

## Review

## Catalysts, mechanisms and industrial processes for the dimethylcarbonate synthesis

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## ABSTRACT

This review reports on the synthesis of dimethylcarbonate (DMC) and deals with the catalysts, the mechanisms as well as the industrial processes and the reactions for producing DMC, within the policy of developing clean and eco-friendly processes. DMC is considered as an environmentally benign chemical due to a negligible ecotoxicity, a low bioaccumulation and a low persistence, so that the production and chemical use of DMC have attracted much attention in the view of the so-called 'sustainable society' and 'green chemistry', mainly for replacing dimethylsulfate and methylhalides in methylation reactions and for replacing the harmful phosgene in polycarbonate and isocyanate syntheses. Special focus is made on the vapour phase oxycarbonylation of methanol by carbon monoxide in substitution to the old phosgenation process abandoned with years, and as an alternative process to both liquid phase methanol oxycarbonylation and methylnitrite carbonylation processes. The catalytic materials consist in high surface area active carbon supported copper chloride-based catalysts and chloride-free zeolite catalysts, both investigated in terms of catalyst preparation, active phase nature, performances and catalytic mechanisms.

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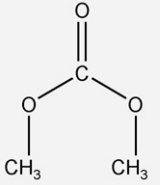
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**Table 1**  
Physico-chemical properties of DMC [1] and its developed formula



Melting temperature (°C)	4.6
Vaporization temperature (°C)	90.3
Density	1.07
Flash point (°C)	21.7
Azeotrop	Water, alcohols
Δ <i>H</i> <sub>vap</sub> (kcal/kg)	88.2
Water solubility (g/100 g)	13.9
Dielectric constant (ε)	3.087
Dipolar moment (μ, D)	0.91

## 1. Dimethylcarbonate (DMC)

Over the last decades, environmental aspects such as the impact of chemical substances over human health have been put forward as major public concern. This more and more important public health and environmental protection pressure resulted in ever stricter legislation requirements related to both use and production of chemicals, carried in the form of bills or resolutions by national or international executives. This led industrials to be involved in developing clean and eco-friendly synthesis processes meeting such environmental restrictions, in adequation with the Green Chemistry approach.

The production and chemical use of dimethylcarbonate (DMC, Table 1) are directly concerned by this policy frame. The 2500 recent reference citations listed by the Chemical Abstract database highlight the growing interest devoted to this research area since few years [2]: the search for more performing catalysts and processes in order to meet the ever increasing standards in the eco-technology field has created a strong incentive, stimulating and driving research in this area. DMC is considered as an environmentally benign chemical, so that its production and its chemical use have attracted much attention in the view of the so-called ‘sustainable society’ and ‘green chemistry’ approaches. This increasing focus is thus mainly due to its biodegradability, with a low bioaccumulation and a low persistence, as well as its low toxicity, DMC being about 1000 times less toxic than phosgene (Table 2). In addition, the great reactivity of DMC towards nucleophilic molecules such as phenols or primary amines renders it a valuable reactant for organic syntheses, mainly for acting as a carbonylation agent for replacing the harmful phosgene in polycarbonate and isocyanate

**Table 3**  
Octane number of fuels containing different alkylcarbonates (3–5 vol.%) [5].

	Dimethylcarbonate	Diethylcarbonate	Dipropylcarbonate	Dibutylcarbonate
Octane number	116	105	106	88

**Table 2**  
Comparison of toxicologic data between DMC and phosgene [1].

Properties	DMC	Phosgene
Toxicity through oral take (rats)	LD <sub>50</sub> 13.8 g/kg	
Toxicity through inhalation (rats)	LC <sub>50</sub> 140 mg/l (4 h)	LC <sub>50</sub> 140 mg/m <sup>3</sup> (75 min)
Mutagen property	Without	
Irritability property	Without	Corrosive
Biodegradability	>90% (28 days)	Rapid hydrolysis into CO <sub>2</sub> and HCl

syntheses, as well as for replacing dimethylsulfate and methylhalides in methylation reactions.

This review thus reports first the main industrial applications of DMC as fuel additive, alternative to phosgene for polycarbonate and isocyanate syntheses, methylation agent and solvent (Section 2), before it describes the industrial synthesis processes, including the old phosgenation process as well as both Enichem liquid phase methanol oxycarbonylation and UBE methylnitrite carbonylation processes (Section 3). The direct synthesis from CO<sub>2</sub> and methanol and the transesterification of ethylene carbonate through urea or methanol are briefly reported in Section 4 as alternative synthesis processes. Finally, Section 5 focuses on the vapour phase oxycarbonylation of methanol, with catalytic materials consisting in high surface area active carbon supported copper chloride-based catalysts and chloride-free zeolite catalysts, investigated in terms of catalyst preparation, active phase nature, performances and catalytic mechanisms.

## 2. Dimethylcarbonate applications

The industrial applications of dimethylcarbonate cover several fields, and the main applications are detailed in this section, such as the use of DMC as fuel additive, alternative substitute for phosgene, methylation agent and solvent.

### 2.1. Fuel additive

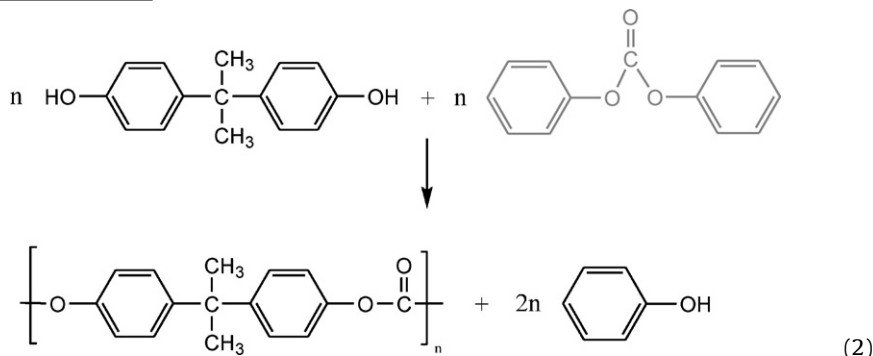
The use of dimethylcarbonate, and more generally of alkylcarbonates, as fuel additive was put forward in numerous patents [3], the first occurrence being the apanage of the Standard Oil Development Co. in 1943 [4], which reported that adding 3 wt.% of diethylcarbonate and butylcarbonate in gazoles allowed both injection and vaporization of gazoles to be improved, by reducing their surface tension. Although butylcarbonate was preferred, dimethylcarbonate was also mentioned. Another determining factor in the fuel formulation is the octane number, which is representative of the capacity of fuel to resist to the self-ignition caused by the com-

pression inside the combustion chamber. Table 3 evidences that adding DMC to fuels significantly increased the octane number compared to other alkylcarbonates, with a high octane number of 116 resulting from the high oxygen content of DMC.

More recently, Union Oil Co. has patented the reduction of the diesel soot particle release for DMC-containing gazole [6,7].

requires an additional restricting separation step during the process.

The search for phosgene-free synthesis routes led thus to propose an alternative process consisting in the transesterification of diphenylcarbonate (DPC) with A-biphenol [8].



A 10–30% decrease in the soot particle release was observed for DMC contents around 5 wt.% inside gazole. In addition, DMC displayed a more valuable efficiency than the usually methyl tert-butyl ether (MTBE) for reducing the exhaust level of carbon monoxide, formaldehyde and unburned hydrocarbons. This was explained by the high oxygen content (53.3 wt.%) of DMC when compared to MTBE (18.2 wt.%), which significantly improved the fuel oxygenation.

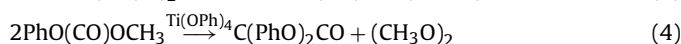
## 2.2. Alternative to phosgene for aromatic polycarbonate and isocyanate syntheses

Phosgene ( $\text{COCl}_2$ ) is widely used in many applications and processes. Its use during WW I as gaseous warfare agent is representative for its high toxicity (Table 2). Ingesting phosgene results in hydrochloric acid formation, which attacks the organism, leading to pulmonary oedema and finally to death. Nowadays, replacing phosgene by low toxicity compounds such as DMC remains thus of immense interest and is therefore highly requested.

### 2.2.1. Aromatic polycarbonate synthesis

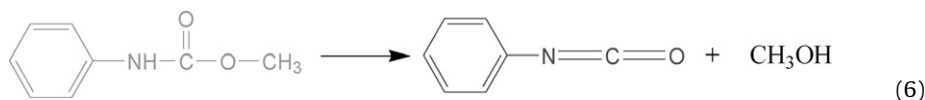
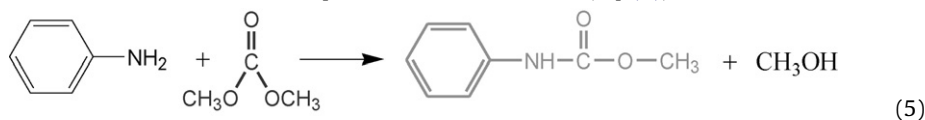
Polycarbonate resins are widely used in the manufacturing of thermoplastic materials, due to suitable mechanical and opti-

In order to fully avoid the use of phosgene, unfortunately also generally involved in the diphenylcarbonate synthesis, the Enichem company developed a liquid phase transesterification–disproportionation process, based on the reaction between DMC and phenol in the presence of titanium alkoxide (Eqs. (3) and (4)) [9]. It can be noted that the use of titanium alkoxide allowed a selectivity to diphenylcarbonate of 99.5% to be achieved, whereas other catalysts based on lead or molybdenum are also efficient.

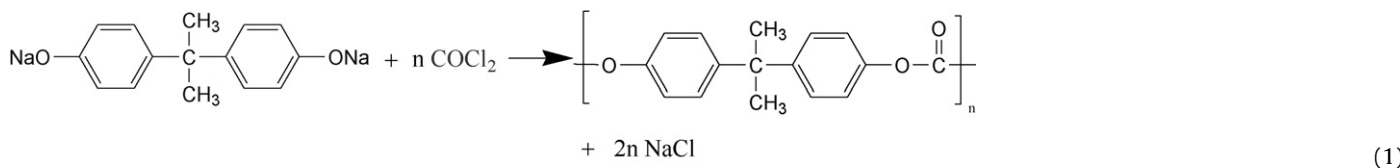


### 2.2.2. Isocyanate synthesis

The reaction of phosgene on a primary or secondary amine led to the formation of the corresponding isocyanate molecule. In this case, like for aromatic polycarbonates, performing the reaction with DMC allowed the use of phosgene to be avoided, by a two-step process passing through the carbamate intermediate [10]. The carbamates are first synthesized by the catalytic reaction between DMC and an amine, as shown by Eq. (5) in the case of the methyl N-phenyl carbamate, using aniline as starting amine reactant. Subsequently, the corresponding isocyanate is obtained by the thermal decomposition of the carbamate (Eq. (6)).



cal properties, with an industrial synthesis based on the reaction between phosgene and a A-biphenol salt (Eq. (1)).



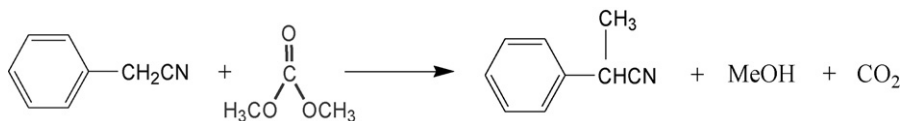
In addition to the use of phosgene, this process suffers from several drawbacks: its design requires the use of large amounts of methylene chloride as solvent that strongly contaminates the washing water. Furthermore, the formation of chloride sodium

Fu and Ono reported that lead oxide is a very efficient catalyst for the synthesis of the carbamate intermediate, with a selectivity

towards methyl N-phenyl carbamate of 99% being obtained at an aniline conversion of 98% after 1 h reaction at 60 °C in a closed vessel [11]. Catalysts such as zinc acetate, mercury salts and aluminium chloride are also reported.

### 2.3. Methylation agent

DMC is also reported to act as an excellent methylation agent for carbon, nitrogen, oxygen and sulfur centres [12], and can thus be an alternative compound to dimethylsulfate or methyl iodide, generally used for this reaction, although displaying a toxic and corrosive nature. In the case of a monomethylation, such as that of phenylacetonitrile in the gas phase (Eq. (7)), using DMC was very efficient, and a phenylacetonitrile conversion of 98% was achieved with a catalytic bed containing potassium carbonate. Yields to monomethyl products of about 70% were obtained at a temperature of 250 °C. Very good performances for the monomethylation of phenols and arylacetonitriles were also reported by Fu and Ono with other basic catalysts such as NaY faujasite zeolites [13].



### 2.4. Solvent

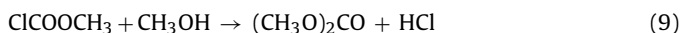
DMC is also considered as a promising alternative to the use of ketones and ester acetates in the field of paints and adhesives, due to a strong solvation power. However, this characteristic of DMC is mainly used only for lithium ion battery applications [14,15]. The electrolytes for such batteries are usually obtained by dissolution of a lithium salt in an organic solvent such as propylene or ethylene carbonates. Such compounds allowed a good dissolution of lithium salts to be achieved, but their strong viscosity remains a very restrictive drawback, by limiting the efficiency of the lithium electrochemical cycle. Adding DMC to the electrolyte significantly increased the conductivity of the electrolyte, due to its great solvation force towards lithium ions and its low viscosity, and the electrolyte resistance is thus consequently diminished.

