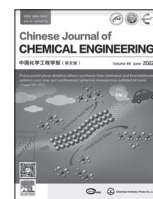




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Full Length Article

Polyoxymethylene dimethyl ethers synthesis from methanol and formaldehyde solution over one-pot synthesized spherical mesoporous sulfated zirconia



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ABSTRACT

The synthesis of polyoxymethylene dimethyl ethers as an ideal diesel fuel additive is the current hot topic of modern petrochemical industry for their expedient properties in mitigating air pollutants emission during combustion. In this work, a series of spherical sulfated zirconia catalysts were prepared by a one-pot hydrothermal method assisted with surfactant cetyltrimethylammonium bromide (CTAB). The prepared sulfated zirconia catalysts were used to catalyze PODE_n synthesis from methanol and formaldehyde solution. Various characterization (XRD, BET, SEM, TGA, NH₃-TPD, FTIR, and Py-IR) were employed to elaborate the structure–activity relationship of the studied catalytic system. The results demonstrated that S/Zr molar ratio in precursor solution played an effective role on catalyst morphology and acidic properties, where the weak Brønsted acid sites and strong Lewis acid sites were favorable to the conversion of methanol and formation of long-chain PODE_n, respectively. The reaction parameters such as catalyst amount, molar ratio of FA/MeOH, reaction time, temperature and pressure were optimized. The speculated reaction pathway for PODE_n synthesis was proposed based on the synergy of Brønsted and Lewis acid sites, which suggested that Brønsted and Lewis acid sites might be advantageous to the activation of polyoxymethylene hemiformals [CH₃(OCH₂)_nOH] and methylene glycol (HOCH₂OH), respectively.

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1. Introduction

Diesel engines are widely adapted in agriculture, transportation and industrial sectors owing to their excellent features such as high thermal efficiency, durability, adaptability and low-operating cost. While, the exhaust emissions of hazardous air pollutants such as nitrogen oxides (NO_x) and particulate matter (PM) derived from diesel combustion are injurious to human health and environment [1,2]. In order to reduce these emissions, the addition of oxygenated compounds to diesel fuel has been proven to be an effective method [3–5]. Polyoxymethylene dimethyl ethers (PODE_n) have been considered as clean and promising diesel fuel additives due to their expedient properties of high oxygen content and high cetane number [6,7]. The utilization of PODE_n in diesel fuel combustion can effectively reduce the harmful emissions of carbon monoxide, hydrocarbon, particulate matter and nitrogen oxide [8–10]. PODE_n as eco-friendly additives can be directly

blended into diesel fuel for usage without modification of the diesel engines [10,11].

PODE_n are oligomers with the structure of CH₃O(CH₂O)_nCH₃, which are comprised of several CH₂O units and capped with one methyl and one methoxy group [7]. PODE_n can be synthesized by the reaction of methyl and methoxy groups supplier with oxymethylene group provider [12]. Several studies demonstrated that methanol (MeOH), methylal (PODE₁) and dimethyl ether (DME) had been widely used as the methyl and methoxy groups suppliers, while formaldehyde (FA), trioxane (TRI) and paraformaldehyde (PF) were considered as the oxymethylene group providers [13–16]. Based on the different end-group suppliers, the liquid-phase synthesis routes of PODE_n can be classified into anhydrous or aqueous production processes. The end-group suppliers for the anhydrous synthesis route include methylal and dimethyl ether, and methanol is used as the capping source in aqueous synthesis of PODE_n [7]. The synthetic routes for PODE_n production are shown in Fig. 1. Water generated in the reaction or existed in the reactant is the main distinction among the aqueous and anhydrous production routes of PODE_n. The synthesis of PODE_n in the presence of

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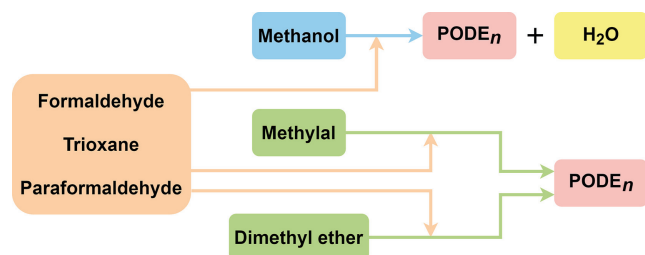


Fig.1. Synthetic routes for PODE_n synthesis via anhydrous and aqueous processes.

water could result in negative effects, including the suppression of long-chain PODE_n formation, reduction of catalytic activity, and difficulty in product separation [13,17–19]. However, PODE_n synthesis from methanol and formaldehyde solution is much more economically advantageous than that of methylal and trioxane [13]. Therefore, large-scale production of PODE_n from methanol and formaldehyde solution is potential and economical in the future.

In general, PODE_n synthesis reaction is not only carried out in the presence of liquid acid catalysts such as sulfuric acid, sulfonic acid and ionic liquids, but also catalyzed by solid acid catalysts, including ion exchange resin, carbon-based material, zeolite and sulfated metallic oxide [14,16,20–25]. Compared to the homogeneous liquid acids, heterogeneous solid acid catalysts are the preferable ones due to their better performance of anti-corrosion, separation and reusability effect. Sulfated metallic oxides, such as $\text{SO}_4^{2-}/\text{SnO}_2$, $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{TiO}_2$ and $\text{SO}_4^{2-}/\text{ZrO}_2$, are known to present super-strong acidity that is efficient for various acid-catalyzed reactions [26–29]. A few previous studies shed light on sulfated metallic oxides catalyzing the PODE_n synthesis reaction. Li *et al.* studied chemical equilibrium and reaction kinetics for the PODE_n synthesis from methylal and trioxane over sulfated titania, demonstrating that the molar ratio of $\text{PODE}_{n+1}/\text{PODE}_n$ in equilibrium was constant and depended on the reaction temperature [30]. They also investigated the sulfated $\text{Fe}_2\text{O}_3\text{-SiO}_2$ catalysts used in the synthesis of PODE_n from methanol and TRI, and reported that the catalytic performance was influenced by the acid strength, ratio of Brønsted to Lewis acid sites and acid density of the catalyst [31]. Liu *et al.* studied the $\text{SO}_4^{2-}/\text{TiO}_2$ catalysts for PODE_n synthesis from methylal and paraformaldehyde (PF), and found that the activity of $\text{SO}_4^{2-}/\text{TiO}_2$ catalysts was influenced by the acid properties, while Brønsted acid sites were active for the whole synthesis reaction [16]. Li *et al.* studied the one-pot synthesized sulfated titania to catalyze the methylal and TRI for PODE_n synthesis and its catalytic performance was comparable to that of CT175 cation-exchange resin [32]. Sulfated zirconia (SZ) is known to possess strong acidic properties and it is an excellent acid catalyst having both Brønsted and Lewis acidity. Even though, SZ had been widely adapted in various acid-catalyzed reactions such as cyclodehydration, esterification, isomerization and Friedel-Craft alkylation [29,33–37]. However, there has been no conducted study concerning the use of SZ as a catalyst for the PODE_n synthesis from methanol and formaldehyde solution.

In this work, spherical mesoporous sulfated zirconia was synthesized by a one-pot hydrothermal method, and it was investigated as a solid acid catalyst in PODE_n synthesis from methanol and formaldehyde solution. The structural and acidic properties of the prepared sulfated zirconia catalysts were analyzed by applying a suite of characterization methods and catalytic performance investigations. The possible reason for the high methanol conversion and PODE₃₋₆ selectivity was discussed based on the results of the characterizations of the catalysts. The effects of various reaction variables such as the molar ratio of FA/MeOH, catalyst amount,

reaction temperature, time and pressure have been investigated. The reusability performance of the catalyst for PODE_n synthesis from methanol and formaldehyde solution has also been conducted. The speculated reaction pathway for PODE_n synthesis from methanol and formaldehyde solution was proposed based on the synergistic effect of Brønsted and Lewis acid sites.

