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The Transesterification of Dimethyl Carbonate with Phenol over Mg−Al-hydrotalcite Catalyst

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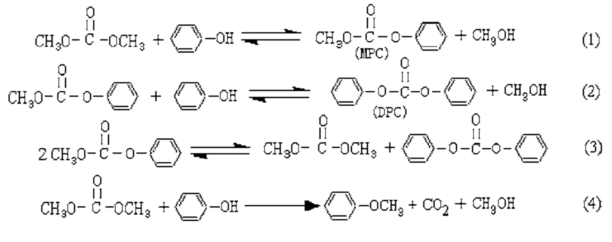
Abstract:

The production of diphenyl carbonate (DPC) by the transesterification of dimethyl carbonate (DMC) with phenol was performed using a variety of solid catalysts. Mg−Al-hydrotalcite was found to have a high activity for this transesterification. A 14.7% yield of DPC and an 11.6% yield of methylphenyl carbonate (MPC) based on DMC were obtained in the presence of Mg−Al-hydrotalcite catalyst. The optimum experimental temperature for this transesterification reaction was between 160 and 180 °C, which was in agreement with the thermodynamic analysis. When the transesterification of DMC with phenol was performed at the molar ratio of phenol to DMC of 2:1, reaction time 10 h, 1.0% of 2:1 Mg−Al-hydrotalcite based on the total weight of reactants, and 160−180 °C, the total yield and selectivity for DPC and MPC were 26.3 and 82.4%, respectively. The yield of anisole was 5.6%.

1. Introduction

Transesterification is an important organic transformation and provides essential synthons for a number of applications in organic processes.[1] The synthesis of aromatic carbonates from dimethyl carbonate (DMC) and phenols is one of the most important tranesterification reactions. It is thought to be the most effective method now, because DMC is achieving increasing importance and interest in the chemical industry, mainly for its versatility as both reagent and solvent and its nontoxicity for human health and the environment.[2] Meanwhile, aromatic carbonates, especially diphenyl carbonate (DPC), are precursors for the production of aromatic polycarbonates by the melt polymerization process which is now the highlight in the polycarbonate industry.[3]

The reactions of DMC with phenol involved in the transesterification reactions are shown in eqs 1−3, and the O-methylation reaction is showed in eq 4:



Tundo et al.[4] reported that the equilibrium constant for eq 1 was 3 × 10^{-4} at 180 °C. This indicates that the transesterification reactions are thermodynamically unfavorable, while the O-methylation reaction is thermodynamically favorable due to the production of gaseous CO_2. To overcome the thermodynamic limitation of the transesterification reactions, many processes have been proposed.[5−12] Catalysts are also very important for transesterification reactions. Traditionally, the homogeneous catalysts for the transesterification of DMC with phenol are Sn, Ti, Al, and Fe organometallic compounds,[13−16] the heterogeneous catalysts are mainly Mo, Ti, Si, and rare earth metal oxides.[17−20] The homogeneous catalysts are unstable and are not easy to separate from the products in this reaction system. The heterogeneous catalysts have low catalytic activities and selectivities. We have found that samarium trifluoromethanesulfonate is an efficient heterogeneous catalyst for the transesterification of DMC with phenol,[21] but it is expensive in commercial application. Therefore, it is desirable to find more efficient and cheap catalysts for transesterification of DMC with phenol in the application of commercial production.

Hydrotalcite-like compounds (HTLCs) consist of brucite-like layers with positively charged metal oxide or hydroxide layers with anions located interstitially. HTLCs catalyze many organic reactions, such as the aldol and Knoevenagel condensations,[22,23] Michael reactions,[24] cyanoethylation of alcohols[25] and nitroaldol reactions.[26] Watanabe and Tatsumi[27] found that hydrotalcite-type materials as base catalysts were

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efficient for the synthesis of dimethyl carbonate from ester exchange of ethylene carbonate and methanol. In this contribution on the basis of our studies on the transesterification of DMC with phenol, we explored Mg−Al-hydrotalcite as catalyst in the transesterification of DMC with phenol and found it was efficient for the transesterification reactions.

2. Experimental Section

2.1. Reagents. DMC (Ube Chemicals, Japan) was fractionally distilled and stored over molecular sieves (4Å). Phenol was of laboratory reagent grade and subjected to drying and purification by a standard procedure.[28] TiO_2/SiO_2 and MoO_3/SiO_2 were prepared according to the literature.[17] MgO, α-Al_2O_3, and Sm_2O_3 were used as received.

