

Dimethyl carbonate for environmentally benign reactions

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Abstract

Dimethyl carbonate (DMC) is a unique molecule having a versatile reactivity. The transesterification of DMC with phenol gives methyl phenyl carbonate, which is converted into diphenyl carbonate (DPC) by disproportionation. $\text{MoO}_3/\text{SiO}_2$ is an active catalyst for both reactions. DPC is an essential monomer in the non-phosgene route for polycarbonates. The methoxycarbonylation of aniline gives methyl *N*-phenyl carbamate in the presence of a lead compound. This reaction offers a non-phosgene route to isocyanates. As a methylating agent, DMC can be a substitute for methyl halides and dimethyl sulfate, toxic and corrosive chemicals. Phenylacetonitrile, aniline and phenol are selectively methylated with DMC over zeolites in the vapor-phase. The reaction of DMC with silica offers a simple and clean method for synthesizing $\text{Si}(\text{OCH}_3)_4$.

Keywords: Dimethyl carbonate; Environmentally benign reactions

1. Introduction

1.1. Environmentally benign reactions

The chemical industry has been one of the major economic activities in this century and will also be so in the coming century. However, the industry has been blamed for producing environmentally hazardous substances, which cause acid rain, a reduction of stratospheric ozone levels and so on. Therefore, many efforts have been focused on eliminating or decreasing environmentally hazardous substances. In fact, the industry as a whole reduced its emissions to air, land, and water by 41% between 1987 and 1991, while the overall production increased by more than 10% [1]. Thus, NO_x and SO_x are one of the major targets in this respect.

Besides these end-of-pipe problems, there are many processes which may require environmental considerations. Much energy is consumed for disposing of by-products or converting them into environmentally non-hazardous substances. Production of such extra energy itself is the cause of the further production of carbon dioxide, NO_x , SO_x and so on.

The processes requiring the handling of dangerous chemicals such as hydrogen fluoride, phosgene, hydrogen cyanide require special efforts for securing the safety. In the processes using sulfuric acid, sodium hydroxide or aluminum chloride, waste water must be neutralized, and a large amount of inorganic products such as ammonium sulfate and sodium chloride are formed as by-products. For example, in the synthesis of 1 ton of ϵ -caprolactam for Nylon 6, about 5.4 tons of ammonium sulfate is formed in the production of hydroxylamine and Beckmann rearrangement of cyclohexanone oxime.

Processes using a large amount of solvents are also those consuming a lot of energy for purification and recycling of the solvents. Multi-step synthesis processes must be short-cut. Non-selective reactions have to be replaced by highly selective reaction systems. In this respect, shape-selective zeolites or highly enantioselective catalysts are extremely important.

These processes which have a burden on the environment must be improved or essentially replaced by more environmentally friendly or compatible processes. The selection of the best synthesis and processes must be determined not only by the rate of the production of the desired products, but also by 'environmental benignness'. The importance of environmentally benign processes has been repeatedly stressed in recent years [2–4].

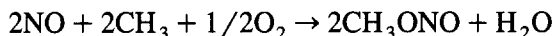
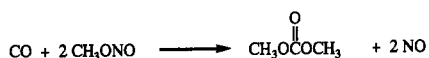
1.2. Chemical characteristics of DMC

Dimethyl carbonate (DMC) has been prepared by the reaction of methanol and phosgene in the presence of a concentrated sodium hydroxide solution.

In 1983, a non-phosgene process for preparing DMC from methanol, carbon monoxide, and oxygen in liquid phase was developed [5].



This reaction may also be carried out in vapor-phase using supported Cu catalysts [5]. Recently, Ube Industries developed a process using butyl nitrite together with Pd catalysts.



DMC has two carbon centers at which a nucleophile may react: the carbonyl and the methyl group. When a nucleophile attacks at carbonyl carbon of DMC, the cleavage of acyl-oxygen bond results in a methoxycarbonyl product. Therefore, DMC can replace phosgene as a safe source for carbonic acid derivatives. Phosgene is a notorious material and difficult to dispose of, although it has a high reactivity. By-products include hydrochloric acid and other chlorides, which present serious corrosion and disposal problems as well. Thus, DMC is used as an intermediate for making polycarbonate resins. DMC may also be used as a replacement of phosgene in making isocyanates.

When a nucleophile attacks at the methyl carbon of DMC, the methylation product is produced by the alkyl-oxygen bond cleavage. Thus, DMC is a useful methylating agent. As a methylating agent, DMC is a safe substitute for dimethyl sulfate.