## 3. Industrial synthesis processes

In 1997, the world production of DMC amounted 1000 bbl/day, corresponding to about 170 t/day. We can estimate that achieving an oxygen content of 1 wt.% in fuel would be required for each *Major* a DMC production of at least 8000 bbl/day (1360 t/day), that largely overshoots the actual world production [3]. This example highlights the need for better DMC production processes. Up to now, only three processes have been transferred to the industrial scale. The old phosgenation process has been totally abandoned with years and the world production remains mainly achieved following two processes developed by the Enichem and the UBE companies, based on the methanol oxycarbonylation and the methyl nitrite carbonylation, respectively.

### 3.1. Phosgenation

Up to the beginning of the 1980s, DMC and more generally dialkylcarbonates, were mainly manufactured by the Bayer company (Germany) and the Société Nationale des Poudres et Explosifs (SNPE, France), through the reaction of methanol on phosgene [16,17]. This reaction was performed following a two-step process, passing through the methylchloroformate intermediate (Eqs. (8) and (9)).



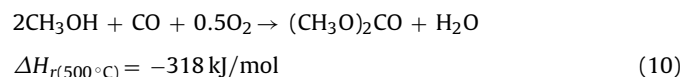
Interesting DMC yields of 82% and 85% were achieved calculated from both methanol and phosgene reactants, respectively [18]. The reaction was usually occurring at 0 °C in an anhydrous solvent such as toluene or dichloromethane, in the presence of pyridine excess, or in excess of an inorganic base (NaOH), both acting as a hydrochloric acid trap, in order to shift the reaction equilibrium towards DMC formation [19]. Without using such bases, the reaction temperature had to be strongly increased up to 50–150 °C.

This process displayed the advantages to reach high yields to DMC. However the use of the unwanted phosgene reactant, together with the need to neutralize large amounts of pyridine and to remove NaCl salts, both requiring strongly restrictive and expensive post-synthesis purification processes, led industry to target and look for less restrictive synthesis processes.

### 3.2. The Enichem process by liquid phase methanol oxycarbonylation

#### 3.2.1. Process

The oxycarbonylation of methanol (as a contraction of oxidative carbonylation) is a catalytic synthesis way, based on the reaction between oxygen, carbon monoxide and liquid methanol, according to Eq. (10)



In 1983, the Enichem company (Italy) industrialized the process in the slurry mode, by exploiting the catalytic properties of copper chloride (I) (CuCl) for the reaction [20]. As shown in Fig. 1, the liquid phase oxycarbonylation of methanol to DMC is performed in a single step inside a slurry reactor, consisting in two columns continuously down-fed with carbon monoxide, oxygen and methanol. The density difference between the up-stream gas inside the column in which the reactants were introduced, and the second column which only contains the liquid phase, causes the transfer of the products between the columns (evidenced by arrows in Fig. 1) [21]. The vaporization of the products formed is assisted by the strong exothermicity of the reaction ( $\Delta H_{r(500^\circ\text{C})} = -318 \text{ kJ/mol}$ ), and thus allows the products to be removed from the reactor, as well as the excess of unreacted reactants. The sole by-products formed are CO<sub>2</sub> and water. CO<sub>2</sub> is recycled as carbonaceous source for the carbon

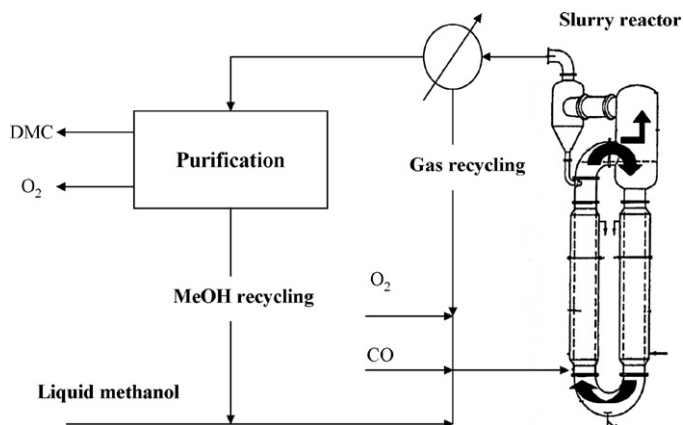


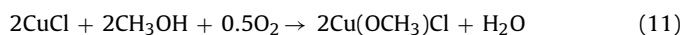
Fig. 1. Schematic view of the Enichem slurry process. Adapted from Rivetti [8,21].

monoxide synthesis, whereas methanol is back-fed to the reactor after separation of the DMC/H<sub>2</sub>O and DMC/MeOH azeotrops. The content of the different condensable products in the reactor outlet stream is around 50–70% for methanol, 30–40% for DMC and 2–5% for water.

The Enichem process is working at a temperature ranging from 120 to 140 °C and under a total pressure between 20 and 40 bar. For instance, at 24 bar and 130 °C, a DMC production of 130 g(l<sup>-1</sup> cat) h<sup>-1</sup> is achieved. During the course of the process, oxygen remains the limiting reactant due to the explosive risk, which could occur if the oxygen content exceeds 4 mol.% in zones where carbon monoxide is the main component [3].

### 3.2.2. Mechanism and catalysts

It is usually admitted that the oxycarbonylation of methanol follows a two-step oxydo-reduction mechanism, through a copper methoxychloride intermediate [22]. The first step consists in the oxidation of copper chloride by oxygen into copper methoxychloride, reaction reported to be of zero order relative to methanol, and of first order relative to oxygen (Eq. (11)):



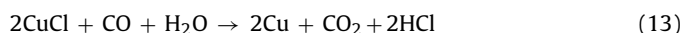
The copper methoxychloride is further reduced by carbon monoxide, allowing thus the copper chloride phase to be regenerated, and a new catalytic cycle to be initiated (Eq. (12)). The reaction is of first order relative to carbon monoxide up to 25 bar, whereas the reaction order decreases down to zero for higher pressures. It can be noted that the reaction rate remains non-depending on the Cu(OCH<sub>3</sub>)Cl amount, because the reaction is performed at the Cu(OCH<sub>3</sub>)Cl solubility equilibrium.



Although this mechanism is well admitted, it seems in total contradiction with that reported in several studies. Delledonne et al. claimed that the reduction of copper methoxychloride by carbon monoxide in an anhydrous media remains difficult, but is favoured by the addition of water and of small amounts of CuCl<sub>2</sub> [2]. The authors observed the formation of diethylcarbonate when Cu(OCH<sub>3</sub>)Cl reacts with carbon monoxide in ethanol. According to that, they advanced that copper methoxychloride cannot be considered as the intermediate by-product such as proposed in Eqs. (11) and (12). Although the mechanism remains uncertain, they put forward a complete catalytic cycle rather than a two-step oxydo-reduction pathway (Fig. 2). In this mechanism, the attack of methanol on the carbon monoxide molecule coordinated

with CuCl<sub>2</sub> formed the carbomethoxy part of DMC. Further, the nucleophilic attack of a second methanol molecule completed the formation of DMC together with that of the copper (I) chloride. The oxidation of the copper (I) chloride by oxygen and methanol resulted in the formation of copper methoxychloride, which acted simultaneously as copper (II) source and as buffer for removing the hydrochloric acid produced during the insertion of methanol inside the carbon monoxide coordinated with CuCl<sub>2</sub>.

The influence of water played a great role on the DMC production. Indeed, the reaction needs to be performed in excess of methanol, because the water produced by the reaction favoured the formation of CuCl<sub>x</sub>OH<sub>y</sub>, nH<sub>2</sub>O-like phases, which are less reactive for DMC production [3]. Water allowed the reduction of copper (I) chloride into metallic copper to be achieved in the presence of carbon monoxide. This caused the deactivation of the catalyst and the loss of chlorine as hydrochloric acid (Eq. (13)) [23].



The existence of an optimum in the DMC production for a water content of 3 wt.%, corresponding to a H<sub>2</sub>O/Cu molar ratio of 0.8, was established by Pacheco and Marshall [3], following previous works by Romano [22,24]. Below such a level, the DMC production strongly increased with increasing the water content. By contrast, the amount of DMC formed decreased drastically above this limit, e.g. being divided by a factor 4 relatively to the optimum for a water concentration of 12 wt.%. As a consequence, the amount of water and its extraction rate from the reactor play a major role in the DMC production and in the design of Enichem reactors.

Fig. 3 shows the evolution of both selectivity and production to DMC as a function of the Cl/Cu ratio, this ratio being depending on the presence (with suitable amounts) of CuCl<sub>2</sub>, Cu(OH)<sub>2</sub> and CuCO<sub>3</sub>. The selectivity pattern displayed a maximum for the Cl/Cu ratio of 1. The behaviour strongly differed for the DMC production, the amount of DMC produced being almost constant for Cl/Cu ratios lower than 1, whereas it decreased for greater ratios. Taking into account both selectivity and production aspects, the optimum in the Cl/Cu ratio is set at 1. Enichem has also patented the use of copper (I) chloride as optimal catalyst for the reaction [25]. The Cl/Cu ratio can be maintained at a constant level during the course of the reaction by adding hydrochloric acid in order to thwart the catalyst deactivation caused by water [26]. However, the presence of HCl can strongly affect the reaction selectivity by leading to the detrimental formation of chloromethane (CH<sub>3</sub>Cl) or of dimethylether (CH<sub>3</sub>OCH<sub>3</sub>).

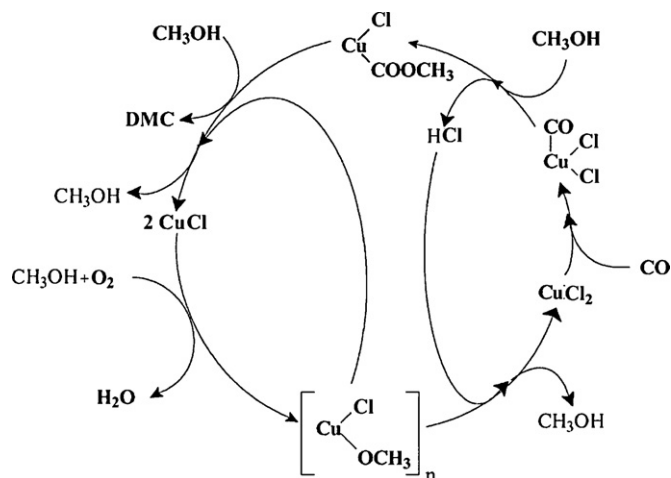


Fig. 2. Catalytic cycle of copper proposed by Delledonne et al. in the DMC synthesis by methanol oxycarbonylation. Reproduced from Delledonne et al. [2].

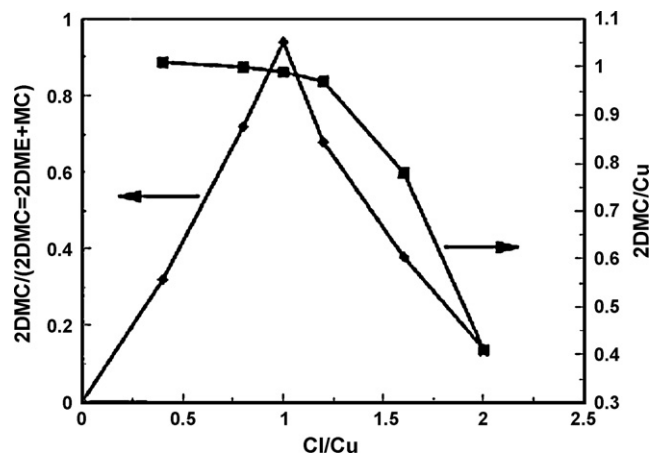


Fig. 3. Evolution of the DMC selectivity (left) and the DMC production (right) as a function of the Cl/Cu molar ratio at 90 °C and 50 bar. MC: chloromethane; DME: dimethylether. Reproduced from Romano et al. [22].

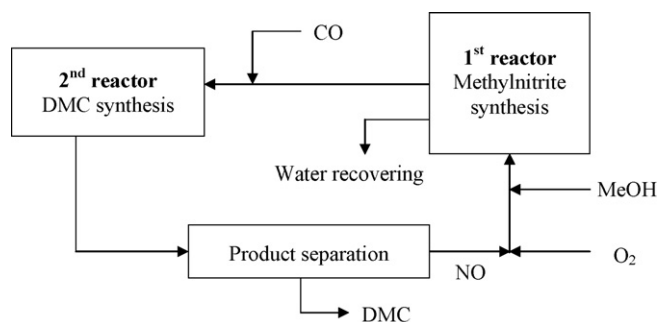
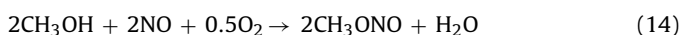


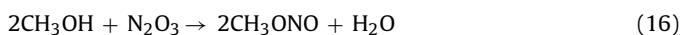
Fig. 4. Schematic view of the UBE process. Adapted from Pacheco and Marshall [3].

### 3.3. The UBE process by methylnitrite carbonylation

Based on its large experience in the dimethyloxalate (DMO) synthesis from nitrogen monoxide, a similar process was developed by the UBE society for synthesizing dimethylcarbonate in the gas phase [27,28]. A production unit was recently erected with a production capacity of 6000 t/year. Fig. 4 shows a simplified schematic view of the UBE process, according to a two-step DMC synthesis. The first step consists in the methylnitrite ( $\text{CH}_3\text{ONO}$ ) synthesis starting from nitrogen monoxide, methanol and oxygen inside Reactor 1 (Eq. (14)).

