SLURRY PHASE OXIDATION OF o-HYDROXYBENZYL ALCOHOL TO o-HYDROXYBENZALDEHYDE AND o-HYDROXYBENZOIC ACID WITH AIR OVER NANOPOROUS ZrV₂O₇ CATALYST

[1]Shweta Kanungo Joshi[*], [2]Neena Sohani, [3]Savita Khare and [4]Rajendra Prasad

[1,2,3,4] School of Chemical Sciences,
Devi Ahilya Vishwavidyalaya, Indore, INDIA

_____

Abstract : Oxidation of o-hydroxybenzyl alcohol was carried out in the liquid phase over nanoporous zirconium vanadate catalyst. Under the optimum conditions catalyst was shown to have good activity to yield reaction products i.e. o-hydroxybenzaldehyde and o-hydroxybenzoic acid. These compounds are of commercial importance. The catalyst was prepared by solution combustion method and characterized with the help of XRD, XPS and Raman analysis. Activity of the catalyst was examined under mild conditions and products were analyzed employing a chemito1000 Chromatograph using FID detector. The catalyst can be separated easily through simple filtration and reused.

Under optimum reaction conditions a maximum conversion of 94.50% of o-hydroxybenzyl alcohol was observed. The catalyst was found to have 85.73 % selectivity for the benzoic acid**.**

Key words **- o-hydroxybenzyl alcohol, ZrV₂O₇, slurry phase oxidation..**

_____

I. INTRODUCTION

Oxidation of o-hydroxybenzyl alcohol to o-hydroxybenzaldehyde (salicylaldehyde) and o- hydroxybenzoic acid (salicylic acid) is important because of their synthetic and pharmaceutical importance. Salicylaldehyde is used as a precursor for the synthesis of catechol, coumarone, 3-carbethoxycoumarin, caroxazone &Trifenagrel, and benzofuran containing Benziodarone. It is also used as a precursor of salen catalyst used for epoxidation of alkenes [1-7].

Salicylic acid is also a compound of pharmaceutical importance. This compound is on the Model list of Essential Medicines (EML) published by World Health Organization (WHO) and considered to be most effective and safe medicine for a health system [8]. Salicylic acid and its derivatives found their applications as skin protectants, analgesics, antipyretics and anti-inflammatory agents. Its para-substituted derivatives and esters are used as food preservatives [9-14].

Oxidation of o-hydroxybenzyl alcohol over supported gold catalyst has been studied by Milone et al. The authors have studied kinetics of the process over Au/Fe_2O_3 as well. They found the kinetics to be of first order for o-hydroxybenzyl alcohol and almost zero order with respect to the air [15, 16].   Traditionally industries were using catalysts based on noble metals like Pt and Pd to oxidize o- hydroxybenzyl alcohol using air as an oxidant. The reaction is mainly carried out in alkaline medium using Pb or Bi as modifiers. Most of these processes are covered by patents [17-20]. Christidis and Vallejos suggested another method for the oxidation of o-hydroxybenzyl alcohol with O_2 in the aqueous alkaline medium (pH 13) using salts of Cu(II), Co(II) , Fe(III), Ni(II) and Mn(II) [21]. R. Rahimi et al reported that copper (II) tetraphenylporphyrin nanoparticles synthesized by mixed solvent method are also found to have good activity [22]. Beside this, some chemical methods like Reimer-Tiemann reaction and Carbonylation etc. are also used for the preparation of o- hydroxybenzaldehyde [23-25].

Drawbacks with the reports mentioned above are that these studies- (1) involves costly metals/ catalysts (2) are in soluble phase where catalyst separation and reuse is tedious (3) patented and (4) report low yield of the product.

In the present work, we have reported oxidation of o-hydroxybenzyl alcohol over nanoporous ZrV_2O_7 catalyst using air as an oxidizing agent. The catalyst is found to have a good efficiency to oxidize o-hydroxybenzyl alcohol to o-hydroxybenzaldehyde and o-hydroxybenzoic acid. It is prepared by solution combustion method by mixing slurry of ammonium meta vanadate and zirconium nitrate using citric acid as fuel. The problem was undertaken with an object (1) to synthesize nanoporous ZrV_2O_7 catalyst (2) to evaluate the activity of the ZrV_2O_7 catalyst prepared by solution combustion method and (3) to optimize the reaction conditions for the oxidation of o-hydroxybenzyl alcohol.

