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Rh^{3+} and Rh^{3+}–diamine complexes intercalated in γ-titanium hydrogen phosphate. Synthesis, characterisation and catalytic activity towards aniline oxidative carbonylation processes

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Abstract

New materials containing Rh(III) ions or Rh(III)–diamine complexes [(L = 2,2′-bipyridyl (bipy); 1,10-phenanthroline (phen); 2,9-dimethyl-1,10-phenanthroline (dmp)] intercalated in γ-titanium phosphate (γ-TiP) are described. The compounds have formula γ-TiPH$_x$Rh$_y$ · tH$_2$O ($x = 2$–$3y$; $0 < y < 0.18$; $1.5 < t < 2.2$), hereafter indicated as γ-TiPRh, and γ-TiPH$_x$Rh$_y$L$_z$ · nH$_2$0 ($x = 2$–$3y$; $0 < y < 0.25$; $0 < z < 0.35$; $2.5 < n < 4.2$), hereafter indicated as γ-TiPRhL. They were prepared by contacting samples of γ-TiP and γ-TiPL with appropriate volumes of Rh(III) solution, at 45°C. The materials were characterised by X-ray diffraction pattern and TG-DTA techniques. Their catalytic activity towards aniline carbonylation was tested. The compounds catalyse the oxidative carbonylation of aniline to diphenylurea (DPU) and/or methylphenylcarbamate (MPC). When the reaction is carried out in methanol or CH$_3$CN, at 70–90°C under moderate pressure of a CO/O$_2$ mixture ($P_{tot} = 0.5 \div 5$ MPa; $P(0_2) = 0.1 \div 0.8$ MPa), aniline is converted to DPU with a yield of 90% with respect to CO. The catalysts recovered and reused do not show any decrease of activity. When more drastic temperature conditions (110–150°C) are used, the carbonylation is not selective and the yield of carbon monoxide fixation is strongly dependent on the solvent. In CH$_3$CN, aniline is converted into DPU with a selectivity of 90% and the yield of CO fixation is still high (85%). Conversely, in methanol, N-phenylmethylcarbamate (MPC) is the main product with relevant amounts of CO$_2$ formed and a CO fixation yield not higher than 70%. Under these conditions, the catalysts when reused have shown a decrease of activity. On the basis of XPS analysis, it has been ascertained that the decrease in activity is due to an irreversible reduction of Rh^{3+} to Rh^o that causes the release of the metal from the support and the consequent deactivation of the catalyst. © 2000 Elsevier Science B.V. All rights reserved.
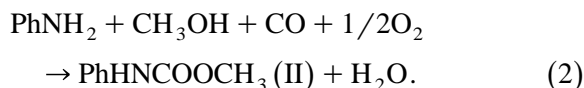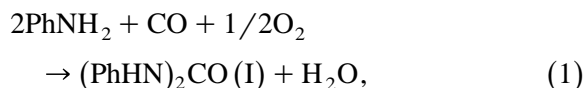
1. Introduction

The aniline carbonylation to diphenylurea (DPU) (Eq. 1) and carbamates (Eq. 2) is of

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interest as it provides a non-phosgene route to the synthesis of compounds that either find a direct practical application [1] or are intermediates for the synthesis of isocyanates:

$$2PhNH_2 + CO + 1/2O_2$$
$$\rightarrow (PhHN)_2CO\,(I) + H_2O, \qquad (1)$$

$$PhNH_2 + CH_3OH + CO + 1/2O_2$$
$$\rightarrow PhHNCOOCH_3\,(II) + H_2O. \qquad (2)$$

In fact, carbamates of primary amines can be converted into isocyanates by thermal decomposition (Eq. 3), while DPU can afford carbamates by alcohols (Eq. 4) and then phenylisocyanate (Eq. 3):

$$PhHNCOOR \rightarrow PhNCO + ROH, \qquad (3)$$

$$(PhHN)_2CO + ROH$$
$$\rightarrow PhHNCOOR + PhNH_2. \qquad (4)$$
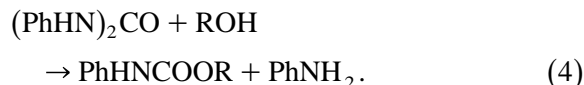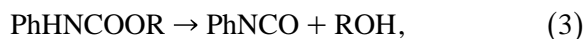
Although, in principle, aniline can be directly either carbonylated to DPU or to carbamate, the latter is more conveniently prepared from DPU. This synthetic strategy is made necessary by the fact that H_2O, which is formed in reaction (2), causes the decomposition of carbamate into CO_2 and aniline (Eq. 5), thus lowering the CO fixation yield:

$$PhHNCOOR + H_2O \rightarrow CO_2 + PhNH_2 + ROH. \qquad (5)$$
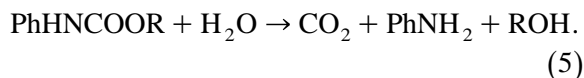
Some catalytic systems have been reported, mainly based on noble metals that work under both homogeneous and heterogeneous conditions and are able to perform the aniline carbonylation to DPU and/or carbamates [2–5].