2. Experimental

2.1. Catalyst synthesis

Spherical mesoporous sulfated zirconia catalyst was prepared by a one-pot hydrothermal method, which was adapted from the catalyst synthesized method proposed by Ciesla *et al.* [38]. In a typical procedure, cetyltrimethylammonium bromide (CTAB, 5 g, 99%, Shanghai Aladdin Bio-Chem Technology Co., Ltd.) was dissolved in a solution of deionized water (230 g) and HCl (49 g, 37%, Shanghai Titan Scientific Co., Ltd.) under stirring for 0.5 h. Zirconium Oxychloride Octahydrate $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (16.11 g, 98%, Shanghai Macklin Biochemical Co., Ltd.) was dissolved in ethanol (50 g, 95%, Shanghai Titan Scientific Co., Ltd.), and then the formed transparent colloid was transferred into CTAB solution. The mixed solution was continuously stirred for 0.5 h. $(\text{NH}_4)_2\text{SO}_4$ (6.61 g, 99%, Shanghai Titan Scientific Co., Ltd.) was dissolved in deionized water (50 g), and then the $(\text{NH}_4)_2\text{SO}_4$ solution was added to the mixed solution. The mixture was stirred for 1 h at room temperature. After fully stirring, the transparent solution was then transferred into a Teflon autoclave, and undergo hydrothermal treatment at 373 K for 48 h. The resulting white precipitate was filtered off, washed with deionized water and absolute ethanol, dried at 373 K overnight, and calcined at 873 K for 5 h under airflow. To investigate the effect of various $(\text{NH}_4)_2\text{SO}_4$ amounts on catalytic activity, the sulfated zirconia catalysts with the different molar ratio of $(\text{NH}_4)_2\text{SO}_4$ to zirconium were prepared. The prepared sulfated zirconia by the hydrothermal method was designed as HSZ-*x*, where *x* represents the molar ratio of S/Zr (MRSZ).

2.2. Catalyst characterization

The crystalline phase of the prepared HSZ catalysts was analyzed by D8 Advance X-ray polycrystalline diffractometer (XRD) (BRUKER AXS) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) within the 2θ range of 10° – 80° . Argon physisorption measurements were carried out on a Micromeritics ASAP 2020 surface area and porosity analyzer. Before the measurement, the samples were degassed for 6 h at 573 K. The specific surface areas and pore sizes were calculated according to the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Thermogravimetric analysis (TGA) was carried out on a Thermo Fisher Thermox 400 instrument with a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ from 308 to 1173 K under $100\text{ ml}\cdot\text{min}^{-1}$ air. The thermal stability of catalysts was investigated by thermogravimetric-mass spectrometry (TG-MS). Samples were heated in a PerkinElmer Pyris 1 TGA equipped with a HIDEN HPR 20 mass spectrometer under Ar flow at $30\text{ ml}\cdot\text{min}^{-1}$ from 323 to 1223 K at a ramp rate of $10\text{ K}\cdot\text{min}^{-1}$. The scanning electron microscopy (SEM) measurements were carried out on an FEI Nova NanoSEM 450 scanning electron microscope with 5.0 kV accelerating voltage. Fourier transform infrared (FT-IR) spectra of the samples were recorded on PerkinElmer Spectrum 100 in KBr pellets between 4000 and 400 cm^{-1} with a resolution of 1 cm^{-1} . The pyridine adsorption FTIR spectra (Py-IR) were performed on BIO-RAD FTS3000 spectrometer to obtain the acid properties of the samples. The powder samples were pressed into translucent disks, degassed in vacuum at 623 K for 1 h, exposed to pyridine vapor, and then cooled down to 298 K. The

Py-IR spectra were then recorded at 423 K, 523 K, 623 K after applying vacuum for 30 min. The sulfate contents of the samples were analyzed by Agilent 725 inductively coupled plasma optical emission spectrometer (ICP-OES). Samples were dissolved by HF before the analysis. The acidity of the samples was determined by temperature-programmed desorption of ammonia (NH₃-TPD), which was performed on a Micromeritics AutoChem II 2920 chemisorption analyzer. Typically, 100 mg of sample was activated under the flow of He at 573 K for 1 h. After cooling down to 333 K in flowing He, the adsorption of NH₃ was performed at 333 K in 10% NH₃/He for 30 min. Subsequently, the evolved ammonia was analyzed by a thermal conductivity detector (TCD) when the temperature was increased to 873 K at a heating rate of 10 K·min⁻¹ in He flow.

2.3. Catalytic activity

The synthesis of polyoxymethylene dimethyl ethers from methanol and formaldehyde solution was performed in a 200 ml batch autoclave. Before the synthesis reaction, the reactants with the various molar ratio of MeOH/FA were prepared by heating the mixture of methanol, water and PF in a 1000 ml flask at 363 K. In a typical reaction procedure, 80 g raw material and the desired amount of HSZ catalyst were taken into the batch autoclave, and the pressure of the autoclave was increased to 1.0 MPa with nitrogen filling. The reaction system was stirred at 600 r·min⁻¹ and rapidly heated to the specified temperature. After the reaction, the spent catalyst was separated from the reaction mixture by centrifuge.

The product was analyzed by a flame ionization detection (FID) of gas chromatography (Shimadzu GC 2014) equipped with the InertCap WAX capillary column (30 m × 0.32 mm × 0.25 μm). Ethanol was determined as the internal standard reagent to quantify the contents of methanol and PODE₁₋₆. The contents of formaldehyde and water were analyzed by the Karl Fischer method and sodium sulfite method, respectively. The methanol conversion (x_{MeOH}), formaldehyde conversion (x_{FA}), PODE_{*n*} selectivity (S_{PODE_n}) and carbon balance (CB) were calculated according to the following equations:

$$x_{\text{MeOH}} = \frac{m_{\text{MeOH,R}} - m_{\text{MeOH,P}}}{m_{\text{MeOH,R}}} \times 100\% \quad (1)$$

$$x_{\text{FA}} = \frac{m_{\text{FA,R}} - m_{\text{FA,P}}}{m_{\text{FA,R}}} \times 100\% \quad (2)$$

$$S_{\text{PODE}_{i-j}} = \frac{2 \times M_{\text{MeOH}} \times \sum_i \frac{m_{\text{PODE}_i,\text{P}}}{M_{\text{PODE}_i}}}{m_{\text{MeOH,R}} - m_{\text{MeOH,P}}} \times 100\%, 1 \leq i \leq j \leq 6 \quad (3)$$

$$\text{CB} = \frac{\frac{m_{\text{MeOH,P}}}{M_{\text{MeOH}}} + \frac{m_{\text{FA,P}}}{M_{\text{FA}}} + \sum_{i=1}^6 \left[(i+2) \times \frac{m_{\text{PODE}_i,\text{P}}}{M_{\text{PODE}_i}} \right] + 2 \times \frac{m_{\text{MF,P}}}{M_{\text{MF}}}}{\frac{m_{\text{MeOH,R}}}{M_{\text{MeOH}}} + \frac{m_{\text{FA,R}}}{M_{\text{FA}}}} \times 100\% \quad (4)$$

where $m_{i,\text{R}}$ and $m_{i,\text{P}}$ are the mass fraction of component *i* in the reactant and product, respectively; M_{MeOH} , M_{FA} , M_{PODE_i} and M_{MF} are the molar mass of methanol, formaldehyde, PODE_{*i*} and methyl formate, respectively.

The carbon balances of all the experiments were over 95%.

3. Results and Discussions

3.1. Catalyst characterization results

The XRD patterns of the HSZ catalysts are shown in Fig. 2. The patterns of these samples calcinated at 873 K exhibited a well-

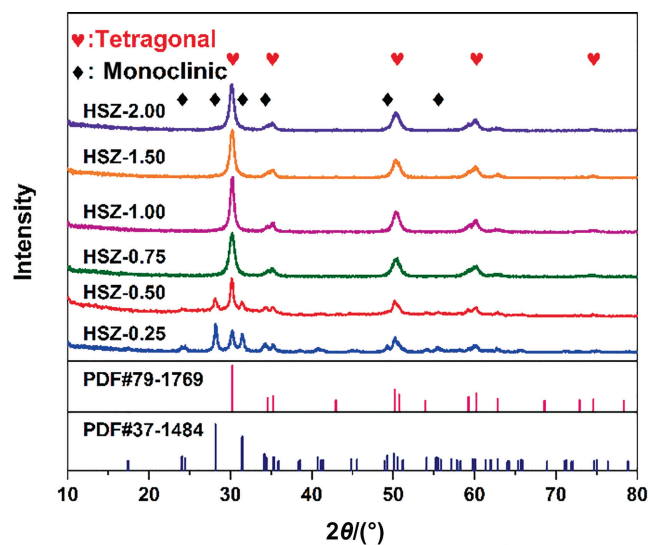


Fig. 2. XRD patterns of the HSZ catalysts.

crystallized character. The diffraction peaks corresponding to the tetragonal zirconia and monoclinic zirconia displayed at $2\theta = 30.2^\circ, 35.3^\circ, 50.2^\circ, 60.2^\circ, 74.6^\circ$ (PDF#79-1769) and $24.4^\circ, 28.2^\circ, 31.5^\circ, 34.2^\circ, 49.3^\circ, 55.6^\circ$ (PDF#37-1484), respectively. As can be seen in Fig. 2, with increasing the MRSZ, the HSZ samples predominantly exhibited the tetragonal phase structure of zirconia, while the HSZ prepared by low MRSZ (0.25, 0.5) contained both monoclinic and tetragonal phases of zirconia. Osatishtiani *et al.* found that the tetragonal phase gradually increased with the increase of sulfate surface coverage [39]. Therefore, the phase transition of zirconia could be influenced by the MRSZ, where the increasing MRSZ was favorable for the increase of sulfur surface coverage so that facilitating the formation of the tetragonal phase of zirconia rather than that of monoclinic zirconia.

