

Article

The Promoting Effect of Ti on the Catalytic Performance of V-Ti-HMS Catalysts in the Selective Oxidation of Methanol

Ley Boon Sim ^{1,†} , Kek Seong Kim ^{1,†} , Jile Fu ^{1,*}  and Binghui Chen ^{1,2,*}

¹ School of Energy and Chemical Engineering, Xiamen University Malaysia, Jalan Sunsuria, Bandar Sunsuria, Sepang 43900, Malaysia

² National Engineering Laboratory for Green Productions of Alcohols-Ethers-Esters, Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

* Correspondence: jile.fu@xmu.edu.my (J.F.); chenbh@xmu.edu.cn (B.C.)

† These authors contributed equally to this work.

Abstract: The effects of Ti modification on the structural properties and catalytic performance of vanadia on hexagonal mesoporous silica (V-HMS) catalysts are studied for selective methanol-to-dimethoxymethane oxidation. Characterizations including N₂ adsorption–desorption (S_{BET}), X-ray diffraction (XRD), UV-Vis diffuse reflectance spectroscopy (DRS UV-Vis), Micro-Raman spectroscopy, FTIR spectroscopy, and H₂ temperature-programmed reduction (H₂-TPR) were carried out to investigate the property and structure of the catalysts. The results show that Ti can be successfully incorporated into the HMS framework in a wide range of Si/Ti ratios from 50 to 10. Ti modification can effectively improve the distribution of vanadium species and thus enhance the overall redox properties and catalytic performance of the catalysts. The catalytic activity of the V-Ti-HMS catalysts with the Si/Ti ratio of 30 is approximately two times higher than that of V-HMS catalysts with comparable selectivity. The enhanced activity exhibited by the V-Ti-HMS catalyst is attributed to the improved dispersion and reducibility of vanadium oxides.

Keywords: mesoporous titanasilicate; hexagonal mesoporous silica (HMS); vanadium catalyst; methanol-selective oxidation



Citation: Sim, L.B.; Kim, K.S.; Fu, J.; Chen, B. The Promoting Effect of Ti on the Catalytic Performance of V-Ti-HMS Catalysts in the Selective Oxidation of Methanol. *Catalysts* **2022**, *12*, 869. <https://doi.org/10.3390/catal12080869>

Academic Editors: Fanhui Meng, Wenlong Mo and Leonarda Francesca Liotta

Received: 30 June 2022

Accepted: 3 August 2022

Published: 6 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Methanol synthesized from syngas is an important building block for the synthesis of many important chemicals, e.g., dimethoxymethane, which is in high demand in various fields, including the pharmaceutical, cosmetics, and petroleum industries, due to its excellent chemical stability, desirable solubility, and low toxicity. The industrial production of dimethoxymethane from methanol involves a two-step, formaldehyde-mediated acidic route, which requires high energy and additional maintenance expenses [1,2]. Therefore, the design of catalysts for one-pot methanol-to-dimethoxymethane processes is of great potential. Continuous endeavors have been dedicated to improving the efficiency of this process [3–5].

Metal oxides comprising metals of high oxidation states generally show high activity in selective oxidation reactions, which can be correlated to the redox pair of the oxides [6]. Among these metal oxides, vanadium oxide stands out for its wide applications in catalytic reactions, including the selective oxidation of o-xylene to phthalic anhydride [7–9], the oxidative dehydrogenation of alkanes [10–12], and the selective oxidation of methanol to dimethoxymethane [13–16]. The performance of vanadium oxide is dramatically influenced by its dispersion degree. Vanadium oxides must be well-dispersed on supports due to the non-selective behavior exhibited by their bulk forms [17–20]. Among the studied supports (e.g., TiO₂, Al₂O₃, ZrO₂, CeO₂, and SiO₂), the use of TiO₂ results in the best catalytic activity due to the synergistic metal-support interaction, which greatly improves the dispersion of

vanadium oxide [15,21–24]. However, the low surface area and poor thermal stability of TiO_2 limit its practical application.

SiO_2 possesses a high surface area and excellent thermal stability, but pure SiO_2 is unsuitable to support vanadium oxides. It is surmised that calcination subjects silica-supported vanadium oxides to agglomeration [25]. Hence, the incorporation of Ti species is suggested to improve the dispersion of vanadium oxides on silica supports and thus result in high catalytic activity. Compared with pure titania or silica supports, titanosilicates have high surface areas that greatly accommodate the dispersion of active components [20,26–28]. Additionally, titanosilicates have high thermal stability up to 800 °C and can stabilize the highly dispersed amorphous vanadium oxides (up to 20 wt%) under a calcination temperature of 500 °C [29].

Many efforts have been made towards the fabrication of titanosilicate-based catalysts. The conventional methods involve the coating of Ti species on the silica surface via the impregnation method, the grafting method, or the atomic layer deposition method [30–35]. The disadvantages of these methods are the complicated procedures and calcination steps that easily contribute to the formation of bulk Ti species, which often block the paths toward the active components [36]. Therefore, the direct integration of Ti species into the silica framework is a desirable alternative to the traditional coating-based methods. Although Ti species have been directly incorporated into mesoporous silicas such as SBA-15 [37–39], HMS [40–42], MCM-41 [43–45], and MCM-48 [46–48], there are few reports on such heterogeneous supports involving vanadium oxide catalysts [12,19], much less in terms of selective methanol-to-dimethoxymethane oxidation applications.

Herein, we prepared the hexagonal mesoporous silica (HMS) and Ti-modified HMS (Ti-HMS), which were used as supports for vanadium oxide to selectively oxidize methanol to dimethoxymethane. Characterizations including X-ray diffraction (XRD), UV-vis diffuse reflectance spectroscopy (DRS), N_2 adsorption–desorption, Raman spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and H_2 -TPR were performed to reveal the effects of Ti species in promoting the structural properties and catalytic performance of V_2O_5 -HMS catalysts.

2. Results and Discussion

2.1. Physicochemical Properties of Supports and Catalysts

The small-angle XRD patterns of Ti-HMS and HMS supports are shown in Figure 1. It can be seen that all the Ti-HMS samples exhibit a small-angle peak at approximately $1\text{--}2^\circ$, which is attributed to the d_{100} diffraction [41,49]. This observation indicates the preservation of the HMS's mesoporous structures after the incorporation of Ti species. With the increasing amount of Ti species, the d_{100} peak shifts to lower angles with increased intensity, suggesting the occurrences of lattice expansion, scattering-domain dimension reduction, and pore diameter enlargement [50]. As the Si/Ti ratio reaches 10, the d_{100} peak becomes poorly resolved, which may be due to the partial destruction of the HMS framework. For all the Ti-incorporated samples, no characteristic peak of TiO_2 is observed (Figure 1b), indicating the high dispersion of Ti on the HMS surface and/or in the HMS framework.

