

Homogeneous Catalysis of the Water Gas Shift Reaction by NiX₂-Tertiary Phosphine Systems

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Received April 11, 1984

Abstract

The NiX₂L₂ (X = Cl, Br; L = PMe₃, PEt₃, PBut₃, P(i-Pr)₃, PMe₂Ph, PEt₂Ph) aqueous-alcoholic solutions, catalyze the water gas shift reaction (W.G.S.R.) under carbon monoxide at atmospheric pressure and temperatures higher than 90 °C. The catalysis is accomplished through the following main reactions: NiX₂L₂ + 3CO + H₂O → Ni(CO)₂L₂ + 2HX + CO₂; Ni(CO)₂L₂ + 2HX → NiX₂L₂ + H₂, which can also be carried out separately. The catalytic activity decreases slowly in time according the sequence: PR₃ < PR₂Ph < PRPh₂. Metallic nickel and phosphine oxide have been recognized in the deactivated solutions. On the most active and lasting NiX₂–PMe₃ systems (X = Cl, Br), the influence of some parameters on the rate of the catalysis has been studied.

Introduction

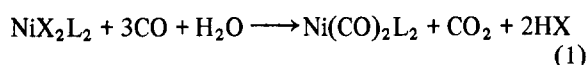
Our recent studies on the carbon monoxide activation have shown that some 2,6-bis(diphenylphosphinomethyl)pyridine Ni(II)-complexes are able to promote the carbon monoxide reactions towards amines and alkoxides to give carbamoyl and alkoxy-carbonyl complexes [1]. We have also reported that the same complexes were able to accomplish the homogeneously catalysed water gas shift reaction [2].

In order to ascertain if these reactions have to be considered as a steric and electronic peculiarity of the 2,6-bis(diphenylphosphinomethyl)pyridine ligand, the behavior of the related monodentate and bidentate phosphine complexes has been examined for the same reactions. We have established [3] that some Ni(II)-tertiary phosphine complexes react with CO, giving Ni(0)-carbonyl complexes via reductive-carbonylation.

We have determined the conditions under which these complexes catalyze the water gas shift reaction, and we shall indicate that this is a property common to many NiX₂-tertiary phosphine complexes.

Results and Discussion

According to previous results [3], CO₂ is the only gaseous product that is obtained (eqn. 1) when the NiX₂L₂ complexes (X = Cl, Br; L = PEt₃, PEt₂-



Ph, PEtPh₂) react with CO in methanol or ethanol water in 95/5 V/V solution at temperatures higher than 70 °C. Now we have found that by carrying out the reaction at temperatures higher than 90 °C, H₂ develops in addition to the CO₂. To begin, the mixture contains more CO₂ than H₂. However, when steady state conditions are reached (1 h), CO₂ and H₂ evolve in a 1:1 molar ratio. On the basis of the previous finding [1–3] and in order to ascertain the evolving hydrogen step, the solutions coming from reaction (1) containing the Ni(0)-carbonyl complexes, were heated at temperatures above 90 °C under argon or nitrogen atmosphere. Hydrogen develops under these conditions (eqn. 2).



Its stoichiometry has been verified by detecting gas-chromatographically the H₂ and CO developed by a known amount of carbonyl complexes, with excess hydrochloric acid (Table I, runs 1–3). Small amounts of CO₂ were observed under these conditions, depending on the phosphine ligand and the reaction time. The aqueous solutions of Ni(CO)₄ ca. 0.1 M, containing two equivalents of phosphine ligand and hydrochloric acid in excess reacted in the same way (Table I, runs 4–5). However by heating the solutions under carbon monoxide, H₂ and CO₂ were obtained catalytically as expected. In fact, the NiX₂-L₂ complexes produced by reaction (2) are reduced via reaction (1) to Ni(0)-carbonyls. Thus the water gas shift reaction was accomplished as catalytic process. The aqueous alcoholic solutions containing Ni(CO)₄, phosphine and hydrochloric acid (one or two equivalents) (Table II, runs 19, 20) also reacted in the same way.

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TABLE I. Hydrogen developed by Ni(0)-carbonyl Systems under Different Conditions.

