Two-step synthesis of diphenyl carbonate from dimethyl carbonate and phenol using MoO_3/SiO_2 catalysts

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Abstract

The transesterification of dimethyl carbonate with phenol to produce methyl phenyl carbonate was carried out in an autoclave using a variety of solid catalysts. MoO_3/SiO_2 was found to have a very high activity for this transesterification. Thus, a 17.1% yield of methyl phenyl carbonate based on phenol was obtained at 433 K in the presence of MoO_3/SiO_2. MoO_3/SiO_2 was also an active catalyst for the disproportionation of methyl phenyl carbonate into diphenyl carbonate and dimethyl carbonate. A 48% yield of diphenyl carbonate was attained over MoO_3/SiO_2 at 443 K. These yield values are probably very close to those at the thermodynamic equilibrium.

Keywords: Diphenyl carbonate; Dimethyl carbonate; Methyl phenyl carbonate; Transesterification; MoO_3/SiO_2 catalyst

1. Introduction

Polycarbonates are important engineering thermoplastics with good mechanical and optical properties as well as electrical and heat resistance useful for many applications [1]. Polycarbonates are commercially produced by the reaction between a bisphenol-A salt in an aqueous caustic solution and phosgene in an organic solution. The main disadvantages of this phosgene process are: (1) The high toxicity and corrosiveness of phosgene, (2) the complex clean-up to remove ionic materials, and (3) the use of a copious amount of methylene chloride, a water-soluble toxic solvent.
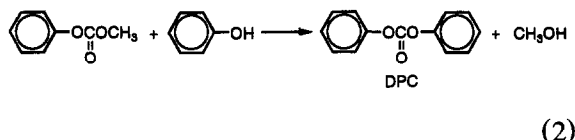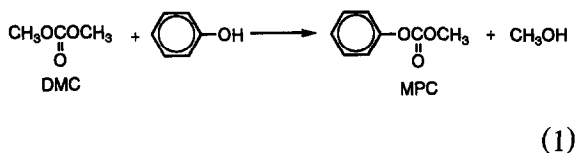
The most practical non-phosgene process for manufacturing polycarbonates is the melt transesterification of diphenyl carbonate (DPC) with bisphenol-A. In this method, no toxic solvents are used and the by-product phenol may be recycled.

DPC has been prepared by the reaction of phenol and phosgene in the presence of bases such as sodium hydroxide [2,3]. The obvious disadvantages of this method are the use of corrosive and toxic phosgene as a raw material and the formation of stoichiometric amount of NaCl.

Dimethyl carbonate (DMC) can be used as a substitute for phosgene in the synthesis of DPC with traditional transesterification catalysts such
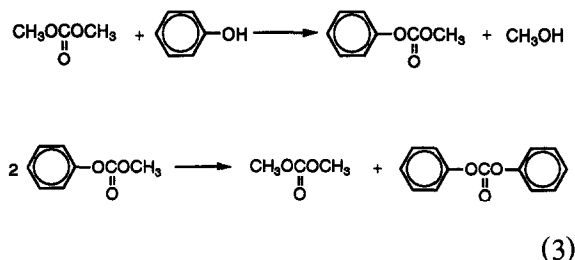
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as Lewis acid and soluble organic Al, Ti, Sn compounds [4–9].

$$CH_3OCOCH_3 + \bigcirc\!\!-OH \longrightarrow \bigcirc\!\!-OCOCH_3 + CH_3OH$$

DMC   MPC

(1)

$$\bigcirc\!\!-OCOCH_3 + \bigcirc\!\!-OH \longrightarrow \bigcirc\!\!-OCO-\!\!\bigcirc + CH_3OH$$

DPC

(2)

Unfortunately, in these homogeneous transesterification systems, the formation of by-products and the difficult separation of catalysts from the products will cause problems. Therefore, the development of active solid catalysts is highly desirable. However, the reports on solid catalysts are very few [10].

