CHAPTER THREE

3.1 Materials and Gasses

3.1.1 Chemicals Brand and Purity:

Chemicals	**Brand**	**Purity (%)**
1. Ammonium molybdate tetrahydrate (mw = 1235.9 g/mol)	Sigma	81.4
2. Ammonium metavanadate (mw = 116.98 g/mol)	Aldrich	99
3. Telluric Acid (mw = 229.64 g/mol)	Aldrich	99
4. Ammonium Niobium Oxalate	H.C. Starck GmbH-Germany	99
5. Nickel (ii) Nitrate hydrate (mw = 290.79 g/mol)	Chempur	99
7. Chromium (iii) nitrate nonahydrate (mw = 400.15 g/mol)	Aeros Organics	99
8. Cobalt (ii) nitrate hexahydrate (mw = 291.04 g/mol)	Chempur	98
13. Citric Acids (mw = 192.12 g/mol)	Sigma	99
14.Ammonium Hydroxide (28-30wt% in water) (mw = 32.04 g/mol)	Aecros	99
15. Poly (ethylene glycol) ~3,000	Sigma	99
17. Hydroxyethyl Cellulose ~ 90,000	Sigma	99

Gases and purity

Type of Gas	Brands	Purity
20. Argon	MOX	99.99
21. Nitrogen	MOX	99.99
22. Oxygen	MOX	99.5
23. Helium	MOX	99.5
24. 5% Hydrogen in Nitrogen	MOX	99.9
25. 5% Oxygen in Helium	MOX	99.9
26. Liquid Nitrogen	MOX	-

3.2 Preparation of unpromoted $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst.

3.2.1 Via amorphous drying method. (Standard recipe)

The catalyst was prepared by an amorphous drying method, which consisted of the preparation of slurry containing salts of four metals: ammonium heptamolybdate, ammonium metavanadate, telluric acid and ammonium niobium oxalate. Initially the ammonium heptamolybdate (25.7 g from Sigma) was dissolved in 420 g deionized water by heating and stirring, followed by the addition of ammonium metavanadate (5.1 g from Aldrich) and telluric acids (7.7 g from Aldrich). This was indicated by a change of color from yellow to orange. The suspension was stirred and heated at 353 K and then leave to cool to room temperature. An aqueous solution of niobium oxalate (17.34 mmol, which is 1.611 g of niobium ammonium oxalate in 114.6 g of aqueous solution) was added to this solution.

The obtained slurry was stirred vigorously for 10 minute, then dried using vacuum rotavapor (Hieldoph) at 323 K, at speed rotation around 150 rpm and pressure of 36 mbar for 2 hours. The catalyst precursor (40 g yield) with chemical composition $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}O_x$ was devided into four parts and precalcined at four different temperature (448, 498, 548 and 598 K) under air by using air oven at heating rate 10 K min^{-1} and hold for 1 hour. The catalyst precursor was calcined at temperatures 873 K under flow of argon (10 ml min^{-1}) using Carbolite CWF 1200 furnace at heating rate of 2 K min^{-1} and hold for 2 hours to generate the active catalyst.

3.2.2 Standard recipe with adding viscosity enhancer

The catalyst was prepared, also according to standard recipe method which is consisted of the preparation of slurry containing the main salt of four metals: ammonium heptamolybdate, ammonium metavanadate, telluric acid, ammonium niobium oxalate with PEG (Polyethylene glycol) or spell out HEC (Hydroxyethyl cellulose) as a viscosity enhancer in the final solution. Ammonium heptamolybdate (3.99 g from Sigma) was dissolved in 65 g of deionizer water by heating and stirring, followed by the additional of the ammonium metavanadate (0.79 g from Aldrich) and telluric acids (1.19 g from Aldrich). The suspension was continues stirred and heated at 353 K, after that cool down to room temperature. An aqueous solution of niobium oxalate (1.25 g of niobium ammonium oxalate in 18 g of aqueous solution) was added to this solution and then PEG or HEC as a viscosity enhancer was added.

