Hydrogenolysis of formic esters with homogeneous and heterogeneous rhenium catalysts

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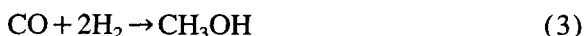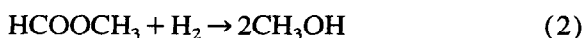
Abstract

The hydrogenolysis of formic esters to methanol, as the second step of the low temperature methanol synthesis from syngas, has been studied using rhenium catalysts. 'Rhenium blacks' containing reduced Re(0) species produced 'in situ' starting from soluble rhenium precursors like Re_2O_7 or $Re_2(CO)_{10}$ are active and generally very selective (99%) in the hydrogenation of the formyl group to methanol. Unfortunately this catalyst suffers from CO poisoning: however, the poisoning is reversible and the catalytic activity can be restored by treatment with pure hydrogen. Rhenium catalysts supported on oxides generally are less active and selective: the acid or basic centres of the support, which strongly interact with the oxophilic rhenium cations, make difficult the generation of the active Re(0) species and on other hand promote the decarboxylation of the formic ester.

Keywords: CO; Formic esters; Hydrogenation; Poisoning; Rhenium
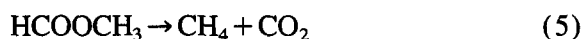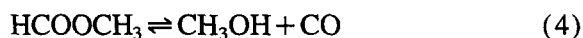
1. Introduction

Several process alternatives have been proposed for converting CO/H_2 to methanol at milder conditions with respect to the current copper-catalyzed process in order to improve the thermodynamic efficiency of the process. Among these alternatives one of the most notable is the synthesis of methanol via an alkyl formate, generally methyl formate [1]:

$$CH_3OH + CO \rightleftharpoons HCOOCH_3 \qquad (1)$$

$$HCOOCH_3 + H_2 \rightarrow 2CH_3OH \qquad (2)$$

$$\overline{CO + 2H_2 \rightarrow CH_3OH} \qquad (3)$$

Methanol is first carbonylated to methyl formate and the subsequent hydrogenolysis results in the gain of a methanol molecule over the total reaction (Eqs. 1–3).

While the carbonylation step is commercially available, the hydrogenolysis, in order to be economically advantageous, must be carried out using a hydrogen feed containing the CO not converted in the carbonylation stage; as a consequence, the hydrogenolysis catalyst must be insensitive to CO poisoning [1]. Furthermore the same catalyst should be able to depress undesired reactions such as decarbonylation and decarboxylations (Eqs. 4–7); reaction (7) follows an intermediate hydrolysis step occurring when water is present:

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$$HCOOCH_3 \rightleftharpoons CH_3OH + CO \qquad (4)$$

$$HCOOCH_3 \rightarrow CH_4 + CO_2 \qquad (5)$$

$$HCOOCH_3 + H_2O \rightleftharpoons CH_3OH + HCOOH \qquad (6)$$

$$HCOOH \rightarrow CO_2 + H_2 \qquad (7)$$

Up to now copper-based catalysts (copper chromite, Cu–Raney, Cu/SiO$_2$) have been extensively studied but they generally were found to be inhibited by CO whereas a contemporary significant decarbonylation of the esters took place [2,3]. Moreover, in the gas phase, the heterogeneous copper hydrogenolysis catalysts were also deactivated by the intermediate formaldehyde, whose polymers deposit on their surface [4].

In this context the hydrogenating activity of homogeneous and heterogeneous rhenium catalysts, never reported in methyl formate hydrogenolysis, has been investigated with the aim at finding new useful catalytic systems.

Rhenium oxides (Re$_2$O$_7$, ReO$_3$, ReO$_2$, Re$_2$O$_3$, ReO) are known to act as hydrogenation catalysts, and are particularly active for ketones, aldehydes, amides and also for acids and carboxylic acids esters [5–8]. By using Re$_2$O$_7$ as precursor, under high hydrogen pressure and at temperatures ranging from 120 to 220°C, a heterogeneous hydrogenation catalyst indicated as 'rhenium black' is obtained, able also to hydrogenate esters and a lot of carboxylic acids to alcohols but not formic acid to methanol [5].

