

Research on direct oxidation of methanol to polyoxymethylene dimethyl ethers over NASICON-based catalytic materials

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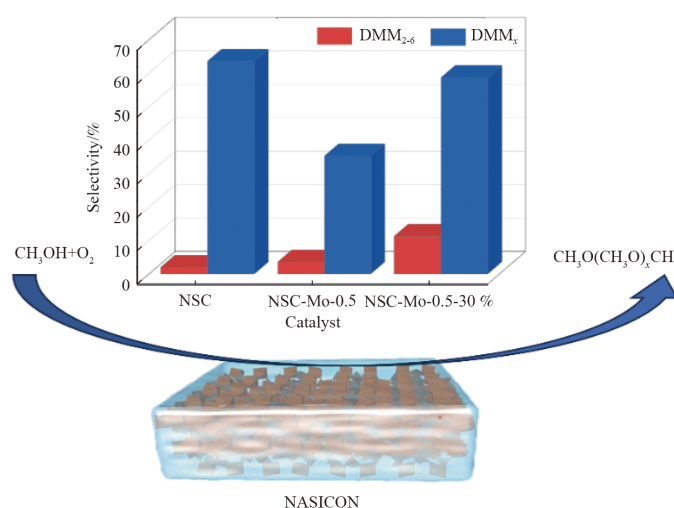
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Abstract: Polyoxymethylene dimethyl ethers (DMM_x) are highly promising clean diesel additives. Compared to the traditional aldol condensation route, the one-step oxidative method for producing DMM_x directly from methanol is a green synthesis route offering significant advantages. However, due to the complexity of the reaction, a balance must be struck between oxidation depth and C–O chain growth efficiency. This imposes specific requirements on the design of catalysts with multifunctional active sites: the catalyst should possess appropriate oxidative activity, suitable acid strength distribution, and effective synergy between these two functions. To address these challenges, this study designed a sulfuric acid-modified molybdenum-doped

NASICON catalyst, which demonstrated favorable catalytic performance in the one-step oxidative synthesis of DMM_x from methanol. Over the NSC-Mo-0.5-30% catalyst, methanol conversion rate of 81.3% and the DMM_x selectivity of 58.7% were achieved, along with the formation of heavier molecules, as evidenced by the DMM₂₋₆ selectivity of 11.3%. The NH₃-TPD, Py-IR and XPS results indicate that the introduction of molybdenum increases the number of weak Lewis acid sites, while sulfuric acid impregnation not only generates gradient-distributed Brønsted acid sites but also promotes the formation of Mo⁵⁺/Mo⁶⁺ redox pairs. The cooperation of the two types of active sites significantly enhances catalyst performance.

Key words: methanol; NASICON material; polyoxymethylene dimethyl ethers; C–O chain growth; oxidation



The selective oxidation of methanol for value-added utilization has become in C1 chemistry and green catalysis. The core challenge lies in precisely regulating the reaction pathway to convert inexpensive methanol into value-added chemicals, such as formaldehyde, formic acid, methyl formate, or polyoxymethylene dimethyl ethers (DMM_x). The DMM_x, with the general chemical formula CH₃O(CH₂O)_xCH₃ (x = 1–8), are internationally recognized as environmentally friendly diesel blending components due

to their high cetane number and high oxygen content, which significantly improve combustion efficiency^[1] and effectively reduce exhaust pollutants and particulate emissions^[2]. Moreover, owing to their strong solvency and eco-friendly characteristics, DMM_x can also be used as green organic solvents, high-end electronic-grade solvents, CO₂ absorbents, etc.^[3]. The synthesis methods for DMM_x mainly include condensation and oxidation. The condensation method involves the liquid-phase

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condensation of methanol^[4–7] or methylal (DMM)^[8–11] with trioxane or paraformaldehyde to produce DMM_x. In contrast, the oxidation method refers to the direct oxidation of methanol^[3] or dimethyl ether^[12] to produce DMM_x. Among these, the direct oxidation of methanol to DMM_x offers advantages such as a concise pathway, good atom economy, low cost and environmental friendliness, making it a promising technological pathway in the coal chemical industry.

The catalysts for the condensation of methylal with trioxane or paraformaldehyde to produce DMM_x mainly include ionic liquids^[9], macroporous strong acid cation exchange resins^[11], and microporous/mesoporous molecular sieve catalysts^[13]. Zhao et al.^[14] investigated the formation mechanism of DMM_x and found that paraformaldehyde first decomposes into CH₂O, and chain growth primarily occurs through the stepwise insertion of individual CH₂O segments. Catalysts for DMM_x synthesis through the reaction of methanol with formaldehyde sources such as paraformaldehyde, mainly include SO₄^{2–}/Fe₂O₃-SiO₂^[4], ZrO₂/γ-Al₂O₃^[5] and Al-MCM-41^[6], etc. Li et al.^[6] proposed that paraformaldehyde first is decomposed into formaldehyde, which then reacts with methanol to form hemiacetal intermediate. Subsequently, this intermediate is attacked by methanol to form dimethoxymethane, with the highest free energy barrier (121.2 kJ/mol), which is regarded as the rate-determining step. Finally, chain growth occurs through the reaction of DMM_{x–1} with formaldehyde to form long-chain DMM_x.

In the field of one-step methanol oxidation for the direct synthesis of DMM_x, relevant studies remain scarce. This reaction pathway involves a complex network, making research particularly challenging due to the difficulty of simultaneously controlling oxidation depth and the efficiency of C–O chain growth. Existing catalytic systems primarily focus on the first C–O chain product, DMM, and the catalysts employed include vanadium-based^[15–16] and molybdenum-based^[17–19] catalysts, among others. To achieve high catalytic efficiency, the key lies in balancing the oxidative activity and acidic sites within the catalyst. This imposes stringent requirements on catalyst design, demanding a simultaneous balance of moderate oxidation activity, a suitable acid strength distribution, and synergy between the dual functional sites.

Our research group has conducted a series of studies on the oxidative synthesis of DMM_x. In the investigation on dimethyl ether (DME) oxidation to DMM_x over solid acid-modified carbon-based catalyst, we found that an appropriate ratio of acid sites on catalyst surface plays a crucial role in C–O chain growth^[20–22]. Gao et al.^[20] achieved the oxidative synthesis of DMM_x from DME by modulating the matching between the surface acid gradient distribution and the redox-active sites on carbon-based catalysts. The results indicate that the Ti(SO₄)_x/AC-N₂ catalyst (AC-N₂ represents the activated carbon treated under N₂ atmosphere) have a high proportion of weak-to-medium strong acid sites and abundant oxygen-containing active groups, significantly promoting the formation of

longer C–O chain products (DMM_{2–3}). To investigate the mechanism of C–O chain growth and achieve the valorization of coal-based chemicals, our further expanded this research to the oxidative conversion of methanol to DMM_x. Wang et al.^[3] designed a core-shell catalyst with an Fe–Mo core and an HZSM-5 zeolite shell, enabling the one-step oxidative conversion of methanol to DMM_x. The results found that the unique core-shell structure, together with the synergy between acid sites with different strengths and redox sites, is essential for facilitating C–O chain growth. Moreover, a moderate amount of medium-strong Brønsted acid sites is crucial for the formation of longer C–O chain DMM_x products. Summary these findings indicate that the efficient synthesis of DMM_x urgently requires the development of multifunctional catalytic materials that integrate both oxidative and acidic functionalities while ensuring effective synergy between them.

Sodium superionic conductor (NASICON) materials are phosphate compounds with the general formula A_xB₂(ZO₄)₃^[23], in which the A sites are typically occupied by alkali or alkaline earth metals, the B sites by multivalent elements (e.g., Zr, Ti, Sc) and the Z sites by phosphorus, silicon, or both. In recent years, NASICON materials have shown significant potential in catalysis due to the presence of multivalent redox-active elements and tunable acid-base properties in their crystal structure. Several studies have reported their application in dehydration, dehydrogenation, and condensation reactions of alcohol molecules^[23–25]. For example, Ermilova et al.^[24] demonstrated that increasing the vanadium content in NASICON catalysts (LiZr₂(VO₄)_x(PO₄)_{3–x}) could shift the primary pathway of methanol conversion from dehydration to dehydrogenation. Recently, our research group synthesized P-Ti-based NASICON materials (H_{1–x}Ti₂(PO₄)_{3–x}(SO₄)_x) and modulated their surface properties by varying synthesis conditions, particularly their acid-base characteristics, enabling the aldol condensation of formaldehyde and acetic acid to produce acrylic acid^[26–27]. Wang et al.^[28] achieved one-step synthesis of acrylic acid from methanol and acetic acid by coating TiO₂ onto NASICON substrate. It found that TiO₂ modification significantly enhanced the surface oxidative dehydrogenation capability of the NASICON material while having minimal impact on its acid-base properties, thus effectively promoting the generation of the intermediate formaldehyde and ultimately improving the selectivity toward acrylic acid. It follows that there are characteristics of both redox-active and acid-base sites for the NASICON materials, which is consistent with the functional requirements of catalysts for the oxidative synthesis of DMM_x from methanol or dimethyl ether.

