Cations in strongly acidic media : Generation, characterization and catalytic application

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Cations in strongly acidic media: Generation, characterization and catalytic application

強酸中における陽イオン種の

形成、特性及び触媒反応への応用

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ABSTRACT

This thesis describes the generation and characterization of a variety of cationic species including carbocations (carbenium ions), metal carbonyl cations and metal nitrosyl cations, and their important roles in catalytic reactions.

Chapter 1 gives a survey and introductory remarks on carbocations, metal carbonyl cations and metal nitrosyl cations related to the present work.

Chapter 2 describes the Koch-type carbonylation of alcohols over Nafion-H, a solid acid catalyst, in which carbenium ions (carbocations) work as the reaction intermediates. Detailed reaction conditions of carbonylation of a variety of alcohols are discussed.

Chapter 3 describes detailed IR, Raman, and NMR spectroscopic characterization on the group 11 metal carbonyl cations over a wide range of temperature and in a variety of strong acids, based on which their molecular structures are determined. Their roles in the catalytic carbonylation of olefins and alcohols are discussed.

Chapter 4 describes the reaction of Cu^0, Cu^I or Cu^{II} compounds with atmospheric NO at room temperature in strong acids, which results in the formation of the copper(II) nitrosyl cation, $[CuNO]^{2+}$. The reductive behavior of NO, depending on the oxidation state of the starting copper compound, is discussed.

Chapter 5 gives general conclusions. The present study indicates that the use of strong acids leads to the formation of a variety of cations including carbocations and metal carbonyl and nitrosyl cations, which work as catalysts or as reaction intermediates in catalytic reactions.

CONTENTS

Chapter 1

Introduction

Cationic species, including carbocations and cationic metal complexes, have recently attracted much attention because it has turned out that they are important not only in various organic and environmentally catalytic reactions but also in biological systems. Although there have been limited reports on cationic species so far, the significance of cationic species in chemistry is increasing. In the present work, strongly acidic media have been used to generate carbocations, metal carbonyl cations and metal nitrosyl cations, and their properties have been investigated using spectroscopic methods and their roles in catalytic reaction have been discussed. This chapter gives a survey and introductory remarks on carbocations, metal carbonyl cations and metal nitrosyl cations related to the present work.

1.1 Carbocations

This section introduces the historical perspective of carbocations and reactions involving carbocations as reaction intermediates, in particular, the Koch-type carbonylation. Koch-type carbonylation is an important reaction in the industry, which produces tertiary carboxylic acids from olefins or alcohols in strong acids.

1.1.1 Historical Perspective

Carbocations including carbenium ions and carbonium cations, which are usually generated in acidic media, are involved in petroleum cracking and refining, coal processing, polymerization chemistry, synthetically important solvolytic reactions, isomerizations and rearrangements, addition reactions, aromatic substitutions, as well as a variety of biosynthetic transformations. Hence, this area is of pivotal importance, ranging from the basic understanding of the nature and behavior of positively charged organic species to the industrial application. Olah, the winner of 1994 Nobel prize in Chemistry, said "One of the most original and significant ideas in organic chemistry was the suggestion that carbocations might be intermediates in the course of reactions that start from nonionic reactants and lead to nonionic covalent products."[1]

Whereas the nature of triarylmethyl cationic salts or some dyes were known since the pioneering studies of Baeyer[2] as well as those of Walden[3], Gomberg[4] and others at the turn of the twentieth century, the more general significance of carbocations in chemistry was not recognized until Hans Meerwein's work[5] in 1922. While studying the Wagner rearrangement of camphene hydrochloride to isobornyl chloride, Meerwein found that the rate of the reaction increased with the dielectric constant of the solvent. Furthermore, he found that certain Lewis acid chlorides—such as $SbCl_5$, $SnCl_4$, $FeCl_3$, $AlCl_3$, and $SbCl_3$ (but not BCl_3 or $SiCl_4$), as well as dry HCl (which promote the ionization of triphenylmethyl chloride by formation of carbocationic complexes) —considerably accelerated the rearrangement of camphene hydrochloride

to isobornyl chloride. Meerwein concluded that the isomerization actually does not proceed by way of migration of the chlorine atom but by a rearrangement of a cationic intermediate. It was the birth of the modern concept of carbocationic intermediates.

In 1962, Olah and co-workers reported the first long-lived alkyl cation salt, i.e., *tert*-butyl hexafluoroantimonate, formed by dissolving $(CH_3)_3CCOF$ in SbF_5, and observed by NMR spectroscopy.[6-8] This breakthrough caused enormous contributions for both fundamental understanding and practical application in the organic chemistry.

$$(CH_3)_3CCOF + SbF_5 \rightleftharpoons (CH_3)_3CCO^+SbF_6^- \xrightarrow{-CO} (CH_3)_3C^+SbF_6^-$$
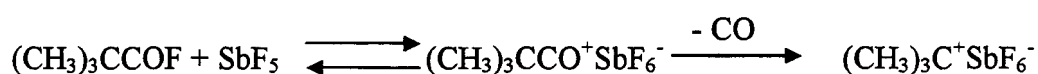
Carbocations have been known as the intermediates in a variety of reactions, especially those with acid catalysts until now. Examples can be found in Friedel-Crafts reactions including substitutions, additions, isomerizations, polymerizations, and a number of other general processes.[9] Friedel-Crafts reactions embrace all electrophilic organic reactions catalyzed by electron-deficient compounds —Lewis acids— and include such reactions as are likewise catalyzed by those proton acids which are strong enough to act somewhat like Lewis acids.[9]

1.1.2 Koch-type Reaction in Strongly Acidic Media

According to the above description, Koch reaction is thought to be one of the Friedel-Crafts reactions. Koch-type carbonylation, which involves carbocations and acylium cations as the reaction intermediates, has been well known for the synthesis of tertiary carboxylic acids from olefins and water, or alcohols, with carbon monoxide in strong acids.[10,11] Generally H_2SO_4, H_3PO_4, HF and $BF_3 \cdot H_2O$ are employed as catalysts and solvents.

In strong acids, for example, the olefin is protonated, or the alcohol is protonated and dehydrated, to form a carbenium ion intermediate, which isomerizes to tertiary

carbocations via the Wagner-Meerwein rearrangement prior to the carbonylation.[9,12]

The protonation of the isomerized olefins is in equilibrium with the deprotonation of the

carbocation.   Polymerization of the olefins and carbocations also occurs as a

competing reaction in this system.
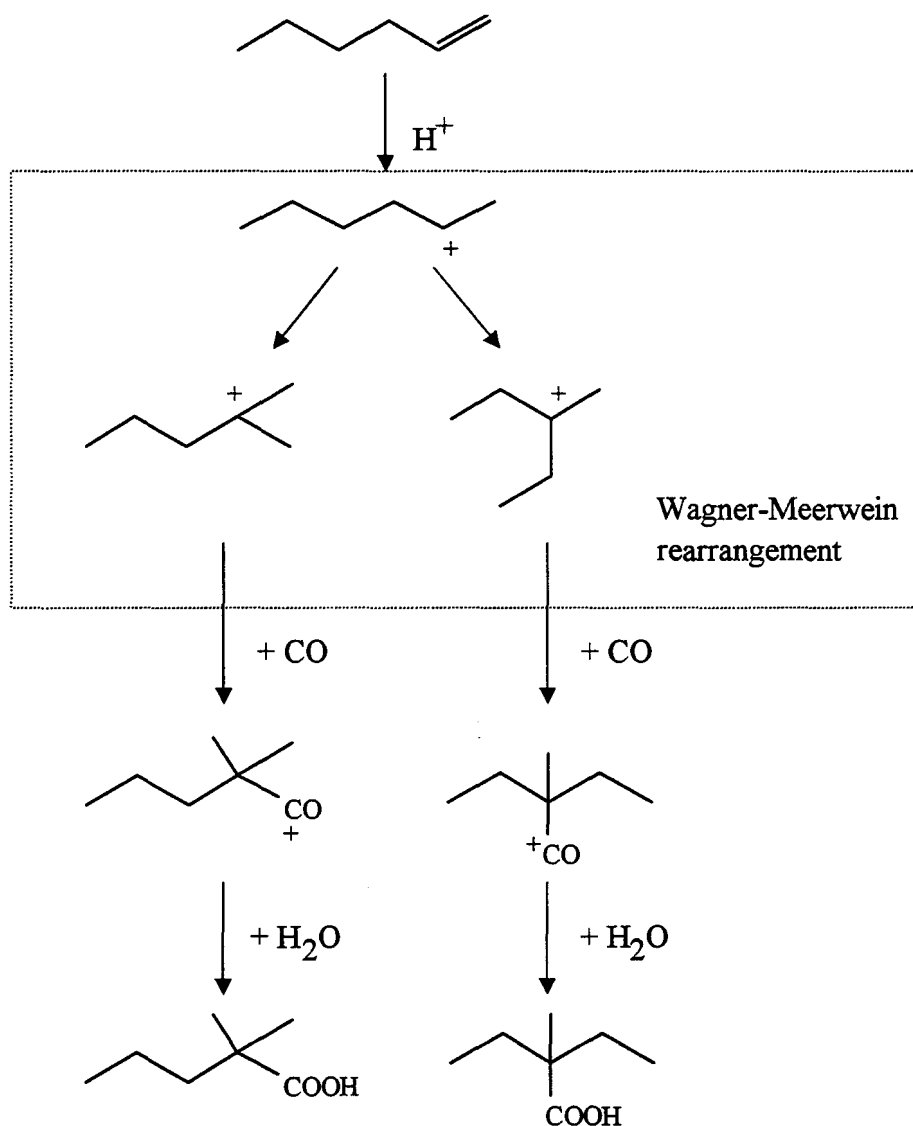
In the original Koch reaction, the direct reaction of the carbocations with the

dissolved CO in the solution leads to the formation of acylium cations, which react with

water to give tertiary carboxylic acids or with alcohols to give the corresponding esters.

At room temperature and atmospheric pressure of CO, olefins are carbonylated to form

the corresponding carboxylic acids in low yields due to the low CO solubility in the

solution and the presence of the polymerization as the competing reaction. Therefore a high CO pressure is indispensable for achieving high yields of carboxylic acids. The process in commercial plants by Esso and Shell was operated at temperature between -20 to 80°C and CO pressure up to 100 atm. One problem in the practical application of Koch-type carbonylation is the severe reaction conditions —high CO pressure and high temperature. In the 1970s Souma *et al.* reported that the addition of Cu(I) and Ag(I) compounds to the acidic solution caused the Koch-type reaction to proceed at room temperature and atmospheric CO pressure. Recently Xu and co-workers found that Au(I), Pd(I), Pt(I) and Rh(I) carbonyl cations also worked as excellent catalysts for the carbonylation of olefins and alcohols at room temperature and atmospheric CO pressure [13-18] (Section 1.2 and Chapter 3).

The other problems arising from the use of the strongly acidic are the corrosion of the equipment, complicated separation procedures for the products and the disposal of huge amount of waste acids. Therefore, the use of solid acid catalysts instead of strong liquid acids has a significant advantage. There have been only few reports on the solid acid-catalyzed carbonylation.[19,20] In the present work, I report the carbonylation of a variety of primary, secondary and tertiary alcohols with CO over Nafion-H, a perfluoroalkanesulfonic acid resin catalyst, which produces tertiary carboxylic acids in high yields[21] (Chapter 2).

1.2   Metal Carbonyl Cations in Strongly Acidic Media

In addition to carbocations, strongly acidic media can also be used to generate metal carbonyl cations and metal nitrosyl cations (Sections 1.2 - 1.3 and Chapters 3 - 4). A number of new homoleptic metal carbonyl cations and their derivatives from groups 6 through 12 have been prepared in acidic or superacidic media or with weakly coordinating anions, in which the CO ligand primarily functions as a σ donor.[13,22,23]

However, solvated cationic carbonyl complexes, in particular, of group 11 metals in strong acids have not been investigated in detail. In the present work, group 11 metal carbonyl cations in strong acids were investigated using spectroscopic methods.[24] This section introduces the historical perspective and properties of metal carbonyl cations in acidic or superacidic media or with weakly coordinating anions.

1.2.1 Historical Perspective

Since the discovery of the first metal carbonyl complexes, $Pt(CO)_2Cl_2$, $Pt_2(CO)_4Cl_4$, and $Pt_2(CO)_3Cl_4$, by Schützenberger in 1868,[25-28] and the discovery of the first homoleptic metal carbonyl, $Ni(CO)_4$, by Mond in 1890 and its immediate industrial application for the preparation of ultrapure nickel,[29-31] metal carbonyls have played a very important role in chemistry and the chemical industry.[10,32] In the 1950-1960s, there appeared examples of cationic transition metal carbonyl species exhibiting $\nu(CO)$ values higher than 2143 cm^{-1}, the value for free CO.

Historically, Manchot and co-workers are the first to systematically investigate the metal carbonyl compounds that were later shown to be primarily σ-bonded. They used a strong protic acid (concentrated H_2SO_4) for the first time to prepare silver carbonyl cations,[33,34] which is the prototype for the recent syntheses of metal carbonyl cations.

As the thermally stable homoleptic carbonyl cations, octahedral $[M(CO)_6]^+$ (M = Mn, Tc, Re) cations were first isolated by Fischer, Hieber and their co-workers in 1961.[35-39] After about 30 years from the first discovery, $[Au(CO)_2]^+$ was discovered as the second isolated species of the homoleptic metal carbonyl cation by an accident in the attempt to prepare the $[HCO]^+$ ion by protonation of CO in the conjugated superacid $HSO_3F-Au(SO_3F)_3$, and for the isolation it was necessary to develop a new carbonylation method in Lewis superacidic media such as SbF_5.[40,41] In SbF_5, a number of thermally stable salts of metal carbonyl cations have subsequently been isolated and

characterized spectroscopically and structurally.[22,42] Several homoleptic metal carbonyl cations have been isolated using weakly coordinating anions such as $[B(OTeF_5)_4]^-$ [43-45] and $[1\text{-}Et\text{-}CB_{11}F_{11}]^-$ [46,47] in organic solvents. In the meantime, a number of metal carbonyl cations have been generated in protic acids, which were spectroscopically characterized and applied as catalysts for the carbonylation of olefins and other organic compounds.[13-18,48-50] In addition, related cationic metal carbonyl species have been found to be formed in zeolites and on the surfaces of metal oxides and halides,[51] and a new laser-ablation technique has recently been successfully employed to isolate a series of metal carbonyl cations in rare-gas matrices which have been characterized in detail by FTIR.[52]

1.2.2 Properties of Metal Carbonyl Cations

The metal-carbonyl bonding is suggested to involve a synergistic interaction between σ-donor bonding from the occupied 5σ molecular orbital of CO into an empty metal orbital with σ symmetry and π-backbonding from occupied metal orbitals into the π* molecular orbitals of CO.[53]

A schematic representation of orbital overlap in the individual (M-CO) segments with terminally bonded CO has been proposed for clarifying the typical metal carbonyls, predominantly π-bonded, highly reduced carbonyl metalates and largely σ-bonded metal carbonyl cations.[42]

In general, the metal carbonyl cations and the cationic carbonyl derivatives display the following distinguishing features in comparison with the typical metal carbonyls:[13]

π

σ

$M^n \longleftarrow C \longrightarrow O$

π

δ^-

Predominantly π-bonded highly reduced carbonylmetalates

$n = -2, -3, -4$ $\nu(CO) < 2080 \ cm^{-1}$

π

σ

$M^n \longleftarrow C = O$

π

Typical metal carbonyls

$n = -1, 0, +1$ $2080 \ cm^{-1} < \nu(CO) < 2180 \ cm^{-1}$

π

σ

$M^n \longleftarrow C \equiv O$

π δ^+

Predominantly σ-bonded metal carbonyl cations

$n = +2, +3, +4$ $\nu(CO) > 2180 \ cm^{-1}$
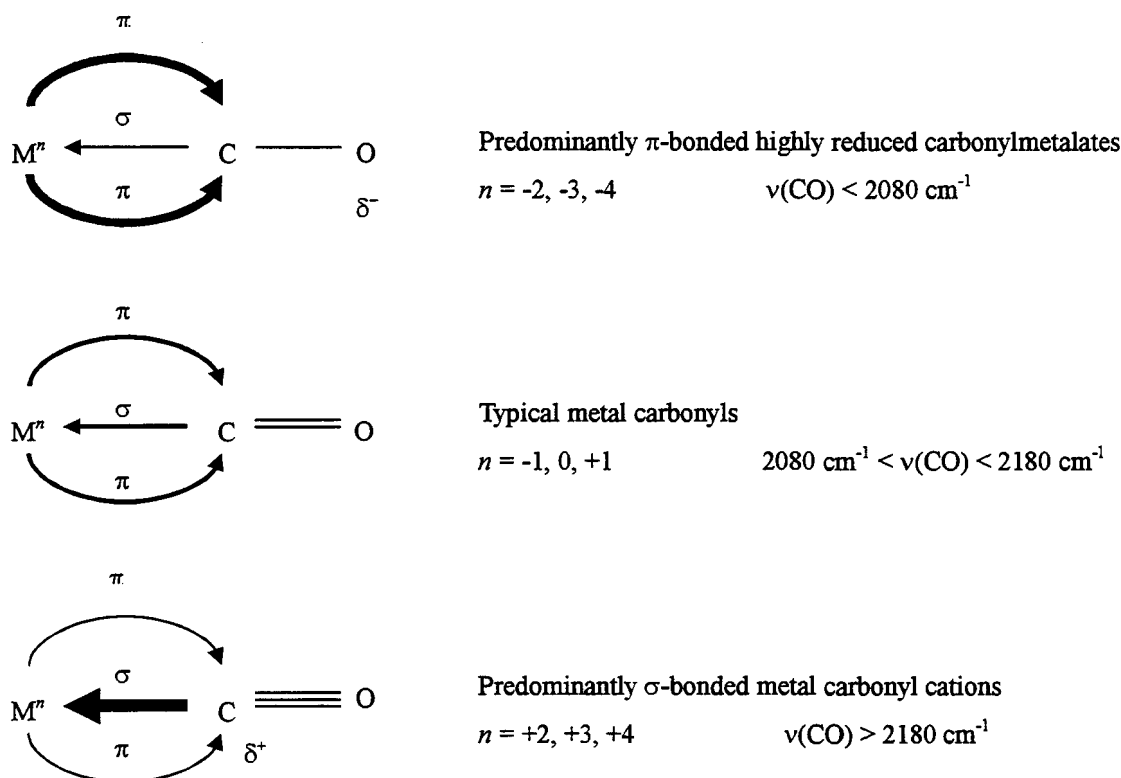
(1) The metal carbonyl cations and the cationic carbonyl derivatives have a high electrophilicity so that they must be generated and stabilized in acidic (superacidic) media or with weakly coordinating anions as described above, or in an unusual environment such as rare-gas matrices, metal cation-exchanged zeolites and surfaces of metal oxides and halides, where no strongly nucleophilic ligands compete with the CO ligands in the coordination to metal.

(2) The unprecedented coordination geometries in metal carbonyl chemistry are observed for the metal carbonyl cations with the electron configurations d^8 and d^{10} with coordination numbers 4 (square-planar coordination) and 2 (linear coordination), respectively, for which the number of valence electrons (16 or 14) violates the noble gas rule, although such geometries have been exhibited by analogous complexes of ligands such as CN$^-$ and PPh$_3$.[53] However, the typical metal carbonyls almost always observe strictly the 18-electron rule (an exception is the 17e molecule V(CO)$_6$).[53]

(3) The cationic metal carbonyl complexes have M-C bond lengths d(MC)

longer than those of the corresponding typical metal carbonyls and short C-O bond lengths d(CO) (usually shorter than 1.128 Å, the value for free CO)[54] with C-O stretching vibrational frequencies v(CO) (up to 2300 cm^{-1}; for most of them higher than 2143 cm^{-1}, the value for free CO)[55] much higher than the values for the corresponding typical metal carbonyls. CO is largely σ-bonded to the metal and the metal-to-CO π-backbonding is highly reduced, whereas the π-backbonding serves to stabilize the M-CO bond for the typical metal carbonyls, especially in the presence of a low formal charge.[53]

(4) The cationic complexes show ^{13}C NMR chemical shifts (up to $\delta(^{13}C) = 121$ ppm; with only few exceptions) high field-shifted from 184 ppm, the value for free CO[41,56,57], whereas a low-field shift from 184 ppm is usually observed for typical metal carbonyls.[42]
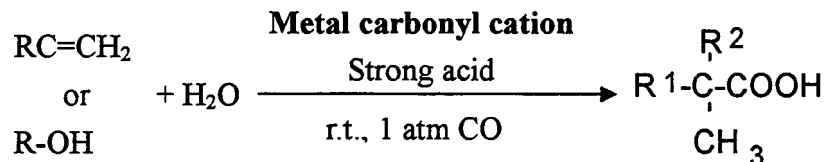
(5) The cationic complexes exhibit high catalytic activities even at room temperature and atmospheric pressure as will be described later. However, reactions (for example, Roelen[58] and Reppe[59] reactions) catalyzed by the typical metal carbonyls such as $Co_2(CO)_8$ or $Ni(CO)_4$ require severe conditions of high temperature and high CO pressure.[10,32]

1.2.3   Group 11 Metal Carbonyl Cations in Protic Acids

Protic acids have been used to generate a number of metal carbonyl cations and cationic carbonyl derivatives as well as molecular adducts of CO to metal cations, as first done by Manchot and co-workers in 1920's.[33,34] The reactions can be divided to three types: (a) solvolysis and carbonylation, (b) reductive carbonylation, and (c) oxidative carbonylation. The two protic superacids HSO_3F and anhydrous hydrogen fluoride HF are very suitable for the preparation of metal carbonyl fluorosulfates and fluorides, which including $Au(CO)SO_3F$,[40] cis-$Pd(CO)_2(SO_3F)_2$,[60,61] cis-$Pt(CO)_2(SO_3F)_2$,[60,62] mer-$Ir(CO)_3(SO_3F)_3$,[63] [$cyclo$-$Pd_2(\mu$-$CO)_2$]$(SO_3F)_2$,[64] and fac-$Ir(CO)_3F_3$.[65,66] In

particular, a number of solvated cationic metal carbonyl complexes such as $Co(CO)_4^+$,[48] $[Rh(CO)_4]^+$,[18,48] $[Pt(CO)_4]^{2+}$,[67] $[cyclo\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$,[16] $[\{Pt(CO)_3\}_2]^{2+}$, [17,49,50] have been prepared in protic acids.

Solvated cationic metal carbonyl complexes of $Cu(I)$,[13,14,24] $Ag(I)$, [13,14,24] $Au(I)$, [13-15,24] have been prepared also in protic acids. In comparison with the $Pt(I)$, $Pd(I)$, $Co(I)$ and $Rh(I)$ carbonyl cations the actual stoichiometry of the group 11 metal carbonyl cations depends on the solvent acid and the temperature; and so far only limited spectroscopic data have been reported.[13,68] In the present work, I report the detailed spectroscopic characterization of the group 11 metal carbonyl cations over a wide range of temperature and in solvents of various acidities, and based on the results, determined their structures.[24] In addition discussion will be given on the active species and reaction mechanism of the metal carbonyl cation-catalyzed carbonylation of olefins and alcohols (Chapter 3).

$$RC{=}CH_2 \;\;\text{or}\;\; R\text{-}OH \;+\; H_2O \;\;\xrightarrow[\text{r.t., 1 atm CO}]{\substack{\textbf{Metal carbonyl cation}\\ \textbf{Strong acid}}}\;\; R^1\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle R^2}{|}}{C}}\text{-}COOH$$

1.3   Metal Nitrosyl Cations in Strongly Acidic Media

The structure, bonding and reactivity of coordinated NO have been considered to be analogous to those of coordinated CO. Although there have recently been remarkable developments in the preparation and characterization of a number of new homoleptic metal carbonyl cations and their derivatives in acidic or superacidic media, so far there have been no direct evidence for the formation of metal nitrosyl cations in strong acids with the only exception being the NO absorption by iron and copper compounds in sulfuric acid observed by Manchot.[69,70] In the present work, the

formation of the copper nitrosyl cation in strong acids was investigated using spectroscopic methods.[71] This section introduces the historical perspective and the M-NO bond properties of metal nitrosyl complexes, including metal nitrosyl cations, in strong acidic media.

1.3.1 Historical Perspective and M-NO Bond Properties of Metal Nitrosyl Complexes

Transition-metal complexes containing nitrogen monoxide have been known for over a century. Although they have not attracted as much attention as metal carbonyls, the study on their preparation and properties is increasing in both quantity and quality. Coordination by NO^+ is directly analogous to metal-carbonyl bonding (CO and NO^+ are isoelectronic) with its synergistic coupling of σ and π bonding. Coordination by NO^-, on the other hand, was proposed to be analogous to that by halide ion and structurally similar to organic nitroso compounds.[72] In general, NO^+ coordinated to the metal center in a linear mode exhibits higher stretching vibrational frequencies v(NO) (usually close to or higher than 1876 cm^{-1}, the value for free NO[73]) than that of NO^- coordinated to the metal center in a bent mode (usually 1500 $\sim$ 1700 cm^{-1}).

Recently, importance of nitrosyl complexes has been widely recognized. Nitrogen monoxide, NO is a molecule of versatility and importance that has united neuroscience, physiology, and immunology, and NO was selected as "the molecule of the year" in 1992. Copper and iron nitrosyl complexes have been reported as pivotal intermediates in biological systems.[74,75]

Metal nitrosyl species have been shown to play an important role also in the processing of nitrogen oxide that is an environmental pollutant. For example, metal-exchanged zeolites have been shown to be excellent catalysts for the decomposition and reduction of NO.[76-78] A number of reports are concerned with these species on solid catalyst, for example, complexes of NO with Cr^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} ion in Y-type zeolite were reported.[76,79-83]

1.3.2 Copper Nitrosyl Cation in Strong Acids

Great attention has been focused on the important role that the metal nitrosyl cations, in particular, copper nitrosyl cations, have played in the processing of an environmental pollutant, nitrogen oxide, because copper-exchanged zeolites have been shown to be excellent catalysts for the decomposition and reduction of NO.[76-78] There have been, however, no direct evidence for the formation of copper nitrosyl cations in strong acids so far.

In the present work, I investigated the reaction of copper powder and a variety of copper compounds in different oxidation state with atmospheric NO at room temperature in strong acids such as concentrated H_2SO_4, FSO_3H, and magic acid $HSO_3F \cdot SbF_5$ (1:1) and found the formation of the copper(II) nitrosyl cation, $[CuNO]^{2+}$ (Chapter 4). The reaction of Cu^0, Cu^I or Cu^{II} compounds with NO results in the formation of the copper(II) nitrosyl cation during which the oxidation of Cu^0 to Cu^{II} is accompanied by the formation of N_2 and N_2O, whereas the oxidation of Cu^I to Cu^{II} results in the formation of N_2O without a significant amount of N_2. These results exhibit the possibility that a number of metal nitrosyl cations might be prepared and isolated using strong acids and superacids or with weakly coordinating anions. In addition, to make clear the reactivity of copper and copper compounds with NO is of great significance in the understanding of the mechanism of the decomposition and reduction of NO by the copper-exchanged zeolite catalysts.

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Chapter 2

Carbocations in Solid Acids
− Carbonylation of Alcohols over Nafion-H, a Solid Perfluoroalkanesulfonic Acid Resin Catalyst

Nafion-H was used as a solid acid catalyst for the Koch-type carbonylation of alcohols, in which carbenium ions (carbocations) work as the reaction intermediates. The carbonylation of a variety of primary, secondary and tertiary alcohols in various solvents such as hexane, cyclohexane, dichloromethane and chlorobenzene produces the corresponding tertiary carboxylic acids in high yields. For example, the conversions of 2-methyl-2-propanol, 1-pentanol and 1-adamantanol to carboxylic acids are 62.5, 64.6 and 76.9%, respectively, at 433 K and 9 MPa CO. The optimum temperature for this reaction is between 433 and 443 K. A high CO pressure is advantageous for the carbonylation. Only small amounts of ethers were observed for the primary alcohols under CO pressure and without water removal, in contrast with the previous report that primary alcohols are converted to ethers over Nafion-H in quantitative yields when CO is absent and water is removed by azeotropic distillation.
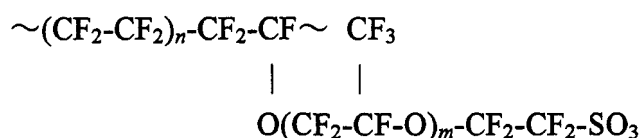
2.1 Introduction

A simple and efficient synthetic method for tertiary carboxylic acids is of industrial importance. Koch first reported that tertiary carboxylic acids can be produced by the reaction of CO with alcohols or with olefins and H_2O in concentrated strong acids (H_2SO_4, $BF_3 \cdot H_2O$, HF) at 253 to 353 K and around 10 MPa.[1-3] We have found that Cu(I), Ag(I), Au(I), Pd(I), Pt(I) and Rh(I) carbonyl cations cause the Koch-type reaction to proceed at room temperature and atmospheric CO pressure.[4-9] However, in the industrial application of the Koch reaction, there are problems such as the corrosion of the equipment, a complicated separation procedure for the products and the disposal of huge amounts of waste acids due to the use of strong acids. Therefore, the use of solid acid catalysts instead of strong liquid acids is of significant advantage.

There have been only a few reports on the solid acid-catalyzed carbonylation, although solid acids have been used as catalysts and are indispensable in many reactions.[10] In 1984, the carbonylation of methanol into methyl acetate, methyl formate and acetic acid was reported on solid acids, but the reaction exhibited either a very low yield (0.3%) under 100% selectivity or a low selectivity (0.8%) with a 34.6% yield with the formation of dimethyl ether via the non-carbonylating route.[11] The carbonylation of formaldehyde has been studied over ion exchange resin catalysts including Nafion-H, Dianion, Amberlyst, and Dowex.[12] Recently, we reported the carbonylation of alcohols over H-zeolites[13] and sulfated zirconia.[14] For the carbonylation of 2-methyl-2-propanol over H-zeolites, H-ZSM-5 gives the highest selectivity for 2,2-dimethylpropanoic acid due to its adequate pore dimensions.[13] With the sulfated zirconia catalyst, tertiary carboxylic acids were obtained from tertiary alcohols in good yields, whereas only ethers were formed from primary alcohols.[14]

The Nafion-H catalyst, a perfluoroalkanesulfonic acid resin first synthesized by DuPont chemists, has the general chemical formula as shown below, where the value of m can be as low as 1 and the value of n ranges between 6 and 13.[15] It has hydrophobic

(-CF$_2$-CF$_2$-) and hydrophilic (-SO$_3$H) regions in its structure and its superacidty is due to the electron withdrawing effect of the perfluoroalkyl backbone to which the sulfonic acid group is attached. The estimated Hammett (H$_0$) value for Nafion-H is comparable to that of 96 - 100% sulfuric acid (H$_0$ = -12.0).[16]

$$\sim(CF_2\text{-}CF_2)_n\text{-}CF_2\text{-}CF\sim \quad CF_3$$
$$| \quad\quad |$$
$$O(CF_2\text{-}CF\text{-}O)_m\text{-}CF_2\text{-}CF_2\text{-}SO_3$$

Nafion-H has been used as a catalyst for various reactions such as transalkylation (Friedel-Crafts reaction), ether synthesis, esterification, the condensation of ketones, and pinacol-pinacolone and Fries rearrangements.[16] There have been few reports on the carbonylation over Nafion-H, however. In this paper, we report the carbonylation of a variety of primary, secondary and tertiary alcohols with CO over the Nafion-H catalyst, which produces tertiary carboxylic acids in high yields.

