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Review

A review on direct synthesis of dimethoxymethane

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ABSTRACT

Polyoxymethylene dimethyl ethers are recognized as the prospective diesel additive to decrease the pollutant emission from the light-duty vehicles, which can be polymerize form the monomer of dimethoxymethane (DMM). The industrial synthesis of DMM is mainly involved two-step process: methanol is oxidized to form the formaldehyde in fixed bed reactor and then reacted with the generated formaldehyde through acetalization in continuous stirred-tank reactor. Due to huge energy consumption, this typical synthesis route of DMM needs to be upgraded and more green routes should be determined. In this review, four state-of-the-art one-step direct synthetic routes, including two upgrading routes (methanol direct oxidation and direct dehydrogenation) and two green routes (methanol diethyl ether direct oxidation and carbon oxides direct hydrogenation), have been summarized and compared. Combination with the reaction mechanism and catalytic performance on the different catalysts, the challenges and opportunities for every synthetic route are proposed. The relationships between catalyst structure and property in different synthesis strategy are also investigated and then the suggestions of the design of catalyst are given about future research directions that efforts should be made in. Hopefully, this review can bridge the gap between newly developed catalysts and synthesis technology to realize their commercial applications in the near future.

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1. Introduction

With the rapid spread of vehicles in recent decades, transportation has become the largest consumer of oil accounting for more than 60% of global consumption. Diesel fuel plays an important role in long-distance transport and 94% of freight relies on diesel engines. The outstanding problem of diesel engine is the exhaust emission of nitrogen oxide (NO_x) and particulate matter (PM), which cause serious air pollution. In 2016, limits and measurement methods for emissions from light-duty vehicles (CHINA 6) was formulated and then promulgated to increase the emission standard. In this context, it is urgent to solve the serious problem of diesel engine exhaust pollution. New research has found that adding oxygenated compounds to diesel can effectively reduce emissions. Therefore, the development and utilization of clean and environmental diesel additives have become the focus of chemical and environmental fields. Among these diesel additives, polyoxymethylene dimethyl ether is the most representative.

Polyoxymethylene dimethyl ethers (DMM_n) is a straight chain of polyether compounds, whose structure is CH₃O(CH₂O)_nCH₃. The oxygen content of DMM_n (3 ≤ n ≤ 5) have high oxygen content, physical properties similar to diesel oil and high cetane. Moreover, the peroxide formed during combustion of the methylene group (—CH₂O—) in DMM_n molecules can significantly mitigate NO_x and PM emissions [1–5]. Further, DMM_{3–5} can allow for replacing conventional diesel or blending into diesel with limited modifications of engine and fuel infrastructure needed [4]. Therefore, they have been considered as a potential diesel additive. The synthesis of DMM_n requires methoxy group and methyl as end groups and methoxyl groups as chain growth groups. In the selection of raw materials for the existing processes, the two substances containing the sealing end groups and the growth groups are considered simultaneously. The former includes methanol (CH₃OH, MeOH), dimethyl ether (CH₃OCH₃, DME) and dimethoxymethane (CH₃OCH₂OCH₃, DMM). The latter includes formaldehyde (CH₂O), triparaformaldehyde ((CH₂O)₃, TOX), paraformaldehyde (HO(CH₂O)_nH, PF). Traditional DMM_{3–5} production is achieved through the reaction of methanol and formaldehyde or its polymers. But the water formed by the condensation of methanol

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and has a negative effect on the synthesis of DMM_n, such as decreasing catalyst activity, promoting side reactions process and increasing the difficulty of product separation. In order to eliminate the negative effect of water on the reaction, an anhydrous route of synthesizing DMM₃₋₅ by reaction of DMM and anhydrous formaldehyde was proposed, where DMM was end group and triparaformaldehyde or paraformaldehyde as a source of anhydrous formaldehyde [6–9]. Besides, DMM is also used as a potential raw material for production of concentrated formaldehyde. Therefore, DMM has a great potential as an intermediate in the value chain for production of environmental diesel fuel additives and other chemicals.

DMM synthesis process mainly includes two methods, indirect synthesis and direct synthesis as shown in Fig. 1(a). Indirect synthesis of DMM mainly involves two steps. The first step is that methanol is oxidized to formaldehyde over iron molybdate catalyst in the gas phase. The second step is that the formed formaldehyde reacts with methanol to produce DMM over acid catalyst in the liquid phase. [5] In this process, acid sites of catalyst are generally considered to be the active sites for the acetalization reaction of methanol and formaldehyde. Many liquid or solid acids with different types of acid centers (Lewis or Brønsted) have been described in scientific patents as acid catalysts for DMM synthesis. For example, conventional liquid acid such as sulfuric acid and hydrochloric acid, which were the first catalysts studied, showed high activity for DMM production [10,11]. Compared with liquid acids, solid acids including ion exchange resins, heteropoly acid and zeolite [12–17], gradually replaced liquid acids because they were easy to recycle and deal with. However, the process of indirect synthesis DMM has a high energy loss. About 57% of the energy is lost in the synthesis of formaldehyde alone, so higher energy losses can be expected in the two-step reaction. In the context of energy conservation and emission reduction, direct synthetic methods were attracting more attention due to the advantages of using fewer operating units and avoiding steps for the recovery and purification of intermediates.

Currently, the direct synthetic methods mainly including methanol direct oxidation, dimethyl ether direct oxidation, methanol direct dehydrogenation, and CO_x hydrogenation in methanol were proposed as shown as Fig. 1 (b). In term of sustainability, coal chemical products methanol and syngas can be recycled with emissions of vehicles CO₂ through photosynthesis, which is in line with sustainable development. In addition, the majority of the reactions are gas–solid catalytic reactions for the easy of catalyst recovery and continuous operation. Researchers have designed a large number of catalysts for each synthesis route and achieved good performance. In this article, we summarize the reaction strategies, catalysts, reaction mechanism and relationship of catalyst structure and property of four synthetic routs in order to provide some basis for the future research, especially for the design of catalyst. Further, we summarize the advantages and situation of the four synthetic routes, which indicate the direction of their future development.

2. Synthesis of DMM via Methanol Direct Oxidation

2.1. Mechanism for methanol direct oxidation

In fact, the method of methanol direct oxidation combines the two steps of the indirect synthesis method into one as shown in Fig. 2. Methanol is oxidized to CH₂O over oxidation sites catalyst firstly followed by acetalization of methanol to yield DMM over acid sites [18–20]. Bifunctional catalysts with oxidation and acid sites are widely used in this reaction. Although the desired active sites of catalyst have been identified, the concentration and relative strength of acid and oxidation sites had a great effect on the conversion of methanol and the selectivity of DMM. As shown in Fig. 3, methanol tends to dehydrate and form DME with acid strength of catalyst increasing. While methanol prefers to be over oxidized to formic acid or even CO₂ if oxidation of catalysts is too strong. In addition, methyl formate (MF) is a by-product that is difficult to avoid in the synthesis of DMM. Therefore, in order

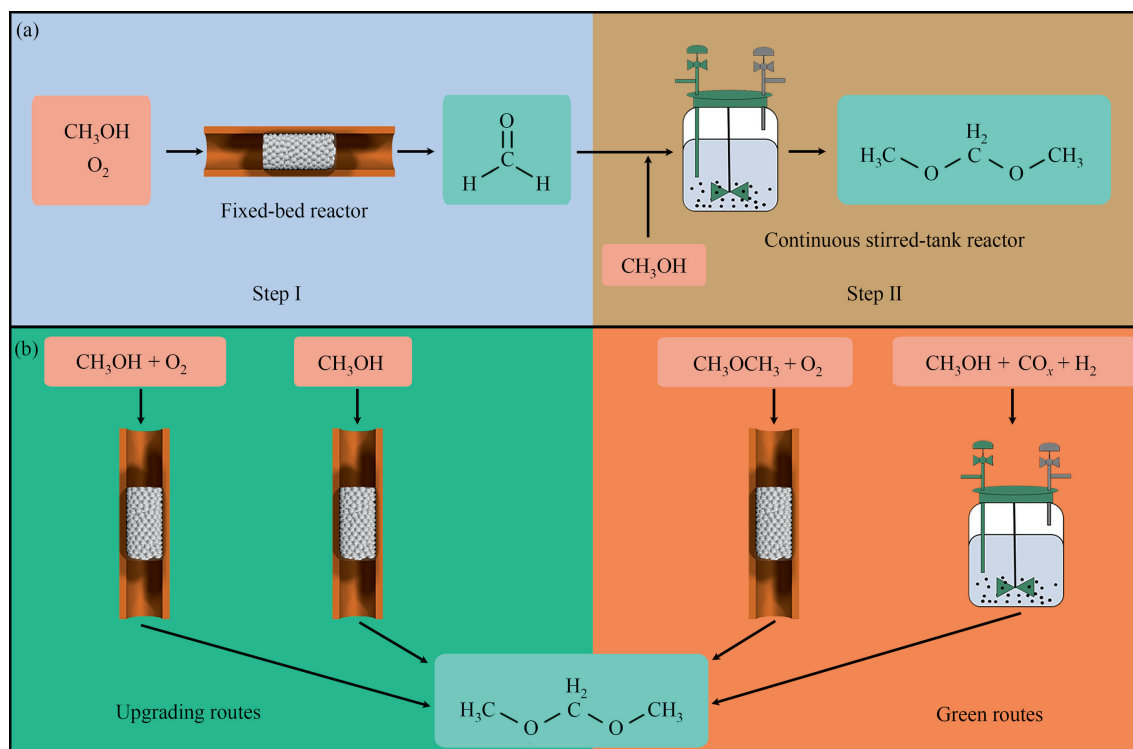


Fig. 1. The synthetic routes of DMM, (a) the indirect synthetic route, (b) direct synthetic route.