Based on the foregoing, a series of NASICON catalysts with varying molybdenum contents (Li_{1–x}Zr₂(PO₄)_{3–x}(MoO₄)_x) were synthesized *via* a sol-gel method and subsequently modified with sulfuric acid. The effects of modification on the crystal structure, surface properties, acidity, and oxidation characteristics were systematically analyzed for the catalysts using XRD, NH₃-

TPD and XPS, and the structure-activity relationship between the catalyst properties and reaction performance was established according to the catalytic performance of these materials for the direct oxidation of methanol to polyoxymethylene dimethyl ethers.

1 Experimental

1.1 Catalyst preparation

1.1.1 Synthesis of molybdenum-doped NASICON materials

NASICON catalysts with varying molybdenum contents ($\text{Li}_{1-x}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{MoO}_4)_x$) were synthesized *via* a sol-gel method^[29]. Using the representative sample $\text{Li}_{0.5}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{MoO}_4)_{0.5}$ (denoted as NSC-Mo-0.5) as an example: 12.89 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 33.664 g of citric acid, 0.37 g of Li_2CO_3 , 5.75 g of $\text{NH}_4\text{H}_2\text{PO}_4$ and 1.77 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were sequentially dissolved in a mixed solvent of ethylene glycol (2 mL) and deionized water (10 mL). Under continuous magnetic stirring, the pH value of the solution was rapidly adjusted to 5 using concentrated ammonia to prevent the precipitation of zirconium phosphate. The resulting sol then underwent a three-step thermal treatment: first, gelation at 95 °C for 24 h; followed by drying at 150 °C for 24 h; and finally, pre-calcination at 350 °C for 4 h. The obtained precursor was thoroughly ground and subsequently calcined in a muffle furnace at 750 °C for 10 h, and the molybdenum-doped NASICON catalyst was obtained. By adjusting the amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ used, a series of catalysts with different molybdenum contents (x values) were prepared using the same procedure and uniformly designated as NSC-Mo- x .

1.1.2 Preparation of sulfuric acid-modified NASICON catalysts

The modified catalyst was prepared by introducing sulfuric acid onto the NSC-Mo-0.5 support *via* an impregnation method. Taking the 30% sulfuric acid loading as an example: first, 1.5 g of concentrated sulfuric acid was slowly added dropwise into 5 g of deionized water under continuous stirring to prepare the impregnation solution. Subsequently, 5 g of the NSC-Mo-0.5 sample was added to this solution. The mixture was ultrasonically dispersed for 10 min to ensure uniform impregnation and then allowed to stand for 6 h. The resulting solid was dried at 120 °C for 6 h to remove moisture, followed by calcination in air at 260 °C for 6 h, ultimately obtaining the sulfuric acid-modified NASICON catalyst. The samples were designated based on the mass percentage of sulfuric acid to the support ($y\%$) as the NSC-Mo-0.5- $y\%$ series.

1.2 Catalyst evaluation

The DMM _{x} synthesis reaction was carried out in a continuous-flow fixed-bed reactor at atmospheric pressure. Catalyst particles (20–40 mesh) with a loading of 1 g were diluted with 1 mL of porcelain rings (20–40 mesh). Typically, prior to the reaction, the catalytic system was purged with oxygen at a gas hourly space velocity (GHSV) of 1800 h⁻¹, and the reactor temperature was gradually raised to 220 °C. After system stabilization, methanol liquid was fed into the catalytic bed at a rate of 0.813 mL/h using a syringe pump. The effluent gas from the reactor outlet was cooled by a condensation unit, allowing for the separation of liquid products and non-condensable gas products.

1.3 Product analysis and quantification

The reaction products were qualitatively and quantitatively analyzed using a system of three gas chromatographs: A GC-2014 unit equipped with a TCD was used to detect oxygen (O₂), formaldehyde (FA), dimethyl ether (DME), methanol (MeOH), water (H₂O), methyl formate (MF) and methylal (DMM). Another GC-2014 unit equipped with an FID was dedicated to the analysis of larger molecule oxygenates like DMM _{x} . A third GC-2014 unit, also equipped with a TCD, was employed to detect oxygen (O₂), hydrogen (H₂), carbon monoxide (CO) and carbon dioxide (CO₂).

The results obtained from the three GC systems were calibrated, normalized, and used to calculate the methanol conversion and the selectivity of various products according to the following formulas:

Methanol conversion:

$$x_{\text{CH}_3\text{OH}} = (Q_{\text{in}} w_{\text{CH}_3\text{OH},\text{in}} - Q_{\text{out}} w_{\text{CH}_3\text{OH},\text{out}}) / Q_{\text{in}} w_{\text{CH}_3\text{OH},\text{in}} \times 100\% \quad (1)$$

where $x_{\text{CH}_3\text{OH}}$: Methanol conversion; Q_{in} : Feed gas flow rate, mol/h; Q_{out} : Effluent gas flow rate, mol/h; $w_{\text{CH}_3\text{OH},\text{in}}$: Mole fraction of methanol in the feed gas; $w_{\text{CH}_3\text{OH},\text{out}}$: Mole fraction of methanol in the effluent gas.

Product selectivity:

$$s_i = a_i n_i / \sum a_i n_i \times 100\% \quad (2)$$

where i : Products FA, DME, MF, DMM, DMM _{x} , CO, CO₂, respectively; s_i : Molar selectivity of product i ; a_i : Number of carbon atoms in a molecule of product i ; n_i : Molar amount of product i in the effluent gas.

1.4 Catalyst characterizations

Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed on an iCAP 6300 instrument. Approximately 0.1 g of the sample was digested at 210 °C using a mixed acid system consisting of 2 mL hydrofluoric acid (HF), 6 mL

hydrochloric acid (HCl) and 2 mL nitric acid (HNO₃). Depending on the estimated elemental concentration, the original solution after constant volume is appropriately diluted (the NSC-Mo-0.5-2% sample was analyzed directly without further dilution, while all other samples were analyzed at their respective dilution factors).

X-ray diffraction (XRD) analysis was performed using a Rigaku MiniFlex 600 X-ray diffractometer (Japan). The measurement was conducted with Cu K α radiation at 40 kV and 15 mA. The scanning range was set from 5° to 90° with a continuous scanning speed of 4(°)/min.

The ammonia temperature-programmed desorption (NH₃-TPD) measurement was conducted on a TP-5080 chemical adsorption analyzer. Place 100 mg of the catalyst sample (20–40 mesh) in the sample tube. The sample was first pretreated by heating to 400 °C under a N₂ atmosphere and holding for 1 h. After cooling to 50 °C, it was exposed to NH₃ (by purging for 10 min followed by a 10 min equilibration period). Subsequently, physically adsorbed NH₃ was removed by purging with N₂ for 30 min. Finally, the temperature-programmed desorption was carried out by heating the sample to 600 °C at a rate of 10 °C/min and the desorption signal was recorded.

The N₂ physisorption-desorption isotherms were obtained through using a BELSORP-MAX II adsorption instrument (BEL, Japan). Prior to the measurement, the sample was pretreated by vacuum degassing at 200 °C. The adsorption-desorption experiment was then conducted in a liquid nitrogen bath at −196 °C.

Raman spectroscopy measurement was performed on a Horiba Evolution spectrometer, using a 532 nm laser for excitation, with a scanning range of −48 to 3778 cm^{−1}.

X-ray photoelectron spectroscopy (XPS) measurement was conducted on a Thermo Fisher ESCALAB 250Xi spectrometer equipped with an Al-K α monochromated flood source. The binding energies were calibrated for charge correction by referencing the C 1s peak to 284.8 eV.

In situ DRIFTS were collected on a Bruker Tensor 27 FT-IR spectrometer, with a spectral range of 4000–800 cm^{−1} under atmospheric pressure. The catalyst powder was placed in the *in situ* cell. Prior to measurement, the sample was degassed under an O₂ flow at 220 °C for 1 h to remove adsorbed impurities, and a background spectrum was collected. The atmosphere was then switched to a methanol vapor, and the spectrum was recorded after stabilizing at 220 °C for 30 min.

Py-IR measurement was performed on a Bruker Tensor 27 spectrometer. The sample was first pressed into a self-supporting wafer, and then the wafer was mounted inside vacuum cell with CaF₂ window pool. Prior to analysis, the sample was degassed under vacuum at 260 °C for 1 h to remove surface adsorbates, followed by cooling to room temperature for background spectrum collection. The sample was then exposed to pyridine vapor at room temperature for 15 min. After this adsorption, a spectrum was collected following a 10 min vacuum treatment at 150 °C. For the temperature-programmed desorption experiment, the temperature was increased stepwise from 50 to 250 °C in 50 °C increments. At each temperature step, the spectrum was collected after a 10 min vacuum treatment.