The textural property of the HSZ catalysts was determined by argon physisorption. The argon-adsorption-desorption isotherm plot and BJH adsorption pore distribution of the HSZ catalysts are displayed in Fig. 3(a) and 3(b), respectively. As shown in Fig. 3(a), the isotherm plot of all HSZ catalysts presented a type IV isotherm with hysteresis loops, confirming the presence of mesopores [40]. Fig. 3(b) displayed the pore distribution of the HSZ catalysts in the mesoporous region. The textural properties of the HSZ catalysts are listed in Table 1. As can be seen from the results, the BET surface area of the HSZ samples increased as the MRSZ increased from 0.25 to 1.00, while further increment of the MRSZ resulted in the decrease of the BET surface area. With increasing the MRSZ, the pore volume of the HSZ catalysts continuously decreased, while the pore diameter was decreasing until the MRSZ reached 0.75 followed by staying constant at around 4.0 nm with a further increase of the MRSZ. Interestingly, the precipitation obtained by the hydrothermal method was gradually increased with the increase of the MRSZ within 0.25–1.00, and there was no precipitation as the MRSZ reached 0. Therefore, the MRSZ could strongly influence the formed precipitation in the catalyst preparation procedure. The sulfur content of the HSZ catalysts decreased with the increase of the MRSZ, however, the sulfur content was increased with further increment. The likely reason could be related to that the less precipitation formed in the low MRSZ (0.25–1.00) was more accessible to sulfate, while the HSZ samples with ordered structure contained more sulfate on the catalyst in higher MRSZ. The changing trend of the BET surface area and pore volume of the HSZ catalysts can be attributed to the fact that the ordered structure of HSZ was gradually formed as the MRSZ increased at the low level (0.25–1.00),

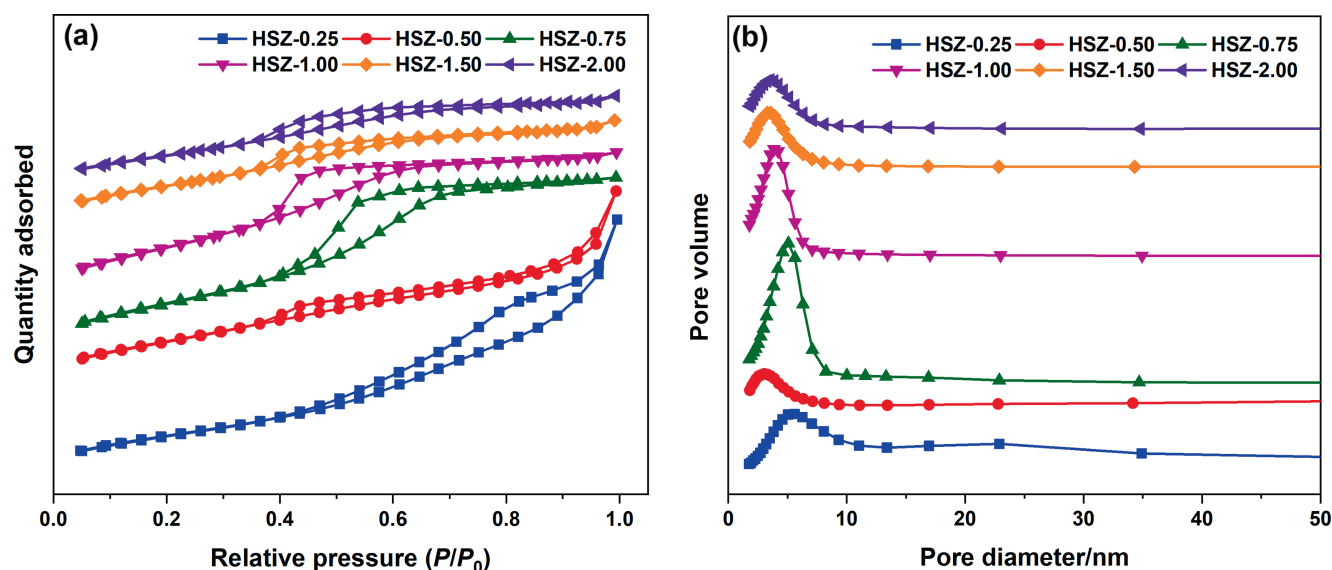


Fig. 3. (a) Argon-adsorption-desorption isotherm plot. (b) Pore size distribution for the HSZ catalysts.

Table 1

Textural properties of the HSZ catalysts

Catalyst	Specific surface area ^① /m ² ·g ⁻¹	Pore volume ^② /cm ³ ·g ⁻¹	Pore diameter ^② /nm	Sulfur mass content ^③ /%
HSZ-0.25	56.78	0.1342	8.2	5.2
HSZ-0.50	65.56	0.0999	6.5	2.7
HSZ-0.75	78.10	0.0957	4.1	1.3
HSZ-1.00	81.57	0.0766	3.6	1.2
HSZ-1.50	59.20	0.0527	3.7	1.6
HSZ-2.00	52.53	0.0478	3.8	1.9

^① Specific surface area was calculated by the BET equation.

^② Pore volume and pore diameter were calculated by the BJH method.

^③ Sulfur content was determined by ICP-OES.

while excessive sulfur amount would result in the mesopores with blockage and collapse [41]. The results indicated that a proper amount of sulfur content could lead to the decrease of the catalyst pore diameter while producing more mesoporous and larger BET surface area.

The surface morphology of the prepared HSZ catalysts was studied by the SEM method, as shown in Fig. 4. As shown in Fig. 4(a), HSZ-0.25 is composed of irregular clustered particles. It can be seen from Fig. 4(b) that the HSZ-0.50 began to show a clear spherical morphology accompanied by partial clustering of nanoparticles. Fig. 4(c)–(f) presented clear spherical morphology of the HSZ catalysts as isolated spherical particles with a diameter of greater than 1 μm . Similar spherical structures of zirconia-based material synthesized by the CTAB-assisted method have been observed in the literature [29,38,42–44]. It was found that the HSZ samples with excessive sulfur amount resulted in the formation of particulates adhering to the catalyst surface, which demonstrated that the decrease of BET surface area and pore volume of the HSZ catalysts was likely ascribed to the pore blockage and collapse. Therefore, the ordered spherical structure of sulfated zirconia formed with the increase of MRSZ, while higher sulfur content would generate excess particulates on the catalyst surface.

The thermal stability of the HSZ catalysts was studied by TGA, as shown in Fig. 5(a). It can be seen that the TGA curves of the HSZ catalysts presented two pronounced mass loss steps. The mass loss between 308 and 773 K of the HSZ samples was assigned to the removal of physisorbed and chemisorbed water, while the mass loss of HSZ samples exceeding 873 K was due to the decomposition of the sulfur species [45–48]. In the first mass loss region,

the release of physisorbed and chemisorbed water from sulfated zirconia took place at about 393 K and between 573 and 773 K, respectively [45]. Profiles of TG-MS for HSZ-0.25 and HSZ-2.00 are presented in Fig. 5(b) and (c). The sulfate species of HSZ samples decomposed to SO_2 over 873 K, demonstrating that the stability of sulfate species could be kept below 873 K. In the range of MRSZ from 0.25 to 1.00, the decomposed sulfur species of the HSZ samples decreased with the increase of MRSZ, which indicates that the HSZ sample prepared by a higher MRSZ possessed less amount of sulfur species. Further increase of MRSZ led to an increase of sulfate species concentration on the surface of HSZ samples, and more polysulfate with higher thermal stability was formed after calcination [45]. The sulfates of HSZ-1.50 and HSZ-2.00 exhibited higher thermal stability than the sulfates of HSZ-1.00, which may be attributed to the formation of polysulfate species on HSZ-1.50 and HSZ-2.00. In the range of MRSZ from 0.25 to 1.00, the temperature of the second mass loss region gradually shifted towards lower temperature with the increase of the sulfur content of the HSZ samples, which could be attributed to the decreased interaction energy between sulfur species and the catalyst surface with the increased sulfur species [49].

