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The effect of titanium dioxide on catalysis Performance, process conceptual design and evaluation

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ABSTRACT

The one-step methanol oxidation to dimethoxymethane (DMM) is a promising method for value-added chemical synthesis. However, vanadium cerium (VCe) catalysts commonly exhibit insufficient DMM selectivity in spite of its moderate high-temperature methanol conversion. In this work, titanium dioxide (TiO_2) with relatively strong acidity was introduced into VCe catalyst to improve the catalysis performance of VCe. The results showed that the addition of TiO_2 enhanced the oxidation reduction and surface acidity of the catalyst, and effectively improved the selectivity and yield of DMM. Furthermore, a scaled-up conceptual process for the one-step oxidation of methanol to DMM was explored, designed and economically evaluated based on the TiO_2 modified catalysts. The entire conceptual process featured that multiple condensation-separation/absorption units offered a complete collection of the DMM. Through the optimization of the process, the generated products and unreacted methanol can be directly stripped from N_2 and O_2, and complete separation of DMM-methanol azeotrope was achieved with only one vacuum distillation unit. The entire process at what catalysis performance (methanol conversion, DMM selectivity, etc.) could bring profit was revealed and discussed. This study emphasizes the interaction between catalyst design, conceptual process design and economic evaluation, providing new ideas for the development of efficient industrial catalysts.

Introduction

Methanol, as one of the most important chemical feedstock, has exhibited excess production capacity with quite low price globally in recent decades. Methanol has been used in producing industrial chemical products such as formaldehyde (FA), methyl formate (MF) and acetic acid. Recent decades, emerging chemicals like dimethoxymethane (DMM) from methanol gains increasing attention. Dimethoxymethane (DMM), conventionally called methylal, is an important intermediate extensively used in many fields, including aerosols, pharmaceuticals, polymers, adhesives, and insecticides [1–5]. The conversion of methanol to value-added DMM becomes a hot issue.

There are mainly two catalytic routes for the conversion of methanol

to DMM. One approach is the indirect synthesis of DMM, which involves the reaction of methanol with formaldehyde (FA) or paraformaldehyde in the presence of a catalyst. This process occurs in two consecutive steps. First, FA is synthesized either through methanol oxidation over iron molybdate or methanol dehydrogenation over a silver (Ag) catalyst. In the second step, DMM is produced via the acetalization of FA and methanol. However, the acetalization is a reversible reaction [6], in which the reaction rate slows down and DMM yield is restricted as approaching equilibrium. To overcome these limitations, in-site removal of DMM by reactive distillation [5–8] has been proposed. During this process, a minimum-boiling azeotrope composed of 92.2/7.8 wt% DMM/MeOH is formed [9], necessitating further purification steps such as extractive or pressure-swing distillations [9–13] to obtain pure DMM.

However, this indirect catalytic process encounters several problems, such as intricate post-processing of the products, high costs, equipment corrosion, and environmental pollution caused by the acidic catalyst [14]. Hence, the one-step direct oxidation of methanol to DMM has gained increasing attention due to its simplicity and environmental benign. The direct route integrates methanol-to-FA reaction (first step) with the subsequent reaction of FA and methanol to DMM (second step) into one step and requires a bi-functional catalyst with both acidic and redox properties. However, design and preparation of such a catalyst, carefully balancing acidity and redox sites, remains a challenge in achieving efficient one-step DMM synthesis.

The catalysts for the one-step methanol-to-DMM process mainly involve rhenium (Re) [15,16], amorphous oxide [17], iron-molybdenum (FeMo) [18–20], vanadium (V) [21–23], Al-P-V-O [24], heteropolyacid [25], et al. In 2000 and 2002, Yuan et al [15,16] gained marked progress in designing $SbRe_2O_6$ and Re-based supported catalysts which achieved methanol conversion of 15 ~ 49 % and DMM selectivity of 88 ~ 94 % at 573 K and 1 atm with a feed composition of $He/O_2/CH_3OH = 86.3/9.7/4.0$ vol%. However, the temperature instability and the scarcity of the Re limits its industrial application in spite of its high catalysis performance. In 2008, Royer et al [17] prepared amorphous oxide catalyst which exhibited methanol conversion of 63 % and DMM selectivity of 89.2 % and achieved a fairly high space–time yield (STY) of 1 kg DMM h^{-1} kgcat^{-1} at 533 K, atmosphere, and GHSV (gas hourly space velocity) = 22,000 mL h^{-1} gcat^{-1}. Thereafter, Gornay et al. [18] adapted the FeMo catalyst conventionally used for MeOH-to-FA process to the one-step MeOH-to-DMM. With a methanol-rich feed instead of methanol-lean one, the conventional FeMo catalyst exhibited 59.9 % methanol conversion and 89.7 % DMM selectivity at 553 K with the highest STY around 4.6 kg DMM h^{-1} kgcat^{-1} at that time. Low reaction temperature is favorable for the DMM synthesis since methanol oxidation to DMM is an exothermic reaction, and therefore the catalyst turns to V/Ti-based system for their low-temperature activity. In 2010, Zhao et al. [23] prepared a series of V_2O_5-TiO_2/SO_4^{2-} catalyst using co-precipitation method, of which the optimized one presented 74 % methanol conversion and 83 % DMM selectivity at 403 K and atmospheric pressure. Chen et al [21] obtained a relatively high methanol conversion and DMM selectivity using impregnation method; And they [24] also designed mesoporous Al-P-V-O catalysts and obtained controllable acidity and redox degrees via adjusting Al/P/V ratio. In 2015, Wang et al prepared V_2O_5/TiO_2-Al_2O_3 catalyst using sol–gel method, which had the best catalysis activity at that time with methanol conversion of 48.9 % and DMM selectivity of 89.9 %.

