



# Vapour phase isomerisation of ortho-toluidine over modified supported V-Mo oxide catalysts: Influence of process parameters and metal loadings on catalytic and thermodynamic properties

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Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

Received 13<sup>th</sup> March 2015, revised 9<sup>th</sup> June 2015, accepted 10<sup>th</sup> July 2015

## Abstract

The vapour phase transformation of o-toluidine isomerisation has been studied over modified V-MO catalyst at different process parameters. The objective of this work is to evaluate the catalytic performance of modified V-MO catalyst carried out by impregnation method with acidic metal salts of Boron and Phosphorus qualitatively and quantitatively also with Mg doped catalyst and compare with parent supported V-Mo catalyst as well as modified catalyst obtained by Mg doping. Catalytic properties (conversion, selectivity) and thermodynamic properties (The Arrhenius activation energy, enthalpy, entropy and Gibbs's free energy) are compared at ambient pressure and at identical reaction parameters using down-flow fixed bed reactor. Catalysts are characterized by x-ray diffractometry for any new phase formation and were ascertained by JCPDS diffraction files. The role of new phase (s) formation in the title reaction is justified.

**Keywords:** O-toluidine, isomerisation, vanadium molybdate, boron, phosphorus, magnesium.

## Introduction

Toluidines are important intermediates for the manufacturing of dyestuffs and agrochemicals and are generally synthesized by electrophilic nitration of toluene followed by reduction of the intermediate nitrotoluenes<sup>1</sup>. A mixture consisting mainly of ortho- and para-toluidines is formed in this process. Meta-toluidine, another important chemical produced in limited quantity in this process<sup>2</sup>. Aniline is primarily used in MDI foams for the automotive and construction industries. Also it has wide application in urethane industry, rubber industries, agricultural and dyes industries. The anilines are generally prepared by nitration of the appropriate methyl benzene followed by reduction of the resulting nitro compound<sup>3</sup>. Mixed oxides catalysts containing molybdenum and vanadium are the preferred catalyst for this investigation. Higher and stable activity seems to be characteristic of combination of vanadium oxides with other metal oxides<sup>4</sup>. The comparison of unique catalytic properties with

Individual metal oxides had drawn attention towards metal oxides system<sup>5</sup>. Researchers have studied the vapour phase reactions for different catalysts on different oxide systems<sup>6-11</sup>.

## Material and Methods

**Materials:** (H<sub>3</sub>BO<sub>3</sub>) was obtained from S. d. Fine chemicals for B doping and H<sub>3</sub>PO<sub>4</sub> was obtained from Sigma Aldrich chemicals for P doping. Magnesium Nitrate (Mg (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was obtained from Loba Chemie for Mg doping.

**Modification of V-MO:** Catalytic performance is highly depends on its preparation method. The modified catalysts prepared in the present work were by using wet impregnation method. The impregnation method is simple and is the most popular catalyst preparation method. For the modification of V-Mo with the precursor solutions were used. A calculated amount of V-Mo was immersed in precursor solutions. The obtained slurry is dried and calcined at the appropriate temperature (At 500°C for 6 h) in a muffle furnace at a heating rate of 10°C min<sup>-1</sup>.

**Table-1**  
Addition of precursors salts for Modification of V-Mo catalyst

Compound	Addition of precursors salts in ml's		
	5 wt %	10wt %	15wt %
H <sub>3</sub> PO <sub>4</sub>	3.387	6.774	10.16
H <sub>3</sub> BO <sub>3</sub>	17.2	34.4	51.6
Mg (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	4	8	12

**Catalyst characterization:** The sample were thoroughly ground to fine powder using pestle and mortar and were subjected for XRD investigation. X-ray diffraction pattern of samples were recorded with Ringaku Dmax/III VC diffractometer using Ni-filtered CuK $\alpha$  ( $\lambda$ = 1.5406 Å) radiation at scanning rate 2° min<sup>-1</sup> in the range 2 $\theta$  of 0 to 100.