2.2 Experimental

2.2.1 Carbonylation of Alcohols over Nafion-H

For the carbonylation of alcohols, commercial Nafion NR-50 (beads, 7-9 mesh, Aldrich) in the H form (ion exchange capacity: ca. 0.8 mequiv g^{-1}; equivalent weight: 1250) was used as the catalyst. The commercial alcohol and solvent reagents were used without further purification. A 120-mL stirred stainless steel autoclave enclosed in an electric furnace was used as the batch reactor. As a general procedure, 2.0 g of Nafion-H beads without pretreatment, 20 mmol of an alcohol, and 50 mL of a solvent were placed in the autoclave. CO was introduced into the autoclave and its pressure

was raised to the desired value. The initial CO pressure at room temperature was varied in the range of 0.1-9 MPa. The autoclave was heated to the desired temperature in 30 min and held at this temperature for 22 h. After the reaction, the products were collected by filtering off the catalyst and then analyzed by GC, GC-MS and NMR and by titration with an ethanol solution of NaOH.

2.2.2. Preparation of Ag-ZSM-5 and Nafion-Ag/H

A 40 g sample of H-ZSM-5 was immersed in 400 mL of a 0.1 mol/L $AgNO_3$ aqueous solution for 15 h, and separated by a centrifugal separator. The immersion was repeated five times. Ag-ZSM-5 was washed five times using water and separated by a centrifugal separator. It was dried at 383 K for 15 h and then dried at 623 K and 1.4 kPa for 3 h. A 2 g sample of Ag-ZSM-5 was stored in a glass bulb, which was then used for the reaction.

A 50 g sample of Nafion-H (NR-50, Aldrich, ion exchange capacity: ca. 0.8 mequiv g^{-1}) was immersed in the aqueous solution in which 20 mmol of $AgNO_3$ was dissolved for 20 h. After the ion-exchange treatment, the supernatant solution of $AgNO_3$ was analyzed by an inductively coupled argon plasma atomic emission spectrophotometer (ICP-575 II, Nippon Jarrell–Ash), and no Ag^+ ion was detected. Therefore, half the $-SO_3H$ groups in the Nafion-H catalyst were changed to $-SO_3Ag$. The Nafion-Ag/H catalyst was washed several times with water dried at 383 K for 20 h and then used for the reaction.

2.3 Results and Discussion

2.3.1 Carbonylation of 2-Methyl-2-Propanol over Nafion-H

Figure 2-1 shows the temperature dependence of the carbonylation of 2-methyl-2-propanol over Nafion-H at 5 MPa CO (initial pressure at room temperature) in chlorobenzene. At room temperature, no carboxylic acids are produced and 2-methyl-2-propanol of 76% remains unreacted after the reaction of 22 h. Isobutene is formed as the main product of the dehydration, the accurate amount of which could not be determined because of its boiling point being lower than room temperature. The conversion of 2-methyl-2-propanol increases with increasing reaction temperature; at 383 K, 2-methyl-2-propanol completely disappears. 2,2-Dimethylpropanoic acid is formed in a yield of 2.1%, while in the dehydration products the dimer (C_8) species are increased. The rapid dehydration of 2-methyl-2-propanol has also been reported for sulfonic acid resins such as Nafion-H,[17] Amberlyst 15 and Dowex 50W.[18] The carbonylation is significantly enhanced at higher temperature; the total yield of the carboxylic acids reaches the maximum at 443 K (T_{max}) and then decreases with increasing temperature. The value of total yield at T_{max} is 51.2%, corresponding to a turnover number of ca. 7 as the ion exchange capacity of the Nafion-H catalyst used is ca. 0.8 mequiv g^{-1}. Besides 2,2-dimethylpropanoic acid, higher-weight carboxylic acids including the C_9 carboxylic acids are also obtained. Similar temperature dependence of the total yield has been observed for the carbonylation of 2-methyl-2-propanol over thermally stable H-zeolites;[13] the appearance of maximum was explained in terms of the fast oligomerization reaction in the high temperature region. Olah *et al.* have shown that Nafion-H catalyst is stable at temperatures up to 483 K while above this temperature the catalytic activity is irreversibly decreased due to its limited thermal stability.[16,17]
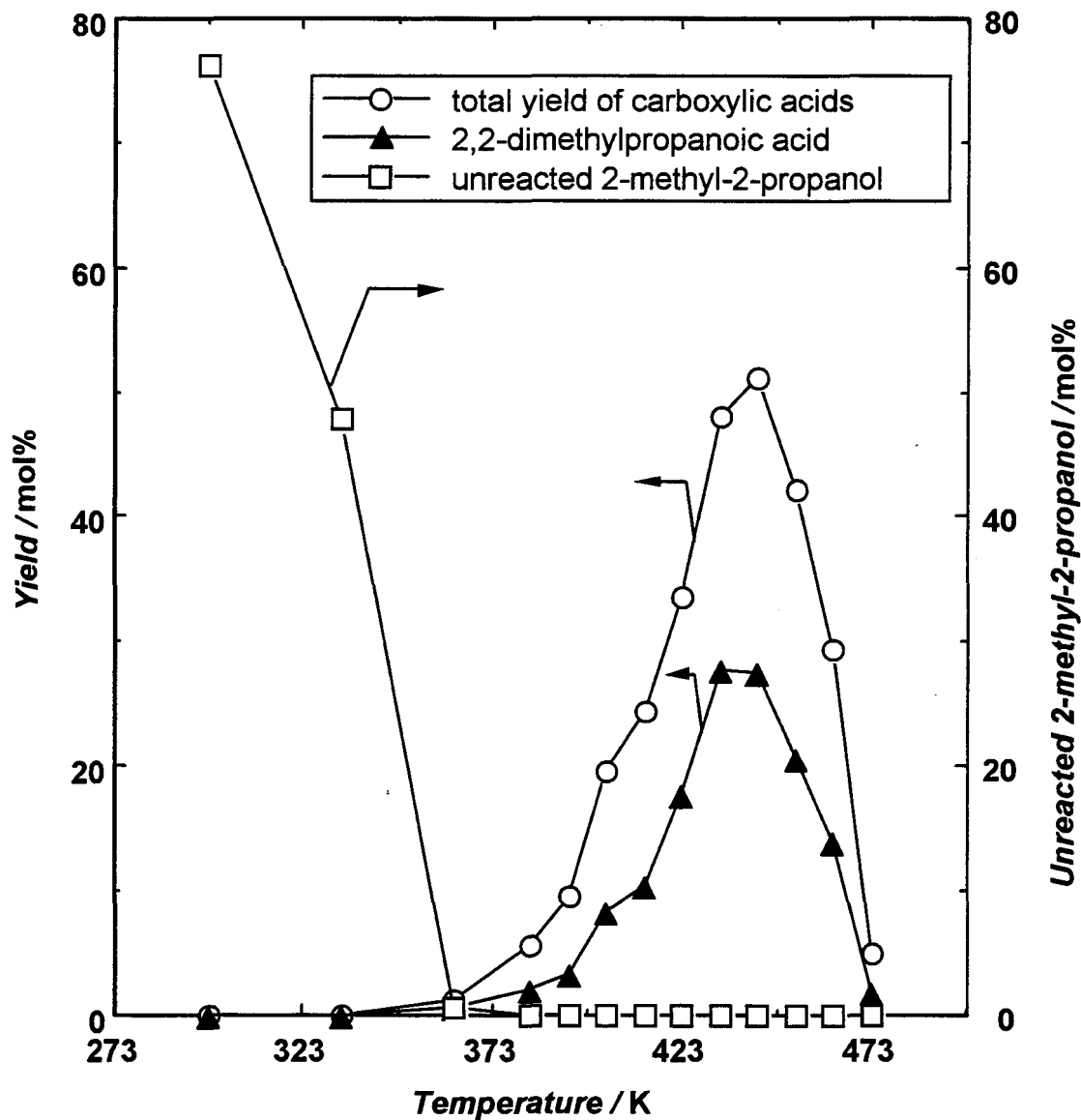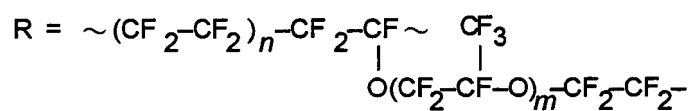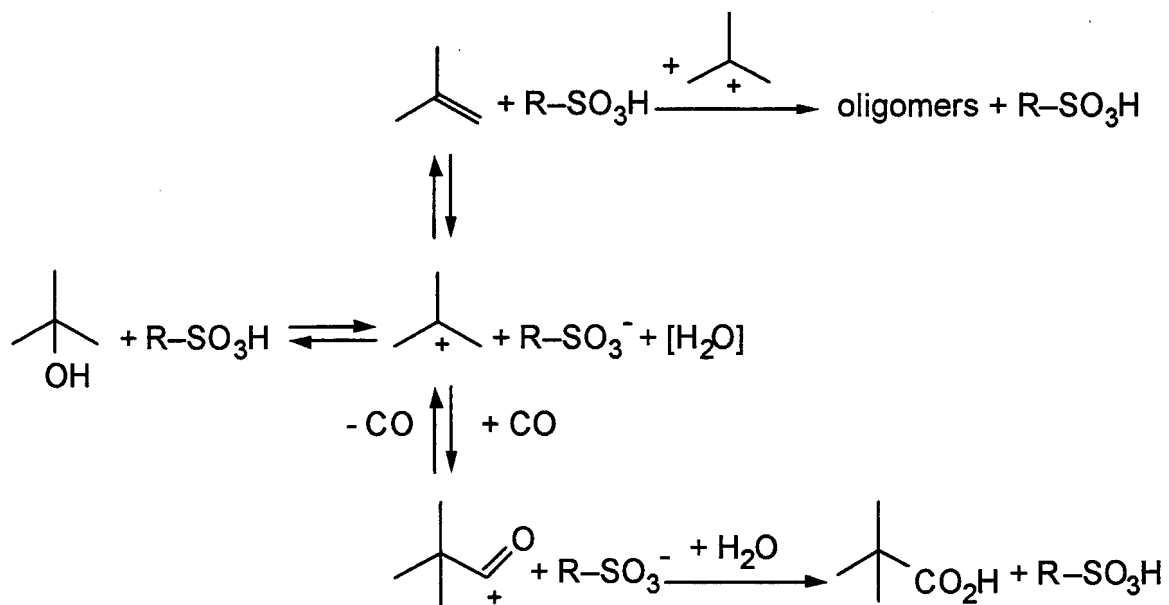
Fig. 2-1 Temperature dependence of the carbonylation of 2-methyl-2-propanol over Nafion-H. Reaction conditions: 2.0 g Nafion-H, 20 mmol 2-methyl-2-propanol, 50 mL chlorobenzene, 5 MPa CO pressure (initial pressure at room temperature), 22 h reaction time.

For investigating the thermal stability of Nafion for the carbonylation of 2-methyl-2-propanol, a Nafion-H catalyst that had been used at 473 K for 22 h was reused at 433 K, which exhibited no significant decrease in the total yield of carboxylic acids and the selectivity of 2,2-dimethylpropanoic acid in comparison with the fresh Nafion-H catalyst. This fact implies that not the thermal instability of Nafion-H but the fast oligomerization accounts for the decrease in the total yield with increasing temperature above T_{max}, as observed for thermally stable H-zeolites.[13] In addition, the observation indicates that the Nafion-H catalyst is reusable for the carbonylation of alcohols at temperatures below 473 K.

The overall reactions of 2-methyl-2-propanol with CO over Nafion-H can be described in scheme 2-1. This scheme includes the dehydration of 2-methyl-2-propanol to form the trimethylcarbenium ion intermediate, which is in equilibrium with both 2-methyl-2-propanol and isobutene. The secondary reaction between isobutene and the trimethylcarbenium ion intermediate gives the dimer (C_8) and the oligomeric species. The reaction of the trimethylcarbenium ion with CO gives rise to the formation of the acylium cation, which reacts with H_2O to form 2,2-dimethylpropanoic acid. The reaction of the unsaturated oligomeric species with CO and H_2O produces higher-weight carboxylic acids. At low temperatures, the carbonylation of the trimethylcarbenium ion intermediate is slow. By raising the temperature, the carbonylation is accelerated, accompanied by an oligomerization enhancement. The observation of the maximum yield of the carboxylic acids can be explained in terms of the fast oligomerization reaction, which prevails over the carbonylation of the trimethylcarbenium ion above T_{max}. A small amount of C_6 and C_7 carboxylic acids are also obtained as by-products, in particular, at high temperatures, which may be formed via dimerization and fragmentation of the carbenium ion intermediates as observed in strong liquid acids.[19,20]

$$R = \sim (CF_2\text{--}CF_2)_n\text{--}CF_2\text{--}CF \sim \quad CF_3$$
$$O(CF_2\text{--}CF\text{--}O)_m\text{--}CF_2\text{--}CF_2\text{--}$$

Scheme 2-1

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No ethers can be detected in contrast to the observation by Olah *et al.* that primary alcohols quantitatively gave ethers over Nafion-H.[21] An S_N2-type reaction mechanism has been proposed for the formation of ethers which involves the in situ formation of an oxonium ion, where Nafion-H converts the hydroxyl group of the alcohol into a better leaving group by protonation, and the ether is then formed by the nucleophilic attack of the alcohol on the oxonium ion in a bimolecular reaction (S_N2-type).[21] Therefore, steric reasons may account for the absence of ethers in the reaction of 2-methyl-2-propanol over Nafion-H. In chlorobenzene, a small amount (3.6% at 433 K) of chlorobenzene alkylation products are formed via the Friedel-Crafts reaction.[17,22]

Table 2-1 shows the pressure dependence of the carbonylation of 2-methyl-2-propanol over Nafion-H at 433 K in chlorobenzene. A high CO pressure is also advantageous for the Koch-type carbonylation over Nafion-H as observed in strong acid solutions[1-3] and observed for H-zeolites.[13] At 0.1 MPa CO (initial pressure at room temperature), no significant amounts of carboxylic acids are formed. By increasing the initial CO pressure to 9 MPa (room temperature), the total yield of the carboxylic acids increases to over 60% and the selectivity of 2,2-dimethylpropanoic acid in the products increases to a value as high as 85%. The increase of selectivity of 2,2-dimethylpropanoic acid with increasing CO pressure results from the enhancement of the carbonylation of the trimethylcarbenium ion prior to the dimerization or oligomerization that gives higher-weight carbonylation products. A higher yield and selectivity of 2,2-dimethylpropanoic acid are expected to be obtained at higher CO pressures.

The solvent effects were also investigated for the carbonylation of 2-methyl-2-propanol over Nafion-H (Table 2-2).

Table 2-1

CO pressure dependence of the carbonylation of 2-methyl-2-propanol over Nafion-H [a]

CO pressure [b] (MPa)	Yield (%)	
	2,2-Dimethylpropanoic acid	Total carboxylic acids
0.1	0	0.1
0.5	2.7	7.5
1	9.2	23.9
2	15.0	32.6
3	20.3	38.3
4	24.5	42.0
5	27.8	48.0
6	30.2	56.1
7	38.1	56.8
8	41.5	59.5
9	53.4	62.5

[a] Reaction Conditions: 2.0 g Nafion-H, 20 mmol 2-methyl-2-propanol, 50 mL chlorobenzene, 433 K, 22 h reaction time.

[b] Initial pressure at room temperature.

Table 2-2

Influence of solvent on the carbonylation of 2-methyl-2-propanol over Nafion-H[a]

Solvent	Temperature (K)	Total yield of carboxylic acids (%)
Dichloromethane	413	21.9
	433	50.3
	453	35.5
Chlorobenzene	413	24.4
	433	48.0
	453	42.2
Hexane	413	21.4
	433	44.4
	453	34.0
Cyclohexane	413	17.7
	433	39.1
	453	26.9

[a] Reaction Conditions: 2.0 g Nafion-H, 20 mmol 2-methyl-2-propanol, 50 mL solvent, 5 MPa CO pressure (initial pressure at room temperature), 22 h reaction time.

The maximum total yields of carboxylic acids are slightly higher in the polar solvents such as dichloromethane (50.3%) and chlorobenzene (48.0%) than those in the nonpolar solvents such as hexane (44.4%) and cyclohexane (39.1%) at 433 K and 5 MPa CO (initial pressure at room temperature). The influence of the solvent polarity on the carbonylation of 2-methyl-2-propanol over Nafion-H, however, is much smaller than that observed by Lange for the carbonylation of di-isobutylmethanol.[23] It was reported that at 423 K and 8 MPa CO the carbonylation of di-isobutylmethanol over Nafion-H gave the corresponding branched carboxylic acid in 39% yield in the polar solvent heptanoic acid, while the yield of the carboxylic acid was as low as 1% in the nonpolar solvent dodecane.

2.3.2   Carbonylation of a Variety of Alcohols over Nafion-H

Table 2-3 summarizes the results of the carbonylation for a variety of alcohols over Nafion-H at 433 K and 9 MPa CO (initial pressure at room temperature). In addition to the carbonylation of 2-methyl-2-propanol as described above, primary and secondary alcohols such as 1-pentanol, 2-pentanol, 1-hexanol and 1-octanol also react with CO to give the corresponding tertiary carboxylic acids, which have been distinctly identified by ^{13}C NMR and GC-MS, in yields as high as 64.6, 52.6, 57.9 and 57.4%, respectively, in the solvent hexane. So far, there have been few examples for the carbonylation of primary and secondary alcohols over solid acid catalysts. The conversion of primary and secondary alcohols to tertiary carboxylic acids indicates the isomerization of the carbenium ion intermediates to form tertiary carbenium ions prior to the carbonylation over Nafion-H. The optimum temperature for the reaction is between 433 K and 443 K. No starting substrates remain unreacted. Besides the major products of the corresponding carboxylic acids having one more carbon atom than the starting materials, tertiary carboxylic acids having more than one extra carbon atom are obtained as minor products, which may be formed via dimerization and

Table 2-3

Carbonylation of a variety of alcohols over Nafion-H [a]

Alcohol	Main product	Yield (%)	
		Main product	Total carboxylic acids
2-Methyl-2-propanol [b]	2,2-Dimethylpropanoic acid	53.4	62.5
1-Pentanol	2,2-Dimethylbutanoic acid	48.2	64.6
2-Pentanol	2,2-Dimethylbutanoic acid	40.4	52.6
1-Hexanol	2,2-Dimethylpentanoic acid	25.8	57.9
	2-Methyl-2-ethylbutanoic acid	22.8	
1-Octanol	2,2-Dimethylheptanoic acid	26.8	57.4
	2-Methyl-2-ethylhexanoic acid	21.6	
1-Adamantanol [b]	1-Adamantanecarboxylic acid	76.8	76.9

[a] Reaction conditions: 2.0 g Nafion-H, 20 mmol alcohol, 50 mL hexane, 433 K, 9 MPa CO pressure (initial pressure at room temperature), 22 h reaction time.

[b] 50 mL chlorobenzene instead of hexane as the solvent.

fragmentation of the carbenium ion intermediates over Nafion-H as observed in strong liquid acids.[19,20] No significant amounts of primary or secondary carboxylic acids are formed as observed in strong liquid acids, in contrast to the NMR observation by Stepanov *et al.* that in H-ZSM-5, the reaction of 1-octene with CO and H_2O results in acid of the $C_8H_{17}COOH$ and $C_{16}H_{33}COOH$ families with predominantly linear hydrocarbon chains although the carbonylation of 2-methyl-2-propanol, isobutyl alcohol and isobutene produces 2,2-dimethylpropanoic acid with high selectivity.[24] The reason for the predominant formation of linear carboxylic acid from 1-octene over H-ZSM-5 was considered to be that 1-octene molecule is too large for the bulky tertiary carbenium ions to be formed and carbonylated in the narrow pores of H-ZSM-5,[24] whereas the pores of Nafion-H are sufficiently large for the carbenium ions formed from the primary and secondary alcohols used in this work to isomerize to tertiary carbenium ions and to be subsequently carbonylated to give tertiary carboxylic acids.

Only small amounts of ethers (< 2%) are formed from the primary alcohols and no ethers are observed for the secondary alcohols. In contrast, over the sulfated zirconia catalyst, no carboxylic acids but high yields of ethers were formed from primary alcohols and neither carboxylic acids nor ethers from secondary alcohols.[14] It was reported by Olah *et al.* that over Nafion-H, primary alcohols gave the corresponding ethers in quantitative yields while secondary alcohols, except for the cyclic alcohols, gave only traces of ethers.[21] The removal of water formed in the reaction by azeotropic distillation was found to be necessary for achieving a high conversion to the ethers. The low conversions of the primary alcohols to the corresponding ethers in this study may be due to the effects of water, which was not removed during the reaction, and/or, to a certain extent, originate from the carbonylation of the alcohols with CO prior to the etherification. The absence of ethers for secondary alcohols may be mainly due to steric reasons, which are disadvantageous for the S_N2-type etherification, as observed for 2-methyl-2-propanol.

No carboxylic acids are obtained from lower alcohols such as methanol, ethanol and 2-propanol. Small amounts (<3%) of alkylation products of chlorobenzene are formed from the low alcohols via the Friedel-Crafts reaction in the solvent chlorobenzene instead of hexane.[17,22] From 1-adamantanol, 1-adamantane carboxylic acid is formed in a yield as high as 76.8%. In chlorobenzene, adamantylchlorobenzene is formed as a by-product in a yield of 15% via the Friedel-Crafts reaction with the solvent, and a small amount of adamantane is also observed.

2.3.3 Carbonylation of Alcohols over Ag-ZSM-5 and Nafion-Ag/H

In order to investigate the effects of the metal ion exchange of the H-type solid acids, the carbonylation of a variety of alcohols was carried out over the 100% Ag ion-exchanged ZSM-5 zeolite and 50% Ag ion exchanged Nafion-H catalysts. Figure 2-2 shows the pressure dependence of the carbonylation of 2-methyl-2-propanol over Ag-ZSM-5 and H-ZSM-5 at 433 K in chlorobenzene. The total yield of carboxylic acids is only slightly higher over Ag-ZSM-5 than that over H-ZSM-5. Table 2-4 summarizes the results of the carbonylation for a variety of alcohols over Nafion-Ag/H and Nafion-H at 433 K and 9 MPa of CO (initial pressure at room temperature). It was found that the catalytic activity of Nafion-Ag/H for the carbonylation of alcohols is almost the same as that of Nafion-H. From the above results, no distinct improvement of catalytic activies of the H-ZSM-5 and Nafion-H catalysts results from the Ag ion-exchange, although it was found that at room temperature $AgCO^+$ can be formed in the Ag-exchanged Nafion catalyst (Appendix I). It seems that at the high reaction temperature (about 433 K) the Ag ions may not form the $AgCO^+$ species, which were expected to improve the catalytic activity of Nafion-H.
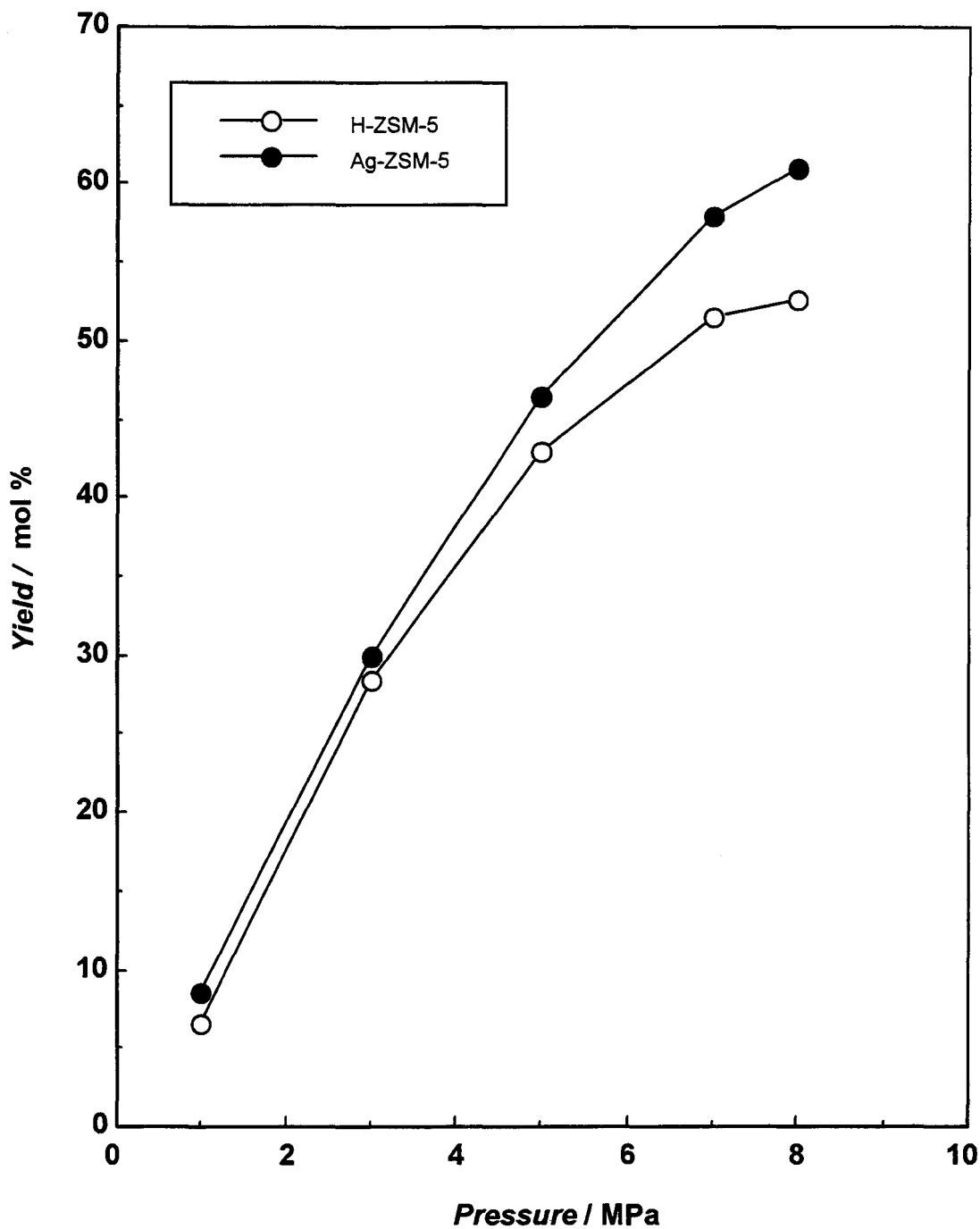
Fig. 2-2   CO pressure dependence of the carbonylation of 2-methyl-2-propanol over Ag-ZSM-5 and H-ZSM-5   Reaction Conditions: 2.0 g catalyst, 20 mmol 2-methyl-2-propanol, 50 mL chlorobenzene, 433 K, 22 h reaction time, (initial CO pressure at room temperature).

Table 2-4

Carbonylation of a variety of alcohols over Nafion-Ag/H and Nafion-H[a]

Alcohol	Total yield of carboxylic acids (%)	
	Nafion-Ag/H	Nafion-H
2-Methyl-2-propanol	60.6	62.5
1-Pentanol	61.8	64.6[b]
2-Pentanol	55.1	52.6[b]
1-Hexanol	59.3	57.9[b]
1-Adamantanol	76.8	76.9

[a] Reaction conditions: 2.0 g catalyst, 20 mmol alcohol, 50 mL chlorobenzene, 433 K, 9 MPa CO pressure (initial pressure at room temperature), 22 h reaction time.

[b] 50 mL hexane instead of chlorobenzene as the solvent.

2.4 Conclusions

The Koch-type carbonylation of alcohols with CO over Nafion-H, a solid perfluoroalkanesulfonic acid resin catalyst, was investigated. Tertiary carboxylic acids are obtained in high yields from not only tertiary but also primary and secondary alcohols. The optimum temperature for this reaction is between 433 and 443 K. A high CO pressure is advantageous for the carbonylation. The catalytic performance can be slightly modified by changing the solvent polarity. The present study indicates the potential industrial application of solid acids instead of strong liquid acids catalysts for the Koch-type reaction to selectively synthesize tertiary carboxylic acids.