Figure 2 shows the wide-angle XRD patterns of the supported catalysts in the range of $10\text{--}90^\circ$. All the supported catalysts present similar well-resolved peaks belonging to crystalline V_2O_5 , suggesting the formation of bulk V_2O_5 and/or V_2O_5 nanoparticles on the surface of the supports. It is noteworthy that the V_2O_5 in the 28V-Ti-HMS(30) catalyst presents less intensive XRD peaks. The relative crystallinity of V_2O_5 for 28V-HMS and 28V-HMS(50) is the highest (14%), followed by 28V-HMS(20) and 28V-HMS(10). 28V-HMS(30) has the lowest relative crystallinity, which is only 8%. This could be due to the better-dispersed V_2O_5 in the 28V-Ti-HMS(30) catalyst compared with the other catalysts.

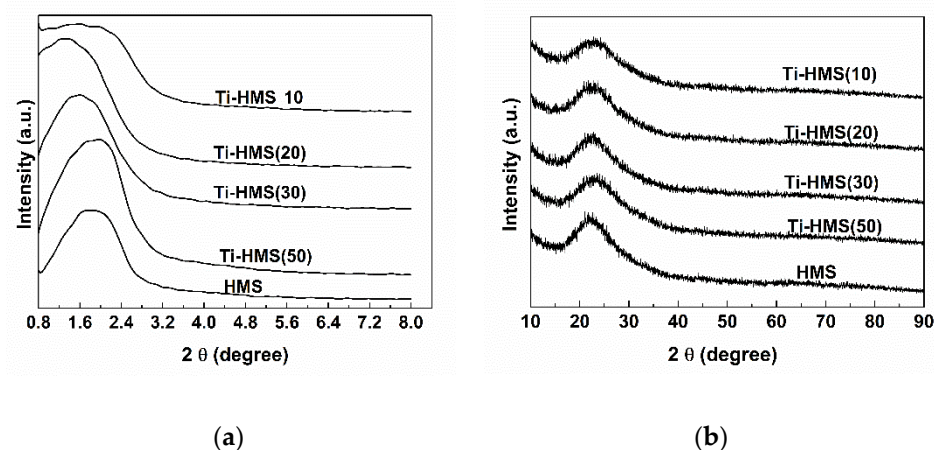


Figure 1. XRD patterns of HMS and Ti-HMS. (a) Low-angle. (b) Wide-angle.

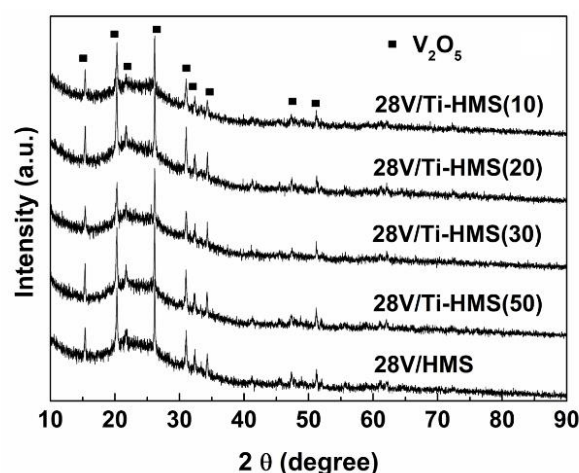


Figure 2. XRD patterns of catalysts with different supports.

Nitrogen physisorption is a practical technique used to study the textural properties of mesoporous materials. The BET specific surface area (S_{BET}) of supports and supported catalysts are summarized in Table 1. The pure HMS demonstrates the highest surface area. After the incorporation of Ti species, the S_{BET} of the supports decreases, while the cumulative pore volume (V_p) and pore diameter increase. This is consistent with the results of the XRD analysis, i.e., the peak position of Ti-HMS slightly shifts to lower angles due to the increasing interplanar distance. The deposition of vanadium species on the supports significantly decreased the S_{BET} , which is commonly observed for impregnated catalysts. Such surface-area loss is ascribed to the partial destruction of the support framework and/or the blocking of catalyst pores by bulk oxide or oxide nanoparticles.

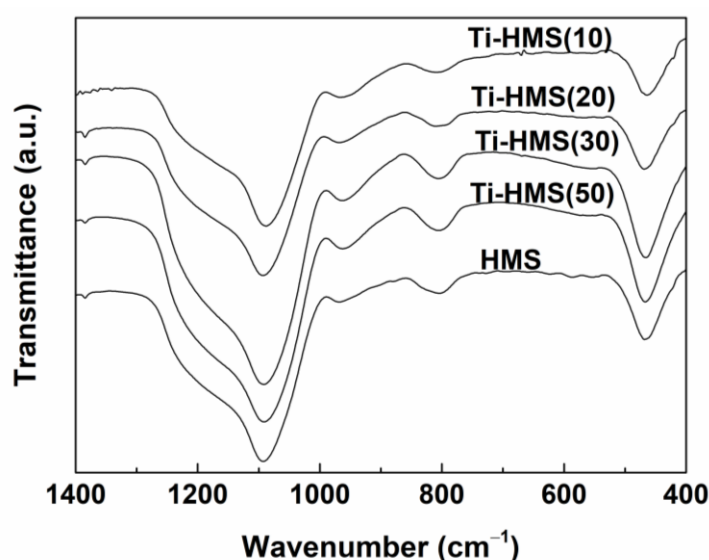
2.2. Confirmation of the Framework Ti

The IR spectra of HMS and Ti-HMS with various Si/Ti ratios in the region of 400–1400 cm^{-1} are shown in Figure 3. All the samples exhibit a symmetric stretching vibration band at 807 cm^{-1} and asymmetric vibration band at 1090 cm^{-1} for the tetrahedral SiO_4^{4-} species. Meanwhile, the pure HMS shows a weak peak at 960 cm^{-1} , which indicates the Si-OH stretching vibration of free silanol groups in the amorphous region [51,52]. For Ti-containing materials, the 960 cm^{-1} band marginally shifts to a lower wavenumber, which has been reported in published studies [53,54]. Additionally, the bulk/crystalline TiO_2 (anatase and/or rutile) with a representative broad band at 600–650 cm^{-1} was not observed. These results suggest that Ti species have been successfully embedded into the HMS framework.

Table 1. Textural properties and E_g of the materials.

Sample	S_{BET} ^a (m ² /g)	V_P ^b (cm ³ /g)	D_{ads} ^c (nm)	E_g ^d (eV)
HMS	764	0.67	3.71	-
Ti-HMS(50)	730	0.97	4.46	-
Ti-HMS(30)	662	0.93	5.22	-
Ti-HMS(20)	662	0.90	4.78	-
Ti-HMS(10)	661	0.59	3.80	-
28V-HMS	382	0.45	4.68	2.47
28V-Ti-HMS(50)	364	0.43	5.66	2.59
28V-Ti-HMS(30)	329	0.38	5.22	2.73
28V-Ti-HMS(20)	345	0.44	5.24	2.57
28V-Ti-HMS(10)	343	0.39	4.84	2.55

^a Specific surface area calculated by the BET method. ^b Total pore volume determined at $P/P_0 = 0.99$. ^c BJH adsorption average pore diameter. ^d Energy of adsorption edge.