The phases reported for V-Mo-O parent catalyst are MoV<sub>2</sub>O<sub>8</sub>,

$(V_{0.22}Mo_{0.88})O_{2.94}$ ,  $(V_{0.22}Mo_{0.88})O_{2.94}$ ,  $Mo_{2.4}V_{3.6}O_{16}$  and  $MoV_2O_8$  with highest  $I/I_0$  values according to JCPDS file no. 18-0851, 74-1508, 84-1952 and 74-2366 respectively.

The phase reported for V-Mo-P-O (10 wt.%) is  $VMo_{0.07}O_{1.67}(PO_4)_{0.93}$  with  $I/I_0 = 0.498$  and for V-Mo-P (15 wt.%) is V-Mo-P-O according to JCPDS file no. 40-0119 and 47-1706 respectively.

The phases reported for V-Mo-Mg-O (10 wt. %) are  $Mg_{2.54}V_{1.08}Mo_{0.92}O_8$ ,  $Mg_{2.5}(VMo)O_8$  and  $Mg_{15}V_6Mo_6O_{48}$  according to the JCPDS file no. 86-1465, 82-2074 and 44-0607 respectively. There are no phases reported in literature for Boron impregnated V-Mo catalyst and therefore it can be said that the catalyst is in the form of physical mixture in this case

