present study, the following ideas can be helpful for the similar works CO oxidation on gold-based catalysts studies of by DRIFTS with MS:

- It was observed that the catalyst powder size and the KBr concentration affect the quality of spectra significantly; hence the optimum values of these parameters should be searched in more details.
- The system should be configured in a way to increase the conversion if the MS and DRIFTS measurements will be coupled.
- CaF_2 powders which are more resistant to moisture can be used instead of KBr in order to increase the intensity of the peak and observe the O-H groups on the catalyst better.
- The effects of feed compositions may be investigated in full details.
- The vacuum systems (and or N_2 purge of the existing systems) can be used to minimize the noise coming from the CO_2 in the atmosphere.

APPENDIX A: SUMMARY OF THE REFERENCE STUDIES

An extensive summary of the FTIR peaks seen during the CO oxidations and the intermediates assigned to these peaks are given in Table A.1.

Table A.1. The peaks (cm^{-1}) in the DRIFTS spectra and their assignment through the reference studies on CO oxidation over various catalysts.

CO	CO ₂	OH region	Carbonate	Other	notes	Catalyst and condition	Reference
2176 2116	2353 2341	3681 3633	-	Bicarbonates: 1621 1220	-	Au/Fe ₂ O ₃ 378 K	Šmit <i>et al.</i> , 2006
2084 (1)	2345	-	1650, 1425 1228	Bicarbonates: 1352 1732	(1) CO on Pt	Fe oxide- promoted Pt/ Al ₂ O ₃ 30 ⁰ C- 90 ⁰ C	Liu <i>et al.</i> , 2002
2185 2181 (1)	-	-	1510, 1370 1576, 1437 1222	-	(1) CO on Ti ⁺⁴	Au/TiO ₂ 50 ⁰ C	Piccolo <i>et al.</i> , 2009
2143 2119	-	3690- 3660 3735 (1)	1450 1300 (m- carbonate) 1562, 1445 1425, 1320	Bicarbonates: 1352, 1732	(1) Hydrx.	Au/TiO ₂ and Au/ZrO ₂ At 200 ⁰ C	Maciejewski <i>et a.l.</i> , 2001
2096 - 1986 (1)	2353	-	1420 1452 Bidentate 1354 Monodentate 1253	Formate: 1569	(1) CO on Au	Au/TiO ₂ At room T	Raphulu <i>et al.</i> , 2010
	2361		Unidentate: 1329	Bicarbonates: 1290 ⁽¹⁾ C-O stretching: 1450-1600	(1) Titanat e nano tube	Au/TN ⁽²⁾ 70 ⁰ C	Ntho <i>et al.</i> , 2009
2100 (1)	2341 2360		1800-1200	Carbonyl: 2450-2000	(1) CO on Au ⁰	At 30 ⁰ C	Zou <i>et al.</i> , 2010
2106 (1) 2058	-	-	-	-	(1) CO on metalli c gold	Au/SiO ₂ At room T	Somodi, 2008
1950 2160	2300 2400	-	1220, 1305, 1430,1610 1340,1400- 1460 1580, 1650 ⁽¹⁾	Bicarbonates: 1455 1660 - 3620 ⁽²⁾	(1) In the prs. of (2) O-H str.vib.	Au/ α - Fe ₂ O ₃ At 80 ⁰ C	Schubert <i>et al.</i> , 2004

Table A.1. The peaks (cm^{-1}) in the DRIFTS spectra and their assignment through the reference studies on CO oxidation over various catalysts (cont.).

CO	CO ₂	OH region	Carbonate	Other	Notes	Catalyst and condition	Reference
-	-	-	H ₂ carbonate ⁽¹⁾ : 1216, 1399 1600 Bidentate: 1583-1297 2880- 2840 ⁽³⁾ other:1330- 1370, 1550 Bidentate ⁽²⁾ : 1583, 1297 H ₂ carbonate: 1214, 1399- 1410	Formate: 2940 2840 Hydroxyl species: 3712-3690 Mono-dentate hydroxyls: 3712-3690	(1) H ₂ carbonate species CO+H ₂ +O ₂ (2) CO ₂ +H ₂ +O ₂ (3) at lower	CuO/CeO ₂ 303 K - 498 K	Gamarra D. and A. Martines-Arias, 2009
2075- 2100 2105 ⁽¹⁾ 2107 ⁽²⁾	2343	-	-	Au ⁰ -CO bond: 2100	(1)On oxidized Au/Al ₂ O ₃ (2)On reduced Au/Al ₂ O ₃	Au/Al ₂ O ₃ At room T	Grisel R.J.H. and B.E. Niewenhuys, 2001,
2180 ⁽¹⁾ 2106 ⁽²⁾ 2060 ⁽³⁾	2352 2358	-	1600-1700 Bidentate: 1620 Carboxilate or bidentate: 1500 Monodentate : 1530-1470 1370-1300	-	(1)CO on TiO ₂ (2) CO on metallic Au (3) CO on negative Au	Au/TiO ₂ 300-373 K	Rasko J. and K.Kiss, 2006
2154 ⁽¹⁾ 2185 ⁽²⁾ 2101 ⁽³⁾	-	-	-	Carbonyls: 2155-2130	(1)H-bonded CO (2)Al ³⁺ -CO (3)Au ⁰ -CO	Au/Al ₂ O ₃ At 673 K	Centeno <i>et al.</i> , 2006
2129 2114 ⁽¹⁾ 2169	2360 2340 2365	-	-	-	(1)CO on metallic Au(Au ⁰)	Au/FePO ₄ At T	Li <i>et al.</i> , 2009
2110 2118	2346	3800-3400	-	-	-	Au/Al ₂ O ₃ At 150 K	Jia <i>et al.</i> , 2001
-	3000-3600 3691 3691	-	1632,1396 1292 C-H bands: 2870-2960	Formate 1576 ⁽¹⁾ 1354 1296	(1)In the presence of H ₂	FeO _x /Pt/TiO ₂ 333 K	Shi <i>et al.</i> , 2007

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