AN INVESTIGATION OF NANOSTRUCTURED TUNGSTATA/VANADIA/TITANIA CATALYSTS FOR THE OXIDATION OF METHANOL

by Vipul Kumar

The use of nanostructured V$_2$O$_5$ / TiO$_2$ and WO$_3$ / V$_2$O$_5$ / TiO$_2$ catalysts was investigated for the low temperature oxidation of methanol. A wet incipient method was used to dope WO$_3$ and V$_2$O$_5$ on the Ishihara ST-01 TiO$_2$ support. The V/Ti mass ratios varied from 0 to 0.10 for the V$_2$O$_5$ / TiO$_2$ catalysts, and the W/Ti mass ratios varied from 0 to 0.10 with constant V/Ti mass ratio = 0.02 for the WO$_3$ / V$_2$O$_5$ / TiO$_2$ catalysts. Characterization of the catalysts using X-ray Diffraction, BET surface area and Raman Spectroscopy showed that the thermal stability of catalysts decreased with increasing V/Ti mass ratio over 0.02 but increased with increasing W/Ti mass ratio. The catalytic activity for methanol oxidation increased with W/Ti mass ratio up to W/Ti = 0.05. The catalyst having 0.05 V/Ti mass ratio and calcined at 400 °C showed the highest catalytic activity.
AN INVESTIGATION OF NANOSTRUCTURED
TUNGSTA/VANADIA/TITANIA CATALYSTS FOR THE OXIDATION OF
METHANOL

A thesis

Submitted to the
Faculty of Miami University
in partial fulfillment of
the requirements for the degree of
Master of Science
Department of Paper Science and Engineering
by
Vipul Kumar
Miami University
Oxford, Ohio
2004

Advisor Dr. Catherine Almquist

Reader Dr. Shashi Lalvani

Reader Prof. Michael H Waller
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<td>Brunauer, Emmett and Teller</td>
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<td>D</td>
<td>Crystal Diameter</td>
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<td>eV</td>
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<td>kV</td>
<td>Kilo Volt</td>
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<td>ms</td>
<td>Milli Second</td>
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<tr>
<td>NH$_4$VO$_3$</td>
<td>Ammonium Metavanadate</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
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<tr>
<td>TiO$_2$</td>
<td>Titanium Dioxide</td>
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<tr>
<td>TRS</td>
<td>Total Reduced Sulfur</td>
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<td>VOC</td>
<td>Volatile Organic Compounds</td>
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<td>$\theta$</td>
<td>Angle</td>
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Acknowledgements:

I take a great pleasure in acknowledging following people for their help and support.

**Department of Paper Science and Engineering**

- Dr. Catherine Almquist
- Dr. Shashi Lalvani
- Prof. Michael H. Waller
- Rodney J Kolb
- Faculty, Staff and Fellow Students of Paper Science

**X-Ray Diffraction Analysis**

- John P Marton (Department of Geology)
- Dr. John Rakovan (Department of Geology)

**BET Analysis**

- Dr. James A. Cox (Department of Chemistry and Biochemistry)
- Ms. Diep Vu Ca (Department of Chemistry and Biochemistry)

**Raman Analysis**

- Dr. Andre J. Sommer (Department of Chemistry and Biochemistry)
1.0 Background:

Volatile organic compounds (VOC), nitrogen oxides and sulfur oxides are major pollutants emitted from process industries. VOCs include a wide range of substances, such as hydrocarbons, halocarbons and oxygenates [1]. These compounds have adverse health effects including eye, nose and throat irritation, headaches and damage to the liver, kidney, and central nervous system [2]. VOCs have adverse effects on the environment. They contribute to global warming and produce ground level or lower atmosphere ozone [1].

Existing and anticipated air pollution laws have forced industries to reduce their air emission. The 1990 Clean Air Act Amendments require pulp and paper mills to report their emissions of volatile organic compounds [3]. MACT (Maximum Achievable Control Technology), which is the air portion of new Cluster Rule, requires old and new paper mills to meet air standards to reduce emissions of toxic air pollutants [4,5]. Methanol, total reduced sulfur (TRS) and chlorinated gases are the main VOC pollutants emitted from paper industries. Emissions of TRS hydrocarbons result in noxious odors. These compounds are emitted in small concentrations but in large volumes. Although a number of process modification and treatment technologies have been implemented to control emissions of VOCs, end-of-pipe treatment methods are still required to control air emissions. Currently available control methods are expensive on the basis of energy cost per mass of pollutant destroyed. Therefore, energy efficient control methods are desirable for the process industries.

Currently, incineration is a widely used method for destroying VOC’s. When VOC concentrations are low and volume is large, incineration is not an economical
method to destroy the pollutants. This process requires very high temperatures generally on the order of 800 °C to 1000 °C. These temperatures are typically maintained by burning fossil fuels, such as coal and methane. Therefore incineration increases the fuel costs and produces carbon dioxide, nitrogen oxides and hazardous organic compounds, which contribute to global warming, acid rain and other detrimental environmental effects.

Due to the high costs of energy and the negative impact combustion has on our environment, industries are looking for possible alternate methods of reducing energy use and greenhouse gas emissions. Process modifications and new technologies are being sought in many process industries, including the pulp and paper industry. The development of new oxidation technologies would lead to energy savings and reduced air emissions.

