

## Characterization and catalytic activity of Ti-MCM-41 for transesterification of dimethyl carbonate with phenol

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**ABSTRACT:** Highly dispersed titanium on MCM-41 molecular sieve catalysts were synthesized by impregnation method. The Ti-MCM-41 catalysts were characterized with different techniques. The catalysts were used for the synthesis of diphenyl carbonate (DPC) by the transesterification of dimethyl carbonate (DMC) with phenol. The characterization results indicate that titanium exists only in the framework. And the six mesoporous structures of MCM-41 were maintained when the titanium content was up to 10 wt %. The catalysts have large surface area and pore size, and contain titanium with four ligands. The Ti-MCM-41 catalyst displayed a high catalytic activity in the synthesis DPC process.

**KEYWORDS:** Diphenyl carbonate; Dimethyl carbonate; Phenol; Transesterification; Ti-MCM-41

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### I. INTRODUCTION

Diphenyl carbonate (DPC) is a green engineering thermoplastic intermediate with low toxicity and no pollution of the circumstance. It is used to produce many organic compounds and polymers, particularly as an intermediate for synthesis of polycarbonate without using phosgene<sup>[1]</sup>. DPC was prepared by these methods such as phosgenation technique, oxidative carbonylation of phenol, and transesterification of phenol and dimethyl carbonate (DMC)<sup>[2]</sup>. The transesterification reaction between dimethyl carbonate (DMC) and phenol is the most promising method for the industrial production of DPC<sup>[3]</sup>. In view of the difficulties in separation and recycling of homogeneous catalysts, much attention is being focused on highly active heterogeneous catalysts for the transesterification reaction between DMC and phenol.

To date, the reported heterogeneous catalysts are mainly composed of single or composite oxides<sup>[4]</sup>, zeolites<sup>[5]</sup>, hydrotalcite-like compounds<sup>[6]</sup> and heteropoly compounds<sup>[7]</sup>. For instance, Wang and coworkers reported that MoO<sub>3</sub>/SiO<sub>2</sub> showed a high activity for both the transesterification step and the disproportionation step while the catalyst recovery was very difficult in the final process<sup>[8]</sup>. Won reported the induction period was greatly shortened when the TiO<sub>2</sub>/SiO<sub>2</sub> catalyst was pretreated with dimethylcarbonate at the reaction temperature<sup>[9]</sup>. Tang and coworkers found that the core-shell TiO<sub>2</sub>@SiO<sub>2</sub> catalyst that is composed of TiO<sub>2</sub> core of diameter 220-300nm and SiO<sub>2</sub> shell of thickness 40-60 nm presented a better catalytic performance, which is due to the formation of Ti-O-Si bonds<sup>[10]</sup>. Other groups developed the catalyst such as Pb<sub>3</sub>O<sub>4</sub>/ZnO, PbO/MgO, and V<sub>2</sub>O<sub>5</sub> catalysts for the DPC synthesis with DMC and phenol. However, the toxic oxides of lead and vanadium are not environmentally benign catalysts<sup>[11]</sup>.

In this study, Ti-MCM-41 was prepared, and characterized by XRD, Raman spectroscopy and Mo K-edge X-ray absorption fine structure (XAFS) measurement. To investigate the relation of local structure and catalytic activity, the transesterification reaction of DMC and phenol was carried out. Our study revealed that Ti-MCM-41 is an efficient, recyclable and environmentally benign heterogeneous catalyst for the synthesis of DPC from the DMC's phenolic transesterification.

## II. EXPERIMENTAL

### 2.1 Chemical reagents

Tetraethyl orthosilicate (TEOS), cetyl trimethyl ammonium bromide (CTAB), titanocene dichloride, chloroform, triethylamine, aqueous ammonia, phenol, and dimethyl carbonate (DMC) were of analytical reagent (AR) grade and directly used in this study.

