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ARTICLE TYPE

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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The catalytic performance of HZSM-5 zeolite in the synthesis of polyoxymethylene dimethyl ethers (PODE$_n$) from dimethoxymethane (DMM) and trioxymethylene (TOM) is closely related to its Si/Al ratio; HZSM-5 with a high Si/Al ratio exhibits high PODE$_{2\text{–}8}$ yield and excellent stability and reusability.

Polyoxymethylene dimethyl ethers (PODE$_n$) are a kind of ether compounds with the formula $CH_3O(CH_2O)_nCH_3$ ($n > 1$). Owing to the well intermiscibility, high oxygen content and cetane number, PODE$_n$ has been recognized as a promising diesel additive, which can improve the combustibility of the diesel oil, enhance the efficiency of combustion, and reduce the release of NO_x and powderous pollutants.[1,2] The presence of –O–CH_2– groups in PODE$_n$ may lead to the formation of hydroperoxides, which can decompose into OH–radicals and then degrade the soot precursors upon combustion.[3,4]

Multitudinous catalysts, both homogeneous and heterogeneous, have been used in the synthesis of PODE$_n$; however, their performances are still somewhat insufficient for the practical application. PODE$_n$ is primitively obtained from methanol (MeOH) and formaldehyde (FA) or polyformaldehydes (PF$_n$) with H_2SO_4 or CF_3SO_3H as the catalysts;[5] with PF$_n$ and methanol as the reactants and CF_3SO_3H as the catalyst, the mass yield of PODE$_{1\text{–}5}$ was 86.6% at 115 °C. However, such liquid acid catalysts are very corrosive. With various ionic liquids as the catalysts, Chen and coworkers reported that the mass yield of PODE$_{2\text{–}8}$ reached 73.3%, by the reaction of MeOH with trioxymethylene (TOM) at 115 °C, with a TOM conversion of 90.1%;[6] however, the high cost of ionic liquids may restrict their large-scale application.

Meanwhile, various solid catalysts including ion exchange resins,[7–9] PVP-stabilized heteropolyacids,[10] and zeolites[11] were also used in the synthesis of PODE$_n$. For the synthesis of PODE$_n$ from dimethoxymethane (DMM) and TOM over CT175 resin, Wang and coworkers reported that the conversion of TOM and selectivity to PODE$_{3\text{–}8}$ at 90 °C reached 89.0% and 64.2%, respectively;[1] however, the hydrothermal stability of resin was unsatisfactory because its –SO_3H groups leach easily. PVP-stabilized heteropolyacids were also found catalytically effective for PODE$_n$ synthesis by TOM methanolysis,[10] whereas the process for the catalyst regeneration and recycling was still some cumbersome. Zhao and coworkers used MCM-22 zeolite as catalyst, MeOH and TOM as raw materials, to synthesize PODE$_n$; the selectivity to PODE$_{3\text{–}8}$ reached 29% at 120 °C.[11] Meanwhile, it was also found that water produced during the reaction with MeOH as the raw material may lead to the formation of hemiformals, which are prejudicial to the property of PODE$_n$.[12]

All these give us a clue that a proper zeolite can be a promising catalyst for the synthesis of PODE$_n$, which is advantageous in structure stability and recycling facility; moreover, the acidity and performance of a zeolite catalyst can be well regulated by altering the Si/Al ratio and crystal morphology. Meanwhile, DMM and TOM could also be ideal raw materials, which do not produce water during the reaction forming PODE$_n$ and then are propitious to get high quality PODE$_n$. In this work, therefore, HZSM-5 zeolite was used as the catalyst for the synthesis of PODE$_n$ from DMM and TOM; the effect of Si/Al molar ratio, reaction time, feed DMM/TOM ratio on the yield of PODE$_n$ were then investigated.

The HZSM-5 zeolites with different Si/Al ratios were synthesized by hydrothermal method with silica white as silicon source (ESI†), as described by Xu and coworkers.[13] The X-ray diffraction (XRD) patterns (Fig. S1, ESI†) illustrate that the as-synthesized HZSM-5 zeolites are well crystallized with the characteristic peaks of MFI structure. The acidity of HZSM-5 zeolites with different Si/Al ratios were measured by temperature-programmed desorption of ammonia (NH_3-TPD) and infrared spectroscopy of pyridine adsorption (Py-IR), as shown in Fig. 1. There are two ammonia desorption peaks in the NH_3-TPD profiles (Fig. 1(I)), one at 120−250 °C and the other at 300−400 °C, corresponding to the weak acid sites and the strong acid sites, respectively. With the increase of the Si/Al ratio, the desorption peaks of both weak and strong acid sites are shifted to lower temperatures,[14] suggesting a decrease of the acidic strength. Meanwhile, the peak intensity representing the density of acid sites is reduced considerably with the increase of Si/Al ratio, especially for the weak acid sites. With a Si/Al molar ratio higher than 580, the ammonia desorption peak for the weak acid sites has almost disappeared and the strength of the strong acid sites is also largely decreased, turning into medium-strong acid sites.