The overall acidity and acid site distribution of the HSZ catalysts were determined by NH_3 -TPD, where Fig. 6 shows the NH_3 -TPD profiles of the HSZ samples. The desorption peaks of ammonia at around 373–573 K, 573–723 K, and 723–873 K were attributed to the desorption of adsorbed ammonia from weak, medium, and strong acid sites, respectively [44,50]. The amount of different strength acid was determined by calculating the desorption peak area of the corresponding acid site [51,52]. As can be seen in

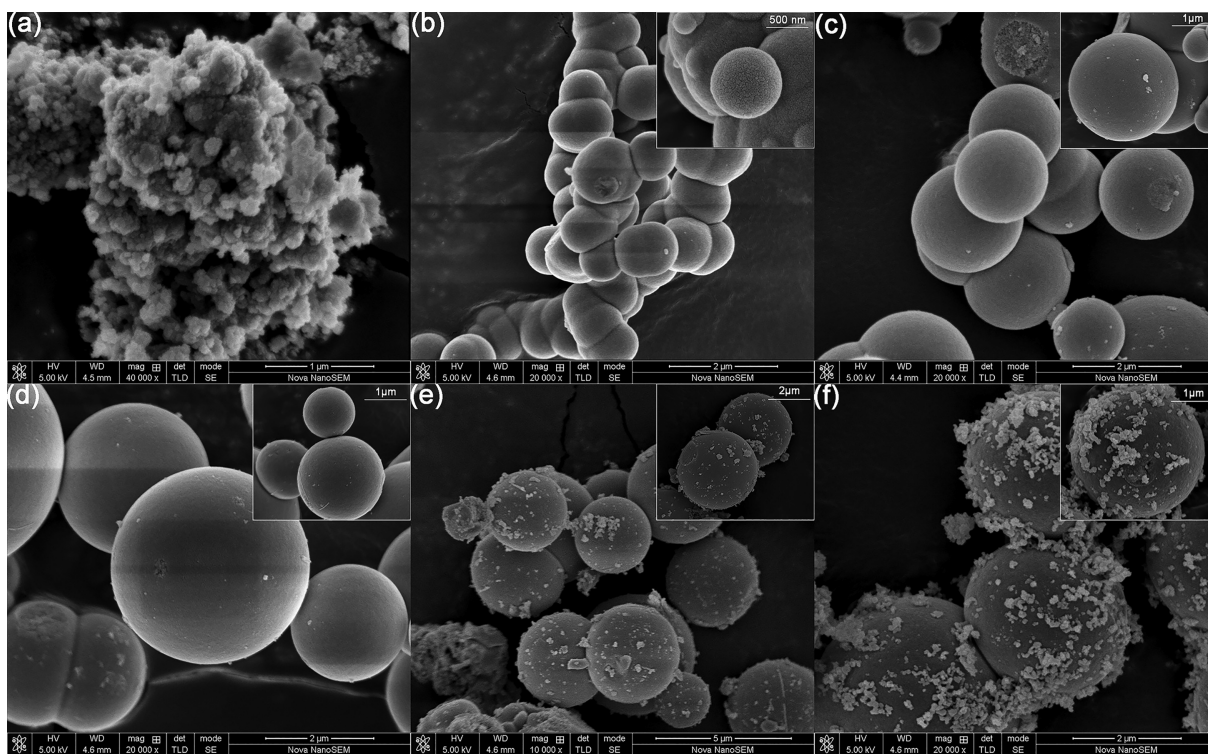


Fig. 4. SEM images of the HSZ catalysts: (a) HSZ-0.25, (b) HSZ-0.50, (c) HSZ-0.75, (d) HSZ-1.00, (e) HSZ-1.50, (f) HSZ-2.00.

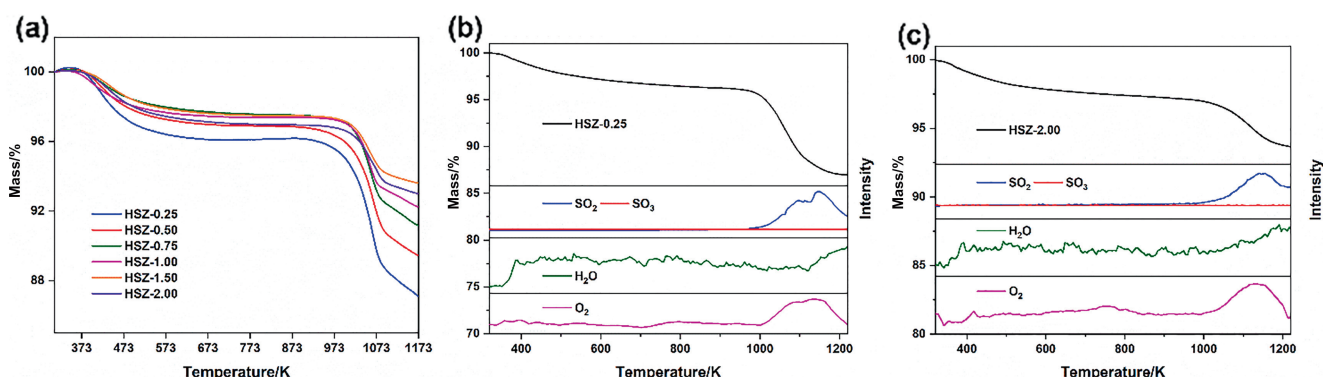


Fig. 5. (a) Thermogravimetric analysis of the HSZ catalysts. Profiles of TG-MS for (b) HSZ-0.25 and (c) HSZ-2.00.

Fig. 6, the HSZ catalysts all possessed weak and strong acid sites, which were ascribed to OH groups and sulfur species on the catalyst surface, respectively [53]. In the range of 0.50–2.00 MRSZ, the amount of weak acid site first increased with the increase of the MRSZ and then decreased when the MRSZ was higher than 1.00. However, in the range of MRSZ from 0.50 to 2.00, the amount of strong acid site progressively increased with the increase of MRSZ, which might attributed to the sulfate content on the surface of HSZ samples increased with the increase of MRSZ. The HSZ-1.00 catalyst had the highest amount of weak acid sites. The obtained result indicated that the MRSZ not only affected the textural properties of the HSZ catalysts but also influenced the nature of acid sites.

The FTIR spectra of the HSZ catalysts are shown in Fig. 7. A broad peak around 3500 cm^{-1} and a peak around 1635 cm^{-1} were attributed to the $\nu(\text{O}-\text{H})$ stretching vibration of the hydroxyl group and $\delta(\text{H}-\text{O}-\text{H})$ bending frequency of water, respectively [54,55]. The characteristic peaks in the region of $1200\text{--}1000\text{ cm}^{-1}$ were attributed to the inorganic chelating bidentate

sulfate ions coordinated to the metal cations [26]. The sulfate bands at around 1240 , 1135 , 1085 and 1048 cm^{-1} were assigned to the stretching vibrations of $\nu(\text{S}=\text{O})$ and $\nu(\text{S}-\text{O})$ [55]. The Brønsted acid sites in sulfated zirconia catalyst were ascribed to the ionic structure of sulfur species [48,55]. The bands that appeared at $800\text{--}500\text{ cm}^{-1}$, characteristic of crystalline zirconia, were associated with the stretching vibrations of the $\text{Zr}-\text{O}-\text{Zr}$ bond [56].