One alternative to incineration for the control of VOC emissions is catalytic oxidation. The key advantage of catalytic oxidation over incineration is that oxidation occurs at lower temperature. Catalysts increase the rate of oxidation reactions which greatly reduces fuel requirements and required temperatures. They can operate at temperatures, on the order of 300 °C, as opposed to the required incineration temperatures of 800 °C - 1000 °C. The catalytic reactor and ancillary equipments are easy to design at these conditions. Catalytic technologies can achieve a higher selectivity of desired end products, lower amount of greenhouse gases, and they do not produce nitrogen oxide gases.

Potential challenges in implementing catalytic technologies are their high cost and their susceptibility to physical and chemical change. Therefore, current research has the
goal of alternative catalysts with more activity and less cost. One way of achieving this goal is through nanotechnology. Catalysts can be made very active in the form of nanoparticles or nanoscale crystals. With the advances in nanotechnology we can systematically organize and manipulate properties and behavior of matter in the atomic and molecular levels [6]. By precisely controlling size, shape, composition and thermal and chemical stability of catalysts we can increase the selectivity and activity of catalysts [7].

The aim of this thesis is to study the oxidation of methanol using nanostructured vanadia/titania (V$_2$O$_5$/TiO$_2$ or V/Ti) and tungst/a vanadia/titania (WO$_3$/V$_2$O$_5$/TiO$_2$ or W/V/Ti) catalysts. V/Ti catalysts are successfully used in selective reduction of NOx [8, 9]. Selective catalytic reduction (SCR) is one of the best proven and widely employed methods in removing NOx from stationary sources due to its efficiency, selectivity and economics [10]. This is applicable to the emissions from different plants, such as power plants, nitric acid plants, stationary diesel engines and urban incinerators [11].

V/Ti catalysts are now drawing considerable attention as selective oxidation catalysts, especially for the oxidation of organic compounds. V/Ti catalyst system has very good catalytic performance in o-xylene oxidation[12]. These catalysts were also found promising for oxidation of other hydrocarbons, such as toluene and its derivative to selective oxidation products[12]. They have also been tested but found to be less effective for the selective oxidation of benzene, olefins, and n-butane [12].

One ternary catalyst system W/V/Ti has also been investigated for the selective catalytic reduction of NOx. It has been demonstrated that tungsta inhibits the initial sintering of anatase TiO$_2$ and the anatase to rutile transition. Studies show that W grants
the ternary catalyst system more stability and higher reactivity in the SCR reaction than
the corresponding binary V/Ti catalyst [13].

Certain factors, such as composition, crystal phase of the TiO₂ support and surface
area, affect the thermal stability and overall catalytic performance. V₂O₅ loading affects
the reactivity of the catalysts. There is a strong interaction between active V₂O₅ and
support TiO₂. The spreading of vanadium over the TiO₂ support modifies the chemical
and physical peculiarities of the former which results in better catalytic properties [14].
Vanadium has potentially rich surface catalytic chemistry, the complete understanding of
which still needs to be investigated. V/Ti catalysts are generally prepared by using
impregnation technique in which V₂O₅ is deposited on commercially available TiO₂. The
overall V₂O₅ amount that can be deposited is largely dependent on surface area of TiO₂.
There are some contradictions about the best V₂O₅ loading. Studies report optimum
loading to be as low as 4% and as high as 30% [15].

TiO₂ support for these catalysts exists in three forms; anatase, brookite and rutile,
which are shown in Figures 1 – 3 [16]. However, anatase and rutile are the forms most
studied in the literature. They differ from each other in structure. Anatase has a more
open crystal structure and rutile has a compact crystal rod like structure. The anatase
form of TiO₂ is metastable and transforms into the thermodynamically stable rutile form
after calcinations. Studies show that small anatase particles with surface area more than
100 m²/g transform into rutile more easily than larger particles [17]. Studies have also
suggested that anatase gives more active and selective catalysts than rutile [18].
Figure 1: *The crystal structure of anatase TiO₂*

Figure 2: *The crystal structure of brookite TiO₂*
The crystal structure of rutile TiO$_2$

The goal of this study is to assess, whether V/Ti and V/W/Ti catalyst systems are useful for oxidizing methanol. Methanol is chosen in this current study because it is the predominant VOC emitted from the pulp and paper industry. Sources of methanol are the recovery boiler, oxygen delignification systems and effluent treatment systems.

The methanol oxidation can form various products depending on the catalyst and reaction temperature. The main intermediate products are formaldehyde (CH$_2$O), dimethyl ether (CH$_3$OCH$_3$), methyl formate (HCOOCH$_3$), methylal ((CH$_3$O)$_2$CH$_2$) and carbon oxides. Formation of formic acid is also observed, but rarely. It is considered an intermediate product in the formation of methyl formate or carbon dioxide. These reactions are shown in Figure 4. However, in our study we did not analyze the reaction products of methanol oxidation, rather we analyzed only the degradation of methanol. The following reactions take place during oxidation of methanol [19].
CH$_3$OH + CH$_3$OH $\rightarrow$ CH$_3$OCH$_3$ + H$_2$O  
+ $\frac{1}{2}$ O$_2$

HCHO + H$_2$O $\rightarrow$ (CH$_3$O)$_2$CH + H$_2$O  
+ 2 CH$_3$OH

(HCOOH) + CH$_3$OH $\rightarrow$ HCOOCH$_3$ + H$_2$O  
- 2 CH$_3$OH

CO$_2$ + H$_2$O

(Oxidation Reactions)  (Dehydration Reactions)

Figure 4: Reactions taking place during oxidation of methanol [19]
2.0 Research Objectives and Tasks:

The overall objective of this study was to assess the feasibility of using nanostructured V / Ti and W/ V/ Ti catalysts for the destruction of methanol, a major pollutant from pulp and paper industries. It was hypothesized that W loading on V/Ti catalysts will improve the thermal stability and reactivity of these catalysts.