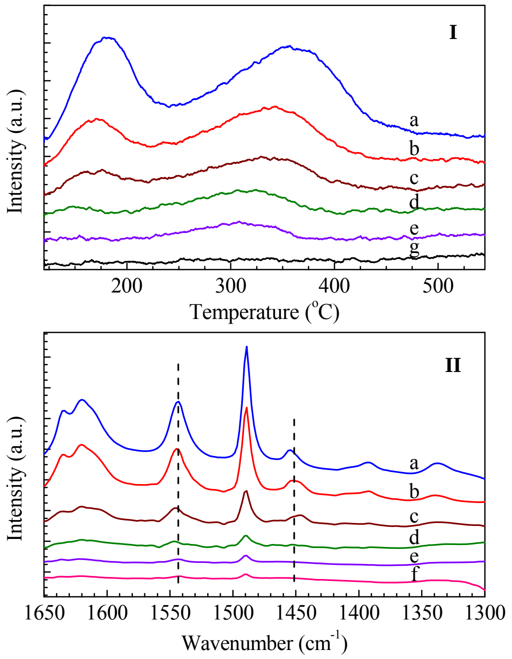


Fig. 1 NH_3-TPD profiles (**I**) and Py-IR spectra (**II**) of the HZSM-5 zeolites with different Si/Al molar ratios: (a) 56; (b) 120; (c) 200; (d) 340; (e) 580; (f) 960; and (g) SiO_2.

The Py-IR spectra of the HZSM-5 zeolites in the region of 1300–1650 cm^{-1} are shown in Fig. 1(II); two absorption peaks located at 1450 and 1540 cm^{-1} are corresponding to the Lewis and Brönsted acid sites, respectively.[15–17] With the increase of Si/Al molar ratio from 56 to 960, the amounts of the Brönsted (B) acid sites and especially the Lewis (L) acid sites are decreased evidently. A quantitative analysis illustrates that the ratio of Brönsted acid sites to Lewis acid sites (B/L) increases from 0.9 to 5.8 with the increase of Si/Al molar ratio from 56 to 960,[18–22] indicating that the Brönsted acid sites turns into the primary acid species on the HZSM-5 zeolite with high Si/Al ratio.

The catalytic performance of HZSM-5 zeolites in the synthesis of PODE$_n$ was tested in a stainless steel autoclave of 100 mL lined with Teflon (ESI†). Typically, 15.2 g DMM, 9 g 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. A series of preliminary tests (Table S1 and Figs. S3 and S4, ESI†) illustrate that such conditions, viz., 120 °C for 45 min, a feed DMM/TOM molar ratio of 2 and catalyst amount of 5 wt.% are appropriate for the synthesis of PODE$_n$. The products and unreacted reactants after reaction 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$_n$, DMM and MeOH; the other one is Shimadzu GC-14B equipped with a TCD detector and Porapak T packed column for FA, HF$_n$, methyl formate (MF), DMM and water. In any case, the mass balance accounts for 95–105%.

As listed in Table 1, both γ-Al_2O_3 and silica are catalytically inactive, whereas the HZSM-5 zeolite exhibits excellent catalytic activity in the synthesis of PODE$_n$ from DMM and TOM. Moreover, the Si/Al ratio of HZSM-5 has a significant effect on the reactant conversion and product distribution. Over the HZSM-5 catalyst with a low Si/Al molar ratio (≤ 200), MF is a prominent product besides PODE$_{2–8}$. With the increase of Si/Al ratio, the selectivity to MF is suppressed markedly and PODE$_{2–8}$ turns to be the primary product. Over the HZSM-5 zeolite with a Si/Al molar ratio of 580, the selectivity to PODE$_{2–8}$ reaches 88.5% with a TOM conversion of 85.3%, whereas the mass selectivity to MF is decreased to 0.5%. With further increasing the Si/Al ratio, however, the selectivity to PODE$_{2–8}$ is decreased gradually, accompanying with an increase of the selectivity to MeOH and FA.