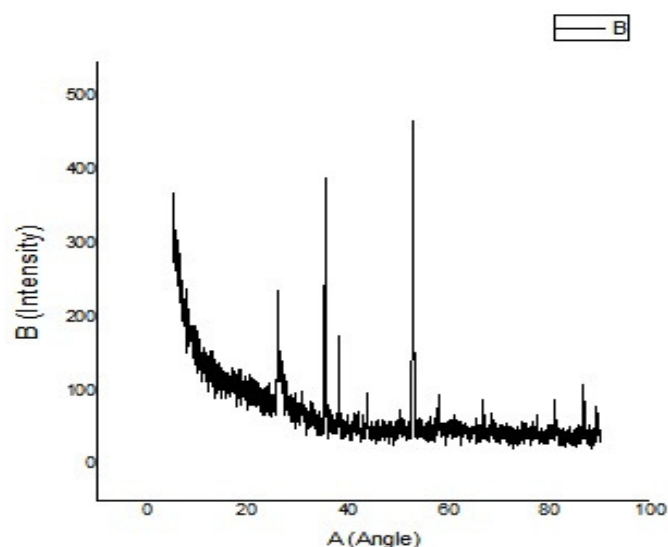


Figure-1  
V-Mo parent XRD Profile

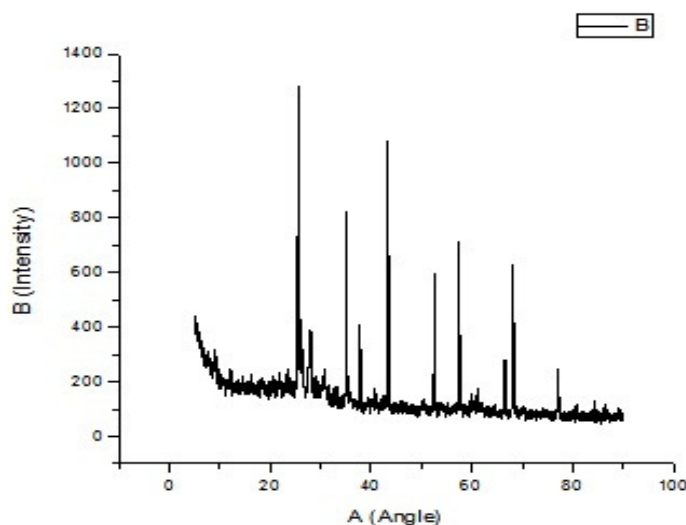


Figure-2  
V-Mo-B (10 wt.%) XRD Profile

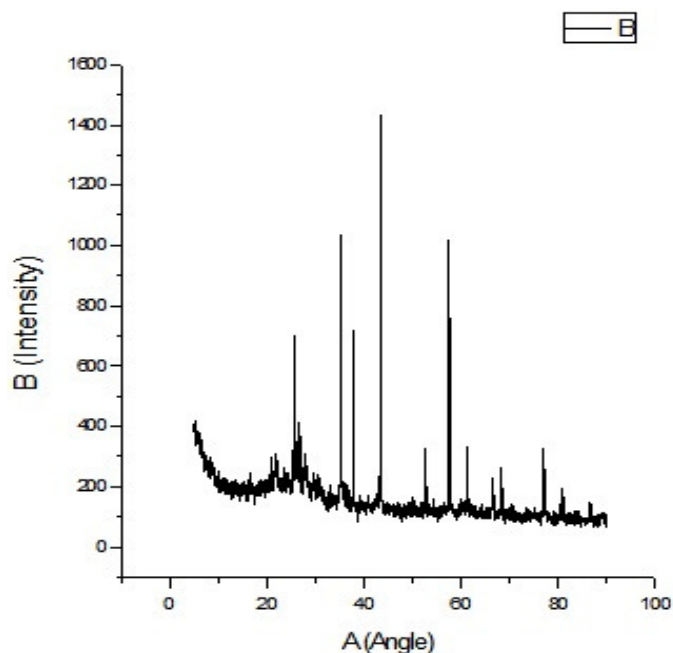


Figure-3  
V-Mo-P (10 wt.%) XRD Profile

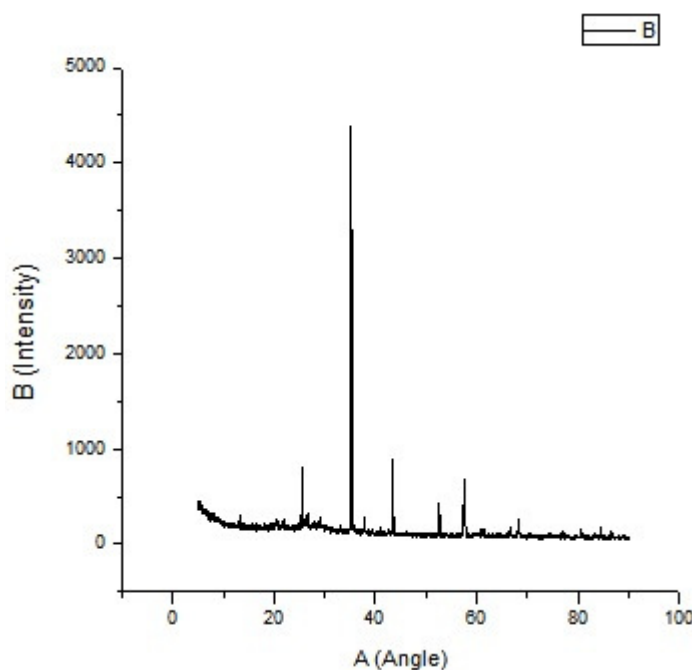
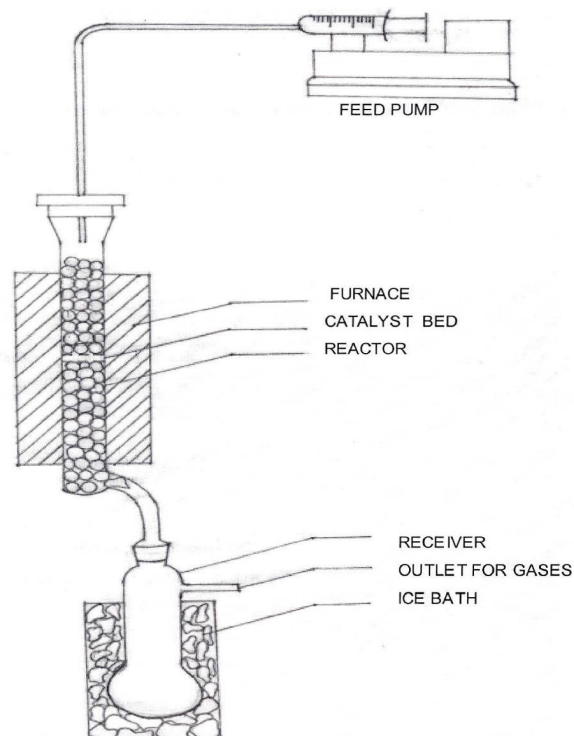