2 Results and discussion

2.1 Evaluation of methanol oxidation performance on NASICON catalysts

Table 1 shows the methanol conversion performance of Mo-doped NASICON catalysts. As shown in Table 1, the undoped NASICON material exhibits the lowest methanol conversion. With increasing Mo content, the methanol conversion rate increases from 34.8% to 49.3%, and the formaldehyde selectivity significantly improves from 23.9% to 45.0%. According to literature^[30], Mo species are able to effectively catalyze methanol dehydrogenation. It can be inferred that the incorporation of Mo likely enhances the oxidative capability of the catalyst, as well supported by the increased selectivity toward the oxidation product methyl formate (MF) from 9.0% to 15.3%. Meanwhile, the dimethyl ether (DME) selectivity rises from 3.4% to 18.1%, while the selectivity to DMM_x decreases markedly from 63.6% to 21.5%. It suggests that the moderate introduction of Mo species can effectively enhance the acid properties of the catalyst, thus promoting the DME formation. When the Mo content is further increased (such as NSC-Mo-0.75), the by-products selectivity increases. The excessively low DMM selectivity restricts its subsequent conversion to DMM₂₋₆^[14], leading to the reduced selectivity for longer-chain DMM₂₋₆. These changes were consistent with the relevant studies^[3,31]: the formation of both DME and DMM_x is closely associated with catalyst acidity.

Table 1 Reaction performance of methanol conversion over NSC-Mo-x catalysts with different Mo

<i>x</i>	CH ₃ OH conversion/%	C-mol selectivity/%						
		FA	DME	MF	DMM	CO _x	DMM ₂₋₆	DMM _x
0	34.8	23.9	3.4	9.0	61.6	0.0	2.0	63.6
0.25	42.8	37.2	10.3	10.2	38.0	0.0	3.0	41.0
0.5	45.3	37.8	16.1	10.8	31.6	0.0	3.6	35.3
0.75	49.3	45.0	18.1	15.3	21.2	0.0	0.3	21.5

Reaction conditions: atmospheric pressure, *t_R*=220 °C, *n*(CH₃OH):*n*(O₂)=1:4, CH₃OH flow rate=0.813 mL/h, GHSV=1800 h^{−1}.

Table 2 shows the sulfur mass fraction in the catalysts prepared with different amounts of sulfuric acid used for impregnation. As can be seen from the table, the actual sulfur content is lower than the theoretical value, indicating a partial loss of sulfur during the calcination process. As the amount of sulfuric acid in the impregnation solution increases, the actual sulfur content in the catalysts gradually increases. Table 3 displays the influence of different amounts of sulfuric acid used for impregnation on the performance of the prepared catalysts. The table reveals that the introduction of sulfuric acid on the material surface leads to significant changes in the catalytic performance. The methanol conversion increases markedly with increasing sulfuric acid dosage (0–10%); when the sulfuric acid dosage exceeds 10%, the growth in conversion levels off. With a 10% addition of sulfuric acid (NSC-Mo-0.5-10%), the methanol conversion increases from 45.3% (before sulfuric acid introduction) to 80.6%. Meanwhile, the formaldehyde (FA) selectivity decreases from 37.8% to 3.1%, but the DMM selectivity increases from 31.6% to 57.9%. As mentioned earlier, the acid sites on the catalyst surface are key factors in promoting C–O chain growth^[3]. Therefore, we infer that the introduction of sulfuric acid modifies both the distribution and strength of the acid sites on the catalyst surface. Furthermore, the selectivity for DMM_{2–6} shows an initial increase followed by a decrease as the sulfuric acid content rises, reaching a maximum value of 11.3% at 30% sulfuric acid impregnation, when the total DMM_x selectivity is 58.7%.

2.2 Catalyst characterizations

2.2.1 XRD characterization

Figure 1 shows the XRD patterns of the prepared catalysts. The patterns indicate that the materials consist primarily of the NASICON phase (PDF #51-0362) with a minor amount of Zr₂P₂O₇ impurity phase (PDF #38-0018). The sharp diffraction peaks observed at $2\theta = 14.1^\circ$, 20.2° , 22.7° , 23.6° , 28.1° , 31.0° , 46.2° and 55.1° match well with the characteristic peaks of the standard NASICON structure, which confirms the successful synthesis of a NASICON-type crystal structure with three-dimensional ion channels^[29,32]. Meanwhile, relatively weak diffraction peaks corresponding to the Zr₂P₂O₇ phase appear near $2\theta = 16.0^\circ$ and 26.7° , suggesting the low content of Zr₂P₂O₇ and its limited impact on the overall material structure. With increasing Mo doping levels, the intensity of the NASICON phase diffraction peaks slightly decreases, indicating a reduction in crystallinity. This phenomenon may be attributed to local structural distortion caused by the difference between MoO₄²⁻ tetrahedra and PO₄³⁻ tetrahedra, which affects the long-range order of the crystal^[29]. Furthermore, compared to the sample without sulfuric acid modification, the NASICON phase diffraction peaks of the acid-treated samples show weakened intensity. This may be attributed to partial dissolution of the particle surfaces in the strongly acidic environment, leading to some degradation of the NASICON framework structure.

Table 2 Actual sulfur content of NSC-Mo-0.5-y% catalyst with different sulfuric acid amounts before and after reaction

y/%	Theory w/%	Before the reaction ^a w/%	After the reaction ^{a,b} w/%
2	0.64	0.46	—
5	1.55	1.09	—
10	2.97	1.56	—
20	5.44	2.66	—
30	7.54	3.88	3.00
40	9.33	4.48	—

^a: ICP-OES determination; ^b: Reaction conditions: atmospheric pressure, $t_R=220^\circ\text{C}$, $n(\text{CH}_3\text{OH}):n(\text{O}_2)=1:4$, CH_3OH flow rate=0.813 mL/h, GHSV=1800 h⁻¹, reaction time of 50 h.

Table 3 Reaction performance of methanol conversion over NSC-Mo-0.5-y% catalysts with different sulfuric acid amounts

y/%	CH ₃ OH conversion/%	C-mol selectivity/%						
		FA	DME	MF	DMM	CO _x	DMM _{2–6}	DMM _x
0	45.3	37.8	16.1	10.8	31.6	0.0	3.6	35.3
2	62.9	5.6	19.5	7.4	60.7	0.0	6.8	67.5
5	70.2	4.6	19.4	9.2	58.7	0.8	7.3	65.0
10	80.6	3.1	18.7	11.8	57.9	0.7	7.8	65.8
20	80.9	6.3	20.3	13.0	49.3	1.2	10.0	59.3
30	81.3	6.8	18.8	14.7	47.5	1.0	11.3	58.7
40	85.4	7.3	18.1	15.6	51.5	1.0	6.5	58.0

Reaction conditions: atmospheric pressure, $t_R=220^\circ\text{C}$, $n(\text{CH}_3\text{OH}):n(\text{O}_2)=1:4$, CH_3OH flow rate=0.813 mL/h, GHSV=1800 h⁻¹.