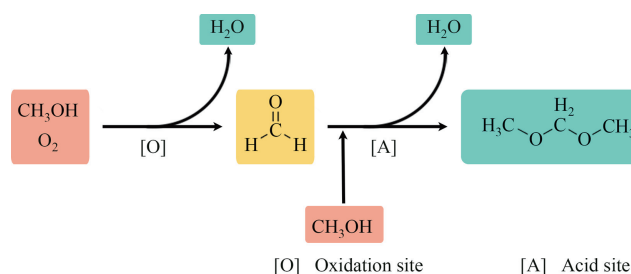


Fig. 2. Mechanism of methanol direct oxidation.

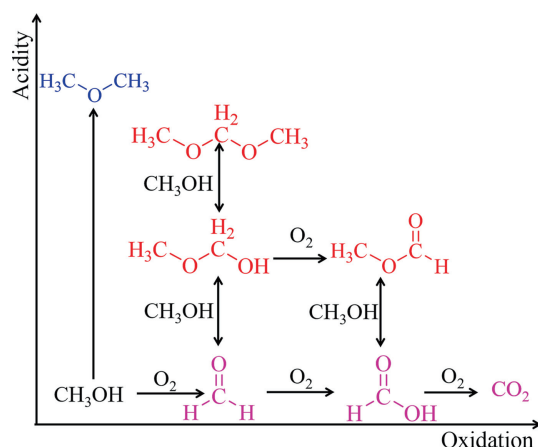


Fig. 3. Proposed reaction network for methanol direct oxidation to DMM [21].

to obtain highly selective DMM, the catalyst needs to achieve the balance between oxidation and acidity.

2.2. Catalysts of methanol direct oxidation

The reaction was usually carried out in a fixed-bed reactor with gaseous methanol and air as feedstocks. The concentration of methanol should be kept below 7% (mol) or above 36% (mol) to prevent methanol explosion [21,22]. In fact, DMM was usually detected as a by-product in the process of methanol oxidation to formaldehyde and MF. Therefore, the catalyst used for methanol oxidation to prepare formaldehyde can also be used for methanol oxidation to synthesize DMM reaction, only need to modify the catalyst or change the reaction conditions. A large number of catalysts have been used for the methanol direct oxidation, mainly including vanadium (V)-based catalysts, molybdenum (Mo)-based catalysts, and novel-metal catalysts. Next, we will describe the characteristics of catalysts, the relationship of catalyst structure and property in detail.

2.2.1. Vanadium-based catalyst

V-based catalyst was initially used in reaction of methanol oxidation to formaldehyde and has been extensively explored. Researchers found that DMM was detected as a by-product in the process of methanol oxidation to formaldehyde and MF over the catalyst of VTi (TiO_2 supported V_2O_5) [16,23–25]. This phenomenon provided a certain basis for the application of VTi catalyst in methanol direct oxidation to synthesis of DMM. However, there is a negative correlation between methanol conversion and DMM selectivity [26]. Shen *et al.* [27] compared the VTi catalyst before and after the modification of $\text{Ti}(\text{SO}_4)_2$. The performance of VTi catalyst was not satisfactory with 40.7% methanol conversion and 10.9 % DMM selectivity. However, the catalyst modified by Ti

$(\text{SO}_4)_2$ expressed good performance with the methanol conversion of 60% and the DMM selectivity of 88.6% (Table 1, row 1 and row 2). It is clear that the addition of SO_4^{2-} over the VTi surface could improve methanol conversion and DMM selectivity. Result of NH_3 -temperature programmed desorption (TPD) might give the interpretation. Catalyst modified by $\text{Ti}(\text{SO}_4)_2$ had stronger acidity and more acid sites which was benefit to acetalization reaction of methanol and formaldehyde, improving the selectivity of DMM. For VTi catalyst, the weaker acidity of catalyst was not enough to generate DMM, which made a large amount of FA and MF generated in the system.

On other hand, the oxidation capability of the catalyst has a great influence on the conversion of the reaction but almost nothing to do with selectivity. The oxidation capability of catalyst is related to the state of VO_x on the surface of support. According to the literature [39–41], three types of vanadium species exist on oxide supports: the first is isolated monomeric VO_x species, which is characterized by three V–O bonds attached to the support and one terminal V = O bond; the second is dimeric or polymeric VO_x species, which is characterized by V–O–V bonds and terminal V = O bond; and the third is crystalline V_2O_5 particles. They all have oxidation capacity and the first three are amorphous VO_x species. Compared with crystalline V_2O_5 , amorphous VO_x is more active for reactant adsorption and C–H bond breaking [42]. There are many factors affecting VO_x species, mainly including preparation method, calcination temperature, vanadium loading, and support properties.

Different preparation methods including coprecipitation (CP) [43,44], evaporation-induced self-assembly (EISA) [45], sol-gel (SG) [28], ultrasonic-assisted impregnation [46], rapid combustion (RP) [25,29], and mechanical grinding (MG) be explored [28]. Among them, the most widely used methods are precipitation and impregnation, they both obtain desired phase through adjusting calcination temperature. But such heat treatment usually leads to agglomeration of active sites, reducing the number of active sites on the catalyst and the oxidation capacity of the catalyst. To overcome this problem, Guo *et al.* proposed the rapidly combustion method and synthesized nanoscale $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst (Table 1, row 3). The more active sites of nanoscale catalyst resulted in the best performance with 48.56% methanol conversion and 91.76 % DMM selectivity at 120 °C [25]. However, catalyst made by grinding method exhibited the lowest activity, probably because mechanical grinding could not mix VOSO_4 and TiO_2 sufficiently [28] (Table 1, row 4 to row 6). In addition, calcination temperature had a significant influence on the dispersity of active sites. Guo *et al.* [29] prepared a series of catalyst at different calcination temperature from 673 K to 973 K. Catalysts calcinated at 723 K and 773 K exhibited best activity with same methanol conversion of 45% and similar DMM selectivity of 90.33% and 91.76% (Table 1, row 7 to row 10). Results of X-ray diffraction (XRD) indicated that the VO_x could be well dispersed on the surface of the catalyst in amorphous state at that calcination temperature. Amorphous VO_x provided more oxidation sites and stronger oxidation capacity, which was consistent with the results of H_2 -temperature program reduction (H_2 -TPR). However, when the calcination temperature exceeded 773 K, VO_x would agglomerate and leading to the formation of large amount of crystalline VO_x , which led to the bad performance of catalyst. Zhao *et al.* [47] also demonstrated the important effect of calcination temperature on catalyst performance. Lu and coworkers [30] prepared (10%, 15%, 20% and 25% (mass) V_2O_5) acid-modified $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts with different vanadium loadings by impregnation (Table 1, row 11 to row 14). XRD showed that the vanadium species on the surface of catalyst were isolated and highly dispersed with the content of was V_2O_5 below 15% (mass). With the content of V_2O_5 increasing, although more surface vana-

Table 1

Catalysts for methanol direct oxidation.

