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Article

Transesterification of dimethyl oxalate with phenol over a $\text{MoO}_3/\text{SiO}_2$ catalyst prepared by thermal spreading

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ABSTRACT

$\text{MoO}_3/\text{SiO}_2$ catalysts for the transesterification of dimethyl oxalate (DMO) with phenol were prepared by both the thermal spreading (TS) and incipient wetness impregnation methods. The results showed that the 10% $\text{MoO}_3/\text{SiO}_2$ catalyst prepared by TS (10% $\text{MoO}_3/\text{SiO}_2$ -TS) exhibited higher catalytic performance compared with the 10% $\text{MoO}_3/\text{SiO}_2$ catalyst prepared by incipient wetness impregnation (10% $\text{MoO}_3/\text{SiO}_2$ -C). The catalysts were characterized by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, pyridine-IR spectroscopy, and NH_3 temperature-programmed desorption. These analyses indicated that weak Lewis acid sites were formed on the catalyst surfaces and that the Mo species were present as monomeric MoO_3 rather than as isolated molybdenum oxide or polymolybdate species on both catalysts, although the 10% $\text{MoO}_3/\text{SiO}_2$ -TS exhibited better dispersion of MoO_3 and a higher surface Mo content than the 10% $\text{MoO}_3/\text{SiO}_2$ -C. Under the optimal transesterification reaction conditions (1.2 g 10% $\text{MoO}_3/\text{SiO}_2$ -TS, $T = 180^\circ\text{C}$, $n(\text{DMO})/n(\text{phenol}) = 2$, $t = 4$ h), the conversion of phenol was 70.9%, and the yields of methyl phenyl oxalate and diphenyl oxalate were 63.1% and 7.7%, respectively.

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1. Introduction

Diphenyl carbonate (DPC) is an important organic intermediate [1] primarily used to synthesize polycarbonates, isocyanates, pesticides, and pharmaceuticals. In recent years, the demand for DPC has increased significantly in conjunction with rapid developments in various economies.

DPC was originally synthesized from phenol using phosgene or methyl chloroformate. The high toxicity of phosgene and

methyl chloroformate, however, has caused serious environmental and safety issues over the years [2] and, since the 1970s, several environmentally benign phosgene-free synthesis routes have been explored and developed [3–10]. Among these, an attractive option is the transesterification of phenol with dimethyl oxalate (DMO) or diethyl oxalate (DEO) to diphenyl oxalate (DPO) followed by decarbonylation of DPO to produce DPC, as developed by Ube Industries Ltd. This process has several advantages, including mild reaction conditions,

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easy separation of products, and the potential to recycle the CO generated during the reaction to synthesize DMO or DEO.

The decarbonylation of DPO to produce DPC is easily accomplished, and selectivity for DPC of nearly 100% with an accompanying yield as high as 95% has been reported [11,12]. For these reasons, the synthesis of DPO has been widely studied. The transesterification synthesis of DPO from DMO generally occurs via a two-step reaction process consisting of the transesterification of DMO with phenol into methyl phenyl oxalate (MPO), followed by further transesterification or disproportionation of the MPO to DPO, as shown in Scheme 1.

Catalyst systems for the phosgene-free synthesis of DPO can be divided into homogeneous and heterogeneous systems. The homogeneous systems generally include $\text{Ti}(\text{OBu})_4$, AlCl_3 , H_2SO_4 , and H_3PO_4 [13], while the heterogeneous systems involve regular or modified molecular sieves, supported metal oxides, N-doped nanoporous carbon materials, and hydrotalcites [14–32]. Among these, the supported MoO_3 catalysts have attracted significant attention because of their excellent catalytic performance [13,22–30]. Traditionally, supported MoO_3 catalysts are prepared by impregnation of the support with a molybdenum salt solution, usually ammonium heptamolybdate, followed by drying and calcination. However, this preparation method also entails certain challenges, such as uneven drying, ammonia emissions during the calcination process, and deposition of MoO_3 crystals on the surface of the support due to agglomeration of Mo species [33,34].

The thermal spreading method (TS), which does not use solvent and does not produce gaseous emissions, can effectively inhibit the agglomeration of active species. The supported MoO_3 or V_2O_5 catalysts prepared by this method are widely used in the metathesis of alkenes, the hydrodesulfurization reaction, oxidation of alcohols, and in other processes [33–40]. To date, however, there have been no reports of the application of $\text{MoO}_3/\text{SiO}_2$ catalysts prepared by the TS method to the transesterification reaction of phenol with DMO. In this work, the catalytic performance of $\text{MoO}_3/\text{SiO}_2$ prepared either by the TS method or the incipient wetness impregnation method was tested in the transesterification of DMO with phenol, and the optimal reaction conditions were investigated.

2. Experimental

2.1. Catalyst preparation

The preparation of the $\text{MoO}_3/\text{SiO}_2$ catalyst via the TS method was as follows [41]. SiO_2 particles were ground to a 100

mesh size and subsequently mixed with MoO_3 in the desired proportion for 30 min. Each mixture was then dried in an oven at 120 °C for 2 h and calcined at 550 °C for 6 h. The samples are denoted herein as $x\text{MoO}_3/\text{SiO}_2\text{-TS}$, where x is the percent loading of MoO_3 .

When applying the incipient wetness impregnation method, the $\text{MoO}_3/\text{SiO}_2$ catalyst was prepared by impregnation of SiO_2 with an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. The impregnated sample was then dried in an oven at 120 °C for 2 h and calcined at 550 °C for 6 h. The sample is referred to as $y\text{MoO}_3/\text{SiO}_2\text{-C}$, where y is the percent loading of MoO_3 .