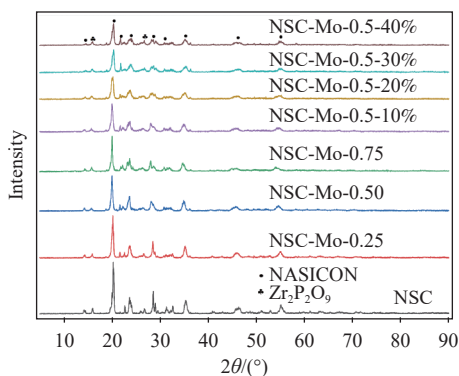


Fig. 1 XRD patterns of catalysts with different Mo and sulfuric acid contents

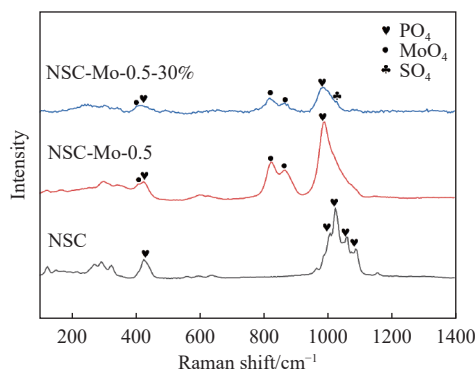


Fig. 2 Raman spectra of catalysts with different Mo and H₂SO₄ contents

2.2.2 Raman characterization

Figure 2 shows the Raman spectra of three NASICON samples: unmodified, Mo-modified and sulfate-modified, respectively. In the typical NASICON structure, ZrO₆ octahedra and PO₄ tetrahedra form a three-dimensional framework network through shared oxygen atoms, and their characteristic peaks are consistent with those reported in the literature^[33–34]. The strong peaks at 1090 and 1060 cm^{−1} correspond to the asymmetric stretching vibrations (ν_3) of the PO₄^{3−} groups, while the peaks at 1026, 1000 and 990 cm^{−1} originate from the symmetric stretching vibrations (ν_1) of PO₄^{3−}. The characteristic peak at 429 cm^{−1} is assigned to the symmetric bending vibration (ν_2) of PO₄^{3−}^[33]. In the modified samples, double peaks at 866 and 824 cm^{−1} can be observed, which include both the asymmetric stretching vibrations (ν_3) of MoO₄^{2−} and the formation of Mo–O–Mo bridging bonds. The peak at 410 cm^{−1} can be attributed to the symmetric bending vibration (ν_4) of MoO₄^{2−}^[35], while the characteristic peak at 1084 cm^{−1} confirms the presence of SO₄^{2−}^[36]. In the low-frequency region (<400 cm^{−1}), the observed vibrational modes mainly arise from lattice translations of Li⁺ and Zr⁴⁺, as well as translational and rotational vibrations of PO₄^{3−} groups^[35]. After modification with MoO₄^{2−} and SO₄^{2−}, new characteristic peaks appear in the spectra, accompanied by shifts in the original peak positions, confirming the successful incorporation of the modifying ions. The above Raman spectra indicate the presence of phosphate, sulfate, and molybdate structures in the catalyst.

2.2.3 N₂ adsorption-desorption characterization

Table 4 summarizes the specific surface area, pore volume, and pore size of the NASICON-based catalyst series, as determined from the measurements. As can be seen from Table 4, the introduction of Mo significantly increases the specific surface area and pore volume of the material, with a moderate improve in average pore size. Considering the decreased diffraction peak intensities observed in XRD, the increase in specific surface area and pore volume can likely be attributed to the formation of more amorphous nanoparticles induced by Mo incorporation, which leads to the formation of additional interparticle pores. With increasing Mo content, both the pore size and specific surface area first increase and then decrease, with the NSC-Mo-0.5 catalyst showing the highest specific surface area and pore volume. Furthermore, the NSC-Mo-0.5-10% catalyst, impregnated with 10% sulfuric acid, shows an increase in pore size but a slight decrease in both specific surface area and pore volume compared to the NSC-Mo-0.5 catalyst, indicating a disruptive effect of sulfuric acid on the material's crystal structure. As the sulfuric acid impregnation amount increases, the NSC-Mo-0.5-20% and NSC-Mo-0.5-30% catalysts exhibit a significant increase in specific surface area, while pore volume and average pore size gradually decrease, suggesting the generation of more amorphous nanoparticles.

Table 4 The textural properties of catalysts with different Mo and sulfuric acid contents

Catalyst	Surface area/(m ² ·g ^{−1})	Volume of pore/(cm ³ ·g ^{−1})	Average pore size/nm
NSC-Mo	4.43	0.07	59.76
NSC-Mo-0.25	10.64	0.20	75.27
NSC-Mo-0.5	11.79	0.22	75.97
NSC-Mo-0.75	11.07	0.17	61.54
NSC-Mo-0.5-10%	6.59	0.15	92.00
NSC-Mo-0.5-20%	12.45	0.16	49.93
NSC-Mo-0.5-30%	15.99	0.13	32.25
NSC-Mo-0.5-40%	7.20	0.12	64.88

The NSC-Mo-0.5-40% catalyst shows a significantly reduced specific surface area and an increased average pore size, which is inferred to result from the agglomeration of some nanoparticles. Correlating with the activity evaluation results, the NSC-Mo-0.5 and NSC-Mo-0.5%-30% catalysts, which possess the highest specific surface areas in their respective series, also exhibit the highest DMM₂₋₆ selectivity in the reaction performance tests. This is because the larger specific surface area of these catalysts exposes more highly dispersed active sites, which facilitates the further conversion of reactants and intermediates and thereby promotes the formation of longer-chain DMM₂₋₆.

2.2.4 NH₃-TPD characterization

The chain growth reaction, as an important acid-catalyzed process, exhibits a strong correlation between its reaction pathways/product distribution and the acidic characteristics of the catalyst surface. NH₃-TPD characterization (Figure 3) reveals that the Mo-free sample shows only weak acidic features. With increasing Mo content, a significant NH₃ desorption peak emerges in the 100–200 °C range, indicating the formation of weak acid sites. However, further Mo addition does not significantly change the number of acid sites, and medium-strong acid sites remain undetected. Given that the sulfate-impregnated catalysts were calcined at 260 °C, the NH₃-TPD temperature program may partially decompose the incorporated sulfate species at higher temperatures, potentially complicating the interpretation of ammonia desorption peaks. Therefore, Py-IR characterization was conducted to further investigate the acidic properties of this catalyst series.

2.2.5 Py-IR characterization

Figure 4 displays the pyridine adsorption infrared spectroscopy (Py-IR) of the NASICON catalyst before and after modification. The characteristic peaks at 1540 and 1450 cm⁻¹ are assigned to the Brønsted acid sites and Lewis

acid sites, and the absorption peak at 1490 cm⁻¹ is related to the co-adsorption of the two^[28]. As shown in Figure 4(a), the vibrational peak attributed to Brønsted acid decreases after Mo doping into NASICON, while the vibrational peak attributed to Lewis acid significantly increases. Furthermore, the number of Lewis acid sites shows a change trend of first increasing and then decreasing with the increased Mo species, and the NSC-Mo-0.5 catalyst exhibits the strongest Lewis acid absorption peak, indicating that the doped Mo species promotes the formation Lewis acid sites as well as changes the original Brønsted acid sites. According to Figure 4(b), the number of Lewis acid centers on the catalyst surface was not significantly changed after sulfuric acid impregnation, but the number of Brønsted acid centers greatly increases. At the 30% impregnation amount, the number of Brønsted acid sites on the catalyst surface is the highest.

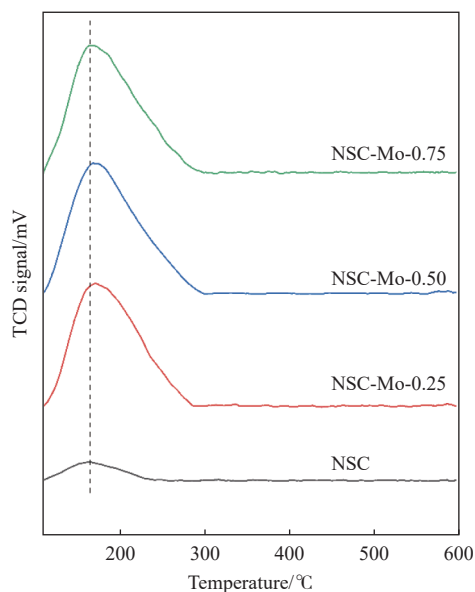
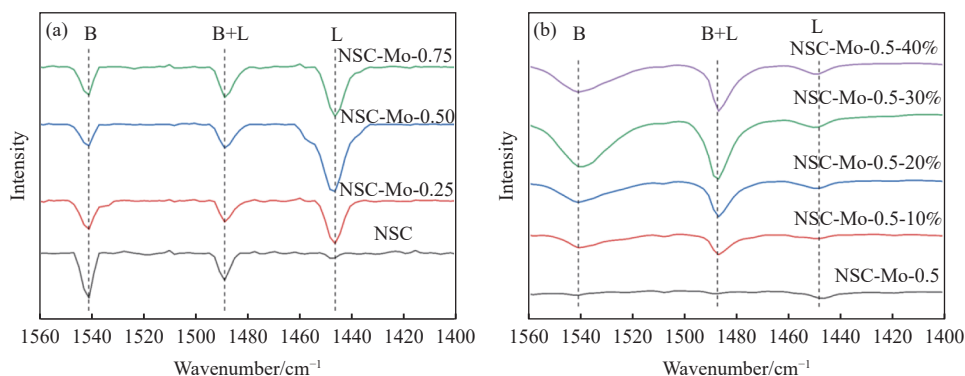


Fig. 3 NH₃-TPD profiles of catalysts with different Mo contents



(a): NSC-Mo-x; (b): NSC-Mo-0.5-y%.