2.2. Preparation of Mg−Al, Calcined Mg−Al-hydrotalcites. The Mg−Al−NO_3-hydrotalcite (Mg−Al-HT) with 2:1 atom ratio of Mg to Al was prepared in a nitrogen atmosphere to avoid carbonation in air. Magnesium nitrate hexahydrate (20.5 g, 0.08 mol) and aluminum nitrate nonahydrate (15.0 g, 0.04 mol) were dissolved in 100 mL of deionised and decarbonated water. The pH of the solution was adjusted to 11.5 by the addition of NaOH (4 M). The slurry was stirred for 2 h under nitrogen at room temperature and then was crystallized for 48 h at 80 °C and filtered under nitrogen and dried under vacuum at 80 °C to get Mg−Al−NO_3-hydrotalcite. Calcined Mg−Al-hydrotalcite was prepared by calcination of Mg−Al-hydrotalcite at 500 °C for 12 h. The particle sizes of Mg−Al-hydrotalcites were 80−90 mesh.

2.3. Typical Procedure of the Synthesis of DPC. The reaction was carried out in a 250-mL three-necked round-bottomed flask equipped with a nitrogen inlet, a thermometer, and a fractionating column (30 cm in length, 3 cm in diameter, filled with small glass beads) connected to a liquid dividing head. In a typical experiment, under nitrogen gas, 47.0 g (0.5 mol) phenol, 22.5 g (0.25 mol) DMC, and 0.7 g Mg−Al-hydrotalcite were added to the flask, with stirring and slowly increasing temperature. When the temperature was about 140 °C, the occurrence of reaction was indicated by the attainment of a temperature 62−63 °C at the top of the column, which corresponded to the 70:30 boiling azeotrope of methanol and DMC. This azeotrope was analyzed by GC once an hour to measure the amount of MeOH and to determine the extent of reaction. The temperature was kept between 160 and 180 °C. The reaction mixture was under refluxing condition between 160 and 180 °C. After filtration to recover the catalyst, the reaction mixture was analyzed by GC−MS.

2.4. Analysis. The structures of Mg−Al-hydrotalcites were characterized by XRD (Rigaku D/MAX-3B). The absolute contents of intercalated NO_3^- and CO_3^{2-} in samples were measured by CHN analysis (CHN-600 Analyzer, LECO). The amount of OH^- was estimated as a balance on the assumption that NO_3^-, CO_3^{2-}, and OH^- neutralize the electric charge on the brucite-like layers. TG-DSC (PEAKIN-ELMER) analysis of Mg−Al-hydrotalcites was performed.

Table 1. **Thermodynamic properties in the transesterification of DMC with phenol at atmospheric pressure**

T/°C	$\Delta_r H_m^0$ kJ·mol^{-1}	$\Delta_r S_m^0$ J·mol^{-1}·K^{-1}	$\Delta_r G_m^0$ kJ·mol^{-1}	K_{eq}
25	64.4	−3.6	65.4	3.5×10^{-12}
100	49.6	65.3	25.2	2.9×10^{-4}
150	45.9	56.0	22.2	1.8×10^{-3}
180	43.0	49.1	20.8	4.0×10^{-3}
220	−45.2	−146.1	26.8	1.4×10^{-3}
250	−41.2	−133.9	28.8	1.3×10^{-3}

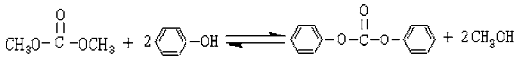
Table 2. **Thermodynamic properties in the O-methylation of phenol with DMC at atmospheric pressure**

T/°C	$\Delta_r H_m^0$ kJ·mol^{-1}	$\Delta_r S_m^0$ J·mol^{-1}·K^{-1}	$\Delta_r G_m^0$ kJ·mol^{-1}	K_{eq}
25	25.9	192.9	−32.6	5.1×10^{5}
100	10.7	151.1	−45.7	2.5×10^{6}
150	13.4	158.2	−53.5	4.1×10^{6}
180	52.5	247.6	−59.7	7.6×10^{6}
220	10.7	154.9	−65.7	9.1×10^{6}
250	14.8	165.6	−71.8	1.5×10^{7}

The distillates during reaction and product mixture were analyzed by gas chromatography (HP 6890) and mass spectroscopy (HP 5973).

