Carbonylation of hydrocarbons and alcohols by cationic metal carbonyl catalysts

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Abstract

tert-Carbocations, which were formed from hydrocarbons and alcohols, react with CO in the presence of catalytic amounts of $Cu(CO)_n{}^+$ to give, following a workup with water *tert*-carboxylic acids upon workup with water catalyst. The salts of the cationic metal carbonyls such as $[Pd(CO)_4][Sb_2F_{11}]_2$, $[Pt(CO)_4][Sb_2F_{11}]_2$, $[OsO_2(CO)_6][Sb_2F_{11}]_2$ and $[Hg(CO)_2][Sb_2F_{11}]_2$ promote the carbonylation of 3-hexanol and *tert*-C_7 carboxylic acids were obtained. Solid superacids such as Nafion, ZSM-5 to SO_4/ZrO_2 were used instead of H_2SO_4, in the catalytic sequence Ag^+ was fixed on these solid superacids to form a silver carbonyl on the surface. The $\nu(CO)$ of the silver carbonyl was observed at $2173\,\mathrm{cm}^{-1}$ on Nafion. The Ag^+-supported solid superacids showed an activity higher than the original solid superacid during the carbonylation of alcohols.
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1. Introduction

The C–H bond activation of hydrocarbons has been mainly studied using a transition metal catalyst. Although the activation of the C–H bond of a saturated hydrocarbon is considered to be difficult. However Pd-Cu mixed catalysts have been developed that enable the carboxylation of alkanes including methane, ethane, and propane to give the corresponding carboxylic acids in trifluoroacetic acid [1]. The direct carbonylation at an sp^2 C–H bond of imidazoles or pyridylbenzene was also studied using a ruthenium carbonyl or rhodium carbonyl catalyst, and ketones were obtained [2].

C–H bond activation has also been accomplished using superacids. The C–H bond cleavage of saturated hydrocarbons by the superacid FSO_3H-SbF_5 was first found by Olah and Lukas [3]. A hydride was abstracted from the saturated hydrocarbons by the superacid to produce carbocations. Paatz and Weisgerber studied the carbonylation of saturated hydrocarbons in HF-SbF_5, and obtained carboxylic acids and ketones [4]. However, the conversion of the saturated hydrocarbons to carbonyl compounds was less than 30% due to the low solubility of carbon monoxide in the strong acids.

It is known that copper(I) carbonyl or silver carbonyl catalysts accelerate the carbonylation of olefins or alcohols to give *tert*-carboxylic acids in high yield at atmospheric CO pressure [5]. Therefore, a copper(I) carbonyl catalyst was used to accelerate the

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carbonylation of saturated hydrocarbons in FSO_3H-SbF_5, and *tert*-carboxylic acids were obtained in high yields as expected [6]. The merit of the application of a copper(I) carbonyl catalyst is the acceleration of the carbonylation of the carbocations. However, further improvement is necessary to solve the corrosive character of the homogeneous acid catalyst. One approach may be heterogenization of the homogeneous acid catalyst to solve the problems of corrosion and separation.

Solid superacids such as Nafion, ZSM-5, and SO_4/ZrO_2 are candidates as alternatives to liquid superacids. Silver was supported on these superacids to form silver carbonyl on the surface. Willner and Aubke found and isolated the white solids of various cationic metal carbonyl complexes in superacidic media [7]. These salts offer the possibility to study the heterogeneous catalytic applications. This paper reports the catalytic carbonylation of alcohols by silver-supported solid superacids and metal carbonyl complexes of $[Pd(CO)_4][Sb_2F_{11}]_2$, $[Pt(CO)_4][Sb_2F_{11}]_2$, $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$, $[Ru(CO)_6][Sb_2F_{11}]_2$, $[OsO_2(CO)_4][Sb_2$-$F_{11}]_2$, and $[Hg(CO)_2][Sb_2F_{11}]_2$.

2. Experimental section

2.1. Carbonylation of saturated hydrocarbons by superacids

2.1.1. Preparation of a copper(I) carbonyl catalyst

FSO_3H and SbF_5 were purchased from the Cationic Co. In a 300 ml three-necked flask equipped with a thermometer and a CO gas burette, 0.858 g of Cu_2O (6 mmol) was placed. The apparatus was evacuated using a rotary pump, and CO was introduced from the gas burette. The mixture was vigorously stirred after 20 ml of FSO_3H and 10 ml of SbF_5 had been added. A colorless copper(I) carbonyl solution was formed by the absorption of CO by Cu_2O. The molar ratio of CO/Cu^+ was 3.7 at 0 °C. The ν(CO) and δ of ^{13}C NMR of $Cu(CO)_4^+$ were 2183 cm^{-1}, and 171.1 ppm, respectively.

2.1.2. Carbonylation of saturated hydrocarbons

From a syringe, 30 mmol of saturated hydrocarbons was added dropwise into the catalyst solution at −2 to 2 °C. The carbon monoxide was immediately absorbed. After the reaction was completed, the mixture was poured over ice. The products were extracted by *n*-hexane, and the total yield of the carboxylic acids was determined by titrating the *n*-hexane extract with a 0.1 mol/l NaOH ethanol solution. The new products were separated by preparative GLPC and analyzed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, as described in a previous paper [5a]. Each product was identified using authentic samples [5a].