Fig. 4 Py-IR spectra of catalysts with different Mo and H₂SO₄ contents

Further Py-IR spectra of the NSC-Mo-0.5 and NSC-Mo-0.5-30% catalysts were recorded at different temperatures. As shown in Figure 5, the peak intensity at 1450 cm^{-1} attributed to Lewis acid vibrations of the NSC-Mo-0.5 catalyst continuously decreases in the range of 50 to $250\text{ }^{\circ}\text{C}$, while the intensity of the peak at 1540 cm^{-1} assigned to the Brønsted acid vibrations shows no significant change. In the spectrum of the sample treated at $200\text{ }^{\circ}\text{C}$, the vibration peak of Lewis acid sites almost disappears, indicating that the introduction of Mo species effectively increases the number of weak Lewis acid centers. This observation is consistent with the increase in the desorption peak within the $100\text{--}200\text{ }^{\circ}\text{C}$ range observed in NH_3 -TPD after Mo doping. The Brønsted acid vibration peak of the NSC-Mo-0.5 catalyst remains essentially unchanged at $250\text{ }^{\circ}\text{C}$ compared to that at $50\text{ }^{\circ}\text{C}$, suggesting that the intrinsic Brønsted acid sites of the NASICON catalyst are of medium-strong strength. However, no significant desorption peak was detected in NH_3 -TPD due to the low acid concentration. The absorption peak of Brønsted acid sites in NSC-Mo-0.5-30% decreases with the increased temperature, but a considerable absorption peak remains even at $250\text{ }^{\circ}\text{C}$, suggesting that the Brønsted acid introduced by sulfuric acid treatment comprises both weak and medium-strong acid sites.

Relevant literature has indicated that both Brønsted and Lewis acid sites contribute to the formation of DMM_{2-6} , with Brønsted acid sites playing a more significant promotional role^[37]. In this study, Mo doping increases the number of weak Lewis acid sites and reduces medium-strength Brønsted acid sites. This change in acidity favors the formation of dimethyl ether, indicating that methanol can dehydrate to form dimethyl ether even on relatively weak Lewis acid sites, thereby affecting the generation of DMM_x . The increased selectivity toward DMM_{2-6} observed with NSC-Mo-0.5 can be attributed to the synergistic effect between the enhanced surface oxidation properties and the preserved acid sites (particular the Brønsted acid sites). Furthermore, sulfuric acid modification increases the amount of medium-strength Brønsted acid sites, which

promotes the condensation reaction between the intermediate product FA and DMM_{x-1} , thereby improving the formation of long-chain DMM_x . Consequently, the NSC-Mo-0.5-30% catalyst with the greater number of Brønsted acid sites exhibits the best performance in the direct oxidation of methanol to synthesize DMM_{2-6} .

2.2.6 In situ DRIFTS characterization

The adsorption and activation behavior of methanol on the catalyst surface were investigated using *in situ* DRIFTS. After introducing methanol vapor at $220\text{ }^{\circ}\text{C}$ for 30 min, the intensities of the characteristic vibration peaks stabilized, indicating that methanol adsorption on the catalyst surface had reached saturation (as shown in Figure 6). In the spectrum (Figure 6(a)), the band at 2865 cm^{-1} originates from gaseous methanol, while the bands at 2981 , 2922 , 2843 and 2827 cm^{-1} correspond to the symmetric/asymmetric stretching and bending vibration modes of the CH_3 group in adsorbed methanol, respectively^[28,38]. It can be observed that after methanol adsorption, the characteristic vibration peaks of the surface groups on the catalyst do not exhibit significant shifts, suggesting that methanol adsorption has minimal impact on the surface groups. Further magnification of the carbonyl vibration region in the $1700\text{--}1800\text{ cm}^{-1}$ range (Figure 6(b)) reveals that the characteristic peaks at 1772 and 1745 cm^{-1} are attributed to gaseous FA, while the peak at 1732 cm^{-1} corresponds to the carbonyl vibration of adsorbed formaldehyde on the catalyst surface^[27]. The intensities of the carbonyl vibration peaks of adsorbed formaldehyde on both series of catalysts initially increase and then decrease, which is attributed to the conversion of surface formaldehyde. Combined with the catalyst evaluation results, the increase in Mo doping significantly enhances FA selectivity from 23.9% to 45% , primarily due to the suboptimal match between the oxidative properties and acidity of catalyst, which inhibits the further conversion of formaldehyde, thereby decreasing the DMM_x selectivity.

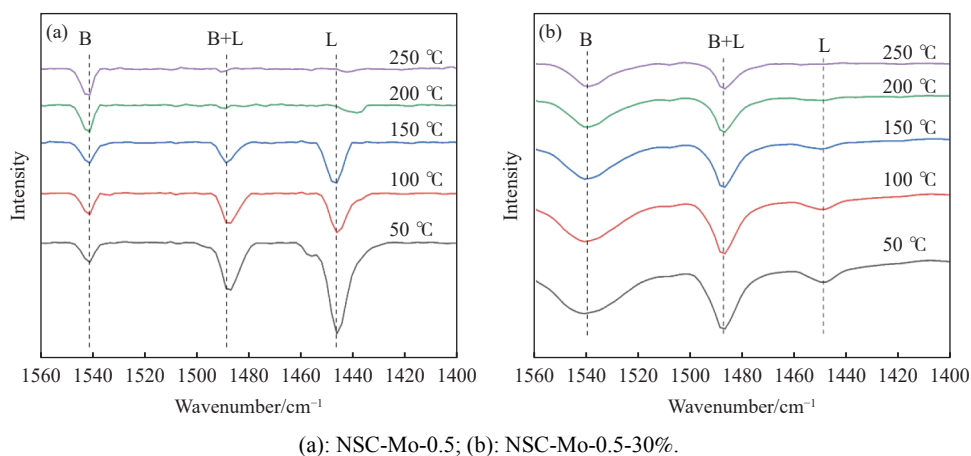
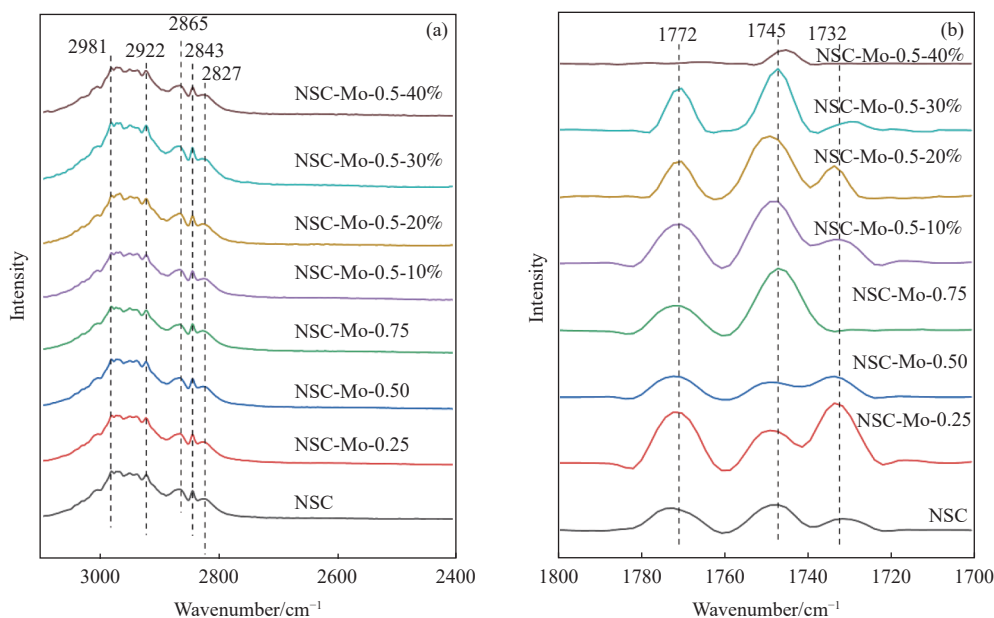


Fig. 5 Py-IR spectra of the catalyst at different temperatures

Fig. 6 *In situ* DRIFTS spectra of methanol on the catalyst

However, after modification with sulfuric acid, the number of Brønsted acid sites on the catalyst increases substantially, promoting further conversion reactions of formaldehyde and other intermediates. As a result, FA selectivity sharply decreases from 37.8% to 3.1%, and the total DMM_x selectivity increases from 35.3% to 65.8%. To further elucidate the synergy between redox properties and acidity, a Mo-free catalyst impregnated with 10% sulfuric acid (NSC-Mo-0-10%) was prepared. Methanol conversion evaluation results in Table 5 indicate that, compared to NSC-Mo-0.5-10%, the Mo-free catalyst exhibits lower methanol conversion and DMM_x selectivity. No FA or long-chain products (DMM₂₋₆) were detected in the products, suggesting weak oxidative capability of the catalyst. Since formaldehyde is a key intermediate in subsequent condensation reactions^[3], the absence of substantial formaldehyde generation implies that chain growth reactions cannot proceed, thereby preventing the formation of DMM₂₋₆. Thus, both the oxidative properties and acidity of the catalyst are crucial, and their effective synergy is essential for the DMM_x synthesis.

