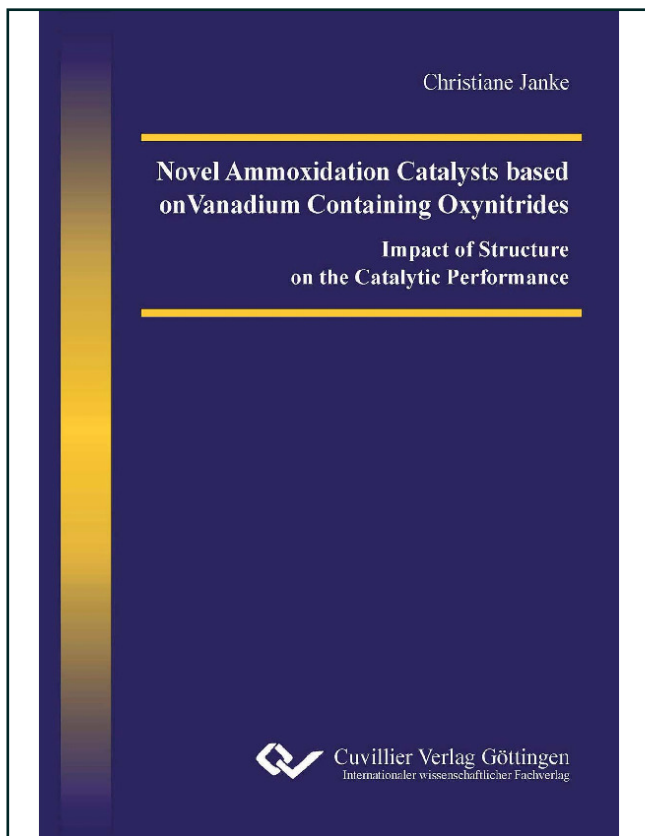




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**Novel Ammoxidation Catalysts based on Vanadium  
Containing Oxynitrides**

Impact of Structure on the Catalytic Performance



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# 1. Introduction and Objectives

Aliphatic, aromatic and heteroaromatic nitriles are important intermediates for producing pharmaceuticals, agricultural pesticides, dyestuffs and textiles.

One economically and ecologically efficient route to synthesize a variety of different nitriles is the ammoxidation of aliphatic or methyl-substituted aromatic and heteroaromatic hydrocarbons in the presence of ammonia and air in the gas phase using suitable solid catalysts. This reaction would be most sustainable, energy-efficient and eco-friendly if it was possible to achieve a nitrile selectivity of 100 % and high space-time yields (STY).

Up to now, this goal is not yet reached. Although conventional catalysts based on mixed oxides of transition metals provide high selectivities at fairly high conversion for selected nitriles such as benzonitrile and 3-cyanopyridine [1], the STY bear still enough potential for improvement.

In the late 1990s, a new class of vanadium oxynitrides (VAION) has been discovered, which however, was only used for ammoxidation of propane to acrylonitrile [2, 3]. Although the nitrile selectivity was somewhat lower compared to MoVTeNbO usually used for this reaction, 5 - 10 times higher STY have been reached with the new VAION catalysts [4–6].

During my preceding diploma work, VAION and VZrON oxynitrides were very successfully tested for the ammoxidation of 3-picoline (3-PIC) to 3-cyanopyridine (3-CP) [7]. The obtained STY exceeded the state of the art by a factor of three [8], though at slightly lower selectivity according to [1]. These promising results inspired us to perform a more comprehensive exploration of V containing oxynitrides for ammoxidation of aromatic hydrocarbons.

It is the aim of this work to elucidate structure-reactivity relationships of vanadium containing oxynitrides in the ammoxidation of 3-PIC to 3-CP, which has been chosen as a model reaction by an integrated approach of catalytic test and characterization studies including in situ spectroscopy. The ultimate goal was to optimize the catalytic performance towards high selectivity and STY.

