

**Electronic supplementary information (ESI) for the manuscript:**

High Si/Al ratio HZSM-5 zeolite: an efficient catalyst for the synthesis of polyoxymethylene dimethyl ethers from dimethoxymethane and trioxymethylene

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**1. More Experimental Details:**

*1.1. Catalyst preparation*

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The ZSM-5 zeolites with different Si/Al ratios and crystal sizes were synthesized by hydrothermal method according to the procedures described by Xu and coworkers.<sup>1</sup> For the synthesis of ZSM-5 with a high Si/Al molar ratio ( $> 200$ ), silica white was used as the silicon source. The zeolite samples were recovered from the crystallization mixture by centrifuging and washed with distilled water under ultrasonic irradiation to remove physically attached templating molecules and silicate/silicoaluminate species. The recovered ZSM-5 zeolite samples were then dried at 110 °C overnight and calcined at 550 °C for 10 h in air. The ZSM-5 zeolite in hydrogen form, i.e. HZSM-5, was obtained through ion-exchanging with aqueous  $\text{NH}_4\text{NO}_3$  solution (1 M,  $m(\text{liquid})/m(\text{solid}) = 30$ ) at 80 °C for 4 h and subsequent calcination at 550 °C for 6 h. The actual Si/Al ratio of zeolite sample was determined by the inductive coupled plasma atomic emission spectrometry (ICP-AES).

### *1.2. Catalyst characterization*

The X-ray diffraction (XRD) patterns of the zeolite catalysts were collected on a Rigaku MiniFlex II desktop X-ray diffractometer with  $\text{CuK}\alpha$  radiation source. The measurements were made in the  $2\theta$  range from 5° to 40° with a scanning rate of 4 °  $\text{min}^{-1}$ .

The nitrogen physisorption on the zeolite catalysts were performed at  $-195.7$  °C with a physisorption analyzer (ASAP 2000, Micromeritics Instrument Co., USA). The catalyst samples were degassed under high vacuum at 200 °C for 8 h prior to the measurement. The surface area was calculated from the adsorption branch in the range of relative pressure from 0.05 to 0.25 by Brunauer–Emmett–Teller (BET) method and the pore size distribution was derived from the adsorption branch by Barrett-Joyner-Halenda (BJH) method; the pore volume was estimated at a relative pressure of 0.99.<sup>2</sup>

The temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) was performed on a

Micromeritics AutoChem II 2920 chemisorption analyzer. Approximately 100 mg of the zeolite sample was used in each measurement, which was first pretreated at 550 °C for 2 h in an argon stream (30 mL min<sup>-1</sup>) and then cooled down to 120 °C. Saturated adsorption of NH<sub>3</sub> on the zeolite sample was then achieved by introducing gaseous NH<sub>3</sub> (5 vol.% in argon, 30 mL min<sup>-1</sup>) into the sample tube for 30 min. After that, the physically adsorbed NH<sub>3</sub> was removed by flushing the sample tube with an argon flow (30 mL min<sup>-1</sup>) at 120 °C for 2 h. To get the NH<sub>3</sub>-TPD profile, the zeolite sample was then heated up from 120 to 550 °C at a ramp of 10 °C min<sup>-1</sup>; the amount of NH<sub>3</sub> released during the heating for desorption was measured by a thermal conductivity detector (TCD).

Fourier transform infrared (FT-IR) spectra were measured on a Bruker Tensor 27 FT-IR spectrometer. The zeolite sample was first pressed into a self-supported wafer. Prior to the measurement, the sample cell was evacuated to 10<sup>-2</sup> Pa at 450 °C for 2 h; the IR spectra were then recorded at room temperature. To get the FT-IR spectra for pyridine adsorption (Py-IR), pyridine vapor was introduced into the cell at room temperature for 1 h. After that, the zeolite samples were degassed for 2 h at 150, 250, and 350 °C and then the spectra was recorded and the background was subtracted. The concentrations of different acidic sites were calculated by following the procedures reported by Madeira and coworkers.<sup>3</sup>

Magic angle spinning (MAS) <sup>27</sup>Al single pulse NMR spectra were recorded on a Bruker Avance III 600 MHz Wide Bore spectrometer operating at a magnetic field of 14.2 T. <sup>27</sup>Al NMR spectra were recorded with a frequency of 156.47 MHz, a spinning rate of 13.0 kHz, and a recycling delay of 1 s. The <sup>27</sup>Al chemical shift is referred to the saturated Al(NO<sub>3</sub>)<sub>3</sub> solution.

