Oxidation and Ammoxidation of Aromatics

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Abstract: An overview of the state of the art in the direct oxygen or nitrogen insertion to aromatic rings and side-chains by hydroxylation, acetoxylation, partial oxidation and ammoxidation is presented. The influence of a variety of catalysts and oxidants on the yields of hydroxylated products of aromatic species is discussed in more detail. The survey is also focussed on the usage of H_2O_2 as an effective oxidising agent for hydroxylation reactions. Acetoxylation of methyl-substituted aromatic compounds to their corresponding esters in a single step is indeed an interesting area from an industrial point of view. Hence, the topics covering benzylic acetoxylation, although they are under a developmental stage for commercial exploitation, are also reviewed. The present contribution also covers the main directions of selective oxidation/ammoxidation of aromatic compounds to useful products, surveys recent developments and provides an updated discussion of the state of the art in the field of oxidation and ammoxidation of aromatics. Additionally, a comparative study of the vapour phase oxidation and ammoxidation of different alkyl aromatics to their corresponding aldehydes and nitriles using various heterogeneous catalysts is presented. Besides, the achievements and limitations of the catalysts/processes are emphasised. Furthermore, the present article includes a discussion of common features and differences in mechanistic steps of oxidation and ammoxidation reactions investigated by *in situ* FITR spectroscopy. The influence of acid-base properties of catalyst surfaces in connection with electronic effects of the substituents on the performance of the catalysts is also described.

Keywords: aromatic hydroxylation; benzylic acetoxylation; electronic effects of substituents; mechanistic aspects by *in situ* FTIR; side-chain oxidation and ammoxidation

1 Introduction

Scientific and technological developments have had a significant effect in the field of catalysis (catalytic processes) in the last two decades on the development of novel catalysts, new types of reactors, reaction engineering aspects, structured beds, etc. Large-scale commodities, organic intermediates as well as special and fine chemicals can be synthesised by oxidation and ammoxidation of various aromatic and heteroaromatic compounds. Usually, catalytic hydrogenation is a method that is frequently applied in the organic synthesis laboratory for the preparation of a variety of valuable chemicals. On the other hand, the use of oxidation catalysis, particularly with heterogeneous catalysts, in the gas phase is not so usual. Because all the products of selective oxidations are intermediates, they are kinetically controlled in mostly various parallel or consecutive ways to total oxidation. Hence, the choice of catalysts and reaction conditions (including control of exothermicity) are very important to get a high selectivity of the desired product at a sufficient production rate. Therefore the review will cover selected reactions which, on the one hand, lead to interesting organic products and, on the other hand, can be carried out with high selectivity.

In the selective oxidation of aromatics one can distinguish between three general reaction types[1]:

1) formation of oxygenates without splitting of ring C–C bonding (e.g., formation of phenols),
2) formation of oxygenates under splitting of ring C–C bonding (e.g., formation of maleic or phthalic anhydride from benzene or naphthalene, respectively),
3) oxidation or ammoxidation of aromatic side-chains (e.g., formation of benzaldehyde or benzonitrile).

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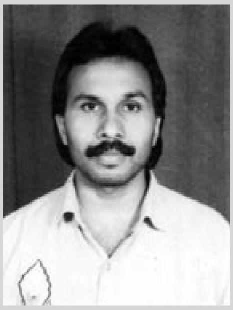
Bernhard Lücke (born in Magdeburg, Germany, 1937) studied chemistry at Humboldt-University Berlin (Master's 1962, PhD on aza-steroids, supervisor A. Rieche 1966). He worked in the pharmaceutical industry from 1965–1969 (syntheses of steroids and derivatives) and switched over to the Central Institute of Organic Chemistry (Academy of Sciences, Berlin), Group of Selective Oxidation (oxidation of butene, butane and of methyl aromatics) in 1970. From 1981 he was group leader and from 1985–1991 director of the C1 Chemistry Department in the same institute (CO hydrogenation, carbonylation, hydrocarbonylation, methanol chemistry etc.). After completion of his habilitation in 1988, he was appointed as professor in 1989. During 1992/1993, he was the scientific director of the Centre for Heterogeneous Catalysis. Soon after the foundation of the Institute for Applied Chemistry Berlin-Adlershof (ACA) in 1994, he became the first scientific director of the institute and from 1995, he was the head of the Catalysis Department of this institute. Since 2000, he is the editor in chief of *Catalysis Communications.* His main research fields are: selective catalytic oxidation, CO chemistry, heterogenisation of homogeneous catalysts. He has published more than 160 articles in different journals of international repute.



