

# Platinum Group Metal-Catalysed Carbonylation as the Basis of Alternative Gas-To-Liquids Processes

## Conversion of stranded natural and associated petroleum gases to marketable products

**By Iren Makaryan\*, Igor Sedov and Valery Savchenko**

The Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Academician Semenov avenue 1, Chernogolovka, Moscow Region, 142432, Russia

\*Email: [irenmak@icp.ac.ru](mailto:irenmak@icp.ac.ru)

Traditional Fischer-Tropsch synthesis for the conversion of gas into liquids for fuels and chemicals is uneconomic for many stranded natural and remote gas sources. This review presents platinum group metal (pgm)-catalysed carbonylation as the basis of a new generation of alternative GTL processes to produce petrochemical products from hydrocarbon gases. The pgm route may allow monetisation of stranded natural and associated petroleum gases by converting them into marketable products with high added value, including for example acetic acid, methyl acetate, ethylidene diacetate, propanal, methyl propanoate, vinyl acetate, oligoketones and oligoesters.

### 1. Introduction

#### 1.1 In Search of Potential New Routes for Gas-to-Liquids

As global energy demand and crude oil prices rise, alternative production routes for hydrocarbons and petrochemicals are becoming more and more economically and ecologically attractive. Thus, gas-to-liquids (GTL) processes intended for the production of synthetic liquid fuels as well as other chemical

and petrochemical products (for example methanol, lubricants and waxes) from hydrocarbon gases have been of interest for the past three decades. This is at least partly driven by a desire to diversify the utilisation of large or stranded gas reserves by gas conversion into marketable products with high added value.

GTL today is largely dominated by Fischer-Tropsch (FT) synthesis converting synthesis gas into synthetic fuels for the transport fuel market. Manufacturing GTL fuels is extremely expensive: conventional FT GTL technologies consist of three steps (1): (a) production of synthesis gas or syngas (carbon monoxide and hydrogen) by oxidation of high purity natural gas or any methane-rich feedstock in the presence of nickel-based catalysts (this step is the most energy intensive and comprises more than 50% of the total GTL capital cost); (b) FT synthesis – the conversion of syngas in the presence of cobalt or iron catalysts to produce a mixture of hydrocarbons in the form of a synthetic crude oil (syncrude) (this step consumes  $\geq 25\%$  of the GTL capital investment); and (c) hydrocracking and hydroisomerisation of the synthesised syncrude using precious metal catalysts and syncrude refining processes to give marketable products (this step comprises 15% to 25% of the total capital cost).

Unfortunately, today the established processes for natural gas transformation into syngas and consequent FT synthesis require large investments which are prohibitive for the exploitation of small and stranded natural gas reservoirs which make up approximately one third of the world's natural gas reserves.

Various attempts are being undertaken by many researchers worldwide to avoid the costly production of syngas required by a conventional GTL route

(hydrocarbon gas → syngas → FT → GTL products). For example, scientists working on the European Union (EU)-funded project “Innovative Catalytic Technologies and Materials for Next Gas to Liquid Processes” (NEXT-GTL) are addressing the main cost and technical challenges associated with conventional GTL processes (2). They are exploring unconventional novel routes for catalytic syngas formation, including H<sub>2</sub> separation by membrane. They are also investigating direct catalytic conversion (without the syngas intermediary) of methane to methanol/dimethyl ether (DME).

Methanol is an important product of GTL technologies. Therefore special attention is paid to the second (in scale of production) route of GTL performance that leads to methanol (gas-to-methanol (GTM) process): hydrocarbon gas → syngas → methanol. The Nobel Prize Winner George Olah proposed the use of methanol as a basic feedstock not only for the chemical industry but also for the whole power industry in the near future (3). Methanol is already a key component of various process flow-sheets allowing a broad range of technologies to be used for manufacturing high value-added products.

Another EU project, “Oxidative Coupling of Methane Followed by Oligomerisation to Liquids” (OCMOL), was aimed at developing a new liquefaction route adapted to the exploitation of small gas reservoirs. The OCMOL process was based on oxidative coupling of methane into ethene followed by subsequent oligomerisation of ethene to linear  $\alpha$ -olefins and synthetic fuels including gasoline and diesel (4). The OCMOL route aimed to develop a process with economic operation at capacities of 100 kT year<sup>-1</sup> and more uniform pressures with low if not zero CO<sub>2</sub> emission.

Among the attempts to develop alternative GTL processes a direct non-catalytic partial oxidation of hydrocarbon gases is of great interest. A new route to convert hydrocarbon gas → methanol without the step of syngas production has been developed at the institutes of the Russian Academy of Sciences (5). Depending on reaction conditions, the oxidative conversion of hydrocarbon gases at temperatures of 700°C–750°C

may lead to formation of olefins (6, 7) which can also be used in a number of reactions. Methanol and olefins produced *via* this method may potentially be involved in carbonylation or oligomerisation reactions in the presence of catalysts, giving a wide assortment of marketable petrochemicals.

At present a number of well-known carbonylation processes are used industrially for large scale production. The most effective carbonylation catalysts are based on platinum group metals (pgms) such as rhodium, iridium and palladium. The aim of this article is to review and discuss pgm-catalysed carbonylation as the basis of a new generation of alternative GTL processes. For the purposes of this article, the term ‘carbonylation’ will refer to all reactions that include CO additions to various substrates. The latter may be methanol, ethene, ethanol, formaldehyde and certain other substrates formed during the direct non-catalytic partial oxidation of hydrocarbon gases.

## 2. Platinum Group Metal Carbonylation Catalysts

As a rule pgm catalysts in carbonylation processes are metal complexes with various organic heteroatom ligands providing selectivity to the required product. Sometimes relatively cheap zeolite catalysts and catalysts based on late transition metals are also used in carbonylation. However, such catalysts are less active in comparison with pgm catalysts and therefore they cannot be effectively used for the carbonylation of mixtures with low substrate content (methanol, ethene). Such mixtures are known to be formed during the partial oxidation of natural hydrocarbon gases.