Specific research objectives are to:

1. Investigate the effect of tungsten oxide loading on the thermal stability of W/ V/ Ti catalysts.
2. Investigate the effect of tungsten oxide loading on the reactivity of W/ V/ Ti catalysts for methanol oxidation.
3. Investigate the effect of calcination temperature on the behavior of catalysts.
4. Comparison of behavior between V/ Ti and W/ V/ Ti catalysts with respect to thermal stability and methanol oxidation.
3.0 Experimental Design and Methods:

3.1 Experimental Design

The following three tasks were conducted to meet the research objectives:

1. Catalyst synthesis

2. Catalyst characterization
   a. X-Ray diffraction
   b. BET surface area
   c. Raman Spectroscopy

3. Catalyst performance

The Tables 1 - 3 show the experimental design to be done to meet the objectives.

**Table 1: Catalyst Synthesis:** [Precursors: TiO$_2$ - Ishihara ST-01 (100% Anatase), V$_2$O$_5$ - Ammonium Metavanadate (Fisher Scientific), WO$_3$ - Tungstic Acid (Sigma-Aldrich)]

<table>
<thead>
<tr>
<th>Method</th>
<th>Catalyst Composition</th>
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<tr>
<td>Wet incipient method</td>
<td>V/Ti ratio,</td>
</tr>
<tr>
<td></td>
<td>V= 0,0.1,0.5,1,2,5,10% of TiO$_2$ mass</td>
</tr>
<tr>
<td>Wet incipient method</td>
<td>W/V/Ti ratio, V= 2%, of TiO$_2$ mass</td>
</tr>
<tr>
<td></td>
<td>W= 0,0.1,0.5,1,2,5,10% of TiO$_2$ mass</td>
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Table 2: Catalyst Characterization

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<th>Catalyst</th>
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<td>All V/Ti and W/V/Ti catalysts</td>
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<tr>
<td>BET Surface Area</td>
<td>All V/Ti and W/V/Ti catalysts</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>Selected V/Ti and W/V/Ti catalysts</td>
</tr>
</tbody>
</table>

Table 3: Performance Testing: [Constants: Methanol Concentration - 9500 ppm, Methanol Temperature - 60 °C, Catalyst Amount - 50 mg, Air flow rate - 10 ml/min, Reaction Time – 2 hours]

<table>
<thead>
<tr>
<th>Catalyst Composition</th>
<th>V/Ti ratio, V= 0,1,2,5,10%</th>
<th>W/V/Ti ratio, V= 2%, W= 0,1,2,5,10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination Temperature</td>
<td>400, 500, 550, 600 °C</td>
<td>400, 500, 550, 600 °C</td>
</tr>
<tr>
<td>Reaction Temperature</td>
<td>100,125,150,175,200,225,250 °C</td>
<td>100,125,150,175,200,225,250 °C</td>
</tr>
</tbody>
</table>
3.2 Experimental Methods:

The experimental methods used to achieve the research objectives are described below.

3.2.1 Catalyst Synthesis:

A number of methods, such as flame synthesis, wet incipient, dry impregnation, sol-gel, precipitation and co-precipitation, are available for catalyst synthesis. Catalysts prepared by different methods have different characteristics. In the wet incipient method metal dopants are placed on the surface of a TiO₂ support while in flame synthesis, metal dopants are placed within the TiO₂ matrix. In our study the wet incipient method was chosen for the synthesis of catalysts. The advantages of the wet incipient method includes: the ease of preparation, uniform composition and V₂O₅ loading at the surface of TiO₂.

3.2.1.1 V₂O₅ / TiO₂ Synthesis:

Five grams of Ishihara ST- 01 TiO₂ (100% anatase) were added to 60 ml of deionized water and stirred and heated in a beaker on a magnetic stirrer. A measured quantity of ammonium metavanadate (Fisher Scientific) was added to the TiO₂ to vary the V/Ti ratio from 0 % to 10%. The slurry was heated to approximately 70 °C until all the water evaporated and the slurry turned to a thick paste. This paste was kept in the oven at 100 °C overnight for drying. After drying, a mortar and pestle was used to crush the V/Ti powder. This powder was divided into five equal aliquots. Four aliquots were calcined in air at 400, 500, 550 and 600 °C for 24 hours and one original V/Ti powder aliquot was left for the future if needed. After calcination, the powder was again crushed and stored in vials for characterization and performance testing.
3.2.1.2 \( \text{WO}_3 / \text{V}_2\text{O}_5 / \text{TiO}_2 \) Synthesis:

A weighed amount of tungstic acid (Sigma-Aldrich) was added to 60 ml of water along with 3-4 drops of ammonium hydroxide. Ammonium hydroxide was used to increase the solubility of tungstic acid in water. A fixed mass of \( \text{TiO}_2 \) (100% anatase) was added to this ammonia solution and stirred using a magnetic stirrer. A measured weight of ammonium metavanadate (Fisher Scientific) was added to slurry to make a 2% V/Ti ratio. V/Ti ratio was fixed at 2% while W/Ti ratio was varied from 0% to 10%. This slurry was heated to approximately 70 °C until it became a thick paste. This paste was kept in an oven at 100 °C overnight for drying. After drying the W/V/Ti powder was crushed using a mortar and pestle and divided into five equal aliquots. Four aliquots were calcined in air at 400, 500, 550 and 600 °C for 24 hours and one was left for future needs. After calcination, the catalysts were again crushed using mortar and pestle and stored in vials for analysis.
3.2.2 Catalyst characterization:

After synthesis, catalyst characterization was done using X-Ray diffraction, BET surface area analysis and Raman Spectroscopy. Each characterized method is discussed below.

