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# Ammoxidation and oxidation of substituted methyl aromatics on vanadium-containing catalysts

Andreas Martin [*], Bernhard Lücke

*Institut für Angewandte Chemie Berlin-Adlershof e.V., Richard-Willstätter-Str. 12, D-12489 Berlin, Germany*

## Abstract

An overview of the state of the art and future trends in vapour phase oxidation and ammoxidation of substituted methyl aromatics and heteroaromatics is presented. The topics mainly contain the conversion of methoxytoluenes, chlorotoluenes and methylpyridines to the corresponding aldehydes and nitriles by vapour phase reaction using V-containing catalysts. Steric and electronic effects of various substituents in combination with acid–base properties of catalyst surfaces on the catalytic performance are discussed; common features and differences in mechanistic steps are demonstrated. The optimum catalyst composition for vapour phase partial oxidation to aldehydes is quite different from that for vapour phase partial ammoxidation to nitriles. ©2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Oxidation; Ammoxidation; Vanadium-containing catalysts; Substituted methyl aromatics; Methyl heteroaromatics; Nitriles; Aldehydes

## 1. Introduction

The selective oxidation of aromatic hydrocarbons both in liquid and vapour phase represents an important class of catalytic reactions and was developed into large scale operations for the production of commodities in the chemical industry [1,2]. Two classes of oxidations of aromatic compounds can be distinguished: (i) the side chain oxidation of alkyl (methyl) aromatics which yields aldehydes, acids or anhydrides without affecting the aromatic nucleus (nucleophilic type oxidation) and (ii) more severe oxidations to synthesise anhydrides or quinones, processing via an oxidative attack on the aromatic ring (electrophilic type oxidation).

First commercial oxidations of aromatics based on vapour phase processes started in the first decades of this century (e.g., phthalic anhydride production by oxidation of naphthalene over vanadium oxide catalysts in 1917). This exemplary reaction is attributed to electrophilic type oxidations whereas the more efficient conversion of *o*-xylene to phthalic anhydride in the vapour phase belongs to the first reaction type [2]. Another aromatic bulk oxygenate, benzoic acid, is produced by a very selective liquid phase side-chain oxidation of toluene (e.g., Amoco process [3]).

The selective production of aromatic aldehydes in vapour phase processes is much more complicated because the aldehydes themselves are consecutively oxidised very fast to acids and deeper oxidised products (e.g., quinones). For example, benzaldehyde is produced in the vapour phase at low toluene conversions (10–20%) per pass at short residence time ($<1$ s); even then, it is only 40–60% of the theoretical yield [4]. This is the main reason why benzaldehyde and various sub-

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[*] Corresponding author. Tel.: +49-30-63924306; fax: +49-30-63924350.
*E-mail address:* a.martin@aca.berlin.de (A. Martin).

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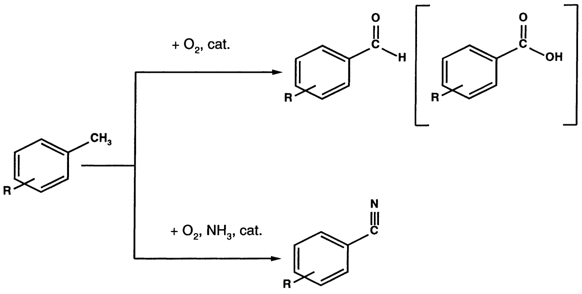
stituted aromatic aldehydes are rather manufactured in liquid phase oxidation processes or by the hydrolysis of benzal chlorides [4] continued to the present.

On the other hand, the vapour phase ammoxidation of aromatic side chains is a very similar process of nucleophilic type oxidations and the most simple and economically most profitable route for the production of aromatic nitriles. This reaction refers to the interaction of ammonia with a reducible organic material (alkanes, alkenes, alkyl aromatic and heteroaromatic compounds) in the presence of oxygen. Especially, the ammoxidation of alkyl aromatics (toluene, isomeric xylenes) to mononitriles (benzonitrile, tolunitriles) and various dinitriles (*o*-phthalodinitrile, iso- and terephthalodinitrile) is intensively studied and applied in the manufacture of bulk chemicals [5]. First communications on this reaction appeared in the 1940s and 1950s. Beside the production of benzonitrile from toluene and dinitriles from xylenes various substituted methyl aromatics as well as heteroaromatics were used as feedstock in such reactions [5–7].