II. RESEARCH METHODOLOGY

2.1 Catalyst preparation

KSE-100 index Nanoporous ZrV_2O_7 catalyst was prepared by Solution combustion method [26-28]. In the typical preparation, salts of zirconium and vanadium were used along with citric acid. Slurry of 1.28g of Ammonium meta vanadate (Sigma-Aldrich), 24.64g of Zirconium nitrate (Sigma-Aldrich) and 25g Citric acid (Merck) was prepared in 150 ml water. Excess of water was evaporated by gentle heating and constant stirring over hot plate where reaction mixture converts into dry gel. The gel was collected and heated in a muffle furnace at 550⁰C for 4 hours.

2.2 Catalyst characterization

The core level X-ray photoelectron spectroscopy (XPS) spectra of ZrV_2O_7 was measured using Omicron Nanotechnology (EA1-25) photoelectron spectrometer with Al Kα radiation (excitation energy = 1486.6 eV) as excitation source. The spectra recorded at pass energy of 40 eV.

The XRD measurements were carried out in the 2θ range 0-90 degree using Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of X-rays was 0.154 nm (Cu Kα). The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker LynxEye detector). The average particle size was calculated from (111) diffraction peak using Debye - Scherer's equation:

$$D = 0.9\lambda / (\beta \cos\theta)$$

Where D is the average crystallite size in nm, λ is the wavelength of source X-ray (0.154 nm), β (in radian) is the full peak width at half maximum.

Raman spectrum of the sample in the range 50-4000 cm^{-1} was recorded over a Labram HR800 micro Raman spectrometer using Labspec software. An Ar^+ source with the wavelength 2.53 eV was used as a source.

2.3 Evaluation of the activity of the catalyst

The reaction was performed in a three necked round bottom flask occupied with a thermometer pocket, a water cooled condenser and an air inlet system in which measured amount of dry air through a manometer could be feed. The flask was kept in a water bath and heated over a magnetic stirrer with hot plate. A magnetic stirrer bar was used for stirring.

In a typical run mixture of 1g o-hydroxybenzyl alcohol, catalyst and solvent (dichloromethane) was refluxed and air was bubbled through the reaction mixture. At the end reactor was cooled. Catalyst was separated by simple filtration. Filtrate (reaction mixture) was distilled in order to separate solvent, reactant and products. Chromatographic analysis of the reaction mixture was performed with the help of a chemito1000 Chromatograph using SE-30 column and FID detector.

III. RESULTS AND DISCUSSION

3.1 Characterization of the catalyst
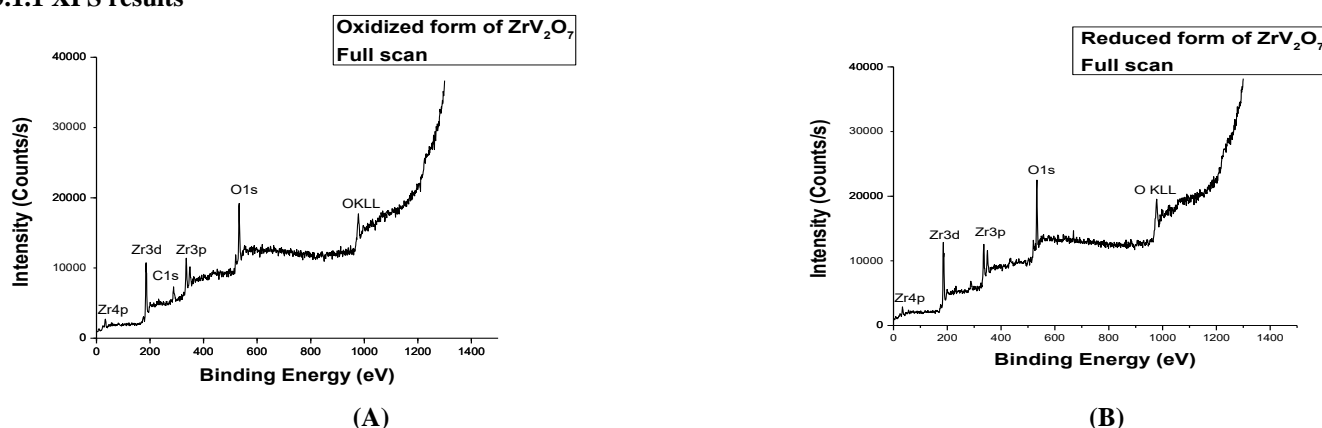
3.1.1 XPS results

Figure 1: Full scan XPS spectra of (A) oxidized and (B) reduced ZrV_2O_7 catalyst.