3.2.2.1 X-Ray Diffraction:

X-Ray diffraction (XRD) method is used to determine the crystal phase of the TiO2 support. We used XRD to access the thermal stability of the catalysts as function of composition and calcination temperature. Our aim was to see how crystal phase changed with,

(a) Calcination temperature
(b) V/ Ti loadings
(c) W/ V/ Ti loadings

The X-Ray Diffractometer (Scintag X1) consists of a voltage and current stabilizer and is connected to a computer and printer. Scintag software is used to calibrate the diffractometer and record the diffraction pattern. A filament current of 35 mA is maintained along with the voltage of 40 kV. Diffractometer scan rate of one degree per minute is used. It takes approximately 70 minutes to complete one test. It gives the ‘raw’ file after the completion of the test. This raw file can be opened in Microsoft Excel.

The X-ray diffraction pattern of a material is like a fingerprint of the material. The powder diffraction method is ideally suitable for characterization and identification of a polycrystalline phase. When X-rays interact with a crystalline material, a diffraction pattern is achieved. Every crystalline material gives a pattern, the same material always gives the same pattern and in a mixture of substances each produces its pattern
independently of the others. The mechanical assembly consisting of a sample holder, detector arm and associated gearing is called a goniometer [20]. It works on the basis of Bragg’s law, which is illustrated in Figure 5.

**Figure 5: Bragg’s Law [21]**

Bragg’s law states that for X-rays scattered from a crystalline solid [21],

$$n \lambda = 2d \sin \theta$$

(1)

Where:

$\theta$ = angle of incidence of X-ray beam (degrees)

d = the distance between atomic layers in a crystal (Å)

$\lambda$ = the wavelength of the incident X-ray beam (Å)

n = an integer

In a goniometer the distance between the X-ray focal spot and the sample is the same as the distance between the sample and the detector. In a $\theta:0$ goniometer, the sample is stationary in the horizontal position. The X-ray tube and the detector both
move simultaneously over the angular range $\theta$. This has been shown in Figure 6.

Figure 6: The $\theta$-$\theta$ Goniometer [16]
XRD results show the change in phase after calcinations at different temperatures. The fraction of anatase phase in the catalysts is calculated using the equation[22],

\[
F = \frac{1}{1 + 1.26(\frac{I_R}{I_A})}
\]  

(2)

Where:

F is the anatase fraction of titania.

\(\frac{I_R}{I_A}\) is the ratio of intensity of the strongest rutile and anatase reflection.

1.26 is a constant determined by Robert A. Spurr and Howard Myers, Hughes research lab, California).

The Scherrer equation was used to estimate the anatase crystal size using the data from the ‘raw’ file after the scanning. According to the Scherrer equation, the mean diameter of an anatase crystallite can be estimated using the following equation [23]

\[
D = k \frac{\lambda}{B_{1/2}} \cos (\theta)
\]

(3)

Where:

D is the diameter of the anatase crystalline particle (Å).

‘k’ is a constant ranging from 0.7 to 1.71. The value of ‘k’ is used as 0.94 in this study.

\(B_{1/2}\) is the half height width of the anatase peak.

\(\lambda\), is the wavelength of the X-Ray. \(\lambda = 1.54\) Å is used.

\(\theta\), is the angle measured from the diffraction pattern (degrees).

The XRD gives the values as intensity (counts per second) versus 2 \(\theta\) (degree). At the 2 \(\theta\) value of 25.5, the anatase titania major feature occurs. So the \(\theta\) value of 12.25 is used in equation (2) to check the crystal size.
3.2.2.2 BET Surface Area:

The BET (Brunauer, Emmett and Teller) is the most commonly used method to characterize the specific surface area of finely divided and porous material. In this study a Coulter SA 3100 surface area analyzer was used to check the specific surface area of catalysts.

Our aim of BET was to assess how the specific surface area of the catalysts varied with:

(a) Calcination temperatures
(b) V/ Ti loadings
(c) W/ V/ Ti loadings

A Coulter SA 3100 analyzer has a built in vacuum pump and a simple touch screen user interface. Initially, outgassing is done to prepare the sample for analysis. Helium is used for this purpose. Outgassing removes adsorbed gases and moisture from the sample surface by evacuating gases with the help of vacuum pumps. Each sample is outgassed for 80 minutes at a furnace temperature of 125 °C. Outgassed samples are used for analysis.

Analysis involves adsorption of nitrogen gas onto the surface and into the pores of outgassed sample. A known amount of nitrogen gas is added into an evacuated tube containing the sample. The quantity of adsorbed gas and the pressure in the sample tube is incrementally increased with a constant tube temperature. After each dose of nitrogen gas, when the pressure in the sample is equilibrated, the data is recorded. Pressure readings are used to calculate the gas volume adsorbed.
The volume of gas adsorbed is measured as a function of relative pressure. Relative pressure is defined as the ratio of pressure in the sample tube to the saturation vapor pressure of adsorbate gas. The sample tube is immersed in a Dewar (vacuum flask) filled with liquid nitrogen to maintain a temperature where liquefaction of nitrogen gas can take place on the sample. The resulting data set is called an adsorption isotherm because measurement is performed at (-196 °C). This isotherm data is used to calculate the surface area.