3 Results and Discussion

3.1. Thermodynamic Analysis. The stoichiometric equation for the transesterification of DMC with phenol is as follows:



(5)

The thermodynamic properties for reactions 5 and 4 were calculated on the basis of references[29−31] and are shown in Tables 1 and 2.

As shown in Table 1, at temperatures below 180 °C, the transesterification reaction 5 is endothermic, and the equilibrium constant (K_{eq}) increases with increase of temperature. Above 180 °C, phenol is vaporized, and reaction 5 becomes exothermic. Between 150 and 250 °C, K_{eq} remains almost unchanged. Thus, the suitable temperature for reaction 5 should be 150−180 °C. As the reaction 4 is endothermic, a higher temperature is preferable for this reaction (see Table 2). The thermodynamic data in Tables 1 and 2 show that the reaction of transesterification of DMC with phenol is thermodynamically unfavorable even at 250 °C, while the reaction of O-methylation of phenol with DMC is thermodynamically favorable at room temperature. Thus, to choose

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Table 3. **Catalytic activity of Mg−Al-hydrotalcite**[a]

catalysts	DMC conv./%	DPC yield/%	MPC yield/%	anisole yield/%	transesterification selectivity[b]/%
Mg−Al-HT	31.9	14.7	11.6	5.6	82.4
MoO_3/SiO_2	7.3	1.2	5.2	0.9	87.7
TiO_2/SiO_2	8.5	1.4	4.8	2.3	72.9
Sm_2O_3	6.6	2.7	3.6	0.3	95.5

[a] Reaction conditions: phenol 47.0 g, DMC 22.5 g, catalyst 0.7 g, 160−180 °C, 10 h. The particle sizes for solid catalysts are 80−90 mesh. [b] Transesterification selectivity: $\frac{\text{(DPC yield + MPC yield)}}{\text{DMC conversion}} \times 100\%$.

Table 4. **Catalytic activities of solid bases**[a]

catalysts	DMC conv./%	DPC yield/%	MPC yield/%	anisole yield/%	transesterification selectivity[c]/%
Mg−Al-HT	31.9	14.7	11.6	5.6	82.4
calcined Mg−Al-HT	15.0	7.5	1.3	6.2	58.7
$MgO-Al_2O_3$[b]	2.9	1.2	0.3	1.4	51.7
$MgO-Al_2O_3$[c]	2.2	0.6	0.1	1.5	31.8
MgO	3.3	1.2	0.4	1.7	48.5
α-Al_2O_3	0.9	0.5	0.2	0.2	77.8

[a] Reaction conditions: phenol 47.0 g, DMC 22.5 g, catalyst 0.7 g, 160−180 °C, 10 h. [b] MgO and α-Al_2O_3 were physically mixed according to $n_{(Mg)}:n_{(Al)} = 2:1$. [c] MgO and α-Al_2O_3 were physically mixed then calcined at 500 °C in air.

suitable catalysts and to design an efficient reaction process are the keys to increasing the yield and selectivity of the transesterification products DPC and MPC.

3.2. The Catalytic Activity of Mg−Al-hydrotalcite. Fu and Ono[17] reported that MoO_3/SiO_2 was an efficient catalyst for the transesterification of DMC with phenol to MPC and the disproportionation of MPC to DPC and DMC in an autoclave. Kim and Lee[18] found that supported TiO_2 was also an active and selective catalyst for the transesterification of DMC with phenol to MPC in an autoclave. The catalytic activity of Mg−Al-hydrotalcite is compared to catalytic activities of these heterogeneous catalysts in a refluxing batchwise reactor. The results are shown in Table 3.

As seen in Table 3, Mg−Al-hydrotalcite is a much more active heterogeneous catalyst for the transesterification of DMC with phenol than MoO_3/SiO_2, TiO_2/SiO_2, and Sm_2O_3. The double-layered hydroxide structure in Mg−Al-hydrotalcite which makes it easy to abstract hydrogen of phenol to form phenoxide seems to be responsible for the higher catalytic activity for the transesterification of DMC with phenol. For MoO_3, TiO_2, and Sm_2O_3, a phenol molecule dissociatively absorbs to coordinate to the surface molybdenum, titanium, or samarium to be activated.[17] This process makes it difficult to abstract hydrogen of phenol to form phenoxide.

Under the same reaction conditions, calcined Mg−Al-HT, $MgO-Al_2O_3$, MgO and α-Al_2O_3 were tested as catalysts in the reaction of DMC with phenol. The results are given in Table 4.

