

VO_x Modified H-Beta Zeolite for Dimethyl Ether Direct Oxidation to Polyoxymethylene Dimethyl Ethers

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Abstract

The catalytic performances of bifunctional vanadium oxide supported on H β zeolite with redox and acid properties were investigated for dimethyl ether (DME) direct oxidation to polyoxymethylene dimethyl ethers (DMM_x) (x=1-2). The best catalytic performance was obtained over 15%V₂O₅/H β . The catalysts were characterized by XRD, BET, NH₃-TPD, H₂-TPR, XPS and FT-IR in order to provide the further insight in the relationship of structure and activity. When the loading content of vanadium oxide was 15%, the presence of oxide species was dominantly the polymeric vanadia. The addition of vanadium oxide to the H-beta zeolite not only provided redox sites, but also changed the acid strength and distribution of H-beta zeolite as confirmed by NH₃-TPD measurement, and the positive correlation was found between the DMM_x selectivity and the ratio of weak and strong acid sites. The introduction of vanadium oxide with appropriate amount to the H-beta zeolite promoted the balance between the acid sites and redox sites, which was very vital for obtaining high DMM_x selectivity.

Keywords: Dimethyl ether; Direct oxidation; VO_x/H-beta; Polyoxymethylene dimethyl ethers

Introduction

Polyoxymethylene dimethyl ethers (DMM_x) have attracted intensive research interest because of their promising properties, such as excellent environmental friendly solvent with low toxicity, low boiling point, good solubility, and the high oxygen content and octane value. DMM_x can effectively improve the engine combustion performance of diesel oil to be beneficial to reduce the CH₄, CO content in the exhaust emissions, therefore, it is considered extremely as the promising green diesel additive in the application [1,2]. Traditionally, the dehydration-condensation of methanol with formaldehyde over the acid catalysts was the main method to synthesize DMM_x. Compared with the aldolization reaction, the researchers proposed the one-step oxidation of methanol to DMM, which was considered to be more environmental and economical advantages. For instance, SbRe₂O₆ [3], heteropolyacids [4], Cu-ZSM-5 [5] and Fe-Mo catalyst [6] were applied. Particularly, the V₂O₅/TiO₂ catalysts have been further studied because of the outstanding catalytic performance in direct oxidation of methanol to DMM [7-9].

In addition, new synthesis routes of DMM_x were put forward including the direct oxidation of dimethyl ether (DME, CH₃-O-CH₃) [10-12]. DME can be synthesized via a one-step process at low cost from syngas generated from coal, biomass and natural gas, and it has been known as a clean fuel and a potential non-petroleum oil route chemical synthesis material [13,14]. It is a very competitive and green route that dimethyl ether as reactant is used to synthesize DMM_x.

In our previous work, we reported the synthesis of DMM_x via the direct oxidation of DME over Re/Sm/Mn modified heteropolyacids catalysts [15,16]. We also proposed the possible mechanism that the formation of CH₃OCH₂OCH₃ may be from the combination of CH₃OCH₂ group generated on the redox sites and CH₃O dissociated over acid sites or the dissociation and recombination of C-O bonds via the aldol condensation with methanol and formaldehyde under the synergistic effects of the acid and redox sites of the catalysts. Hence, designing a catalyst including the acid sites and the redox sites into one system was in favor of high DMM_x selectivity to make the most use of the bifunctional components.

Compared with the heteropolyacids, zeolites have drawn great attention as the acid catalysts, due to their high surface area, specific pore structure, high thermal stability and eco-friendly nature. In particular, the HBEA zeolite dominated by weak acid sites should be in favor of the selective oxidation reaction of DME according to our previous research [15]. At the same time, the redox sites are provided by vanadium oxide that has very important redox properties in catalysts due to the capacity to adopt multiple oxidation states. Vanadium oxide-based catalysts are widely used in catalytic oxidation, such as the selective oxidation of methanol to formaldehyde [17], oxidation of SO₂ to SO₃ [18] and oxidative dehydrogenation of propane [19]. So vanadium oxide modified H-beta catalyst is applied to the selective oxidation of DME to DMM_x, and the related work is seldom reported, in addition, we observed the formation of DMM₂, indicating that the further growth of C-O occurred in our research.