Substituted aromatic nitriles as well as aldehydes are of widespread use in fine chemical production. They can be converted to commercially interesting and valuable intermediates for the synthesis of several pharmaceuticals and dyestuffs as well as pesticides and final products of these lines.

Coming back to the distinguishing feature of catalytic oxidations, i.e., nucleophilic or electrophilic type of oxidation, the nucleophilic oxidation reaction proceeds with the co-operation of lattice oxide ions $O^{2-}$. Such lattice species have no oxidising properties and they does not attack π bonds of hydrocarbon molecules as known from electrophilic oxygen species ($O_2$, $O_2{}^{-}$ and $O^{-}$). Lattice oxide ions $O^{2-}$ act as nucleophilic reactants and can be inserted into activated hydrocarbons (e.g., allyl or benzyl species [1] generated by the co-operation of Me=O oxo groups) to form oxygenates. Consequently, the oxide catalyst is reduced and in a separate step the catalyst lattice is reoxidised by vapour phase oxygen. A mechanistic cycle of this type was suggested by Mars and van Krevelen in the 1950s [8] studying the oxidation of aromatics on $V_2O_5$ catalysts. Up to now, V-containing catalysts are of prime importance in the oxidation as well as ammoxidation of light paraffins, olefins and aromatics as also shown recently by Grasselli [9] in a review on advances and future trends in selective oxidation and ammoxidation catalysis, concerning commodities and fine chemicals.

This review gives a survey on the progress of the last decade in the synthesis of fine chemicals by vapour phase oxidation processes for the production of aromatic and heteroaromatic aldehydes and nitriles, respectively.

## 2. Discussion

### 2.1. Oxidation of substituted methyl aromatics and heteroaromatics to aldehydes

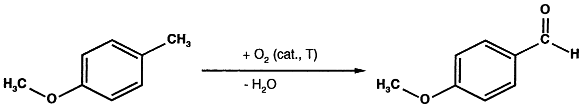
Liquid phase oxidations of methyl aromatics are well established processes in industry. Nevertheless, the synthesis of substituted benzaldehydes is carried out in traditional way of the organic chemistry, e.g., by the above mentioned hydrolysis of substituted benzal chlorides [4]. Additionally, other routes to synthesise the corresponding aldehydes became known; e.g., the indirect oxidation of substituted methyl aromatics by electrochemical means using Co, Mn or Ce redox couples in the presence of a suitable solvent [10,11]. However, these processes produce many waste causing environmental problems and, additionally, the efficiencies of these routes are not so high.

Some work has been done in the last decade to find promising catalyst compositions for the oxidation of toluene in the vapour phase and to increase the benzaldehyde selectivity; e.g., the use of $V_2O_5$–$K_2SO_4$ catalysts [12,13], the synthesis and application of novel ultrafine complex Mo-based oxide particles [14] and new $V_2O_5$–$TiO_2$ oxide phases doped with Te or $K_2SO_4$ [15] as well as the application of V-containing micro- and mesoporous materials [16] and Fe–Mo substituted deboronated borosilicates [17]. A similar future trend will begin to emerge in the partial oxidation of substituted toluenes. Some efforts were already made in the past to develop the vapour phase route using vanadium oxide-containing catalysts. Simultaneously, the application of extensive catalyst characterisations using various in situ methods (FTIR, ESR) reveal a deeper insight in reactant–catalyst interaction [18–21] that may help to improve catalytic performance.

Some selected examples should prove the progress; the synthesis of 4-methoxybenzaldehyde and 4-chlorobenzaldehyde play an outstanding role.