In the recent years, our interest has been focused on finding suitable methods for synthesizing compounds, I and II [6–8]. Taking into account the advantages of heterogeneous vs. homogeneous catalysts, mainly in terms of catalyst separation and recycling, we have searched for simple, selective, efficient and stable heterogeneous catalytic systems.

The acid phosphates of tetravalent metals, α- or γ-zirconium phosphates (α- or γ-ZrP) and

γ-titanium phosphate (γ-TiP), are well-known either as ion exchangers or as agents able to intercalate organic molecules [9,10]. Such materials can include transition metal systems (naked ions or complexes). Metal ions can either be fixed on the inorganic matrix or co-ordinate organic molecules in situ with formation of intercalated complexes [11–15]. This behaviour can be used as an alternative route to heterogenize on an inorganic support metal complexes that are active homogeneous catalysts.

We have already investigated the properties of supported metal ions or complexes on α- and γ-zirconium hydrogen phosphate and tested the heterogenized catalysts towards carbonylation reactions [16]. Recently, we have reported that α- and γ-zirconium hydrogen phosphates (α- and γ-ZrP) containing Rh^{3+} ions or Rh^{3+} complexes, under suitable temperature and solvent conditions, act as stable and effective catalysts for the oxidative carbonylation of aniline. The reaction mechanism is identical with that of homogeneous systems [17,18]. In the present paper, we described the catalytic activity tested by recycling the catalyst of new materials obtained by heterogenizing Rh^{3+} ions and Rh^{3+}– diamine complexes on γ-titanium phosphate, $\gamma\text{-}Ti(PO_4)(H_2PO_4) \cdot 2H_2O$, an inorganic layered ion exchanger structurally similar to γ-ZrP [19]. The preparation and the solid state characterisation of these materials are also reported.

2. Experimental

2.1. Chemicals

Rhodium(III) nitrate, bipy, phen, dmp, methanol, acetonitrile and aniline were Fluka products and were used as received.

2.2. Materials

γ-TiP was prepared, characterised and stored as described in the literature [15]. The intercala-

tion compounds γ-Ti(PO$_4$)(H$_2$PO$_4$)bipy$_{0.40}$ · 0.35H$_2$O, (γ-TiPbipy$_{0.40}$); γ-Ti(PO$_4$)(H$_2$PO$_4$)- phen$_{0.45}$ · 1.6H$_2$O (γ-TiPphen$_{0.45}$); and γ- Ti(PO$_4$)(H$_2$PO$_4$)dmp$_{0.22}$ · 3H$_2$O (γ-TiPdmp$_{0.22}$) were prepared as previously described [15].

2.3. Physical measurements and chemical analysis

Rh^{3+} uptake was monitored by following the concentration change in the supernatant solutions after contact with the exchanger, using the GBC 903 atomic adsorption.

The compounds obtained were characterised by X-ray diffraction pattern by using a Philips diffractometer (Ni-filtered, Cu K radiation). The diamine ligands, the water content and the thermal behaviour of various materials were determined using the simultaneous apparatus, TG-DTA Stanton Model 750 Redcroft (ignition up to 1100°C, to reach a constant weight, in an air flow), heating rate 10°C/min.

X-ray photoelectron spectra were taken on a Leybold LHS 10 spectrometer (Centro Interdipartimentale di servizi nel settore della Spettroscopia, Università di Bari) employing Al K$\alpha_{1.2}$ excitation (1486.6 eV) at a residual pressure of 10^{-8} mbar. The samples were dusted and pressed onto a thin copper pellet to minimize charging effects. The binding energy calibration of the spectrometer was made with respect to both the $4f_{7/2}$ gold line at 84.0 eV and $2p_{3/2}$ copper line at 932.6 eV. Sample charging was corrected by referencing to C1s line of the contamination carbon, taken at 284.8 eV. The binding energies were considered to be accurate to ± 0.1 eV. The spectra were recorded in the fixed analyser transmission (FAT) mode at 50 eV. Data analysis of high-resolution spectra was performed using two packages, both running on Compaq Deskpro386. The first one [20] was employed in the preliminary stage of analysis (satellite and background subtraction and curve synthesis). The outputs of this stage were used as initial estimates of peak parameters in the

second software package, a nonlinear least-squares fitting program [21].

GLC quantitative analyses of methylcarbamates (MPC) and aniline were carried out with a Varian Vista 6000 gas chromatograph using a 30-m 0.53 mm ID DB5 capillary column. Reaction conditions: oven, 80°C (hold 2 min) to 180°C; carrier gas N2 (20 ml/s), and toluene as internal standard. DPU was isolated by filtration, analyzed and weighted.

An HP 5890 gas chromatograph with a thermal conductivity detector connected to a Varian 4270 integrator was used for gas analyses. Analyses of CO and O$_2$ were performed with a molecular sieve 5 A column; a porapak Q column was used for analysing CO$_2$. Methane was used as internal standard.

2.4. Rh^{3+} exchange procedure

γ-TiPRh and γ-TiPRh-L were prepared by contacting at 45°C for a week the corresponding material with a proper volume of a Rh^{3+} solution. The suspension was then filtered, the supernatant analysed for the rhodium content. A fast evaluation of uptaken rhodium (III) was obtained by measuring the pH decrease due to the Rh^{3+}/H^+ ion exchange process of the incoming metal ions with the di-hydrogen phosphate groups.