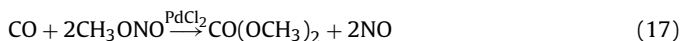


This reaction is generally performed in the liquid phase at  $60^\circ\text{C}$  without any catalyst and with usual contact times ranging from 0.5 to 2 s. It can be decomposed into two consecutive oxidative reactions, such as that of nitrogen monoxide by oxygen into  $\text{N}_2\text{O}_3$  (Eq. (15)) and that of methanol by  $\text{N}_2\text{O}_3$  into the final methylnitrite product (Eq. (16)).



At this stage, it is necessary to remove the water formed from the reaction media in order to perform the DMC synthesis in a fully anhydrous media, so that the activity of the catalyst could be maintained with time on stream.

The second step consists in the vapour phase catalytic reaction between methylnitrite and carbon monoxide (both reactants with contents around 5–30 vol.%) over an activated charcoal supported palladium chloride ( $\text{Pd}^{\text{II}}\text{Cl}_2$ ) catalyst in a fixed-bed reactor. The reaction is performed in the presence of small amounts of chloride compounds diluted in an inert gas. The catalytic reaction between methylnitrite and carbon monoxide at  $100\text{--}120^\circ\text{C}$  and at 0.5–1 MPa formed DMC according to Eq. (17). The DMC production was ranging from 200 and  $600 \text{ kg}[\text{m}^3 \text{ cat}] \text{ h}^{-1}$  for a contact time within the 0.5–5 s range. The operational life-time of the catalyst was around one year, taking into account regeneration processes.



The outlet stream of reactor 2 containing DMC and the dimethyloxalate ( $\text{CH}_3\text{OOC}-\text{COOCH}_3$ ), methylformate and methylal by-products is consecutively separated into non-condensable (methylnitrite, nitrogen monoxide) and condensable products over an adsorption column. The nitrogen monoxide and the remaining methylnitrite are further injected back to reactor 1. This process exhibited the great advantage to avoid the restricting contact between water, methanol and DMC molecules, which generally results in separation problems due to the azeotrop equilibrium formed between the three products.

A large variety of catalysts has been evaluated for the DMC production according to the UBE process, as shown in Table 4.

Table 4

Performances obtained for the DMC synthesis following the UBE process. Reaction conditions: Pd = 1 wt.% and Cu = 1.2 wt.% impregnated on activated charcoal,  $T = 120^\circ\text{C}$ ,  $P = 3 \text{ kg cm}^{-2}$ , gas hourly space velocity =  $4000 \text{ h}^{-1}$ , CO = 20 vol.%, methylnitrite = 10 vol.% and balance  $\text{N}_2 = 70 \text{ vol.}\%$ , DMO = dimethyloxalate. Adapted from Matsuzaki and Nakamura [23].

Catalyst	DMC production (mol/l cat/h)	DMO production (mol/l cat/h)	Hourly DMC yield (g/l cat/h)
Pd (0)	0.31	1.37	28
Pd-Cl	2.03	0.1	183
Cu-Cl	0.04	0	4
Pd-Cu-Cl	6.14	0.25	553
Pd-Cu-Br	5.81	0.33	523
Pd-Cu-AcO	0.58	1.88	52
Pd-Cu- $\text{NO}_3$	0.78	2.18	70

It should be noted that dimethyloxalate remained the sole by-product obtained during the UBE process, with a formation favoured by the presence of metallic palladium. It can be put forward that the copper chloride-based catalysts used in the Enichem process showed very poor performances for the UBE synthesis, although coupling palladium and copper with chlorine as ligand allowed an increase in performances to be obtained. This trend was explained by the great slow down, due to the presence of copper, of the reduction of palladium (II) into metallic palladium, known to be inactive for the DMC synthesis. The ligand nature was also essential, since chloride bimetallic catalysts exhibited a DMC productivity 10 times lower than that obtained with the similar catalysts containing acetate ligands.

A mechanistic reaction pathway has been established taking into account and integrating the necessary presence of chlorine [2] (Fig. 5). The  $\text{Pd}(\text{COOCH}_3)(\text{NO})\text{Cl}_2$  reaction intermediate is produced starting from palladium chloride ( $\text{PdCl}_2$ ) by successive reactions with methylnitrite and carbon monoxide. During a third step, this intermediate reacts with methylnitrite again to form DMC and nitrogen monoxide.

Formation of small amounts of methylchloroformate ( $\text{ClCOOCH}_3$ ) was observed by Manada et al. [29], and attributed to the decomposition of the  $\text{Pd}(\text{COOCH}_3)(\text{NO})\text{Cl}_2$  intermediate into methylchloroformate, nitrogen monoxide and metallic palladium. The resulting metallic palladium aggregates are the cause of the catalyst deactivation. However, the catalyst activity can be restored by adding small amounts of methylchloroformate (Eq. (18)) or HCl (Eq. (19)) during the reaction.

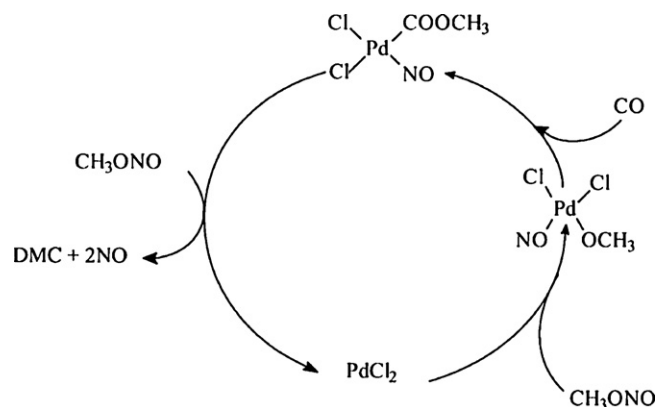
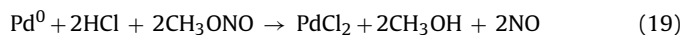
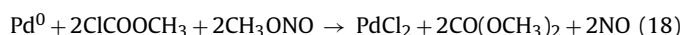


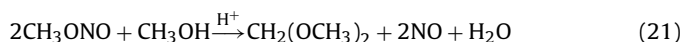
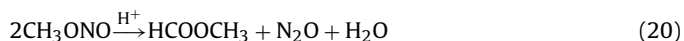
Fig. 5. Catalytic cycle during the DMC synthesis by methylnitrite carbonylation. Reproduced from Delledonne et al. [2].

The previous reaction equations evidenced the double role played by the methyl nitrite. It acts (i) as a reactant for synthesizing DMC, and (ii) as an oxidizing agent for keeping the palladium under the PdCl<sub>2</sub> form and thus for limiting the catalyst deactivation by metallic palladium formation.

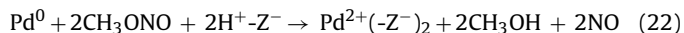
Numerous other material supports for CuCl<sub>2</sub>–PdCl<sub>2</sub> bimetallic catalysts, such as zeolites, silica or γ-alumina, have been tested for the synthesis of DMC [30,31]. Their catalytic efficiencies can be ranked as:

Active carbon > γ-alumina > Y zeolite > silica

Active carbon exhibits the best performances nowadays, although no explanation has been proposed up to now, except that both the specific surface area and the porous nature of the support should influence the performances of the catalyst. The acido-basic characteristics of a support are also reported to play a great role in the UBE synthesis. Indeed, it has been observed that methyl nitrite can be decomposed to methylformate (Eq. (20)) and methylal (Eq. (21)) over acid supports. Also, basic supports favour the formation of dimethyl oxalate.



Using zeolites is very interesting, even if the selectivity to DMC remains lower than that observed on activated carbon (85% vs. >95%). Zeolites exchanged with palladium (II) by ionic exchange show the great advantage to be active for synthesizing DMC starting from methyl nitrite in the absence of ligands such as chlorine [32,33]. In addition, the metallic palladium formed during the reaction can be re-oxidized through the methyl nitrite and the zeolitic proton (formed after the palladium reduction) (Eq. (22)).



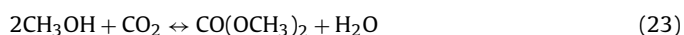
#### 4. Other synthesis processes

Amongst the synthesis ways having been reported up to now for producing dimethyl carbonate, very few of them can be considered for industrial development. Two synthesis processes remain promising and are studied since few years: the direct synthesis of DMC from carbon dioxide and the reactions of transesterification of both urea and ethylene carbonate.

##### 4.1. Direct synthesis from CO<sub>2</sub>

This direct synthesis enters in the strategy of using CO<sub>2</sub> as carbon resource targeting simultaneously the environment protection and an efficient synthesis chemistry, usually labelled also as CO<sub>2</sub> valorisation. The possibility to convert CO<sub>2</sub> into environmentally friendly chemicals could not only limit the greenhouse environmental damages resulting from the continuous release of CO<sub>2</sub> into the atmosphere and thus the consequent stratospheric ozone depletion, but could also lead to consider CO<sub>2</sub> as a carbon source alternative to petroleum, natural gas and coal. In addition, the large scale availability and the low cost of CO<sub>2</sub> are great advantages for using CO<sub>2</sub> as precursor for synthesizing useful chemical products.

The direct synthesis of DMC by reaction between CO<sub>2</sub> and methanol is studied since the 1980s [34] (Eq. (23))



However, both activation and use remain still highly challenging due to the thermodynamical stability and the kinetic inertness of the CO<sub>2</sub> molecule, and to the detrimental decomposition of the catalysts and hydrolysis of the carbonate. As a resulting of

this 'sustainable society' Graal, this research area could contribute by itself to a self-sufficient review. We recommend the recent and detailed review of Sakakura and Kohno on the synthesis of organic carbonates from carbon dioxide [35], from which Table 5 has been extracted for summarising and compiling catalysts, dehydrating agents, reaction conditions and performances reported in the literature. Solving the thermodynamic restrictions mentioned above could be performed by shifting the equilibrium by pressurizing the CO<sub>2</sub> and determining effective dehydrating agents, and by accelerating the reaction by pressurizing CO<sub>2</sub> and developing effective catalysts. Since the yield to DMC remains very low (lower than 2% based on MeOH) when no dehydrating agents are used, two kinds of dehydrating agents are investigated: (i) non-recyclable agents like orthoesters (orthoacetate, Si(OMe)<sub>4</sub>), Mitsunobu's reagent and dicyclohexylcarbodiimide (DCC) and (ii) recyclable agents like acetals or molecular sieves.

Briefly, in the case of orthoester dehydrating agents, with a reaction catalysed by metal alkoxides and onium salts, Bu<sub>2</sub>Sn(OMe)<sub>2</sub> is a more efficient catalyst than Bu<sub>3</sub>SnOMe, and requires CO<sub>2</sub> pressures over the critical pressure. The main drawbacks remain the use of high-cost orthoesters as dehydrating agent, which in addition is difficult to regenerate from alcohols and esters. The same problems limit the use of other dehydrating agents like DCC, Si(OMe)<sub>4</sub> or Mitsunobu's reagent. Therefore, within the research trend to target more recyclable and available organic dehydrating agents, the use of acetals is studied, mainly due to an easy regeneration of acetals from ketones. Typical catalysts are dialkyltin dialkoxides, trialkyltin alkoxides being again poor catalysts as when using the orthoester agent, although the toxic nature of tin-based compounds remains a critical driving force for targeting catalysts based on less toxic metals, like zirconium or titanium. Molecular sieves have been also used as inorganic dehydrating agent with up to now no spectacular results.

It should also be mentioned that adding a small amount of an acidic catalysts (like Sc(OTf)<sub>3</sub> or Ph<sub>2</sub>NH<sub>2</sub>OTf) significantly accelerates the reaction of DMC formation when using acetals as dehydrating agent in the presence of a weakly basic tin-based catalyst (like Bu<sub>2</sub>Sn(OMe)<sub>2</sub> or Bu<sub>2</sub>SnO). Moreover, adding acid catalysts to tin-free oxide catalytic systems was also reported to strongly enhance the performances in terms of yields to DMC, regardless to the use of acetals. A very large variety of catalysts and systems have been investigated up to now, including, e.g. organometallic compounds [36], metal tetra-alkoxides [37], potassium carbonate [38], ZrO<sub>2</sub> [39,40], H<sub>3</sub>PW<sub>12</sub>O<sub>4</sub>–ZrO<sub>2</sub> [41], CeO<sub>2</sub> [42], SiO<sub>2</sub> and VSO supported Cu–(Ni,V,O) and Cu–Ni systems [43,44] as well as bimetallic Cu–Ni active phases supported on carbon nanotubes and thermally expanded graphite [45,46].

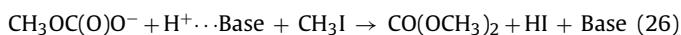
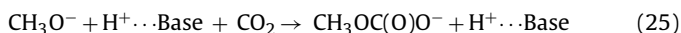
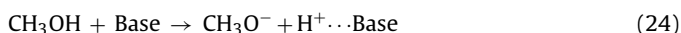
Detailing all the catalytic systems and associated reaction conditions investigated for valorising CO<sub>2</sub> into DMC could therefore, as previously introduced, consist in a separate review, since topic remains highly challenging for the worldwide community, which considers that this synthetic route – if it could be successfully managed first at the laboratory scale and further at the industrial one – is believed to be the most economic one. Let us here only focus on basic catalytic systems and on zirconia. Fang and Fujimoto evidenced the efficiency of the reaction on a basic catalyst in the presence of methyl iodide, acting as a promoter [38]. The reaction was performed in a closed vessel at a temperature of 100 °C and under 50 atm. Amongst the different basic catalysts evaluated for the reaction, the K<sub>2</sub>CO<sub>3</sub> carbonate potassium appeared to be the most interesting candidate, dimethylether (CH<sub>3</sub>OCH<sub>3</sub>) being the sole by-product obtained together with DMC. Decreasing the reaction temperature down to 80 °C allowed a DMC selectivity of 97% to be reached compared to only 67% at 100 °C. The mechanism reaction pathway proposed passes through a methanol deprotonation step (Eq. (24)) followed by the insertion of CO<sub>2</sub> (Eq. (25)), the HI

**Table 5**  
DMC synthesis by direct synthesis from CO<sub>2</sub> (dehydrative condensation of CO<sub>2</sub>), reproduced from Sakakura and Kohno [35].