2.2. Carbonylation of 3-hexanol using salts of cationic metal carbonyls

2.2.1. Preparation of metal carbonyl cations

The preparation of $[Pd(CO)_4][Sb_2F_{11}]_2$ [8], $[Pt(CO)_4][Sb_2F_{11}]_2$ [8], $[Fe(CO)_6][Sb_2F_{11}]_2$ [9], $[Ru(CO)_6][Sb_2F_{11}]_2$ [11], $[OsO_2(CO)_4][Sb_2F_{11}]_2$ [10] and $[Hg(CO)_2][Sb_2F_{11}]_2$ [12] were carried out according to the literature procedures. A typical example of the preparation is as follows.

$[Pt(CO)_4][Sb_2F_{11}]_2$: Into a well-dried round bottom glass flask of about 60 ml volume, fitted with a PTFE-valve and a magnetic stirring bar, 390 mg Pt powder (2.00 mmol) is placed. In vacuo, 2 ml HSO_3F and 1 ml $S_2O_6F_2$ are transferred into the reactor using liquid nitrogen. At 100 °C and with stirring, the platinum powder is dissolved within 1 day. After cooling to room temperature, the most volatile components of the brown solution ($S_2O_5F_2$ and $S_2O_6F_2$) are pumped off. Subsequently, 6 ml SbF_5 is condensed on top of the solution and CO is introduced to give a total pressure of 2 atm at 80 °C. The content is stirred for 2 days and the CO atmosphere is replaced a few times. After the suspension is completely colorless, all the volatile materials are pumped off at 50 °C and 2300 mg (2.00 mmol $[Pt(CO)_4]$ $[Sb_2F_{11}]_2$) of a white powder is left in the glass bulb. The ν(CO) and ^{13}C NMR chemical shift δ of $[Pt(CO)_4][Sb_2F_{11}]$ were observed at 2244 cm^{-1} and 137 ppm, respectively. The other cationic metal carbonyl complexes were obtained using the same procedure. The ν(CO) and δ of $[Pd(CO)_4][Sb_2F_{11}]_2$ were observed at 2248 cm^{-1} and 144 ppm, respectively. The ν(CO) and δ of $[Fe(CO)_6][Sb_2F_{11}]_2$ were observed at 2204 cm^{-1} and 179 ppm, respectively. The ν(CO) and δ of $[Ru(CO)_6][Sb_2F_{11}]_2$ were observed at 2199 cm^{-1} and 166 ppm, respectively. The ν(CO) and δ of $[Hg(CO)_2][Sb_2F_{11}]_2$ were observed at 2278 cm^{-1} and 169 ppm, respectively.

2.2.2. Carbonylation of 3-hexanol

As all salts of the cationic metal carbonyl complexes are very moisture sensitive, they were stored in sealed glass ampoules and handled in a glove box. A three-necked flask, connected with a CO gas burette, was placed in the glove box. A certain amount of the cationic metal carbonyl complex was placed in the three-necked flask, and 3-hexanol was added dropwise into the mixture with stirring by magnetic stirrer without solvent at room temperature and atmospheric CO pressure. The IR spectra during the reaction were measured on thin films between two silicon discs using a JASCO FT/IR-230 spectrometer. After the reaction was finished, water was added. The products were extracted by *n*-hexane, analyzed by GC, and identified using authentic samples [5a]. The total yield of the carboxylic acids were determined by titrating the *n*-hexane extract with a 0.1 mol/l NaOH ethanol solution.

2.3. Carbonylation of alcohols by solid superacids

2.3.1. Preparation of silver carbonyl on Nafion

Nafion loaded with silver ions was prepared by ion-exchange of the SO_3H protons in Nafion with Ag^+. A 0.3 g piece of Nafion 112 film (ion-exchange capacity: 0.9 meq./g, Aldrich) was immersed into 50 ml of a 0.01 mol/l $AgNO_3$ aqueous solution for 20 h. After the ion-exchange treatment was over, the supernatant solution of $AgNO_3$ was analyzed using an inductively coupled argon plasma atomic emission spectrophotometer (ICAP-575 II) by Nippon Jarrell–Ash, and it was found that 0.23 mmol of Ag^+ remained. A 0.27 mmol amount of Ag^+ was used for the ion-exchange, and it was then confirmed that all protons were exchanged by the silver ions. The Ag/Nafion was washed several times by demineralized water, dried at 110 °C for 3 h, and then cooled in a desiccator. The Ag/Nafion was dried again in an especially designed IR cell having KBr windows as shown in Fig. 1 at 140 °C under 10 mmHg for 7 h. After the cell was cooled to room temperature, 190 mmHg of CO was introduced into the IR cell and the Ag/Nafion was exposed to the CO for 30 min, then the IR absorption of the AgCO/Nafion was measured by a JASCO FT/IR-230 spectrometer. The blank IR absorption of the CO gas was subtracted from the obtained spectrum. The ν(CO) of AgCO on Nafion was 2173 cm^{-1}.

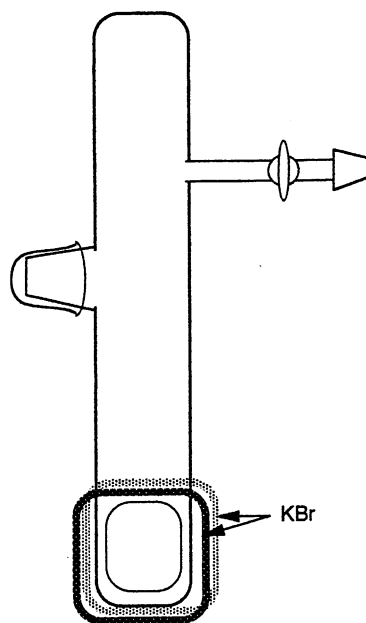
Fig. 1. The designed IR cell.