Dimethyl sulfate, used in pharmaceutical manufacture, also yields by-products that are hard to dispose of. A comparison of the toxicological values of dimethyl sulfate with those for DMC shows that for dimethyl sulfate LD50 (rat) for oral dose is 440 mg kg⁻¹, while for subcutaneous injection it is 30 mg kg⁻¹. The corresponding values for DMC are: oral, 12 800 mg kg⁻¹; subcutaneous injection, 8500 mg kg⁻¹ [6].

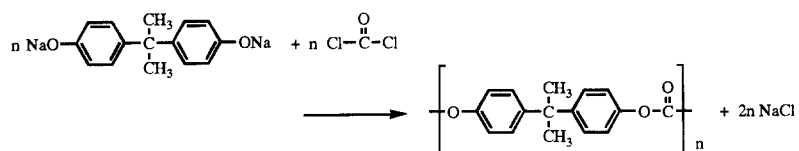
Thus, DMC is a non-toxic intermediate that is being touted as a possible replacement for toxic intermediates, phosgene and dimethyl sulfate. DMC can also be used as an octane enhancer.

In this review, several representative examples where DMC serves as an environmentally benign intermediate will be described.

2. Dimethyl carbonate as a substitute for phosgene

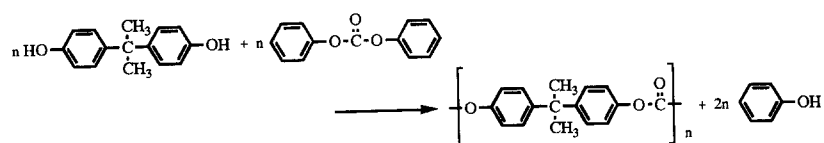
2.1. New route for polycarbonate

Polycarbonate resins are important engineering thermoplastics with good mechanical and optical properties as well as electrical and heat resistance useful for many engineering applications. Polycarbonates have been commercially produced by the interfacial polycondensation between a bisphenol-A salt in an aqueous caustic solution and phosgene in an organic solution as follows:



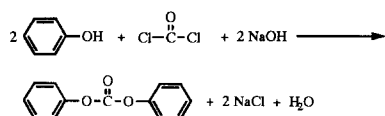
The main disadvantages of this phosgene process are: (1) Use of the high toxicity and corrosiveness of phosgene. (2) Use of copious amounts of methylene chloride solvent (10 times the weight of the product). This solvent is water soluble, so it contaminates the wash water. (3) The complex clean-up to remove ionic materials.

The most practical non-phosgene process for manufacturing polycarbonates is the transesterification of diphenyl carbonate (DPC) with bisphenol-A.



In this method, no toxic solvents are used and the by-product phenol may be recycled [7].

Diphenyl carbonate is usually prepared by the reaction of phosgene in the presence of bases.



The obvious disadvantages of the method are again the use of phosgene as a raw material and the formation of stoichiometric amounts of NaCl.

In order to avoid the use of phosgene, non-phosgene routes to diphenyl carbonate have been sought. One of the methods is the oxidative carbonylation of phenol with carbon monoxide and oxygen in the presence of a Pd catalyst.

The other and more practical method is the use of DMC as a substitute for phosgene in the

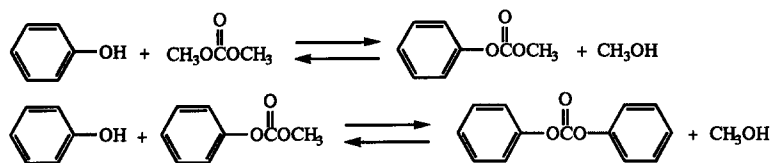
Table 1

The catalytic activities of metal oxides supported on silica for transesterification of DMC with phenol (yields based on phenol) ^a

Catalyst	Yield (%) ^b		
	MPC	DPC	AN
MoO ₃	17.1	0.2	0.0
Ga ₂ O ₃	12.7	0.3	3.5
V ₂ O ₅	12.0	0.3	0.1
PbO	11.6	2.2	0.9
Pr ₆ O ₁₁	11.5	0.2	0.2
ZrO ₂	11.3	1.3	1.3
TiO ₂	10.8	0.4	0.4
CdO	8.4	0.1	0.7
Sm ₂ O ₃	8.3	0.2	0.2
Fe ₂ O ₃	7.8	0.1	0.9

^a Reaction conditions: 433 K, 4 h, DMC/PhOH = 5.0, PhOH = 23.8 mmol. Oxides were supported on silica in 10 wt%.^b MPC, methyl phenyl carbonate; DPC, diphenyl carbonate; AN, anisole.