The slurry was continuously stirred vigorously for 10 minute and then dried the using vacuum rotavapor (Hieldoph) at 323 K, speed of rotation 150 rpm and pressure of

36 mbar for 2 hour. After that, the sample was precalcine at 548 K under air with heating rate 10 K min^{-1} and hold for 60 minutes. Activate the catalysts at 873 K under a flow of argon (10 ml min^{-1}) using Carbolite CWF 1200 furnace at heating rate 2 K min^{-1} for 2 hours.

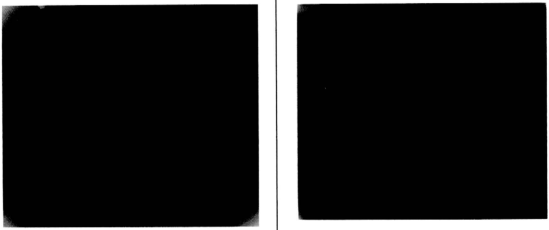
3.2.3 Via Citric Acid Route.

The catalyst precursor was prepared by amorphous drying method involving the preparation of metal citrate solution containing three metals with citrate as a precursor; molybdenum-citrate, vanadium-citrate and telluric-citrate at molar or weight ratio 1:1 and 1:2 metal to citric acids. The molarity of each metal citrate solution was 0.025 M. Metal citrate solution was prepared as follows: ammonium heptamolybdate (4.4 g from Sigma) was dissolved in 10 ml of citrate solution (4.8 g of citric acid for ratio 1:1 and 9.6 g for ratio 1:2) for preparing Mo-citrate solution, ammonium metavanadate (2.9 g from Aldrich) in 10 ml of citrate solution (4.8 g of citric acid for ratio 1:1 and 9.6 g for ratio 1:2) for the vanadium-citrate solution and telluric acid (5.7 g from Aldrich) was dissolved in 10 ml aqueous solution of citric acid (4.8 g of citric acid for ratio 1:1 and 9.6 g for ratio 1:2) for preparing Te-citrate solution . The stable solution, did not precipitate with citric acid was viewed under microscope (Figure 3.1, 3.2 and 3.3)

Heat and stir each of the solution to make it concentrate. After that, the solution was cool down to room temperature. Adjust the pH for each of metal citrate solutions to pH 5 by adding of 0.5 M ammonium hydroxide solution (28-30 wt% in water). Mixed all the citrate solutions at room temperature and the suspension was continuously stirred. An aqueous solution of niobium oxalate (1.38 g of niobium ammonium oxalate in 19.91 g of aqueous solution) was added to this mixture.

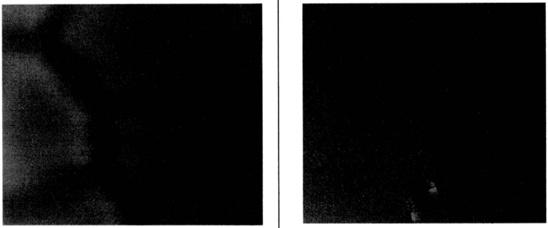
Dry the slurry using vacuum rotavapor (Hieldoph) at 323 K, speed of rotation around 150 rpm and pressure of 36 mbar for 2 hour. The catalyst precursor (10 g yield) was precalcined at 548 K under air at heating rate of 10 K min^{-1} and hold for 1 hour after which the sample was activated at 873 K under flow of argon (10 ml min^{-1}) using Carbolite CWF 1200 furnace with heating rate 2 K min^{-1} and hold for 2 hours to generate an active catalyst.