From the reviews above, it can be concluded that the low-temperature instability and scarcity of the Re limit its progress. Heteropolyacid commonly possesses strong acidity, resulting in high DME selectivity, meanwhile, heteropolyacid has low specific surface area and can be easily dissolved in polar solvent, but suffers of recycle difficulty. The FeMo catalyst presents good reactivity with the highest STY at least in the open literatures, but it requires relatively high temperature and its stability for this reaction has not been fully demonstrated. The vanadium-based catalysts exhibit low-temperature activity, which is favorable for the exothermic DMM synthesis. Meanwhile, it has also been recognized that methyl formate (MF) is less harmful to the environment and owns a higher market price compared with FA. Therefore, the production of DMM with MF as a co-product is highly desirable. However, most of the above-mentioned vanadium-based modified catalysts have yielded significant amounts of dimethyl ether (DME), despite achieving relatively high methanol conversion and DMM selectivity. Hence, the DMM synthesis accompanying with MF co-product but without DME is the focus of this work.

Moreover, vanadium suffers from relatively low stability and a small specific surface area, which hinder its usage as support. Our previous study [26] revealed that the Vanadium-Cerium (VCe) catalysts offers a relatively high DMM selectivity without the formation of DME. However, the DMM selectivity is insufficient high, which is mainly because of the relatively weak acidity of the V-Ce catalyst. Hence, it is desirable to introduce TiO_2 to enhance acidity, which would increase DMM selectivity.

Besides the catalyst research, conceptual process design and evaluation based on lab-scale catalytic performance are rarely reported. We have studied the effect of TiO_2 on the Vanadium-Cerium catalysis performance, and successfully synthesized two types of concentrated products in the reactor effluent: DMM/MF/CO$_x$, or even DMM/CO$_x$ along. From the standpoint of process engineering, this concentrated selectivity with low methanol conversion commonly offers process economic advantage. However, this raises the questions of whether such catalysis performance and what catalytic metrics—with high DMM selectivity but low methanol conversion—can yield profitability. Addressing this requires ongoing process design and evaluation to inform further catalyst development. Unfortunately, to avoid the explosion limit and alleviate the oxidation effect, there commonly exists so excessive oxygen (O_2) and methanol (MeOH) unreacted and inert nitrogen (N_2) that a stream with only dilute DMM and much unreacted methanol in the reactor effluent is obtained, and that a large amount of gas needs to be recycled. Meanwhile, a complete separation of dilute DMM from a stream containing large amounts of oxygen and nitrogen presents challenge. Additionally, DMM and methanol form a minimum azeotrope with 92.20 wt% DMM at atmospheric pressure, making conventional distillation unsuitable for this separation.

Focusing on these two challenges, Cai et al. [27] explored the process integration of the one-step oxidation of methanol-to-DMM. However, the presence of numerous co-products, including formaldehyde (FA), and dimethyl ether (DME), significantly increased the separation difficulty, potentially leading to higher capital investment and operating costs, despite a high total yield of DMM and MF at 80.2 %. Nevertheless, the methanol absorption technique proposed by Cai et al. [27] for completely washing down the formed DMM still an effective method, which should be applied for solving the problem one. To address the second problem of the separation of DMM and methanol, Wang, Yu, Xia and Xu [11–13,28] developed the extractive distillation using DMF as a heavy entrainer, the pressure-swing distillation, and the novel extractive dividing-wall column also with the DMF entrainer. However, these works mainly related the so-called special distillation, and two-column sequence or complex column is commonly required, resulting in high capital investment costs or control/operation difficulty. Recently, Xia [29] proposed a pinch zone analysis method for the quantification of the pressure-sensitive system, which justifies the feasibility of one-column distillation that should simplify the process. Hence, the basis of process design and development is now in place, which is significant and necessary to guide the catalyst design and development.

In this work, to improve the VCe-based catalysis performance, a serial of catalysts with various Ti contents in ($TiO_2 + CeO_2$) (0, 25, 50, 75 and 100 wt%) were firstly prepared in details. The effect of Ti addition on the reactivity is investigated. Furthermore, taking the effluent of the reactor with good experimental prospect as the research object, the entire conceptual process of one-step oxidation of methanol to DMM was conceptually designed and evaluated for five cases of only DMM and CO$_x$ and DMM/MF/CO$_x$ products. Furthermore, with fictitious catalysis performance postulated by changing methanol conversion and maintaining a relative high DMM selectivity (~90 %), the question at what methanol conversion this technology can bring benefit is well answered. The rough but meaningful economic evaluations of the methanol to DMM process light the way towards the industrial catalyst design.

Experiments and simulations

Catalyst preparation

All the catalysts were prepared by using sol–gel method, with a brief procedure stated below [26]. The preparation process of 15 wt%V/CeO$_2$ was as follows: (i)1.29 g NH$_4$VO$_3$ and 1.47 g citric acidic solution were

added to 100 mL distilled water, and then heated and stirred until NH_4VO_3 was completely dissolved, denoted as S1; (ii)14.31 g Ce $(NO_3)_3 6H_2O$ and 4.41 g citric acid solution were added to 100 mL distilled water to obtain S2. The two solutions were uniformly mixed, and then diluted with 300 mL distilled water, denoted as S3. The S3 was kept at 60 ℃ for around 48 h, gelatinous solution was formed, which was dried at 120 ℃ for 12 h and roasted at 400 ℃ for 4 h. The various V_2O_5 mass content (5, 10, 15, 20, and 30 wt%) in the preparation corresponded to catalysts 5VCe, 10VCe, 15VCe, 20VCe, and 30VCe. The 15VCe catalyst would be modified via introducing TiO_2 because of its relative high DMM selectivity but relatively low methanol conversion, as revealed previously [26]. The Ti-modified catalyst was prepared by the same method except that a certain amount of tetrabutyl titanate(TBT) was added to S2, and anhydrous ethanol was used instead of solvent distilled water. The various mass content of TiO_2 (0, 25, 50, 75, and 100 wt%) in the TiO_2 and CeO_2 mixture corresponded to the catalysts VCe, VCe$_{0.75}$Ti$_{0.25}$, VCe$_{0.50}$Ti$_{0.50}$, VCe$_{0.25}$Ti$_{0.75}$, and VTi.

