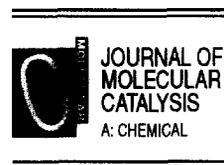




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Intercalation compounds of α -zirconium hydrogen phosphate with Rh^{3+} ions and Rh^{3+} -diamine complexes. Part II. Their behaviour towards CO, CO_2 and H_2 and their use in the CO catalytic oxidation

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Abstract

The reactivity of Rh^{3+} ions and Rh^{3+} -diamine $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ complexes intercalated in α -zirconium hydrogen phosphate towards small molecules (CO , O_2 , H_2) was studied. The compounds only containing Rh^{3+} ions, of composition $\text{ZrH}_x\text{Rh}_y(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($x = 2 - 3y$; $0 < y \leq 0.66$) react with CO at atmospheric pressure and temperatures ranging from 80 to 100°C, and undergo selective reduction of Rh^{3+} to Rh^{1+} . The resulting materials containing Rh^{1+} are reoxidized to Rh^{3+} by molecular dioxygen under the same pressure and temperature conditions. The simultaneous action of a CO/O_2 mixture determines the catalytic oxidation of the CO to CO_2 and the system acts as a stable catalyst of this reaction. At higher temperatures, the reduction of Rh^{3+} is no longer selective and in these conditions Rh^0 is formed, which escapes from the support and causes its deactivation. Similar behaviour is found in systems containing Rh^{3+} -diamine complexes, which react with CO at temperatures higher than 120°C and undergo an irreversible reduction of Rh^{3+} to Rh^0 . The reaction with H_2 ($70 < T < 100^\circ\text{C}$) also causes a non selective reduction of the Rh^{3+} to Rh^{1+} and Rh^0 . The progress over time of the catalytic activity of some compounds with different contents of Rh^{3+} in converting CO to CO_2 has shown not only that these materials maintain a constant catalytic activity, indicating the stability of the systems to the loss of metal during working cycles, but also that Rh^{3+} supported in these matrixes is more active and selective in this type of reaction than Rh^{3+} in solution.

Keywords: Zirconium hydrogen phosphate; Intercalation; Rhenium complexes; Catalytic oxidation

1. Introduction

We have recently ascertained that the activity of Pd^{2+} -ions or of some Pd^{2+} -diamine com-

plexes in catalyzing the oxidative carbonylation of amines, is not inhibited when they are intercalated by means of ion exchange into planes of α -zirconium acid hydrogen phosphate, an inorganic ion-exchanger used as support [1]. However, these systems were found not to be very

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stable, as in conditions of catalysis the support slowly loses palladium and deactivates.

In the endeavour to find more stable and active systems in analogous or other reactions, we prepared and characterized some new intercalation compounds of α -zirconium hydrogen phosphate with Rh^{3+} ions and Rh^{3+} -diamine complexes [2] and studied their reactivity in reductive and oxidative conditions.

Rhodium was chosen because it can be involved in processes in which the redox pair $\text{Rh}^{3+}/\text{Rh}^{1+}$ is present. The presence of ion species, even in a reduced state (Rh^{1+} and not Rh^0), could in our opinion be sufficient to maintain the metal in the support and avoid its deactivation.

2. Experimental

2.1. Materials

Phosphoric acid and ZrOCl_2 were ERBA RP ACS (highest purity) products. Rhodium (III) nitrate and aromatic diamines 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp) were Fluka "purissimum" products. All were used as received.

The layered α -zirconium hydrogen phosphate, $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ($\alpha\text{-ZrP}$) and the $\alpha\text{-ZrP}$ -aromatic diamine intercalation compounds $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot (\text{bipy})_{0.25} \cdot 1.5\text{H}_2\text{O}$ ($\alpha\text{-ZrP-bipy}$), $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot (\text{phen})_{0.5} \cdot 2\text{H}_2\text{O}$ ($\alpha\text{-ZrP-phen}$) and $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot (\text{dmp})_{0.5} \cdot 2.5\text{H}_2\text{O}$ ($\alpha\text{-ZrP-dmp}$) were prepared as reported previously [2].