Figure-4  
V-Mo-P (15 wt.%) XRD Profile

### Reaction Procedure

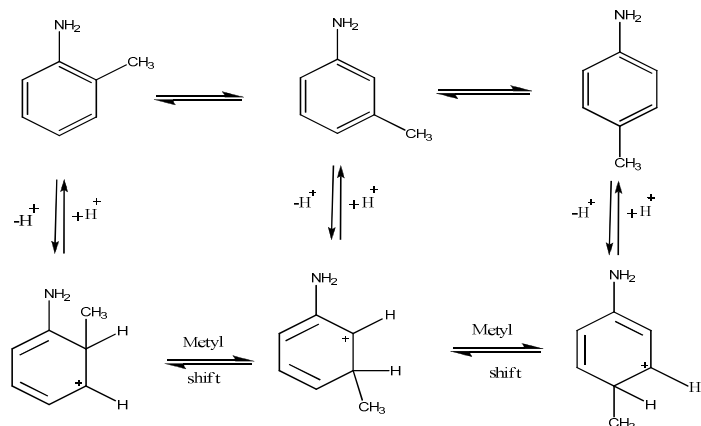
The Catalyst  $V_2O_5-MO_3$  (varying  $V_2O_5/MO_3=2.1$ ) supported on Si-Al support (85%) and remaining (15%) is active material was modified with nitrate solution of B and P solutions quantitatively

and qualitatively by impregnation method at water bath temperature (96-98°C). These were evaporated to dryness and brought to room temperature. These modified catalysts were calcined in the muffle furnace at the specific calcination program (Room temperature -10°C/min, Calcination temperature-500°C, hold time-6 hrs) uniformly. After bringing to room temperature these were subjected to XRD investigation for any new phase formation. The new phases that are formed were ascertained by JCPDS standards diffractions files. These catalysts are planned to investigate for isomerisation of o-toluidine reaction by vapour phase using downflow silica reactor at atmospheric pressure. The extent of modified species on newly inorganic phase formed at these calcination temperatures will be presented. In the reaction of o-toluidine isomerisation, it is reported in the literature that two main reactions i. e. isomerisation and Disproportionation are taking place. In our study we will investigate the effect of reaction temperature, flowrate (WHSV h<sup>-1</sup>) on the extent of Isomerisation and Disproportionation reaction. The catalyst modified with alkali, alkaline earth and parent catalyst would be compared for their activity and selectivity to different products. The performance indicator (ratio of Isomerisation product / Disproportionation product) expected to throw light due to acidic and basic nature of different catalysts in the evaluation of catalytic performance will be calculated. The Arrhenius activation energy, enthalpy of reaction and entropy of reaction will be correlated by standard expressions and presented for qualitative and quantitative impregnation. 3 gm of catalyst was positioned in a down-flow integral fixed bed reactor (length 37cm; i.d. = 12 mm with thermocouple well of length 14 cm and i.d. = 6mm) maintained at constant temperature. The catalyst was packed either side with porcelain beads and was activated in a flow of dry air at the rate of 25 cc min<sup>-1</sup> at the desired temperature 500°C for 4 h. This was cooled then desired reaction temperature in the flow of nitrogen at 20 cc min<sup>-1</sup>. The L/D ratio of catalytic bed was 0.6745. The o-toluidine was fed from the top of the reactor using pulse injection at desired rate. Liquid product was condensed in a receiver using ice cold trap



**Figure-5**  
**Reactor assembly**

**Reaction scheme:** The products form in the reaction i.e. (selectivity to different products) will be correlated with type and extent of modified species (especially new formed inorganic phases, if any). The isomerisation of o-toluidine is a unimolecular reaction. However, formation of DMAs (dimethyl aniline) is a bimolecular reaction and proceeds via di-aryl intermediate. Thus, in this case monomolecular mechanism involving successive 1, 2 -methyl shifts around the ring and protonate benzenium ion can be visualized. At high temperature, the protonated benzenium ion (sigma complex) is formed followed by a single or successive 1,2-methyl shifts resulting in the formation of meta and para isomers of toluidine as shown in above scheme<sup>12</sup>.