The surface acidity of the sulfated zirconia was measured by defusing reflectance FTIR spectroscopy using pyridine as probe molecule at successively higher temperatures ($323\text{--}523\text{ K}$) and shown in Fig. 8. The IR absorption bands at around 1445 and 1535 cm^{-1} were attributed to the Lewis acid site and Brønsted acid sites, respectively [57,58]. Moreover, the two other IR absorption bands located at around 1608 cm^{-1} and 1490 cm^{-1} were assigned to pyridine adsorbed on either Lewis or Brønsted acid sites [55,59]. The quantified result of Lewis and Brønsted acid sites are listed in Table 2. HSZ-0.25 catalyst with the highest sulfur content had a rel-

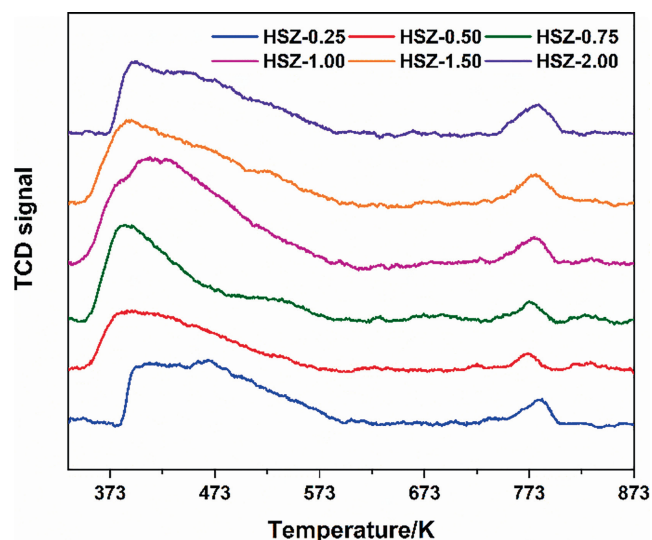


Fig. 6. NH_3 -TPD profiles of the HSZ catalysts.

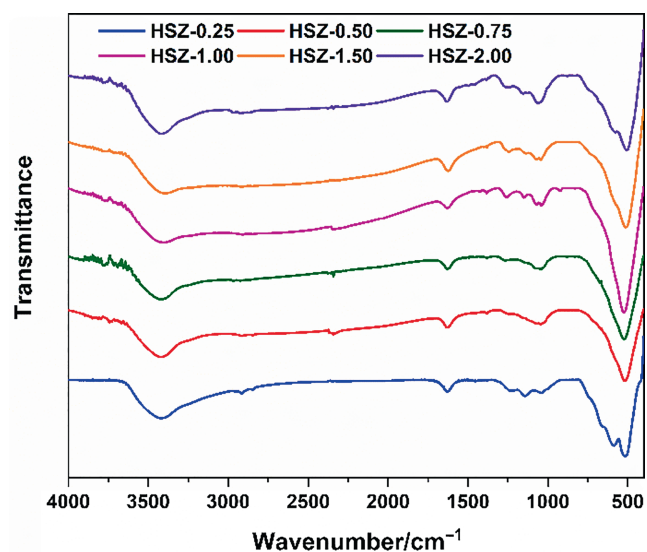


Fig. 7. FTIR spectra of the HSZ catalyst.

atively small amount of Brønsted acid sites, which may be ascribed to the high sulfur loading on the catalyst surface inhibiting the formation of Brønsted acid sites. The amount of Lewis and Brønsted

acid sites progressively increased within the range of 0.50–1.00 MRSZ and decreased with a further MRSZ increase. The different amount of Brønsted acid sites of the HSZ catalysts possibly resulted from the different combination of sulfur species with zirconium and hydration degree [55]. The obtained result demonstrated that the Lewis and Brønsted acid sites could be adjusted by the applied MRSZ used in the catalyst preparation.

3.2. Synthetic scheme for spherical sulfated zirconia

The speculated synthetic procedure for the HSZ catalysts is presented in Fig. 9. In detail, the cationic surfactant CTAB was dissolved in hydrogen chloride aqueous solution, and the hydrophilic group formed spherical micelles outward [60]. The transparent sol, obtained by the addition of zirconium oxychloride in 95% (mass) ethanol aqueous solution, was added to the CTAB aqueous solution, thus Zr^{4+} accumulated inside the CTAB spherical micelles to form a surfactant-stabilized zirconium sol. Next, a designed amount of $(\text{NH}_4)_2\text{SO}_4$ aqueous solution was mixed well with the obtained sol. The surface of surfactant-stabilized zirconium sol was affected by $(\text{NH}_4)_2\text{SO}_4$ species. SO_4^{2-} ions were adsorbed on the outer surface of the spherical zirconium sol. The electrostatic interaction between SO_4^{2-} and hydrophilic groups of CTAB in the solution reduced the electrostatic repulsion between the hydrophilic groups of CTAB and increased the stability of surfactant-stabilized zirconium sol. Therefore, the enhancement of the low concentration of ammonium sulfate in the precursor solution for the structural stability of the surfactant-stabilized zirconium sol was relatively low. Finally, the transparent solution was treated under the hydrothermal condition to form the white precipitation of $\text{Zr}(\text{OH})_4$. In the precursor solution with lower MRSZ, the $\text{Zr}(\text{OH})_4$ gel continuously formed during the hydrothermal procedure might undermine the spherical micelle structure of CTAB and accumulated to form disordered clusters. Meanwhile, more SO_4^{2-} might exist in the bulk phase of the $\text{Zr}(\text{OH})_4$ gel during the accumulation of the gel, resulting in higher sulfur content in the HSZ sample. In the hydrothermal procedure, the unstable spherical $\text{Zr}(\text{OH})_4$ could be generated at the lower MRSZ and was dissolved easily in the water again. Notably, there was no $\text{Zr}(\text{OH})_4$ gel generated after the hydrothermal treatment if ammonium sulfate was not added to the precursor solution. All these indicated that the concentration of SO_4^{2-} played an important role in stabilizing the spherical micelle structure of CTAB. The higher concentration of ammonium sulfate in the precursor solution was conducive to the stability of the CTAB spherical micelle structure. However, excessive ammonium sulfate produced particles adhering to the catalyst surface, affecting the structure and properties of the catalyst. After drying in a convection oven, the precipitation was calcinated at 873 K for 5 h under air atmosphere. The

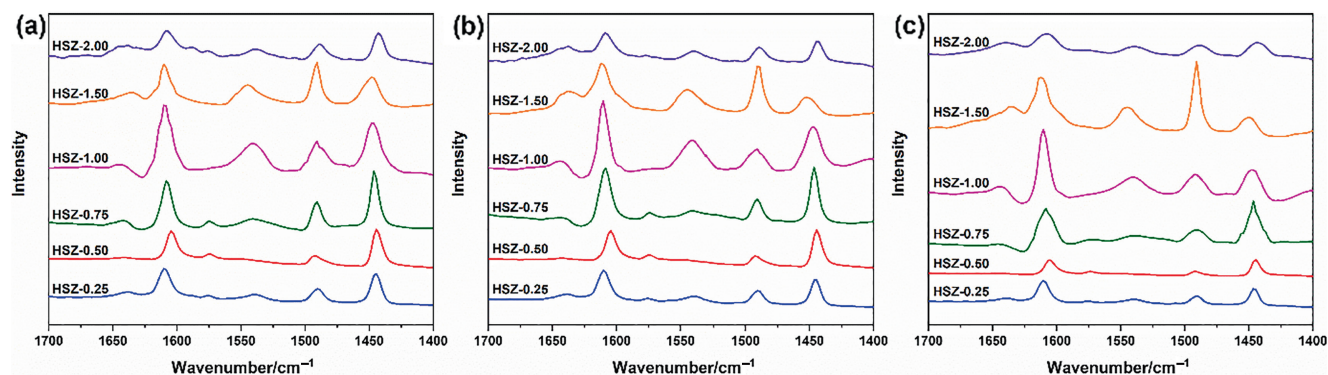
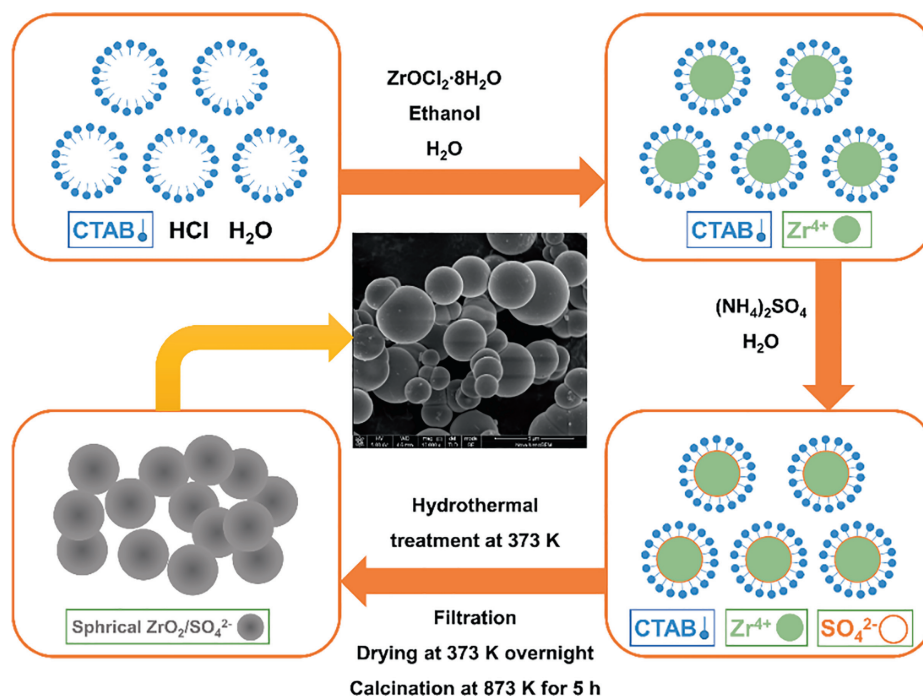


