

## Role of vanadium in Keggin heteropoly molybdate supported on titania catalysts for oxidation reactions

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**Abstract.** Vanadium-incorporated molybdophosphoric acid catalysts supported on titania were prepared and characterized by FT-IR, X-ray diffraction and laser Raman spectroscopy. Characterization data reveals the incorporation of vanadium into the primary structure of Keggin ion of MPA. Catalysts activities were evaluated for oxidation of 1,2-benzenedimethanol using  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  as oxidants. Vanadium-containing catalysts showed high activity compared to their parent heteropoly acids. Oxidation ability depended on the number of V atoms present in Keggin heteropoly molybdate. Effect of reaction parameters on the oxidation ability was also evaluated.

**Keywords.** Molybdophosphoric acid; titania; vanadium; 1,2-benzenedimethanol.

### 1. Introduction

Heteropolyacids (HPAs) are inorganic acids as well as strong oxidizing agents which mostly exist as Keggin structure. Keggin HPAs consists of a central cation (e.g., P, Si, Ti, etc.) that is surrounded by 12 metal oxide cations (e.g., W, Mo, etc.).<sup>1</sup> Each metal oxide cation possesses one terminal M-O bond, four bridging M-O-M bonds, and one long M-O-P bond. The negatively charged mixed metal oxide Keggin anion is balanced by surface protons. Molecular and structural chemistry of Keggin HPAs can be tuned by substitution of different cations or by exchanging its protons with cations.<sup>2</sup> For example, one or more of the primary  $\text{Mo}^{6+}$  cations in the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  Keggin structure can be substituted by  $\text{V}^{5+}$  cations, and charge imbalance is compensated by additional surface protons or even surface inorganic cations in the surrounding secondary structure of Keggin.<sup>3</sup> Addition of vanadium to  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  (MPA) Keggin enhances its catalytic partial oxidation properties because vanadium introduces redox character to MPA.<sup>4</sup>

Lactones of five and larger rings are important compounds because of their applications in building up biologically active compounds which exhibit various pharmacological activities.<sup>5,6</sup> They can be used in the synthesis of polyesters. There are a number of

methods concerning lactonization of diols.<sup>7</sup> Many catalytic methods including heterogeneous liquid phase lactonization of diols were studied.<sup>8</sup> Among them, vanadomolybdophosphoric acid immobilized on polyaniline,<sup>9</sup> sodium bromate–hydrobromic acid system, palladium<sup>10</sup> and gold-based catalysts<sup>11</sup> have been reported. Most of these systems required long reaction times and tedious work-up procedures.

Although oxidation of alcohols has been widely used in the synthesis of various chemicals, oxidation of diols to lactones usually requires fierce reaction conditions and specific oxidants. The reaction can occur under mild conditions only in the presence of organic cooxidants such as toluene, PhBr,  $\alpha,\beta$ -unsaturated ketone, allyl methyl carbonate, *N*-methylmorpholine *N*-oxide or acetone. Catalytic oxidation of diols to lactones using molecular oxygen or air as the green oxidant is highly suitable.

The objective of the present study is to examine catalytic functionalities of vanadium substituted MPA (MPAV) supported on titania catalysts for oxidation of 1,2-benzenedimethanol using  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  as oxidants. Titania was chosen as a support because it preserves the Keggin unit even at higher temperature than its unsupported form. Another important aspect of the titania support is that it is capable of releasing oxygen from the surface due to mobility of lattice oxygen and to form oxygen vacancies at relatively mild conditions. The influence of V content on the oxidation ability is also one of the aims of the present study.

