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Catalysis in C_1 chemistry: future and prospect

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This work summarizes the most relevant facets of the current knowledge of the principal catalytic processes involved in one carbon-atom conversions. Without doubt, natural gas (or methane) chemical conversion into high molecular weight hydrocarbons via oxidative coupling (OCM) or partial oxidation into C_1 oxygenates (POM) currently represents a great chemical and technological challenge for petrochemistry. Although the catalyst systems and the basic principles of the two types of processes are well known, a greater effort is needed towards the development of more efficient and stable catalysts under the severe operation conditions imposed by the reaction itself, as well as the need for suitable reaction design to minimize the extent of the homogeneous reaction. The alternative process is to obtain synthesis gas (CO/H_2) in a first step through steam reforming followed by a second Fischer–Tropsch hydrogenation step. However, the unfavorable energetic balance of the reforming step and the absence of selective catalysts in the latter to obtain a narrow molecular weight distribution currently leads to compromise in solutions. Among these, the high molecular weight alcohol synthesis and the recently developed Shell middle distillate synthesis (SMDS) appear to be very attractive. Of no less importance are the reactions which incorporate a CO molecule into alcohols or olefins via carbonylations and hydroformylations. Within this framework, the use of organometallic complexes anchored to functionalized polymeric matrices initiated a very intense research activity, particularly in the development of stable catalysts.

Keywords: C_1 chemistry; methane oxidative coupling; methane partial oxidation; CO hydrogenation; methanol conversion; higher alcohol synthesis

1. Introduction

The organic and inorganic molecules containing a C-atom (CO, CO_2, CH_4, CH_3OH, HCOH) have found wide application in modern chemical industry in recent years. Several processes, such as the steam reforming of methane to produce CO/H_2 mixtures and the pyrolysis of methane to yield acetylene have been well known for many years. Other alternatives for using C_1 compounds in the synthesis of certain petrochemical products such as monomers, intermediates and liquid fuels have been widely developed in more recent years. In particular, the conversion of methane to gasoline and the condensation of methane into ethylene (and ethane) and C_1 oxygenates in a single catalytic step represent some of the most important technological challenges posed in the chemical industry in the last decades [1].

Research in this field is spread over a wide range, although the principal pathways can be arranged along the lines: (i) new reactions of C_1 compounds; (ii) development of efficient catalysts for such reactions; (iii) development of the industrial processes. Without doubt, the expectations are enormous although it must be recognized that the unsolved chemical problems are considerable. The central problem in all these processes is selectivity [2]. In particular, the activation of the C–H bond in CH_4 appears to be extremely difficult owing to the high stability of the CH_4 molecule imposed by the sp^3 hybridization of the C-atom. As a consequence, the thermal activation of CH_4 occurs at very high temperatures, which restricts the control of selectivity to products of interest. Similarly, CO hydrogenation usually yields a wide product distribution, with a resultant complicated and expense incurring separation process required.

Concerning the abundant literature on the particular aspects of the subject of this review [3–5], there is no intention of analyzing it critically but to offer the reader a compilation of the progress attained in recent years as well as the authors appreciation of the possible directions of C_1 chemistry in the near future.

2. Relevant processes based on C_1 chemistry

The production of long chain hydrocarbons (C_nH_y, $n \geqslant 2$) from molecules containing only one C-atom constitutes an enormously attractive chemical and technological alternative to the existing processes. This intention is even more appropriate considering the large reserves of natural gas (mainly composed of methane), which are available worldwide and which eventually well outpass crude oil as a hydrocarbon resource in the long-range future (fig. 1). As the proven natural gas reserves exceed 10^{14} m^3, this evolution allows for the assumption that the ultimate resources are considerable [6]. This tendency will continue into the near future, shifting towards the use of natural gas as a feedstock for the large scale manufacture of liquid fuels and even petrochemicals. Recognition of this situation is concluded in new emerging technologies which can efficiently convert natural gas into liquids and higher added-value products. Other incentives to produce liquids from natural gas stem from using such technologies directly at the remote natural gas fields and thereby saving on expensive gas transportation costs. Such an alternative could thus compete favourably with liquefied natural gas (LNG), which represents the prime means of gas transportation to consumers from remote gas fields. Moreover, natural gas can be readily purified on-site to yield a very clean and H-rich source of hydrocarbons. The absence of heteroatoms, metals and polyaromatic structures makes natural gas more interesting for the production of clean fuel products.

Various processes, all based on natural gas conversion, are either already com-

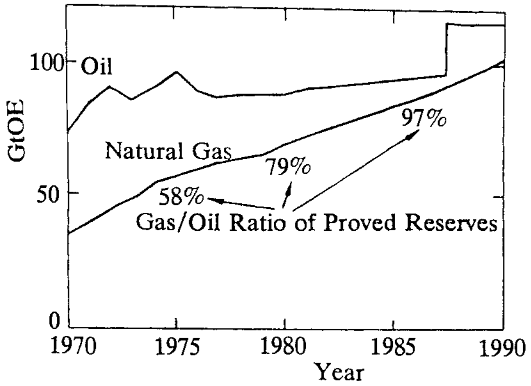


Fig. 1. Evolution of oil and natural gas reserves in the world. The ordinate represents the ratio between the known reserves of natural gas and oil, which was 58% in 1975, 79% in 1980 and 97% in 1987. The increase of oil reserves in 1987 was due to a sudden revalorisation of known reserves.

mercial or at an advanced stage of development. The first step in these processes requires the steam reforming to produce CO / H_2, followed by further processing to obtain the desired liquid product. Since reforming is a highly energy-consuming step, considerable research into alternative direct routes has been carried out as to avoid this necessity. One of the most promising direct conversion routes is the oxidative coupling of methane (OCM) (fig. 2). The primary products are ethylene and ethane (C_{2+}) but the yields are not high enough. Although the literature on the OCM is abundant, the C_{2+} yields rarely exceed 15%. An interesting exception has been already documented recently by the Repsol, S.A. company, which reported C_{2+} yields of 20.1% under steady state conditions [7].

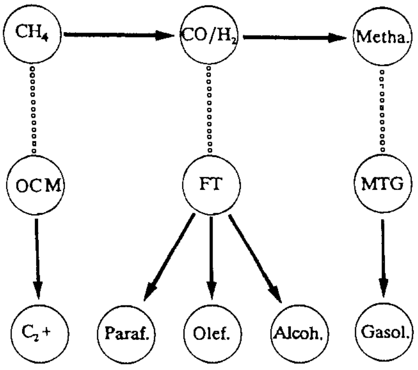


Fig. 2. Schematic representation of several catalytic developments of which the origin lies in natural gas.