About the nature of the active species present in the 'rhenium black' metal Re(0), or Re(IV) species, when water or acetic acid are the reaction media, have been suggested [5].

Another interesting characteristic of the homogeneous and heterogeneous rhenium catalysts is their activity in the hydrogenation of CO to ethylene glycol and methanol [9,10] and in the hydroformylation of olefins [11] which suggests a possible maintenance of the hydrogenating ability also in the presence of CO.

Finally, a recent patent has reported the resistance of rhenium catalysts to formaldehyde poisoning [12], a possible drawback in formic esters

hydrogenolysis, where formaldehyde is produced as intermediate; however, the catalyst employed in that study (Re/C) was unable to hydrogenolyze alkyl formates, their decomposition to alcohol and CO being the only reaction detected.

2. Experimental

2.1. Materials

NH$_4$ReO$_4$ (Strem), Re$_2$O$_7$ (Fluka), Re$_2$(CO)$_{10}$ (Fluka) were used as received.

[Re (CO)$_3$ (OH)]$_4$ [13], [Bu$_4$N] [Re$_2$ (CO)$_6$ (OMe)$_3$] [14], H$_3$ Re$_3$ (CO)$_{12}$ [15] and H$_4$ Re$_4$ (CO)$_{12}$ [16] were prepared according to literature methods.

Supported Re catalysts were prepared by wet impregnation of the support with slightly warm solutions of ammonium perrhenate and successive drying at 250°C for 8 h.

The following supports were used: SiO$_2$ (Akzo Si-4-5p; surface area: 400 m^2/g), Al$_2$O$_3$ (Akzo p29440; surface area: 200 m^2/g), MgO (Carlo Erba; surface area: 80 m^2/g), TiO$_2$ (Fluka; surface area: 55 m^2/g), Nb$_2$O$_5$ (CBMM; surface area: 164 m^2/g).

The determination of rhenium content in the various supported catalysts was carried out spectrophotometrically according to literature procedure [17].

2.2. Apparatus and procedure

The hydrogenolysis reactions were carried out in a 190 ml Hastelloy C rocking autoclave filled with a glass vial and heated in an oil bath and equipped with devices for removal of liquid and gas samples during the runs.

2.3. Analysis

Liquid and gas products were analyzed by GLC (Perkin Elmer Sigma 3B) as reported previously [18].

IR spectra were carried out with a Perkin Elmer 1750 Fourier transform infrared spectrometer. The infrared cell was interfaced to a gas manifold to maintain the recovered catalyst under argon.

3. Results and discussion

3.1. Hydrogenolysis of methyl formate with soluble rhenium precursors

The most utilized soluble rhenium precursors reported in the literature are the $Re(VII)$ oxide, Re_2O_7, and the $Re(0)$ carbonyl $Re_2(CO)_{10}$.

Hydrogenolysis runs on methyl formate, carried out with Re_2O_7 reduced in situ to 'Re black' at 200°C and 10 MPa of hydrogen, displayed good selectivity to methanol (up to 99%), being very limited the decomposition of the formic moiety to CO or CO_2 (run 1, Table 1).

The recycled 'rhenium black' catalyst did not lose significantly activity and selectivity in successive hydrogenolysis cycles (Table 1, run 2).

The hydrogenolysis of methyl formate took place very rapidly also under milder temperature conditions (150°C, but at higher pressures and rhenium concentrations) and also using THF as solvent (Table 1, run 5 and 6).

In contrast, when the hydrogenolysis was carried out in the presence of initial CO (H_2/CO: 10) (Table 1, run 3), a marked decrease of the catalytic activity was observed. Contemporary a great part ($\approx 60\%$) of the catalyst was trans-formed into $Re_2(CO)_{10}$ present in solution or adsorbed on the solid catalyst. This result gave an indirect confirmation of the prevailing $Re(0)$ nature of 'rhenium black' and prompted us to accomplish a new synthesis route of $Re_2(CO)_{10}$ from Re_2O_7 under mild conditions in the presence of CO/H_2 mixtures [19].