Catalyst	Dehydrating agent	Conditions	DMC yield or TON
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	None (self cat.)	100 °C, 30 bar	TON 0.10
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	None (self cat.)	100 °C, 50 bar	TON 0.98
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	None (self cat.)	150 °C, 66 bar	TON 0.32
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	DCC	150 °C, 25 bar	TON 1.2
Bu <sub>2</sub> Sn(OBu) <sub>2</sub>	Molecular sieves	150 °C, 25 bar	TON 3.2
Bu <sub>2</sub> Sn(OMe) <sub>2</sub> + Bu <sub>4</sub> PI	Orthoester	180 °C, 300 bar	70% based on orthoester
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	Acetal(2,2-dimethoxypropane) <sup>a</sup>	180 °C, 300 bar	6% based on MeOH, TON 30, (57% based on acetal)
ZrO <sub>2</sub>	None	100 °C, MeOH:CO <sub>2</sub> = 1:3	1% based on MeOH
Ni(OAc) <sub>2</sub>	None (self cat.)	140 °C, 74 bar	2.1% based on MeOH
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	None (self cat.)	145 °C, 50 h, MeOH:CO <sub>2</sub> = 0.8:1	TON 1
ZrO <sub>2</sub> + H <sub>3</sub> PO <sub>4</sub>	None (self cat.)	130 °C, MeOH:CO <sub>2</sub> = 0.99:1	0.62% based on MeOH
ZrO <sub>2</sub> + CeO <sub>2</sub>	None (self cat.)	110 °C, MeOH:CO <sub>2</sub> = 0.2:1	1.6% based on MeOH
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	MS3A <sup>a</sup>	180 °C, 72 h, 300 bar	45% based on MeOH (equilibrium yield)
ZrO <sub>2</sub> + CeO <sub>2</sub>	Acetal <sup>a</sup>	130 °C, 140 h, MeOH:CO <sub>2</sub> = 0.99:1	4.3% based on MeOH (41% based on acetal)
Nb(OR) <sub>5</sub>	None (self cat.)	137 °C, 30 h, 55 bar	2% based on MeOH
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	Si(OMe) <sub>4</sub>	150 °C, 12 h, 200 bar	TON 3.0
H <sub>3</sub> PO <sub>4</sub> + V <sub>2</sub> O <sub>5</sub>	None (self cat.)	140 °C, MeOH:CO <sub>2</sub> = 1:0.5	1.8% based on MeOH
CuCl + MeOC(O)ONa	DCC	65 °C, 24 h, 50 bar	0.8% based on MeOH (83% based on DCC)
Cu–Ni + VSO	None (self cat.)	180 °C, MeOH:CO <sub>2</sub> = 1:0.5	2.6% based on MeOH
Cu <sub>1.5</sub> PMo <sub>12</sub> O <sub>40</sub> (hetero-polyacid)	None (self cat.)	50 °C, 1.2 bar	1.6% based on MeOH
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> + Ce–Ti–O	None (self cat.)	170 °C, 12 h, 50 bar	5% based on MeOH
None	Mitsunobu reagents	100 °C, 8 h, 1 bar	Unsymmetrical carbonate synthesis from CO <sub>2</sub>
Cu–Ni/VSO photoirradiation	None (self cat.)	120 °C, UV irradiation	4% based on MeOH
Bu <sub>2</sub> Sn(OMe) <sub>2</sub> + acid	Acetal <sup>a</sup>	180 °C, 24 h, 300 bar	40% based on MeOH (equilibrium yield)
Ti(OMe) <sub>4</sub> + acid	Acetal <sup>a</sup>	180 °C, 24 h, 300 bar	24% based on MeOH
Ti(OMe) <sub>4</sub> + polyether	Acetal <sup>a</sup>	180 °C, 24, 300 bar	55% based on MeOH (equilibrium yield)
Sn/SBA-15 (immob. cat.)	None (self cat.)	183 °C, 10 h, 200 bar	TON 1.1
Mg	None (self cat.)	180 °C, 12 h, 150 bar	1% based on MeOH

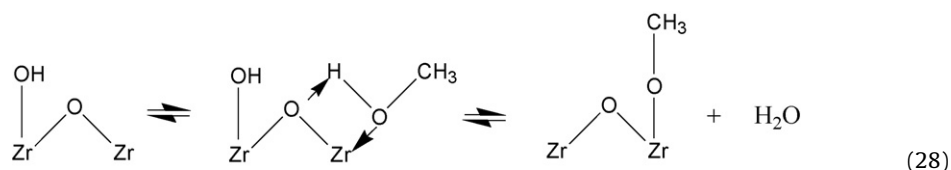
<sup>a</sup> Recyclable – TON: turn over number.

species formed at the end of the catalytic cycle course (Eq. (26)) reacting with methanol to recover the CH<sub>3</sub>I promoter (Eq. (27)).

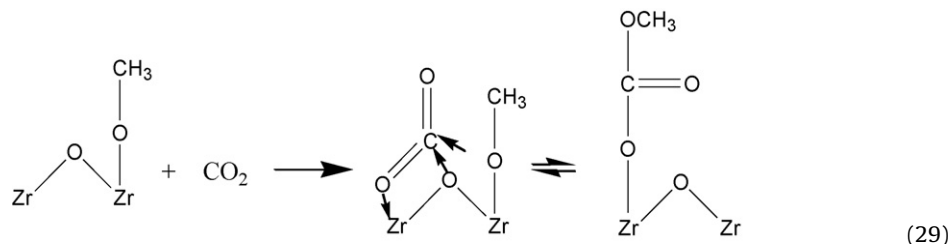


Zirconia was also reported to be an excellent catalyst for the overall reaction (Eq. (23)), with a total selectivity towards DMC (calculated from methanol) being obtained around 140–190 °C and under 50 MPa, without the addition of any promoters [40]. Based

on an *in situ* Infra Red study, Jung and Bell have proposed a reaction mechanism, during which the adsorption of methanol occurred first on the oxygen atoms of Zr<sup>+</sup> cations. The dissociation of the adsorbed methanol molecule led to the formation of a methoxy (CH<sub>3</sub>O<sup>-</sup>) functional group and of a proton, this latter reacting with a hydroxyl surface group of zirconia to give a water molecule (Eq. (28)).



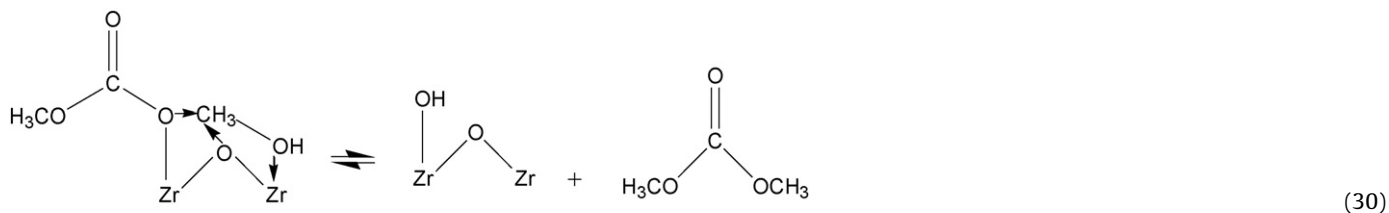
The insertion of CO<sub>2</sub> is achieved at the level of the Zr–O binding, assisted by the interactions between carbon and the oxygen atoms of the Zr–O groups. This led to the formation of a methylcarbonate group intermediate (Eq. (29)).



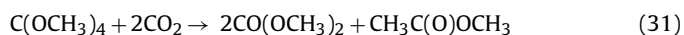
Subsequently, the insertion of a second molecule of methanol on the methylcarbonate functional group follows a similar pathway than that of CO<sub>2</sub>, resulting to the dimethylcarbonate formation (Eq. (30)). It is interesting to note that monoclinic zirconia led to higher performances when compared to tetragonal zirconia, due to a greater force of the Zr<sup>4+</sup>–O<sup>2-</sup> centres, which allowed to improve



the insertion kinetic for methanol and CO<sub>2</sub> [47].



However, the DMC production obtained through this alternative one-step synthesis way remains still limited due to the equilibrium nature of the reaction Eq. (23), being unfortunately in favour of the reactants, to the difficulty in activating CO<sub>2</sub> and to the catalyst deactivation by *in situ* produced water. It should be mentioned that Sakakura proposed the use of dehydrated derivatives of methanol such as trimethylorthoacetate over Bu<sub>2</sub>Sn(OMe)<sub>2</sub> catalysts for (i) overcoming the equilibrium constraint and (ii) avoiding the catalyst deactivation [48] (Eq. (31)).



#### 4.2. Transesterification of ethylene carbonate and urea

This synthesis way is based on a transesterification reaction, consisting in the reaction of methanol either on ethylene carbonate or on urea. Concerning the ethylene carbonate, this led to the catalytic formation of DMC and ethylene glycol (Eq. (32)). It should be mentioned that this transesterification process suffers from the expensive cost of the ethylene carbonate raw reactant, but is however industrialized by companies such as Texaco, Shell and others in China.

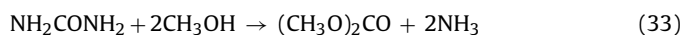


This reaction is usually occurring in a batch mode at temperatures ranging from 100 to 150 °C under an 80 bar pressure. The interesting study of Kniton reported the efficiency of numerous homogeneous catalysts based on zirconium complexes, such as for instance ZrCl<sub>4</sub> or zirconium acetylacetonate, or based on titanium such as titanium acetylacetonate [49]. Selectivities towards methanol around 98% (calculated from the methanol conversion) can be achieved. Bhanage et al. showed that basic oxides and magnesium oxide especially, were excellent catalysts for this reaction, with total selectivity towards DMC [50]. However, the reaction equilibrium, strongly in favour of the reactants, remains a restricting drawback for DMC production, and leads to separation problems for the resulting product/reactant mixture. In order to overcome this major drawback, the equilibrium can be shifted towards the products by removing them by distilling the methanol/DMC azeotrop [51]. The Bayer company patented in 1993 a similar derivative process, in which a catalytic bed-based column was maintained at a temperature greater than the boiling temperature of both methanol and DMC, but lower than that of both ethylene glycol and ethylene carbonate [52]. In this process, ethylene carbonate is introduced at the top of the column whereas methanol is counter-injected in the gas phase at the bottom of the column. The reactor temperature being set as intermediate between the boiling temperatures of the different compounds involved, ethylene glycol is separated at the bottom of the column together with ethylene carbonate, whereas both DMC and methanol are released in the gas phase at the top of the column. During the course of the process, the ethylene glycol formed can be recycled by its reaction with urea to get ethy-

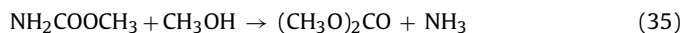
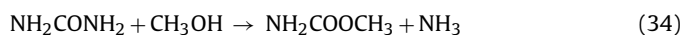
lene carbonate, which can be fed back to the transesterification process.

Although this relatively unexplored reaction compared other ways of synthesizing DMC, like, e.g. directly from CO<sub>2</sub> could be considered as an environmentally friendly alternative for the replacement of harmful and undesirable compounds and could be an interesting path for the production of a great number of chemical intermediates, only few solids have been investigated for being used as catalysts under mild conditions (atmospheric pressure and low temperature). One can mention alkalimetals [53], zeolite [50], smectites [54], hydrotalcites [55], basic salts such as Na<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> [56], quaternary ammonium salts [57], composites [58], ionic liquids [59] or basic Na-containing aluminates derived from heat-treated NaAlCO<sub>3</sub>(OH)<sub>2</sub> dawsonites [60]. The main advantage of the transesterification route remains the co-production of monoethylene glycol exclusively and the absence of diethylene glycol and polyethylene glycols as in the conventional route of ethylene glycol production by hydration of ethylene oxide. The considerable commercial interest of ethylene glycol in the manufacture of polyester fibre and films, associated to the fact that ethylene carbonate can be obtained by reaction of ethylene oxide with CO<sub>2</sub> or via bio-ethylene obtained by dehydration of biomass-fermented alcohol, could open a new 'renewable' route for producing DMC and ethylene glycol.

DMC synthesis by transesterification can be also performed via urea. In contrary to the ethylene carbonate way, the process benefits from the abundant resource and the low cost of the raw reactants. However, like for the ethylene carbonate transesterification, the very high free enthalpy of the reaction ( $\Delta G_{100^\circ\text{C}} = 13.8 \text{ kJ/mol}$ ) transferred the reaction equilibrium in favour of the reactants (Eq. (33)).