Then, O₂ purging was employed to the catalyst pre-saturated with methanol adsorption, and the dynamic changes of adsorbed species were monitored in real time using *in situ* DRIFTS spectroscopy (Figure 7, the arrow direction indicates the prolonged purging time). The results show that the amount of adsorbed methanol on all catalyst surfaces decreases as the purging time increases. The

intensity of methanol adsorption peaks on the surfaces of NSC (Figure 7(a)) and NSC-Mo-0.5 (Figure 7(b)) catalysts rapidly decline under O₂ purging, indicating the weak interaction between the methanol and these surfaces. In contrast, the decay rate of methanol adsorption peaks slows down on sulfuric acid-modified catalysts (Figure 7(c)–(f)), and this effect becomes more pronounced with the increased sulfuric acid impregnation amount. Furthermore, the decay rate of the vibration peaks also reduces. This phenomenon confirms that sulfuric acid modification can effectively enhanced methanol adsorption on the catalyst surface. Meanwhile, this enhancement also is beneficial to stabilize reaction intermediates and promote subsequent catalytic conversion, which is one of the main reasons for the higher activity of sulfuric acid-modified NASICON catalysts in methanol conversion reactions.

2.2.7 XPS characterization

The catalyst samples were subjected to surface chemical analysis using X-ray photoelectron spectroscopy (XPS), with all test data charge-corrected based on the standard C 1s peak position (284.8 eV). As shown in Figure 8(a), the spectrum of the Zr 3d orbital can be fitted into two characteristic peaks: Zr 3d_{5/2} at 183.0 eV and Zr 3d_{3/2} at 185.6 eV, with a spin-orbit splitting energy of 2.6 eV^[39–40].

Table 5 Reaction performance of methanol conversion over sulfuric acid-impregnated NASICON catalysts with varying Mo contents

Catalyst	CH ₃ OH conversion/%	C-mol selectivity/%						
		FA	DME	MF	DMM	CO _x	DMM ₂₋₆	DMM _x
NSC-Mo-0.5-10%	80.6	3.1	18.7	11.8	57.9	0.7	7.8	65.8
NSC-Mo-0-10%	35.4	0.0	60.3	0.0	39.7	0.0	0.0	39.7

Reaction conditions: atmospheric pressure, $t_R=220$ °C, $n(\text{CH}_3\text{OH}):n(\text{O}_2)=1:4$, CH₃OH flow rate=0.813 mL/h, GHSV=1800 h⁻¹.

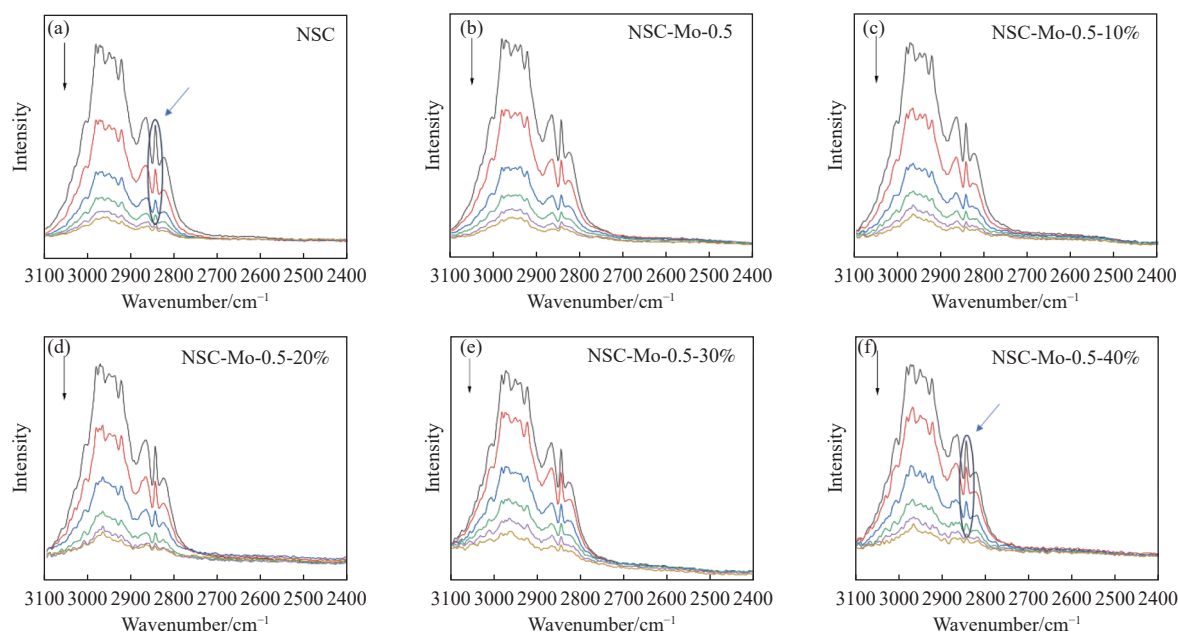
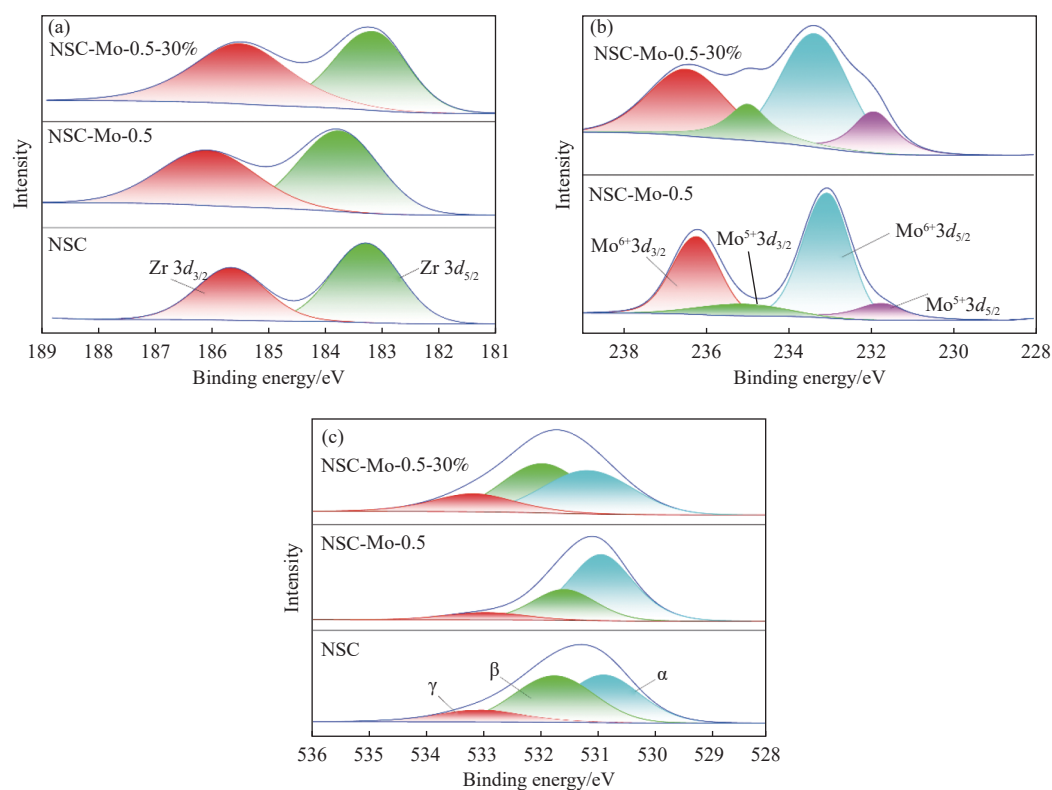


Fig. 7 *In situ* DRIFTS spectra of methanol adsorption under O₂ flow



(a): XPS-Zr 3d; (b): XPS-Mo 3d; (c): XPS-O 1s.

Fig. 8 XPS spectra of the catalyst

Compared with the unmodified NSC catalyst, the binding energy of Zr 3d in the Mo-doped NSC-Mo-0.5 catalyst shifts to a higher value, which is attributed to the altered coordination environment around Zr due to the introduction of Mo. However, the Zr 3d binding energy shifts back toward lower values with the subsequent introduction of

sulfuric acid (sample NSC-Mo-0.5-30%). This reversible change suggests that the introduction of sulfuric acid may have affected the Mo-Zr interaction. These shifts in binding energy reflect the transfer of the electron structure of the Zr active centers on the catalyst surface during the modification process.

