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# Dispersion and Catalytic Activity of $MoO_3$ on $TiO_2$-$SiO_2$ Binary Oxide Support

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*The authors present results of an investigation into the dispersion of $MoO_3$ on $TiO_2$-$SiO_2$ composite and its reactivity in transesterification of dimethyl oxalate (DMO) with phenol to produce methyl phenyl oxalate (MPO) and diphenyl oxalate (DPO). They examined the effects of support composition, $MoO_3$ content, and reaction time on activities of the transesterification. The results show that $MoO_3/TiO_2$-$SiO_2$ is more active and selective than $MoO_3/TiO_2$, $MoO_3/SiO_2$, and $TiO_2/SiO_2$ catalysts in the transesterification reaction. The best catalytic performance is obtained over a 12%$MoO_3$/8%$TiO_2$-$SiO_2$, providing a 71.8% DMO conversion and 59.0%, 40.1% selectivities for MPO and DPO, respectively. Through employing X-ray diffraction and inductively coupled plasma-optic emission spectrometry, they show evidence strongly suggesting that improvement of catalytic reactivity over the $TiO_2$-modified $SiO_2$ support can be ascribed to the enhanced metal oxide support interactions and the increased dispersion capacity of $MoO_3$ phase. They also present evidence showing that incorporation of $TiO_2$ in $SiO_2$ can elevate the monolayer dispersion capacity of $MoO_3$ on $SiO_2$. Thus, they conclude that increased DPO selectivity from $MoO_3/TiO_2$-$SiO_2$ catalysts can be primarily attributed to the improvement of $MoO_3$ dispersion and the synergistic effect between amorphous $MoO_3$ and amorphous $TiO_2$.* © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 741–749, 2008

*Keywords: diphenyl carbonate, diphenyl oxalate, methyl phenyl oxalate, transesterification, dimethyl oxalate, slurry impregnation, supported $MoO_3$ catalyst, $TiO_2$-$SiO_2$ composite, amorphous*

## Introduction

Polycarbonates (PCs) resins are important engineering thermoplastics with excellent mechanical, optical, electrical, and heat resistance properties.[1] Currently, the worldwide production capacity of PCs is more than 1.5 million ton/year, and construction of new PC plants is very likely to continue.[2,3] PCs have been commercially produced by the interfacial polycondensation of bisphenol-A with phosgene. One of the major disadvantages of the conventional phosgene process from environmental point of view is the use of copious amount of methylene chloride as the solvent, about 10 times products weight, and highly toxic phosgene as a reagent.

Recently, there has been increasing demand for improvement or essential replacement of those processes, which place burden on the environment, by more environmentally friendly or compatible processes for PC synthesis. One of the

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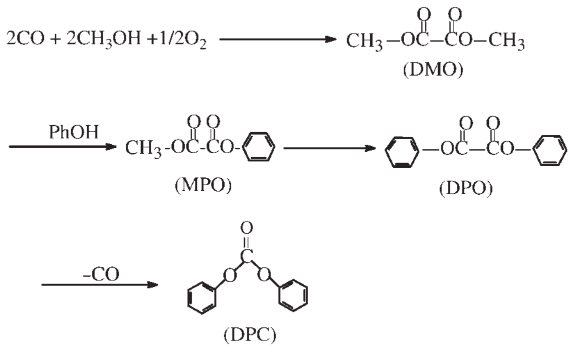
most practical processes is the synthesis of diphenyl carbonate (DPC) followed by transesterification of DPC with bisphenol-A.[4] In this process, no toxic solvents are used and the by-product, phenol, can be recycled. Unfortunately, commercially DPC is prepared by the reaction of phenol and phosgene in the presence of bases such as sodium hydroxide.[5] Obviously, this traditional process for DPC has the same environmental concerns as mentioned above due to the use of phosgene. Thus, in order to produce PCs without social effects of pollution, the key technology is preparation of DPC via a green process.

Among several developed or proposed alternative nonphosgenated approaches for DPC synthesis,[6–17] the transesterification of dimethyl oxalate (DMO) with phenol to prepare diphenyl oxalate (DPO), followed by the decarbonylation of DPO to produce DPC, is a promising route due to the high efficiency, the use of nontoxic feedstock, and no hazard to the environment.[18,19] Additionally, the coproducts, methanol and CO, can be separated easily and be reused in the DMO production via oxidative carbonylation of methanol[20,21] as shown in reaction 1.



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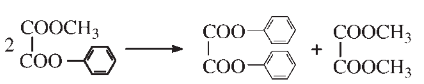

(3)

For synthesis of DPC from the transesterification of DMO with phenol, the decarbonylation of DPO to produce DPC could be carried out easily over a $PPh_4Cl$ catalyst, and the yield of DPC is up to 99.5%.[22,23] Moreover, the synthesis of DPO from the transesterification of phenol with DMO follows a two-step reaction consisting of the transesterification of DMO with phenol into methyl phenyl oxalate (MPO), followed by the production of DPO via the disproportionation of MPO, as shown in the reactions 2 and 3.

