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Ammoxidation of 3-picoline to nicotinonitrile over VPO catalysts

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ABSTRACT

Industrial vanadium phosphate (VPO) samples (vanadyl phosphate hemihydrate precursor compound, freshly calcined and equilibrated vanadyl pyrophosphate solids) shaped with polysilicic acid (PSA) were characterized and used as catalysts for the ammoxidation of 3-picoline to nicotinonitrile. Catalyst characterization with N_2-adsorption, XRD, IR spectroscopy, UV–Vis-DRS and XPS provide information on BET surface area and pore size, crystalline properties and vanadium oxidation state data in bulk and near-to-surface region. BET surface area is dramatically increased by calcination of the precursor but catalytic operation drops the surface area again, moreover, deactivation by carbon deposits was observed. The deactivation is also demonstrated by decrease in V^{5+} portion in the equilibrated catalyst. Ammoxidation test runs showed quite good performance for the calcined vanadyl pyrophosphate sample; the used and precursor sample revealed poor performance only. Interestingly, characterization of samples used in ammoxidation showed phase alteration in particular for precursor sample proving phase change towards NH_4-ion containing VPO phase.

1. Introduction

In general, ammoxidation reactions are industrially important hydrocarbon conversions for producing a variety of nitriles, which are very useful organic intermediates for further manufacture of different commercial compounds [1]. Olefins, alkyl aromatics and heteroaromatics can be used as reactants. Besides the large scale production of acrylonitrile starting from propene and nowadays from propane, the conversion of alkyl (methyl) aromatics and in particular heteroaromatics lead to interesting intermediates as well as final products belonging to fine chemicals sector, in particular agrochemicals and pharmaceuticals area (e.g. [2]).

Ammoxidation of heteroaromatics (e.g. picolines [3–5], 2-methyl pyrazine [6–10]) is an intensively investigated field studied by various industrial companies and research groups using different types of catalysts. Among them, vanadium-containing oxides are preferentially used as supported, bulk or multi-component catalysts for such ammoxidations. Usually, V/Ti, V/Mo, V/Fe, V/Sb, V/Sn oxides, which are sometimes supported on various oxides or promoted by further transition metals are used as effective catalysts ([6–13] and refs. therein). Among them, VTiO catalysts are extensively investigated for ammoxidation of methyl pyrazine and picoline by various research groups (e.g. [7,8,14–16]). Bondareva et al. [7] reported on the effect of VTiO solids during ammoxidation of 2-methyl pyrazine to the corresponding amidopyrazine and cyanopyrazine. The selectivity of both the target products always reached 90–95%. Proportions of carbon oxides and pyrazine appearing as destruction products increase at conversions higher than 70–80%. Andersson et al. [14,15] claimed 90% conversion of 3-picoline with 75–85% selectivity of nicotinonitrile over VTiO catalysts. A 3-picoline conversion of ca. 75% at almost 100% selectivity of nicotinonitrile was reported over monolayer V_2O_5/TiO_2 catalysts [16]. Recently, some Chinese researchers [17,18] also reported ca. 90% conversion of 3-picoline with ≥90% selectivity of nitrile again on V_2O_5/TiO_2 catalysts. Additionally, metal fluoride supported catalysts are also reported recently to be highly active and selective catalysts [19,20]. Furthermore, bulky metal phosphates such as VPO, MoPO and FePO are known as suitable catalysts from the literature [4,9,21]. However, vanadium phosphate (VPO) catalysts, better known from maleic anhydride manufacture process (e.g. [22]), are also very effective even for ammoxidation of 3-picoline [1,2,23–26]; pyridine–carbonitrile yields from 80 to nearly 100% were reached at almost total conversions. Molybdenum phosphate (MoPO) catalysts are also checked for their performance in this reaction. Lee et al. reported superior catalytic properties of X-ray amorphous MoPO materials enabling total conversion and selectivities higher than 90% for all three picoline isomers [21].

Nicotinonitrile (NN; also known as pyridine-3-carbonitrile, 3-cyanopyridine) is the precursor compound of nicotinic acid (C_5H_4N-COOH) or the corresponding amide (C_5H_4N-$CONH_2$); both are essential vitamins (vitamin B3) and called niacin as the generic

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name. Scheme 1 shows the formation of nicotinonitrile by the ammoxidation of 3-methyl-pyridine (3-picoline). First heterogeneously catalyzed ammoxidation research taking such reactants is known since ca. 40 years [27]; Beschke et al. from Degussa gave a relevant review on catalysts, reaction conditions and applications some years later [3]. Besides the early work of Moll and Fischer using V_2O_5 supported catalysts [27] and that of Degussa researchers using $VTiSbSiO_x$ catalysts [4,28], some Russian groups also reported on ammoxidation of heteroaromatics (e.g. [6–8,29]). First use of VPO solids as catalysts for such reactions was reported 20 years ago [5]. The approximate worldwide demand for nicotinic acid and its derivatives amounts to ca. 10 kt/a. A nice overview is given on the developments in nicotinate technology over the past 10–15 years by Chuck from Lonza [30].

Intensive research on kinetics and mechanism of NN formation on vanadium oxide (VO_x) containing catalysts was first reported from the group of Andersson in the 1980s (e.g. [31–33]). Prasad and Kar [34] and Arntz et al. [35] reported on further investigations on reaction kinetics and reaction mechanism. Formation of by-products (pyridine due to demethylation and CO_x due to decarbonylation/decarboxylation) and the effect of additional dosing of water to the feed were in the focus.