**Figure- 6**

**Reaction mechanism of o-toluidine isomerisation**

Formule:

% conversion of O-Toluidine =

$$\frac{\text{mole of o - toluidine feed} - \text{moles of o - toluidine in product}}{\text{moles of o - toluidine feed}}$$

% selectivity of p - toluidine =

$$\frac{\text{mole of p - toluidine produced}}{\text{Conversion of o - toluidine}} \times 100$$

Selectivity Ratio  $S_R$  =

Selectivity of Isomerisation product (paratoluidine + metatoluidine)

Selectivity of Disproportionation product (aniline + dimethylaniline)

$$\% \text{ selectivity of (Aniline + Dimethyl Aniline) = } \frac{\text{moles of (Aniline + Dimethyl Aniline) Produced}}{\text{Conversion of o-toluidine}}$$

## Results and Discussion

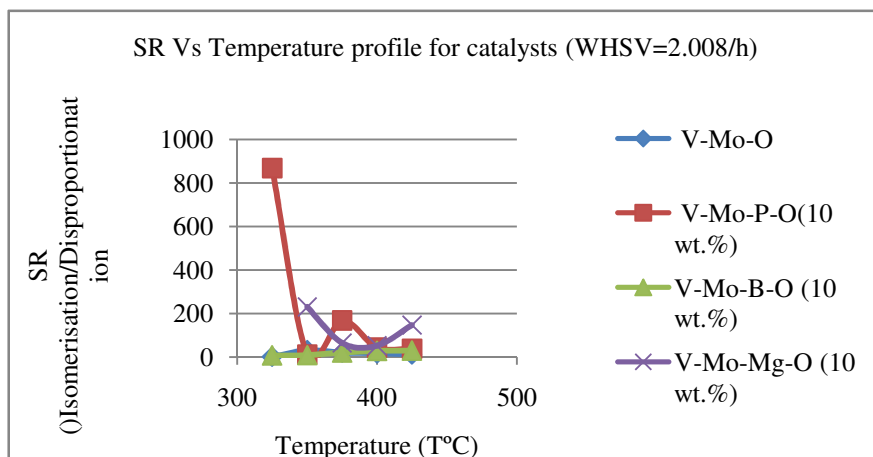
**Product analysis:** Catalytic activity evaluation experiments were carried at atmospheric pressure using fixed bed down flow integral silica reactor. Products were analyzed by gas chromatography using FID, Column- HP-5% column 50 m × 200 μm (o. d.) × 0.33 μm (film thickness) and FID Injection Temperature- 250 °C, Instrument Name- Hewlett Packard HP 6890, Column material- Stationary phase- 5% phenyl polymethyl siloxane.

Table-2 shows the catalytic performance of o-toluidine isomerisation as a function of variation in reaction temperature. These tables also compare the effect of variation in WHSV over V-Mo catalyst. It may be noted that at low temperature of 325 °C (WHSV=2.008 h<sup>-1</sup>) the conversion of o-toluidine is higher (42.024%) and at higher temperature (425 °C) the higher conversion shown for higher WHSV=3.012 h<sup>-1</sup>. Lower WHSV