Run ^a	Systems	mM (Ni)	Temp. °C	Time/h	mM (H ₂)	mM (CO)	mM (H ₂ /Ni)	mM (CO/Ni)
1	Ni(CO) ₂ (PPh ₃) ₂ + HCl (1:10)	0.20	150	8	0.19	0.38	0.95	1.90
2	Ni(CO) ₂ (PEtPh ₂) ₂ + HCl (1:10)	0.15	150	8	0.15	0.28	1.00	1.87
3	Ni(CO) ₂ (PEt ₃) ₂ + HCl (1:10)	0.18	150	8	0.19	0.35	1.06	1.94
4	Ni(CO) ₄ + PBut ₃ + HCl (1:2:10)	0.22	150	8	0.21			
5	Ni(CO) ₄ + PEt ₃ + HCl (1:2:10)	0.22	150	8	0.20			
6	Ni(CO) ₄ + PMe ₃ + HCl (1:2:2)	0.11	130	1	0.053			
7	Ni(CO) ₄ + PMe ₃ + HCl (1:2:4)	0.11	130	1	0.062			
8	Ni(CO) ₄ + PMe ₃ + HCl (1:2:5)	0.11	130	1	0.081			
9	Ni(CO) ₄ + HCl (1:2)	0.11	130	1	0.030			
10	Ni(CO) ₄ + HCl + PMe ₃ (1:2:0.5)	0.11	130	1	0.038			
11	Ni(CO) ₄ + HCl + PMe ₃ (1:2:1)	0.11	130	1	0.045			

^aThe runs 1–3 were performed under argon atmosphere, the others under carbon monoxide.

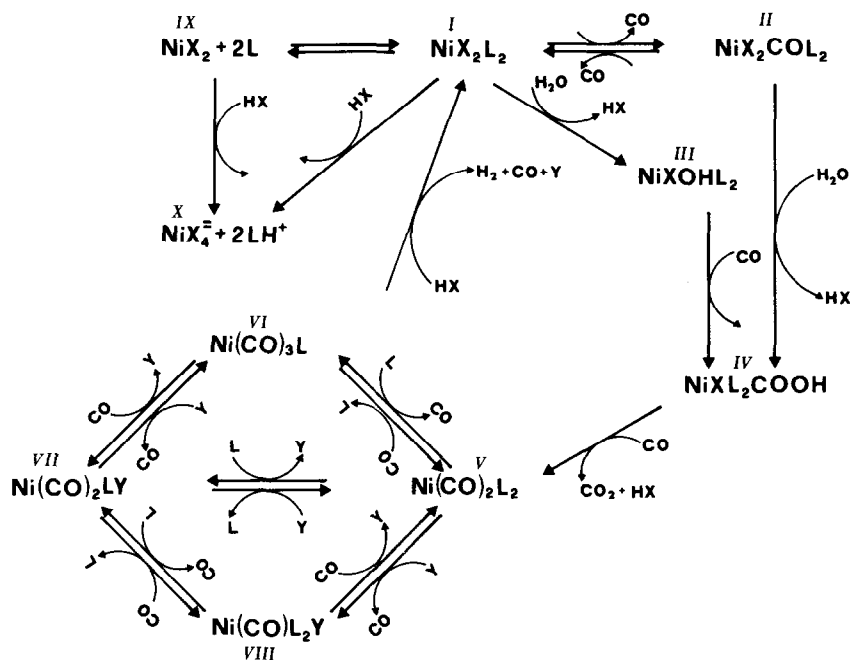
TABLE II. W.G.S. Catalysis for Different Systems. T = 130 °C; P_{co} = Atmospheric Pressure at 20 °C.