Catalysts	Temperature/K	GHSV/ml·g ⁻¹ ·h ⁻¹	Methanol Cov./%	Selectivity/%					Ref.
				DMM	DME	FA	MF	COx	
10 %V ₂ O ₅ /TiO ₂	433	11400	40.70	10.90	0.70	61.00	27.50	0.00	[27]
10 %V ₂ O ₅ /TiO ₂ -Ti(SO ₄) ₂	433	11400	60.00	88.60	0.40	1.20	9.80	0.00	[27]
VTiS-RC	393	5000	48.56	91.76	0.57	1.98	5.63	0.00	[25]
VTiS-CP	413	11400	42.00	93.00	1.00	0	6.00	0.00	[28]
VTiS-SG	433	11400	47.00	89.00	1.00	0.00	10.00	0.00	[28]
VTiS-MG	433	11400	21.00	88.00	8.00	1.00	9.60	0.00	[28]
VTS-673	393	n.a	45.00	66.64	3.36	20.35	8.92	0.73	[29]
VTS-723	393	n.a	45.00	90.33	0.94	3.23	5.16	0.34	[29]
VTS-773	393	n.a	45.00	91.76	0.57	1.98	5.63	0.07	[29]
VTS-873	393	n.a	45.00	64.46	1.23	19.90	14.09	19.90	[29]
5 %V ₂ O ₅ /TiO ₂ -H ₂ SO ₄	423	n.a	36.00	92.30	n.a	n.a	n.a	n.a	[30]
10 %V ₂ O ₅ /TiO ₂ -H ₂ SO ₄	423	n.a	49.00	92.80	n.a	n.a	n.a	n.a	[30]
15 %V ₂ O ₅ /TiO ₂ -H ₂ SO ₄	423	n.a	34.00	92.50	n.a	n.a	n.a	n.a	[30]
20 %V ₂ O ₅ /TiO ₂ -H ₂ SO ₄	423	n.a	29.00	92.80	n.a	n.a	n.a	n.a	[30]
SO ₄ ²⁻ -30VO _x -TiO ₂	423	1650	55.00	85.00	3.00	0.00	12.00	0.00	[31]
SVTNT-673	513	11400	58.00	92.00	0.00	2.00	6.00	0.00	[32]
WVTNT-673	513	11400	44.00	55.00	19.00	26.00	0.00	0.00	[32]
PVTNT-673	513	11400	31.00	85.00	0.00	0.00	1.00	0.00	[32]
VO _x /g-C ₃ N ₄	473	n.a	40.00	95.20	n.a	n.a	n.a	n.a	[33]
FeMo	553	n.a	55.70	89.70	5.30	4.20	0.70	0.1	[34]
Fe ₂ O ₃	528	16000	7.00	0	0	20	80	0	[22]
MoO ₃	528	16000	7.00	80	n.a	n.a	n.a	n.a	[22]
FeMo ₄	528	16000	45.00	80	n.a	n.a	n.a	n.a	[22]
Mo:Fe(2)/HY	503	15000	17.30	70.80	1.02	7.60	19.80	0.78	[35]
Mo:Fe(2)/Al ₂ O ₃	503	15000	20.50	55.00	1.61	28.10	15.20	0.19	[35]
Mo:Fe(2)/HZSM-5(40)	503	15000	28.50	58.00	1.91	7.81	31.70	0.58	[35]
Mo:Fe(2)/HZSM-5(40)	503	15000	22.60	68.20	1.09	9.81	20.70	0.20	[35]
Mo:Fe(2)/SiO ₂	503	15000	21.90	8.30	0.00	79.70	8.70	3.29	[35]
Mo:Fe(2)/HZSM-5(80 + 80)	503	15000	87.44	93.00	0.21	2.05	4.17	0.57	[35]
SbRe ₂ O ₆	573	10000	6.50	92.50	6.30	0.00	1.20	0.00	[36]
Re/V ₂ O ₅	513	40000	21.50	93.70	4.30	0.00	0.00	2.00	[36]
Re/α-Fe ₂ O ₃	513	40000	15.50	90.50	1.00	2.00	6.00	0.50	[36]
Re/γ-Fe ₂ O ₃	513	40000	48.40	91.00	1.00	2.40	4.60	1.00	[37]
4.4 %RuO ₂ /Al ₂ O ₃	393	n.a	14.90	57.60	0.00	11.60	30.10	1.00	[38]
4.1 %RuO ₂ /ZrO ₂	393	n.a	17.60	5.60	0.00	6.60	70.70	16.80	[38]
2.2 %RuO ₂ /TiO ₂	393	n.a	14.50	4.10	0.00	25.20	69.90	0.90	[38]

n.a: not available.

dium species are produced, the polymerization of vanadium species is intensified to form crystalline vanadium species resulting in low catalytic activity. This phenomenon was consisted with the research of Zhao *et al.* [48].

Moreover, the performance of the catalyst is closely related to the properties of the support [49–55]. For example, Kaichev and coworkers [56] loaded VO_x on different metal oxides (ZrO₂, TiO₂, SiO₂ and γ-Al₂O₃) through impregnation method and applied them to methanol oxidation direct synthesis of DMM. Catalyst of VO_x/TiO₂ expressed best activity among them although these catalysts are all active for the reaction. Various characterization results indicated that the nature of the support determines the structure of the VO_x species. The monomeric and polymeric VO_x surface species formed on the surfaces of ZrO₂ and TiO₂ are more active than the crystalline phase of V₂O₅ formed on SiO₂ and γ-Al₂O₃ supports. Monomeric VO_x on ZrO₂ and TiO₂ manifest similar activity, and polymeric forms on TiO₂ are considerably more active. They thought that the lower energy of V–O–support than V–O–V was facilitated to proton detachment from the methoxy group CH₃–O–VO_x which was the rate-limiting step. Zhao *et al.* [49] also demonstrated this phenomenon. Liu *et al.* [31] prepared mesoporous VO_x-TiO₂ with high surface area by combining evaporation-induced self-assembly and ammonia post-treatment. VO_x-TiO₂ material had a high specific surface area with pore-size of 4 nm. The larger specific surface area was favorable for VO_x to be highly dispersed on the support, even the content of VO_x was up to 30% (Table 1, row 15). The catalyst SO₄²⁻-30VO_x-TiO₂ showed good selectivity of DMM (85%) with the conversion of methanol

was 55% at 423 K. In addition, TiO₂ nanotubes (TNT) [32,57] and Titanium silicalite (TS-1) [58,59] with high specific surface area are usually used to highly dispersed active sites too. In particular, the special structure of carbon nanotubes is conducive to the high dispersion of V₂O₅ [32]. V₂O₅ can obtain a nearly monolayer dispersed V₂O₅ loading of up to 20%, which enables the very high conversion of methanol to reach 58% with the DMM selectivity of 92% (Table 1, row 16). Ma *et al.* [33] prepared a composite material VO_x/g-C₃N₄. Various characterization results proved that VO_x grafted to the surface of g-C₃N₄ through the interaction between V or O atoms and characteristic groups on the surface of g-C₃N₄ to achieve molecular level dispersion. Highly dispersed VO_x/g-C₃N₄ has effective catalytic activity and high selectivity for methanol oxidation to DMM with a turnover frequency (TOF) of 44.9 mol·mol⁻¹·h⁻¹ and the DMM selectivity of 95.2% (Table 1, row 19).

The acidity of catalyst mainly affects the selectivity of DMM. Although the introduction of sulfate species can improve the yield of DMM, the performance of the catalyst is dependent on the content of acid sites and the strength of acid. The content of sulfate and calcination temperature both affect the acidity of the catalysts. Guo *et al.* [25] prepared VO_x-TiO₂ catalysts with different sulfate contents by rapid combustion method. The results showed that when the sulfate content was lower than 4% (mol), the sulfate was highly dispersed on the catalyst surface, and when the sulfate content was higher than 4% (mol), the sulfate aggregated on the catalyst surface. The results of NH₃-TPD showed that the different sulfate loading did not change the acid strength, but only changed

the number of acid sites. When the content of sulfate was 4% (mol), the selectivity of DMM was the highest, reaching 91.76%, which mainly due to the largest number of acid sites. In addition, calcination temperature also affected the sulfate species on the support. Guo *et al.* found that the sulfate was highly dispersed on the support when the calcination temperature of catalyst was 723 and 773 K [29]. As described by the H_2 -temperature program reduction mass spectrometry (H_2 -TPR-MS), bidentate sulfate species formed on VTiS calcined at 723 or 773 K, whereas aggregated pyrosulfates were present on VTiS calcined above 773 K. In addition, different acid promoters also affect the performance of the catalyst. Cai *et al.* [32] introduced different acidic promoters (H_2SO_4 , H_3PO_4 , $H_3PW_{12}O_{40}$) (Table 1, row 16 to row 18) in Titania-nanotubes (TNT) supported V_2O_5 catalysts (VTNT) respectively. Only VTNT calcinated at 673 K after sulfuric acid modification showed significantly enhanced selectivity to DMM with the higher conversion of methanol. Some sulfate groups strongly interact with vanadium species were produced during calcination, which enhanced the surface acidity of vanadium species without weakening their oxidation reduction ability. The addition of H_3PO_4 and $H_3PW_{12}O_{40}$ could enhance the surface acidity of V_2O_5/TiO_2 while weakening its oxidation reduction ability, which is harmful to the target reaction.

2.2.2. Molybdenum -based catalyst

Ferro-molybdenum catalysts are used industrially to produce formaldehyde with low concentrations of methanol feeds (<7.5% (mol)) [60]. The conversion of methanol is 99% with the formaldehyde selectivity of 94%. It is interesting that a small amount of DMM was detected as by-product, which provided a certain basis for the application of Mo-based catalyst in the direct synthesis of DMM by methanol oxidation.

Gornay *et al.* [34] demonstrated excellent performance of an industrial FeMo catalyst [MoO_3 - $Fe_2(MoO_4)_3$] in methanol directly oxide to DMM. The concentration of the raw material has a great influence on the selectivity of the product with little influence on the conversion of methanol under same reaction conditions. The selectivity of DMM was only 3% at poor feedstocks of 7.5% (mol) methanol. But the DMM selectivity was greatly improve to 90% at rich feedstock of 40% (mol) (Table 1, row 20). It is clear that methanol not been oxidized to formaldehyde reacts with the formaldehyde to form DMM. Subsequently, this group further explored the relationship between the structure and properties of catalysts [22]. In order to investigate the role of Fe and Mo in the catalytic process, the two components were investigated separately. For Fe_2O_3 , the conversion of methanol was 7% with the MF selectivity of 80% and no selectivity to DMM (Table 1, row 21). Whereas, the selectivity of DMM was increased to nearly 80% and the conversion of methanol was almost unchanged under the catalysis of MoO_3 (Table 1, row 22). These results indicated that both Fe_2O_3 and MoO_3 had oxidation sites to convert methanol into formaldehyde, while only MoO_3 had acidic sites to catalyze the acetalization reaction between methanol and formaldehyde to form DMM. When the two are combined with each other, the yield of DMM was increased to about 40% still maintaining high selectivity (Table 1, row 23). It is obvious that MoO_3 and Fe_2O_3 have an excellent synergistic effect to improve the yield of DMM. In addition, the result of *in situ* X-ray photoelectron microscopy (XPS) showed that Fe^{3+} was reduced to Fe^{2+} in the reaction process, while Mo did not change valence state. So, Fe^{3+} rather than Mo^{6+} was considered as the redox site.