Analysis results are written to the diskette automatically during analysis. Output to the diskette is in ASCII format and COULTER SA-VIEW Microsoft Windows based program was used for reviewing data files. Figure 7 shows the SA 3100 Analyzer. [24]

Figure 7: SA 3100 COULTER Surface Area Analyzer [24]
With the increase of calcination temperature, small particles come together and form bigger particles, thus increasing particle size. With an increase in particle size, surface area decreases.

3.2.2.3 Raman Spectroscopy:

Raman Spectroscopy is used to characterize the different functional groups present on the catalyst. In this study it was used to characterize V and W groups present on TiO\textsubscript{2}. A Raman spectrometer works on the basis of inelastic light scattered by molecules. A sample is illuminated with the help of a laser beam. The molecules present in the sample vibrate or rotate at characteristic frequencies. The molecules scatter back the light. A shift in the frequency of the light is observed as per the specific nature of the molecule. This scattered light is collected with the help of a window probe and the concentration of the components is analyzed in a spectrographic detector with computer. In Raman Spectroscopy the spectra is very specific and sharp. It minimizes the interference between molecules. The results obtained are qualitative as well as quantitative. Although in our study, Raman was used only qualitatively. After the analysis a graph is obtained between intensity and wave number.
3.2.3 Performance testing:

After the synthesis and characterization, the performance of each catalyst was tested. The oxidation of methanol was chosen as a measure to assess the performance of the catalysts.

Our aim of this testing was to analyze the oxidation of methanol at different temperatures. It includes,

- The temperature at which methanol shows total destruction
- The effect of calcination temperatures on methanol destruction
- The effect of different V/Ti loadings on methanol destruction
- The effect of different W loading on V/Ti in the destruction of methanol

A schematic of the test system used to assess the catalyst performance is shown in Figure 8. Performance constants and variables are listed in Table 3.

![Schematic Diagram of experimental setup for Thermo Catalytic Process](image)

**Figure 8:** Schematic Diagram of experimental setup for Thermo Catalytic Process

It consists of a mass flow controller to control the flow of air through the test system at 10 ml/min. 50 mg of catalyst was placed as a plug in a ¼” OD alumina reaction
tube, which was secured in a tube furnace. The temperature of the furnace varied from 100 °C to 250 °C. A Gas-Chromatograph (GC) (HP 6890) with a thermal conductivity detector (TCD) was used to detect the various components present in the gas coming from the reactor. The GC is connected to a computer to store and analyze the data. Software, called Chemstation, is used for this purpose. It gives the different peak areas corresponding to the concentration of different components present in the reactor effluent.

Figure 9 shows the Lindberg/Blue Reaction tube furnace and HP 6890 Gas-Chromatograph is shown in Figure 10.

Figure 9: Lindberg /Blue Reaction Tube Furnace
Figure 10: HP 6890 Gas-Chromatograph
Methanol vapors were generated using a diffusion cell, shown in Figure 11. The diffusion cell consists of a glass vial filled with methanol connected to the air flow line with a 12.065 cm long, 0.3175 cm ID Teflon tube. A stable methanol concentration in the inlet air flow to the reactor was obtained using the diffusion cell. The rate of diffusion of methanol is defined as[25]:

\[
N_A = \frac{D_{AB} P}{RT} \frac{(z_2 - z_1) \ln (P - p_{A2})}{(P - p_{A1})}
\]  

(4)

Where:

- \(N_A\) is rate of diffusion, (moles/sec/cm²)
- \(D_{AB}\) is diffusivity of methanol (cm²/s)
- \(P\) is total pressure (Pa)
- \(p_{A1}\) and \(p_{A2}\) are partial pressure of methanol (Pa)
- \(p_{B1}\) and \(p_{B2}\) are partial pressure of air (Pa)

**Figure 11: Diffusion of Methanol in Air**
A linear response of the GC peak areas to methanol concentration was verified. The flow of the air was varied to change the concentration of methanol in the air, and the peak area of the methanol was analyzed. The peak area varied with respect to methanol concentration. The system was checked before each run for any possible leakage. Methanol was heated to 60°C in a water bath to maintain a sufficiently high methanol concentration such that it can be analyzed by the GC.
4.0 Results and Discussion:

4.1 Thermal Stability:

X-Ray diffraction study resulted in the following outcome for V/Ti and W/V/Ti catalysts:

- Anatase to rutile phase change
- Anatase crystal size change

We assessed the thermal stability of the catalysts by investigating the TiO$_2$ crystal phase change from anatase to rutile with calcination temperature. The anatase TiO$_2$ fraction in each prepared catalyst was determined using XRD spectra. Figure 12 shows the anatase fraction of the V/Ti catalysts as functions of composition and calcination temperature. At V/Ti ratios up to 0.01, no phase change is observed, even following calcination at temperatures up to 600 °C. However, the phase transformation from anatase to rutile occurs as the V/Ti ratio increases to 0.02 and above. For example, at a V/Ti ratio of 0.10, slight phase conversion is noted following calcinations at 500 °C. At V/Ti ratios of 0.05, and 0.10, complete conversion from anatase to rutile is observed following calcinations at 550 °C and 600 °C. At a V/Ti ratio of 0.02, significant phase transformation is observed following calcinations at 600 °C. These results support the conclusion presented by Balikdjian, et al. [17] that a minimal amount of surface V species is required to decrease the temperature at which phase transformation occurs.
Figure 12: Fraction Anatase vs. V/Ti ratio at different calcination temperatures for V/Ti catalysts