Run ^a	System	Solvent	Time/h	ml (H ₂)	ml (CO ₂)	Activity ^b
1	NiCl ₂ (PMe ₃) ₂	Ethanol	4	10.12	10.13	23
2	NiBr ₂ (PMe ₃) ₂	Ethanol	4	9.90	9.90	22.5
3	NiBr ₂ CO(PMe ₃) ₂	Ethanol	4	9.68	9.69	22
4	NiBr ₂ (PMe ₃) ₂	Propanol	4	10.12	10.11	23
5	NiCl ₂ (PEt ₃) ₂	Ethanol	8	6.16	6.15	7
6	NiBr ₂ (PEt ₃) ₂	Butanol	8	6.60	6.61	7.5
7	NiCl ₂ (PBut ₃) ₂	Ethanol	8	5.72	5.71	6.5
8	NiBr ₂ (PBut ₃) ₂	Ethanol	8	5.28	5.29	6
9	NiBr ₂ (PBut ₃) ₂	Methanol	8	6.15	6.16	7
10	NiCl ₂ [P(i-Pr) ₃] ₂	Ethanol	8	4.41	4.42	5
11	NiCl ₂ (PMe ₂ Ph) ₂	Ethanol	8	5.27	5.27	6
12	NiBr ₂ (PMe ₂ Ph) ₂	Ethanol	8	5.28	5.27	6
13	NiBr ₂ (PMe ₂ Ph) ₂	Pentanol	8	5.71	5.71	6.5
14	NiCl ₂ (PEt ₂ Ph) ₂	Ethanol	8	3.52	3.52	4
15	NiCl ₂ (PEtPh ₂) ₂	Ethanol	8	—	0.1	0
16	NiCl ₂ (PPh ₃) ₂	Ethanol	8	—	0.05	0
17	NiCl ₄ (PEt ₃ H) ₂	Ethanol	8	0.43	0.44	0.5
18	Ni(PEt ₃) ₄ + HCl (1:2)	Ethanol	8	5.28	5.26	6
19	Ni(CO) ₄ + PEt ₃ + HCl (1:2:1)	Ethanol	8	3.52	3.50	4
20	Ni(CO) ₄ + PBut + HCl (1:2:2)	Ethanol	8	4.41	4.39	5

^aSee Experimental. ^bExpressed in milliliter of H₂/millimole of Ni complex per h.

The first example of an active catalytic system able to effect the homogeneous catalysis of the w.g.s.r. was that described by Ford and co-workers [4]. Since then several systems that are active in basic, neutral or acid media and in aqueous organic solvents or directly in pure water have been found. Most systems are transition metal carbonyls, mono and poly-nuclear [5] complexes or transition metal phosphine complexes [6] and in some cases also

transition metal salts [7]. For the simplicity of the two main component reactions (1, 2), which can be also carried out separately, the systems described herein offer themselves as suitable models for the shift reaction catalysis. Furthermore, the generality of these two reactions, *viz.* the reduction of a metallic ion by carbon monoxide and its oxidation by H⁺ ion, suggests that other NiX₂-tertiary phosphine systems, apart from those investigated, could exhibit



Scheme 1.

catalytic activity for the shift reaction. The results of our investigation show, however, that the following is essential:

i) The dissociation of the complexes (I–IX in the scheme) normally present in aqueous alcoholic solution, should be partial. The lack of the reduction observed with the $\text{NiX}_2(\text{PPh}_3)_2$ complexes [3], which are completely dissociated under experimental conditions, is in agreement with this view.

ii) The conditions for the reaction (2) should be such as not to cause the decomposition of the resulting Ni(II)–phosphine complexes. In the range of the available phosphine it has been observed that the oxidation of the $\text{Ni}(\text{CO})_2(\text{PR}_3)_2$ [$\text{R} = \text{Me}, \text{Et}, \text{n-But}, \text{is-Prop}$] and $\text{Ni}(\text{CO})_2(\text{PR}_2\text{Ph})_2$ [$\text{R} = \text{Et}, \text{Me}$] does not require acidic conditions different from those produced in reaction (1). On the contrary, additional amounts of hydrochloric acid are necessary for the $\text{Ni}(\text{CO})_2(\text{PEtPh}_2)$ oxidation. Consequently, the decomposition of the resulting $\text{NiCl}_2(\text{PEtPh}_2)_2$ complex occurs, nullifying the beneficial effect of the catalysis. The results of the different systems are summarized in Table II. Their catalytic activity, expressed in volume (ml) of H_2 or CO_2 /mmol of nickel complex per hour, was determined considering the gas evolved in steady state conditions, during the first ten hours of catalysis. For a longer reaction time, the activity slowly decayed (see later). The catalytic activity, as shown in Table II, is phosphine-dependent and decreases in the sequence: $\text{PR}_3 < \text{PR}_2\text{Ph} < \text{PRPh}_2$; it declines with time in the same sequence. No

influence on the halide and on the alcoholic solvent was observed.