In this paper, we designed and prepared H-beta zeolite supported vanadium oxide catalyst with different loading content of vanadium oxide, and investigated its catalytic performance in the direct oxidation of DME to DMM_x. The catalysts were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller isotherms (BET), temperature-programmed desorption of NH₃ (NH₃-TPD), temperature-programmed reduction of H₂ (H₂-TPR), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) to provide the further insight in the influence of structure and surface properties on the activity of VO_x/H-beta.

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Experimental Methods

Catalysts preparation

Commercial H-beta zeolite (Nankai University Catalyst Company, China, SiO₂/Al₂O₃=26) was initially calcined at 823 K for 5 h. The VOx/H-beta zeolite was prepared by the incipient wetness impregnation method. Briefly, a certain amount of ammonium metavanadate (ammonium metavanadate: oxalic acid molar ratio=1:2) were dissolved in oxalic acid solution at the temperature of 333 K in the water bath, then was added by H-beta zeolite. The slurry was kept at room temperature for 12 h, dried overnight at 110 °C, and finally calcined in air at 673 K for 5 h before being crushed to 20-40 mesh.

Catalytic oxidation of DME

The catalytic oxidation of DME was carried out in a continuous flow type fixed-bed reactor. The catalyst (3 ml, 20-40 mesh) was diluted with ground quartz to prevent over-heating of the catalyst due to exothermic reaction. The catalyst was pretreated in flow of O₂ (30 ml/min) for 1 h before reaction. The reactant mixture consisted of DME and O₂ with molar ratio of O₂:DME=1: 1. The reaction products were analyzed by gas chromatography GC-9A (Shimadzu Co.) equipped with flame ionization detector (30 m × 0.32 mm, PEG-40M), GC-4000A with thermal conductivity detector (Porapak T column) and GC-4000A (TDX-01 column) with thermal conductivity detectors. The data of the entire work was calculated based on carbon balance, and the carbon balances of most experiments were within 90-95%.

Catalytic characterization

X-ray diffraction (XRD) measurements were carried out on a Rigaku mini Flex II De X-ray Diffractometer scanning from 5° to 70° at a rate of 4°/min using a Cu Kα radiation source. The applied voltage and current were 30 KV and 30 mA, respectively. The BET surface area and pore volume of the zeolite samples were determined by N₂ adsorption-desorption at -196°C in Micromeritics TriStar II 3020 equipment.

The acid sites of the catalysts were quantified by ammonia temperature-programmed desorption (NH₃-TPD). The NH₃-TPD profiles were obtained in Tianjin XianQuan company tp-5080 type automatic adsorption instrument with a thermal conductivity detector. In all experiments, 100 mg of sample was pretreated at 873K under N₂ flow (30 ml/min) for 30 min, then cooled down to 373K, at this temperature, NH₃ was introduced into the flow system till saturation, then the sample was flushed with N₂ at 373K for 2 h to remove excess ammonia. The NH₃-TPD profiles were recorded from 373 to 873K at a rate of 10 K/min.

The H₂-TPR measurements were taken by using tp-5080 type automatic adsorption instrument with a thermal conductivity detector (TCD) in Tianjin Xian Quan Company. In all experiments, 50 mg of sample was pretreated at 573K under N₂ flow (30 ml/min) for 1 h, then cooled down to 303K, the TPR measurement was carried out using H₂/

N₂ as reducing gas mixture, the H₂-TPR profiles were recorded from 303 to 1123K at a rate of 5 K/min.

The X-ray photoelectron spectra (XPS) were measured on Kratos AXIS Ultra DLD spectrometer equipped with Al anode (Al Kα hv=1486.6 eV) powered at 150 W. The detection area analyzed was 700 × 300 μm. FT-IR measurements were recorded with BRUKER TENSOR 27, in the 4000-600 cm⁻¹ range, with a resolution of 2 cm⁻¹ and using 64 scans. The samples were measured before activation in situ at 673K under the atmosphere of Ar.