Evaluation apparatus

The methanol oxidation reaction occurred in a fixed-bed reactor with 5-mm inner diameter. The loading of the catalyst with 20–40 mesh was 1 mL, with an identical volume of fine quartz sand diluted for avoiding sintering due to the super heat caused by high exothermicity. Prior to reaction, the catalyst should be activated at 673 K in 10/90 vol% O_2/Ar (80 mL/min). Methanol feed supplied from a metering pump was firstly mixed with a stream of 10/90 vol% O_2/Ar, which was heated and vaporized at 373 K in a heating unit, and then fed to the reactor. The methanol flow rate was 1.95 mL/h, and the feed composition was maintained as Ar: O_2: CH_3OH = 84.02:9.33:6.63 vol%, and thus WHSV of methanol was 1.542 g/mLcat/h. Hence, total feed WHSV was 16280 h^{-1}. The reactor effluent were analyzed by on-line gas chromatography (GC-950) using a Propack T column and a TDX-01 column connected to TCD detector and FID detector, respectively (Fig. 1). The generated products including formaldehyde (FA), dimethyl ether (DME), methyl formate (MF), dimethoxymethane (DMM), water (H_2O) and the unreacted methanol (CH_3OH) were fed to a Propack T column connected to TCD detector. The generated CO and CO_2, converted to methane (CH_4) by a reformer, was fed to a TDX-01 column and then detected by FID.

Fundamentals of process development

Thermodynamic methods

It is of vital importance to select a suitable thermodynamic method to describe this system precisely and accurately. The non-random two-liquid (NRTL) method are mainly utilized to describe the vapor–liquid equilibrium since almost all the components in this system are common. The nitrogen, oxygen, and carbon dioxide in this system are considered as the Henry's components, with the Henry's constant retrieved from Aspen Plus (Table S1, SI). Several comparisons of T-xy vapor–liquid equilibrium of methanol and DMM from the experimental by Albert [30], Dong[31] and the simulated datum is made, which have $|\Delta y|$ of 0.029 and $|\Delta T|$ of 1.09 K below, suggesting the capability of NRTL method (Table S2 and Fig. S2, SI).

Economic basis

Since this work aims to conduct process economic evaluation for offering useful guideline to the catalyst improvement, the evaluation criteria roughly considers operation cost related to the intrinsic process, and the marketing factor involving products value and feedstock costs. Thus, the profit for the scale-up project of this technology can be estimated as below,

$$\text{Profit} = \text{Products Value} - \text{Feedstock Costs} - \text{Operating Cost} \tag{1}$$

In which the unit of all the variables above is in USD/h or RMB/h, and the profit indicates the static economic index for preliminary comparison. Products Value in the project is the summation of DMM and
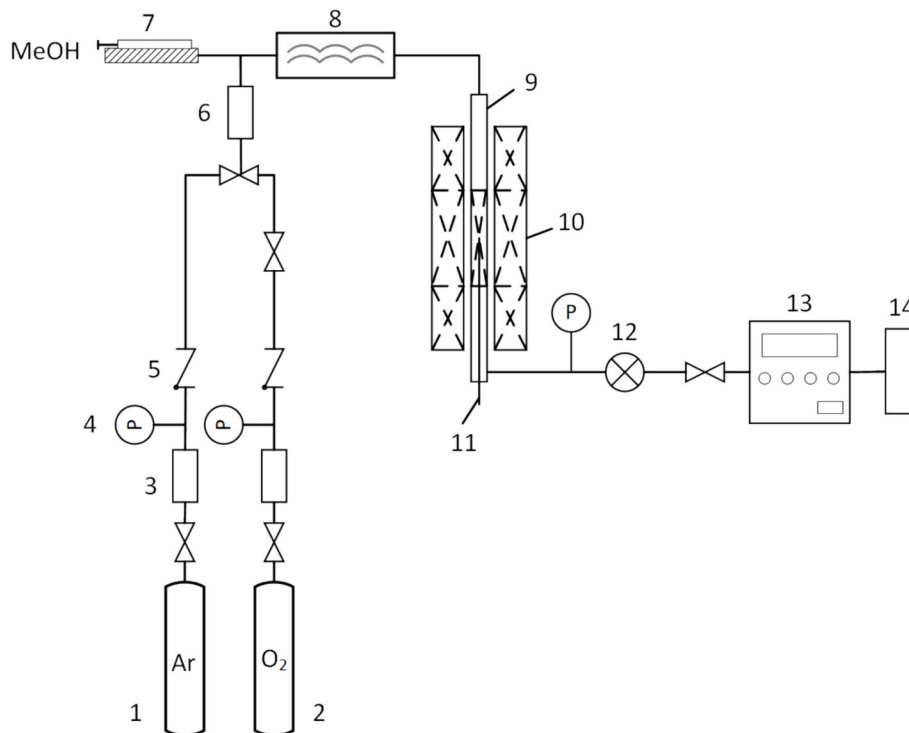

Fig. 1. Schematic apparatus for methanol oxidation reaction: (1)Ar cylinders, (2) O_2 cylinders, (3)filter, (4)pressure gauge, (5)check value, (6)mass flowmeter, (7) metering pump, (8) evaporator, (9) reactor, (10) three-zone heater, (11) thermocouple, (12) system pressure regulator, (13) gas chromatography, (14) foam flowmeter.

