Catalytic fuel production using water and coal.

Authors : J. Drapier, A.J. Hubert and Ph. Teyssié

Contract number : EED.2.326.B (RS)

Duration : 30 mois 1 Mai 1981 - Octobre 1983

Head of Project : Ph. TEYSSIE, Université de Liège

Contractor : Université de Liège

Adress : Université de Liège
Institut de Chimie
SART TILMAN 4000 LIEGE

Summary

The present investigation is devoted to the search for novel or improved catalysts for the efficient and selective synthesis of oxygenated chemicals (> C_2) directly from CO and H_2. In this project, the preparation of methanol homologues (eg ethanol, propanols, butanols) is a particularly attractive challenge because these alcohols would be interesting fuels but could be also easily converted to valuable olefins (ethylene, propylene, butenes) : such an achievement would be significant in relation with the problem of the replacement of petroleum by coal. Preparation of other oxygenated compounds and of olefins would be also of interest. In the present report, we summarize the preliminary study of some modified and original catalytic systems (Rh, Ru derivatives associated to a Lewis acid or to CuBr; (Cobalt complexes), some of them (particularily Co catalysts) giving promising results in the context of oxygenated product preparation.

The apparatus used for the present study will be described briefly together with a short discussion of the mechanistic aspects of the reactions.

Introduction

Since the impact of the petroleum crisis on the economy of the western countries, important efforts have been devoted to the search for novel energy supplies. The use of coal as a fuel precursor is known since a very long time and received much attention when problems of energy shortage were particularly accute.

The general conditions for considering the replacement of petroleum by coal are again encountered in our countries.

However, two different approaches of the problem are intensively investigated in the industry :

- the more classical one consists in transforming coal to CO and hydrogen (water gas) and use the synthesis gas for the preparation of a hydrocarbons mixture analoguous to gasoline.
- the second approach consists in using synthesis gas for the preparation of more valuable chemicals which up to now are mainly available from petroleum or valuable biological resources : as examples we have the preparation of olefins (which is reasonably controlled at the present stage) and of oxygen containing chemicals such as : methanol, ethanol, higher homologues (propanol, C_4 alcohols, ...) acetic acid, esters, ethers ...

The problem of methanol preparation from synthesis gas is already an important process at the industrial level.

The preparation of acetic acid from methanol is no more a problem since the discovery of the Monsanto process and the conversion of methanol to hydrocarbons (synthetic gasoline) is also possible (Mobil process).

However the discovery of selective and economically efficient processes for the direct synthesis from synthesis gas (without the preparation of methanol as an intermediate step) of more elaborated molecules such as ethanol, acetic acid or of their homologues (propionic acid, butyric acid, propanol, n- and t-butyl-alcohols) remains an unsolved problem.

In fact there are several indications that these challenges will receive solutions in the next future : several patents report on the preparation of ethanol from $CO:H_2$ with reasonable selectivities but relatively large amounts of very expensive catalysts (Rhodium)[+] are required in these processes (1, 2).

It is noteworthy that ethylene glycol production directly from $CO:H_2$ has been well studied by Union Carbide but the process has not been developped further than the pilot stage because of the economical drawback due to the use of the expensive Rhodium catalyst and very high pressure.

The use of less expensive metals than Rhodium seems therefore to be requisite for industrial application except if the life and efficiency of rhodium based systems could be substantially improved, the more important drawback of the existing processes being however the lack of selectivity (the undesirable formation of hydrocarbons being the main side reaction).

[+] Hoechst process uses 11 g of $RhCl_3$ on 40 g of support.

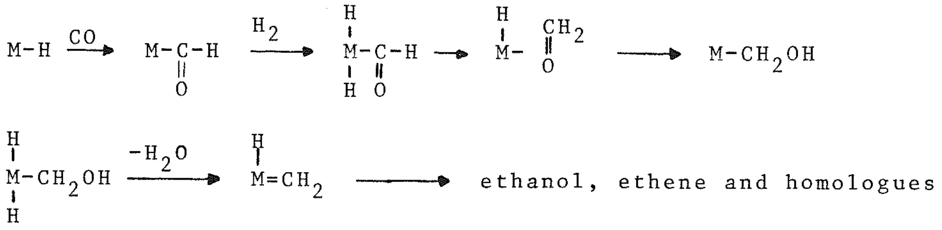
Cobalt catalysts may meet these requirements if their selectivity could be improved (cobalt catalysts are in fact efficient for the homologation reaction of methanol to ethanol and of course much cheaper than rhodium based catalysts).

