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A new process for the synthesis of diphenyl carbonate from dimethyl carbonate and phenol over heterogeneous catalysts

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The two-step synthesis of diphenyl carbonate (DPC) from dimethyl carbonate (DMC) and phenol has been compared in liquid phase and gas phase, both over heterogeneous catalysts. In the first step, equilibrium yields of methyl phenyl carbonate (MPC) in the transesterification of DMC and phenol were very low at low temperatures in the liquid phase although reaction rates were fast. This endothermic reaction was more favorable at high temperatures in the gas-phase reaction. Titanium oxide catalysts supported on SiO_2 or activated carbon were found to be effective in a continuous gas flow reactor. In case of the second step, the disproportionation of MPC, selective formation of DPC was not feasible in the gas-phase reaction due to extensive side reactions. However, there was no by-product in the liquid-phase reaction over the TiO_2/SiO_2 catalyst. Therefore, our proposed two-step synthesis process consists of the gas-phase transesterification of DMC and phenol followed by the liquid-phase disproportionation of MPC to DPC, both over the TiO_2/SiO_2 catalyst.

Keywords: gas-phase transesterification, methyl phenyl carbonate (MPC), disproportionation, diphenyl carbonate (DPC), TiO_2/SiO_2 catalyst

1. Introduction

Polycarbonate has been conventionally produced by the interfacial polycondensation of bisphenol-A and phosgene. One of the major drawbacks of the conventional phosgene process is an environmental and safety problem involved in using copious amounts of methylene chloride as the solvent, which is ten times the weight of the products, and highly toxic phosgene as the reagent [1]. However, phosgene-free processes for polycarbonate have been proposed that employ melt transesterification [2–5] or solid-state polymerization [1,6] using bisphenol-A and diphenyl carbonate (DPC) with the latter synthesized in a phosgene-free process.

Diphenyl carbonate, a convenient intermediate for the synthesis of polycarbonate without using phosgene, has often been synthesized via a two-step reaction from dimethyl carbonate (DMC) and phenol [7–10], since the direct synthesis of DPC (simultaneous reactions (1) and (2) in one reactor) is limited due to low equilibrium constants for the forward reaction [8]. Hence, DPC is obtained efficiently with two reactions of the transesterification of DMC and phenol (reaction (1)) followed by the disproportionation of formed methyl phenyl carbonate (MPC) into DPC and DMC (reaction (3)).

$$\begin{aligned}&CH_3O(C{=}O)OCH_3 + C_6H_5OH \rightleftharpoons\\&\quad C_6H_5O(C{=}O)OCH_3 + CH_3OH\end{aligned}\tag{1}$$

$$\begin{aligned}&C_6H_5O(C{=}O)OCH_3 + C_6H_5OH \rightleftharpoons\\&\quad C_6H_5O(C{=}O)OC_6H_5 + CH_3OH\end{aligned}\tag{2}$$

$$\begin{aligned}&2C_6H_5O(C{=}O)OCH_3 \rightleftharpoons\\&\quad C_6H_5O(C{=}O)OC_6H_5 + CH_3O(C{=}O)OCH_3\end{aligned}\tag{3}$$

Generally, the transesterification of DMC and phenol and the disproportionation of MPC are carried out in the liquid phase using homogeneous catalysts such as organic Pb, Sn, or Ti compounds. However, an active solid catalyst is more desirable in the aspect of separation and regeneration of the catalyst. As one of a few reports on the development of active solid catalysts, Fu et al. [10] reported that molybdenum oxide supported on silica showed the highest activity for both the transesterification and the disproportionation in the liquid-phase reaction. Nevertheless, there exists a critical thermodynamic limitation for the synthesis of DPC from DMC and phenol, especially in reaction (1). Much efforts have been devoted to increasing the yield of MPC by employment of complicated reaction processes such as catalytic distillation [7–9], but it is desirable to devise a more improved catalytic system that could increase the yield of MPC from the reaction itself under modified reaction conditions. In this work, we propose a new process for the synthesis of DPC from DMC and phenol that employs the unprecedented gas-phase transesterification of DMC and phenol followed by the liquid-phase disproportionation of MPC. Both reactions proceed over a new heterogeneous TiO_2/SiO_2 catalyst which performs better than catalysts re-

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ported previously in the literature to be active in similar reactions.