$\text{NiX}_2\text{--PMe}_3$ Systems

Among the $\text{NiX}_2\text{--PR}_3$ systems used, those with trimethylphosphine were by far the most active and the most lasting. For these reasons the $\text{NiCl}_2\text{--}(\text{PMe}_3)_2$ and $\text{NiBr}_2(\text{PMe}_3)_2$ complexes were utilized to study the influence on the rate of the catalysis of the following parameters: temperature, carbon monoxide pressure, acids and nitrogen bases. Furthermore, the $\text{NiX}_2(\text{PMe}_3)_2$ complexes ($\text{X} = \text{Cl}, \text{Br}$), contrary to the related ones involving the trialkyl and dialkyl-phenyl-phosphine ligands, were not reduced by CO at temperatures lower than 70°C . Within the temperature range $70\text{--}80^\circ\text{C}$ only CO_2 develops. Hydrogen and carbon dioxide, in an almost 1:1 ratio, were however produced at higher temperatures.

Influence on the Rate of the Catalysis

i) Temperature: In Table III the catalytic activity values within the temperature range $90\text{--}160^\circ\text{C}$ are given. Higher temperatures were not explored since rapid deposition of metallic nickel occurs. The steady increase of the catalytic activity with temperature differs from that found previously [2] for the $\text{NiX}_2\text{--}2,6\text{-bis(diphenylphosphinomethyl)pyridine}$ system, for which it reaches a maximum at around 75°C and decreases at higher temperatures. This trend suggests that in the temperature range experienced, the position of the equilibrium (I–II in scheme)

TABLE III. W.G.S. at Different Temperatures.

Run ^a	System	Temp. °C	Time/h	ml (H ₂)	ml (CO ₂)	Activity ^b
1	NiCl ₂ (PMe ₃) ₂	90	8	0.44	0.48	0.5
2	NiCl ₂ (PMe ₃) ₂	110	8	7.92	7.90	9
3	NiBr ₂ (PMe ₃) ₂	110	8	7.92	7.90	9
4	NiCl ₂ (PMe ₃) ₂	130	4	10.12	10.10	23
5	NiBr ₂ (PMe ₃) ₂	140	4	8.80	8.79	20
6	NiCl ₂ (PMe ₃) ₂	150	4	16.72	16.70	38
7	NiCl ₂ (PMe ₃) ₂	160	2	10.34	10.30	47

^aSee Experimental. ^bAs in Table II.TABLE IV. W.G.S. Catalysis at Different Acidity Ratios; T = 130 °C; P_{co} = Atmospheric Pressure at 25 °C.

Run ^a	System	mM Acid/mM Ni	Time/h	ml(H ₂)	ml (CO ₂)	Activity ^b
1	NiCl ₂ -2PMe ₃ + HCl	0.5	4	10.40	10.38	26
2	NiCl ₂ -2PMe ₃ + HCl	1	4	7.20	6.98	18
3	NiCl ₂ -2PMe ₃ + HCl	1.5	8	6.40	6.41	8
4	NiCl ₂ -2PMe ₃ + HCl	2.5	8	—	0.10	—
5	NiCl ₂ -2PMe ₃ + Et ₃ NHCl	1	4	9.60	9.62	24
6	NiCl ₂ -2PMe ₃ + Et ₃ NHCl	2.5	8	8.00	8.10	10
7	NiCl ₂ -2PMe ₃ + C ₆ H ₅ NH ₃ Cl	1	4	7.98	8.00	20
8	NiCl ₂ -2PMe ₃ + C ₆ H ₅ NH ₃ Cl	2.5	4	2.81	2.82	7
9	NiCl ₂ -2PMe ₃ + C ₆ H ₅ NH ₃ Cl	5	8	0.80	0.81	1
10	NiCl ₂ -2PMe ₃ + C ₅ H ₅ NHCl	1	4	8.81	8.79	22
11	NiCl ₂ -2PMe ₃ + C ₅ H ₅ NHCl	2.5	8	6.40	6.38	8
12	NiCl ₂ -2PMe ₃ + C ₅ H ₅ NHCl	5	8	1.20	1.21	1.5