2.5. Catalytic reactions

All reactions were performed in a 55.6-ml stainless-steel autoclave mounted in an electrical oven having a magnetic stirrer in its base. Catalyst, co-catalyst and reagents were introduced in a Pyrex test tube placed inside the autoclave in order to prevent any contact with the metal. After reaction, under the conditions indicated in Table 2, the autoclave was cooled and the solids, DPU and γ-TiPRh, filtered off, washed with CH$_3$CN and weighted. Treating the solid residue with dimethyl formamide that dissolves DPU was possible to recover the catalyst. The DPU amount was used for estimating the turnover frequency (TOF) expressed as mole

of aniline reacted per gram of rhodium per hour. The catalyst was reused in another reaction for testing its efficiency and stability. The liquid and gas phases, containing, respectively, aniline and carbamate, the first one, and CO, O_2 and CO_2, the second, were fully analyzed to evaluate the selectivity of the process.

2.6. Reactions under mild temperature conditions

DPU was synthesized using different conditions and solvents.

2.6.1. Reaction in CH_3CN

In a typical experiment, the autoclave was charged with the catalyst (40 mg of γ-TiPH$_{1.46}$-Rh$_{0.18}$ · 2.2H$_2$O), co-catalyst (32.1 mg of PhNH$_3^+$I$^-$; I/Rh = 6), aniline (3 ml) and CH_3CN (7 ml). The autoclave was sealed, air was evacuated and then O_2 (0.8 MPa) and CO up to a total pressure of 5 MPa were admitted. After reaction, 1 h at 80°C, the autoclave was cooled and the content analyzed as described above. As an example, we can consider entry 2 in Table 2: reacted aniline, 7.2 mmol; diphenylurea, 3.6 mmol (100% selectivity); reacted CO, 4.0 mmol (90% yield); formed CO_2, 0.3 mmol.

2.6.2. Reaction in methanol

The reaction was carried out according to the above procedure using the same amounts of reactants and methanol in place of CH_3CN. Results (Table 2, entry 4): reacted aniline, 8.1 mmol; diphenylurea, 3.9 mmol (97% selectivity); reacted CO, 4.4 mmol (89% yield); formed CO_2, 0.6 mmol.

2.7. Reaction under more drastic temperature conditions

2.7.1. DPU synthesis in CH_3CN

The autoclave was charged as previously described using the same amounts of reactants and was heated to the desired temperature (110–150°C). Results (entry 12): reacted aniline, 16.7

mmol; diphenylurea, 7.5 mmol (90% selectivity); reacted CO 8.8 mmol (85% yield); formed CO_2, 1.5 mmol.

2.7.2. Methylphenylcarbamate synthesis in methanol

The reaction was carried out as described above using methanol as solvent. Results (entry 14): reacted aniline, 18.6 mmol; diphenylurea, 0.9 mmol (10% selectivity); methylphenylcarbamate, 13.8 mmol (74% selectivity); reacted CO, 21.1 mmol (70%); total selectivity of carbonylate aniline (DPU + MPC) 84%; formed CO_2, 6.2 mmol.

3. Results and discussion

3.1. Uptake of Rh^{3+} by γ-TiP and γ-TiP–diamine: synthesis and characterisation of corresponding Rh-intercalated materials

The materials were obtained as deep yellow, well-crystalline compounds and were characterised by X-ray powder diffraction patterns and thermal analysis.

In the case of the material derived from γ-TiP, it was not possible to obtain the completely exchanged phase γ-titanium–rhodium phosphate. Only a part of the phosphate groups was involved in the exchange, most of them remaining in the hydrogenphosphate form. The maximum Rh^{3+} uptake was reached after 1 week and a material with the chemical composition γ-Ti(PO$_4$)(H$_{1.46}$Rh$_{0.18}$PO$_4$) · 3.2H$_2$O was obtained. The latter shows a interlayer distance similar to that of γ-TiP, as demonstrated by X-rays analysis (Table 1).

If Rh^{3+} were kept in contact with compounds of type γ-TiPL, obtained by intercalation of dinitrogen ligands in γ-TiP, the exchange Rh^{3+}/H$^+$ was accompanied by the elution of intercalated diamine. The amount of both Rh^{3+}-exchanged and -leached ligand was dependent on the time of contact. Starting from γ-TiPphen$_{0.45}$, about 30% of phen ligand was

Table 1
Chemical composition and interlayer distance of some materials

Materials	d_{002} (Å)
γ-TiP $\cdot$ 2H$_2$O	11.60
γ-TiPH$_{1.46}$Rh$_{0.18}$ $\cdot$ 3.2H$_2$O	11.60
γ-TiPbipy$_{0.40}$ $\cdot$ 0.35H$_2$O	14.59
γ-TiPH$_{1.25}$bipy$_{0.33}$Rh$_{0.25}$ $\cdot$ 2.55H$_2$O	14.59
γ-TiPphen$_{0.45}$ $\cdot$ 1.6H$_2$O	17.46
γ-TiPH$_{0.95}$phen$_{0.35}$Rh$_{0.35}$ $\cdot$ 3.7H$_2$O	17.30
γ-TiPdmp$_{0.22}$ $\cdot$ 3H$_2$O	18.02
γ-TiPH$_{1.44}$dmp$_{0.04}$ $\cdot$ Rh$_{0.186}$ $\cdot$ 4.2H$_2$O	18.00

eluted after 1 week and the rhodium uptake was such as to obtain a material with a molar ratio Rh^{3+}/(diamine intercalated) = 1, as demonstrated by analysis of uptaken metal and leached diamine.