I. Mechanistic aspects

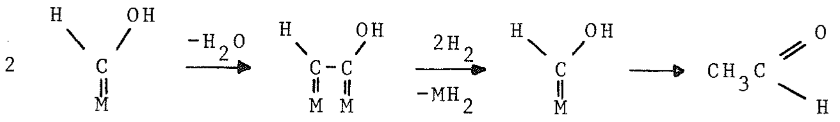
The CO hydrogenation mechanism is a challenging problem for chemists and constitutes in fact the most remarkable intellectual achievement of the last few years, comparable in fact to the study of the Ziegler and metathesis reactions.

However, the problem of the understanding of CO hydrogenation is not yet completely solved : several mechanisms have been recognized to be acting under different conditions.

It is now rather well accepted that most of the Fischer-Tropsch related processes are proceeding through the formation of carbenoid intermediates, as example in the Olive's mechanism :

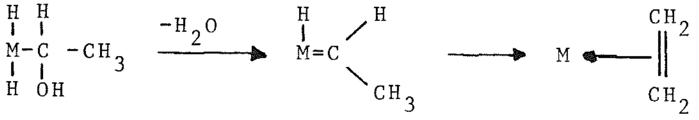


Oxygenated products would result from the formation of metal formyl species or more probably (for thermodynamic reasons according to some authors) as hydroxy carbenoids (4)



The polycondensation of hydroxy carbenoids may explain the formation of oxygenated products, the reduction of the monomeric species giving methanol.

Dehydration of hydroxylated intermediates leads to carbenes and the formation of olefins can thus be explained.



But olefins such as ethylene can also result from β-eliminations :

$$M\text{-}CH_2\text{-}CH_3 \longrightarrow M\text{-}H \quad + \quad CH_2{=}CH_2$$

Alcanes (eg ethane) result from hydrogenolysis of alkyl-metal bonds.

Insertion of CO into the metal-alkyl bonds has been proposed in other mechanistic proposals (eg : Olive's mechanism, see above).

According to Pettit (5) unusual selectivities such as the formation of C_3 and C_4 olefins would be the result of the reaction of lower olefins with methylene carbenoid (ethylene → propylene → C_4...). This author stressed the role of bridged methylene carbenoïds in such reactions.

However, the high selectivity for propene may be probably best explained by the oligomerisation of three carbenoid units on clusters presenting particularly well defined structural and dimensional features except if a particularly strong preferential reactivity of ethylene as compare to propylene is postulated.

Formaldehyde has however been proposed as an intermediate particularly in ethylene glycol synthesis (6). In the actinide series, the "side coordination" of CO has been proposed to explain the formation of oxycarbenes which dimerize readily to give stable dimeric complexes.

II. Instrumentation :

Most of the efforts related to the first period of the present contract have been devoted to the installation of proper high pressure equipment and to devise adequate techniques, particularly to solve the intricate analytical problems.

Our experiments are run under two main sets of conditions :

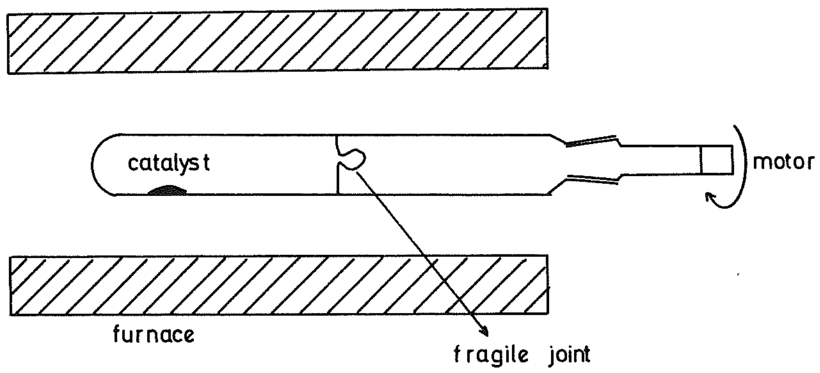
1. Static experiments :