Rh(III) -zirconium phosphate materials with chemical composition $\alpha\text{-ZrH}_x\text{Rh}_y(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($x = 2 - 3y$; $0 < y \leq 0.66$), hereafter indicated as $\alpha\text{-ZrP-Rh}_y$, were obtained by contacting the metastable ethanolic form of the exchanger $\alpha\text{-Zr}(\text{HPO}_4)_2(\text{EtOH})_2$ ($\alpha\text{-ZrPEtOH}$) with proper volumes of $\text{Rh}(\text{NO}_3)_3$ solution. The Rh(III) -diamine-zirconium-phosphate compounds with formulae $\alpha\text{-ZrH}_x\text{Rh}_y\text{L}_z(\text{PO}_4)_2 \cdot$

$t\text{H}_2\text{O}$ ($x = 2 - 3y$; $0 < y \leq 0.66$; $\text{L} = \text{bipy}$, phen, dmp; $0.25 < L < 0.5$; $1.8 < t < 3.1$) were obtained from the Rh(III) -nitrate solutions and the respective $\alpha\text{-ZrP-L}$ intercalation compounds. The insertion of Rh^{3+} in $\alpha\text{-ZrP-phen}$ and $\alpha\text{-ZrP-dmp}$ causes a partial elution of the respective diamine from the solids. Phen and dmp are the more released to the contact solution the higher the $\text{Rh}^{3+}/\text{H}^+$ exchange. Full details on the preparation and characterization of all of the materials have been reported in Ref. [2].

2.2. Physical measurements

A HP 5890 gas chromatograph with a thermal conductivity detector connected to a Varian 4270 integrator was used for analysis of gas mixtures. Analyses (CO , H_2 , O_2) were achieved on a molecular sieve 5A column (2 ft \times 0.25 in.); a porapak Q column (12 ft \times 0.125 in.) was used to analyze CO_2 .

X-ray photoelectron spectra were taken on a Vacuum Generator ESCALAB MK II spectrometer (Servizio Esca, C.N.R., Area della Ricerca, Rome) employing $\text{Al K}\alpha_{1,2}$ excitation (1486.6 eV) at a residual pressure of 10^{-9} Pa. The samples were dusted as a thin film onto gold or steel plate to minimize changing effects. The binding energy calibration was made with respect to the $4f_{7/2}$ gold line at 83.7 eV and sample charging was corrected by referencing to C 1s line of the containing oil carbon, taken at 285.0 eV. The binding energies were considered to be accurate to ± 0.05 eV. Cooling of the samples to liquid nitrogen temperature was performed as a precaution against possible secondary decomposition effects owing to the X-ray source. The spectra were usually recorded in the fixed analyser transmission (fat) mode at 20 eV. The collection and the fit of the XPS spectra were made by DEC PDP 11/24 data system [3]. X-ray powder diffraction patterns were taken on a Philips 1130 PW diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation (2θ angles accurate 0.05°).

Table 1
CO₂ developed by α -ZrP-Rh_y samples with different Rh content

Compound	Rh (mmol)	Time (h)	V(CO ₂) (ml) ^a
α -ZrP-Rh _{0.42}	0.35	2	5.5
α -ZrP-Rh _{0.42}	0.35	8	7.5
α -ZrP-Rh _{0.66}	0.40	3	7.1
α -ZrP-Rh _{0.66}	0.40	8	8.4

^a Values corrected for the solubility of CO₂ in reaction conditions.

2.3. Reaction of ZrP-Rh_y or ZrP-Rh_y-ligand with CO

All reactions were carried out in a glass vessel reactor of known volume (45.7 ml) provided with a jacket for thermostating. In a typical experiment, 0.255 g of α -ZrP-Rh_{0.66} (0.40 mmol of Rh) were added to 10 ml of an oxygen free ethanol-H₂O (5%) mixture, saturated with CO. The reactor was connected by teflon stopcocks to a vacuum manifold and a gas burette, and then thermostatted at 20°C. Carbon monoxide was added to the suspension which was left under stirring for 10 min. No reaction takes place under these conditions. The reactor was charged with a CO pressure equal to atmospheric pressure and was then connected with a bath thermostatted at 80°C and allowed

to react under stirring. After the reaction went to completion (about 6–8 h), the reactor was cooled and its temperature thermostatted at 20°C. Under these conditions CO or N₂ were added to the reactor, through the gas burette, to restore the atmospheric pressure. Known volumes of the gas were analyzed gas chromatographically and the CO₂ present was measured. The results were corrected for the solubility of CO₂ in reaction medium by means of a calibrated curve obtained in the same reaction conditions. Volumes of CO₂ developed by two samples at different times are shown in Table 1.

The inorganic matrix in suspension was filtered and XPS analyzed for the oxidation state of the rhodium. The spectrum shows signals characteristic of Rh¹⁺ indicating completion of the reaction (see Table 2 and Fig. 1b referring to α -ZrP-Rh_{0.66} sample).

The reactions under H₂ were carried out in the same conditions and at the end of the reaction the material was filtered and XPS analyzed (Fig. 1d).