The pgms are used to catalyse many reactions involving CO, H<sub>2</sub> and even molecular nitrogen (8). In general, pgm catalysts are active under milder conditions and show much higher selectivity compared to other metals. The pgms have many other key characteristics and are widely applied in industrial catalysis, despite their high prices (Table I).

Previous research at the Institute of Problems of Chemical Physics of the Russian Academy of Sciences

**Table I Johnson Matthey Base Prices<sup>a</sup> (9)**

Platinum Group Metal	Pt	Pd	Rh	Ir	Ru
US\$ per oz	1264.69	782.87	1229.31	583.30	58.96

<sup>a</sup> Month average for all time zones, October 2014

(IPCP RAS) includes the development of catalysts based on pgms (Pd, Pt, Rh, Ir). These catalysts were intended for a number of processes, particularly liquid-phase hydrogenation and dehydrochlorination of organic compounds (10, 11), activation of C–H bonds (12) and copolymerisation of ethene and CO (13).

### 3. Examples of Platinum Group Metal Catalysed Conversion of Oxidation Products

Possible products of oxidative conversion of hydrocarbon gases, including methanol, ethene and CO, may undergo various reactions to form products which are in high demand. There are currently a range of oxidative conversion processes at different stages of commercialisation. The most promising for alternative GTL processes are addition reactions of CO to low molecular weight substrates, such as carbonylation of methanol to acetic acid and methyl acetate; production of ethylidene diacetate; hydroformylation of ethene to propanal; formation of methyl propanoate during ethene methoxycarbonylation and vinyl acetate by reaction of ethene with acetic acid; and the cooligomerisation of ethene and CO with formation of oligoketones and oligoesters.

#### 3.1 Production of Acetic Acid from Methanol and Carbon Monoxide

The carbonylation of methanol to acetic acid is one of the major commercialised processes using CO, Equation (i):



The process was described by BASF in 1913 and was modified in 1941 to use late transition metal carbonyl complexes in place of transition metal salts. Co-catalysed carbonylation was initially commercialised by BASF in 1963. The use of Co-based catalysts required extremely harsh process conditions (~250°C, 600 bar) with an acetic acid yield up to 90% based on methanol and up to 70% based on CO (14).

In the 1960s Monsanto developed an improved low pressure method for methanol carbonylation using an iodide-promoted rhodium complex catalyst with much higher catalytic activity and selectivity, allowing for milder reaction conditions (~175°C, 30 bar) (15). The first plant based on this technology was put into operation in Texas City, USA, in 1970. This process has since become used in all industrialised countries. The achieved selectivity is more than 99% (based on

methanol) due to the catalytic mechanism proceeding on Rh active species. This mechanism may be achieved when the catalyst is promoted by iodide ions because methanol itself cannot participate in the basic catalytic cycle (**Figure 1**).

The selectivity of the process is about 85% to CO. The low selectivity is caused primarily by the occurrence of the water gas shift reaction (WGSR), Equation (ii):



Because this reaction is also catalysed by Rh complexes, it cannot be avoided by changing the operating conditions. Catalysts based on Ir complexes do not have this shortcoming.

The effect of hydrogen (syngas) on methanol carbonylation has also been investigated (17, 18). It was shown that the availability of hydrogen cannot prevent the carbonylation of methanol to acetic acid and methyl acetate.

In 1983 Eastman Chemical developed a process of acetic anhydride production by Rh-catalysed iodide-promoted carbonylation of methyl acetate, with a plant capacity of 320,000 tons per year (15, 19). Production of methyl acetate is performed using standard acetic acid production technology supplemented by esterification of excess methanol under reactive distillation conditions.

Another option to produce acetic acid *via* methanol carbonylation is the Cativa™ process developed by BP Chemicals in the early 1990s. This process applies an Ir-based catalyst and a ruthenium promoter. The technology was commercialised in 1995. The catalytic cycle of methanol carbonylation includes Ir-containing active species. In contrast to the Monsanto process, the oxidative addition of methyl iodide to Ir-based catalysts proceeds 150 times faster than for Rh catalysts (20). The selectivity to acetic acid may exceed 99% because the Ir catalyst prevents the formation of propanoic acid as a side product.

The production of acetic acid by carbonylation of methanol is considered the most economical of all commercial methods (oxidation of acetaldehyde and oxidation of C<sub>4</sub>–C<sub>7</sub> hydrocarbons). All new plants under construction based on this technology have a capacity of about 0.5 million tons acetic acid per year for each plant. The capital cost of such plants is estimated at US\$500 million each.

The global acetic acid market was valued at US\$6 billion in 2011 and is expected to reach US\$10 billion by 2018, growing at an annual growth rate of 9.3% over the forecast period from 2012 to 2018 (21). Global demand