After removal of the adsorbed $Re_2(CO)_{10}$, the residual solid catalyst was used in a successive hydrogenolysis cycle under pure H_2 (Table 1, run 4): its activity (expressed as TN and taking into account the loss of soluble Re) and selectivity toward MeOH were completely restored. This indicates that 'rhenium black' can be regenerated under pure H_2. IR spectrum of the solid catalyst recovered from run 4 indicates the complete absence of carbonyl species.

To better clarify the phenomenon of CO-induced catalyst inhibition, the hydrogenolysis of methyl formate was also investigated starting from homogeneous rhenium metal carbonyl complexes.

Catalysts originated from $Re_2(CO)_{10}$ were less active both in pure methyl formate and in THF with respect to the corresponding catalysts obtained from Re_2O_7 working under analogous conditions (compare runs 7–8, Table 2 with runs 5–6, Table 1).

The selectivity to methanol was always >95% being CH_4 and CO_2 the only by-products; no decarbonylation reaction of methyl formate was noticed.

Table 1
Hydrogenolysis of methyl formate with Re_2O_7

Run	1	2	3	4	5	6 [a]
Catalyst charged	Re_2O_7	'Re black' from run 1	'Re black' from run 2	'Re black' from run 3	Re_2O_7	Re_2O_7
Methyl formate/Re (w/w)	200	200	200	500	60	60
$p\,H_2$ (MPa)	10	10	10	10	15	15
$p\,CO$ (MPa)	–	–	1	–	–	–
T (°C)	200	200	200	200	150	150
Time (h)	8	8	8	8	4	4
Conversion (%)	79.7	77.9	4.2	33.1	70.0	89.0
MeOH (Selectivity %)	98.6	99.7	100	95.8	98.0	98.5
TN (h^{-1}) [b]	10.5	10.3	0.5	10.5	8.3	10.8

[a] Solvent: THF (THF/MF = 2/1 v/v).
[b] TN (h^{-1}): g MeOH/(g Re × h).

Table 2
Hydrogenolysis of methyl formate with $Re_2(CO)_{10}$[a]

Run	7[b]	8	9[b]	10[b]	11[b]
Methyl formate/Re (w/w)	60	60	60	60	40
Promoter	–	–	Et_3N	p-tolylsulphonic acid	Me_3NO
Promoter/Re (molar ratio)	–	–	2	5	3
Time (h)	4	4	7	7	4
Conversion (%)	42	33	35	29	23
MeOH (Selectivity %)	96.0	97.3	97.0	95.3	82.1
TN (h^{-1})[c]	3.9	3.1	1.9	1.5	1.1

[a] Reaction conditions: temperature: 150°C; pressure (H_2): 15 MPa.
[b] Solvent: THF (THF/MF = 2/1 v/v).
[c] TN (h^{-1}): g MeOH/(g Re × h).

The IR spectroscopic analysis of the discharged solution revealed the presence of a part of unconverted $Re_2(CO)_{10}$ and little amount of $[Re(CO)_3(OH)]_4$ (produced by reaction of rhenium carbonyl with moisture impurity); solid 'rhenium black' was also separated.

Working in the presence of CO (CO/H_2:1/12) complete inactivity was observed and no solid 'rhenium black' was formed.

The addition of bases, such as Et_3N, did not promote the expected formation of hydrido-carbonyl species which could increase the hydrogenating activity; analogously the addition of strong acids, such as p-tolyl sulphonic acid, did slightly inhibit the catalytic activity (runs 9–10, Table 2).

The difficulty in activating rhenium carbonyl prompted us to investigate the effect of the addition of species (such Me_3NO) able to subtract CO from the metal with formation of CO_2. The activity of the modified system was very scarce and the selectivity to methanol was lower than 85%: in this case significant decarbonylation of methyl formate was observed (run 11, Table 2).