To this end, the following sub-tasks have been considered in the thesis:

- Development of novel VZrAlON catalysts by combination of the most active (VZrON) and selective (VAION) catalysts,



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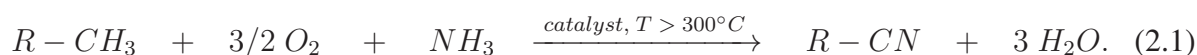
- Investigation of the influence of incorporation of phosphorus into VZrON catalysts,
- Examination of the influence of mixing VMON and  $\text{Mo}_x\text{O}_y\text{N}_z$  catalysts (M = Al or Zr),
- Evaluation of the impact of redox-active M in VMON catalysts (M = Mo or Sb).



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## 2. State of the Art

**The ammoxidation** belongs to the class of heterogeneous catalytic gas phase reactions and has been investigated for more than 60 years [9, 10]. In presence of ammonia, air and a suitable catalyst alkanes and alkenes as well as methyl-substituted aromatics and heteroaromatics R-CH<sub>3</sub> are transferred into nitriles at temperatures higher than 300 °C. The ammoxidation can be regarded as oxidative ammonolysis. Besides the desired nitrile only water is produced as by-product at 100 % selectivity according to the reaction:



Conventional catalysts contain supported or unsupported redox active transition metals such as V, Mo, or Cr as key components in the form of pure oxides [11–14], oxyfluorides [15–17] or phosphor containing oxides [18–22].

In Table B.3 a short overview is given on some heteroaromatic ammoxidation reactions to clarify the still persistent research interest in this kind of reaction. In particular, active and selective catalysts for the ammoxidation of dimethoxytoluene to dimethoxybenzotrile are still missing up to now. In addition, the synthesis of aliphatic dinitriles such as adiponitrile via ammoxidation is of great interest. Processes starting from cyclohexane, cyclohexene or methylcyclohexane are reported, but conversions and selectivities did not exceed 40 % [23–25].

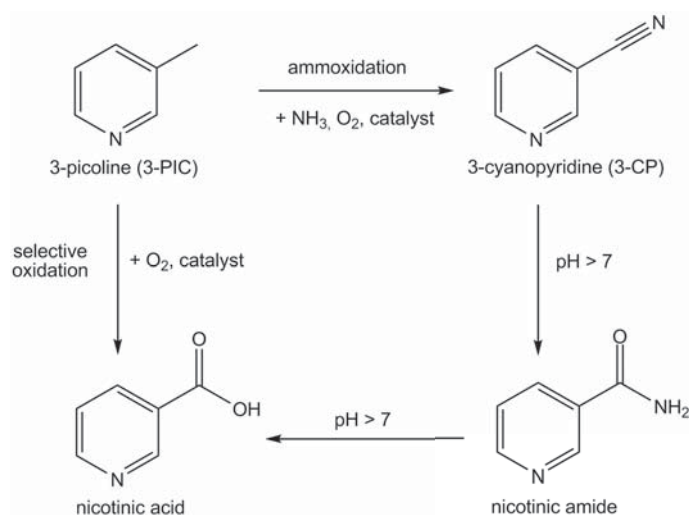
On the contrary, a story of success possesses the oxidative ammonolysis of propene to acrylonitrile, which was the first industrially implemented and commercialized ammoxidation technology [26, 27]. From the late 1950s still up to now, the worldwide demand on polyacrylonitrile fibers is almost covered by the production of acrylonitrile via this process [11], but an efficient alternative route for producing acrylonitrile is needed due to e.g. the advancing scarcity of propene [28]. One promising route seems to be the ammoxidation of propane to acrylonitrile. However, the development of functional, highly active and selective catalysts for activation of an alkane is experimentally challenging due to its higher activation energy [29–31].

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One active class of catalysts for this reaction is the oxynitride VAION [2, 3]. Propane conversions around 60-80 % and selectivities to acrylonitrile about 50 - 65 % are reported at high space velocities (GHSV). Although the nitrile selectivity was somewhat lower compared to MoVTenbO, higher STY (up to 10 times) have been reached with the new VAION catalysts [4–6, 32].