Results and Discussion

Surface structures

The XRD spectra show that the structure of the BEA zeolite was maintained after impregnation of VOx. The marked peaks (20.3°, 34.3° and 51.4°) corresponded to crystallites of V₂O₅. The characteristic diffraction peaks of crystalline V₂O₅ were not detected when the content of vanadium oxide was lower than 15%, suggesting that the VOx species were dispersed highly on the zeolite. The peaks of crystalline V₂O₅ appeared when the loading content exceeded 15%, which can be explained by the agglomeration of the polymeric vanadium oxide with the increase of loading content, but when the content was 15%, the intensity of the diffraction peak at 20.3° was ambiguous, manifesting that the proportion of crystalline V₂O₅ was very low. The structure of surface vanadium species supported on the HBEA zeolite depended on the loading content. Below 15%, both monomeric and polymeric species were present, while above 15%, the polymeric vanadia species turned into crystalline vanadium oxide. This could be confirmed by FT-IR providing more detailed information. Structure properties of VOx/Hβ catalysts are given in Table 1. The BET surface area continuously decreased from 558 to 397 m²g⁻¹ with the gradual increase in the loading content of vanadium oxide, while the surface area of 25% V₂O₅/Hβ sample went up slightly compared with the 20% V₂O₅/Hβ, maybe due to the assembly of VOx reducing the blocking of the zeolite pore under the conditions of high loading content. The variation of pore volume also could prove this phenomenon. The results were consistent with the analysis of XRD (Figure 1).

In Figure 2 displays the FT-IR spectra of the prepared catalysts. The catalysts were first treated by high temperature under the atmosphere of Ar, therefore, the influence of hydration on the supported vanadium oxide could be excluded. Through the comparison of the pure zeolite and the catalysts with different loading content of vanadium oxide, the peak at 1023 cm⁻¹ appeared when the vanadium oxide loading content reached 15%, and the intensity gradually enhanced with the increasing content of vanadium oxide. Combining with the XRD results and the literature [20], the band at 1023 cm⁻¹ was considered as the V=O characteristic stretching band of crystalline V₂O₅. For all catalysts except pure zeolite, the band at 894 cm⁻¹ possibly assigning to V-O-V linkage was observed according to the variation tendency,

Catalysts	S _{BET} ^a (m ² g ⁻¹)	S _{micro} ^b (m ² g ⁻¹)	D _{pore} ^b (nm)	V _{micro} ^a (cm ³ g ⁻¹)
Hβ	558	458	2.34	0.183
5%V ₂ O ₅ /Hβ	503	410	2.28	0.164
10%V ₂ O ₅ /Hβ	476	406	2.30	0.162
15%V ₂ O ₅ /Hβ	437	371	2.35	0.148
20%V ₂ O ₅ /Hβ	397	319	2.58	0.127
25%V ₂ O ₅ /Hβ	404	324	2.67	0.129

^acalculated using BET method; ^bcalculated by t-plot method

Table 1: Structure properties of VOx/Hβ catalysts.

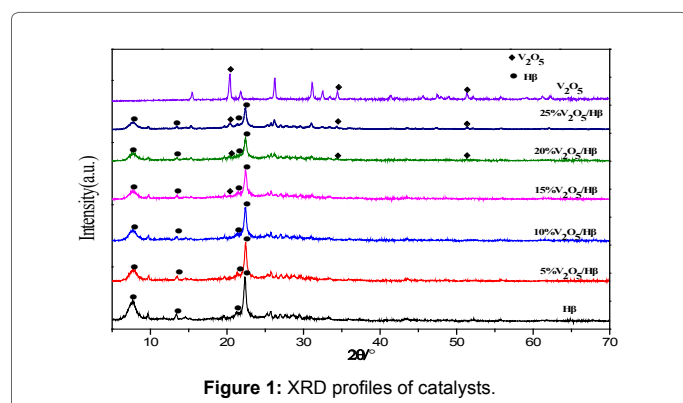


Figure 1: XRD profiles of catalysts.