Formation of Silver(I) Carbonyl Cation, Ag(CO)$^+$, on Nafion-Ag

I found that the reaction of Nafion-Ag with CO results in the formation of the silver(I) carbonyl cation, Ag(CO)$^+$. A 0.3 g sample of Nafion 112 (film, Aldrich) in the H form (ion exchange capacity: ca. 0.9 mequiv g^{-1}) was immersed in 50 mL of a 0.01 mol/L AgNO$_3$ aqueous solution for 20 h. The Nafion-Ag was washed several times with water, and dried at 383 K for 3 h and then cooled in a desiccator. The Nafion-Ag was put in the A side of a special hand-made vacuum-tight IR cell with KBr windows as shown in Fig. 2-3 and dried again at 413 K under 1.3 kPa for 7 h. After the cell was cooled to room temperature, 25.3 kPa of CO was introduced into the IR cell and the Nafion-Ag was exposed to the CO for 30 min. After moving the sample to the B side the IR spectrum was measured on a JASCO FT/IR-230 spectrometer. The IR absorption of the CO gas was subtracted from the observed spectrum, giving the IR absorption of the silver(I) carbonyl cation, Ag(CO)$^+$, on Nafion-Ag at 2173 cm^{-1} as shown in Fig. 2-4.

| (a) | (b) | (c) |
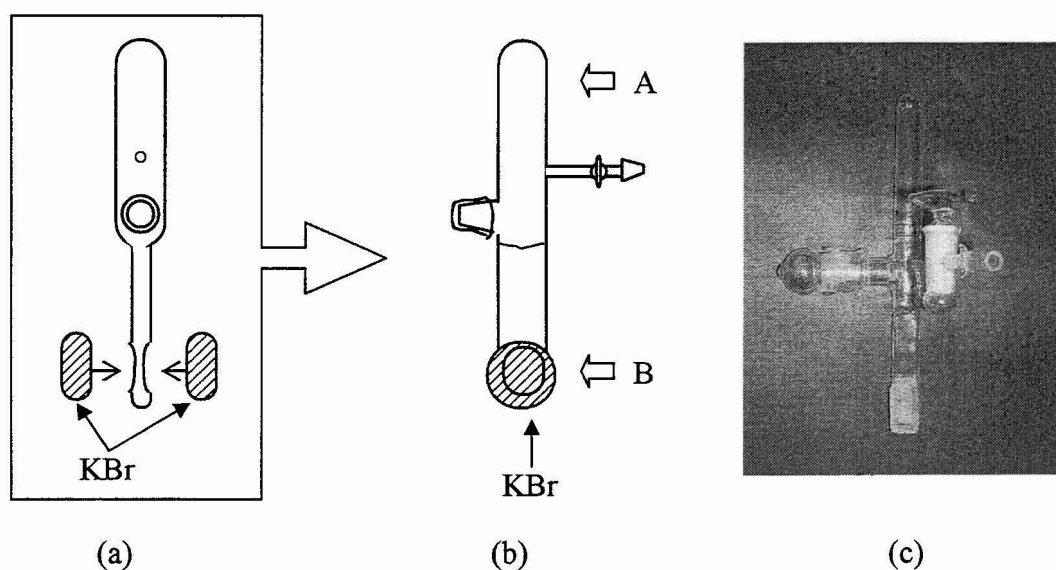
Fig. 2-3   The special hand-made vacuum-tight IR cell with KBr windows
(a) side view, (b) front view, (c) photograph

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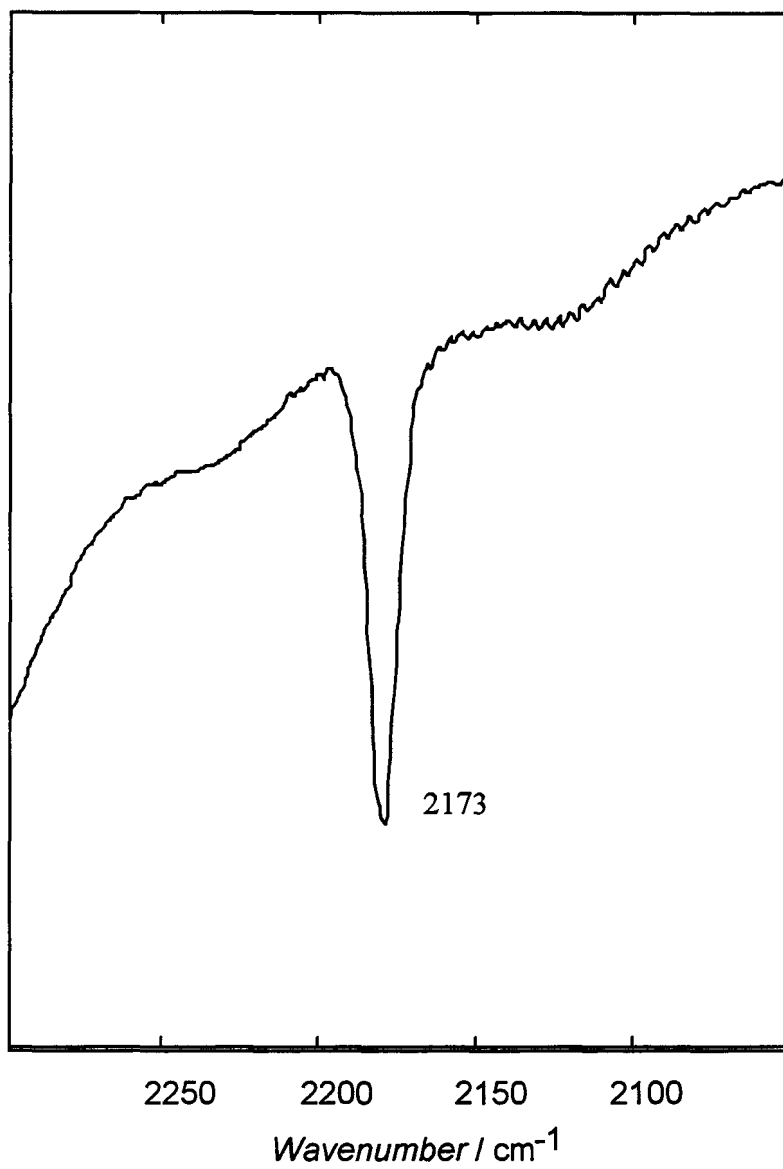
Fig. 2-4   The IR spectrum of the silver(I) carbonyl cation, Ag(CO)$^+$, on Nafion-Ag

References to Chapter 2

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Chapter 3

Copper(I), Silver(I) and Gold(I) Carbonyl Cations in Strong Acids
– Spectroscopic Characterization and Catalytic Application

Detailed IR, Raman, and NMR spectroscopic characterization has been carried out on the group 11 metal carbonyl cations, $Cu(CO)_n^+$ (n = 1, 2, 3, 4), $Ag(CO)_n^+$ (n = 1, 2, 3), and $Au(CO)_n^+$ (n = 1, 2), over a wide range of temperature and in a variety of strong acids, based on which their molecular structures were determined. Comparison and discussion of their stabilities are given. The active species have been determined to be $Cu(CO)_2^+$ (and $Cu(CO)_3^+$ as a minor species) instead of the previously assigned $Cu(CO)_3^+$, $Ag(CO)^+$ instead of the previously assigned $Ag(CO)_2^+$, and $Au(CO)_2^+$, respectively, for the copper(I), silver(I) and gold(I) carbonyl cation-catalyzed carbonylation of olefins and alcohols in concentrated sulfuric acid. The reaction mechanism previously proposed for the metal carbonyl cation-catalyzed carbonylation has been modified to involve an olefin-metal-monocarbonyl (e.g., for Ag) or an olefin-metal-polycarbonyl (e.g., for Cu or Au) intermediate.

3.1 Introduction

Carbon monoxide is one of the most important and versatile ligands in transition metal chemistry.[1] Since the discovery of the first metal carbonyl complexes, $Pt(CO)_2Cl_2$, $Pt_2(CO)_4Cl_4$, and $Pt_2(CO)_3Cl_4$, by Schützenberger in 1868,[2-5] metal carbonyls have played a very important role in chemistry and the chemical industry.[6,7] Many industrial processes employ CO as a reagent and transition metal compounds as heterogeneous or homogeneous catalysts and involve the intermediates of metal carbonyls.[8-12] The metal-carbonyl bonding has been suggested to involve a synergistic interaction between σ-donor bonding from the occupied 5σ molecular orbital of CO into an empty metal orbital with σ symmetry and π-backbonding from occupied metal orbitals into the π* molecular orbitals of CO.[1]

Recently, there has been a remarkable development in the synthesis and characterization of new homoleptic metal carbonyl cations and their derivatives from groups 6 through 12 in acidic or superacidic media or with weakly coordinating anions, in which the CO ligand primarily functions as a σ donor.[13-21] Protic acids have been used to generate a number of metal carbonyl cations and cationic carbonyl derivatives as well as molecular adducts of CO to metal cations,[22,23] many of which have been used as catalysts for the carbonylation of olefins and alcohols.[17,21] In strongly acidic solutions, Cu_2O, Ag_2O and Au_2O_3 absorbed carbon monoxide to give colorless, cationic carbonyl complexes of the general formula $[L_mM(CO)_n]^+$ (M = Cu, Ag, Au; L denotes the solvent ligand probably being the conjugate base of the solvent acid or a closely related species), which show high catalytic activities for the carbonylation of olefins and alcohols.[24-28] For the sake of brevity, the solvated cations that should exist in the form of $[L_mM(CO)_n]^+$ will hereafter be simply formulated as $M(CO)_n^+$. The actual stoichiometry of the group 11 metal carbonyl cations depends on the solvent acid and the temperature; so far only limited spectroscopic data have been reported.[21,29]

In this paper, we report the detailed spectroscopic characterization of the group 11

metal carbonyl cations over a wide range of temperature and in solvents of various acidities, based on which, their structures have been determined. In addition, discussions are given on the active species and reaction mechanism of the metal carbonyl cation-catalyzed carbonylation of olefins and alcohols.

3.2 Experimental

3.2.1 Chemicals

Cu_2O (Wako Pure Chemical Industries), Ag_2O (Wako Pure Chemical Industries), Au_2O_3 (Rare metallic Co.), H_2SO_4 (96%, Kanto Chemical Co.), HSO_3F (Wako Pure Chemical Industries), $HSO_3F \cdot SbF_5$ (1:1) (Aldrich Chemical Company) and CO (Nippon Sanso) were used. The chemicals were high-purity grade and were used without further purification.

3.2.2 General Procedures

Preparation of the metal carbonyls was performed with a 100-mL three-necked flask connected to a carbon monoxide gas buret. The apparatus containing a mixture of a metal compound (2 mmol, based on the metal atom) and a strong acid (10 mL) was evacuated by a rotary pump to remove air, and after carbon monoxide was introduced from the gas buret, the mixture was stirred vigorously until the completion of the reaction. The amount of absorbed CO was measured by the gas buret. In 96% H_2SO_4, HSO_3F or magic acid, $HSO_3F \cdot SbF_5$ (1:1), clear solutions were obtained for silver(I) and gold(I) carbonyl cations. Stable heterogeneous suspensions were formed from Cu_2O or Cu under CO atmosphere, which were used as prepared for the spectroscopic measurements. All the manometric and spectroscopic measurements were performed under CO atmosphere unless the spectra for the evacuated samples

were obtained under argon atmosphere. For temperature-variable measurements, the sample was first prepared at room temperature and then cooled or heated to each temperature, where the sample was rigorously stirred under CO atmosphere until reaching the equilibrium.

3.2.3 Instrumentation

In situ FT-IR spectra were recorded using a ReactIR1000 System (ASI, Millersville, MD) with a spectral resolution of 2 cm^{-1} on a Zirconia attenuated total reflection (ATR) sensor (ZirComp) (for Cu and Ag) or a Diamond ATR sensor (DiComp) (for Au).

FT-Raman spectra were recorded on a Nicolet FT-Raman 960 spectrometer with a spectral resolution of 2 cm^{-1} using the 1064 nm exciting line (~600 mV) of a Nd:YAG laser (Spectra Physics, USA). Standard canula transfer techniques were used for the sample manipulations for the room-temperature Raman measurements, for which liquid Raman samples were contained in a 5-mm o.d. NMR tube. For *in situ* temperature-variable Raman measurements, the liquid samples were contained in a Pyrex tube connected to the three-necked flask and mounted on the cryostat.

^{13}C NMR spectra were recorded using a JEOL JNM-AL400 spectrometer operating at 100.40 MHz. $CDCl_3$ was contained as an external reference and a lock in sample tubes of 5 mm o.d., in which coaxial inserts containing liquid samples were placed. Standard canula transfer techniques were used for the sample manipulations. Carbon monoxide of natural abundance was used for ^{13}C NMR measurements. Chemical shifts are given in δ unit (parts per million) downfield from tetramethylsilane.

3.3 Results and Discussion

3.3.1 Copper(I) Carbonyls

It was known that a number of copper(I) compounds absorb carbon monoxide with a CO/Cu stoichiometric ratio ≤ 1.0 to form Cu(CO)X under various conditions.[30-36] Souma *et al.* previously reported the formation of $Cu(CO)_4^+$, $Cu(CO)_3^+$ and $Cu(CO)^+$ from Cu_2O in strong acids such as H_2SO_4, CF_3SO_3H, HSO_3F, HF and $BF_3 \cdot H_2O$, while $Cu(CO)_2^+$ was not considered for reasons that are not clear.[24] We report here the detailed spectroscopic investigation of this system, which shows the formation of $Cu(CO)_n^+$ ($n = 1, 2, 3, 4$).

When Cu_2O or Cu reacts with atmospheric CO in 96% H_2SO_4, HSO_3F or magic acid, $HSO_3F \cdot SbF_5$ (1:1), a heterogeneous suspension is formed at room temperature; Cu(II) compounds, such as CuO and $CuSO_4$, do not react with CO in these acids. The actual CO/Cu^+ stoichiometry depends on the temperature and the acid solvent. With increasing acidity of the solution or decreasing temperature, the CO/Cu^+ stoichiometry was increased: under atmospheric CO pressure, 1.5 at 23 °C and 2.1 at -10 °C in 96% H_2SO_4; 2.8 at 23 °C and 3.9 at -70 °C in HSO_3F; 3.6 at 23 °C and 3.9 at -40 °C in magic acid, $HSO_3F \cdot SbF_5$ (1:1) (Fig. 3-1). *In situ* infrared and FT-Raman spectra at varying temperatures exhibit obvious evidence for the formation of the copper(I) carbonyl cations, $Cu(CO)_n^+$ ($n = 1, 2, 3, 4$), under atmospheric pressure of CO. The equilibra shown below are shifted to the right as the temperature decreases.

$$Cu_2O \text{ (or Cu)} \longrightarrow Cu^+ \xrightarrow{+ CO} Cu(CO)^+ \underset{- CO}{\overset{+ CO}{\rightleftharpoons}}$$

$$Cu(CO)_2^+ \underset{- CO}{\overset{+ CO}{\rightleftharpoons}} Cu(CO)_3^+ \underset{- CO}{\overset{+ CO}{\rightleftharpoons}} Cu(CO)_4^+$$
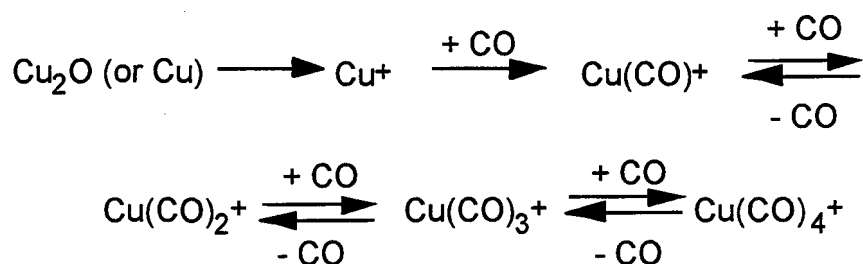
In 96% H_2SO_4 solution at room temperature, where $CO/Cu^+ = 1.5$, the IR
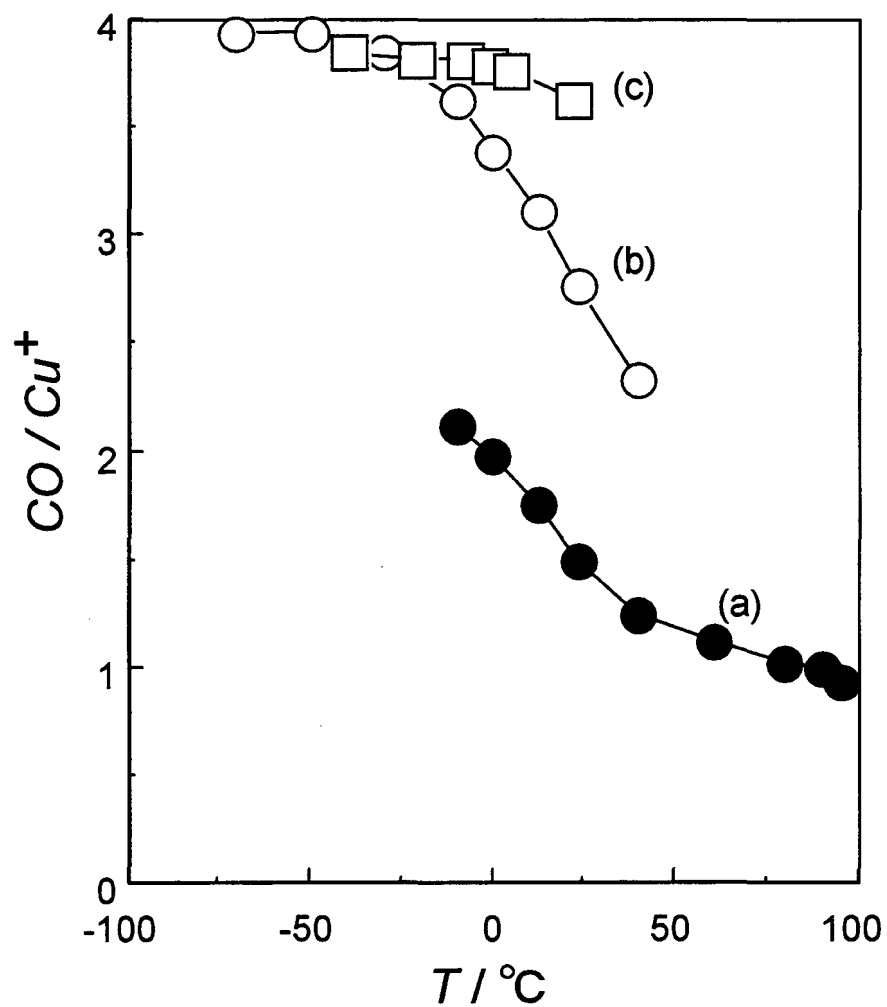
Fig. 3-1   CO uptake of Cu₂O dissolved in (a) 96% H₂SO₄, (b) HSO₃F, and (c) magic

acid, HSO₃F · SbF₅ (1:1), at varying temperatures under atmospheric pressure of CO.
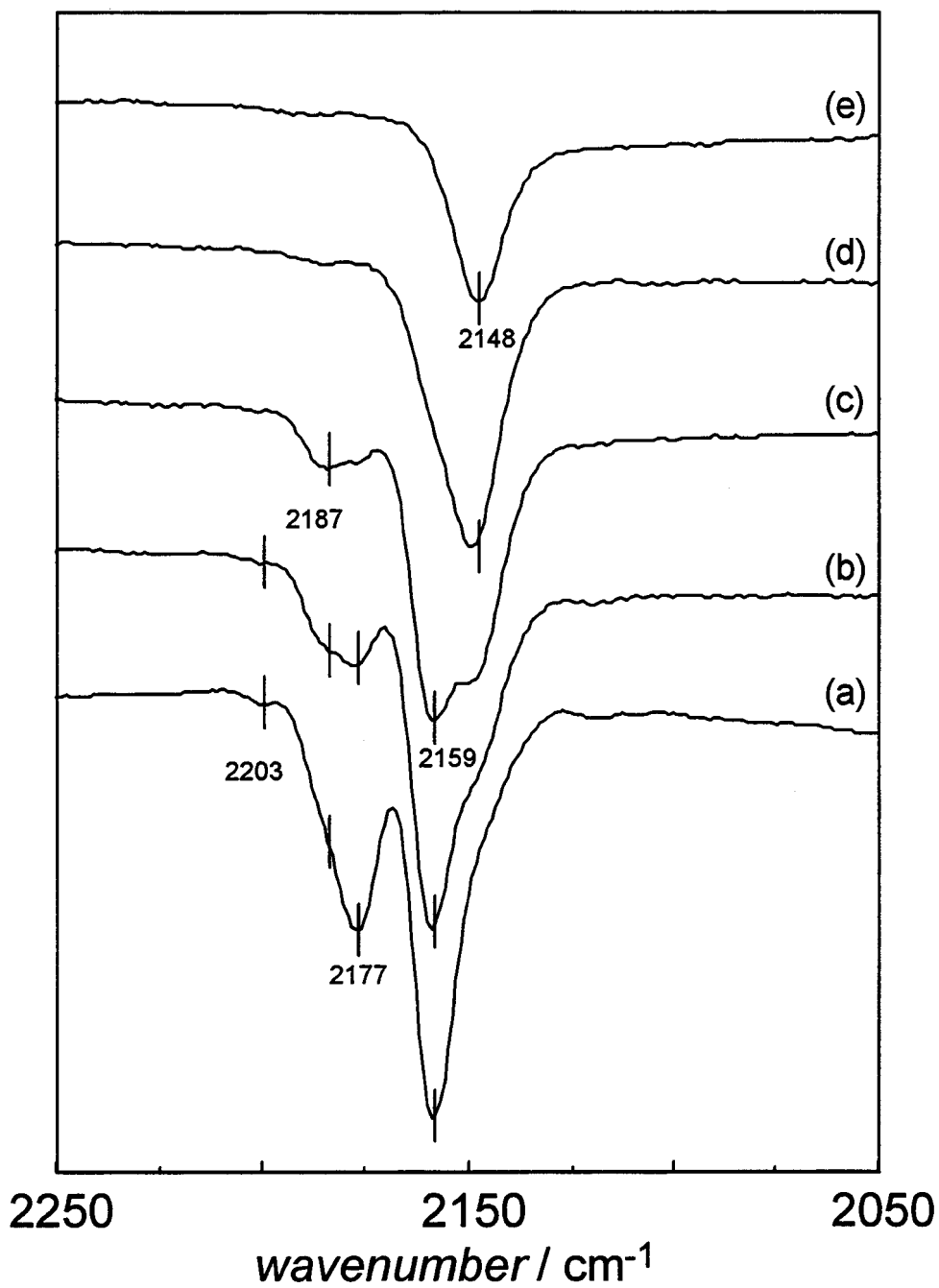
Fig. 3-2　IR spectra of copper(I) carbonyl cations in 96% H_2SO_4 at (a) -10 °C, (b) 12 °C, (c) 23 °C, and (d) 80 °C under atmospheric pressure of CO, and (e) after evacuating the sample at 23 °C for 10 min.
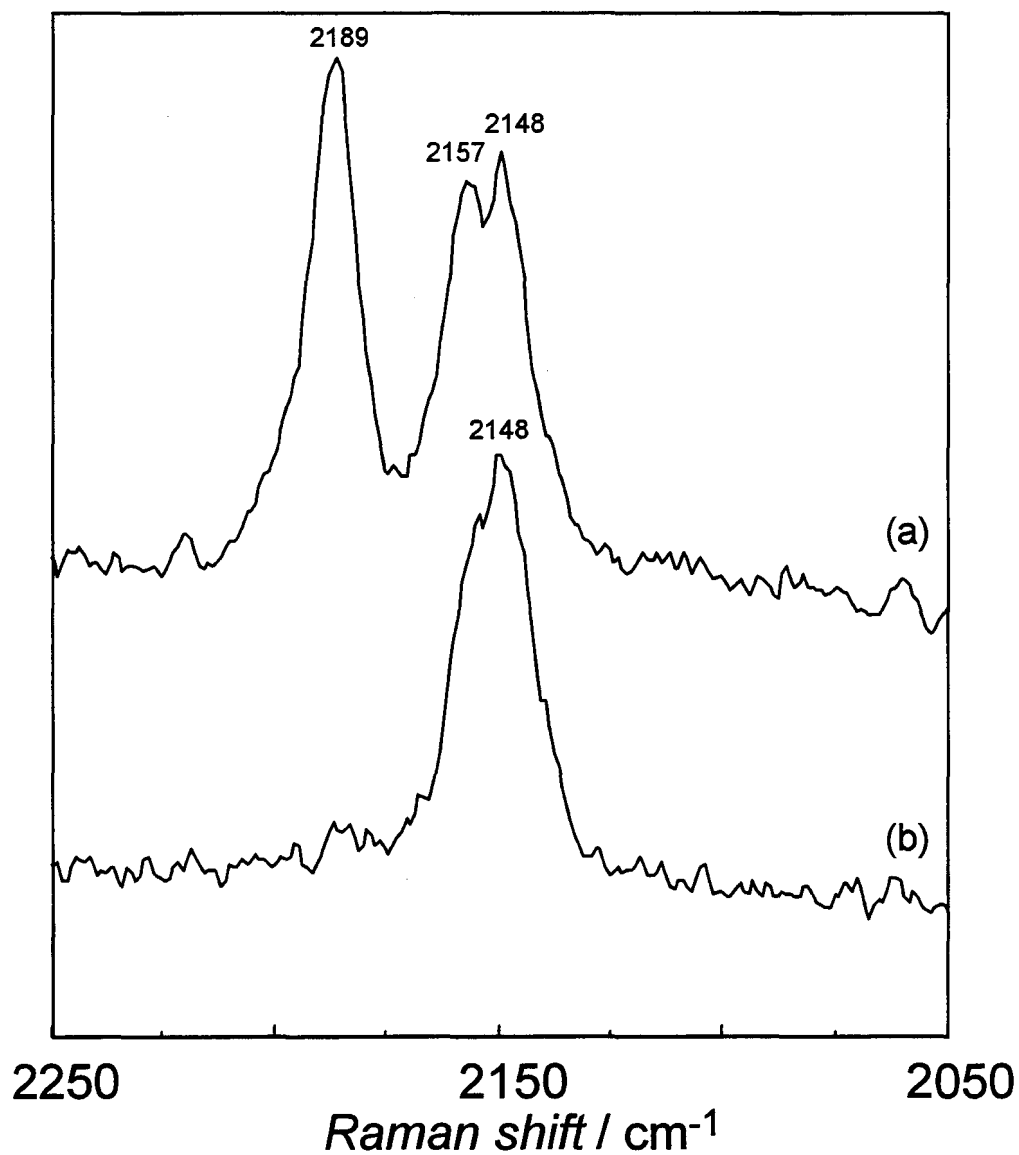
Fig. 3-3 Raman spectra of copper(I) carbonyl cations in 96% H_2SO_4 (a) at 23 °C under atmospheric pressure of CO, and (b) after evacuating the sample at 23 °C for 10 min.

spectrum exhibits a strong $\nu(CO)$ band at 2159 cm^{-1} and a weak IR band at 2187 cm^{-1} (Fig. 3-2c), and the corresponding Raman spectrum shows a weak band at 2157 cm^{-1} and a strong band at 2189 cm^{-1} (Fig. 3-3a), which are attributed to Cu(CO)$_2^+$. According to the "mutual exclusive rule",[37] the IR/Raman coincidences indicate a non-linear symmetry (bent, C_{2v}) for Cu(CO)$_2^+$. The IR bands at the higher frequencies decrease in intensity and the shoulder at 2148 cm^{-1} grows in intensity, accompanied by the CO evolution, with increasing temperature; at 80 °C, the band at 2148 cm^{-1} has the largest intensity (Fig. 3-2d). In addition, by a brief evacuation of the sample at room temperature, only the IR band at 2148 cm^{-1} (Fig. 3-2e) along with its corresponding Raman band at the same frequency (Fig. 3-3b) is left, which is assigned to the copper(I) monocarbonyl cation, Cu(CO)$^+$. At room temperature, a $\nu(CO)_{IR}$ shoulder is observed at 2177 cm^{-1}, which grows, along with the band at 2203 cm^{-1}, with decreasing temperature (Figs. 3-2a, 3-2b). These two bands are attributed to Cu(CO)$_3^+$, in which the three CO ligands are out of plane (C_{3v}). Note that in 96% H$_2$SO$_4$ solution at room temperature, the copper(I) mono-, di- and tri- carbonyl cations, Cu(CO)$_n^+$ (n = 1, 2, 3), coexist in equilibrium and the dicarbonyl cation, Cu(CO)$_2^+$, rather than Cu(CO)$_3^+$, is the major species, whereas in the previous reports Cu(CO)$_2^+$ was not considered and Cu(CO)$_3^+$ was assigned as the active species for the carbonylation of olefins and alcohols in concentrated H$_2$SO$_4$ (*vide infra*).[25] At room temperature, only a single resonance appears at 168 ppm in the ^{13}C NMR spectrum, for which the rapid CO exchange on the NMR time scale between the species, Cu(CO)$_n^+$ (n = 1, 2, 3), would account. By removing the ambient CO by evacuation, the solution gives a single peak at 166 ppm, which is attributed to Cu(CO)$^+$.