Materials with a Rh/diamine molar ratio < 1 were derived from γ-TiPbipy$_{0.40}$ (Table 1). If γ-TiPdmp$_{0.22}$ was used, the exchange Rh^{3+}/H^{+} caused a severe ligand leaching ($\sim$ 80%). The rhodium intercalation does not causes any change of the X-ray powder diffraction pattern of the Ti compound. All materials are crystalline, except the γ-TiPdmp-rhodium phase that is quite amorphous.

Table 1 shows the chemical composition and the interlayer distance, d_{002}, of some of the prepared materials.

It is quite clear that the intercalation of naked ion Rh(III) does not perturb the interlayer distance. A major deviation comes by the intercalation of diamine ligands. The uptake of Rh ions by the intercalated ligands does not cause further distortion.

3.2. XRDP

The X-ray powder diffraction pattern of the yellow crystalline materials containing rhodium shows the same layered structure of their precursors. Such a structure was maintained upon heating up to 250°C. Rising the temperature to 900°C, Rh$_2$O$_3$ reflections at d_{hkl} = 2.57–2.73–3.86 Å appear that disappear if the temperature is further increased. The disappearance occurs at 1200°C for the materials derived from γ-TiP and at 1100°C for those derived from γ-TiP-phen.

New peaks appear, under these conditions, at d_{hkl} = 2.20 and 1.90 Å, that are ascribed to Rh°.

On the basis of these data, it can be said that the ligand lowers the temperature of formation of Rh° of about 100°C with respect to the materials containing only the Rh. Fig. 1 shows the XRDP of γ-TiPH$_{0.95}$phen$_{0.33}$Rh$_{0.35}$ $\cdot$ 3.7OH$_2$O at 900°C (dark line) and at 1100°C
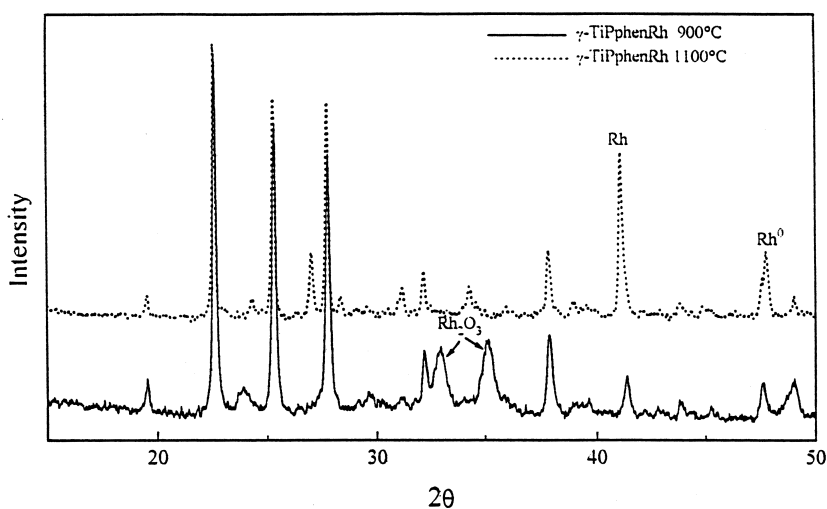

Fig. 1. X-ray diffraction patterns of: (—) γ-TiPphenRh at 900°C; ($\cdots$) γ-TiPphenRh at 1100°C.

(light line) with the related peaks of Rh_2O_3 and Rh^o, respectively.