**Figure 3.** Infrared spectra of HMS and Ti-HMS samples with different Si/Ti ratios.

The incorporation of Ti species into the HMS framework was further verified by UV-vis DRS. This technique has been extensively employed for the characterization of the nature and coordination of Ti^{4+} ions in titanosilicates [55]. The corresponding spectra of the Ti-substituted supports are displayed in Figure 4, along with pure HMS and anatase (bulk). The band at ~ 210 nm is assigned to the titanium-to-silica charge transfer, which is used to confirm the Ti^{4+} framework sites. The broad absorption band at ~ 325 nm denotes the presence of bulk TiO_2 (anatase) [56]. It is apparent from Figure 4 that the HMS shows no adsorption band. The incorporation of Ti species introduces a peak centered at 210 nm with gradually strengthening intensity with increased Ti content. Despite the high loading of Ti for Ti-HMS(10), no visible peak at 325 nm is observed. Such a phenomenon strongly demonstrates that most Ti species successfully occupy the isolated site positions in the HMS framework in a wide range of Si/Ti ratios from 50 to 10. However, it is noticeable that the position of the 210 nm band shifts to a higher wavelength when the Si/Ti ratio is 10.

2.3. Effect of Ti on the Vanadia Dispersion

Figure 5 presents the UV-vis DRS spectra of the supported catalysts. The abrupt variation of all the spectra at 350 nm is due to the change of light source during detection. All the spectra consist of several ligand-to-metal charge transfer absorption bands characterizing the V_2O_5 constituted siliceous surface. The d-d absorption bands in the region of 495–660 nm representing the vanadium (+IV) are not detected, which confirms the fact that all the vanadium species were successfully oxidized to vanadium (+V). The region of 170–290 nm is attributed to the

presence of coordinated tetrahedral vanadium species, whereas the 290–410 nm range features the O_h point group vanadium species (square-pyramidal or octahedral) [57]. These results indicate that the well-dispersed and bulk-like vanadium species coexisted in all the catalysts. Therefore, to further understand the vanadium's state, the absorption-edge energies (E_g) of the spectra are obtained to retrieve information regarding the type and number of ligands neighboring the core metal ion of the first coordination sphere, as there is a linear relationship between E_g and the number of bridging V-O-V bonds in bulk vanadium species [19,58].

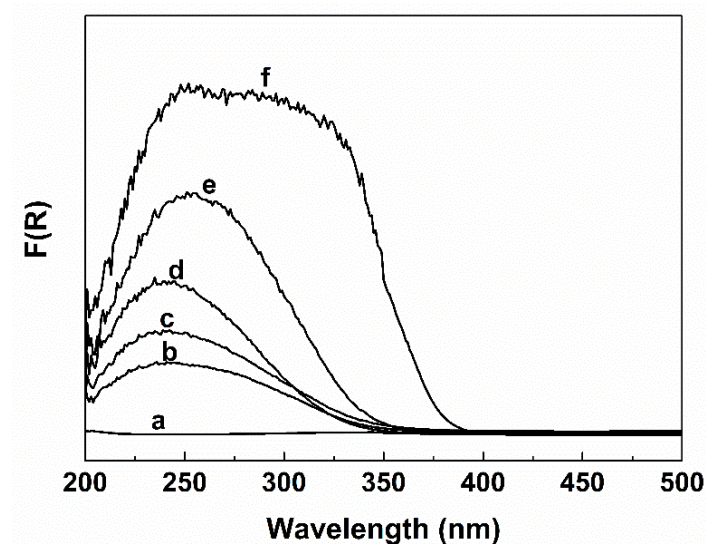


Figure 4. UV-vis spectra of calcined Ti-containing materials (a) HMS, (b) Ti-HMS(50), (c) Ti-HMS(30), (d) Ti-HMS(20), (e) Ti-HMS(10), and (f) anatase.

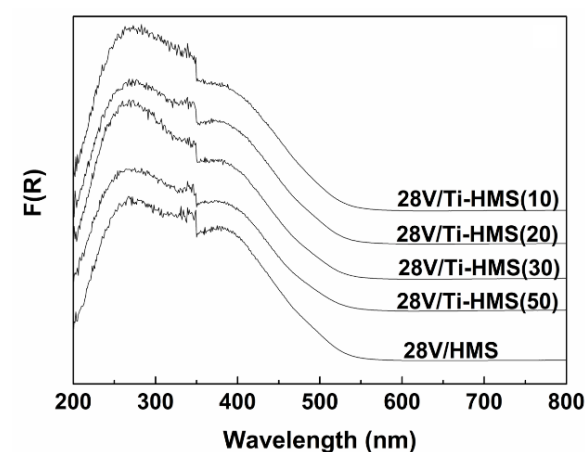


Figure 5. UV-vis spectra of catalysts with different supports.

The E_g of the supported catalysts are tabulated in Table 1, and the spectra of V-HMS and V-Ti-HMS in the form of $[F(R\infty)h\nu]^2$ -against- E_g plot are depicted in Figure 6. Tian et al. [59] have demonstrated the use of E_g values to qualitatively monitor vanadium species polymerization. It has been verified that a high E_g value reflects the high dispersion of vanadium species. As shown in Table 1, Ti-HMS-supported V_2O_5 catalysts have higher E_g values than pure-HMS-supported catalysts, wherein Ti-HMS(30) exhibits the highest E_g value. Our results thus suggest the better dispersion of vanadium species supported on Ti-HMS catalysts than those on pure HMS catalysts.

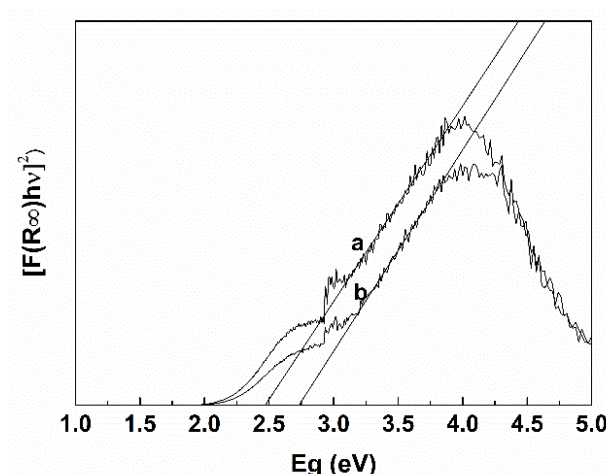


Figure 6. UV-vis spectra of catalysts with different supports. (a) 28V/HMS. (b) 28V/Ti-HMS (30).