2. Experimental

2.1. Catalysts preparation

All catalysts were prepared by an impregnation method. γ-Al_2O_3 (Strem 93-1338), TiO_2 (Aldrich 23203-3) and SiO_2 (Aldrich 23683-7) were impregnated to incipient wetness with aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich 22123-6), $Cr(NO_3)_3\cdot 9H_2O$ (Aldrich 23925-9), and $(NH_4)_6W_{12}O_{39}\cdot xH_2O$ (Aldrich 35897-5). The metal precursors were loaded to give 10 wt% of metal and samples were dried in an oven at 383 K for 12 h to remove the moisture and calcined in a quartz reactor at 773 K for 4 h with an air stream of 89 μmol s^{-1}. Impregnation with NH_4VO_3 (Aldrich 39812-8) was carried out in an excess of the solution with a small quantity of oxalic acid and the sample was dried at 323 K in vacuum. The calcination procedure was the same as for the other samples.

When activated carbon (Aldrich 24227-6) was employed as the support for molybdenum, it was impregnated with a solution of the Mo precursor (20 wt% Mo) to incipient wetness and dried at 383 K in an oven for 12 h, then treated in a quartz reactor at 773 K for 4 h with a He stream of 89 μmol s^{-1}. Following the treatment, it was found by XRD that the Mo species on activated carbon was molybdenum dioxide, MoO_2. Carbon-supported molybdenum nitride and carbide were prepared using the temperature-programmed reaction (TPR) method, which was described in detail elsewhere [11,12].

In order to prepare the Sn and Ti catalysts, SiO_2, MgO (Alfa 88290) and activated carbon were impregnated with solutions of $SnCl_2$ (Aldrich 20472-2) and tetrabutoxytitanium (Aldrich 24411-2) dissolved in methanol and toluene, respectively. Samples (10 wt% by metal) were dried in an oven at 383 K for 12 h to remove the organic solvent and calcined in a quartz reactor at 773 K for 4 h with an air stream of 89 μmol s^{-1}. In case of titanium supported on silica, tetraethoxytitanium (J&M Co.), tetraisopropoxytitanium (Aldrich 20527-3) and tetrachlorotitanium (Aldrich 20856-6) were also used as titanium precursors.

2.2. The transesterification of DMC and phenol

For a gas-phase reaction, the catalysts were pretreated under the flow of nitrogen gas at a rate of 15 μmol s^{-1} at 773 K for 1 h just prior to the delivery of the mixture of DMC and phenol. The reactant mixture was a solution of DMC (Aldrich D15292-7) and phenol (Aldrich 18545-0), which was mixed at a ratio of 5 mol DMC to 1 mol phenol. The reactants were introduced into the flow of nitrogen gas of 15 μmol s^{-1} via a syringe pump (Sage Instruments, model 361) at a pumping rate of 1.0 cm^3 h^{-1} at atmospheric pressure. Identification and quantitative analysis of reaction products were carried out using an on-line HP 5890II gas chromatograph (GC) equipped with a flame ionization detector (FID) and using a HP 5890II-HP5972MSD GC–mass spectrometer (GC/MS). A sample was injected into the GC every 20 min by a six-port sampling valve attached to the effluent stream line.

For a liquid-phase reaction, a 300 cm^3 autoclave (Parr) was employed as a batch reactor. The catalyst and the mixture of DMC and phenol were charged into the reactor. While stirred, the reactor was flushed with nitrogen gas several times and pressurized with nitrogen gas. The reactor was heated to a reaction temperature at a rate of 10.8 K min^{-1}. When temperature reached the desired reaction temperature, it was assumed to be the start of reaction. Sampling was performed every hour by using two sampling valves attached on the sampling loop. The liquid products were filtered into a microsyringe and analyzed by GC and GC/MS as described above.

2.3. The disproportionation of MPC

As a reactant, a high-purity MPC was obtained from methylchloroformate and phenol by the method described elsewhere [13]. By GC and GC/MS analysis the product was found to be a mixture of 94.3 wt% MPC containing 5.7 wt% of unreacted phenol. Using this mixture, the disproportionation of MPC was performed in gas and liquid phases as in the first step. In the liquid-phase reaction, an excess amount of n-hexane was employed as a solvent.