Another disadvantage of the direct transesterification of DMC with phenol into DPC is that the formation of DPC is not thermodynamically favored [11]. A two-step process, consisting of the transesterification to MPC into methyl phenyl carbonate (MPC) and the disproportionation of MPC into DPC and DMC offers the most attractive route to DPC [12],[13].

$$CH_3OCOCH_3 + \bigcirc\!\!-OH \longrightarrow \bigcirc\!\!-OCOCH_3 + CH_3OH$$

$$2\,\bigcirc\!\!-OCOCH_3 \longrightarrow CH_3OCOCH_3 + \bigcirc\!\!-OCO-\!\!\bigcirc$$

(3)

In this work, we attempted to search active solid catalysts for the transesterification and the disproportionation. Here, we report that MoO_3/SiO_2 is an effective catalyst for both the transesterification of DMC with phenol and the disproportionation of MPC into DPC.

2. Experimental

2.1. Catalysts

MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts were prepared by conventional impregnation of SiO_2 (101 m^2 g^{-1}, average pore size 31 nm) with an aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and NH_4VO_3 (Kanto Chemical), respectively. The water was evaporated to dryness at 333 K using a rotary evaporator, followed by drying the solid in an oven at 393 K overnight and calcining it in a muffle furnace at 823 K overnight. The surface areas of SiO_2, 10 wt% MoO_3/SiO_2 and 25 wt% MoO_3/SiO_2 were 101, 84, 75 m^2 g^{-1}, respectively.

MoO_2/SiO_2 was prepared by reducing MoO_3/SiO_2 in flowing hydrogen at 673 K for 4 h, and the formation of MoO_2 was confirmed by XRD.

TiO_2/SiO_2 and ZrO_2/SiO_2 catalysts were prepared by impregnating SiO_2 with a benzene solution of titanium isopropoxide and zirconium butoxide (Kanto Chemical), respectively, followed by drying to remove the solvent and heating in an oven at 573 K overnight.

Nb_2O_5/SiO_2 was prepared by impregnating SiO_2 with an aqueous solution of niobium oxalate, followed by drying at 393 K overnight and calcining at 773 K in air overnight.

$Y(OAc)_3/SiO_2$, $La(OAc)_3/SiO_2$, $Pr(OAc)_3/SiO_2$ and $Sm(OAc)_3/SiO_2$ were prepared by impregnating SiO_2 with an aqueous solution of the corresponding acetate, followed by heating at 523 K. The anhydrous rare earth acetates were reported to be stable at 523 K and decomposed only above 673 K [14].

Y_2O_3/SiO_2, Pr_6O_{11}/SiO_2, Nd_2O_3/SiO_2, Sm_2O_3/SiO_2 were prepared by calcining the corresponding acetates supported on SiO_2 at 723 K, 993 K, 1073 K, and 1023 K, respectively. The other metal oxides on SiO_2 were also prepared by calcining the corresponding acetates supported on SiO_2.

A mesoporous silica, FSM-16, was a kind

gift of Dr. S. Inagaki of Toyota Central R&D Labs.

NaOEt/Al_2O_3 and CsOH/Al_2O_3 was prepared according to the procedures reported in literature [15,16], respectively.

Al (powder) and zirconium acetylacetonate (guaranteed reagent grade, Kanto Chemical) were used as received.

2.2. Reaction procedures

The transesterification of phenol and DMC was carried out as follows: Phenol, DMC and a catalyst were introduced into an autoclave (50 ml), and air in autoclave was replaced by nitrogen. The autoclave was heated to the reaction temperature at a rate of 7 K min^{-1}. After the reaction, the autoclave was cooled to room temperature, and the products were filtered and analyzed with a gas chromatograph equipped with a capillary column (50 m, OV101) and a flame ionization detector.

The disproportionation of MPC was conducted in an autoclave (50 ml) or in a flask (30 ml) equipped with a distillation apparatus.

3. Results and discussion

3.1. Transesterification of DMC with phenol

#### 3.1.1. Catalytic activities of various catalysts

A variety of catalysts were prepared and examined their catalytic activities for the transesterification (Eq. (1)). The reaction was carried out in an autoclave. The reaction conditions were as follows; reaction temperature = 433 K, phenol = 2.24 g (23.8 mmol) and DMC/phenol = 5.0.