In HSO$_3$F at room temperature, where CO/Cu$^+$ = 2.8, the IR spectrum exhibits a strong $\nu(CO)$ band at 2184 cm^{-1} and a shoulder at 2207 cm^{-1} (Fig. 3-4c) and the corresponding Raman spectrum shows a weak band at 2185 cm^{-1} and a strong band at 2209 cm^{-1} (Fig. 3-5a). These bands can be attributed to Cu(CO)$_3^+$ having a structure
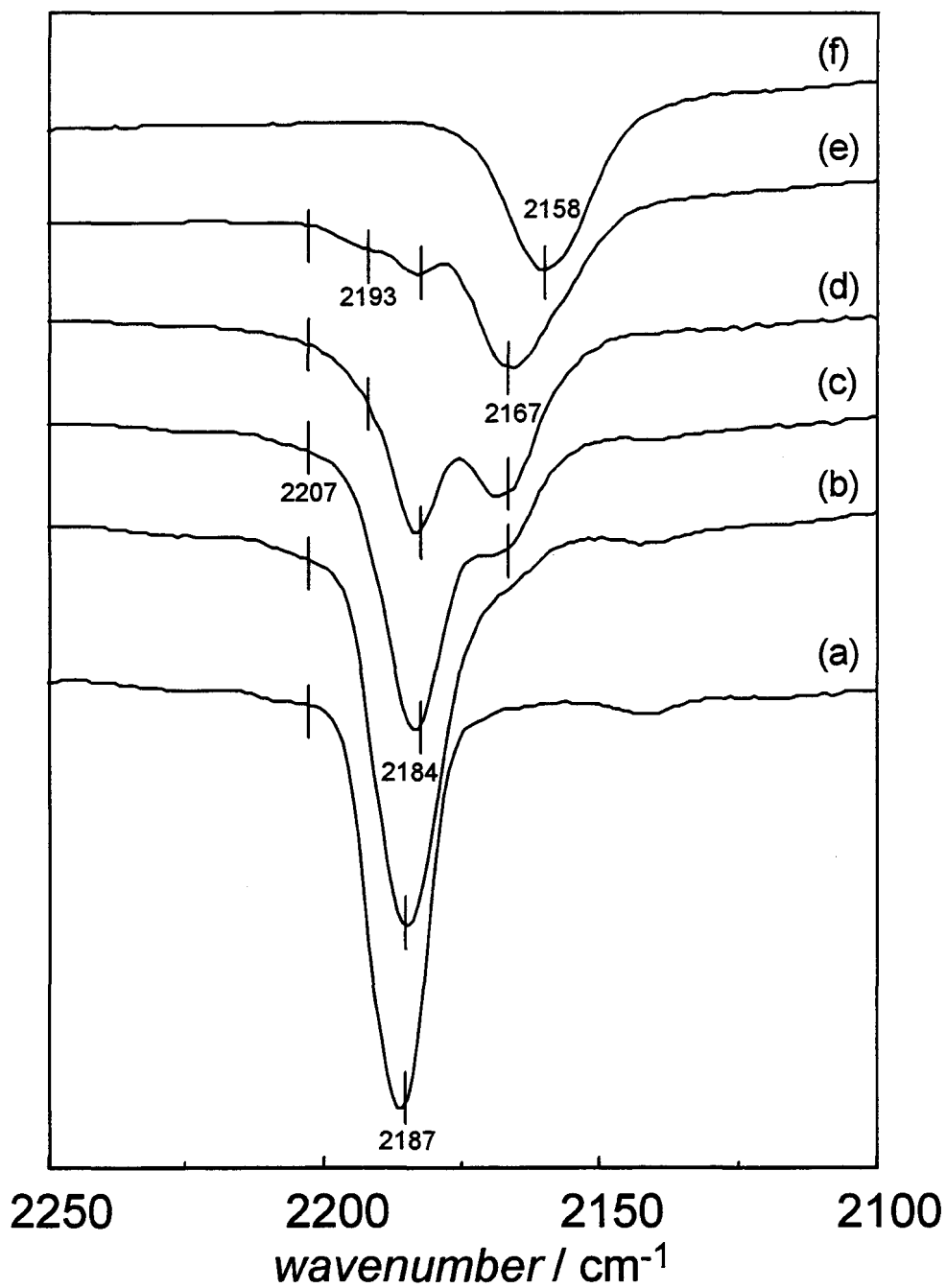
Fig. 3-4   IR spectra of copper(I) carbonyl cations in HSO_3F at (a) -70 °C, (b) 0 °C, (c) 24 °C and (d) 40 °C under atmospheric pressure of CO, and after evacuating the sample at 24 °C (e) for 5 sec and (f) for 10 min.
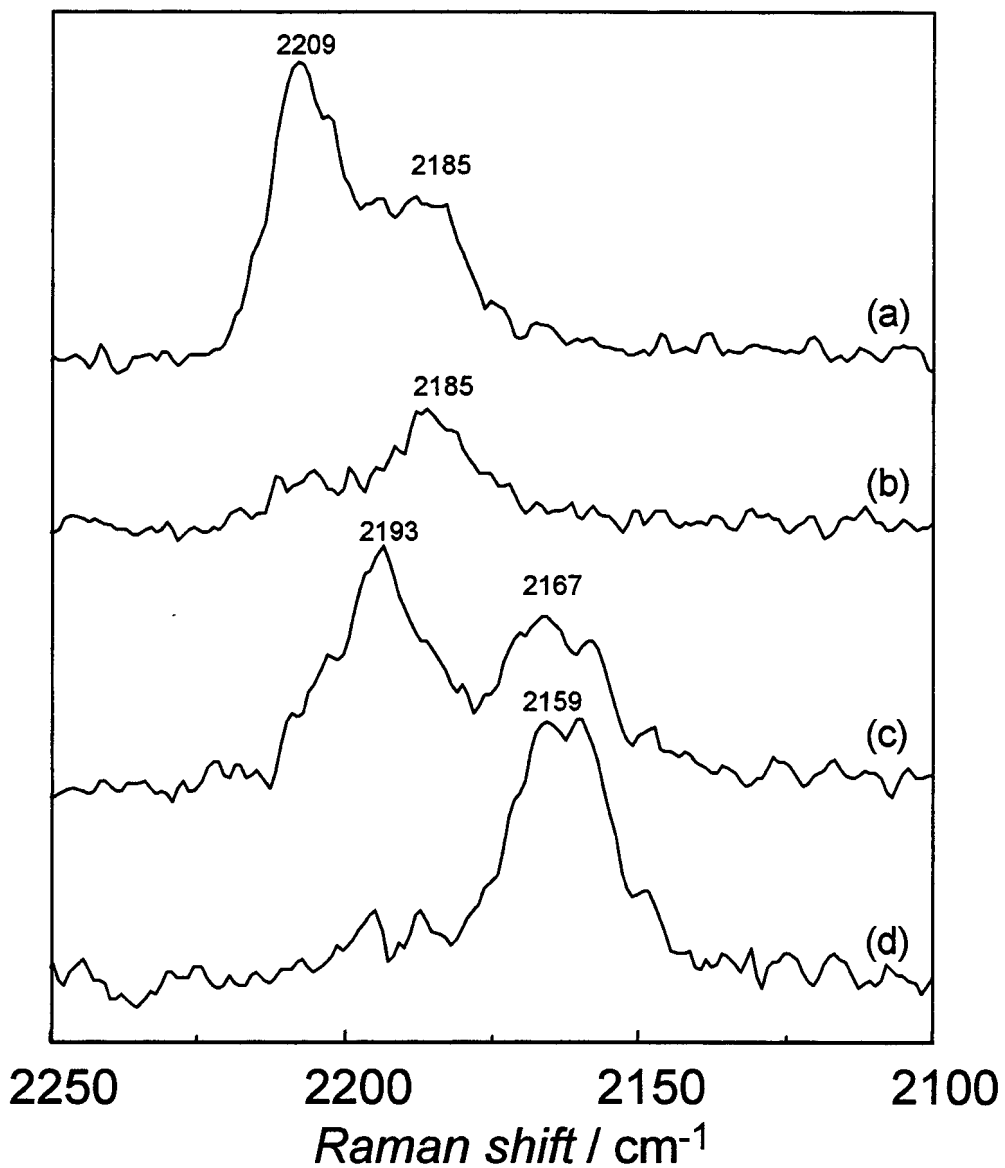
Fig. 3-5 Raman spectra of copper(I) carbonyl cations in HSO_3F with (a) 0 °
and (b) 90 ° polarization filters at 24 °C under atmospheric pressure of CO, and after
evacuating the sample at 24 °C (c) for 5 sec and (d) for 10 min.

(C_{3v}) with an out-of-plane deviation from a trigonal plane (D_{3h}). The Raman band at 2209 cm^{-1} is strongly polarized (Figs. 3-5a, 3-5b), which, along with its IR counterpart at 2207 cm^{-1}, is assigned to the symmetric CO stretch. The Raman band at 2185 cm^{-1} is depolarized, which, along with its IR counterpart at 2184 cm^{-1}, is assigned to the asymmetric CO stretch. The IR band at 2184 cm^{-1} due to $Cu(CO)_3^+$ slightly shifts to 2187 cm^{-1} on decreasing the temperature from 24 to -70 °C (Figs. 3-4c~3-4a). However, for CO/Cu$^+$ = 3.9 at -70 °C, no IR band due to $Cu(CO)_4^+$ was observed, due to its low solubility as also observed in magic acid (*vide infra*). By raising the temperature from room temperature, the IR bands at higher frequencies decrease in intensity and the shoulder at 2167 cm^{-1} grows in intensity, accompanied by CO evolution (Figs. 3-4c, 3-4d). At 40 °C where the CO/Cu$^+$ ratio is 2.3, the IR band at 2167 cm^{-1} with an intensity comparable to that at 2184 cm^{-1} and a shoulder at 2193 cm^{-1} are observed (Fig. 3-4d). In addition, by a brief evacuation for 5 sec at room temperature, the IR band at 2184 cm^{-1} is remarkably decreased and the IR bands at 2167 and 2193 cm^{-1} are enhanced (Fig. 3-4e); the corresponding Raman spectrum shows a band at 2167 cm^{-1} and a band at 2193 cm^{-1} with a larger intensity (Fig. 3-5c), which are attributed to $Cu(CO)_2^+$ with a non-linear structure (bent, C_{2v}). Upon an evacuation for 10 min at room temperature, the high-frequency bands disappear and a new IR band at 2158 cm^{-1} (Fig. 3-4f) with the corresponding Raman band at 2159 cm^{-1} (Fig. 3-5d) appears, which can be assigned to $Cu(CO)^+$. It is noted that in HSO$_3$F, the copper(I) mono-, di- and tri- carbonyl cations, $Cu(CO)_n^+$ (n = 1, 2, 3), coexist in equilibrium and the tricarbonyl cation, $Cu(CO)_3^+$, is the major species at room temperature. At room temperature, only a single resonance appears at 169 ppm in the ^{13}C NMR spectrum, for which the rapid CO exchange on the NMR time scale between the species, $Cu(CO)_n^+$ (n = 1, 2, 3), would account. By removing the ambient CO by evacuation, the solution gives a single peak at 166 ppm due to the stable $Cu(CO)^+$.

In magic acid, HSO$_3$F·SbF$_5$ (1:1), at atmospheric pressure of CO and room

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temperature, a white suspension is formed with $CO/Cu^+ = 3.6$. A $\nu(CO)$ band at 2190 cm^{-1} in the IR spectrum (Fig. 3-6a), two strong bands at 2187 and 2211 cm^{-1} and a shoulder at 2192 cm^{-1} in the Raman spectrum (Fig. 3-7b) were observed. The IR band at 2190 cm^{-1} decreases in intensity with decreasing temperature; at -40 °C, it mostly disappears (Figs. 3-6a∼3-6d). We assign the IR band at 2190 cm^{-1} along with the corresponding Raman bands at 2192 and 2211 cm^{-1} to $Cu(CO)_3^+$. The lack of an IR counterpart of the Raman band at 2211 cm^{-1} indicates $Cu(CO)_3^+$ has an almostly trigonal-planar (D_{3h}) structure, in contrast with the out-of-plane structure for $Cu(CO)_3^+$ in concentrated H_2SO_4 or HSO_3F, probably owing to the lower nucleophilicity of magic acid. The Raman band at 2187 cm^{-1} is assigned to $Cu(CO)_4^+$ even though we could detect only one Raman band instead of the two predicted for $Cu(CO)_4^+$ with tetrahedral geometry (T_d). The Raman band at 2187 cm^{-1} grows in intensity with decreasing temperature and therefore increasing the concentration of $Cu(CO)_4^+$ (Fig. 3-7a). It is considered that the lack of an IR $\nu(CO)$ band corresponding to the Raman band at 2187 cm^{-1} for $Cu(CO)_4^+$ is due to its low solubility because the attenuated total reflection (ATR) IR sensor can detect only soluble species while both soluble and insoluble species can be detected in the Raman measurements. This assignment is supported by the examination with evacuation of the solution. By only a brief evacuation (5 min) at -20 °C, the white solids in the suspension immediately disappear, giving a clear and colorless solution. The IR band at 2190 cm^{-1} increases in intensity due to the evacuation (Figs. 3-6e, 3-6f). We believe that $Cu(CO)_4^+$, the white solids in the suspension, undetectable by the ATR IR sensor, readily release one CO ligand by evacuation to form $Cu(CO)_3^+$, which is soluble and detectable by the ATR IR sensor. At room temperature, no ^{13}C NMR signal was detected from the clear solution obtained by decanting the suspension from the solution prepared with CO of natural abundance, because most of the Cu^+ has been precipitated as $Cu(CO)_4^+$ so that the concentration of $Cu(CO)_3^+$ in the solution is too low to be detected. By a brief evacuation for 30 sec at
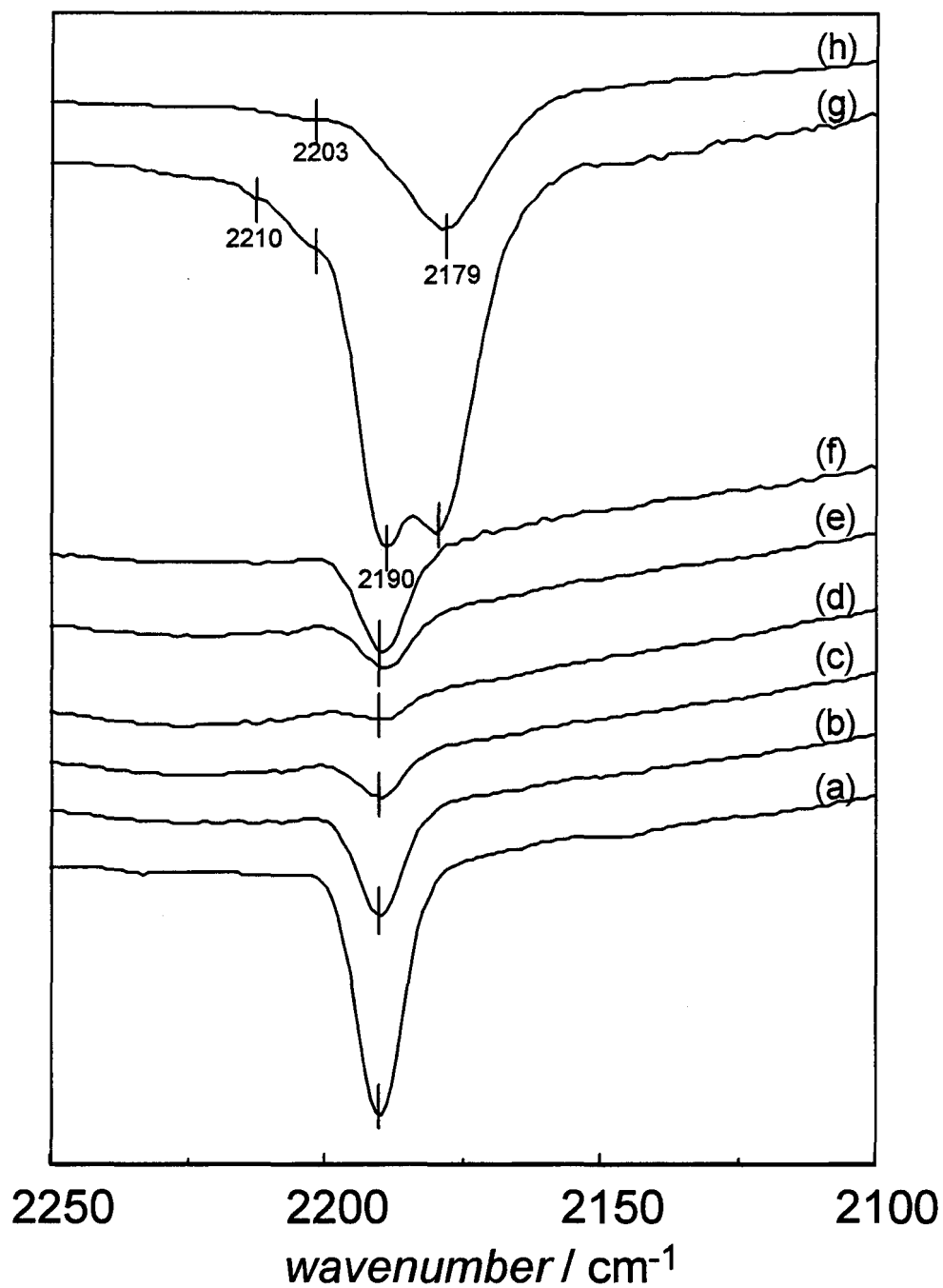
Fig. 3-6 IR spectra of copper(I) carbonyl cations in magic acid, $HSO_3F \cdot SbF_5$ (1:1), at (a) 23 °C, (b) 0 °C, (c) -20 °C and (d) -40 °C under atmospheric pressure of CO, and after evacuating the sample at -20 °C (e) for 5 min and (f) for 3 h, and after evacuating the sample at 23 °C (g) for 2 h and (h) for 6 h.
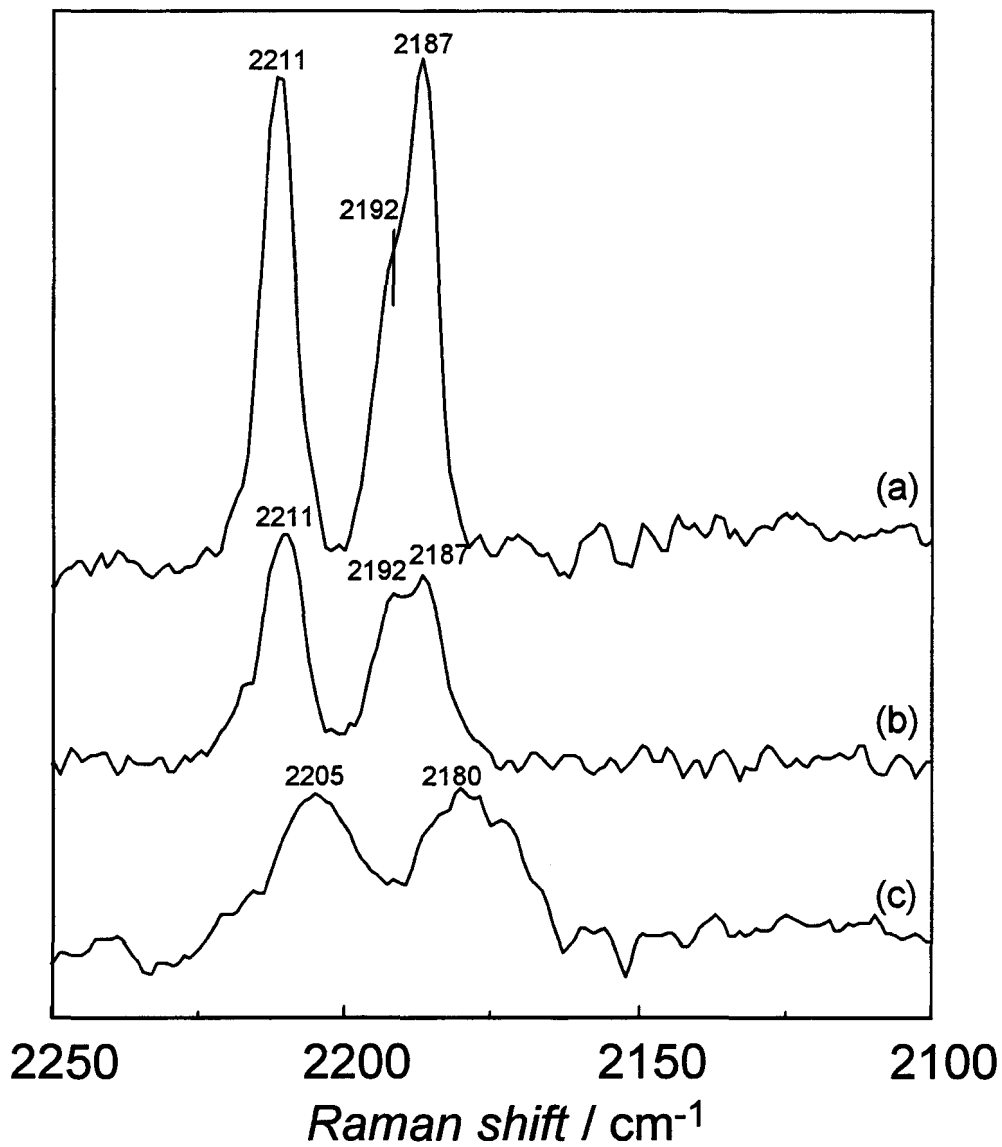
Fig. 3-7 Raman spectra of copper(I) carbonyl cations in magic acid, $HSO_3F \cdot SbF_5$ (1:1), at (a) -20 °C, (b) 23 °C, and (c) after evacuating the sample at 23 °C for 6 h.

room temperature, the white solids in the suspension quickly disappear, giving a colorless, clear solution which exhibits a ^{13}C NMR resonance at 169 ppm due to $Cu(CO)_3^+$. Further prolonged evacuation of the solution leads to the loss of one CO ligand from $Cu(CO)_3^+$ to form $Cu(CO)_2^+$, which has a non-linear structure (bent, C_{2v}); two IR bands at 2179 (strong) and 2203 (weak) cm^{-1} (Figs. 3-6g, 3-6h) and two corresponding Raman bands at 2180 and 2205 cm^{-1} (Fig. 3-7c) were observed, as observed in concentrated H_2SO_4 and HSO_3F. $Cu(CO)_2^+$ in magic acid exhibits a ^{13}C NMR resonance at 166 ppm.

All the IR and Raman $v(CO)$ values observed for $Cu(CO)_n^+$ ($n = 1$-4) are higher than 2143 cm^{-1}, the value for free CO,[37] indicating reduced π-backbonding, as observed for a series of metal carbonyl cations, whereas typical metal carbonyls exhibit much lower $v(CO)$ values.[16] The ^{13}C NMR chemical shifts shown by the copper(I) carbonyl cations are high field-shifted from 184 ppm, the value for free CO,[38] as observed for a series of metal carbonyl cations, whereas a low-field shift from 184 ppm is usually observed for typical metal carbonyls.[16] It is noted that $Cu(CO)_2^+$ is bent (C_{2v}) in all these acids whereas $Cu(CO)_3^+$ is non-planar (C_{3v}) in concentrated H_2SO_4 and HSO_3F but almostly trigonal planar (D_{3h}) in magic acid. Therefore, in a solution being sufficiently nucleophilic, Cu^+ tends to assume a tetrahedral coordination geometry, in which the coordination sites unoccupied by CO ligands are occupied by the solvent molecules. In comparison, the two-coordinate, linear structure ($D_{\infty h}$) for $Cu(CO)_2^+$ and the three-coordinate, trigonal-planar structure (D_{3h}) for $Cu(CO)_3^+$ are observed in solid $[Cu(CO)_n][AsF_6]$ ($n = 2$, 3)[39] and in the rare-gas matrices,[40] but the bent $Cu(CO)_2^+$ and non-planar $Cu(CO)_3^+$ are observed in zeolites[41-43] and in $Cu(CO)_n(N(SO_2CF_3)_2)$ ($n = 2$, 3)[44] (Fig. 3-8). The copper(I) tetracarbonyl cation, $Cu(CO)_4^+$, may be tetrahedral (T_d), as observed for solid $[Cu(CO)_4][1\text{-}Et\text{-}CB_{11}F_{11}]$[45] or the isoelectronic $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$.[46]

It seems that the stability of the copper(I) carbonyls increases with increasing

(a) 2148
2148
2187 2159
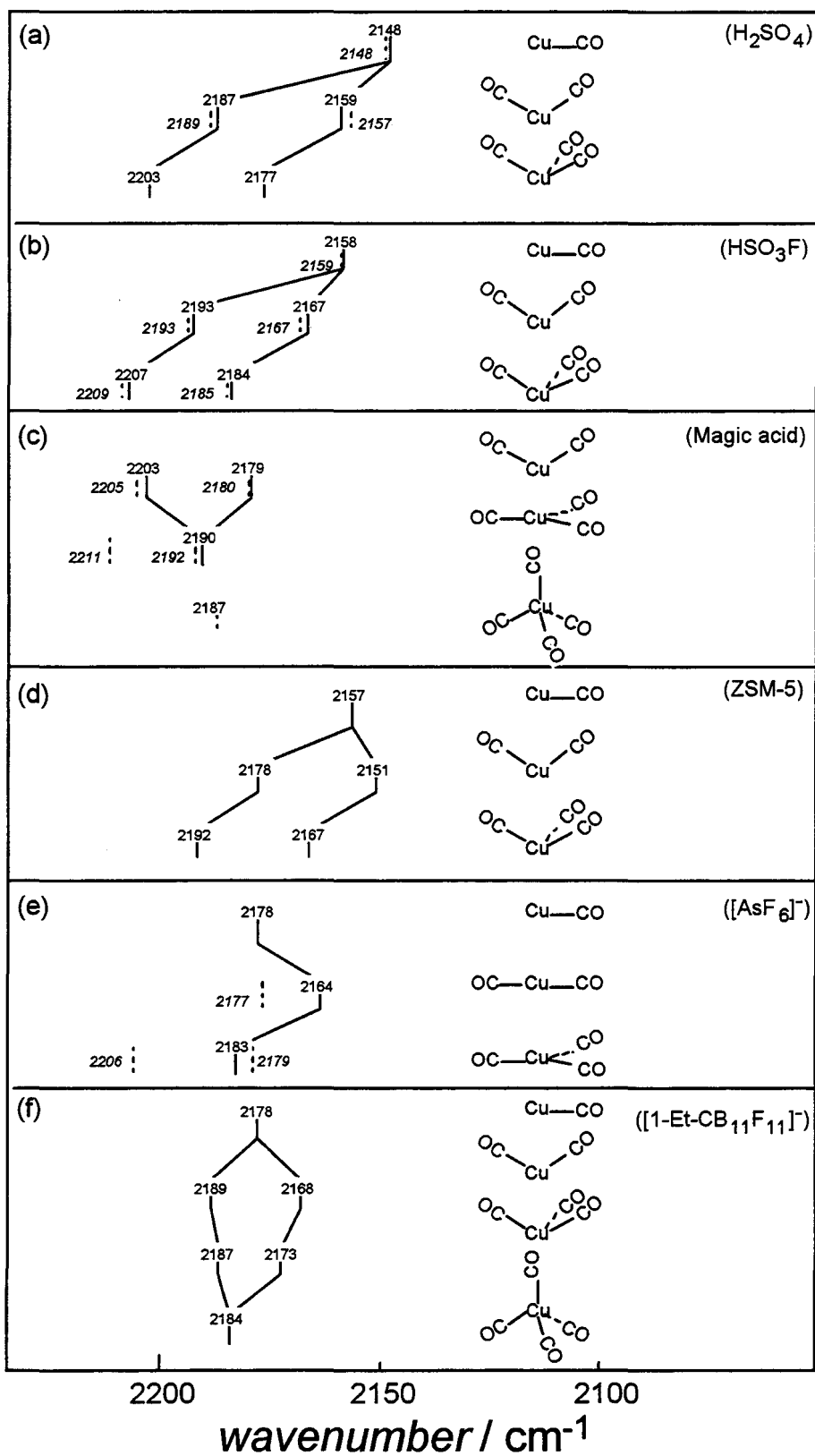*2189* *2157*
2203 2177

Cu—CO (H₂SO₄)

(b) 2158
2159
2193 2167
2193 *2167*
2207 2184
2209 *2185*

Cu—CO (HSO₃F)

(c) (Magic acid)
2203 2179
2205 *2180*
2190
2211 *2192*
2187

(d) 2157
2178 2151
2192 2167

Cu—CO (ZSM-5)

(e) 2178
2177 2164
2183 *2179*
2206

Cu—CO ([AsF₆]⁻)
OC—Cu—CO
OC—Cu<CO CO

(f) 2178
2189 2168
2187 2173
2184

Cu—CO ([1-Et-CB₁₁F₁₁]⁻)

2200   2150   2100

wavenumber / cm⁻¹

Fig. 3-8   Schematic representations of Cu(CO)ₙ⁺ (n = 1-4) species and corresponding CO vibrational frequncies in (a) 96% H₂SO₄, (b) HSO₃F, (c) magic acid, HSO₃F·SbF₅ (1:1), (d) the ZSM-5 zeolite, (e) the salt of [AsF₆]⁻, and (f) the salt of [1-Et-CB₁₁F₁₁]⁻.   Full and dashed segments represent IR and Raman data, respectively.

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acidity of the solvent acid. The monocarbonyl $Cu(CO)^+$ is stabler than $Cu(CO)_2^+$ and $Cu(CO)_3^+$ in concentrated H_2SO_4 solution; the unstable polycarbonyls readily release CO ligands to form $Cu(CO)^+$ upon brief evacuation, but $Cu(CO)^+$ survives even after continuous evacuation over 24 hours. Also in HSO_3F, only $Cu(CO)^+$ survives upon evacuation, but in magic acid, $Cu(CO)_2^+$ remains unchanged after prolonged evacuation. Note that the lower stability was observed in the solid than in solution as the solid $[Cu(CO)][AsF_6]$ releases CO to form $CuAsF_6$ at 0 torr CO,[39] although $[AsF_6]^-$ is less nucleophilic than the above acid solutions.

3.3.2 Silver(I) Carbonyls

Manchot *et al.* first reported that Ag_2SO_4 reversibly absorbed CO in concentrated H_2SO_4 in the 1920's.[22,23] A CO/Ag stoichiometric ratio of 0.5 was achieved at 0 °C and 1 atm of CO. Souma *et al.* reported that Ag_2O in neat HSO_3F, $BF_3 \cdot H_2O$, and other strong acids absorbed up to 2 equivalents CO per equivalent Ag, the exact stoichiometry being dependent on temperature and pressure; only the dicarbonyl $Ag(CO)_2^+$ but not the monocarbonyl $Ag(CO)^+$ was considered in the strong acids for reasons that are not clear, which was assigned as the active species for the carbonylation of olefins, alcohols and saturated hydrocarbons.[24,47] Strauss and co-workers have isolated the $Ag(CO)^+$ and $Ag(CO)_2^+$ cations by the direct but reversible CO addition to the silver(I) salts of $[B(OTeF_5)_4]^-$, $[Zn(OTeF_5)_4]_2^-$, $[Nb(OTeF_5)_6]^-$, and $[Ti(OTeF_5)_6]_2^-$ under different CO pressures; single-crystals of $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$ were obtained from the very weakly coordinating solvent $1,1,2-C_2Cl_3F_3$, and their low temperature X-ray diffraction studies revealed nearly linear Ag-C-O arrays in both of the salts and a linear structure for $[Ag(CO)_2][B(OTeF_5)_4]$.[48-50] Furthermore, the direct but reversible CO addition to metal salts with weakly coordinating anions at high pressures of CO results in the formation of $[Ag(CO)_3][Nb(OTeF_5)_6]$.[51] Very recently, Willner and co-workers reported that the anion, $[B(CF_3)_4]^-$, is very weakly coordinating,

as demonstrated by the low equilibrium CO pressure over the $[Ag(CO)_n][B(CF_3)_4]$ ($n = 1, 2$) salts and the formation of $[Ag(CO)_n][B(CF_3)_4]$ ($n = 3, 4$) at higher CO pressures.[52] Here we report detailed spectroscopic investigation of the silver(I) carbonyl cations in a variety of strongly acidic solutions and show that in 96% H_2SO_4, only the monocarbonyl cation, $Ag(CO)^+$, is formed and in HSO_3F or magic acid, the tricarbonyl complex, $Ag(CO)_3^+$, is formed in addition to $Ag(CO)_n^+$ ($n = 1, 2$) at atmospheric pressure of CO.