Ammonium Heptamolybdate – Citric Acid



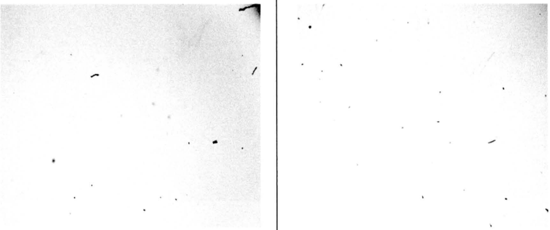
Mo-Citrate (1:1)

Mo-Citrate (1:2)



Mo-Citrate (1:1) close up

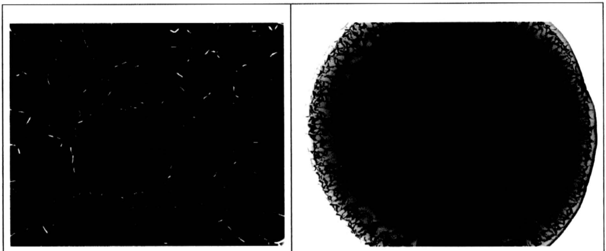
Mo-Citrate (1:2) close up



Mo-Citrate (1:1) at pH5

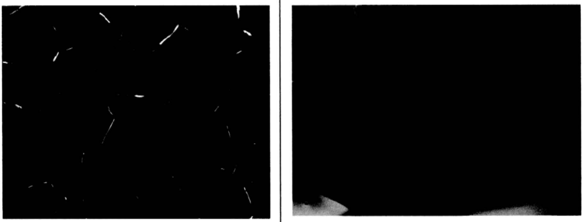
Mo-Citrate (1:2) pH 5

Figure 3.1: The stability of Molybdenum-Citrate solution after pH adjustment.



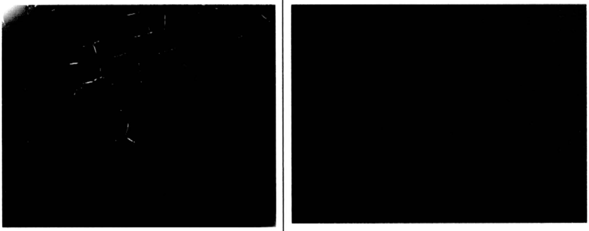
V-Citrate (1:1)

V-Citrate (1:2)



V-Citrate (1:1) close up

V-Citrate (1:2) close up



V-Citrate (1:1) pH5

V-Citrate (1:2) pH5

Figure 3.2: The stability of Vanadium-Citrate solution after pH adjustment.

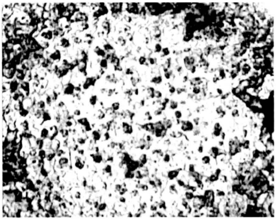
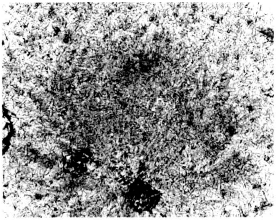
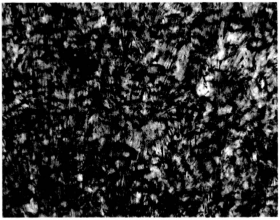
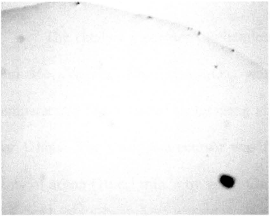
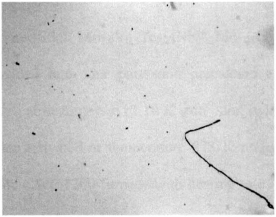
 Te-Citrate (1:1)	 Te-Citrate (1:2)
 Te-Citrate (1:1) close up	 Te-Citrate (1:2) close up
 Te-Citrate (1:1) pH 5	 Te-Citrate (1:1) pH5

Figure 3.3: The stability of Telluric-Citrate solution after pH adjustment.

3.3 Preparation of promoted $Mo_{1.0}\,V_{0.3}\,Te_{0.23}\,Nb_{0.12}\,O_x$ catalyst

3.3.1 Via amorphous drying method with various transition metal as a promoter.

The $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}Me_{0.05}O_n$ and $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}Me_{0.005}O_n$ catalysts were also prepared according to standard recipe method with the addition of various transition metal salts as a promoter (Ni, Co, and Cr). These metals salt are all in the nitrate precursor and prepared at two different weights loadings of 0.005M and 0.05M. The promoter was introduced to the first slurry solution similar as in the last procedure, where the slurry solutions containing ammonium heptamolybdate, ammonium metavanadate and telluric acid was prepared concurrently. After that, the solution of niobium oxalate was added and this slurry solution was continuously stirred for 10 minute. The slurry was dried using rotavapor vacuum (Hieldoph) at 323 K, around 150 rpm and pressure of 36 mbar for 2 hour.