The IR analysis of the discharged solutions revealed that $Re_2(CO)_{10}$ was in this case completely converted into other carbonyl species such as $[Re(CO)_3(OH)]_4$ and $[Re_2(CO)_6(OMe)_{3-x}(OH)_x]^-$ ($x = 0-3$) [14,20,21]. Furthermore, separate runs using $[Re(CO)_3(OH)]_4$ and $[Bu_4N][Re_2(CO)_6(OMe)_3]$ as catalytic

precursors showed that they were very stable and unable to catalyze the hydrogenolysis of methyl formate (not reported in the table): this indicates that they should not correspond to active species.

Other hydrido rhenium carbonyl precursors, such as $H_3Re_3(CO)_{12}$ and $H_4Re_4(CO)_{12}$ were not able to hydrogenate methyl formate; the addition of Me_3NO favoured only the production of $[Re(CO)_3(OH)]_4$.

In conclusion, the following points have been ascertained about the catalytic activity of rhenium catalysts produced from homogeneous precursors:

(i) 'rhenium black' heterogeneous catalyst, formed from Re_2O_7 under pure hydrogen and likely consisting of metal Re, is active and very selective in the hydrogenation of the formic moiety. A reversible CO poisoning is observed working under CO/H_2 mixtures.

(ii) the presence of CO ligands in the precursor compounds makes more difficult the reduction to 'rhenium black'.

(iii) rhenium(I) species, such as $[Re(CO)_3(OH)]_4$ and $[Re_2(CO)_6(OMe)_3]^-$ are catalytically inactive.

3.2. Hydrogenolysis of formic esters with supported heterogeneous rhenium catalysts

In order to diminish rhenium concentration and attain a better dispersion of metal, heterogeneous catalysts, prepared by wet impregnation of different supports with ammonium perrhenate, were prepared and tested after a preactivation with 10 MPa of hydrogen at 200°C in n-hexane. Acid, neutral and basic supports were used.

When Re/SiO_2 was used in the hydrogenolysis of methyl formate, the activity and selectivity toward MeOH appeared reduced with respect to catalysts prepared from homogeneous precursors (compare run 12, Table 3 with run 1, Table 1) and a significant formation of CO_2 and methane was observed.

The solid catalyst recycled in successive HCOOMe hydrogenolysis tests maintained

Table 3
Hydrogenolysis of methyl formate with supported rhenium catalysts [a]

Run	12	13	14	15	16
Catalyst charged	Re/SiO$_2$ [b]	Re/SiO$_2$ from run 12	Re/SiO$_2$ from run 13	Re/SiO$_2$ from run 14	Re/Al$_2$O$_3$ [c]
p H$_2$ (MPa)	10	10	10	10	10
p CO (MPa)	–	–	1	–	–
Conversion (%)	46.1	43.0	4.8	40.9	12.1
Reaction products	Selectivity %				
MeOH	90	90	67.5	90.4	60.5
CO$_2$	7.0	5.0	14.5	5.9	9.7
CO	–	–	–	–	–
CH$_4$	3.0	5.0	18.0	3.7	12.0
TN (h^{-1}) [d]	1.1	1.0	0.1	0.9	0.2

[a] Reaction conditions: temperature: 200°C; methyl formate/Re: 118; time: 24 h.

[b] Re/SiO$_2$: 4.77% Re.

[c] Re/Al$_2$O$_3$: 4.29% Re.

[d] TN (h^{-1}): g MeOH/(g Re × h).

almost unchanged its catalytic activity and selectivity (Table 3, run 13). When the hydrogenolysis of methyl formate was carried out with H$_2$ stream containing CO (H$_2$/CO: 10/1) a marked decrease of the catalytic activity and an increase of the selectivity to CO$_2$ and CH$_4$ formation were observed (Table 3, run 14).