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis of the catalysts was performed using a Philips X'pert PRO MPD with $\text{Cu K}\alpha$ (40 kV, 40 mA) radiation, with a scan range of $2\theta = 10^\circ\text{--}80^\circ$ and a scanning velocity of $2^\circ/\text{min}$. The specific surface areas, total pore volumes, and average pore diameters of the catalysts were determined from N_2 adsorption/desorption isotherms at -196°C (Quantachrome). Before each measurement, the sample was degassed under vacuum at 300 °C for 3 h. Raman spectra of the catalysts were recorded on a Renishaw Invia Raman microscope using an argon laser ($\lambda = 514\text{ nm}$) as the excitation source. X-ray photoelectron spectroscopy (XPS) was carried out using an XSAM 800 spectrometer (Kratos) with an $\text{Al K}\alpha$ ($h\nu = 1486.6\text{ eV}$) X-ray source, and the binding energies were corrected using the C 1s peak at 284.6 eV. The infrared (IR) spectroscopic measurements of adsorbed pyridine were performed on a Nicolet 560 Fourier transform IR (FT-IR) spectrometer. Prior to each measurement, the catalyst sample was evacuated to remove any physically adsorbed contaminants. After the saturated adsorption of pyridine, the sample was allowed to out-gas, and the IR spectrum was recorded at room temperature. NH_3 -TPD profiles were obtained with a TP5080 chemical adsorption spectrometer (Tianjin Xianquan Industry and Trade Development Co., Ltd., China). The catalyst sample was heated to 400 °C under a flow of N_2 for 1 h and then cooled to room temperature. NH_3 adsorption was then carried out at 50 °C until the material was saturated. NH_3 was replaced with N_2 , and the sample was heated to 600 °C at a rate of $10^\circ\text{C}/\text{min}$ while the desorption signal was monitored by TCD.

2.3. Catalytic testing and product analysis

The transesterification synthesis of DPO was conducted in a 250 mL glass flask equipped with a thermometer, a distillation

Scheme 1. Transesterification of DMO with phenol to synthesize DPO.

apparatus, and a stirrer under atmospheric pressure. After the phenol, DMO, and the catalyst were added in the desired proportions, inert gas was introduced to purge the air from the reaction system, and the flask was heated to the specified temperature. The reaction products and distillates were analyzed using a GC-112A gas chromatograph (Shanghai Precision Scientific Instrument Co., Ltd., China) equipped with an SPB™-5 (Supelco) capillary column and a flame ionization detector.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Specific surface area measurements

The surface areas of the 10%MoO₃/SiO₂ catalyst and the support material were determined from N₂ adsorption-desorption isotherms using the BET method. As shown in Fig. 1, the N₂ adsorption-desorption isotherms of the 10%MoO₃/SiO₂-TS and 10%MoO₃/SiO₂-C catalysts both displayed type-IV isotherms with an H1-type hysteresis loop, which is typical for a mesoporous structure according to the IUPAC method of classification.

The textural properties of the 10%MoO₃/SiO₂-TS and 10%MoO₃/SiO₂-C catalysts, as well as the support, are listed in Table 1. Compared with the support material, the 10%MoO₃/SiO₂-C catalyst exhibited a decreased specific surface area, likely because the MoO₃ species occupied the pores of the support. In the case of the 10%MoO₃/SiO₂-TS catalyst, however, the extreme decreases in the specific surface area and average pore diameter may be due to a decrease in the number of micropores, because of plugging of pores by migration of additional MoO₃ to the surface.

Fig. 1. N₂ adsorption-desorption isotherms of 10%MoO₃/SiO₂ catalysts and support.

Table 1

Textural characteristics of the 10%MoO₃/SiO₂ catalysts.

Catalyst	S_{BET}^a (m ² /g)	V_p (cm ³ /g)	D_p^b (nm)
SiO ₂	198	0.96	21.2
10%MoO ₃ /SiO ₂ -TS	89	0.25	11.2
10%MoO ₃ /SiO ₂ -C	135	0.90	26.7

^a BET specific area.

^b Average pore diameter calculated by the BJH method.

Fig. 2. XRD patterns of catalysts SiO₂ (1), 10%MoO₃/SiO₂-TS (2), and 10%MoO₃/SiO₂-C (3).

3.1.2. XRD patterns of MoO₃/SiO₂ catalysts

The XRD patterns of the 10%MoO₃/SiO₂-TS and 10%MoO₃/SiO₂-C catalysts are shown in Fig. 2. The diffraction peaks observed at $2\theta = 12.8^\circ, 23.3^\circ, 25.7^\circ, 27.4^\circ, 33.1^\circ, 33.7^\circ, 39.0^\circ, 39.7^\circ, 45.7^\circ, 46.3^\circ,$ and 49.2° can be attributed to the presence of an orthorhombic MoO₃ phase (JCPDS 05-0508) in the 10% MoO₃/SiO₂-C catalyst. However, no molybdenum phase is evident in the 10%MoO₃/SiO₂-TS catalyst, indicating that the Mo species were either well dispersed on the SiO₂ surface or in a highly amorphous state.