Recently, a report was published on the dependence of the catalyst performance on the oxidation state and V_2O_5 proportion in the V_2O_5/TiO_2 catalysts used for ammoxidation of 3-picoline [16]. Furthermore, similar characterization studies using VPO catalysts and conventional MoO_3–V_2O_5/Al_2O_3 solids were carried out by Manohar and Reddy [36]. They claimed that the redox couple between $(VO)_2P_2O_7$ (V^{4+}) and $VOPO_4$ (V^{5+}) phases appears to be responsible for the good ammoxidation activity and selectivity of VPO catalysts. This corresponds to own experiments on VPO's showing a decreasing activity by a vanadium surface oxidation state to lower than +4, otherwise an optimum activity for $(VO)_2P_2O_7$ was found at an oxidation state of ca. +4.3, further increase in surface oxidation state led to a dramatic increase in total oxidation [37].

The aim of the present study was to evaluate industrially synthesized bulk VPO samples in the ammoxidation of 3-picoline because those solids can be effective ammoxidation catalysts. The motivation for these studies was supported by the intention to reveal different catalytic, surface and bulk behaviors due to different genesis. Therefore, VPO solids were used in the form of precursor, calcined (i.e. fresh sample), and equilibrated material. The equilibrated material was obtained from n-butane to maleic anhydride reaction carried out in the DuPont recirculation reactor, which separates oxidation/reduction steps (e.g. [38]). The parent sample was shaped with polysilicic acid (PSA). The objective is also to carry out basic solid-state characterization in a systematic way to throw some more light on the catalytic performance.

2. Experimental

2.1. Catalysts

Three polysilicic acid (PSA) coated VPO catalysts samples (e.g. [39]) were included in the investigations: (A) vanadyl phosphate hemihydrate precursor compound (VHP, $VOHPO_4 \cdot 1/2\ H_2O$/9.05 wt% SiO_2), (B) fresh (i.e. calcined) vanadyl pyrophosphate (VPPf, $(VO)_2P_2O_7$/10 wt% SiO_2), (C) equilibrated vanadyl pyrophosphate (VPPe, $(VO)_2P_2O_7$/10 wt% SiO_2). All the samples were supplied by DuPont (U.S.A.). The precursor material A was obtained by spray drying from the synthesis slurry, the fresh catalyst B by calcination of A and equilibrated catalyst sample C from long-term operation in manufacture of maleic anhydride from n-butane feed. The equilibrated sample was under operation in a continuous industrial plant (Asturias, Spain) for over 2 years, however, operating conditions are changed as and when required during time-on-stream studies and on some occasions certain amount of fresh catalyst was also added to make up for losses due to attrition. The reaction temperatures applied were up to 400 °C, pressure was ca. 4 bar and n-butane and oxygen concentrations were typically in the order of 6% and 12%, respectively.

The as-received industrial catalysts (A–C) were shaped for ammoxidation test runs by using a hydraulic press (20 MPa, 30 s), crushed and a sieve fraction of 1–1.25 mm was used for the catalytic experiments. Some of the solids used in ammoxidation reaction were additionally characterized with the methods described below and will be denoted as A_{aox}, B_{aox} and C_{aox}.

2.2. Characterization methods

BET surface areas and pore volumes of the different samples were determined by nitrogen adsorption at 77 K (ASAP2010).

Phase analysis of all solids was carried out using X-ray diffraction (XRD, STADIP, Stoe) using Cu Kα1 radiation (1.5406 Å).

IR spectroscopic studies were carried out in ATR (attenuated total reflection) technique. The spectra were recorded using Nicolet 6700 spectrometer. Catalyst powder was directly pressed by stamp on a diamond crystal and measured.

The XPS data were recorded with a VG ESCALAB 220iXL unit using Mg Kα radiation ($E = 1253.6$ eV) at a base pressure of the UHV chamber. Peak position and area were determined after satellite and background subtraction and fitting with Gaussian–Lorentzian curves. The amount of a component and the composition of the near-surface region were determined from the peak area after dividing it by the element-specific Scofield factor and the analyzer-specific transmission function.

UV–Vis investigations in diffuse reflectance mode were recorded under ambient conditions using Varian Cary 400 spectrometer. $BaSO_4$ reflectance standard (Merck) was chosen as diluent to minimize absorbance as well as used as baseline standard. Diffuse reflectance spectra were analyzed by Kubelka–Munk treatments.

2.3. Catalytic tests

A laboratory test unit containing a plug-flow reactor was used for the catalytic investigations. Gases (air (5.0, Air Liquide) and ammonia (5.0, Messer-Grießheim)) were metered using mass flow controllers (Bronkhorst). 3-Picoline (99%, Aldrich) was fed as an aqueous solution with a fixed molar ratio of 1:8 (3-picoline:H_2O) by a syringe pump. The reactor ($V = 15$ ml) was made of quartz glass and equipped with an inner guiding tube for moving a thermocouple along the bed to measure bed temperature. In every test, 5.4 ml catalyst was loaded between the layers of quartz glass beads. In general, the following reaction conditions were applied: T(oven) = 330–380 °C, GHSV = 1804 h^{-1} (residence time = 2 s), molar ratio: 3-picoline:air:ammonia:water = 1:22:4.6:8. The reaction products were quenched and analyzed by GC (Shimadzu GC-17A equipped with autosampler Shimadzu AOC-20i; column: FS-SE-54) using FID. The carbon oxides were continuously monitored by on line non-dispersive infrared analyzer (Rosemount, BINOS 100 2M). An average value of five analyses was taken into account for further calculations. 3-Picoline conversion (X) and nicotinonitrile yields (Y) were calculated from GC peak areas and calibration factors developed from mixtures of known 3-picoline and nicotinonitrile concentrations. Selectivities were calculated from moles of formed product divided by moles of reacted compound, multiplied by carbon number of product and divided by that of reactant, to get stoichiometric corrected values.

Some blank tests were carried out initially by loading the reactor with glass beads in equal amounts as catalyst particles and