A wide variety of catalytic systems (primarily homogeneous) have been proposed for the transesterification reaction.[18,19] Considering the disadvantages of separation and regeneration of catalysts and the potential environmental effects caused by using homogeneous catalysts, development of active solid catalysts with excellent catalytic performance is highly desirable. Supported $MoO_3$ is an important catalyst or a catalyst precursor in a number of industrially relevant reactions.[24–28] Recently, it has attracted much attention due to its good performance in the transesterification of DMO with phenol.[16] Since the type of support plays an important role on catalytic properties, for a given reaction, activity and selectivity of the catalyst can be improved by using an appropriate support oxide.[27] In our previous study,[29] we presented results of investigations on various $MoO_3$ catalysts supported on alumina, active carbon, and silica with different $MoO_3$ loadings in the transesterification reactions and showed that $MoO_3/SiO_2$ performed best. However, DPO selectivity and yield are not very satisfactory from industrialized point of view. Therefore, development of active solid catalysts that combine good catalytic activity with desirable DPO selectivity is necessary.

On the basis of abundant literature evidence, it is well established that supported $MoO_3$ catalyst is one kind of so-called monolayer-dispersed systems and coverage of active component in a catalyst is closely correlated with catalytic activity. The optimized content of active component is usually close to its monolayer dispersion capacity, which has been discussed previously over a $MoO_3/SiO_2$.[16,30] Poor dispersion of active metal oxide, $MoO_3$, on the $SiO_2$ surface was observed, which can be ascribed to the weak interaction between the $MoO_3$ and the $SiO_2$ support.[30] As a matter of fact, $TiO_2$ shows strong interaction with transition metal oxides and is a representative of strong metal-support interaction support.[31] Furthermore, Xie et al. showed that highly dispersed titanium on silica can improve the interaction between $MoO_3$ and $SiO_2$ and increase the dispersion capability of $MoO_3$ on $SiO_2$.[32–34] On the other hand, as shown previously, besides $MoO_3/SiO_2$, $TiO_2/SiO_2$ is another active and stable catalysts system with alike performance in the transesterification reaction (e.g., high DMO conversion with low DPO selectivity).[35,36] Moreover, supported $MoO_3$ catalysts on $TiO_2$-$SiO_2$ and other composite supports have been attempted in a number of industrially important catalytic reactions such as hydrodesulfurization of dibenzothiophenes,[37] isomerization of butanes,[38] dehydration of cyclohexanol,[39] and selective catalytic reduction of $NO_x$.[40] High activity and selectivity are usually provided by a catalyst consisting of two or more mixed oxides as a composite support. These facts give us some credence to the possibility that highly dispersed $MoO_3$ on $TiO_2/SiO_2$ ($MoO_3/TiO_2$-$SiO_2$) provides a preferable performance in the transesterification reaction.

Therefore, in this article, we present results on the dispersion of $MoO_3$ over $TiO_2$-$SiO_2$ binary oxide and its reactivity in transesterification of DMO with phenol. We prepared a $TiO_2$-$SiO_2$ composite by conventional impregnation, where titania over-layers are coated on silica supports. Also, from an environmental point of view, the active component $MoO_3$ was supported on $TiO_2$-$SiO_2$ composite by slurry impregnation, which is an environmentally friendly process and a simple, clean, effective alternative to the conventional preparation using a solution of $(NH_4)_6Mo_7O_{24}$ (ammonium heptamolybdate, AHM).[29,41,42] In identification of $TiO_2$-containing support that would promote the catalytic efficiency by enhancing interactions of $MoO_3$ with support and further improving dispersion of $MoO_3$, $MoO_3/TiO_2$-$SiO_2$ catalysts with different support compositions were characterized by X-ray diffraction (XRD) and inductively coupled plasma-optic emission spectrometry (ICP-OES).

## Experimental

### *Catalyst preparation*

Commercial $SiO_2$ (average particle size 0.2–0.3 mm) and $TiO_2$ are used as the supported materials. Before impregnation they were calcined at 393 K for 2 h. This treatment results in $SiO_2$ and $TiO_2$ with surface areas of 231 and 4 $m^2/g$, respectively, as measured by nitrogen adsorption.

The $TiO_2$-$SiO_2$ binary oxide support was prepared by a conventional impregnation method with an excess ethanol solution of $Ti(OBu)_4$. For this purpose, 15 g of the silica support was impregnated with about 100 mL of the salt solution until dry. After impregnation, the samples were dried and calcined in a muffle furnace at 393 K for 4 h and then 823 K for 5 h. The $TiO_2$-$SiO_2$ composite are given in weight percentage based on $TiO_2$ content [$TiO_2/(TiO_2+SiO_2)$] and labeled as 2%Ti-Si, 4%Ti-Si, 8%Ti-Si, 10%Ti-Si, and 12%Ti-Si, respectively.

$MoO_3$ was ground in an agate mortar before use. Mixtures of the appropriate amount of $MoO_3$, support (Ti-Si, pure $SiO_2$, or pure $TiO_2$), and an excess amount of distilled water were prepared in a set of rotary flasks. Each mixture was heated under a rotary evaporator to 363 K for several hours depending on the loading amount, for example, for a 16 wt % $MoO_3$, the sample is heated for ~24 h until fine gray powder of $MoO_3$ disappears. After impregnation, the water was vacuum-removed at 353 K until dry followed by calcining samples in a muffle furnace at 433 K for 6 h. $MoO_3$ nominal loadings are varied in a range of 1–20 wt %. The composition of $MoO_3$ is expressed in wt % of $MoO_3$ based on the weight percentage of $MoO_3$ content [i.e., $MoO_3/(MoO_3+\text{support})$]. The resultant catalysts are named as $MoO_3$/Ti-Si, $MoO_3/SiO_2$, and $MoO_3/TiO_2$, respectively.