Since no water is formed, the reaction mixture (in the overhead product) does not form any methanol–water–DMC ternary azeotrop, and the subsequent separation and purification of DMC is easy. This synthesis is performed in two steps via a methylcarbamate intermediate. The first step consists in the reaction between methanol and urea to get methylcarbamate at a temperature close to 100 °C (Eq. (34)). Further, the methylcarbamate reacts with methanol to form DMC between 180 and 190 °C (Eq. (35)).



Both Eqs. (34)/(35) reactions are catalyzed by an equimolar mixture of a Lewis acid like Al(*i*Bu)<sub>2</sub>H and of a Lewis base like PPh<sub>3</sub>, and are performed consecutively.

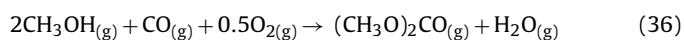
## 5. Vapour phase methanol oxycarbonylation

### 5.1. The vapour phase methanol oxycarbonylation reaction

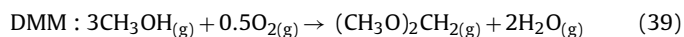
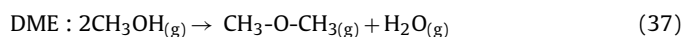
The processes for synthesizing DMC at the industrial scale suffer from several drawbacks. In the Enichem process, the presence of large amounts of copper (I) chloride causes the formation

of hydrochloric acid. This implies that the conception and the design of the reactor should take into account phenomena of plant-corrosion under the simultaneous action of water and of hydrochloric acid. A vapour phase process like the UBE process seems more economical than a batch process. But, although the methylnitrite carbonylation could avoid the formation of large amounts of CO<sub>2</sub> from CO and could lead to a higher productivity to DMC, the UBE process suffers from safety problems, with risks of explosion related to the use of the Pd/NO/O<sub>2</sub> mixture, and also due to the strong toxicity of the methylnitrite reactant. Indeed, concentrations greater than 50 ppm cause nausea and loss of consciousness, so that methylnitrite is considered as more toxic than carbon monoxide [61].

In order to overcome all those drawbacks, the Dow Chemical company studied since the end of the 1980s a vapour phase process of oxycarbonylation of methanol [62,63]. This process, directly derived from the liquid phase Enichem process, is based on the same reaction (Eq. (36)).



The hydrocarboned by-products are dimethylether (DME), methylformate (MF), dimethoxymethane (DMM) and methylacetate (MA), obtained according to Eqs. (37)–(40), respectively.



Methanol is generally injected into a vaporization chamber through a pump, before to be fed into a fixed-bed catalytic reactor with carbon monoxide and oxygen. The reaction is usually performed at temperatures ranging from 100 to 130 °C under middle pressures (10–30 bar). The temperature remains limited to about 130 °C, since non-catalytic oxidation of carbon monoxide cannot be considered as negligible for higher temperatures [64]. This process is in keeping with the general pattern of the transfer of the methanol oxycarbonylation from the liquid to the gas phase, in order to replace the Enichem process.

The catalytic materials located inside the reactor are generally composed of a support (activated charcoal, zeolite, etc.) on which is deposited or grafted an active phase based on copper. Many supports and active phases have been investigated and patented for this reaction. The most valuable ones are reported in the following section.

## 5.2. Active carbon supported chloride-containing catalysts

Activated charcoal remains the most widely used catalyst support in the case of chloride catalysts in the vapour phase methanol oxycarbonylation. Although it leads to the best initial performances, its stability/deactivation behaviour as a function of time on stream is an important and critical parameter to review.

### 5.2.1. With copper (II) chloride

Curnutt and Harley can be considered as pioneers in the development of vapour phase DMC synthesis processes for the Dow Chemical company. They studied catalysts prepared by impregnating on activated charcoal CuCl<sub>2</sub> copper chloride with ethanol, or a copper methoxychloride-based pyridine complex [C<sub>5</sub>H<sub>5</sub>NCu(OCH<sub>3</sub>)Cl] with pyridine [64]. They have investigated many supports, and amongst them, activated charcoal exhibited the most interesting performances (Fig. 6), assigned to:

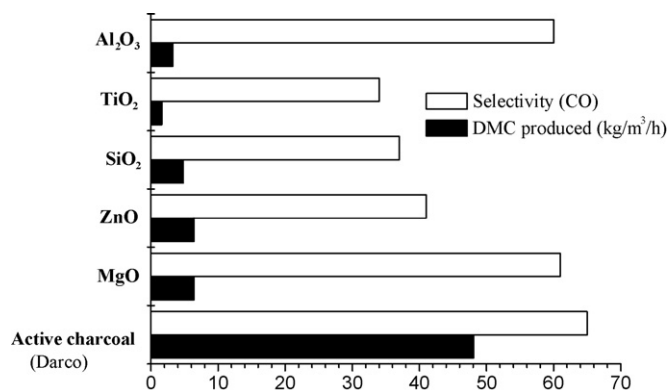
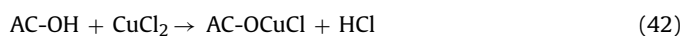


Fig. 6. Influence of the support nature on the DMC synthesis. Conditions:  $T = 100^\circ\text{C}$ ,  $P = 20.68$  bar, impregnation with C<sub>5</sub>H<sub>5</sub>NCu(OCH<sub>3</sub>)Cl (2 wt.% Cu), GHSV = 1800 h<sup>-1</sup>. The selectivity was calculated relatively to the carbon monoxide, taking into account DMC and CO<sub>2</sub> as reaction products. Adapted from Curnutt and Harley [64].

- The unstability of the active phase by the surface oxygen atoms (or the surface hydroxyl groups) in the case of inorganic oxides [3].
- A better stabilisation of the active phase on the activated charcoal due to its electrical conductivity (although weak compared to other forms of carboned supports), which would help the transfer of the electrons involved in the oxydo-reduction mechanism of the DMC synthesis. However, no experimental proof could evidence such a hypothesis.

The X-ray diffraction pattern of activated charcoal impregnated with copper chloride (CuCl<sub>2</sub>) shows the total absence of any diffraction peaks assigned to copper chloride for concentrations lower than 10 wt.%. In the case of higher concentrations, the diffraction peaks observed and corresponding to copper chloride allowed its crystallite size to be derived. This latter increased with the copper content, being calculated at 30 and 37.4 nm, for loadings of 12.3 and 19.7 wt.%, respectively [65]. The absence of any diffraction peaks at low loading was as usually attributed to the good dispersion of copper at the activated charcoal surface. The Cl/Cu molar ratio was generally reported to be lower than the theoretical value of 2 after the catalyst impregnation and the drying procedure, although it can near this value for increasing copper loadings [66,67]. Indeed, Tomigishe et al. observed a Cl/Cu molar ratio of 1.2 and 1.8 for 2.5 and 7.5 wt.% of Cu, respectively [64]. A possible explanation of this chloride loss after the catalyst drying resulted from the EXAFS study conducted by Kriventsov et al. and was related to the interaction between the copper (II) chloride and the oxygenated surface groups of activated charcoal (AC-COOH and AC-OH), which caused a loss in hydrochloric acid molecules (Eqs. (41) and (42)) [68].

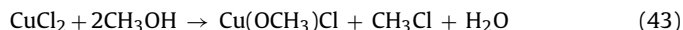


For a copper content lower than 5 wt.%, copper would be mainly linked to the oxygenated surface groups of activated charcoal (corresponding to a CuCl stoichiometry), while a multilayer coverage would be formed for higher copper contents, built on a CuCl<sub>2</sub> stoichiometry. Yamamoto et al. evidenced by EXAFS and XANES the presence of copper (I) coordinated by three atoms of chlorine at the surface of catalysts containing 1.2 wt.% of Cu, and they considered both carboxylic and hydroxyls groups at the carbon surface as reducing centres, promoting the Cu<sup>II</sup>Cl<sub>2</sub> to Cu<sup>I</sup>Cl reduction and leading to the observed loss of chlorine [67].

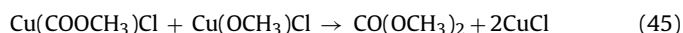
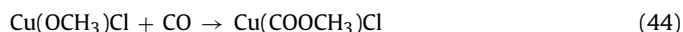
From a catalytic activity point of view, the optimum in copper content is ranging from 5 to 10 wt.% depending on the authors. Han et al. obtained a methanol conversion of 21% at a DMC selectivity of

80%, calculated from the methanol conversion, whatever the copper loading in the case of copper contents greater than 5 wt.% [69]. By contrast, at lower amounts, Punnoose et al. reported that the activity was increasing with the copper content [70]. They observed that the carbon monoxide desorption curve becomes non-sensitive to the copper content after this 5 wt.% level, due to a constant number of available active sites. They considered that the copper deposit turned from a monolayer to a multilayer coverage system, thus explaining the stagnation of the activity at high copper loadings.

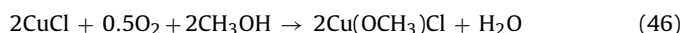
**5.2.1.1. Reaction mechanism.** Curnutt et al. have proposed a three-step mechanism, in which the methanol reacted first with the copper chloride catalyst to form a copper methoxychloride [64] following the reaction Eq. (43).



The methoxychloride intermediate further incorporated a carbon monoxide molecule (Eq. (44)) before finally reacting with a second methoxychloride molecule to obtain the DMC (Eq. (45)). The insertion of the carbon monoxide molecule follows a similar reaction pathway than that reported in the Enichem process.

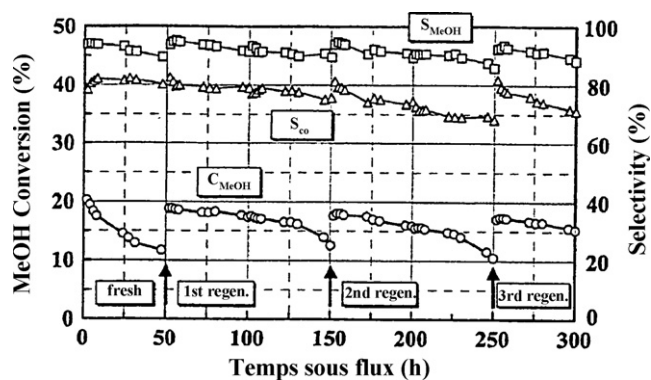


The initial copper (II) state is recovered by oxidizing the copper (I) chloride by oxygen into copper (II) methoxychloride together with water formation (Eq. (46)).



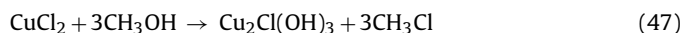
Kinetic studies reported that the reaction of DMC formation was of zero order relative to oxygen [64,71], whereas the reaction orders relative to carbon monoxide and methanol were ranging from 0.8 to 1, and 1 to 1.4, respectively. The oxidation of copper (I) by oxygen seems to be more rapid than the formation of copper methoxychloride and than the insertion of carbon monoxide. The optimal formation of DMC thus occurred with a reactant feed containing methanol and carbon monoxide in large excess relatively to oxygen. This was confirmed by investigating the influence of the reactant ratios within the reaction feed, with an optimal yield to DMC being achieved for CO/MeOH and O<sub>2</sub>/MeOH molar ratios greater than 4 and set at 0.1, respectively [72]

**5.2.1.2. Catalyst deactivation and regeneration.** The literature reports that activated charcoal supported CuCl<sub>2</sub> catalysts suffer from the deactivation of the catalyst as a function of time on stream, although it remains scarcely studied and quantified. Itoh et al. showed that the DMC yield decreased from 50% after 50 h of reaction on stream [72]. Numerous authors, including Curnutt and Harley [64] especially, claimed that the catalyst deactivation resulted from a particle sintering and an aggregation process, forming 0.2–1 μm size particles, and from a massive chlorine loss. Indeed, the Cl/Cu weight ratio for a catalyst containing 10.3 wt.% of CuCl<sub>2</sub>, decreased from the initial theoretical ratio of 1.12 down to 0.24 after 90 h of time on stream. This decrease in the Cl/Cu weight ratio was accompanied by the formation of two new crystallized phases, i.e. the Cu<sub>2</sub>(OH)<sub>3</sub>Cl paracatamite and Cu(OH)Cl. Within the structure of both phases, the copper atoms were only linked to oxygen atoms [73], so that substitution of chlorine atoms by hydroxyl groups occurred. Some authors revealed the presence of trace amounts of copper (II) oxide. This chlorine loss could result either from the direct reaction of methanol with copper (II) chloride to form paracatamite and chloromethane (Eq. (47)), or from the hydrolysis of chlorine into hydrochloric acid with formation of



**Fig. 7.** Influence of time on stream and of regenerative treatments on the catalytic performances. Conditions: 5 mol.% HCl/N<sub>2</sub>, T = 140 °C, P = 9.4 bar, CH<sub>3</sub>OH/CO/O<sub>2</sub> reactant ratios = 1/3/0.06. Reproduced from Itoh et al. [72].

chloromethane by further reacting with methanol. The formation of chloromethane was thus related to the catalyst deactivation.



A regenerative treatment of the catalyst with HCl diluted in nitrogen or with other chloride molecules (CH<sub>3</sub>Cl, etc.) was reported to be efficient for recovering almost the initial methanol conversion, and also for improving the catalyst stability, even after several successive regenerations (Fig. 7). According to Itoh et al., the loss of chlorine during the impregnation step would be overcome during successive regenerations, so that the catalyst stability could be even improved compared to that shown by freshly prepared catalysts [72].

