# Coordination chemistry of rhodium and iridium in constrained zeolite cavities: methanol carbonylation

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Abstract - Faujasites - like structure zeolites, possessing in their three dimensional framework, void cavities of 12-13 Å diameter, were found effective for anchoring soluble rhodium and iridium carbonyl compounds. $Rh^I(CO)_2$ and $Ir^I(CO)_2$ were in-situ synthesized by reacting $Rh^{III}$ and $Ir^{III}$ exchanged NaY zeolite with CO. The complexes were identified by infrared spectroscopy and other techniques. Reaction at high temperature with $CO-H_2$, $CO-H_2O$ mixture led to the formation of $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$ metal carbonyl clusters. The zeolite framework not only allows the heterogenization of these soluble compounds but also allows excess of charge on the Rh or Ir metal atoms. The mononuclear monovalent Rh and Ir dicarbonyls entrapped in the zeolite cavities were active for the vapor phase carbonylation of methanol in the presence of methyl iodide. The interesting feature of these systems was that methyl chloride can be used as promoter.

## INTRODUCTION

The literature has now shown that the catalytic properties of soluble transition metal complexes can be retained when immobilized on both organic and inorganic supports. It should be noted that the support is not innocent but plays the role of a ligand and as such could affect the catalytic reaction. Rhodium-based soluble compounds showed interesting catalytic activity in the methanol carbonylation in the presence of methyl iodide (ref. 1). Several attempts to heterogenize these catalysts have been made. Carbon attached (ref. 2) and polymer bound (ref. 3) rhodium carbonyls have been explored. The major disadvantages of these systems were the low dispersion and the low stability of the catalyst. More recently zeolites have been used to anchor rhodium carbonyl complexes which showed interesting catalytic properties in the vapor phase carbonylation of methanol (ref. 4,5,6,7).

We report in this paper the synthesis and the characterization of mono and polynuclear rhodium and iridium carbonyl compounds entrapped in the zeolite cavities. The effect of the zeolite ligand on the charge density at the metal atom will be traced through the infrared stretching frequencies of CO. In addition we will report on the carbonylation of methanol over entrapped-$Rh^I$ and $Ir^I$ carbonyl complexes. The reaction occurred with an appreciable rate when methyl iodide was used as promoter. The unexpected and interesting result was that methyl chloride could also be used with the zeolite heterogenized catalyst.

## MONONUCLEAR Rh$^I$ AND Ir$^I$ DICARBONYLS FORMATION IN ZEOLITE

Earlier work (ref. 8) has shown that $[Rh(NH_3)_5Cl]^{2+}$ exchanged NaY zeolite, which has been activated in oxygen to remove $NH_3$ ligands, reacts with CO at 293 K with the subsequent reduction of $Rh^{III}$ to $Rh^I$. The reduction was demonstrated by XPS studies. Indeed the XPS peak at 310.8 eV corresponding to the binding energy of $Rh^{III}$ 3d5/2 was shifted to 308.1 eV ($Rh^I$3d5/2) after CO reaction. Infrared studies indicated the formation of $CO_2$. Furthermore in the CO stretching region two intense doublets appeared at 2116-2048 and 2101-2022 cm$^{-1}$. These IR bands were due to the formation of two different $Rh^I(CO)_2$ complexes within the zeolite cavities. The dicarbonyl monovalent rhodium complexes were formed according to the reactions:

$$Rh^{III}(H_2O) + CO \longrightarrow Rh^I + 2H^+ + CO_2$$

$$Rh^I + 2CO \longrightarrow Rh^I(CO)_2$$
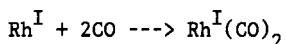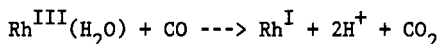
The structures of the rhodium carbonyl complexes were specified recently (ref. 9). It was proposed that the low frequency doublet 2101-2022 cm$^{-1}$ could be assigned to $Rh^I(CO)_2$ bonded to two zeolite lattice oxygen, while the high frequency doublet 2116-2048 cm$^{-1}$ was due to $[(O^{2-})(HO) Rh^I(CO)_2]$. Hence one may suggest that the charge density at the rhodium atom will be high when the complex is bonded to the zeolite lattice.