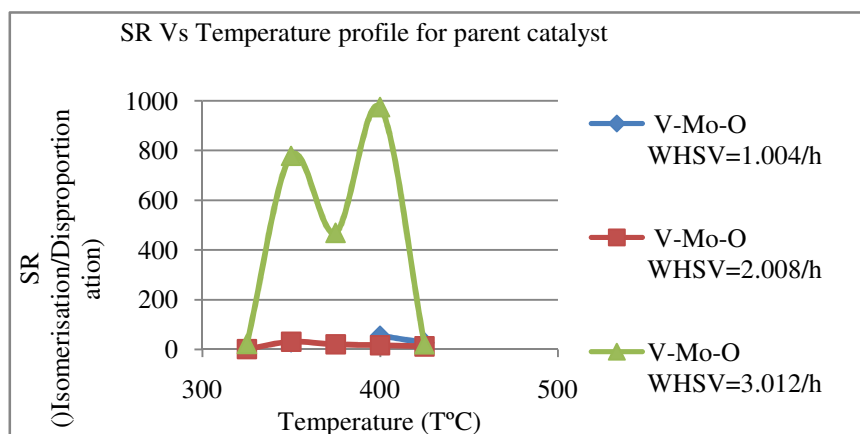
linearly decrease conversion level upto 375 °C and there is a increased at high temperature 425 °C. However for intermediate WHSV 2.008 h<sup>-1</sup> the o-toluidine conversion was tremendously decrease upto 2.3%. A notable observation is at 400, there is a linear increase from 10.5% to 33.6% in o-toluidine conversion as WHSV was increased from 1.004 to 3.012 h<sup>-1</sup>. At lower WHSV (1.004 h<sup>-1</sup>) there is a no detection of Disproportionation. However above 350 °C it has occurred. The selectivity ratio (S<sub>R</sub>) of (Isomerisation/Disproportionate) linearly increased from 350 to 400 °C (S<sub>R</sub> varied from 27.9 to 55%) WHSV=1.004 h<sup>-1</sup>) and at 425 °C, it is dropped to 26.13. Thus 400 °C is the optimum temperature in view of isomerisation reaction as supported by selectivity ratio. The Arrhenius activation energy is negligible nearing to 1 Kcal/gm mole. For WHSV=2.008 h<sup>-1</sup> although S<sub>R</sub> is higher at 350 °C. There is a drastic enhancement of Ea=44 Kcal/gm mole. At WHSV=2.008 h<sup>-1</sup> beyond temperature 350 °C there is a drastic decrease in the S<sub>R</sub> of (Isomerisation/Disproportionation) products implying that this conditions of WHSV and reaction temperature favoured Disproportionate of o-toluidine. At higher WHSV of 3.012 h<sup>-1</sup> there is a absence of Disproportionate. The value of ΔG suggests that WHSV=2.008 h<sup>-1</sup> is preferred in view of isomerisation.

**Table-2**  
**Effect of o-toluidine isomerisation over V-Mo-O parent catalyst:**

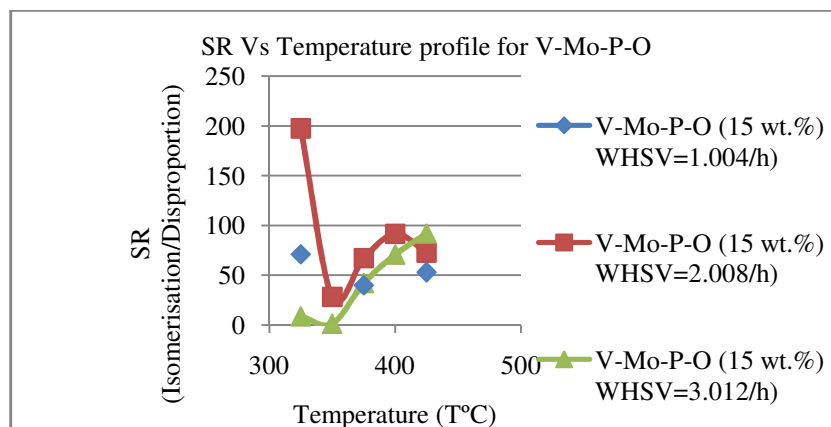
T (°C)	325	350	375	400	425
% conversion o-toluidine V-Mo-O (WHSV=1.004 h <sup>-1</sup> )	30.311	7.47	5.748	10.49	30.42
% conversion o-toluidine V-Mo-O (WHSV=2.008 h <sup>-1</sup> )	42.02	17.062	13.45	25.42	2.33
% conversion o-toluidine V-Mo-O (WHSV=3.012 h <sup>-1</sup> )	30.39	31.059	25.916	33.614	30.38
% conversion o-toluidine V-Mo-P-O (15 wt%) (WHSV=1.004 h <sup>-1</sup> )	21.1	-	10.59	-	4.46
% conversion o-toluidine V-Mo-P-O (15 wt%) (WHSV=2.008 h <sup>-1</sup> )	15.47	8.837	18.78	17.12	18.92
% conversion o-toluidine V-Mo-P-O (15 wt%) (WHSV=3.012 h <sup>-1</sup> )	16.355	42.886	5.968	7.079	3.806
% conversion o-toluidine V-Mo-P-O (10 wt%) (WHSV=2.008 h <sup>-1</sup> )	33.625	15.575	49.532	35.38	23.82
% conversion o-toluidine V-Mo-B-O (10 wt%) (WHSV=2.008 h <sup>-1</sup> )	22.341	15.566	5.529	15.461	5.594
% conversion o-toluidine V-Mo-Mg-O(10 wt%)(WHSV=2.008 h <sup>-1</sup> )	-	15.51	8.74	7.1	3.78