Further peak-fitting analysis was performed on the XPS Mo 3d orbital. As shown in Figure 8(b), the Mo 3d binding energy spectrum can be fitted into four characteristic peaks. Where the peaks at 236.2 and 233.1 eV are ascribed to the Mo^{6+} 3d_{3/2} and 3d_{5/2} orbitals, while the peaks at 235.1 and 231.8 eV are attributed to the Mo^{5+} 3d_{3/2} and 3d_{5/2} orbitals^[19,41]. Quantitative analysis reveals the coexistence of both Mo^{6+} and Mo^{5+} species on the catalyst surface (Table 6). After sulfuric acid modification, the relative content of Mo^{5+} in the catalyst increases from 17.2% to 23.6%. As previously indicated by N_2 adsorption-desorption results, the specific surface area of the NSC-Mo-0.5 sample increases from 11.79 to 15.99 m²/g after 30% sulfuric acid impregnation (NSC-Mo-0.5-30%), which promotes the dispersion of Mo to some extent^[42]. Moreover, the introduced sulfuric acid can dissolve partial Mo, leading to its redispersion. These highly dispersed Mo species undergo changes in its local coordination environment^[43] due to their strong interaction with the NASICON material, resulting in the increased content of Mo^{5+} species in the catalyst. According to literature, the increased $\text{Mo}^{5+}/\text{Mo}^{6+}$ redox pair can enhance the oxidative properties of the catalyst^[41]. Thus, the introduction of sulfuric acid not only increases the number of Brønsted acid centers but also enhances the oxidative properties of the catalyst, which is conducive to enhance the synergistic action of oxidizing and acidic sites, thereby promoting the formation of long-chain DMM_x .

From the XPS O 1s spectra of the catalysts (Figure 8(c)), three oxygen species can be identified: lattice oxygen (O_a) with a binding energy (BE) at 531 eV, chemisorbed oxygen (O_β) at 532 eV, and hydroxyl oxygen (O_γ) at 533 eV^[28]. Quantitative analysis of these oxygen species was summarized in Table 7. It is indicated that the doped Mo significantly increases the proportion of O_a in the NASICON material, while sulfuric acid impregnation treatment reduces its relative. Additionally, the sulfuric acid impregnation leads to a notable increase in O_γ content, which is in accordance with the observed gradient Brønsted acid sites in the Py-IR characterization. This further confirms the enhancement of surface acid sites on the material.

Table 6 XPS analysis of Mo 3d spectra for the catalyst

Catalyst	$\text{Mo}^{6+}/\%$	$\text{Mo}^{5+}/\%$
NSC-Mo-0.5	82.8	17.2
NSC-Mo-0.5-30%	76.4	23.6

Table 7 XPS analysis of O 1s spectra for the catalyst

Catalyst	$\text{O}_a/\%$	$\text{O}_\beta/\%$	$\text{O}_\gamma/\%$
NSC	42.5	44.1	13.5
NSC-Mo-0.5	63.4	28.2	8.4
NSC-Mo-0.5-30%	41.9	41.2	16.9

2.3 Catalyst Stability

A 50 h stability test was performed for the NSC-Mo-0.5-30% catalyst, as shown in Figure 9. The result indicates that the methanol conversion remains consistently around 85% and the overall selectivity for DMM_x remains stable at approximately 60% during the 50 h reaction process, indicating that the structure of the catalyst remains largely intact. However, the selectivity for DMM_{2-6} gradually decreases with increasing reaction time. To further clarify its nature, the ICP-OES analysis was performed on the catalyst after reaction (Table 2). The results reveal that the sulfur content of the catalyst after the reaction decreases from 3.88% to 3.00%, which may lead to changes in the acidic sites of the catalyst, thereby weakening its chain growth capability and resulting in the decline of DMM_{2-6} selectivity.

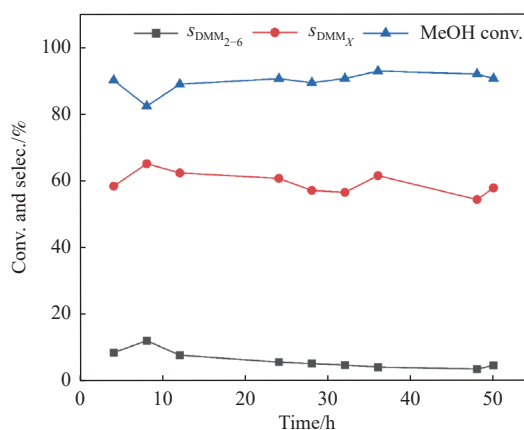


Fig. 9 Catalyst stability of NSC-Mo-0.5-30%

3 Conclusion

In this study, a series of sulfuric acid-impregnated (Mo-doped) NASICON-type catalysts were designed and prepared, and the effects of oxidative and acidic regulation on methanol oxidation performance were systematically investigated. The evaluation results show that 30% sulfuric acid-impregnated $\text{Li}_{0.5}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{MoO}_4)_{0.5}$ (NSC-Mo-0.5-30%) catalyst achieves the methanol conversion rate of 81.3% at 220 °C, with the DMM_{2-6} selectivity of 11.3% and the overall DMM_x selectivity of 58.7%. The characterization results indicate that the doped Mo effectively increases the number of weak Lewis acid sites on the catalyst surface, and the sulfuric acid impregnation not only successfully constructs gradient-distributed Brønsted acid sites but also significantly increases the content of $\text{Mo}^{5+}/\text{Mo}^{6+}$ redox pairs. The synergistic effect between these uniquely gradient-distributed acid sites and the abundant $\text{Mo}^{5+}/\text{Mo}^{6+}$ redox pairs effectively enhances the catalytic performance. This study provides a new approach for the targeted construction of multifunctional active sites in NASICON materials, offering important