3.3. Thermal behaviour

The thermal behaviour of all the materials containing rhodium was very similar. Fig. 2 shows the simultaneous curves TG-DTA of γ-
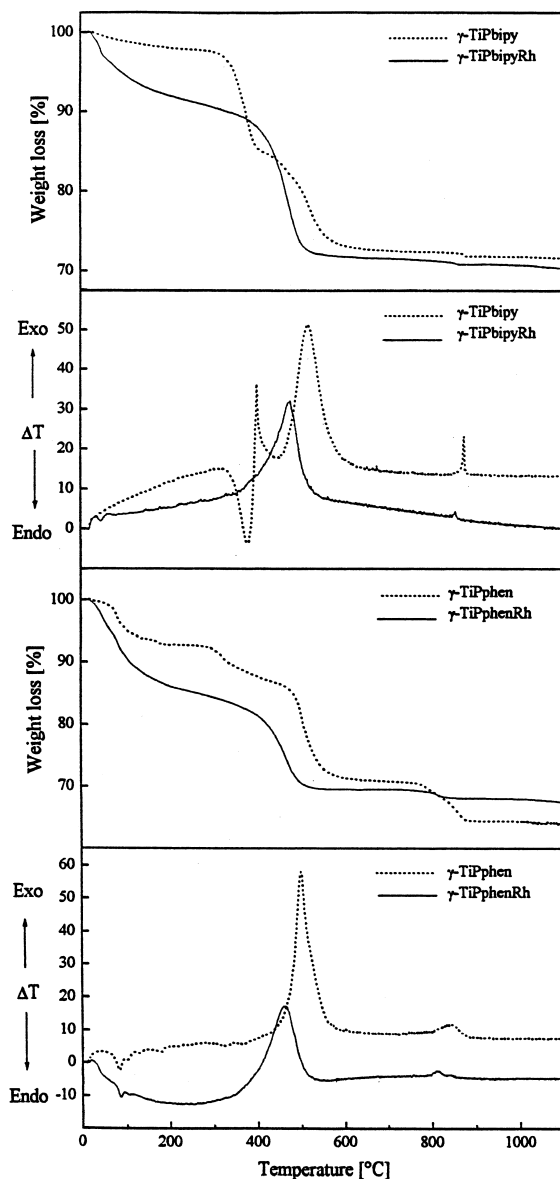

Fig. 2. TG-DTA curves of γ-TiPbipy-rhodium and γ-TiPphen-rhodium phase by comparison with those of their precursors.

TiPbipy-rhodium and γ-TiPphen-rhodium phase compared with those of their precursors. The TG curves of the rhodium-charged materials show an increase of loss of water at 200°C, with respect to the parent compound. This is due to the loss of water co-ordinated to rhodium ions. This loss overlaps with ligand decomposition, at 400°C. If the precursors are considered, the water loss is neatly separated from the ligand decomposition.

The water loss observed at 800°C is related to the condensation of phosphate groups to pyrophosphates. This loss starts at 400°C, and may be hidden by the loss of ligands.

The DTA curve of the γ-TiPphen-rhodium phase shows a clear exothermic peak at 440°C, corresponding to the phen decomposition. In the phase γ-TiPphen$_{0.45}$, such decomposition occurs at 510°C. It seems that the presence of rhodium catalyses the decomposition of the ligand that occurs at a lower temperature ($\sim$ 70°C). The same trend is observed when materials derived from γ-TiPbipy$_{0.40}$ are used.

The last exothermic peak at 800°C is related, in this case, to the transition phase of the layered pyrophosphates to the alpha cubic. Also, in this case, we have noted that with the rhodium materials, this transformation occurs at lover temperature (ca. 70°C) than for the parent compounds.

3.4. Catalytic behaviour

All the compounds have shown interesting catalytic properties for the oxidative carbonylation of aniline to DPU (Eq. 1). In a typical run, a suspension in CH_3CN or methanol was reacted with aniline and a CO/O_2 mixture under atmospheric or higher pressure, at 70–120°C, in the presence of $PhNH_3^+I^-$ as co-catalyst. The most significant results are summarised in Table 2. The catalytic activity increases with the pressure of the CO/O_2 mixture (entries 2, 6, 7), the temperature (entries 2, 3, 11, 12) and the ratio $PhNH_3^+I^-/Rh^{3+}$ (entries 5, 8, 9, 10). The best

Table 2
Oxidative carbonylation of aniline to DPU and MPC[a]

n	Compound	Solvent	I^-/Rh	T [°C]	P_{tot} [MPa]	Aniline Reacted (mmol)	DPU (mmol)	MPC (mmol)	TOF
1	γ-TiP	CH_3CN	6	100	5	0.95	–	–	–
2	γ-TiPRh$_{0.18}^b$	CH_3CN	6	80	5	7.2	3.6(100)[c]	–	2.89
3	γ-TiPRh$_{0.18}^b$	CH_3CN	6	90	5	7.9	3.9 (99)	–	3.17
4	γ-TiPRh$_{0.18}^b$	CH_3OH	6	90	5	8.1	3.9 (96)		3.25
5	γ-TiPRh$_{0.18}^b$	CH_3CN/CH_3OH	6	100	5	8.4	4.0 (95)	0.20 (2)	3.37
6	γ-TiPRh$_{0.18}^b$	CH_3CN	6	80	4	6.3	3.1 (98)	–	2.53
7	γ-TiPRh$_{0.18}^b$	CH_3CN/CH_3OH	6	80	3	5.3	2.6 (98)	–	2.13
8	γ-TiPRh$_{0.18}^b$	CH_3CN	3	100	5	7.1	3.4 (96)	–	2.85
9	γ-TiPRh$_{0.18}^b$	$CH_3CN/$	2	100	5	6.2	2.9 (94)		2.49
10	γ-TiPRh$_{0.18}^b$	CH_3CN	8	100	5	8.3	3.9 (94)	–	3.33
11	γ-TiPRh$_{0.18}^b$	CH_3CN	6	130	5	11.4	5.4 (95)	–	4.58
12	γ-TiPRh$_{0.18}^b$	$CH_3CN/$	6	150	5	16.7	7.5(90)		6.71
13	γ-TiPRh$_{0.18}^b$	CH_3OH	6	130	5	11.7	1.5 (26)	7.7 (66)	4.71
14	γ-TiPRh$_{0.18}^b$	CH_3OH	6	150	5	18.6	0.9 (10)	13.8 (74)	7.45
15	γ-TiPRh$_{0.25}$bipy$_{0.33}^d$	CH_3CN	6	100	5	9.1	4.3 (95)	–	3.21
16	γ-TiPRh$_{0.25}$bipy$_{0.33}^d$	CH_3CN	6	130	5	11.9	5.6 (94)	–	4.20
17	γ-TiPRh$_{0.25}$bipy$_{0.33}^d$	CH_3OH	6	150	5	20.7	0.6 (6)	17.0 (82)	7.31
18	γ-TiPRh$_{0.35}$phen$_{0.33}$ 3.86H$_2$O	CH_3CN	6	130	5	14.9	7.0 (94)		4.18
19	γ-TiPRh$_{0.35}$-phen$_{0.33}$ · 3.86H$_2$O	CH_3CN/CH_3OH	6	100	5	11.3	5.4 (96)		3.17
20	γ-TiPRh$_{0.186}$dmp$_{0.04}$ · 4.2 H$_2$O	CH_3CN	6	90	5	7.1	3.5 (98)	–	3.19