Colorless solutions were obtained when Ag_2O was dissolved in 96% H_2SO_4, HSO_3F and magic acid, $HSO_3F \cdot SbF_5$ (1:1), under atmospheric pressure of CO. As shown in Fig. 3-9, with increasing acidity of the solution or decreasing temperature, the CO/Ag stoichiometry is increased: 0.21 at 22 °C and 0.62 at -10 °C in 96% H_2SO_4; 0.59 at 22 °C and 2.3 at -70 °C in HSO_3F; 2.1 at 22 °C and 2.5 at -30 °C in magic acid. It is noted that the CO/Ag stoichiometry is higher than 2.0, meaning that $Ag(CO)_3^+$ may be formed, in HSO_3F and magic acid at low temperatures under atmospheric pressure of CO. *In situ* infrared spectra at varying temperatures exhibit obvious evidence for the formation of the silver(I) carbonyl cations, $Ag(CO)_n^+$ ($n = 1, 2, 3$), under atmospheric pressure of CO (*vide infra*). The binding of CO to Ag^+ in these acids is reversible as observed in the solids or a 1,1,2-$C_2Cl_3F_3$ solution of $AgNb(OTeF_5)_6$.[50] The equilibra shown below are shifted to the right as the temperature decreases.

$$Ag_2O \longrightarrow Ag^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} Ag(CO)^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} Ag(CO)_2^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} Ag(CO)_3^+$$
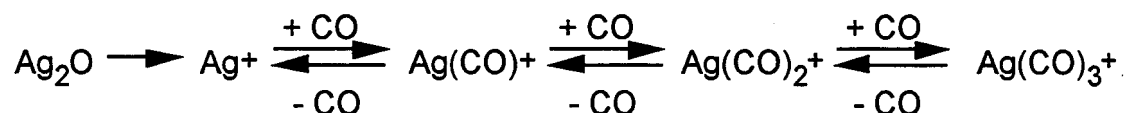
In 96% H_2SO_4 solution, a $\nu(CO)$ band was observed at 2186 cm^{-1} in the IR spectrum at room temperature, which grows in intensity at the same frequency with decreasing temperature and decreases in intensity with increasing temperature (Fig. 3-10). The corresponding Raman band is observed at 2186 cm^{-1} (Fig. 3-11a), which
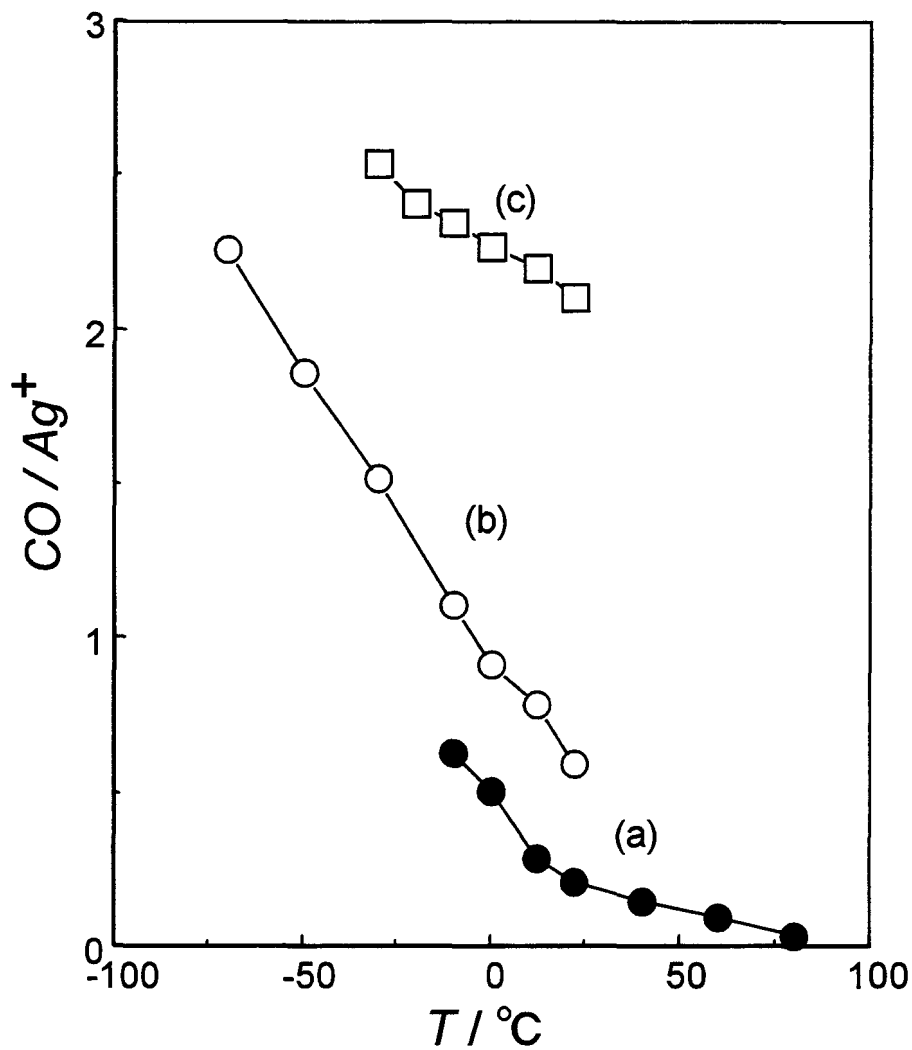
Fig. 3-9 CO uptake of Ag_2O dissolved in (a) 96% H_2SO_4, (b) HSO_3F and (c) magic acid, $HSO_3F \cdot SbF_5$ (1:1), at varying temperatures under atmospheric pressure of CO.
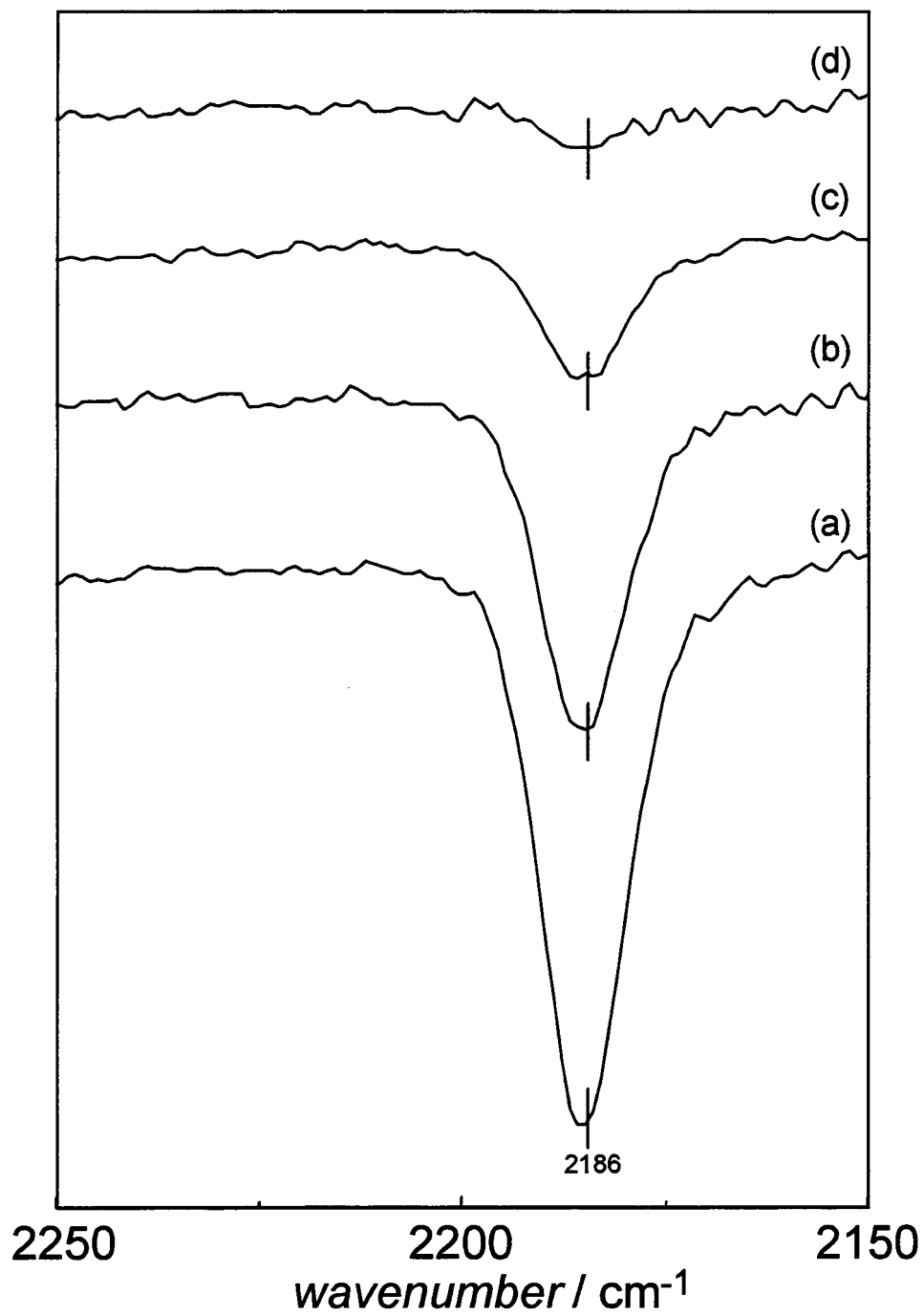
Fig. 3-10   IR spectra of $Ag(CO)^+$ in 96% H_2SO_4 at (a) -10 °C, (b) 12 °C, (c) 25 °C, and (d) 80 °C under atmospheric pressure of CO.

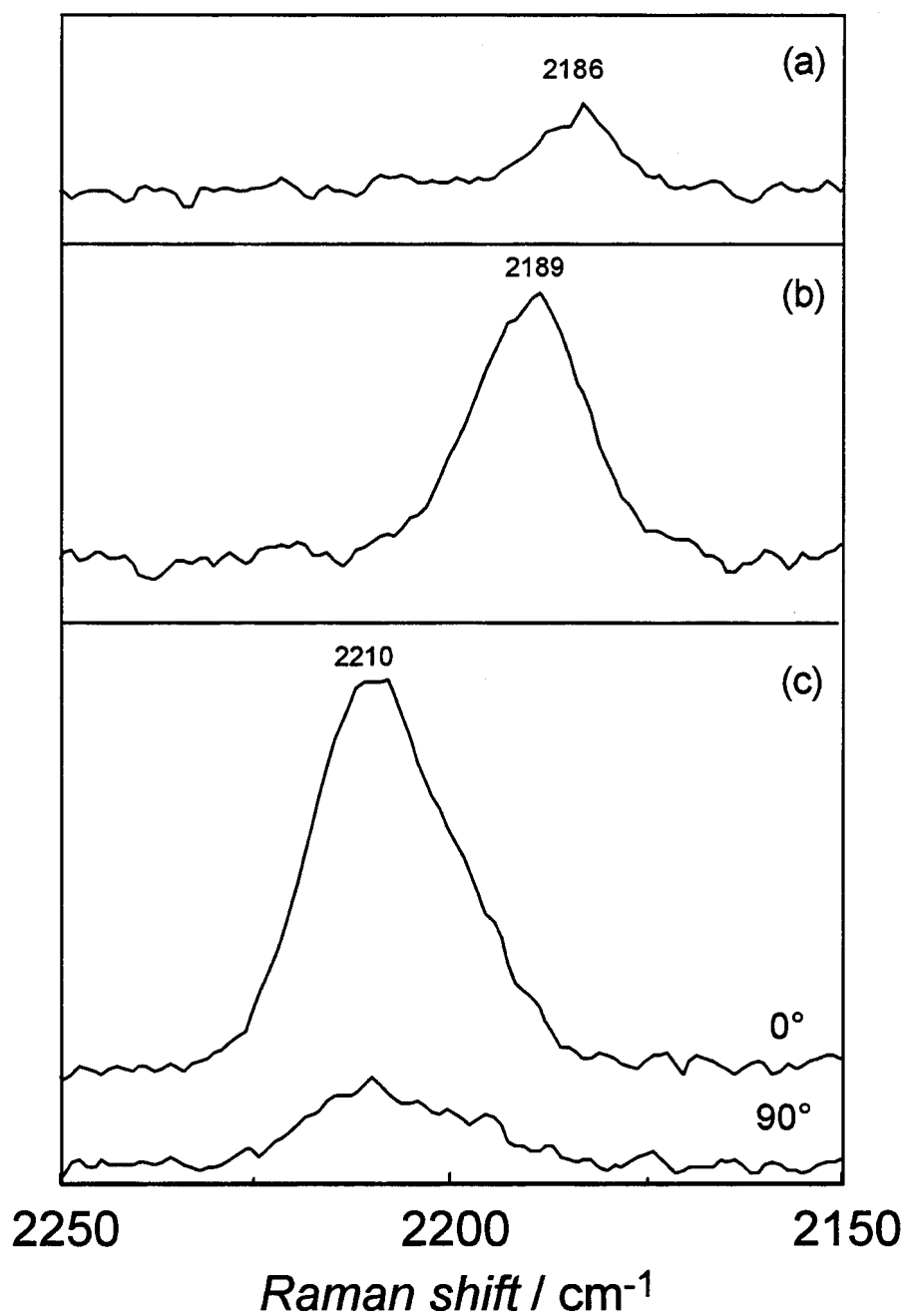Fig. 3-11　Raman spectra of silver(I) carbonyl cations in (a) 96% H_2SO_4, (b) HSO_3F, and (c) magic acid, $HSO_3F \cdot SbF_5$ (1:1), (upper with 0 ° polarization filter and bottom with 90 ° polarization filter) at room temperature under atmospheric pressure of CO.

should be attributed to the silver(I) monocarbonyl cation, $Ag(CO)^+$. Note that no $Ag(CO)_2^+$ species is formed in the 96% H_2SO_4 solution. Similarly to that in solid salts with weakly coordinating anions,[48-50] $Ag(CO)^+$ is unstable in contrast with the high stability of $Cu(CO)^+$ in strong acids; the CO ligand is readily removed under vacuum at -10 °C.

In HSO_3F, a $v(CO)$ IR band at 2189 cm^{-1} (Fig. 3-12a) with the corresponding Raman band at 2189 cm^{-1} (Fig. 3-11b) was observed for $Ag(CO)^+$ at room temperature. The IR band first shifts to higher energy with the convolution of the $v(CO)$ bands for $Ag(CO)^+$ and $Ag(CO)_2^+$ until the temperature is decreased to -60 °C where a $v(CO)$ band was observed at 2192 cm^{-1} for $Ag(CO)_2^+$ (Fig. 3-12b, 3-12c). At -60 °C, the $v(CO)$ band begins to shift to lower energy with decreasing temperature and reaches 2190 cm^{-1} at -80 °C (Fig. 3-12d, 3-12e). Our interpretation is that $Ag(CO)_3^+$, which exhibits a $v(CO)$ band lower than that for $Ag(CO)_2^+$ (2192 cm^{-1}), is formed below -60 °C, consistent with the CO uptake (Fig. 3-9b). At -80 °C, the band at 2190 cm^{-1} shifts to 2192 cm^{-1} with a brief evacuation (Fig. 3-12f), reflecting that one CO ligand can be readily removed from $Ag(CO)_3^+$ to form $Ag(CO)_2^+$, but the latter remains unchanged even after evacuation for 3 h.

Figure 3-13 shows IR spectra of silver(I) carbonyl cations in magic acid, $HSO_3F \cdot SbF_5$ (1:1), under atmospheric pressure of CO at temperatures that range from room temperature to -40 °C. At room temperature, a $v(CO)$ band was observed at 2203 cm^{-1} (Fig. 3-13a), and a strongly polarized Raman band was observed at 2210 cm^{-1} (Fig. 3-11c); the IR band is attributed to the asymmetric CO stretch (Σu^+ normal mode) and the Raman band to the symmetric CO stretch (Σg^+ normal mode) of the silver(I) dicarbonyl cation, $Ag(CO)_2^+$, which should have a linear structure ($D_{\infty h}$), as observed for solid $[Ag(CO)_2][B(OTeF_5)_4]$.[50] Note that the bent OC-Ag-CO species (C_{2v}) has been observed in zeolites.[53] One CO ligand is readily removed to form $Ag(CO)^+$ (2198 cm^{-1}) under vacuum (Fig. 3-13e), but a small amount of $Ag(CO)^+$ remains after an
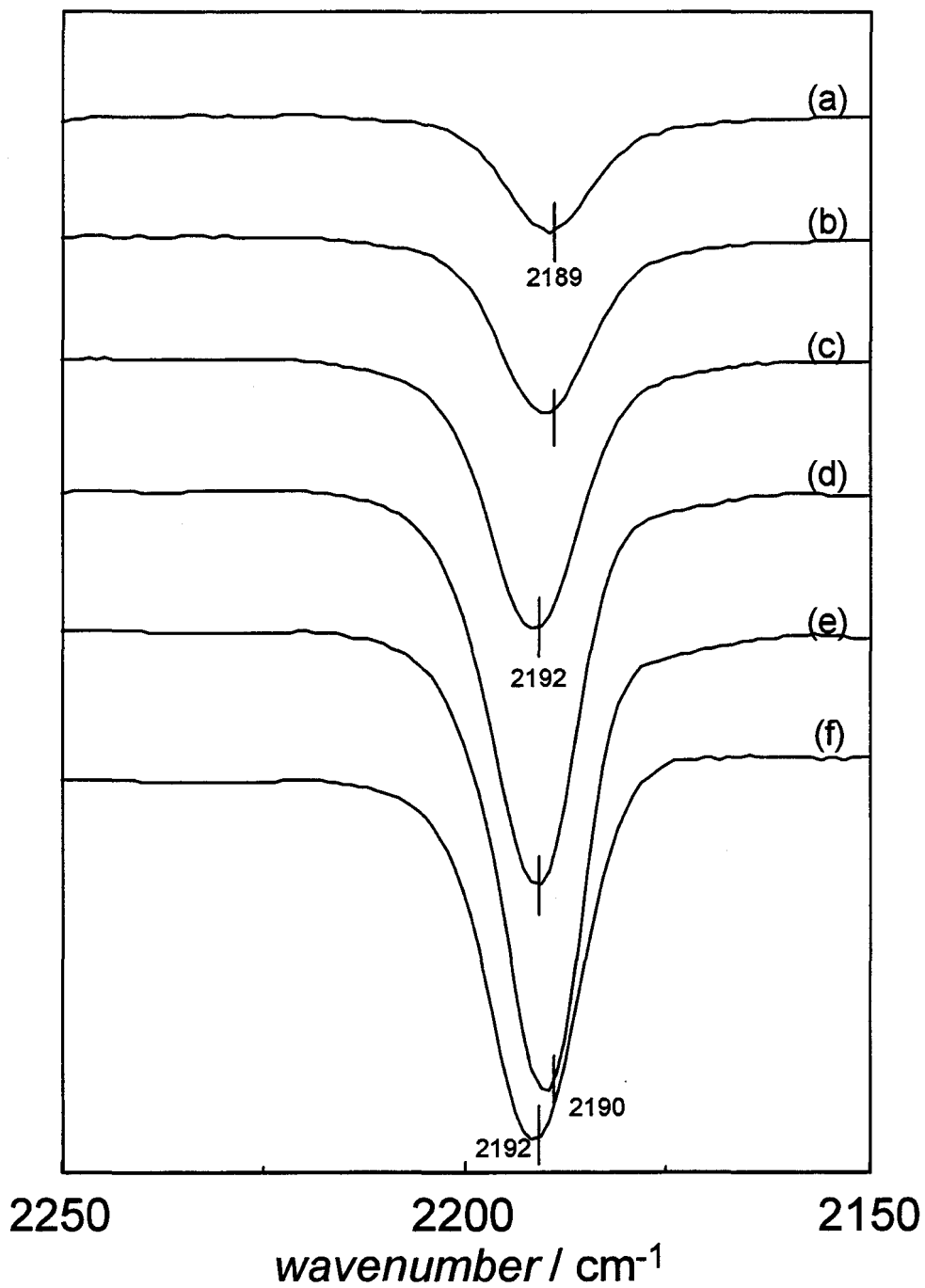
Fig. 3-12　IR spectra of silver(I) carbonyl cations in HSO₃F at (a) 23 °C, (b) 0 °C, (c) -60 °C, (d) -70 °C, (e) -80 °C and (f) after evacuating the sample at -80 °C for 3 h.
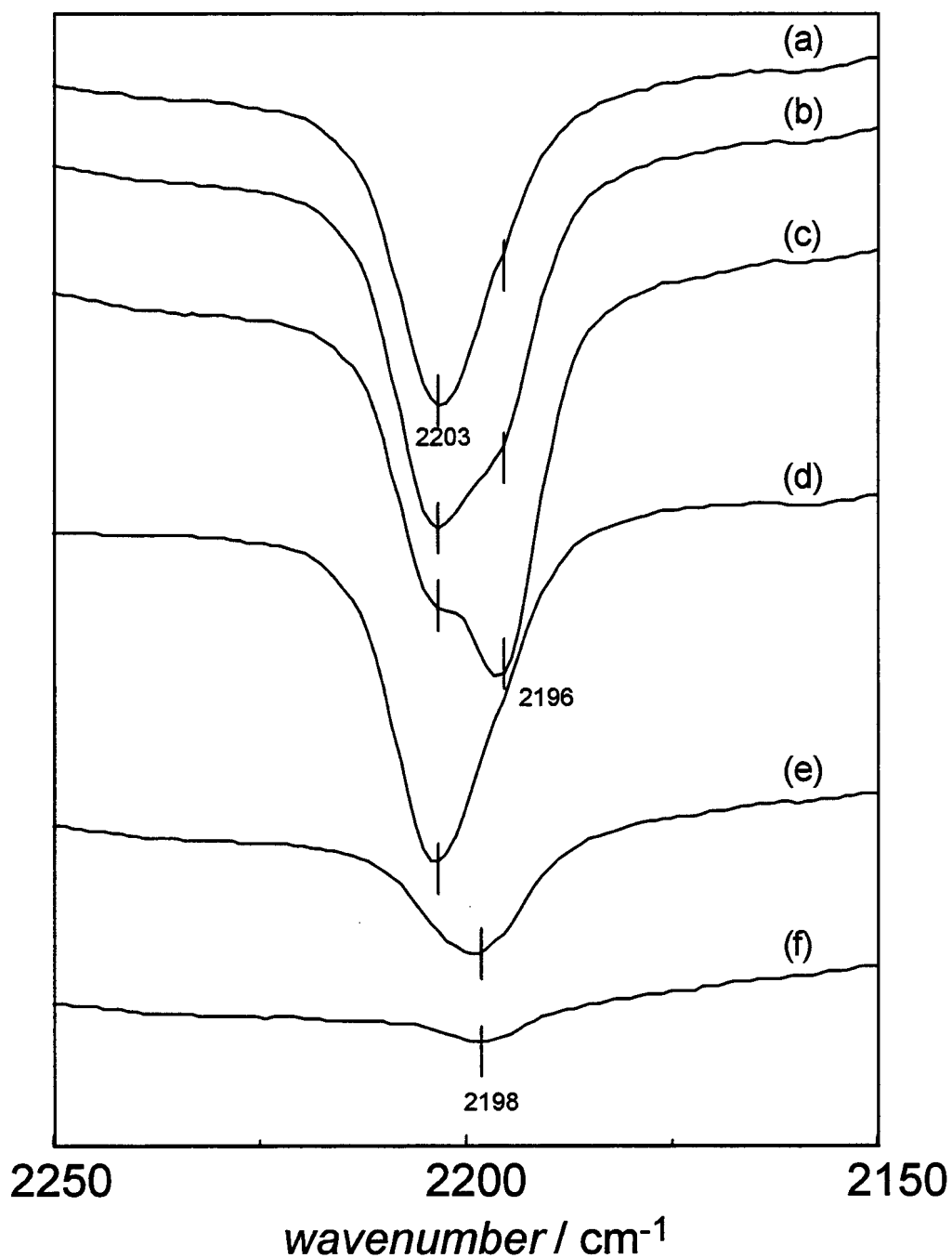
Fig. 3-13 IR spectra of silver(I) carbonyl cations in magic acid, $HSO_3F \cdot SbF_5$ (1:1), at (a) 21 °C, (b) -20 °C and (c) -40 °C under atmospheric pressure of CO, (d) after evacuating the sample at -40 °C for 15 min, and after evacuating the sample at 21 °C (e) for 15 min and (f) for 1h.

evacuation for 1 h at room temperature (Fig. 3-13f). With decreasing temperature, the IR absorption at 2203 cm^{-1} decreases, and a separate and distinct $v(CO)$ band, which is assigned to $Ag(CO)_3^+$, grows in intensity at 2196 cm^{-1} (Figs. 3-13b, 3-13c). At -40 °C, one CO ligand is readily removed from $Ag(CO)_3^+$ by brief evacuation to form $Ag(CO)_2^+$ (Fig. 3-13d), but $Ag(CO)_2^+$ survives even after an evacuation for 3 h. Almost the same results were obtained for AgF dissolved in magic acid.

All the IR and Raman $v(CO)$ values observed for $Ag(CO)_n^+$ ($n = 1$-3) are higher than 2143 cm^{-1}, the value for free CO, and the ^{13}C NMR chemical shifts shown by the silver(I) carbonyl cations are high-field-shifted from 184 ppm, the value for free CO. Single $v(CO)$ IR bands are observed for each complex, suggesting a linear structure ($D_{\infty h}$) for $Ag(CO)_2^+$ (Σu^+ normal mode) and a three-coordinate, trigonal-planar structure (D_{3h}) for $Ag(CO)_3^+$ (E' normal mode), as observed in $[Ag(CO)_n][Nb(OTeF_5)_6]$ ($n = 1$-3),[48-51] and in rare-gas matrices[54] (Fig. 3-14). Only for $Ag(CO)_2^+$ in zeolites is the bent structure (C_{2v}) observed.[53] It appears that, in HSO_3F or magic acid, the stability of the complexes is in the order of $Ag(CO)^+ > Ag(CO)_2^+ > Ag(CO)_3^+$, whereas a theoretical calculation (MP2 level) predicted that $Ag(CO)_2^+$ is the stablest.[55] With decreasing acidity of the solution, the $v(CO)$ bands for each of the silver(I) carbonyl cations shift to low energy. In HSO_3F or magic acid, the $v(CO)$ bands are in the order of $Ag(CO)_2^+ > Ag(CO)^+ > Ag(CO)_3^+$. In contrast, the $v(CO)$ bands for $[Ag(CO)_n][Nb(OTeF_5)_6]$ are 2208, 2198, and 2192 cm^{-1} for $n = 1$, 2 and 3, respectively, in the order of $Ag(CO)^+ > Ag(CO)_2^+ > Ag(CO)_3^+$.[48-51] The effects from the solvents (although probably being very weakly coordinating) seem to be important with respect to the observations. Armentrout et al. have reported metal carbonyl bond energies for the gas phase complex ions $Ag(CO)_n^+$ ($n = 1$-4): $(CO)_xAg^+$-CO bond energies at 0 K were found to be 21(1), 26(1), 13(2) and 11(4) kcal mol^{-1} for $x = 0$, 1, 2 and 3, respectively.[56] This finding predicts that the bond energy for $Ag(CO)_4^+$ may be close to that for $Ag(CO)_3^+$, which has been recently verified by the formation of
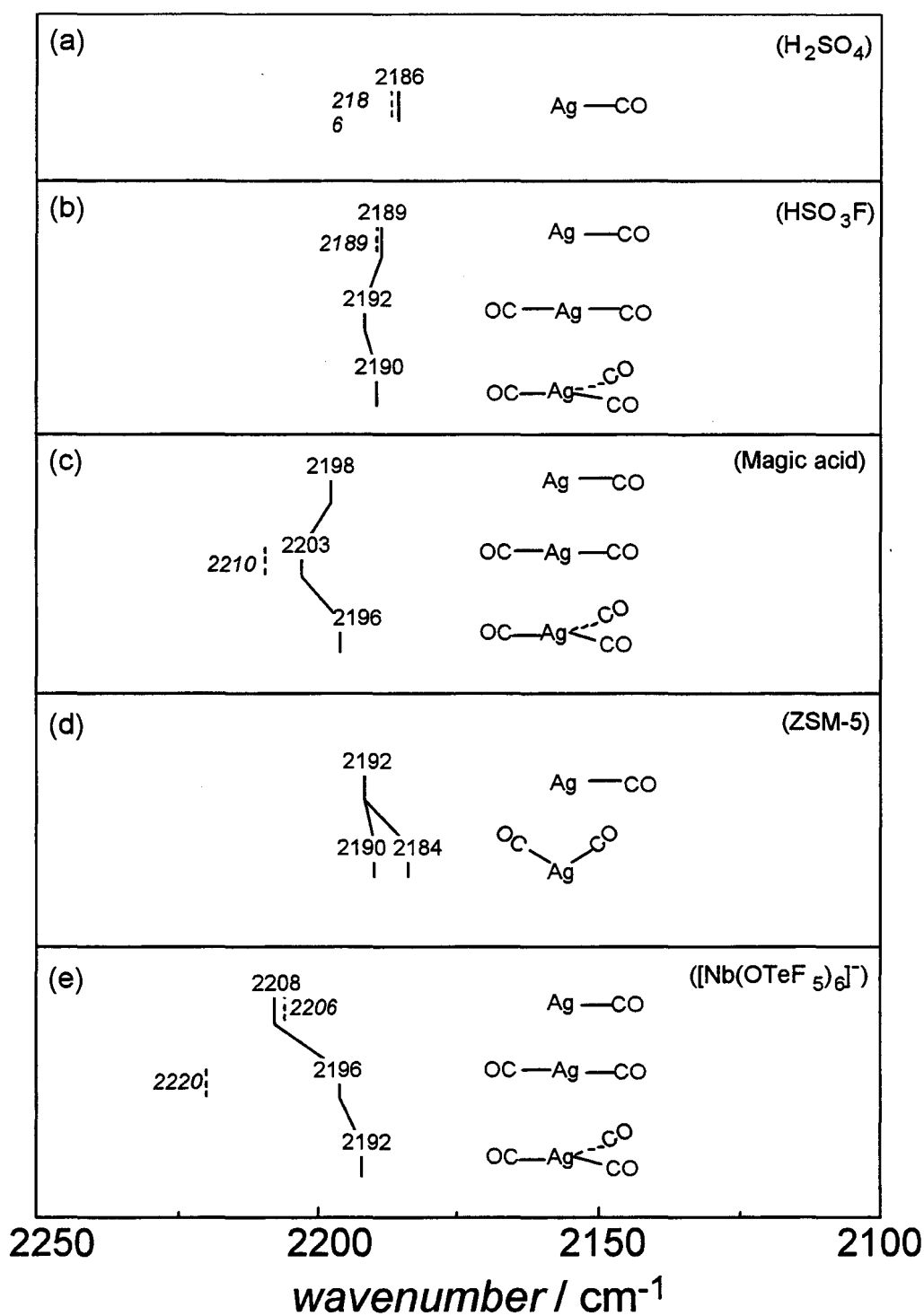
(a)   2186   (H$_2$SO$_4$)
2186   Ag —CO

(b)   2189   (HSO$_3$F)
2189   Ag —CO
2192   OC —Ag —CO
2190   OC—Ag$\stackrel{CO}{CO}$

(c)   2198   (Magic acid)
Ag —CO
2210 2203   OC—Ag —CO
2196   OC—Ag$\stackrel{CO}{CO}$

(d)   2192   (ZSM-5)
Ag —CO
2190 2184   OC⌄Ag⌄CO

(e)   2208   ([Nb(OTeF$_5$)$_6$]$^-$)
2206   Ag —CO
2196   OC —Ag —CO
2220   2192   OC—Ag$\stackrel{CO}{CO}$

2250   2200   2150   2100

wavenumber / cm^{-1}

Fig. 3-14   Schematic representations of Ag(CO)$_n^+$ (n = 1-3) species and corresponding CO vibrational frequencies in (a) 96% H$_2$SO$_4$, (b) HSO$_3$F, (c) magic acid, HSO$_3$F · SbF$_5$ (1:1), (d) the ZSM-5 zeolite, and (e) the salt of [Nb(OTeF$_5$)$_6$]$^-$. Full and dashed segments represent IR and Raman data, respectively.