Table 1: Observed peaks (eV) and their assignments in XPS spectra of ZrV_2O_7 catalyst

Peak position (eV)	Assignments
517	V2p3/2
524.4	V2p1/2
537	O 1s
291.5	C 1s
340.1	Zr 3p3/2
353.3	Zr 3p1/2

The XPS spectra is represented in Fig. 1 and assignments of the spectrum are given in Table 1. It confirms   the presence of Vanadium, Oxygen and Zirconium [29]. V2p1/2 generally appears at 523 eV. Its shifting to 524.4 eV can be attributed to change in oxidation state from V^{4+} to V^{5+}.
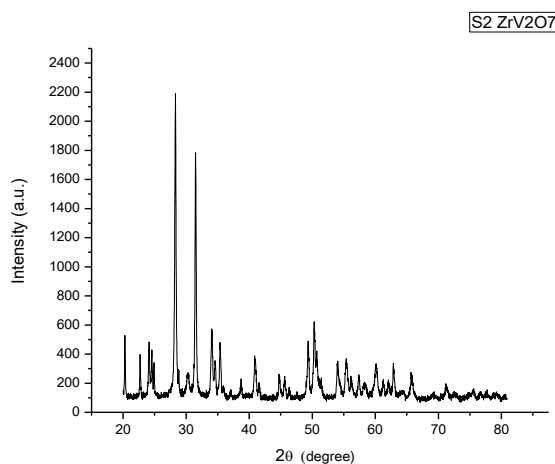
3.1.2 XRD results

Figure 2: XRD patterns of ZrV$_2$O$_7$ catalyst

Table 2: Observed peaks (2θ) and their assignments in XRD patterns of ZrV$_2$O$_7$ catalyst

Peak position (2θ)	Assignments
25 (m)	ZrV$_2$O$_7$
28.31 (s)	ZrO$_2$ tetragonal
34.07 (s)	ZrO$_2$ monoclinic

The Powder XRD pattern of the sample is shown in Fig. 2. The sample seems to be highly crystalline. The pattern appeared around 2θ value of 25 can be assigned to ZrV$_2$O$_7$. The strong peak appeared at 2θ value of 28.31   can be ascribed to tetragonal ZrO$_2$. Peak appeared at 2θ value of 34.07 can be ascribed to monoclinic ZrO$_2$ [30].
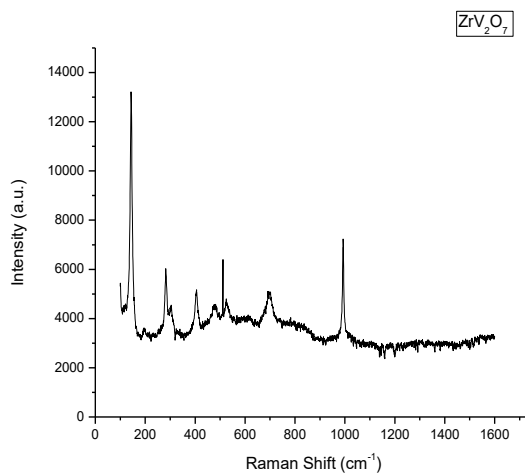
3.1.3 Raman spectroscopy

Figure 3: Raman spectra of prepared ZrV$_2$O$_7$ catalyst

Table 3: Observed bands (cm^{-1}) and their assignments in Raman spectra of ZrV$_2$O$_7$ catalyst

Observed bands (cm^{-1})	Assignments
100 (s) , 143 (s)	Lattice vibrations
282 (s), 299 (m)	ZrO$_6$ (symmetric)
405 (w)	ZrO$_6$ (asymmetric)
511 (s), 524 (w), 691 (s)	ZrO$_2$ (tetragonal)
993 (s)	VO$_4$ (symmetric)