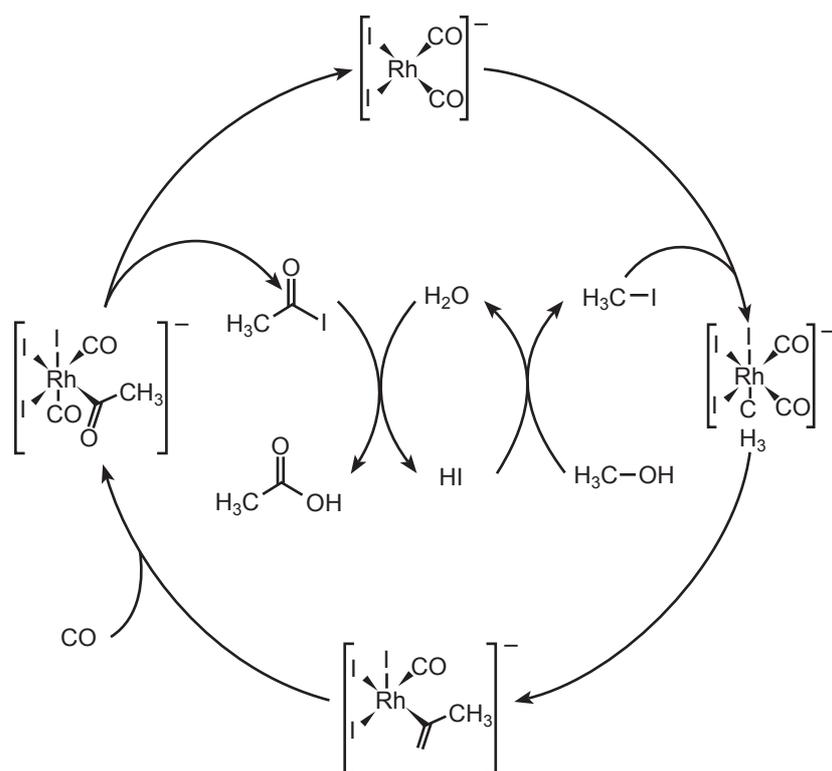
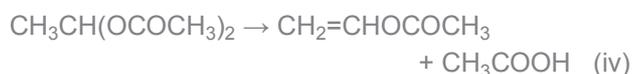
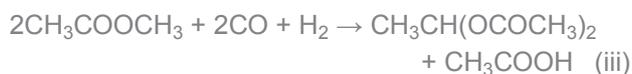


Fig. 1. Catalytic cycle for rhodium-complex-catalysed methanol carbonylation (Monsanto) (16)

for acetic acid has been steadily increasing over the last ten years (10.25 million tons in 2011 compared to 6.11 million tons in 2000) and is estimated to reach 15.5 million tons by 2020. Demand in advanced countries has largely stabilised, while emerging economies like China and India have huge consumption potential in acetic acid downstream segments such as vinyl acetate monomer, purified terephthalic acid, ethyl acetate and acetic anhydride (22).

### 3.2 Production of Vinyl Acetate *via* Ethylidene Diacetate

As mentioned above, when carbonylation is carried out in excess methanol, methyl acetate may be synthesised as well as acetic acid (23). Further reductive carbonylation of methyl acetate leads to formation of ethylidene diacetate (24), which after hydrolysis yields vinyl acetate. Vinyl acetate monomer is well-known as one of the most important chemical raw materials (25), Equations (iii) and (iv):



These syntheses were first proposed by Halcon in the 1980s. It was found that they are 30%–40% more efficient than traditional reaction routes. It has recently been shown (26) that the best feedstock for production of ethylidene diacetate and vinyl acetate is DME (24) which ensures the highest selectivity, because the WGS is not possible (27).

### 3.3 Hydroformylation of Ethene

Hydroformylation (oxo synthesis) of unsaturated substrates was discovered by Otto Roelen in 1938 (28, 29) and was originally performed using a heterogeneous Co catalyst. Further research revealed a range of metals (Rh, Co, Ir, Ru, Mn and Fe) able to catalyse the process (**Table II**) (30).

In commercial processes different metal-based catalysts are used and the most effective among them are Rh-based complexes. As can be seen from **Table II**, the activity of the Rh catalyst  $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$  exceeds that of the Co catalyst  $[\text{HCo}(\text{CO})_4]$  by three orders of magnitude. The Rh-based catalyst is more selective (linear:branched aldehyde ratio 19:1 compared with 4:1) and can be operated at lower pressures (7 atm–25 atm compared with 200 atm–300 atm) (31). The benefit of using a

**Table II Relative Activity of Different Metals in Hydroformylation (30)**

Metal	Rh	Co	Ir	Ru	Mn	Fe
Lg A	3	0	-1	-2	-4	-6

Rh-based catalyst in hydroformylation is economic efficiency, especially after the two-stage Ruhrchemie/Rhone-Poulenc (RCH/RP) process was developed, eliminating the need to separate the used catalyst from the products (21).

At present commercial hydroformylation is the key step in production of fatty alcohols based on dimers and trimers of propylene and butenes.

### 3.4 Cooligomerisation of Ethene and Carbon Monoxide

Alternate copolymerisation of olefins and CO is usually carried out in the presence of Pd-containing catalysts and leads to the formation of 1,4-polyketones ( $\gamma$ -polyketones). The latter represent copolymers with unique properties (high crystallinity, excellent mechanical properties and high chemical stability) (32, 33).

Shell developed commercial production of the first polyketone in 1996, but discontinued it in 2000 (34, 35). The product, marketed under the trade name of Carilon<sup>®</sup>, was an olefin/CO alternate copolymer containing ethene and a small amount (5%–10%) of propylene units. Today SRI International, USA, offers polyketone thermoplastic polymers. The material is currently produced under the brand name Karilon by industrial conglomerate Hyosung Corporation, South Korea, in a pilot plant, but there are plans for a continuous plant that would come on-stream in 2015 (36).

A similar reaction of ethene and CO proceeding in methanol can lead to low molecular weight products. The latter represent valuable raw materials for the production of methyl methacrylate, among them methyl propanoate (37) and diethyl ketone as a 'green' solvent (Figure 2) (38). These reactions are catalysed by Pd complexes with phosphine ligands under relatively low pressures (39, 40). A source of hydrogen that leads to

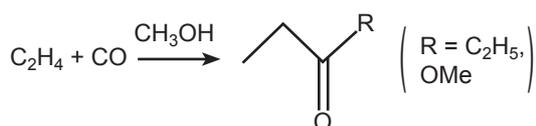


Fig. 2. Feasible products during interaction of CO and ethene in methanol in the presence of pgm catalysts

chain termination and the formation of diketones may help the WGS. The reaction was therefore promoted by the addition of amines into the reaction mixture. Both selectivity of oligomerisation and the chain length of products obtained strongly depend on the nature and the structure of the phosphine ligand (33).

One of the low molecular weight products which can be formed during the cooligomerisation of ethene and CO in the presence of methanol, involving the isomerisation of active centres, is methyl propanoate. Synthesis of methyl propanoate by methoxycarbonylation of ethene requires the participation of equimolar quantities of ethene, methanol and CO (Figure 2, R = OMe). The synthesis is catalysed by Pd complexes with the sterically bulky bidentate phosphine ligands.