### *1.3. Catalytic tests*

The catalytic performance of the HZSM-5 zeolites in the synthesis of polyoxymethylene dimethyl ethers (PODE<sub>n</sub>) was tested in a stainless steel autoclave of 100 mL lined with Teflon. Typically, 15.2 g dimethoxymethane (DMM), 9 g trioxymethylene (TOM) and 1.2 g HZSM-5 were loaded into the autoclave; the reaction mixture was heated to 120 °C and kept at this temperature for 45 min under vigorous stirring.

To consider the influence of HZSM-5 Si/Al ratio on the conversion of TOM and product distribution, the dissociation of TOM alone was also conducted over the HZSM-5 zeolites with different Si/Al ratios in a stainless steel autoclave of 25 mL lined with Teflon. For each test, 10.0 g CH<sub>2</sub>Cl<sub>2</sub>, 1.0 g TOM and 0.15 g HZSM-5 were loaded; the mixture was stirred continuously at 120 °C for 0.75 h.

The products after reaction, including PODE<sub>n</sub>, MeOH, HF<sub>n</sub>, FA, and unreacted reactants, were measured with decane as an internal standard by two gas chromatographs: one is Shimadzu GC-2014C equipped with a FID detector and DB-1 capillary column for determining PODE<sub>n</sub>, DMM, MeOH, etc.; the other one is Shimadzu GC-14B equipped with a TCD detector and Porapak T packed column for formaldehyde (FA), polyformaldehydes (PF<sub>n</sub>), methyl formate (MF), DMM, water, etc. In any case, the mass balance accounts for 95–105%.

The conversions of DMM ( $x_{\text{DMM}}$ ) and TOM ( $x_{\text{TOM}}$ ) are determined by

$$x_{\text{DMM}} = (n_{\text{DMM,feed}} - n_{\text{DMM,product}}) / n_{\text{DMM,feed}} \times 100\%,$$

$$x_{\text{TOM}} = (n_{\text{TOM,feed}} - n_{\text{TOM,product}} - n_{\text{FA,product}}/3) / n_{\text{TOM,feed}} \times 100\%,$$

and the mass selectivity to each product is determined by

$$s_i = m_{i,\text{product}} / \sum m_i \times 100\%.$$

For example, the mass selectivity to PODE<sub>2-8</sub> is

$$S_{\text{PODE}_{2-8}} = m_{\text{PODE}_{2-8},\text{product}} / \sum m_i \times 100\%,$$

where  $m_i$  is the mass of species  $i$  ( $m_{\text{PODE}_{2-8}}$ , the mass of PODE<sub>2-8</sub>) in the products and  $\sum m_i$  is the mass of all the liquid products trapped after the reaction test.

Turnover frequency (TOF), the number of TOM molecules converted per active site and second, is estimated on the basis of total Al content in the HZSM-5 zeolite, i.e.,

$$\text{TOF} = \frac{[\text{Number of converted reactant molecules}]}{[\text{Number of active sites}] \times [\text{Time}]} = \frac{n_{\text{TOM,feed}} \times x_{\text{TRI}}}{m_{\text{cat}} \times \frac{w_{\text{Al}}}{M_{\text{Al}}} \times t},$$

where  $m_{\text{cat}}$  is the mass of HZSM-5 zeolite,  $w_{\text{Al}}$  means the mass percentage of Al element in the HZSM-5 which is analyzed by ICP-AES,  $M_{\text{Al}}$  is the atomic mass of Al atom (27.0) and  $t$  means the reaction time (s).