MF values, in which each value can be estimated by the product marketing price (Table S3, SI) multiplies its production. Feedstock Costs in the project is the summation of methanol, oxygen, and nitrogen costs, in which each value can be estimated by the feedstock marketing price (Table S4, SI) multiplies the corresponding consumption. Operating Cost in the project mainly involves steam, electricity, refrigeration including chilled water (Table S5, SI). The costs is the summation of the feedstock costs and the operating costs. Herein, cooling water costs is neglected since it is much inexpensive compared with refrigeration.

Results and discussions

Catalyst performance analysis

Catalyst characterization

Fig. 2 presented a Raman spectra of the Ti-modified VCe catalyst, in which there existed a typical Raman shift of CeO_2 at 457 cm^{-1}. As the content of TiO_2 increased, the intensity of the CeO_2 peak became weak while the typical Raman shift of anatase TiO_2 appeared at 152, 395, 510, and 635 cm^{-1}. Additionally, a peak of aggregated VO_x at 1010 cm^{-1} observed on all the catalysts indicated that the increase in TiO_2 content almost had no influence on the state of the vanadium oxide.

Temperature programmed reduction (TPR) was an useful technique to probe the reducibility of metal oxides. The H_2-TPR spectra of the catalyst was given in Fig. 3. On the VCe catalyst there existed two reduction peak at 723 and 908 K, representing the reductions of the surface vanadium species and the bulk-phase CeO_2, respectively. With the addition of TiO_2, the low-temperature reduction peak shifted toward lower temperature, suggesting that the redox capacity of the vanadium oxide was enhanced on the VCe_xTi_y catalysts. Meanwhile, as the TiO_2 content increased, the high-temperature reduction peak of the modified catalyst became weaker and further disappeared over the $VCe_{0.25}Ti_{0.75}$. This is possibly caused by the replacement of CeO_2 by TiO_2, and once the CeO_2 was totally replaced by TiO_2 a new reduction peak arose at 860 K, which possibly corresponded to the reduction of titanium oxide.

The acidity of the catalyst was characterized by NH_3-TPD technology (Fig. 4 and Table 1). There were one type of peaks around 430–490 K for VCe, $VCe_{0.75}Ti_{0.25}$, $VCe_{0.50}Ti_{0.50}$, and $VCe_{0.25}Ti_{0.75}$, corresponding to the weak acidic site. The acid sites markedly increase with the addition of TiO_2, and the more TiO_2 was added, the more weak acidic sites there were. VTi catalyst had the maximum amount acidity of 259.95 μmol/g, with strong acidity peak arose at 606 K. These phenomenon suggest that the addition of TiO_2 enhanced the acidity of the VCe catalyst.

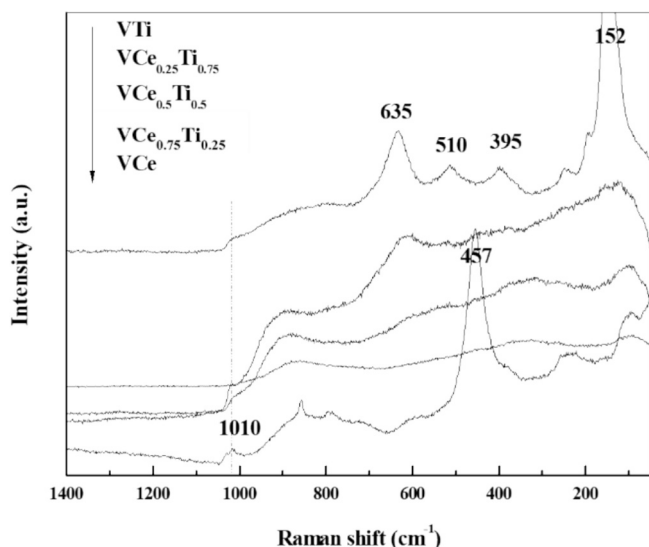**Fig. 3.** H_2-TPR profiles of the catalysts with different TiO_2 content.

Fig. 4. NH_3-TPD profiles of the catalysts with different TiO_2 content.

Table 1
NH_3-TPD result of the catalysts with different TiO_2 content.

Catalyst	Weak acid		Middle Strong acid	
	T(K)	NO. (μmol/g)	T(K)	NO. (μmol/g)
VCe	435	208.57	–	–
$VCe_{0.25}Ti_{0.75}$	416	215.83	–	–
$VCe_{0.50}Ti_{0.50}$	425	233.35	–	–
$VCe_{0.75}Ti_{0.25}$	415	248.83	–	–
VTi	443	259.95	606	52.33

Catalytic performance

Fig. 5a gave the influence of TiO_2 content on methanol conversion. It was observed that the addition of TiO_2 slightly increased the low-temperature (<440 K) activity of the modified VCe catalysts at the almost same reaction temperature whereas at high temperature zone (> 440 K) an abnormal conversion decrease was observed that remains a mysterious.

As the mass ratio of TiO_2 to CeO_2 was below 1 the methanol conversion slowly increased over the Ti-modified VCe catalyst. Methanol

Fig. 2. Raman spectra of the catalysts with different TiO_2 content.