2.4. Reaction with O₂

0.331 g of α -ZrP-Rh_{0.42} (0.35 mmol of Rh) suspended in 10 ml of an oxygen free ethanol-

Table 2
XPS characterization of surface rhodium for α -ZrP-Rh_{0.66} (A) and α -ZrP-Rh_{0.66} previously reduced for 6 h in CO flow (B), under various atmospheres

Treatment	Rh 3d _{5/2}			Rh ³⁺ /Rh ¹⁺	Rh ³⁺ /Rh ⁰
	Rh ³⁺	Rh ¹⁺	Rh ⁰		
As prepared	309.7	—	—		
(A) In CO flow					
At 80°C; 2 h	309.7	308.8	—	0.3	
At 80°C; 6 h	—	308.7	—		
(A) In CO/O ₂ flow					
At 80°C; long time	309.6	—	—	0.4	
(B) In O ₂ flow	309.7	308.5		2	
At 80°C; 6 h					
(A) In H ₂ flow					
At 70°C; 1 h	309.7	308.6	307.5	4.4	
At 100°C; 1 h ^a	309.6	308.6		3.1	3.7

^a For α -ZrP-Rh_{0.66}-bipy_{0.25} in the same operative conditions were obtained the following results: Rh³⁺/Rh¹⁺ = 0.9.

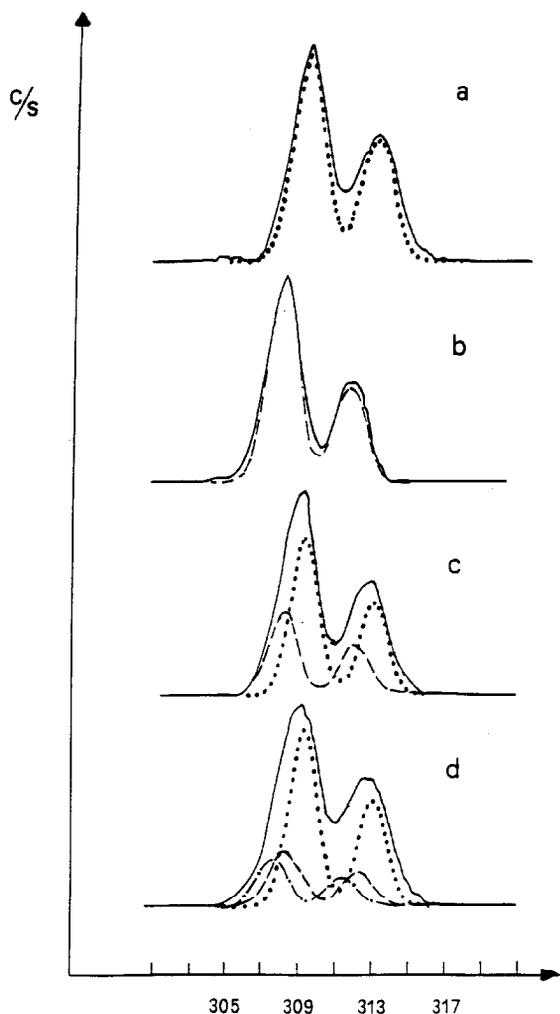


Fig. 1. Photoelectron spectra of the Rh $3d_{5/2}$ levels of: (a) α -ZrP-Rh_{0.66}; (b) α -ZrP-Rh_{0.66} 6 h under CO at 80°C; (c) the previous material 6 h under O₂ at 80°C; (d) α -ZrP-Rh_{0.66} 1 h under H₂ at 100°C.

H₂O (5%) mixture, was left to react under CO as described above. After reaction, the gas phase was purged and firstly N₂ and then O₂ were slowly bubbled through the suspension at room temperature for 5 min. The reactor was charged with O₂ at atmospheric pressure and left to react under stirring at 80°C for 10 h. At the end of this time the reactor was cooled, the temperature was thermostatted at 20°C and the atmospheric pressure was restored through the gas burette with N₂. 2.7 ml of gas corresponding to 70% of the O₂ required to oxidize the initial

Rh¹⁺ to Rh³⁺, according to the stoichiometry of reaction (3), were necessary to restore the pressure. The suspension was filtered and the residue was analyzed by XPS spectrum. The intensity of the signal related to Rh³⁺ was about three times higher than that of Rh¹⁺, which agrees with the volume of reacted dioxygen, too.

The reactions with α -ZrP-Rh_y-ligand were carried out according to the above described procedure.

2.5. Catalytic reaction

General procedure: reactions were achieved in a glass reactor of known volume (135.4 ml) which was charged under N₂ with a weighed amount of ZrP-Rh_{0.66} and 20 ml of an ethanol-H₂O (5%) mixture. A 2/1 mixture of CO/O₂ was bubbled for 2 min, then the reactor was closed at atmospheric pressure and allowed to react at the temperature and for the time desired. After reaction, the reactor was cooled at 20°C and the inside pressure was restored through a gas burette. Both the CO/O₂ and N₂ were used as restoring gas. In the first case only the CO₂ formed in the reaction can be detected, in the other, the amount of reacted CO and O₂ can also be obtained. In all experiments, the amounts of CO₂ produced and CO and O₂ consumed were according to the stoichiometry of the reaction (4).