Similarly $Ir^I(CO)_3$ and/or $Ir^I(CO)_2$ (ref. 10,11) were generated when exchanged $Ir^{III}$ - NaY zeolite reacted with CO at 443 K. At room temperature the rate of formation of $Ir^I(CO)_2$ was very low in contrast with the high reactivity of $Rh^{III}$ in zeolite. The monovalent iridium carbonyl complex was identified by the doublet vCO IR bands at 2086 and 2001 cm$^{-1}$. In summary of these results one may conclude that in situ synthesis of $Rh^I(CO)_2$ and $Ir^I(CO)_2$ complexes was feasible starting from $Rh^{III}$ or $Ir^{III}$ exchanged NaY zeolite. The zeolite framework not only exerted a stabilizing effect on these complexes but also, due to the negatively charged framework, increased, to some extent, the charge density at the central metal atom of the carbonyl complex.

## POLYNUCLEAR METAL CARBONYL CLUSTERS FORMATION IN ZEOLITE

Zeolite-attached $Rh^I(CO)_2$ although relatively stable in CO atmosphere, was rapidly trans-formed into rhodium carbonyl clusters when it was treated at 323-373 K in $CO-H_2O$ or $CO-H_2$ atmosphere. The transformation of $Rh^I(CO)_2$ was followed by the disappearance of the IR bands due to $Rh^I(CO)_2$ and the subsequent growth of IR bands at around 2090-2030 cm$^{-1}$ and at 1830 and 1760 cm$^{-1}$. In fact the band at 1830 cm$^{-1}$ decreased rapidly while the 1760 cm$^{-1}$ band increased, as the reaction temperature was increased from 323 to 373 k. By comparison with the IR data of the well known $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ it was concluded that both $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ were produced within the zeolite cavities, $Rh_4(CO)_{12}$ being easily converted into $Rh_6(CO)_{16}$ by raising up the reaction temperature (ref. 12). The in-situ synthesis of $Ir_4(CO)_{12}$ cluster, starting from $[Ir(NH_3)_5Cl]NaY$ samples was also performed (ref. 13). As in the case of Rh-NaY, the reaction of IrIII-NaY with $CO-H_2$ mixture or $CO-H_2O$, resulted in the formation of $Ir_4(CO)_{12}$. Indeed the solid turned yellow, $CO_2$ gas was formed and intense narrow infrared bands were detected at 2073-2030 cm$^{-1}$. Quantitative measurement of the CO uptake during the reaction, and isotopic exchange experiments, $^{12}$CO ligands of the metal

cluster being replaced by [13]CO, showed that the CO/Ir ratio characterizing the metal cluster is equal to 3. Furthermore, by refluxing the zeolite-supported iridium carbonyl in toluene, a yellow compound was extracted showing infrared bands at 2070-2020 $cm^{-1}$ due to terminal CO ligands. This IR spectrum was similar to the one exhibited by $Ir_4(CO)_{12}$ in cyclohexane. It was concluded that $Ir_4(CO)_{12}$ was generated within the zeolite cavities.

The negatively charged zeolite matrix exerts a significant effect on the charge density at the Ir metal atoms. It is known that while $Ir_4(CO)_{12}$ showed only terminal CO ligands, $Ir_4(CO)_{11}X^-$, where one CO has been replaced by one negatively charged ligand, exhibited both terminal CO and bridged CO, with the appearance of an IR band at around 1800 $cm^{-1}$ (ref. 14). $Ir_4(CO)_{12}$ in hydrated NaY zeolite as indicated above showed only terminal CO. However upon dehydration in vacuo at 293 K, which resulted in the removal of $H_2O$ present in the cavities, a narrow intense IR band at 1813 $cm^{-1}$ appeared due to bridged CO. It is concluded that the zeolite matrix exerts on $Ir_4(CO)_{12}$ cluster the same effect as a negatively charged ligand. When the zeolite cavities are partially filled with water, $Ir_4(CO)_{12}$ is surrounded by water molecules and thus protected from the electrostatic field of the zeolite. Removal of $H_2O$ molecules leads to a strong interaction of the $Ir_4(CO)_{12}$ cluster with the negatively charged zeolite framework. Thus an excess of electron charge around iridium atoms appears and several CO ligands are transformed from terminal to bridged configuration.