Table 1 shows the activities of solid acid and base catalysts. In general, solid acids and bases are not active for the transesterification and give anisole as the main product, instead. Especially, K_2CO_3 and CsOH supported on alumina were very selective for the formation of anisole.

Amberlyst 15, a well-known transesterifica-

tion catalyst, gave a MPC yield of 1.2%, an anisole yield being 26.1%. H-ZSM-5 showed almost the same results as Amberlyst 15.

It was reported that acids and bases catalyzed the decarboxylation of MPC to yield anisole [17,18]. Therefore, anisole may be formed by the direct methylation of phenol with DMC as well as by the decarboxylation of primary product (MPC) catalyzed by acid or base as shown below.
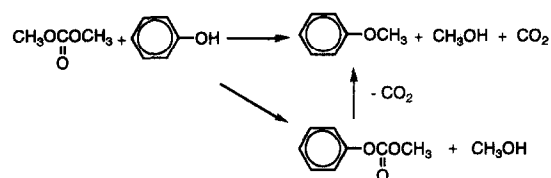
The catalytic activities of silica-supported metal acetates for the transesterification are listed in Table 2. The loading amount of the acetate was 10 wt% of the support. It was confirmed that silica gel showed almost no activity for the formation of MPC as well as anisole. The acetates of rare earth metals gave reasonable yields of MPC, though the formation of anisole was always observed. Nd$(OAc)_3$ gave a MPC yield of 15.9%, an anisole yield being 4.2%. Fe(OH)$(OAc)_2$ and Cd$(OAc)_2$ gave high selectivities for MPC. Fe(OH)$(OAc)_2$ gave a 10.7% yield of MPC, an anisole yield being 0.3%. The acetates of alkaline earth metals showed low selectivity for MPC.

The catalytic activities of metal oxides supported on silica are listed in Table 3, in which the oxides are listed in the most probable form at the corresponding calcination temperatures. The loading amount of the precursor compounds was 10 wt% of the support as the corresponding oxides.

Among the supported oxides, MoO_3/SiO_2, V_2O_5/SiO_2, ZrO_2/SiO_2, and PbO/SiO_2 showed high activities and selectivities. MoO_3/SiO_2 revealed the highest activity and selectivity for the transesterification. The yields of MPC and DPC based on phenol were 17.1%

Table 1
The catalytic activities of solid acids and bases for transesterification of dimethyl carbonate with phenol

Catalyst	Weight (g)	Time (h)	Phenol conversion (%)	Yields (%)		
				MPC	DPC	AN
H-ZSM-5	0.5	4	36.8	4.5	0.0	32.3
Amberlyst 15	0.5	4	29.1	1.2	0.0	26.1
K_2CO_3	0.17	4	83.5	0.5	0.0	83.0
$CaCO_3$	0.12	4	1.3	0.8	0.0	0.5
$BaCO_3$	0.24	4	9.0	5.0	0.0	4.0
$Ca(OH)_2$	0.09	4	14.5	4.5	0.0	10.0
$MgOAl_2O_3$	0.15	4	27.6	1.3	0.2	26.1
$NaOEt/Al_2O_3$	0.5	14	49.1	0.4	0.0	48.7
$CsOH/Al_2O_3$	0.5	16	94.0	0.0	0.0	94.0

MPC: methyl phenyl carbonate, DPC: diphenyl carbonate, AN: anisole.
Reaction temperature = 433 K, DMC/PhOH = 5.0, PhOH = 23.8 mmol.

and 0.2%, respectively, while only trace amount of anisole was observed as a by-product. A very small yield of DPC is due to the thermodynamic limitation.