### 2.2 Catalyst preparation

#### 2.2.1. Preparation of Si-MCM-41<sup>[12]</sup>

Ti-MCM-41 catalyst was synthesized using a TEOS as Si source. CTAB was used as a template and ammonia water was used to provide alkalinity of the reaction. CTAB (2.0 g) and deionized water (65 ml) were added in a three-necked flask of 500 ml. The mixture was continually stirred at 40 °C for half an hour until the CTAB was dissolved completely. The pH of the solution was adjusted to 11 with aqueous ammonia. Then, 8.5 g TEOS was slowly added into the solution. After the mixture was stirred for 2 h, it was aged at ambient temperature for 24 h. The mixture was then heated at 110 °C for 24 h in the reaction kettle. The resulting product was filtered and washed with deionized water. Finally, the Si-MCM-41 white powder was obtained by calcining in air at 650 °C for 3.5 h.

#### 2.2.2. Preparation of Ti-MCM-41

The titanium-loaded MCM-41 catalysts were synthesized following a controlled loading process. The dried Si-MCM-41 powder and triethylamine were added to chloroform under the continuous stirring. Then, titanocene dichloride was added to the above mixture which was then strongly stirred for 3 h. After filtration, washing and removing the excess titanocene dichloride, the product was dried. Then, the obtained product was calcined at 500 °C for 2 h and 650 °C for 3.5 h under air, respectively. Samples with different titanium contents can be obtained by changing ratio of the reagents.

### 2.3 Characterization

Powder X-ray diffraction (XRD) analyses were carried out on a Rigaku D/max-2500 X-ray diffraction equipped with Cu-K<sub>α</sub> radiation. The experimental conditions were as follows: voltage 40 kV, current 100 mA. Fourier transform infrared (FT-IR) absorption spectra were recorded on a VER TEX 70 using KBr pellet. N<sub>2</sub> adsorption-desorption isotherms were recorded at 77K on a Micromeritics ASAP 2020. UV-Vis measurements were recorded on a Lambda 650S spectrometer, and the referenced BaSO<sub>4</sub> were used for the measurements. Transmission electron microscopy (TEM) experiments were conducted on a JEM-3010. X-ray photoelectron spectroscopy (XPS) was recorded by a VG ESCALAB5 multi-function electronic energy spectrometer with Al-K<sub>α</sub> ray under CAE mode.

### 2.4 Reaction procedure

The reaction was carried out in a 100 mL three-neck round-bottomed flask, equipped with a magnetic stirring bar, a nitrogen inlet, a dropping funnel, and a fractionating column connected to a liquid dividing head. Under nitrogen gas, phenol and a catalyst were introduced into the flask. After the mixture was heated to 180 °C, DMC was added drop-wise. The reaction mixture was under refluxing condition at 180 °C. During the reaction, a distillate of DMC and methanol was collected slowly in a receiver flask attached to the liquid dividing head and for analysis. After the reaction, the mixture was cooled to room temperature and the catalyst was filtered, and then the filtrate was analyzed by gas chromatography.

### 2.5 Product analysis

The azeotrope of DMC and methanol and the reaction system were analyzed by gas chromatography equipped with a capillary column (30 m) and a flame ionization detector (FID). Identification analysis of the reaction system was conducted on a 6890/5973 GC-Mass spectrometer.

## III. RESULT AND DISCUSSION

### 3.1 Catalyst structure

Fig. 1 shows small angle XRD spectra of samples and Fig. 2 shows big angle XRD spectra of samples. For all samples, a strong peak at 2.3° was presented and two weak peaks were in the range of 2° to 5.5°. The weak and broad peak at 23° was observed due to the existence of amorphous SiO<sub>2</sub>. The low-range diffraction shows that mesoporous structure of MCM-41 molecular sieve was formed for all samples and has a better long-range order and crystallinity. The peak intensity of the modified sample decreases and the peak position also slightly migrates, which indicates the metallic elements have entered into the framework of the molecular

sieve and changed the long-range order of the silicon molecular sieve. With the increase of Ti content, the characteristic peak slightly decreased. From the big angle XRD spectra of samples can be seen that spectrum has not been obviously changed when the titanium content reached up to 10%. The characteristic peak of crystalline  $\text{TiO}_2$  was not been found, which indicated that titanium existed only in the framework of molecular sieve.