**Figure-7**  
Shows  $S_R$  Vs Temperature profile for catalyst



**Figure-8**  
Shows  $S_R$  Vs Temperature Profile for catalyst



**Figure-9**  
Shows  $S_R$  Vs Temperature Profile for P doped catalyst

**Effect of o-toluidine isomerisation over boron and phosphorus doped supported V-Mo-O catalyst:** The comparison of  $B_2O_3$  and  $P_2O_5$  doped supporting V-Mo-O catalyst with parent show that at low temperature of 325°C, the

conversion of o-toluidine is lowered for  $P_2O_5$  doped sample than the parent one and it is almost 50% for  $B_2O_3$  doped catalyst. However at higher temperature beyond 400°C the  $P_2O_5$  and  $B_2O_3$  (10 wt.% doping amount), the conversion is in the order V

Mo>P<sub>2</sub>O<sub>5</sub>>B<sub>2</sub>O<sub>3</sub> but at 425°C boron shows more than 2 fold activities. In general the selectivity ratio for P<sub>2</sub>O<sub>5</sub> doped sample is higher than B<sub>2</sub>O<sub>3</sub> doped sample at the equivalent metal loading and B<sub>2</sub>O<sub>3</sub> doped catalyst shows higher values for SR at all temperatures than the supported V-Mo catalyst is shown in figure-7,8 and 9. It also shows that P<sub>2</sub>O<sub>5</sub> doped sample is dominant in respect of isomerisation activities than the B<sub>2</sub>O<sub>3</sub> doped sample. This again is attributable to new phase formation due to P<sub>2</sub>O<sub>5</sub> loading i.e. VMo<sub>0.03</sub>P<sub>1.1</sub>O<sub>4.84</sub>, VMo<sub>0.07</sub>O<sub>1.67</sub>(PO<sub>4</sub>)<sub>0.93</sub>, V-Mo-P-O [JCPDS File no. 47-1705, 40-0119, 47-1706].

The reaction rate constant [K<sub>r</sub> [mol/gm/hr]] were calculated by using following expression. The Arrhenius plots of the runs are depicted in fig. From these the activation energy was computed using following expression

$$K_r = \frac{F}{W} \ln \frac{1}{(1-X)}$$

Where: F=reactant feed passed in moles per hours, W=weight of catalyst in gram, X= Fractional conversion (%)

From the data, the plot of -ln K<sub>r</sub> Vs 1/T °K were drawn. The -ln K<sub>r</sub> Vs 1/T °K plot for V-Mo-Mg (10 wt.%) is shown in

figure-10. The Arrhenius activation energies from the slopes of the plots were calculated by

$$\text{Slope} = \frac{-E_a}{2.303 \times 3 R}$$

Where: R=Molar gas constant, E<sub>a</sub>= Activation energy kcal/gmole.

Thermodynamic activation parameters such as enthalpy ΔH, entropy ΔS and free energy ΔG are important for any chemical transformation,