3.1.2. Effect of supports

Table 4 shows the effect of supports on the catalytic activity of MoO_3 at 433 K. The unsupported MoO_3 catalyst showed a very low activity probably because of the low surface area (7 m^2/g). When MoO_3 was supported on SiO_2, ZrO_2 and TiO_2, higher MPC yields were obtained. When MoO_3 was supported on SiO_2–Al_2O_3, Al_2O_3 and CaO, MPC yields were quite low with high yields of anisole. In these cases, high yields of anisole are plausibly due to the

Table 2
The catalytic activities of metal acetate supported on silica for transesterification of dimethyl carbonate with phenol

Catalyst	Phenol conversion (%)	Yields (%)		
		MPC	DPC	AN
$Mg(OAc)_2$	17.3	8.1	0.2	8.9
$Ca(OAc)_2$	13.6	9.4	0.1	4.1
$Y(OAc)_3$	14.6	11.5	0.1	3.0
$La(OAc)_3$	14.2	9.9	0.1	4.1
$Sm(OAc)_3$	17.2	13.7	0.1	3.3
$Pr(OAc)_3$	16.4	8.5	0.1	7.5
$Nd(OAc)_2$	15.9	11.6	0.1	4.2

MPC: methyl phenyl carbonate, DPC: diphenyl carbonate, AN: anisole. Acetates were supported on silica in 10 wt%.
Reaction temperature = 433 K, reaction time = 4 h, DMC/PhOH = 5.0, PhOH = 23.8 mmol.

decarboxylation of MPC into anisole catalyzed by the basic or acidic sites on the supports [17,18]. Among the supports, silica was found

Table 3
The catalytic activities of metal oxides supported on silica for transesterification of dimethyl carbonate with phenol

Catalyst	Phenol conversion (%)	Yields (%)		
		MPC	DPC	AN
MoO_3	17.3	17.1	0.2	0.0
Ga_2O_3	16.7	12.7	0.3	3.5
V_2O_5	12.4	12.0	0.3	0.1
PbO	14.5	11.6	2.2	0.9
Pr_6O_{11}	12.8	11.5	0.2	0.2
ZrO_2	14.3	11.3	1.3	1.3
TiO_2	11.6	10.8	0.4	0.4
CdO	9.2	8.4	0.1	0.7
Sm_2O_3	8.7	8.3	0.2	0.2
Fe_2O_3	8.9	7.8	0.1	0.9
CuO	9.6	7.6	0.3	1.3
Y_2O_3	11.4	5.9	0.0	5.1
MgO	15.8	5.7	0.0	9.8
Mn_3O_4	7.0	5.6	0.0	1.4
NiO	5.8	5.3	0.0	0.5
ZnO	15.6	7.2	0.0	8.4
Nd_2O_3	5.4	5.1	0.0	0.3
Co_2O_3	6.6	5.0	0.1	1.5
RuO_2	5.1	4.7	0.0	0.4
Nb_2O_5	2.5	2.5	0.0	0.0
Cr_2O_3	1.4	1.0	0.0	0.4
Al(powder) [a]	11.9	10.9	0.2	0.8
$Zn(acac)_4$ [a]	10.6	10.4	0.0	0.2

MPC: methyl phenyl carbonate, DPC: diphenyl carbonate, AN: anisole. Oxides were supported on silica in 10 wt%. Reaction time = 4 h, catalyst = 0.2 g except Al (0.03 g) and $Zn(acac)_4$ (0.05 g), DMC/PhOH = 5.0, PhOH = 23.8 mmol.
[a] Not supported. Reaction temperature = 433 K.

Table 4

Effect of supports on the catalytic activities of MoO_3 for the transesterification of dimethyl carbonate with phenol

Catalyst	Phenol conversion (%)	Yields (%)		
		MPC	DMC	AN
MoO_3(0.02 g)	3.8	3.8	0.0	0.0
MoO_3/SiO_2	17.3	17.1	0.2	0.0
MoO_3/FSM-36	14.7	14.3	0.1	0.3
MoO_3/ZrO_2	13.9	13.5	0.1	0.3
MoO_3/TiO_2	9.3	8.9	0.0	0.4
MoO_2/SiO_2-Al_2O_3	18.3	4.3	0.0	12.9
MoO_3/Al_2O_3	20.0	3.6	0.0	15.3
MoO_3/CaO	23.2	2.0	0.0	20.9

MPC: methyl phenyl carbonate, DPC: Diphenyl carbonate, AN: anisole. Loading of MoO_3 on supports: 10 wt%. Catalyst = 0.2 g, reaction temperature = 433 K, reaction time = 4 h, DMC/PhOH = 5.0, PhOH = 23.8 mmol.

to be the best with respect to both the yield of and the selectivity for MPC.