The XRD patterns of MoO₃/SiO₂-TS catalysts with a range of MoO₃ loadings between 2% and 18% are presented in Fig. 3. When MoO₃ loadings are below 10%, no characteristic peaks associated with an orthorhombic MoO₃ phase are observed, indicating that the Mo species were well dispersed or in a highly amorphous state. Diffraction peaks corresponding to the bulk MoO₃ phase were however observed in the 14%MoO₃/SiO₂-TS catalyst. With increasing levels of MoO₃ loading, the diffraction peaks corresponding to the MoO₃ phase became both more apparent and sharper as the formulation approaches the 18%MoO₃/SiO₂-TS catalyst, suggesting an obvious increase in the sizes of the MoO₃ crystallites.

Fig. 3. XRD patterns of MoO₃/SiO₂-TS catalysts with different MoO₃ loadings (x). (1) 0; (2) 2%; (3) 6%; (4) 10%; (5) 14%; (6) 18%.

3.1.3. Raman spectra of MoO₃/SiO₂ catalysts

Raman spectra of the MoO₃/SiO₂ catalysts prepared by the TS and incipient wetness impregnation methods are shown in Fig. 4. All the MoO₃/SiO₂ catalysts displayed characteristic bands associated with MoO₃ at 666, 819, and 995 cm⁻¹ [34,35,40]. Among these, the bands at 666 and 819 cm⁻¹ can be ascribed to Mo–O–Mo bridge bond vibrations, while the 995 cm⁻¹ band results from the stretching mode of terminal Mo=O groups. There are no bands at 874, 959, or 981 cm⁻¹, which suggests the presence of Mo in the MoO₃ monomeric form but not as isolated molybdenum oxide or polymolybdate species [40].

3.1.4. XPS of 10%MoO₃/SiO₂ catalysts

The XPS results obtained for the 10%MoO₃/SiO₂ catalysts are summarized in Table 2. Both catalysts exhibited the same Mo 3d_{5/2} binding energies, while the Mo 3d_{3/2} peak binding energies were only slightly different at 235.7 and 235.6 eV. There was therefore no apparent shift in the Mo 3d binding energy [22,25], suggesting that the molybdenum compounds were present only in the (VI) oxidation state as MoO₃. This result is in accordance with the information obtained from Raman spectroscopy. In addition, it can be seen that a higher Mo/Si ratio was obtained on the surface of the 10%MoO₃/SiO₂-TS catalyst than on the 10%MoO₃/SiO₂-C material, indicating that the TS method favors the migration of Mo species to the surface. Combined with the XRD results, which showed that no orthorhombic MoO₃ phase had formed on the 10%MoO₃/SiO₂-TS catalyst, it is evident that the MoO₃ species exhibited better dispersion in the 10%MoO₃/SiO₂-TS catalyst than in the 10%MoO₃/SiO₂-C catalyst.

Fig. 4. Raman spectra of MoO₃/SiO₂ catalysts. (1) 6%MoO₃/SiO₂-TS; (2) 10%MoO₃/SiO₂-TS; (3) 10%MoO₃/SiO₂-C; (4) 18%MoO₃/SiO₂-TS.

Table 2

Mo 3d binding energies and surface element compositions of the 10%MoO₃/SiO₂ catalysts.

Catalyst	Binding energy (eV)		Mo ^a (mol%)	Mo/Si atomic ratio ^a
	Mo 3d _{3/2}	Mo 3d _{5/2}		
10%MoO ₃ /SiO ₂ -C	235.7	232.6	0.63	0.024
10%MoO ₃ /SiO ₂ -TS	235.6	232.6	0.82	0.033

^a Calculated from XPS data.

3.1.5. Pyridine-IR of 10%MoO₃/SiO₂ catalysts

FT-IR analysis of adsorbed pyridine allows a clear distinction to be made between types B and L acid sites. In general, the IR band at 1450 cm⁻¹ is attributed to pyridine adsorbed on L acid sites, while the band at 1540 cm⁻¹ is associated with adsorption on B sites [22]. From Fig. 5, it can be seen that both catalysts exhibit a peak at approximately 1450 cm⁻¹, indicating that there were only L acid sites on both.

3.1.6. NH₃-TPD of 10%MoO₃/SiO₂ catalysts

In NH₃-TPD curves, desorption peaks are generally found within two regions [13,24]: either below or above 400 °C, referred to as the low- and high-temperature regions, respectively. The peaks in the low-temperature region can be attributed to desorption of NH₃ from weak acid sites, while the peaks in the high-temperature region are due to desorption of NH₃ from strong acid sites. As shown in Fig. 6, the desorption peaks of the two catalysts appear at 192.6 and 190.9 °C, suggesting that only weak acid sites were present on both materials [22,30]. Furthermore, the total NH₃ desorptions from the 10%MoO₃/SiO₂-TS and 10%MoO₃/SiO₂-C catalysts were approximately 0.088 and 0.092 mmol/g (calculated on the basis of the peak integration), respectively. These data suggest that there were no significant differences in the total amounts of acid between the two catalysts.

Fig. 5. IR spectra of pyridine adsorbed on the catalysts. (1) 10%MoO₃/SiO₂-C; (2) 10%MoO₃/SiO₂-TS.

Fig. 6. NH₃-TPD profiles of 10%MoO₃/SiO₂-C (1) and 10%MoO₃/SiO₂-TS (2).