In a typical experiment α -ZrP-Rh_{0.66} (0.13 mmol of Rh) were left to react for 15 h. The following values were obtained: CO₂ (corrected for the solubility), 10.0 ml (0.45 mmol; turnover number (TN) = 5.5 mol/mol Rh × day); CO, 10.3 ml; O₂, 5.2 ml.

Catalysis with other compounds and in different conditions were achieved according to the procedures described.

The experiments at higher than atmospheric pressures were carried out in a stainless steel autoclave of known volume (55.6 ml) which was heated with an electrical oven having a magnetic stirrer built into its base.

2.6. Decomposition of $\alpha\text{-ZrP}(\text{dmp})\text{Rh}^{1+}-(\text{CO})_2$

$\alpha\text{-ZrH}_{0.44}\text{Rh}_{0.52}(\text{dmp})_{0.37}(\text{PO}_4)_2 \cdot 3.1\text{H}_2\text{O}$ (0.274 g, 0.30 mmol of Rh) were allowed to react with CO in an ethanol–H₂O mixture. After reduction the compounds show IR bands at 2095 (m) and 2038 (m) cm⁻¹. N₂ was bubbled into the reaction mixture to remove the CO, then I₂ or an aqueous HCl solution were added (I₂ or HCl/Rh = 10) and the system was heated at 130°C. The gas developed was gas chromatographically recognized as CO and its volume was measured by a gas burette. 12 ml of CO (0.53 mmol; CO/Rh = 1.76), corresponding to 88% of the expected value, were obtained with both reactants.

3. Results and discussion

3.1. Reaction with CO, O₂, H₂

The reactivity of the $\alpha\text{-ZrP-Rh}_y$, and $\alpha\text{-ZrP-Rh}_y\text{-L}_z$ systems towards the small molecules CO, O₂, H₂, alone or in mixtures, was investigated in order to gain some indication as to their possible use in reductive and/or oxidative catalytic processes.

The eventual modifications of oxidation state undergone by the various Rh³⁺-containing samples have been followed by means of XPS experiments. Depending on the treatment undergone by the samples the XPS analyses of the Rh 3d_{5/2} core levels showed the presence of one, two or three components falling at 309.7 ± 0.2 eV, 308.6 ± 0.2 eV and 307.5 ± 0.2 eV. While the last binding energy value (307.5 eV) can be assigned to zerovalent rhodium, the first two (309.7 and 308.6 eV) are respectively assigned to tri- and monovalent metal ion in agreement with literature data [4]. The value of binding energy ascribed to Rh³⁺ (309.7 eV) is also obtained for Rh(NO₃)₃ in our XPS experiments.

Alfa-ZrP-Rh_y materials suspended in a mixture of ethanol–water (5%), undergo the reductive action of the carbon monoxide at 80°C and

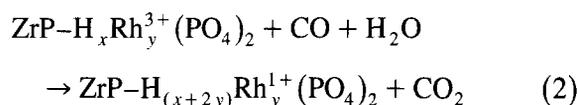
atmospheric pressure and transform into the corresponding systems containing Rh¹⁺ (reaction (1)).



The reduction of a metallic ion by carbon monoxide is fairly common among transition metals (see for example Ref. [5]) and is often used to prepare carbonyl- and non-carbonyl-complexes, in lower oxidation states. RhCl₃·hydrate itself reacts with CO to give the well known dimer [RhCl(CO)₂]₂ [6].

Reaction (1) was ascertained both analyzing the CO₂ in the reaction gaseous mixture and analyzing the residual inorganic matrix in which Rh¹⁺ was found.

The protons produced in the reaction bond to the phosphate groups of the solid according to the constancy of the pH before and after reaction. In this view, reaction (1) is better described in reaction (2).

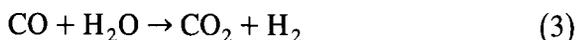


The quantity of CO₂ two hours after the start of the reaction approximately corresponds to the 70% of the amount of Rh³⁺ initially present in the matrix and agrees with the XPS analysis of the resulting material which shows the presence of Rh¹⁺ together with residual Rh³⁺. Longer reaction times lead to completion of the reaction with the disappearance of Rh³⁺ from the solid. Rh⁰ is never present.

The XPS analyses of the Rh 3d_{5/2} core level for $\alpha\text{-ZrP-Rh}_{0.66}$, as prepared and after 2 and 6 h treatment at 80°C in CO flow are summarized in Table 2, where are also reported the results of the reaction of $\alpha\text{-ZrP-Rh}_{0.66}$ with H₂ in which Rh⁰ is formed (see after). The Rh³⁺/Rh¹⁺ and Rh³⁺/Rh⁰ atomic ratios are also reported.