Recently, it was found that VAION and VZrON oxynitrides also bear a high activity and STY in the ammoxidation of heteroaromatics, e.g. 3-picoline (3-PIC) to 3-cyanopyridine (3-CP) [7, 8]. However, the latter ammoxidation was already industrialized in 1983 by Degussa [33]. A vanadium containing long-term stable catalyst with the general formula  $Sb_aV_bTi_cX_d$  supported on  $SiO_2$  ( $X =$  alkali metal) is used. A selectivity to 3-CP ( $S_{3-CP}$ ) of 95.8 % at nearly full conversion of 3-PIC ( $X_{PIC}$ ) is obtained at 370 °C with a maximum STY of 156 g/lh [1, 34].

In contrast to acrylonitrile being a bulk chemical 3-CP belongs to fine chemicals. The latter compound is used as intermediate to produce nicotinic acid and amide by hydrolysis (see Fig. 2.1). 14 000 ton of nicotinic acid and 8000 ton of the related nicotinic amide were globally manufactured in 1995 [35]. In 2006 the worldwide production of both increased to about 35 000 to 40 000 ton [18]. Up to now, the direct oxidation of 3-PIC to nicotinic acid in the gas phase is not established (see Fig. 2.1) since sufficient catalysts are missing and side-reactions like decarboxylation are occurring. Also, the low sublimation temperature of nicotinic acid may be a problem in implementation of an industrial process [35].



**Figure 2.1.:** Heterogeneous catalytic gas phase routes to nicotinic acid starting from 3-PIC [35]

Nicotinic acid and its derivatives are needed in different fields. Most notably, nicotinic acid is applied as additive. In animal nutrition it is supposed to improve the natural capability of productive livestock, and it is also added to beverage, food and cosmetic products. Humans can not produce nicotinic acid (vitamin B<sub>3</sub>) and amide on its own; and the importance of nicotinic



acid ingestion was not recognized until 2nd decade in 1900. Thitherto, many humans suffered from the disease called pellagra due to an insufficient ingestion of vitamin B<sub>3</sub>, resulting mostly from undernourishment. However, nowadays this disease is still not extinct [36,37].

**The mechanism of heteroaromatic ammoxidation** over oxide catalysts has been investigated for several years, starting with the early work of Andersson et al. [38], while no such studies are available for oxynitrides.

For oxide catalysts it has been proposed that the ammoxidation starts with adsorption of the aromatic ring followed by hydrogen abstraction from the alkyl group, formation of a benzyl-like intermediate and in situ generation of an -OH group that converts gaseous NH<sub>3</sub> to NH<sub>4</sub><sup>+</sup> by proton transfer. In due course, it was suggested that NH<sub>4</sub><sup>+</sup> is supposed to react with the benzyl-like intermediate to a benzylamine species, which is transformed to the nitrile and desorbs from the surface of the catalyst. A Mars-van Krevelen mechanism proceeds during this reaction including participation of lattice oxygen [39–45]. Also, imido =NH or amido -NH<sub>2</sub> species on the catalyst surface are considered as active N-insertion species, however their role in the aromatic ammoxidation is still not fully elucidated [41,46,47].

From extensive studies of toluene ammoxidation over phosphor and vanadium containing oxide catalysts it was proposed that highly active and selective catalysts must fulfill four crucial features: i) They should provide chain- or layer-like surface vandyl units; ii) These units should be located at a proper distance to enable adsorption of the aromatic ring and reaction of the methyl group at the neighboring site, iii) The mean surface V valence state should be close to +4 and iv) the catalyst must be able to incorporate NH<sub>3</sub> from the gas phase [40].