3.2. Catalytic performance

3.2.1. Effect of preparation methods on the transesterification reaction

The effects of preparation methods on catalytic performance during the transesterification of DMO with phenol are shown in Fig. 7. Compared with the pure MoO_3 catalyst, the conversion of phenol increased from 26.7% to 43.8% on the 10% $\text{MoO}_3/\text{SiO}_2\text{-C}$ catalyst using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ as the precursor. When the 10% $\text{MoO}_3/\text{SiO}_2\text{-TS}$ was used as the catalyst, the conversion of phenol reached 56.2% and the selectivities for MPO and DPO were 89.0% and 10.9%, respectively.

The Raman spectra of the catalysts demonstrated that the element Mo was in the monomeric MoO_3 form on the catalysts and that isolated molybdenum oxide species or polymolybdate species were not present. Moreover, the results of pyridine-IR and $\text{NH}_3\text{-TPD}$ studies indicated that the 10% $\text{MoO}_3/\text{SiO}_2$ catalyst contained weak Lewis acid sites, suggesting that such sites produced by the interaction of MoO_3 and SiO_2 were responsible for the transesterification reaction. It was reported by Ma et al. [22] that the catalytic performance of $\text{MoO}_3/\text{SiO}_2$ catalysts is closely associated with the dispersion state of MoO_3 . The appearance of agglomerated MoO_3 particles in the catalyst is therefore not favorable with regard to the formation of MPO and DPO [23,28]. Based on the results of XRD and XPS analyses, the 10% $\text{MoO}_3/\text{SiO}_2\text{-TS}$ catalyst exhibited better dispersion of MoO_3 and a higher surface Mo content than the 10% $\text{MoO}_3/\text{SiO}_2\text{-C}$ catalyst, meaning that it had a greater quantity of weak Lewis acid sites on its surface. Consequently, the 10% $\text{MoO}_3/\text{SiO}_2\text{-TS}$ catalyst exhibited enhanced catalytic performance compared with the 10% $\text{MoO}_3/\text{SiO}_2\text{-C}$ catalyst.

3.2.2. Effect of MoO_3 loadings on the transesterification reaction

The effect of MoO_3 loadings on the performance of $\text{MoO}_3/\text{SiO}_2\text{-TS}$ catalysts is summarized in Fig. 8. The conversion of phenol and the selectivity for DPO both increased continuously before decreasing as the MoO_3 loading went from 2% to 18%. The selectivity for MPO, however, exhibited the opposite trend. Compared with the 10% $\text{MoO}_3/\text{SiO}_2\text{-TS}$ catalyst, the 14% and 18% $\text{MoO}_3/\text{SiO}_2\text{-TS}$ catalysts did not show better catalytic per-

Fig. 7. Effect of preparation methods on the performance of catalysts. Reaction conditions: 0.12 g MoO_3 , 0.2 mol DMO, 0.2 mol phenol, $T = 180^\circ\text{C}$, $t = 3$ h.

Fig. 8. Effect of MoO_3 loadings on the performance of $\text{MoO}_3/\text{SiO}_2\text{-TS}$ catalysts. Reaction conditions: 0.2 mol DMO, 0.2 mol phenol, 1.2 g catalyst, $T = 180^\circ\text{C}$, $t = 3$ h.

formance because the orthorhombic phase MoO_3 formed on the surface covered the existing active sites to some extent. Similar phenomena have been reported in $\text{TiO}_2/\text{SiO}_2$, $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$, and $\text{MoO}_3/\text{SiO}_2$ catalysts prepared by the slurry impregnation method [21,23,27,28].

3.3. Optimization of reaction conditions on the 10% $\text{MoO}_3/\text{SiO}_2\text{-TS}$ catalyst

3.3.1. Effect of catalyst amount

The effect of catalyst amount on the transesterification reaction is shown in Fig. 9. The conversion of phenol increased from 33.6% to 56.2%, and the selectivity for DPO also increased from 2.8% to 10.9%, whereas the selectivity for MPO decreased from 97.1% to 89.0% when increasing the amount of catalyst from 0.3 g to 1.2 g. The total transesterification selectivity was kept at 99.8%. When the amount of catalyst was 1.5 g, the conversion of phenol decreased slightly, and therefore the optimal amount of catalyst is 1.2 g.

3.3.2. Effect of reaction temperature

The effect of reaction temperature on the transesterification

Fig. 9. Effect of catalyst amount on transesterification. Reaction conditions: 0.2 mol DMO, 0.2 mol phenol, $T = 180^\circ\text{C}$, $t = 3$ h.

Fig. 10. Effect of reaction temperature on transesterification. Reaction conditions: 0.2 mol DMO, 0.2 mol phenol, 1.2 g catalyst, $t = 3$ h.

was studied, and the experimental results are presented in Fig. 10. When the reaction temperature was below 140 °C, the transesterification reaction did not proceed to any appreciable extent. The conversion of phenol and the selectivity for DPO, however, both increased sharply with further increases in reaction temperature, suggesting that the transesterification reaction can be improved by operating at higher temperatures, and that the transesterification and disproportionation reactions of MPO are endothermic. The conversion of phenol and the yields of MPO and DPO all reached their maximum values at 180 °C, and hence this appears to be the optimal temperature.

3.3.3. Effect of $n(\text{DMO})/n(\text{phenol})$

The effect of the $n(\text{DMO})/n(\text{phenol})$ ratio on the transesterification was also investigated. As shown in Fig. 11, the selectivities for MPO and DPO changed somewhat as the $n(\text{DMO})/n(\text{phenol})$ ratio was varied, while the conversion of phenol increased as the ratio was increased from 0.5 to 2. When the $n(\text{DMO})/n(\text{phenol})$ was further increased to 2.5, the phenol conversion leveled off and so the optimal $n(\text{DMO})/n(\text{phenol})$ ratio is 2. A phenol conversion value of 65.6% along with selectivities of 89.3% and 10.6% for MPO and DPO were obtained when using the 10%MoO₃/SiO₂-TS catalyst.