The indirect routes via CO/H_2 have progressed substantially in terms of commercial development. Process technology based on FT catalysts was successfully developed in Germany in the 40's using coal as the source of the hydrocarbon feedstock. This technology was then developed and applied on a large commercial scale in South Africa by the Sasol company also using coal as the feed for CO/H_2 production. The FT route can potentially produce a large variety of products, including olefins, paraffins and alcohols. The product distribution can be modulated to some degree depending on the catalyst system used. More recently the Shell company [8] has developed the Shell middle distillate synthesis (SMDS) which uses natural gas and therefore results in a more hydrogen rich CO/H_2 mixture than is produced from coal. Since the FT catalysis involves a chain growth mechanism which obeys Anderson–Schulz–Flory kinetics, this poses the problem in designing the process to produce a narrow carbon number range product. This intrinsic limitation has been partly solved in the SMDS process by applying two consecutive catalytic steps: a first in which a high molecular weight wax is produced by FT catalysis and a second in which the wax is hydrocracked to a middle distillate boiling point range. The first commercial SMDS plant will be constructed in Malaysia making use of a remote natural gas field to provide the methane for the reforming step. A synthetic gas oil product of very high cetane number and no aromatic structures or heteroatoms (S, N, V, Ni) is produced by this process. Another important natural gas conversion process is the methanol-to-gasoline (MTG) process developed by Mobil (fig. 2) [9]. This process is based on the selective conversion of methanol using the shape selective zeolite ZSM-5 to yield an aromatic product which boils in the gasoline range. The methanol is selectively produced from syngas over copper-based catalysts using proven technology. The first commercial unit based on this technology is successfully operating in New Zealand allowing formation of liquid fuels similar to gasoline in two consecutive processes. In the meantime Mobil has developed a more advanced process which utilizes fluid bed reactors for improved selectivity and heat removal.

3. Methane partial oxidation

3.1. METHANE OXIDATIVE COUPLING

The mayor difficulty to be overcome in CH_4 conversion is the strength of the first C–H bond (ca. 435 kJ mol^{-1}). For this reason, the direct pyrolitic route to H_2 and C_2H_2 will be disfavored thermodynamically and requires high temperatures, consequently resulting in poor selectivity. As pointed out by Pitchai and Klier [10], the CH_4 partial oxidation to an oxygenated product such as formaldehyde or methanol is favored thermodynamically. Table 1 compiles the important thermodynamic equilibria taking place in the gas phase during methane partial oxidation (MPO). It can be seen in table 1 that methanol, formaldehyde and even C_{2+} hydro-

Table 1
Gibbs free energies and enthalpies (kJ mol^{-1}) of reactions of methane with oxygen

Reaction		ΔG°_{298}	ΔH°_{298}
$CH_4 + \frac{1}{2}O_2 \rightleftharpoons CH_3OH$	(1)	−111.6	−126.2
$CH_4 + O_2 \rightleftharpoons CH_2O + H_2O$	(2)	−287.2	−282.6
$CH_4 + \frac{1}{4}O_2 \rightleftharpoons \frac{1}{2}C_2H_6 + \frac{1}{2}H_2O$	(3)	−64.0	−87.8
$CH_4 + \frac{1}{2}O_2 \rightleftharpoons \frac{1}{2}C_2H_4 + H_2O$	(4)	−143.0	−140.4
$CH_4 + \frac{3}{2}O_2 \rightleftharpoons CO + H_2O$	(5)	−543.0	−518.7
$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$	(6)	−800.0	−801.3

carbons are thermodynamically feasible, but carbon oxides are even more favoured. As a consequence, the utilization of MPO reaction for the production of useful products becomes a problem of kinetic stabilization of these products. Accordingly, catalytic research in this field has been directed in recent years towards the selective production of C_1 oxygenates, on one hand, and on the production of C_{2+} hydrocarbons, on the other.

Keller and Bhasin [11] were the first to report a significant production of C_{2+} hydrocarbons by the direct MPO reaction over several metal oxide catalysts. These authors used cyclic feeding of methane and oxygen to minimize secondary oxidation of C_{2+} products. Even the importance of optimizing the gas phase reactions to maximize C_{2+} yields was recognized. More recent studies have used continuous cofeeding of the two reactants with the development of catalysts which give moderately high selectivity to C_{2+} hydrocarbons together with high CH_4 conversions. Following this methodology, the works of Baerns et al. [12,13] on supported PbO catalysts and of Ito and Lunsford [14] on Li/MgO catalysts, on which high C_{2+} yields were found, were followed by an intense research activity on three catalytic systems for the MPO reaction: (i) redox oxides [15–22], (ii) alkaline and alkaline-earth oxides [23–32] and (iii) lanthanide oxides [33–45]. In parallel with this effort, many studies related to the MPO reaction have been conducted. Although this reaction can take place over a wide range of catalysts, certain common features of the mechanism can be discerned. The results of Tyler and Luckey [46] for the MPO on a Li/MgO catalyst are typical and are compiled in fig. 3. These data show: (i) the formation of C_{2+} hydrocarbons occurs only at temperatures above 870 K; (ii) the highest selectivity to C_{2+} is attained at low CH_4 conversions; (iii) the increase in temperature or the decrease in CH_4/O_2 ratio in the feed increases the CH_4 conversion; (iv) at high conversions the C_{2+} selectivity decreases although the C_2H_4/C_2H_6 ratio increases; (v) the CO_x ($CO + CO_2$) yield also increases with temperature and oxygen molar ratio in the feed. Although Keller and Bhasin [11] originally considered that the coupling process took place only on the catalyst surface, Ito et al. [15] attempted to explain the above observations assuming the formation of methyl radicals (CH_3) by abstraction of a H-atom from CH_4 molecule. When

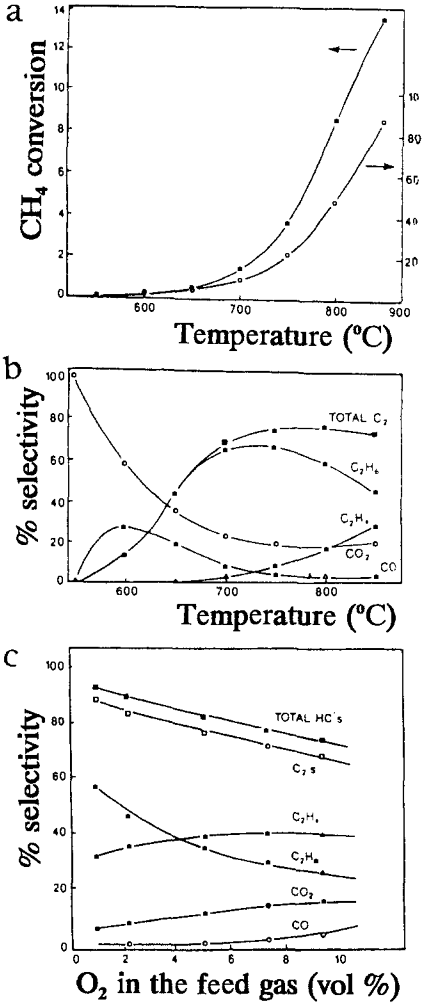


Fig. 3. Effect of the temperature on the CH_4 and O_2 conversions (a) and on the product distributions (b) in the OCM reaction over a Li/MgO catalyst (feed: 50% CH_4 and 5% O_2; $W/F = 0.05$ g cm^{-3} s^{-1}). Effect of the O_2 concentration on the product distribution (c) (feed: 90% CH_4, N_2 balance; $W/F = 1.5$ g cm^{-3} s^{-1}). Adapted from ref. [44].