Reaction (1) represents the first stage of some well known catalytic processes like the oxidation of CO to CO₂ (reaction (6)) and the water gas shift reaction (reaction (3)) achieved for the first time effectively with Ru₃(CO)₁₂ by Ford

and co-workers [7], in which the rhodium has been proved to be effective, too [8].

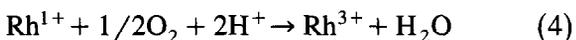


A reaction similar to reaction (1) can also constitute the initial step of other carbonylation processes which can be performed by substituting water with other nucleophiles.

As the catalysis in these processes requires the reoxidation of the Rh^{1+} to Rh^{3+} to reform the initial active species and to close the catalytic cycle, we investigated the behaviour of systems containing Rh^{1+} with molecular oxygen.

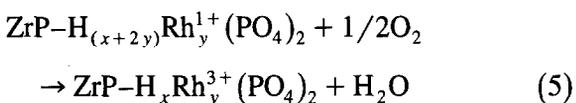
Thus, a hydro-alcoholic solution containing the sample $\alpha\text{-ZrP-Rh}_{0.66}$ was first allowed to react for 6 h under CO at atmospheric pressure and at a temperature of 80°C , and then put under dioxygen at atmospheric pressure under the same temperature condition for 6 h.

XPS analysis of the resulting matrix (see Table 2) showed that part of the Rh^{1+} formed in the first reductive step (reaction (1) or (2)) is reoxidized to Rh^{3+} (ratio signals intensity $\text{Rh}^{3+}/\text{Rh}^{1+} = 2$) probably in agreement with the stoichiometry of reaction (4).

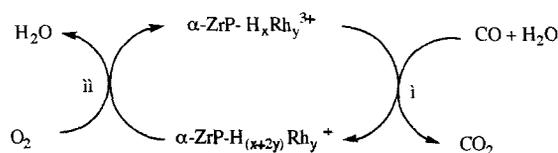


Longer reaction times are not sufficient to re-oxidize all the Rh^{1+} present to Rh^{3+} .

As the re-oxidation of Rh^{1+} to Rh^{3+} causes an increase of positive charge inside the ion-exchanger, 2 mol of H^+ per mol of re-oxidized Rh^{1+} must move from phosphate groups and pass in solution. Thus, reaction (4) should be more correctly described with reaction (5).



These results indicate that the oxidative step of Rh^{1+} to Rh^{3+} is slower than the reductive one. Support for this comes from the XPS analysis of samples allowing to react for a long time under CO/O_2 mixture (see below) showing a greater quantity of Rh^{1+} ($\text{Rh}^{3+}/\text{Rh}^{1+} = 0.4$).



Scheme 1. Scheme 1

The overall reaction of these two processes (reactions (2) and (5)) constitutes the catalytic oxidation of CO to CO_2 (reaction (6)).



We realized this reaction continuously and in a catalytic fashion by allowing a mixture of CO/O_2 (2:1) to react at atmospheric pressure with a sample containing Rh^{3+} or a sample previously reduced under CO, containing Rh^{1+} . We found that oxidation of CO to CO_2 occurs with a turnover number of 5.5 mol/mol rhodium per day. It's quite probable that, under these conditions, the conversion of CO into CO_2 occurs through a redox process whose main steps are outlined in Scheme 1.

The carbon dioxide is formed in the reductive step (i) (reaction (1) or (2)), while the catalytically active Rh^{3+} species is restored in the oxidative process, step (ii), reaction (4) or (5).

In order to be sure that Rh^{1+} is the only reduced species when the CO is the reductant, $\alpha\text{-ZrP-Rh}_{0.66}$ was treated with H_2 for one hour at 70 and 100°C . At 70°C the XPS results give account only for a reduction to Rh^{+1} , while the treatment at 100°C produces Rh^{+1} and Rh^0 , the former in a slightly higher amount. The reduction to Rh^0 causes a blackening of the material. However, metallic rhodium is not evidenced in the XRD pattern, probably because of the high dispersion of the material in the solid. In Fig. 1 are reported the $\text{Rh}3d_{5/2}$ spectra of: (i) $\alpha\text{-ZrP-Rh}_{0.66}$ as prepared (a); (ii) $\alpha\text{-ZrP-Rh}_{0.66}$ treated with CO for 6 h at 80°C (b); (iii) the previous material reoxidized with O_2 for 6 h at 80°C (c); (iv) $\alpha\text{-ZrP-Rh}_{0.66}$ treated with H_2 at 100°C for 1 h (d).