$$\Delta H = E_a - RT \text{ cal/gmole}$$

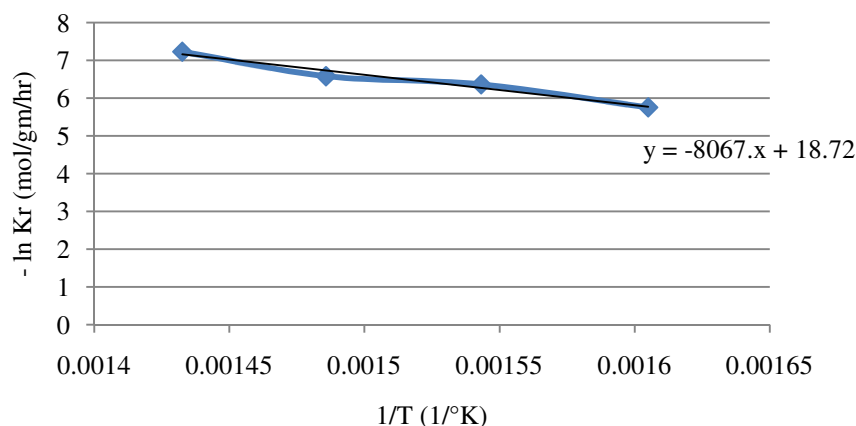
$$\Delta S = \left[ \Delta H + \frac{Rh}{K \ln Kr} \right] / T_{\text{and}} \quad \Delta G = \Delta H - T \Delta S$$

Where: ΔH= Change in enthalpy Kcal/mole, ΔG=Gibbs free energy Kcal/mole, ΔS=Change in entropy Cal/mole, K = Boltzmann constant i.e. 1.3805 × 10<sup>-23</sup>, Kr = Rate constant of reaction at optimum reaction temperature, h = planks constant i.e. 6.625 × 10<sup>-34</sup>.

The thermodynamic properties of reaction are shown in table-3.

**Table-3**  
**Thermodynamic properties of Reactions**

Catalyst	E <sub>a</sub> Kcal/gmole	ΔH Kcal/mole	ΔS (e.u) Cal/° mole	ΔG cal/mole
V-Mo (WHSV=1.004 h <sup>-1</sup> )	0.90286	0.90152	1.34	0.035
V-Mo (WHSV=2.008 h <sup>-1</sup> )	43.9484	43.9472	70.54	0.022
V-Mo (WHSV=3.012 h <sup>-1</sup> )	0.70334	0.70201	1.0430	0.0637
V-Mo-B (10 wt %) WHSV=2.008 h <sup>-1</sup>	23.0175	23.0161	32.97	0.069
V-Mo-Mg (10 wt %) WHSV=2.008 h <sup>-1</sup>	36.9150	36.9138	59.25	1.09
V-Mo-P (10 wt %) WHSV=2.008 h <sup>-1</sup>	1.23462	1.03905	1.7375	0.025
V-Mo-P (15 wt %) WHSV= 1.004 h <sup>-1</sup>	31.382	31.380	52.47	2.94
V-Mo-P (15 wt %) WHSV=2.008 h <sup>-1</sup>	8.60299	8.60180	14.38	0.048
V-Mo-P (15 wt %) WHSV=3.012 h <sup>-1</sup>	38.4251	38.4237	55.022	0.127



**Figure-10**  
**Arrhenius plot of -ln K<sub>r</sub> Vs 1/T for V Mo Mg catalyst**

## Conclusion

Influence of  $P_2O_5$  loading indicated that as the contact time was decreased (WHSV increased from 1.004 to 3.012  $h^{-1}$ ) at 325°C, there is higher percentage conversion of O-toluidine. However at higher WHSV there is a marginal difference at 375°C. The conversion was higher at intermittent WHSV=2.008  $h^{-1}$  at low temperature of 325°C. There is no activity for either for disproportionation and isomerisation in case of 15 wt.%  $P_2O_5$  doped catalyst at 375°C, however, higher contact time showed lower SR (39.95) at 375°C. Comparison of equivalent metal loading of Boron and Phosphorus (10 wt. %) shows that  $P_2O_5$  loaded sample is dominant in term of selectivity ratio (Isomerisation/Disproportionation) than the Boron loaded sample. This behavior of V-Mo-P-O (10 wt. %) is attributed to the inorganic phases formed namely  $VMo_{0.03}P_{1.1}O_{4.84}$ ,  $VMo_{0.07}O_{1.67}(PO_4)_{0.93}$  and V-Mo-P-O [JCPDS File no: 47-1705, 40-0119 and 47-1706 respectively]<sup>13</sup>.

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