[a] In all the experiments, 40 mg of catalyst, 3 ml of aniline, 7 ml of solvent were used. $pO_2 = 8$ atm; $t = 1$ h.
[b] The sample contains 2.2 mol H_2O/mol complex.
[c] Selectivity in parentheses.
[d] The sample contains 2.55 mol H_2O/mol complex.

results were obtained with a molar ratio I^-/Rh^{3+} between 5 and 6. Materials containing only Rh^{3+} were more active than those containing Rh–diamine complexes.

Comparing the titanium-phosphate-supported materials to the analogous zirconium-phosphate species previously described [18], we can say that, in general, TOF values are slightly lower for titanium.

The temperature plays an important role. In fact, the aniline conversion reaches 95–100% selectivity only working at $T < 100$°C in CH_3CN. At higher temperatures, the selectivity decreases owing to the direct oxidation of aniline that appears to be more significant in methanol. The carbon monoxide conversion yield depends on the solvent and temperature. In CH_3CN, the conversion of CO is very high (85–90%). In methanol, relevant amounts of CO_2, which increases with the temperature, are found in the gaseous phase. Under these condi-

tions, the yield with respect to CO is 65–70% (see Section 2).

The formation of CO_2 is an intriguing point. In fact, the compounds may catalyse the direct oxidation of CO to CO_2 (Eq. 6) [17]. Nevertheless, the formation of the latter cannot be ascribed entirely to this reaction. A direct experiment has shown that CO_2 is formed only in small amounts when the materials are reacted with CO/O_2 in alcohol in absence of aniline, under the same pressure and temperature conditions:

$$CO + 1/2O_2 \rightarrow CO_2. \qquad (6)$$

This finding supports the view that CO_2 can originate from the hydrolysis of DPU or MPC to carbamic acid (PhHNCOOH) that then converts into CO_2 and aniline (Scheme 1). Control experiments have shown that remarkable amounts of CO_2 are formed when DPU or DMP are heated in a methanol–aqueous solution.

$$CO(NHPh)(Y) + H_2O \xrightarrow{\ \ HY\ \ } CO(NHPh)(OH)$$

(y=NHPh, OR)

$$\downarrow$$

$$CO_2 + PhNH_2$$

Scheme 1.
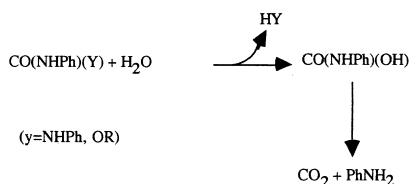
In order to verify the stability of catalysts, their TOF has been monitored over the time. Thus, the catalysts have been used under the conditions indicated in Table 3 for 1–2 h and thereafter recovered and reused. The trend of the TOF after each cycle shows that the catalyst stability depends on the temperature and solvent. The activity remains constant for several cycles if the catalysis is performed at $T < 100°C$ in CH_3CN or methanol. After six cycles, activity is still very close to the initial value and the slight decrease is most likely due to a loss of catalyst during handling and transferring of materials (Table 3). That rhodium is not lost during the catalytic run is demonstrated by the fact that it is not found in the concentrated mother liquor.

In contrast, the catalysts recovered from experiments carried out at $T > 100°C$ show a slow but steady lowering of activity starting from the second cycle, in both CH_3CN and CH_3OH. The decrease of activity is larger in methanol and is due to the fact that rhodium migrates from the inorganic phase into the solution that shows some catalytic activity.

3.5. The fate of Rh(III)

The Rh 3d high-resolution XPS spectra of the catalysts recovered from the catalytic cycles performed at $T < 100°C$ display two signals ascribed to Rh^{3+} and Rh^{1+}. Noteworthy, the analogous catalysts obtained by insertion in α- and γ-zirconium phosphate show only Rh^{3+} components [18].