Different reactivity was found with samples containing Rh^{3+} -diamine complexes. Those

containing the bipy or phen ligand do not catalyze the oxidation of CO, as at 80°C the CO is not able to reduce Rh^{3+} to Rh^{1+} . The use of higher temperatures ($T \geq 120^\circ\text{C}$) leads to the formation of a dark material due to metallic rhodium which scatters inside the matrix.

Also, the sample containing the dmp ligand, although reduced by CO, is inactive to catalyze its oxidation as the reaction product is stable to the re-oxidation by molecular dioxygen. This compound can be safely formulated as a dicarbonyl complex of Rh^{1+} , $\alpha\text{-ZrP}-(\text{dmp})\text{Rh}^{1+}-(\text{CO})_2$ on the basis of IR and XPS spectral data and CO evolved upon decomposition. Its IR spectrum shows the presence of two carbonyl bands of medium intensity centered at 2095 and 2038 cm^{-1} , characteristic of a Rh^{1+} [9]; XPS signals are consistent for Rh^{1+} ion and a molar ratio CO/Rh of about two, was obtained upon chemical (iodine or HCl) decomposition of the material (see experimental).

The behaviour of systems with molecular H_2 in the temperature range 70–100°C was also investigated. All of the samples behave as those

without ligands. Thus, Rh^{3+} is partially reduced in a non-selective way to Rh^{1+} and Rh^0 . The ratio between the two forms steadily increases in favour of Rh^0 with increasing temperature and reaction times. In all the examined cases the Rh^0 must be finely scattered in the material as it was not visible at X-ray diffraction. The samples reduced at 70°C, which contained more Rh^{1+} than when reduced at 100°C, were slightly dark and found to be active to CO oxidation even after treatment with HCl (see below). Those reduced at 100°C were dark, presented no signals ascribed to Rh^{1+} and had no catalytic activity even after treatment with acid. In Fig. 2 are reported the Rh 3d_{5/2} photoelectron spectra of $\alpha\text{-ZrH}_{1.52}\text{Rh}_{0.16}\text{-bipy}_{0.25}(\text{PO}_4)_2 \cdot 1.9\text{H}_2\text{O}$ as prepared (a) and treated under H_2 at 70°C for 1 h (b).

3.2. Catalytic activity and stability of the $\alpha\text{-ZrP-Rh}_y$ systems

Catalytic oxidation of CO to CO_2 (reaction (6)) is a well known reaction and several catalytic systems, mostly noble metal based, working in homogeneous and heterogeneous conditions, have been realized [10]. The CO oxidation has also been observed in catalytic systems working under oxidative carbonylation conditions ($\text{CO} + \text{O}_2$), as an undesirable side-effect. The oxidative carbonylation of methanol to give dimethyl carbonate provides an example [11].

To examine the possibility of using these systems as catalysts in carbonylation reactions, we have studied their catalytic activity over time in converting CO to CO_2 . In fact, a decrease of the catalytic activity over time involving the elution of the metal would cause the deactivation of system.

The activity of three samples of $\alpha\text{-ZrP-Rh}_y$, with different contents of rhodium (see Table 3), was monitored for twenty days. The systems were left to react in catalytic conditions (CO/O_2 , 2:1 at atmospheric pressure; $T = 80^\circ\text{C}$) for 10–15 hours *per day*. Each day, which we will consider as a working cycle, the CO_2 de-

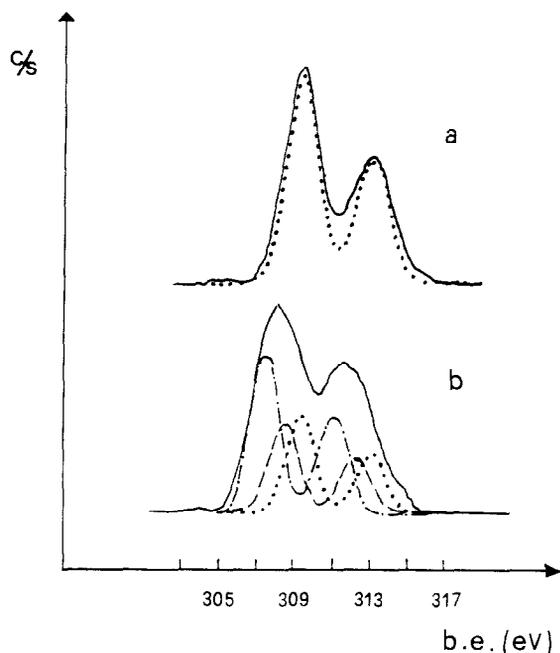


Fig. 2. Photoelectron spectra of: (a) $\alpha\text{-ZrP-Rh}_{0.16}\text{-bipy}_{0.25}$ as prepared; (b) 1 h under H_2 at 70°C.

veloped was measured and the catalytic activity was determined by means of the TN. After every working cycle, the catalyst was recovered by filtration and used in a new cycle with a fresh hydro-alcohol solution to prevent any rhodium, escaped from the matrix and present in the solution, from helping to maintain the catalytic activity.

