

One Step Synthesis of Acetonitrile from Ethanol *via* Ammoxidation over Sb-V-P-O/Al₂O₃ Catalyst

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Selective synthesis of acetonitrile in one step from ethanol by ammoxidation is reported, for the first time, using alumina supported and antimony promoted vanadium phosphorus oxide catalyst.

Ethanol is a versatile feedstock for a variety of intermediate and end products such as ethylene, butadiene, acetaldehyde, ethoxides and ethers.¹ Ethanol to acetonitrile in one step has however, not been reported so far. Acetonitrile is normally produced either by catalytic dehydration of acetamide^{2,3} or catalytic dehydrogenation of ethylamine,^{4,5} both of which are produced by amination of acetic acid and ethanol respectively.²⁻⁵ In this communication we report selective synthesis of acetonitrile from ethanol in one step *via* ammoxidation over alumina supported and antimony promoted vanadium phosphorus oxide (VPO) catalyst.

The investigated Al₂O₃ supported and antimony promoted VPO catalyst (V : P : Sb : Al = 1.4 : 1 : 3.3 : 10) was prepared by a deposition precipitation method. The requisite quantities of ammonium metavanadate (Fluka, AR grade) and antimony trioxide (Loba Chemie, AR grade) were suspended in deionized water, to which a stoichiometric 85% orthophosphoric acid (Loba Chemie, AR grade) was also added and refluxed for 6 h. To the resulting light-green slurry suspension the desired quantity of gamma alumina (ACC, India, surface area 104 m² g⁻¹) fine powder (-200 mesh fraction) was added

and heated further to concentrate the suspension to obtain a paste. The paste was then oven dried at 120 °C for 16 h and calcined at 750 °C for 4 h in an open air furnace. The resulting catalyst had a N₂ Brunauer-Emmett-Teller (BET) surface area of 16 m² g⁻¹.

Catalytic tests were carried out in a previously described⁶ flow microreactor system operating at atmospheric pressure. For each run about 2-3 g of catalyst sample (<0.5 mm particle size) was used and was prereduced at 350 °C for 6 h with a mixture of ammonia and air (1:1 v/v) at a flow rate of 40 ml min⁻¹. Pure ethanol (Merck, AR grade) diluted with water (1:2 v/v) was fed at a rate of 4-6 ml h⁻¹. The reaction temperature was maintained at 400 °C and an air-ammonia gas mixture (1:2.1 mole ratio) was passed at a space velocity of 3580 h⁻¹. The reaction products were analysed quantitatively by gas chromatography (OV-17 column, flame ionization detector) and qualitatively by NMR and mass spectrometry.

Activity and selectivity of the catalyst for ethanol to acetonitrile conversion is illustrated in Table 1. About 84% conversion of ethanol with 96% selectivity to acetonitrile is obtained under the experimental conditions employed in this study. Thus, Sb-V-P-O/Al₂O₃ appears to be a promising system for this reaction. Vanadium phosphorus oxide in combination with various promoter atoms and support materials is known to be a unique catalyst in recent times for the selective oxidation of butane/butenes to maleic anhydride.⁷⁻⁹ Silica supported VPO as well as unsupported VPO has also proved to be an effective catalyst system for the selective ammoxidation of methyl substituted *N*-heteroaromatic compounds to their corresponding nitriles.¹⁰⁻¹² The present study illustrates further the significance of the VPO catalyst for this novel title reaction.

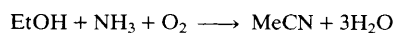
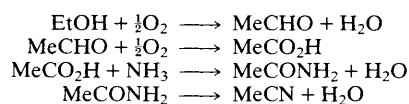
In order to ascertain the mechanism of this reaction a few additional experiments were also carried out by taking

Table 1 Activity and selectivity results on Sb-V-P-O/Al₂O₃ catalyst at 400 °C

Reactant	Con- version (%)	Selectivity (%)				
		Aceto- nitrile	Acetal- dehyde	Acetic acid	Acet- amide	Ethyl- amine
Ethanol	84	96	Trace	Trace	Trace	—
Acetaldehyde	92	97	8 ^a	2	—	—
Acetic acid	99	99	—	Trace ^a	Trace	—

^a Unreacted.

acetaldehyde and acetic acid as the starting reactants instead of ethanol; the conversion and selectivity to various products are also shown in Table 1. The results are consistent with the reaction sequence in Scheme 1, which we feel is more likely than a sequence involving ethylamine as an intermediate.



Scheme 1

In these reactions, acetaldehyde, acetic acid and acetamide are the intermediates and whose presence were also noted in the reaction products when ethanol was used as the reactant (Table 1). When the reaction was conducted in the absence of gas phase ammonia acetaldehyde and acetic acid were observed as the main products. Under identical conditions when the reaction was carried out in the absence of air ethylamine was the main product obtained. However, in the presence of both air and ammonia, acetonitrile was the selective product with some traces of acetaldehyde, acetic acid and acetamide as shown in Table 1. In addition, when acetaldehyde or acetic acid were used as starting reactants

total conversion with more than 97% selectivity to acetonitrile was observed.

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