For most of the catalytic tests, the reaction time was 45 min (2700 s), and the quantities of DMM and TOM in the feed were 15.2 g and 9.0 g (0.1 mol), respectively. As an example for the synthesis of PODE <sub>$n$</sub>  over HZSM-5 with a Si/Al molar ratio of 200 at 120 °C, the catalyst weight was 1.2 g in which the mass percentage of Al is 0.22 wt.%. As the conversion of TOM was 86.7%, the TOF can be calculated as:

$$\text{TOF} = (0.1 \times 0.867) / (1.2 \times 0.0022 / 27.0) / 2700 = 0.33 \text{ (s}^{-1}\text{)}.$$

## 2. More Results of Catalyst Characterization and Reaction Tests:

### 2.1. More catalyst characterization results

The XRD patterns shown in Fig. S1 illustrate that all the as-synthesized HZSM-5

zeolites are well crystallized with the characteristic peaks of MFI structure.

**{Fig. S1}**

As well known, the acid sites on a zeolite catalyst mainly come from Al atoms at different locations of the zeolite framework. To investigate the location of Al atoms in HZSM-5 with different Si/Al ratios,  $^{27}\text{Al}$  MAS NMR spectra are depicted in Fig. S2. It was reported that Al species in four-, five-, and six-coordination states exhibit signals at 55–60, 30, and 0 ppm, respectively.<sup>4,5</sup> Here three HZSM-5 samples all exhibit a symmetrical and narrow signal at about 55 ppm, indicating that most of the Al species are in tetrahedral coordination ( $\text{Al}^{\text{IV}}$ ), which is located in the framework of the HZSM-5 lattice.<sup>6</sup> However, the HZSM-5 sample with a Si/Al molar ratio of 56 shows a distinct signal at about 0 ppm, suggesting that the hex-coordinated or extra-framework Al species exist in the HZSM-5 zeolite with a low Si/Al ratio. It may be speculated that the framework Al species with four-coordination structure act mainly as the Brønsted acid sites that are active for the synthesis of  $\text{PODE}_n$ , whereas the hex-coordinated or extra-framework Al species promote the formation of MF.

**{Fig. S2}**

*2.2. Selection of appropriate reaction conditions*

The effect of the reaction time on the reactants conversion and products distribution in the synthesis of  $\text{PODE}_n$  over HZSM-5 with a Si/Al molar ratio of 580 was considered. As shown in Fig. S3, when the reaction time exceeds 0.75 h, the conversions of DMM and TOM and mass selectivity to  $\text{PODE}_{2-8}$  keep roughly the same level, suggesting that a reaction time of 45 min is sufficient and appropriate for the synthesis of  $\text{PODE}_n$  over the HZSM-5 zeolites.

### {Fig. S3}

The effect of the HZSM-5 catalyst amount on the reactants conversion and products distribution in the synthesis of PODE<sub>n</sub> over HZSM-5 with a Si/Al molar ratio of 580 was also considered. As shown in Fig. S4, DMM conversion decreases and TOM conversion increases gradually with the increase of catalyst usage up to 5.0 wt.%, whereas the mass selectivity to PODE<sub>2-8</sub> keeps roughly the same level. Over that, for example, when the amount of catalyst used reaches 10 wt.%, the mass selectivity to PODE<sub>3-8</sub> is decreased, probably suggesting that excessive amount of the acid catalyst may promote the decomposition of long-chain PODE<sub>n</sub> products. As a result, the optimized amount of catalyst used in the reaction is about 5 wt.%, which gives the highest yield of PODE<sub>2-8</sub>.

### {Fig. S4}

The effect of the feed DMM/TOM molar ratio ranging from 1.5 to 5 on the reactants conversion and products distribution in the synthesis of PODE<sub>n</sub> over HZSM-5 with a Si/Al molar ratio of 340 was considered. As listed in Table S1, a DMM/TOM molar ratio of 2 is appropriate to get high yield of PODE<sub>2-8</sub>.