## CARBONYLATION OF METHANOL IN THE PRESENCE OF CH₃I, CH₃CL PROMOTERS

The carbonylation reaction of methanol, catalyzed by soluble carbonyl $Rh^I$ complexes, was found to be promoted by $CH_3I$ (ref. 1). The mechanism of the reaction was elucidated by combining kinetics and infrared studies (ref. 15). The following steps for the reaction were proposed: oxidative addition of $CH_3I$ to $[Rh(CO)_2I_2]^-$ which is the rate determining step followed by methyl migration to form rhodium acetyl. Methylacetate and acetic acid were produced by methanolysis or hydrolysis of the acetyl moiety (ref. 15). Substitution of $CH_3I$ by $CH_3Cl$ or by pentachlorobenzenethiol lowered considerably the reaction rate. Indeed under similar experimental conditions the rate of methanol carbonylation decreased by a factor of $10^2$ with $C_6Cl_5SCH_3$ (ref. 17) promoters. In this paragraph the vapor phase carbonylation of methanol catalyzed by zeolite-entrapped rhodium or iridium carbonyl complex is discussed. Kinetic studies of the methanol carbonylation reaction over Rh-NaY and Ir-NaY gave rate expressions identical to those proposed for the reaction in solution (ref. 6,7).

$$r = k[Rh]^1 [CH_3I]^1 (P_{CH3OH})^0 (P_{CO})^0 \qquad r = k[Ir]^1 [CH_3I]^0 (P_{CH3OH})^1 (P_{CO})^0$$

Although rhodium-based catalysts were preferred for the carbonylation of methanol in the liquid phase, iridium-based catalysts also were active for this reaction (ref. 18,20). However the mechanism of the reaction over iridium halides and $CH_3I$ as promoter was found more complex and involved at least two different cycles depending on the experimental conditions which influenced the structure of the active iridium complex (ref. 20). By increasing the concentration of $CH_3I$ the iridium species changed from the neutral complex $Ir(CO)_3I$ to anionic species $HIr(CO)_2 I_3^-$ and $Ir(CO)_2I_2^-$. Our results showed that zeolite-supported iridium catalyst was also active for the carbonylation of methanol in the vapor phase. In table 1 are listed the turnover numbers measured over Rh-NaY and Ir-NaY catalysts. The rate of methanol carbonylation over Ir-NaY is almost five time larger than over Rh-NaY with $CH_3I$ as promoter. The difference of activity between Ir-NaY and Rh-NaY is even more pronounced when $CH_3Cl$ is used as promoter.

Table 1. Turnover number in hour$^{-1}$ for $CH_3OH$ carbonylation
on Rh-NaY and Ir-NaY.

|  | Promoter | |
| --- | --- | --- |
| Catalyst | $CH_3I$ | $CH_3Cl$ |
| Rh-NaY (1.5 % Rh) | 18 | 0.6 |
| Ir-NaY (1.2-1.7 % Rh) | 95 | 25 |

$T_R$ = 423 K - Flow rate = 5-9 l h$^{-1}$ - $P_{CH3X}$ = 8.8 torr

$P_{CH3OH}$ = 6.5 torr - $P_{CO}$ = 300 torr ($CH_3I$), 45 torr ($CH_3Cl$).

Recently interest has been centered on finding promoters which could have an effect, on the methanol carbonylation, analogous to that of $CH_3I$, while being less corrosive, easily separated from the products by distillation. The carbonylation of methanol in the presence of rhodium chloride as the catalyst occurred when methyl bromide (ref. 21) pentachlorobenzenethiol (ref. 3) were used as promoters. However the rate of carbonylation with these promoters was almost two order of magnitude less than with $CH_3I$. These features were explained by the less effectiveness of $CH_3Br$ to dissociate and consequently to oxidatively add on Rh$^I$ complexes. The rate determining step being the oxidative addition of $CH_3X$ one could understand that $CH_3Br$ will be a less effective promoter than $CH_3I$. In this research it was thought that a solid matrix like zeolite, showing strong ionizing properties, could enhance the rate of the chloride abstraction in $CH_3Cl$ thus increasing the effectiveness of $CH_3Cl$ promoter during the carbonylation of methanol. Table 1 shows that both Rh$^I$ and Ir$^I$ carbonyl complexes catalyzed the carbonylation of methanol in the presence of methyl chloride promoter. Furthermore comparison with $CH_3I$ promoter indicates that, within the zeolite matrix, $CH_3Cl$ is relatively as effective as $CH_3I$ to promote the methanol carbonylation by the heterogenized rhodium or iridium complexes. In contrast, in liquid phase the activity of Rh-$CH_3Cl$ was 10$^5$ less than that of Rh-$CH_3I$ (ref. 16).