### *2.1.1. Synthesis of methoxybenzaldehydes*

Beside various attempts on the heterogenisation of the partial oxidation of toluene to benzaldehyde, reports on the oxidation of substituted methyl aromatics to their aldehydes in the vapour phase are rather rare but appearing since ca. 25 years. First results of intensive efforts on the vapour phase oxidation of 4-methoxytoluene (4-MeOT) to 4-methoxybenzaldehyde (4-MeOBA) were published in the 1970s by Japanese researchers of Tanabe Seiyaku Co. ([22,23], see Eq. (1)).



(1)

4-MeOBA is an important chemical intermediate in the production of cosmetics and pharmaceuticals. The authors used V–P–Cu–O catalysts doped with potassium sulphate and gave 4-MeOBA yields up to ca. 70 wt.%. The commercialisation of this reaction by Nippon Shokubai and Kagaku Kogyo using an alkali metal-containing vanadium catalysts was recently reported [24].

In between, mainly Japanese groups reported on the role of acid and base properties of vanadium oxide catalysts, containing base metal oxides (M = K, Rb, Cs, Tl, Ag) for partial oxidation of 4-MeOT and other substituted toluenes [25–27]. The most effective base metal oxide studied was the rather hazardous $Tl_2O$. In general, they stated that the selectivity to substituted benzaldehydes is closely related to the basic properties of the catalyst whereas the activity strongly depends on the amount and strength of acid sites.

This finding matches the results of own studies on the oxidation of toluene to benzaldehyde on the rather acidic $(VO)_2P_2O_7$ [20]. This solid generates under working conditions a large proportion of surface OH groups by hydrolysis of V–O–V and/or V–O–P bonds. These OH groups (Brønsted sites) are responsible for a strengthening of the chemisorptive interaction of the formed aldehyde and the catalyst surface in addition to the molecule sorption by co-ordinatively unsaturated sites (Lewis sites); the reason is the generation of hydrogen bonding between the formed carbonyl group of the aldehyde species and neighboured OH groups [21]. This action could be proven by the admixture of pyridine to the feed that preferentially blocks the acid OH groups; the result is a threefold increase of benzaldehyde selectivity at nearly the same conversion rate [21], i.e., the Lewis sites are not significantly affected. In the same direction, the addition of alkali metal salts to vanadium catalysts [13] makes the desorption of the desired products easier and, additionally, alkali cations block Brønsted acid sites.

Recently, Reddy et al. [28,29] proposed the application of base supports for vanadium oxide used in the above mentioned reaction; but the use of $V_2O_5$ on CaO–MgO supports results in rather poor 4-MeOBA yields of ca. 10–15%. 4-Methoxybenzoic acid was always formed as deeper oxidation product in equal selectivities. The authors noticed that both acid–base properties coupled with the redox function are essential for good conversion and high aldehyde selectivity. Furthermore, Reddy et al. [30,31] reported on the use of $V_2O_5$ supported on binary oxides (e.g., $Ga_2O_3$–$TiO_2$; 1:5) that interestingly reveals high 4-MeOBA yields of ca. 70%.

Table 1 gives a short summary on used catalyst compositions published and key dates of catalytic tests.

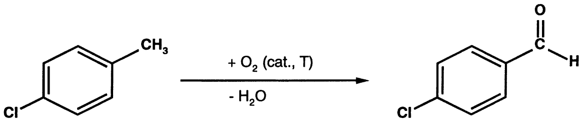
### *2.1.2. Synthesis of chlorobenzaldehydes*

Apart from the synthesis of 4-MeOBA the heterogeneously catalysed formation of 4-chlorobenzaldehyde (4-ClBA) from 4-chlorotoluene (4-ClT) received a