### {Table S1}

#### 2.3. Characterization of used and re-generated catalysts

Among the major virtues of HZSM-5 as a catalyst in PODE<sub>n</sub> synthesis are its high stability, good recyclability and facility for regeneration. In this work, the HZSM-5 catalyst exhibits excellent stability and reusability; the mass yield to PODE<sub>2-8</sub> only displays a very slight decrease after being reused for 15 cycles upon a simple centrifugation separation. After that, the activity of the used catalyst can be recovered by a calcination process at 550

°C for 5 h and then keeps the same trend like that of the fresh catalyst in the next runs. Compared with the fresh catalyst, further XRD and IR characterizations of the used and re-activated HZSM-5 catalysts illustrate that the structure and properties changes little, except that the used catalyst upon a centrifugation separation may still have certain reactants, products or intermediates adsorbed on the zeolite surface which however only have a minor effect on the catalytic activity.

For example, the fresh HZSM-5 catalyst with a Si/Al molar ratio of 580 has a surface area of  $376 \text{ m}^2 \text{ g}^{-1}$  and micropore volume of  $0.114 \text{ mL g}^{-1}$ . After being used for 15 cycles, the surface area and micropore volume of the spent HZSM-5 catalyst are slightly decreased to  $353 \text{ m}^2 \text{ g}^{-1}$  and  $0.093 \text{ mL g}^{-1}$ , respectively; after re-generation through the calcination activation at  $550 \text{ }^\circ\text{C}$ , they are recovered to  $365 \text{ m}^2 \text{ g}^{-1}$  and  $0.107 \text{ mL g}^{-1}$ , respectively.

Fig. S5(I and II) shows the FT-IR spectra of the HZSM-5 zeolites before and after the reaction. The absorption bands at  $1225$ ,  $550$  and  $450 \text{ cm}^{-1}$  are the characteristic of the ZSM-5 crystalline structure,<sup>7-8</sup> whereas the peaks around  $800$ ,  $1105$  and  $1200 \text{ cm}^{-1}$  are ascribed to the  $\text{SiO}_4$  tetrahedron units. Obviously, the absorption bands around  $905$  and  $935 \text{ cm}^{-1}$  in the used catalyst should be attributed to the polyformaldehyde species adsorbed on the catalyst surface,<sup>9</sup> whereas the bands at  $2900\text{--}3000 \text{ cm}^{-1}$  is corresponded to  $\text{PODE}_n$  species ( $2980 \text{ cm}^{-1}$  for  $\nu_{\text{as}}[\text{CH}_3\text{O}]$  and  $2918 \text{ cm}^{-1}$  for  $\nu_{\text{as}}[\text{CH}_2]$ ). The adsorbed reactants and products may be one cause for the decline of the catalyst activity after being used. However, these bands ascribed to the adsorption of polyformaldehyde and  $\text{PODE}_n$  species disappear after a re-generation process through calcination at  $550 \text{ }^\circ\text{C}$ ; both the re-activated catalyst and the fresh catalyst are actually identical in their IR spectra.

**{Fig. S5}**



The Py-IR spectra of the catalysts before and after the reaction are also shown in Fig. S5(III). The Lewis and Brönsted acid peaks for the used catalyst are some less intense than that of the fresh catalyst, however, they are restored effectively after the calcination treatment. All these illustrate that the HZSM-5 zeolite with an appropriate Si/Al ratio is effective in the synthesis of PODE<sub>n</sub> from DMM and TOM; it exhibits high stability and excellent reusability. Compared with the fresh catalyst, the used and activated HZSM-5 catalysts have little changes in their structure and properties, except that the used catalyst upon a simple centrifugation separation may still have certain reactants, products or intermediates adsorbed on the zeolite surface which however only have a minor effect on the catalytic activity. Moreover, the activity of the used catalyst can also be effectively restored through a calcination process.

### **Acknowledgments**

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**Table S1.** Effect of the feed DMM/TOM molar ratio on the reactants conversion and products distribution in the synthesis of PODE<sub>*n*</sub> over HZSM-5 with a Si/Al molar ratio of 340<sup>*a*</sup>

DMM/TOM molar ratio	Conversion (%)		Mass selectivity to PODE <sub><i>n</i></sub> <sup><i>b</i></sup> (%)				
	DMM	TOM	PODE <sub>2</sub>	PODE <sub>3</sub>	PODE <sub>4</sub>	PODE <sub>5</sub>	PODE <sub>2-8</sub>
1.5	57.7	79.8	28.9	20.5	14.1	9.7	86.0
2	43.8	86.4	36.6	22.8	13.9	7.8	88.2
3	24.3	92.0	45.9	21.2	10.1	4.2	84.2
5	12.4	94.2	51.7	20.8	7.6	3.0	83.7

<sup>*a*</sup> The reaction was carried out at 120 °C for 45 min, with a catalyst amount of 5 wt.% in the feed.