The strong Bronsted basic sites (hydroxyl groups) in double layers of Mg−Al-HT[27] lead to the high catalytic activity for transesterification of DMC with phenol. The calcined Mg−Al-hydrotalcite is a Mg−Al mixed oxide. The presence of coordinatively unsaturated O^{2-} ions acting as Lewis basic sites in calcined hydrotalcite may be responsible for their activities.[32]

Table 5. **Effect of atom ratio of Mg−Al on the yield of DPC**[a]

Mg:Al	DMC conv./%	DPC yield/%	MPC yield/%	anisole yield/%	transesterification selectivity/%
1:1	21.1	9.6	3.8	7.7	63.5
2:1	31.9	14.7	11.6	5.6	82.4
3:1	39.5	12.9	3.6	23.0	41.8
4:1	35.6	12.2	7.0	16.4	53.9
5:1	40.2	12.8	4.9	22.5	44.0
6:1	26.1	9.9	5.3	10.9	58.2

[a] Reaction conditions: phenol 47.0 g, DMC 22.5 g, catalyst 0.7 g, 160−180 °C, 10 h.

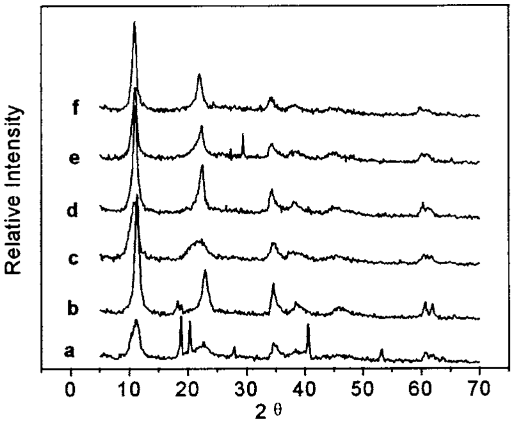

Figure 1. **Effect of molar ratio of Mg to Al. Preparation conditions of Mg−Al-hydrotalcites: under nitrogen atmosphere, pH of the solution 11.5, crystallization time 48 h at 80 °C. Spectra a, b, c, d, e, f are corresponding to $n_{(Mg)}/n_{(Al)} = 1, 2, 3, 4, 5, 6$, respectively.**

3.3. The Effect of Atom Ratio of Mg to Al in Hydrotalcite. The different atom ratio of Mg−Al in hydrotalcite is related with the catalytic activity of Mg−Al in hydrotalcite. The effect of this ratio on the transesterification of DMC with phenol is given in Table 5.

It was reported that the amount of basicity on hydrotalcite-type materials increased with decreasing concentration of Al in the brucite-like layers.[33] For 1:1 and 6:1 Mg−Al-hydrotalcites, although they have higher selectivities for transesterification, the transesterification yield is lowest (see Figure 1). This shows that the highest or lowest basicity for Mg−Al-hydrotalcite is not favorable for the transesterification of DMC with phenol. Mg−Al-hydrotalcite with a 2:1 atom ratio of Mg to Al has the highest catalytic activity, while Mg−Al-hydrotalcites with 3:1 to 5:1 Mg/Al catalyze O-methylation of phenol with DMC more favorably. These results indicate that Mg−Al-hydrotalcite with moderate basicity performs good catalytic activity for the transesterification of DMC with phenol. The XRD pattern for 2:1 Mg−Al-hydrotalcites consists of sharp and symmetrical peaks, being characteristic of a layered structure and similar to the

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Table 6. **Effect of molar ratio of phenol to DMC**[a]

n(phenol):n(DMC)	DMC conv./%	DPC yield/%	MPC yield/%	anisole yield/%	transesterification selectivity/%
1:2	3.8	0.5	1.7	1.6	57.9
1:1	20.0	6.1	6.4	7.5	62.5
2:1	31.9	14.7	11.6	5.6	82.4
3:1	26.1	10.8	9.5	5.8	77.8
4:1	13.6	6.1	4.3	3.2	76.5

[a] Reaction conditions: 2:1 Mg−Al-hydrotalcite 0.7 g, 160−180 °C, 10 h. The total amounts of DMC and phenol are constant.