Table 1
Partial oxidation of 4-methoxytoluene (4-MeOT) to 4-methoxybenzaldehyde (4-MeOBA) on vanadium oxide-containing catalysts

| Catalyst | *T* (K) | Conversion (%) (4-MeOT) | Yield (%) (4-MeOBA) | Reference |
|---|---|---|---|---|
| VPO–CuO–$K_2SO_4$ | 733–768 | | ≤72.5 | [22] |
| VPO–CuO–$K_2SO_4$ | 725 | 75 | 48 | [23] |
| $V_2O_5$–$Tl_2O$ | 703 | 83 | 63 | [25,26] |
| $V_2O_5$–CaO–MgO | 673 | 30 | 16 | [28] |
| $V_2O_5$–$Ga_2O_3$–$TiO_2$ | 673 | 72 | 65 | [30] |

similar attention (Eq. (2)), however, reports on such work are very limited in the literature.



(2)

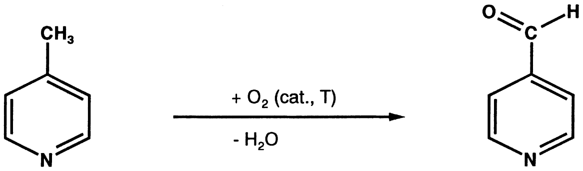
The early investigations of Chopra and Ramakrishna [32] on the partial oxidation of the chlorotoluene isomers on Bi–Mo–O catalysts yields in amazing high selectivities up to 88% for 4-ClBA at 93% conversion of 4-ClT at 723 K. However, these high yields could never be reproduced. A recent patent application by Hoechst AG [33] picked up this reaction again. The authors applied catalyst compositions, mainly consisting of V–Cs–Fe–O doped with various transition metals. The catalyst composition also reflects the combination of acid, base and redox functions. The reaction was carried out at ca. 673–773 K and in dependence on the reaction conditions the 4-ClT conversion reaches values up to 68% but the 4-ClBA yield does not markedly exceed ca. 20%.

In contrast to the ammoxidation of the mentioned compounds to the corresponding nitriles (the nitrile group formed during the ammoxidation reaction reveals a strong electron-withdrawing effect) as shown later it seems likely that the rather electron-withdrawing effect of the halogen substituent prevents high product selectivities at high conversion in contrast to electron-donating substituents like methoxy or phenoxy groups. Similar suggestions were also reported by Ueshima et al. [26,27]. They compared their results of aldehyde formation using different alkyl toluenes and 4-MeOT with a correlation between the ionisation potential of the reactant and its reactivity in vapour phase oxidation according to Dadyburjor et al. [34]. From these studies, it is supposed that the rate determining step is the electron transfer from the reactant molecule to the sorption site (Lewis site), i.e., molecules with electron-donating groups are best suited [26]. Otherwise, a quick desorption of the formed aldehyde seems to be essential and should improve the product selectivity but a too strong chemisorption of the reactant as well as the partial oxygenated intermediate may promote a deeper oxidation.

The main reason for such behaviour might be on the one hand for partial oxidation the demand on a basic catalyst surface as far as possible to accelerate desired product desorption and to block acid sites beside the needed presence of acidic Lewis sites for reactant sorption (the more basic methoxytoluene is better suited then the less basic chlorotoluene) whereas on the other hand in the case of the later discussed ammoxidation a more acidic catalyst surface is needed to chemisorb sufficiently ammonia as ammonium ions and to desorb the more acidic nitrile easier the less basic chlorotoluenes are more favoured in comparison to the more basic methoxytoluenes.

### 2.1.3. Synthesis of pyridinecarbaldehydes

Beside the above mentioned examples of the partial oxidation of toluene derivatives also little is known on the conversion of methyl heteroaromatics to their aldehydes. The synthesis of pyridine-4-carbaldehyde (4-PyA) by vapour phase oxidation of 4-methylpyridine (4-MPy, see Eq. (3)) was investigated in our group [35].