<sup>*b*</sup> The mass selectivity to a given product is defined as its weight divided by the weight of all products.

## Captions

**Table S1.** Effect of the feed DMM/TOM molar ratio on the reactants conversion and products distribution in the synthesis of PODE<sub>n</sub> over HZSM-5 with a Si/Al molar ratio of 340.

**Fig. S1.** XRD patterns of the HZSM-5 zeolites with different Si/Al molar ratios: (a) 56; (b) 120; (c) 200; (d) 340; (e) 580; (f) 960.

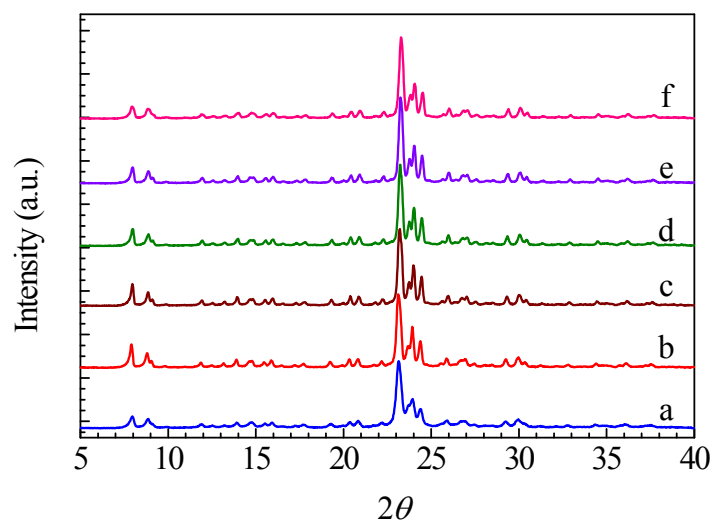
**Fig. S2.** <sup>27</sup>Al MAS NMR spectra of the HZSM-5 zeolites with different Si/Al molar ratios: (a) 56; (b) 580; (c) 960.

**Fig. S3.** Effect of the reaction time on the reactants conversion and products distribution in the synthesis of PODE<sub>n</sub> over HZSM-5 with a Si/Al molar ratio of 340: (a) DMM conversion; (b) TOM conversion; (c) mass selectivity to PODE<sub>2-8</sub>. The reaction was carried out at 120 °C, with a feed DMM/TOM molar ratio of 2 and catalyst amount of 5 wt.%.

**Fig. S4.** Effect of the HZSM-5 catalyst amount on the reactants conversion (**I**) and products distribution (**II**) in the synthesis of PODE<sub>n</sub> over HZSM-5 with a Si/Al molar ratio of 340. The reaction was carried out at 120 °C for 45 min, with a feed DMM/TOM molar ratio of 2.

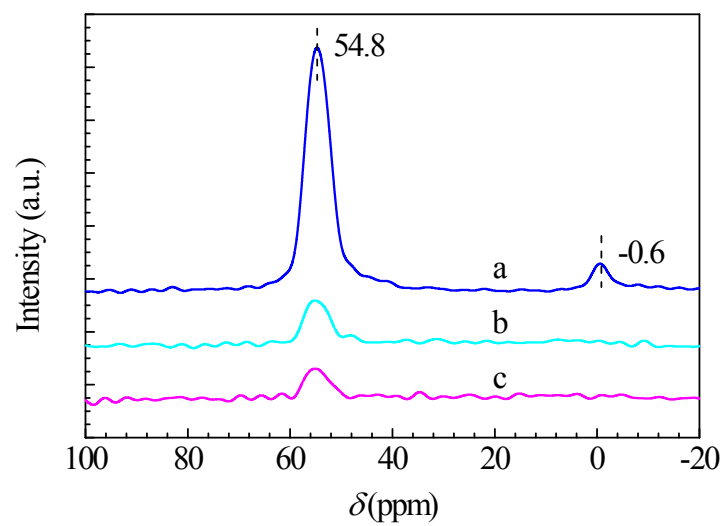
**Fig. S5.** FT-IR spectra at 1500–400 cm<sup>-1</sup> (**I**), FT-IR spectra at 4000–2600 cm<sup>-1</sup> (**II**), and Py-IR spectra (**III**) of the HZSM-5 catalyst with a Si/Al molar ratio of 280 at different stages: (a) fresh catalyst; (b) used catalyst after 15 reaction cycles upon centrifugation separation; (c) re-activated catalyst through calcination at 550 °C for 5 h.