2.3.2. Preparation of Ag/ZSM-5

A 40 g sample of ZSM-5 was immersed to 400 ml of 0.1 mol/l $AgNO_3$ for 15 h, and separated by centrifugal separator. The immersion was repeated five times. Ag/ZSM-5 was washed five times using demineralized water and separated by a centrifugal separator. It was dried at 110 °C for 15 h, then dried at 350 °C under 10^{-2} mmHg for 3 h. A 2 g sample of Ag/ZSM-5 was stored in a glass bulb.

2.3.3. Preparation of SO_4/ZrO_2 and $Ag/SO_4/ZrO_2$

A 200 g sample of $ZrO(NO_3)_2 \cdot 2H_2O$ was dissolved in 5 l of water, and neutralized by 25% aqueous ammonia up to pH 8. The precipitate was washed with 3 l of water and filtered. A 115 g of $Zr(OH)_4$ was obtained after drying at 100 °C for 24 h. A 30 ml aliquot of 1N H_2SO_4 was added to 2 g of $Zr(OH)_4$ on a filter and the solid was then dried for 15 h at room temperature. SO_4/ZrO_2 was obtained by heating the solid at 600 °C for 3 h, and then sealed in a glass bulb. $Ag/SO_4/ZrO_2$ was prepared by immersing 2 g of SO_4/ZrO_2 in 30 ml of 0.02 M Ag_2SO_4, and dried at 600 °C.

2.3.4. Preparation of Ag/H/Nafion

Ag/H/Nafion was prepared by exchanging half the SO_3H protons with Ag^+. A 50 g sample of Nafion

NR-50 beads (7–9 mesh, 0.8 meq./g, Aldrich) was immersed in an aqueous solution in which 3.4 g (0.02 mol) of $AgNO_3$ had been dissolved for 20 h. The supernatant solution was analyzed by ICAP-575 II, and Ag^+ was not detected. The Ag/H/Nafion was washed several times with demineralized water, and dried at 110 °C for 20 h, then used for the reaction.

2.3.5. Carbonylation of alcohols by solid superacids

For carbonylation of the alcohols, a 120 ml stirred stainless steel autoclave enclosed in an electric furnace was used. As a general procedure, 2 g of Ag/H/Nafion, 20 mmol of an alcohol, and 50 ml of a solvent were placed in the autoclave. The initial CO pressure at room temperature was varied in the range of 1–90 atm. 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 and GC–MS and by titration with an ethanol solution of 0.1 mol/l NaOH. The carbonylations of the alcohols by Nafion, ZSM-5, Ag/ZSM-5, SO_4/ZrO_2 and $Ag/SO_4/ZrO_2$ were carried out in the same way.

3. Results and discussion

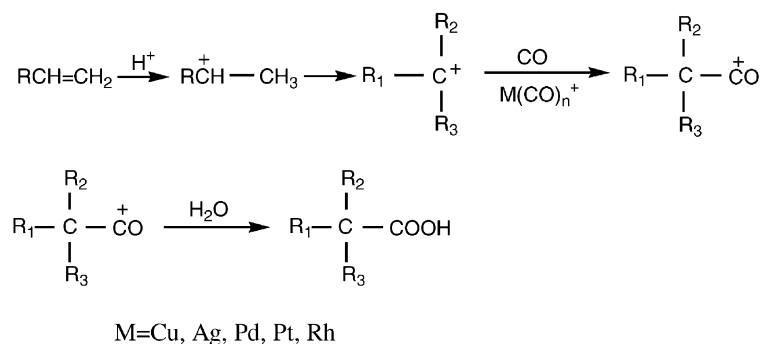### 3.1. Carbonylation of saturated hydrocarbons by superacid

The copper carbonyl catalyst, $Cu(CO)_n^+$ ($n = 2, 3,$ and 4), and silver carbonyl catalyst, $Ag(CO)^+$ ($n = 1, 2$), accelerate the carbonylation of olefins or alcohols in sulfuric acid to give *tert*-carboxylic acids

[5]. Recently, the catalytic properties of $Au(CO)_2^+$, $[Pd_2(CO)_2]^{2+}$, $[Pt_2(CO)_6]^{2+}$, and $[Rh(CO)_4]^+$ in sulfuric acid were also studied with respect to their effect on the carbonylation of olefins or alcohols [13]. In this Koch reaction, carbocations are first formed by protonation of the olefin and then rearrange to the most stable *tert*-carbocation, and finally reacted with CO to give *tert*-carboxylic acid (Scheme 1).
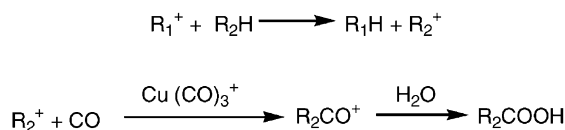
In these cationic metal carbonyls, the $\nu(CO)$ in the IR spectrum was observed at a higher wavenumber compared to the free CO (2143 cm^{-1}), and the ^{13}C NMR chemical shifts δ were observed at a higher field compared to the free CO (184 ppm). The $\nu(CO)$ of $Cu(CO)_3^+$, $Ag(CO)^+$, $Au(CO)_2^+$, $[Pd_2(CO)_2]^{2+}$, $[Pt_2(CO)_6]^{2+}$ and $Rh(CO)_4^+$ were observed at 2175, 2186, 2208, 2167, 2174 and 2139 cm^{-1}, respectively, in H_2SO_4. The δ values of the above complex were observed at 169.2, 172.9, 175, 177, 166.3, and 171.5 ppm, respectively, in H_2SO_4. The theoretically predicted C–O stretching frequencies are shifted toward higher wavenumbers in $M(CO)_n^+$, which agrees with the experimentally observed vibrational spectra [24]. It is known that the M–C bond of these metal carbonyl cations were mainly formed by the σ-dative bond of CO, and the π-back bonding from the metal is negligibly small [7,14,15,24].