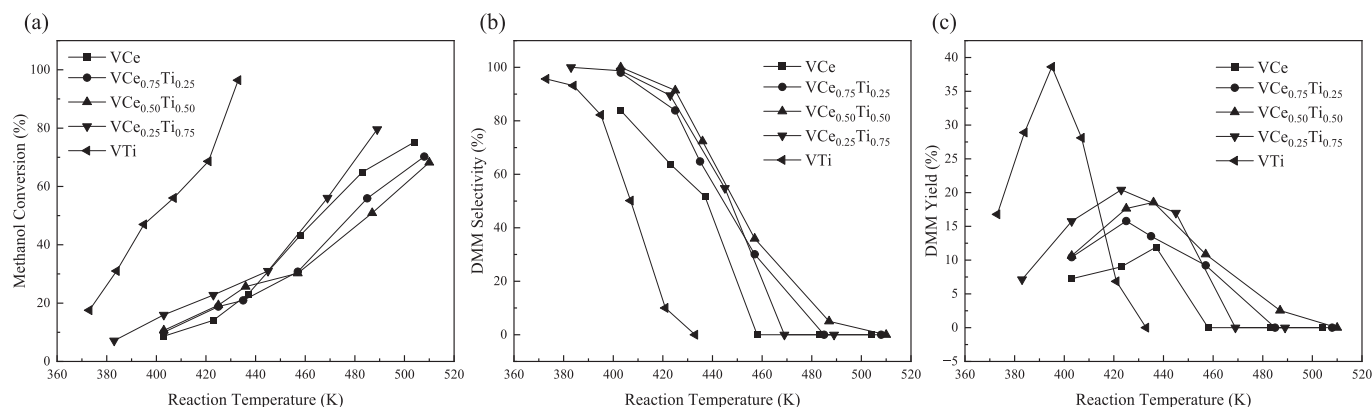**Fig. 5.** Influence of TiO$_2$ content on (a) methanol conversion, (b) DMM selectivity, (c) DMM yield WHSV = 16211 h^{-1} with feed composition of Ar: O$_2$: CH$_3$OH = 84.02:9.33:6.63 vol%.

conversion over the catalysts VCe, VCe$_{0.75}$Ti$_{0.25}$, VCe$_{0.50}$Ti$_{0.50}$ was almost the same as around 10 % at 403 K, while at 504 K the methanol conversion over VCe and VCe$_{0.50}$Ti$_{0.50}$ increased to 75.23 % and 68.23 % with an abnormal conversion decrease of 7 %. As the mass ratio of TiO$_2$ to CeO$_2$ increased to 3, the methanol conversion substantially increased over VCe$_{0.25}$Ti$_{0.75}$ and the temperature required for the identical methanol conversion decreased. Specifically, over VCe$_{0.25}$Ti$_{0.75}$ catalyst 392 K offered 10 % methanol conversion, while only 490 K achieved 80 % methanol conversion.

How reaction temperature influences DMM selectivity and yield were given in Fig. 5b and 5c (Table S8, SI). The DMM selectivity decreased with increasing temperature. This is because increasing temperature made much more methanol converted to FA, MF or CO$_x$. Moreover, the selectivity and yield of DMM increased as the content of TiO$_2$ increased, which should be related to variation in redox and surface acidity of the various catalysts. According to the H$_2$-TPR and NH$_3$-TPD results as in Fig. 3 and Fig. 4, the addition of TiO$_2$ enhanced the redox and surface acidity sites, and therefore effectively catalyzed and balanced the first step (MeOH to FA) and the second step (MeOH and FA to DMM) in DMM synthesis, resulting in the increases in the selectivity and yield of DMM.

From the Raman results, the addition of TiO$_2$ has no influence on the state of vanadium species as revealed from Fig. 2. We contended that the enhancement of DMM selectivity and methanol conversion was primarily ascribed to the formation of active sites at the VO$_x$-TiO$_2$ interface, namely V-O-Ti and V-O bonds. The V-O-Ti bonds, offered enhanced acidity sites as shown in Fig. 4, facilitated the reaction of the formed FA and methanol to increase the formation of DMM. The V-O bonds, not only facilitated the cleavage of C–H bonds in methoxy intermediates but also considerably enhanced the redox performance as shown in Fig. 3 by regulating the electronic structure of VO$_x$, thereby improving methanol conversion.[32,33] The Cerium may act to regulate the electronic structure of VO$_x$, and thus influenced the redox performance.

We also calculated the thermodynamic equilibrium of the reaction 2MeOH + FA = DMM + H$_2$O using the REquil Module in Aspen Plus. It was found that the formation of DMM is significantly influenced by the reaction temperature and the molar ratio of MeOH to FA. Specifically, as shown in Fig. 6. The equilibrium yield of DMM decreases with increasing reaction temperature, indicating that lower temperatures are more favorable for the reaction (Fig. S3). The acidity of the catalyst surface may promote the formation of FA, the formed FA and methanol further dimerized to form DMM. As methanol: FA = 0.14:0.02 (mol/mol), the equilibrium yield of DMM is about 15 % at 400 K. As the decrease of MeOH: FA ratio to 0.1:0.06 and 0.06:0.01, the equilibrium yield at 400 K is significantly increased to be 32 % and 38 %. These results suggested that the perfect matching between first and second steps determined the MeOH: FA ratio over active site of the TiO$_2$-modified catalyst which

Fig. 6. DMM equilibrium yield at various reaction temperatures at the different molar ratios of MeOH and FA.

further influenced the DMM yield. Inherently, the required redox of the explored catalyst should be high enough to generate sufficient FA which further completely reacted with MeOH over matching acidic sites to generate the target DMM.

Process design based on catalyst performance

For the methanol selective oxidation to DMM route, process conceptual design and evaluations based on the laboratory experiment are also of significance for its guideline of catalyst development. Since both methanol conversion and DMM selectivity have marked impact on the process conceptual design and economics and several Ti-Ce catalysts exhibit high DMM selectivity with a little two other co-products (MF and CO$_x$), only the Ti-Ce catalysts forming DMM, MF, and CO$_x$ are considered for process conceptual design. The DMM and MF products are targeted to type b and type a respectively due to their much high prices (Table S3 and S4, SI).

