

## Selective Liquid Phase Ammoxidation of Aromatic Aldehydes to Aromatic Nitriles with VPO Titania Heterogeneous Catalysts in Air

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**ABSTRACT:** Preparation of 2-Chlorobenzonitrile, and benzonitrile are reported here from the corresponding 2-Chlorobenzaldehyde and benzaldehyde by the reaction of ammonium hydroxide/VPO titania, VPO bulk (ammonium metavanadate) CuCr catalyst/air system in methanol. All these catalysts showed better conversions with reasonable selectivity to aromatic. The results prove that BET surface area results show VPO is present on the catalysts surface which has high surface area, attributed to increase in activity of the catalysts.

**KEY WORDS:** Ammoxidation, 2-chlorobenzaldehyde, 2-chlorobenzonitrile, VPO,  $\text{NH}_4\text{OH}$ .

### INTRODUCTION

Ammoxidation of aldehydes is an economical and ecologically favourable route to valuable intermediates in organic synthesis like: dyestuffs, pharmaceuticals, pesticides, hence undeniably an industrially and academically important reaction [1]. The conventional two stage method for obtaining nitriles from the corresponding aldehydes is through oximation of aldehyde with hydroxyl amine followed with dehydration of the resulting aldoxime using various dehydrating agents such as acetic anhydride,  $\text{P}_2\text{O}_5$ , dicyclohexylcarbodiimide etc. [2]. The yields of nitriles with traditional synthetic methods are known to be high at the expense of hazardous reagents feed components and solvents resulting in waste salts [3]. Using iodine in Ammonia in water is also reported [4]. Das, B., et al. [5] reported ammoxidation of aldehydes using microwave irradiation using ammonium acetate.

The present work highlights the ammoxidation of 2-chlorobenzaldehyde to 2-chlorobenzonitrile in VPO contains ammonium metavanadate and VPO supported and CuCr catalyst in methanol and a base such as sodium hydroxide in ammonium hydroxide solution under mild reaction conditions.

### EXPERIMENTAL

#### Materials

All chemicals used in this project were pure and available from (Fluka).

#### Preparation of the Catalyst

Bulk VPO precursors (0.95P/V) mainly consisting of  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  ammonium metavanadate (VHP) phase is prepared in an organic medium as described by Martin A. et al. [1].

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Further VPCoO, VPO-TiO<sub>2</sub>, and VPO Alumina were also prepared by impregnation method by these authors [1].

#### Typical reaction procedure

In a 3 neck round bottom flask equipped with magnetic bar, and reflux condenser, and oxygen bubbler, were placed VPO catalyst 3.85 mol, and aldehyde 0.04 mol, 0.42 mol NH<sub>4</sub>OH solution, Sodium hydroxide 0.03 mol, and methanol 35 mL are charged into the reaction medium and heated at 50-55 °C and the reaction is followed and at the end analysed 2-chlorobenzonitrile is obtained by usual workup. The authenticity of the individual nitrile obtained was confirmed by comparison of its retention time in GC and molecular weight fragmentation in mass and the IR absorption of the nitrile functional group.

#### Characterisation of catalysts

The BET surface area characterization was carried by BET equation.

## RESULTS AND DISCUSSION

#### BET result

BET surface area of VPO bulk and VPO supported catalysts were carried out on Brunnauer-Emmett Teller Equation [6-11]. Which are presented in table 1.

#### Dependence of Time

Amoxidation of 2-chlorobenzaldehyde to 2-chlorobenzonitrile was studied in time dependence for various catalysts as mentioned in table 3. With CuCr catalyst the yield was 55 %. Selectivity >95 in 4 h. With VPO Bulk (0.95 e/v) the yield reached was 72 %, and selectivity 90 % in 6 h, for 50 % VPOTiO<sub>2</sub>, 77 % yield, Selectivity-100 %. From these results we conclude that as the time is increasing the rate of the reaction is also increased due to the active acidic sites, on the surface of the catalyst.

## CONCLUSIONS

In conclusion the liquid phase amoxidation is a convenient method to synthesize aromatic nitriles from aromatic aldehydes, (table 2). The BET results conclusively demonstrate that VPO is present which are active for amoxidation of aldehydes to nitriles.

VPO catalysts after calcinations, produce active sites such as oxides of vanadium which are acidic in nature

**Table 1: BET Surface areas and pore volumes of catalysts used in the present study.**

Catalyst	BET-SAm <sup>2</sup> /g	Pore Volume (cm <sup>3</sup> /g)
VPCoO3C/N <sub>2</sub>	31.7	0.306
50 % VPO-TiO <sub>2</sub>	37	-
25 % VPO <sub>γ</sub> /Al <sub>2</sub> O <sub>3</sub>	69.3	0.166
VPO Bulk (0.95 e/v)	40.0	0.113
25 % VPMoO/TiO <sub>2</sub>	58.6	0.204
25 % VPCrO/TiO <sub>2</sub>	60.6	0.240
CuCr	-	-

**Table 2: Amoxidation of 2-chlorobenzaldehyde to 2-Chlorobenzonitrile in liquid phase employing various catalysts at 50-55 °C for 24 hrs.**

S. No	Catalysts	Conv %
1.	VPCoO3CN <sub>2</sub> *	40 %
2.	25% VPO TiO <sub>2</sub>	20 %
3.	50% VPO TiO <sub>2</sub>	35 %
4.	25% VPO-γ-Al <sub>2</sub> O <sub>3</sub> *	70 %
5.	50% VPO-γ-Al <sub>2</sub> O <sub>3</sub> *	76 %
6.	25% VPO MoO TiO <sub>2</sub> *	65 %
7.	50% VPO MoO TiO <sub>2</sub> *	75 %
8.	25% VPCrOTiO <sub>2</sub> *	60 %
9.	50% VPCrOTiO <sub>2</sub> *	71 %

\* No base is used.

**Table 3: Time dependence study during the amoxidation of 2-chlorobenzaldehyde to 2-Chlorobenzonitril in liquid phase employing various catalysts at 50-55 °C.**

Catalyst	Time	Yield	Selectivity
CuCr	4 h	55.6 %	100 %
	2 h	-	-
	1 h	-	-
VPCo-O3C/N <sub>2</sub> *	5 h	78.2 %	>95
	4 h	42 %	
	3 h	21 %	
	2 h	22 %	
	1 h	30 %	
50 % VPOTiO <sub>2</sub> *	6 h	18.5 %	-
	2 h	77 %	
25 % VPMoO/TiO <sub>2</sub>	5 h	26 %	>95 %
	2 h	83 %	
	1 h	18 %	
25 % VPCrO/TiO <sub>2</sub> *	23 h	60.0 %	>97
	4 h	46 %	
	3 h	52.9 %	
	1 h	46.3 %	
VPO Bulk (0.95 P/V)*	6 h	72 %	90
CuCr	6 h	70 %	93

resulting in ammoxidation reaction. The chloro group present in 2<sup>nd</sup> position does not hinder the aldehyde group which is easily converted to nitriles in liquid phase conditions, which is a very convenient route for the synthesis of a very useful 2-chlorobenzonitrile from 2-chloro-benzaldehyde.

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