Methoxycarbonylation of ethene was commercialised while developing the Lucite Alpha process in 2008 (41). The first step is interaction of ethene, CO and methanol to produce methyl propanoate; the second step is the reaction of methyl propanoate and formaldehyde to form methyl methacrylate (Figure 3). The carbonylation step has a complex highly selective mechanism with two kinds of catalytic cycles starting from both methoxy- and hydrido-Pd species (Figure 4). This reaction is catalysed by adducts of Pd salts with biphosphine that have tertiary substituents at the phosphorus atom allowing the polymerisation process to be suppressed (42). The commercial Lucite Alpha process uses 1,2-bis(di-*tert*-butylphosphinomethyl)-benzene as a phosphine ligand.

Methyl methacrylate monomer is an important marketable product. Its main applications are the production of polymethylmethacrylate and acrylic resin. Global growth in the consumption of methyl methacrylate is forecast to be 4.0% on average annually during 2011–2017 and its global market will reach 3.2 million tons by 2017 (43).

It is worth mentioning carbonylation processes which do not use CO as a direct raw material (44). In such cases different carbonyl-containing compounds (most often formates) are used as carbonyl group donors. An example is the formation of methyl propanoate by reaction of ethene with methyl formate, catalysed by Ru

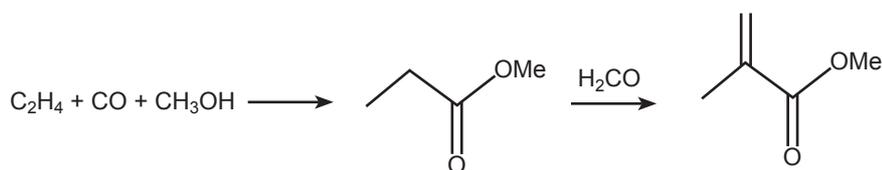


Fig. 3. Scheme of Lucite Alpha methyl methacrylate process

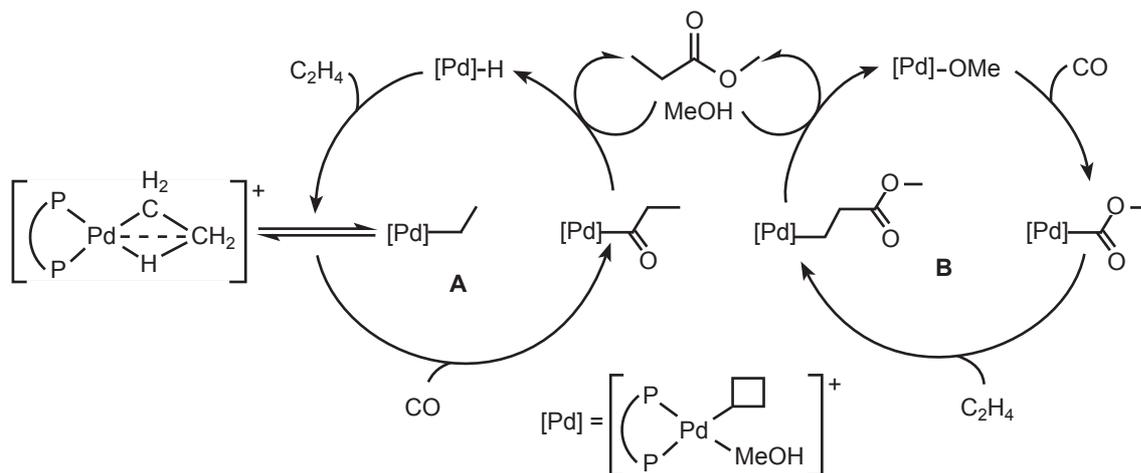


Fig. 4. Mechanism of ethene methoxycarbonylation

catalysts (Figure 5). This reaction is more ecologically friendly than the reaction that directly uses CO. The methyl formate needed for this reaction may be formed by copper-catalysed methanol carbonylation (45).

Synthesis of methyl formate and further formation of methyl propanoate taken together represent an alternative to methoxycarbonylation processes.

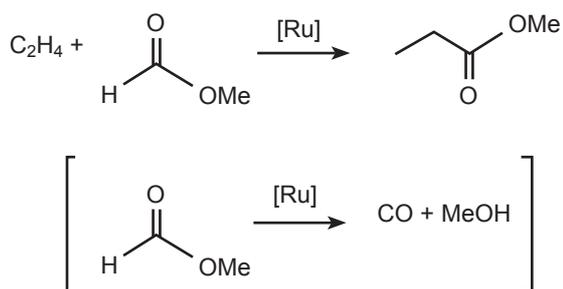


Fig. 5. Ruthenium-catalysed reaction of ethene and methyl formate

### 3.4.1 Preparation of Vinyl Acetate

Vinyl acetate is another important monomer for the production of various polymers. Its world production

is estimated as 6.5 million tons per year (46). The global vinyl acetate monomer market is expected to grow at an average rate of 5% over the forecast period from 2012 to 2020, and at a much higher rate in the Asia-Pacific region, particularly in China. Process modernisation means that BP has decreased its operating costs by a factor of three; similarly, Celanese managed to increase productivity by 95% (Praxair – by 5%) and to decrease costs by 15%.

In addition to the production of vinyl acetate from ethylidene diacetate which in turn can be produced by the reductive carboxylation of methyl acetate, vinyl acetate can be produced by the reaction of ethene with acetic acid (Figure 6). This reaction is catalysed by the homogeneous catalyst PdCl<sub>2</sub>/CuCl<sub>2</sub> at optimal temperatures of 110°C–130°C and pressures of 30 atm–40 atm. However, such operating conditions are extremely corrosive to the processing equipment. Heterogeneous Pd/Au catalysts have now been developed that avoid this shortcoming. The newly designed catalysts ensure selectivity of up to 94% to ethene and up to 99% to acetic acid. When the process is carried out in a fluidised bed reactor the capital costs may decrease by 30% (46). Recently a



Fig. 6. Palladium-catalysed vinyl acetate production from ethene and acetic acid

number of large scale vinyl acetate plants have been constructed in China, India, Iran and Saudi Arabia.