### *Transesterification of DMO with phenol*

The reaction was conducted in a 250-mL glass flask equipped with a thermometer, a distillation apparatus, and a stirrer under refluxing condition at atmospheric pressure. The top of distillation column was kept at 353 K by flowing recycled hot water through it to remove methanol from the reaction system. Thus, the reaction equilibrium limitation in reaction 2 is broken and the reaction is accelerated in the desired direction. The reaction mixture contained 0.1 mol DMO, 0.3 mol phenol, and 1.8 g catalyst. After the raw materials and catalyst were placed into the batch reactor, nitrogen gas was flowed at 30 SCCM to purge air from the reaction system. After 10 min, nitrogen flow was stopped and the flask was heated at a rate of 8 K/min. The reaction was conducted at 453 K at atmospheric pressure. Qualitative and quantitative analyses of reaction products and distillates were carried out on an HP5890-HP5971MSD and a SP3420 gas chromatogram equipped with a flame ionization detector. A HP-5 capillary column (Hewlett-Packard Company, 15 m × 0.53 mm × 1.5 $\mu$m) was used to separate products for GC analysis. The products were predominantly DPO, MPO, and anisole (AN). An internal standard qualitative analysis method was used, where ethyl benzoate was chosen as an internal standard material. The conversions were reported on the basis of the limiting reagent, DMO, and defined as the ratio of the moles of converted DMO to the moles of DMO fed initially to the reactor. The selectivities for MPO and DPO were defined as the moles of MPO and DPO produced per 100 mol of consumed DMO, while the yields of MPO and DPO were obtained from multiplication of DMO conversion by the selectivities to MPO and DPO, respectively. The experimental uncertainties based on reactivity measurements are ~3%.

### *Catalysts characterization*

Powder XRD crystalline phases were determined at room temperature. A diffractometer (PANalytical X'Pert Highscore, Holland) equipped with a Co Ka radiation anode ($k$ = 1.78901 Å, 40 kV, and 40 mA) was used for these measurements. Intensity data were acquired by step scanning with a scanning rate of 12°/min from $2\theta = 5°$ to $2\theta = 80°$.

Further elemental analysis of catalysts performed on an ICP-OES (Varian Vista-MPX) was operated at a high frequency emission power of 1.5 kW and a plasma airflow of 15.0 L/min ($\lambda_{Si}$ = 251.611 nm, $\lambda_{Mo}$ = 202.032 nm, $\lambda_{Ti}$ = 336.122 nm). Samples were dissolved in the hydrofluoric acid solution (40%) first, followed by dilution with a boracic acid aqueous solution.

## Results and Discussion

### *Activities of oxide catalysts and conventional ester exchange catalysts*

Table 1 shows the catalytic activities of different catalysts for the transesterification of DMO with phenol. Initially, in the absence of any catalysts, no yield of DPO was achieved and only a trace amount of DMO was converted (entry 1). This result suggests that it is difficult for direct transesterification to shift the equilibrium from the raw materials to the products. It is interesting that, for $SiO_2$, despite low DMO conversion observed (1.7%), 100% selectivity to MPO is obtained. Moreover, as shown previously, catalytic efficiency of metal oxides can be promoted when the formation of AN is suppressed by using $SiO_2$ as a support (entries 2–10).[16,29,43,44] It is notable that, although $TiO_2$ support has a small surface area of 4 $m^2/g$, the $MoO_3/TiO_2$ shows significant activity (59.5% of DMO conversion) and selectivity (88.1%, 11.4% for MPO and DPO, respectively) (entry 11). Another issue we need to address here is that, as reported elsewhere,[44] we used $SnO_2$ as an additive and found that $SnO_2$ could promote the catalytic performance of $MoO_3/SiO_2$ (entries 6,8). Indeed, the DMO conversion markedly increased over $MoO_3$–$SnO_2/SiO_2$ catalysts, whereas the selectivity to DPO was still unsatisfactory with different Mo:Sn mass ratios.[44] As shown in entry 10, $MoO_3$/Ti-Si catalyst shows best catalytic efficiency among all the supported active solid catalysts (entries 6–11). It motivates us to further explore and discuss the effect of $MoO_3$ and $TiO_2$ contents on catalytic activities in the transesterification of DMO with phenol over $MoO_3$/Ti-Si catalysts.

For purpose of comparison of catalytic activities between conventional homogeneous catalysts and solid catalysts

Table 1. Acticities of Various Catalysts for the Transesterification of Dimethyl Oxalate with Phenol*