^aSee Experimental. ^bAs in Table II.

does not influence the rate of the catalysis. Our data are not sufficient to say that the reductive carbonylation (reaction 1) proceeds via-coordination of a water molecule (I–III in scheme) followed by CO insertion in Ni–OH bond (III–IV), rather via a nucleophilic attack of a water molecule on the Ni(II)–CO species (II). In fact the results would be in agreement with both the routes if as is probable the oxidation of Ni(o) to Ni(II) (reaction 2) were the rate determining step. Higher temperatures, in order to verify an eventual reversal of the rate, were not tested due to the decomposition of the complexes.

ii) Acidity: The results in Table IV show that the catalytic activity increases slowly for ratios acid added/Ni-complex < 1. A steady decrease was observed with an increasing ratio. Using hydrochloric acid and ratios ≥ 2 the activity fell nearly to zero. On the contrary, using more weak acids, *viz.* Et₃NHCl, C₆H₅NH₃Cl, C₅H₅NHCl, the same results were obtained at higher ratios. Very low activity was also observed using NiCl₂(PEt₃H)₂ compound (run 17 Table II) as catalyst, according to the fact that it can be

considered as NiCl₂(PEt₃)₂–2HCl. If one considers the effect of the acidity on the two main reactions (1, 2) of the catalysis, then these trends can be explained. The runs 6–8 in Table I show the amount of H₂ developed in one hour by the specified Ni(o)–carbonyls (or Ni(CO)₄ + 2PMe₃ system), using different amounts of hydrochloric acid. The increase in hydrogen with increasing acidity shows that the rate of reaction (2), which we have supposed to be the rate determining step, is accelerated. On the other hand, acidity must exercise a negative influence because it promotes the decomposition of Ni(II)-complexes (reactions IX–X and I–X in the scheme). The catalytic activity values suggest that for low acidity ratios, the kinetic effect prevails.

iii) Nitrogen Bases: The addition to the catalytic alcohol solution of nitrogen bases such as pyridine, aniline and triethylamine caused an increase in the rate of catalysis at temperatures <130 °C. At higher temperatures the effect was less evident so that at 160 °C no influence was observed. In Table V have been summarized the results at different tempera-

TABLE V. W.G.S. Catalysis: Influence of the Nitrogen Bases (Base/Ni = 2) at Different Temperatures. P_{CO} = Atmospheric Pressure.

Run ^a	System	Temp °C	Time/h	ml (H ₂)	ml (CO ₂)	Activity ^b
1	NiCl ₂ (PMe ₃) ₂ + C ₆ H ₅ NH ₂	110	4	5.72	5.73	13
2	NiCl ₂ (PMe ₃) ₂ + C ₆ H ₅ NH ₂	130	4	12.32	12.31	28
3	NiCl ₂ (PMe ₃) ₂ + C ₆ H ₅ NH ₂	150	2	8.58	8.56	39
4	NiCl ₂ (PMe ₃) ₂ + C ₅ H ₅ N	110	4	6.16	6.19	14
5	NiCl ₂ (PMe ₃) ₂ + C ₅ H ₅ N	130	2	6.60	6.58	30
6	NiCl ₂ (PMe ₃) ₂ + C ₅ H ₅ N	160	2	10.56	10.55	48
7	NiCl ₂ (PMe ₃) ₂ + Et ₃ N	110	4	6.16	6.17	14
8	NiCl ₂ (PMe ₃) ₂ + Et ₃ N	130	4	12.76	12.74	29
9	NiCl ₂ (PMe ₃) ₂ + Et ₃ N	150	2	8.80	8.49	40

^aSee Experimental. ^bAs in Table II.