$[Ag(CO)_n][B(CF_3)_4]$ ($n = 3$, 4) at higher CO pressure.[52]

3.3.3. Gold(I) Carbonyls

A small number of carbonyl derivatives of gold have been synthesized to date. For more than 65 years, the only isolable gold(I) carbonyl was Au(CO)Cl, first prepared by Manchot and Gall in 1925.[57] Willner et $al.$ reported the isolation of the gold(I) carbonyl cation, $Au(CO)_2^+$, using Lewis superacidic media such as SbF_5; its discovery resulted as an accident from the attempts to prepare the $[HCO]^+$ ion by protonation of CO in the conjugated superacid $HSO_3F-Au(SO_3F)_3$.[58,59] Strauss and co-workers determined that a new IR band at 2212 cm^{-1}, assigned to $[Au(CO)_3][Sb_2F_{11}]$, appears when the dicarbonyl complex, $[Au(CO)_2][Sb_2F_{11}]$, is exposed to 100 atm CO pressure.[60]

We found a facile synthetic method for gold(I) carbonyls suitable for the catalytic carbonylation of olefins and alcohols; the direct reductive carbonylation of gold(III) oxide, Au_2O_3, with CO leads to the formation of $Au(CO)_n^+$ ($n = 1$, 2).[61] Alternative routes to the formation of the gold(I) carbonyl cations in H_2SO_4 are the oxidation carbonylation of metallic gold with SO_3 as an oxidizing agent and the solvolysis and carbonylation of AuOH. As shown in Fig. 3-15a, with decreasing temperature, the CO/Au stoichiometry is increased: 1.7 at 23 °C and 2.0 at -10 °C in 96% H_2SO_4. At room temperature, an IR $\nu(CO)$ band at 2194 cm^{-1} and the corresponding Raman band at 2196 cm^{-1} were observed (Figs. 3-15b, 3-15c), which are attributed to $Au(CO)^+$. The mutually exclusive IR and Raman $\nu(CO)$ bands at 2208 and 2247 cm^{-1} indicate a linear coordination ($D_{\infty h}$) for $Au(CO)_2^+$, the former due to the asymmetric CO stretch (Σu^+ normal mode) and the latter due to the symmetric CO stretch (Σg^+ normal mode). The linear structure has been observed in $[Au(CO)_2][Sb_2F_{11}]$[59] and $[Au(CO)_2]_2[SbF_6][Sb_2F_{11}]$.[62] $Au(CO)^+$ and $Au(CO)_2^+$ coexist in concentrated H_2SO_4 solution. $Au(CO)^+$ is stabler than $Au(CO)_2^+$; the unstable $Au(CO)_2^+$ readily releases one CO ligand to form $Au(CO)^+$ upon brief evacuation
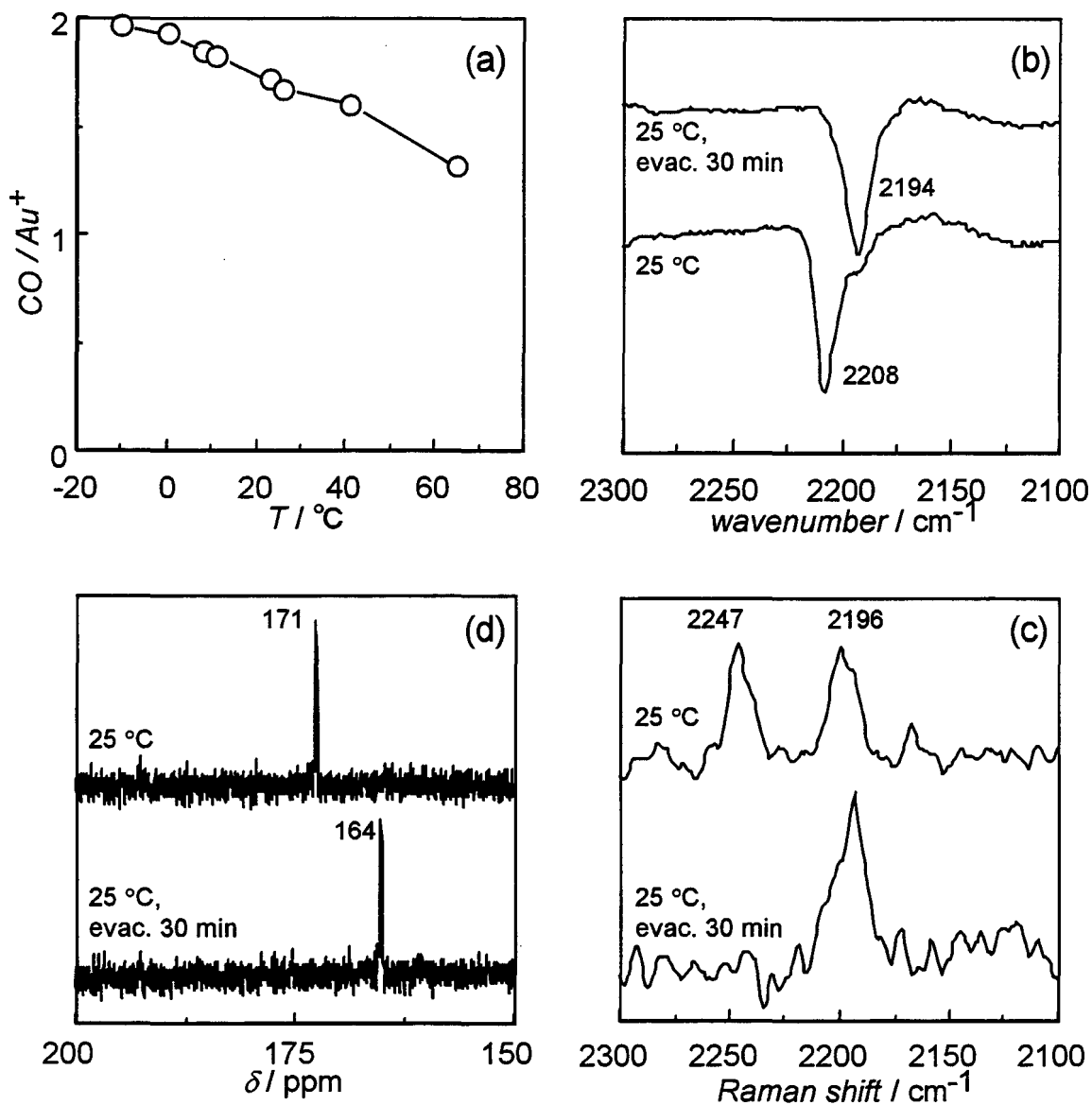
Fig. 3-15 (a) CO uptake of Au_2O_3, and (b, bottom) IR, (c, upper) Raman, and (d, upper) ^{13}C NMR spectra of $Au(CO)_n^+$ (n = 1, 2) in 96% H_2SO_4 at room temperature under atmospheric pressure of CO (natural abundance), and (b, upper) IR, (c, bottom) Raman, and (d, bottom) ^{13}C NMR spectra after evacuating the sample at room temperature for 30 min.

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(Figs. 3-15b, 3-15c), while $Au(CO)^+$ remains unchanged even after a continuous evacuation over 24 hours. A resonance at 171 ppm appears in the ^{13}C NMR spectrum at room temperature (Fig. 3-15d). After removing the ambient CO by evacuation, the solution gives a single peak at 164 ppm, which is due to $Au(CO)^+$. An equilibrium process between $Au(CO)^+$ and $Au(CO)_2^+$, which undergoes rapid CO exchange on the NMR time scale, would account for the single resonance. The chemical shift of $Au(CO)_2^+$ can be calculated to be 175 ppm by taking into consideration the CO/Au ratio.

$$Au_2O_3 \xrightarrow{+\ CO} Au^+ \xrightarrow{+\ CO} Au(CO)^+ \underset{-\ CO}{\overset{+\ CO}{\rightleftharpoons}} Au(CO)_2^+$$
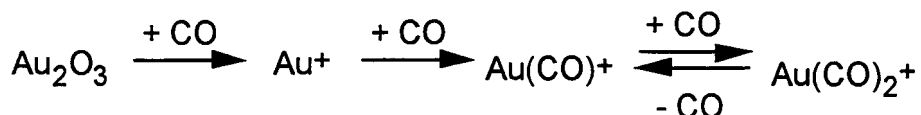
In HSO_3F, the CO/Au stoichiometry reaches 2.0 at room temperature and remains the same value at lower temperatures. An IR $\nu(CO)$ band at 2211 cm^{-1} (Fig. 3-16a) and a strongly polarized Raman band at 2249 cm^{-1} (Figs. 3-16d, 3-16e) were observed. These mutually exclusive IR and Raman $\nu(CO)$ bands indicate a linear coordination ($D_{\infty h}$) for $Au(CO)_2^+$, the former due to the asymmetric CO stretch (Σu^+ normal mode) and the latter due to the symmetric CO stretch (Σg^+ normal mode). $Au(CO)_2^+$ is stabler in HSO_3F than in concentrated H_2SO_4; it needs more than 14 h to remove one CO ligand to form $Au(CO)^+$, which shows an IR $\nu(CO)$ band at 2198 cm^{-1} (Fig. 3-16c). In the ^{13}C NMR spectrum at room temperature, a resonance at 174 ppm is observed for $Au(CO)_2^+$, in agreement with the previous observation.[59] After an evacuation for 14 h, the solution gives a single peak at 169 ppm due to a mixture of $Au(CO)^+$ and $Au(CO)_2^+$, which undergoes rapid CO exchange on the NMR time scale.

In magic acid, $HSO_3F \cdot SbF_5$ (1:1), the CO/Au stoichiometry reaches 2.0 at room temperature and remains the same value at lower temperatures. An IR $\nu(CO)$ band at 2216 cm^{-1} (Fig. 3-17a) and a strongly polarized Raman band at 2252 cm^{-1} (Figs. 3-17d, 3-17e) were observed. As observed in HSO_3F, the mutually exclusive IR and Raman
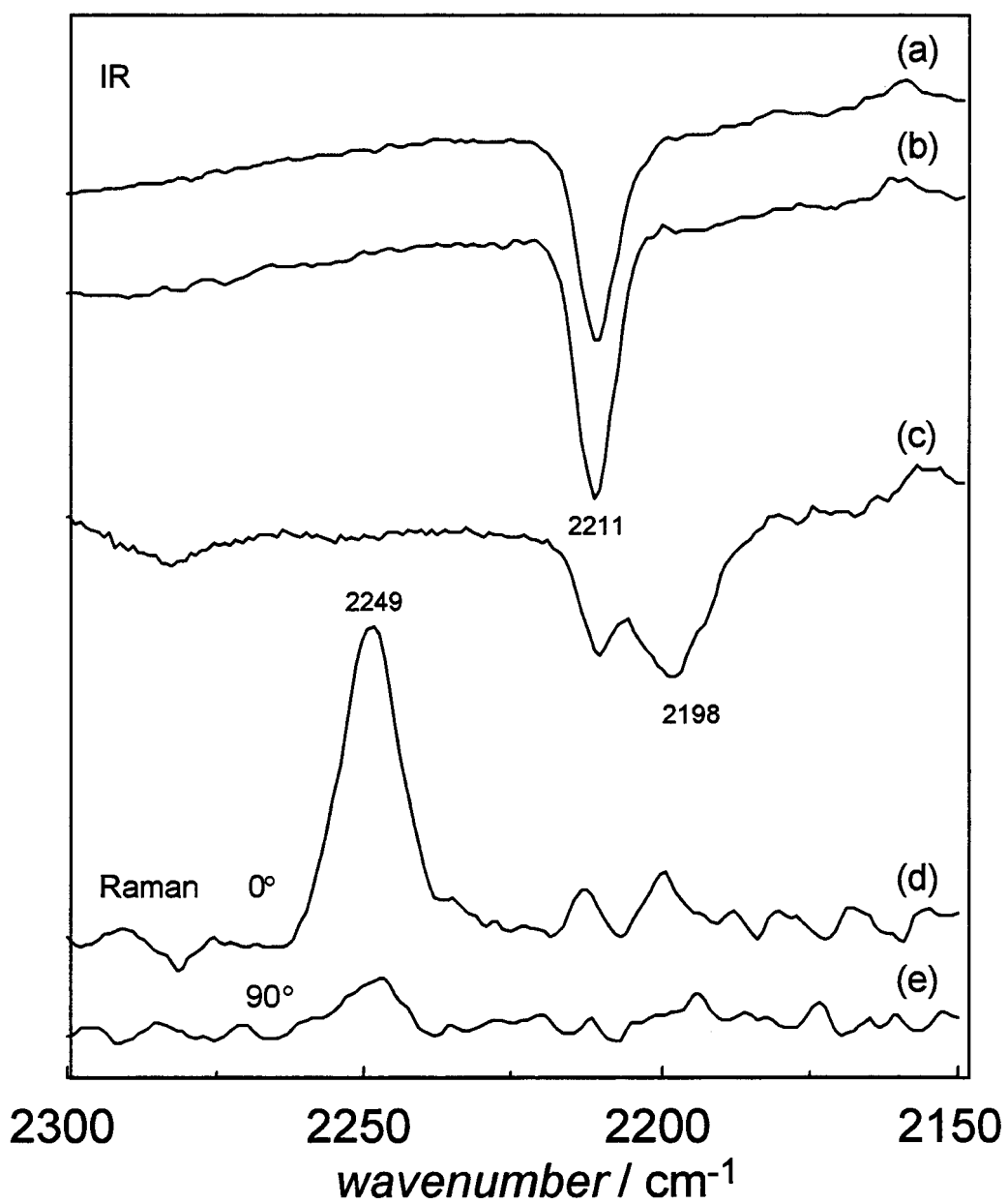
Fig. 3-16   IR spectra of gold(I) carbonyl cations in HSO₃F at (a) 25 °C and (b) -70 °C under atmospheric pressure of CO, and (c) after evacuating at room temperature for 14 h, and Raman spectra of the sample a with (d) 0 ° and (e) 90 ° polarization filters.
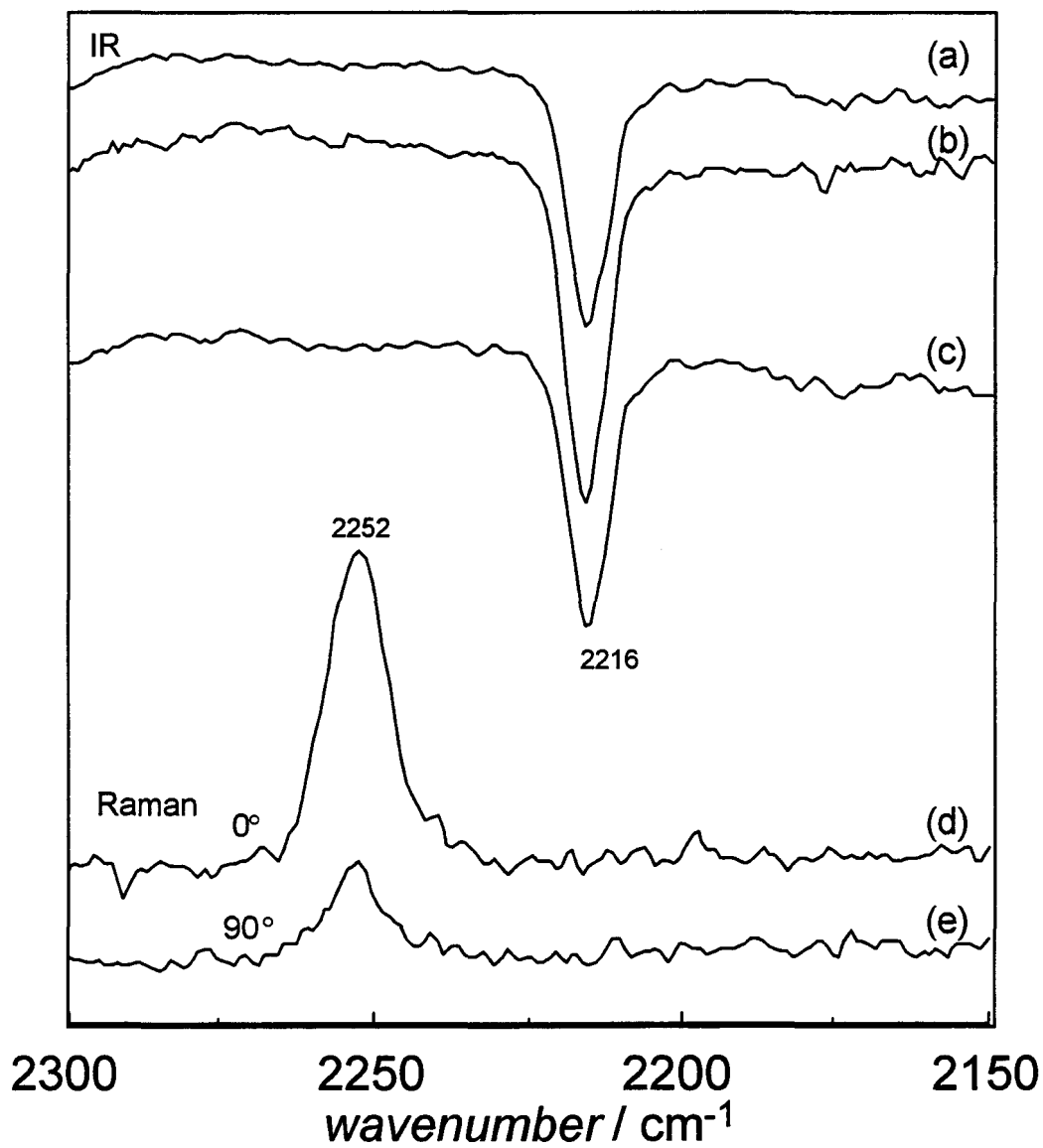
Fig. 3-17   IR spectra of gold(I) carbonyl cations in magic acid, $HSO_3F \cdot SbF_5$ (1:1), at (a) 25 °C and (b) -23 °C under atmospheric pressure of CO, and (c) after evacuating at room temperature for 13 h, and Raman spectra of the sample a with (d) 0 ° and (e) 90 ° polarization filters.

$v(CO)$ bands indicate a linear coordination $(D_{\infty h})$ for $Au(CO)_2^+$, the former due to the asymmetric CO stretch (Σu^+ normal mode) and the latter due to the symmetric CO stretch (Σg^+ normal mode). $Au(CO)_2^+$ is stabler in magic acid than in HSO_3F; it remains unchanged even after an evacuation of 13 h (Fig. 3-17c). In the ^{13}C NMR spectrum at room temperature, a resonance at 172 ppm is observed for $Au(CO)_2^+$.

All the IR and Raman $v(CO)$ values for $Au(CO)_n^+$ ($n = 1, 2$) are much higher than 2143 cm^{-1}, the value for free CO. The ^{13}C NMR chemical shifts shown by the gold(I) carbonyl cations are high-field-shifted from 184 ppm, the value for free CO. It is noted that, with increasing acidity of the solvent $v(CO)$ shifts to a higher frequency and $\delta(^{13}C)$ shifts to a higher field. The structure for $Au(CO)_2^+$ in all the three solvents is linear $(D_{\infty h})$ (Fig. 3-18).

3.3.4 Comparison of Copper(I), Silver(I), and Gold(I) Carbonyls

It is very interesting that we could not observe $Au(CO)_3^+$ and $Au(CO)_4^+$ although $Cu(CO)_n^+$ ($n = 1$-4) and $Ag(CO)_n^+$ ($n = 1$-3) have been observed in strongly acidic solutions at atmospheric CO pressure, and the mono- and di- carbonyl cations of gold(I), $Au(CO)_n^+$ ($n = 1, 2$), are stabler than those of copper(I) and silver(I). These findings are in agreement with the properties of the metal-carbon bondings previously investigated by both experimental and theoretical methods. Armentrout and co-workers estimated metal-carbonyl bond energies for the gas phase complex ions $Cu(CO)_n^+$ and $Ag(CO)_n^+$ ($n = 1$-4): $(CO)_xCu^+CO$ bond energies at 0 K of 36, 41, 18, and 13 kcal/mol for $x = 0, 1, 2$, and 3, respectively; $(CO)_xAg^+CO$ bond energies at 0 K of 21, 26, 13, and 11 kcal/mol for $x = 0, 1, 2$, and 3, respectively.[56] Veldkamp and Frenking calculated (MP2 level of theory) $(CO)_xAg^+CO$ bond energies of 21, 27, and 12 kcal/mol for $x = 0, 1$, and 2, respectively; $(CO)_xAu^+CO$ bond energies of 45, 50, and 9 kcal/mol for $x = 0, 1$, and 2, respectively.[55] Zhou and Andrews reported calculations (B3LYP) of dissociation energies of $(CO)_xCu^+CO$ of 34.8, 35.6, 20.4, and 17.4 kcal/mol
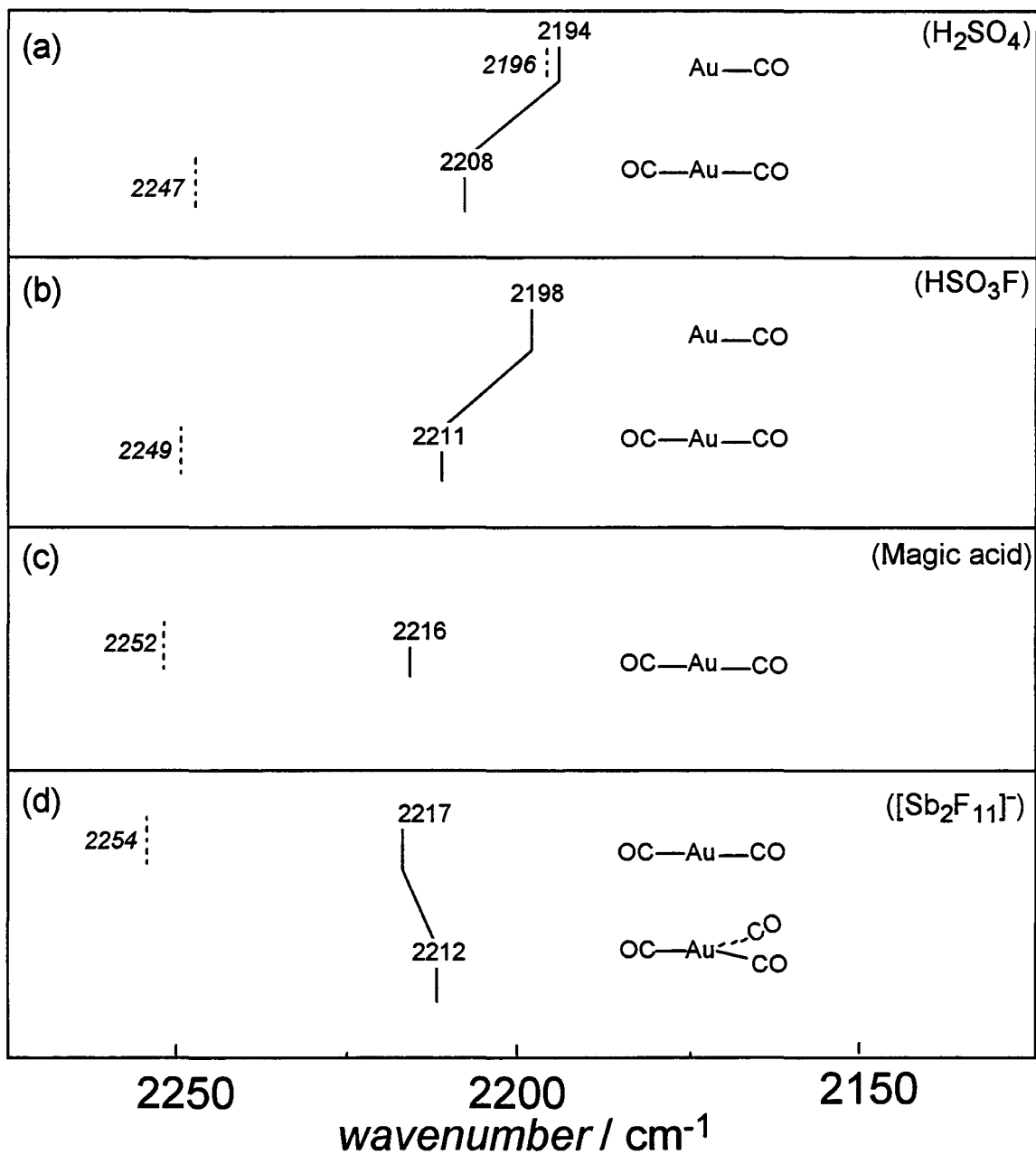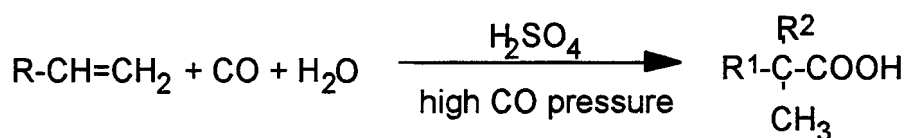
Fig. 3-18   Schematic representations of $Au(CO)_n^+$ (n = 1-3) species and corresponding CO vibrational frequencies in (a) 96% H_2SO_4, (b) HSO_3F, (c) magic acid, $HSO_3F \cdot SbF_5$ (1:1), and (d) the salt of $[Sb_2F_{11}]^-$. Full and dashed segments represent IR and Raman data, respectively.

for x = 0, 1, 2, and 3, respectively.[40]   These results predicted that the stability of $M(CO)^+$ and $M(CO)_2^+$ is in the order of Ag < Cu < Au, but the stability of $M(CO)_3^+$ is in the order of Au < Ag < Cu, in good agreement with the findings of the present work. The order for M-CO bond energies of $M(CO)_2^+$ has been explained by Strauss *et al.* using the s-d_σ energy gaps (corresponding to the lowest energy $d^9s^1 \leftarrow d^{10}$ electronic transition energies for the gas-phase M^+ cation; 2.7, 4.9, and 1.9 eV, respectively, for Cu, Ag, and Au) and d-subshell energy levels (corresponding to the second ionization energies; 20.3, 21.5, and 20.5 eV, respectively, for Cu, Ag, and Au).[60]   For two-coordinate d^{10} metal complexes, sd_σ mixing results in a shift of electron density from the z axis (the metal-ligand axis) to the xy plane and decreases the σ-repulsion which allows for shorter, stronger metal-ligand σ-bonds.   Among the three metals, Au(I) has the smallest s-d_σ energy gap, and therefore the Au-C σ-bonds in $Au(CO)_2^+$ are particularly strong.   The reason why the third M-CO bond is so weak for gold may be that the d-orbital participation in M-C σ-bonding is so effective in $Au(CO)_2^+$ that bending the molecular framework is more destabilizing than for $Cu(CO)_2^+$ or $Ag(CO)_2^+$, as well observed for Au(I) which has a much reduced tendency to form three-coordinate complexes relative to Ag(I) and Cu(I).[60]

3.3.5   Application of Copper(I), Silver(I) and Gold(I) Carbonyl Cations to Carbonylation of Olefins and Alcohols

The Koch reaction has been well-known for the synthesis of tertiary carboxylic acids from olefins and water, or alcohols, with carbon monoxide in strong acids.[7,63] This reaction occurs at temperatures between -20 to 80 °C and pressures up to 100 atm. Generally, H_2SO_4, H_3PO_4, HF and $BF_3 \cdot H_2O$ are employed as catalysts and solvents.   In concentrated H_2SO_4, for example, the olefin is protonated, or the alcohol is protonated and dehydrated, to form a carbenium ion intermediate, which isomerizes to tertiary carbenium ions via the Wagner-Meerwein rearrangement prior to the carbonylation.[64,65]
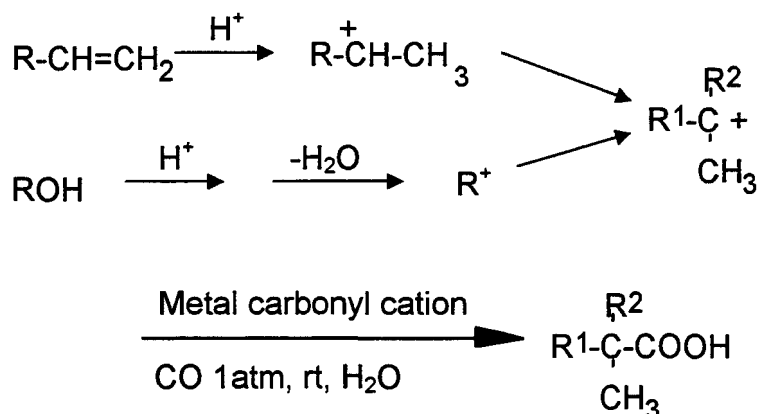
The carbonylation of the carbenium ions leads to the formation of acylium cations, which react with water to give tertiary carboxylic acids or with alcohol to give the corresponding esters. However, olefins are converted to carboxylic acids in a yield lower than 10% under atmospheric CO pressure owing to the presence of olefin oligomerization as a competitive reaction. To achieve a high conversion to the corresponding carboxylic acids, a high CO pressure is needed. Haaf developed an alternative pressure-free variant with formic acid as the CO source.[66, 67] However, this method has been restricted to the laboratory due to the high cost of formic acid.

$$R\text{-}CH{=}CH_2 + CO + H_2O \xrightarrow[\text{high CO pressure}]{H_2SO_4} R^1\text{-}\underset{CH_3}{\overset{R^2}{\underset{|}{\overset{|}{C}}}}\text{-}COOH$$

The previous work by Souma et $al.$ showed that copper(I) and silver(I) carbonyls in strong acids catalyze the carbonylation of olefins and alcohols to give tertiary carboxylic acids in high yields at room temperature and atmospheric pressure.[25-28] The polycarbonyl cations, $Cu(CO)_3^+$ and $Ag(CO)_2^+$, were assigned as the active species, respectively, in the carbonylation of olefins and alcohols in concentrated H_2SO_4.[47] The present work reveals that when the copper(I) compounds are solved under CO atmosphere in concentrated H_2SO_4, $Cu(CO)_2^+$ is mainly formed with $Cu(CO)_3^+$ as the minor species, and when the silver(I) compounds are dissolved under CO atmosphere in concentrated H_2SO_4, only $Ag(CO)^+$ (no $Ag(CO)_2^+$) is formed. Therefore, $Cu(CO)_2^+$ (and $Cu(CO)_3^+$ as a minor species) and $Ag(CO)^+$ should be assigned as the active species, respectively, for the copper(I) and silver(I) carbonyl cation-catalyzed carbonylation of olefins and alcohols.