IR analysis of the discharged solution (from run 14, Table 3) excluded the formation of soluble Re$_2$(CO)$_{10}$ or other carbonyl derivatives. On the contrary the IR spectrum of the solid discharged catalyst provided evidence for the presence of a strong band at 2030 cm^{-1} due to linear Re–CO species, to be compared with the strong band at 2035 cm^{-1} reported in the literature for CO linearly bound to Re supported crystallites; absorptions assignable to oxidized rhenium carbonyl species were nearly absent (Fig. 1) [22,23].

The formation of Re(0) carbonyl species should indicate the presence of metal Re(0) in the preactivated catalyst and of weak interactions between rhenium and SiO$_2$ which facilitate its reduction [24]. The lower catalytic activity of the supported catalyst with respect to 'rhenium black' is probably related to residual not fully reduced rhenium species, dissolved into bulk SiO$_2$ [25].

The residual solid catalyst, used in a successive recycle under pure H$_2$, restored again nearly completely its activity and selectivity (run 15, Table 3).

The acid γ-Al$_2$O$_3$ was also used as support for rhenium catalysts in the hydrogenolysis of methyl formate. The catalyst was very little active in this reaction whereas promoted an extensive ester decomposition (decarbonylation and decarboxylation), favoured by the acid character of the support (Table 3, run 16).

These negative performances point out once again the relevance of reducing Re completely: the reduction of rhenium on γ-Al$_2$O$_3$ is in fact reported to be more difficult with respect to Re/SiO$_2$ due to the oxophilic nature of the rhenium cations which are strongly bonded to the support oxide surface [26,27]. These strong metal support interactions (SMSI) prevent the reduction step [28,29], causing a significant decrease of the catalytic activity of the hydrogenolysis reaction. Residual activity could be assured by the presence of very low amounts of Re(0), as also observed in related spectroscopic studies [30].

To gain more information on the hydrogenation of the formyl moiety some experiments were then carried out using formic esters of higher alcohols.

Thus Re/SiO$_2$ catalysts were tested in the hydrogenolysis of ethyl formate and n-butyl formate (Table 4, runs 17–18): lower activity with
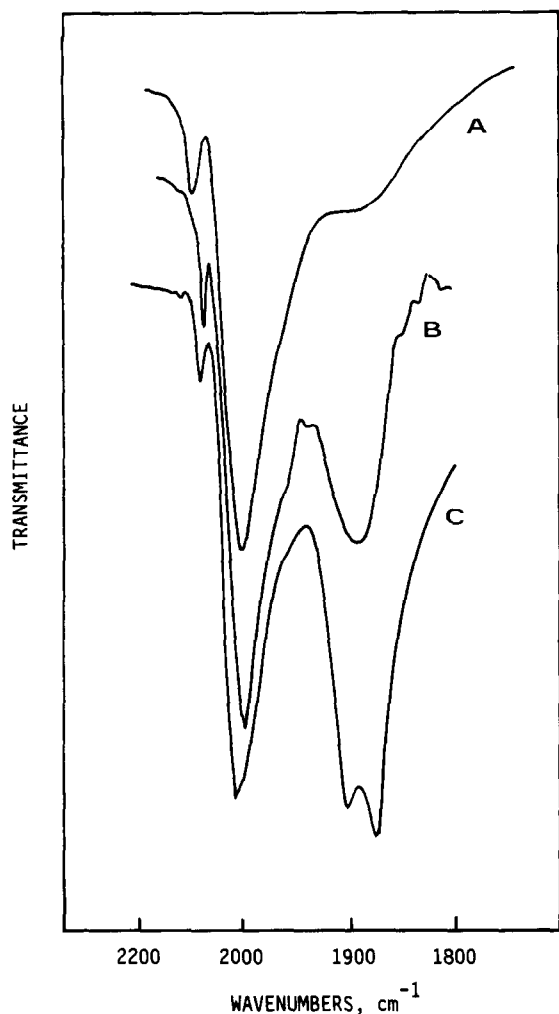
Fig. 1. Infrared spectra in the carbonyl region of: (A) Re/SiO$_2$ catalyst recovered after run 14 carried out in the presence of CO; (B) Re/TiO$_2$ catalyst recovered after run 20 carried out in the presence of CO. (C) Re/Nb$_2$O$_5$ catalyst recovered after run 23 carried out in the presence of CO.

