Applied Catalysis A: General 443–444 (2012) 111–118

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Metal vanadate catalysts for the ammoxidation of 2-methylpyrazine to 2-cyanopyrazine

Naresh Dhachapally, Venkata N. Kalevaru, Angelika Brückner, Andreas Martin*

Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany

ARTICLE INFO

Article history:
Received 19 April 2012
Received in revised form 24 July 2012
Accepted 25 July 2012
Available online 2 August 2012

Dedicated to Professor Dr. Bernhard Lücke on the occasion of his 75th birthday.

Keywords:
Metal vanadates
Ammoxidation
2-Methylpyrazine
2-Cyanopyrazine
XRD
XPS
Pyridine-FTIR
ESR

ABSTRACT

The ammoxidation of 2-methylpyrazine to 2-cyanopyrazine was carried out in a fixed bed metal reactor in the temperature range of 320–460 °C using a series of metal vanadate-containing solids (MV) as catalysts. These solids named as $AlVO_4$, $FeVO_4$, $CrVO_4$, $NbVO_5$, $LaVO_4$ and $BiVO_4$ were prepared with a nominal V/M ratio = 1 always using the same synthesis procedure. Fresh and spent solids were characterized by X-ray diffraction, UV–vis DRS, XPS and pyridine-FTIR & ESR spectroscopy. The results revealed that the phase composition, near-surface-region behaviour and catalytic properties strongly depend on the nature of the metal used in MV solids. XRD showed the formation of crystalline MV phases in case of $LaVO_4$ and $BiVO_4$; whereas $FeVO_4$ and $CrVO_4$ exhibited poor crystallinity only. $AlVO_4$ sample revealed the clear formation of crystalline V_2O_5 whereas in $NbVO_5$ only a small proportion of V_2O_5 was detected. XPS depicted that the enrichment of vanadium in the near-surface-region is clearly dependent on the type of MV. It can be concluded that high near-surface-region V/M molar ratios promote the selectivity to cyanopyrazine but reduce the catalytic activity and vice versa. $NbVO_5$ showed the best catalytic performance compared to all other MVs. Almost 69% yield of 2-cyanopyrazine at total conversion could be successfully obtained.

1. Introduction

The ammoxidation of various alkanes, olefins and aromatics is an industrially important reaction for the production of different N-functionalized intermediates and final products, in particular the corresponding nitriles [1,2]. The heterogeneously catalyzed ammoxidation of various aromatics and hetero aromatics to such nitriles has been the subject of great interest in recent years due to their extensive applications in the syntheses of a variety of fine and specialty chemicals including dyestuffs, plastics, resins, pesticides, pharmaceuticals, etc. [2,3]. The ammoxidation of 2-methylpyrazine (MP) to 2-cyanopyrazine (CP), in particular, is of high commercial significance [4]. CP is an intermediate compound to synthesize pyrazinamide (PyA), an effective anti-tubercular drug [5]. About one third of the world's population is currently infected with *M. tuberculosis* (TB) and new infections occur at a rate of about one per second. Thus, the TB problem requires an urgent attention and there is a need to develop potential drugs like PyA in an effective manner.

The ammoxidation reaction is usually carried out using different heterogeneous catalysts systems [e.g. 1]. A large number of such catalytic systems have been developed. They mostly contain transition metal oxides; mainly vanadium-containing oxides are preferentially used as supported, bulk or multi-component catalysts for the ammoxidation of aromatic compounds. For example, the well known vanadium phosphorus oxide (VPO) catalysts that are normally used for the industrial manufacture of maleic anhydride from n-butane are also reported to be active and selective for different ammoxidation reactions [1,6,7]. These VPO solids are usually applied in their bulk form.

Literature survey reveals that a good number of papers have been published on the vapour phase ammoxidation of MP to CP using various supported and bulk catalysts [8–14]. Among the catalysts employed, the V–Ti oxide system was found to be widely used for this reaction. Bondareva et al. have carried out much research on V–Ti oxide catalysts for the synthesis of PyA or CP from MP by ammoxidation [9,10]. Heteropolyacids are another class of catalysts that are also applied for this reaction. However, the disadvantages of the latter solids are low thermal stability and possible water solubility and thereby leaching of active components during the course of the reaction, because water is an unavoidable by-product of the reaction [11,12]. In recent times, efforts were also made to use metal phosphate (e.g. $FePO_4$) based

* Corresponding author. Fax: +49 381 1281 51246.
E-mail address: andreas.martin@catalysis.de (A. Martin).

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http://dx.doi.org/10.1016/j.apcata.2012.07.029

catalysts for the ammoxidation of MP. However, the main drawback of these solids is a low conversion level of MP [13,14]. Another class of bulk catalysts for ammoxidation purpose are metal vanadate-containing solids (MV) which also have been used very recently for the ammoxidation of MP to CP [15,16]. However, certain bulk MVs are already used as catalysts in the oxidative dehydrogenation of lower alkanes [17,18] and for methanol oxidation [19,20]. Guerrero-Pérez et al. have proven that MVs, in particular the $SbVO_x$ system is a prospective catalyst for the production of acrylonitrile from propane by ammoxidation [21]. In addition, $SbVO_x$ phases also play an important role in the manufacture of active and selective industrial catalysts for ammoxidation of 3-picoline [e.g. 22]. Thus, the vanadium containing binary metal oxide systems (e.g. MVs) are creating keen interest in the oxidation and ammoxidation reactions and showing great concern from both industrial and academic points of view.

In view of this, the attention is paid by us on further developing highly active and selective catalytic systems for the ammoxidation of MP. Accordingly, we have applied the potential of MV catalysts (V/M molar ratio = 1) for the direct synthesis of CP. In this connection, we have focused in this work on a detailed characterization of fresh and spent catalyst samples by using various techniques to uncover properties mainly influencing the catalytic behaviour.