According to Curnutt and Harley, another way for limiting the deactivation of the catalyst consisted in promoting the CuCl<sub>2</sub>/AC catalyst with MgCl<sub>2</sub> or KCl (about 5 wt.%) [64]. The reaction between the promoter and the copper chloride favoured the formation of chlorocuprates such as KCuCl<sub>3</sub> or MgCuCl<sub>4</sub>·6H<sub>2</sub>O. Such chlorocuprates displayed a higher Cl/Cu ratio than copper chloride, and would be less sensitive to chlorine extraction, and thus would limit the catalyst deactivation.

**5.2.1.3. Counter-ions and active phase nature effects.** As reported before, the presence of chlorine seems essential for designing a catalyst with a high activity. This essential role of chlorine seems in agreement with the study of the role of counter-ions performed by Dunn et al., using different copper salts impregnated on activated charcoal for the synthesis of diethylcarbonate (DEC) in autoclave conditions (Fig. 8) [74]. Replacing copper (II) chloride by copper acetate or nitrate led to form 4 times less of DEC, and around only half when copper (I) chloride was used.

According to Curnutt and Harley, the presence of the γ-Cu<sub>2</sub>Cl(OH)<sub>3</sub> paracatamite phase on the catalyst could be responsible for the deactivation of the catalyst [64], although the literature remained very controversial on this point, since numerous authors [69,75,76] have reported that a second impregnation of CuCl<sub>2</sub>/AC by a hydroxide solution promoted the formation of Cu<sub>2</sub>Cl(OH)<sub>3</sub> after drying and resulted in catalysts with higher performances than in the case of the CuCl<sub>2</sub>/AC reference, as reported by Ma et al. (Table 6 [76]).

The nature of the counter-cation (K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, etc.) used during the impregnation of the hydroxide did not significantly influence the conversion and the selectivity to DMC. By contrast, the Cu/OH molar ratio appeared to be a crucial parameter to control, being directly related to the DMC production. Several studies showed that a value of 1 led to the best catalytic performances [76,77]. In parallel, Han et al. have reported that the crystallographic structure of the Cu<sub>2</sub>Cl(OH)<sub>3</sub> was depending on the Cu/OH molar ratio,

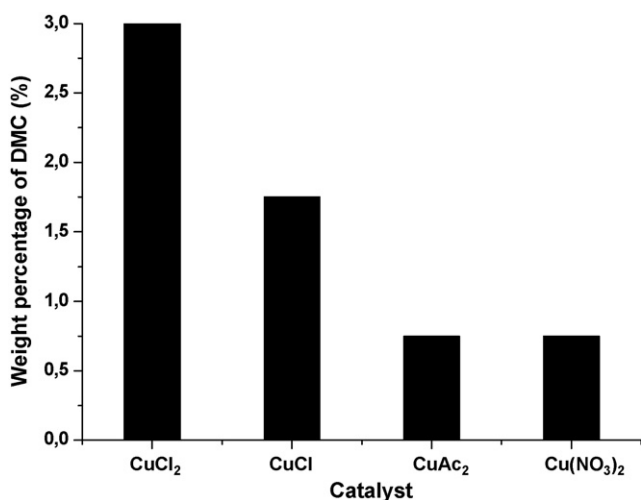


Fig. 8. Influence of the counter-cation on the catalytic activity in the DEC synthesis. Conditions in close vessel: 0.5 g of catalyst, 3.6 g of ethanol,  $T=170^{\circ}\text{C}$ ,  $\text{CO}/\text{O}_2/\text{N}_2 = 1/1.5/2.5$ . Adapted from Dunn et al. [74].

$\text{Cu}_2\text{Cl}(\text{OH})_3$  existing with two different crystallographic structures: the  $\alpha$ - $\text{Cu}_2\text{Cl}(\text{OH})_3$  atacamite and the  $\gamma$ - $\text{Cu}_2\text{Cl}(\text{OH})_3$  paratacamite, with orthorhombic and rhombohedral structures, respectively [78]. X-ray diffraction and Spectroscopy X studies evidenced that atacamite was the main phase for a Cu/OH ratio of 2, whereas this was reversed for a Cu/OH ratio of 1. This was in agreement with the work of Punnoose et al., who explained that the amount of DEC formed (similar synthesis than for DMC, by substituting methanol by ethanol) was directly linked to the intensity of the X-ray diffraction peak assigned to the paratacamite phase, with a maximum for a Cu/OH ratio of 1 [70]. Two non-exclusive hypotheses have been proposed for explaining this behaviour. The greater activity shown by the paratacamite relatively to the atacamite and the copper (II) chloride would result from: (i) a more important adsorption of carbon monoxide on the paratacamite surface, according to the temperature-programmed desorption study performed by Han et al. [78], (ii) a more easy reduction of the copper (II) into copper (I) within the paratacamite structure [79]. Cu/OH ratios greater than 1 resulted in a lower amount of paratacamite phase together with larger amounts of salt crystals (NaCl, KCl, etc.) blocking the access of the reactants to the active centers.

From an industrial point of view, the impact on the catalytic activity of the feed contamination by-products or impurities has to be taken into account [72]. Nitrogen, hydrogen and carbon dioxide have no effect on the catalytic process. By contrast, adding water to the feed has a detrimental effect, by decreasing the methanol conversion, a water content of 5.5 wt.% in the methanol feed resulting in a drastic drop of the methanol conversion from a half. According to Itoh et al., this could be attributed to the hydrolysis of DMC (Eq. (48) [72]).

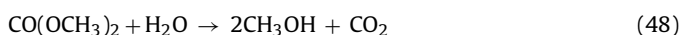


Table 6

Effect of adding hydroxyde to  $\text{CuCl}_2/\text{CA}$  catalysts. Conditions:  $T=110^{\circ}\text{C}$ ,  $P=7$  bar,  $\text{GHSV}=1346\text{ h}^{-1}$ , 3 wt.% Cu,  $\text{Cu}/\text{OH}=1$ . Adapted from Ma et al. [76].

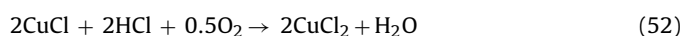
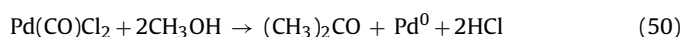
Catalysts	Hydroxydes	MeOH conversion (%)	DMC selectivity (%)
$\text{CuCl}_2/\text{CA}$	–	2.4	43.4
$\text{CuCl}_2/\text{hydroxyde}/\text{CA}$	NaOH	5.6	79.5
$\text{CuCl}_2/\text{hydroxyde}/\text{CA}$	KOH	5.4	78.4
$\text{CuCl}_2/\text{hydroxyde}/\text{CA}$	LiOH	5.6	78.1

The catalytic performances are thus strongly limited by the amount of water in the reactor and its removal outside of the catalytic bed is an important process parameter, like for the Enichem process.

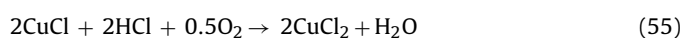
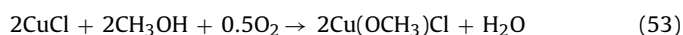
### 5.2.2. With $\text{CuCl}_2$ - $\text{PdCl}_2$ bimetallic chlorides

$\text{CuCl}_2$ - $\text{PdCl}_2$  bimetallic catalysts, usually labelled as Wacker-type catalysts, are often used for the low temperature oxidation of carbon monoxide [80,81]. The use for the DMC synthesis by vapour phase oxycarbonylation of methanol, of such catalysts supported on high surface area activated charcoal ( $\text{CuCl}_2$ - $\text{PdCl}_2/\text{AC}$ ), obtained by co-impregnation with copper (II) and palladium (II) chlorides, led generally to an increase in the DMC production when compared to that obtained on the corresponding  $\text{CuCl}_2/\text{AC}$  and  $\text{PdCl}_2/\text{AC}$  single systems. Dunn et al. have observed that the weight percentage of DMC was increasing from 3% to 9.5% on  $\text{CuCl}_2$  and  $\text{CuCl}_2$ - $\text{PdCl}_2$ , respectively [74]. However, this remained controversial in the literature, other authors observing the reverse phenomena. The selectivity to DMC calculated from carbon monoxide also decreased, due to the larger amounts of carbon dioxide formed [69].

5.2.2.1. Reaction mechanisms. The reaction mechanisms proposed to explain the high reactivity of Wacker-type catalysts and the synergy effect between palladium and copper, are similar to those established for the oxidation of carbon monoxide (Eqs. (49)–(52)). The insertion of carbon monoxide occurs on the palladium chloride to form the  $\text{Pd}(\text{CO})\text{Cl}_2$  intermediate [82] that can further react with methanol to form DMC and metallic palladium, subsequently re-oxidized by the copper (II) chloride with the formation of copper (I) chloride. This later reacts with oxygen to form copper (II) chloride. The temperature-programmed reduction study performed by Cao et al. also evidenced the greater reducibility of copper (II) into copper (I) in the bimetallic system compared to that in the  $\text{CuCl}_2/\text{AC}$  single system [83]. By X-ray diffraction analysis, the absence of any diffraction peaks assigned to copper or palladium species confirmed the good dispersion of the phases at the support surface



Jiang et al. explained the great reactivity of bimetallic catalysts by the occurrence of two distinct mechanisms [84]. DMC would be produced following the mechanism reported above, and by a mechanism close to that proposed by Curnutt et al., and only involving copper (Eqs. (53)–(55)). The copper (I) chloride phase, which initiates this second mechanism, would result from the oxidation of palladium by the copper (II) chloride (Eq. (51)).



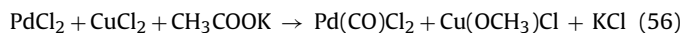
XPS studies performed by Jiang et al. over different  $\text{CuCl}_2/\text{AC}$ ,  $\text{PdCl}_2/\text{AC}$  and  $\text{CuCl}_2$ - $\text{PdCl}_2/\text{AC}$  systems evidenced the presence of the Cu(I)/Cu(II) and Pd(0)/Pd(II) couples in the  $\text{CuCl}_2/\text{AC}$  and  $\text{PdCl}_2/\text{AC}$  catalysts, respectively. The reduction process leading to the reduction of Pd(II) to metallic palladium were similar to that already reported in the case of the copper reduction on activated charcoal. By contrast, all the previously cited species were observed in the  $\text{CuCl}_2$ - $\text{PdCl}_2/\text{AC}$  mixed system, except metallic palladium. This was explained by a preferential reduction of copper (II) on the activated charcoal sites, relatively to that of palladium (II), due

to a strongly weaker redox potential for the  $\text{Cu}^{2+}/\text{Cu}^+$  (0.15 V vs.  $\text{Ag}^+/\text{AgCl}$ ) when compared to that of the  $\text{Pd}^{2+}/\text{Pd}^0$  couple (0.82 V) [84].

**5.2.2.2. Promoter effects.** Numerous promoters such as sodium hydroxide, potassium chloride or different acetates have been used with bimetallic systems [64,85–87]. Impregnation with a soda solution allowed also the paratacamite phase to be obtained, like in the case of  $\text{CuCl}_2/\text{AC}$  catalysts, whereas a subsequent addition of potassium chloride increased also the catalytic performances. Indeed, the yield into diethylcarbonate (DEC) increased from 17 wt.% to more than 31 wt.% for a  $\text{NaOH-CuCl}_2\text{-PdCl}_2/\text{AC}$  catalyst with addition of potassium chloride. Adding KCl initiates the transformation of a part of the  $\text{Cu}_2(\text{OH})_3\text{Cl}$  paratacamite into the  $\text{Cu}(\text{OH})\text{Cl}$  phase, which, due to its suitable structure, allowed a very rapid electron transfer between copper and palladium (with a short length Cu–Cl binding) [88]. Consequently, both oxidation and reduction processes, for palladium and copper, respectively, were thus more rapid. In the case of a single promoter (*i.e.* in the absence of sodium hydroxide), potassium acetate appeared to be a better promoter than potassium chloride, according to Jiang et al. [87], the DMC production reaching more than  $200 \text{ g l}^{-1} \text{ h}^{-1}$  with potassium acetate, when it amounted only  $70 \text{ g l}^{-1} \text{ h}^{-1}$  with potassium chloride. However, differences within the acetate family were evidenced, the influence of acetates on the DMC synthesis being ranked following the basicity order:



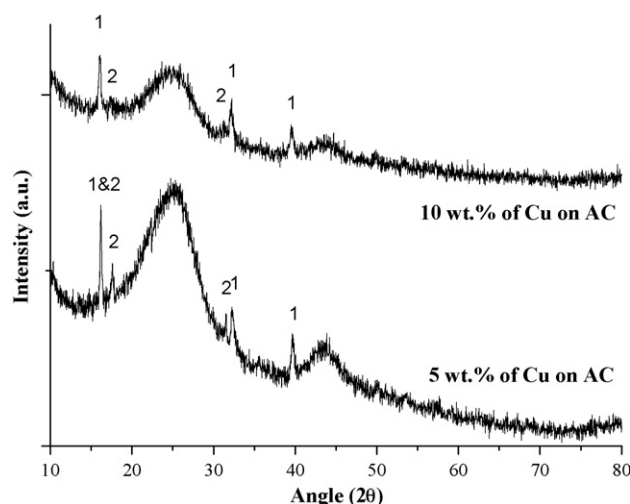
The beneficial effect of acetates was attributed to the combination of several phenomena. The loss of chloride during the impregnation step could be limited by the reaction between acetate and both copper and palladium chlorides (Eq. (56)), allowing simultaneously the formation of intermediate phases, reactive for the DMC synthesis.