respect to methyl formate hydrogenolysis was ascertained; the lower selectivity toward free MeOH (30%) was due to the transesterification reaction to methyl formate (Eq. 8):

$$HCOOR + MeOH \rightleftharpoons HCOOMe + ROH \qquad (8)$$

Re/TiO$_2$ catalysts, reported in the literature as active in the CO hydrogenation to methanol [23] and consequently insensitive to CO poisoning, were also tested in the ethyl formate hydrogenolysis: they showed a catalytic activity analogous to that observed with Re/SiO$_2$, but the extent of the

decarboxylation reaction was higher and a CO reversible poisoning was again observed (Table 4, run 20).

The infrared spectrum of the discharged catalyst (Fig. 1 B) showed not only the absorption at 2030 cm^{-1} due to CO occupying sites on the metal surface, but also the presence of a broad band centered at 1900 cm^{-1} probably due to an oxidized rhenium carbonyl species on the titanium oxide.

Also the less known Re/Nb$_2$O$_5$ catalyst, claimed to be active in the hydrogenation of CO$_2$ to methanol [31], was tested in the hydrogenolysis of ethyl formate: in this case the formic moiety was prevailingly decomposed to CO$_2$, due to the high acidity of the support [32]. The IR spectrum of the catalyst, recovered after the run carried out in the presence of CO, indicated the presence of CO linearly bound to supported Re(0) (νCO: 2030 cm^{-1}) but also the prevailing presence of oxidized carbonyl species, with νCO bands at 2030, 1920 and 1885 cm^{-1}, assignable to species of general formula [Re(CO)$_3$][ONb]$_{3-x}$ [HONb]$_x$ [33–35]. The presence of these species at the expenses of Re(0) is likely the cause of the low hydrogenolyzing ability.

Finally a basic support as MgO was used. Also for this oxide several studies [33,34,36–38] revealed the easy formation of the [Re (CO)$_3$][OMg]$_{3-x}$[HOMg]$_x$ species thus indicating the presence of strong interactions preventing complete rhenium reduction.

In effect also in this case a scarce hydrogenolyzing activity and a significant decomposition of the formic moiety to CO$_2$ were observed (Table 4, runs 25–27).

In conclusion, the use of supported rhenium catalysts always resulted in a decrease of the overall activity (TN) with the supported catalysts suffering from the same CO poisoning as 'rhenium black': moreover the supports, especially acid and basic ones which strongly interact with rhenium oxides, make difficult the reduction to the active Re(0) species. Thus, the best support appears to be silica where Re(0) species can be easily generated and stabilized; similar conclusions were

Table 4
Hydrogenolysis of ethyl and butyl formate with supported rhenium catalysts [a]

Run	17	18	19	20	21	22	23	24	25	26	27
Catalyst charged	Re/SiO$_2$ [b]	Re/SiO$_2$ [b]	Re/TiO$_2$ [c]	Re/TiO$_2$ from run 19	Re/TiO$_2$ from run 20	Re/Nb$_2$O$_5$ [d]	Re/Nb$_2$O$_5$ from run 22	Re/Nb$_2$O$_5$ from run 23	Re/MgO [e]	Re/MgO from run 25	Re/MgO from run 26
Ester	HCOOEt	HCOOBu	HCOOEt	HCOOEt	HCOOEt	HCOOEt	HCOOEt	HCOOEt	HCOOEt	HCOOEt	HCOOEt
p H$_2$ (MPa)	10	10	10	10	10	10	10	10	10	10	10
p CO (MPa)	–	–	–	1	–	–	1	–	–	1	–
Conversion (%)	41.7	44.9	62.4	14.7	76.3	66.7	25.6	71.0	69.7	11.5	63.2
Reaction products	**Selectivity %**										
MeOH	29.6	25.2	31.2	2.1	43.9	23.1	5.3	30.4	25.7	–	24.5
HCOOMe	55.7	60.0	48.2	59.6	23.5	21.7	44.9	22.9	23.3	11.8	30.4
CO$_2$	7.0	8.0	17.7	18.1	28.0	40.6	37.5	31.4	36.8	60.2	32.8
CO	–	–	–	–	–	–	–	–	3.6	–	3.7
CH$_4$	7.7	6.8	2.9	20.2	4.6	14.6	12.3	15.3	10.5	28.0	8.0
TN (h^{-1}) [f]	0.8	0.6	1.0	0.2	1.0	0.6	0.2	0.8	0.8	0.3	0.7