The catalyst precursor of chemical composition $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}Me_{0.05}O_n$ and $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}Me_{0.005}O_n$ was divided into four parts and precalcine at temperatures 548 K under air by using air oven at heating rate of 10 K min^{-1} and hold for 1 hour. The catalyst precursor was further activated at temperature 873 K under flow of argon (10 ml min^{-1}) by using Carbolite CWF 1200 furnace with heating rate 2 K min^{-1} and hold for 2 hours.

3.4 General Characterisation Equipment

3.4.1 Nitrogen Physisorption measurements

From the catalysis point of view, the rate of product formation over a catalyst is a function of the accessible surface area of the active phase for materials not limited by mass transport of reactants to the active phase. Thus it is important to be able to quantify the surface area of this active phase, and the adsorption of inert gases makes this measurement possible [54].

In spite of the oversimplification of the model on which the theory in based, the B.E.T. method is the most widely used standard procedure for the determination of surface area of finely divided and porous material [55]. The BET equation applicable at low p/p_o range is customarily written in linear form as:

$$\frac{p}{n^{a}\,(p_o-p)} = \frac{1}{n_m{}^{a}\,C} + \left(\frac{C\text{-}1}{n_m{}^{a}C}\right)\frac{p}{p_o} \qquad [56].$$

where n^a is the amount of the gas adsorbed at the relative pressure p/p_o, $n_m{}^a$ is the monolayer capacity and C is the so-called BET constant which , according to the BET theory, is related to the enthalpy of adsorption in the first adsorbed layer and gives information about the magnitude of adsorbent-adsorbate interaction energy [57]. If the information is applicable, a plot of $p/[n^a\,(p_o-p)]$ *vs.* p/p_o should yield a straight line with intercept $1/n_m{}^aC$ and slope $(C\text{-}1)/\ n_m{}^aC$. The value of $n_m{}^a$ and C may then be obtained from a plot of a single line, or regression line, through the points [58]. The volume of the monolayer having been determined allows the surface area of the sample to be determined by a single adsorbate molecule, a value derived from the assumption of close packing at the surface by the formula:

$$a_s\,(\mathrm{BET}) = \frac{n_m{}^{a}\,.\,L\,.\,a_m}{m} \qquad [56].$$

where a_s is the specific surface area, L is Avogadro's number (6.023×10^{23} mol^{-1}), m is the mass of the adsorbent, and a_m is the cross sectional area of the adsorbate molecule, for which a value of 0.162 nm^2 $molecule^{-1}$ for N_2 is widely accepted. The assumptions in the BET equation break down if the BET plot is not linear, and the plot is usually restricted to the linear part of the isotherm over the p/p_o range of 0.05- 0.3 [56].

There are six different types of isotherms and four types of hysteresis loops as shown in Figure 4.1.2 [56]. For the possible isotherm to be amenable to BET analysis, the value of C is neither too low nor too high, *i.e.* $20< C <200$, and the BET plot must be linear for the p/p_o region taken for calculations.

Experimental procedure

Before the analysis was carried out, about 200 to 400 mg of catalysts powder was degassed at 393 K for 5 hours. Then, the total surface area of the catalyst was measured by Brunauer-Emmet-Teller (BET) method using nitrogen adsorption at 77 K. This experimental was done using Sorptometic 1990 instrument.

3.4.2 Scanning electron microscopy (SEM-EDX)

In scanning electron microscopy, a fine beam of electron is used to scan back and forth across the specimen surface. The low-energy, secondary electrons generated are then are collected by a scintillator crystal that converts each electron impact into a flesh of light. Each of these light flashes in the crystal is then amplified by a photo multiplier tube and used to build the final image on a fluorescent screen. The scan of the beam used to form this image is driven in synchrony with that of the electron-exciting beam that scans the specimen, so the resulting image (formed in much the same way as the picture on the television cathode ray tube) is a faithful representation of the specimen surface as imaged by altering the size of the area scanned by the scanning beam [59].