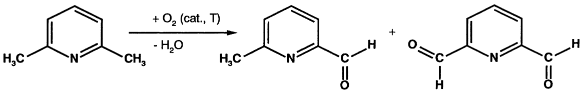


(3)

We have used $(VO)_2P_2O_7$ as catalyst and a maximum 4-PyA selectivity of ca. 55% was reached at a 4-MPy conversion of about 80 mol% (ca. 690 K). Mainly pyridine was analysed as by-product that is stable under the oxidative reaction conditions. Pyridine and 4-MPy are also able to block acidic OH groups being generated during the reaction. This blockade accelerates the aldehyde desorption; additionally, the co-operation of the nitrogen single electron pair during chemisorption could be responsible for changed sorption mechanism as shown later.

Kulkarni et al. [36,37] reported on results obtained by using V-containing AlPO and SAPO molecular sieves at 673–693 K. 4-PyA selectivities up to ca. 70% were obtained at a nearly complete 4-MPy conversion. Another vapour phase synthesis of a heterocyclic aldehyde was carried out by Prasad and Subrahmanyam [38] by using a V–Mo–O catalyst. The authors reported on the conversion of 3-hydroxy-4-methylpyridine to 3-hydroxy-4-pyridinecarbaldehyde at 673 K with 35 mol% conversion and 75% aldehyde selectivity. The relating acid was the main by-product.

Recently, the vapour phase oxidation of 2,6-dimethylpyridine was reported by Abele et al. [39,40]. Supported V–Mo–O catalysts, containing various promotors were used. The main partial oxidation products always formed were 2,6-pyridinedicarbaldehyde and the corresponding mono aldehyde (6-methyl-2-pyridine- carbaldehyde, see Eq. (4)). On catalysts promoted with silver oxide or bismuth oxide both aldehydes were synthesised in equal amounts. Best results were obtained at ca. 673 K with ca. 65% total selectivity of both aldehydes (the yield of both aldehydes depends on the reaction conditions and the two values are in a ratio of 1:2 to 2:1) at approx. 95% conversion. The influence of the V(IV) content and the surface acidity on the aldehyde formation were discussed.



(4)

Alkaeva et al. [41] carried out the vapour phase oxidation of 3-methylpyridine on binary V–Ti–O catalysts being known as rather stronger oxidation catalysts. Consequently, the main product obtained was nicotinic acid and the corresponding aldehyde was formed only in minor proportions.

## 2.2. Ammoxidation of substituted methyl aromatics and heteroaromatics to nitriles

The formation of aromatic as well as heteroaromatic nitriles by vapour phase oxidation of the corresponding methyl substituted reactants in the presence of ammonia proceeds in its activation in equal pathways to the described partial oxidation to aldehydes [42–45]. It is generally accepted that such reactions are of the same kind as the so-called allylic oxidation [1], i.e., the reaction starts on a methyl group that is neighboured to an olefinic or aromatic double bond: So a methylene-like (benzyl) species is formed from a methyl aromatic reactant after H-abstraction; this specimen is converted to a benzaldimine (R–CH=NH) intermediate either by dehydrogenation of an intermediately generated benzylamine ($R–CH_2NH_2$) that could be formed from a benzyl species and a co-ordinated ammonia or by the more likely condensation of ammonia with benzaldehyde e.g. [43]. The nitrile can also be formed by oxidation of the benzaldehyde intermediate to the corresponding acid with subsequent acid amide formation ($R–CONH_2$) and dehydration according to Ref. [46].

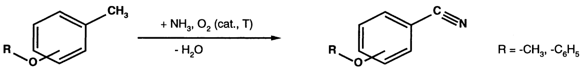
Intensive in situ FTIR studies of the ammoxidation of toluene on vanadyl pyrophosphate used as catalyst led us to the conclusion that benzaldimine is preferential formed by the reaction of co-ordinated ammonia (ammonium ions) and benzaldehyde intermediate [47,48]. Actually, these investigations showed that adsorbed benzylamine did not react to the desired nitrile under similar reaction conditions [47]. To substantiate the co-operation of co-ordinated ammonia, we found in pulse ammoxidation experiments with $^{15}N$-ammonia on a $^{14}NH_4^+$ ion-containing vanadyl pyrophosphate catalyst that ammonium ions may react with the chemisorbed aldehyde intermediate to form the nitrile [49].