Figure 13 shows the anatase fraction in the W/V/Ti catalysts as functions of both the W/V/Ti mass ratio and calcination temperature. Note that in these catalysts, the V/Ti ratio was held constant at 0.02, while the W/Ti ratio varied between 0 and 0.1. Based upon the results shown in Figure 13, the addition of W to the catalysts inhibited the phase transformation. Fraction anatase increased with increase in W loadings at calcination temperature of 600 °C. Only exception was the catalyst with 0.005 W/Ti ratio. It seems an outlier. At a W/Ti ratio of 0.05 and 0.10, very little to no phase transformation from anatase to rutile was observed following calcinations at 600 °C. This data supports the conclusions made by S.Djerad, where they found that W/Ti loading of 0.05 and 0.09 inhibited the phase transformation of TiO₂ [26].
The anatase crystal size of each catalyst was also estimated based upon XRD spectra using equation (3). This equation can be used only for anatase crystal size. As shown in Figure 12, at V/Ti ratios of 0.05 and 0.1, anatase was converted completely to rutile at calcination temperatures of 550 °C and 600 °C. Anatase crystal size could not be calculated for these catalysts.

The affect of calcination temperature was significant in all the catalysts. Anatase crystal size increased with a increase in calcination temperature. It indicates that anatase sintering takes place and particles come closer to form a large crystal. At low V concentration (≤ 2%) the crystal size did not increase significantly. As shown in Figures 14 and 15, the anatase crystal size increases with increasing V loadings, especially at 5% and 10%. This is in agreement with previous observations by G. Madia et al. that vanadia promotes the increase in crystal size [27]. However, the addition of W to the catalysts
does not seem to significantly affect the anatase crystal size of the W/V/Ti catalysts, as shown in Figures 16 and 17.

**Figure 14:** *Anatase Crystal Size vs. V/Ti ratio for V/Ti catalysts*

**Figure 15:** *Anatase Crystal Size vs. Calcination Temperature for V/Ti catalysts*
Figure 16: Anatase Crystal Size vs. W/Ti ratio ($V=2\%$) for W/V/Ti catalysts

Figure 17: Anatase Crystal Size vs. Calcination Temperature for W/V/Ti catalysts
Figure 18 shows the reduction in BET surface area as functions of calcination temperature and V/Ti ratios. As shown, there is little effect of V/Ti ratio on BET surface area reduction at V/Ti mass ratios up to 1%, suggesting that the catalysts with low amounts of V species on the surface sinter to the same extent as catalysts without V. At a V/Ti ratio of 2%, the catalyst surface area significantly reduces to less than 5 m$^2$/g following calcinations at 600 °C. However, at V/Ti ratios of 5% and 10%, the reduction in surface area to below 10 m$^2$/g occurs following calcinations at 500 °C. Therefore, the BET surface area reduction, or degree of sintering, increases with increasing V/Ti mass ratio. Besselmann, et al. [28] observed that the V species on the surface of V/Ti catalysts when present in low concentrations are predominantly monomeric and polymeric species in strong interaction with the TiO$_2$ support. At high V concentrations, the V species on the surface of the catalysts are predominantly polymeric and crystalline vanadia species. Considering the BET surface area and XRD data for our catalysts, and the observations by Besselmann, et al. [28], monomeric and polymeric species in strong interaction with the TiO$_2$ may indeed inhibit phase transformation, whereas crystalline and polymeric vanadia at the surface of the catalysts (likely present in our catalysts with V/Ti ratios of 2%, 5%, and 10%) promote sintering and anatase to rutile phase transformation.
Figure 18: Specific Surface Area vs. Calcination Temperature for V/Ti catalysts

Figure 19 shows the change in specific surface area as a function of calcination temperatures for W/V/Ti catalysts. Surface area decreases with increase in calcination temperatures for all the catalysts. Figure 20 shows the effect of W/Ti ratios on surface area. Catalyst surface area increases slightly as the W/Ti ratios increase. Therefore, the addition of tungsta appears to inhibit catalyst sintering somewhat, especially at higher (5% and 10%) W/Ti ratios. This is in good agreement with measurements made in previous studies by S. Djerad, that tungsta loadings hinders the sintering process and increases surface area[26].
Figure 19: Specific Surface Area vs. Calcination Temperature for W/V/Ti catalysts

Figure 20: Specific Surface Area vs. W/Ti ratio (V=2%) for W/V/Ti catalysts
Raman spectra of the V/Ti and W/V/Ti catalysts were obtained. As per literature the crystalline vanadia is characterized by a Raman band at 995 cm \(^{-1}\)[28]. Terminal V=O groups of bulk vanadia are represented by this Raman band. Figure 21 shows the Raman results for V/Ti (500 °C) catalysts. Peaks for V species were observed in catalysts with V loadings of 5% and 10% at approximately 995 cm \(^{-1}\) frequency.

![Raman Spectroscopy results for V/Ti (500 °C) catalysts showing V species, A= Anatase](image)

**Figure 21:** Raman Spectroscopy results for V/Ti (500 °C) catalysts showing V species, A= Anatase
Phase change and reduction in surface area are also observed at 5% and 10% V loadings. It supports the conclusion of Besselmann et al. [28], that crystalline V groups present on Ti enhance degree of sintering and phase transformation.