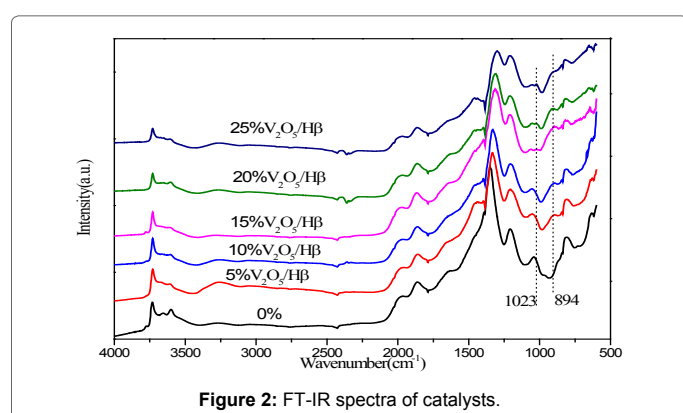


Figure 2: FT-IR spectra of catalysts.

and the intensity of the band increased along with the increase content of surface vanadium oxide, while it did not changed more after the formation of crystalline V_2O_5 .

In Figure 3 presents the binding energies of $V2p_{3/2}$ and the results of vanadium species analyzed by $V2p_{3/2}$ peak-fitting from the XPS spectra. Two BE positions were obtained by peak fitting of $V2p_{3/2}$ line at 517.8 eV and 516.9 eV, which were ascribed to two different components V_2O_5 and V_2O_4 species, respectively. Among the sample, V^{4+} possessed 20%, which may be resulted from the interaction between vanadium and surface atom of zeolite or the combination exposure to air and water vapor, according to the report of Terán-Escobar et al. [21]. The coexistence and shift of V^{4+} and V^{5+} oxidation states prompted the catalytic oxidation cycles, moreover, Tokarz-Sobieraj et al. [22] considered that V^{4+} could be more effective owing to the more available oxygen vacancies and the higher electron density of vanadium that would improve the redox capability to facilitate the oxidation reaction.

Surface acidity

NH_3 -TPD was used to analyze the strength and distribution of the surface acidity of the catalysts. The temperature region of 400-600K was attributed to the weak acid sites, while 600-800K belonged to the strong acid sites as shown in Figure 4. The results were obtained by the integration from the NH_3 -TPD spectra. The profiles showed that the weak acid sites dominated in H-beta zeolite, and the amount of the weak acid sites mounted up, then decreased with the increasing content of vanadium oxide impregnated on the HBEA support, whereas, the intensity of weak acid sites was higher than that of parent zeolite. Addition of vanadium oxide to the H-beta zeolite decreased the strong acid sites distinctly due to the overlapping, which in turn favored the

increase of weak acid sites because of the weak acidity generated by vanadium oxide. However, when the loading content exceeded 20%, the agglomeration of the polymeric vanadium oxide induced the contrary results that 25% $V_2O_5/H\beta$ had more strong acid sites than the low loading content catalyst. The possible explanation could be the exposure afresh of the strong acid sites because of the increase proportion of crystalline V_2O_5 . Thus, the ratio of weak acid and strong acid sites presented the volcanic type with the various content of vanadium oxide, and the maximum ratio was 2.77 when the loading content of VOx was 20%, similar to the 15% $V_2O_5/H\beta$.

As described in Figure 5 for 3300-3800 cm^{-1} region of FT-IR profiles, the intensity of these bands at 3600, 3662, 3782 cm^{-1} weakened obviously and even vanished after the introduction of low loading vanadium oxide content. The band at 3600 cm^{-1} was corresponding to the bridging hydroxyl groups (Si-(OH)-Al), and the features at 3662 and 3782 cm^{-1} were assigned to two kinds of Al-OH groups in which Al atoms belonged to EFAL species and tricoordinated Al atoms linked to the framework by two O atoms, respectively [23]. Thus, VOx species mainly anchored to the bridging hydroxyl groups (Si-(OH)-Al) and Al-OH groups which supported the strong acid sites, and the results were in agreement to the literature [24]. These adequately interpreted the variation of the ratio of W/S in line with the results of NH_3 -TPD (Table 2).