When saturated hydrocarbons having a *tert*-hydrogen were mixed with olefins in the $Cu(CO)_n^+/H_2SO_4$ catalyst solution, *tert*-hydrogen was abstracted by the carbocation formed by the olefin [16]. The resulting *tert*-carbocation reacted with CO to then give the *tert*-carboxylic acid (Scheme 2).
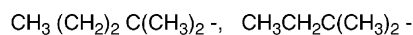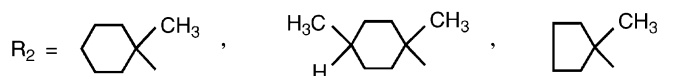
Olefins or alcohols were used as the sources of the carbocations. A portion of the olefin and alcohol
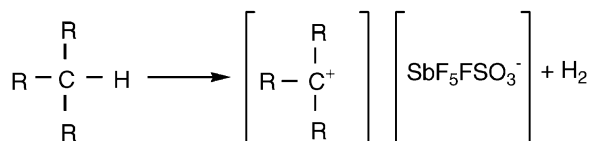

M=Cu, Ag, Pd, Pt, Rh

Scheme 1.

$$R_1^+ + R_2H \longrightarrow R_1H + R_2^+$$

$$R_2^+ + CO \xrightarrow{\text{Cu(CO)}_3^+} R_2CO^+ \xrightarrow{\text{H}_2\text{O}} R_2COOH$$

R_1 = general alkyl (n -, sec -, *tert*-)

R_2 =

$CH_3(CH_2)_2 C(CH_3)_2$ -, $CH_3CH_2C(CH_3)_2$ -

Scheme 2.

Scheme 3.

also gave *tert*-carboxylic acids. The results of the carbonylation of saturated hydrocarbons are shown in Table 1. With an increase in the H_2SO_4 concentration to greater than 85%, a greater amount hydride abstract took place. The hydride abstract easily took place at 20–40 °C.

No *tert*-carboxylic acid was formed in H_2SO_4 when the saturated hydrocarbons did not contain a *tert*-hydrogen, and the superacid FSO_3H-SbF_5 is necessary to abstract hydride from the saturated hydrocarbons as Olah and Lukas reported [3] (Scheme 3).

Hydride abstract took place in the order: primary hydrogen < secondary hydrogen < tertiary hydrogen. The characteristic tendency in the superacid reaction is the easy cleavage of the C–C bond and rearrangement to the *tert*-carbocation. When the copper

carbonyl catalyst was added to the FSO_3H-SbF_5, carbonylation of the saturated hydrocarbons were accelerated to give *tert*-carboxylic acid. The reaction rapidly proceeded at −2 to 2 °C. These results are shown in Table 2.

3.2. Carbonylation of 3-hexanol with salts of cationic metal carbonyl complexes

Willner and Aubke prepared various metal carbonyl complexes such as $[Au(CO)_2][Sb_2F_{11}]$ [17], $[Pd(CO)_4][Sb_2F_{11}]_2$ [8], $[Pt(CO)_4][Sb_2F_{11}]_2$ [8], $[Fe(CO)_6][Sb_2F_{11}]_2$ [9], $[OsO_2(CO)_4][Sb_2F_{11}]_2$ [10], $[Hg(CO)_2][Sb_2F_{11}]_2$ [12], etc. in superacidic media and isolated them as white thermally stable salts. Some of them were used to promote the carbonylation of 3-hexanol at room temperature and atmospheric pressure. These results are shown in Table 3 (Scheme 4).

A solvent and protonation reagent were not used for the reaction. The carbocation is assumed to be formed as follows, and then further carbonylation took place (Scheme 5).
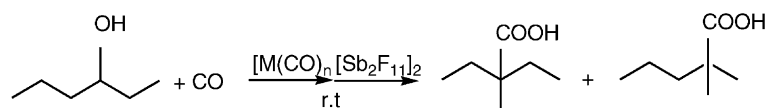
M = Pd, Pt, Fe, Ru, Os, Hg

Scheme 4.

Table 1
tert-Carboxylic acids from saturated hydrocarbons by copper(I) carbonyl catalyst[a]