Analysis of the performance of V-Ce-TiO$_2$ catalyst

Based on the performance of the catalyst (Table 2), a separation problem with a feed from the reactor effluent is formed for producing DMM and MF at their marketing specifications. Upon the differences in products selectivity of the reactions over the catalysts, the separation

Table 2
Catalysis performances over the catalysts with various TiO_2/CeO_2 ratio.

TiO_2/CeO_2 (wt/wt)	Reaction Temp.(K)	MeOH Conv. (%)	Selectivity (%)					DMM Yield (%)	No.
			FA	DME	MF	DMM	CO_x		
50	425	19.30	0.00	0.00	8.60	91.40	0.00	17.64	1
75	403	15.96	0.00	0.00	0.00	98.74	1.26	15.76	2
	423	22.80	0.00	0.00	9.53	89.53	0.94	20.41	3
100	373	17.55	0.00	0.00	3.93	95.67	0.40	16.78	4
	384	31.01	0.00	0.00	6.63	93.17	0.19	28.89	5

problem can be classified to three cases, viz,

(1) The highest selectivity of DMM (only CO_x co-product) and lowest conversion of methanol probably simplified the flowsheet in spite of low DMM yield and large methanol recycle. No. 2 is in this case.

(2) As the methanol conversion increases, DMM selectivity slightly decreases and MF arises, in which a flexible balance between the two products should exist. No. 1, 3–5 are in this case.

(3) Other possible improvement. This means that novel catalyst needs to be explored once the technology based on the performance of V-Ce-TiO_2 catalyst does not bring profit.

Process design and economic

There exists so many components, MeOH, O_2, N_2, DMM, FA, MF, CO_x and water (W), involving several azeotropes in the effluent of the methanol to DMM reactor that it is quite difficult to completely achieve this separation (Table S6, SI). Meanwhile, a large amount of feedstock and diluted gas (N_2) needs to be recycled for material reuse due to the relatively low conversions of both methanol and oxygen.

(1) Preliminary screening and analysis

The process flowsheet diagram of the entire process including reaction/pre-separation, product separation and the unreacted feedstock/inert gas recycling units is given in Fig. 7, as described below. The first and important unit should be the product condensation and collection, in which a conventional cooler-separator 1 is capable to this job. However, the reactor effluent is a mixture with a low dew point because of the quite low oxygen conversion and the large amount of the inert gas such that even a low-temperature condenser (cooler 1) cannot make the non-gas products completely condensed. So there still exists products and unreacted feedstock in the vapor escaped from the separator that must be recovered and recycled. Fortunately, an absorption unit is quite suitable for the vapor/gas with dilute DMM by using suitable absorbent. According to the "like dissolves like" rule, and the principle of no addition of other components, methanol is selected as a suitable absorbent, recommended by Cai. [27] A total stage of 10 roughly assumed can achieve this separation with a DMM recovery of ~ 99.0 % at an absorbent flowrate around 2865.1 kg/h methanol. The vapor out of the top of the absorber still contains little products and unreacted methanol because of their saturated vapor pressures. Hence, a further cooler-separator 2 at a lower temperature is required to reduce the loss of the products and unreacted methanol.

The vapor from separator 2 rich in the unreacted oxygen and nitrogen is recycled by using a recycle compressor. The collected liquid streams from separator 1, separator 2, and absorber are mixed and entered into a stripper for the removal of the solute gas, from the bottoms of which a liquid stream rich in the products and unreacted methanol can be obtained. Since there exists several azeotropes in the liquid stream, conventional distillation cannot completely achieve this separation. Fortunately, various special distillation systems such as extractive distillation [11], pressure-swing distillation [13], and even the advanced column called extractive dividing-wall column [12,28] have been explored to complete this separation. For simplicity of process and avoidance of the entrainer addition, the pressure-swing distillation
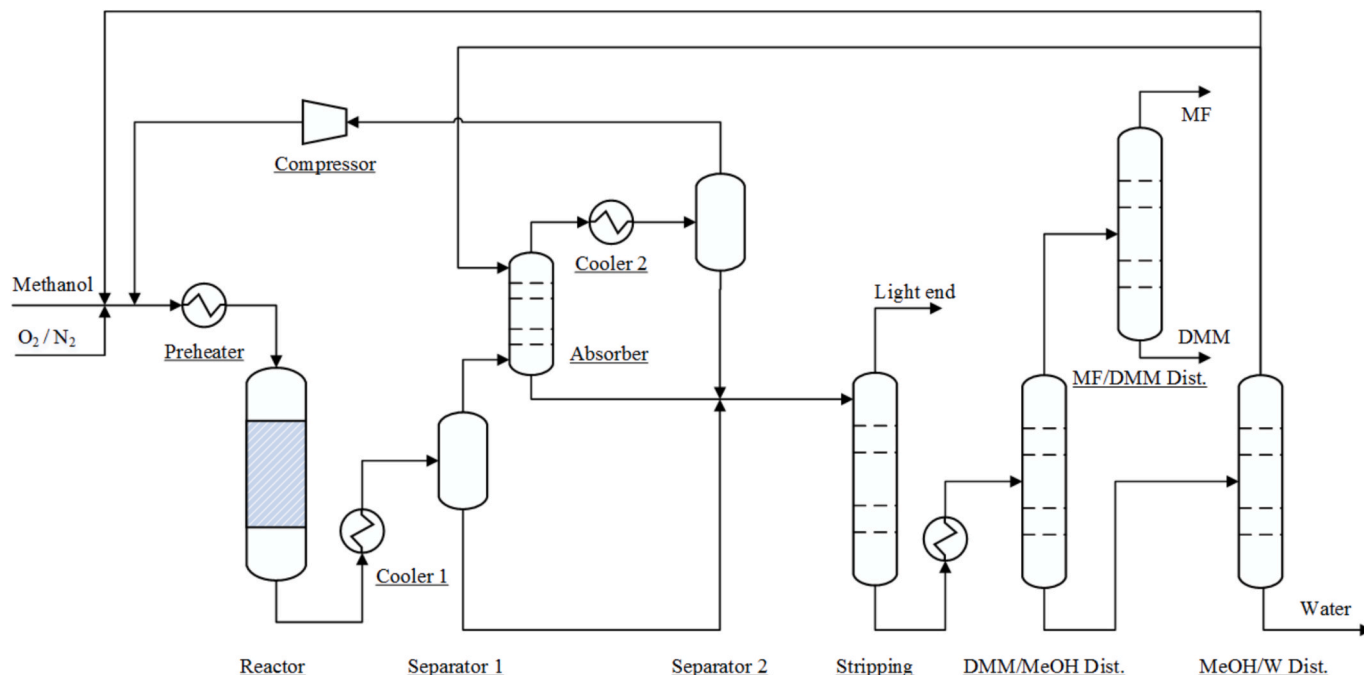