In fact, most of our investigations are performed in stainless steel autoclaves, a pressure of CO/H_2 mixture being applied at the beginning of the experiment. In fact, it is necessary to study the catalytic activity of our catalysts under a large scale of pressures as the efficiency and selectivity can be dramatically affected by this factor :

a) High pressure experiments (300 bars) are currently run at the present stage in our laboratory in small autoclaves (125-250 ml).
The autoclaves are heated with an electrical furnace and mechanically shaken. (Prolabo system).
The original autoclaves have been modified to allow the direct injection of air sensitive catalysts. Higher pressures (up to 1000 bars) are now available in our laboratory by using a compressor (NOVA) in association with an autoclave of 1000 bars.

b) Low pressure autoclaves (up to 15 bars) are also available. They have been constructed in the University.

c) A few experiments have been run in sealed glass tubes. This technique was useful for studying very sensitive catalysts under low pressure (1 bar) (eg Ti Br_4 - Ru or Rh carbonyl). The tube is heated while rotating in an electrical furnace.



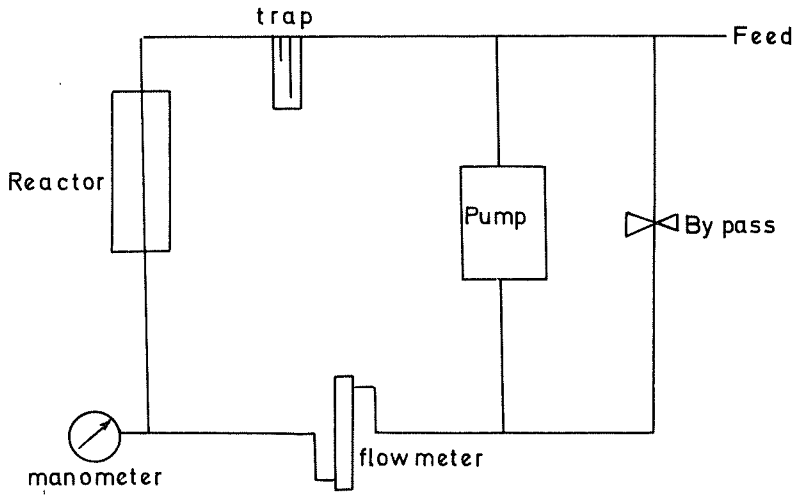
The gases are analysed by GLC and MS after breaking the fragile joint with a magnet.

d) This technique was used only in some exploratory experiments and is no more applied in our laboratory.

2. Dynamic experiments :

When the expected compounds are not very stable under the operating conditions, it is of interest to remove them as readily as possible from the reaction medium. We have therefore built two devices A and B for low pressure experiments (glass reactors and traps), whereas a system suitable for working under 100 bars is under construction (the whole apparatus is made in stainless steel and the feed of gas will be assumed by a manostat.

The low pressure apparatus A, suitable to work at 1 - 1,5 bars, can be used for comparison of our catalysts with the Ichikawa and Hoechst processes.



The low pressure apparatus B is used for liquid phase experiments with catalysts dissolved or in suspension in a high boiling solvent.

The high pressure system will be used to run experiments under the Hoechst's patent conditions : the general scheme will be very similar to (A) but the working pressure will be maintained at 100 bars.

3. Analytical techniques : The reactions run in the low pressure circulating system are followed directly by gas chromatography. The liquid portion collected in the cool trap is injected into the chromatograph when the reaction is finished.

The reaction products of the experiments run in high pressures autoclaves are analysed after completion of the reaction. The gas is analysed by GLC by using freon as a standard, whereas the liquid phase is condensed in a cool trap, the autoclave being heated under vacuum during this operation.