3.1.3. Effect of the loading amount of MoO_3 on SiO_2

Fig. 1 shows the effect of MoO_3 loading on the phenol conversion. The reaction temperature was 433 K and the weight of the catalyst was 0.01 g. The catalytic activity increased with increasing the MoO_3 loading up to 20 wt% where the maximum activity was observed. In any case, the formation of anisole was not
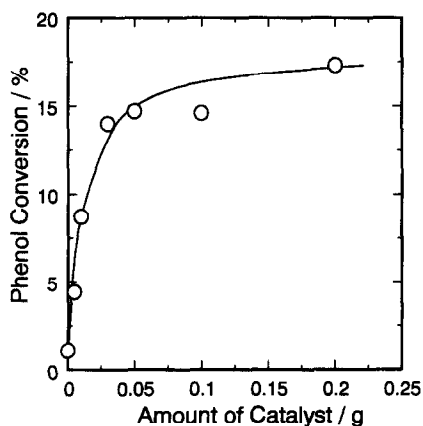

Fig. 1. The effect of MoO_3 loading on SiO_2 on the phenol conversion in the transesterification of dimethyl carbonate with phenol. Reaction conditions: Catalyst = 0.01 g, temperature = 433 K, reaction time = 4 h, DMC/PhOH = 5, phenol = 23.8 mmol.
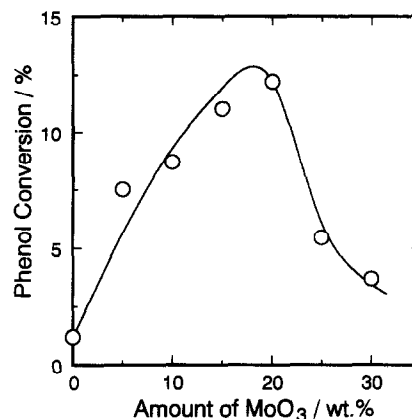

Fig. 2. The effect of the amount of the catalyst used on the phenol conversion in the transesterification of dimethyl carbonate with phenol. Reaction conditions: Catalyst = MoO_3(10 wt%)/SiO_2, 433 K, reaction time = 4 h, DMC/PhOH = 5, phenol = 23.8 mmol.

observed. Thus, the optimum loading of MoO_3 on SiO_2 was around 20 wt%. It was confirmed by XRD that the oxide on the silica surface actually exists in the form of MoO_3.

3.1.4. Effect of catalyst amount on the MPC yield

Fig. 2 shows the effect of the amount of MoO_3/SiO_2 catalyst at 433 K and 4.0 h. The loading amount of MoO_3 on SiO_2 was 10 wt%. Increasing MoO_3/SiO_2 weight from 0.005 g to 0.02 g led to the increase in a MPC yield. Above 0.03 g, the yield increased very slowly with increasing MoO_3/SiO_2 weight. With 0.2 g of the catalyst, the yield of MPC reached 17.1%. This value is probably very close to the equilibrium yield obtained by thermodynamic estimation at this temperature. In any case, the formation of anisole was not observed.

3.1.5. Effect of the temperature on the MPC yield

The effect of temperature on the activities of MoO_3/SiO_2 (0.03 g) was examined. The other reaction conditions were same as the one given in Table 4. At 433 K and 4.0 h, the MPC and DPC yields were 13.8% and 0.2%, respectively.

When the reaction was conducted at 473 K for 8.0 h, MPC and DPC yields were 17.6% and 1.5%, respectively, but anisole was formed at a yield of 1.5%. Therefore, to avoid the formation of anisole as a by-product, the favorable temperature was around 430 K.