theoretical foundations and practical guidance for the design of active sites in the one-step oxidative conversion of methanol to DMM_x.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] LIU H, WANG Z, ZHANG J, et al. Study on combustion and emission characteristics of polyoxymethylene dimethyl ethers/diesel blends in light-duty and heavy-duty diesel engines[J]. Appl Energy, 2017, 185: 1393–1402.
- [2] WANG J, WU F, XIAO J, et al. Oxygenated blend design and its effects on reducing diesel particulate emissions[J]. Fuel, 2009, 88(10): 2037–2045.
- [3] WANG X, GAO X, SONG F, et al. Direct oxidation of methanol to polyoxymethylene dimethyl ethers over FeMo@HZSM-5 core-shell catalyst[J]. ACS Catal, 2024, 14(2): 1093–1097.
- [4] LI H, SONG H, CHEN L, et al. Designed $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3\text{-SiO}_2$ solid acids for polyoxymethylene dimethyl ethers synthesis: The acid sites control and reaction pathways[J]. Appl Catal B: Environ, 2015, 165: 466–476.
- [5] ZHANG J, FANG D, LIU D. Evaluation of Zr–alumina in production of polyoxymethylene dimethyl ethers from methanol and formaldehyde: Performance tests and kinetic investigations[J]. Ind Eng Chem Res, 2014, 53(35): 13589–13597.
- [6] LI G, NING J, XU C, et al. Identification of reaction path for the synthesis of polyoxymethylene dimethyl ethers from methanol and paraformaldehyde catalyzed by Al-MCM-41 zeolite[J]. Comput Theor Chem, 2021, 1200: 113248.
- [7] NING J X, QIU Q Y, MA H X, et al. Development and catalytic mechanism of ionic liquid catalysts for polyoxymethylene dimethyl ethers[J]. Chem Phys Lett, 2023, 822: 140471.
- [8] LI H, SONG H, ZHAO F, et al. Chemical equilibrium controlled synthesis of polyoxymethylene dimethyl ethers over sulfated titania[J]. J Energy Chem, 2015, 24(2): 239–244.
- [9] WU Q, WANG M, HAO Y, et al. Synthesis of polyoxymethylene dimethyl ethers catalyzed by Brønsted acid ionic liquids with alkanesulfonic acid groups[J]. Ind Eng Chem Res, 2014, 53(42): 16254–16260.
- [10] LIU F, WEI R, WANG T F. Effects of water and methanol on synthesis of polyoxymethylene dimethyl ethers from dimethoxymethane and paraformaldehyde[J]. Chem Eng Sci, 2022, 248: 117057.
- [11] BURGER J, STROFER E, HASSE H. Chemical equilibrium and reaction kinetics of the heterogeneously catalyzed formation of poly(oxymethylene) dimethyl ethers from methylal and trioxane[J]. Ind Eng Chem Res, 2012, 51(39): 12751–12761.
- [12] ZHANG Q, TAN Y, LIU G, et al. Rhenium oxide-modified $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ catalysts for selective oxidation of dimethyl ether to dimethoxy dimethyl ether[J]. Green Chem, 2014, 16(11): 4708–4715.
- [13] ZHAO Q, WANG H, QIN Z, et al. Synthesis of polyoxymethylene dimethyl ethers from methanol and trioxymethylene with molecular sieves as catalysts[J]. J Fuel Chem Technol, 2011, 39(12): 918–923.
- [14] ZHAO Y P, XU Z, CHEN H, et al. Mechanism of chain propagation for the synthesis of polyoxymethylene dimethyl ethers[J]. J Energy Chem, 2013, 22(6): 833–836.
- [15] MENG Y, WANG T, CHEN S, et al. Selective oxidation of methanol to dimethoxymethane on $\text{V}_2\text{O}_5\text{-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts[J]. Appl Catal B: Environ, 2014, 160: 161–172.
- [16] BAI Y L, DAI X Y, ZENG X J, et al. Efficient one-step synthesis of dimethoxymethane from methanol on bifunctional vanadium oxide/carbon hybrid catalyst[J]. Chem Eng J, 2025, 511: 162122.
- [17] YUAN M, CHE Y J, TANG R Y, et al. One-step synthesis of methylal via methanol oxidation by Mo: Fe(x)/HZSM-5 bifunctional catalyst[J]. Fuel, 2020, 261: 116416.
- [18] THAVORNPRASERT K A, CAPRON M, JALOWIECKI-DUHAMEL L, et al. Highly productive iron molybdate mixed oxides and their relevant catalytic properties for direct synthesis of 1, 1-dimethoxymethane from methanol[J]. Appl Catal B: Environ, 2014, 145: 126–135.
- [19] WANG J, GAO X, SONG F, et al. Effect of molybdenum valence in low Mo/Sn ratio catalysts for the oxidation of methanol to dimethoxymethane[J]. J Fuel Chem Technol, 2024, 52(1): 38–46.
- [20] GAO X J, WANG W F, GU Y Y, et al. Synthesis of polyoxymethylene dimethyl ethers from dimethyl ether direct oxidation over carbon-based catalysts[J]. Chemcatchem, 2018, 10(1): 273–279.
- [21] FENG R, GAO X, YANG Q, et al. Effects of calcination temperature on the catalytic performance of $\text{Ti}(\text{SO}_4)_2/\text{CS}$ for DME direct oxidation to polyoxymethylene dimethyl ethers[J]. J Fuel Chem Technol, 2021, 49(1): 72–79.
- [22] GAO X J, ZHANG J F, SONG F E, et al. Biomass-based carbon-supported sulfate catalyst for efficient synthesis of dimethoxymethane from direct oxidation of dimethyl ether[J]. J Phys Chem Lett, 2021, 12(49): 11795–11801.
- [23] IL'IN A B, NOVIKOVA S A, SUKHANOV M V, et al. Catalytic activity of NASICON-type phosphates for ethanol dehydration and dehydrogenation[J]. Inorg Mater, 2012, 48(4): 397–401.
- [24] ERMILOVA M M, OREKHOVA N V, MIRONOVA E Y, et al. Methanol transformations on framework lithium zirconium vanadate phosphates[J]. Russ J Inorg Chem, 2016, 61(8): 940–945.
- [25] DANILOVA M N, PYLININA A I, KASATKIN E M, et al. Reactions of isobutanol over a NASICON-type Ni-containing catalyst activated by plasma treatments[J]. Kinet Catal, 2015, 56(4): 476–479.
- [26] GAO Q L, ZHENG K W, LI C, et al. Highly efficient acrylic acid production from formaldehyde and acetic acid over the NASICON-type catalyst[J]. Chem Commun, 2023, 59(11): 1489–1492.
- [27] ZHENG K W, GAO Q L, LI C, et al. A novel and environmentally friendly NASICON-type material: Efficient catalyst for condensation of formaldehyde and acetic acid to acrylic acid and methyl acrylate[J]. Chem Eng J, 2022, 446: 137324.
- [28] WANG J H, GAO Q L, LI C, et al. Direct synthesis of acrylic acid from methanol and acetic acid over a constructed TiO_2 -coated NASICON catalyst[J]. J Catal, 2024, 436: 115612.
- [29] ILIN A B, ERMILOVA M M, OREKHOVA N V, et al. Conversion of aliphatic C1-C2 alcohols on In-, Nb-, Mo-doped complex lithium phosphates and $\text{HZr}_2(\text{PO}_4)_3$ with NASICON-type structure[J]. J Alloys Compd, 2018, 748: 583–590.

- [30] BOWKER M, HOLROYD R, HOUSE M, et al. The selective oxidation of methanol on iron molybdate catalysts[J]. Top Catal, 2008, 48(1/4): 158–165.
- [31] JIANG J, SUN S, WANG X, et al. Synthesis of dimethyl ether from methanol over heteropoly acid/nanocrystalline HZSM-5 complex solid acidic catalyst[J]. Acta Chim Sin, 2013, 71(5): 810–814.
- [32] ZHANG Y B, CHEN K, SHEN Y, et al. Enhanced lithium-ion conductivity in a $\text{LiZr}_2(\text{PO}_4)_3$ solid electrolyte by Al doping[J]. Ceram Int, 2017, 43: S598–S602.
- [33] KAMALI K, RAVINDRAN T R. Temperature and pressure dependent phase transitions of β' - $\text{LiZr}_2(\text{PO}_4)_3$ studied by raman spectroscopy[J]. J Phys Chem A, 2016, 120(12): 1971–1977.
- [34] REDDY I N, AKKINEPALLY B, REDDY C V, et al. A systematic study of annealing environment and Al dopant effect on NASICON-type $\text{LiZr}_2(\text{PO}_4)_3$ solid electrolyte[J]. Ionics, 2020, 26(9): 4287–4298.
- [35] WANG M, WANG C H, WANG J, et al. Temperature-dependent raman spectroscopic study of the double molybdate $\text{KBi}(\text{MoO}_4)_2$ [J]. Materials, 2020, 13(23):5453.
- [36] TRUSSOV I A, MALE L L, SANJUAN M L, et al. Understanding the complex structural features and phase changes in $\text{Na}_2\text{Mg}_2(\text{SO}_4)_3$: A combined single crystal and variable temperature powder diffraction and Raman spectroscopy study[J]. J Solid State Chem, 2019, 272: 157–165.
- [37] XUE Z. Study on the preparation, characterization and application of catalysts for the synthesis of polyoxymethylene dimethyl ethers[D]. Qingdao: China University of Petroleum (East China), 2017.
- [38] WANG C Y, OUYANG M Y, LI M W, et al. Low-coordinated Pd catalysts supported on Zn1Zr1Ox composite oxides for selective methanol steam reforming[J]. Appl Catal A: Gen, 2019, 580: 81–92.
- [39] TAHERI P, LILL K, DE WIT J H W, et al. Effects of zinc surface acid-based properties on formation mechanisms and interfacial bonding properties of zirconium-based conversion layers[J]. J Phys Chem C, 2012, 116(15): 8426–8436.
- [40] PONOMAREVA M, DUCHOSLAV J, STIFTER D, et al. Effect of surface pretreatments on the formation of Zr-Based conversion layers on Zn-Al-Mg alloy-coated steel[J]. Mater Corros, 2025, 76(4): 510–518.
- [41] WANG W, GAO X, XIONG P, et al. Low-temperature oxidation of methanol to dimethoxymethane over Mo-Sn catalyst[J]. J Fuel Chem Technol, 2021, 49(10): 1487–1494.
- [42] LIU W, ZHAI Y, LIAN P, et al. The dispersity of molybdenum on the surface of Mo/Al-CLM and its hydrodesulfurization activity[J]. Acta Per Sin, 2000, 16(3): 27–32.
- [43] GAO J, ZHENG Y T, JEHNG J M, et al. Identification of molybdenum oxide nanostructures on zeolites for natural gas conversion[J]. Science, 2015, 348(6235): 686–690.

NASICON 基催化材料上甲醇直接氧化制聚甲氧基二甲醚研究

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摘要: 聚甲氧基二甲醚(DMM_x)是一种极具前景的清洁柴油添加剂。相比于传统的醇醛缩合路线, 以甲醇为原料通过一步法氧化直接制取 DMM_x 是一条优势显著的绿色合成路线。由于反应的复杂性, 存在氧化深度与 C-O 链增长效率之间的平衡问题, 因此, 催化剂设计需满足多功能活性位点的协同需求, 即催化剂应具备适度的氧化活性、适宜的酸强度分布以及两者之间的良好协同。针对以上挑战, 本研究设计了一种硫酸改性的钼掺杂 NASICON 催化剂, 该催化剂在甲醇一步氧化合成 DMM_x 反应中表现出较好的催化活性。在 NSC-Mo-0.5-30% 催化剂上, 甲醇转化率为 81.3%, DMM_x 的选择性达 58.7%, 并且实现了更大分子的合成, DMM₂₋₆ 选择性为 11.3%。NH₃-TPD、Py-IR 和 XPS 结果表明, 钼的引入增加了弱 Lewis 酸位点, 而硫酸浸渍不仅构建了梯度分布的 Brønsted 酸位点, 同时促进了 Mo⁵⁺/Mo⁶⁺ 氧化还原对的生成, 两者的共同作用明显促进了催化剂性能的提升。

关键词: 甲醇; NASICON 材料; 聚甲氧基二甲醚; C-O 链增长; 氧化

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