The activation of NH<sub>3</sub> from the gas feed via transient incorporation into the catalyst lattice during toluene ammoxidation has been evidenced by isotopic labeling experiments using the Temporal-Analysis-of-Products (TAP) reactor and <sup>15</sup>NH<sub>3</sub> as gaseous feed component [48]. For VAION catalysts, TAP experiments with labeled <sup>15</sup>NH<sub>3</sub> in the ammoxidation of propane have shown, too, that N insertion into hydrocarbons occurs via surface N sites [49]. Thus, the insertion of N as well as O via a double Mars-van Krevelen mechanism is considered to be responsible for their high catalytic performance in the ammoxidation of propane. The structure-reactivity relationship proposed for ammoxidation of 3-PIC to 3-CP over VZrON and VAION catalysts also confirms that such N insertion process is of great importance in the ammoxidation of 3-PIC [8]. This structure-reactivity relationship is described in-depth later on.

In general, transition metal oxide catalysts are only capable of catalyzing selective oxidation reaction via a Mars-van Krevelen redox cycle if oxygen anions of the lattice are highly mobile



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and migrate. Thus, a well-directed incorporation of anionic defects and vacancies (point defects as well as 2-D and 3-D defects) in transition metal oxides might not only support electron migration and therefore influence the redox-activity of the transition metal site but also support the migration of O and N containing species.

Moreover, it was considered that the surface acidity of V containing catalysts has a crucial impact on the catalytic performance in the partial oxidation of heteroaromatics [50]. This is also true for the ammoxidation of heteroaromatics since a benzyl-like intermediate is formed. Different strategies are known to influence the surface acidity and basicity of a solid material. One common way is to dope oxide compounds with basic ions such as  $\text{Na}^+$  or  $\text{K}^+$  [51, 52]. A second strategy is based on the idea to modify the anionic lattice via introduction of anions such as fluoride [53] or nitride [54–56].

**Metal nitrides and oxynitrides** are accessible via nitridation of the corresponding metal oxide precursor [57, 58]. This reaction in pure ammonia implies the substitution of three oxygen anions by two nitride anions leaving one vacancy in the anionic lattice according to the following equation:



A high flow of ammonia is generally used to remove the water from the equilibrium and adjust the balance state to the right side of the reaction. In principle, the nitridation of metal oxide precursors might be an excellent route to synthesize effective ammoxidation catalysts since this reaction introduces anionic defects and nitrogen containing sites such as  $\text{N}^{3-}$  into the catalyst, modifies the surface acidity and reduces the valence state of redox-active metal sites.

Moreover, nitrides and oxynitrides are promising materials in various fields of applications due to their outstanding physical and chemical properties [58]. Compared to oxides, metal nitrides possess superior physical properties such as hardness, mechanical and tensile strength and high melting points. In addition, they provide electronic and magnetic properties resembling those of metals, such as electronic conductivity, Hall coefficient, magnetic susceptibility and heat capacity [59]. Their extreme hardness and excellent corrosion resistance make them suitable as cutting tools and hard coatings [60–62]. Among nitrides and oxynitrides also non-metal compounds such as phosphorus nitride and carbon nitrides  $\text{CN}_x$  have attracted considerable attention. L. Chen et al. [63] succeed the synthesis of amorphous  $\text{P}_3\text{N}_5$  hollow spheres, which might have a great potential for encapsulation and delivery in drugs.  $\text{CN}_x$  coatings are used in

thin film-Schottky-solar cells and computer hard discs of IBM, as layers in humidity sensors and electrochemical gas detectors [64].

As already indicated, transition metal nitrides and oxynitrides have also received considerable attention in the field of heterogeneous catalysis. In ammonia synthesis [65, 66], Fischer-Tropsch [67], hydrodenitrogenation [68, 69], hydrodesulfurization [70] and ammoxidation [4–6], they are proved to be active, and in some cases they possess superior selectivity, stability and resistance to poisoning. For example, the decomposition of hydrazine being traditionally catalyzed over iridium supported on alumina, is also efficiently catalyzed over  $\text{MoN}_x\text{O}_y$  catalysts [71]. Nitrides and oxynitrides are proved to be active in photo catalytic water splitting to hydrogen, too [72, 73].