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## 2. Experimental

### 2.1 Catalyst preparation

2.1a Preparation of  $H_{3+x}PMo_{12-x}V_xO_{40}/TiO_2$ : Vanadium-incorporated molybdophosphoric acid catalysts were prepared according to the reported procedure.<sup>12</sup> In the synthesis of  $H_4PMo_{11}VO_{40}$  (MPAV<sub>1</sub>), hot aqueous solutions of disodium hydrogen phosphate and sodium metavanadate were mixed in required proportions. The mixture was cooled and acidified with concentrated sulphuric acid. To this mixture an aqueous solution of sodium molybdate dihydrate was added. Concentrated sulphuric acid was subsequently added slowly with stirring and the colour changed from dark red to light red. The MPAV<sub>1</sub> formed was extracted with diethyl ether since the heteropoly acid was present in the middle layer as a heteropoly etherate. Ether was removed by passing air through the solution. The orange solid obtained was dissolved in water and concentrated until crystals appeared. Preparation of catalysts with two and three V atoms is also followed similar to that of MPAV<sub>1</sub> except by taking the required amount of sodium metavanadate and sodium molybdate. Titania-supported catalysts were prepared by impregnation method. Required quantity of MPAV<sub>x</sub> ( $y = 1, 2, 3$ ) was dissolved in minimum amount of water and this solution was added to support with constant stirring. Excess water was removed on water bath and catalyst masses were dried in an air oven at 120°C for 12 h. Finally, catalysts were calcined at 300°C for 2 h. These catalysts were denoted as MPAV<sub>x</sub>/TiO<sub>2</sub> ( $x = 1, 2, 3$ ). The active component content on TiO<sub>2</sub> was kept constant at 20 wt% for all the samples.

### 2.2 Characterization of catalysts

The FT-IR spectrum was recorded on a Bio-rod Excalibur series spectrometer using the KBr disc method.

X-ray powder diffraction patterns were recorded on Rigaku Miniflex diffractometer using Cu K $\alpha$  radiation (1.5406 Å) at 40 kV and 30 mA and secondary graphite monochromatic. Measurements were obtained in steps of 0.045° with account time of 0.5 s and in the  $2\theta$  range of 10–80 degrees.

Confocal micro-Raman spectra have been recorded at room temperature in the range of 200–1200 cm<sup>-1</sup> using a Horiba Jobin-Yvon Lab Ram HR spectrometer with a 17 mW internal He–Ne (helium–neon) laser source of excitation wavelength 632.8 nm. Catalyst samples in powder form (about 5–10 mg) were usually loosely spread onto a glass slide below the confocal microscope for Raman measurements.

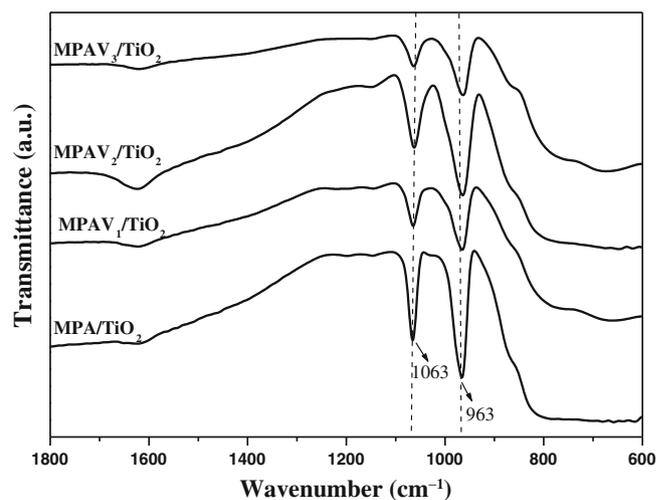
### 2.3 General reaction procedure

In a typical reaction procedure, 1, 2-benzenedimethanol (1 mmol), 30% H<sub>2</sub>O<sub>2</sub> (4 mmol) and dichloroethane (3 ml) were taken in a 25-ml round bottom flask. About 50 mg of catalyst was added to the reaction mixture and stirred at 80°C on oil bath. In the case of O<sub>2</sub> as oxidant, reaction was conducted under O<sub>2</sub> atmosphere. Progress of the reaction was monitored by using thin-layer chromatography. The products were identified by GC-MS (SHIMADZU-2010) analysis by separating products on a DB-5 column.