The products are identified by the GLC-MS method. By combining four different columns (see below), it is possible to solve satisfactorily the analytical problems encountered in the present study.

Quantitative analysis of the liquid fraction is performed by using propanol as a standard : the chromatogram of a sample of the analysed liquid fraction is compared to the chromatogram of the same sample to which an known amount of propanol has been added.

APPARATUS	Detector	Column	ANALYSED PRODUCTS
INTERSMAT IG 120	FID	PORAPAK 70-220°C(10°/min)	liquids gases
IDEM	IDEM	FFAP 60-220°C(10°/min)	liquids
VARIAN 3 700	CATHAR	SPHERO CARB ISOTH.50° (6 min) 50-150°C(10°/min)	H_2O, O_2, N_2, CO, CH_4, CO_2
IDEM	IDEM	CHROMOSORB 102 60-220°C(10°/min)	alcohols water

III. Progress of work and results

Beside the solution of technical problems, the first period of the present program was devoted to an exploratory approach of novel catalytic systems for CO hydrogenation with particular attention centred on alcohols (eg ethanol) synthesis.

The early exploratory approach was based on low pressure experiments as the high pressure equipment was not fully operative. Most of the first investigated catalysts appeared to be very inefficient and most of the results were poorly reproducible (eg. attemps with CuBr-KBr and with $M_x(CO)_y$ on Al_2O_3-$TiCl_4$).

More reproducible results were however obtained with $TiBr_4$ - $Ru(CO)_{12}$ see below) but the best performances as far as alcohols (and particularly ethanol) formation is concerned are obtained with supported (expensive) rhodium catalysts.

However, promising results for oxygenated compounds synthesis were also obtained by using reduced cobalt catalysts.

Summary of the preliminary experiments :

1. The use of fused salts where an acidic (Lewis acid) cocatalyst is present : according to Muetterties (8), such catalysts lead to unusual selectivities in alkanes but the production of oxygenated compounds has not been reported with his systems (Ruthenium, Rhodium and Iridium carbonyl in very strong Lewis acid such as $AlCl_3$) : in fact the extremely acidic conditions render the existence of oxygenated products extremely improbable.

Our approach consisted in using CuBr, a much weaker Lewis acid than $AlCl_3$, as cuprous salts are known to coordinate efficiently CO.

The CuBr-KBr eutectic (mp 190°C) was used in association with $Ru_3(CO)_{12}$. (composition of the catalyst : CuBr (3.10^{-3} moles) KBr ($7.6\ 10^{-3}$ m) - $Ru_3(CO)_{12}$ (3.10^{-5} m).

The reaction was run in glass reactors (p = 1-2 atm) and in autoclaves (p = 10-15 atm, T=180-200°C).

The synthesis gas was a (1:3) mixture of CO and H_2.

We have thus observed the formation of water, propene, propane, methyl and ethyl bromide, methanol, ethanol and n-propanol in some cases.

Problems related to autoclave corrosion (with formation of potential catalytic species) and sublimation of $Ru_3(CO)_{12}$ lead to considerable variation of product compositions : hydrocarbons (C_1-C_5) are formed in these cases.

A typical experiments was performed under the following conditions :

CuBr : 430 mgm
KBr : 913 mgm
KI : 60 mgm
$Ru_3(CO)_{12}$: 19

$CO/H_2 = 2/1$ (120 bars)
T = 200°C
t = 190 h

The liquid condensed in a cool trap after reaction contained CH_3OH (15%), C_2H_5OH (11), C_3H_7OH (42), acetic acid (23), C_2H_5COOH (10) (no calibration, rel %).

An attempt without potassium iodide and based on Rhodium catalyst afforded also oxygenated products :

CuBr : 430 mgm
KBr : 913 mgm
$Rh_6(CO)_{16}$: 32

$CO/H_2 = 1/1$ (150 bars)
T = 200°C
t = 190 h

The following mixture of oxygenated products was obtained : CH_3OH (7,5%), C_2H_5OH (11), iso C_3H_7OH (?)(7) n.C_3H_7OH (27), CH_3COOH (40), C_2H_5COOH (7,5).