The Raman spectra of the samples in the region of 200 to 1200 cm^{-1} are presented in Figure 7. The distinctive Raman characteristics of crystalline V_2O_5 are the bands centered at 282, 301, 405, 478, 525, 700, and 995 cm^{-1} , which appear for all samples [31] and thus agree well with the XRD results as shown in Figure 2 where well-resolved V_2O_5 patterns are observed. It is notable that a new band at 1035 cm^{-1} , which is identified as the terminal mono-oxo $\text{V}=\text{O}$ bond of isolated surface vanadium species bonded to the surface silica species ($\text{O}=\text{V}(\text{OSi})_3$) [60], is only observed for the Ti-modified catalysts. This finding further confirms that the dispersion of V_2O_5 over the Ti-modified catalysts, especially for V-Ti-HMS(30), is better than that over the Ti-free catalysts. This result is consistent with the outcomes of UV-vis DRS studies.

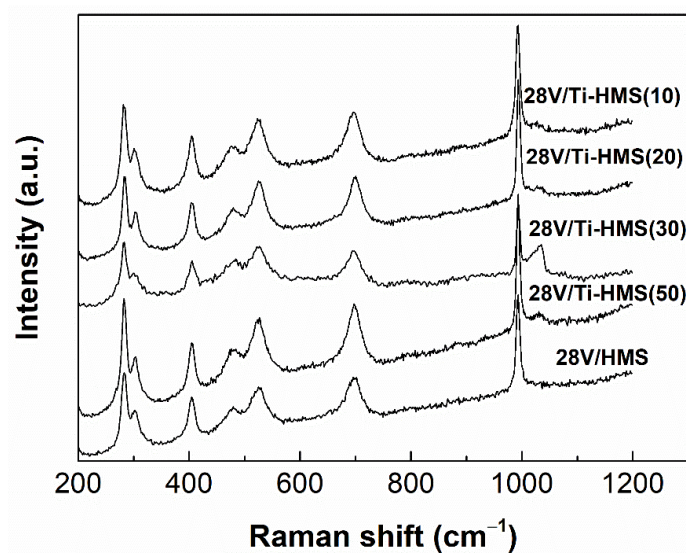


Figure 7. Raman spectra of vanadia-supported catalysts with different supports.

2.4. Redox Property and Catalytic Performance of Catalysts

The TPR profiles of different catalysts are presented in Figure 8. Since no reduction peak was observed for Ti-HMS and HMS, the corresponding TPR files are not shown here. As surmised, the addition of Ti species can improve the redox properties of catalysts. The main H_2 consumption peak of V-HMS catalysts emerges at ~ 890 K, with a shoulder occurring at ~ 860 K. After the incorporation of Ti species into the HMS framework, the main reduction peaks shift to lower temperatures (~ 865 K). Further increasing the amount of Ti, a slight increase in the reduction temperature is observed for V-Ti-HMS(10), which may be attributed to the destruction of HMS. Besselmann et al. [61] associated the change in redox

properties with the different types of vanadium species. The crystalline and polymeric vanadium species are more challenging to reduce than their monomeric counterparts. The resultant spectra of both UV-vis DRS and Raman spectroscopy revealed the improved dispersion of V_2O_5 over the Ti-HMS supports compared with that over the pure HMS supports. Therefore, it is reasonable to believe that modification using Ti species improves the dispersion of V_2O_5 and thus enhances the reducibility of catalysts.

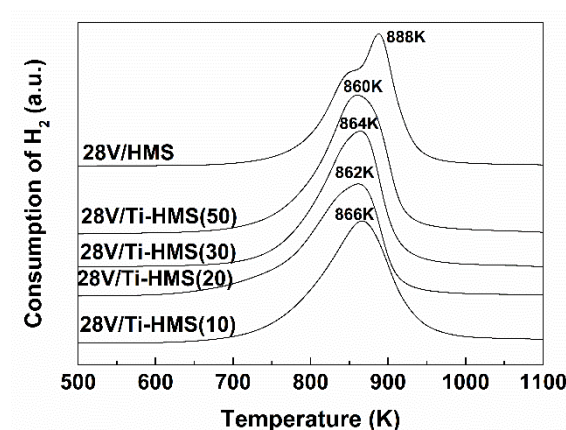


Figure 8. Temperature programmed reduction (TPR) profiles of catalysts with different supports.

Table 2 presents the catalytic performance of various catalysts at a low temperature (413 K). The V-HMS (without Ti) shows much lower catalytic activity with merely 6% of methanol conversion. It is evident that Ti modification can enhance catalysts' methanol conversion to a value higher than 10% without a significant loss in selectivity. Among the Ti-modified catalysts, V-Ti-HMS(30) exhibits the best catalytic performance with the methanol-to-dimethoxymethane conversion and selectivity of 15% and 87%, respectively. The improvement in catalytic performance is not related to the specific surface area since all the samples have similar specific surface area. Well-dispersed VO_4 oxides (isolated and polymeric surface species) are considered to be the catalytically active sites for the selective oxidation of methanol [62]. Additionally, the selectivity for DMM is mainly determined by the acidity of the catalysts [15]. According to the characterization results above, the incorporation of Ti significantly improved the dispersion of vanadia, which had minor effect on the acidity. The V-Ti-HMS(30) with the best V_2O_5 dispersion exhibits the best catalytic behaviors. Hence, the high dispersion of V_2O_5 is likely the key reason for the high activity observed for the Ti-modified catalysts. With the improvement in the dispersion of V_2O_5 , the catalysts become more reducible, which has been confirmed by the TPR results. Based on the Mars-van Krevelen mechanism [63], the lattice oxygen of vanadia participates in oxidation. With the improved reducibility, both the oxidation of methanol and the re-oxidation of catalysts becomes easier. Therefore, the excellent dispersibility and high reducibility are most likely the major contributions to the improved catalytic performance of the V-Ti-HMS catalysts. Additionally, the reusability of V-Ti-HMS(30) was also tested for 50 h. The results in Figure 9 indicate the high stability of the catalysts.

Table 2. Performance of catalysts in the methanol oxidation reaction.

Sample	Conversion (%)	Selectivity (%)				
		DMM	MF	FA	DME	CO _x
28V-HMS	6	89	2	6	3	0
28V-Ti-HMS(50)	12	85	7	6	2	0
28V-Ti-HMS(30)	15	87	4	7	2	0
28V-Ti-HMS(20)	11	84	5	8	3	0
28V-Ti-HMS(10)	8	81	5	12	2	0

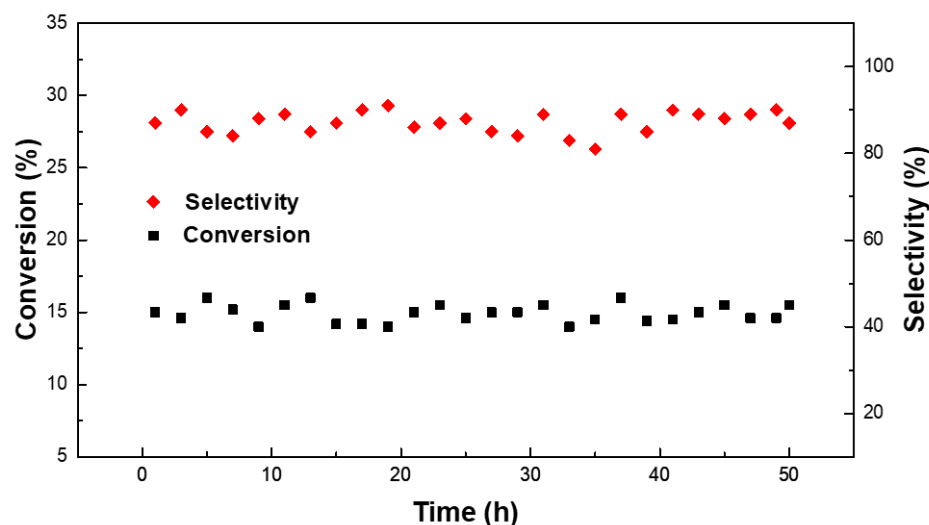


Figure 9. Conversion of methanol and selectivity of DMM using V-Ti-HMS(30) in the methanol oxidation.