It can be found from the above investigation that iron oxide and molybdenum oxide can be used as active sites for the direct oxidation of methanol to synthesize DMM. Some supports had been applied to disperse these active components in order to improve the performance of the catalyst. Yuan *et al.* [61]

explored the performance of Mo: Fe (2)/HZSM-5 in a fluidized bed though dispersing the active components on HZSM-5 and the effects at different reaction temperature were explored. The experimental results showed that the high reaction temperature was not conducive to the formation of the target product DMM. The BET, TEM and other characterization methods were used to investigate the reason. The results showed that the high reaction temperature led to the agglomeration of metal oxides on the catalyst surface, blocking the channel and reducing the specific surface area, and destroyed the acid active site on the catalyst surface. In addition, the influences of supports including SiO_2 , Al_2O_3 , HY zeolite and HZSM-5 (ratio of Si/Al = 80, 40) (Table 1, row 24 to row 28) were further investigated [35]. The DMM yield was up to 81.33% under the catalyst Mo:Fe(2)/HZSM-5 (80 + 80) (Mo:Fe(2)/HZSM-5 (80) mixed with HZSM-5 (80)). Compared with Mo:Fe(2)/HZSM-5 (80), the introduction of HZSM-5 (80) increased the amount of acid sites especially B acid sites. Therefore, it was not different to find that the B acid site played a key role in the selective catalysis of the target product, and a higher B/L ratio was in favor of improving the catalytic activity and selectivity of the target product. On the other hand, the Mo loading affected MoO_x species dispersed on TiO_2 support which was similar to the V-based catalyst. Faye *et al.* [62] found that MoO_x existed in an amorphous state when the Mo loading was less than 14% (mass) though the results of XRD and Raman spectroscopy. H_2 -TPR results showed that with the increase of the content of Mo, the number of oxidation site of the catalyst first increased and then decreased and reached the highest with the Mo content at 8%. Moreover, the introduction of MoO_x increased the number acid site of the catalyst by forming Mo-O-Ti bond with TiO_2 support and presented the same trend of change with oxidation sites. When the MoO_x loading was 8%, the oxidation and acidity of the catalyst are coordinated, resulting the catalyst has the best performance with the conversion of methanol at 5% and the selection of DMM at 80%.

2.2.3. Noble-metal catalyst

Yuan *et al.* explored the performance of $SbRe_2O_6$ for selective oxidation of methanol to DMM [36]. The catalyst expressed very good performance with methanol conversion of 6.5% and DMM selectivity of 92.5% at 300°C, which could be ascribed to the ReO_x connected with Sb-O chains (Table 1, row 30). To further clarify the role of the catalyst, pulse experiments were used to further explore the reaction mechanism. Methanol can still be oxidized to DMM in the absence of oxygen, which indicated that the lattice oxygen in $SbRe_2O_6$ was involved in the oxidation of methanol. In addition, the results of O_2 -TPD showed that two types of lattice oxygen in the catalyst were involved in the reaction of synthesis of DMM. So, it can be inferred that the lattice oxygen was firstly consumed and then regenerated by oxygen molecules during the reaction. However, the low specific surface area ($1\text{ m}^2\cdot\text{g}^{-1}$) of $SbRe_2O_6$ could limit the performance of the catalyst. To improve the performance of the catalyst, rhenium oxide is loaded on different supports, including V_2O_5 , SiO_2 , α - Al_2O_3 , TiO_2 -rutile, TiO_2 -anatase, ZrO_2 , α - Fe_2O_3 , γ - Fe_2O_3 , and MoO_3 [37]. When rhenium oxide is loaded on V_2O_5 , α - Fe_2O_3 , γ - Fe_2O_3 , the catalysts showed good selectivity of DMM more than 90% at 513 K (Table 1, row 31 to row 33). Compared V_2O_5 , α - Fe_2O_3 , the Re/γ - Fe_2O_3 displayed the highest methanol conversion of 48.4%, which was attributed to its largest specific surface facilitating the dispersion of rhenium oxide. For α - Fe_2O_3 , with the increase of rhenium loading, rhenium oxides were dispersed as tetrahedral $Re^{7+}O_4$ species (<0.7% (mass)), active Re-Fe-O mixed-oxide clusters (>1% (mass)) and ReO_2 crystallites (>6% (mass)) respectively, which was consistent with literatures [63]. However, for γ - Fe_2O_3 support, higher specific surface area favored the dispersion of rhenium oxide, and ReO_2 was not

observed. The rhenium oxide species on the support was generally considered as the active center for methanol oxidation to DMM. In order to determine the specific active components, XPS was used to measure the fresh catalyst (FC), the used catalyst (UC) after the reaction in the absence of oxygen. The Re^{4+} strength of UC increased significantly while the strength of catalyst Re^{6+} and Re^{7+} decreased. And the Re^{6+} and Re^{7+} increased again after the oxygen was introduced in the system. So, it can be inferred from the above that the redox capability of rhenium oxides $\text{Re}^{6-7+} \leftrightarrow \text{Re}^{4+}$ was responsible for the catalytic performance.

Liu *et al.* [38] prepared bifunctional catalysts by loading RuO_2 on oxide supporting including SnO_2 , ZrO_2 , TiO_2 , Al_2O_3 , and SiO_2 to explore the performance to directly oxidize methanol to DMM at low temperature (60–120 °C). It was found that the catalyst $\text{RuO}_2/\text{Al}_2\text{O}_3$ displayed the best performance with maximum DMM selectivity of 67% (Table 1, row 35). For the SnO_2 , ZrO_2 and TiO_2 , the weaker acidity of them was more favorable to the formation of MF (Table 1, row 36 to row 38). Yu *et al.* [64] prepared a highly dispersed ruthenium oxide clusters catalyst $\text{RuO}_2 \cdot x\text{H}_2\text{O}/\text{CNT}$ through a homogeneous oxidation precipitation method in which RuCl_3 was oxidized by H_2O_2 in liquid phase. The highly dispersion of ruthenium oxide clusters was ascribed to the oxygen-containing species located on the surface of functionalized CNT. With the increase of heat treatment temperature, $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ gradually dehydrated into anhydrous RuO_2 , and the selectivity of DMM decreased from 49% to 6%. In addition, Li *et al.* [65] used RuCl_3 as catalyst to synthesize DMM via methanol oxidation in the liquid phase. The methanol conversion was 49.8% and the DMM selectivity was 79.8%. These results indicated that RuCl_3 was a novel catalyst for the selective oxidation of methanol to DMM in liquid phase, when only molecular oxygen was used as the sole oxidant. The authors proposed the hypothesis that Ru^{3+} provided oxidation sites for methanol to be oxidized to formaldehyde with being reduced to Ru^{2+} , followed oxidized to Ru^{3+} by oxygen molecule. Moreover, The Lewis acid sites of RuCl_3 provided the active site for the acetalization reaction of methanol with formaldehyde.

3. Synthesis of DMM via Methanol Direct Dehydrogenation

3.1. Mechanism of methanol direct dehydrogenation

The method of methanol direct dehydrogenation is that methanol dehydrogenated to produce CH_2O over the dehydrogenation site, which further reacted with methanol to obtain DMM, hydrogen and water over the acid site, as shown in Fig. 4. The gas phase by-product H_2 of this reaction can not only react with CO_2 to generate methanol, but also is a kind of clean energy with high recycling value. In addition, compared with the direct oxidation of methanol, the oxygen-free environment also avoids the risk of methanol explosion and having higher safety.

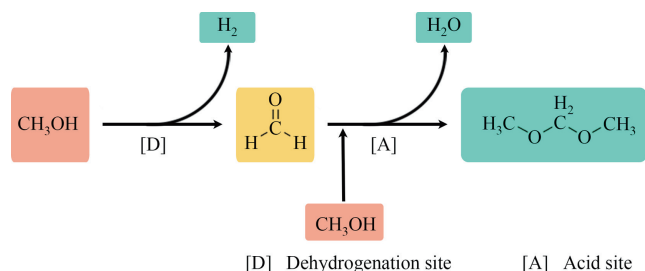


Fig. 4. Mechanism of methanol direct dehydrogenation.

3.2. Catalysts of methanol direct dehydrogenation

The reaction of methanol direct dehydrogenation is carried out in a fixed-bed reactor or autoclave reactor. In fact, DMM is often detected as a by-product of methanol liquid phase dehydrogenation in the presence of Ru-based catalysts [66–69]. This provides a feasibility of direct synthesis of DMM by methanol dehydrogenation, although the selectivity of DMM was very low. There are only a few articles on this subject. In general, the reaction can be divided into two categories, that is, in the gas phase and in the liquid phase. For the catalysts used in these two reaction systems, metal Cu provides dehydrogenation sites, and metal oxides or zeolite to provide acid sites. The catalysts used in these two reaction systems are described in detail next.