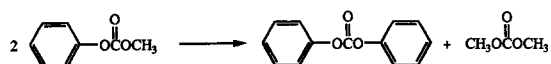
traditional synthesis of diphenyl carbonate. The transesterification is usually carried out in two steps because of the low equilibrium constants for the products.



As the catalysts for the esterification reactions, homogeneous catalysts such as Sn or Ti compounds have been proposed [8]. Only few reports on solid catalysts are known. Onoda et al. showed that SiO₂-TiO₂ can be used as a solid catalyst [9].

Fu and Ono attempted to search for active solid catalysts for the transesterification of DMC with phenol [10]. Table 1 shows the catalytic activities of metal oxide supported on silica. The reaction was carried out in an autoclave. Molybdenum oxide supported on silica (MoO₃/SiO₂) showed the highest activity for the transesterification. The main product was methyl phenyl carbonate and the yield of diphenyl carbonate was very small because of the thermodynamic limitation. The formation of MoO₃ phase was confirmed by XRD.

Another method to obtain diphenyl carbonate is the disproportionation of methyl phenyl carbonate rather than the two-step transesterification.



As shown in Table 2, MoO₃/SiO₂ showed a high activity and selectivity also for this disproportionation [10]. Formation of anisole as a by-product was not observed at 433 K. MoO₂/SiO₂, which was prepared by reduction of MoO₃/SiO₂ with hydrogen, showed a low catalytic activity. The leaching of Mo species to the solution phase was not observed.

Table 2

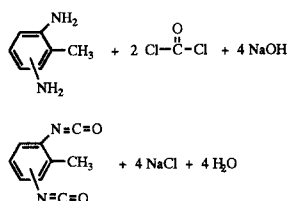
The catalytic activities of supported MoO₃ for the disproportionation of methyl phenyl carbonate (MPC)^a

Catalyst	Temperature (K)	Time (h)	Yield (%) ^b	
			DPC	AN
MoO ₃ /SiO ₂ (20 wt%)	433	4	44.2	0.0
	433	7	48.2	0.0
	473	4	48.6	0.1
	473	7	51.0	0.2
MoO ₃ /SiO ₂	433	4	13.8	0.0
MoO ₃ /Al ₂ O ₃	433	4	12.3	10.5

^a Catalyst = 0.2 g, MPC = 38.7 mmol.^b DPC, diphenyl carbonate; AN, anisole.

2.2. New route to isocyanates

One of the most important uses of phosgene is the production of isocyanate for polyurethane. For example, toluene diisocyanate is produced by the reaction of diaminotoluene with phosgene.



The obvious drawbacks of this method are the high toxicity of phosgene and the need to handle of a large amount of hydrogen chloride. Therefore, several methods for synthesizing isocyanates (or carbamate ester as a precursor) without using phosgene have been sought. The carbonylation of nitro- or amino-compounds offers routes to the corresponding carbamates.

The carbamates can also be synthesized from amines and alkyl carbonates such as DMC.



This synthesis method has been paid little attention to since DMC has been synthesized from phosgene and methanol. Because a process for preparing DMC from CO, O₂, and methanol was

Table 3

The activities and selectivities for the methoxycarbonylation of aniline with dimethyl carbonate^a

Catalyst	Amount (mmol as Pb)	Aniline conversion (%)	Carbamate yield (%)	Selectivity (%)
PbO (yellow)	2.68	96.8	95.0	98.1
PbO (red)	2.68	97.9	96.7	98.8
Pb ₃ O ₄	2.78	96.0	94.7	98.6
PbCO ₃	2.70	96.0	94.2	98.1
2PbCO ₃ · Pb(OH) ₂	2.51	96.9	95.0	98.0
Pb(OAc) ₂	2.68	95.0	95.1	98.4
Pb(OAc) ₂ · Pb(OH) ₂	2.65	94.7	93.1	98.3

^a Reaction temperature = 433 K, reaction time: 1 h, aniline = 2 ml, DMC/aniline = 5.4.