However, even if the loss of chloride during the impregnation step remained limited, the catalyst deactivation on stream due to the loss of chloride was not inhibited during the reaction.

In parallel, according to Cao et al., the potassium acetate would promote the formation of paratacamite by neutralizing acidic groups located at the activated charcoal surface, reported to inhibit the paratacamite formation. Indeed, activated charcoal supports treated with water, potassium hydroxide or by reduction with hydrogen contained numerous basic surface groups, contrarily to supports treated with nitric acid or oxidized under air, for which the main surface groups are acidic carboxylic functional groups. The X-ray diffraction study performed by Yang et al. evidenced the relationship between the chemical groups at the support surface and the active phase formed during the impregnation process [75]. Indeed, supports with many basic surface groups favoured the formation of paratacamite, while supports with many acidic surface groups were paratacamite-free. This was in agreement with the catalytic testing, which highlighted that the activity of the catalysts was increasing with increasing the amounts of paratacamite.

**5.2.2.3. Solvent effects.** The nature of the solvent used for impregnating the support seemed also to play an important role. The catalysts impregnated with an ethanolic solution displayed a greater activity than those prepared with a pure aqueous solution. The order in the different impregnation steps, including the promoter ( $\text{CH}_3\text{COOK}$ , etc.), the copper and the palladium precursors, also influenced the dispersion of the active phase, and consequently the catalytic activity of the systems [83]. However, such studies remained very scarcely reported.

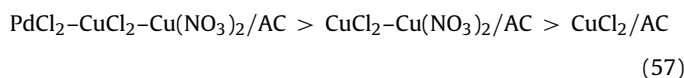


**Fig. 9.** X-ray diffraction pattern of activated charcoal supported  $\text{Cu}_2(\text{OH})_3\text{Cl}$  catalysts for 5 and 10 wt.% of copper. Beside the broad peaks attributed to carbon, peaks indexed by (1) and (2) were assigned to the paratacamite and atacamite  $\text{Cu}_2(\text{OH})_3\text{Cl}$  phases, respectively.

### 5.2.3. With $\text{Cu}_2(\text{OH})_3\text{Cl}$ and bimetallic $\text{Cu}_2(\text{OH})_3\text{Cl-PdCl}_2$ chloride catalysts

The  $\text{Cu}_2(\text{OH})_3\text{Cl}$  phase was usually obtained by adding  $\text{Cu}(\text{NO}_3)_2$  copper nitrate to the  $\text{CuCl}_2$  copper chloride onto the active carbon support material as described by Park et al. [81]. After the co-impregnation of both copper salts and a first drying at room temperature, the  $\text{Cu}_2(\text{OH})_3\text{Cl}$  phase was obtained after helium treatment at  $150^\circ\text{C}$  for 2 h. Fig. 9 shows the X-ray diffraction patterns of activated charcoal supported  $\text{Cu}_2(\text{OH})_3\text{Cl}$  catalysts for 5 and 10 wt.% of copper as examples. Beside the broad peaks attributed to high surface area activated carbon, they evidenced the main  $\text{Cu}_2(\text{OH})_3\text{Cl}$  crystallographic phases usually observed, *i.e.* the paratacamite and the atacamite phases.

Over activated carbon-based catalysts, adding palladium chloride, mainly using the palladium tetraamine chloride as precursor, allowed an increase in the DMC production to be obtained when compared to the palladium chloride-free catalyst, with a significant increase both in the methanol conversion and in the selectivity to DMC calculated from methanol. Indeed, a gain in STY of almost a half was usually observed. The results reported led to establish a ranking as follows in terms of DMC production (Eq. (57)):



However, adding palladium caused a drastic decrease in the selectivity to DMC calculated from CO, as a result of the strong increase in the oxygen conversion with massive production of  $\text{CO}_2$ , due to the good performances shown by such catalytic systems for the low temperature CO oxidation, for which Park et al. have proposed a reaction mechanism reported in Fig. 10 [81]. This model proposed that the palladium chloride could interact with the  $\text{Cu}_2(\text{OH})_3\text{Cl}$  phase through a chlorine atom and a hydroxyl group. The attack of palladium chloride by carbon monoxide led to substituting chlorine atoms by a carbon monoxide molecule and a hydroxyl group together with the production of hydrochloric acid. It has been shown that water favoured the oxidation of carbon monoxide [89], and in the present case, water could directly result from the synthesis of DMC or from secondary reactions. Then  $\text{CO}_2$  produced from carbonyl and hydroxyl ligands induced the reduction of palladium (II) into metallic palladium, subsequently easily reoxidized through the copper (II) of the  $\text{Cu}_2(\text{OH})_3\text{Cl}$  phase ( $\text{Cu}^{2+} + \text{Pd}^0 \rightarrow \text{Cu}^+ + \text{Pd}^{2+}$  oxydo-reduction reactions). The last step

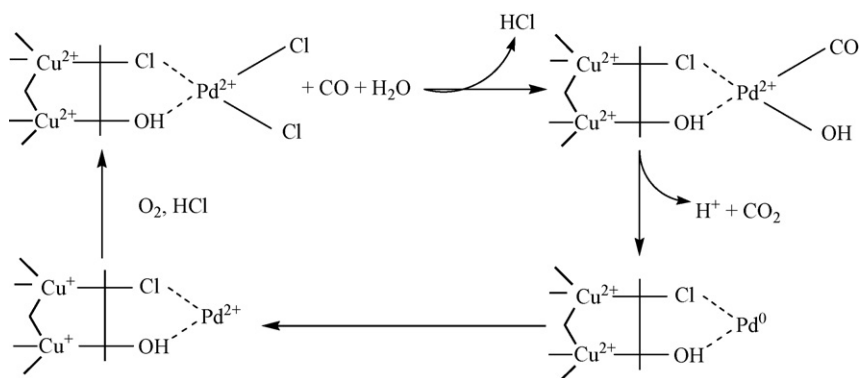


Fig. 10. Mechanism for the carbon monoxide oxidation proposed by Park et al. over  $\text{Cu}_2(\text{OH})_3\text{Cl}-\text{PdCl}_2/\text{AC}$  catalysts. Adapted from Park et al. [81].

consisted in the reoxydation of copper (I) of the  $\text{Cu}_2(\text{OH})_3\text{Cl}$  structure by oxygen. Unfortunately, oxygen from the reaction feed was used mainly for producing  $\text{CO}_2$ , and strongly limited the formation of DMC, even if a moderate increase in the DMC production was observed. This remained the main drawback of bimetallic Cu–Pd catalytic systems applied to the vapour phase oxycarbonylation of methanol, *i.e.* the competition between the direct oxidation of carbon monoxide and the synthesis of DMC. This competition was strongly marked by the fact that both reactions occurred through a similar mechanism, thus limiting the number of active sites available for synthesizing DMC. Fig. 11 described the mechanism proposed by Zhang et al. for the synthesis of diethylcarbonate, here adapted to the synthesis of DMC [88], and similar to that proposed by Park et al. for the direct oxidation of carbon monoxide, by substituting water by methanol. In addition, one should not forget that the large increase in the exothermic carbon monoxide oxidation reaction resulted in a strong increase in the temperature of the catalyst bed, especially when high surface activated charcoal with low thermoconductivity was used, leading to a possible temperature boom till no oxygen remained available in the feed at the catalyst level.

### 5.3. Chlorine-free zeolite-based catalysts

Zeolitic materials are aluminosilicates made by  $\text{AlO}_2^-$  and  $\text{SiO}_2$  tetrahedra, following a  $\text{M}_x/\text{n}^{n+} (\text{Al}_x\text{Si}_y\text{O}_2(x+y))^{x-} \cdot z\text{H}_2\text{O}$  overall formula, in which M represents an exchangeable cation (alkaline, alkaline-earth, transition metal, proton, etc.). This cationic exchange characteristic directly results in the use of zeolite in catalysis. Copper-exchanged zeolites have been used as catalysts notably for the selective reduction of nitrogen oxide [90,91], gazole desulfuration [92] or as adsorbent [93]. However, very few works

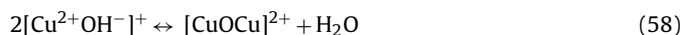
have been reported on the use of copper-exchanged zeolites for synthesizing DMC.

In 1996, King was the first author to show that the acidic form of the Y zeolite (labelled as H-Y) exchanged with copper was an active catalyst for synthesizing DMC by the vapour phase methanol oxycarbonylation at  $130^\circ\text{C}$  [94]. Three main copper exchange procedures are reported: liquid phase, HAR high-temperature anhydrous reaction and vapour phase exchanges.

#### 5.3.1. Liquid phase copper exchange

This exchange mode remains the main process described by the literature, and is usually performed with copper (II) nitrates as copper source dissolved into water, followed by a drying around  $100^\circ\text{C}$ . Without any post-treatments, no activity for synthesizing DMC around  $130^\circ\text{C}$  could be observed. This inactivity is attributed by King to the stability of the  $\text{Cu}^{2+}$  ion, that cannot be reduced into the  $\text{Cu}^+$  cupric ions. This inhibited the  $\text{Cu}^+/\text{Cu}^{2+}$  catalytic cycle, that could not lead to DMC through the  $(\text{CH}_3\text{O}-\text{Cu})^+\text{Y}^-$  intermediate [95].

The inactivity of liquid phase copper-exchanged zeolites for the DMC synthesis rendered necessary the use of post-synthesis activation treatments. ESR studies by Takahashi et al. [93] and Gédéon et al. [96] showed that a part of  $\text{Cu}^{\text{II}}$  could be self-reduced in  $\text{Cu}^{\text{I}}$  at  $450^\circ\text{C}$  under helium, with 50% and 75% of reduction efficiency for 1 and 12 h treatments, respectively. The self-reduction mechanism generally admitted is as follows [97,98]:



Numerous authors used carbon monoxide as reduction agent [99,100]. Larsen et al. showed that a CO/He (4 mol.%) treatment at

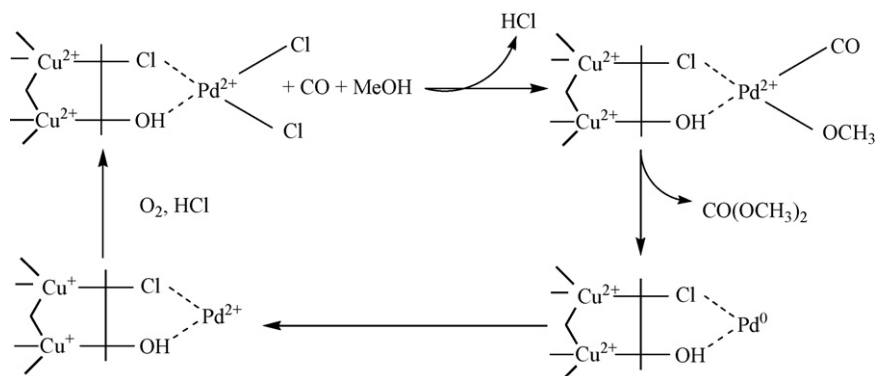


Fig. 11. Mechanism adapted for the DMC formation, derived from that proposed by Zhang et al. over  $\text{Cu}_2(\text{OH})_3\text{Cl}-\text{PdCl}_2/\text{AC}$  catalysts for the diethylcarbonate (DEC) production [88].

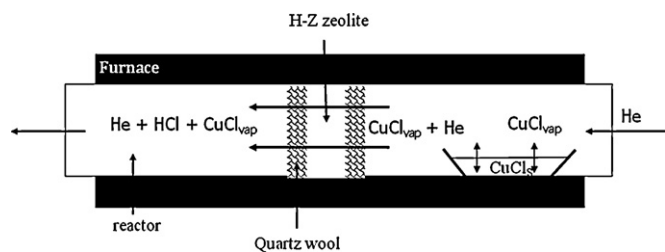


Fig. 12. Schematic view of the vapour phase copper exchange process.

45 °C over a Cu-ZSM5 zeolite obtained by liquid phase exchange with nitrates led to 75% reduction efficiency into Cu<sup>I</sup> [101].

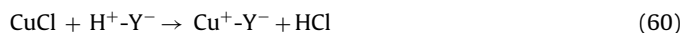
However, the performances for the DMC synthesis remained limited by the relatively low amount of copper exchanged following the liquid phase procedure. The dissolution of copper salts in water caused the formation of hydrolyzed species such as Cu(OH)<sup>+</sup>, Cu(OH)<sub>3</sub><sup>-</sup> or Cu(OH)<sub>4</sub><sup>2-</sup>, hindering the suitable exchange with the zeolite because of steric limitations [102]. Performing the exchange at acidic pH (lower than pH 6 especially) led to limit the presence of the hydrolyzed species, whereas increasing the solution exchange temperature allowed an increase in the amount of exchanged copper. However, this temperature increase can result in the detrimental destroy of the zeolitic structure. The search for more suitable exchange procedures is therefore of high interest.