K. V. Narayana was born in Seethampeta, Andhra Pradesh State (AP), India and graduated from Kakatiya University, Warangal (AP, India). After his Masters, he worked as lecturer for some time in Sidhartha Degree College (India), teaching chemistry to the graduate students. Then he joined Birla Institute of Scientific Research, Hyderabad as Research Fellow and rendered his services for two years (June 1990 to June 1992) dealing with various analytical methods including AAS, FTIR, etc. Then he joined the Indian Institute of Chemical Technology (IICT), Hyderabad to carry out his doctoral work on ammoxidation of various alkylaromatics/heteroaromatics and optimisation of process parameters using statistically designed experiments. He was awarded a Ph. D. degree in Chemistry (Heterogeneous Catalysis) from Osmania University, Hyderabad, India in March 1998. After his Ph. D., he joined AP state Electricity Board (a Government body) (from June 97 to April 2000) and then moved to Germany to carry out his post-doctoral research. He is presently working as a post-doctoral fellow at the Institute for Applied Chemistry, Adlershof-Berlin e. V. (ACA) in the group of Dr. Andreas Martin (from April 2000 to the present). His main research interests are catalyst syntheses, characterisation and catalyst evaluation for various oxidation and ammoxidation reactions, in particular mechanistic aspects of catalysis on mixed and supported oxides. He holds several patents and publications in the field of ammoxidation. His research interests also include supercritical fluids.

Andreas Martin was born in Wilkau-Haßlau, Germany and graduated from the Technical University (TU) Dresden. His Master's thesis was on "Chemistry of 2-Aminothiophenes". After his M.Sc., he worked as a research fellow at Central Institute of Organic Chemistry (Berlin) of the Academy of Sciences (Organic Intermediates Department) on oxidation and ammoxidation of methylaromatics and methylheteroaromatics where he carried out his doctoral work. He was awarded a Ph. D. degree in Chemistry (Heterogeneous Catalysis) from the Academy of Sciences, Berlin in 1986. After his Ph. D. he was engaged in the C_1 Chemistry Department of the Central Institute of Organic Chemistry (Berlin) in MTG/MTO catalysis and pyrolysis of hydrocarbons on zeolites. From 1989–1990 he was the head of the research group "Zeolite Catalysis" (C_1 Chemistry Department). 1990/1991 he joined the University Bremen as a post-doctoral research fellow (Zeolite chemistry and catalysis). In 1992, he moved again to Berlin and worked at the Centre for Heterogeneous Catalysis – Berlin as head of the project group "Zeolite Catalysis" (Zeolite-catalysed amination and O/N transformation of organic compounds). In 1994 he joined the Institute of Applied Chemistry Berlin-Adlershof (ACA) as a research fellow (ammoxidation of methylaromatics). In 1997 he became head of project group "Catalysis in multi-phases and supercritical fluids" (heterogeneously catalysed oxidation reactions in SCF, catalytic wet oxidation, high-pressure reactions, partial oxidations, oxidation and ammoxidation of methylaromatics) and in 2002 head of the R & D area "Catalytic processes and catalysts". He holds several patents and more than 120 publications in various fields of catalysis.

Klaus Jähnisch studied chemistry at the TH Merseburg, and received his doctorate from the Institut für Organische Chemie, Berlin-Adlershof in 1972 with E. Schmitz on the amination of olefins and ketones. From 1980 to 1983, he worked as a group leader at the Cuban Academy of Science in Havana. He habilitated in 1991 at the TH Merseburg. He has been working as a scientist at the Institut für Angewandte Chemie Berlin-Adlershof e. V., Berlin since 1994. His research interests include the asymmetric synthesis of amino acid derivatives, the functionalisation of arenes and the chemistry in micro-structured reactors.

The oxidation of aromatic compounds under splitting of ring C–C bonds represented a milestone in the heterogeneously catalysed oxidation technology. Thus, the first commercial production of phthalic anhydride started in 1916 (vapour phase oxidation of naphthalene over vanadium oxide), and also maleic anhydride was produced from benzene during the earlier industrial period starting in 1933.[1] At present both industrial processes are only of historical interest and this reaction type is also not of interest from the viewpoint of the organic synthesis. Therefore, the review will only deal with the first and the third reaction types.

This paper also covers the main directions of the oxidation of aromatic compounds, particularly with air and in the gas phase, under the special viewpoint of organic synthesis. In this light, it can be stated that preferentially the ammoxidation of aromatic side-chains may be a reliable tool for the direct synthesis of differently substituted nitriles, whereas the oxidation of side-chains to benzyl alcohols (*via* oxidative acetoxylation) or to benzaldehydes is still under development and is not so versatile in its commercial application as nitrile syntheses.

Additionally, the direct hydroxylation by oxidation of the aromatic nucleus is indeed a big challenge and hence the state-of-art for this reaction is presented here for the different approaches both in liquid and gas phase reactions.