In order to characterize the intermediate species formed by the interaction of $CH_3I$ with zeolite-supported Rh$^I(CO)_2$ or NaY-Ir$^I(CO)_2$ infrared spectroscopy has been used. Fig. 1 and 2 show the infrared spectra, in the carbonyl stretching region, of the intermediate complexes formed. Spectrum 1a due to $(O^{2-})_2Rh^I(CO)_2$ vCO at 2101-2022 cm$^{-1}$ and $[(O^{2-})(OH)Rh^I(CO)_2]$, vCO at 2116-2050 cm$^{-1}$ was altered, after $CH_3I$ adsorption, into spectrum 1b. The removal of the two previous doublet with the subsequent formation of one doublet at 2109-2040 cm$^{-1}$ was attributed to the conversion of the two initial carbonyl species into the unique complex $[(O2-)(CH_3I)RhI(CO)_2]$ where non dissociated $CH_3I$ interacts with Rh. Both at 25° and at 100°C a slow transformation occurred, the doublet at 2109-2040 cm$^{-1}$ decreased slowly while it appeared two new IR bands at 2090 cm$^{-1}$ and 1725 cm$^{-1}$ the latter being unambiguously assigned to the rhodium acetyl moiety (Fig. 1c). Thus it is shown that $CH_3I$ bound to Rh$^I(CO)_2$ is slowly dissociated into $(CH_3)$ and $(I)$ fragments oxidatively adsorbed on

Rh$^I(CO)_2$, this step being rapidly followed by methyl migration to form the acetyl moiety $[(O^{2-})(I)(CH_3CO)Rh^{III}(CO)]$ as already proposed in (ref. 15).

The behaviour of Ir$^I(CO)_2$ was quite different. Indeed the infrared spectra represented in Fig. 2a and 2b show that upon addition of $CH_3I$ the doublet at 2088-2003 cm$^{-1}$ due to Ir$^I(CO)_2$ bound to lattice oxygens is replaced by two sets of doublet at 2152-2105 cm$^{-1}$ and 2124-2080
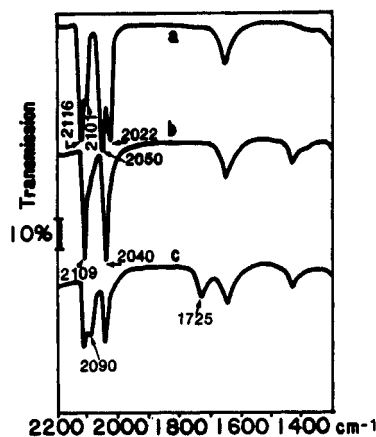
Fig. 1. IR Spectra of NaY-encaged $Rh^I(CO)_2$
(a) interacting with 15 Torr $CH_3I$ at room
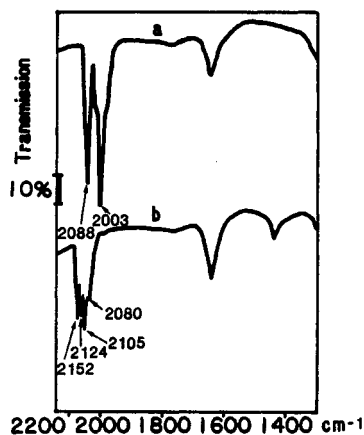temperature: (b) after 5 min contact
(c) after 2 hr contact



Fig. 2. IR Spectra of NaY-encaged
$Ir^I(CO)_2$ (a) interacting with
5 Torr $CH_3I$ at room temperature (b).

$cm^{-1}$ the relative intensity of these two sets of doublet depending on the $CH_3I$ concentration and Ir content. In no case an IR band around 1700 $cm^{-1}$ could be detected. From these results it is concluded that zeolite-bound $Ir^I(CO)_2$ experienced a rapid oxidative addition when it was reacted with $CH_3I$ to form $[(O^{2-})(CH_3)(I)Ir^{III}(CO)_2]$. In the absence of $CH_3OH$ and/or CO the latter complex shows no tendency to isomerize to an acetyl iridium species even on heating at 100°C.