However, the formed nitrile is much more stable than the aldehyde stage, significantly higher product selectivities are obtainable in the presence of the base ammonia and an easier preparation of acidic catalysts for this reaction is possible; these are the main reasons why much more successful work on vapour phase ammoxidation of methyl aromatics and heteroaromatics is carried out in comparison to the partial oxidation route.

Mainly, the ammoxidation of toluene and the isomeric xylenes to benzonitrile and the dinitriles, respectively, is intensively studied, commercialised and well established [5,46,50] but other methylbenzenes are also subject to ammoxidation reaction; for example, Sai Prasad et al. [51] reported on the ammoxidation of mesitylene to 1,3,5-tricyanobenzene on V–Sn–O catalysts with yields up to ca. 30%. Beside the usually used V–Ti–O materials that can contain further transition metal components the application of catalysts on the basis of V-containing zeolites is described [52–55]. However, also the vapour phase ammoxidation of various substituted toluenes grows in importance. Some selected examples should examine this trend.

### 2.2.1. Synthesis of methoxybenzonitriles

Cavani et al. [46] reported on the 4-MeOT ammoxidation with 4-methoxybenzonitrile (4-MeOBN) selectivities up to ca. 55% at high conversions using V–Ti–O catalysts. A paper of Ivanov et al. [56] described the vapour phase ammoxidation of isomeric phenoxy toluenes and 4-MeOT to the corresponding nitriles (see Eq. (5)) using V–Sb–Cr–O catalysts up to ca. 635 K. The selectivity to 4-MeOBN amounted to ca. 40–60% depending on the reaction temperature at 50–75% 4-MeOT conversion.



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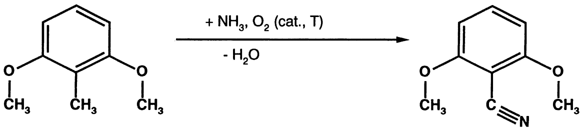
Own results using defined vanadium phosphorus oxides as catalysts revealed a 4-MeOBN selectivity of ca. 70% at a nearly complete conversion at 703 K [57]. We also studied the influence of the position of the second substituent (methoxy) on the toluene molecule concerning reactivity and product distribution under comparable conditions. Evidently, the 4-isomer showed highest conversion and selectivity to the desired nitrile whereas these data are significantly declined for the 2- and 3-isomers (4- » 2- > 3-). This row mirrors the different accessibility and reactivity in dependence on the position of the substituents; additionally, this ranking is influenced by a different electronic stabilisation of reaction intermediates beside the electronic effect (electron-donating or electron-withdrawing) of the substituents themselves [56].

Moreover, the introduction of another substituent of the same kind (Eq. (6)) may strengthen these effects, such as shown for 2,6-dimethoxytoluene. On the one hand, the methyl group can be covered by the large substituents and on the other one, the electronic effects (electron-donating in the case of the methoxy group) can lead to a stronger adsorption of reactants, intermediates as well as products. Inevitably, the stronger adsorption results in deeper oxidation. These actions result in low reactivity and nitrile selectivity; in the case of 2,6-dimethoxytoluene only traces of the desired nitrile were obtained at ca. 25 mol% conversion [57].



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### 2.2.2. Synthesis of chlorobenzonitriles

Cavani et al. [46] also reported on the 4-ClT ammoxidation on V–Ti–O catalysts as well. High 4-chlorobenzonitrile (4-ClBN) selectivities up to ca. 85% were reached at high conversions.