Saturated compounds	Olefin or alcohol	Product	Yield (%)
Methylcyclohexane	1-Hexene	Methylcyclohexanecarboxylic acid	5.5[b]
		tert-C$_7$ acids[c]	1.5[b]
2-Methylpentane	1-Octene	2,2-Dimethylpentanoic acid	40
		2-Methyl-2-ethylbutanoic acid	20
		tert-C$_9$ acids[d]	30
2-Methylbutane	1-Octene	2,2-Dimethylbutanoic acid	30
		tert-C$_9$ acids[d]	60
		2,2-Dimethylpropionic acid	5
Methylcyclopentane	1-Octene	Methylcyclopentanecarboxylic acid	55
		tert-C$_9$ acids[d]	26
Methylcyclohexane	1-Hexene	Methylcyclohexanecarboxylic acid	51
		tert-C$_7$ acids[c]	30
Methylcyclohexane	1-Octene	Methylcyclohexanecarboxylic acid	65
		tert-C$_9$ acids[d]	30
Methylcyclohexane	2-Propanol	Methylcyclohexanecarboxylic acid	20
		2-Methylpropionic acid	5
Methylcyclohexane	*tert*-Butyl alcohol	Methylcyclohexanecarboxylic acid	33
		2,2-dimethylpropionic acid	10
Methylcyclohexane	1-Hexanol	Methylcyclohexanecarboxylic acid	43
		tert-C$_7$ acids[c]	29
Methylcyclohexane	1-Octanol	Methylcyclohexanecarboxylic acid	70
		tert-C$_9$ acids[d]	10
1,4-Dimethylcyclohexane	1-Hexene	1,4-Dimethylcyclohexanecarboxylic acids (*cis* to *trans*, 1:1)	55
		tert-C$_7$ acids[c]	26
Octane	1-Hexene	*tert*-C$_9$ acids[d]	0
		tert-C$_7$ acids[c]	64
2,2,4-Trimethylpentane	1-Hexene	*tert*-C$_9$ acids[d]	1
		tert-C$_7$ acids[c]	85
Cyclohexane	1-Hexene	*tert*-C$_7$ acids[c]	80

[a] In most cases, 0.2 mol of saturated hydrocarbon, 0.2 mol of olefin or alcohol, 0.02 mol of Cu_2O, and 105 ml of 98% H_2SO_4 were used. The reaction temperature was ∼30 °C, and the reaction time varied from 1 to 2 h. The pressure of carbon monoxide was 1 atm.

[b] Copper(I) compound was not used.

[c] The ratio of 2,2-dimethylpentanoic acid to 2-methylbutanoic acid was 2:1.

[d] The ratio of 2,2-dimethylheptanoic acid to 2-methyl-2-ethylhexanoic acid to 2-methyl-2-propylpentanoicacid was 4:2:1.

With the addition of 3-hexanol, the pale yellow color of $[Pd(CO)_4]$ $[Sb_2F_{11}]_2$ (**1**) changed to black. This suggested the partial formation of zero valent palladium in the solid. At the same time, the characteristic IR absorption of $\nu(CO)$ 2248 cm^{-1} of **1** disappeared, and a new species (**2**) having absorptions at 2146 and 2168 cm^{-1} was observed during the carbonylation and

$$ROH + [Sb_2F_{11}^-] \longrightarrow [R^+][SbF_6^-] + [HOSbF_5]^-$$

$$R^+ + CO \xrightarrow{[M(CO)_n]^{2+}} RCO^+ \xrightarrow{OH^-} RCOOH$$

Scheme 5.

tert-C$_7$ carboxylic acid was obtained in 15%. When H_2SO_4 was added as the protonation reagent, the yield of *tert*-C$_7$ carboxylic acid increased to 23%. We carried out the carbonylation of the olefin in sulfuric acid in the presence of the $[c$-$Pd_2(\mu CO)_2]^{2+}$ catalyst. Following the addition of 1-hexene, a new complex was observed at 2144 and 2167 cm^{-1}, and δ was 177 ppm, which indicates that the active species is $[Pd_2(CO)_2]^{2+}$ [13b]. From these results, the newly observed complex (**2**) was postulated to be an active species of $[Pd_2(CO)_2]^{2+}$ (Scheme 6).

When $[Pt(CO)_4][Sb_2F_{11}]_2$ (**3**) was used to promote the carbonylation, the characteristic absorption at 2244 cm^{-1} decreased with the addition of 3-hexanol,
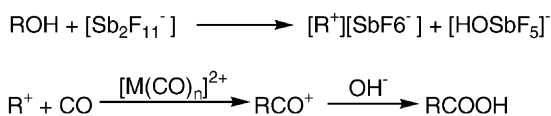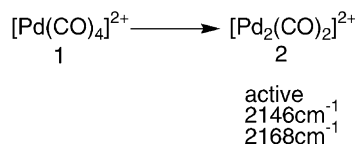
Table 2
Carbonylation of saturated hydrocarbons[a]

Substrate	Product	Yield (%)
Methylcyclopentane	1-Methylcyclopentanecarboxylic acid	45
	Cyclohexanecarboxylic acid	40
Methylcyclohexane	1-Methylcyclohexanecarboxylic acid	5
	Mixture of methylcyclohexanecarboxylic acid and ethylcyclopentanecarboxylic acid	90
Cyclohexane	Cyclohexanecarboxylic acid	45
Hexane	2,2-Dimethylpentanoic acid	55
	2-Methyl-2-ethylbutanoic acid	35
	2,2-Dimethylbutanoic acid	11
	2,2-Dimethylpropionic acid	17
	Cyclohexanecarboxylic acid	25
2-Methylpentane	2,2-Dimethylpentanoic acid	45
	2-Methyl-2-ethylbutanoic acid	30
2-Methylbutane	2,2-Dimethylbutanoic acid	20
	Mixture of 2,3-dimethylbutanoic acid and 4-methylpentanoic acid	40
Octane	2,2-Dimethylpropionic acid	195
Decane	2,2-Dimethylpropionic acid	102
	2,2-Dimethylbutanoic acid	20
	Mixture of 2-pentanecarboxylic acid and 3-pentanecarboxylic acid	30
	2,2-Dimethylpentanoic acid	30
	2-Methyl-2-ethylbutanoic acid	10