Redox properties

In Figure 6 shows H_2 -TPR profiles of VOx/H β with different V_2O_5 content. From the comparison of the TPR profiles of the catalysts, it was observed that the reduction temperature of impregnated vanadium oxide shifted to higher value with the surface vanadium oxide coverage increasing. Meanwhile, the area of hydrogen consumption peak to some extent went up. In the TPR profiles, the reduction peaks exhibited one single peak. Different vanadia species such as monomeric, polymeric and crystalline VOx species may coexist due to different loading content of the vanadium oxide on the surface species of the VOx/H β system. Thus, the peaks did not necessarily represent different steps of reduction of the same species but should rather be considered to result from a superposition of different reduction steps of several species [25]. In addition, when the vanadium loading content was beyond 20%, the reduction peak was asymmetric with left-hand shoulder that may be ascribed to the reduction of dispersed polymeric vanadium species which were more easily reduced than crystalline V_2O_5 formed on the surface of zeolite, which was confirmed by XRD and FT-IR.

DME selective oxidation to DMMx

In Table 3 presents the catalytic performance of the pure zeolite and H-beta zeolite supported vanadium oxide catalysts in the DME direct oxidation to DMMx (x=1-2). For pure H β zeolite, DME primarily underwent hydrolysis reaction to produce methanol over the acid sites, while the target products were obtained after the introduction of vanadium oxide, suggesting the redox sites provided by vanadium oxide played an importance role in the formation of DMMx from DME oxidation. With the increasing loading content of vanadium oxide, the enhanced selectivity of DMMx was contributed to an increase in the number of active sites. The optimum catalytic performance was achieved over 15% $V_2O_5/H\beta$, and the total selectivity of DMM and DMM₂ reached 46.0% with DME conversion of 12.4%. As the vanadium loading amount further up to 20%, the selectivity of DMM and DMM₂ hardly changed. Routray et al. [26] pointed out that the decrease in activity above monolayer coverage resulted from the low reactivity of crystalline V_2O_5 compared to the surface vanadium

Catalysts	Total acid (mmol NH ₃ /g)	Tm ¹ /K	Weak acid (mmol NH ₃ /g)	Tm ² /K	Strong acid (mmol NH ₃ /g)	WA / SA
Hβ	0.341	505	0.219	653	0.122	1.79
5%V ₂ O ₅ /Hβ	0.397	506	0.278	644	0.119	2.33
10%V ₂ O ₅ /Hβ	0.407	510	0.287	638	0.119	2.41
15%V ₂ O ₅ /Hβ	0.373	502	0.273	615	0.100	2.72
20%V ₂ O ₅ /Hβ	0.360	496	0.264	603	0.096	2.77
25%V ₂ O ₅ /Hβ	0.340	504	0.238	637	0.102	2.34

Table 2: Results of NH₃-TPD profiles integration.

Catalysts	DME Conversion/%	Selectivity/%							
		DMM ^a	DMM ₂ ^b	FA ^c	MF ^d	CH ₃ OH	CO	CO ₂	CH ₄
Hβ	8.6	0	0	0	0	66.5	18.5	15.0	0
5%V ₂ O ₅ /Hβ	13.1	14.4	0	12.4	5.3	43.7	14.4	9.8	0
10%V ₂ O ₅ /Hβ	12.1	41.1	1.7	9.2	10.4	24.4	8.3	5.0	0
15%V ₂ O ₅ /Hβ	12.4	43.5	2.5	7.6	15.4	17.9	7.2	6.0	0
20%V ₂ O ₅ /Hβ	14.5	43.3	2.1	8.8	18.0	18.3	6.2	3.3	0
25%V ₂ O ₅ /Hβ	21.4	22.3	1.3	40.6	8.7	21.7	3.4	2.0	0

Reaction conditions: T=473 K, Atmospheric pressure, n_{DME}:n_{O₂}=1:1; GHSV=800 h⁻¹; ^aDMM: CH₃OCH₂OCH₃, ^bDMM₂: CH₃OCH₂OCH₂OCH₃, ^cFA: HCHO, ^dHCOOCH₃.

Table 3: Effects of different V₂O₅ content on the activity of V₂O₅/Hβ for DME catalytic oxidation to DMMx.

