One-step Synthesis of Adiponitrile by Catalytic Ammoxidation over Antimony–Vanadium Phosphorus Oxide/γ-Alumina Catalyst

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The selective synthesis of adiponitrile from cyclohexanol, cyclohexanone, cyclohexane and n-hexane in a single step by vapour-phase ammoxidation over an antimony-promoted vanadium phosphorus oxide catalyst supported on alumina is reported.

Adiponitrile (1,4-dicyanobutane) is an important intermediate in the chemical, pharmaceutical, food and perfumery industry;[1] however, the largest quantities are mainly utilized in the manufacture of Nylon 6.6. Industrially, adiponitrile is produced by a two-step process: oxidation of a cyclohexanol–cyclohexanone mixture to adipic acid, followed by reaction of adipic acid with ammonia.[1,2] Several alternative routes have also been attempted in the literature involving aromatic hydrocarbons, olefinic compounds and alkanes on various catalyst systems.[3–8] However, the conversions and product selectivities obtained are very small.

In this communication, we describe the synthesis of adiponitrile in a single-step by an ammoxidation route over an antimony-promoted vanadium phosphorus oxide (VPO) catalyst supported on γ-alumina. The VPOs are perhaps the most unique catalysts known today for the selective oxidation of n-butane or butene to maleic anhydride.[9,10] Supported VPO catalysts are also reported to be active in the selective ammoxidation of picolines and 2-methylpyrazine.[11,12]

The Sb-promoted and γ-Al_2O_3-supported VPO catalyst was prepared by a precipitation deposition method in aqueous media. In a typical experiment ammonium metavanadate (24 g) (Fluka, AR grade) and antimony(VI) oxide (60 g) (Loba Chemie, GR grade) were suspended in *ca.* 500 ml of deionized water to which 85% orthophosphoric acid (23.8 g) (Loba Chemie, GR Grade) was added and refluxed for 8 h. To the resulting light-green slurry γ-Al_2O_3 fine powder (74 g) (ACC, India; surface area 104 $m^2 g^{-1}$; −200 British Standard Sieve mesh fraction) was added and the suspension was further heated to obtain a paste. The residue was oven-dried at 120 °C for 16 h and calcined at 750 °C for 3 h in an open air furnace. The obtained catalyst had a N_2 BET (Brunauer–Emmett–Teller) surface area of 16 $m^2 g^{-1}$ and was further characterized by means of X-ray diffraction (Philips PW 1051 instrument with Ni-filtered Cu-Kα radiation), electron spin resonance (Bruker ER 200D-SRC × band spectrometer with 100 kHz modulation) and ammonia uptake measurements.[13] Activity and selectivity studies were carried out in a previously described fixed-bed microreactor at atmospheric pressure.[14] For each run *ca.* 3 g of catalyst sample was used and the products were collected after establishing steady-state conditions. All the reaction products were analysed by gas chromatography with a 10% OV-17 column (l = 2 m) on Chromosorb G-AW. The feed mixture consisting of reactant, air and ammonia was passed through the catalyst bed at a space velocity of 1624–2450 h^{-1}.

Total conversion of various substrates and their product selectivities to adiponitrile and hexanenitrile (1-cyanopentane) at 425 °C temperature are shown in Fig. 1. Various additional side products (not shown in Fig. 1) were also observed depending on the nature of substrate used. The ammoxidation reaction was carried out at various temperatures ranging from 300–500 °C, however, the best results were noted at 425 °C. Above this temperature the formation of CO and CO_2 in large quantities occurred in addition to hydrocarbon cracking products which play a major role in opening the ring of the cyclic compounds. The total conversion and selectivities of various substrates were found to depend on the mole ratio of air : ammonia. Better results shown in Fig. 1 were obtained at an air : ammonia mole ratio of 2.8 : 1. Reactivity trends of various substrates were as follows: cyclohexanol > cyclohexane > cyclohexanone > n-hexane.

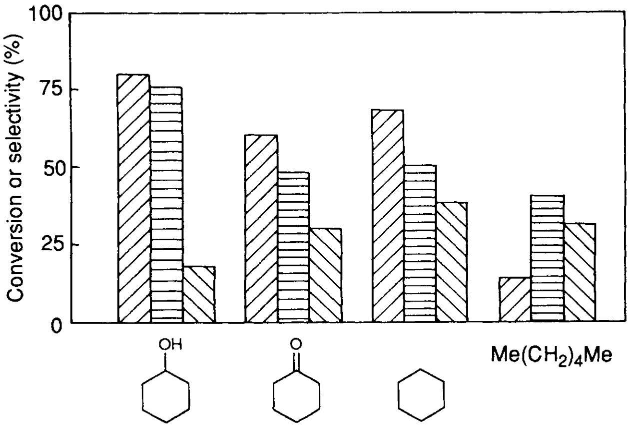

Fig. 1 Total conversion (▨) of various substrates and their product selectivities to adiponitrile (▤) and hexanenitrile (▧) at 425 °C with feed composition (mol) of substrate : air : ammonia = 0.6–1.0 : 4.2 : 1.5.

The greater reactivity of cyclohexanol than other substrates is primarily due to the presence of –OH groups which are known to facilitate the interaction of the reactant molecule with the catalyst surface. The reaction apparently proceeds *via* a mechanism involving dehydration or oxidative dehydrogenation to yield cyclic or straight chain olefins, followed by oxidative ammonolysis to corresponding nitriles as suggested by Kim *et al.*[15]

X-Ray powder diffraction patterns of the catalyst sample revealed the presence of $(VO)_2P_2O_7$ as the major phase along with α-$VOPO_4$ and other phases in minor quantities. An ESR spectrum of this sample showed the presence of the V^{4+} species in large quantity. Ammonia uptake at 150 °C showed that the catalyst possessed a greater number of acid sites. As reported by Busca *et al.*[16] the working VPO catalyst generally contains a mixture of a well-crystallized $(VO)_2P_2O_7(V^{4+})$ phase and an amorphous VPO (V^{5+}) phase; a dynamic equilibrium has to be maintained between $V^{4+} \rightleftharpoons V^{5+}$ states during the course of reaction. As envisaged earlier[11] the role of support is to enhance the exposed area of $(VO)_2P_2O_7$ phase with a preferential exposure on the surface of the (020) plane, which is known to be active in the redox processes.

Thus, the Sb-VPO/Al_2O_3 appears to be an efficient catalyst for the one-step synthesis of adiponitrile from cyclohexanol along with other substrates.

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