The ammoxidation of the isomeric chlorotoluenes and dichlorotoluenes was also intensively studied in our group using defined vanadium phosphate catalysts [57–60]. Activity and selectivity are shown to depend on the position of the Cl-substituents (see Table 2) causing a changed accessibility of the methyl group

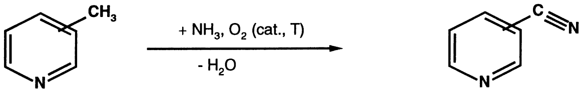
Table 2
Ammoxidation of various isomeric chlorotoluenes and dichlorotoluenes on a defined V–P–O catalyst [57]

| Reactant | $T$ (K) | Toluene conversion (%) | Nitrile selectivity (%) |
|---|---|---|---|
| 2-Chlorotoluene | 703 | 70 | 70 |
| 3-Chlorotoluene | 703 | 62 | 57 |
| 4-Chlorotoluene | 703 | 98 | 95 |
| 3,4-Dichlorotoluene | 688 | 85 | 52 |
| 2,4-Dichlorotoluene | 688 | 85 | 54 |
| 2,3-Dichlorotoluene | 688 | 78 | 41 |
| 2,5-Dichlorotoluene | 688 | 64 | 39 |
| 2,6-Dichlorotoluene | 688 | 55 | 28 |

and a possible different electronic stabilisation of the reaction intermediates as discussed above. In contrast to the usage of methoxytoluenes as reactant, the halogen substituent of the chlorotoluenes reveals a rather electron-withdrawing effect; the result is that the nitrile selectivities can be increased by a faster desorption of the nitrile molecule. This behaviour is in line with the ideas suggested above on the interaction of reactants being different in their acid–base properties with more acid catalyst surface of an ammoxidation catalyst and with the more base surface of an oxidation catalyst.

### 2.2.3. Synthesis of heteroaromatic nitriles

As early as the 1980s both Andersson and Andersson [61] and Baiker and Zollinger [62] gave in summarising reports the state of the ammoxidation of alkylpyridines to the corresponding nitriles (see Eq. (7)), being well established processes in industry to produce valuable intermediates for pharmaceutical syntheses. Mainly V–Ti–O catalysts were used and intensively characterised, especially concerning the formation of special vanadia–titania phases, their V/Ti ratio and the vanadium oxidation state.



(7)

Nevertheless, various papers were published in the 1990s reporting on the ammoxidation of methylpyridines revealing the interest in improving of established processes. Ramachandra Rao et al. [63] reported on the ammoxidation of 3-methylpyridine (3-MPy) to 3-cyanopyridine (3-CPy; nicotinonitrile) on crystalline/amorphous V-containing zeolite catalysts. A V-containing SAPO material showed the highest 3-CPy yield of 76%. The SAPO framework helps to enhance the desired product yield by decreasing the proportion of higher boiling products due to its shape selective properties. Similar results on the ammoxidation of 3-MPy and 4-MPy were reported by Kulkarni et al. [36,37] also using V-containing SAPO and AlPO molecular sieve catalysts.

Narayana et al. [64,65] studied the ammoxidation of 3-MPy over vanadia–titania (anatase) catalysts. Optimum catalysts contain a vanadia monolayer coverage with nitrile selectivities close to 100% at ca. 70% 3-MPy conversion. Higher vanadia loadings reveal declined activity and nitrile selectivity; this is due to the coverage of monomeric $VO_x$ species. Co-ordinatively unsaturated sites (Lewis sites) on vanadia are responsible for oxidation and ammoxidation reaction.

Kanta Rao et al. [66] reported on the use of ceria–titania (rutile and anatase) catalysts for the ammoxidation of 3-MPy and 4-MPy. Anatase supported catalysts exhibited higher ammoxidation activities then rutile supported ones. The authors noted a marked steric effect in 3-MPy and 4-MPy reactivity. Best results were obtained on 20% ceria on anatase showing 3-MPy conversion of 37% (89% for 4-MPy) and 45% 3-CPy selectivity (77% for 4-CPy).