Table 1 Catalytic performance of the HZSM-5 zeolites with various Si/Al ratios in the synthesis of PODE$_n$ from DMM and TOM [a]

Si/Al molar ratio	Conversion (%)		Mass selectivity [b] (%)				TOF [c] (s^{-1})
	DMM	TOM	PODE$_{2–8}$	MF	MeOH	FA	
γ-Al_2O_3	0	0					
56	27.5	97.1	47.2	47.3	2.9	2.6	0.10
120	37.4	91.6	73.7	18.8	3.0	4.5	0.21
200	42.2	88.0	80.4	10.1	3.1	6.4	0.33
340	43.8	86.4	88.2	2.0	3.2	6.6	0.55
580	47.5	85.3	88.5	0.5	3.7	7.3	0.94
960	48.0	84.7	87.4	0.2	4.0	8.4	1.53
2200	47.1	80.0	84.4	0.0	5.5	10.1	3.33
4500	11.5	3.0	71.4	0.0	19.6	9.0	0.25
SiO_2	0	0					

[a] The reaction was carried out at 120 °C for 45 min, with a feed DMM/TOM molar ratio of 2 and catalyst amount of 5 wt.%.
[b] The mass selectivity to a given product is defined as its weight divided by the weight of all products.
[c] The turnover frequency (TOF) is the number of TOM molecules converted over per active site and second, estimated on the basis of total Al contents in the HZSM-5 (ESI†).

Since the synthesis of PODE$_n$ is an acid-catalyzed reaction,[10,11] the catalytic performance of HZSM-5 zeolite should be related to its acidic properties, viz., the density, strength, circumstance and type of the acid sites, which are dependent on the HZSM-5 Si/Al ratio. The acid sites on a zeolite generally originate from the bridged linkage of Si-(OH)-Al (Brönsted) and defect Al sites (Lewis) and the acidic density decreases with the increase of Si/Al ratio, i.e. with the decrease of Al content. Table 1 illustrates that the turnover frequency (TOF, ESI†) for PODE$_n$ production is almost proportional to the Si/Al molar ratio. Through associating the reaction tests (Table 1) with the acidic characterization (Fig. 1), it can be found that the acid sites on HZSM-5 with high Si/Al ratio is propitious to the conversion of TOM and DMM to PODE$_n$; these acid sites are characterized by relatively low density, medium-strong strength, and mainly Brönsted ones. However, as the number of acid sites per unit catalyst is decreased with the Si/Al ratio, the overall catalytic performance of HZSM-5 with an extortionate Si/Al molar ratio (e.g. > 960) begins to deteriorate quite seriously. As a compromise, a Si/Al molar ratio of 580 gives the HZSM-5 zeolite highest performance in the synthesis of PODE$_n$ from TOM and DMM. HZSM-5 with lower Si/Al molar ratio (eg. < 200) is provided with large amounts of both weak and strong acid sites, which consists of a large fraction of Lewis acid sites and favors the formation of MF by consuming mainly TOM. On the contrary, the acid sites on HZSM-5 with higher Si/Al molar ratio (eg. > 2200) is rather scanty, which promotes the formation of MeOH by consuming mainly DMM and shows a low overall activity in the synthesis of PODE$_n$.

Fig. 2 displays the distribution of PODE$_n$ products (n = 2–8) over the HZSM-5 catalyst with different Si/Al ratios. The PODE$_n$ products over the HZSM-5 catalysts with a Si/Al molar ratio from 200 to 2200 all follow the Schulz-Flory distribution,[2] though the HZSM-5 zeolite with a Si/Al molar ratio of 580 gives the highest yield of PODE$_{2-8}$. An excessively low or overly high Si/Al ratio is ineligible for the production of PODE$_{2-8}$. As the PODE$_n$ product distribution is controlled by the chain propagation, it is unlikely to get a specific PODE$_n$ product in a single reaction step with very high yield. However, a suitable HZSM-5 catalyst with an appropriate Si/Al ratio is effective in suppressing the formation of some by-products like MF and MeOH and meanwhile possesses high activity for the chain propagations forming PODE$_n$.