3. Results and discussion

3.1. Thermodynamic consideration

Thermodynamic data for materials involved in reactions (1)–(3) are rare and their reliability is questionable. An investigation of the thermodynamics of reaction (1) in the liquid phase was described by Harrison et al. [8]. They reported an equilibrium constant for the reaction of 2.6×10^{-3}. However, the conditions of their calculations that were employed to obtain this value were not specified. Their typical reaction conditions were 491 K, 75 psia and equimolar DMC to phenol. Tundo et al. [14] reported the reaction of DMC with phenol for the synthesis of anisole in the gas phase. They suggested that the transesterification between DMC and phenol was not favorable thermodynamically with K_{eq} of ca. 3×10^{-4} at 453 K. The basis of this value was not described again, yet typical reaction conditions were 453 K, atmospheric pressure and 1.2 mol of DMC per mole of phenol.

We investigated the thermodynamic properties of the reaction (1) in the gas phase over the temperature range of 298–800 K at atmospheric pressure with an assumption of the ideal gas state [15]. Since there was no available thermodynamic data of DMC and MPC, we applied the functional group contribution method by using the Aspen Plus

Table 1
Activities of various catalysts (10 wt% metal loading) for the transesterification of DMC and phenol in the gas-phase reaction.[a]

Catalyst	Conv.[b] (%)	Yield[c] (%)	Selectivity[d] (%)						
			BZ	TN	AN	Cr	MPC	MMB	DPC
MoO_x/Al_2O_3[e]	2.1	0.7	0	0	35.6	29.6	34.6	0	0
MoO_x/TiO_2[e]	0.9	0.5	0	0	42.5	0	57.6	0	0
MoO_3/SiO_2	20.5	8.4	1.9	0.7	29.3	17.3	40.8	5.1	5.0
CrO_x/SiO_2	29.9	5.0	0.5	0.7	19.5	51.9	16.8	1.1	4.3
WO_x/SiO_2	12.1	3.4	1.2	2.0	21.8	7.9	27.7	5.4	4.4
VO_x/SiO_2	6.0	2.9	1.9	2.2	24.0	24.8	47.7	0	0
MoO_2/C[e,f]	28.6	13.6	1.0	0.7	43.1	7.0	47.4	0.7	0
Mo_2N/C[e,f]	16.8	3.1	2.2	0.8	61.0	17.8	18.2	0	0
Mo_2C/C[e,f]	17.5	4.3	1.9	1.1	55.6	16.5	24.5	0	0
SnO_x/SiO_2	20.7	11.0	0	0	35.0	9.4	52.9	0	2.6
TiO_x/MgO	24.3	9.0	0	0	35.3	26.3	37.1	1.3	0
TiO_2/C	30.4	27.7	0	0	5.9	1.6	91.2	0	1.2
TiO_2/SiO_2	37.2	31.7	0	0	8.8	4.0	85.1	0.4	1.7
$TiO_2(E)/SiO_2$[g]	30.4	25.8	0	0.4	6.6	5.6	84.9	0	2.4
$TiO_2(I)/SiO_2$[g]	28.9	23.2	0	0	7.7	8.4	80.4	1.0	2.5
$TiO_2(C)/SiO_2$[g]	32.4	28.5	0	0	8.2	2.5	87.9	0	1.4

[a] Reactant mixture feeding rate $= 1.0\ cm^3\ h^{-1}$, the mole ratio of DMC to phenol $= 5$, N_2 flow rate $= 15\ \mu mol\ s^{-1}$, catalyst loading $= 0.48$ g, reaction temperature $= 723$ K.
[b] Based on phenol converted.
[c] Yield of methyl phenyl carbonate (MPC).
[d] BZ: benzene, TN: toluene, AN: anisole, Cr: cresol, MPC: methyl phenyl carbonate, MMB: multimethylbenzenes, DPC: diphenyl carbonate.
[e] Catalyst loading $= 1.0$ g.
[f] 20 wt% Mo loading.
[g] Silica-supported titanium dioxide catalysts derived from tetraethoxytitanium (E), tetraisopropoxytitanium (I) and tetrachlorotitanium (C), respectively.

(version 9.2-1) package. The enthalpies of formation at 298 K were estimated to be -554.75, -421.42, -200.66 and $-90.83\ kJ\,mol^{-1}$ for DMC, MPC, methanol and phenol, respectively. Consequently, the standard heat of reaction (1) in the gas phase was estimated to be $23.5\ kJ\,mol^{-1}$. This endothermic reaction should be more favorable for a high yield of MPC at relatively high temperatures.