| Entry | Catalysts | Conversion[†] (%) | Selectivity (%) AN | Selectivity (%) MPO | Selectivity (%) DPO | Yield (%) MPO | Yield (%) DPO |
|---|---|---|---|---|---|---|---|
| 1 | None | 1.3 | 0 | 82.1 | 17.9 | 1.1 | 0.2 |
| 2 | $MoO_3$[‡] | 54.1 | 2.1 | 42.7 | 13.0 | 23.1 | 7.0 |
| 3 | $SnO_2$ | 2.8 | 7.2 | 57.1 | 35.7 | 1.6 | 1.0 |
| 4 | $SiO_2$ | 1.7 | 0 | 100 | 0 | 1.7 | 0 |
| 5 | $TiO_2$ | 32.1 | 0.6 | 79.9 | 19.5 | 25.7 | 6.3 |
| 6 | $SnO_2/SiO_2$[§] | 46.7 | 0.8 | 76.7 | 22.5 | 35.8 | 10.5 |
| 7 | $MoO_3/SiO_2$[¶] | 39.0 | 0.9 | 88.2 | 10.9 | 34.4 | 4.2 |
| 8 | $MoO_3$-$SnO_2/SiO_2$[**] | 56.7 | 0.6 | 86.7 | 12.7 | 49.1 | 7.2 |
| 9 | $TiO_2/SiO_2$[††] | 54.5 | 0.8 | 81.8 | 17.4 | 44.6 | 9.5 |
| 10 | $MoO_3/TiO_2$-$SiO_2$[‡‡] | 69.2 | 0.8 | 66.9 | 32.3 | 46.3 | 22.4 |
| 11 | $MoO_3/TiO_2$[§§] | 59.5 | 0.5 | 88.1 | 11.4 | 52.5 | 6.8 |
| 12 | $Ti(OBu)_4$[¶¶] | 92.5 | 0 | 20.6 | 2.8 | 19.0 | 2.6 |
| 13 | $SnOBu_2$[¶¶] | 25.7 | 2.2 | 80.8 | 12.5 | 20.8 | 3.2 |
| 14 | $C_{32}H_{64}O_4Sn$[¶¶] | 54.1 | 1.8 | 21.0 | 13.7 | 11.4 | 7.4 |

*Reaction conditions: catalyst 1.8 g (except homogeneous catalyst 0.01 mol), phenol 0.5 mol, DMO 0.1 mol, reaction time 2 h, and reaction temperature 453 K.

[†] Based on DMO converted.

[‡] Benzyl alcohol and methyl phenol were formed as main by-products besides anisole.

[§] $SnO_2$ was supported on $SiO_2$ in 13% weight.

[¶] $MoO_3$ was supported on $SiO_2$ in 15% weight.

[**] $MoO_3$ and $SnO_2$ were supported on $SiO_2$ in 15 and 13% weight, respectively.

[††] $TiO_2$ were supported on $SiO_2$ in 10% weight.

[‡‡] $MoO_3$ and $TiO_2$ were supported on $SiO_2$ in 16% and 10% weight.

[§§] $MoO_3$ was supported on $TiO_2$ in 4% weight.

[¶¶] Conventional homogeneous catalysts for the transesterification of DMO with phenol.

MPO, methyl phenyl oxalate; DPO, diphenyl oxalate; AN, anisole.

studied in this article, we also tested reactivities of homogeneous $Ti(OBu)_4$, $SnOBu_2$, and $C_{32}H_{64}O_4Sn$ catalysts and the results are shown in entries 12–14.[17] Generally, they were somewhat effective for the transesterification reaction, but the selectivities for MPO and DPO were relatively low. Moreover, as we mentioned earlier, an issue brought out by a homogeneous system that we need to concern is to separate catalyst from products.

### *Effect of $TiO_2$ content on the activity of the transesterification of DMO with phenol*

A series of batch tests were carried out for different sample with the same $MoO_3$ nominal loading (16 wt %) but different $TiO_2$ nominal content ranging from 2 to 12 wt % and the results are shown in Table 2. Generally, $MoO_3$/Ti-Si catalysts exhibit excellent catalytic activities along with high DPO selectivity with different $TiO_2$ contents compared with $MoO_3/SiO_2$ catalyst. Under the same experimental conditions, a 16%$MoO_3/SiO_2$ catalyst provides 61.8% DMO conversion contrasting with 70.9%, the DMO conversion offered by a 16%$MoO_3$/8%Ti-Si catalyst. Further, a low DPO yield of 10.7% is observed using 16% $MoO_3/SiO_2$, whereas the 16%$MoO_3$/8%Ti-Si catalyst produces a much higher DPO yield (27.6%). It is notable that total selectivities for MPO and DPO keep around 99% all along for both $MoO_3/SiO_2$ and $MoO_3$/Ti-Si catalysts.

The results shown in Table 2 also demonstrate that, in the case of $MoO_3$/Ti-Si catalyst, DMO conversion increased with the $TiO_2$ content ranging from 2 to 8 wt %, followed by a decrease to 66.7% at a 12 wt % $TiO_2$ content. The optimized $TiO_2$ loading is determined to be 8 wt % based on the amount of DMO converted (70.9%). It is notable that the selectivity and yield of DPO increase remarkably with the addition of $TiO_2$ below 8 wt %. The maximum value of 38.9% and 27.6% (DPO selectivity and yield) are reached at 8 wt % $TiO_2$ content. Interestingly, the selectivity and yield of MPO show almost an opposite trend compared with those of DPO, indicating that much more MPO are converted into DPO over a $MoO_3$/8%Ti-Si catalyst. Accordingly, these reactivity data show a distinct turning point (at 8 wt % $TiO_2$ content), which may be related to a so-called threshold effect.[32]

Table 2. Effect of $TiO_2$ Content on the Activity of Transesterification of DMO with Phenol*

| Catalysts | Conversion[†] (%) | Selectivity (%) AN | Selectivity (%) MPO | Selectivity (%) DPO | Yield (%) MPO | Yield (%) DPO |
|---|---|---|---|---|---|---|
| 16%$MoO_3/SiO_2$ | 61.8 | 0.5 | 82.2 | 17.3 | 50.8 | 10.7 |
| 16%$MoO_3$/2%Ti-Si | 67.3 | 0.6 | 68.2 | 31.2 | 45.9 | 21.0 |
| 16%$MoO_3$/4%Ti-Si | 69.5 | 0.8 | 63.8 | 35.4 | 44.3 | 24.6 |
| 16%$MoO_3$/8%Ti-Si | 70.9 | 0.9 | 60.2 | 38.9 | 42.7 | 27.6 |
| 16%$MoO_3$/10%Ti-Si | 68.4 | 0.8 | 67.3 | 31.9 | 46.0 | 21.8 |
| 16%$MoO_3$/12%Ti-Si | 66.7 | 1.0 | 70.6 | 28.4 | 47.2 | 18.9 |

*Reaction conditions: catalyst 1.8 g, phenol 0.3 mol, DMO 0.1 mol, reaction time 2 h, and reaction temperature 453 K.