The Raman spectrum of the catalyst calcined at 550°C in the region 4000-100 cm^{-1} is reproduced in Fig. 3.   Assignment of the observed spectrum is based on the basis of comparison with the spectra of molecules available in literature. Bands appeared at 100 cm^{-1} and 143 cm^{-1} are assigned to lattice vibrations. Band appeared at 282 cm^{-1} with the shoulder at 299 cm^{-1} is assigned to ZrO$_6$ symmetric stretching vibrations.   The band appeared at 405 cm^{-1} is assigned to ZrO$_6$ asymmetric stretching mode. Bands appeared at 511 cm^{-1}, 524 cm^{-1} and 691 cm^{-1} can be assigned to ZrO$_2$ tetragonal mode. The strong band appeared at 993 cm^{-1} is due to VO$_4$ symmetric stretching in bulk V$_2$O$_5$ [28, 30].

3.2 Catalyst evaluation

3.2.1 Effect of catalyst loading on the performance of ZrV_2O_7 catalyst
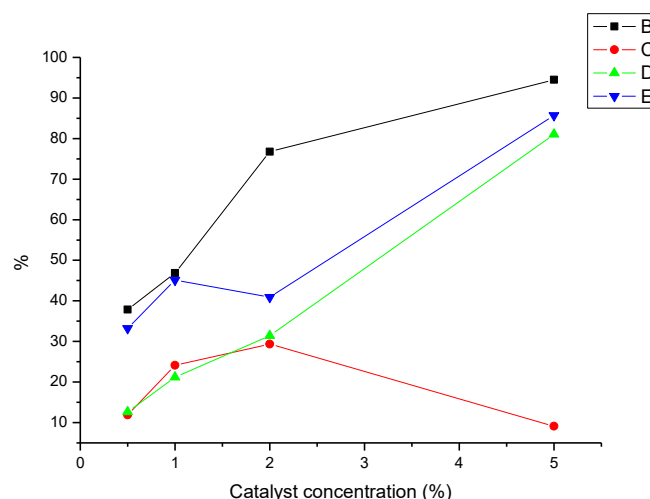

Figure 4: Effect of catalyst loading on the performance of ZrV_2O_7 catalyst in the air oxidation of o-hydroxybenzyl alcohol. B=Conversion, C= o-hydroxybenzaldehyde, D= o-hydroxybenzoic acid, E= Selectivity for o-hydroxybenzoic acid, Time of run : 8 hrs, temperature : 80^0C, air flow rate : 30 lt.hr^{-1}

        Effect of catalyst loading on the performance of ZrV_2O_7 catalyst in the oxidation of o-hydroxybenzyl alcohol was examined at a temperature of 80^0C and air flow rate of 30 lt.hr^{-1}.   The conversion of o-hydroxybenzylalcohol increases with increase in catalyst concentration. Maximum conversion was observed with the 5% catalyst loading. Conversion to o-hydroxybenzaldehyde increases up to 2% catalyst loading and decreased thereafter. Conversion in to o-hydroxybenzoic acid as well as its selectivity increased with catalyst loading. This can be attributed to further oxidation of aldehyde to acid.

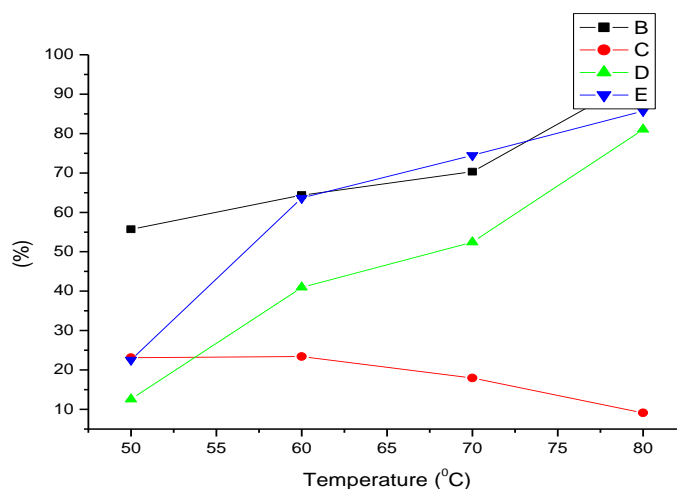**3.2.2 Effect of Temperature on the performance of ZrV_2O_7 catalyst**

Figure 5: Effect of Temperature on the performance of ZrV_2O_7 catalyst in the oxidation of o-hydroxybenzyl alcohol. B=Conversion, C= o-hydroxybenzaldehyde, D= o-hydroxybenzoic acid, E= Selectivity for o-hydroxybenzoic acid, Time of run : 8 hrs, o-hydroxybenzyl alcohol feed rate: 1g.h^{-1}, Air flow rate: 30 lt.hr^{-1}.