#### 4. Commercial Carbonylation of Methanol and Ethene

Those pgm-catalysed carbonylation processes mentioned above that have been successfully commercialised are listed in Table III. It can be seen from Table III that there is significant commercial experience in the realisation of processes including pgm-catalysed carbonylation to form a wide range of valuable petrochemicals. A number of these processes may be performed only in the presence of pgm catalysts. Hydroformylation was originally catalysed

by Co; however, pgm catalysts are increasingly being used. Such catalysts possess higher activity and selectivity, ensuring higher relative efficiency of the whole process.

#### 5. Carbonylation as a Component Part of a New Gas-to-Liquid Process

A new route for alternative GTL based on carbonylation has been proposed recently by the present authors (55). It consists of direct partial oxidation of hydrocarbon gases into methanol and/or ethene followed by catalytic carbonylation of the latter. The main steps of conventional GTL and the suggested alternative GTL process are shown in Figure 7.

The first step of the suggested alternative GTL process consists of direct oxidative conversion; for example: the partial oxidation of methane to methanol (56); the partial oxidation of heavy components of associated petroleum gas to methanol and CO (57); or the oxidative cracking of heavy components of associated petroleum gas to form ethene and CO

Table III Commercial Processes Including the Step of Methanol and Ethene Carbonylation

Process	Products	Metal/Catalyst	Operating temperature, °C	Operating pressure, atm	Licensor	Start-up time	Production	Reference
Hydroformylation of ethene and propylene (oxo-synthesis)	Aldehydes, alcohols	Rh H[Rh(CO) (PAr) <sub>3</sub> ]	100	20	Union Carbide Company Ruhchemie/ Rhone-Poulenc	1948 1986	overall on Rh ~2.3×10 <sup>6</sup> t/a (2002)	(47, 29)
Carbonylation of methanol	Acetic acid, methyl acetate	Rh [Rh(CO) <sub>2</sub> I <sub>2</sub> ] <sup>-</sup> (active species) Ir [Ir(CO) <sub>2</sub> I <sub>2</sub> ] <sup>-</sup>	180	30	Monsanto Celanese BP (Cativa™ process)	1970 1996	~10.5×10 <sup>6</sup> t/a (2012)	(22, 48, 49)
Interaction of ethene and acetic acid	Vinyl acetate	Pd PdCl <sub>2</sub> /CuCl <sub>2</sub> or supported Pd/Au	130	40	National Distillers Products Bayer-Hoechst	1986	~3.5×10 <sup>6</sup> t/a (2007)	(50–52)
Ethene-CO copolymerisation	Polyketone	Pd various Pd-phosphine complexes	100	20	Shell (Carilon®) BP (Ketonex®)	1996	7000 t/a (discontinued in 2000)	(53)
Ethene Carbomethoxy-ation	Methyl methacrylate	Pd Pd <sub>2</sub> (dba) <sub>3</sub> + 1,2-bis(di-tert-butylphosphino-methyl) benzene	120	20	Lucite (Alpha process)	1998	0.1×10 <sup>6</sup> t/a (2008) 0.1×10 <sup>6</sup> t/a (under construction)	(41, 54)

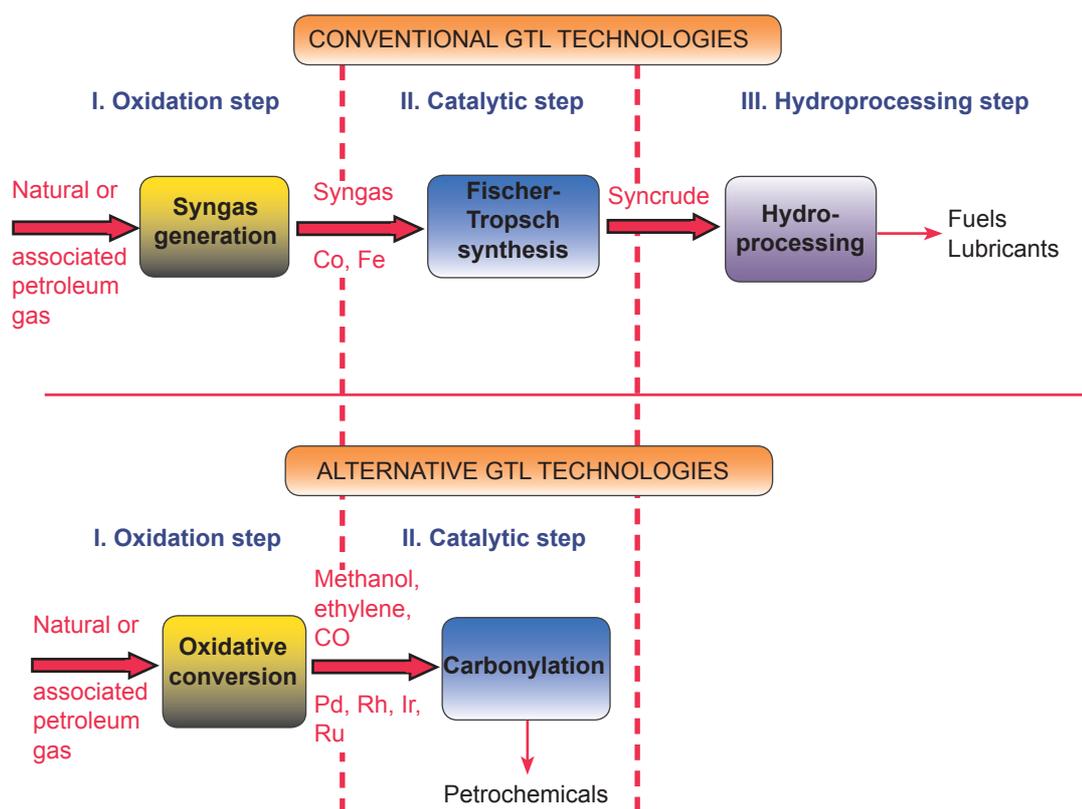


Fig. 7. The main steps of conventional and suggested alternative GTL-technologies

(58). The further processing of gas-vapour mixtures containing methanol, ethene and CO may give a broad assortment of value-added GTL products.