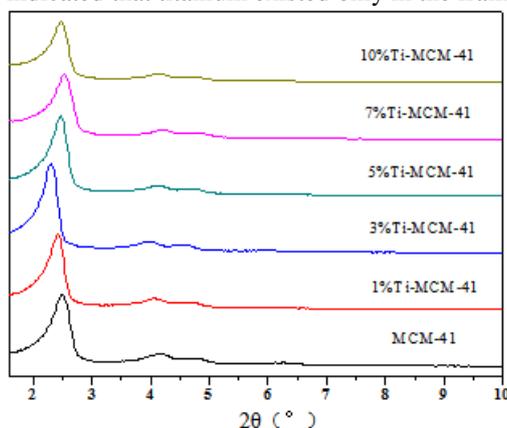


Fig.1 XRD patterns of the samples(Small angle area)

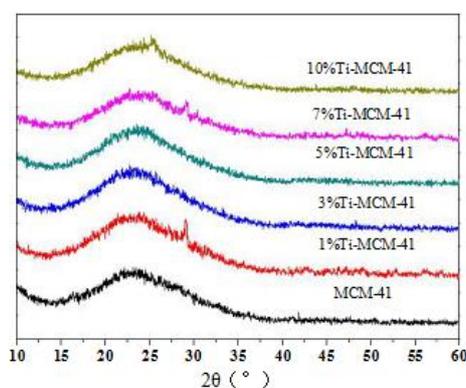


Fig.2 XRD patterns of the samples(big angle area)

### 3.2 FT-IR analysis

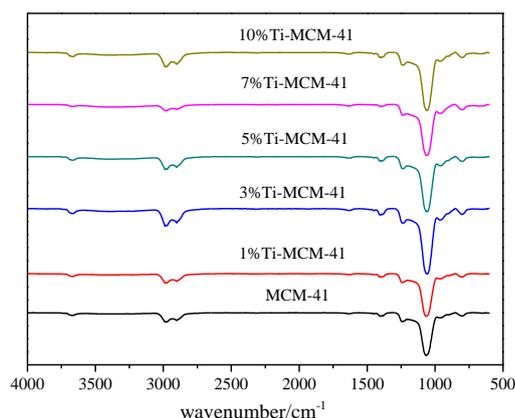


Fig. 3 FT-IR spectra of the samples

Fig.3 shows FT-IR spectra of MCM-41 and Ti-MCM-41. Two bands appear at the same position of MCM-41 and Ti-MCM-41 spectra. The characteristic peak around  $1085 \text{ cm}^{-1}$  is observed, which is corresponded to the asymmetric stretching vibration of Si-O-Si bond. The other characteristic peak around  $800 \text{ cm}^{-1}$  is observed, which may be caused by the symmetric stretching vibration of Si-O-Si bond. The intensity of Si-O-Si bond is enhanced due to the introduction of Ti. The main reason is that the molecular sieve asymmetry structure

was increased by the larger titanium, and thus distortion and vibration of the silicon-oxygen tetrahedron were formed. In addition, for all samples the peak at  $652\text{ cm}^{-1}$  was not found, which indicates titanium exists in the skeleton state. With the increase of Ti atom, Ti atom replaces Si or O atom and the peak at  $1085\text{ cm}^{-1}$  decreased gradually. The above obtained results indicate that the mesoporous structure of MCM-41 is not affected after titanium atom is introduced.

### 3.3 Pore Structure and Specific Surface Area

Fig.4 shows the nitrogen adsorption-desorption isotherm of Ti-MCM-41. The sample exhibits a type IV isotherms pattern with a pronounced hysteresis loop starting at  $0.3\text{ p/p}_0$ , which indicates the structure of Ti-MCM-41 remains intact after the active component of titanium was introduced in the carrier.