2. Experimental

2.1. Catalyst preparation

The preparation of several MVs was carried out under identical conditions to get comparable samples; it involves two steps (cf. [20]). The 1st step deals with the preparation of the metal solution. The requisite quantities (for a nominal molar ratio of V/M = 1) of appropriate metal nitrates (M = Al, Fe, Cr, La, Bi) and $NH_4NbO(C_2O_4)_2$ in case of niobium were dissolved in distilled water, to which a desired amount of citric acid (CA) was added (molar ratio of M/CA = 3). Then the mixture was stirred at room temperature (r.t.) until a clear solution is obtained. The 2nd step involves the preparation of the vanadium solution using NH_4VO_3 (AMV) as a precursor. The required amount of AMV was taken in distilled water and a suitable amount of oxalic acid (OA) was added to it (molar ratio of OA/AMV = 1.5). The above solution was then heated to 60 °C under stirring and kept at the same temperature for 10 min. This solution was added drop wise to the metal-citric acid solution at 60 °C with constant stirring. After complete addition, the mixture was heated to 80 °C and then slowly evaporated to dryness on a hot plate. The solids thus obtained were further dried at 110 °C for 16 h in an oven and calcined in air (4 l/h) at 500–600 °C for 4–48 h. They are named as $AlVO_4$, $FeVO_4$, $CrVO_4$, $NbVO_5$, $LaVO_4$ and $BiVO_4$. The information on the type of metal precursors used, calcination conditions applied and elemental analysis (ICP values) are presented in Table 1. More details on the catalyst preparation are described elsewhere [16]. The elemental analysis (ICP-OES) showed the expected V/M ratio, only in the case of Nb the V content was slightly increased, which could be related to the use of oxalate instead of nitrate salt.

2.2. Catalysts characterization

The X-ray diffraction (XRD) patterns were obtained on a X-ray diffractometer STADIP (Stoe) using Ni-filtered CuK_α radiation (λ = 1.5418 Å). The crystalline phases were identified by referring to the database ICDD. Crystallite sizes were calculated using the Scherrer equation (mean error range is ±10%).

The surface areas (BET) and pore size distribution of the catalysts were determined on NOVA 4200e (Quantachrome) instrument by N_2-physisorption at −196 °C. Prior to the measurements, the sample (~200 mg) was evacuated for 2 h at 200 °C to remove physically adsorbed water.

FTIR measurements in transmission using pyridine as probe molecule for acidity characterization were carried out on a Bruker Tensor 27 spectrometer using self-supporting wafers (d = 20 mm, wt. = 50 mg). A heatable homemade reaction cell with CaF_2 windows was used. Before pyridine adsorption, the samples were pretreated in synthetic air (400 °C, 30 min), cooled down to room temperature and then, pyridine was adsorbed until saturation. The physisorbed pyridine was removed by flushing with He and then, the infrared spectra were recorded.

UV–vis DR spectra were recorded on an Avaspec-2048 (Avantes) fiber optical instrument using a reflectance probe. For recording the baseline, $BaSO_4$ (spectroscopic grade) was used as a reference material.

The X-ray photoelectron spectroscopic (XPS) measurements were done with a VG ESCALAB 220iXL (Thermo Scientific) unit using MgK_α radiation (E = 1253.6 eV) at 10^{-7} Pa. The C 1s binding energy of 284.6 eV was used as a reference for determining the binding energies.

Electron spin resonance (ESR) spectra were recorded in X-band ($\nu \approx 9.5$ GHz) with a cw-spectrometer ELEXSYS 500-10/12 (Bruker) using microwave power of 6.3 mW at r.t. and also at −196 °C. The modulation frequency was 100 kHz and the modulation amplitude was 0.5 mT. The magnetic field was measured with respect to the standard 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH).

2.3. Catalytic tests

The catalytic tests were carried out in a top-down flow, fixed bed stainless steel reactor (i.d. = 9.4 mm, l = 250 mm) in vapour phase at atmospheric pressure. In a typical experiment, 1 g of the pressed and grinded catalyst (0.5–0.8 mm size) diluted with equal amount of corundum with the same size were loaded in the reactor. The diluted catalyst was placed between two quartz wool plugs in the middle of the reactor. Also the upper and lower portions of the catalyst bed were filled with corundum. The liquid feed of MP and H_2O mixture (molar ratio of H_2O/MP = 13) was metered using a HPLC pump and was vaporized in a preheating zone. Air, NH_3 and N_2 (for dilution) supplied were commercially available gases from

Table 1
Calcination conditions, types of precursors used and V/M ratios of various MV catalysts.

Sample	Calcination	Metal precursor	Composition V/M ratio (mole)		
			Nominal	Calcined[a]	Used[*]
$AlVO_4$	600 °C/48 h	$Al(NO_3)_3{\cdot}9\,H_2O$	1.0	1.03	1.06
$FeVO_4$	550 °C/4 h	$Fe(NO_3)_3{\cdot}9\,H_2O$	1.0	0.94	1.04
$CrVO_4$	550 °C/4 h	$Cr(NO_3)_3{\cdot}9\,H_2O$	1.0	1.14	1.21
$NbVO_5$	500 °C/12 h	$NH_4NbO(C_2O_4)_2{\cdot}$ x H_2O	1.0	1.51	1.49
$LaVO_4$	600 °C/15 h	$La(NO_3)_3{\cdot}6\,H_2O$	1.0	1.06	1.03
$BiVO_4$	500 °C/5 h	$Bi(NO_3)_3{\cdot}6\,H_2O$	1.0	0.92	1.02

[a] Determined from ICP-OES analysis.