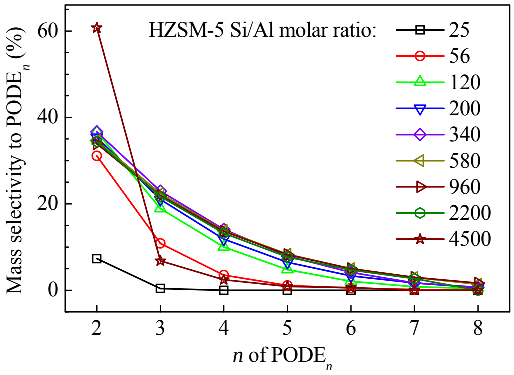


Fig. 2 Distribution of PODE$_n$ products over the HZSM-5 catalysts with different Si/Al ratios. The reaction was carried out at 120 °C for 45 min, with a feed DMM/TOM molar ratio of 2 and catalyst amount of 5 wt.%.

The effect of Si/Al ratio on the TOM conversion and product selectivity for the dissociation of TOM alone over HZSM-5 (ESI†) are shown in Fig. 3. It was further confirmed that the conversion of TOM dissociation decreases with the increase of HZSM-5 Si/Al ratio, i.e. with the decrease of acidic density. However, over the HZSM-5 zeolite with a low Si/Al ratio, MF is the primary product. The selectivity to MF decreases considerably with the increase of Si/Al ratio; over the HZSM-5 catalyst with a Si/Al molar ratio over 580, MF almost disappears in the product, whereas FA that can take part in the chain propagation forming PODE$_n$ turns to be the dominating product. The 27Al MAS NMR tests (Fig. S2, ESI†) further illustrate that the Al species in tetrahedral coordination on the HZSM-5 zeolite with a high Si/Al ratio may act as the Brönsted acid sites that are active for the formation of PODE$_n$, whereas the Al species in hexahedral coordination or extra-framework Al species may promote the conversion of TOM to MF that is deleterious to the formation of PODE$_n$.

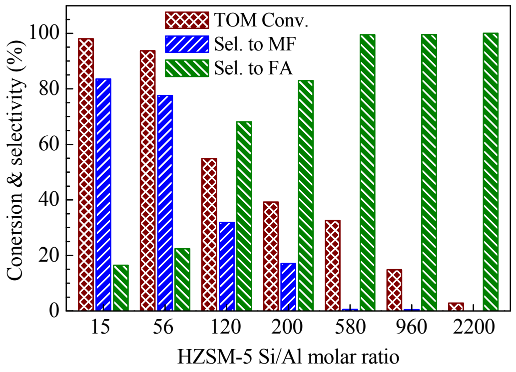


Fig. 3 Influence of the Si/Al ratio on TOM conversion and product selectivity for TOM dissociation over the HZSM-5 zeolites. For each test, 10.0 g CH_2Cl_2, 1.0 g TOM and 0.15 g HZSM-5 were loaded into a 25 mL Teflon-lined autoclave; the reaction lasted for 45 min at 120 °C.

Among the major virtues of the HZSM-5 zeolite as a catalyst in the synthesis of PODE$_n$ are its high stability, good recyclability and facility for regeneration. As shown in Fig. 4, the HZSM-5 catalyst exhibits excellent stability and reusability; the mass yield to PODE$_{2-8}$ 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 (Fig. S5, ESI†) illustrate that their structure and properties changes little upon the reaction tests, 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. The excellent stability and reusability may imply that the synthesis of PODE$_n$ can be conducted in a continuous tank reactor with an accessorial filter for the separation of catalyst and discharging of products.

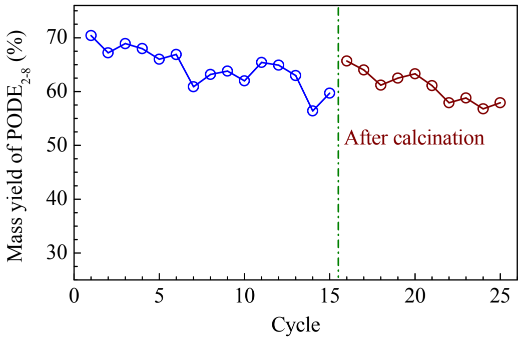
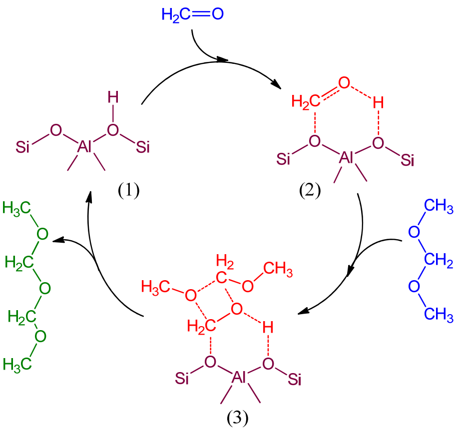


Fig. 4 Reusability of the HZSM-5 catalyst (with a Si/Al molar ratio of 280). The reaction was carried out at 120 °C for 45 min, with a feed DMM/TOM molar ratio of 2 and catalyst amount of 5 wt.%. After each test, the catalyst is re-used in next run upon a simple centrifugation separation; the catalyst was subject to an activation process through calcination at 550 °C for 5 h after first 15 cycles.