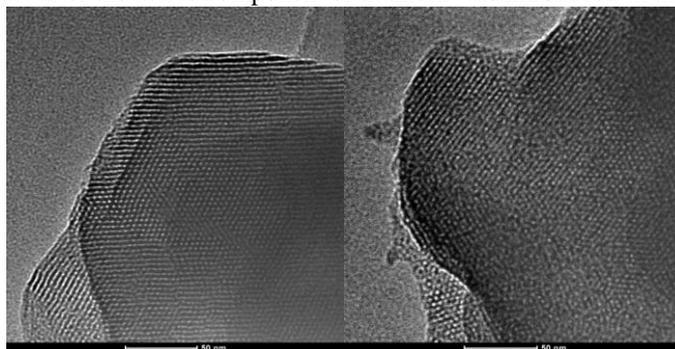


Fig.4 TEM images of Ti-MCM-41(a) TEM images of 5%Ti-MCM-41(b)

The textural properties of the catalyst sample are listed in Table 1. Due to loading Ti atom onto MCM-41, the BET surface area and pore volume decrease to  $975.43\text{ m}^2/\text{g}$  and  $0.80\text{ cm}^3/\text{g}$ , respectively. The slight decrease in the BET surface area ( $S_{\text{BET}}$ ) and pore volume ( $V_p$ ) of Ti-MCM-41 may be due to the titanium into the internal surface of MCM-41.

Table 1 Pore structure analysis of Ti-MCM-41

Catalyst	SBET ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	BJH pore size (nm)
MCM-41	1012	0.96	3.5
5%Ti-MCM-41	975.43	0.80	3.26

### 3.4 Transmission Electron Microscope

The morphology of the catalysts was observed by TEM, and the images are shown in Fig.5. The TEM images clearly reveal that the microstructure of the samples was not changed after loading the active components of titanium and the original pore structure was maintained.

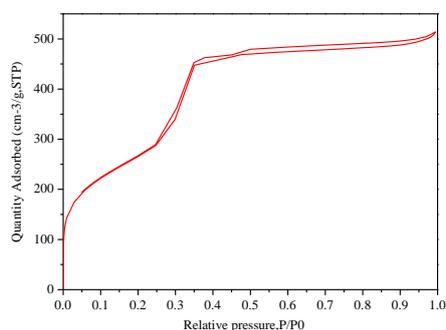


Fig.5  $\text{N}_2$  adsorption-desorption isotherm of 5% Ti-MCM-41

### 3.5 X-ray Photoelectron Spectroscopy Analysis

In order to obtain chemical state information of the active components in the catalysts, XPS analysis has been carried out as shown in Fig.6. Two strong peaks were at  $459.71\text{ eV}$  and  $465.31\text{ eV}$  from Fig.6a, respectively. The peak at  $459.71\text{ eV}$  is attributed to Ti  $2\text{P}_{3/2}$  and the peak at  $465.31\text{ eV}$  is assigned to Ti  $2\text{P}_{1/2}$ . The

results further confirm titanium atom has entered into the framework of molecular sieve.

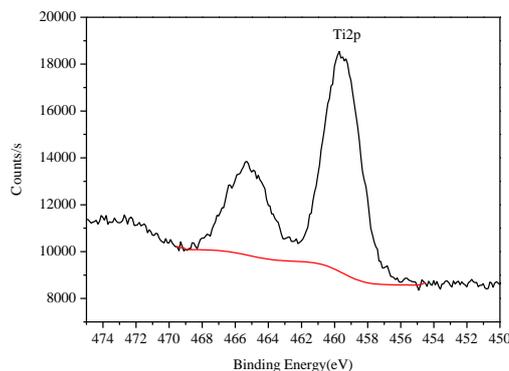


Fig.6 XPS spectra of 5% Ti-MCM-41 for the catalyst(a)

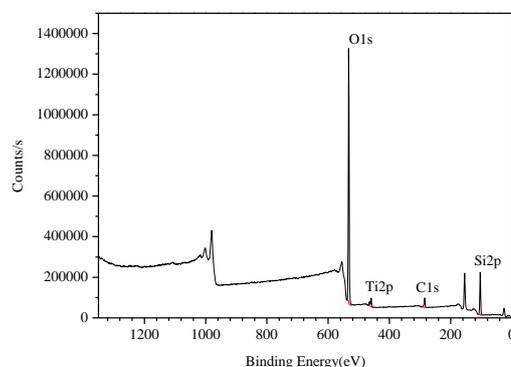


Fig.6 XPS spectra of 5% Ti-MCM-41 for the catalyst(b)