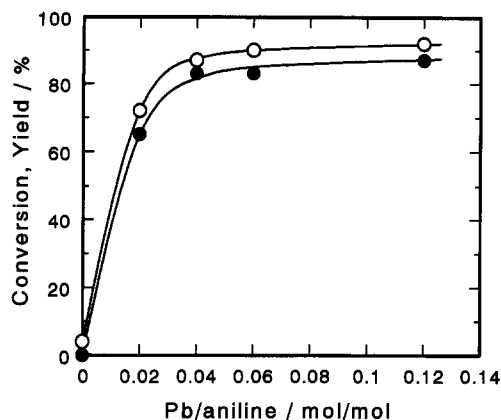


Fig. 1. The effect of the amount of $\text{Pb}(\text{OAc})_2 \cdot \text{Pb}(\text{OH})_2$ on the conversion (○) and the carbamate yield (●) at 433 K. Aniline = 4 ml (44.1 mmol), DMC/aniline = 2, reaction time: 1 h.

industrialized, the use of alkyl carbonate is becoming an attractive route for the carbamates synthesis. In this method of the synthesis, the reaction can be carried out under much milder conditions compared with the carbonylations of nitro- or amino-compounds.

Lissel et al. reported that aniline can be methoxycarbonylated with DMC in the presence of K_2CO_3 and 18-crown 6-ether [11]. Several patents have been disclosed for the synthesis of carbamates from dialkyl carbonates and amines including aniline [12]. The various catalysts including Ti, Sn, and Zn compounds are known to be active for carbamate synthesis.

Fu and Ono reported that various lead compounds are highly effective catalysts for the synthesis of methyl *N*-phenyl carbamate from aniline and DMC [13]. The reactions were carried out in an autoclave at 433 K for 1 h and the results are shown in Table 3. Lead compounds studied showed very high activities together with high selectivities for the carbamate ester. For example, upon using red PbO as the catalyst, the aniline conversion of 98% with the ester selectivity of 99% was obtained.

The effect of the DMC/aniline ratio on the carbamate yield in the reaction using $\text{Pb}(\text{OAc})_2 \cdot \text{Pb}(\text{OH})_2$ as the catalyst was examined. The reaction was carried out at 433 K for 1 h. At DMC/aniline ratio of unity, the carbamate yield was 65%. With increasing the DMC/aniline ratio, the aniline conversion and the carbamate yield increased. At the DMC/aniline ratio of 4, the carbamate yield reached 92%.

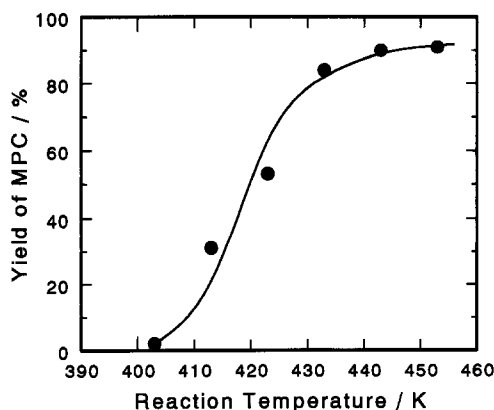


Fig. 2. The effect of reaction temperature on the carbamate yield in the presence of $\text{Pb}(\text{OAc})_2 \cdot \text{Pb}(\text{OH})_2$ (1.32 mmol). Aniline = 2.0 ml (22.1 mmol), DMC/aniline = 5.4, reaction time: 1 h.

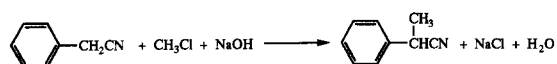
The effect of the amount of the catalyst, $\text{Pb}(\text{OAc})_2 \cdot \text{Pb}(\text{OH})_2$ is shown in Fig. 1. The conversion of aniline and the carbamate yield increased with the amount of the catalyst up to Pb/aniline ratio of 0.04 and almost unchanged with further increase of the catalyst amount.

Fig. 2 shows the effect of the reaction temperature on the carbamate yield with use of $\text{Pb}(\text{OAc})_2 \cdot \text{Pb}(\text{OH})_2$ as the catalyst and at the DMC/aniline ratio of 2.0. The carbamate was not obtained at all at 403 K, and over 413 K, the carbamate yield increased with increasing reaction temperature. It reached 92% based on aniline at 453 K. Under the reaction conditions, the selectivity for the carbamate based on aniline was 94.8% and the DMC conversion was 55%, the selectivity for the carbamate based on DMC being 84%.