Fig. 8. Py-IR spectrum of the HSZ catalysts. (a) 423 K, (b) 523 K, (c) 623 K.

Table 2

Amount of Lewis and Brønsted acid sites determined by Py-IR.

Catalyst	Amount of Lewis acid/ $\mu\text{mol}\cdot\text{g}^{-1}$		Amount of Brønsted acid/ $\mu\text{mol}\cdot\text{g}^{-1}$		Total amount acid/ $\mu\text{mol}\cdot\text{g}^{-1}$		B/L
	Weak	Strong	Weak	Strong	Lewis	Brønsted	
HSZ-0.25	36.6	20.6	18.1	12.8	57.2	31.0	0.54
HSZ-0.50	50.3	23.4	6.6	5.1	73.7	11.7	0.16
HSZ-0.75	37.8	55.2	39.3	28.3	93.0	67.6	0.73
HSZ-1.00	57.4	66.1	81.4	65.3	123.5	146.7	1.19
HSZ-1.50	53.7	36.9	50.1	59.4	90.6	109.6	1.21
HSZ-2.00	24.2	26.1	20.6	28.1	50.2	48.7	0.97

**Fig. 9.** Synthetic scheme for spherical sulfated zirconia.

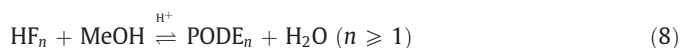
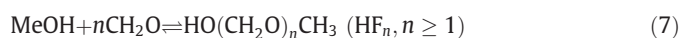
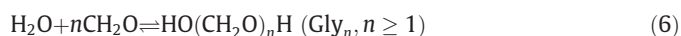
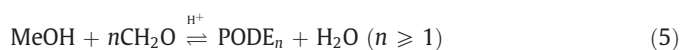
ordered spherical sulfated zirconia could be obtained by adjusting the MRSZ. The formed morphology of HSZ catalysts was strongly influenced by the concentration of $(\text{NH}_4)_2\text{SO}_4$ in the solution.

Therefore, the speculation about the difference in morphology of the HSZ catalysts prepared by different MRSZ was as follows. (1) Lower MRSZ in the precursor solution resulted in the poor stability of micelles with similar core-shell structure formed by CTAB and Zr^{4+} , and the $\text{Zr}(\text{OH})_4$ gel generated during the hydrothermal process continuously accumulated to form disordered clusters, which contained much sulfate content in the bulk phase. (2) With the increase of MRSZ in the precursor solution, the SO_4^{2-} concentration on the surface of semi-stable CTAB spherical micelles increased, strengthening the stability of the micelles and benefiting for $\text{Zr}(\text{OH})_4$ gel to grow inside micelles and form the stable spherical structure. (3) The excessive MRSZ had no significant effect on the basic spherical morphology of $\text{Zr}(\text{OH})_4$ gel, while the higher SO_4^{2-} concentration on the surface of $\text{Zr}(\text{OH})_4$ gel would result in the formation of particles adhering to the surface of HSZ samples and polysulfate on the catalyst surface after calcination.

3.3. Catalyst performance evaluation

In this experiment, the catalytic performance evaluation of sulfated zirconia catalysts for the synthesis of PODE_n using methanol and formaldehyde solution as reactant was carried out. The global

reaction and detailed acetalization reaction for the synthesis reaction are described as Eq. (5) and Eqs. (6)–(8), respectively [7,61].



The catalytic performance of the studied sulfated zirconia and sulfonated cation resin (SR) on the synthesis of PODE_n from methanol and formaldehyde solution is presented in Fig. 10. The experiments were carried out under catalyst amount of 3.0% (mass), 2.0 h of reaction time, 393 K of reaction temperature, 1.5 molar ratio of formaldehyde to methanol, and 1.0 MPa of pressure. From the result of Fig. 10, the catalytic activity of HSZ was continuously improved by increasing the MRSZ within the range of 0.50–1.00, while further increment resulted in the inhibition on the catalytic performance. The acidic properties of catalysts have played an important role in the PODE_n synthesis reaction [14,62–64]. Therefore, the catalytic results demonstrated that the MRSZ strongly influenced the acidic properties of the HSZ catalysts, which in turn affected the methanol conversion and PODE_{3-6} selectivity. The

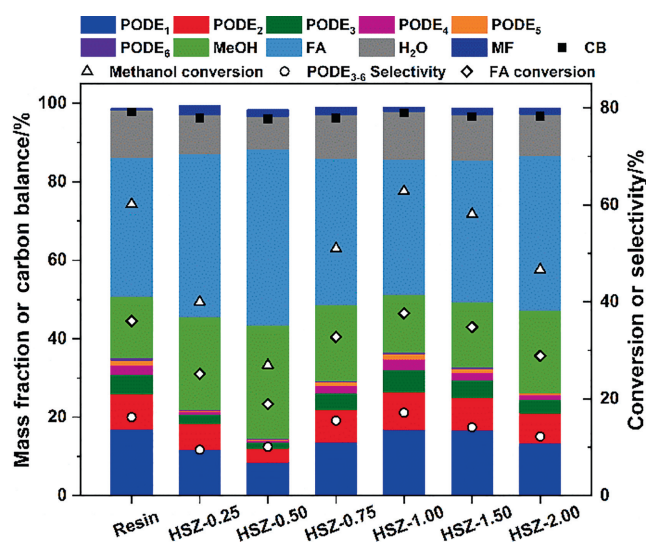


Fig. 10. Catalytic performance of sulfonated acid cation resin and sulfated zirconia in the synthesis of PODE_n from methanol and formaldehyde solution.

HSZ-1.00 exhibited the best reaction performance among the sulfated zirconia catalysts, which could probably be attributed to the excellent acidic property. Comparatively, the sulfonated acid cation resins were strongly active for the PODE_n synthesis reaction, and exhibited a similar methanol conversion and PODE_{3-6} selectivity with the HSZ-1.00, indicating that the catalytic activity of HSZ-1.00 was comparable to that of the efficient sulfonated acid cation resin catalyst. Combining the Py-IR results and catalytic perfor-

mance of HSZ catalysts, it could be found that methanol conversion and PODE_{3-6} selectivity might be related to the Brønsted acid sites and Lewis acid sites, respectively. HSZ catalyst with more Brønsted acid sites exhibited higher methanol conversion. By further analyzing the influence of the Brønsted acid strength on methanol conversion, HSZ-2.00 contained the same amount of strong Brønsted acid sites and less weak Brønsted acid sites compared to HSZ-0.75, and exhibited better performance on methanol conversion. This indicated that the higher amount of weak Brønsted acid sites might result in the promotion of methanol conversion for PODE_n synthesis from methanol and formaldehyde solution. Wang *et al.* demonstrated that Brønsted acid sites with weak acid strength might be the main active sites for PODE_n synthesis reaction [14]. Considering the influence of weak and strong Lewis acid sites on PODE_{3-6} selectivity, it was found that the higher PODE_{3-6} selectivity of HSZ-1.00 was more likely to be attributed to its much more strong Lewis acid sites than HSZ-1.50. Baranowski *et al.* found that the Lewis acid sites could activate formaldehyde to promote the insertion of formaldehyde into PODE_n [62]. Therefore, methanol conversion and PODE_{3-6} selectivity might be influenced by weak Brønsted acid sites and strong Lewis acid sites, respectively. HSZ-1.00 was chosen for all of the following experiments, which were carried out for the determination of optimal reaction conditions.