[†] Based on DMO charged.

MPO, methyl phenyl oxalate; DPO, diphenyl oxalate; AN, anisole.

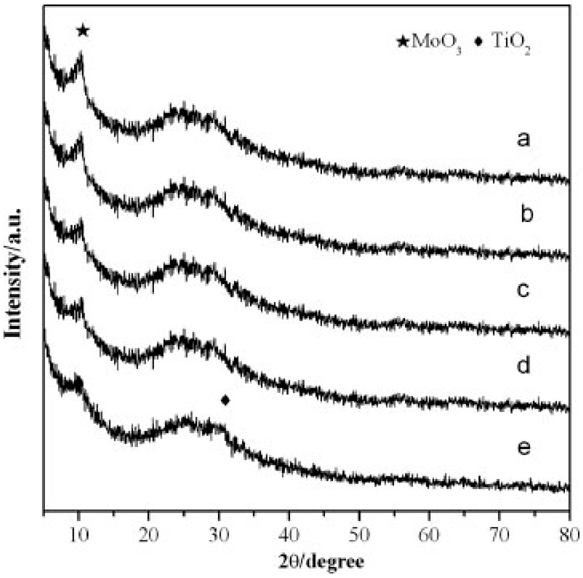

**Figure 1. XRD spectra of $MoO_3/SiO_2$ and $MoO_3$/Ti-Si catalysts with different $TiO_2$ contents.**

(a) 16%$MoO_3/SiO_2$; (b) 16%$MoO_3$/2%Ti-Si; (c) 16%$MoO_3$/8%Ti-Si; (d) 16%$MoO_3$/10%Ti-Si; (e) 16%$MoO_3$/12%Ti-Si.

On the basis of these experimental results, we can speculate that excellent activity and DPO selectivity from $MoO_3$/Ti-Si catalyst could be ascribed to the synergistic effect between $MoO_3$ and $TiO_2$. However, a $TiO_2$ support has no pore system with small specific surface area compared to silica, alumina, and so on. Thus, the monolayer dispersion capability of $MoO_3$ on $TiO_2$ would be considerably low and the synergic effect between $MoO_3$ and $TiO_2$ may be weakened, which results in the unsatisfactory activity and selectivity of $MoO_3/TiO_2$ compared to $MoO_3$/Ti-Si (Table 1, entry 11). These observations and the speculation motivated the following work to further explore surface properties of $MoO_3$/Ti-Si catalysts.

### *Powder XRD analysis*

As mentioned earlier, a small amount of $TiO_2$ plays an important role in improving catalytic performance, while a large amount of $TiO_2$ might show a negative effect. Therefore, XRD analysis was undertaken to determine the composition and crystalline state of $MoO_3$ on $MoO_3/SiO_2$ and $MoO_3$/Ti-Si. As XRD pattern of all the samples shown in Figure 1, characteristic peaks of crystalline molybdenum oxide are observed for a 16%$MoO_3/SiO_2$ sample, possibly due to the overloading of $MoO_3$ on $SiO_2$. On the other hand, the appearance of polymolybdate species also implies the weak interaction between $MoO_3$ and silica. Comparatively, for $MoO_3$/Ti-Si sample, a better dispersion of Mo species on Ti-Si can be suggested due to the decrease of bulk $MoO_3$ species. Furthermore, the $MoO_3$ peak intensity apparently decreases with $TiO_2$ content increasing up to 8 wt %, followed by remaining almost constant independent of $TiO_2$ content. This implies that 8 wt % is the optimal $TiO_2$ content where the highest $MoO_3$ dispersion capacity is reached. Another interesting feature is that weak XRD peak of anatase can be detected only when $TiO_2$ content is higher that 12 wt %, suggesting that $TiO_2$ species is also highly dispersed on silica surfaces below 12 wt % $TiO_2$ content. These results provide evidence that amorphously dispersed $TiO_2$ on surfaces of $SiO_2$ can significantly improve dispersion state of $MoO_3$. Therefore, it can be deduced that increasing $TiO_2$ content (below the monolayer dispersion capability) leads to reduce crystalline $MoO_3$ and increase the extent of amorphously dispersed $MoO_3$ on the $SiO_2$. However, further addition of $TiO_2$ may result in the formation of crystalline $TiO_2$. In a previous study on $TiO_2/SiO_2$ catalysts, Wang et al. showed that $TiO_2$ crystallite, which appears at high loadings, is unfavorable for the disproportionation of MPO into DPO and results in a decrease in DPO selectivity.[36] It is interesting that the similar phenomenon has also been observed on $MoO_3/SiO_2$ catalysts.[30] Therefore, based on these results from previous studies, we can conclude that highly dispersed (amorphous) $MoO_3$ on $TiO_2$-modified $SiO_2$ is desirable for transesterification of DMO with phenol (more amorphous $MoO_3$ and $TiO_2$ on $SiO_2$ provide more catalytically active centers.). In addition, it seems that synergetic effect of amorphous $MoO_3$ with amorphous $TiO_2$ may promote the disproportionation of MPO into DPO that leads to a further increase in DPO selectivity. Accordingly, the highest yield of DPO is obtained over a $MoO_3$/Ti-Si catalyst with an 8 wt % of $TiO_2$, which is approximately the monolayer dispersion capacity of $TiO_2$ on $SiO_2$.[36]

