Facile synthesis of 2,6-dichlorobenzonitrile by vapour phase ammoxidation

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Ammoxidation of different alkyl aromatics and heteroaromatics to their corresponding nitriles in a single step process is gaining lot of industrial interest in recent times. In general, these reactions have been the subject of many industrial applications for producing a variety of commercially useful chemicals. Selective synthesis of 2,6-dichlorobenzonitrile (DCBN) from 2,6-dichlorotoluene (DCT) is of particular importance for manufacturing a series of highly efficient pesticides and special kind of engineering plastics. Despite such growing interest and commercial significance, only a few scientific studies exist in the literature on this particular reaction. In this contribution, we intend to present some of the important results obtained over vanadium phosphorous oxide (VPO) catalysts with a special emphasis devoted to the influence of P/V ratio on the catalytic performance.

Bulk VPO precursors were prepared through an organic route as described elsewhere [1]. The P/V ratios of these materials are varied over a wide range from 0.5 to 2.0 and calcined at 450 °C for 3 h in nitrogen atmosphere. All these samples are characterised by N_2 adsorption (BET-surface areas), FTIR and XRD. Catalytic tests were performed in a fixed bed glass reactor at ambient pressure and at 360 to 440 °C. The product stream was analysed off-line by GC equipped with FID.

BET surface areas increased gradually from ca. 15 to 40 m^2/g with increase in P/V ratio close to stoichiometric ratio of $(VO)_2P_2O_7$ (i.e. 0.95 P/V) and then decreased to 11 m^2/g with further increase in P/V ratio to 2. XRD showed the formation of $VOHPO_4 \cdot 0.5\ H_2O$ in all the precursors and $(VO)_2P_2O_7$ phase (VPP) in the calcined samples. FTIR further confirmed the formation of VPP from the appearance of bands at around 970 cm^{-1}, which can be assigned to reduced vanadium sites (V^{4+}=O). The conversion of DCT is found to decrease at a slower rate from 98 to 92 % up to stoichiometric P/V ratio and then significantly beyond this ratio. The selectivity of DCBN is varied in the range from 57 to 70 %. In other words, the catalysts with low P/V ratios exhibited high conversions but low selectivities and vice versa. The lower activity of the high P/V solids can be ascribed to increased stabilisation of reduced vanadium species by enhanced phosphorous contents. Results suggest that the P/V ratio of 0.95 seems to be somewhat optimum and hence the influence of various reaction parameters (e.g. effects of reaction temperature, NH_3/DCT mole ratio, air/DCT mole ratios) on the performance of this sample was further investigated. These studies revealed some interesting results.

On the whole, it can be stated that the ratio of phosphorous to vanadium (P/V) displayed strong influence on the catalytic performance of the present VPO catalysts. Selective synthesis of DCBN (S = ca.60 %) at significantly high conversion of DCT (>90 %) could be achieved.

1. A. Martin, V.N. Kalevaru, B. Lücke, D. van Deynse, M. Belmans, F. Boers, WO 03/101939 A2 (2003) (Tessenderlo Chemie S.A.).