3. Materials and Methods

3.1. Synthesis of the Supports

The hexagonal mesoporous silica (HMS) and hexagonal mesoporous titanosilicate (Ti-HMS) were synthesized under ambient conditions using dodecylamine ($C_{12}H_{25}NH_2$, Aldrich 98%) as a surfactant [56]. Generally, different ratios of tetraethyl orthosilicate (TEOS) to titanium tetrabutoxide (TBOT) were added to the solution of dodecylamine (DDA) in water and ethanol under vigorous stirring. The molar composition of the reaction mixture is xTi : 1.0 Si: 0.2 DDA: 9.0 EtOH: 160 H_2O . The reaction mixture was aged under ambient temperature under vigorous stirring for 24 h to obtain crystalline products. The Si/Ti molar ratios (denoted as y) used for the preparation of Ti-HMS(y) were 50, 30, 20, and 10. Pure HMS samples without Ti content were also prepared accordingly. All samples were filtered, washed thoroughly with water, dried under ambient temperature, and calcined at 923 K for 4 h.

3.2. Preparation of the Catalysts

The vanadium oxide species were introduced onto the support using the conventional wet impregnation method. NH_4VO_3 was dissolved in the oxalic acid solution and then impregnated onto the HMS or Ti-HMS supports. After drying at 383 K for 12 h and calcined at 673 K for 3 h, zV-HMS or zV-Ti-HMS(y) catalysts were obtained, where a and b are the Si/Ti molar ratio and loading of V_2O_5 (z wt%), respectively. The powdered vanadium catalysts were dissolved in a solution with 5% aqua regia and 30% hydrogen peroxide for 10 min. Then the percentage of V_2O_5 in the obtained catalysts was confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES) in the range of 27.5 wt% to 28.6 wt%. This is consistent with the estimated loading (28 wt%).

3.3. Characterization Methods

Powder XRD analysis was conducted using a Philips PANalytical X'pert Pro diffractometer equipped with the Cu $K\alpha$ radiation at $\lambda = 0.1542$ nm, 40 kV, and 30 mA. The nitrogen adsorption–desorption isotherms were obtained using the Tristar 3000 equipment. Prior to the experiments, the samples were degassed at 543 K under vacuum for 5 h. The volume of the adsorbed N_2 was normalized to the standard temperature and pressure. The specific surface area (S_{BET}) was calculated by applying the BET equation in the relative pressure range of $0.05 < P/P_0 < 0.30$. The average pore diameter was calculated by applying the Barret-Joyner-Halenda (BJH) method to the adsorption branches of the N_2 isotherms. The cumulative pore volume was obtained from the isotherms at $P/P_0 = 0.99$.

DR UV-vis spectra were collected using a Varian Cary 5000 UV-vis-NIR spectrometer equipped with diffuse-reflectance accessories in the range of 200–1000 nm, and dehydrated BaSO₄ was used as the reference. All the samples were dehydrated at 473 K overnight and then stored in a sealed serum bottle to prevent the hydration of vanadium species. The Fourier transform infrared (FTIR) spectra were recorded in the range 400–1400 cm^{−1} using 32 scans and a resolution of 4 cm^{−1} on the VERTEX 70 of spectroscopic grade potassium bromide (KBr). Raman spectra were obtained using the Renishaw inVia Raman System equipped with a CCD detector and a Leica DMLM microscope. The excitation was provided by a 532 nm Ar⁺ ion laser. The range and resolution were 100–1200 and 0.5 cm^{−1}, respectively.

H₂-TPR measurements were carried out in a continuous mode using a quartz micro-reactor (3.5 mm in diameter). A sample of ~50 mg was contacted with an H₂:Ar mixture (5% volume of H₂ in Ar) at a total flow rate of 20 ml min^{−1}. The sample was heated at a rate of 10 K min^{−1} from room temperature to 1073 K. The hydrogen consumption was monitored using a thermal conductivity detector (TCD). The reducing gas was first passed through the reference arm of the TCD before entering the reactor. The exit flow of the reactor was directed through a trap filled with Mg(ClO₄)₂ for dehydration, and then the flow proceeded to the second arm of the TCD.

3.4. Catalytic Activity Measurements

The selective oxidation of methanol was carried out at the atmospheric pressure in a fixed-bed microreactor (glass) with an inner diameter of 8 mm. Methanol was introduced into the reaction zone by bubbling O₂/N₂ (1/4) through a glass saturator filled with methanol (99.9%) maintained at 288 K. In each test, 0.2 g of catalyst was loaded, and the gas hourly space velocity (GHSV) was 11,400 ml g^{−1} h^{−1}. The feed composition was maintained as 1 methanol:1 O₂:4 N₂ (v/v). Methanol, dimethoxymethane, formaldehyde, and other organic compounds were analyzed using a GC equipped with an FID detector connected to Porapak N columns. CO and CO₂ were detected using a TDX-01 column. The gas lines were kept at 393 K to prevent the condensation of reactants and products.

4. Conclusions

In this study, Ti was successfully incorporated into the HMS framework with a wide range of Si/Ti ratios from 10 to 50. Compared with pure HMS, the Ti-HMS-supported vanadium oxide catalysts exhibited higher activities with a similar selectivity in the selective oxidation of methanol to dimethoxymethane. It was revealed that the incorporation of Ti rendered the well-dispersed oxides on the catalyst surface and hence increased the catalysts' reducibility. Excellent dispersibility and high reducibility are most likely the major contributions to the improved performance of the V-Ti-HMS catalysts.

Author Contributions: Conceptualization, J.F. and B.C.; methodology, L.B.S.; validation, L.B.S.; formal analysis, L.B.S. and J.F.; investigation, L.B.S. and K.S.K.; resources, B.C.; data curation, K.S.K.; writing—original draft preparation, L.B.S. and K.S.K.; writing—review and editing, J.F. and B.C.; visualization, L.B.S.; supervision, J.F. and B.C.; project administration, J.F.; funding acquisition, J.F. and B.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Xiamen University Malaysia Campus, XMUMRF/2021-C8/IENG/0040.