Very recently, Xu and co-workers reported that the gold(I) carbonyl cations serve as an excellent catalyst, with which olefins readily react with CO to produce tertiary carboxylic acids in high yields at ambient CO pressure and temperature. $Au(CO)_2^+$ has been suggested to be the active species.[61] It is the first application of

gold(I) carbonyls to organic syntheses; very few gold catalysts have been reported so far. Furthermore, it has been found that the palladium(I), rhodium(I) and platinum(I) carbonyl cations are excellent catalysts for the carbonylation of olefins and alcohols, for which $Pd_2(CO)_2{}^{2+}{}_{(solv)}$, $Rh(CO)_4{}^{+}$ and $[\{Pt(CO)_3\}_2]^{2+}$ are the active species, respectively.[68-73]

$$R\text{-}CH\text{=}CH_2 \xrightarrow{H^+} R\text{-}\overset{+}{C}H\text{-}CH_3 \searrow$$

$$ROH \xrightarrow{H^+} \xrightarrow{-H_2O} R^+ \nearrow \quad \underset{CH_3}{R^1\text{-}\overset{R^2}{\underset{|}{C}}} +$$

$$\xrightarrow[\text{CO 1atm, rt, } H_2O]{\text{Metal carbonyl cation}} \quad \underset{CH_3}{R^1\text{-}\overset{R^2}{\underset{|}{C}}\text{-}COOH}$$

A CO-carrier model was originally proposed for the reaction mechanism, in which the unstable metal polycarbonyl cations were considered to act merely as a *CO carrier* which transports CO from the gas phase to the H_2SO_4 solution, resulting in a high CO concentration in the solution and consequently accelerating the carbonylation of olefins and alcohols via the pathway of the original Koch reaction.[25] However, in contrast with the Cu(I), Ag(I), Au(I) and Rh(I) carbonyl cations, which require only a brief evacuation to remove the reversible CO ligands as described above, $Pd_2(CO)_2{}^{2+}{}_{(solv)}$ and $[\{Pt(CO)_3\}_2]^{2+}$, from which a prolonged evacuation (*ca.* one day) is required to remove the CO ligands,[68,73] are so stable that they cannot act as a mere CO carrier to transport CO from the gas phase and readily release the CO ligands to the H_2SO_4 solution. In addition, the conversions of olefins and alcohols to tertiary carboxylic acids by Pt(I) and Pd(I) carbonyl catalysts are comparable to those by the Cu(I), Ag(I), Au(I), and Rh(I) carbonyl catalysts. Furthermore, it has recently been found that $[Ir_4(CO)_{12}H_2]^{2+}$ holding tightly bound CO ligands also exhibits catalytic activity for the carbonylation of olefins in strong acids at room temperature and

atmospheric CO pressure.[74]   These observations conflict with the *CO carrier* model.

A reaction mechanism involving an olefin-metal-polycarbonyl intermediate has been proposed for the metal carbonyl cation-catalyzed carbonylation of olefins and alcohols in strong acids.[17,61]

As described above, in concentrated H_2SO_4 only silver(I) monocarbonyl, $Ag(CO)^+$, is observed and therefore assigned as the active species for the carbonylation of olefins and alcohols, whereas polycarbonyl cations are observed for copper(I) and gold(I).   This finding suggests that an olefin-metal-monocarbonyl (not only olefin-metal-polycarbonyl[9] may also be an intermediate involved in the metal carbonyl cation-catalyzed carbonylation, leading to a modification of the reaction mechanism as follows (Scheme 3-1).   When the olefin is added to the strong acid H_2SO_4, it forms a carbenium ion, which isomerizes to the carbenium ion **2**.   An equilibrium process exists between the carbenium ion **2** and the isomerized olefin **3**, a part of which oligomerizes to give higher weight molecules in a competitive reaction.   **3** coordinates to M to form the π complex **4**.   As described above, for Cu, $n = 2, 3$; for Ag, $n = 1$; and for Au, $n = 2$.   In the complex **4**, because the tertiary and primary carbons are unsymmetrically bridged, a relatively positive charge should be located at the tertiary carbon.   CO migrates to the partially positively charged tertiary carbon via the intermediate **5**, which transforms into the acylium cation **6**.   The acylium cation **6** consequently reacts with water to give the carboxylic acid **7**.   Such an olefin-metal-carbonyl intermediate has not been directly observed but similar organometallic ions such as ethylene-, norbornylene- and cyclohexene- mercurium ions, which were prepared from Hg^{2+}, the isoelectronic ion of Au^+, have been observed by Olah *et al.* in superacidic media.[75-78]   Theoretical studies (B3LYP level of theory) have supported the reaction mechanism involving the olefin-metal-carbonyl intermediate.[79]
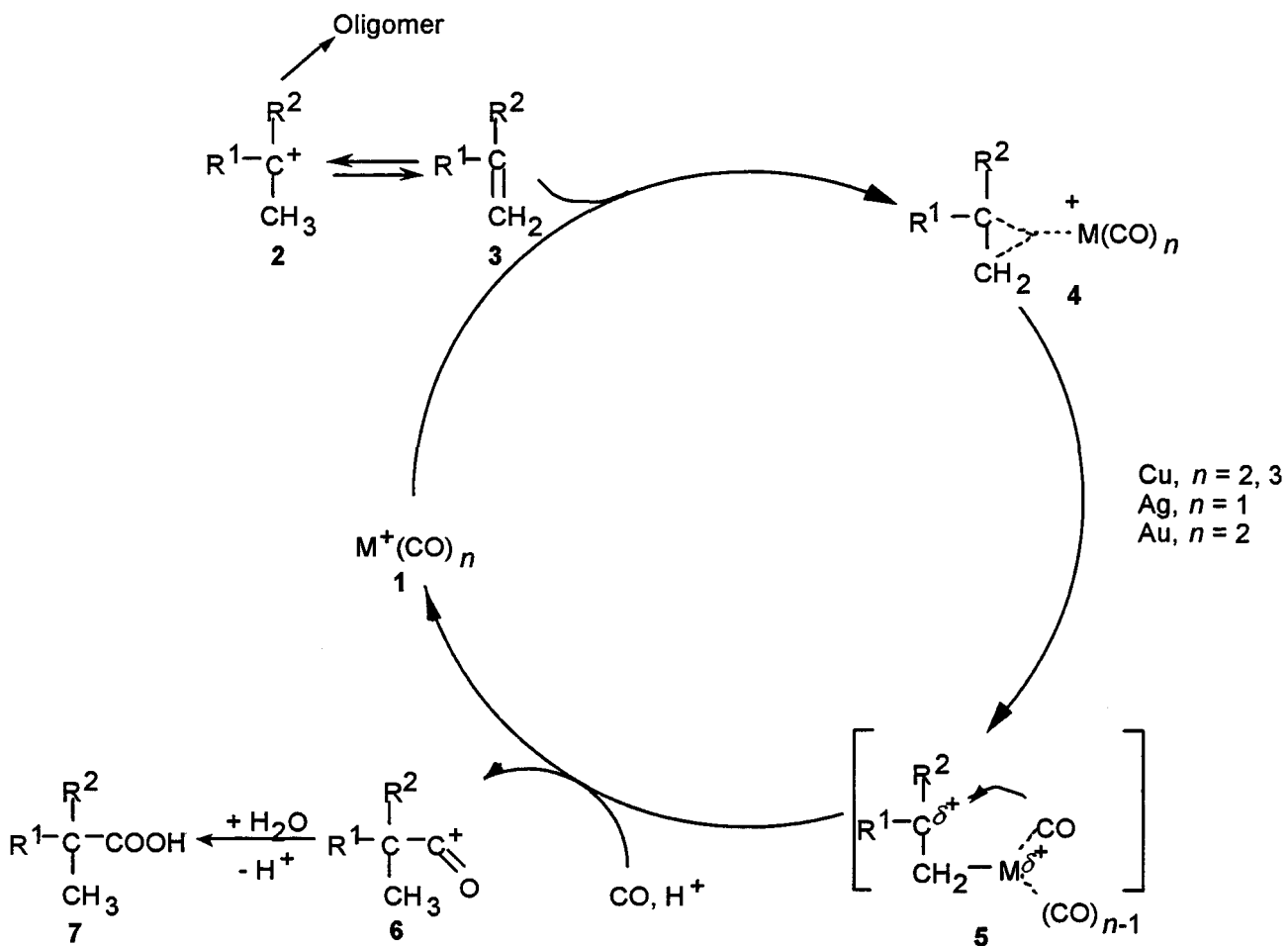
Scheme 3-1

3.4 Conclusions

Detailed IR, Raman, and NMR spectroscopic characterization has been carried out on the group 11 metal carbonyl cations, $Cu(CO)_n^+$ ($n = 1, 2, 3, 4$), $Ag(CO)_n^+$ ($n = 1, 2, 3$), and $Au(CO)_n^+$ ($n = 1, 2$), over a wide range of temperature and in solvents of different acidities. Based on the spectroscopic data, the molecular structures of copper(I), silver(I) and gold(I) carbonyl cations have been determined. The $Cu(CO)^+$, the bent $Cu(CO)_2^+$ (C_{2v}) and the non-planar $Cu(CO)_3^+$ (C_{3v}) are formed in concentrated H_2SO_4 and HSO_3F, whereas the bent $Cu(CO)_2^+$ (C_{2v}), the trigonal-planar $Cu(CO)_3^+$ (D_{3h}) and the tetrahedral $Cu(CO)_4^+$ (T_d) are formed in magic acid. The $Ag(CO)^+$, the linear $Ag(CO)_2^+$ ($D_{\infty h}$) and the trigonal-planar $Ag(CO)_3^+$ (D_{3h}) cations are formed in HSO_3F and magic acid, but only $Ag(CO)^+$ is formed in concentrated H_2SO_4. The linear $Au(CO)_2^+$ and $Au(CO)^+$ are observed in all the acids, but no $Au(CO)_3^+$ and $Au(CO)_4^+$ were formed under atmospheric CO pressure.

This work reveals that in concentrated H_2SO_4 under CO atmosphere at room temperature, $Cu(CO)_2^+$ is formed as the major species and $Cu(CO)_3^+$ as the minor species for Cu(I), and only $Ag(CO)^+$ (no $Ag(CO)_2^+$) is observed for Ag(I). The active species are therefore determined to be $Cu(CO)_2^+$ (and $Cu(CO)_3^+$ as a minor species) instead of the previously assigned $Cu(CO)_3^+$, $Ag(CO)^+$ instead of the previously assigned $Ag(CO)_2^+$, and $Au(CO)_2^+$ for the copper(I), silver(I) and gold((I) carbonyl cation-catalyzed carbonylation of olefins and alcohols. The reaction mechanism previously proposed for the metal carbonyl cation-catalyzed carbonylation of olefins and alcohols has been modified to involve an olefin-metal-monocarbonyl (e.g., for Ag) or an olefin-metal-polycarbonyl (e.g., for Cu or Au) intermediate.

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Chapter 4

A Copper(II) Nitrosyl Cation
in Strong Acids
– Generation and Spectroscopic Characterization

The reaction of nitrogen monoxide with copper(0) powder, and copper(I) and copper(II) compounds in concentrated sulfuric acid was investigated. The NO reduction by Cu^0 is accompanied by the formation of N_2 and N_2O, whereas the NO reduction by Cu^I results in the formation of N_2O without the evolution of a significant amount of N_2. Both Cu^0 and Cu^I are oxidated to Cu^{II}, to which the coordination of NO leads to the formation of the copper(II) nitrosyl cation, $[CuNO]^{2+}$. The present findings enrich the understanding of the reaction mechanism of the direct decomposition of NO into N_2 and O_2 over copper-exchanged zeolites.

4.1 Introduction

Nitrogen monoxide, NO, is an important bioregulatory molecule and copper-nitrosyl adducts are implicated as pivotal intermediates in biological systems, including $[CuNO]^{2+}$ which is purported to be an intermediate during copper nitrite reductase turnover.[1] Great attention has been noted on the important role that the copper-nitrosyl species have played in the environmentally significant nitrogen oxide processing as copper-exchanged zeolites have been shown to be excellent catalysts for the decomposition and reduction of NO.[2-4] However, the direct observation for the $[CuNO]^{a+}$ (a = 1, 2) cations remains limited to the adsorbed species[4,5] or the isolated species in matrices.[6] So far there have been no evidence for the formation of metal nitrosyl cations in strong acids with the only exception being the NO absorption by iron and copper compounds in sulfuric acid observed by Manchot,[7,8] while there has been a rapid development in the synthesis and characterization of metal carbonyl cations, including $Cu(CO)_n^+$ (n = 1-4), which are usually generated in strong acids, superacids or with weakly coordinating anions.[9-11] To make clear the reactivity of copper compounds with NO is of great significance in the understanding of the copper-exchanged zeolite catalysts. In the present study, we investigated the reaction of nitrogen monoxide with copper(0) powder, and copper(I) and copper(II) compounds in strong acids.

4.2 Experimental

The Cu(II) nitrosyl cation is prepared using commercial reagents. Natural abundance (Sumitomo Seika Chemical Co., Ltd) and 99.8 atom% (Shoko Co., Ltd) ^{15}N-enriched NO were used without further purification. A mixture of copper powder or a copper compound (4 mmol based on Cu atom) and 96% H_2SO_4 (5 mL) in a 200-mL three necked flask was stirred and then evacuated by a rotary pump to remove the air.

Nitrogen monoxide was introduced from a gas balloon so that the flask was kept constantly at 1 atm of NO. The mixture was rigorously stirred for 3 hours at room temperature whereupon a purple suspension was formed.

Standard canula transfer techniques were used for all sample manipulations for the spectroscopic measurements. The infrared spectra were obtained at room temperature on thin films between two silcon disks on a Bio-rad FTS 6000 spectrometer. Raman spectra were recorded at room temperature on liquid samples contained in a 5-mm o.d. NMR tube on a Nicolet FT-Raman 960 spectrometer. ESR spectra were recorded at room temperature using a Bruker ESP 300e spectrometer. The NO, N_2 and N_2O gases were analyzed on a gas chromatograph (SHIMADU GC-14B) with molecular sieve 13X (3 m) (carrier gas: He; column temperature: 50-180 °C (raising rate: 10 °C/min)).

4.3 Results and Discussion

4.3.1 Formation and Characterization of the Copper(II) Nitrosyl Cation, $[CuNO]^{2+}$

In concentrated H_2SO_4, the reaction of copper powder and a variety of copper compounds with atmospheric NO at room temperature results in the formation of the copper(II) nitrosyl cation, $[CuNO]^{2+}$ (for sake of brevity, a solvated cation that should exist in the form of $[CuNO(L)_m]^{a+}$ (L denotes the weakly coordinating ligand probably being the conjugate base of the solvent acid or a closely related species) is simply formulated as $[CuNO]^{a+}$), of which the formulation is based on IR, Raman and ESR spectroscopy. An IR absorption was observed for the v(NO) stretching at 1929 cm^{-1} (v(^{15}NO) at 1894 cm^{-1}) with the corresponding Raman band at 1930 cm^{-1} (v(^{15}NO) at 1894 cm^{-1}), indicating the formation of a copper mononitrosyl complex (Fig. 4-1). The resulting complex readily releases the NO ligand upon brief evacuation (2-3 min) to
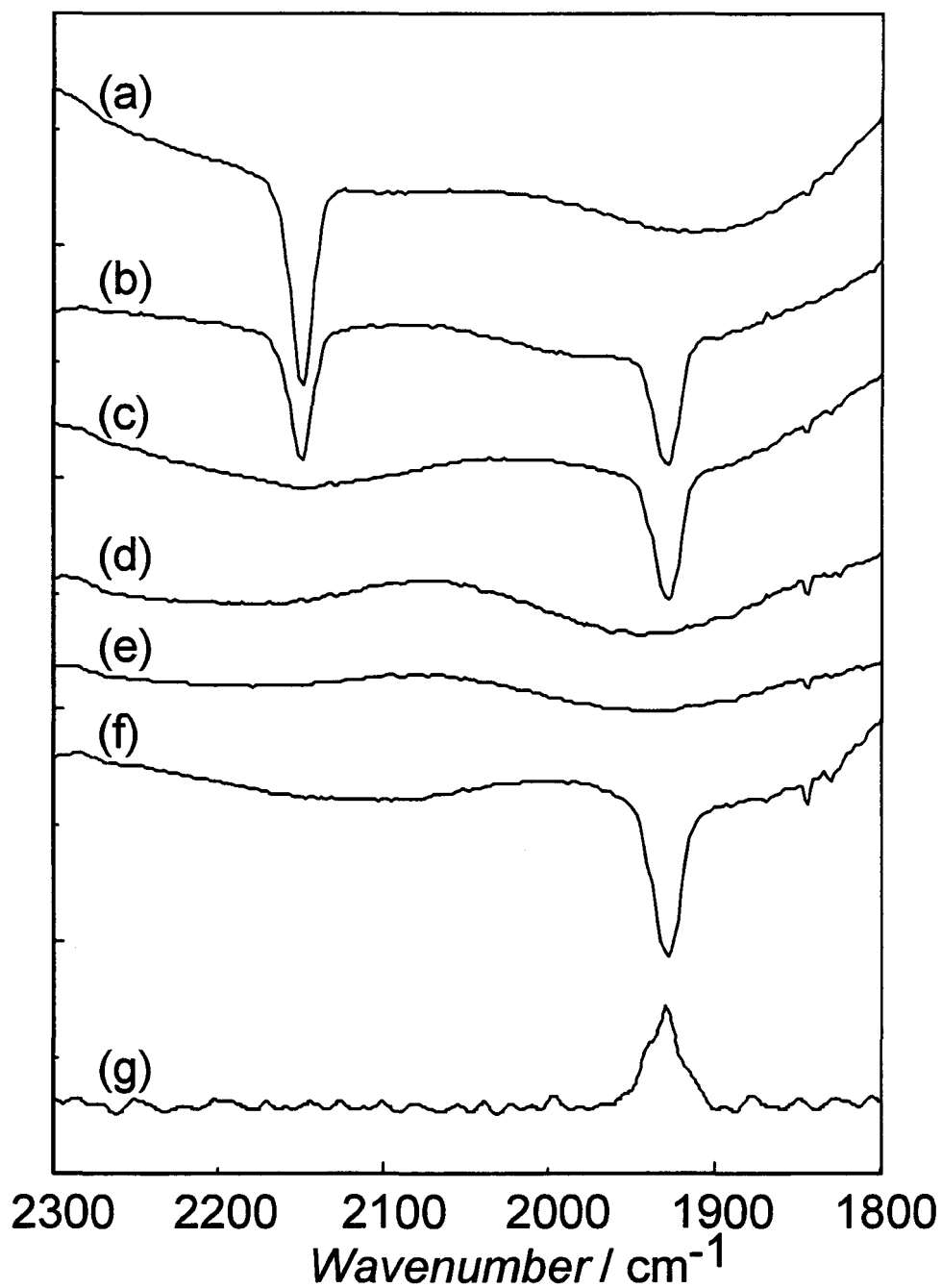
Fig. 4-1 IR spectra of the carbonyl and nitrosyl regions at room temperature for Cu₂O in concentrated H₂SO₄ obtained (a) after the reaction with atmospheric CO and subsequent evacuation; (b) after a 1-h reaction with NO following (a); (c) after a 16-h reaction with NO following (a); (d) after a 5-min evacuation following (c); (e) after stirring under a CO atmosphere for 1 h following (d); and (f) after a 30-min reaction with NO following (e); and (g) the corresponding Raman spectrum of (c).

give a colorless heterogeneous suspension showing no ν(CO) bands, which reintroducing NO. No ^{15}N NMR signal due to the resulting complex was observed even using 99.8 atom% ^{15}N-enriched NO, probably owing to it low concentration in concentrated H_2SO_4. The II oxidation state of copper is deduced from both the examination using CO as the probe molecule and the ESR study.

The reaction of Cu_2O with atmospheric CO in concentrated H_2SO_4 leads to the formation of $Cu(CO)_n^+$ (n = 1-3), which releases the reversible CO ligands upon brief evacuation to give the stable $Cu(CO)^+$ (ν(CO) = 2148 cm^{-1}; see Fig. 4-1a).[12] By introducing atmospheric NO, the CO ligand of $Cu(CO)^+$ is gradually replaced by NO to give a purple heterogeneous suspension exhibiting an IR ν(NO) band at 1929 cm^{-1} (Figs. 4-1b $\sim$ 4-1c). The resulting complex readily releases the NO ligand upon brief evacuation (2-3 min) to give a colorless heterogeneous suspension showing no ν(CO) bands (Fig. 4-1d,), whereas NO is not desorbed from $[CuNO]^{2+}$ in the zeolite by brief evacuation at room temperature.[13] No CO species is observed by reintroducing CO into the above solution (Fig. 4-1e), leading to the conclusion that Cu^I has been oxidized to Cu^{II} as it is found that a Cu^I compound such as Cu_2O but not a Cu^{II} compound such as $CuSO_4$ absorbs CO in concentrated H_2SO_4; CO has also been used as a probe molecule diagnostic for the Cu^+ sites on the Cu-zeolites.[14] The copper(II) nitrosyl cation, $[CuNO]^{2+}$, is reformed by reintroducing NO suggesting an equilibrium between $[CuNO]^{2+}$ and Cu^{2+} under the NO atmosphere in concentrated H_2SO_4. (Fig. 4-1f, Eq. 4-1).

$$[CuNO]^{2+} \underset{+\,NO}{\overset{-\,NO}{\rightleftharpoons}} Cu^{2+} \qquad \text{Eq. 4-1}$$
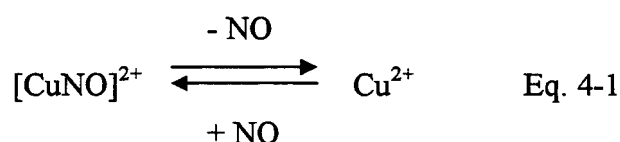
The ESR study confirmed the II oxidation state of Cu in the resulting complex. As shown in Fig. 4-2a, the strong resonance characteristic of Cu^{2+} is observed at g = 2.2359 for the clear solution obtained by decanting and filtering the suspension of
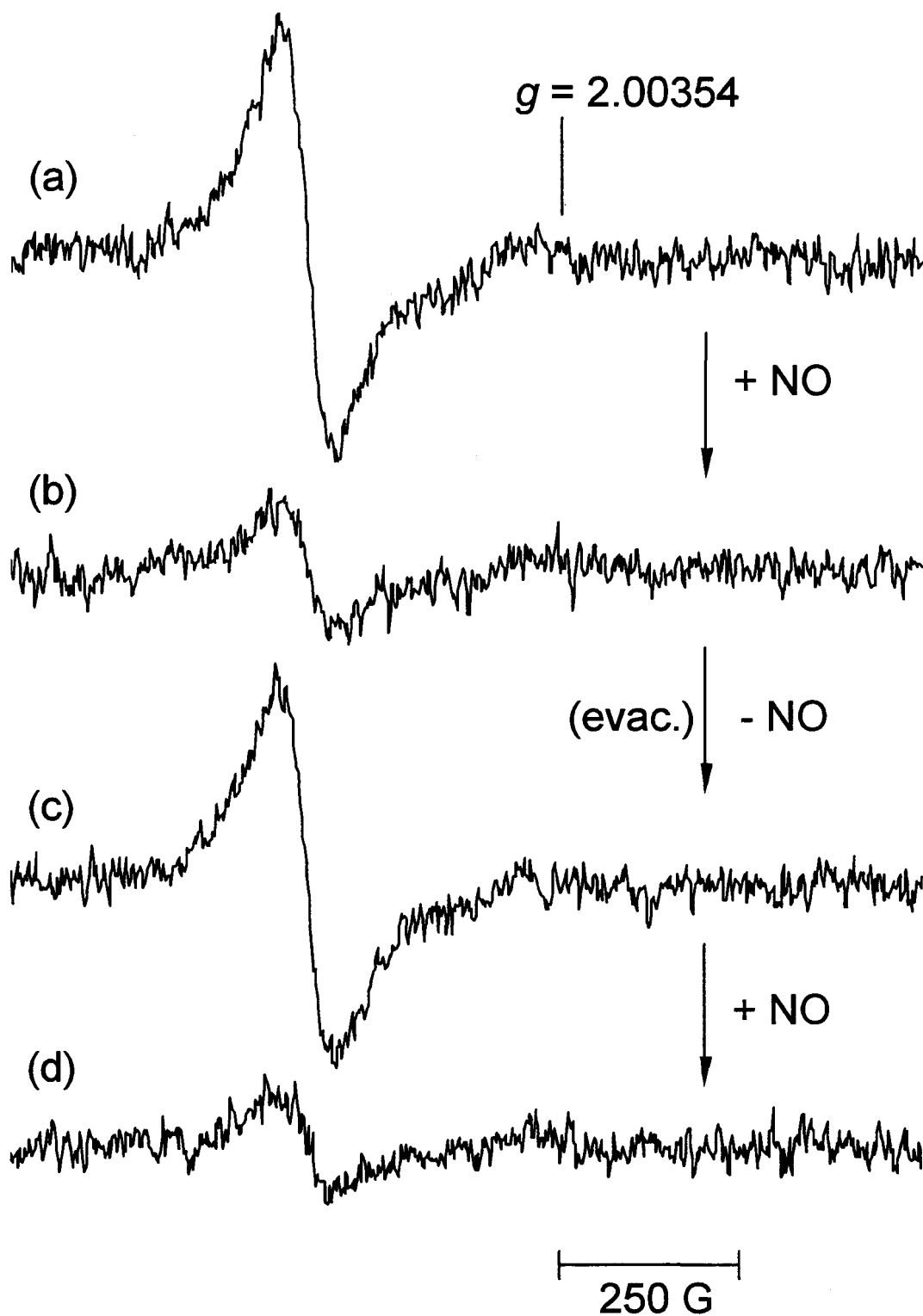
Fig. 4-2 ESR spectra of (a) the clear solution obtained by decanting and filtering the suspension of CuSO₄ in concentrated H₂SO₄; (b) after a 40-min reaction with NO following (a); (c) after a 30-min evacuation following (b); and (d) after a 2-h reaction with NO following (c).

$CuSO_4$ in concentrated H_2SO_4. Introducing NO to this clear solution leads to a significant decrease in the intensity of the ESR signal (Fig. 4-2b) owing to the formation of the diamagnetic $[CuNO]^{2+}$; the weak ESR signal remains observable due to the existence of a small amount of Cu^{2+} in equilibrium with $[CuNO]^{2+}$ (Eq. 4-1). The intensity of the ESR signal for Cu^{2+} is increased upon a brief evacuation (Fig. 4-2c), but significantly decreases again by reintroducing NO (Fig. 4-2d).