Experimental procedure

The sample was adhered on the aluminium stub using carbon conductive tape. The stub was then mounted on the stub holder and loaded into the chamber and evacuated for analysis. Images were recorded at COMBICAT with a Quanta 200 FEI microscope instrument and INCA-Suite version 4.02 for ECK analysis. The following settings were used:

Accelerating voltage: 5 kV
Detector type: ETD-SE
Working distance: 8-10 mm

3.4.3 X-Ray Powder Diffraction (XRD) Analysis

X-ray Powder diffraction (XRD) is one of the most frequently applied techniques in catalyst characterization. X-ray with wavelengths in the Å range, is sufficiently energetic to penetrate solid and are well suited to probe their internal structure. XRD is used to identify bulk phase and to estimate particle sizes [60].

An x-ray source consists of a target, which is bombarded with high-energy electrons. The emitted x-rays arise from two processes. Electron slow down by the target emits a continuous background spectrum of Bremsstrahlung. Superimposed on this are characteristic narrow lines. The Cu Kα line arises when a primary electron creates a core hole in the K shell, which is filled by an electron from the L shell (Kβ: the K-hole is filled from the M-shell, etc) under emission of an x-ray quantum [61].

XRD is an elastic scattering of x-ray photons by atoms in a periodic lattice. The scattered monochromatic x-rays that are in phase give constructive interference. The XRD pattern of a powdered sample is measured with a stationery x-ray source (usually Cu Kα) and a movable detector, which scan the intensity of the diffracted beams radiation as a function of the angle 2θ between the incoming and the diffracted beams. When working with powdered sample, an image of diffraction lines occurs because a small fraction of the powder particle will be oriented such that by chance a certain crystal plane (*hkl*) is at the right angle with the incident beams for constructive interference [61].

The width of diffraction peaks carries information on the dimensions of the reflecting planes. Diffraction lines from perfect crystals are very narrow. For crystallite sizes below 100nm, however line broadening occurs due to incomplete destructive interference in scattering directions where the x-ray is out of phase [61].

Experimental procedure

The powder XRD analysis was carried out using a Bruker X-ray Diffraction model D-8 to obtain a crystalline phase of the precursors and catalysts, at ambient temperature. About 200 – 500 mg of sample powder was mounted on a plastic sample holder. Diffraction patent were obtained by employing CuK_α radiation (λ = 1.54019 Å) generated by Bruker glass diffraction X-ray tube broad focus 2.7 kW type. The sample was continuously scanned at the range of $2\Theta = 2 - 80^o$ with a scanning rate of 0.02^o sec^{-1}. The values of the d-spacing, intensity and full width at half maximum (FWHM) were calculated using basic process version 2.6 software. The diffractograms obtained were matched against the Joint Committee on Powder Diffraction Standards (JCPDS) PDF 1 database version 2.6 to confirm the precursor and catalytic phase.

3.4.4 Temperature-Programmed Reduction (TPR)

Temperature-programmed reduction (TPR), form a class of a technique in which chemical reaction is monitored whiles the temperature increase linearly in time. These techniques are applicable to real catalysts and single crystals and have the advantage that they are experimentally simple and inexpensive in comparison to many other spectroscopies. Interpretation in a qualitative base it rather straight forward [62].

The basic set up for TPR consists of a reactor and a thermal conductivity/detector to measure the hydrogen content in TPR, of the gas mixture before and after reaction. More sophisticated TPR equipment content a mass spectrometer for the detection of reaction product [61]. The area under a TPR curve represent the total hydrogen consumption and is commonly expressed in terms of moles of H_2 or O_2 consumed per mol of atoms (H_2 / Mol). TPR provides a quick characterization of metallic system. This method gives information on the phases present the eventual degree of reduction. For bimetallic catalysts, TPR pattern often indicate if the two components are mixed or not. In principle one can also determined the energy of the adsorption bond, however applying rather involved computations [62].