### 5.3.2. Solid exchange by high-temperature anhydrous reaction (HAR)

This exchange method consists in a high-temperature treatment (650 °C) under an inert atmosphere of a mechanical mixture of the zeolite and of a solid copper source (Cu<sub>2</sub>O, Cu<sup>I</sup>Cl, Cu<sup>II</sup>O, and Cu<sup>II</sup>Cl<sub>2</sub>), so that the migration of copper atoms and their exchange with the proton of the zeolitic Y<sup>-</sup> framework can occur. The oxidation degree of copper within the zeolite is directly related to the copper solid source used for the exchange. According to the works of King, only the Cu(I)-Y zeolites prepared by HAR are active for producing DMC [95,103], eliminating the use of Cu<sup>II</sup>O and Cu<sup>II</sup>Cl<sub>2</sub> for directly preparing a Cu(I)-based catalyst. It remains also impossible to get a pure Cu(II)-Y zeolite by the HAR treatment, due to the self-reduction of Cu(II) into Cu(I) at high temperature [93]. HAR treatments can suffer from separation problems, due to the use of a mechanical mixture, and therefore performing the exchange in the vapour phase is an efficient alternative.

### 5.3.3. Vapour phase exchange

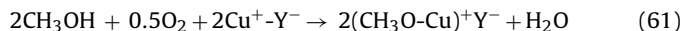
This exchange mode is the direct transposition of the HAR exchange method to the vapour phase, and is based on the reaction at 650 °C through the whole Y zeolite material with gaseous CuCl fed with helium, previously obtained by vaporizing solid CuCl as Cu(I) solid source at the same temperature (Eq. (60) and Fig. 12).



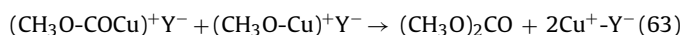
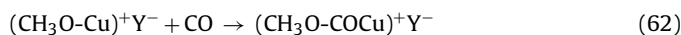
This method displays several advantages: (i) it allows to avoid a direct contact between the host zeolite and the copper solid source; (ii) the gaseous copper source after vaporization is directly passing through the whole zeolite material; (iii) the low exchange temperature (650 °C) compared to the vaporization temperature of CuCl (1490 °C) led to a progressive and thus controllable vaporization inside the reactor; (iv) the low fusion temperature of CuCl compared to that of Cu-based impurities (such as Cu<sub>2</sub>O or CuO) led to create of pure CuCl<sub>g</sub>/He flow.

The main interest of using copper-exchanged zeolites for the DMC synthesis results from the absence of chlorine when compared to catalysts based on activated charcoal. Indeed, the chlorine element is playing an essential role in catalysts based on activated

charcoal, while Cu(I)-Y catalysts prepared using Cu<sub>2</sub>O as copper source, also exhibited an activity for synthesizing DMC. It has been advanced that the Y zeolite framework, negatively charged, played the same role than the chlorine element in the CuCl<sub>2</sub>/AC catalysts [94,103]. A mechanistic study by *in situ* Infra Red revealed the presence of the (CH<sub>3</sub>-O-Cu)<sup>+</sup> methoxide group, already evidenced in the mechanism proposed by Romano et al. for the Enichem process. Those observations were recently confirmed by Anderson and Root [104]. During the first step, methanol adsorbed on the zeolite could react with oxygen to form the methoxide intermediate (Eq. (61)).



The second step could consist in the insertion of the carbon monoxide at the methoxide level to form the carbomethoxyde (Eq. (62)), which react further with the methoxide to form DMC (Eq. (63)). The insertion of carbon monoxide would be the rate limiting step for the DMC formation. Kinetic studies performed by Anderson and Root showed that competition occurred between the direct adsorption of carbon monoxide on the Cu<sup>+</sup>-Y<sup>-</sup> sites of the zeolite (which would not take part to the DMC formation) and the reaction of carbomethoxyde by insertion of carbon monoxide [104]. This competition led to a decrease in the DMC production, especially for high pressure carbon monoxide.

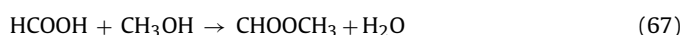
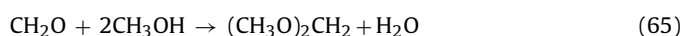


The presence of water is a limiting factor in the DMC synthesis. Indeed, at too high vapour pressure, water molecules adsorb on the catalytic sites of the zeolite, leading to diminish the methoxide coverage rate at the catalyst surface, thus decreasing the methanol adsorption.

Very few different zeolites have been studied for this reaction, the most stable and efficient catalysts having been prepared by HAR exchange with copper (I) chloride and faujasite structure zeolites. Increasing activity was observed with decreasing the Si/Al atomic ratio (for Y and X-like zeolites), this behaviour being explained by a more important number of Cu(I)-Y sites. Beside to the absence of any chloride atoms within the catalyst, the great advantage of such systems is that no deactivation was observed for 80 h on stream. King claimed that such a catalytic performance could be similar to that shown by CuCl<sub>2</sub>/AC (5 wt.% of Cu), the carbon dioxide formation resulting from the direct oxidation of carbon monoxide. Selectivities, calculated from methanol, achieved 80% towards DMC and 20% towards (CH<sub>3</sub>O)<sub>2</sub>CH<sub>2</sub> dimethoxymethane, respectively, whereas trace amounts of CHOOCH<sub>3</sub> methylformate were only detected. The formation of formaldehyde on the Cu(I) sites of the zeolites could consist in the first step of the formation of secondary by-products (Eq. (64))



According to Anderson and Root [105], formaldehyde reacts with methanol on the (H<sup>+</sup>-Y<sup>-</sup>) acidic sites of the zeolite to get dimethoxymethane (Eq. (65)). Its hypothesis for the methylformate synthesis is based on reaction between the formic acid, resulting from formaldehyde following Eq. (66), and methanol on copper (0) sites (Eq. (67)).



The works of Anderson evidenced that it would be necessary to perform the reaction at a temperature higher than 130 °C to improve the reaction yield. However, it has recently been shown that the decomposition of dimethylcarbonate occurred above

130 °C, leading to a decrease in the reaction yield [106], methanol and formaldehyde being formed during the DMC decomposition. In addition, reacting DMC with oxygen to form carbon dioxide and water is also thermodynamically favoured under such conditions. The decomposition reaction is directly proportional to the DMC partial pressure and takes place on the residual Brønsted sites resulting from the incomplete exchange of the zeolite. Unfortunately neutralizing the remaining unexchanged sites by adsorbing pyridine or trimethylphosphine did not allowed the DMC production to be improved. By contrast, a complementary exchange of those sites by the lithium (I) ion diminishes the DMC decomposition rate of about 30%, without being detrimental to the activity level obtained on  $\text{Cu}^+ \text{-Y}^-$ .

In the case of vapour phase exchanged zeolite catalysts, a close relationship was established between the amount of DMC produced and the copper exchange rate, so that zeolites with large amounts of cationic sites such as the Y zeolite especially, displayed a higher DMC production than other zeolites such as ZSM-5 or mor-denites. In addition to that, the presence of residual acid sites as a result from a partial exchange of the cationic sites of the zeolite, was responsible for the formation of secondary by-products such as DME and DMM.

The great advantage of vapour phase CuCl exchanged Y zeolite catalysts was that stable performances could be obtained on-stream, with no deactivation being observed as it was usually observed for all carbon supported copper-based catalysts. The absence of any chlorine atoms in the catalyst was also very positive, since this resulted in the absence of any on-stream corrosion phenomena inside the micropilot, which remained very detrimental in terms of chemical processes over carbon-based catalysts.

One should note that supporting a copper-exchanged Y zeolite on medium surface area ( $10 \text{ m}^2/\text{g}$ ) silicon carbide material was recently performed [107]. First, this aimed at the improvement of the catalyst shaping. Further, the thermoconductive nature of the medium surface area  $\beta$  silicon carbide support helped in the control of the temperature of the catalyst bed, so that the usual increase in temperature observed on bulk zeolites could be avoided. This resulted in a decrease in the formation of unwanted by-products such as DME and  $\text{CO}_2$ , even at high temperature. Relatively to the real amount of zeolite anchored on the silicon carbide support, very interesting space time yields to DMC were obtained – higher than for the similar unsupported copper-exchanged Y zeolite. However, since only low amounts of zeolite crystals could be deposited and strongly anchored onto the medium surface area silicon carbide support (about 8 wt.%), the DMC production and therefore the overall space time yields to DMC per gram of catalyst (active phase + support material) remained largely in favour of the bulk zeolite material. If the amount of Y zeolite deposited at the surface of the silicon carbide material could be strongly enhanced in the future, then it could be possible to obtain a significative increase in terms of DMC production and of space time yields to DMC per gram of overall catalyst, up to getting a higher productivity than that shown by the bulk zeolites.

## 6. Conclusion

The synthesis of DMC was reviewed with focus on the catalysts, the mechanisms as well as the industrial processes and the reactions involved. The negligible ecotoxicity of DMC with low

bioaccumulation and low persistence, led to consider DMC as an environmentally benign chemical, that could enter into the policy of developing clean and eco-friendly processes, so that an increasing interest was devoted to the chemical use and the production ways of DMC. Replacement of dimethylsulfate and methylhalides in methylation reactions, and of the harmful phosgene in polycarbonate and isocyanate syntheses by acting as carbonylation agent, could be considered as the main targeted uses. For producing DMC by other ways than through the old phosgenation process, abandoned with years, we highlighted the interest of developing the vapour phase oxycarbonylation of methanol by carbon monoxide as an alternative to liquid phase methanol oxycarbonylation and methylnitrite carbonylation processes. The catalytic systems could be classified into two main classes, depending on their chloride contents. The chloride-containing catalytic materials consisted of high surface area active carbon supported copper-based catalysts, with either  $\text{CuCl}_2$  or  $\text{Cu}_2(\text{OH})_3\text{Cl}$  supported copper-based phases. Palladium as  $\text{PdCl}_2$  could be added and coupled to both catalytic systems for very significantly increasing the DMC production level, although competition in terms of active sites then occurred between the oxidation of carbon monoxide and the formation of DMC, since very similar reaction mechanisms are involved on such mixed catalytic systems. It should be stressed that the chloride-containing catalytic systems displayed a very high activity at the beginning of their life-time, but irreversibly suffered from a rapid *on-stream* loss of chloride, that resulted in corrosion problems inside pilots, and in a drastic *on-stream* drop of performances. Temporary alternatives could be found, by modifying the supported copper-based active phase, but the different stratagems that could be used remained only time-delaying and more or less pronounced deactivation of the catalysts could not be avoided.

The chloride-free catalysts remained a promising alternative, which consisted in copper-exchanged zeolitic systems. The more interesting system was that obtained with Y zeolite and through the vapour phase exchange with solid  $\text{Cu}^{(I)}\text{Cl}$  precursor. The main advantage of such systems remained the very good *on-stream* stability of the catalytic performances, and the absence of any chlorine loss and of any corrosion problem inside the pilots, although the DMC production was unfortunately still low when compared to chlorine-containing activated charcoal-based catalysts.

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## Appendix A. Calculation appendix

The methanol conversion was usually defined taking into account the different products formed (DMC, DME, DMM, MF, MA, and  $\text{CH}_3\text{Cl}$ ) and the respective stoichiometric coefficients of their formation reactions (Section 5.1):

$$C_{\text{CH}_3\text{OH}} = \frac{x_{\text{CH}_3\text{Cl}} + 2 \times x_{\text{DME}} + 2 \times x_{\text{MF}} + 3 \times x_{\text{DMM}} + 3 \times x_{\text{MA}} + 2 \times x_{\text{DMC}}}{(x_{\text{CH}_3\text{Cl}} + 2 \times x_{\text{DME}} + 2 \times x_{\text{MF}} + 3 \times x_{\text{DMM}} + 3 \times x_{\text{MA}} + 2 \times x_{\text{DMC}}) + x_{\text{CH}_3\text{OH}}}$$

The selectivity  $S_j$ , of the reaction to the  $j$  product could thus be calculated from the CO or from the methanol reactants, giving  $S_{j/\text{CO}}$  and  $S_{j/\text{MeOH}}$ , respectively:

$$S_{j/\text{CO}} = \frac{x_j}{x_{\text{CO}_2} + x_{\text{DMC}}} \times 100\% \quad \text{with } j = \text{CO}_2 \text{ or DMC}$$

$$S_{j/\text{MeOH}} = \frac{\nu_j \times x_j}{x_{\text{CH}_3\text{Cl}} + 2 \times x_{\text{DME}} + 2 \times x_{\text{MF}} + 3 \times x_{\text{DMM}} + 3 \times x_{\text{MA}} + 2 \times x_{\text{DMC}}} \times 100\%$$



with  $j = \text{CH}_3\text{Cl}$ , DME, MA, MF, DMM, and DMC.  $v_j$  the number of methanol molecules necessary for forming the  $j$  product.

The reaction yield to DMC was thus usually expressed as:

$$R_{\text{DMC}} = C_{\text{MeOH}} \times S_{\text{DMC/MeOH}} \times 100\%$$

The hourly weight yield to dimethylcarbonate (STY – space time yield) was usually industrially defined as the weight amount of DMC produced by 1 l of catalyst per hour, which corresponds to the catalyst productivity towards DMC

$$\text{STY}(\text{g/h/l}) = \frac{WF_{\text{MeOH}} \times MW_{\text{DMC}} \times Y_{\text{DMC}}}{MW_{\text{MeOH}} \times 2 \times V_{\text{cat}}}$$

with  $WF_{\text{CH}_3\text{OH}}$ : weight flow of methanol (g/h);  $MW_{\text{DMC}}$  and  $MW_{\text{MeOH}}$ : molar weights of DMC and methanol, respectively;  $Y_{\text{DMC}}$ : reaction yield to DMC;  $V_{\text{cat}}$ : volume of the catalyst (l).

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