Acknowledgments: The authors would like to thank the support from Xiamen University Malaysia Campus.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ahmad, W.; Chan, F.L.; Chaffee, A.L.; Wang, H.; Hoadley, A.; Tanksale, A. Dimethoxymethane Production via Catalytic Hydrogenation of Carbon Monoxide in Methanol Media. *ACS Sustain. Chem. Eng.* **2020**, *8*, 2081–2092. [[CrossRef](#)]
2. Ftouni, K.; Lakiss, L.; Thomas, S.; Daturi, M.; Fernandez, C.; Bazin, P.; El Fallah, J.; El-Roz, M. TiO₂/Zeolite Bifunctional (Photo)Catalysts for a Selective Conversion of Methanol to Dimethoxymethane: On the Role of Brønsted Acidity. *J. Phys. Chem. C* **2018**, *122*, 29359–29367. [[CrossRef](#)]

3. Peláez, R.; Marín, P.; Ordóñez, S. Effect of formaldehyde precursor and water inhibition in dimethoxymethane synthesis from methanol over acidic ion exchange resins: Mechanism and kinetics. *Biofuel Bioprod. Biorefin.* **2021**, *15*, 1696–1708. [\[CrossRef\]](#)
4. To, A.T.; Wilke, T.J.; Nelson, E.; Nash, C.P.; Bartling, A.; Wegener, E.C.; Unocic, K.A.; Habas, S.E.; Foust, T.D.; Ruddy, D.A. Dehydrogenative Coupling of Methanol for the Gas-Phase, One-Step Synthesis of Dimethoxymethane over Supported Copper Catalysts. *ACS Sustain. Chem. Eng.* **2020**, *8*, 12151–12160. [\[CrossRef\]](#)
5. Sun, R.; Delidovich, I.; Palkovits, R. Dimethoxymethane as a Cleaner Synthetic Fuel: Synthetic Methods, Catalysts, and Reaction Mechanism. *ACS Catal.* **2019**, *9*, 1298–1318. [\[CrossRef\]](#)
6. Reddy, K.P.; Choi, H.; Kim, D.; Choi, M.; Ryoo, R.; Park, J.Y. The facet effect of ceria nanoparticles on platinum dispersion and catalytic activity of methanol partial oxidation. *Chem. Commun.* **2021**, *57*, 7382–7385. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Akbari, A.; Alavi, S.M. The effect of cesium and antimony promoters on the performance of Ti-phosphate-supported vanadium(V) oxide catalysts in selective oxidation of o-xylene to phthalic anhydride. *Chem. Eng. Res. Des.* **2015**, *102*, 286–296. [\[CrossRef\]](#)
8. Wellmann, A.; Grazia, L.; Bermejo-Deval, R.; Sanchez-Sanchez, M.; Lercher, J.A. Effect of promoters on o-xylene oxidation pathways reveals nature of selective sites on TiO₂ supported vanadia. *J. Catal.* **2022**, *408*, 330–338. [\[CrossRef\]](#)
9. Dias, C.R.; Portela, M.F.; Bañares, M.A.; Galán-Fereres, M.; López-Granados, M.; Peña, M.A.; Fierro, J.L.G. Selective oxidation of o-xylene over ternary V-Ti-Si catalysts. *Appl. Catal. A Gen.* **2002**, *224*, 141–151. [\[CrossRef\]](#)
10. Jiang, X.; Zhang, X.; Purdy, S.C.; He, Y.; Huang, Z.; You, R.; Wei, Z.; Meyer, H.M.; Yang, J.; Pan, Y.; et al. Multiple Promotional Effects of Vanadium Oxide on Boron Nitride for Oxidative Dehydrogenation of Propane. *JACS Au* **2022**, *2*, 1096–1104. [\[CrossRef\]](#)
11. Kazerooni, H.; Towfighi Darian, J.; Mortazavi, Y.; Khadadadi, A.A.; Asadi, R. Titania-Supported Vanadium Oxide Synthesis by Atomic Layer Deposition and Its Application for Low-Temperature Oxidative Dehydrogenation of Propane. *Catal. Lett.* **2020**, *150*, 2807–2822. [\[CrossRef\]](#)
12. Wang, C.; Chen, J.-G.; Xing, T.; Liu, Z.-T.; Liu, Z.-W.; Jiang, J.; Lu, J. Vanadium Oxide Supported on Titanosilicates for the Oxidative Dehydrogenation of n-Butane. *Ind. Eng. Chem. Res.* **2015**, *54*, 3602–3610. [\[CrossRef\]](#)
13. Chen, S.; Ma, X. The role of oxygen species in the selective oxidation of methanol to dimethoxymethane over VOx/TS-1 catalyst. *J. Ind. Eng. Chem.* **2017**, *45*, 296–300. [\[CrossRef\]](#)
14. Wang, T.; Meng, Y.; Zeng, L.; Gong, J. Selective oxidation of methanol to dimethoxymethane over V₂O₅/TiO₂-Al₂O₃ catalysts. *Sci. Bull.* **2015**, *60*, 1009–1018. [\[CrossRef\]](#)
15. Lu, X.; Qin, Z.; Dong, M.; Zhu, H.; Wang, G.; Zhao, Y.; Fan, W.; Wang, J. Selective oxidation of methanol to dimethoxymethane over acid-modified V₂O₅/TiO₂ catalysts. *Fuel* **2011**, *90*, 1335–1339. [\[CrossRef\]](#)
16. Fan, Z.; Guo, H.; Fang, K.; Sun, Y. Efficient V₂O₅/TiO₂ composite catalysts for dimethoxymethane synthesis from methanol selective oxidation. *RSC Adv.* **2015**, *5*, 24795–24802. [\[CrossRef\]](#)
17. Mamedov, E.A.; Cortés Corberán, V. Oxidative dehydrogenation of lower alkanes on vanadium oxide-based catalysts. The present state of the art and outlooks. *Appl. Catal. A Gen.* **1995**, *127*, 1–40. [\[CrossRef\]](#)
18. Khodakov, A.; Yang, J.; Su, S.; Iglesia, E.; Bell, A.T. Structure and properties of vanadium oxide-zirconia catalysts for propane oxidative dehydrogenation. *J. Catal.* **1998**, *177*, 343–351. [\[CrossRef\]](#)
19. Setnička, M.; Čičmanec, P.; Bulánek, R.; Zukal, A.; Pastva, J. Hexagonal mesoporous titanosilicates as support for vanadium oxide—Promising catalysts for the oxidative dehydrogenation of n-butane. *Catal. Today* **2013**, *204*, 132–139. [\[CrossRef\]](#)
20. Santacesaria, E.; Cozzolino, M.; Di Serio, M.; Venezia, A.M.; Tesser, R. Vanadium based catalysts prepared by grafting: Preparation, properties and performances in the ODH of butane. *Appl. Catal. A Gen.* **2004**, *270*, 177–192. [\[CrossRef\]](#)
21. Meng, Y.; Wang, T.; Chen, S.; Zhao, Y.; Ma, X.; Gong, J. Selective oxidation of methanol to dimethoxymethane on V₂O₅-MoO₃/γ-Al₂O₃ catalysts. *Appl. Catal. B* **2014**, *160–161*, 161–172. [\[CrossRef\]](#)
22. Kaichev, V.V.; Popova, G.Y.; Chesalov, Y.A.; Saraev, A.A.; Andrushkevich, T.V.; Bukhtiyarov, V.I. Active component of supported vanadium catalysts in the selective oxidation of methanol. *Kinet. Catal.* **2016**, *57*, 82–94. [\[CrossRef\]](#)
23. Kropp, T.; Paier, J.; Sauer, J. Support Effect in Oxide Catalysis: Methanol Oxidation on Vanadia/Ceria. *J. Am. Chem. Soc.* **2014**, *136*, 14616–14625. [\[CrossRef\]](#)
24. Yoon, S.; Oh, K.; Liu, F.; Seo, J.H.; Somorjai, G.A.; Lee, J.H.; An, K. Specific metal-support interactions between nanoparticle layers for catalysts with enhanced methanol oxidation activity. *ACS Catal.* **2018**, *8*, 5391–5398. [\[CrossRef\]](#)
25. Jaegers, N.R.; Wan, C.; Hu, M.Y.; Vasiliu, M.; Dixon, D.A.; Walter, E.; Wachs, I.E.; Wang, Y.; Hu, J.Z. Investigation of Silica-Supported Vanadium Oxide Catalysts by High-Field 51V Magic-Angle Spinning NMR. *J. Phys. Chem. C* **2017**, *121*, 6246–6254. [\[CrossRef\]](#)
26. Castillo, R.; Koch, B.; Ruiz, P.; Delmon, B. Influence of the Amount of Titania on the Texture and Structure of Titania Supported on Silica. *J. Catal.* **1996**, *161*, 524–529. [\[CrossRef\]](#)
27. Gao, X.; Wachs, I.E. Molecular Engineering of Supported Vanadium Oxide Catalysts Through Support Modification. *Top. Catal.* **2002**, *18*, 243–250. [\[CrossRef\]](#)
28. Gao, X.; Bare, S.R.; Fierro, J.L.G.; Wachs, I.E. Structural Characteristics and Reactivity/Reducibility Properties of Dispersed and Bilayered V₂O₅/TiO₂/SiO₂ Catalysts. *J. Phys. Chem. B* **1999**, *103*, 618–629. [\[CrossRef\]](#)
29. Mahipal Reddy, B.; Mehdi, S.; Padmanabha Reddy, E. Dispersion and thermal stability of vanadium oxide catalysts supported on titania-silica mixed oxide. *Catal. Lett.* **1993**, *20*, 317–327. [\[CrossRef\]](#)
30. Chakraborty, S.; Nayak, S.C.; Deo, G. TiO₂/SiO₂ supported vanadia catalysts for the ODH of propane. *Catal. Today* **2015**, *254*, 62–71. [\[CrossRef\]](#)