The results obtained, apart from small variations which could be ascribed to different stirring efficiency, indicate that the three systems maintain their activity practically constant. Table 3 (entries 1–3) shows the average TN values after twenty working days.

During this time, the colour of the samples gradually changed from dove-grey to dark-brown. XPS analysis showed no Rh^0 signal, which would have justified the chromatic change. Indirect tests (see below), intended to ascertain the presence of metal rhodium so finely scattered as to be invisible at X-ray, were in agreement with the absence of Rh^0 also.

In fact, when the dark material containing the finely scattered Rh^0 , prepared by pre-reducing $\alpha\text{-ZrP-Rh}_{0.42}$ under H_2 at 100°C , was used as

catalyst, it was found to be poorly active in CO oxidation to CO_2 (Table 3, entry 4). Addition of HCl to the reaction medium ($\text{HCl/Rh} = 2$) determined some increase in the catalytic activity (entry 5). The activity remained constant only if the material is maintained in the presence of its originating mother liquor but is practically null if the catalyst is recovered by filtration and reused for a new catalytic cycle (entry 6). In contrast, when a sample of $\alpha\text{-ZrP-Rh}_{0.42}$ was left to work for ten days in catalytic conditions and then was subjected to acid treatment ($\text{HCl/Rh} = 2$), not only its catalytic activity was not lost, when the hydro-alcoholic solution was changed, but even an increase in turnover number was observed (entry 7).

These results indicate that:

– Metallic rhodium is poorly active in catalyzing the oxidation of CO to CO_2 under those conditions in which intercalated Rh^{3+} is effective. Rhodium (0) probably operates via mechanisms different from those involving the $\text{Rh}^{3+}/\text{Rh}^{1+}$ pairs (Scheme 1).

– The increased activity in an acidic medium is probably due to oxidation of the metallic

Table 3
Oxidative carbonylation of CO by $\alpha\text{-ZrP-Rh}_x$ systems^a

No.	Catalyst composition	Medium	CO_2 (mmol)	Time (h)	Temp. ($^\circ\text{C}$)	CO/O_2	P_{tot} (atm)	TN (mol/mol Rh day)
1	$\alpha\text{-ZrP-Rh}_{0.30}$	ethanol- H_2O	0.42	15	80	2	1	5.2
2	$\alpha\text{-ZrP-Rh}_{0.42}$	ethanol- H_2O	0.40	15	80	2	1	4.9
3	$\alpha\text{-ZrP-Rh}_{0.66}$	ethanol- H_2O	0.44	15	80	2	1	5.4
4	$\alpha\text{-ZrP-Rh}_{0.42}$ ^b	ethanol- H_2O	0.20	30	80	2	1	0.9
5	$\alpha\text{-ZrP-Rh}_{0.42}$ ^b	$\text{HCl/Rh} = 2$	0.56	30	80	2	1	3.5
6	$\alpha\text{-ZrP-Rh}_{0.42}$ ^c	$\text{HCl/Rh} = 2$	trace	30	80	2	1	—
7	$\alpha\text{-ZrP-Rh}_{0.42}$ ^d	$\text{HCl/Rh} = 2$	0.55	15	80	2	1	6.8
8	$\alpha\text{-ZrP-Rh}_{0.42}$ ^d	$\text{HCl/Rh} = 3$	0.57	15	80	2	1	7.1
9	$\text{RhCl}_3(0.13)$ ^e	$\text{HCl/Rh} = 3$	0.50	30	80	2	1	3.1
10	$\text{RhCl}_3(0.13)$	$\text{HCl/Rh} = 3$	0.40	15	80	2	1	4.9
11	$\text{RhCl}_3(0.13)$	$\text{HCl/Rh} = 4$	0.41	15	80	2	1	5.1
12	$\alpha\text{-ZrP-Rh}_{0.42}$	$\text{HCl/Rh} = 4$	0.48	15	90	2	1	6.0
13	$\alpha\text{-ZrP-Rh}_{0.42}$	$\text{HCl/Rh} = 4$	0.51	15	100	2	1	6.3
14	$\alpha\text{-ZrP-Rh}_{0.42}$	$\text{HCl/Rh} = 4$	0.60	15	9	$P(\text{O}_2) = 3$ atm	10	7.5
15	$\alpha\text{-ZrP-Rh}_{0.42}$	$\text{HCl/Rh} = 4$	0.64	15	90	$P(\text{O}_2) = 5$ atm	15	7.9
16	$\alpha\text{-ZrP-Rh}_{0.42}$	$\text{HCl/Rh} = 4$	0.66	15	100	$P(\text{O}_2) = 5$ atm	15	8.2

^a The amount of catalyst employed in all the experiments contains 0.13 mmol Rh.