Fig. 11. Effect of $n(\text{DMO})/n(\text{phenol})$ on transesterification. Reaction conditions: 0.2 mol phenol, 1.2 g catalyst, $T = 180$ °C, $t = 3$ h.

Fig. 12. Effect of reaction time on transesterification. Reaction conditions: 1.2 g catalyst, 0.2 mol phenol, $n(\text{DMO})/n(\text{phenol}) = 2$, $T = 180$ °C.

3.3.4. Effect of reaction time

The transesterification reaction was also monitored while changing the reaction time. As shown in Fig. 12, the conversion of phenol increased significantly while the selectivities for MPO and DPO changed only slightly when the reaction time was increased from 1 to 4 h, suggesting that reaction time was beneficial to transesterification and has little effect on the disproportionation of MPO. After 4 h, the conversion of phenol reached 70.9%, and the yields of MPO and DPO were 63.1% and 7.7%, respectively. Increasing the reaction time to 5 h only slightly improved the conversion of phenol and so the optimal reaction time is 4 h.

4. Conclusions

Compared with the 10%MoO₃/SiO₂-C catalyst, the 10%MoO₃/SiO₂-TS catalyst exhibited better dispersion of MoO₃, higher surface Mo content, and better catalytic performance during the transesterification of DMO with phenol. Under the optimal reaction conditions, consisting of a catalyst amount of 1.2 g, a reaction temperature of 180 °C, a DMO to phenol molar ratio of 2, and a 4 h reaction time, the conversion of phenol was 70.9%, while the yields of MPO and DPO were 63.1% and 7.7%, respectively. The thermal spreading method is both simple and environmentally friendly and therefore will play an important role in future with regard to the preparation of supported MoO₃ catalysts.

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Graphical Abstract

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Transesterification of dimethyl oxalate with phenol over a $\text{MoO}_3/\text{SiO}_2$ catalyst prepared by thermal spreading

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A 10% $\text{MoO}_3/\text{SiO}_2$ catalyst prepared by thermal spreading exhibits higher catalytic performance compared with a 10% $\text{MoO}_3/\text{SiO}_2$ catalyst prepared by incipient wetness impregnation during the transesterification of dimethyl oxalate with phenol to synthesize methyl phenyl oxalate (MPO) and diphenyl oxalate (DPO).

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热扩散法制备 $\text{MoO}_3/\text{SiO}_2$ 催化草酸二甲酯和苯酚酯交换反应

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摘要: 采用热扩散法(TS)和等体积浸渍法制备了 $\text{MoO}_3/\text{SiO}_2$ 催化剂用于草酸二甲酯和苯酚酯交换反应。结果表明, 热扩散法制备的10% $\text{MoO}_3/\text{SiO}_2$ -TS催化剂较等体积浸渍法制备的10% $\text{MoO}_3/\text{SiO}_2$ -C催化剂具有更好的催化性能。运用X射线衍射、Raman光谱、X射线光电子能谱分析、吡啶吸附红外光谱、 NH_3 程序升温脱附等手段对催化剂进行了表征, 发现虽然两种方法制备的催化剂都只有弱Lewis酸中心, 钼均以氧化钼单体形式存在, 未形成解离和聚合, 但是10% $\text{MoO}_3/\text{SiO}_2$ -TS催化剂较10% $\text{MoO}_3/\text{SiO}_2$ -C催化剂表面钼含量更高且 MoO_3 分散得更好。在苯酚用量为0.2 mol, 10% $\text{MoO}_3/\text{SiO}_2$ -TS催化剂用量为1.2 g, 反应温度为180 °C, 草酸二甲酯与苯酚的摩尔比为2, 反应时间为4 h的优化条件下, 苯酚转化率可达70.9%, 甲基苯基草酸酯和草酸二苯酯的收率分别达63.1%和7.7%。

关键词: 热扩散法; $\text{MoO}_3/\text{SiO}_2$ 催化剂; 甲基苯基草酸酯; 草酸二苯酯; 酯交换

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1. 前言

碳酸二苯酯(DPC)作为一种重要的有机化工中间体^[1], 主要用作合成聚碳酸酯、异氰酸酯及农药、医药等。近年来, 随着我国经济的高速发展, 国内对DPC的需求不断增加。

DPC的合成最初是采用苯酚与光气或氯甲酸甲酯反应, 但光气及氯甲酸甲酯均为剧毒, 存在严重的环境和安全隐患^[2]。上世纪70年代以来, 国内外陆续开发了多条非光气清洁生产工艺路线^[3–10], 其中日本Ube公司开发的利用草酸二甲酯(DMO)或草酸二乙酯和苯酚先进行酯交换合成草酸二苯酯(DPO), 然后DPO再脱羰生成DPC这一工艺路线颇具吸引力。该过程具有反应条件温和、产物易分离及生成的CO可回收合成原料草酸二甲酯或草酸二乙酯等优点。

DPO脱羰制备DPC较易进行, 催化剂选择性几乎为100%, DPC收率可达95%以上^[11,12]。因此, 酯交换合成DPO受到更多关注。以草酸二甲酯为例, 一般认为草酸二甲酯和苯酚酯交换过程分为两步: 首先, 草酸二甲酯与苯酚生成甲基苯基草酸酯(MPO); 其次, 甲基苯基草酸酯发生歧化或者进一步与苯酚酯交换生成草酸二苯酯, 有关反应方程式见图式1。