3.4. Reaction conditions optimization and reusability studies

The effects of the reaction parameters, such as reaction temperature, reaction time, catalyst amount, molar ratio of FA/MeOH, and reaction pressure on the catalytic activity were investigated. As shown in Fig. 11(a), the methanol conversion and PODE_{3-6} selectivity significantly increased as the reaction temperature was raised from 373 to 393 K. However, by further increasing the reaction

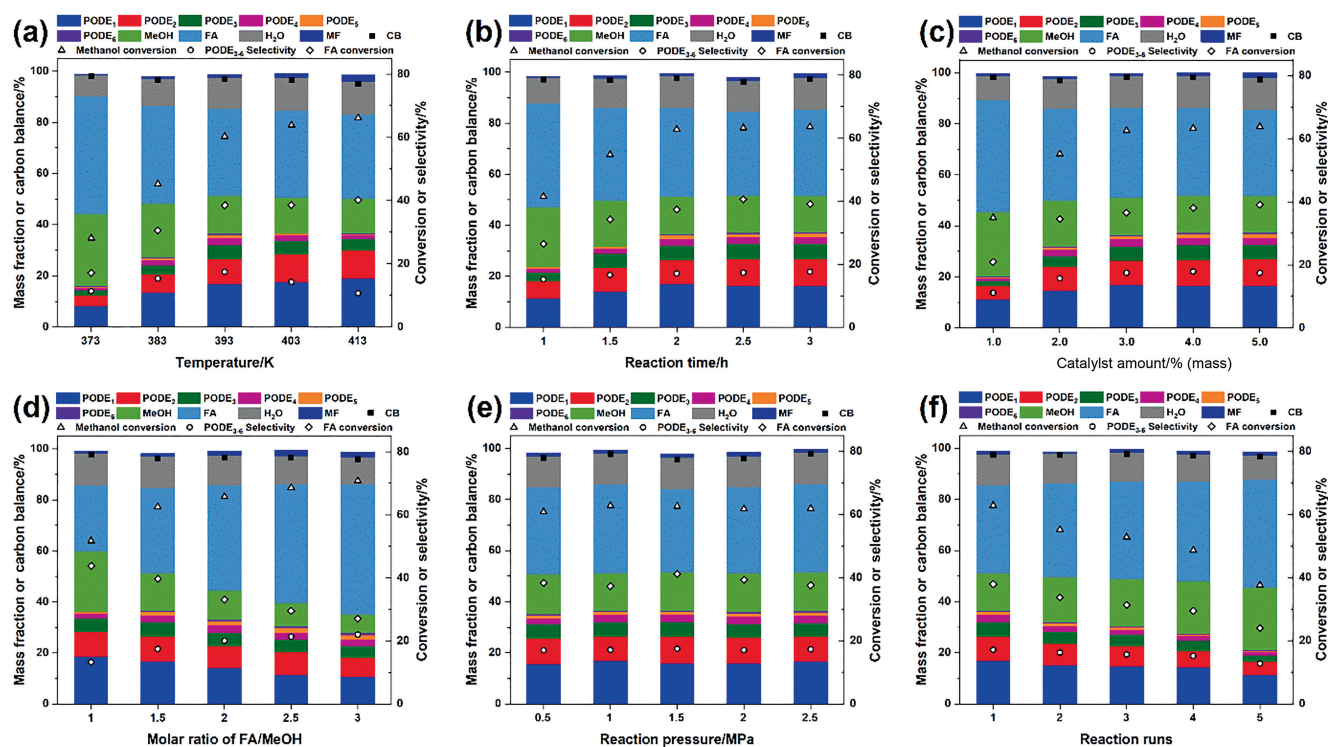


Fig. 11. Effects of reaction parameters on the catalytic activity of HSZ-1.00 in the synthesis reaction of PODE_n from methanol and formaldehyde solution. (a) Effects of reaction temperature (reaction time 2.0 h, catalyst amount 3.0% (mass), molar ratio of FA/MeOH 1.5, reaction pressure 1.0 MPa); (b) Effects of reaction time (reaction temperature 393 K, catalyst amount 3.0% (mass), molar ratio of FA/MeOH 1.5, reaction pressure 1.0 MPa); (c) Effects of catalyst amount (reaction temperature 393 K, reaction time 2.0 h, molar ratio of FA/MeOH 1.5, reaction pressure 1.0 MPa); (d) Effects of molar ratio of FA/MeOH (reaction temperature 393 K, reaction time 2.0 h, catalyst amount 3.0% (mass), reaction pressure 1.0 MPa); (e) Effects of reaction pressure (reaction temperature 393 K, reaction time 2.0 h, catalyst amount 3.0% (mass), molar ratio of FA/MeOH 1.5); (f) Reusability of the HSZ-1.00 catalyst.

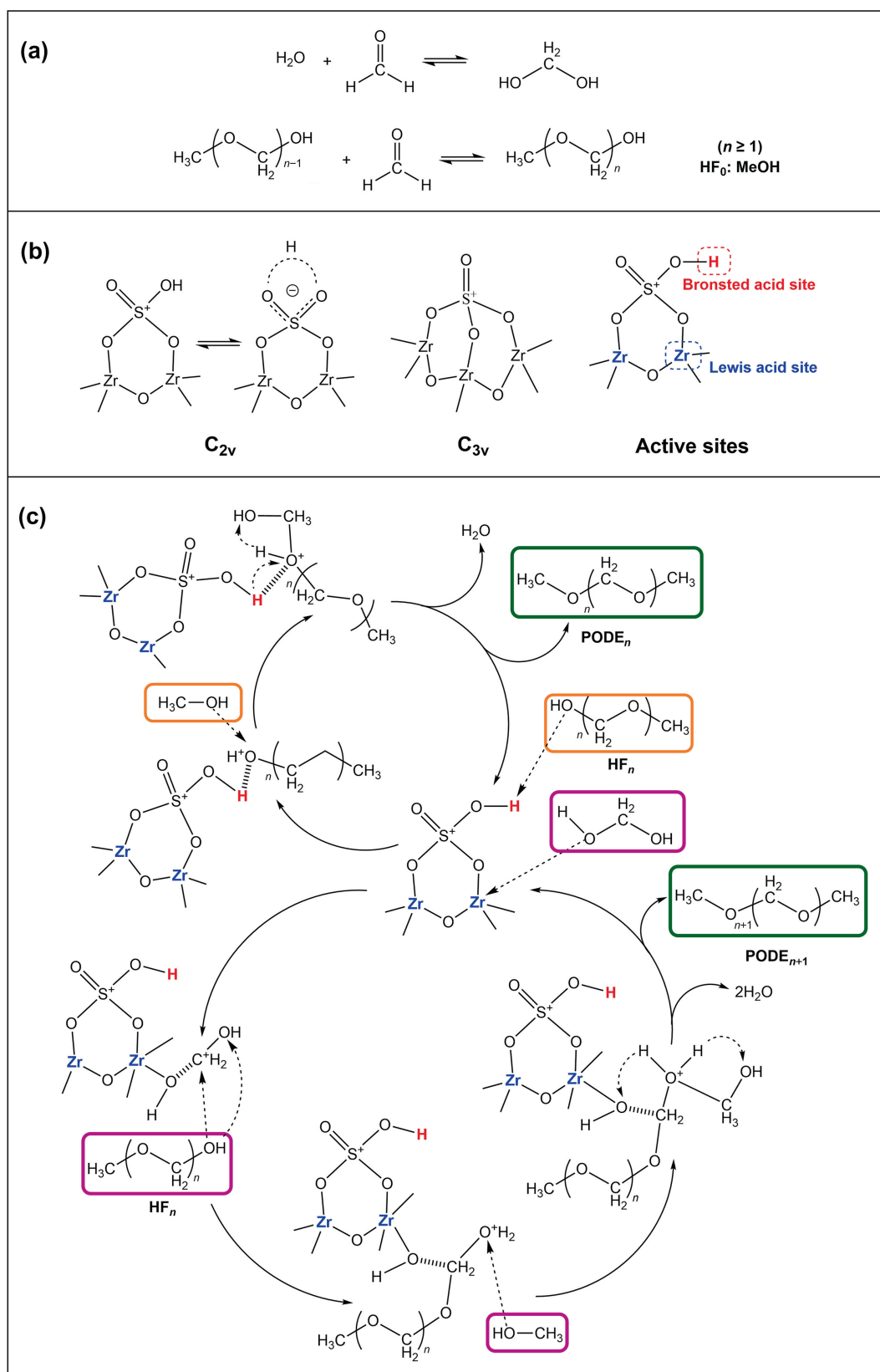


Fig. 12. Speculated reaction pathway for PODE_n synthesis from methanol and formaldehyde solution over HSZ catalyst. (a) Equilibrium reactions in the reactant; (b) Possible sulfate species geometry of sulfated zirconia and active sites of HSZ catalyst; (c) Proposed reaction pathway on Brønsted and Lewis acid sites.