Own results concerning the ammoxidation of the isomeric methylpyridines are summarised in Table 3 using vanadium phosphate catalysts [57,67]. The significance of steric conditions is very well demonstrated considering the catalytic results of the 2-MPy ammoxidation. In contrast to the other isomers a large proportion of the reactant is converted to pyridine; this is probably caused by a steric hindrance of the reaction due to the co-operation of the ring nitrogen electron pair during the formation of the adsorbate complex. Similar mechanistic ideas on the inclusion of the additional electron pair of the ring nitrogen in the chemisorption state during the conversion of methylpyridines to the corresponding nitriles on defined vanadium phosphate catalysts are discussed by Matsuura [68].

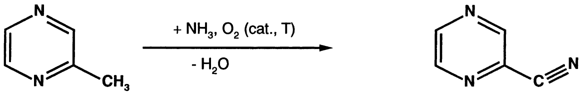
Beside the ammoxidation of methyl pyridine derivatives only little is known on the synthesis of other heteroaromatic nitriles. However, some work is published on the ammoxidation of methylpyrazines [69]. More recently, Bondareva et al. [70] suggested the use of V-containing heteropoly compounds as catalysts for

Table 3
Ammoxidation of the isomeric methylpyridines on a defined V–P–O catalyst [57,67] at 703 K

| Reactant | Methylpyridine conversion (%) | Nitrile selectivity (%) |
|---|---|---|
| 2-Methylpyridine | 87 | 65[a] |
| 3-Methylpyridine | 90 | 81 |
| 4-Methylpyridine | 98 | 93 |

[a] Pyridine was observed as the main by-product.

the ammoxidation of 2-methylpyrazine (see Eq. (8)); a maximum selectivity towards 2-cyanopyrazine of ca. 70% at 90% conversion is reported. Amirkhanova et al. [71] used Mo–Ce–Ti–O catalysts for the ammoxidation of 2,5-dimethylpyrazine but, surprisingly, no nitrile was found in the outlet stream; main products instead of this were pyrazinedicarboxamide and a pyrazine polyamide at higher temperatures.



(8)

## 3. Outlook

The vapour phase oxidation and ammoxidation of substituted aromatic compounds will be continuously of interest. The reason for this is given by the growing importance of the application of heterogeneous catalysts for the production of fine chemicals on the one hand and of the future growth in the supply of aromatics by the expected change in the petroleum processing on the other hand. The efficiency of these processes will be improved with more selective catalysts; the amount of waste as well as the formation of undesired by-products will be significantly limited and complicated separation operations can be replaced by simpler ones.

More efficiency means less severe, less energy intensive processes, including the application of new and cheaper raw materials. For a broader application of heterogeneous catalysts particularly in the selective oxidation of substituted aromatic compounds the catalyst performance must be improved to carry out reactions under distinct milder conditions, leading to an increase in selectivity. Particularly, the catalyst design must be adapted for the selective oxidation of compounds with more complicated structure, e.g., with substituents having unfavourable electronic and/or steric properties. To develop such adapted catalysts with qualified structure and suited promotors better information are necessary (i) on the catalytic active structures and sites, (ii) on their electronic and steric architecture and (iii) their altering during the catalytic reaction.

Furthermore, the interaction between the reactants and the intermediates with the catalyst surface and the reaction course should be studied in detail. Substantial information on the chemisorption steps and the mechanistic features will be obtained by in situ investigations using suitable spectroscopic methods. The target is the development of sophisticated multifunctional highly active and selective catalyst.

The development of new catalytic materials for emerging oxidation processes, e.g., effective catalysts supported on microporous or mesoporous materials [72–74] or nanostructured noble metal catalyst [75–78] combined with a deeper insight in catalyst chemistry and its surface properties [79–81] may open the way for further development. Additionally, new reaction media, such as the usage of supercritical fluids for partial oxidations [82–85] or thermomorphic solvent systems (with temperature dependent change form biphasic systems to single phases) [86] may give new impulses for the improvement of catalytic selective oxidations.

More sophisticated reactions might be realised in the future using such new adapted catalysts and new reaction engineering concepts [87–89], e.g., partial oxidations of complicated and highly substituted compounds; additionally, technical achievements are to expect with the use of multifunctional reactors [90,91].

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