3.2.1. Catalysts used in liquid phase

Compared the reaction in the gas phase, methanol dehydrogenation in the liquid phase has an obvious advantage that hydrogen can be removed from the liquid in time, Pushing equilibrium in the direction of the positive reaction. Shinoda *et al.* [70] investigated the performance of $\text{Cu-ZnO}/\text{SiO}_2$ in the liquid phase dehydrogenation of methanol. MF was the main product with selectivity at almost 100 % when catalyst was calcined in air. While the catalyst was calcined in N_2 , the main product was DMM. The results of XRD and XPS showed that the catalysts calcined in N_2 produced Cu^0 and Cu^+ whereas only Cu^{2+} existed when the catalyst was calcined in air. The catalysts burned in N_2 showed better catalytic performance, which may be related to the weak adsorption capacity of FA on Cu^+ . Therefore, the intermediate FA easily desorbed from Cu^+ and trapped by methanol in the liquid phase, and then reacted with methanol to form DMM. Wu *et al.* [71] studied the performance of Cu/SiO_2 catalyst in methanol dehydrogenation. They found that there was a large amount of DMM production with almost 100 % selectivity in the liquid phase. Based on XRD and XPS results, the reaction pathway was speculated. Supercritical methanol dehydrogenated to formaldehyde at Cu^0 and Cu^+ , and then reacted with methanol in the liquid phase to form DMM.

3.2.2. Catalysts used in gas phase

There are only a few reports in gaseous phase reaction. To *et al.* [72] first proposed the coupling of methanol dehydrogenation to prepare DMM, in which Cu/ZrAlO had the highest activity. The yield of DMM was 3%, which was 40% of the equilibrium limit under experimental conditions (equilibrium yield was 7%). For $\text{Cu}/\text{Al}_2\text{O}_3$ and Cu/ZrO_2 catalysts, DME and MF are the main products with a large amount of CO_x (CO and CO_2). CO_x was probably related to the alkaline sites on the catalyst. The higher yield of Cu/ZrAlO may be related to the more medium and strong acid sites of catalyst. Significantly, these results further proved that Cu nanoparticles could promote efficient dehydrogenation of methanol at low temperature (usually at 500–800 °C [73]). Sun *et al.* [74] demonstrated that H β with high ratio of Si/Al was more suitable as a support, achieving the conversion of methanol at 3.6% and the selectivity of DMM at 80.3%. Compared $\text{Cu}/\text{ZSM-5}$ (200–400) and Cu/HY (80), the higher selectivity of DMM over $\text{Cu}/\text{H}\beta$ (836) was ascribed to its weaker acidity. But for $\text{Cu}/\text{silicalite-1}$, whose acidity was the weakest, the MF is main product, which was consistent with the work of Yang *et al.* [75] In summary, it is not difficult to find that the high selectivity of DMM is related to the appropriate acid intensity on the catalyst. Moreover, the effect of spatial position of catalytic functionalities was also explored. No matter the mixture of two functional catalysts or the piecwise addition, the highly selective products could be not obtained. This demonstrated that tailored proximity and interaction of Cu and H β (836) are required for efficient catalysts. *In situ* fourier transform infrared spectroscopy (FTIR) was used to speculate the reaction

mechanism. With the time going, the $\text{CH}_3\text{O-Si}$ and $\text{CH}_2\text{O-Si}$ was detected successively, which proved that methanol underwent a process of dehydrogenation into formaldehyde. However, during this process, the DMM and MF was not detected, possibly because the concentration was too low, which was below the detection line. Isotope labeled methanol (CD_3OH) was used in this experiment to further speculate on the reaction mechanism. The generation of HD demonstrated that methanol underwent the breaking of O–H and C–D bond, and further supporting the hypothesis that methanol dehydrogenated to CH_2O intermediate. The group of Mebrahtu further modified H β , which was dealuminated by different concentrations of HNO_3 solution [76]. It was found that the H β with high ratio of Si/Al had weaker acidity, which was benefit to improve the selectivity of DMM. The result of Py-IR showed that only Lewis acidic sites were on the catalyst. And an optimal amount of Lewis acidic sites of catalyst led to the high DMM selectivity of 81.5 %. In addition, CO-DRIFTS was used to detect valence state of Cu. For fresh catalyst, there was no characteristic peak of CO-Cu^+ . However, the characteristic peaks of CO-Cu^+ were observed for the catalyst after methanol flow in situ at 200 °C for 1 h. Therefore, the author proposed that the Cu^0 was gradually oxidized to Cu^+ , which will lead to increased concentration of adsorbed methoxy species available for condensation.

4. Synthesis of DMM via DME Direct Oxidation

4.1. Mechanism of DME direct oxidation

Dimethyl ether is a non-toxic chemical raw material which could be used to synthesize various oxygen-containing chemicals. Among them, one-step oxidation of DME to DMM is a green and competitive route with good atomic economy and low carbon emissions. According to the literatures [77], there are two possible pathways for DME direct oxidation to DMM. As shown in Fig. 5, the one is that DME firstly dissociates into $-\text{CH}_3\text{O}$ at the acid site. Then the DME is oxidated to CH_3OCH_2 over the oxidation site. Finally, the formed CH_3OCH_2 reacted with CH_3O to form DMM. Another possible pathway is that the formed $-\text{CH}_3\text{O}$ can further generate methanol and FA over the acid site and oxidation site respectively. Then the methanol can react with FA over the acid site to form DMM.

4.2. Catalysts of DME direct oxidation

The reaction of DME direct oxidation is usually carried out in a continuous flow fixed-bed reactor. Due to the chemical stability of methyl ether, direct oxidation of methyl ether to DMM at low temperatures is very challenging. The low temperature or the oxidation of the catalyst is not enough to break a large amount of C–O and C–H, resulting in a very low conversion of dimethyl ether. However, high temperature or strong oxidation of the catalyst will lead to the complete fracture of C–O and C–H, resulting in the formation of a large amount of CO_x . So, it is very difficult to break the C–O and C–H bonds of DME while maintaining the stability of C–O–C–O–C of DMM. In 2003 Liu *et al.* [78] firstly proposed the scheme of direct oxidating DME to synthesis DMM and the synthesis of DMM, and found that the bifunctional catalyst with oxidation site and acid site played a very important role. Later, many scientific researchers participated in this study and made great progress. These catalysts can be roughly divided into three categories: Heteropoly acids catalyst, carbon supported catalyst and zeolite supported catalyst.

4.2.1. Heteropoly acids catalyst

Heteropoly acids (HPA) are negatively charged oxide clusters with Keggin structures, W, Mo, or V as addenda atoms, and P, Si, Or B as central atoms [78,79]. When the negative charge of framework is balanced by protons, the material has acidity. Heteropoly acids were used to catalyze this reaction because they provide both oxidation and acid sites. Liu *et al.* [78] used different heteropoly acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$) in the oxidation of DME. Among three catalysts, the main products of oxidation of DME were CH_3OH with a small amount of DMM and CH_2O under $\text{H}_3\text{PW}_{12}\text{O}_{40}$. While, for $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, the selectivity of DMM was substantially improved, 46% and 56%, respectively, although the conversion of DME was only 2% and 1.8%. Compared $\text{H}_3\text{PW}_{12}\text{O}_{40}$, the higher oxidation ability of latter two can improve the oxidation rate of DME and generate more CH_2O , further reacted with DME to produce DMM, improving the selectivity of DMM. But the small specific surface of heteropoly acid ($<10 \text{ m}^2\cdot\text{g}^{-1}$) is not conducive to the dispersion of active sites, resulting in a very low reaction rate. So, loading the heteropoly acids on porous materials like SiO_2 , carbon-based materials, zeolite

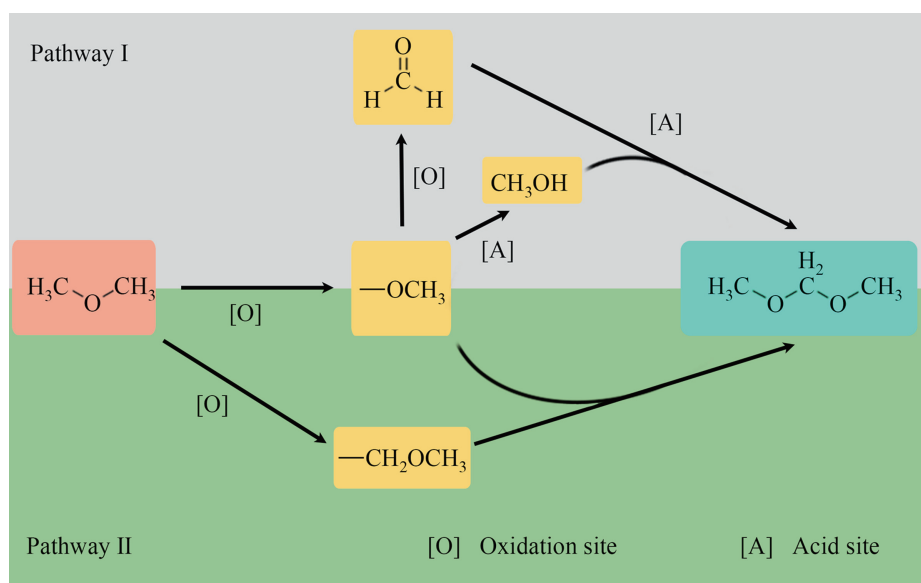


Fig. 5. Mechanism of DME direct oxidation.

can disperse active sites to a large extent, which is beneficial to improve the performance of catalysts.