3.1.6. Reaction mechanism

Since the acid or base catalysts do not give MPC from DMC and phenol, the coordination of a reactant/s to the coordinatively unsaturated molybdenum species seems essential for the transesterification. The tentative mechanism may be expressed as follows:
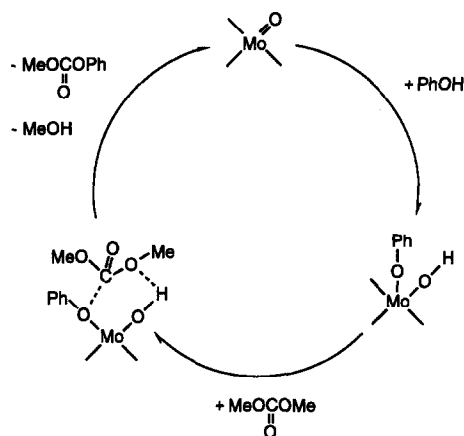
A phenol molecule dissociatively adsorbs to coordinate to the surface molybdenum. A DMC molecule, a polar molecule, interacts with adsorbed phenoxide to form the transesterification product.

3.2. Disproportionation of MPC into DPC and DMC

3.2.1. Activities of SiO_2 supported catalysts

Disproportionation of MPC into DPC and DMC [Eq. (3)] was studied, using MoO_3/SiO_2 as the catalyst in an autoclave. As shown in Table 5, MoO_3/SiO_2 catalyzed the disproportionation of MPC as well as the transesterifica-

Table 5
The catalytic activities of supported MoO_3 for the disproportionation of methyl phenyl carbonate (MPC)

Catalyst	Temperature (K)	Time (h)	MPC conversion (%)	Yields (%)	
				DPC	AN
MoO_3/SiO_2	433	4	44.2	44.2	0.0
	433	7	48.2	48.2	0.0
	473	4	48.7	48.6	0.1
	473	7	51.3	51.0	0.2
MoO_2/SiO_2	433	4	13.8	13.8	0.0
MoO_3/Al_2O_3	433	4	23.1	12.3	10.5
$Y(OAc)_3$	433	4	36.7	33.6	3.1

DPC: diphenyl carbonate, AN: anisole. Catalyst = 0.2 g, MPC = 38.7 mmol.

tion (Eq. (2)). The yields given in Table 5 were based on the phenyl group.

Over 20 wt% MoO_3/SiO_2, the conversions of MPC at 433 K in 4 h and 7 h were 44.1% and 48.2%, respectively, and DPC and DMC were formed with a molar ratio of 1.0. The formation of anisole as a by-product was not observed at 433 K. The MPC conversions at 473 K in 4 h and 7 h were 48.7% and 51.3%, respectively. At this temperature, the selectivity for DPC formation was slightly lower than 100% because of the formation of a small amount of anisole. The equilibrium conversions of MPC are 49% and 51% at 433 K and 473 K, respectively. Therefore, the disproportionation proceeds to the equilibrium under the experimental conditions.

When a MoO_3/SiO_2 catalyst was reduced with hydrogen, the formation of MoO_2 was confirmed by XRD. In the presence of MoO_2/SiO_2, the MPC conversion was much lower (13%), indicating that MoO_3 is an active component, and that MoO_2 has much lower activity for the disproportionation.

When MoO_3 was supported on Al_2O_3, the activity was much lower than MoO_3/SiO_2 and an appreciable amount of anisole was formed, as in the case of the transesterification.

The result with $Y(OAc)_3/SiO_2$, which showed a high activity for the transesterification

Table 6
Effect of MoO_3 loading on SiO_2 on the catalytic activity for the disproportionation of methyl phenyl carbonate (MPC)

MoO_3 loading (wt%)	MPC conversion (%)	Yields (%)	
		DPC	AN
5	22.0	22.0	0.0
10	33.0	33.3	0.0
15	42.2	42.2	0.0
20	44.2	44.2	0.0
25	39.7	39.7	0.0

DPC: diphenyl carbonate, AN: anisole. Reaction temperature: 433 K, reaction time = 4 h, catalyst: 0.2 g, MPC = 38.7 mmol.

of DMC with phenol, is also listed in Table 5. It gave 33.6% DPC with a conversion of 36.7%.