3.2. Transesterification of DMC and phenol: reaction (1)

Table 1 shows activities of various catalysts in the gas-phase reaction at a time on stream of ca. 8.5 h. The catalyst systems of titania supported on activated carbon and silica reached steady-state activities within 6 h, but the other catalysts were deactivated by coking until the end of the reaction. It was observed that the major by-products were anisole and cresol, which could be formed via methylation of phenol by DMC. More anisole was produced than cresol for most of the catalysts through a nucleophilic attack on methyl group in DMC by the phenoxy compound. However, little diphenyl carbonate (DPC) was produced in most cases, indicating that there was insufficient contact time of reactants and catalyst for the consecutive reactions (1) and (2) to occur significantly. It was found that the formation of DPC became appreciable as the space velocity of reactants decreased [16]. The most efficient catalyst was TiO_2 supported on activated carbon or silica. Furthermore, the performances of all TiO_2/SiO_2 catalysts were similar independent of the titanium precursors employed for the catalyst preparation. It was found that MPC selectivity could be increased to 94% with 29.5% phenol conversion at 673 K over 10 wt% TiO_2/SiO_2 catalyst. Anisole was produced with a selectivity of about 3.5% and DPC with a selectivity of 1.5%. It is worth noting that the TiO_2/SiO_2 and TiO_2/C catalysts showed a well-defined induction period unlike the others. These catalysts had the similar activity trend with time on stream, a rapid decrease of activity at the beginning of the reaction and a marked increase in selectivity up to steady-state values after an induction period of ca. 2–3 h. This particular behavior was found to be related to the rapid carbon deposition in the early stage of the reaction and will be reported in detail in a forthcoming publication [17]. The MoO_3/SiO_2 catalyst which was reported by Fu et al. [10] to be the best catalyst for the liquid-phase transesterification showed a mediocre selectivity to MPC in the gas-phase reaction.

Figure 1 and table 2 represent the activity of the transesterification over MoO_2/C, MoO_3/SiO_2 and TiO_2/SiO_2 catalysts in the liquid-phase reaction in a batch reactor. For MoO_2/C reported in figure 1, by-products were anisole and a little cresol. The rate of MPC formation was much faster than that of anisole, but anisole was formed irreversibly with reaction time. The formation of anisole showed a linear increase with reaction time, implying a zeroth-order reaction, while MPC yield approached ca. 5.2% which was believed to be close to the equilibrium value. This value should be less than the yield that would have been obtained when no by-product were formed. For the catalysts consisting of Mo or Ti supported on silica, as shown in table 2, MPC yields of ca. 7% were obtained which were again believed to be the equilibrium yield. The slightly different value of equilibrium yield from that for MoO$_2$/C may be due to the great difference in by-product composition. The reaction rates were so fast, compared to that of MoO$_2$/C, that the equilibrium yield was obtained within 2 h with minimal formation of anisole as the sole by-product.

In the liquid phase, the transesterification of DMC and phenol has a critical thermodynamic limitation in obtaining high MPC yields. The equilibrium yield of MPC is close to 7% under the present conditions although the reaction rate is fast. Hence, the development of a more efficient catalyst system for the liquid-phase reaction would not exert any significant impact on the improvement of MPC yield. Since reaction (1) is endothermic, higher temperatures are desirable for higher MPC yields. Due to the boiling point of phenol (454 K), however, the reaction should be carried out in gas phase and development of a new catalyst is required that works effectively under drastically altered reaction conditions. We found that TiO$_2$/SiO$_2$ or TiO$_2$/C employed in a continuous gas flow reactor is a suitable catalyst for the purpose. The detailed results of catalyst characterization and a kinetic study for the gas-phase transesterification over TiO$_2$/SiO$_2$ are subjects of a forthcoming publication [16].

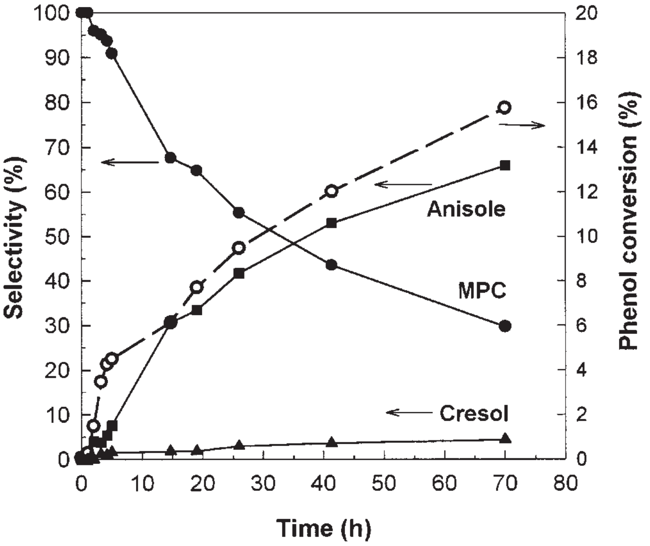

Figure 1. The transesterification of DMC and phenol in the liquid phase over 20 wt% MoO$_2$/C. Charge of DMC = 714.0 mmol, charge of phenol = 142.8 mmol, catalyst loading = 2.0 g, stirring rate = 400 rpm, initial pressure = 6.8 atm of N$_2$ at 293 K, reaction temperature = 433 K.