The binding energy values of $3d_{5/2}$ core levels are 309.5 and 308.2 eV for Rh^{3+} and Rh^{1+}, respectively (Fig. 3b). The Rh^{3+}/Rh^{1+} area ratio equals 9.5 and remains practically constant over several catalytic cycles. It is worth to recall that newly prepared catalysts show only the Rh^{3+} component at 309 eV (Fig. 3a).

The Rh 3d region of materials recovered from catalytic reactions carried out at $T > 100°C$ also exhibit two components at 309.2 and 306.6 eV (Fig. 3c) that are attributed to the binding energy of Rh^{3+} and Rh^o, respectively. Moreover, the Rh^o component is more intense than the Rh^{3+} one.

In the latter case, the intensity of both Rh^{3+} and Rh^o components decreases after each cycle and the signals disappear after five to six cycles.

Table 3
Turnover number frequency after recycle
In all the cycles, the catalyst was kept to react for 2 h, Pt = 5 MPa.

| Number of cycles	Catalysts	Solvent	T [°C]	TOF
2	γ-TiPRh$_{0.18}$	CH_3CN	80	2.92
3	γ-TiPRh$_{0.18}$	CH_3CN	90	3.0
4	γ-TiPRh$_{0.18}$	CH_3CN	100	3.28
5	γ-TiPRh$_{0.18}$	CH_3CN	80	2.89
2	γ-TiPRh$_{0.25}$bipy$_{0.33}$	CH_3CN	100	3.20
4	γ-TiPRh$_{0.25}$bipy$_{0.33}$	CH_3CN	100	3.19
4	γ-TiPRh$_{0.35}$phen$_{0.35}$	CH_3CN	80	2.52
2	γ-TiPRh$_{0.18}$	CH_3CN/CH_3OH	130	4.1
4	γ-TiPRh$_{0.18}$	CH_3CN/CH_3OH	130	2.8
6	γ-TiPRh$_{0.18}$	CH_3CN/CH_3OH	130	0.7
3	γ-TiPRh$_{0.35}$phen$_{0.35}$	CH_3CN/CH_3OH	150	2.7
6	γ-TiPRh$_{0.35}$phen$_{0.35}$	CH_3CN/CH_3OH	150	0.3
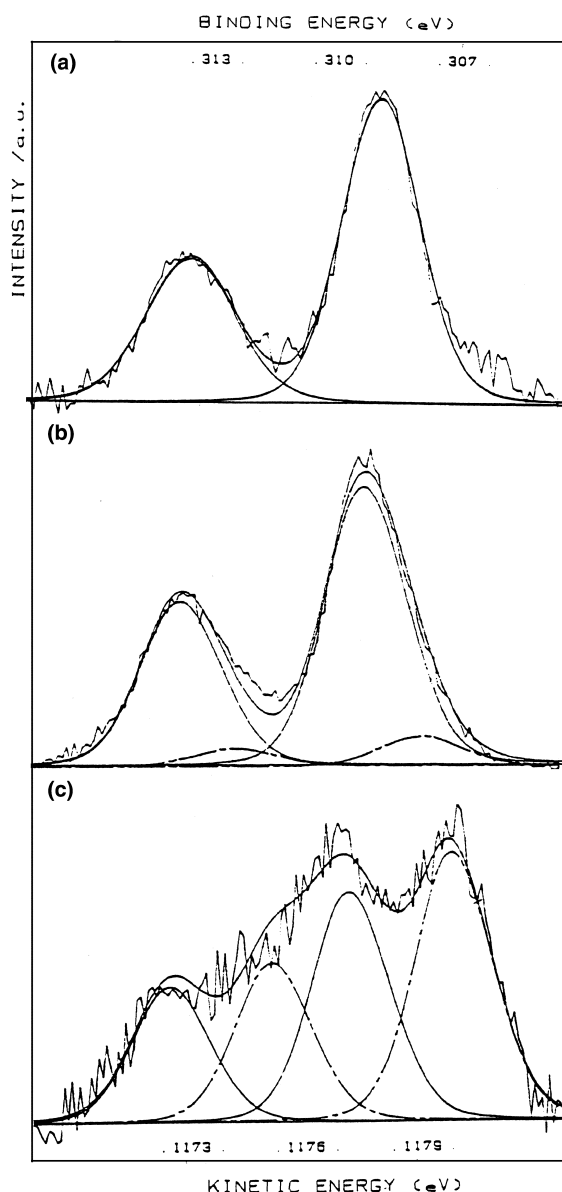
Fig. 3. Photoelectron spectra of the Rh $3d_{5/2}$ levels of: (a) γ-TiPRh as prepared; (b) after one catalytic cycle at $T < 100°C$; (c) after catalysis at $T = 150°C$.

The resulting material does not show any catalytic activity.