### *Inductively coupled plasma-optical emission spectroscopy analysis*

Measurements on element contents of Mo, Ti, and Si in $MoO_3/TiO_2$-$SiO_2$ catalysts were carried out by employing ICP-OES technique. The ICP results of $MoO_3$ and $TiO_2$ actual contents as a function of nominal $TiO_2$ loading are

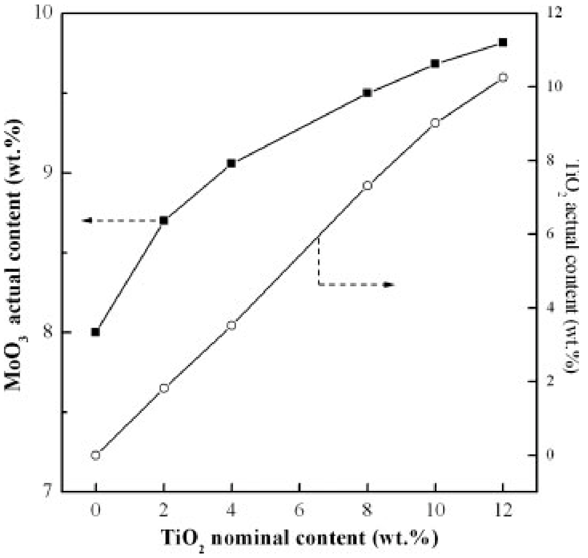

**Figure 2. The $MoO_3$ and $TiO_2$ actual contents as a function of nominal $TiO_2$ content on $MoO_3/SiO_2$ and $MoO_3$/Ti-Si catalysts.**

shown in Figure 2. It can be seen that the actual $MoO_3$ loadings are less than the nominal amount (16 wt %) for all the samples and increase linearly with the addition of $TiO_2$, while the actual loadings of $TiO_2$ are rather close to the corresponding nominal loadings. It is interesting to note that the actual loading of $MoO_3$ on the $MoO_3/SiO_2$ is only about 7.5 wt %, which is far from its nominal loading (16 wt %). According to the preparation procedure of supported $MoO_3$ catalysts by the slurry impregnation discussed earlier in the experimental section, all $MoO_3$/support samples with 16 wt % $MoO_3$ loading were prepared under the same condition and were ensured full impregnation. Therefore, it is not very likely that the difference between actual and nominal loading amounts of $MoO_3$ can be ascribed to the insufficient impregnation. As established in literature, slurry impregnation is a special impregnation method based on equilibrium adsorption of $MoO_3$.[29,45,46] The maximum amount of $MoO_3$ that can be deposited by slurry impregnation corresponds to the formation of "saturated adsorption monolayer." A higher loading than saturated adsorption monolayer is not attainable by this slurry impregnation method (However, we can obtain such a high loading by conventional impregnation with AHM[46]). Evidence for this argument is shown in previous studies on $MoO_3/Al_2O_3$, $MoO_3/MgO$, $MoO_3$/active carbon, and $MoO_3/ZrO_2$ catalysts.[41,46] However, to the best of our knowledge, there are few reports on $MoO_3/SiO_2$ in this respect.

The dense monolayer dispersion model shows that the interspace occupied by one $MoO_3$ molecule is same as that occupied by two oxygen anions, if size of $Mo^{6+}$ cation is negligible compared with $O^{2-}$ anion.[31] As the radius of the oxygen anion is 0.14 nm, it can be calculated that the theoretical monolayer capability of $MoO_3$ on $SiO_2$ surfaces is about 0.117 g $MoO_3$/100 $m^2$ $SiO_2$. Previous experimental studies by Zhou et al.[47] and Zhao et al.[48] showed that the highest monolayer dispersion capacity of $MoO_3$ on the surfaces of $SiO_2$ is 0.032 g $MoO_3$/100 $m^2$ $SiO_2$, which is only 27% of the theoretical monolayer dispersion threshold. Specifically, as for the $SiO_2$ sample with a surface area of 231 $m^2/g$, the monolayer dispersion of $MoO_3$ is ~6.9 wt %, which basically agrees with our experimental value (8.0 wt %). Regarding the difference of monolayer dispersion capacity between theoretical (6.9 wt %) and experimental (8.0 wt %) studies, it can probably be ascribed to the slurry impregnation we used in this study. One issue we need to mention here is that the resultant solution after the impregnation contains some dissociative $MoO_3$ species, and upon heating sample (to remove water) some left $MoO_3$ species clings to the external surface of support forming crystalline $MoO_3$,[46] which can be confirmed by the appearance of sharp characteristic peaks corresponding to crystalline $MoO_3$ from XRD measurements. Indeed, we have also prepared a series of $MoO_3/SiO_2$ samples in such a way that the resultant solution after impregnation is directly decanted instead of being dried. The highest loading of $MoO_3$ obtained by this method is ~6.6 wt %, which agrees well with the theoretical monolayer dispersion threshold (6.9 wt %). So it can be presumed that the "saturated adsorption monolayer" theory concerning the slurry impregnation also fits the $MoO_3/SiO_2$ samples. Furthermore, as we mentioned earlier, $MoO_3$ actual loadings steadily increase with the addition of $TiO_2$. This observation provides evidence that incorporation of $TiO_2$ can somewhat promote dispersion capability of $MoO_3$ on $TiO_2$-$SiO_2$ composite and elevate the monolayer dispersion threshold of $MoO_3$.