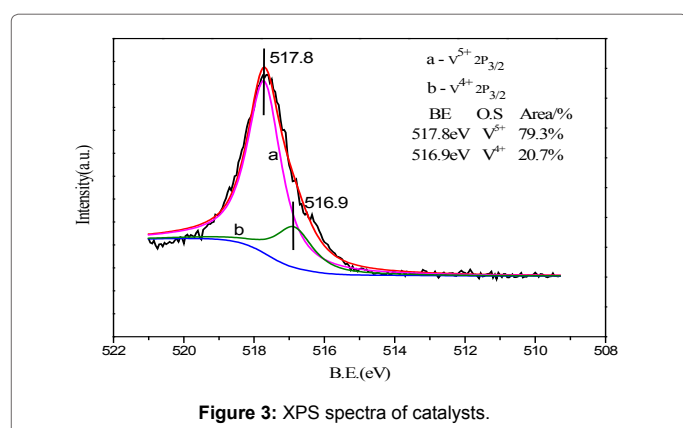


Figure 3: XPS spectra of catalysts.

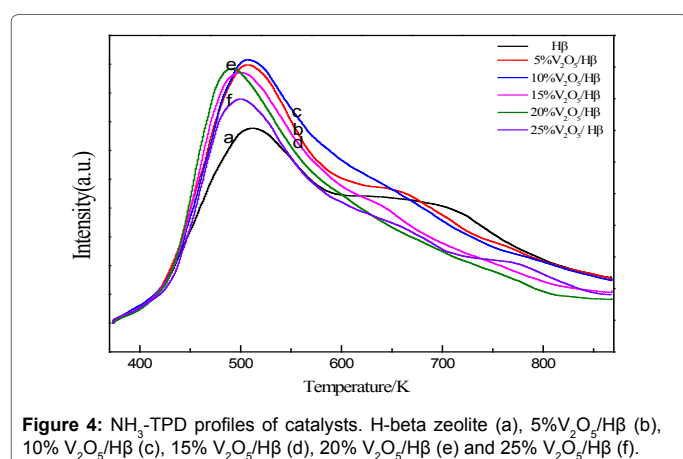


Figure 4: NH₃-TPD profiles of catalysts. H-beta zeolite (a), 5%V₂O₅/Hβ (b), 10% V₂O₅/Hβ (c), 15% V₂O₅/Hβ (d), 20% V₂O₅/Hβ (e) and 25% V₂O₅/Hβ (f).

oxide species. Higher vanadium loading content could promote the conversion of DME but it resulted in more redox sites than acid sites, which accelerated the formation of formaldehyde.

From the H₂-TPR profiles, the presence of reduction peak exhibited the redox properties. With the surface vanadium coverage increasing, the area of hydrogen consumption peak gradually went up, which

provided more and more redox sites for methoxy group or methanol to form HCHO. The appropriate value of redox sites facilitated the formation and transform of HCHO. The excess VOx species leads to the imbalance between redox and acid sites, and further inhibited the synthesis of DMM and DMM₂. The impregnation of vanadium oxide not only provided the redox sites, but also changed somewhat the acid strength and distribution of H-beta zeolite as confirmed by NH₃-TPD measurement. The oxide reduced the number of strong acid sites, and simultaneously increased the amount of weak acid sites, which resulted in the difference of the ratio of weak and strong acid sites. The selectivity of DMMx was compared with the ratio of W/S, and the high ratio of weak and strong acid site was in favor the formation of DMMx (x=1-2) which was coincident with our previous results [15]. When the ratio was similar between 15% and 20%V₂O₅/Hβ, the selectivity of target product was almost the same. These adequately explained the importance role of weak acid site of H-beta zeolite adjusted by VOx in the DME oxidation reaction. Hence, the formation of DMM and DMM₂ was attributed to two types of active sites offered by oxide/zeolite catalyst exhibiting complementary properties.