TABLE VI. W.G.S. Catalysis at Different Carbon Monoxide Pressures and Temperatures.

Run ^a	System	P_{CO}	Temp. °C	Time/h	ml (H ₂)	ml (CO ₂)	Activity ^b
1	NiCl ₂ (PMe ₃) ₂	400 (Torr)	90	8	4.39	4.40	5
2	NiCl ₂ (PMe ₃) ₂	510 (Torr)	90	8	3.52	3.54	4
3	NiCl ₂ (PMe ₃) ₂	761 (Torr)	90	8	0.44	0.48	0.5 ^c
4	NiCl ₂ (PMe ₃) ₂	610 (Torr)	110	8	9.68	9.67	11
5	NiCl ₂ (PMe ₃) ₂	760 (Torr)	110	8	7.92	7.90	9 ^c
6	NiCl ₂ (PMe ₃) ₂	3 (atm.)	130	8	14.10	13.90	16
7	NiCl ₂ (PMe ₃) ₂	760 (Torr)	130	4	10.12	10.10	23 ^c
8	NiCl ₂ (PMe ₃) ₂	5 (atm.)	150	4	15.40	15.38	35
9	NiCl ₂ (PMe ₃) ₂	760 (Torr)	150	4	20.68	20.59	47 ^c

^aSee Experimental. ^bAs in Table II. ^cFrom Table III.

tures, being the ratio base/Ni-complex = 2. Using higher base/Ni ratios, some decomposition of the complexes was observed.

iii) Carbon Monoxide Pressure: A negative influence of the CO pressure on the rate of catalysis was observed (Table VI). At lower atmospheric pressure values the catalysis can also be carried out at 85 °C. If one consider the equilibrium V–VI (see scheme), this will be shifted to the right with increasing carbon monoxide pressures. The observed trend could be explained if the rate constant for the Ni(CO)₃L oxidation (react. VI–I) were lower than that of the corresponding Ni(CO)₂L₂. On the other hand the electronic density on the Ni(o)–tricarbonyl must be lower than for Ni(o)–dicarbonyl because the carbon monoxide is a π -acceptor ligand stronger than a phosphine ligand. We found that an alcoholic solution of Ni(CO)₄, containing two equivalents of HCl, evolved amounts of H₂ increasing with the phosphine (Table I, run 6 and 9–11). Furthermore the different reactivity of the Ni(CO)₂L₂ and Ni(CO)₃L could also explain the influence of the nitrogen bases.

The bases could promote the formation of the more oxidizable species VII and VIII (see scheme; y = nitrogen base).

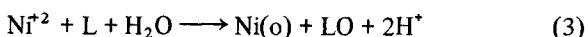
The same species will show the effect of their greater reactivity at lower temperatures, as reported above.

In order to ascertain the causes of the catalyst decomposition, the I.R. spectrum of the reacting solution was recorded every 5 hrs. This displays in the carbonyl region a series of three bands at 2065, 1995, 1925 cm⁻¹, the strongest being the 1995 cm⁻¹. No significant shift was observed on going from one phosphine ligand to another. The pattern of the spectrum is that as derived from the presence in solution of the NiL₂(CO)₂ and NiL(CO)₃ mixture [3]. The band between 2015 and 2030 cm⁻¹ (assignable to the NiX₂(CO)L₂ [8]), present in the initial solution was not observed during the catalysis. Also the electronic spectrum displayed no bands, relative to the NiL₂X₂ species, in the 400–600 nm range. The absence of these bands is in agreement with the above mentioned view, that is to

say the reaction (1) is far quicker than reaction (2).

However, by heating under argon or nitrogen atmosphere, the solutions were enriched in NiX_2L_2 species, as evidenced by its electronic spectrum [9c]*. Under these conditions, the low carbon monoxide pressure preserves the Ni(II) -complex against reduction to Ni(o) . The intensity of the three carbonyl bands decreased slowly with the time for all systems tested. No bands were observed in deactivated systems.