The results could not be reproduced when contact between the catalyst and the stainless steel autoclave was suppressed by using a glass tube inside the reactor.

In some attemps, acetone, t-butanol, propene and an unidentified product ($C_7H_{12}O$) were obtained as the main components.

However, the lack of reproductibility of these results led us to postulate the participation of active species formed by reaction of the salts with the autoclaves.

Attempts performed with a strong Lewis acid such as $TiBr_4$ and $Ru_3(CO)_{12}$ led to the formation of hydrocarbons as main reaction products (propane, isobutane, isopentane and C_6) together with halogenated products (methyl, ethyl and propyl bromides).

Table I

$TiBr_4$-$Ru_3(CO)_{12}$ $CO/H_2=1/2$(1 bar) T = 190°

Hydrocarbons	Flask (IL) (relative %) 24h	14h	sealed tube (20 mL) (absolute %) * 7 days
C_1	-	0	0,6
CH_3Br	11	-	-
C_2	-	0	0,8
C_2H_5Br	12	-	-
C_3	6	12	0,8
C_3Br	2	-	-
C_4	43	49	0,9 (iso:0,5;n:0,4)
C_5	26	31	0,45 (neo?0,006;iso?0,25 n?,0,20)
C_6	19	7	0,02
Ru	5 mgm		20
Ti	300		150

* absolute % calculated by using freon as a standard for GLC determination.

In opposition to Muetterties' results, we did not observed the simultaneous formation of methane and ethane, the C_4 and C_5 hydrocarbons being predominant when the reaction was run under a pressure of 1.5 bar in a glass (1L) apparatus.

The halogenated products are formed at the very beginning of the reaction whereas the C_4 and C_5 fractions increase with time. It seems therefore that halogenated products could be the precursors of higher alkanes in this case : the absence of CH_4 and C_2H_6 during the early stages of the reaction could thus be explained by the ready formation of the higher alkanes from CH_3Br and C_2H_5Br.

The use of $Ir_4(CO)_{12}$ or $Mn_2(CO)_{10}$ instead of $Ru_3(CO)_{12}$ (in sealed tubes) leads to the preferential formation of C_1 and C_2 hydrocarbons. (Table II).

Table II

$C_{\underline{n}}H_{2n+2}$	$Rh_6(CO)_{16}$:10 mgm $TiBr_4$: 300	$Ir_4(CO)_{12}$:20 $TiBr_4$: 100	$Mn_2(CO)_{10}$:10 $TiBr_4$: 200
1	0,25% *	3	6
2	0,16	0,06	0,02
3	0,6	0,9	
4	0,25		
5	0,6		
6	0,8		
7	0,3		

* absolute % calculated by adding freon as an internal standard after reaction.

The experiments performed in flask gave reproducible results as far as the qualitative composition of the gas phase is concerned whereas the attempts in sealed tubes were poorly reproducible but as these $TiBr_4$ based catalysts did not afford oxygenated products, they did not fit therefore with the general objective of the present program and were consequently no more investigated.

However, further experiments (eg in the presence of added alkyl bromides to the reaction medium to check their eventual participation to alkanes formation) could be of interest and will be eventually studied latter.

2. Reduced Metal systems :

Blanchard, Petit and Mortreux (9) publications on a cobalt (II) - AlR_3 catalyst generated in the presence of butadiene suggest the participation of cobalt species similar to those reported by Bönneman (10) for acetylenes-nitriles co-cyclotrimerizations to pyridines rather than clusters as suggested by the french authors.

We have therefore prepared reduced metal catalysts by treating the corresponding salts by $NaBH_4$ (in methanol or acetonitrile) in the presence of ligands. The mixture was evapored in vaccuo and used directly for the experiments. The salts used for the catalyst preparation are : $CoCl_2$, $RuCl_3$, $NiCl_2$, $MnCl_2$. (Table III)

Table III : (experiments 1,2,3,4 of the first progress report) Reduced transition metal salts as catalysts for CO hydrogenation (preliminary experiments). Solvent : CH_3OH.