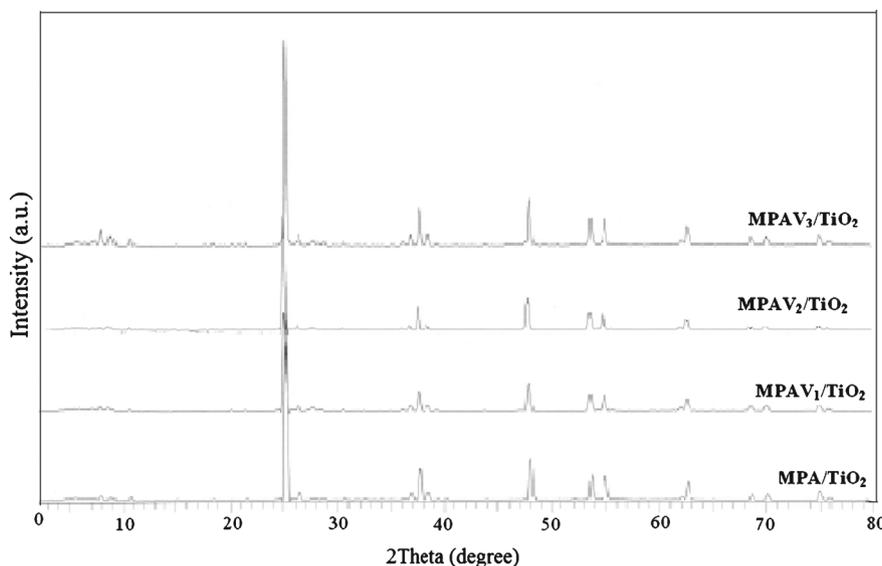
## 3. Results and discussion

FT-IR spectra of the titania-supported vanadium-incorporated molybdophosphoric acid catalysts are presented in figure 1. Spectra of MPA supported on titania (without vanadium) is also presented for sake of comparison. Catalysts mainly exhibited bands at 1063, 963 and 863 that are assigned to stretching vibrations of P–O<sub>a</sub> (O<sub>a</sub> = oxygen atoms bound to three Mo atoms and to P) Mo–O<sub>t</sub> (O<sub>t</sub> = terminal oxygen), Mo–O<sub>b</sub>–Mo (O<sub>b</sub> = corner sharing bridging oxygen), respectively.<sup>13</sup> The TiO<sub>2</sub> support absorbs the IR signal below 800 cm<sup>-1</sup> that prevents collection of weak Keggin vibrations in this region. The P–O and Mo–O bands shifted toward lower wave numbers compared to parent MPA due to reduced structure symmetry.<sup>14</sup> The shift in wave number suggests possible incorporation of V into the primary structure.

XRD patterns of titania-supported MPA and MPAV<sub>x</sub> catalysts are presented in figure 2. The XRD patterns



**Figure 1.** FT-IR spectra of molybdophosphoric acid and vanadium-incorporated molybdophosphoric acid supported on titania catalysts.



**Figure 2.** XRD patterns of molybdophosphoric acid and vanadium-incorporated molybdophosphoric acid supported on titania catalysts.

are dominated by the peaks of crystalline anatase phase of  $\text{TiO}_2$ . Only small diffraction lines at  $2\theta$  values of  $10^\circ$  and  $25^\circ$  indicate the presence Keggin ion structure of  $\text{MPAV}_x$ . These results indicate that the active component  $\text{MPAV}_x$  is well-dispersed on titania.