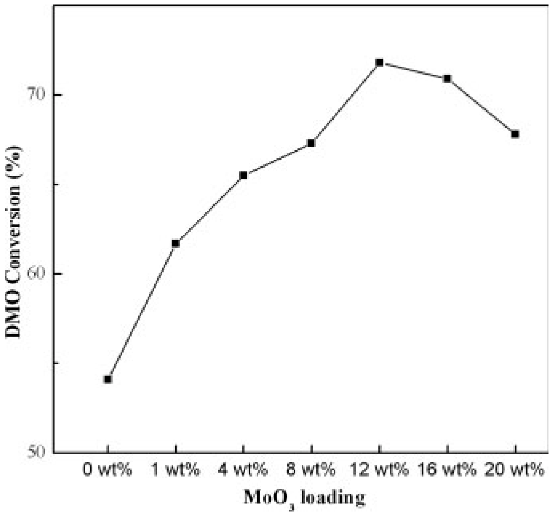

**Figure 3. Effect of $MoO_3$ loading on DMO conversion over $MoO_3$/Ti-Si catalysts.**

### *Effect of $MoO_3$ loading on the activities of transesterification of DMO with phenol*

In a previous publication, we investigated the effect of loading amount of $MoO_3$ on $MoO_3/SiO_2$ catalysts for the transesterification reaction and found an optimized $MoO_3$ loading.[30] However, as will be discussed later, for the $MoO_3$/Ti-Si catalyst, the incorporation of $TiO_2$ can affect the influence of $MoO_3$ loading on the transesterification activity and thus shift optimal $MoO_3$ loading somehow. Considering the highest activity from the $MoO_3$/8%Ti-Si catalyst, here we selected 8%Ti-Si as a support and further investigated the effect of $MoO_3$ loading on the reactivities of the transesterification reaction.

DMO conversion, MPO and DPO selectivities, and yields over $MoO_3$/8%Ti-Si catalysts with different $MoO_3$ loadings are shown in Figures 3–5, respectively. For purpose of comparison, the activities of 8%Ti-Si are also provided as well. Generally, deposition of $MoO_3$ on a $TiO_2$-$SiO_2$ (8 wt % $TiO_2$) composite makes it more catalytically active compared with a bare $TiO_2$-$SiO_2$ (8 wt %). Also, volcano profiles are observed for DMO conversion and DPO selectivity over $MoO_3/TiO_2$-$SiO_2$ catalysts. As shown in Figure 3, DMO conversion promotes from 61.7% to 71.8% with $MoO_3$ loadings ranging from 1 to 12 wt % and decreases upon further increasing $MoO_3$ loading to 20 wt %.

Regarding DPO selectivity and yield, as presented in Figures 4 and 5, both of them reach maximum values at a 12 wt % $MoO_3$ loading, followed by durative decrease with further increase in $MoO_3$ loading. However, selectivity and yield of MPO show opposite tendencies with respect to $MoO_3$ loading. Total selectivity for MPO and DPO usually keep up to 99%, while AN is the only observed by-product with a selectivity less than 1%.

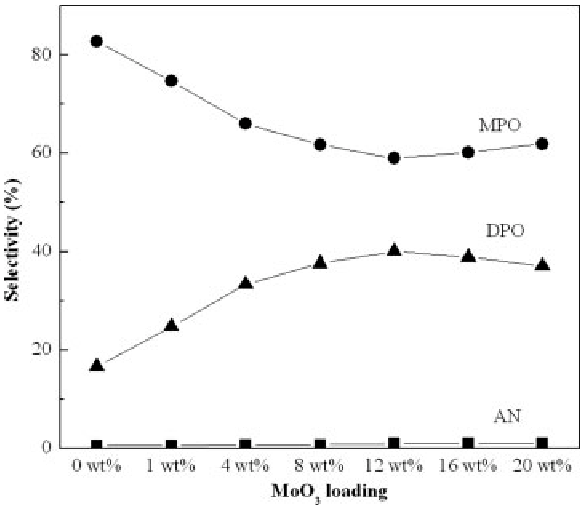

**Figure 4. Effect of $MoO_3$ loading on the selectivities to DPO, MPO, and AN over $MoO_3$/Ti-Si catalysts.**

### *Effect of reaction time on the activity of transesterification of DMO with phenol*

The effect of reaction time on the transesterification reaction was studied in the presence of 16%$MoO_3$/8%Ti-Si and 16%$MoO_3/SiO_2$, respectively. Figure 6 shows the results of DMO conversion, DPO selectivity, and DPO yield as a function of reaction time varied from 2 to 6 h. As expected, DMO conversion, DPO selectivity, and yield increase constantly as the reaction proceeds up to 6 h for both 16%$MoO_3$/8%Ti-Si and 16%$MoO_3/SiO_2$ catalysts. In addition, increasing extents of both DMO conversion and DPO yield from $MoO_3$/Ti-Si are greater than those from $MoO_3/SiO_2$ with increasing reaction time, which strongly suggests that $MoO_3$/Ti-Si is more active and stable than $MoO_3/SiO_2$. Longer reaction time would help improve DMO conversion and DPO yield for the $MoO_3$/Ti-Si catalyst.