The research group of Zhang carried out a series of studies on HPA/SiO₂ [77,80–83]. As shown in the first row of Table 2, the H₃PW₁₂O₄₀(40%)/SiO₂ were very active during DME oxidation, but the DMM selectivity was only 1.3%, while the selectivity of CO and CO₂ was as high as 65.6%. It may be that DMM was strongly adsorbed on the catalyst, resulting in excessive oxidation of DME to CO_x. Then, the H₃PW₁₂O₄₀(40%)/SiO₂ catalyst was modified by Cs, K. [80]. Among them, the Cs_{2.5}H_{0.5}PW₁₂O₄₀ (40%)/SiO₂ catalyst showed the best performance with the conversion of DME at 20% and the selectivity of DMM at 34.8% (Table 2, row 2 and row 3). But after 7 h of reaction, the selectivity of DMM decreased by more than half and the selectivity of methanol and formaldehyde increased greatly. For this phenomenon, the results of NH₃-TPD provide an answer. Compared with the fresh catalyst, the number of acid sites of the reacted catalyst is reduced, which affects the subsequent acetalization reaction of methanol and formaldehyde. The results of Scanning Electron Microscope (SEM) show that the used catalyst has obvious agglomeration, which is also one of the reasons for deactivation of the catalyst. Subsequently, this research group [83] explored the catalytic performance of different heteropoly acids modified by MnCl₂. The order of catalytic activity was MnCl₂-H₄SiW₁₂O₄₀/SiO₂ > MnCl₂-H₃PW₁₂O₄₀/SiO₂ > MnCl₂-H₃PMo₁₂O₄₀/SiO₂. Compared with the unmodified catalyst, the modified catalyst has stronger oxidation capacity and weaker acidity, which may be the reason of increasing of DMM selectivity. It is not difficult to find that the strong acidity would lead to that the dimethyl ether was excessively oxidized to CO_x. Sm₂O₃ is often used to adjust the acidity and improve the oxidation of catalysts [84,85]. Tan *et al.* reported that Sm₂O₃ modified γ -Al₂O₃ has more weak acid sites [92]. On this basis, the Sm₂O₃ was introduced in molybdenum-modified HPA/SiO₂ catalyst to adjust oxidation and acid. As shown in in rows 7 and 8 of Table 2, the selectivity of DMM improved from 36.3% to 60.3%, which was attributed to the increased number of Lewis acid sites and weak acid sites [82].

Rhenium oxide is widely used in oxidation reactions because of its characteristic oxidation and acidity. It has been demonstrated that 5%Re–20%PW₁₂/TiO₂ was active to the DME oxidation to DMM [83]. It is important to note that DMM₂ is formed in this

reaction, although the selectivity is only 3.7% (Table 2, row 9). It is also the first report of direct oxidation of DME to DMM₂. But the low specific surface area of TiO₂ limits the dispersion of active components, and the catalyst will agglomerate during the reaction, which both limit the performance of catalyst. According to the chain growth mechanism, synthesis of long chain DMM_n requires a large amount of formaldehyde monomer and capping group. Carbon nano-tubes (CNT) has good electrical conductivity, thermal stability and large specific surface area, it was selected as support to disperse active sites [93]. For Re/CNTs, the selection of DMM was only 4.2% while there was a lot of FA with selection of 73.7% (Table 2, row 10). Although rhenium oxide is somewhat acidic, it is not sufficient to catalyze the synthesis of DMM from formaldehyde and DME, resulting in the retention of large amounts of formaldehyde. So, H₃PW₁₂O₄₀ was used to modify Re/CNTs to increase acidity of catalyst, and the selectivity of DMM increased to 55% with the conversion of DME was 8.9% (Table 2, row 11).

4.2.2. carbon-supported catalyst

Oxidation and acidity are two important factors in DME oxidation. Considering the good physical and chemical properties of carbon material, its large specific surface area can be used to disperse the active components well, and its good electrical conductivity is conducive to electron transfer in redox reactions. For this reason, carbon materials (active carbon, AC; graphene, G; CNTs; *etc.*) are often used as support or catalysts. Normally, oxygen-containing functional groups on the surface of carbon materials are considered to be active sites for activating O₂ molecules. If AC is used as catalyst, CH₃OH and CH₂O were the main products, which indicated that AC had acid and oxidation (Table 2, row 13). But, the acid of AC was not strong enough to form DMM_n [94]. So, the acidic titanium sulfate was used to modify the carbon material to improve the acidity of the catalyst. A series of carbon material catalysts modified with titanium sulfate were prepared by impregnation [86,94,95]. For 40% Ti(SO₄)₂/CNT the selectivity of DMM, DMM₂ was 63.6% and 0.4% respectively. In order to further explore the formation mechanism of DMM₂, the different feedstock was explored. the selectivity of DMM₂ was further improved to 89.4% under new ratio of feedstock (DME: DMM: O₂ = 1:1.2:1.3). It is not difficult to find that DMM is the intermediate of DMM₂ synthe-

Table 2
Catalysts for DME oxidation.

Catalysts	Temperature/K	WHSV /h ⁻¹	DME Cov./%	Selectivity/%								
				DMM	DMM ₂	DMM ₃	FA	MF	CH ₃ OH	CO _x	C _x H _x	Ref.
H ₃ PW ₁₂ O ₄₀ (40%)/SiO ₂	633	360	49.00	1.30	0.00	0.00	6.60	0.40	23.8	65.60	2.3	[84]
K _{2.5} H _{0.5} PW ₁₂ O ₄₀ (40%)/SiO ₂	633	360	37.20	2.50	0.00	0.00	2.40	2.40	12.50	63.80	3.4	[84]
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ (40%)/SiO ₂	633	360	20.00	34.80	0.00	0.00	5.30	1.60	16.60	38.60	3.1	[84]
MnCl ₂ (5%(mass))-H ₄ SiW ₁₂ O ₄₀ /SiO ₂	593	360	8.60	39.10	0.00	0.00	8.50	9.30	33.00	6.60	3.6	[85]
MnCl ₂ (5%(mass))-H ₃ PMo ₁₂ O ₄₀ /SiO ₂	593	360	52.00	0.00	0.00	0.00	7.80	5.20	10.50	73.20	3.3	[85]
MnCl ₂ (5%(mass))-H ₃ PW ₁₂ O ₄₀ /SiO ₂	593	360	14.90	12.00	0.00	0.00	15.20	9.60	28.90	33.40	0.9	[85]
Mn-SiW ₁₂ /SiO ₂	593	360	9.40	36.30	0.00	0.00	8.40	5.40	31.20	15.20	3.5	[80]
Mn-(1%Sm + SiW ₁₂)/SiO ₂	593	360	9.50	60.30	0.00	0.00	2.30	5.20	6.30	22.60	3.30	[80]
5%Re–20%PW ₁₂ /TiO ₂	513	3600	3.10	42.20	3.70	0.00	33.60	2.90	6.90	9.70	1.00	[83]
Re/ CNTs	513	1800	4.20	6.20	0.00	0.00	73.70	3.50	16.20	0.00	0.00	[86]
5%Re–30%PW ₁₂ O ₄₀ /CNTs	513	1800	8.90	55.00	4.00	0.00	31.40	5.40	4.20	0.00	0.00	[86]
40%Ti(SO ₄) ₂ /CNTs	513	3600	3.80	63.60	0.40	0.00	2.40	0.00	33.60	0.00	0.00	[87]
AC	513	3600	6.80	0.00	0.00	0.00	45.80	0.00	54.20	0.00	0.00	[88]
30%Ti(SO ₄) ₂ /G	513	3600	7.20	0.00	0.00	0.00	18.40	0.00	81.60	0.00	0.00	[88]
30%Ti(SO ₄) ₂ /AC	513	3600	8.40	77.50	6.8	0.00	8.80	0.00	6.90	0.00	0.00	[88]
30%Ti(SO ₄) ₂ /PC-H ₂ SO ₄	513	3600	9.70	89.10	7.60	0.00	0.40	0.00	2.90	0.00	0.00	[89]
10%V ₂ O ₅ /H-beta-673 K	503	3600	12.00	55.40	12.20	0.00	0.00	6.60	25.80	0.00	0.00	[90]
10%V ₂ O ₅ /H-beta-773 K	503	3600	10.50	49.90	21.60	1.60	0.10	3.20	23.60	0.00	0.00	[90]
10%V ₂ O ₅ /H-beta-823 K	503	3600	9.20	52.10	22.10	0.00	0.00	0.60	25.20	0.00	0.00	[90]
10%V ₂ O ₅ /H-beta-873 K	503	3600	9.40	73.50	3.60	0.00	0.00	3.60	19.3	0.00	0.00	[90]
10%V ₂ O ₅ /H-MOR	503	3600	14.40	37.40	20.40	2.20	3.20	4.20	12.10	20.4	0.00	[91]
10%V ₂ O ₅ /mm-H-MOR	503	3600	11.20	49.00	22.00	1.50	0.80	6.10	11.30	9.40	0.00	[91]
10%V ₂ O ₅ /deAlmm-H-MOR	503	3600	10.60	50.10	26.80	1.30	0.40	6.80	14.70	0.00	0.00	[91]

sis from DME oxidation. Among those catalysts, the performance of 30% $\text{Ti}(\text{SO}_4)_2/\text{PC}-\text{H}_2\text{SO}_4$ was best with the selectivity of DMM, DMM₂ were 89.1% and 7.6% respectively. PC has a large number of microporous structures, which can make $\text{Ti}(\text{SO}_4)_2$ better dispersed on the surface of the support and improve the activity of the catalyst.