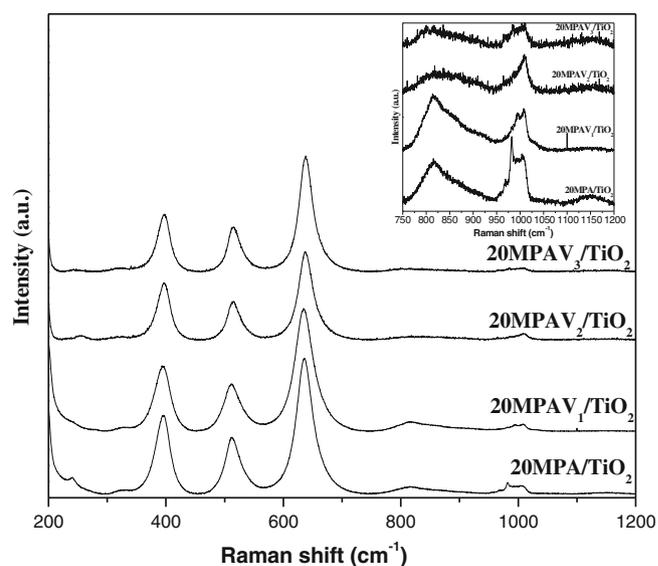
Figure 3 shows the Raman spectra of  $\text{MPAV}_x/\text{TiO}_2$  and  $\text{MPA}/\text{TiO}_2$  catalysts. Characteristic bands of titania are dominant in the spectra. Characteristic bands of Keggin were not seen. Predominant bands at 392, 510 and  $632\text{ cm}^{-1}$  originated from anatase phase of  $\text{TiO}_2$  were seen for all the samples. Only small band at  $1003\text{ cm}^{-1}$  related to  $\text{M}=\text{O}_t$  vibration of Keggin ion of  $\text{MPAV}$  is seen. Bands related to  $\text{M}=\text{O}_t$  vibrations are shown in the inserted figure for the sake of clarity. The absence of a band around  $1034\text{ cm}^{-1}$  indicates that there was no free  $\text{V}_2\text{O}_5$  on the surface of  $\text{MPA}$ .<sup>15</sup> FT-IR and Raman results suggest that V is incorporated into the primary structure of  $\text{MPA}$  Keggin ion.

### 3.1 Oxidation of 1,2-benzenedimethanol

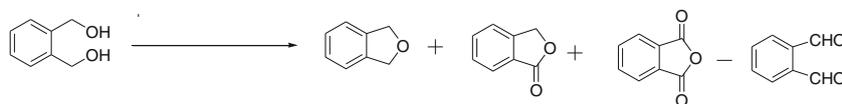
Activity of  $\text{MPA}/\text{TiO}_2$  and  $\text{MPAV}_x/\text{TiO}_2$  catalysts were studied for oxidation of 1,2-benzenedimethanol reaction. Oxidation of 1,2-benzenedimethanol leads to the formation of different products as shown in scheme 1. For this reaction, both  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  were used as oxidants. Selectivity of the products is varied with oxidizing agents. Phthalide is the main product under  $\text{H}_2\text{O}_2$  and 1,3-dihydroisobenzofuran in  $\text{O}_2$ . In  $\text{O}_2$  oxidizing conditions, only small amounts of by-products phthalaldehyde and phthalic acid were

formed. Formation of phthalide proceeds via two steps: initial chemoselective oxidation to 1,2-benzenedimethanol, to give 1,3-dihydroisobenzofuran-1-ol, and then oxidation of 1,3-dihydroisobenzofuran-1-ol to phthalide. Phthalaldehyde could be oxidized to phthalic acid. Dehydration of 1, 2-benzenedimethanol gave 1,3-dihydroisobenzofuran. Catalytic performance and optimization of reaction conditions are based on the yield of phthalide.

Initially, oxidation of 1,2-benzenedimethanol was studied at  $80^\circ\text{C}$  by using  $\text{H}_2\text{O}_2$  and molecular  $\text{O}_2$  as



**Figure 3.** Raman spectra of molybdophosphoric acid and vanadium-incorporated molybdophosphoric acid supported on titania catalysts.



**Scheme 1.** The oxidation products of 1, 2 benzenedimethanol.

oxidizing agents, to determine oxidizing abilities of the catalysts.

### 3.2 Oxidation of 1,2-benzenedimethanol by using $H_2O_2$

Oxidation of 1,2-benzenedimethanol reaction was studied by using titania-supported MPA and  $MPAV_x$  and using  $H_2O_2$  as oxidizing agent and the results are shown in table 1.