the catalyst was Li/MgO, the site responsible for H-abstraction was thought to be $[Li^+\text{–}O^-]$ [24]. Later on, the gas-phase methyl radicals were identified in the partial oxidation of methane over MgO and Li/MgO catalysts using matrix isolation resonance spectroscopy (MIESR). These radicals then recombine in such a way that at least 40% of the ethane produced could be accounted for by gas phase coupling [47]. Therefore, the simplified reactional scheme is

$$CH_4 + s \rightarrow CH_3\cdot + H\text{–}s \qquad (7)$$

$$2CH_3\cdot \rightarrow C_2H_6 \ . \tag{8}$$

Isotopic studies have provided direct evidence for the participation of gas phase reactions in the coupling of radicals. In the exchange between CH_4 and CD_4 on Bi_2O_3, Amenomiya et al. [48,49] found that only one H-atom is exchanged in one adsorption–desorption cycle, suggesting the relevance of CH_3 radicals in the mechanism. In parallel, Cant et al. [26] found a kinetic isotopic effect of 1.5 on Li/MgO catalysts at 1023 K, demonstrating that C–H bond scission must be the rate-determining step in the MOC reaction. Similarly, Nelson et al. [50] measured the distribution of deuterated ethylene and ethane in the products of MOC reaction of a $CH_4 + CD_4$ feed mixture, and found only C_2H_6, CH_3CD_3 and C_2D_6 ethanes, demonstrating that the reaction took place almost exclusively by gas-phase methyl coupling. Moreover, as $CH_2{=}CH_2$, $CD_2{=}CH_2$ and $CD_2{=}CD_2$ were the only detected ethylenes, they concluded that gas-phase dehydrogenation of ethane was the likely source of ethylene. Exchange studies have also provided insight into the mechanism of CO_x formation. For such a purpose, Nelson and Cant [51] dosed pulses of ^{13}C-labeled ethylene and ethane to the CH_4/O_2 feed in a recirculating reactor containing a Li/MgO catalyst. By analyzing the amount of $^{13}CO_x$ produced they were able to conclude that above 1013 K between 30 and 80% of CO_x could be formed from gas-phase oxidation of C_2 molecules.

In the gas-phase oxidation of hydrocarbons Warnatz [52] identified two regimes of reaction. In the first, radical-poor regime, the chemistry is strongly influenced by the rate of the chain-inititiating step,

$$CH_4 + O_2 \rightarrow CH_3\cdot + HO_2\cdot \ . \tag{9}$$

The second stage is the radical-rich regime characteristic of rapid oxidation. Without doubt the most important of this regime are the propagation reactions in which the radicals H, OH, O, and to a lesser extent, HO_2 attack the hydrocarbon. Since the MOC reaction is generally carried out in extremely fuel-rich conditions (typically CH_4/O_2 may be between 2 and 20) and at relatively low CH_4 conversions, it might be considered that the reaction takes place in the radical-poor situation.

The rapid progress achieved in recent years in the precise determination of rate constants for the elementary processes had lead to various reaction models for the MOC. A detailed reaction model for the MOC to produce C_2 hydrocarbons should be capable of modeling in detail the C_1 and C_2 chemistry. Except at high pressures, yields of C_{3+} hydrocarbons are small so that simplified mechanisms for the C_{3+} chemistry can be tolerated. On the basis of kinetic modeling of fuel-rich oxidation, fig. 4 shows the important routes in oxidative coupling of CH_4 through the C_2 products. Because of the large amount of CH_3 radicals entering the gas-phase from the catalyst surface, the major reaction routes differ considerably from those in near stoichiometric methane flames [53]. Methyl radicals desorbing into the gas-phase first couple to form ethane, which may then undergo attack by CH_3 radi-

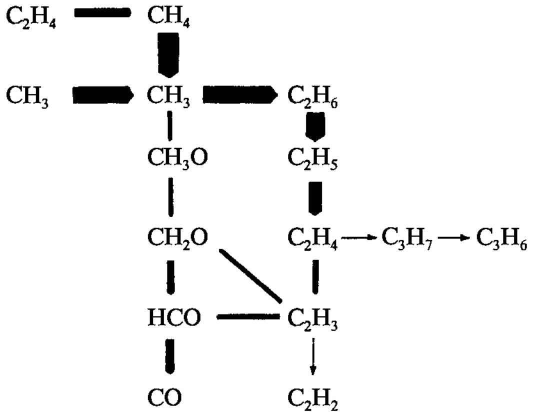


Fig. 4. Flow chart showing the principal reaction pathways for the OCM in the gas phase for a constant rate of desorption of $CH_3\cdot$ radicals. A stirred tank reactor at 928°C, $t_{res} = 0.15$ s, $P = 50$ Torr (22% CH_4, 3.5% O_2, balance Ar) was considered in the calculations. The area of the arrows is proportional to the flow of molecules through a given route.

cals to form C_2H_5 radicals followed by a unimolecular scission to C_2H_4 and H. This hydrogen atoms attack rapidly the CH_4 and also undergo chain branching with O_2. Whilst a considerable portion of methyl radicals combine to produce ethane, which then leads to ethylene, a significant number of CH_3 radicals react with O_2. The consequence of this is the production of CO_x although formaldehyde is an important intermediate in this process. Very recently, Zanthoff and Baerns [54] presented a detailed reaction model comprising 164 elementary reactions including C_3 species to predict the products of oxidative coupling at high pressure, while Mackie et al. [55] have developed a detailed model to demonstrate the inhibition of C_2 oxidation in an excess of methane.

In comparison with the higher temperature oxidative coupling to C_2 hydrocarbons, the gas-phase partial oxidation of methane to produce C_1 oxygenates is carried out at a lower temperature (ca. 723 K) and higher pressure (30–50 bar), conditions which favour reactions of methylperoxy radicals. Although initiation takes place according to eq. (7), methyl radicals rapidly equilibrate with O_2 according to

$$CH_3\cdot + O_2 \rightleftharpoons CH_3O_2\cdot \ . \tag{10}$$

Because of the relative stability and high population of methylperoxy radicals against thermal decomposition, the propagation of the oxidation initially takes place through

$$CH_3O_2\cdot + CH_4 \rightarrow CH_3OOH + CH_3\cdot \tag{11}$$

$$CH_3OOH \rightarrow CH_3O\cdot + OH\cdot \ . \tag{12}$$

As illustrated in fig. 5, methanol is principally produced by abstraction of a H-atom from CH_4 by methoxy radicals, but it can also be formed through termination reactions,

$$CH_3O\cdot + CH_4 \rightarrow CH_3OH + CH_3\cdot \tag{13}$$

$$CH_3O\cdot + CH_3O\cdot \rightarrow CH_3OH + CH_2O\cdot\ . \tag{14}$$

Similarly, formaldehyde arises principally by H-abstraction from the radical $CH_2OH\cdot$ oxygen,

$$CH_2OH\cdot + O_2 \rightarrow CH_2O + HO_2\cdot\ . \tag{15}$$

The reactions summarized by the schemes in figs. 4 and 5 only represent a small fraction of the overall reaction pathway proposed to describe the gas-phase reactions either in the MOC at pressure near to atmospheric or in the partial oxidation to C_1 oxygenates. Despite the uncertainties in accurately measuring the specific reaction constants, detailed reaction models have proven useful in predicting methane conversion and product selectivities in the partial oxidation to oxygenates.