        Effect of temperature on the performance of ZrV_2O_7 catalyst in the oxidation of o-hydroxybenzyl alcohol was examined at an air flow rate of 30 lt.hr^{-1} and 5% catalyst loading. Results are graphically shown in Fig.4. Higher temperature led to higher conversion of o-hydroxybenzyl alcohol increases with increase in temperature. Conversion to the o-hydroxybenzaldehyde decreases at higher temperature while conversion to o-hydroxybenzoic acid increases with increase in the temperature. Also selectivity of the catalyst for o-hydroxybenzoic acid observed to be increased with increase in temperature.
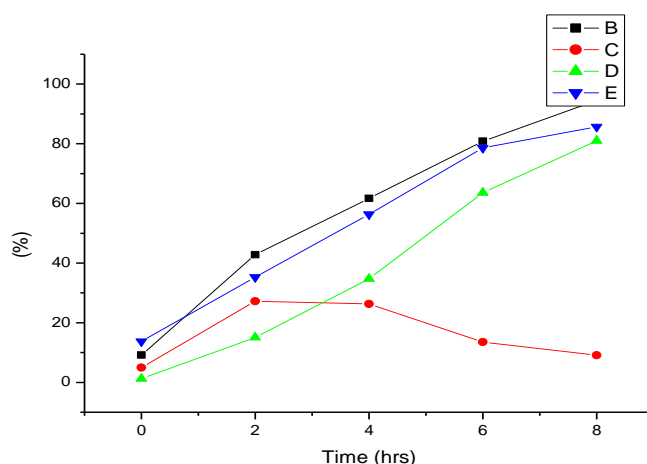
3.2.3 Effect of Time on stream on the performance of ZrV₂O₇ catalyst

Figure 6: Effect of Time on stream on the performance of ZrV₂O₇ catalyst in the oxidation of o-hydroxybenzyl alcohol. B=Conversion, C= o-hydroxybenzaldehyde, D= o-hydroxybenzoic acid, E= Selectivity for o-hydroxybenzoic acid, temperature: 80^0C, Air flow rate: 30 lt.hr^{-1}

Effect of time on stream on the performance of ZrV₂O₇ catalyst was observed and results indicate that conversion increases with increased time on stream. Formation of o-hydroxybenzaldehyde increases up to 2 hrs. and then decreased thereafter perhaps due to its conversion to o-hydroxybenzoic acid. Conversion to o-hydroxybenzoic acid and selectivity for it increases with increase in time on stream.

3.3. Conclusion

From the results it may be concluded that Nanoporous ZrV₂O₇ catalyst synthesized by Solution combustion method is having a good activity for the oxidation of o-hydroxybenzyl alcohol. Under optimum conditions catalyst was shown to have 85.73 % selectivity for the o-hydroxybenzoic acid with a maximum conversion of 94.50% of o-hydroxybenzyl alcohol. This catalyst works at moderate reaction conditions and its efficiency for the particular oxidation reaction provides a green option for the synthesis of carbonyl compounds.