Fig. 7. Process flowsheet diagram of the conceptual design based on the lab-scale experimental datum.

is preferred. However, the pressure-swing distillation by Yu [13] featured one column operating at 101.33 kPa and the other column at 1200 kPa, and considered NRTL method with the binary parameters built-in Aspen for the DMM/MeOH separation without the experimental VLE validation, which could weaken its technology feasibility. Herein, the method proposed by Xia [29] is utilized for "pinch or not?" judgment and revealed that the DMM/MeOH azeotrope could disappear with the narrow pressure reduction from 101.33 kPa to 10 kPa, which indicates a conventional vacuum distillation enable this complete separation that could improve the technology feasibility (Fig. S1, SI).

The separations of MF-DMM and methanol–water systems can be achieved by using conventional distillation respectively, from which the DMM and MF products can be obtained. The obtained methanol splits to two streams, of which the one acts as the absorbent for the absorber and the other as recycled feed is mixed with the fresh methanol for further conversion.

(2) Process selection and its economics

The selections of the key process parameters are listed in Table 3 under the design specification of each major unit (Table S7, SI). The conventional distillation column include DMM/MeOH distillation C3, MF/DMM distillation C5, and MeOH/W distillation C4, the total stages of which are arbitrarily set at 60, 60, and 40 due to the relatively hard and moderate separation difficulty. Herein, the pressures of the columns C4 and C5 are upon its upstream, whereas the pressure of the column C3 reduces to 10 kPa since the azeotrope could disappear and the separation becomes ease. The total stage of absorber C1 is roughly specified at 10 with its pressure upon its upstream. The total stage of stripper C2 is set at 5 since the stripper C2 is employed for light end removal and thus easy separation. Other minor items are used dependent on the entire process flowsheet. The process does not consider any heat integration with a consideration of rough economic evaluations for simplicity.

On the basis of the experimental 5 cases, the feedstock and products prices, and the energy prices under the desired specifications, the economics of the conceptual design are investigated in details as below in Table 4. Unfortunately, none of all the 5 cases can bring profit at the boundary conditions above. However, there exists somewhat trend that can be used to guide the catalyst design or modifications. That is, the highest DMM selectivity with the lowest methanol conversion (case 2) is not beneficial for the profit, which is abnormal to our intuition. This is because the absorption of such more dilute DMM from the reactor effluent requires quite heavier methanol flowrate per ton/h DMM produced, which have to be distilled to a high purity and further recycled for reuse, suggesting large partition of energy consumption. At high DMM selectivity (>90 %), the DMM selectivity hardly has an effect on the profit with low methanol conversion (<18 %), whereas the methanol conversion has significant effect on the profit with high methanol

conversion (>18 %).

The most promising but still non-profitable one is the case 5, indicating the importance of the increasing the methanol conversion with a relative high DMM selectivity (>90 %) being maintained. To higher the methanol conversion, the redox of catalyst should be properly increased, while to maintain the relatively high DMM selectivity (>90 %), the acidity should be kept almost fixed. It should be noticed that it seems that although the additions of TiO₂ could produce only DMM and MF, or even only DMM, the process economic indicates that this type of modification would hardly bring profit, and therefore does not work. Hence the question what catalysis index can make money should be well answered as the torch for lighting the catalyst design and modification.

Conceptual designs over the fictitious catalyst (the catalysts with ideal modifications)

It should be reasonable to investigate the effect of the single-pass conversion of methanol (40, 50, 60, 85, 100 %) with the selectivity being maintained at 90/9/1 % DMM/MF/CO$_x$ on the products value, costs, and profit, as given in Table 5. Since we considered the absolute production of DMM at 1000 kg/h with MF co-product, the products values of all the cases 6–10 are the same. However, as the single-pass conversion of methanol increased, the feedstock and operation costs are substantially reduced due to the considerable saving in steam consumption per ton DMM. Thus, the profit markedly increased with the increasing single-pass conversion of methanol.

With the cases 1–10 entirely considered in spite of the differences in selectivity of the case 1–5, how the single-pass conversion of methanol effect the economic index in terms of products value, costs (feedstock and operation), and profit can be revealed, as given in Fig. 8. For a fixed DMM production of 1000 kg/h even with MF co-product, the products value are almost kept constant in a narrow zone, while the feedstock and operation costs substantially decrease with increasing single-pass methanol conversion. Therefore, the profit considerably increases from the loss (−3063 RMB/t DMM) to gain (531 RMB/t DMM) with the single-pass methanol conversion increasing from 19.3 to 40 %, and further gradually increase from 531 to 2720 RMB/t DMM with the single-pass methanol conversion from 40 % to 100 %. Obviously, a single-pass methanol conversion of ∼ 35 % is the break-even point which critically determines the profitability of this technology at the boundary conditions as above-mentioned.