For the formation of PODE$_n$ over the cation exchange resins, Zheng and coworkers proposed that FA molecule was protonated at the carbonyl group and then the protonated carbonyl group reacted with PODE$_n$ to form PODE$_{n+1}$ via an intermediate with the help of electroaffinity.[9] Fang and coworkers also found that the synthesis of PODE$_n$ was strongly related to the acidity and involved the transfer of protons.[10] The formation of higher PODE$_n$ is controlled by the chain propagation and then the PODE$_n$ products follow the Schulz-Flory distribution.[2] In this work, the HZSM-5 catalyst with a Si/Al molar ratio of about 580 is provided with sufficient medium-strong acid sites of Brönsted type, which can effectively promote the dissociation of TOM to FA species and meanwhile suppress the conversion of FA to MF. Moreover, the acid sites on HZSM-5 are also very active for the chain propagation, in which the FA species react with DMM and/or lower PODE$_n$, forming higher PODE$_n$. As illustrated in Scheme 1, when a FA molecule is adsorbed on the Brönsted acid site of HZSM-5 zeolite (1), a weakly hydrogen-bonded complex (π complex) is formed (2);[23] the DMM molecule or a lower PODE$_n$ then interacts with CH_2OH species by the electroaffinity, forming a new transition state (3); after that, the new transition state may decompose into PODE$_2$ or a higher PODE$_n$ and the acid site is then released for a new catalytic cycle.[24]



Scheme 1 Proposed reaction pathways for the synthesis of PODE$_n$ from TOM and DMM on the Brönsted acid sites of the HZSM-5 zeolite.

In conclusion, HZSM-5 zeolite of high Si/Al ratio is effective in the synthesis of PODE$_n$ from DMM and TOM. The yield of PODE$_n$ is closely related to the Si/Al ratio; over the HZSM-5 catalyst with a Si/Al molar ratio of 580, the mass selectivity to PODE$_{2–8}$ reaches 88.5% with a TOM conversion of 85.3%, after reaction for 45 min at 120 °C with a feed DMM/TOM molar ratio of 2. Moreover, the HZSM-5 catalyst exhibits high stability and excellent reusability.

HZSM-5 zeolite with an appropriate Si/Al ratio is provided with sufficient medium-strong acid sites of Brönsted type, which can effectively promote the dissociation of TOM to FA species; meanwhile, the acid sites on HZSM-5 are also active for the chain propagation, in which FA species react with DMM and lower PODE$_n$, forming higher PODE$_n$. As the strong Lewis acid sites are largely eliminated, the conversion of FA species to MF and formation of other byproducts is then suppressed. All these may contribute to the excellent catalytic performance of HZSM-5 in the synthesis of PODE$_n$. This approach may open a new green path to produce PODE$_n$ diesel additives effectively and cheaply.

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Notes and references

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Graphic Abstract

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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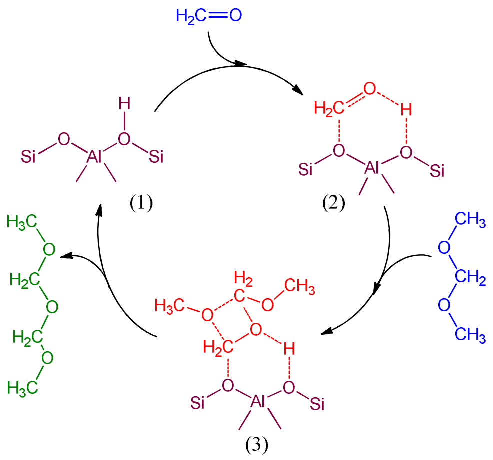

High Si/Al ratio HZSM-5 zeolite exhibits excellent catalytic performance in the synthesis of polyoxymethylene dimethyl ethers from dimethoxymethane and trioxymethylene.

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