According to G. Madia et al., the W units are characterized by the band around 800 cm\(^{-1}\) [27]. This peak indicates the presence of W-O-W stretching of W units on the surface of catalyst. Figure 22 shows the Raman results for catalysts with different W/V/Ti catalysts calcined at 600 °C. W peaks were observed at around 800 cm\(^{-1}\) for catalysts with 5% and 10 % W loadings on Ti.

Raman results also show the phase change with change of W loadings on Ti in catalysts calcined at 600 °C. Maximum rutile behavior is observed in 0% W/V/Ti catalysts. As W increased from 0-10 %, the anatase phase is restored from rutile. At 5 % and 10% W loadings very little or no rutile phase is observed. It indicates that W addition inhibits phase transformation. These results are also observed in XRD analysis, as shown in Figure 13.
Figure 22: Raman Spectroscopy result for 10% W/V/Ti (600 °C) catalysts showing W species, $A =$ Anatase, $R =$ Rutile
In summary, the thermal stability apparently degrades with increasing V/Ti ratios over 0.02 but improves with increasing W/Ti ratio. In our study, the thermal stability of catalysts with V/Ti of 0.02 was greatest with W/Ti ratios of 0.05 and 0.10, as indicated by lower TiO$_2$ phase transformation temperatures and lower extents of surface area reduction.
4.2 Catalyst Performance

Catalyst performance was investigated with catalysts with V loadings of 0%, 1%, 2%, 5%, 10% and W loadings of 0%, 1%, 2%, 5%, and 10%. The fraction of methanol oxidized was used as a measure of catalyst performance. However, in this study, no differentiation was made between partial and deep oxidation of methanol. Catalysts with V loadings of 0.1% and 0.5% were not tested because their physical characteristics were very similar to that of 1% V loading.

The results for the destruction of methanol over V/Ti catalysts that show the effect of V/Ti ratio are shown in Figures 23 – 27 and those that show the effect of calcination temperature for the same catalysts are shown in Figures 28 - 31. Note that in the control runs, where methanol destruction was investigated in an empty reaction tube and in a reaction tube with the quartz wool plugs but without catalyst, very little degradation of methanol was observed at temperatures up to 250 ºC. These results ensure that the observed degradation of methanol is due to the presence of the catalysts in the reaction tube.
Figure 23: *Un-reacted Methanol vs. Reaction Temperature for 0% V/Ti catalysts*

Figure 24 *Un-reacted Methanol vs. Reaction Temperature for 1% V/Ti catalysts*
Figure 25: Un-reacted Methanol vs. Reaction Temperature for 2% V/Ti catalysts

Figure 26: Un-reacted Methanol vs. Reaction Temperature for 5% V/Ti catalysts
Figure 27: Un-reacted Methanol vs. Reaction Temperature for 10% V/Ti catalysts

Figure 28: Un-reacted Methanol vs. Reaction Temperature for V/Ti (400 °C) catalysts
Figure 29: Un-reacted Methanol vs. Reaction Temperature for V/Ti (500 ºC) catalysts

Figure 30: Un-reacted Methanol vs. Reaction Temperature for V/Ti (550 ºC) catalysts
Figure 31: Un-reacted Methanol vs. Reaction Temperature for V/Ti (600 °C) catalysts

Three observations are made by comparing Figures 23 - 27 and Figures 28 – 31:

(i) The presence of V on Ti significantly enhances the performance of the catalysts for the oxidation of methanol.

(ii) As the calcination temperature increases, the V/Ti ratio of the best performing catalyst decreases. For example, following calcinations at 400 °C, the best performing catalyst has a V/Ti ratio of 0.05. Following calcination at 550 °C, the best performing catalyst has a V/Ti ratio of 0.02. Following calcination at 600 °C, the best performing catalyst has a V/Ti ratio of 0.01.

(iii) The best performing catalyst for the oxidation of methanol was calcined at 400 °C and has a V/Ti ratio of 0.05.

These observations, when considered with the crystal phase and surface area of each catalyst, suggest that the predominant factor for catalyst activity is the surface interaction of monomeric V species with anatase TiO₂.
Following calcination at 400 °C, the catalyst performance increased with V/Ti ratio up to 0.05, but then decreased at a V/Ti ratio of 0.10. The catalyst with a V/Ti ratio of 0.05% performed better than the catalyst with a V/Ti ratio of 0.10, even though both catalysts were anatase and the surface areas were comparable. This observation suggests that monomeric layers of V (more likely at lower V/Ti ratios) are more effective for the oxidation of methanol than polymeric layers of V (more likely at V/Ti ratio of 0.10).

Following calcination at 500 °C, the catalysts with V/Ti ratios of 0.02 and 0.05 were both anatase, but the surface area of the catalyst with a V/Ti ratio of 0.02 was significantly greater than that with a V/Ti ratio of 0.05. However, both catalysts had similar performance for the oxidation of methanol. This observation suggests that the presence of active sites, where monomeric V species is present on the surface of TiO₂ (likely to be greater in number at V/Ti ratio of 0.05 than at V/Ti ratio of 0.02), play a more prominent role than surface area.

Following calcination at 550 °C, catalysts with V/Ti ratios of 0.05 and 0.10 were rutile, whereas catalysts with V/Ti ratios up to 0.02 were still anatase. The catalyst with a V/Ti ratio of 0.02 performed best under these conditions for the oxidation of methanol. This observation strongly suggests that the anatase crystal phase is very important for catalyst activity.