3.2.2. Effect of MoO_3 loading on SiO_2

The effect of MoO_3 loading on a SiO_2 support is shown in Table 6. The sample of 20 wt% loading showed the highest activity, which was consistent with the results of transesterification of phenol with DMC. At every MoO_3 loading, anisole was not formed. Thus, the favorable MoO_3 content was around 20 wt%.

3.2.3. Regeneration of the used catalyst

When the reaction was carried out at 433 K for 4.0 h, the MPC conversion was 44.2%. After the reaction, the catalyst was separated by filtration and calcined at 823 K. Then, the reaction was carried out with the regenerated catalyst. The MPC conversion was 39.7%, indicating that the catalyst is basically regenerable.

3.2.4. Disproportionation with distillation

Since the disproportionation of MPC is an equilibrium process, the DPC yield can be increased by removing DMC from the system during the reaction. The reaction was carried out under the atmospheric pressure in the distillation apparatus, where DMC could be distilled off. A 66% MPC conversion was obtained at 463 K in 8.0 h.

4. Conclusions

MoO_3/SiO_2 showed a high activity and selectivity for the transesterification of DMC with phenol as well as the disproportionation of MPC into DPC and DMC. In the transesterification, the yields of methyl phenyl carbonate and diphenyl carbonate were 17.1% and 0.2%, respectively, in 4 h at 433 K. In the disproportionation, the conversion reached 48.2% in 7 h at 433 K. These values are very close to those at equilibrium estimated from the thermodynamics.

References

[1] W.F. Christopher and D.W. Fox, Polycarbonates (Reinhold Publishing Co., New York, 1962) p. 6.
[2] Kirk-Othmer, Encyclopedia of Chemical Technology, Vol 18 (1982) p. 487.
[3] M. Janatpour and S.J. Shafer, Eur. Pat. 228,672 (1987).
[4] A.-A.G. Shaikh and S. Sivaram, Ind. Eng. Chem. Res. 31 (1992) 1167.
[5] M. Komoritani and A. Horiguchi, Jpn. Kokai Tokkyo Koho, JP 93 123,579 (1993).
[6] T. Nakano, Jpn. Kokai Tokkyo Koho, JP 92 07,035 and 92 122,451 (1992).
[7] Belg. Pat. 1,006,062 (1994).
[8] H.J. Buysch, N. Schoen and J. Rechner, Eur. Pat. 560,169 (1993).
[9] S. Fukuoka, Jpn. Kokai Tokkyo Koho, JP 82 183,745 (1982).
[10] T. Onoda, K. Tano and Y. Hara, Jpn. Kokai Tokkyo Koho, JP 79 125,617 (1979).
[11] P. Tundo, F. Trotta, G. Molaglio and F. Ligorati, Ind. Eng. Chem. Res. 27 (1988) 1565.
[12] S. Fukuoka and R. Deguchi, Jpn. Kokai Tokkyo Koho, JP 91 200,736 and 91 236,354 (1991).
[13] S. Fukuoka, R. Deguchi and M. Tojo, US. Pat. 5,166,393 (1992).
[14] K.C. Patil, G.V. Chandrashekhar, M.V. George and C.N.R. Rao, Can. J. Chem. 46 (1968) 257.
[15] N. Yoshihara, T. Kitagawa, I. Ihara, S. Hasegawa and T. Hasegawa, Bull. Chem. Soc. Jpn. 65 (1992) 1185.
[16] K. Sukata, Bull. Chem. Soc. Jpn. 56 (1983) 3309.
[17] P. Braunstein, M. Lakkis, D. Matt and S. Lecolier, J. Mol. Catal. 42 (1987) 353.
[18] G. Barcelo, D. Grenouillat, J.-P. Senet and G. Sennyey, Tetrahedron 46 (1990) 1848.