The coordination of NO to Cu^{2+} involves the electron transfer of the unpaired electron from the antibonding π^* orbital of NO to a 3d orbital of Cu^{2+}, resulting in the spin pairing between NO and Cu^{2+}, and therefore, the diamagnetism for $[CuNO]^{2+}$.[15] The observed $v(NO)$ value (1929 (IR); 1930 (Raman) cm^{-1}) is higher than 1876 cm^{-1}, the value for free NO,[16] corresponding to a partially positive NO species and a linear Cu-N-O bond angle.[17] Although the spin pairing has occurred as revealed by ESR, the charge transfer from NO to Cu^{2+} is, however, far from being complete, which should be followed by a lone pair donation from NO and π back-bonding to the NO orbitals, as the observed $v(NO)$ value is lower than that of NO^+ (2340 cm^{-1}).[18] Hence $[CuNO]^{2+}$ may be denoted as $Cu^{(1+\delta)} + (NO)^{\delta'+}(\delta + \delta' = 1)$. Based on the classification proposed by Enemark et al. for MNO complexes by the number of d-type electrons present in the complex, $[CuNO]^{2+}$ would be written as $\{CuNO\}^{10}$, which may have a pseudo-tetrahedral geometry with a linear Cu-N-O group and three solvent ligands.[17]

In HSO_3F and magic acid, $HSO_3F \cdot SbF_5$ (1:1), $[CuNO]^{2+}$ is also formed from the Cu^0, Cu^I or Cu^{II} compounds under an NO atmosphere. $[CuNO]^{2+}$ exhibits higher $v(NO)$ values in HSO_3F (1933 (IR); 1936 (Raman) cm^{-1}) and magic acid (1946 (IR); 1950 (Raman) cm^{-1}) due to a decrease in the π back-bonding as observed for metal carbonyl cations in strong acids.[9-12] It is confirmed that no IR or Raman n(NO) bands appear in the range of 1500 - 2200 cm^{-1} in the absence of Cu in these acids. $[CuNO]^{2+}$ is remarkably more stable in HSO_3F and magic acid than in concentrated H_2SO_4; it remains unchanged even after a prolonged evacuation of 4 h. The attempt to isolate

$[CuNO]^{2+}$ as a crystalline salt is currently underway. Interestingly, no $[CuNO]^{+}$ species is observed in these strong acids while both $[CuNO]^{+}$ and $[CuNO]^{2+}$ are observed in zeolites.[5]

4.3.2 Reduction of NO by Copper(0) and Copper(I) Compounds

It is worth noting that during the formation of $[CuNO]^{2+}$ in concentrated H_2SO_4 at room temperature, distinct behavior in the reduction of NO is observed for the starting materials with different oxidation states, as shown in scheme 4-1.

$$
\left.\begin{array}{c} Cu^0 \\ \text{or} \\ [Cu^I] \\ \text{or} \\ [Cu^{II}] \end{array}\right\} + \xrightarrow{\text{concd. } H_2SO_4} [CuNO]^{2+} + \left\{\begin{array}{c} N_2 + N_2O \\ \text{or} \\ N_2O \end{array}\right.
$$

$$[Cu^I] = Cu_2O, \ CuCl, \ Cu(CO)^+, \ Cu(CH_3COO)$$
$$[Cu^{II}] = CuO, \ CuCl_2, \ CuF_2, \ Cu(CH_3COO)_2, \ CuSO_4$$
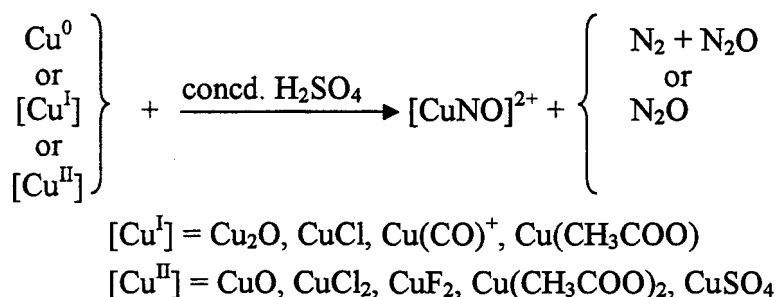
Scheme 4-1

As shown in Fig. 4-3, the oxidation of Cu^0 (copper powder) is accompanied by the reduction of NO to almost equal amounts of N_2 and N_2O, while no significant N_2 but N_2O is observed during the reaction of the Cu^I compound, $Cu(CO)^+$, with NO. Neither significant N_2 nor N_2O has been observed for the reaction with the Cu^{II} compound, $CuSO_4$, as the starting material. The small amount of N_2O observed for the reaction of NO with $CuSO_4$ in concentrated H_2SO_4, or without copper metal or a copper compound in concentrated H_2SO_4, might be due to the disproportionation of NO to N_2O and NO_2, as it has been reported that the disproportionation reaction of NO, $3NO(g) \rightarrow N_2O(g) + NO_2(g)$, has a free energy of -24.6 kcal, indicating that NO is not thermodynamically stable and the disproportionation rate can be increased under certain conditions such as in the presence of catalysts in spite of the kinetic stability of NO at room temperature
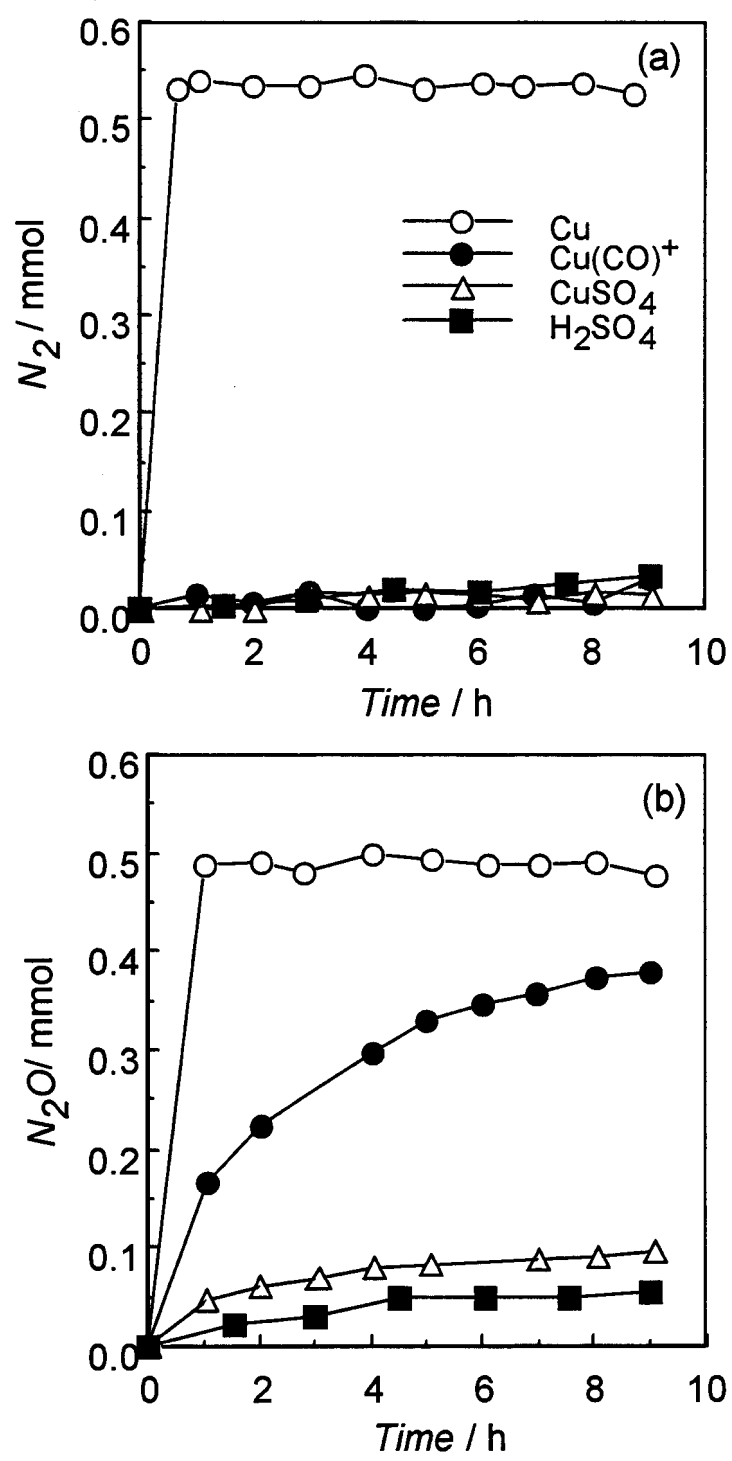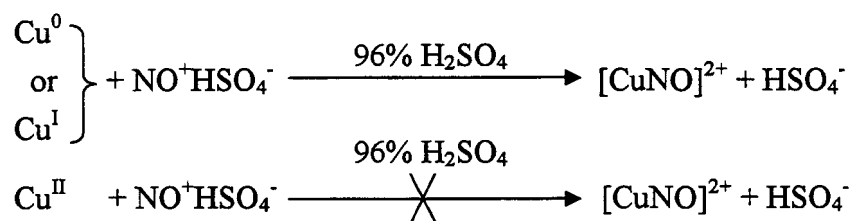
Fig. 4-3 Formation of (a) N_2 and (b) N_2O during the reaction of NO with copper powder and copper(I) and copper(II) compounds in concentrated H_2SO_4 at room temperature.

and 1 atm.[19]   Similar results have been obtained for the reaction with the Cu^I

compounds such as CuCl, Cu_2O, and $Cu(CH_3COO)$, and for the reaction with the Cu^{II}

compounds such as $CuCl_2$, CuO, and $Cu(CH_3COO)_2$, as the starting materials,

respectively.   These observations suggest that during the reduction of NO in

concentrated H_2SO_4 the formation of N_2 is related to the oxidation of Cu^0 to Cu^I and the

formation of N_2O is related to the oxidation of Cu^I to Cu^{II}. Cu^+ has been considered as

the active center, and a neighboring Cu^+ site has been proposed to be important in the

copper-exchanged zeolites.[5]   On the other hand, it has been reported that the

Cu-ZSM-5 catalysts with excess loading of copper ions above 100% exchange level are,

in particular, much more active for the decomposition of NO than the catalysts with

exchange level of copper ion below 100%.[5,13,20]   Our present findings indicate the

importance of Cu^0 in the reduction of NO and suggest the possibility that Cu^0, which

may be generated by the disproportionation of two Cu^+ sites, might play an important

role in the catalytic direct decomposition of NO to N_2 and O_2.

4.3.3   Formation of $[CuNO]^{2+}$ using $NOHSO_4$

There is another way to form $[CuNO]^{2+}$.   I found that the reaction of copper

powder or Cu^I compounds with nitrosonium hydrogen sulphate, $NO^+HSO_4^-$, in 96%

H_2SO_4 under atmospheric Ar pressure results in the formation of the copper(II) nitrosyl

cation, as shown in scheme 4-2. Cu^{II} compounds do not react with $NO^+HSO_4^-$ in 96%

H_2SO_4 under atmospheric Ar pressure.   It seems that the oxidation of Cu^0 or Cu^I to Cu^{II}

is accompanied by the reduction of NO^+ to NO.

$$\left. \begin{array}{c} Cu^0 \\ or \\ Cu^I \end{array} \right\} + NO^+HSO_4^- \xrightarrow{\ 96\%\ H_2SO_4\ } [CuNO]^{2+} + HSO_4^-$$

$$Cu^{II} + NO^+HSO_4^- \xrightarrow{\quad 96\%\ H_2SO_4 \quad}\!\!\!\!\!\!\!\!\times\ \ [CuNO]^{2+} + HSO_4^-$$

Scheme 4-2

4.4 Conclusions

In the present study, we prepared and spectroscopically characterized the copper(II) nitrosyl cation, $[CuNO]^{2+}$, in strong acids. It was found that the reaction of Cu^0 powder with NO in strong acids results in the formation of a significant amount of N_2 and N_2O whereas the reaction of Cu^I compounds is accompanied with only a significant amount of N_2O. These findings might enrich the understanding of the reaction mechanism of the direct decomposition of NO into N_2 and O_2 over copper-exchanged zeolites.

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Chapter 5

General Conclusions

Cationic species generated in strongly acidic media, on which only limited studies have been reported so far, have peculiar properties and exhibit unusual reactivities in contrast with those in neutral and basic media. In the present work, I focused on the keywords "cations" and "strong acids" and dealt with three types of cationic species, i.e., carbocations, metal carbonyl cations and metal nitrosyl cations. From this work, it turned out that all of these cationic species play important roles as reaction intermediates or catalysts in catalytic reactions such as carbonylation of alcohols in solid acids, carbonylation of olefins and alcohols in strong acids and NO reduction and decomposition in zeolites.
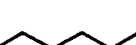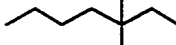
5.1 Carbocations in Solid Acids
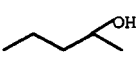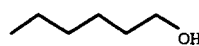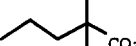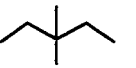
The Koch reaction, which involves carbocations and acylium cations as the reaction intermediates, is a simple and efficient synthetic method for synthesizing tertiary carboxylic acids.[1,2] For overcoming the problems arising from the use of the strongly acidic solutions Nafion-H was used as a solid acid catalyst for the Koch-type carbonylation of alcohols in the present work (Scheme 5-1).[3]

$$\text{R'-OH} + \text{R-SO}_3\text{H} \rightleftharpoons \overset{+}{\text{R'}} + \text{R-SO}_3^- + [\text{H}_2\text{O}] \rightleftharpoons$$

$$\overset{+}{\text{R'}} \underset{+\,\text{CO}}{\overset{-\,\text{CO}}{\rightleftharpoons}} \overset{+}{\text{R'}}\text{CO} + \text{R-SO}_3^- \xrightarrow{+\,\text{H}_2\text{O}} \text{R'}\text{CO}_2\text{H} + \text{R-SO}_3\text{H}$$

$$R = \sim(CF_2\text{-}CF_2)_n\text{-}CF_2\text{-}CF\sim \quad CF_3$$
$$\mathop{|}\limits \qquad \mathop{|}\limits$$
$$O(CF_2\text{-}CF\text{-}O)_m\text{-}CF_2\text{-}CF_2\text{-}$$
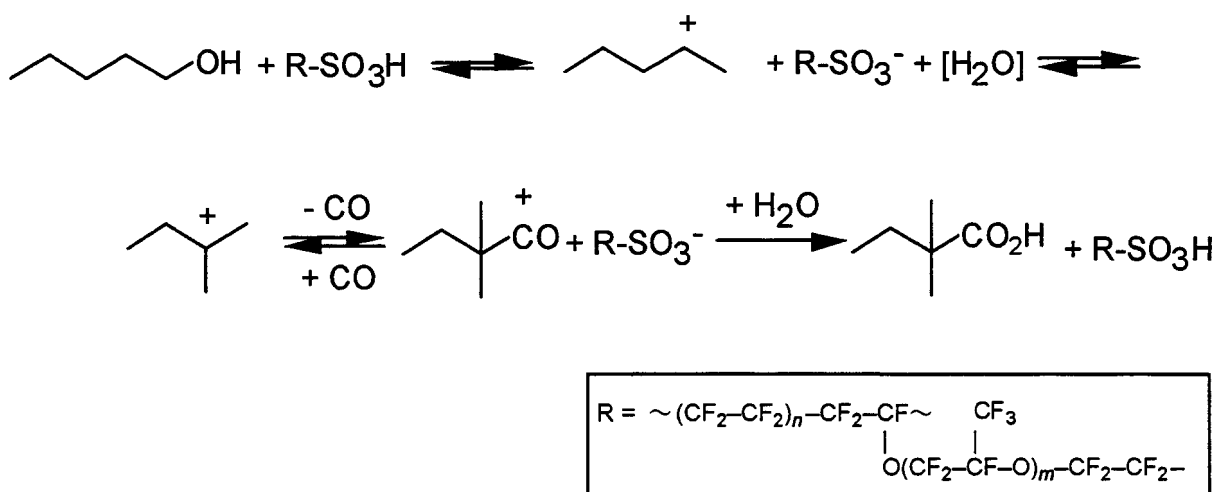
Scheme 5-1

The carbonylation of a variety of primary, secondary and tertiary alcohols in various solvents such as hexane, cyclohexane, dichloromethane and chlorobenzene produces the corresponding tertiary carboxylic acids in high yields (Table 5-1). For example, the conversions of 2-methyl-2-propanol, 1-pentanol and 1-adamantanol to carboxylic acids are 62.5, 64.6 and 76.9%, respectively, at 433 K and 9 MPa CO. The optimum temperature for this reaction is between 433 and 443 K. A high CO pressure is advantageous for the carbonylation. The yields of carboxylic acids are slightly higher in the polar solvents than those in the nonpolar solvents. This work indicates the potential industrial application of solid acids instead of strong liquid acid catalysts for the Koch-type reaction to selectively synthesize tertiary carboxylic acids.

Table 5-1　Carbonylation of a variety of alcohols over Nafion-H

Substrate	Main Product (%)	Total Yield of Carboxylic Acids (%)
(structure) OH	(structure) CO₂H 53.4	62.5
(structure) OH	(structure) CO₂H 48.2	64.6
(structure) OH	(structure) CO₂H 40.4	52.6
(structure) OH	(structure) CO₂H 25.8　(structure) CO₂H 22.8	57.9
(structure) OH	(structure) CO₂H 26.8　(structure) CO₂H 21.6	57.4
(structure) OH	(structure) CO₂H 76.8	76.9

2.0 g Nafion-H, 20 mmol alcohol, 50 mL hexane, 433 K, 9.0 MPa, 22 h,

5.2　Copper(I), Silver(I) and Gold(I) Carbonyl Cations in Strong Acids

Apart from the carbocations, solvated cationic carbonyl complexes, in particular, of group 11 metals in strong acids have not been investigated in detail so far. In the present work detailed IR, Raman, and NMR spectroscopic characterization has been carried out on the group 11 metal carbonyl cations, $Cu(CO)_n^+$ (n = 1, 2, 3, 4), $Ag(CO)_n^+$ (n = 1, 2, 3), and $Au(CO)_n^+$ (n = 1, 2), over a wide range of temperature and in solvents of different acidities. Based on the spectroscopic data, the molecular structures of copper(I), silver(I) and gold(I) carbonyl cations have been determined.[4]

The $Cu(CO)^+$, the bent $Cu(CO)_2^+$ (C_{2v}) and the non-planar $Cu(CO)_3^+$ (C_{3v}) are formed in concentrated H_2SO_4 and HSO_3F, whereas the bent $Cu(CO)_2^+$ (C_{2v}), the trigonal-planar $Cu(CO)_3^+$ (D_{3h}) and the tetrahedral $Cu(CO)_4^+$ (T_d) are formed in magic acid. The $Ag(CO)^+$, the linear $Ag(CO)_2^+$ ($D_{\infty h}$) and the trigonal-planar $Ag(CO)_3^+$ (D_{3h}) cations are formed in HSO_3F and magic acid, but only $Ag(CO)^+$ is formed in concentrated H_2SO_4. The linear $Au(CO)_2^+$ and $Au(CO)^+$ are observed in all the acids,

but no $Au(CO)_3^+$ and $Au(CO)_4^+$ are formed under atmospheric CO pressure (Scheme 5-2)

	H_2SO_4	HSO_3F	Magic acid
Cu	Cu—CO (OC)Cu(CO) [major species] (OC)Cu(CO)(CO)	Cu—CO (OC)Cu(CO) (OC)Cu(CO)(CO)	(OC)Cu(CO) OC—Cu(CO)(CO) OC—Cu(CO)(CO)(CO)
Ag	Ag—CO [major species]	Ag—CO OC—Ag—CO OC—Ag(CO)(CO)	Ag—CO OC—Ag—CO OC—Ag(CO)(CO)
Au	Au—CO OC—Au—CO [major species]	Au—CO OC—Au—CO	OC—Au—CO
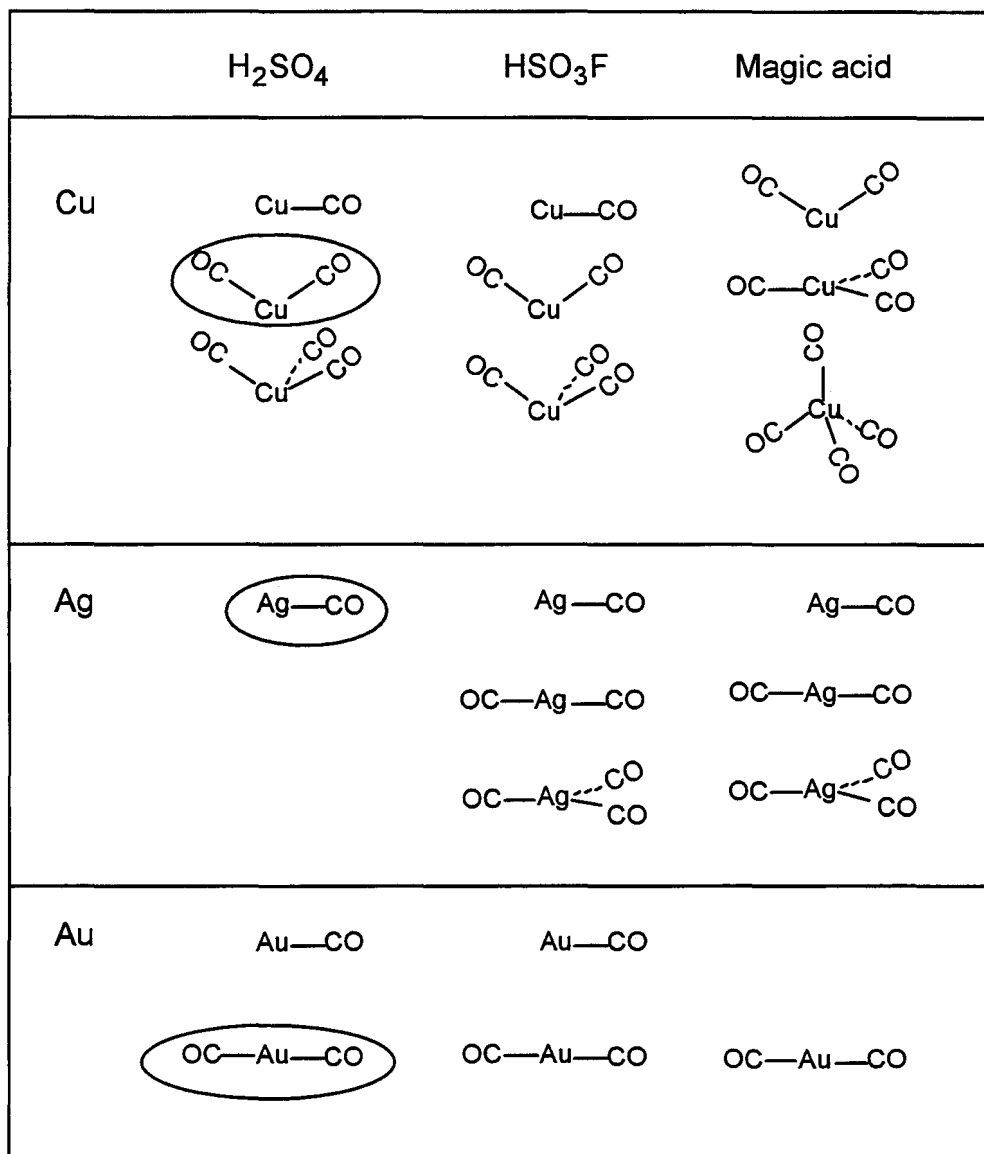
⬭ : Major species in concentrated H_2SO_4 at room temperature

Scheme 5-2

Because copper(I), silver(I) and gold(I) carbonyl cations in concentrated H_2SO_4 have been used as catalysts for the carbonylation of olefins and alcohols, the active

species and reaction mechanism are of great interest. Previously the formation of $Cu(CO)_2^+$ and $Ag(CO)^+$ was not considered and $Cu(CO)_3^+$ and $Ag(CO)_2^+$ were assigned as the active species, although the reason is unclear.[5] This work revealed by detailed spectroscopic analyses that in concentrated H_2SO_4 under CO atmosphere at room temperature, $Cu(CO)_2^+$ was formed as the major species and $Cu(CO)_3^+$ as the minor species for Cu(I), and only $Ag(CO)^+$ (no $Ag(CO)_2^+$) was observed for Ag(I). These results indicate that major active species for the copper(I) and silver(I) carbonyl cation-catalyzed carbonylation of olefins and alcohols are $Cu(CO)_2^+$ and $Ag(CO)^+$ instead of the previously assigned species, respectively.

This work:
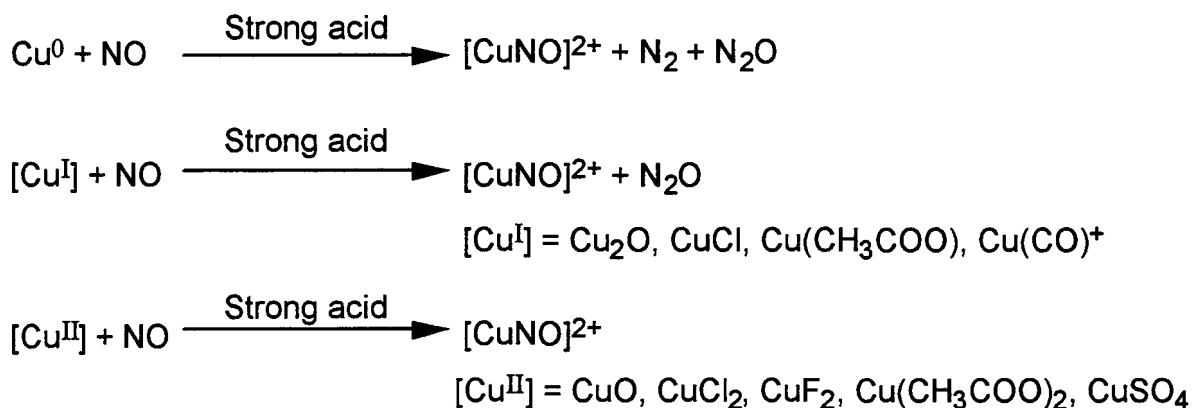Cu, $n = 2$, (3)
Ag, $n = 1$
Au, $n = 2$
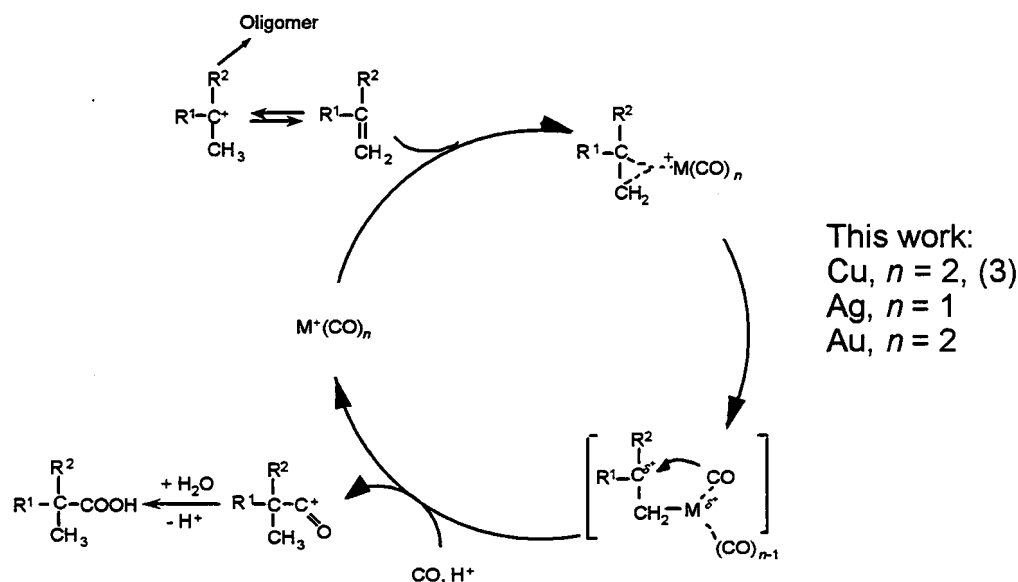
Scheme 5-3

A reaction mechanism involving an olefin-metal-polycarbonyl intermediate was previously proposed for the metal carbonyl cation-catalyzed carbonylation of olefins and alcohols in strong acids.[6] However, the present work revealed that in silver(I) cation-catalyzed carbonylation, only monocarbonyl species ($Ag(CO)^+$) is involved in contrast with the catalytically active polycarbonyl cations of copper(I) and gold(I). Therefore, the reaction mechanism for the metal carbonyl cation-catalyzed

carbonylation of olefins and alcohols has been modified to involve an olefin-metal-monocarbonyl (e.g., for Ag) or an olefin-metal-polycarbonyl (e.g., for Cu or Au) intermediate (Scheme 5-3).

5.3 Copper(II) Nitrosyl Cation, $[CuNO]^{2+}$, in Strong Acids

The first direct evidence for the formation of metal nitrosyl cations in strong acids was shown in the present study. I prepared the copper(II) nitrosyl cation, $[CuNO]^{2+}$, in strong acids, which was well-characterized by IR, Raman and ESR spectroscopy (Scheme 5-4, Table 5-2).[7]

$$Cu^0 + NO \xrightarrow{\text{Strong acid}} [CuNO]^{2+} + N_2 + N_2O$$

$$[Cu^I] + NO \xrightarrow{\text{Strong acid}} [CuNO]^{2+} + N_2O$$

$$[Cu^I] = Cu_2O, \ CuCl, \ Cu(CH_3COO), \ Cu(CO)^+$$

$$[Cu^{II}] + NO \xrightarrow{\text{Strong acid}} [CuNO]^{2+}$$

$$[Cu^{II}] = CuO, \ CuCl_2, \ CuF_2, \ Cu(CH_3COO)_2, \ CuSO_4$$

Scheme 5-4

The coincidence of the observed IR ($1929 \ cm^{-1}$) and Raman ($1930 \ cm^{-1}$) $\nu(NO)$ stretching frequencies indicates the formation of a copper mononitrosyl complex. The $\nu(NO)$ values higher than $1876 \ cm^{-1}$, the value for free NO, correspond to a partially positive NO species and a linear Cu-N-O bond angle. The II oxidation state of copper is deduced from both the examination using CO as the probe molecule and the ESR study.

Table 5-2 $v(NO)$ value of $[CuNO]^{2+}$ in strong acids

Solvent	$v(NO)$ IR (cm^{-1})	$v(NO)$ Raman (cm^{-1})
H_2SO_4	1929	1930
FSO_3H	1933	1936
Magic acid	1946	1950

It was found that the reaction of Cu^0 powder with NO in strong acids results in the formation of a significant amount of N_2 and N_2O, whereas the reaction of Cu^I compounds is accompanied by only a significant amount of N_2O.[7]   These findings are expected to enrich the understanding of the reaction mechanism of the direct decomposition of NO into N_2 and O_2 over copper-exchanged zeolites (Scheme 5-4).[8]

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List of Publications

1. "Carbonylation of olefins by copper or silver carbonyl supported catalysts at room temperature and atmospheric pressure"

   Y. Souma* and N. Tsumori,

   Sekiyu Gakkaishi, **41**, 411-412 (1998).

2. "Carbonylation of *tert*-butyl alcohol over H-zeolites"

   Q. Xu*, S. Inoue, N. Tsumori, H. Mori, M. Kameda, M. Tanaka,

   M. Fijiwara and Y. Souma,

   Journal of Molecular Catalysis A: Chemical, **170**, 147-153 (2001).

3. "Carbonylation of alcohols over Nafion-H, a solid perfluoroalkanesulfonic acid resin catalyst"

   N. Tsumori, Q. Xu*, Y. Souma and H. Mori,

   Journal of Molecular Catalysis A: Chemical, **179**, 271-277 (2002).

4. "Formation of the copper(II) nitrosyl cation, $[CuNO]^{2+}$, in strong acids"

   N. Tsumori and Q. Xu*,

   Bulletin of the Chemical Society of Japan, **75**, 1861-1862 (2002).

5. "Carbonylation of hydrocarbons and alcohols by cationic metal carbonyl catalysts"

   Y. Souma*, N. Tsumori, H. Willner, Q. Xu, H. Mori and T. Morisaki,

   Journal of Molecular Catalysis A: Chemical, **189**, 67-77 (2002).

6. "Spectroscopic characterization and catalytic application of copper(I), silver(I) and gold(I) carbonyl cations in strong acids"

N. Tsumori, Q. Xu*, M. Hirahara, S. Tanihata, Y. Souma, Y. Nishimura,

N. Kuriyama and S. Tsubota,

Bulletin of the Chemical Society of Japan, 75, 2257-2268 (2002).

7. "A neutral molecule with some boron-boron triple bond character"
M. F. Zhou*, N. Tsumori, Z. H. Li, K. N. Fan, L. Andrews and Q. Xu*,

Journal of the American Chemical Society, 124, 12936-12937 (2002).

8. "The infrared spectra of BCO, B(CO)$_2$ and OCBBCO in solid argon"

M. F. Zhou*, N. Tsumori, L. Andrews and Q. Xu*,

Journal of Physical Chemistry A, submitted.

List of Presentations

1. "Carbonylation of alcohols by Nafion catalyst."

   ○N. Tsumori, H. Mori and Y. Souma,

   78th National Meeting of The Chemical Society of Japan (Funabashi), March/29/2000

2. "Carbonylation of alcohols by Nafion and a [Ag(CO)]$^+$/Nafion catalyst"

   ○N. Tsumori, H. Mori and Y. Souma,

   International Chemical Congress of Pacific Basin Societies (PACIFICHEM 2000) (Honolulu), December/16/2000

3. "Formation of copper(II) nitrosyl cation in concentrated sulfuric acid"

   ○N. Tsumori and Q. Xu,

   79th National Meeting of The Chemical Society of Japan (Kobe), March/29/2001

4. "Carbonylation of alcohols over Nafion-H, a solid perfluoroalkanesulfonic acid resin catalyst"

   ○N. Tsumori, H. Mori, Q. Xu and Y. Souma,

   International Symposium on Acid-Base Catalysis IV (ABC IV) (Matsuyama), May/9/2001

5. "Spectroscopic evidence for the formation of the copper(II) nitrosyl cation in strong acid"

   ○N. Tsumori and Q. Xu,

   81th National Meeting of The Chemical Society of Japan (Tokyo), March/29/2002

6. "Spectroscopic evidence for the formation of the copper(II) nitrosyl cation, $[Cu(NO)]^{2+}$, in strong acids"

○N. Tsumori and Q. Xu,

35th International Conference on Coordination Chemistry (ICCC 35) (Heidelberg),

July/25/2002

7. "Formation of molybdenum carbonyl cation and tungsten carbonyl cation in strong acids"

○N. Tsumori and Q. Xu,

52th The Annual Meeting of Japan Society of Coordination Chemistry (Tokyo),

September/25/2002

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