Following calcination at 600 °C, catalysts with V/Ti ratios of 0.02 and greater were rutile, whereas catalysts with V/Ti ratios up to 0.01 were still anatase. The catalyst with a V/Ti ratio of 0.01 performed best under these conditions for the oxidation of methanol. This observation also strongly suggests that the anatase crystal phase is very important for catalyst activity.
Goutam Deo observed that as the V loading is increased the catalytic activity increases. Oxidation activity of V/Ti catalysts increased with increase in V/Ti ratio from 0 to 0.7. But catalyst with 0.02 V/Ti ratio performed better than the catalyst with 0.03 V/Ti ratio [29].

The results for the destruction of methanol over W/V/Ti catalysts that show the effect of W/Ti ratio are plotted in Figures 32 - 36 and those that show the effect of calcination temperature are shown in Figures 37 - 40. At 400 °C calcination temperature catalysts with different tungsta loadings shows methanol destruction up to 96% at 200 °C reaction temperature. However catalysts with 1% to 5% W loadings at 500 °C calcination temperature show complete destruction of methanol at 200 °C reaction temperature. At 200 °C reaction temperature catalysts calcined at 550 °C temperature with low tungsta concentration( up to 2%) show 97% destruction but complete methanol destruction is observed at high concentrations of 5 % & 10%.

All the W/V/Ti catalysts calcined at 600 °C performed poorly. At 225 °C reaction temperature, catalyst with 1% W loading showed only 52% methanol destruction and other catalysts with higher W loadings showed destruction up to 95%. Even at 250 °C reaction temperature, total destruction was not observed. This can be explained by the fact that, surface area reduced from (~ 33m²/gm) at 550 °C calcination temperature to (~3-10 m²/gm) at 600 °C calcination temperature. As shown in Figure 13, following calcination up to 550 °C all the catalysts were anatase but rutile phase was observed at 600 °C calcinations temperature, which also resulted in poor performance.

In all cases, the addition of tungsta up to a W/Ti ratio of 0.05 enhanced the performance of the catalysts for the oxidation of methanol. The catalyst performances at
W/Ti ratios of 0.05 and 0.10 were similar. As calcination temperature increased, however, the degree of catalyst performance enhancement diminished.

In addition, the W/V/Ti catalysts that were calcined at 500 °C and 550 °C performed best for the oxidation of methanol. The presence of W loadings on 2% V/Ti increased the activity of W/V/Ti catalysts. For all the calcination temperatures, catalysts with different W loadings performed better than the catalyst with only 2% V loading (i.e. 0% W/V/Ti).

Figure 32: *Un-reacted Methanol vs. Reaction Temperature for 0% W/V/Ti catalysts*
Figure 33: Un-reacted Methanol vs. Reaction Temperature for 1% W/V/Ti catalysts

Figure 34: Un-reacted Methanol vs. Reaction Temperature for 2% W/V/Ti catalysts
Figure 35: Un-reacted Methanol vs. Reaction Temperature for 5% W/V/Ti catalysts

Figure 36: Un-reacted Methanol vs. Reaction Temperature for 10% W/V/Ti catalysts
**Figure 37:** Un-reacted Methanol vs. Reaction Temperature for W/V/Ti (400 ºC) catalysts

**Figure 38:** Un-reacted Methanol vs. Reaction Temperature for W/V/Ti (500 ºC) catalysts
Figure 39: *Un-reacted Methanol vs. Reaction Temperature for W/V/Ti (550 °C) catalysts*

Figure 40: *Un-reacted Methanol vs. Reaction Temperature for W/V/Ti (600 °C)*
5.0 Conclusion and Recommendations:

This investigation shows that V/Ti and W/V/Ti catalysts can be used to achieve methanol oxidation at moderate temperatures (< 300ºC). The data also show that there is a significant increase in the overall activity for methanol oxidation as the V/Ti mass ratio increased to 0.05 when calcined at 400 ºC. In addition, our data support that V₂O₅ species on the surface of anatase TiO₂ are responsible for higher catalytic activity for the oxidation of methanol.

The addition of W on the catalysts enhances the thermal stability of the catalysts, as indicated by the higher TiO₂ phase transformation temperatures and lower extents of sintering or surface area reduction. Catalysts with different W loadings on V/Ti performed better than with only 2% V/Ti loading.

Based on the results obtained, W/V/Ti catalysts performed best at the calcination temperatures of 500 ºC and 550 ºC. Catalyst performance was not good at 600 ºC calcination temperature for all the catalysts. Addition of tungsta up to 5% loading improved the activity of catalysts in all cases. Catalysts with W/Ti ratios of 5% and 10% behaved very similarly.

A catalyst having 5% V/Ti ratio and calcined at 400 ºC showed the best catalytic activity. In future study with tungsta, this work should be repeated with 5% vanadia loading. In future, catalysts with only tungsta loading on titania (W/Ti) should be compared with V/Ti and W/V/Ti catalysts.

Future work with this system should also include a detailed analysis of the reaction products and kinetics. This will help in assessing the selectivity of the catalysts.
in minimizing the formation of undesired products. It will also allow us to find the type of compounds for which this destruction method can be used.

Another important area for future study is effect of moisture content. Moisture present can affect the behavior of catalysts. It will help in finding the factors effecting the oxidation and formation of undesirable products during the reaction. To see the change in characteristics and behavior of catalysts, other methods such as flame synthesis should be used in future studies.
6.0 References:

http://ruby.colorado.edu/~smyth/min/tio2.html


21. http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html