Catalyst	Gas *	Liquid
$CoCl_2$	$C_4>>C_2 \approx C_3>C_4>$ $C_3H_6>C_5>C_4H_8>C_5>$ $C_6>C_2H_4$	Organic layer:C_3 - C_{14} Aqueous layer:traces of CH_3OH,C_2H_5OH,n-propanol, n-butanol
$RuCl_3$	C_1-C_6, CO_2	Org.:C_4 - C_{13} Aq.:CH_3OH>n-butyrald(ehyde)> n-propionald, >acetald, >n-propanol>ethanol
$NiCl_2$	CO-H_2	Org.:0 Aq.:traces of CH_3OH
$CoCl_2$ + $MnCl_2$	$C_1>C_3>C_4>C_2>$ $C_5>C_6>C_7$	Org.:$C_7>C_6>C_5>C_4$ (+ unidentified products) Aq.:CH_3OH>butyrald >propionald>acetald >n-propanol>ethanol

* Cn correspond to alkanes (n given), CnH_2n refers to olefins.

A typical attempt in acetonitrile as solvent afforded the distribution of products reported in Table IV in the presence of an added ligand.

Table IV

$CoCl_2$ (5mmoles), $NaBH_4$ (10 mmoles)
CH_3CN : 20 ml, L : 10 mmoles
CO/H_2 = 1/2, P_o = 120 bars, P_F = 50 bars
T = 200°C, t = 62 hr

Gas		Liquid *	
CH_4	133 mgm	CH_3OH C_2H_5OH	3%(relative)
C_2H_6	28	propanols	33
C_3H_8	51	butanols	15
C_4H_{10}	32	pentanols ?	12
C_5H_{12}	20	XYZ $^+$	35
C_6H_{14}	14		

* other compounds than alcohols and unidentified products

In fact, the cobalt catalysts gave the best results as far as alcohols are concerned and their optimalisation is presently studied.

3. Preformed reduced CO species :

The results obtained with reduced metal salts prompted us to investigate preformed pure complexes presenting a low oxidation state, our present research is in fact mainly centered on this aspect.

4. Supported catalysts :

Preliminary experiments : A series of exploratory experiments have been performed by dispersing the catalysts on different supports.

a) Lewis acid containing systems :

1) The dispersion of $RuCl_3$ (50 mgm) on Al_2O_3 (10 g) was treated with $TiCl_4$.
The CO hydrogenation reaction was run at 180°C under 10 bars ($CO:H_2$ = 1:3).
The conversion is very low (0.01%) but the distribution of hydrocarbons favours again the C_3, C_4 and C_5(?) fractions. Substantial amounts of olefins are present.

Table V

	$TiCl_4$: 5.10^{-4} mole	$TiCl_4$: 2 ml
	t = 24 h	t = 72 h
Products	% *	% *
C_3 : propene	44	56
propane	2,5	9
C_4 : butenes		12
other C_4		10
C_5 : ?		13
unknown	41,5 and 12	
Conversion	0,01	0,01

% * : relative peak area of each components calculated on the sum of volatile components detected in the chromatogram .

2) A dispersion of $Ru_3(CO)_{12}$ on Al_2O_3 was treated with $TiCl_4$(5.10^{-4} moles) at 180° under 10 bars (CO : H_2 = 3).

Table VI

Products	(%) *	
	t = 24 h	144 h
C_3 : propene	75	39
propane	10,5	30
C_4 : butenes	10,5	12,5
other C_4	4	2,5
unknown		16
Conversion	0,1	0,3%

% * : see Table V.

These results are not very reproducible and corrosion products of the autoclave seem again to be acting as catalysts. Moreover , the absence of oxygenated products prompted us to stop further investigations of these systems.

b) Complexes dispersed on oxides

The dispersion of transition metal complexes (eg derivatives of Rh, Ru, ...) on metal oxides (Al_2O_3, ZrO_2, TiO_2, SiO_2 SiO_2-MnO) leads to different selectivities.