酯交换合成草酸二苯酯催化剂可分为均相催化体

系和多相催化体系。均相催化体系主要包括钛酸四丁酯、氯化铝及硫酸、磷酸等^[13], 多相催化体系主要包括分子筛及改性分子筛、负载型金属氧化物、多孔碳材料和类水滑石等^[14–32]。其中, 负载型三氧化钼催化剂由于具有较好的催化性能引起了研究者广泛关注^[13,22–30]。传统上制备负载型 MoO_3 催化剂多采用浸渍法。然而, 浸渍法也存在着一些缺陷, 比如干燥过程中难以保持均匀, 在后期焙烧过程中会产生氨气, 制备的催化剂易出现活性物种团聚^[33,34]。

热扩散法(TS)不需要任何溶剂且不产生氨气, 能有效降低催化剂活性物种的团聚。该法制备的负载型 MoO_3 和 V_2O_5 等催化剂广泛应用在烯烃复分解、加氢脱硫及醇的氧化等反应中^[33–40]。截止目前, TS法制备负载型 MoO_3 催化剂在草酸二甲酯与苯酚酯交换反应体系中尚未见报道。

本文分别采用TS法和等体积浸渍法制备了 $\text{MoO}_3/\text{SiO}_2$ 催化剂, 并比较了它们的催化性能, 在此基础上优化了草酸二甲酯与苯酚酯交换反应的工艺条件。

2. 实验部分

2.1. 催化剂制备

热扩散法(TS)制备 $\text{MoO}_3/\text{SiO}_2$ 催化剂参照文献^[41]。将 SiO_2 粉碎成100目粉末后, 取一定量与 MoO_3 混合, 研

磨30 min, 置于马弗炉中120 °C干燥2 h, 然后加热至550 °C并保持6 h. 所得催化剂记为 $x\text{MoO}_3/\text{SiO}_2\text{-TS}$ (x 表示 MoO_3 的负载量).

对于等体积浸渍法, 配制一定浓度的钼酸铵溶液浸渍100目 SiO_2 粉末, 静置过夜, 然后置于马弗炉中120 °C干燥2 h, 再加热至550 °C并保持6 h. 所得催化剂记为 $y\text{MoO}_3/\text{SiO}_2\text{-C}$ (y 表示 MoO_3 的负载量).

2.2. 催化剂表征

催化剂晶相分析在Philips X'pert PRO MPD型X射线衍射仪(XRD)上进行, Cu 靶, K_α 辐射源, 管电压40 kV, 管电流40 mA, 入射狭缝(1/6)°, 扫描速度2°/min, 扫描范围10°–80°. 比表面积分析在美国Quantachrome公司全自动NOVA1000e型比表面和孔隙度分析仪上进行, 分析结果采用BET法计算. Raman光谱测试在InVia型激光拉曼光谱仪(英国雷尼绍公司)上进行, 激发光波长为514.5 nm. 样品的X射线电子能谱测定在英国Kratos公司XSAM 800型X射线光电子能谱仪(XPS)上进行, 以 $\text{Al } K_\alpha$ (1486.6 eV)为激发光源, 样品的荷电效应以 C1s (284.6 eV)为内标加以校正. 催化剂吸附吡啶红外光谱表征在傅里叶红外光谱仪(美国Nicolet 560)上进行, 先将脱去表面物理吸附杂质的样品置于含有吡啶蒸气的密闭容器中, 充分吸附后再在真空条件下180 °C加热2 h, 冷却后测量. $\text{NH}_3\text{-TPD}$ 表征在TP5080型全自动化学吸附仪(天津先权工贸发展有限公司)上进行, 用高纯氮气400 °C吹扫1 h后降至室温, 在50 °C化学吸附 NH_3 至饱和, 再切换成氮气以10 °C/min从50 °C升温至600 °C, 然后降至室温, 用热导检测 NH_3 脱附信号.

2.3. 催化剂性能评价

草酸二苯酯合成在带有搅拌器和分馏柱的250 mL三颈烧瓶中进行. 分别将一定量的苯酚、草酸二甲酯和催化剂按比例加入, 通惰性气体保护, 升温到反应温度. 反应结束后的釜液和馏分用带有FID检测器的气相色谱GC112A (上海精密科学仪器有限公司)分析, 分离色谱柱型号为 $\text{SPB}^{\text{TM}}\text{-5}$ (SUPELCO).

3. 结果与讨论

3.1. 催化剂表征结果

3.1.1. 比表面积测试

图1为载体 SiO_2 和10% $\text{MoO}_3/\text{SiO}_2$ 催化剂的 N_2 吸附-脱附曲线. 可以看出, 热扩散法和等体积浸渍法制备的 $\text{MoO}_3/\text{SiO}_2$ 催化剂与载体 SiO_2 的吸附-脱附等温线形状相似. 根据IUPAC吸附等温线的分类标准, 10% $\text{MoO}_3/$

$\text{SiO}_2\text{-TS}$ 和10% $\text{MoO}_3/\text{SiO}_2\text{-C}$ 均为IV型等温线, 且出现了明显的H1型滞后环, 表明两种催化剂仍保持了典型的介孔结构.