[a] The reaction was carried out using 20 ml of FSO_3H, 10 ml of SbF_5, 0.858 g of Cu_2O and 30 mmol of saturated hydrocarbons at -2 to 2 °C for 2 h at 1 atm of CO.

then new species (**4**) having a strong absorption at 2167 cm^{-1} and another species (**5**) having ν(CO) values at 2219 and 2189 cm^{-1} increased. The *tert*-C$_7$ carboxylic acids were then obtained in 38% yield. We carried out the carbonylation of the olefins in the presence of a platinum carbonyl catalyst in H_2SO_4 solution [13c,13e]. It was found that the active species of $[Pt_2(CO)_6]^{2+}$ having a ν(CO) at 2174 cm^{-1}, and an inactive species of *cis*-$[Pt(CO)_2]^{2+}$ having ν(CO) values at 2218 and 2182 cm^{-1} were formed at the

$$[Pd(CO)_4]^{2+} \longrightarrow [Pd_2(CO)_2]^{2+}$$
$$\quad 1 \qquad\qquad\qquad 2$$
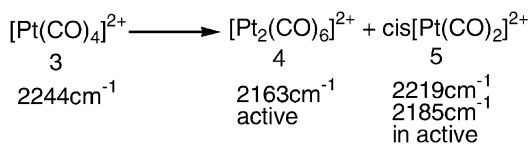
active
2146 cm^{-1}
2168 cm^{-1}

Scheme 6.

Table 3
Carbonylation of 3-hexanol catalyzed by white salts of cationic metal carbonyls[a]

Complex	Amount of complex (mmol)	3-Hexanol (mmol)	ROH/complex	Time (h)	Yield of *tert*-C$_7$ acids (%)[b]
$[Pd(CO)_4][Sb_2F_{11}]_2$	0.41	2.0	5.0	6	15
	0.04	1.0	24	6	5
$[Pt(CO)_4][Sb_2F_{11}]_2$	0.41	1.0	2.4	6	38
	0.41	2.0	5.0	6	29
$[Fe(CO)_6][Sb_2F_{11}]_2$	0.08	1.0	12	5	0
$[Ru(CO)_6][Sb_2F_{11}]_2$	0.24	1.0	4.2	4	0
$[Os_2(CO)_6][Sb_2F_{11}]_2$	0.25	1.3	5.0	6	7
$[Hg(CO)_2][Sb_2F_{11}]_2$	0.31	1.0	3.1	2	31

[a] CO 1 atm, RT.
[b] Based on 3-hexanol.

$[Pt(CO)_4]^{2+} \longrightarrow [Pt_2(CO)_6]^{2+} + cis[Pt(CO)_2]^{2+}$

3   **4**   **5**

$2244 cm^{-1}$ $2163 cm^{-1}$ $2219 cm^{-1}$

                    active $2185 cm^{-1}$

                                      in active

Scheme 7.

same time. From these results, it is postulated that **3** decomposed into the active species $[Pt_2(CO)_6]^{2+}$ (**4**) and inactive species *cis*-$[Pt(CO)_2]^{2+}$ (**5**) with the addition of the nucleophilic 3-hexanol. Compound **4** is the first dinuclear homoleptic metal carbonyl cation with only terminal CO ligands (Scheme 7).

As soon as nucleophilic 3-hexanol was added to $[Hg(CO)_2][Sb_2F_{11}]_2$ (**6**), the white powder changed to brown, and **6** decomposed. No absorption corresponding to the metal carbonyl was observed in the $2100-2300 cm^{-1}$ region. However, 31% of the *tert*-C_7 carboxylic acid was obtained. The mercury carbonyl seems to be very unstable in the presence of nucleophilic reagents. A similar phenomenon was observed for the carbonylation of 1-hexene in H_2SO_4. When $Hg[CH_3COO]_2$ was used as a catalyst in conc. H_2SO_4, 52% of the *tert*-C_7 carboxylic acids was obtained. Although no IR absorption corresponding to the mercury carbonyl was observed by the analysis on thin film between two silicon discs, mercury carbonyl is assumed to be formed by the in situ reaction [18].

When 3-hexanol was added to $[OsO_2(CO)_4]$ $[Sb_2F_{11}]_2$ (**7**), **7** was decomposed, and 7% of the *tert*-C_7 carboxylic acids was obtained. A specific IR absorption (2210 and $2253 cm^{-1}$) of **7** disappeared, and new absorptions (2188, 2172, and $2134 cm^{-1}$) were observed, but the new structure is not yet known. When 3-hexanol was added to $[Ru(CO)_6][Sb_2F_{11}]_2$ and $[Fe(CO)_6][Sb_2F_{11}]_2$, both white powders changed to brown, and decomposed, no carboxylic acids were obtained.

Better results are expected when a dehydrated alcohol or dry non-polar solvents are used in these carbonylations.

3.3. Carbonylation of alcohols by solid superacid catalysts

Solid superacid catalysts are convenient for the easy separation and recycling of catalysts in industrial applications. Zeolite, H/Nafion and sulfated zirconia were used for the Koch reaction, and *tert*-carboxylic acids were obtained [19–21].