In the reaction conducted with $CH_3Cl$, the addition of the methyl chloride to $Rh^I(CO)_2$ bound to the lattice oxygens led to a non dissociative interaction and the formation of the unique complex $[(O^{2-})(CH_3Cl)Rh^I(CO)_2]$ characterized by the doublet at 2112-2045 $cm^{-1}$ (Fig. 3). In contrast with $CH_3I$ addition, the oxidative addition of $CH_3Cl$ on $Rh^I(CO)_2$ was not observed by IR which confirms that with Rh-based catalysts $CH_3Cl$ promoter is less effective than $CH_3I$.

The effectiveness of $CH_3Cl$ in oxidative addition on $Ir(CO)_2$-NaY was demonstrated by the infrared results shown in Fig. 4 which illustrate the reaction between $CH_3Cl$ and $[(O^{2-})_2Ir(CO)_2]$. At 25°C, $CH_3Cl$ is bound to the Ir atom without dissociation, the new adduct formed being characterized by a doublet at 2095-2024 $cm^{-1}$ (Fig. 4b). The interaction was
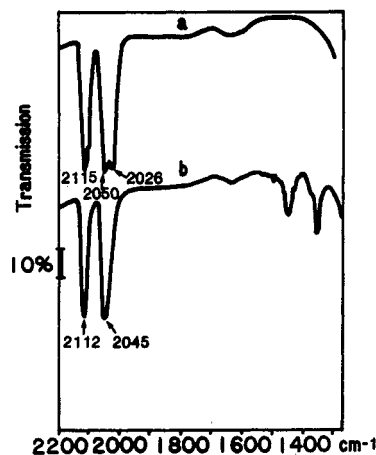


Fig. 3. IR Spectra of NaY-encaged $Rh^I(CO)_2$
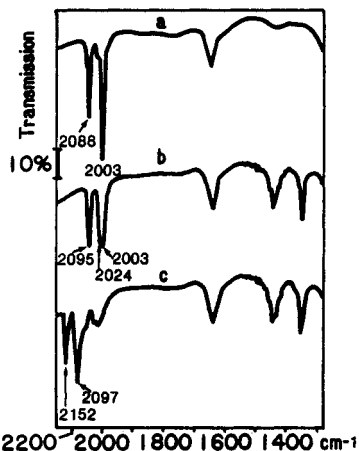(a) interacting with 12 Torr $CH_3Cl$ in the
temperature range 293-373 K (b)



Fig. 4. IR Spectra of NaY-encaged $Ir^I(CO)_2$
(a) after contacting with 6 Torr $CH_3Cl$ at
293 K (b) and at 393 K for 1 hour (c).

reversible and strongly dependent on the $CH_3Cl$ concentration, increasing the pressure of $CH_3Cl$ decreasing further the intensity of the IR doublet at 2088-2003 $cm^{-1}$. At 120°C the IR bands around 2095-2024 $cm^{-1}$ were removed and it appeared two new bands at 2152-2097 $cm^{-1}$ attributed to the dissociation of $CH_3Cl$ bound to $Rh^I(CO)_2$ followed by the oxidative addition on the central iridium atom to form the carbonylation reaction intermediate $[(O^{2-})(CH_3)(I)Ir^{III}(CO)_2]$.

The effect of the matrix in facilitating the oxidative addition of $CH_3Cl$ to the $Ir^I(CO)_2$ species can be explained by a concerted mechanism. On one hand, the matrix is thought to interact via $O^{2-}$ ions with $CH_3Cl$ undissociatively bound to $Ir^I(CO)_2$, thus strongly polarizing the $CH_3$-Cl bond:

$$Zeol-O^{2-} \text{ --- } \overset{\delta+}{CH_3}-\overset{\delta-}{Cl} \text{ --- } Ir^I(CO)_2.$$
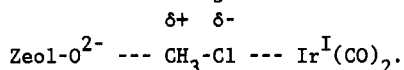
On the other hand, an increase of the charge density at the Ir atom due to the coordination of the Ir complex to donating $O^{2-}$ ions of the matrix should favor the attack of the methyl group on the Ir atom and should undergo the oxidative addition of $CH_3Cl$. These two effects would enhance the reactivity of methyl chloride compared to what was observed for the homogeneous process.

In conclusion, this work has shown that the vapor phase carbonylation of methanol with iridium based catalysts is promoted by  as $CH_3I$ and $CH_3Cl$ as well when zeolites are used as supports.

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