3.2. METHANE SELECTIVE OXIDATION C_1 OXYGENATES

The production of C_1 oxygenates (methanol and formaldehyde) through selective oxidation of methane can be grouped in two categories: (i) homogeneous reaction at high pressure, and (ii) fully-catalytic reaction. The production of methanol according to reaction (i) was studied by Hunter et al. [56] and by Burch et al. [57] who addressed the problem of improving the yield of methanol from the high pres-

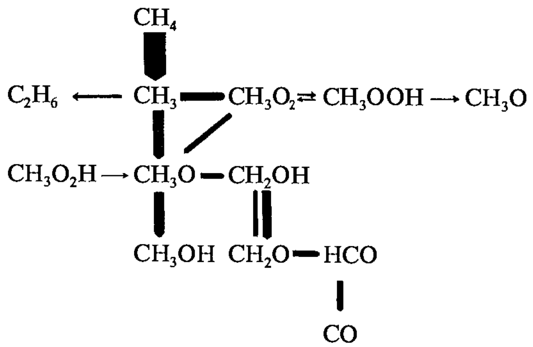


Fig. 5. Flow chart showing the principal reaction pathways for the CH_4 oxidation to methanol and formaldehyde in the gas phase. A stirred tank reactor at 467°C, $t_{res} = 1$ s, $P_{CH_4} = 36$ bar and $P_{O_2} = 1$ bar was considered in the calculations.

sure homogeneous process. Both groups have looked at the influence of the reactor wall and concluded that metals are undesirable since these lead to at least some degree of combustion.

The heterogeneous process has long been studied with some success on metal oxide catalysts. Otsuka and Hatano [58] have measured the activity of a range of oxides, and tried to correlate it with the electronegativity of the respective cation. They proposed a simple scheme for methane oxidation,

$$CH_4 \xrightarrow{1} CH_{4-x} \xrightarrow{2} HCHO \xrightarrow{3} CO_x , \tag{16}$$

which assumes abstraction of hydrogen in a first step and insertion of oxygen in the second one, implying quite different properties in catalytic sites. One might expect that a compromise oxide with sites having a little of the character needed for both steps would be the best. According to this, Otsuka and Hatano [58] found the highest CH_4 conversion over Ga_2O_3 and B_2O_3 which lay in the middle of the electronegativity plot (fig. 6a). On the other hand, maximising HCHO yield implies minimising the rate of step 3, compared to step 2, and the selectivity to HCHO

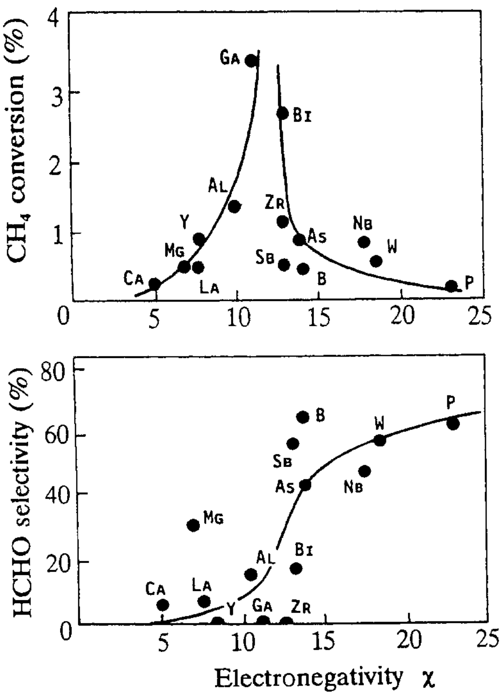


Fig. 6. CH_4 conversion (a) and HCHO selectivity (b) versus the electronegativity of the metal cation for several metal oxides. Adapted from ref. [56].

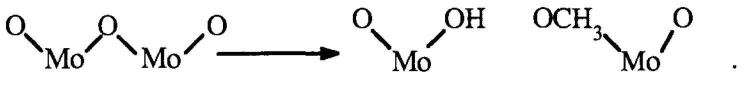
was consistently higher for the highly-electronegative oxides, those of B,P and W (fig. 6b).

Among the variety of the oxide systems proposed for the reaction, and collected in the review by Brown and Parkyns [1], the MoO_3/SiO_2 catalysts were found to be very attractive. As shown by Spencer [59], the selectivity to HCHO is inversely proportional to CH_4 conversion, and the selectivity/conversion data could be plotted on a common curve, being independent of space velocity and only slightly temperature-dependent [59,60]. In contrast, V_2O_5/SiO_2 catalysts showed a marked dependence on temperature [61]. Also, in a recent study [62,63] it has been reported that both MoO_3 surface concentration and impregnation pH are important parameters in the genesis of these catalysts since they control to some extent the type and relative abundance of specific molybdenum species which are active in the CH_4 selective oxidation. It has been found that the SiO_2 carrier alone has much lower activity, and formaldehyde yield, for methane oxidation than that of the supported catalysts under the same experimental conditions [64,65].

The use of a double layered catalyst bed has been proposed as an alternative to increase the HCHO yield. Thus, Sun et al. [66] reported the results for CH_4 oxidation over a double layered bed of the Sr/La_2O_3 coupling catalyst as the first layer followed by the very selective methane-to-oxygenates MoO_3/SiO_2 catalyst for cogeneration of C_2 hydrocarbons and formaldehyde with much higher space time yield than that from the individual catalysts. The highest HCHO yields (ca. 6.7%) appear in a Japanese patent [67]. It is stressed that such a level is only obtained by saturating the CH_4/air mixture with water vapour at room temperature. The best catalyst was a mixture of the oxides (10% each) of Fe(III), Ni(II), Bi, Mg and Mo, the remaining 50% being SiO_2. The molybdenum oxides appear to be involved in the active phase since a similar catalyst, without MoO_3, yielded a very small proportion of formaldehyde under the same experimental conditions.

Other Mo-based catalysts have been found interesting for the methane selective oxidation. By combining the ideas of CH_3 generation from an Mo=O centre with elements of olefin metathesis catalysts, Amir-Ebrahimi and Rooney [68] proposed the $MoCl_5/R_4Sn$ systems, where R is an alkyl group supported on silica, which produced exceptionally active and selective catalysts at 973 K (HCHO yield ca. 16%). Unfortunately, attempts to reproduce these catalysts were unsuccessful [69]. The UV-photoassisted oxidation of methane at moderate temperatures appears to be quite attractive [70]. For instance, at 453 K, the HCHO yield was ca. 3% in the absence of CO_x on an MoO_3/SiO_2 catalyst.

The mechanisms of MPO reaction in the gas-phase at elevated temperatures were briefly described in the preceding section. Concerning the surface processes, the amount of mechanistic work is rather limited but some common features are discernible for Mo-containing catalysts. Yang and Lunsford [71] suggested a mechanism whereby a switch in valence between Mo(IV)/Mo(VI) was responsible for the oxidation of methanol to formaldehyde, the species for this oxidation step being a bridging-oxygen between two Mo(V) atoms,



More recently, Bañares et al. [72] in a mechanistic oxygen-18 tracer study of the CH_4 selective oxidation to HCHO found that the reaction proceeds via a redox mechanism, the oxygen incorporated into HCHO comes from MoO_3 lattice. The CH_4 oxidation with $^{16}O_2$ or $^{18}O_2$ yielded always $HCH^{16}O$, but if the reaction is conducted with $^{16}O_2$ over a catalyst to which ca. 1/3 of O-atoms have been replaced by ^{18}O, through a first reduction in hydrogen at 773 K followed by a further reoxidation with $^{18}O_2$, $HCH^{18}O$ and $HCH^{16}O$ were observed in the gas-phase. As illustrated in fig. 7, the formaldehyde produced attains a maximum and disappears for longer reaction times due to its combustion on the catalyst surface induced by recirculating reactants and products.