表1列出了两种不同方法制备的10% $\text{MoO}_3/\text{SiO}_2$ 催化剂比表面积和孔结构参数. 与载体相比, 等体积浸渍法制备的催化剂比表面积和孔体积出现了下降, 表明有 MoO_3 进入并堵塞了载体孔道, 而TS法制备的催化剂比表面积和孔体积下降更为明显, 这可能是由于更多的 MoO_3 向载体表面迁移时堵塞了微孔.

3.1.2. XRD表征

图2为TS法和等体积浸渍法制备的10% $\text{MoO}_3/\text{SiO}_2$ 催化剂XRD谱图. 可以看出, 等体积浸渍法制备的10% $\text{MoO}_3/\text{SiO}_2$ 催化剂在 $2\theta = 12.8^\circ, 23.3^\circ, 25.7^\circ, 27.4^\circ, 33.1^\circ, 33.7^\circ, 39.0^\circ, 39.7^\circ, 45.7^\circ, 46.3^\circ$ 和 49.2° 等处出现了明显的正交相 MoO_3 (JCPDS 05-0508)特征衍射峰. 而相同负载量经TS法制备的催化剂则未出现正交相 MoO_3 的特征衍射峰, 这可能是由于 MoO_3 以高分散形式或者无定形态分布在载体表面.

图3为不同 MoO_3 负载量时 $\text{MoO}_3/\text{SiO}_2\text{-TS}$ 催化剂的XRD谱图. 可以看出, 当 MoO_3 负载量为2%, 6%和10%时, 所有催化剂均未观察到正交相 MoO_3 的特征衍射峰, 表明 MoO_3 以高分散形式或无定形态存在; 当 MoO_3 负载量为14%时, 有较弱的正交相 MoO_3 特征衍射峰出现; 继续增大 MoO_3 负载量至18%时, MoO_3 晶粒的衍射峰变得更尖锐, 表明 MoO_3 晶粒变大.

3.1.3. Raman表征

图4为TS法和等体积浸渍法制备的 $\text{MoO}_3/\text{SiO}_2$ 催化剂的Raman谱图. 从中可以看出, 两种方法制备的 $\text{MoO}_3/\text{SiO}_2$ 催化剂均在666, 819和995 cm^{-1} 处出现了明显的 MoO_3 特征峰^[34,35,40]. 其中666和819 cm^{-1} 为 MoO_3 中 Mo-O-Mo 桥键振动峰, 995 cm^{-1} 为末端 Mo=O 官能团伸缩峰. 在874, 959和981 cm^{-1} 处并未出现峰, 意味着两种方法制备的催化剂表面活性物种均以 MoO_3 单体形式出现, 未发生解离和聚合^[40].

3.1.4. XPS表征

表2为TS法和等体积浸渍法制备的10% $\text{MoO}_3/\text{SiO}_2$ 催化剂表面XPS分析结果. 可以看出, TS法和等体积浸渍法制备的催化剂表面 Mo 的 $3d_{3/2}$ 结合能分别为235.7和235.6 eV, 而 $3d_{5/2}$ 结合能均为232.6 eV, 与文献中^[22,25]报道的 MoO_3 中 $3d_{3/2}$ 、 $3d_{5/2}$ 结合能一致, 无明显位移, 意味着两种方法制备的催化剂中钼都以 MoO_3 形式存在, 与Raman表征结果一致. 此外, 表2还列出了两种方法制备

的10%MoO₃/SiO₂催化剂表面钼含量。显然, 10%MoO₃/SiO₂-TS催化剂表面Mo含量比10%MoO₃/SiO₂-C催化剂更高, 说明TS法有利于MoO₃向催化剂载体表面迁移。结合XRD谱图结果, 10%MoO₃/SiO₂-TS催化剂未出现MoO₃特征衍射峰, 而10%MoO₃/SiO₂-C催化剂出现了MoO₃晶粒特征衍射峰, 表明10%MoO₃/SiO₂-TS催化剂中活性组分MoO₃较10%MoO₃/SiO₂-C催化剂分散的更好。

3.1.5. 吡啶吸附IR表征

吡啶吸附红外光谱可以有效区分催化剂上的酸型。通常1450 cm⁻¹附近出现的特征吸收峰为Lewis酸中心, 1540 cm⁻¹附近出现的特征吸收峰为B酸中心^[22]。图5为TS法和等体积浸渍法制备的10%MoO₃/SiO₂催化剂吡啶红外谱图。可以看出, 两种方法制备的催化剂在1450 cm⁻¹附近出现吸收峰, 在1540 cm⁻¹附近没有出现特征吸收峰。这说明10%MoO₃/SiO₂-TS和10%MoO₃/SiO₂-C均产生了L酸中心而无B酸中心。

3.1.6. NH₃-TPD表征

在NH₃-TPD曲线中, 低于400 °C的峰对应着催化剂的弱酸中心, 而大于400 °C的峰对应着催化剂强酸中心^[13,24]。图6为10%MoO₃/SiO₂催化剂的NH₃-TPD图谱。可以看出, 10%MoO₃/SiO₂-C催化剂和10%MoO₃/SiO₂-TS催化剂脱附峰温变化较小, 分别出现在190.9和192.6 °C, 意味着两种催化剂都只存在弱L酸中心, 无强酸中心出现^[22,30]。通过对氨脱附的峰面积进行分析, 发现10%MoO₃/SiO₂-TS和10%MoO₃/SiO₂-C的氨脱附量分别为0.088和0.092 mmol/g, 即两种催化剂所具有的总酸量相差不大。