Some of these systems have been reported as displaying high selectivities in oxygenated products (eg ethanol). We are therefore studying the dispersion of the efficient catalysts on different supports.

However it appears that the use of static conditions leads to low yield of oxygenated products. The use of a dynamic reactor is therefore a requirement.

The low pressure apparatus described in Fig.2 is therefore used for such experiments. Of course the high pressure device would be particularly useful.

1) Static experiments

a) $Rh_6(CO)_{16}$ (0.05 g) was dispersed on La_2O_3 (10 g) according to Ichikawa procedure (1) by evaporation of a THF solution of the Rh complex on the support, followed by heat treatment (180°C in vaccuo) and reduction by hydrogen (200°C). The mixture was heated at 220°C during 90 h under an atmosphere of CO : H_2 (1:3) (initial pressure at 25°C=150 bars - end pressure = 80 bars).

Products : - the gas phase contains a mixture of CO, H_2, CO_2, paraffinic and olefinic hydrocarbons ($CH_4 > C_3H_8 > C_4H_{10} > C_3H_6 > C_2H_6 > C_5H_{12} > C_6H_{14}$).

- the liquid phase (0,8 g) is an aqueous solution of traces of methanol, ethanol, n-propanol, n-butanol (and possibly pentanol and hexanol ?)

b) $RhCl_3.3H_2O$ (0.62 g), $MnCl_2.4H_2O$ (0.25g) were dispersed on ZrO_2 (20 g).
One gramme of this catalyst was activated by reduction under hydrogen at 200°C during one hour.
The CO - H_2 (1:2) reaction was run at 200°C during 60 h (initial p = 120 bars, end p = 80 bars).

Products : - the gas phase is a mixture of CO, H_2 and saturated hydrocarbons $CH_4 > C_2H_6 > C_3H_8 >$ n-$C_4H_{10} >$ iso-C_4H_{10} no CO_2 and olefins were detected).

- the liquid phase (0,2 g) is an aqueous solution of traces of aldehydes (acetaldehyde, propanal, isobutanal) and alcohols (methanol, ethanol).

2) Dynamic experiments :

Experiments run in the low pressure circulator (Fig.2) using Ichikawa catalyst afforded only hydrocarbons.
However the use of one of the catalysts disclosed in a Hoechst patent (2) was efficient for CO hydrogenation (CO = H_2 = 1 : 2) even under atmospheric pressure, the product analysis being under investigation.
Catalyst : $MgCl_2$ on SiO_2 sintered at 950°C was used as support for $RhCl_3$.
The catalyst was activated by hydrogenation at 200°C in the reactor and the CO-H_2 (1:2) reaction was run during 24 hours.
The circulating device is now operating and will be extensively used for testing our catalysts (eg the cobalt based systems).
A comparison with experiments run with high pressure (100 bars or above) recycling system will be particularly interesting.
These catalysts afford reproducible results at least as far as the distribution of oxygenated products is concerned and they are therefore still investigated.

Analysis of results

The results obtained with the different classes of studied catalysts show that very different products distributions are obtained according to the nature of the metal of the catalyst and its oxidation state. The use of Lewis acid cocatalysts has also a deep effect on the product formation. As example, we observed in some cases the preferential formation of C_4 and C_5 hydrocarbons without the simultaneous formation of methane and ethane by using $TiBr_4$ instead of the Muetterties system ($Ru_3(CO)_{12}$ - $AlCl_3$).

The use of CuBr-KBr-Ru system leads to the formation of alcohols (C_1, C_2 and C_3) together with propane, propene and alkyl bromides. In some cases, acetone and t-butanol or carboxylic acids were even obtained but these results were not reproducible.

Active species are in fact very probably formed by corrosion of the stainless steel autoclaves as these results could not be reproduced when the reactors were fitted with glass protections.

The reduced metal systems show that the product distribution depends strongly on the type of metal and the type of added solvent, systems based on cobalt giving the more interesting results at the present stage and are receiving much attention together with modified supported rhodium catalysts.