3.3. FUTURE TENDENCIES ON METHANE CONVERSION

The intense work developed in recent years on the heterogeneous MOC reaction has outlined the approaches which will be taken with regards to research in the near future. It is apparent that the C_{2+} yield begins to pass the magic barrier of 20% with the most efficient catalytic systems in a single pass and stationary-state conditions. These yields, close to the 26% estimated for a commercially feasible pro-

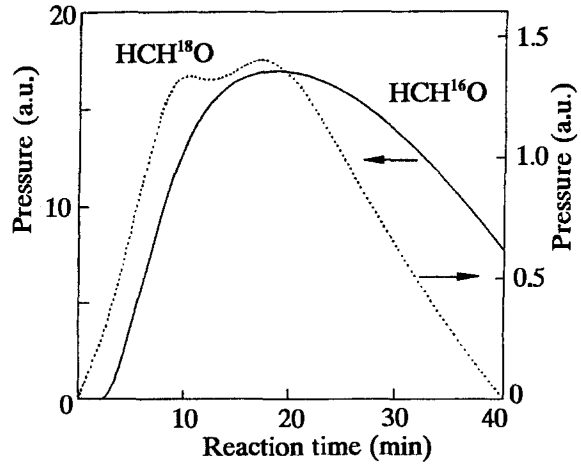


Fig. 7. Composition changes for $HCH^{16}O$ and $HCH^{18}O$ after contact with a 1.9 Mo nm^{-2} silica catalyst, in which ca. 1/3 of ^{16}O atoms were deliberately replaced by ^{18}O, with 100 Torr of a $CH_4 + O_2$ (CH_4/O_2 = 5 molar) mixture at 600°C. Adapted from ref. [66].

cess, can even be improved by proper design of the reactor and catalysts. As the operation temperatures are usually high enough ($T > 923$ K), the thermal and chemical stability are imperative to preserve both activity and selectivity for long periods on-stream. In addition to this, a rigorous kinetic analysis, computer-assisted simulation techniques and development methodologies for detecting intermediate reaction products will help to achieve such an objective. Moreover, other routes for activation of methane would be explored. The solid superacids appear particularly attractive since they can form CH_5^+ intermediates, which yield hydrogen and methyl radicals,

$$CH_4 + s{-}H^+ \rightarrow s{-}CH_5^+ \rightarrow s{-} + H_2 + CH_3\cdot \quad . \tag{17}$$

Although all these aspects are valid for the MOC reaction, thoughts now turn to CH_4 (or natural gas) conversion into CO/H_2 mixtures since large amounts of hydrogen are expected to be consumed by the fuel cells, which are being developed at a great rate.

In respect to the oxidation of methane to C_1 oxygenates it is clear from the progress being made, that there are no catalysts in prospect that will convert CH_4 into methanol or formaldehyde in high yields in a single pass. The homogeneous oxidation at high pressures still holds the best prospects, but confirmatory data are still needed. In the absence of a breakthrough in the present technology, novel reactor designs for working at low conversion and high selectivity may be the best alternatives. In accordance with this, novel concepts of operation of reactor are under investigation: (i) pressure swing reactor (PSR), and (ii) membrane reactor. Type (i) reactor operates under an alternating pressure regime, initially at high pressure in the presence of a good catalyst for methanol formation. The reactor will also contain a zeolite, which would preferentially adsorb methanol, from which the alcohol might be recovered on the depressurisation step of the cycle. Type (ii) reactor is a porous membrane [73,74] of controlled size between 4 and 5 nm. The methanol formed in the inner wall coated with a catalyst would migrate preferentially to the outside of the tube by surface diffusion and collected continuously. It is remarked that although no results are yet available, the direction of these alternatives seems very attractive and promising.

4. Direct synthesis

The production of hydrocarbons and oxygenate compounds from syngas (FT synthesis) has been studied and used on an industrial scale for more than 50 years. As a result of its relevance, the different catalytic, kinetic mechanistic and economic aspects of the process have been frequently reviewed in detail. Although the literature on the subject is abundant, the most complete information can be found in several reviews [75–80]. Most of the characteristics of the FT synthesis indicate that the mechanism is complicated. The reaction, which includes dissociation of adsorbed molecules, transforms the CO and H_2 into compounds containing C–C and C–H bonds. In general, numerous compounds, differing not only in chain length but also in functional groups, are obtained. The appearance of different functional groups implies different reactional pathways and participation of different intermediates. The relative amounts of products vary with the catalyst, temperature and pressure, and the different pathways are favoured by a specific group of reaction conditions.

4.1. THE SYNTHESIS PROCESSES

The thermodynamics for the production of hydrocarbons from carbon oxides has been calculated and discussed in detail [81]. With the exception of a few compounds such as acetylene and formaldehyde, the ΔG° values at 298 K are negative; therefore it is theoretically possible to produce a large variety of compounds at reasonable reaction temperatures. Some of the typical and most desirable reactions of the hydrogenation of CO are summarized in table 2. Other products such as acids, ketones, aldehydes and aromatics can also be produced by similar reactions. From table 2, it is clear that the stoichiometric feed ratio H_2/CO is 3 for the methanation reaction whereas for the synthesis of high molecular weight hydrocarbons and alcohols, the H_2/CO usage ratio approaches a limiting value of 2.

A number of competing reactions can occur concurrently with the synthesis of hydrocarbons and alcohols. Since water is a primary product in most of the synthesis reactions, the water–gas shift reaction can occur between this water and CO from the feed, which changes the O-containing by-products from water to carbon dioxide and alters the stoichiometry of the CO and H_2 in the feed stream. Carbon deposits can be formed at the catalyst surface by the direct disproportionation of CO and also by the direct reaction of CO with H_2.

The production of different compounds can be achieved today by a careful design of the catalyst and an appropriate control of the temperature and pressure. In general, metal catalysts favor the production of paraffins, whereas metal oxides and doped metal oxides are required for the production of alcohols. The synthesis of alcohols, and particularly higher alcohols $C_{2+}OH$, via FT processes appears to

Table 2
Reactions which can occur during hydrogenation of CO

desirable	methanation:	$3H_2 + CO \rightarrow CH_4$	(18)
	hydrocarbons:	$2nH_2 + nCO \rightarrow C_nH_{2n}\ (C_nH_{2n+2})$	(19)
	alcohols:	$2nH_2 + nCO \rightarrow C_nH_{2n+1}OH$	(20)
undesirable	water–gas shift:	$CO + H_2O \rightarrow CO_2 + H_2$	(21)
	Boudouard reaction:	$2CO \rightarrow C + CO_2$	(22)
	coke formation:	$CO + H_2 \rightarrow C + H_2O$	(23)

be very attractive since they are clean fuels which can be added to gasoline. A few catalytic systems useful for these processes are examined below.