31. Shee, D.; Mitra, B.; Chary, K.V.R.; Deo, G. Characterization and reactivity of vanadium oxide supported on TiO₂-SiO₂ mixed oxide support. *Mol. Catal.* **2018**, *451*, 228–237. [\[CrossRef\]](#)
32. Hamilton, N.; Wolfram, T.; Tzolova Müller, G.; Hävecker, M.; Kröhnert, J.; Carrero, C.; Schomäcker, R.; Trunschke, A.; Schlögl, R. Topology of silica supported vanadium–titanium oxide catalysts for oxidative dehydrogenation of propane. *Catal. Sci. Technol.* **2012**, *2*, 1346–1359. [\[CrossRef\]](#)
33. Kwak, J.H.; Herrera, J.E.; Hu, J.Z.; Wang, Y.; Peden, C.H.F. A new class of highly dispersed VO_x catalysts on mesoporous silica: Synthesis, characterization, and catalytic activity in the partial oxidation of ethanol. *Appl. Catal. A Gen.* **2006**, *300*, 109–119. [\[CrossRef\]](#)
34. Keränen, J.; Carniti, P.; Gervasini, A.; Iiskola, E.; Auroux, A.; Niinistö, L. Preparation by atomic layer deposition and characterization of active sites in nanodispersed vanadia/titania/silica catalysts. *Catal. Today* **2004**, *91–92*, 67–71. [\[CrossRef\]](#)
35. Keränen, J.; Auroux, A.; Ek, S.; Niinistö, L. Preparation, characterization and activity testing of vanadia catalysts deposited onto silica and alumina supports by atomic layer deposition. *Appl. Catal. A Gen.* **2002**, *228*, 213–225. [\[CrossRef\]](#)
36. Bérubé, F.; Kleitz, F.; Kaliaguine, S. Surface properties and epoxidation catalytic activity of Ti-SBA15 prepared by direct synthesis. *J. Mater. Sci.* **2009**, *44*, 6727–6735. [\[CrossRef\]](#)
37. Chen, Y.; Huang, Y.; Xiu, J.; Han, X.; Bao, X. Direct synthesis, characterization and catalytic activity of titanium-substituted SBA-15 mesoporous molecular sieves. *Appl. Catal. A Gen.* **2004**, *273*, 185–191. [\[CrossRef\]](#)
38. Devi, P.; Das, U.; Dalai, A.K. Production of glycerol carbonate using a novel Ti-SBA-15 catalyst. *Chem. Eng. J.* **2018**, *346*, 477–488. [\[CrossRef\]](#)
39. Bérubé, F.; Nohair, B.; Kleitz, F.; Kaliaguine, S. Controlled Postgrafting of Titanium Chelates for Improved Synthesis of Ti-SBA-15 Epoxidation Catalysts. *Chem. Mater.* **2010**, *22*, 1988–2000. [\[CrossRef\]](#)
40. Zepeda, T.A.; Pawelec, B.; Fierro, J.L.G.; Halachev, T. Removal of refractory S-containing compounds from liquid fuels on novel bifunctional CoMo/HMS catalysts modified with Ti. *Appl. Catal. B* **2007**, *71*, 223–236. [\[CrossRef\]](#)
41. Düzenli, D.; Sahin, Ö.; Kazıcı, H.Ç.; Aktaş, N.; Kivrak, H. Synthesis and characterization of novel Ti doped hexagonal mesoporous silica catalyst for nonenzymatic hydrogen peroxide oxidation. *Microporous Mesoporous Mater.* **2018**, *257*, 92–98. [\[CrossRef\]](#)
42. Zepeda, T.A.; Infantes-Molina, A.; de Leon, J.N.D.; Obeso-Estrella, R.; Fuentes, S.; Alonso-Núñez, G.; Pawelec, B. Synthesis and characterization of Ga-modified Ti-HMS oxide materials with varying Ga content. *J. Mol. Catal. A Chem.* **2015**, *397*, 26–35. [\[CrossRef\]](#)
43. Wang, S.; Shi, Y.; Ma, X.; Gong, J. Tuning Porosity of Ti-MCM-41: Implication for Shape Selective Catalysis. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2154–2160. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Peng, R.; Zhao, D.; Dimitrijevic, N.M.; Rajh, T.; Koodali, R.T. Room Temperature Synthesis of Ti-MCM-48 and Ti-MCM-41 Mesoporous Materials and Their Performance on Photocatalytic Splitting of Water. *J. Phys. Chem. C* **2012**, *116*, 1605–1613. [\[CrossRef\]](#)
45. Song, H.; Wang, J.; Wang, Z.; Song, H.; Li, F.; Jin, Z. Effect of titanium content on dibenzothiophene HDS performance over Ni₂P/Ti-MCM-41 catalyst. *J. Catal.* **2014**, *311*, 257–265. [\[CrossRef\]](#)
46. Zhao, D.; Budhi, S.; Rodriguez, A.; Koodali, R.T. Rapid and facile synthesis of Ti-MCM-48 mesoporous material and the photocatalytic performance for hydrogen evolution. *Int. J. Hydrog. Energy* **2010**, *35*, 5276–5283. [\[CrossRef\]](#)
47. Peng, R.; Wu, C.-M.; Baltrusaitis, J.; Dimitrijevic, N.M.; Rajh, T.; Koodali, R.T. Ultra-stable CdS incorporated Ti-MCM-48 mesoporous materials for efficient photocatalytic decomposition of water under visible light illumination. *Chem. Commun.* **2013**, *49*, 3221–3223. [\[CrossRef\]](#)
48. Huang, F.; Hao, H.; Sheng, W.; Dong, X.; Lang, X. Embedding an organic dye into Ti-MCM-48 for direct photocatalytic selective aerobic oxidation of sulfides driven by green light. *Chem. Eng. J.* **2022**, *432*, 134285. [\[CrossRef\]](#)
49. Tanev, P.T.; Pinnavaia, T.J. A Neutral Templating Route to Mesoporous Molecular Sieves. *Science* **1995**, *267*, 865–867. [\[CrossRef\]](#)
50. Zepeda, T.A.; Fierro, J.L.G.; Pawelec, B.; Nava, R.; Klimova, T.; Fuentes, G.A.; Halachev, T. Synthesis and Characterization of Ti-HMS and CoMo/Ti-HMS Oxide Materials with Varying Ti Content. *Chem. Mater.* **2005**, *17*, 4062–4073. [\[CrossRef\]](#)
51. Davis, R.J.; Liu, Z. Titania–Silica: A Model Binary Oxide Catalyst System. *Chem. Mater.* **1997**, *9*, 2311–2324. [\[CrossRef\]](#)
52. Schraml-Marth, M.; Walther, K.L.; Wokaun, A.; Handy, B.E.; Baiker, A. Porous silica gels and TiO₂/SiO₂ mixed oxides prepared via the sol-gel process: Characterization by spectroscopic techniques. *J. Non-Cryst. Solids* **1992**, *143*, 93–111. [\[CrossRef\]](#)
53. Boahene, P.E.; Soni, K.; Dalai, A.K.; Adjaye, J. Hydrotreating of coker light gas oil on Ti-modified HMS supports using Ni/HPMo catalysts. *Appl. Catal. B* **2011**, *101*, 294–305. [\[CrossRef\]](#)
54. Soni, K.; Boahene, P.E.; Chandra Mouli, K.; Dalai, A.K.; Adjaye, J. Hydrotreating of coker light gas oil on Ti-HMS supported heteropolytungstic acid catalysts. *Appl. Catal. A Gen.* **2011**, *398*, 27–36. [\[CrossRef\]](#)
55. Boccuti, M.R.; Rao, K.M.; Zecchina, A.; Leofanti, G.; Petrini, G. Spectroscopic Characterization of Silicalite and Titanium-Silicalite. In *Studies in Surface Science and Catalysis*; Morterra, C., Zecchina, A., Costa, G., Eds.; Elsevier: Amsterdam, The Netherlands, 1989; Volume 48, pp. 133–144.
56. Zhang, W.; Fröba, M.; Wang, J.; Tanev, P.T.; Wong, J.; Pinnavaia, T.J. Mesoporous Titanosilicate Molecular Sieves Prepared at Ambient Temperature by Electrostatic (S⁺I⁺, S⁺X⁺I⁺) and Neutral (S⁰I⁰) Assembly Pathways: A Comparison of Physical Properties and Catalytic Activity for Peroxide Oxidations. *J. Am. Chem. Soc.* **1996**, *118*, 9164–9171. [\[CrossRef\]](#)
57. Bulánek, R.; Čapek, L.; Setnička, M.; Čičmanec, P. DR UV–vis Study of the Supported Vanadium Oxide Catalysts. *J. Phys. Chem. C* **2011**, *115*, 12430–12438. [\[CrossRef\]](#)