3. Dimethyl carbonate as a substitute for dimethyl sulfate

3.1. Alkylation reactions

Alkylation reactions are very important in the synthetic organic chemistry. For methylations, methyl chloride or dimethyl sulfate is conventionally used as a methylating agent. For example, the methylation of phenylacetonitrile by methyl chloride is expressed as follows.



The reaction has the following drawbacks with respect to the environment.

1. Methyl chloride and dimethyl sulfate are toxic and corrosive chemicals. It is desirable to conduct alkylations by using environmentally benign methylating agents.
2. The reaction requires a stoichiometric amount of a base and produces a stoichiometric amount of sodium chloride. It is desirable to make the reactions catalytic, instead of using a stoichiometric amount of a base.
3. The reactions are performed in the liquid phase. Therefore, tedious workup procedures are required for separating the products from solvents or by-products. This disadvantage can be overcome by performing the reactions in the vapor-phase over solid catalysts.

Zeolites are materials of versatile nature and have been used as catalysts for many organic reactions. Fu and Ono have tried to use zeolites as catalysts for methylations in the vapor-phase. As the methylating agents, was used DMC, which is much less toxic than methyl halides or dimethyl sulfate as described earlier. In this way, we can avoid the drawbacks of the conventional alkylation reactions as described above. Here, the vapor-phase methylations of phenylacetonitrile, aniline, and phenol over zeolites will be described. The reactions were carried out in a fixed-bed flow reactor at atmospheric pressure.

3.2. Methylation of phenylacetonitrile

Alkylation of active methylene compounds is a widely used procedure in organic synthesis. For example, the α -monomethylation of phenylacetonitrile (PAN) is a very important step for the synthesis of the arylacetic acid moieties, used for drugs, etc. As described above, the alkylation of PAN has been carried out using alkyl halides in the presence of a stoichiometric amount of strong

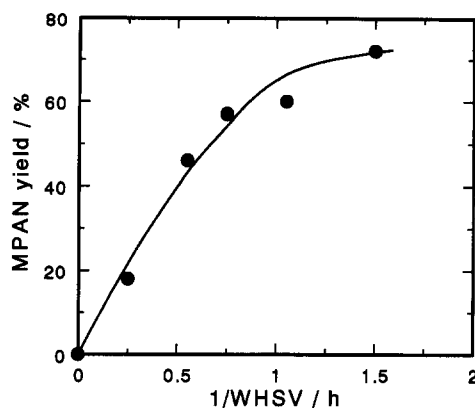
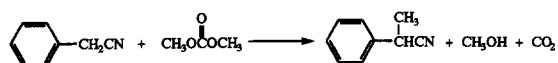


Fig. 3. The change in the yield of α -methylphenylacetonitrile (MPAN) with contact time in the methylation of phenylacetonitrile with dimethyl carbonate at 533 K. Catalyst: NaY, DMC/PAN = 1.0, PAN = 23.1 kPa.

bases such as NaNH_2 and NaOH [14–16]. Furthermore, the reactions are not selective, noticeable amounts of doubly alkylated derivatives being formed as by-products.

Fu and Ono examined the possibility of methylating PAN into α -methylphenylacetonitrile (MPAN) with DMC with the use of zeolites as solid base catalysts [17].



In Fig. 3 is shown the change in the yield of MPAN with contact time in the methylation with DMC over NaY at 533 K. At $1/\text{WHHSV} = 1.50$ h, the MPAN yield was 72%. The selectivity for MPAN with respect to DMC was ca.80%. A striking feature of the methylation of PAN over NaY is that no doubly methylated product was formed, in contrast with liquid phase methylation with methyl iodide.

This example clearly shows that zeolites can be very potential catalysts for methylation of organic substance with DMC.

3.3. *N*-Methylation of aniline

The vapor-phase methylation of aniline by methanol has been extensively studied. However, both the ring- and *N*-alkylation occur simultaneously, leading to the formation of *N*-methylaniline (1),

Table 4
The reaction of aniline with DMC over alkali-exchanged zeolites

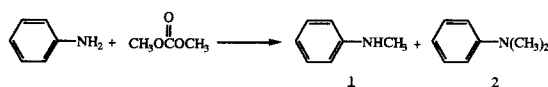
Catalyst	Temperature (K)	DMC/AN ratio	WHHSV (h^{-1})	AN conversion (%)	Selectivity	
					1	2
KY	453	1.25	0.37	99.6	93.5	6.5
	478	1.25	0.37	100	86.8	13.2
NaX	508	2.0	0.10	100	11.5	88.5
	513	2.5	0.13	100	4.4	95.6

Table 5
Reaction of phenol with DMC over alkali-exchanged zeolites ^a

Catalyst	Phenol conversion (%)	Selectivity (%)
NaX	96	94
KX	86	95
CsX	51	90

^a Reaction conditions: 533 K, WHSV = 3.7 h⁻¹, phenol = 24.7 kPa, DMC/phenol = 1.0.