[a] Reaction conditions: temperature: 200°C; alkyl formate/Re: 118; time: 24 h; all catalysts were used after a preactivation step carried out under H$_2$ in n-hexane at 200°C.
[b] Re/SiO$_2$: 4.77% Re.
[c] Re/TiO$_2$: 4.5% Re.
[d] Re/Nb$_2$O$_5$: 4.3% Re.
[e] Re/MgO: 4.2% Re.
[f] TN (h^{-1}): $\dfrac{\text{g of formed MeOH (as free MeOH + MeOH in MF)}}{\text{g Re} \times \text{h}}$.

also achieved in a study on the hydrogenation of CO$_2$ with supported rhenium catalysts on different oxides [39].

3.3. General conclusions

The present work shows that heterogeneous dispersed rhenium catalysts, i.e. Re(0) 'rhenium black', is an active (TN: 10 g MeOH/(g Re × h) and selective (selectivity > 99%) catalyst for the hydrogenation of the HCO group to methanol under not too drastic conditions (T: 150–200°C, P: 10–15 MPa).

Unfortunately, the active metal rhenium is poisoned, albeit in a reversible manner, by CO with formation of rhenium carbonyl species: the carbonylation may proceed up to the formation of soluble Re$_2$(CO)$_{10}$.

The 'rhenium black' upon recycle maintains unchanged its catalytic activity and after poison-ing by CO can be restored by treatment at high temperature (200°C) with pure H$_2$.

The formation of oxidized rhenium(I) species corresponds to the occurrence of less active catalysts, both in the homogeneous (species [Re (CO)$_3$ (OH)]$_4$ and [Re$_2$ (CO)$_6$ (OMe)$_{3-x}$ (OH)$_x$]$^-$), and in the heterogeneous phase (species [Re (CO)$_3$] [OM*]$_{3-x}$ [HOM*]$_x$ (x=0–3; M* = Al, Mg,).

Thus, only neutral and almost inert matrices can be proposed as supports for the rhenium catalysts to be used in the hydrogenation of the formyl moiety of the formic esters without causing their decarboxylation to CO$_2$ and CH$_4$.

References

[1] M.S. Wainwright, Stud. Surf. Sci. Catal., 36 (1988) 95.

[2] R.J. Gormley, V.U. Rao, Y. Soong and E. Micheli, Appl. Catal. A, 87 (1992) 81.

[3] J.W. Evans, P.S. Casey, M.S. Wainwright D.L. Trimm and N.W. Cant, Appl. Catal., 7 (1983) 31.

[4] D.M. Monti, N.W. Cant, D.L. Trimm and M.S. Wainwright, J. Catal., 100 (1986) 17.

[5] H.S. Broadbent, G.C. Campbell, W.J. Bartley and J.H. Johnson, J. Org. Chem., 24 (1959) 1847

[6] H.S. Broadbent and J.H. Johnson, J. Org. Chem., 27 (1962) 4400.

[7] H.S. Broadbent and J.H. Johnson, J. Org. Chem., 27 (1962) 4402.

[8] H.S. Broadbent and W.J. Bartley, J. Org. Chem., 28 (1963) 2345.

[9] M. Ishino, T. Deguchi, T. Takano and S. Nakamura, J. Mol. Catal., 49 (1989) 315.