3.3. Disproportionation of MPC: reaction (3)

Table 3 shows the reactivity of MPC over TiO$_2$/SiO$_2$ catalyst in the gas-phase reaction. The reaction yields various and complicated reaction products. Reaction (3) predicts co-production of DMC and DPC. However, DMC was not detected, indicating that the formed DMC was promptly converted into DME and CO$_2$ through the decarboxylation of DMC. Furthermore, anisole could be produced through the decarboxylation of MPC. It is worthy to mention the enormous quantity of phenol produced even though the reactant mixture initially contained phenol of only 5.7 wt%. The MPC adsorbed on the catalyst surface is expected to be cleaved into surface species such as PhO*, CH$_3^*$ and CO$_2$, where $*$ denotes an adsorption site on the catalyst surface. The surface species CH$_3^*$ has the possibility of further surface reactions such as coupling with PhO* to anisole, the methylation of aromatic compounds and the thermal dehydrogenation into carbon deposit and surface hydrogen. Hence, phenol could be produced through the surface reaction of PhO* and surface hydrogen. At any rate, due to these extensive side reactions, selective synthesis of DPC from gas-phase disproportionation of MPC is not feasible.

Figure 2 represents the disproportionation of MPC in the liquid phase over TiO$_2$/SiO$_2$ and MoO$_3$/SiO$_2$ catalysts. In both cases, MPC disproportionated into DMC and DPC with selectivity of 99.8% or better. The TiO$_2$/SiO$_2$ catalyst reached an equilibrium conversion of ca. 47% within 20 h, but the MoO$_3$/SiO$_2$ showed a slower rate giving 20% conversion in 25 h.

In case of the disproportionation of MPC, the selective formation of DPC was not feasible in the gas-phase reaction due to the extensive side reactions. However, there were negligible amounts of by-product in the liquid-phase reaction that showed a high yield of DPC over the TiO$_2$/SiO$_2$ catalyst. Hence, a liquid-phase reaction over TiO$_2$/SiO$_2$ is our choice for the disproportionation of MPC to DPC.

Table 2
Conversion of phenol and selectivity to MPC of catalysts for the transesterification of DMC and phenol after 3 h in the liquid-phase reaction.[a]

	Catalyst			
	MoO$_3$/SiO$_2$[b]	TiO$_2$(B)/SiO$_2$[c]	TiO$_2$(I)/SiO$_2$[c]	TiO$_2$(C)/SiO$_2$[c]
Phenol conversion (%)	7.1	6.3	5.7	6.7
MPC selectivity (%)	99.7	99.3	99.4	99.7

[a] Charge of DMC = 595.0 mmol, charge of phenol = 119.0 mmol, catalysts loading = 1.0 g, stirring rate = 400 rpm, initial pressure = 6.8 atm of N$_2$ at 293 K, reaction temperature = 433 K.

[b] 20 wt% Mo-loaded MoO$_3$/SiO$_2$ catalyst.

[c] 10 wt% Ti-loaded TiO$_2$/SiO$_2$ catalysts derived from the precursors of tetrabutoxytitanium (B), tetraisopropoxytitanium (I) and tetrachlorotitanium (C), respectively.

Table 3
The disproportionation of MPC over 10 wt% TiO_2/SiO_2 catalyst in the gas phase.[a]

Temp.	Product distribution[b] (%)											
(K)	DME	Me	BZ	TN	XN	AN	Ph	Cr	DMP	MPC	MMB	DPC
613	0.64	2.44	0	0	0	7.83	53.6	23.0	3.47	2.43	5.70	0.35
643	1.41	0.82	0	0.12	0	4.16	50.9	23.8	3.43	3.67	8.20	1.07
673	2.22	0.33	0.28	0.44	0.21	2.54	49.5	24.2	2.97	4.10	8.00	2.58
703	3.56	0	1.63	2.35	1.23	1.23	46.6	25.4	1.96	3.23	4.20	3.97
743	6.56	0	11.9	10.4	2.73	1.03	37.3	10.7	0.18	0.71	4.00	6.32
773	8.34	0	19.1	9.90	1.62	0.51	35.1	3.50	0	0	7.20	8.32