N,N-dimethylaniline (2) and toluidines, respectively. Studies on the selective *N*-methylation are rather scarce. The methylation of aniline with DMC over zeolites was studied by Fu and Ono [18].



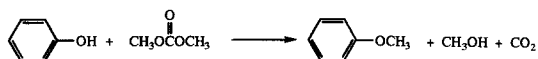
As shown in Table 4, alkali ion-exchanged faujasites showed very high activities for the methylation. Furthermore, *N*-methylation occurred exclusively, toluidenes not being formed at all. The selectivity for *N*-methylaniline and *N,N*-dimethylaniline depended on the zeolites used and the reaction conditions. A 93.5% selectivity for *N*-methylaniline was obtained at aniline conversion of 99.6% over KY at 453 K. On the other hand, *N,N*-dimethylaniline was obtained in a 95.6% yield over NaX at 513 K.

3.4. *O*-Methylation of phenol

Anisole is an important industrial chemical as a starting material for the production of dyes and agrochemicals or stabilizers for plastics. Anisole could be obtained by the Williamson ether synthesis, which requires methyl halide and a stoichiometric amount of sodium hydroxide.

The vapor-phase methylation of phenol with methanol using metal oxides or zeolites as catalysts has been extensively studied. The products are usually mixtures of anisole (the product of *O*-methylation) and cresols (the products of ring methylation).

The catalytic activities of alkali ion-exchanged zeolites on the methylation of phenol with DMC in the vapor phase are compared at 553 K in Table 5 [19].



As shown in Table 5, NaX gave a high and stable activity among alkali ion-exchanged zeolites. KX showed higher activity than NaX in the beginning, but the activity decayed quickly with time on stream. Under the reaction conditions of 553 K, WHSV = 1.85 h⁻¹, phenol pressure of 24.7 kPa and DMC/phenol = 1.0, the anisole yield reached 91% at phenol conversion of 95% over NaX.

4. Direct synthesis of tetramethoxysilane from silica and dimethyl carbonate

Alkoxysilanes are very important in the production of ceramics by the sol–gel process in which metal alkoxides are polycondensed and the resulting sol is calcined to afford a gel. They are also used

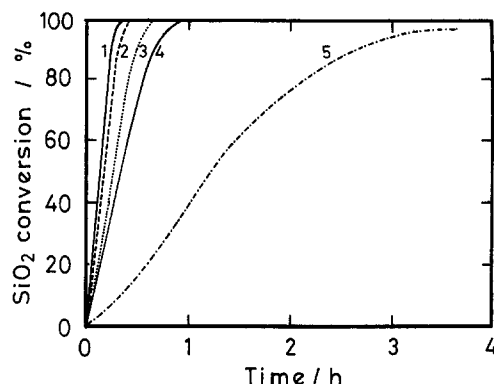


Fig. 4. Change in the conversion of silica gel into $\text{Si}(\text{OCH}_3)_4$ with reaction time. Catalyst: 5% KOH, reaction temperature: (1) 600, (2) 575, (3) 550, (4) 525, (5) 500 K.

as starting materials for pure silica. They are usually prepared from alcohols and silicon chlorides, which are, in turn, prepared via metallic silicon from silica.

Ono et al. found that silica gel reacts with DMC to give tetramethoxysilane at 500–600 K in the presence of a catalyst loaded on silica, the catalyst being an alkali hydroxide or alkali halide [20–22].



Silica gel loaded with the catalyst was placed in a fixed bed reactor, and DMC was fed at a constant rate. Fig. 4 shows how the silica conversion increases with reaction time at various temperatures. The complete conversion of silica gel was attained in 30 min at 600 K upon using potassium hydroxide as the catalyst. The silicon source can be impure, like rice hull ash [22].

The solid–gas reaction offers a simple and clean route for the synthesis of tetramethoxysilane. The reaction of silica gel with diethyl carbonate gives tetraethoxysilane [22], and the reaction of titanium dioxide with diethyl carbonate gives $\text{Ti}(\text{OEt})_4$ [23].

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