Conclusions and future developments

In fact, our exploratory work has led us to the selection of one novel catalytic system which is susceptible to lead to oxygenated products with good selectivity : in fact, large amounts of such products relatively to hydrocarbons were formed in some experiments with Co reduced species.
The problems of efficiency and improved selectivity in one oxygenated derivative are still unsolved.

The future development of the present work is devoted to the evaluation of reduced cobalt complexes under different conditions (pressure, added ligands, solvents, ...).

The role of supports will be further considered mainly in connection with Hoechst patent where Magnesium containing silicates appeared as particularly beneficial. In this approach, we shall try to decrease as much as possible (and ideally to cancel completely) the use of the very expensive Rh salts (Hoechst catalyst uses very large amount of this metal (11g/40g of catalyst) by replacing them by cobalt derivatives.

The use of rhodium associated with another metal (cobalt at the present time) is therefore presently investigated under different conditions in order to try to reach this objective.
The use of methanol synthesis catalyst (ZnO-CuO) in association with a methanol homologation catalyst (eg Rh, Co) will be also considered.

References :

1. M. ICHIKAWA, Bull.Chem.Soc.Japan, 51, 2273 (1978); M. ICHIKAWA, K. SHIKURA, K. SEKIZAWA and K. TANAKA, European Patent 22358, 03/07/80.
2. H.J. SCHMIDT, F. WUNDER, H.J. ARPE and E.I. LEUPOLD, European Patent 4653, 31/03/79.
3. H.M. FEDER and J.W. RATHKE, Annals N.Y. Acad.Sciences, 45 (1980); C. MASTERS, Adv. Organomet. Chem., 17 , 61 (1979); E.L. MUETTERTIES and J. STEIN, Chem. Reviews, 79, 479 (1979).
4. R.B. ANDERSON, Catalysis, ed. P.H. EMMETT, Reinhold, New York, Vol. 4, 29 (1956); H.H. NIJS, P.A. JACOBS, J. Catal. 66, 401 (1980).
5. R.C. BRADY III, R. PETTIT, J. Amer. Chem. Soc., 102, 6181 (1980).
6. B.D. DOMBEK, J. Amer. Chem. Soc., 102, 6855 (1980); D.R. FAHEY, J. Amer.Chem.Soc., 103, 136 (1981); J.F. KNIFTON, J.C.S. Chem. Comm. 188 (1981).
7. P.T. WOLCZANSKI, J.E. BERCAW, Acc. Chem. Res. 13, 121 (1980).
8. G.C. DEMITRAS and E.L. MUETTERTIES, J. Amer. Chem. Soc., 99, 2796 (1977).
9. M. BLANCHARD, D. VANHOUE, A. MORTREUX and F. PETIT, J. Chem. Soc., Chem. Comm., 908 (1980).
10. H. BONNEMANN, Ang. Chem. Int. Ed. Engl., 17, 505 (1978).

DISCUSSION

Question - Dr Jacobs, KUL : Concerning the CH_4 formation on Manganese carbonyl, do you have data to distinguish whether this is a catalytic reaction or just a stoichiometric reaction : i.e. just a consumption of the ligand of the complex ?

Answer The amount of CH_4 formed in this reaction is within the range of a stoichiometric process and may include therefore a consumption of the ligand.

Question - Dr Jacobs, KUL : For the selective synthesis of propane on supported and promoted Ru dodecacarbonyl, have you an idea about the carbon mass balance under these conditions : is all the carbon entering the reactor as CO converted to propylene or is an appreciable amount of it left on the catalyst ?

Answer Due to the very small amount of catalysts used in the reaction and the low conversion, a mass balance for carbon cannot be evaluated.

Question - Dr Pilavachi, CEC : Why do you obtain a conversion as low as 0.01 in the Lewis supported case catalyst (table 1) ?

Answer The conversion is very low because the conditions are rather smooth (low pressure). We believe also that products (eg water) may inhibit the Lewis acid catalyst (hydrolysis of $TiCl_4$).