-
58. Gao, X.; Wachs, I.E. Investigation of Surface Structures of Supported Vanadium Oxide Catalysts by UV–vis–NIR Diffuse Reflectance Spectroscopy. *J. Phys. Chem. B* **2000**, *104*, 1261–1268. [[CrossRef](#)]
 59. Tian, H.; Ross, E.I.; Wachs, I.E. Quantitative Determination of the Speciation of Surface Vanadium Oxides and Their Catalytic Activity. *J. Phys. Chem. B* **2006**, *110*, 9593–9600. [[CrossRef](#)]
 60. Magg, N.; Immaraporn, B.; Giorgi, J.B.; Schroeder, T.; Bäumer, M.; Döbler, J.; Wu, Z.; Kondratenko, E.; Cherian, M.; Baerns, M.; et al. Vibrational spectra of alumina- and silica-supported vanadia revisited: An experimental and theoretical model catalyst study. *J. Catal.* **2004**, *226*, 88–100. [[CrossRef](#)]
 61. Besselmann, S.; Freitag, C.; Hinrichsen, O.; Muhler, M. Temperature-programmed reduction and oxidation experiments with V_2O_5/TiO_2 catalysts. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4633–4638. [[CrossRef](#)]
 62. Kim, T.; Wachs, I.E. CH_3OH oxidation over well-defined supported V_2O_5/Al_2O_3 catalysts: Influence of vanadium oxide loading and surface vanadium–oxygen functionalities. *J. Catal.* **2008**, *255*, 197–205. [[CrossRef](#)]
 63. Kaichev, V.V.; Popova, G.Y.; Chesalov, Y.A.; Saraev, A.A.; Zemlyanov, D.Y.; Beloshapkin, S.A.; Knop-Gericke, A.; Schlögl, R.; Andrushkevich, T.V.; Bukhtiyarov, V.I. Selective oxidation of methanol to form dimethoxymethane and methyl formate over a monolayer V_2O_5/TiO_2 catalyst. *J. Catal.* **2014**, *311*, 59–70. [[CrossRef](#)]