Catalyst without vanadium  $MPA/TiO_2$  exhibited poor activity. Catalysts with vanadia showed high yield towards the desired product. It is interesting to note that the MPA modified with V results in high oxidation ability with  $H_2O_2$  as oxidant within reasonable reaction time. This enhancement in the activity of catalysts might be due to the presence of  $V^{5+}$  in MPA which facilitates generation of more reactive lattice oxygen associated with the Mo-O-V species.<sup>16</sup>

Ability of these catalysts can be explained by the role of vanadium which is known for its redox properties. The oxidation reaction proceeds such that the polyoxometallate [ $PMo_{12-x}V_xO_{40}$ ] through transfer of two electron and two protons from the organic substrate to the catalyst to yield the oxidized product and reduced polyoxometallate. The catalyst is reoxidized by oxidizing agent.<sup>16</sup>

The number of vanadium atoms per Keggin unit is also an impact on oxidation ability. Oxidation over the vanadium-containing molybdenum-based heteropoly acids showed that conversion increases with incorporation of vanadium into MPA and maximum selectivity attained for the catalyst with two vanadium atoms in MPA. It is also reported that in the case of molybdenum-based heteropoly acids, substitution of more than two vanadium atoms causes a decrease in the activity. It has been rationalized that the HPA Keggin structure can only tolerate two vanadium per Keggin unit since higher vanadium content destabilizes the crystalline molecular structure of Keggin.<sup>17</sup>

### 3.3 Oxidation of alcohol by using $O_2$ atmosphere

Oxidation of 1,2-benzenedimethanol reaction was also studied using oxygen as oxidizing agent over

$MPAV_x/TiO_2$  catalysts and results are shown in table 2. Using  $O_2$  as oxidant, the main products are dehydration product and aldehyde. In these conditions,  $MPA/TiO_2$  catalyst also gave very low conversion. The  $MPAV_2/TiO_2$  catalyst showed high activity at a high reaction time of 12 h. Compared to the activity obtained by using  $H_2O_2$  oxidant, the activity obtained by  $O_2$  is less because the activation of molecular  $O_2$  is difficult and takes longer time. Generally, noble metal catalysts gave high selectivity when  $O_2$  was used as oxidant.<sup>18</sup> Oxidation ability of these catalysts even in presence of  $O_2$  reiterates the high oxidation ability of  $MPAV_x/TiO_2$  catalysts.

### 3.4 Influence of reaction temperature

Influence of reaction temperature on oxidation of 1,2-benzenedimethanol over  $MPAV_2/TiO_2$  was evaluated by varying the reaction temperature from 40°C to 80°C by using  $H_2O_2$ ,  $O_2$  as oxidizing agents and results are shown in table 3. Conversion of 1,2-benzenedimethanol increased with increase in temperature for both the oxidants. At higher temperature, formation of phthalide is predominant when  $H_2O_2$  is used as oxidant. High conversion cannot be achieved when the temperature is lower than 80°C. Therefore, 80°C was chosen as the optimal reaction temperature because  $H_2O_2$  would decompose at temperatures higher than 80°C. If  $O_2$  used as oxidizing agent, the maximum selectivity is towards dihydrobenzofuran.

### 3.5 Effect of catalyst weight

The effect of catalyst weight also studied for this reaction using  $O_2$  oxidant and results are shown in table 4. In  $H_2O_2$  oxidation conditions, only small amount of catalyst was used because  $H_2O_2$  has stronger oxidation ability than  $O_2$ . High activation energy is required for molecular  $O_2$ . Increase in catalyst amount from 0.05 to 0.15 g leads to increased conversion and remained consistent after further increase in catalyst weight. Formation of 1,3-dihydrobenzofuran increased with increase in catalyst amount and at the same time a decrease in phthalide is observed.