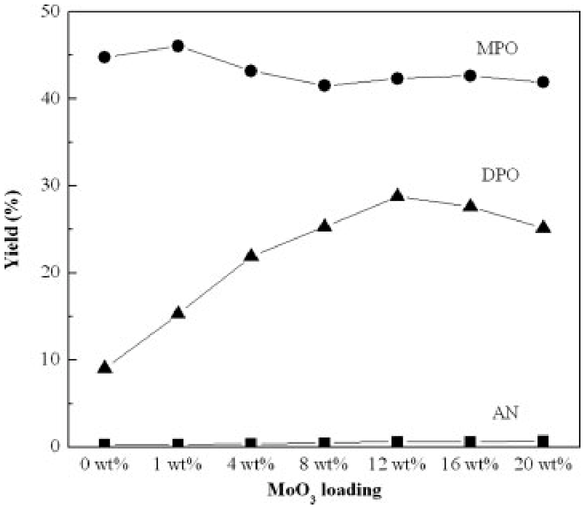

**Figure 5. Effect of $MoO_3$ loading on the yield of DPO, MPO, and AN over $MoO_3$/Ti-Si catalysts.**

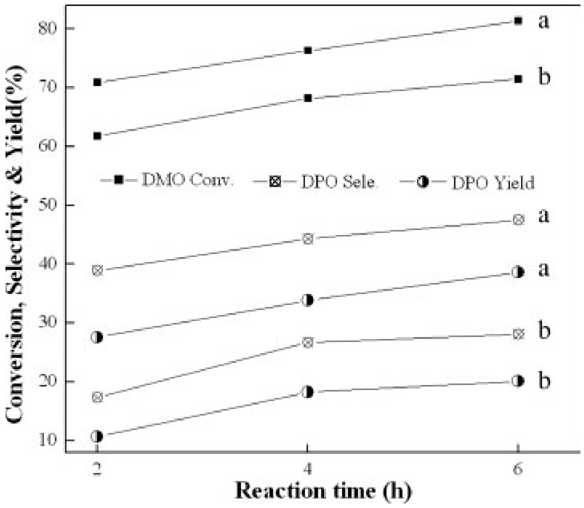

**Figure 6. Effect of reaction time on transesterification of DMO with phenol over $MoO_3$/Ti-Si catalysts.**

(a) 16%$MoO_3$/8%Ti-Si; (b) 16%$MoO_3/SiO_2$.

### *Regeneration of $MoO_3/TiO_2$-$SiO_2$ catalyst*

To study regeneration of catalyst, a 16%$MoO_3$/8%Ti-Si sample was selected. As shown in Table 3, a freshly prepared 16%$MoO_3$/8%Ti-Si sample produces a 70.9% DMO conversion. The catalyst after the reaction was separated by filtration and calcined at 823 K for 5 h. The following active test on this recovered catalyst provides a DMO conversion of 66.2%. We repeated same catalyst regeneration and active test cycle and found that DMO conversion keeps around 59.4% after two more recycles (Table 3), indicating that the catalyst is stable and basically recoverable. On the other hand, it is notable that all the Ti-Si supported $MoO_3$ catalysts in this article were analyzed by the ICP measurements before and after the reactions. Comparing ICP data of fresh and regenerated catalysts (not shown here), we found that only a trace amount of Mo and Ti species were leached to the reactant solution, further indicating the stability of $MoO_3$/Ti-Si catalyst.

## Conclusions

In this article, we present results of investigations into the dispersion of $MoO_3$ on $TiO_2$-$SiO_2$ composite and its reactivity in transesterification of DMO with phenol to produce MPO and DPO. In particular, we examined the effects of

**Table 3. The Catalytic Activities of the Regenerated Catalyst***

| Regenerated Times | DMO Conversion (%) |
|---|---|
| 0 | 70.9 |
| 1 | 66.2 |
| 2 | 62.8 |
| 3 | 59.4 |
| 4 | 59.2 |

*Reaction conditions: catalyst (16%$MoO_3$/8%Ti-Si) 1.8 g, phenol 0.3 mol, DMO 0.1 mol, reaction time 2 h, and reaction temperature 453 K.

support composition, $MoO_3$ content, and reaction time on activities of the transesterification. It has been shown that $MoO_3$/Ti-Si catalyst is a quite stable, active, and selective heterogeneous catalyst for transesterification of DMO with phenol. $MoO_3$/Ti-Si catalyst provides higher DMO conversion, DPO selectivity, and DPO yield than what have been reported on other solid active catalysts. We showed evidence suggesting that the maximum value of deposited $MoO_3$ from slurry impregnation corresponds to the formation of saturated adsorption monolayer. Although, for $MoO_3/SiO_2$, the maximum deposition amount of $MoO_3$ by slurry impregnation is relatively low, incorporation of $TiO_2$ can improve it to some extent. XRD and ICP-OES measurements show that incorporation of $TiO_2$ on $SiO_2$ can significantly elevate the monolayer dispersion capacity of $MoO_3$. Thus, it can be deduced that increased DPO selectivity from $MoO_3$/Ti-Si catalysts could be ascribed to the improvement of $MoO_3$ dispersion and the synergic effect between amorphous $MoO_3$ and amorphous $TiO_2$.

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