[a] MPC feeding rate $= 0.2\ cm^3\,h^{-1}$, N_2 flow rate $= 15\ \mu mol\,s^{-1}$, 10 wt% Ti-loaded TiO_2/SiO_2 catalyst loading = 0.48 g, temperature-ramping rate $= 0.017\ K\,s^{-1}$. The feed mixture was made of 94.3 wt% MPC and 5.7 wt% phenol as described above.

[b] DME: dimethyl ether, Me: methanol, BZ: benzene, TN: toluene, XN: xylene, AN: anisole, Ph: phenol, Cr: cresol, DMP: dimethylphenol, MPC: methyl phenyl carbonate, MMB: multimethylbenzene, DPC: diphenyl carbonate.

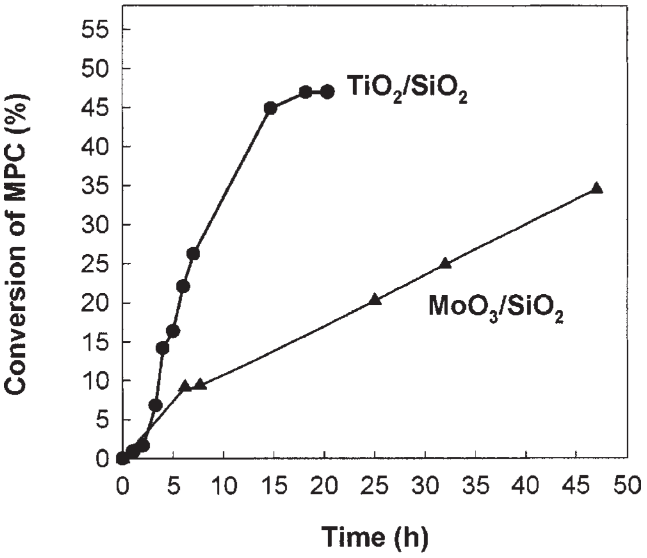

Figure 2. The disproportionation of MPC over 10 wt% TiO_2/SiO_2 and 20 wt% MoO_3/SiO_2 catalysts in the liquid-phase reaction. Charge of MPC = 31.2 mmol, catalyst loading = 0.5 g, stirring rate = 400 rpm, initial pressure = 6.8 atm of N_2 at 293 K, reaction temperature = 433 K, solvent charge of n-hexane = 612.7 mmol. The feed mixture was made of 94.3 wt% MPC and 5.7 wt% phenol.

3.4. A new process scheme of diphenyl carbonate synthesis from dimethyl carbonate and phenol

Due to the recent success of solid-state polymerization of diphenyl carbonate and bisphenol-A to produce fiber-grade polycarbonate [6], an efficient synthesis process of diphenyl carbonate without using phosgene is the subject of great interest. In order to circumvent the thermodynamic limitation of the reactions involved, catalytic distillation using homogeneous liquid-phase catalysts has been commonly proposed. In this paper, we propose an alternative process and a new catalyst. The proposed two-step process consists of the gas-phase transesterificaton of dimethyl carbonate and phenol followed by the liquid-phase disproportionation of methyl phenyl carbonate to diphenyl carbonate and dimethyl carbonate over the same TiO_2/SiO_2 solid catalyst.

4. Conclusions

In the liquid phase, the transesterification of DMC and phenol has a critical thermodynamic limitation in increasing the MPC yield. The equilibrium yield of the MPC is very low although the reaction rate is fast. Alternatively, gas-phase reaction at higher temperatures drives the equilibrium toward higher MPC yields. New catalysts of TiO_2/SiO_2 and TiO_2/C were found to be efficient in a continuous gas flow reactor.

In case of the disproportionation of MPC, selective DPC formation was not feasible in the gas-phase reaction because of the extensive side reactions. However, there was negligible by-product formation in the liquid-phase reaction that showed a high yield of DPC over TiO_2/SiO_2 catalyst. Hence, we propose a new scheme of diphenyl carbonate synthesis from dimethyl carbonate and phenol that consists of the gas-phase transesterification followed by the liquid-phase disproportionation both over TiO_2/SiO_2 catalyst.

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