4.2. SYNTHESIS OF ALCOHOLS

Mixed oxides with spinel or perovskite structure, possessing one or more reducible cations during the FT reaction, have been shown useful for the production of alcohols [82–85]. One of the cations which displays this property is Cu^{2+}. In its reduced state, copper adsorbs CO molecule in a molecular form, thus being exploited in the development of active and selective catalysts for methanol synthesis.

The Co(Ni)/Cu mixed oxide systems, containing a trivalent oxide and an alkaline oxide dopant, have been developed by the Institute Francais du Petrole. The coprecipitation of metal nitrates with a basic reactant yields a compound constituted by a phase with hydrotalcite-like structure and by an amorphous phase [86]. After calcination, both phases transform into spinels with general formula AB_2O_4 ($A = M^{2+}$ and $B = M^{3+}$) while CuO segregates. Under syngas reaction mixture the spinel is strongly depleted in B, yielding highly divided Cu–B clusters, which have been proposed as the active sites for alcohol formation. Fig. 8 shows the effect of composition in the alkalinized ternary system Cu–Co–Cr on the selectivity [87]. Methanol is obtained as the main product both in the Cu-rich and in the Cr-rich

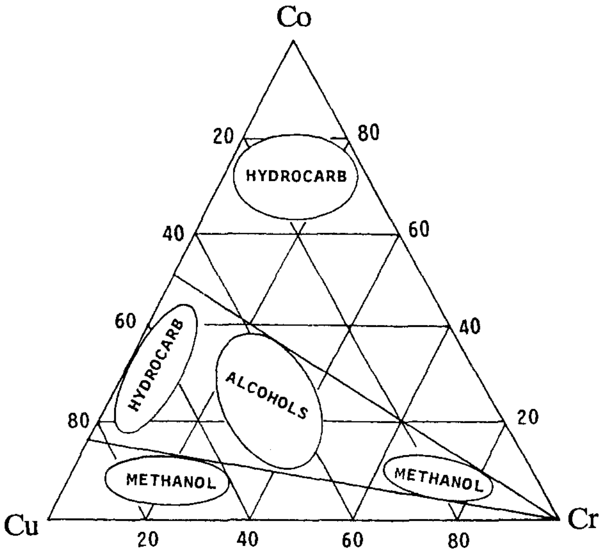


Fig. 8. Effect of the composition on the selectivity for CO hydrogenation on Cu–Cr–Co oxide catalysts.

regions, the activity being much higher for Cu-rich compositions. A FT behaviour is observed in the Co-rich region with methane as the main product. For intermediate composition ($1 \leqslant Cu/Co \leqslant 3$ and $Co/Cr \geqslant 0.5$) active and selective catalysts for the synthesis of light alcohols C_1–C_5 are obtained. Alkalinization is required to arrive at selective catalysts. In the case of hydrotalcite-like catalysts the basic function has been incorporated by Mg^{2+} cations of the oxide lattice [88].

Low temperature Cu-based catalysts alkalinized with Cs or K have been studied by Klier and co-workers [89,90] and others [91–93]. Doping the conventional Cu/ZnO and Cu/ZnO/M_2O_3 methanol synthesis catalysts with cesium causes the rate of CO conversion and selectivity to C_2 oxygenates to pass through a maximum as a function of the cesium concentration. The maximum has been attributed to the bifunctional character of these catalysts, namely hydrogenation and basicity. The alcohols most promoted by Cs were 1-propanol and 2-methyl-1-propanol, while ethanol and 1-butanol apparently were affected only marginally.

The crystalline structure of perovskite oxides with its capability to accommodate many different cations [83,84] affords an interesting frame of reference to test the substitution of B cations by copper in the perovskite on the catalytic behavior for the hydrogenation of CO. This idea was first developed by Broussard and Wade [94] and then by Brown-Bourzutschky et al. [95] who noted that substitution of Mn by Cu in $LaMnO_3$ shifted the product distribution from 100% hydrocarbons to methanol and small amounts of C_{2+} oxygenates. Later on, Rojas et al. [96,97] synthesized copper-containing perovskites of the type $LaM_{1-x}Cu_xO_3$ (M = Mn, Ti) with the aim of studying the effect of partial replacement of Mn or Ti by copper on the activity and product distribution of the hydrogenation of CO.

Activity data for CO hydrogenation as a function of the substitution degree (x) are summarized in table 3 [84,98]. It can be observed that the conversion level of CO strongly depends on the Cu substitution, attaining the highest values in the composition range $0.5 \leqslant x \leqslant 1.0$ and the lowest for $x = 0$. The product distribution was also influenced by copper substitution. Methane, ethane, dimethyl ether and alcohols were the principal organic products. Table 3 also summarizes the product

Table 3
Activity and product distribution for CO hydrogenation over $LaTi_{1-x}Cu_xO_3$ perovskite-type oxides [a]

Catalyst	x_{CO} (%)	Selectivity (%)					
		MeOH	CO_2	CH_4	C_2H_6	DME	$C_{2+}OH$
$LaTiO_3$	0.6	31	31	29	–	9	–
$LaTi_{0.8}Cu_{0.2}O_3$	12.7	39	34	9	6	10	2
$LaTi_{0.5}Cu_{0.5}O_3$	22.4	78	13	5	1	1	2
$LaTi_{0.4}Cu_{0.6}O_3$	21.0	83	10	4	1	1	2
$LaCuO_{2.5}$	21.3	73	15	7	2	1	1
Cu/La_2O_3	7.7	18	38	25	10	9	–

[a] Reaction conditions were: $T = 573$ K; $H_2/CO = 3$; overall pressure = 5 MPa.

distribution observed at a fixed set of reaction conditions. The unsubstituted $LaTiO_3$ produced methanol, methane and carbon dioxide with selectivities of about 30%, and a substantially lower proportion of dimethyl ether. Upon incorporation of Cu, the alcohol selectivity increased whereas that of methanation decreased. Interestingly, for $x = 0.5$ and 0.6 selectivity to methanol ranged from 78 to 83%, while that of CO_2 varied from 13 to 10%. The product distribution obtained with the reference lanthana-supported Cu catalyst gave quite a dissimilar result to that of the perovskites $x = 0.5$ and 0.6. In particular, methanol selectivity decreased markedly whereas CO_2, CH_4, C_2H_6 and DME followed an opposite trend.

The drastic increase of CO hydrogenation activity with increasing Cu substitution is similar to that reported by Broussard and Wade [94] for a $LaM_{0.5}Cu_{0.5}O_3$ (M = Mn, Ti) perovskite and by Brown-Bourzutschky et al. [95] for the $LaMn_{1-x}Cu_xO_3$ catalyst series. The methanol synthesis rate was observed to pass through a maximum at substitution $x = 0.6$, for which the methanol synthesis rate was 9.7×10^{-2} g/h m^2, which is similar to the one found by Sheffer and King [99] for a 1.2 at% K promoted unsupported Cu catalyst using similar reaction parameters. All these findings indicate clearly the importance of copper for both activity and selectivity toward methanol.