**Fig. S1.**



**Fig. S1.** XRD patterns of the HZSM-5 zeolites with different Si/Al molar ratios: (a) 56; (b) 120; (c) 200; (d) 340; (e) 580; (f) 960.

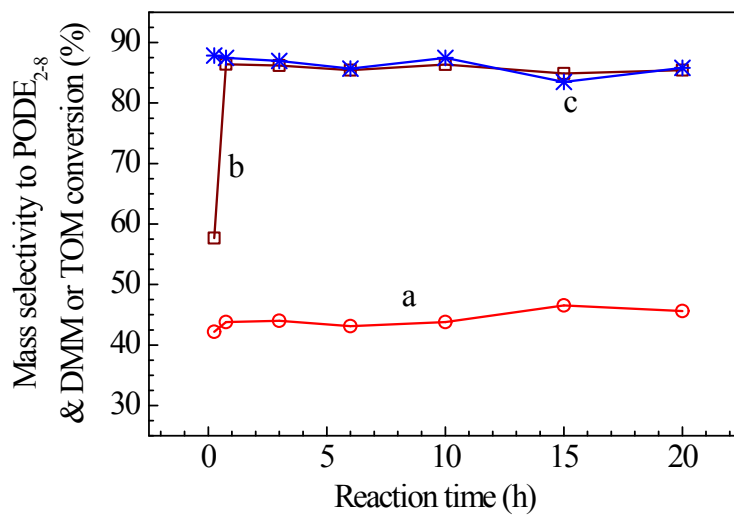
**Fig. S2.**



**Fig. S2.**  $^{27}\text{Al}$  MAS NMR spectra of the HZSM-5 zeolites with different Si/Al molar ratios:

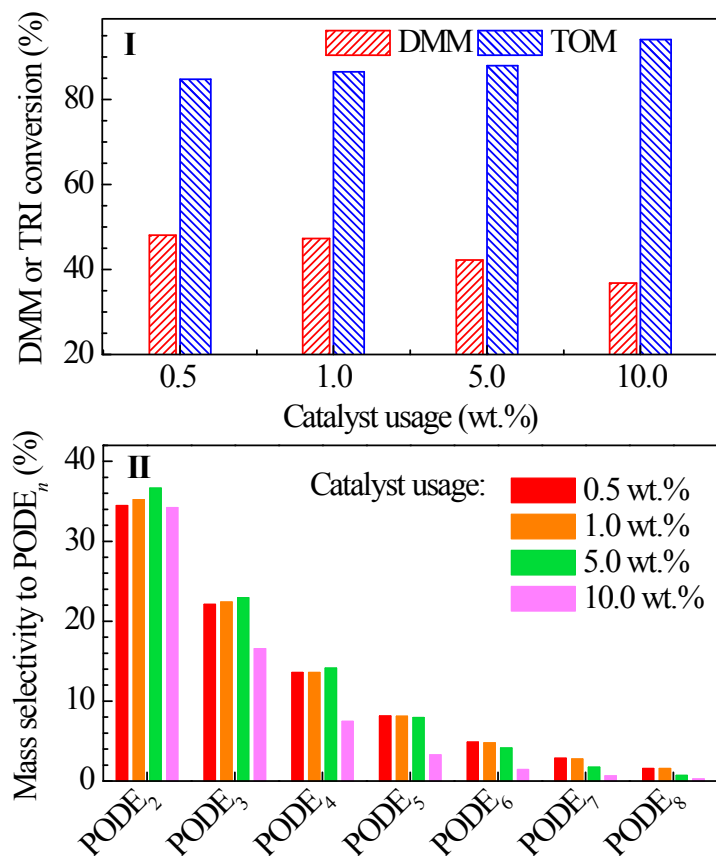
(a) 56; (b) 580; (c) 960.