This approach to gas conversion is particularly attractive because CO can be formed, along with the substrates (methanol and ethene), during the partial oxidation of natural gas in quantities sufficient for a further carbonylation step. Therefore there is no need for energy consuming steam conversion or oxidation of methane into syngas. This allows the development of an integrated two-stage gas conversion process that gives a broad range of GTL products such as diethylketone, methylacetate, dimethylcarbonate, methylpropanoate, ethylidene diacetate, oligoketones and polyketones (Figure 8), without the need to separate intermediate products.

## 6. Challenges for Commercial Fischer-Tropsch and Carbonylation Processes

Shell, Sasol, ChevronTexaco, Retch, Syntroleum Corp, Statoil and other petrochemical companies are currently

developing GTL technologies for the production of sulfur-free synthetic fuels with high octane numbers (59). Among them the only companies with industrial scale FT GTL facilities are Shell (Malaysia and Qatar), Sasol (South Africa and Qatar), PetroSA (South Africa) and Chevron (Nigeria).

Current FT-based GTL technologies are most effective as large scale projects with a capacity of 30,000–150,000 barrels per day (bpd). GTL plants in use at Oryx GTL and Pearl GTL (Qatar), Escravos (Nigeria) and Nippon GTL (Japan), as well as Bintulu (Malaysia) and Mossel Bay (South Africa) which are under construction at the time of writing, represent extremely complex and energy- and capital-intensive facilities. The capital cost of the megaproject Shell Pearl in Qatar with a capacity of 140,000 bpd exceeds US\$20 billion, meaning that the capital cost per 1 bpd of synthetic oil is more than US\$140,000. Chevron Escravos in Nigeria had a total capital cost of US\$8.4 billion, i.e. the capital cost per 1 bpd of synthetic oil is around US\$200,000. The evolution of GTL processes using Fe and Co

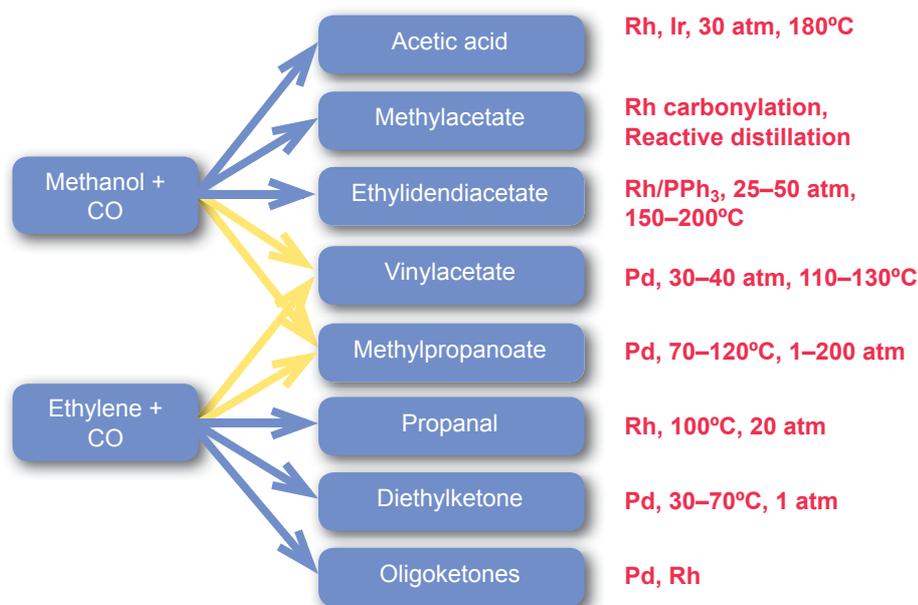


Fig. 8. Potential marketable products of catalytic carbonylation

catalysts seems unlikely due to the difficulty of increasing their productivity any further.

Thus, despite the interest, the main challenges and restrictions to the broad expansion of GTL-FT technologies are capital costs, changes in the oil/gas price ratio and volatile prices of GTL products. GTL products also have to compete with cheaper products from crude oil (gasoline, diesel, jet and stove fuel) in the consumer market. In recent years, the stimulus of GTL has turned to another force: the desire to transform stranded or flared natural gases into money by converting these into high value-added marketable chemicals.

For example, Sasol’s GTL-FT facilities are flexible for the production of not only synthetic liquid fuels but

also a broad assortment of different petrochemicals with high added value (60). This approach lowers the investment risks in comparison with production of synthetic fuel as the only marketable product. Sasol produces more than 100 products (acids, alcohols, ketones, olefins) from its high-temperature FT process for supply to the market, among them only a few fuels. This demonstrates the potential for alternative GTL to produce value-added products.

The operating characteristics of conventional GTL technologies based on FT synthesis in comparison with the suggested integrated process including carbonylation in the presence of pgm catalysts are given in **Table IV**.