**Structure-reactivity relationship of VAION and VZrON in the ammoxidation of 3-PIC** VAION and VZrON catalysts synthesized via co-precipitation and nitridation were proved to be active in the ammoxidation of 3-PIC to 3-CP [7, 8]. Results for the catalytic testings showed that the catalytic performance of these two systems differ significantly. VAION catalysts are less active, but more selective than VZrON catalysts. A maximum STY of 399 g/lh was reached using VZrON catalysts with a ratio of V/Zr = 0.25. In comparison to the benchmark catalyst with the general formula  $\text{Sb}_a\text{V}_b\text{Ti}_c\text{X}_d/\text{SiO}_2$  ( $\text{X} = \text{K}^+$ ) STY could be triplicated using VZrON oxynitrides. Both catalyst classes, VZrON and VAION, suffer from a lower selectivity compared to the latter benchmark catalyst.

By a multitude of ex situ characterization techniques such as XPS and UV/Vis-DRS and in situ EPR spectroscopy, it was possible to elucidate the structural differences in these two catalyst classes under working state and to build up structure-reactivity relationship.

In contrast to VAION catalysts, VZrON oxynitrides are characterized by a higher polymerisation degree of  $\text{VO}^{2+}$  sites indicated by results derived from EPR spectroscopy, UV/Vis-DRS and XPS. The chemical composition calculated from XPS suggested a surface enrichment of V for VZrON, but not for VAION. Additionally a higher mean oxidation state of V was observed for VZrON, which was close to  $\text{V}^{5+}$ . In contrast, two different V sites could be detected by XPS for VAION catalyst. Both V sites in VAION differ in their mean V oxidation state, one V valence close to +3 and the second close to +4. Additionally, only for VAION with  $\text{V}/\text{Al} \geq 0.25$  a nitrogen site with a binding energy being typical for  $\text{N}^{3-}$  could be detected by XPS. As opposed to this, the near surface region of VZrON catalyst was N-free.

Moreover in situ EPR investigations on VZrON and VAION suggested that the latter catalyst can provide a significant higher amount of  $\text{VO}^{2+}$  under reaction conditions. In combination with





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results derived from UV/Vis-DRS and XPS, it was concluded, that the main amount of V in VZrON catalysts must be present as  $V^{5+}$  and not as  $V^{3+}$  or  $V^{4+}$  under reaction conditions.

**Development of strategies** Based on the knowledge gained from the structure-reactivity relationship of VAION and VZrON different strategies were followed to improve the selectivity and to increase the conversion and STY in the ammoxidation of 3-PIC.

Firstly, three different routes were investigated to generate N containing surface sites in highly active VZrON catalysts to improve the selectivity of this catalyst class without losing the activity:

- Since for VAION catalysts nitride sites could be detected on the surface, it was assumed that adding Al in VZrON might help to stabilize surface nitrogen species. For this reason, VZrAlON catalysts were synthesized by simultaneous co-precipitation of V, Al and Zr.
- VPO catalysts are well known for their superior catalytic performance in the ammoxidation of heteroaromatics [18–22]. Moreover, it is well known from literature, that ZrPON oxynitrides possess a variety of nitrogen surface sites in contrast to VZrON catalysts [55, 74]. For these reasons the impact of adding phosphor into VZrON was investigated.
- Different types of molybdenum nitrides are known. VMO (M = Al or Zr) precursors mechanically mixed with  $MoO_3$  were nitrated by a defined nitridation protocol described in literature to form molybdenum nitrides besides VZrON and VAION, respectively [75–77]. With the help of this route a defined amount of nitride site was supposed to be introduced into VMON catalysts.

Secondly, it was additionally focused on novel VMON oxynitrides. Since active ammoxidation catalysts contain beside V as redox-active site also Sb [34, 78], it was decided to elucidate the potential of VSbON catalysts in the ammoxidation of 3-PIC. Finally, the two redox-active metal sites, V and Mo, were combined via an aqueous route to investigate the impact of VMoON catalysts in the ammoxidation of heteroaromatics.