3.2. 催化剂性能

3.2.1. 制备方法的影响

制备方法对MoO₃/SiO₂催化性能的影响见图7。以MoO₃作为催化剂时, 苯酚转化率仅为26.7%。以钼酸铵为前驱体等体积浸渍法制备的10%MoO₃/SiO₂-C为催化剂时, 苯酚转化率为43.8%。而以TS法制备的10%MoO₃/SiO₂-TS为催化剂时, 苯酚转化率大幅增加到56.2%, MPO和DPO选择性分别达89.0%和10.9%。

催化剂Raman表征表明10%MoO₃/SiO₂-TS催化剂和10%MoO₃/SiO₂-C催化剂上钼元素均以MoO₃单体形式存在, 未发生解离和聚合; 吡啶红外光谱和NH₃-TPD表征表明MoO₃与SiO₂相互作用产生的弱Lewis酸中心是草酸二甲酯和苯酚酯交换反应的活性中心。马新宾等^[22]研究发现MoO₃/SiO₂催化剂性能与MoO₃的分散状态有

关。催化剂表面上团聚的MoO₃晶粒越多, 越不利于产物MPO和DPO的生成^[23,28]。结合催化剂的XRD和XPS表征结果, 10%MoO₃/SiO₂-TS较10%MoO₃/SiO₂-C表现出更高的催化性能归因于10%MoO₃/SiO₂-TS催化剂表面钼含量更高且MoO₃分散得更好, 可产生更多的弱酸中心。

3.2.2. MoO₃负载量对MoO₃/SiO₂-TS催化剂性能的影响

不同MoO₃负载量对酯交换反应的影响见图8。可以看出, 随着催化剂中MoO₃含量增加, 苯酚转化率和DPO选择性先逐渐增大然后下降, 而MPO选择性则出现完全相反的趋势。当MoO₃负载量为10%时, 苯酚的转化率和DPO选择性达最大, MPO选择性为最低, 表明此时有较多的MPO转化成DPO。与10%MoO₃/SiO₂-TS催化剂相比, 14%MoO₃/SiO₂-TS和18%MoO₃/SiO₂-TS催化剂没有表现出更好的催化性能, 可能是由于MoO₃负载量过高时, 催化剂表面形成的正交相MoO₃晶粒一定程度上覆盖了原有的活性位。类似的现象在TiO₂/SiO₂催化剂体系、MoO₃/γ-Al₂O₃催化体系和泥浆浸渍法制备的MoO₃/SiO₂催化体系中也有报道^[21,23,27,28]。

3.3. 10%MoO₃/SiO₂-TS催化酯交换反应条件优化

3.3.1. 催化剂用量

图9为10%MoO₃/SiO₂-TS催化剂用量对草酸二甲酯与苯酚酯交换反应的影响。可以看出, 随催化剂用量从0.3 g增加到1.2 g, 苯酚的转化率由33.6%增加到56.2%, DPO选择性由2.8%增加至10.9%, 而MPO选择性则由97.1%降至89.0%, 酯交换总选择性在99.8%以上。当催化剂用量为1.5 g时, 苯酚转化率反而稍有下降, 但酯交换总选择性基本保持不变。这表明较适宜的催化剂用量为1.2 g。

3.3.2. 反应温度

图10为反应温度对酯交换的影响。可以看出, 当温度为140 °C, 酯交换几乎不能进行。随着体系反应温度逐渐升高, 苯酚转化率和DPO选择性急剧增大, MPO选择性不断下降, 说明提高反应温度有利于酯交换反应和MPO歧化反应的进行, 这与酯交换和歧化反应均为吸热反应相吻合。当反应温度为180 °C, 苯酚转化率和产物MPO和DPO收率达最大值。因此, 适宜的酯交换反应温度为180 °C。

3.3.3. 草酸二甲酯与苯酚摩尔比

图11为原料中DMO与苯酚摩尔比对酯交换反应的影响。可以看出, 当草酸二甲酯过量时, 随着DMO与苯酚摩尔比由0.5增大到2, 产物MPO和DPO的选择性变化

不明显, 但苯酚转化率明显提高, 表明DMO用量增加有利于苯酚的转化; 继续增大摩尔比到2.5时, 苯酚转化率增加较小. 因此, 适宜的草酸二甲酯与苯酚摩尔比为2. 此时, 苯酚转化率可达65.6%, MPO和DPO的选择性分别为89.3%和10.6%.

3.3.4. 反应时间

图12为反应时间对酯交换反应的影响. 可以看出, 随着反应时间的延长, 苯酚转化率逐渐增加, 而MPO和DPO选择性均变化较小, 表明延长反应时间有利于酯交换的进行而对MPO歧化反应影响不大. 反应4 h时, 苯酚转化率已达70.9%, MPO和DPO收率分别达63.1%和

7.7%. 继续延长反应时间至5 h时, 苯酚转化率增加幅度较小. 因此, 较佳的反应时间为4 h.

4. 结论

与等体积浸渍法相比, 热扩散法制备的10%MoO₃/SiO₂-TS催化剂表面钼含量更高且活性组分MoO₃分散得更好, 在草酸二甲酯与苯酚酯交换反应中表现出更好的催化性能. 在优化的工艺条件下, 苯酚转化率可达70.9%, MPO和DPO收率分别达63.1%和7.7%. 热扩散法处理过程简单, 绿色环保, 为开发负载型MoO₃催化剂提供了选择, 具有重要的意义.