A careful study of the deactivation time was not made; however, one goes approximately from *ca.* 20 hrs for $\text{NiX}_2\text{-PR}_2\text{Ph}$ system, 2–3 days for $\text{NiX}_2\text{-PR}_3$ system, up to 7–10 days for $\text{NiX}_2\text{-PMe}_3$ system, depending upon the temperature. It is difficult to establish with certainty the reactions leading to the destruction of the catalyst. Metallic nickel and phosphine oxide however were always found (see experimental N.M.R.) in the deactivated solutions. Blank runs concurrently were carried out on aqueous-alcoholic solutions containing the NiL_2X_2 or the Ni(CO)_4 , under nitrogen or carbon monoxide. Metallic nickel was found as a residue. Phosphine oxide could be formed by reaction (3) which occurs easily with 1,2-bis(diphenylphosphino)-



ethane, in basic medium [3]. With the examined phosphines, it was not observed in mild conditions [3] but it could occur with more drastic conditions of catalysis. The lack of hydrocarbon (ethane, propane ecc. depending upon alcoholic solvents) in the gas phase, and of acetone in solution when the catalysis was carried out in iso-propanol, also suggests that the solvents are not responsible for the deactivation of the catalyst. Some methane, also present in solvents different from methanol, were recognized on the runs at higher temperatures**.

Experimental

The alcoholic solvents (reagent-grade quality) were deoxygenated by bubbling through pure argon before use. Literature methods were employed for preparations of NiX_2L_2 [9], $\text{NiBr}_2\text{CO(PMe}_3)_2$ [8], NiP_4 [10], $\text{NiCl}_4(\text{PEt}_3\text{H})_2$ [3], $\text{Ni(CO)}_2(\text{PPh}_3)_2$ [11].

All the other $\text{Ni(CO)}_2\text{L}_2$ complexes were obtained in solution as previously reported [3]. The Ni(CO)_4 (Matheson) was used as purchased. A Carlo Erba Fractovap C gas chromatograph, with a thermal

conductivity detector connected to a Hewlett Packard 3380 A integrator was used for analysis of gas mixtures. Separation of gases (H_2 , CO , CH_4 , CO_2) was achieved on a Porapak Q 3.5 m column; H_2 was better analysed on a molecular sieve 5 A column using N_2 as an internal calibrant. G.L.C. analysis of the solutions were made using a Varian Vista 6000 connected to a Varian 4270 integrator and a 20 m capillary column. Infrared spectra were recorded in solution using CaF_2 cells on a Perkin-Elmer 577 spectrophotometer. A Varian Cary 219 spectrophotometer was used for electronic spectra. ^{31}P NMR spectra were recorded on a Varian XL 200, operating in FT mode. The solutions coming from catalysis were placed in a 10-nm tube containing D_2O as external lock.

The Water Gas Shift Reaction

1) NiX_2L_2 System

Typically: a 55.6 ml stainless steel autoclave, containing 5 ml of the aqueous ethanolic solution (95:5 V/V), 0.10–0.12 mM of NiX_2L_2 complex and a teflon-coated magnetic stirring bar, was charged with CO at atmospheric pressure. The autoclave was mounted in an electrical oven having a magnetic stirrer built into its base, and was heated at the specified temperature for one hour. Then the system was rapidly cooled and the gas was pumped out. Quantitative analysis showed that the CO_2 was higher than H_2 . The autoclave was recharged with CO and heated. The temperatures and the times were those specified in Table (II) and Table (III). After cooling at room temperature the gas was introduced in a burette and H_2 and CO_2 were quantitatively analysed.

2) $\text{Ni(CO)}_4 + \text{PR}_3 + \text{HCl}$ System

The autoclave containing the aqueous ethanolic 0.1 M solution of Ni(CO)_4 1 ml, PEt_3 2ml and HCl 2ml, was charged with carbon monoxide and heated following the procedure described for NiX_2L_2 system. In this case, the gas that evolved during the first hour of catalysis contained more H_2 than CO_2 .

3) $\text{NiCl}_2(\text{PMe}_3)_2 + \text{Nitrogen Base and NiCl}_2\text{-(PMe}_3)_2 + \text{Acidity}$

The autoclave was charged under carbon monoxide atmosphere with 5 ml of an aqueous ethanolic solution containing 0.10 mM of $\text{NiCl}_2\text{-(PMe}_3)_2$. The base or the acid was added in the ratio specified in Table IV and V. The runs were achieved following the procedure described for NiX_2L_2 .