XRD pattern of 1.8:1 Mg−Al-hydrotalcite reported in the literature.[27]

3.4. The Effect of Temperature. As the reaction of transesterification of DMC with phenol is thermodynamically unfavorable and endothermic, it should proceed at high temperature to increase the yields for DPC and MPC. Experimentally, the transesterification reaction initiates at 160 °C, as indicated by the presence of MPC and DPC in the flask, DMC and methanol at the top of distillation column. The temperature was gradually increased from 160 to 180 °C in about 10 h. During this period, methanol was very slowly removed from the reaction system. The removal of methanol out of reaction system could shift the reaction to the direction of MPC and DPC. The reaction was also performed under refluxing conditions between 160 and 180 °C due to the existence of excess amount of phenol. Under refluxing conditions, Mg−Al-HT activates phenol to form the active intermediate (PhO^-) which nucleophilically attacks the carbonyl group in DMC to produce methylphenyl carbonate (MPC). Another PhO^- continuously reacts with MPC to produce DPC. Fukuda and McIver[34] found that the reaction at the carbonyl group was enhanced by the presence of solvent. DMC is both reagent and solvent under refluxing conditions in this reaction. Memoli et al.[35] also thought that the transesterification of DMC with phenol prevailed over the O-methylation of phenol with DMC under refluxing conditions. Therefore, the suitable temperature range for the transesterification of DMC with phenol is 160−180 °C, which is in agreement with the thermodynamic analysis (150−180 °C).

3.5. The Effect of Molar Ratio of DMC to Phenol on the Synthesis of DPC. The effect of molar ratio of phenol to DMC on the transesterification of DMC with phenol is shown in Table 6.

When the molar ratio of phenol to DMC is 2:1 and 3:1, the yields and selectivities of DPC and MPC are higher, but the former is highest. Although the molar ratio 2:1 of phenol to DMC is stoichiometric according to eq 5, the amount of phenol is slightly in excess compared with the amount of DMC due to the discharge of a little amount of DMC from the flask with methanol during reaction. This result shows that a little excess amount of phenol can enhance the transesterification. In addition, the excess of phenol can decrease the discharge of DMC and keep a high temperature in the flask. But the large excess of phenol [n(phenol): n(DMC) = 4:1] may cause a higher acidity in the reaction mixture, which is unfavorable for the transesterification. The excess of DMC leads to vaporisation of DMC easily from 160 to 180 °C. The vapor-phase reaction of DMC with phenol is favorable for producing anisole by O-methylation of phenol with DMC.[36]

Table 7. **Effect of reaction time on transesterification**[a]

time/h	DMC conv./%	DPC yield/%	MPC yield/%	anisole yield/%	transesterification selectivity/%
7	21.8	9.2	7.8	4.8	78.0
10	31.9	14.7	11.6	5.6	82.4
12	33.2	17.2	7.5	8.5	74.4
16[b]	32.7	13.5	4.2	15.0	54.1

[a] Reaction conditions: phenol 47.0 g, DMC 22.5 g, 2:1 Mg−Al-hydrotalcite 0.7 g, 160−180 °C. [b] Reaction temperature 160−190 °C.

3.6. Effect of Reaction Time on Transesterification. Because the transesterification of DMC with phenol is reversible and the reaction rate is slow, the effect of reaction time on it was studied. The results are given in Table 7.

The data indicate that after 10 h, the conversion of DMC does not change very much, but the yields of DPC, MPC, and anisole do change. After 10 h, the temperature reached approximately 180 °C, and the disproportionation of MPC to DMC and DPC over Mg−Al-hydrotalcite caused the increase in the yield of DPC and the decrease in the yield of MPC, from 10 to 12 h. After 12 h, the temperature increased further, DMC and phenol were vaporized, the vapour-phase reaction of DMC with phenol increased the O-methylation reaction,[36] and subsequently the yield of anisole increased. The decarboxylation of MPC and DPC at higher temperatures also led to decreases in the yields of MPC and DPC. Therefore, the best reaction time for the transesterification of DMC with phenol over Mg−Al-hydrotalcite is from 10 to 12 h.

4. Conclusions

For the transesterification of DMC with phenol, Mg−Al-hydrotalcites were found effective as catalysts. When the reaction was carried out between 140 and180 °C, with a molar ratio of phenol to DMC of 2:1, a reaction time 10 h, the yield and selectivity for transesterification reaction were 26.3 and 82.4%, respectively, over 2:1 Mg−Al-hydrotalcite. Mg−Al-hydrotalcites are cheap, easy to prepare, and separate from the products, and they are also reusable; thus, they have great potential in the application of transesterification reactions.

Note Added after ASAP Publication: In the version published on the Internet 4/17/2004, the names of some authors were inadvertently omitted from a few references. The final version published 4/23/2004 and the print version are correct.

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