Additionally, the structure, surface properties and morphology were further explored by different characterizations. Take $\text{Ti}(\text{SO}_4)_2/\text{CNT}$ as an example, the results of XRD showed that $\text{Ti}(\text{SO}_4)_2$ could be well dispersed on the surface of CNT calcinated at 240 °C. Besides, the number of catalyst weak acid sites is most (though $\text{NH}_3\text{-TPD}$) when the content of SO_4^{2-} is 40%, which is the reason that the performance of 40% $\text{Ti}(\text{SO}_4)_2/\text{CNT}$ is best. On the other hand, the modification of titanium sulfate also affects the oxidation of carbon materials. Introduction of $\text{Ti}(\text{SO}_4)_2$ improved the activation ability of CNT to oxygen, and the O_2 on the surface of adsorbed CNTs was not completely desorbed, part of them might become oxygen group on the surface of CNTs though results of oxygen temperature-programmed desorption mass spectrometry ($\text{O}_2\text{-TPD-MS}$). DME-TPRS-MS was used to explore specific oxidation sites, CH_3OH , MF, FA and DMM is detected without O_2 introduced in reaction system, which proved that oxygen-containing functional groups on the surface of the carbon material participate in the reaction. So, oxygen group located at the surface defect plays an important role in this the process of DME oxidation. In summary, oxygen group located at the surface of the carbon material provided oxidation sites for the reaction, while $\text{Ti}(\text{SO}_4)_2$ provided acid sites.

4.2.3. Zeolite-supported catalyst

Based on the above results, it is not difficult to find that weak acid sites and oxide sites play an important role in the formation of DMM_n, but the role of acid site type is still unclear. Bifunction catalysts H-beta zeolite supported vanadium oxide catalysts were prepared at different calcination temperature to evaluate the reaction of oxidation of DME [87]. Different calcination temperatures affect the VO_x species on the support, as described in Section 2.2.1. The vanadium oxides can be well dispersed on the support in an amorphous state with the calcination temperature below 923 K. XPS results showed that V^{5+} and V^{4+} coexisted on the surface of catalysts. Additionally, the number of V^{4+} of catalysts calcinated at 673 K and 773 K were more than that of catalysts at higher calcination temperature, which could increase the number of oxygen vacancies and improve the oxidation capacity of the catalyst [58]. The oxidation of catalyst mainly affects the conversion of DME, which is similar to the process of methanol oxidation. In addition, with the increase of heat treatment temperature, the ratio of B/L acid sites gradually increased, and the selectivity of DMM_n increased from 67.6% to 77.1%. In addition, the selectivity of DMM_n is linearly related to the ratio of B/L acid sites. Moreover, the introduction of vanadium oxides reduced the acid strength, which may be due to the interaction of dispersed vanadium oxide and hydroxyl groups of H-beta zeolite. For 10% $\text{V}_2\text{O}_5/\text{H}\beta$, the conversion of DME is 10.5%, and the selectivity of DMM, DMM₂ and DMM₃ was 49.9%, 21.6% and 1.6%, respectively (Table 1, row 18). It is noteworthy that this is the first report on the formation of DMM₃ during the oxidation of DME. The results of $\text{NH}_3\text{-TPD}$ may give the reason, more strong acid sites of 10% $\text{V}_2\text{O}_5/\text{H-beta-773 K}$ were conducive to promoting the rupture of C—O, thus promoting the chain growth of DMM_n.

On the other hand, a series of H-MOR with different pore structures were prepared as supports to explore the effect of pore structure on catalyst [89]. H-MOR treated with an alkali solution is denoted as mm-H-MOR, and mm-H-MOR further treated with an acid solution is denoted as deAlmm-H-MOR. Compared with 10%

$\text{V}_2\text{O}_5/\text{H-MOR}$, the selection of 10% $\text{V}_2\text{O}_5/\text{deAlmm-H-MOR}$ significantly increased the selectivity of DMM_n from 60.0% to 78.2%, while the selectivity of CO decreased to zero (Table 2, row 21 to row 23). For 10% $\text{V}_2\text{O}_5/\text{H-MOR}$, the presence of eight-membered rings ($0.26 \times 0.57 \text{ nm}$) channels in H-MOR seriously hindered the diffusion of reactants and products, resulting in the formation of more by-products, which is consistent with the research of other literatures [90,96]. More mesoporous of 10% $\text{V}_2\text{O}_5/\text{mm-H-MOR}$ was beneficial to the dispersion of vanadium oxide species. In addition, larger porous size promotes the diffusion of products and intermediates, which is conducive to the subsequent reaction. These may be the reasons that the selectivity of DMM_n improves from 60.0% to 72.5%. The acid treatment of mm-H-MOR can remove extra-framework Al species in the channel, and further improve the mesoporous volume of the catalyst. The larger porous diameter and volume of 10% $\text{V}_2\text{O}_5/\text{deAlmm-H-MOR}$ allow the selectivity of DMM_n to increase 72.5% to 78.2%.

5. Synthesis of DMM via CO_x Direct Hydrogenation in Methanol

5.1. Mechanism of CO_x direct hydrogenation in methanol

Direct synthesis of DMM using CO_x and H_2 is a sustainable development path, conforming to the principle of carbon neutrality and reducing dependence on fossil fuels. For this reaction, the key step is the hydrogenation of CO_x to the intermediate FA. There are only a few literatures on this reaction, and two possible pathways are proposed, as showed as Fig. 6. For the two pathways, the first step of the reaction both is CO_x hydrogenation to formaldehyde over the hydrogenation. And the last step is the same too, which is that methanol reacts with hemiacetal on the acid site to form DMM. The process from formaldehyde to the next intermediate hemiacetal can be divided into two ways. The first is that formaldehyde first changes to MF, and then the MF reacts with hydrogen to form hemiacetal. The other pathway is that methanol reacts with the formed formaldehyde to generate hemiacetal.

5.2. Catalysts of CO_x direct hydrogenation in methanol

The reaction of CO_x direct hydrogenation in methanol is usually carried out in autoclave reactor. As early as 2003, Vlasenko *et al.* [91] directly synthesized DMM via syngas using Cu/Pd/Ps (60) zeolite catalyst which provided an argument for CO hydrogenation synthesis of DMM. Bahmanpour *et al.* [97,98] demonstrated the synthesis of formaldehyde by hydrogenation of carbon monoxide in water and methanol under the catalysis of $\text{Ru-Ni/Al}_2\text{O}_3$. In methanol medium, the generated FA was stabilized as hemiacetal, which could react with methanol to form DMM over acid site. What's more, the hemiacetal produced by CO can react with methanol to form DMM under the catalysis of acid catalyst [98]. On the other hand, CO_2 hydrogenation is easier to methanol and formic acid because of their thermodynamic advantages. Consequently, the method that CO_2 hydrogenation to formic acid and its esterification with methanol to form methyl formate as intermediate is a favorable way. The catalysts used in this reaction are mainly divided into homogeneous and heterogeneous catalysts. Next, we will introduce these two types of catalysts in detail.

5.2.1. Homogeneous catalysts

In 2016, Thenert *et al.* [88] firstly reported the method of synthesis DMM via CO_2 hydrogenation in methanol. In this work, the multifunctional catalysts include ruthenium catalyst for hydrogenation step and acid co-catalysts for esterification and acetalization steps. More specifically, the ruthenium catalyst was [Ru

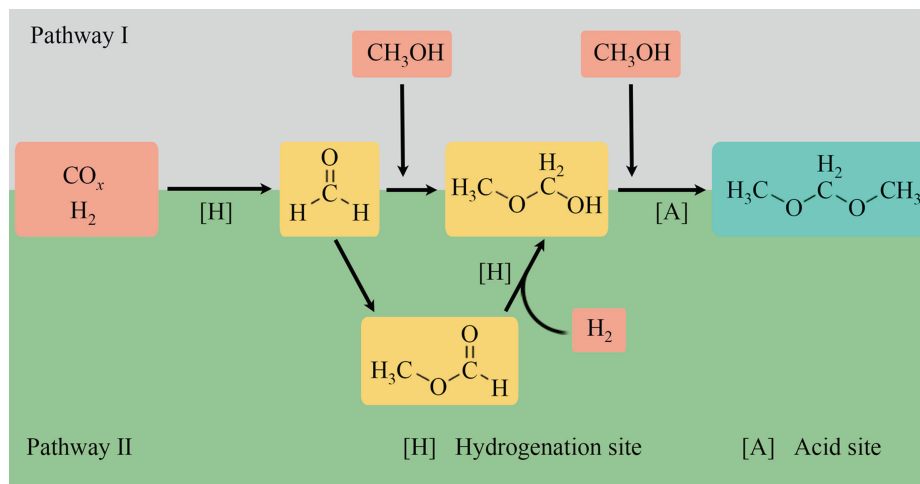


Fig. 6. Mechanism of CO_x direct hydrogenation in methanol.