4) $\text{NiCl}_2(\text{PMe}_3)_2$ at Different Carbon Monoxide Pressure

a) Runs below atmospheric pressure. Typically: 0.0305 g (0.11 mM) of $\text{NiCl}_2(\text{PMe}_3)_2$ and 5 ml of

*A band at 475 nm relative to $\text{NiCl}_2(\text{PMe}_3)_2$ was recorded.

**Experiments are in progress in order to obtain selective formation of methane.

the aqueous ethanolic solution were introduced in the autoclave under argon atmosphere. The autoclave was connected to a gas burette by a three-way stopcock and the argon was pumped out. A known volume of carbon monoxide under ambient conditions (e.g. 29.3 ml for the run 1 Table VI) was introduced through the gas burette; then argon was added to restore the atmospheric pressure.

b) Runs above atmospheric pressure. The autoclave containing the complex (0.11 mM) and 5 ml of the ethanolic solution was charged with carbon monoxide at the specified pressure.

Reaction of $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ with HCl

$\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$, 10 ml (2 mM), of an aqueous ethanolic 0.1 M HCl solution and 0.128 g (0.20 mM) of $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ were introduced in the autoclave under argon atmosphere. The mixture was heated at the temperature specified in Table I, and H_2 and CO were analysed.

The reactions with the related dicarbonyl complexes were achieved in the same way.

Reaction of $\text{Ni}(\text{CO})_4$ with HCl and Phosphine

To a 1 ml of an aqueous ethanolic 0.1 M solution of $\text{Ni}(\text{CO})_4$ were added ethanolic solutions of HCl (0.1 M) and PMe_3 (0.1 M) in the ratio specified in Table I. The mixture was introduced in the autoclave and then was allowed to react under the conditions specified in Table I.

^{31}P NMR Spectra

The chemical shifts were relative to 85% H_3PO_4 , with downfield shifts being positive.

$\text{NiCl}_2(\text{PEt}_3)_2$ System

Ethanolic solutions recorded after: i) One hour under catalysis at 130 °C: signals at +46.7 and +20.3 ppm. The reported values for $\text{Ni}(\text{CO})_3\text{PEt}_3$ and $\text{Ni}(\text{CO})_2(\text{PEt}_3)_2$ are respectively +47.0 and +20.7 ppm [12]. ii) Further heating (~2 h) under argon at 150 °C produced signals at +46.7, +20.3 and +15.3 ppm, with a decreasing intensity for the 46.7 and 20.3 being observed. The literature value for $\text{NiCl}_2(\text{PEt}_3)_2$ is +15.7 ppm [13]. iii) Deactivated solutions: signals at +46.7, +20.3 and +49.2 ppm, with 46.7 and 20.3 ppm intensity signals being very low. The literature value for Et_3PO is 48.3 ppm [14].

$\text{NiCl}_2(\text{Bu}_3\text{P})_2$ System

i) Not deactivated system spectrum: signals at +33.4 and +13.2 ppm. The literature value for $\text{Ni}(\text{CO})_2(\text{Bu}_3\text{P})_2$ is 12.1 ppm [12]. ii) Deactivated system spectrum: signal at +47.3 ppm, reported values for Bu_3PO are 45.8 [14] and 46.9 [15].

$\text{NiCl}_2(\text{PMe}_3)_2$ System

i) Spectrum of the catalytically active solution: signal at 49.1 ppm. The spectrum of an ethanolic

solution containing $\text{Ni}(\text{CO})_4$ and PMe_3 in the 10:1 ratio displayed signals at +49.2 and -61.1 ppm. The reported signal for PMe_3 is -62 [16]. ii) Deactivated solution: signal at +42.4 ppm. The literature value for Me_3PO is 41.9 [15].

Acknowledgements

The authors wish to express their thanks to Professor Adriano Sacco for the helpful discussions and suggestions. The work was partially supported by the C.N.R. (Rome).

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