^b Prereduced under H_2 at 100°C .

^c Recovered from experiment 5.

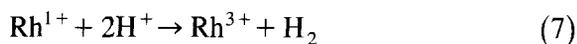
^d Kept for 10 days to work under catalysis conditions.

^e mmol Rh in parentheses.

rhodium, via a reaction similar to reaction (4), which determines the formation of the most active ion pairs during catalysis.

– The deactivation of the system after filtration, makes the acid treatment a valid test for ascertaining the formation of metallic rhodium not detectable by X-ray analysis.

In order to obtain some insight into the role played by acid we compared the catalytic activity of supported systems with that of a solution containing an equal quantity of RhCl_3 . Surprisingly, the results show that the Rh^{3+} in solution is less active (entry 9) and its reduction is also not selective. Metallic rhodium, as a fine dark suspension, was found in the reaction mixture. Only when the oxidation of CO with RhCl_3 was carried out in the presence of HCl with a molar ratio $\text{HCl}/\text{Rh}^{3+}$ ranging from 3 to 4, the precipitation of metallic rhodium could be prevented. The catalytic activity under these conditions was comparable to that of supported systems (entry 10–11). However, H_2 was also found among gaseous products. This suggests that the re-oxidation of Rh^{1+} to Rh^{3+} is likely to proceed via reaction (7) that combined with reaction (1) shows that RhCl_3 partially acts as water gas shift catalyst (Eq. (3)). The lack of H_2 in the reactions with $\alpha\text{-ZrP-Rh}_y$, indicates that the conversion of CO to CO_2 with these systems proceeds only by direct oxidation of carbon monoxide (reaction (6)).



The greater activity of supported systems could imply an increase in the oxidative step rate, which is the rate determining catalysis step (see above). It is not clear how this may occur but, on the basis of the positive influence exerted by acidity, it may be hypothesized that the oxidation of Rh^{1+} is in some way assisted by the $\text{PO}_3\text{-OH}$ group of the solid. Attempts to isolate $\text{Rh}^{1+}\text{-O}_2$ adducts, not unusual in rhodium chemistry [12], so as to observe any $(\text{O}_2)\text{-PO}_3\text{-OH}$ interaction, failed.

The stability of $\alpha\text{-ZrP-Rh}_y$ in more drastic conditions of acidity, temperature and CO pres-

ures was also investigated. The use of $\text{HCl}/\text{Rh} > 2$ ratios determines an increase in activity up to values of $\text{HCl}/\text{Rh} = 3$ (entry 8); higher values cause a gradual deactivation of the material due to rhodium passing into the solution through a $\text{Rh}^{3+}/\text{H}^+$ or $\text{Rh}^{1+}/\text{H}^+$ ion exchange process. As regards temperature, no diminution in stability was observed in the range 80–100°C, in which the system gives the best results (entries 12–13). Higher temperatures cause its deactivation, fairly rapidly in an acidic medium ($\text{HCl}/\text{Rh} = 2$) and more slowly in a neutral medium. Finally, an increase in the pressure of gas mixtures does not alter the stability of the system over time and, in the range investigated, determines an increase in TN (entries 14–16).

4. Conclusions

Trivalent rhodium ion inserted between the layers of α -zirconium hydrogen phosphate behaves as a stable and selective catalyst for the oxidation of CO to CO_2 under relatively mild conditions. The oxidation occurs through a mechanism involving a redox process (Scheme 1) whose two main steps have been also carried out separately. Carbon dioxide is formed in a reductive step where Rh^{3+} is reduced to Rh^{1+} (reaction (1)), while the catalytically active Rh^{3+} species is restored in an oxidative step by dioxygen (reaction (3)).

Analogous materials containing Rh^{3+} bonded to bipy, phen or dmp ligands are less effective and require higher temperatures that cause irreversible reduction of Rh^{3+} to Rh^0 .

This study enabled us to confirm that anchoring metallic ions inside an α -zirconium hydrogen phosphate matrix not only does not alter their activity but in some cases even enhances it, probably thanks to the assistance of the mono-hydrogen phosphate group.

Furthermore, the stability of $\alpha\text{-ZrP-Rh}_y$ to the loss of metal when it is involved in reactions in which there is participation of the ion pair $\text{Rh}^{3+}/\text{Rh}^{1+}$, on the one hand makes the idea of

using the inorganic matrix as a heterogeneous support seem a feasible proposition, and on the other, suggests that its efficiency is determined by maintaining of the system in ionic form.

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