(Triphos)(TMM)], [Triphos = 1,1,1-Tris-(Diphenylphosphino methyl) ethane, TMM = trimethylene methane] and acid co-catalysts were trifluoromethanesulfonylimide (HNTf_2) and $\text{Al}(\text{OTf})_3$. Firstly, they explored the synergistic effect of co-catalysts with $[\text{Ru}(\text{Triphos})(\text{TMM})]$ and founded that $\text{Al}(\text{OTf})_3$ expressed the better performance. Temperature also had a great influence on the experiment. When the temperature exceeded 100°C , the yield of DMM decreased, probably because the excessively high temperature would lead to the generation of MF and DME. In addition, the concentration of $[\text{Ru}(\text{triphos})(\text{TMM})]$ and $\text{Al}(\text{OTf})_3$ were also investigated. In the combination of $6.0\ \mu\text{mol}$ $[\text{Ru}(\text{triphos})(\text{TMM})]$ and $25\ \mu\text{mol}$ $\text{Al}(\text{OTf})_3$, the yield of DMM is the highest with a turnover number (TOF) of 214 at 80°C . Nonlabeled CO_2 , H_2 and labeled methanol ($^{13}\text{CD}_3\text{OD}$) were used in this experiment to explore the reaction mechanism. Only $^{13}\text{CD}_3\text{OCOCH}_3$, $^{13}\text{CD}_3\text{OCH}_2\text{OH}$ and $^{13}\text{CD}_3\text{OCH}_2\text{O}^{13}\text{CD}_3$ were detected, which demonstrated the hypothesis that CO_2 was successively hydrogenated to DMM through intermediate MF and hemiacetal as shown as Fig. 7. More recently, Trapp *et al.* [99] prepared the catalyst (ruthenium/*N*-triphos/ $\text{Al}(\text{OTf})_3$) and optimized the reaction conditions for CO_2 hydrogenation in methanol to obtain DMM and MF. In this work, the influence of reaction conditions on temperature, H_2 and CO_2 partial pressures, reaction time, additives, catalysts and Lewis acid concentration was studied. Finally, the TOF of DMM was 786 under optimized reaction conditions [99]. In 2017, non-noble metal catalysts were applied to hydrogenation of CO_2 in methanol to form DMM [100]. The authors found that $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was the most active precursor combined with triphos ligand and the acidic catalyst

HNTf_2 for hydrogenation of DMM using MF as substrate with a TOF of 373. Subsequently, the same catalyst system was used for the CO_2 -based reaction with a TOF 92 for DMM at 100°C and a partial pressure H_2/CO_2 of 6/2 MPa. In addition, the influence of other triphos ligand on the reaction was also explored. The TOF of DMM was up to 157 with the triphos^{Tol} (1,1,1-tris(bis(4-methylphenyl phosphino) methyl) ethane) used as the ligand, which was comparable to the activity of noble metal Ru based catalyst.

5.2.2. Heterogeneous catalysts

Heterogeneous catalysts attracted more attention because they were easier to separate from the reaction system. Based on their previous work, Ahmad *et al.* [101] loaded Ru, Ru-Ni and Ru-Cu on were supported on H-ZSM-5 and H β by impregnation method to explore the performance for the hydrogenation of CO in methanol to synthesis DMM. Although the yields of 1%Ru/H β and 1%Ru/H-ZSM-5 were almost identical, the former had a higher initial reaction rate and used shorter time to reach equilibrium. The low initial reaction rate of 1%Ru/H-ZSM-5 might be due to the higher acidity of H-ZSM-5, leading to a higher rate of competitive reactions, such as the dehydration of formaldehyde to methyl ether. The introduction of Ni and Cu could improve the performance of catalysts, with DMM yield of Ru-Ni/H β and Cu-Ru/H β was $5.11\ \text{mmol} \cdot (\text{g cat})^{-1} \cdot (\text{L methanol})^{-1}$ at $393\ \text{K}$ and $5.34\ \text{mmol} \cdot (\text{g cat})^{-1} \cdot (\text{L methanol})^{-1}$ at $323\ \text{K}$, respectively. Although, the yields of these two catalysts were almost same, the lower temperature was needed for Ru-Ni/H β catalysts. In addition, for Ru-Ni/H β , the initial reaction rate increased with reaction temperature, indicating that the initial reaction rate is limited by kinetics, and the higher initial reaction rate may be related to the better activation of hydrogen by Ni. However, the DMM yield of Cu-Ru/H β catalyst decreased with increasing temperature, which may be attributed to the decomposition of FA on Cu at higher temperature.

Later, the same group compared the performance of different materials (CO and CO_2) in the synthesis of DMM over 3%Ru/H β catalyst [102]. When CO_2 as a raw material, the highest yield of DMM and DMM₂ were 7.42 and $2.13\ \text{mmol} \cdot \text{g}^{-1} \cdot \text{L}^{-1}$, respectively, at 150°C , $7.5\ \text{MPa}$ and H_2/CO_2 molar ratio of 3. In order to validate reaction pathway, CO_2 and deuterated CD_3OCD_3 were used to explore the reaction pathway. Intermediates CHOOH and deuterated dimethoxymethane dimethyl ether $\text{CD}_3\text{OCH}_2\text{OCD}_3$ were detected. Based on the above findings, the authors proposed the following reaction path, as shown in the Fig. 8. However, Thenert *et al.* [88] proposed a reaction path in which CO_2 first hydrogenated to generate MF intermediate in CH_3OH , and then MF is hydro-

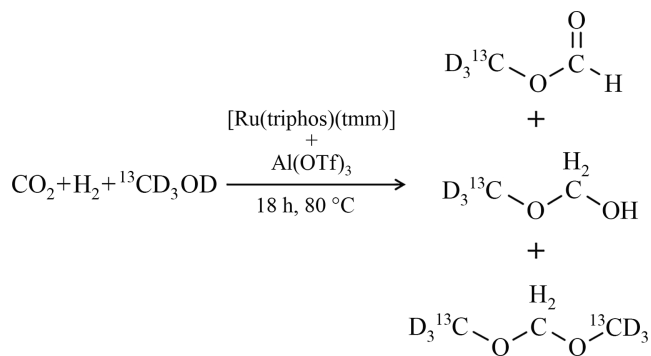


Fig. 7. Isotopic labeling observed by NMR spectroscopy for the synthesis of DMM from $^{13}\text{CD}_3\text{OD}$.

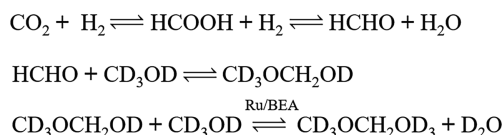


Fig. 8. Proposed reaction pathway [102].

generated to methoxy methanol. Finally, methoxy methanol reacted with methanol to generate DMM. To verify which path is dominant, two groups of experiments were conducted with paraformaldehyde (PF) which decomposed to form a lot of FA and MF as raw materials respectively. The DMM yield of the experiment using PF as feedstocks was much higher than that of the experiment using MF as raw material. So, the reaction path with formaldehyde as intermediate was dominant. In addition, the effect of catalyst pore size on the reaction was also explored [103]. Compared to commercial zeolite beta (CBEA) and desilicated zeolite beta (HBZDS), hierarchical zeolite beta (HBEASX, synthesized with steam assisted conversion) has better performance due to the largest pore size.

6. Conclusions and Outlook

Due to the high energy consumption and complex operation in the typical synthesis process, four state-of-the-art one-step direct synthetic routes of DMM, including two upgrading routes (methanol direct oxidation and methanol direct dehydrogenation) and two green routes (diethyl ether direct oxidation and carbon oxides direct hydrogenation) are summarized in this review. In the four processes, the methanol oxidation pathway is considered as the efficient technology to replace the typical routes because of the superior conversion and selectivity (both more than 90 %). However, high produced water increases the separation cost of DMM and limits stability of catalysts. To decrease the water content, another upgrading route is also developed with the only reactant methanol. Limited by the equilibrium of reaction, low conversion of methanol and selectivity of DMM inhibit the development of this route. For other two novel methods, although these routes are green and competitive route with good atomic economy, low performances of the catalysts still make the corresponding researches at the experimental stage.

In terms of the prospective of direct routes in the synthesis of DMM, we propose the following focuses to improve the possibility for industrial application:

(1) High-performance catalyst design. For both four direct routes, the catalysts suffer from the practical application problems. The catalysts in methanol direct oxidation need to maintain superior water resistance with the while still keeping the high conversion and selectivity. For example, through surface structure engineering, decreasing the water wettability around the active sites might be an efficient way to rapidly move the produced water molecules. As for other three routes, finding and designing the suitable catalysts are the key to enhance the catalytic performances. It is known that both dual sites play important role in the reaction systems. How to balance and achieve the oriented design of the dual sites is worth researchers to think about based on the relationship between reaction and active sites.

(2) Reactor design. For methanol direct dehydrogenation, limited by the equilibrium of reaction, the maximum efficiency in this system is still lower than other routes. To improve the practical efficiency, whether this equilibrium can be break out *via* reactor design. In this system, hydrogen is also produced as the second energy if it can be used. There is an idea to try to move produced hydrogen out the system, which breaks the equilibrium and

reduces the separation cost of hydrogen. For instance, membrane reactor might be suitably combined with this system.

(3) Mechanism determination. For both two green routes, more than one reaction mechanism is proposed in the reaction. So it is a meaningful work to determine what happens on the catalyst surface. In this part, theoretical calculation and *in situ* characterization can be combined to advance the mechanism powerful. Density functional theory (DFT) can reveal the interactions between catalyst surface and reactant molecules through comparing adsorption energy and possible pathway *via* analyzing the reaction barrier at transient state calculation. *In situ* fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) are also established and employed to investigate the surface properties of catalyst in the whole reaction process. The clear mechanism for every route is beneficial to design high-performance catalysts, thus enhancing the possibility of practical application.

Data Availability

No data was used for the research described in the article.

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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