IV. **Acknowledgments**

References

[1] Brühne, F. and Wright, E. 2012. Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH.
[2] Hansen, T .V. and Skattebøl, L. 2005. Ortho-Formylation of Phenols; Preparation of 3-Bromosalicylaldehyde. Organic Syntheses, 82: 64-68.
[3] Janeš , D. and Kreft, S. 2008. Salicylaldehyde is a characteristic aroma component of buckwheat groats. Food Chemistry, 109(2): 293–298.
[4] Dakin, H. D. 1923. Catechol. Organic Syntheses, 3: 28.
[5] Burgstahler, A. W. and Worden, L. R. 1966. Coumarone. Organic Syntheses, 46: 28.
[6] Rap, E. 1895. "Sull' α-Benzoilcumarone" [On the α-Benzoylcoumaron]. Gazzetta Chimica Italiana , 2(4):285–290.
[7] Horning, E. C., Horning, M. G. and Dimmig, D. A. 1948. 3-Carbethoxycoumarin. Organic Syntheses, 28: 24.
[8] WHO Model List of Essential Medicines (19th List), 2015.World Health Organization.
     https://www.who.int/medicines/publications/essentialmedicines/en/ .
[9]   WHO Model Formulary 2008, World Health Organization, **2009**.
[10] Madan, R. K. and Levitt, J. 2014. A review of toxicity from topical salicylic acid preparations. Journal of American Academy of Dermatology, 70 (4): 788-892.
[11] Schrör, K. 2016. Acetylsalicylic Acid (2 ed.), John Wiley & Sons.
[12] Norn, S., Permin, H., Kruse, P. R. and Kruse, E.2009. From willow bark to acetylsalicylic acid. Dansk Medicinhistorisk Årbog (in Danish), 37: 79–98.
[13] Goldberg, D. R. 2009. "Aspirin: Turn-of-the-Century Miracle Drug". Chemical Heritage Foundation.
[14] Hemel, P. B. and Chiltoskey, M. U. 1975. Cherokee Plants and Their Uses – A 400 Year History, Sylva. NC: Herald Publishing Co.
[15] Milone, C., Ingoglia, R., Pistone, A., Neri, G. and Galvagno, S. 2003. Activity of gold catalysts in liquid-phase oxidation of o-hydroxybenzyl alcohol. Catalysis. Letters, 87: 201-209.
[16] Milone, C., Ingoglia, R., Neri, G., Pistone, A. and Galvagno, S. 2001. Gold catalysts for the liquid phase oxidation of o-hydroxybenzyl alcohol. Applied Catalysis A: General, 211(2): 251-257.
[17] Di bella, E. P. 1972. US patent 3673257.

[18] Ludec J L. 1977. US Patent 4,026,950.

[19] Bauer, K., Mölleken, R., Fiege, H. and Wedemeyer, K. 1978. US Patent 4,119,671.

[20] Lanfranc, H. 1997. US Patent 5,689,009.

[21] Christidis, Y. and Vallejos, J. C. 1984. US Patent 4,481,374.

[22] Rahimi, R., Gholamrezapor, E., Naimi-Jamal, M. R. and Rabbani, M. 2012. Oxidation of o-chloro and o-hydroxy benzyl alcohols catalyzed by copper (II) tetraphenylporphyrin nanoparticles synthesized by mixed solvent method. Current Chemistry Letters, 1: 101–108.

[23] Hamada, K. and Suzukamo, G. 1984. US Patent 4,469,894.

[24] Hamada, K., Suzukamo, G., Masuko, F. and Nakamura, M. 1984. US Patent 4,584,410.

[25] Weisse, L., Neuntefeul, R., Nenndorf, B. and Strutz, H. US Patent 5,395,978.

[26] Aruna, S. T. and Mukasyan, A. S. 2008. Combustion synthesis and nanomaterials. Current Opinion in Solid State & Material Science, 12: 44-50.

[27] Kumarsrinivasan, S., Verma, A. and Gopinath, C. S. 2012. Molecular oxygen-assisted oxidative dehydrogenation of ethylbenzene to styrene with nanocrystalline $Ti_{1-x}V_xO_2$. Green Chemistry, 14: 461-471.

[28] Verma, A., Dwivedi, R., Prasad, R. and Bartwal, K. S. 2013. Microwave-Assisted Synthesis of Mixed Metal-Oxide Nanoparticles. Journal of Nanoparticles, Article ID 737831, 11 pages. http://dx.doi.org/10.1155/2013/737831

[29] Kantcheva, M. 2000. Spectroscopic characterization of vanadium(v) oxo species deposited on zirconia. Physical Chemistry Chemical Physics, 2(13): 3043–3048.

[30] Khodakov, A., Yang, J., Su, S., Iglesia, E. and Bell, A. T. 1998. Structure and properties of vanadium oxide-zirconia catalysts for propane oxidative dehydrogenation. Journal of Catalysis, 177(2): 343–351.