Table IV Comparative Data on Conventional FT GTL and Integrated Process including Platinum Group Metal Catalysed Carbonylation		
Parameter	Conventional FT GTL	Carbonylation based GTL
Temperature, °C	220–330	100–200
Pressure, atm	20–30	10–60
Catalysts	Co, Fe	pgm
Specific activity of catalyst, kg/kg h	1.1–0.3 (conventional); Up to 2 (microchannel)	250–400 (for Rh-catalysed hydroformylation)

(Continued)

**Table IV Comparative Data on Conventional FT GTL and Integrated Process including Platinum Group Metal Catalysed Carbonylation (Continued)**

Parameter	Conventional FT GTL	Carbonylation based GTL
Reactor size	Huge	Ordinary
Expensive step for syngas production	Required	Not required
Oxidant (industrial O <sub>2</sub> )	Steam conversion: no need for O <sub>2</sub> ; Partial oxidation and ATR: need for O <sub>2</sub>	Need for O <sub>2</sub>
Additional step for reductive isomerisation	Required	Not required
Final products	Syncrude, fuels, lubricants	Petrochemicals
Product purification	Required	Required
Availability for small-scale production or direct use in oil/gas fields	Economically unreasonable	Economically reasonable
Capital cost per unit, US\$/bpd	>140,000	~50,000

## Conclusion

The present review indicates that in some cases alternative GTL processes based on carbonylation will be able to take their own segment in the existing petrochemical markets, especially for remote areas and short life oil/gas pools. In order to perform such alternative processes it is advisable to use pgm catalysts because of their high activity and selectivity. This type of process can be used for the monetisation of stranded natural and associated petroleum gases by converting them into marketable products with high added value.

## References

1. E. F. Sousa-Aguiar, F. B. Noronha and A. Faro, Jr, *Catal. Sci. Technol.*, 2011, **1**, (5), 698
2. NEXT-GTL Result In Brief, 'Making Better Use of Natural Gas', Project Reference 229183, Record Number 91099, Community Research and Development Information Service (CORDIS), Luxembourg, 4th July, 2014
3. G. A. Olah, A. Goeppert and G. K. S. Prakash, "Beyond Oil and Gas: The Methanol Economy", 2nd Edn., Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2009
4. 'Periodic Report Summary 2', Oxidative Coupling of Methane followed by Oligomerisation to Liquids (OCMOL), Project reference 228953, Record Number 53847, Community Research and Development Information Service (CORDIS), Ghent, Belgium, 28th May, 2014
5. V. S. Arutyunov and O. V. Krylov, *Russ. Chem. Rev.*, 2005, **74**, (12), 1111
6. R. N. Magomedov, A. Yu. Proshina and V. S. Arutyunov, *Kinet. Catal.*, 2013, **54**, (4), 383
7. R. N. Magomedov, A. Yu. Proshina, B. V. Peshnev and V. S. Arutyunov, *Kinet. Catal.*, 2013, **54**, (4), 394
8. T. A. Bazhenova and A. E. Shilov, *Coord. Chem. Rev.*, 1995, **144**, 69
9. Johnson Matthey base prices in US\$ per troy oz: <http://www.platinum.matthey.com/prices/price-tables> (Accessed on 24th October 2014)
10. V. I. Savchenko, I. A. Makaryan and V. G. Dorokhov, *Platinum Metals Rev.*, 1997, **41**, (4), 176
11. V. I. Savchenko and I. A. Makaryan, *Platinum Metals Rev.*, 1999, **43**, (2), 74
12. A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, 1997, **97**, (8), 2879
13. O. M. Chukanova, K. A. Alpherov and G. P. Belov, *J. Mol. Catal. A: Chem.*, 2010, **325**, (1–2), 60
14. W. Reppe, H. Friederich, N. von Kutepow and W. Morsch, BASF AG, 'Process for the Production of Aliphatic Oxygen Compounds By Carbonylation of Alcohols, Ethers, and Esters', *US Patent 2,729,651*; 1956
15. A. Haynes, *Adv. Catal.*, 2010, **53**, 1
16. A. Behr and P. Neubert, "Applied Homogeneous Catalysis", Wiley-VCH Verlag & Co KGaA, Weinheim, Germany, 2012
17. K. G. Moloy and J. L. Petersen, *Organometallics*, 1995, **14**, (6), 2931
18. B. Liu and S. F. Ji, *Adv. Mater. Res.*, 2012, **610–613**, 2600