It was reported that copper carbonyls were formed on Cu^+-ZSM-5 by the CO absorption and a precise IR absorption study of $Cu(CO)_n^+$ ($n = 1$, 2, and 3)
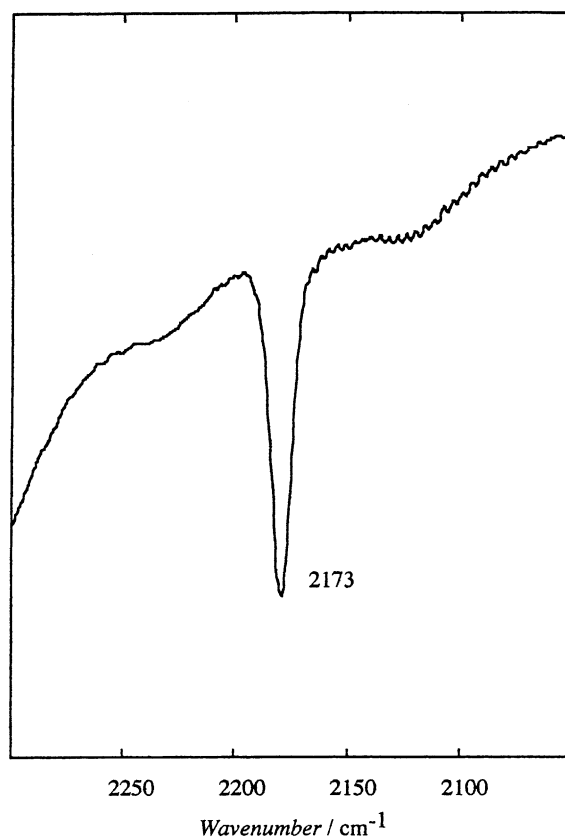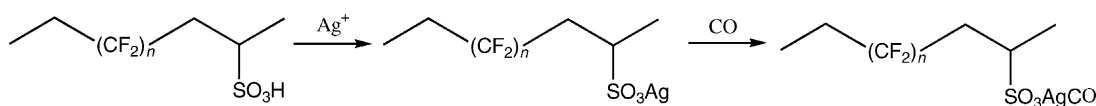
Fig. 2. Formation of silver carbonyl on Nafion. CO 190 mmHg, $20 °C$.

Scheme 8.

was carried out [22,23]. The ν(CO) of copper carbonyls on ZSM-5 were observed at a higher wavenumber than 2143 cm^{-1}, similar to the neat cationic metal carbonyls [5–15].

We prepared Ag/H/Nafion, Ag/ZSM-5 and Ag/SO$_4$/ZrO$_2$ by ion-exchange. These solid superacids were exposed to CO to form silver carbonyl on the surface. When Ag/Nafion was exposed to CO, silver carbonyl was expected to be formed as in Scheme 8. The ν(CO) of silver carbonyl on Nafion was observed at 2173 cm^{-1} as shown in Fig. 2. Solid superacids such as Ag/H/Nafion, Ag/ZSM-5 and Ag/SO$_4$/ZrO$_2$ were used for the carbonylation of alcohols. The results are shown in Table 4. The yield of the *tert*-carboxylic acid increased when Ag$^+$-supported solid superacids were used. The influence of CO pressure on the carbonyla-

tion of 2-methyl-2-propanol using the Ag/H$^+$/Nafion catalyst is shown in Fig. 3 The Koch reaction is an acid-catalyzed reaction by a proton. The amount of proton should then be the same for comparing the reactivity. Therefore, 1 g of Nafion NR-50 and 2 g of Ag/H/Nafion NR-50 were used to compare the reactivity. With the increase in CO pressure, the catalytic activity increased. When Ag/H/Nafion was used, a higher amount of 2,2-dimethylpropanoic acid was obtained. The influence of CO pressure on the carbonylation of 2-methyl-2-propanol by the Ag/ZSM-5 catalyst is shown in Fig. 4. With the increase in CO pressure, the catalytic activity increased. When Ag/ZSM-5 was used as a catalyst, the yield of 2,2-dimethylpropanoic acid was higher than that obtained using ZSM-5. Silver carbonyl seems to accelerate the carbonylation,
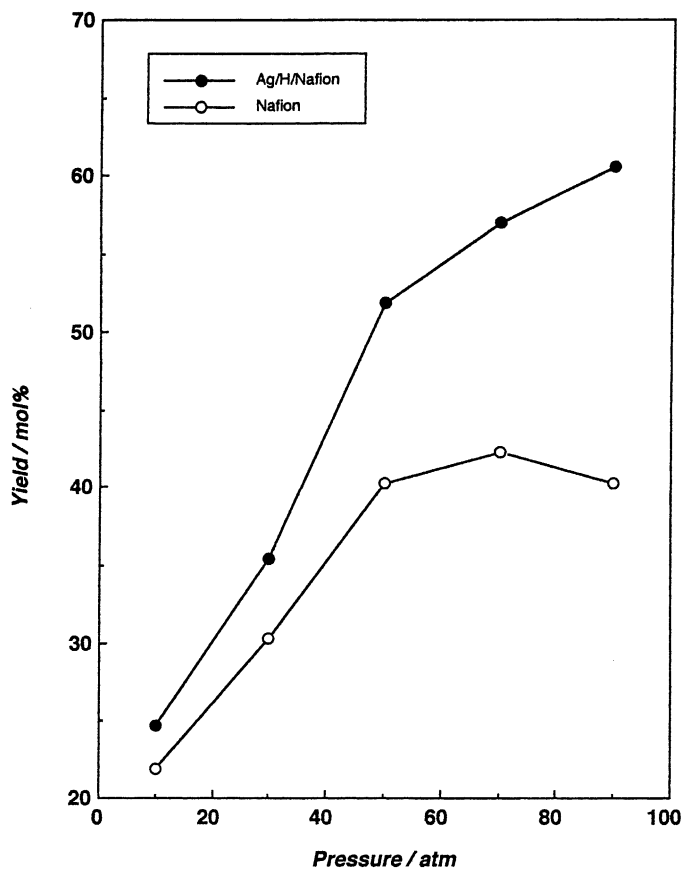

Fig. 3. The influence of CO pressure on the carbonylation of 2-methyl-2-propanol by Ag/H/Nafion catalyst. Reaction conditions: H/Nafion, 1 g; Ag/H/Nafion, 2 g; 2-methyl-2-propanol, 20 mmol; chlorobenzene, 50 ml; 160 °C, 22 h, CO pressure is initially at room temperature.