**Table 1.** Oxidation of 1,2-benzenedimethanol by using H<sub>2</sub>O<sub>2</sub>.

Catalyst	Conversion (%)	Yield (%)			
		Phthalide	1,3-Dihydrobenzofuran	Phthalic anhydride	Phthalaldehyde
20MPA/TiO <sub>2</sub>	6.5	3.4	3	-	-
20MPAV <sub>1</sub> /TiO <sub>2</sub>	73.3	64.3	9	-	-
20MPAV <sub>2</sub> /TiO <sub>2</sub>	88.3	71.5	12.2	-	-
20MPAV <sub>3</sub> /TiO <sub>2</sub>	81.3	67.4	13.7	-	-

Reaction conditions: 1,2-benzenedimethanol (1 mmol); 30% H<sub>2</sub>O<sub>2</sub> (4 mmol); catalyst weight (50 mg); temperature 80°C; DCE (3 ml); reaction time 6 h

**Table 2.** Oxidation of 1,2-benzenedimethanol by using O<sub>2</sub>.

Catalyst	Conversion (%)	Yield (%)			
		Phthalide	1,3-Dihydrobenzofuran	Phthalic anhydride	Phthalaldehyde
20MPA/TiO <sub>2</sub>	6.4	-	6.4	-	-
20MPAV <sub>1</sub> /TiO <sub>2</sub>	50.5	9.7	25.6	-	17.5
20MPAV <sub>2</sub> /TiO <sub>2</sub>	85.7	16.3	32.7	12.3	28.5
20MPAV <sub>3</sub> /TiO <sub>2</sub>	82.0	16.5	25.8	12.1	27.4

Reaction conditions: 1,2-benzenedimethanol (1 mmol); catalyst weight (200 mg); temperature: 80°C; DCE (solvent): 3 ml; time: 12 h

**Table 3.** Influence of reaction temperature on oxidation of 1,2-benzenedimethanol.

Temperature (°C)	Oxidant	Reaction time (h)	Conversion (%)	Phthalide yield (%)	1,3-Dihydrobenzofuran yield (%)	Phthalic anhydride yield (%)	Phthalaldehyde yield (%)
40	H <sub>2</sub> O <sub>2</sub>	6	21.0	19.04	2.4	-	-
	O <sub>2</sub>	12	10.8	2.0	6.8	-	1.2
60	H <sub>2</sub> O <sub>2</sub>	6	34.5	32.5	4.5	-	-
	O <sub>2</sub>	12	45.0	12.0	25.5	2.5	5.0
80	H <sub>2</sub> O <sub>2</sub>	6	88.3	71.5	12.2	-	-
	O <sub>2</sub>	12	85.7	16.3	32.7	12.3	28.5

Reaction conditions: 1,2-benzenedimethanol (1 mmol); 30% H<sub>2</sub>O<sub>2</sub> (4 mmol); catalyst weight (50 mg for H<sub>2</sub>O<sub>2</sub> and 200 mg for O<sub>2</sub>); DCE (3 ml)

**Table 4.** Effect of catalyst weight oxidation on 1,2-benzenedimethanol by using O<sub>2</sub>.

Catalyst weight (g)	Conversion (%)	Yield (%)			
		Phthalide	1,3-Dihydrobenzofuran	Phthalaldehyde	Phthalic anhydride
0.05	60.2	23.4	30.9	4.4	1.4
0.10	67.0	19.2	34.1	8.8	4.7
0.15	82.5	16.4	32.7	23.9	2.6
0.20	85.7	13.3	38.9	28.5	10.3
0.25	86.4	12.5	33.0	27.1	13.8

Reaction conditions: 1,2-benzenedimethanol (1 mmol); temperature: 80°C; DCE (solvent): 3 ml; time: 12 h.

#### 4. Conclusions

Titania-supported Keggin-type molybdophosphates with different vanadium content were prepared. These catalysts exhibited high oxidation activity towards 1,2-benzene dimethanol using  $H_2O_2$  and  $O_2$  oxidants. These catalysts are highly active and selective to phthalide under mild conditions within short reaction time using  $H_2O_2$  as oxidant. Activity of catalysts depends on the amount of V present in the heteropoly molybdate and catalysts with two V atoms showed high activity. These catalysts were also active even in the oxidation of 1,2-benzene dimethanol using molecular oxygen as oxidant.

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