19. J. R. Zoeller, *Catal. Today*, 2009, **140**, (3–4), 118
20. A. Haynes, P. M. Maitlis, G. E. Morris, G. J. Sunley, H. Adams, P. W. Badger, C. M. Bowers, D. B. Cook, P. I. P. Elliott, T. Ghaffar, H. Green, T. R. Griffin, M. Payne, J. M. Pearson, M. J. Taylor, P. W. Vickers and R. J. Watt, *J. Am. Chem. Soc.*, 2004, **126**, (9), 2847
21. 'Acetic Acid Market for VAM, PTA, Acetate Esters, Acetic Anhydride and Other Applications – Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2012–2018', Transparency Market Research, Albany, New York, USA, 3rd October, 2013
22. 'Global Acetic Acid Market Estimated to Reach 15.5 Million Tons by 2020', Plastemart, Mumbai, India, 14th February, 2013
23. P. Cheung, A. Bhan, G. J. Sunley and E. Iglesia, *Angew. Chem. Int. Ed.*, 2006, **45**, (10), 1617
24. D. Liu, X. Huang, L. Hu, D. Fang, W. Ying and D. Chen, *J. Nat. Gas Chem.*, 2010, **19**, (2), 165
25. N. Rizkalla and R. Vale, The Halcon SD Group, Inc, 'Preparation of Carboxylic Acid Anhydrides', *US Patent* 4,483,803; 1984
26. F. J. Waller, Air Products and Chemicals, Inc, 'Process for Converting Dimethyl Ether to Ethylidene Diacetate', *European Patent* 0,566,371; 1993
27. A. Haynes, 'Acetic Acid Synthesis by Catalytic Carbonylation of Methanol', in "Catalytic Carbonylation Reactions", ed. M. Beller, Topics in Organometallic Chemistry, Springer-Verlag, Berlin, Heidelberg, Germany, 2006, Vol. 18, pp. 179–205
28. O. Roelen, Chemische Verwertungsgesellschaft, 'Verfahren zur Herstellung von sauerstoffhaltigen Verbindungen', *German Patent* 849,548; 1938
29. B. Cornils, W. A. Herrmann and M. Rasch, *Angew. Chem. Int. Ed.*, 1994, **33**, (21), 2144
30. K.-D. Wiese and D. Obst, 'Hydroformylation', in "Catalytic Carbonylation Reactions", ed. M. Beller, Topics in Organometallic Chemistry, Springer-Verlag, Berlin, Heidelberg, Germany, 2006, Vol. 18, pp. 1–33
31. "Aqueous-Phase Organometallic Catalysis: Concepts and Applications", 2nd Edn., eds. B. Cornils and W. A. Herrmann, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2004
32. G. P. Belov and E. V. Novikova, *Russ. Chem. Rev.*, 2004, **73**, (3), 267
33. E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, (2), 663
34. H. Seifert, *Kunststoffe*, 1998, **88**, 1154
35. F. Garbassi, *Chemtech*, 1999, **29**, (10), 48
36. 'Polyketone returns', *Injection World*, November/December 2013, p. 36
37. G. R. Eastham, R. P. Tooze, M. Kilner, D. F. Foster and D. J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.*, 2002, (8), 1613
38. V. N. Zudin, G. N. Il'inich, V. A. Likholobov and Y. I. Yermakov, *J. Chem. Soc., Chem. Commun.*, 1984, (8), 545
39. G. Cavinato, L. Toniolo and A. Vavasori, 'Carbonylation of Ethene in Methanol Catalysed by Cationic Phosphine Complexes of Pd(II): from Polyketones to Monocarbonylated Products', in "Catalytic Carbonylation Reactions", ed. M. Beller, Topics in Organometallic Chemistry, Springer-Verlag, Berlin, Heidelberg, Germany, 2006, Vol. 18, pp. 125–164
40. R. A. M. Robertson and D. J. Cole-Hamilton, *Coord. Chem. Rev.*, 2002, **225**, (1–2), 67
41. B. Harris, 'Acrylics for the Future', *Ingenia*, December 2010, Issue 45, p. 19
42. P. W. N. M. van Leeuwen and Z. Freixa, 'Bite Angle Effects of Diphosphines in Carbonylation Reactions', in "Modern Carbonylation Methods", ed. L. Kollár, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2008
43. 'Methyl Methacrylate: A Global Strategic Business Report', Global Industry Analysts Inc, San Jose, California, USA, February, 2013
44. T. Morimoto and K. Kakiuchi, *Angew. Chem. Int. Ed.*, 2004, **43**, (42), 5580
45. L. He, H. Liu, C.-x. Xiao and Y. Kou, *Green Chem.*, 2008, **10**, (6), 619
46. G. Roscher, 'Vinyl Esters' in "Ullmans's Encyclopedia of Industrial Chemistry", Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2007
47. S. N. Bitzzari, R. Gubler and A. Kishi, 'Oxo Chemicals', in "Chemical Economics Handbook", SRI International, Report number 682.7000, 2002, pp. 1–121
48. K. Weissermel and H.-J. Arpe, "Industrial Organic Chemistry", 4th Edn., Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2003
49. I. Conn, 'Refining & Marketing Welcome', Refining and Marketing Investor Day, BP Plc, Pangbourne, UK, 30th November, 2011
50. I. I. Moiseev, M. N. Vargaftik and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 1960, **133**, 377
51. H. Fernholz, H.-J. Schmidt, F. Wunder, Hoechst AG, 'Process for the Manufacture of Vinyl Esters of Carboxylic Acids', *German Patent* 1,296,138; 1967

52. R. E. Robinson, National Distillers, 'Process for Preparing Esters', *US Patent* 3,190,912; 1965
53. E. Brulé, J. Guo, G. W. Coates and C. M. Thomas, *Macromol. Rapid Comm.*, 2011, **32**, (2), 169
54. G. R. Eastham, M. Waugh and P. I. Richards, Lucite International UK Limited, 'Carbonylation of Ethylenically Unsaturated Compounds', *World Appl.* 2007/057,640
55. V. I. Savchenko, I. A. Makaryan, I. G. Fokin, I. V. Sedov, R. N. Magomedov, M. G. Lipilin and V. S. Arutyunov, *Neftepererabotka i Neftechimiya*, 2013, (8), 21
56. V. Arutyunov, "Direct Methane to Methanol: Foundations and Prospects of the Process", Elsevier BV, Amsterdam, The Netherlands, 2014
57. V. S. Arutyunov, E. V. Sheverdenkin, V. M. Rudakov and V. I. Savchenko, *Stud. Surf. Sci. Catal.*, 2004, **147**, 703
58. V. S. Arutyunov and R. N. Magomedov, *Russ. Chem. Rev.*, 2012, **81**, (9), 790
59. D. A. Wood, C. Nwaoha and B. F. Towler, *J. Nat. Gas Sci. Eng.*, 2012, **9**, 196
60. A. P. Steynberg, R. L. Espinoza, B. Jager and A. C. Vosloo, *Appl. Catal. A: Gen.*, 1999, **186**, (1–2), 41

## The Authors



Iren A. Makaryan obtained her PhD in Chemistry from the Institute of Problems of Chemical Physics at the Russian Academy of Sciences (RAS), Chernogolovka, Moscow Region, Russia, under the supervision of Professor Valery I. Savchenko. She is currently Head of the Techno-Economic and Market Research Group. Her research interests include kinetics and mechanism of pgm catalysed reactions, commercialisation of newly designed processes and market analysis.



Igor V. Sedov obtained his PhD in Chemistry from the Institute of Problems of Chemical Physics RAS, Chernogolovka, under the supervision of Professor Petr E. Matkovskiy in 2011. He is now Head of the Petrochemical Processes Laboratory at the institute. His interests include organometallic catalysis, chemical technology and engineering.



Professor Valery I. Savchenko has been Head of the Department of Chemical Technology at the Institute of Problems of Chemical Physics RAS, Chernogolovka, since 1991. He also lectures on Modern Petrochemical Processes at the Lomonosov Moscow State University, Russia. His research is devoted to a wide range of problems in the field of chemical physics and chemical technology, including catalysis, kinetics, reaction mechanisms and reaction engineering. He has helped develop and commercialise a number of novel chemical and petrochemical processes.