**Fig. S3.**



**Fig. S3.** Effect of the reaction time on the reactants conversion and products distribution in the synthesis of PODE<sub>n</sub> over HZSM-5 with a Si/Al molar ratio of 340: (a) DMM conversion; (b) TOM conversion; (c) mass selectivity to PODE<sub>2-8</sub>. The reaction was carried out at 120 °C, with a feed DMM/TOM molar ratio of 2 and catalyst amount of 5 wt.%.

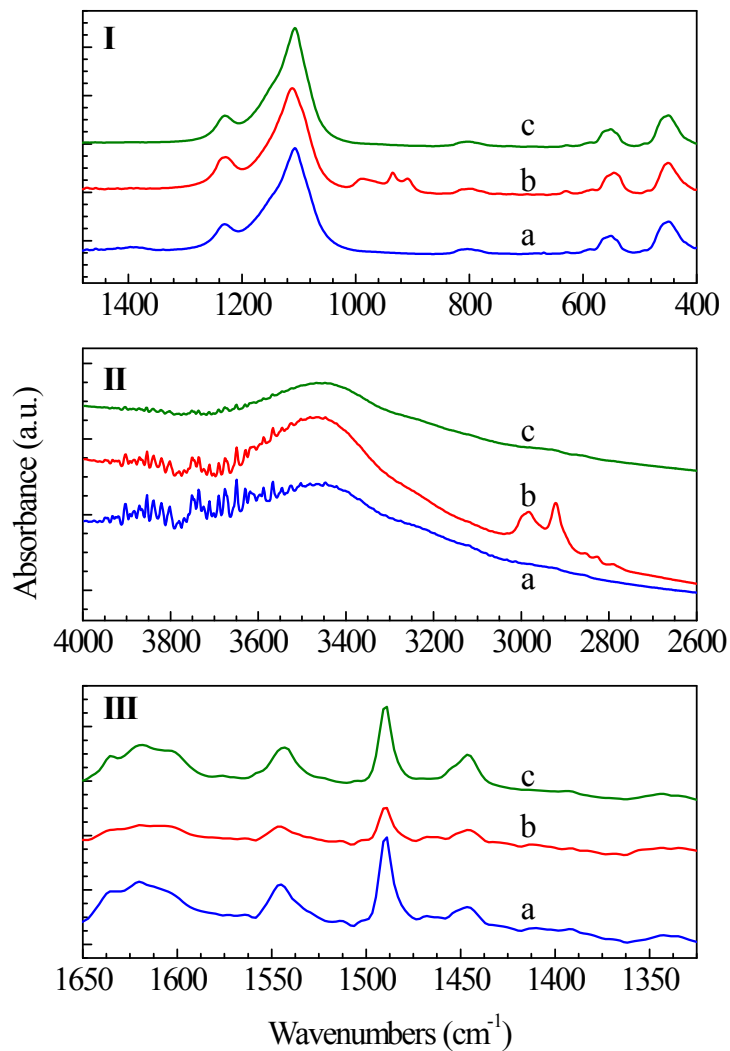
**Fig. S4.**



**Fig. S4.** Effect of the HZSM-5 catalyst amount on the reactants conversion (I) and products distribution (II) in the synthesis of PODE<sub>n</sub> over HZSM-5 with a Si/Al molar ratio of 340. The reaction was carried out at 120 °C for 45 min, with a feed DMM/TOM molar ratio of 2.



**Fig. S5.**



**Fig. S5.** FT-IR spectra at 1500–400 cm<sup>-1</sup> (**I**), FT-IR spectra at 4000–2600 cm<sup>-1</sup> (**II**), and Py-IR spectra (**III**) of the HZSM-5 catalyst with a Si/Al molar ratio of 280 at different stages: (a) fresh catalyst; (b) used catalyst after 15 reaction cycles upon centrifugation separation; (c) re-activated catalyst through calcination at 550 °C for 5 h.