Table 4
Carbonylation of alcohols by solid superacids

Substate[a]	Product	Yield (%)	Catalyst[b]	Temperature (°C)	CO pressure (MPa)[c]	Time (h)	Solvent[d]
tert-Butanol	2,2-Dimethylpropanoic acid	12	SO_4/ZrO_2	150	5	18	*n*-Hexane
tert-Butanol	2,2-Dimethylpropanoic acid	16	$Ag/SO_4/ZrO_2$	150	5	18	*n*-Hexane
1-Adamantanol	1-Adamantanecarboxylic acid	77	Nafion	160	9	22	Chlorobenzene
1-Adamantanol	1-Adamantanecarboxylic acid	82	Ag/H/Nafion	160	9	22	Chlorobenzene
tert-Butanol	2,2-Dimethylpropanoic acid	55	ZSM-5	160	7	22	Chlorobenzene
tert-Butanol	2,2-Dimethylpropanoic acid	58	Ag/ZSM-5	160	7	22	Chlorobenzene

[a] Alcohols 20 mmol.
[b] Catalysts 2 g.
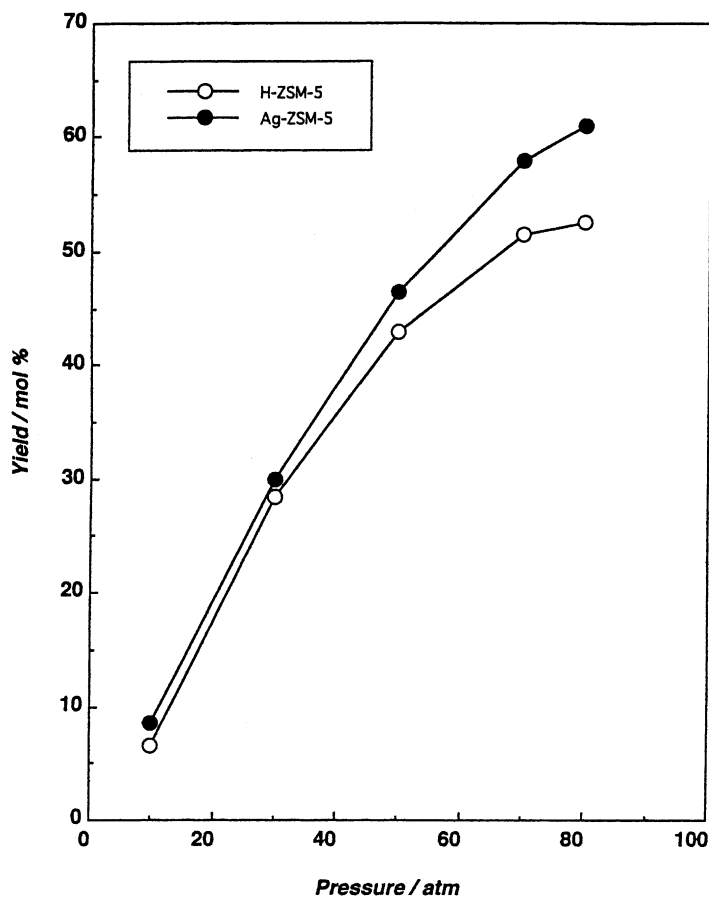[c] Initial pressure at room temperature.
[d] 50 ml.

Fig. 4. Carbonylation of 2-methyl-2-propanol by Ag/ZSM-5 catalyst. Reaction conditions: ZSM-5, 2 g; Ag/ZSM-5, 2 g; 2-methyl-2-propanol, 20 mmol; chlorobenzene, 50 ml; H_2O, 20 mmol.

but further research is necessary to improve the conditions.

4. Conclusions

The C–H bond activation of saturated hydrocarbons was studied in $Cu(CO)_n{}^+/FSO_3H\text{-}SbF_5$, and *tert*-carboxylic acids were obtained after hydride abstraction, and subsequent carbonylation of the carbocation. Solid cationic metal carbonyl complexes such as $[Pd(CO)_4][Sb_2F_{11}]_2$, $[Pt(CO)_4][Sb_2F_{11}]_2$, $[OsO_2(CO)_6] [Sb_2F_{11}]_2$, and $[Hg(CO)_2] [Sb_2F_{11}]_2$ promoted the carbonylation of 3-hexanol, and *tert*-C_7 carboxylic acids were obtained. When Ag/H/Nafion, Ag/ZSM-5 and Ag/SO$_4$/ZrO$_2$ were used as the solid superacid, the yield of the *tert*-carboxylic acid increased compared to those obtained with of Nafion, ZSM-5 and SO$_4$/ZrO$_2$. The ν(CO) of silver carbonyl on Ag/Nafion was observed at $2173\,cm^{-1}$. The carbonylations of alcohols and saturated hydrocarbons were accelerated in the presence of cationic metal carbonyl catalysts.

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