[10] M. Komiyama, Y. Ogino, Y. Akai and M. Goto, J. Chem. Soc. Faraday Trans., 79 (2) (1983) 1719.

[11] E.H. Homeier, US Pat. 3 948 999 (1976), to Universal Oil Products.

[12] J.A. Broussard, Eur. Pat. Appl. 0 373 938 (1989) to Hoechst Celanese Co.

[13] M. Herberhold and G. Süss, Angew. Chem., Int. Ed. Engl., 14 (1975) 700.

[14] A.A. Ioganson, B.V. Lokshin, E.E. Kolobova and K.N. Anisimov, Zh. Obsch. Kh., 44 (1974) 23.

[15] M.A. Andrews, S.W. Kirtley and H.S. Kaesz, Inorg. Synth., 17 (1977) 66.

[16] J.R. Johnson and H.D. Kaesz, Inorg. Synth., 18 (1978) 60.

[17] M. Valigi and G. Minelli, J. Less Common Metals, 51 (1977) 271.

[18] G. Braca, G. Sbrana, A.M. Raspolli Galletti and S. Berti, J. Organomet. Chem., 342 (1988) 245.

[19] M. Marchionna, M. Lami, A.M. Raspolli Galletti and G. Braca, Gazz. Chim. Ital., 123 (1993) 107.

[20] G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, J. Organomet. Chem., 152 (1978) 85.

[21] W.A. Hermann, D. Mihalios, K. Öfele, P. Kiprof and F. Belmedjahed, Chem. Ber., 125 (1992) 1795.

[22] C. Bolivar, H. Charcosset, R. Frety, M. Primet, L. Tournayau, C. Betizeau, G. Leclercq and R. Maurel, J. Catal., 45 (1976) 163.

[23] M. Komiyama, T. Okamoto and Y. Ogino, J. Chem. Soc. Chem. Commun., (1984) 618.

[24] M. Valigi, A. Cimino and G. Minelli, Chim. Ind (Milan), 60 (1978) 810.

[25] D.J.C. Yates and J.H. Sinfelt, J. Catal., 14 (1969) 182.

[26] H.C. Yao and M. Shelef, J. Catal., 44 (1976) 392.

[27] R.M. Edreva-Kardjieva and A.A. Andreev, J. Catal., 94 (1985) 97.

[28] A.S. Fung, P.A. Tooley, M.J. Kelley, D.C. Koningsberger and B.C. Gates, J. Phys. Chem., 95 (1991) 225.

[29] S. Engels, H. Lausch and H.W. Meiners, React. Kinet. Catal. Lett., 44 (1991) 251.

[30] F. Solymosi and T. Bànsàgi, J. Phys. Chem., 96 (1992) 1349.

[31] T. Iizuka, M. Kojima and K. Tanabe, J. Chem. Soc., Chem. Commun., 638 (1983).

[32] T. Iizuka, K. Osawara and K. Tanabe, Bull. Chem. Soc. Jpn., 56 (1983) 2927.

[33] P.S. Kirlin, F.B.M. van Zon, D.C. Koningsberger and B.C. Gates, J. Phys. Chem., 94 (1990) 8439.

[34] P.S. Kirlin, F.A. De Thomas, J.W. Bailey, H.S. Gold, C. Dybowski and B.C. Gates, J. Phys. Chem., 90 (1986) 4882.

[35] L. Guczi, A. Beck, Z. Zsoldos and S. Dobos, J. Mol. Catal., 56 (1989) 50.

[36] C.J. Papile and B.C. Gates, Langmuir, 8 (1992) 74.

[37] A. Honji, L.U. Gron, J.R. Chang and B.C. Gates, Langmuir, 8 (1992) 2715.

[38] A. Cimino, D. Gazzoli, G. Minelli and M. Valigi, Z. Anorg. Allg. Chem., 494 (1982) 207.

[39] Z. Xu, Z. Qian, K. Tanabe and H. Hattori, Bull. Chem. Soc. Jpn., 64 (1991) 1664.