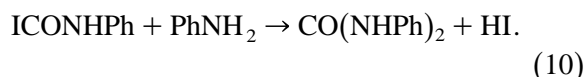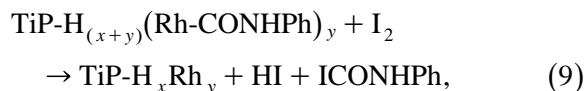These data are in agreement with our finding that the deactivation is due to the release of Rh metal [16–18].
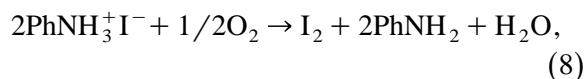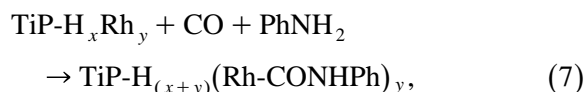
The loss of rhodium is caused by its reduction from Rh^{3+} to Rh^o. The latter has no further interaction with the matrix.

The lack of a component attributable to Rh^o in the samples whose catalytic activity is maintained after recovery and reuse, is in line with our hypothesis that the loss of metal must be attributed to an irreversible reduction of Rh^{3+} to Rh^o.

3.6. The reaction mechanism

As far as the carbonylation mechanism is concerned, the path (Scheme 2) recently proposed for zirconium phosphate compounds [17] can be also operative for the analogous titanium compounds.

Thus, the key intermediate is a Rh^{3+}–carbamoyl complex (Eq. 7) that reacts with molecular iodine, formed by in situ oxidation of the iodide co-catalysts (Eq. 8), to afford iodoformamide intermediate, ICONHPh (Eq. 9). The latter reacts with aniline to afford the final products (Eq. 10):

$$TiP\text{-}H_xRh_y + CO + PhNH_2$$
$$\rightarrow TiP\text{-}H_{(x+y)}(Rh\text{-}CONHPh)_y, \tag{7}$$

$$2PhNH_3^+I^- + 1/2O_2 \rightarrow I_2 + 2PhNH_2 + H_2O, \tag{8}$$

$$TiP\text{-}H_{(x+y)}(Rh\text{-}CONHPh)_y + I_2$$
$$\rightarrow TiP\text{-}H_xRh_y + HI + ICONHPh, \tag{9}$$

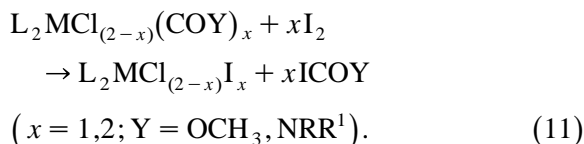$$ICONHPh + PhNH_2 \rightarrow CO(NHPh)_2 + HI. \tag{10}$$

However, the actual role of iodide co-catalyst is to promote the cleavage of the rhodium–
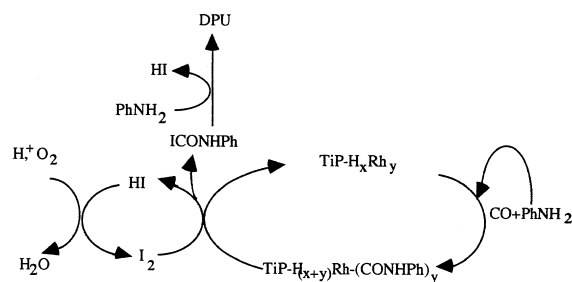

Scheme 2.

carbon bond of the carbamoyl ligand and its elimination as iodoformamide. This suggestion is in line with our recent findings indicating that several alkoxo-carbonyl- and carbamoyl complexes of Ni and Pd, react with halogens, Cl_2 and I_2, to give chloro- or iodo-formamide, respectively (Eq. 11) [22–24]:

$$L_2MCl_{(2-x)}(COY)_x + xI_2$$
$$\rightarrow L_2MCl_{(2-x)}I_x + xICOY$$
$$\left(x = 1,2; Y = OCH_3, NRR^1 \right). \tag{11}$$

The Rh^{+1} found in the material can be formed by a side reaction involving the direct oxidation of CO to CO_2 (Eq. 12) [17],

$$Rh(III) + CO + H_2O \rightarrow Rh(I) + CO_2 + 2H^+. \tag{12}$$
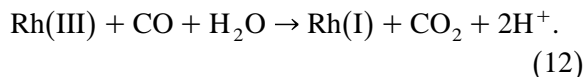
Under drastic temperature conditions, Rh^{+3} can be the catalyst until it is present in the material. A different mechanism based on Rh^o escaped from layers and present as dispersed particles in solution can be postulated. The oxidative addition of aniline to Rh^o, as proposed by Fukuoka and Chono [2] for analogous systems working under drastic conditions, can be the key step, followed by the iodine-promoted elimination of carbamoyl ligand as iodoformamide.

4. Conclusions

Rh^{3+} can be intercalated in both γ-TiP and γ-TiPL, where L is an aromatic diamine. In the first case, the uptaken rhodium does not exchange all the protons of the phosphate groups. In the second case, the amount of the Rh intercalated depends on the diamine present. The rhodium materials have the same interlayer distance with respect to the precursors and a quite different thermal behaviour. In particular, rhodium influences both the temperature of decomposition of the intercalated ligand, and the temperature of formation of the alpha cubic pyrophosphate.

Heterogenized Rh(III) is able to catalyse the oxidative carbonylation of amines. Moreover, γ-TiPRh is stable when used at temperature below 100°C. The advantage of using heterogenized Rh catalysts over the homogeneous catalysts is represented by a longer life and higher selectivity.

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