In order to assess the chemical state of copper, the catalysts after on-stream have been examined by X-ray photoelectron spectroscopy. Fig. 9 shows the copper core level spectra of various $LaTi_{1-x}Cu_xO_3$ catalysts used in reaction. From this figure, it appears that the binding energy (BE) values of Cu 2p electrons are very similar from catalyst to catalyst and somewhat lower than that of Cu^{2+} ions. Cupric ions can be distinguished by the appearance of a shake-up satellite line by ca. 10 eV above the principal Cu 2p peaks. As can be noted, for $x = 1.0$, and to a lesser extent for $x = 0.6$, a satellite peak is observed. The presence of Cu^{2+} ions, together with Cu^0, is expected since for these compositions the two CuO and La_2CuO_4 phases have been detected by XRD, but the reduction in hydrogen at 573 K only eliminates the CuO phase, according to the equation

$$CuO + La_2CuO_4 + H_2 \rightarrow Cu^0 + La_2CuO_4 + H_2O \ , \qquad (24)$$

while the La_2CuO_4 appears to be stable up to 673 K.

The identification of the reduced copper species, i.e., Cu^0 and/or Cu^+, becomes extremely difficult, if not impossible, by XPS data alone since the BE for Cu^0 and Cu^+ are almost the same, appearing at ca. 1.3 eV below that of Cu^{2+} ions. This is feasible only through observation of the L_3VV X-ray induced Auger parameter of copper. The modified Auger parameter α_A, defined by the equation $\alpha_A = h\nu + KE_{LMM} - KE(Cu\ 2p_{3/2})$, is generally used. KE_{LMM} and $KE(Cu\ 2p_{3/2})$ are the kinetic energies of the L_3VV X-ray induced Auger emitted electrons and the Cu $2p_{3/2}$ photoemitted electrons, respectively. The X-ray induced Auger spectrum for a representative $LaMn_{0.5}Cu_{0.5}O_3$ catalyst prereduced and used in CO hydrogenation at 573 K was found to have the Cu L_3VV peak at 1849.2 eV. As no other

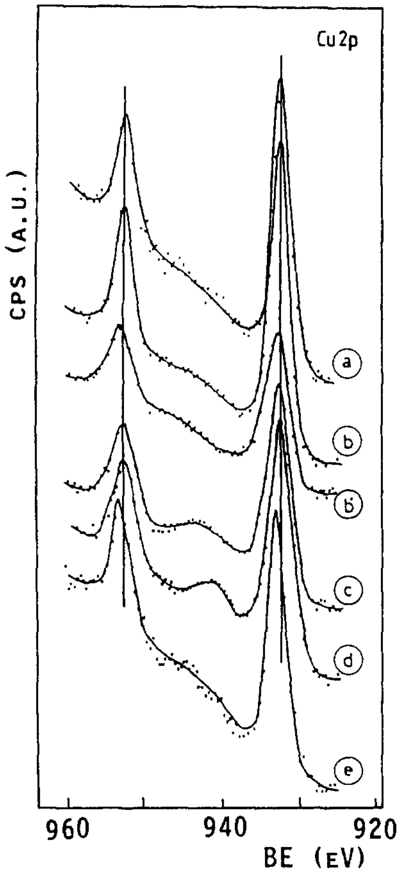


Fig. 9. Cu 2p core level spectra of several $LaTi_{1-x}Cu_xO_3$ catalysts prereduced at 300°C and used in CO hydrogenation. (a) $x = 0.2$; (b) $x = 0.5$; (c) $x = 0.6$; (d) $x = 1.0$; (e) Cu/La_2O_3. For comparative purpose, the Cu 2p spectrum (b′) of the parent $LaMn_{0.5}Cu_{0.5}O_3$ catalyst is also included.

peak was observed at energies up to 1851.0 eV, where both Cu^0 and Cu^{2+} species are expected to appear, it can be concluded that Cu^+ is the dominant copper species in the spent catalyst.

On the basis of this spectroscopic analysis, and considering that substitutions of the element M by copper in the range $x = 0.5$–1.0 in $LaM_{1-x}Cu_xO_3$ compounds result in active and selective catalysts toward methanol synthesis it can be inferred that Cu^+ locations should be responsible for methanol synthesis. The mechanism by which the perovskite lattice stabilizes Cu^+ ions can be derived from the analysis of temperature-programmed reduction profiles. These profiles for the $LaM_{1-x}Cu_xO_3$ (M = Mn, Ti) [96,97] catalyst series demonstrated that Cu^{2+} ions placed in the perovskite lattice become reduced at temperatures much higher than in massive CuO. Consequently, the extent of reduction is inhibited and the sintering of the resulting reduced phase is retarded with respect to the reduced bulk CuO or conventional supported catalysts.

The quite different catalytic behavior of $LaTi_{1-x}Cu_xO_3$ and the reference Cu/La_2O_3 catalyst suggests that under the reaction conditions the structure and probably the chemical state of copper are different. As large Cu^0 particles have been found in the Cu/La_2O_3 catalyst it seems that formation of hydrocarbons very likely occurs on metallic Cu. Since CO does not dissociate over Cu^0 [100], reaction probably proceeds via hydrogenation of CO to form H_xCO intermediates, which then undergo dissociation to yield H_yC fragments, thus constituting the precursor of hydrocarbons. Even though the dominant Cu species in the spent lanthana-supported copper catalyst is metallic Cu, in line with the high proportion of hydrocarbons in the product distribution, the presence of a small part of ionic copper on the surface of Cu crystals, or in close contact with them, cannot be excluded since it seems an important requirement for the methanol synthesis.

5. Organometallic complexes in C_1 reactions

There are numerous reactions catalysed by homogeneous organometallic complexes in which simple molecules containing only one C-atom are involved. Several tendencies of this chemistry are sketched below.

5.1. REACTIONS WITH PARTICIPATION OF CO

The liquid phase conversion of CO has already been achieved under such conditions that two stoichiometric reactions can occur simultaneously with organometallic complexes,

$$L_2MX_2 + CO + H_2O\,(+2L) \rightarrow L_4M + CO_2 + 2HX \tag{25a}$$

$$L_4M + 2HX\,(-2L) \rightarrow L_2MX_2 + H_2\ . \tag{25b}$$

The incorporation of reactions (25a) and (25b) in a close cycle yields the reaction balance:

$$CO + H_2O \rightarrow CO_2 + H_2\ . \tag{26}$$

In particular, Pd complexes of the type $[Pd(PPh_3)_2(OAc)_2]$ appear exceptionally active under very mild reaction conditions, i.e., 373 K and at CO pressures close to 1 bar [101].

Similarly, the catalytic synthesis of hydrogen peroxide can be achieved through the coupled oxidation of CO and H_2O in a close cycle by means of Pd–phosphine complexes. The final balance can be formulated:

$$CO + O_2 + H_2O \rightarrow CO_2 + H_2O_2 \ , \tag{27}$$

in which the endothermic oxidation of H_2O into H_2O_2 is compensated to a certain extent by the exothermic oxidation of CO. Reaction (27) has been performed in practice in the two-phase H_2O–CH_2Cl_2 system: Ti^{4+} sulphate, which traps the H_2O_2 formed, in the first reaction, and the Pd complex and free phosphine in the second [102].