temperature to 413 K, a noticeable reduction for PODE₃₋₆ selectivity was observed while the methanol conversion stayed almost constant. The effect of the reaction time in the range of 1.0–3.0 h on the catalytic activity is depicted in Fig. 11(b). The methanol conversion and PODE₃₋₆ selectivity increased from 41.51% and 15.22% in 1.0 h to 62.82% and 17.12% in 2.0 h, respectively, and remained almost constant upon further increase of the reaction time to 3.0 h. As shown in Fig. 11(c), the methanol conversion was obviously improved with the amount of the catalyst loading. An increase in catalyst amount from 1.0% (mass) to 3.0% (mass) resulted in the increment of methanol conversion from 34.96% to 62.57% and PODE₃₋₆ selectivity from 11.13% to 17.48%, which may be attributed to the increase of active acid sites. By further increasing the catalyst amount to 5.0% (mass), the methanol conversion and PODE₃₋₆ selectivity remained almost constant. The effect of molar ratio of FA/MeOH on the methanol conversion and PODE₃₋₆ selectivity was also studied and shown in Fig. 11(d). It can be seen that the methanol conversion and PODE₃₋₆ selectivity increased gradually by increasing the molar ratio of FA/MeOH in the reactant. However, the solubility of the reactant was decreased by the reduced methanol content, which could result in the polymerization of high concentration formaldehyde. Therefore, the molar ratio of FA/MeOH in the reactant was not suitable to be too low. The effect of reaction pressure on the PODE_n synthesis from 0.5 to 2.5 MPa is presented in Fig. 11(e). The results showed that the reaction pressure had a negligible influence on the catalytic performance of HSZ-1.00. The vaporization of the reactant could be suppressed when the pressure of the reactor reached 1.0 MPa. Therefore, the optimal reaction results catalyzed by HSZ-1.00 could be obtained under the optimized reaction conditions of 393 K reaction temperature, 2.0 h reaction time, 3.0% (mass) catalyst amount, 1.5 molar ratio of FA/MeOH, and 1.0 MPa reaction pressure.

Besides the catalytic activity, stability and reusability are also the essential factors influencing the performance of the acidic catalysts in the PODE_n synthesis reaction. In this work, successive reaction runs were used to evaluate the stability and reusability of the prepared HSZ catalysts. After each catalytic reaction, the separated catalysts were washed repeatedly with methanol to remove the residuary reactant and product on the catalyst and then dried at 383 K overnight. The PODE_n synthesis reaction was performed under the investigated optimal reaction conditions. As seen in Fig. 11(f), a gradual decrease in the methanol conversion and PODE₃₋₆ selectivity was observed during five reaction runs. The slight deactivation of the HSZ-1.00 was attributed to the loss of sulfate species, which resulted in the decrease in the acidity of the catalyst [16,29].

3.5. Possible reaction pathway for PODE_n synthesis

Considering the reactant used in this work, the actual substances polyoxymethylene glycols $[\text{HO}(\text{CH}_2\text{O})_n\text{H}, n \geq 1, \text{Gly}_n]$ and polyoxymethylene hemiformals $[\text{CH}_3(\text{OCH}_2)_n\text{OH}, n \geq 1, \text{HF}_n]$ could be generated by the two equilibrium reactions of formaldehyde with water and methanol with formaldehyde, respectively [61]. The equilibrium reactions for the aqueous solution of methanol and formaldehyde are shown in Fig. 12(a). Hammache *et al.* proposed the structure of calcinated sulfated zirconia that possessed both Lewis and Brønsted acid sites, which have a synergistic effect on *n*-butane isomerization [65]. Zirconia with tetragonal and monoclinic phases facilitated the coordination with sulfate species in C_{2v} and C_{3v} geometric structures, respectively [34]. The possible sulfate structures of sulfated zirconia in C_{2v} and C_{3v} geometry and active sites of HSZ are presented in Fig. 12(b).

Based on the results in the current study and our previous investigations [66], the possible reaction pathway for PODE_n synthesis from methanol and formaldehyde solution over the HSZ-

1.00 catalyst is presented in Fig. 12(c). The reaction mechanism for PODE_n synthesis has been studied by different groups. Liu *et al.* proposed the reaction mechanism for PODE_n synthesis from paraformaldehyde and methylal based on the synergy of Brønsted and Lewis acid sites, and found that Brønsted acid sites were effective for the whole reaction pathway [16]. Wang *et al.* found that weak Brønsted acid sites of citric acid-modified beta zeolite were predominant active sites for PODE_n synthesis [14]. Therefore, in the Brønsted acid-catalyzed reaction cycle $\text{HF}_n [\text{CH}_3(\text{OCH}_2)_n\text{OH}]$ was first activated by Brønsted acid sites to form oxonium cation $[\text{CH}_3(\text{OCH}_2)_n\text{O}^+\text{H}_2]$, which then reacted with methanol to form water and PODE_n. Baranowski *et al.* investigated the synergistic effect of Brønsted and Lewis acid sites on PODE_n synthesis reaction, demonstrating that the interaction between Lewis acid sites and formaldehyde facilitated the insertion of formaldehyde into PODE_n [62]. Pezzotta *et al.* believed that the adsorption of reactant containing active hydroxyl group on Lewis acid sites was achieved by bonding with the oxygen atom of the hydroxyl group [67]. Consequently, considering the Lewis acid-catalyzed reaction cycle, one hydroxyl group of the methylene glycol (HOCH_2OH) could be activated by Lewis acid sites to form carbon cation HOC^+H_2 , which was followed by reacting with $\text{HF}_n [\text{CH}_3(\text{OCH}_2)_n\text{OH}]$ to form the oxonium cation $[\text{CH}_3(\text{OCH}_2)_{n+1}\text{O}^+\text{H}_2]$. The formed oxonium cation $[\text{CH}_3(\text{OCH}_2)_{n+1}\text{O}^+\text{H}_2]$ interacted with methanol to form PODE_{n+1} and water. In the suggested reaction pathway, Brønsted acid sites were active for PODE_n synthesis reaction by the direct activation of $\text{HF}_n [\text{CH}_3(\text{OCH}_2)_n\text{OH}]$, while Lewis acid sites might be more inclined to activate the methylene glycol (HOCH_2OH).

4. Conclusions

Spherical sulfated zirconia with mesopores for PODE_n synthesis from methanol and formaldehyde solutions were prepared by a one-pot hydrothermal method assisted with CTAB surfactant. The results demonstrated that the MRSZ not only controlled the formation of ordered spherical morphology of catalysts but also affected the acidic properties of the HSZ catalysts. The properties and catalytic activity of all the HSZ catalysts were compared, where the best catalyst HSZ-1.00 had the highest activity among all of the HSZ catalysts. According to the results of catalytic performance, acidic properties of the HSZ catalysts could strongly influence the activity, which increased firstly and then decreased with MRSZ increased from 0.50 to 2.00. The methanol conversion and PODE₃₋₆ selectivity of PODE_n synthesis reaction from methanol and formaldehyde solution over the HSZ catalysts were possibly influenced by the weak Brønsted acid sites and strong Lewis acid sites, respectively. Based on the synergy of Lewis and Brønsted acid sites, the speculated reaction pathway was proposed, which demonstrated that the Brønsted and Lewis acid sites could be beneficial to the activation of polyoxymethylene hemiformals $[\text{CH}_3(\text{OCH}_2)_n\text{OH}]$ and methylene glycol (HOCH_2OH), respectively. Accordingly, the obtained results could provide some guidance for designing acidic catalysts that could be applied in PODE_n synthesis reaction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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