Conclusions

In this work, TiO₂ was introduced to improve the performance of the VCe catalyst for the direct oxidation of methanol to DMM, and the relationship between the structure, properties and performance of the Ti-modified catalyst was revealed. The results showed that the addition

Table 3
Selections of the key process parameters for the rough process evaluation.

	Parameters, unit / Major items	Theoretical stage, 1	Operating pressure, kPa	Stage pressure drop, kPa	Temperature, K
Columns	Absorber C1	10	597	0.7	/
	Stripper C2	5	500	0.7	/
	DMM/MeOH distillation C3	60	10	20(Column pressure drop)	/
	MeOH/W distillation C4	40	101.33	0.7	/
	MF/DMM distillation C5	60	101.33	0.7	/
Tanks	Separator V1	1			293.15
	Separator V2	1			278.15
Reactor	R1	/	740		403
Heat exchangers	Heater H1	/	740		403.15
	Cooler C1	/	597		403
	Cooler C2	/	589		278.15
Compressor	K1	/	730		303.1
Pumps	P31	/	120		289
	Psp	/	700		293.47

Table 4

Process economics of the conceptual design based on the 5 cases (1000 kg DMM/h).

			Case 1		Case 2		Case 3		Case 4		Case 5	
Products		Price, RMB/t	Flowrate, t/h	Value, RMB/h	Flowrate, t/h	Value, RMB/h	Flowrate, t/h	Value, RMB/h	Flowrate, t/h	Value, RMB/h	Flowrate, t/h	Value, RMB/h
	DMM	6000	1	6000	1	6000	1	6000	1	6000	1	6000
	MF	11,000	0.1105	1215.52	0	0	0.1253	1378	0.0483	531	0.0837	921
Income, total				7215.52		6000		7378		6531		6921
Consumed		Price[a]	Unit consumed[b]	Cost, RMB/h	Unit consumed	Cost, RMB/h	Unit consumed	Cost, RMB/h	Unit consumed	Cost, RMB/h	Unit consumed	Cost, RMB/h
	MeOH	2000	1.41	2826	1.29	2585	1.42	2837	1.35	2691	1.37	2742
	Oxygen	350	0.28	99	0.25	87	0.31	107	0.26	90	0.27	93
	Nitrogen	175	0.07	12	0.07	13	0.06	10	0.07	12	0.04	7
	LPS	100	60.16	6016	66.25	6625	52.98	5298	61.52	6152	37.75	3775
	Chilled water	30.26	9.27	281	10.52	318	7.85	238	9.83	297	5.36	162
	Refrigeration	53.89	11.93	643	13.22	712	10.62	572	12.49	673	8.48	457
	Electricity	0.55	733.47	403	820.47	451	633.73	349	771.39	424	446.98	246
	Costs, total	/	/	10,279		10,792		9411		10,341		7483
Profit	RMB/h	/	/	−3063		−4792		−2033		−3809		−562

Table 5

Influence of the fictitious catalysts' performance on the profit (1000 kg DMM/h also with MF).

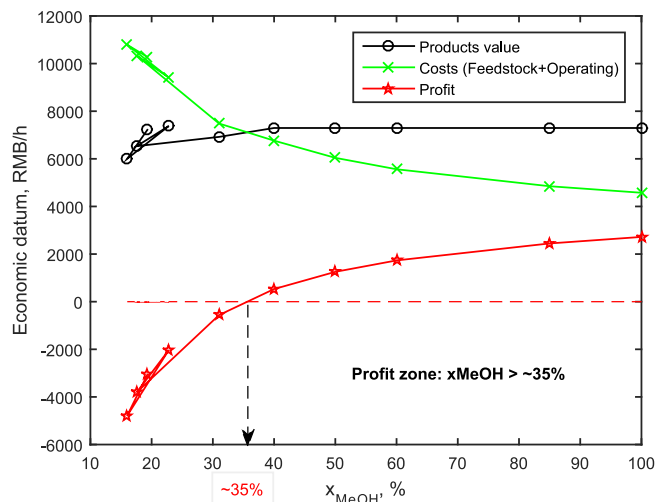|		Case 6	Case 7	Case 8	Case 9	Case 10
$X_{MeOH, s}$, %		40	50	60	85	100
S_{DMM}; S_{MF}; S_{COx}, %				90; 9; 1		
Products Value (DMM + MF), RMB/t DMM		7295	7295	7295	7295	7295
Costs (Feedstock + Operating), RMB/t DMM		6763	6041	5562	4849	4575
Profit	RMB/t DMM	531	1254	1733	2446	2720
	USD/t DMM	77.7	183.6	253.7	358.1	398.2

Fig. 8. The influence of single-pass conversion of methanol on the economic datum and its corresponding profit zone with a relative high DMM selectivity (~90 %) being maintained.

of TiO₂ enhanced the redox site and the surface acidity site, which effectively catalyzed the first step of DMM synthesis (MeOH to FA) and the second step (MeOH reacted with FA to form DMM). Furthermore, based on the performance of the preferred TiO₂ modified catalysts, a scaled-up conceptual process for the one-step oxidation of methanol to DMM was explored, designed and economically evaluated. The entire conceptual process featured that multiple condensation-separation/absorption units offered a complete collection of the DMM, and complete separation of DMM-methanol azeotrope was achieved with only one vacuum distillation unit. It was shown that about a single-pass

methanol conversion of ~ 35 % while maintaining high DMM selectivity and MF as the primary by-product (90 % DMM and 9 % MF) are at the break-even point, beyond which lab-scale catalysts can be profitable. Additionally, increasing the single-pass methanol conversion significantly improved the profit of the process. Specifically, the technology is profitable as the single-pass methanol conversion is increased to be 40 % more.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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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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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jiec.2025.05.042.

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