Experimental procedure

A Thermofinnigan TPDRO 1100 instrument is used to carry out the temperature-programmed reduction. About 100 -200 mg of the catalyst was pre-treated by heating it at 393 K under N_2 flow (1 bar, 20 cm^3 min^{-1}) and hold for 45 minutes to eliminate possible contaminants and completely oxidised the metal portion of the catalyst. It was then cooled to room temperature. After that, the flow was switch to 5% hydrogen in argon (1 bar, 20 cm^3 min^{-1}). The temperature was raised from ambient to 923 K at a heating rate of 3 K min^{-1} and hold under flow of gas for 30 minute. The reduction was measured by monitoring the hydrogen consumption with the TCD detector.

3.4.5 Thermogravimetric (TGA) analysis

Thermogravimetric analysis is the measure on the gain or loss in weight of a material as a function of the composition of the atmosphere and the temperature. It is a very useful technique for the study of solid-gas system. This technique use in the chemistry of solid to characterize phase transformations and, if necessary, to dose them with selected probe is well known [63, 64, 65, 66 & 67]. Most physical, chemical or physicochemical phenomena are characterize by variations in the masses of reactive samples where these sample are subjected to various environments, whether fixed or changing, such as temperature, atmosphere, vacuum, magnetic field, pressure and irradiation. A recorded, continuous and precise weighing can follow the change in a substance under these environmental conditions, which are also recorded continuously [68].

As the main parameter is often the temperature, thus the common name of thermogravimetry. The measuring instrument is therefore a weighing device. It has no memory that changes in the mass of the sample clearly imply evaluation or uptake of matter by the sample. In weighing the sample it assumed that it can be connected to the weighing device. The method only works well if the sample is in compact form.

Generally this is a solid or a powder; sometimes a liquid placed in an open crucible or even fixed on a solid phase. In practice, the sample can be a) liquid or homogenous solid (solid solution), b) adsorbed phases at the surface of a solid or liquid in pores, c) distinct solid phases in granular solid (metal), d) layer on surface (oxide films) or e) heterogeneous liquids (emulsions). It is always advantageous to complement thermogravimetry with other method of analysis [68].

Experimental procedure

To investigate the thermal stability of the catalyst the measurement was done using Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). The TGA analysis was carried out using Mettler Toledo TGA/SDTA851^{e} thermobalance. An open alumina crucible of 100 μl was used for the measurements. About 10 to 50 mg of catalysts was used to characterise. The TGA temperature program was run dynamically from ambient to 773 K at a heating rate of 5 K min^{-1} under two variables, air and nitrogen with flow rate of 50 ml min^{-1}.

3.4.6 Differential Scanning Calorimetry (DSC) analysis

Differential Scanning Calorimeters is a technique in which the differences in an energetic behavior between the substance and references material are measured as a function of the temperature when the substance and the reference material undergo a controlled temperature program. The differential scanning calorimeters can be; i) either flowmatic, e.i, derived from the Tian-Calvet calorimeter [69, 70] or ii) power compensation DSC, in which each of the two cells, references and sample, has a specific heating element; the heat supplied to one cell only is measured, according to the principle of power compensation; a signal, proportional to the difference in the heat supplied to the sample and to the reference, dH / dt, is record as a function of the temperature (t) [71]. A DSC can measure not only enthalpy changes, but also the rates of reaction, which lead, in principle, to kinetic parameter and to reaction mechanisms [71].

Experimental procedure

The differential scanning calorimetry analysis was performed using Mettler Toledo DSC822^{e} equipment with an intra cooler. About 10-50 mg of catalyst was used to characterise. This sample was measured in hermetically sealed crucible, in a self-generated atmosphere by piercing a 50 μm hole in the aluminium lid of a sealed crucible. The temperature program was run dynamically from ambient to 823 K at heating rate of 5 K min^{-1} under nitrogen flow (50 ml min^{-1}).