### 3.6 Catalytic activity

The evaluation experiment of the catalyst was carried out in a reactive distillation unit. A similar set of catalytic reactions was investigated via catalyst with different titanium contents as shown in table. 2. The blank experiment showed very low conversion of DMC (0.82%) and did not form DPC at all. The results imply that the raw material conversion rate is very low in the blank experiment while the conversion and selectivity are improved after adding the catalyst samples. When the amount of Ti atom was increased from 1% to 5%, DMC conversion was increased from 11.24% to 32.13%, the DPC yield was increased from 3.87% to 9.77%, and the MPC yield was enhanced from 7.23% to 22.21%. More weak acid sites are favorable for improving the catalytic properties, which were assigned to the small particle size, large surface area and plenty of Ti (IV) active centers inside the framework<sup>[13]</sup>. However, when the amount of Ti atom was further increased, DMC conversion, DPC and MPC yield were all decreased. The results indicate that with the introduction of active components of titanium atom, the catalysts presented high catalytic activity and high selectivity. However, the performance of the catalyst is related to the content of titanium atom. Whether the quantity of catalyst is low or too high, the selectivity and conversion rate are low and higher yield can be obtained only when the quantity is appropriate. So an appropriate amount of Ti ( 5%) supported on MCM-41 was obtained when the best results of MPC and DPC in 22.21% and 9.77% yields were given. Correlated with the analysis results of catalyst characterization, the titanium exists in the skeleton of zeolite and the framework titanium has catalytic activity in the reaction. The activity of catalyst is related to the structure of catalyst. With the increase of titanium content on the catalyst, the specific surface area, pore volume and pore size were affected and the catalyst presented different catalytic activity. The Si-O-Ti was active sites for reaction, and the interaction mode between Ti-O-Si and DMC was main factor to determine carboxymethylation and methylation<sup>[14]</sup>. Therefore the titanium content of catalyst should be appropriate and a good catalytic activity can be ensured.

**Table 2** the catalytic activity of the catalysts in the transesterification reaction

Catalyst	DMC Conversion (%)	MPC Selectivity (%)	DPC Selectivity (%)	MPC Yield (%)	DPC Yield (%)	Transesterification Selectivity (%)
Blank	0.82	40.12	0	0.33	0	40.12
1%Ti-MCM-41 <sup>a</sup>	11.24	64.36	34.46	7.23	3.87	98.82
3%Ti-MCM-41	20.4	65.97	33.03	12.85	6.94	99.0
5%Ti-MCM-41	32.13	69.14	30.42	22.21	9.77	99.56
7% Ti-MCM-41	19.71	68.38	30.92	13.48	6.09	99.3
10% Ti-MCM-41	14.52	66.41	32.79	9.64	4.76	99.2

<sup>a</sup>Note: The 1%Ti-MCM-41 in the table denotes the catalyst has a titanium content of 1%.

<sup>b</sup>Note: Reaction conditions were as follows: phenol 30.0g, DMC 30.0g, catalyst 0.5g, reaction temperature 180°C, reaction time 8h.

#### IV. CONCLUSION

The reaction between phenol and DMC was promoted by Ti-MCM-41. An appropriate amount of Ti (5%) supported on MCM-41 gave the best results of producing MPC and DPC in 22.21% and 9.77% yields at 8h. The six mesoporous structures of MCM-41 molecular sieve have better long-range order and crystallinity and the reaction selectivity is strengthened. The absorption peak intensity of the modified sample decreases, and the peak position also slightly migrates, which indicates the metallic element (Ti) has entered into the framework of zeolite and Si-O-Ti bond was formed. The structures and chemical state of titanium species in Ti/MCM-41 had been investigated by XRD and XPS. The titanium of catalyst still exists as Ti (IV) species up to 10 wt % loading. The species of Si-O-Ti was activity sites for transesterification reaction. And the interaction mode between Ti-O-Si and DMC was main factor to determine carboxymethylation and methylation reactions.

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