5.2. HYDROFORMYLATION REACTIONS ON IMMOBILIZED CATALYSTS

The immobilization of homogeneous hydroformylation catalysts on solid polymeric and inorganic materials represents an interesting alternative to recover and reuse these types of catalysts [103–108]. In particular, polymers can be easily functionalized with phosphine groups, which usually constitute the ligands of many complexes. Polymer containing groups similar to the phosphine ligands used in transition metal complex catalysts are prepared by routes known from organometallic synthesis. For example, phosphine-functionalized poly(styrene-divinylbenzene) is an often used polymer support since, when it is brought in contact with metal complexes like $Rh(PPh)_3Cl$ it undergoes phosphine–phosphine ligand exchange and forms metal containing polymers. These polymers have chemical and catalytic properties similar to those of their soluble analogues. Many acid, basic, and metal-containing polymers have been prepared [106]. Some syntheses are shown in fig. 10.

Although the relevance of such an alternative is widely accepted, the chemical stability of the complex anchored to polymer must be improved. In recent studies [107,108], attention was focused on the stability of Rh(I) complexes containing Cl^- or $SC_6F_5^-$ bridge ligands anchored to (2% DVB)-polystyrene. A careful analysis of the profiles of elements by the SEM-EDX technique, and the surface composition by XPS showed that complexes containing Cl^- ligands form a weak bond with $-PPh_2$ groups of polystyrene, whereas this bond is stronger in that prepared with $SC_6F_5^-$ ligands. The catalytic behaviour for hydroformylation of 1-heptene appeared strongly influenced by these chemical differences. Although both activity and product distribution do not differ significantly at short reaction times, important changes in the catalyst lifetimes are observed. Whereas supported complexes ex-chloride were used in four cycles of reaction, the ex-pentafluorophenylthiolate homologues preserved their activity after eleven cycles. Moreover, both SEM-EDX and XPS techniques revealed leaching of Rh(I) complex to the reaction medium in the former case while this complex remained essentially unchanged in the latter. Apart from the chemical stability of the complex, other important factors such as the mechanical strength of the polymeric matrices, the extent of swelling by solvent molecules and the transport of reactants and products to and from the surface of the heterogenized catalysts, need to be investigated in detail. Therefore, more and more efforts are required to clarify these aspects.

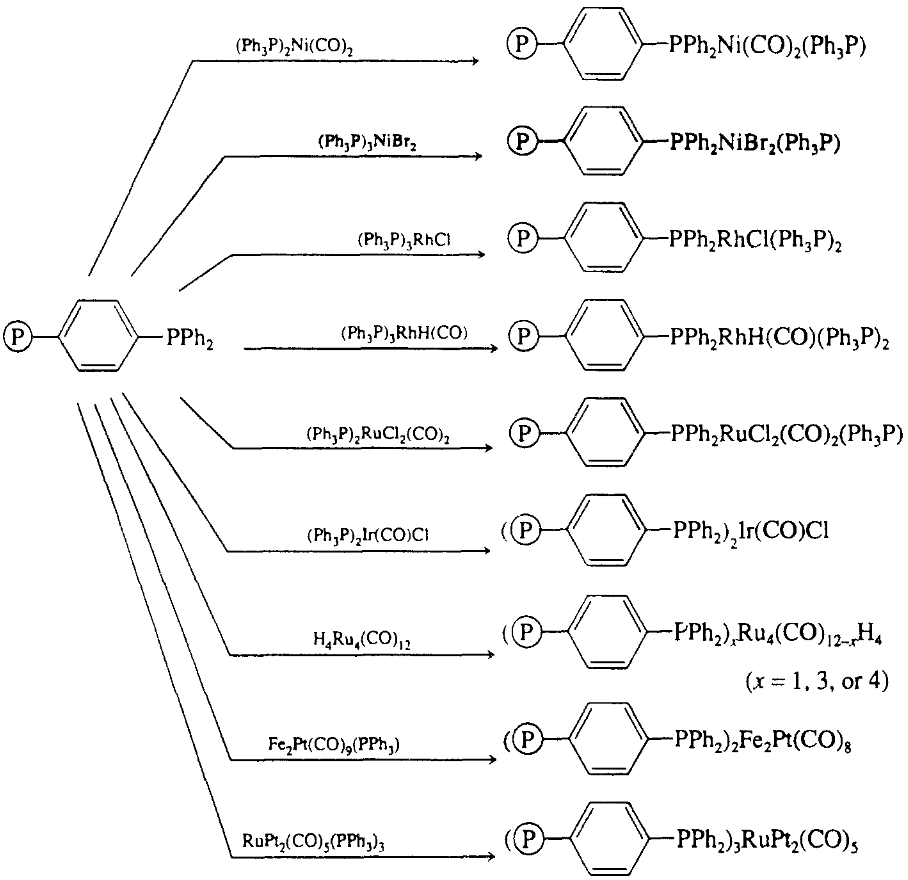


Fig. 10. Polymer-anchored organometallic complexes prepared by ligand exchange of metal complexes and clusters with phosphinated polystyrene (P) cross-linked with DVB.

6. Conclusion

This overview tries to summarize the advances attained in recent years in several processes which involve simple molecules containing one C-atom. Without doubt, the direct conversion of natural gas, in a single catalytic step, in C_{2+} hydrocarbons via MOC reaction or in C_1 oxygenates via MPO reaction constitutes nowadays an extraordinary contribution to the overall energetic system. In respect to the MOC reaction, the most efficient systems begin to overcome the barrier of 20% yield to C_{2+} hydrocarbons when operating in a single pass and under stationary-state conditions. This level, which approaches the 26% yield required for its commercialization, can even be improved by proper design of catalysts thermal and chemical stability, and of the reactor. Moreover, other routes of CH_4 activation, including solid superacids, must be explored. In addition, a rigorous kinetic, analysis, computer-assisted simulation techniques and development methodologies for detecting intermediate reaction products will help to achieve such an objective. No less important is the reaction engineering. The use of membrane reactors requires very precise techniques for incorporating the active ingredients into the porous structure, as well as a strict control of the operation variables. Similarly, the conversion of CH_4 into CO/H_2 via partial oxidation must be developed since it provides the hydrogen required for the fuel cells, which are being developed rapidly. On the other hand, catalysts for CH_4 oxidation into C_1 oxygenates are, with a few exceptions, highly inefficient. The homogeneous oxidation at high pressure to obtain methanol appears to be more promising. New reactor designs and operation modes are being explored with high methanol yields. The indirect alternatives to produce syngas in a first step (fig. 2), followed by a second one of hydrogenation to methanol or hydrocarbons (FT) are classic processes. The indirect FT alternative to produce middle distillates according to the SMDS processes represents a qualitative innovation to the classic ones. Another interesting option is the higher alcohol synthesis from CO. As the $C_{2+}OH$ product is a clean fuel, it can be added to other liquid fuels, thus decreasing the dependence of petroleum sources.

Although not so much attention was paid to these processes, methanol conversion via non-oxidative dehydrogenation [109,110], alkylation (MTBE) [111], etc., together with the MTG and MTO processes, will play an important role within the overall energy scheme. Important efforts will also be devoted to methanol carbonylation and hydroformylation of terminal olefins, all of these catalysed by organometallic complexes immobilised in polymers and inorganic materials. The innovation of these processes and technologies of C_1 chemistry will be crucial for the petrochemistry industry since, on one hand, it needs to implement the decrease in oil reserves and, on the other, to supply the market with clean fuels as demanded by a more and more rigid environmental legislation.

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