For the reaction mechanism, the literature [27] pointed out that the reaction began with the molecular chemisorption of methanol on the V⁵⁺ cations. The adsorbed molecules dissociated to form the methoxy species, the following oxidation of the methoxy species led to the formation of adsorbed formaldehyde, which can transform into the surface dioxymethylene species. The further reaction of dioxymethylene species with either the methoxy species or methanol generated dimethoxymethane. The formation of the species was accompanied by the shift of the vanadium oxidation state. However, in our research, we inferred that HCHO formed over the redox sites of polymeric VOx species desorbed when the reaction temperature was higher than what Kaichev et al. reported [27], and then transported to the near weak acid site afforded by the H-beta zeolite support, where DMM and DMM₂ were formed via the acetalization reaction of methanol with the desorbed formaldehyde. When DME proceeded over 15%V₂O₅/Hβ, the major products were formaldehyde and methanol, but they did not further reacted over the active sites of VOx species with the coexistence of formaldehyde and methanol so that dimethoxymethane was not detected under the same reaction conditions. The results above forcefully proved the speculation. The weak acid sites and redox

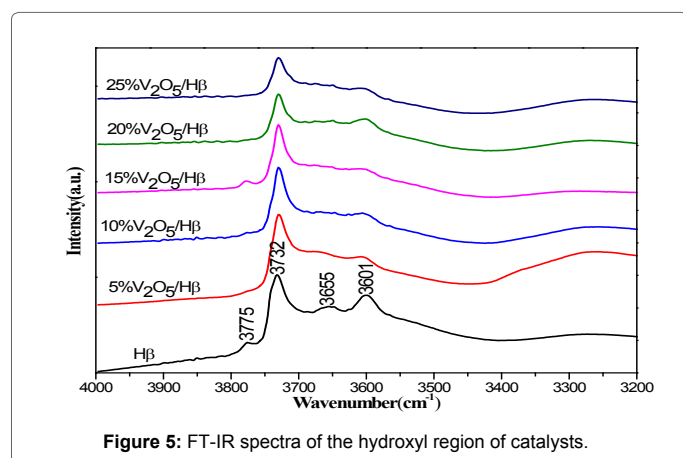


Figure 5: FT-IR spectra of the hydroxyl region of catalysts.

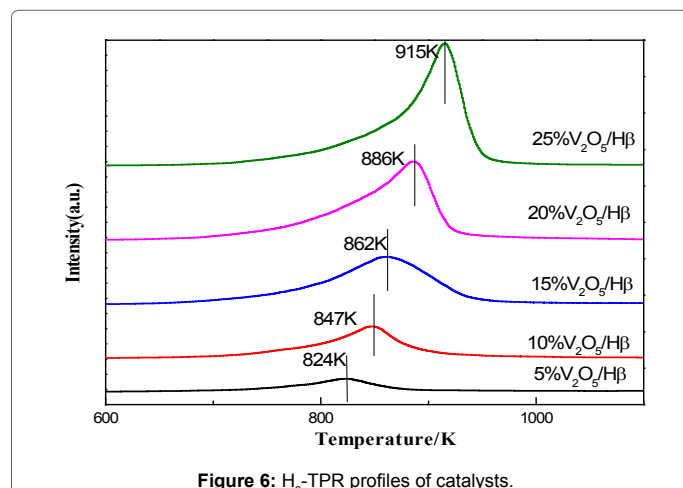


Figure 6: H₂-TPR profiles of catalysts.

properties supported by VOx species were considered to be responsible for the formation of DMMx.

Conclusion

H-beta zeolite supported vanadium oxide was applied in DME direct oxidation to DMMx (x=1-2), the best catalytic performance were obtained and the total selectivity of DMM and DMM₂ reached 46.0% with the DME conversion of 12.4% over 15%V₂O₅/Hβ.

After the impregnation of 15% vanadium oxide on the H-beta zeolite, the polymeric vanadia was the dominant species from the analysis of XRD and FT-IR spectra. The addition of vanadium oxide offered redox sites, and concurrently influenced the acidic strength and distribution of H-beta zeolite as shown by H₂-TPR and NH₃-TPD. Comparing the selectivity of DMMx with the ratio of weak and strong acid sites, they presented the positive correlation. Thus, the appropriate balance between the acid sites and the redox sites played an important role in achieving high DMMx selectivity.

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