Industrial aspects of the selective oxidation of aromatic compounds are not dealt in this article, for more information we refer to the relevant literature, e.g., "*The Technology of Catalytic Oxidations*" by P. Arpentinier, F. Cavani, F. Trifiro.[2]

For the development and application of catalysts the activation mechanism and the different oxygen species on the catalyst surface are important; however, this is not covered in this survey as it is more related to the organic reaction and its limitations. The activation of oxygen is described in detail elsewhere.[3–5]

Therefore, the main topics of the survey are:

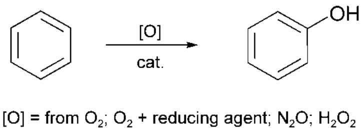
- direct hydroxylation of aromatic compounds,
- acetoxylation of methyl-substituted aromatic compounds,
- synthesis of aldehydes by side-chain oxidation,
- ammoxidation of aromatic side-chains.

2 Direct Hydroxylation of Aromatic Compounds

The direct and selective introduction of the hydroxy group into aromatic compounds is one of the most challenging fields in oxidation chemistry today. Multi-step processes are used in many cases for the technical production of hydroxylated aromatic compounds. Thus, most of the phenol produced worldwide is prepared by the Hock process. Apart from the disadvantage of a multi-step process, acetone is also formed in equimolar amounts.

Owing to the importance of the direct oxidation of aromatics, there is a multitude of studies in this field, which will be discussed in this review in the following sections. Various oxidation agents are used in gas- or liquid-phase reactions in the presence of catalysts. In the present review article, the hydroxylation of benzene is discussed first, followed by the hydroxylations of phenol, toluene, xylene, halogenated aromatics and benzonitrile.

The direct catalytic oxidation of benzene to phenol has been examined with a large variety of oxidants as shown in Scheme 1.



Scheme 1. The direct catalytic oxidation of benzene to phenol with a large variety of oxidants.

More than 100 years ago, Friedel and Crafts examined the conversion of benzene to phenol using oxygen. The experiments carried out in 1888 were conducted in the gas phase in the presence of aluminium chloride.[6] Later studies used molybdenum, tungsten, copper, uranium, and vanadium oxides as catalysts.[7,8] The selectivities obtained were very low and hence they are of no importance with regard to practical applications. The use of Cu-supported ZSM-5 catalysts afforded a maximum phenol yield of 1.5%.[9] An increase in the yield up to 4.3% could also be achieved by the use of V-Mo-O/SiO_2 catalysts.[10] Investigations on the oxidation of benzene with oxygen in the liquid phase in the presence of

CuCl,[11] iron or palladium in heteropoly acids,[12,13] or palladium acetate[14] gave also only low selectivities.

These examples show that the direct oxidation of benzene to phenol using oxygen as oxidant – one of the 10 "challenges for catalysis" – as mentioned in the literature[15,16] proceeds with very low selectivity to hydroxylated products due to opening of the benzene ring as the total oxidation with formation of CO_2 and water is the predominant reaction. However, the selectivity of the hydroxylation of benzene to phenol can be improved if the reaction is carried out in the presence of reducing agents. Thus, already in 1954, Udenfriend could show that the Fe/EDTA/ascorbate complex can be used for the hydroxylation of aromatics.[17] In later studies, the reaction has been analysed more thoroughly and the mechanism has been clarified.[18–21] The homogeneously catalysed liquid-phase reaction proceeds *via* OH radicals with the formation of phenol or hydroquinone giving very low conversion. In several other studies, iron was replaced by other redox metals. Thus, studies have been performed in the presence of Cu-supported zeolites,[22] Cu-supported MCM-41 catalysts,[23] and CuO-Al_2O_3[24] but yields obtained were still lower than 1%. Higher yields of phenol are also reported when iron is replaced by vanadium catalysts. A maximum benzene conversion of 3.6% with a selectivity of 98.1% has been obtained using oxygen in the presence of VCl_3 in the two-phase system water-benzonitrile/benzene.[25] The highest phenol yield amounted to about 9% when V/Al_2O_3 catalysts are used in 80% acetic acid for the hydroxylation with oxygen as oxidant and ascorbic acid as reductant.[26] A drawback of this process is that vanadium penetrates into the liquid phase by leaching. The use of other reductants such as hydroquinone, pyrocatechol, dithiothreitol, or 2-mercaptoethanol resulted in considerably lower yields of phenol.

On the whole it can be stated that the hydroxylation of benzene to phenol in the presence of organic compounds as reducing agents is interesting from a scientific point of view but is not yet suited for practical applications because of the low yields obtained. Several authors have also studied the activation of oxygen in the presence of reducing gases such as hydrogen or carbon monoxide. Probably, hydrogen peroxide is formed *in situ*, which reacts with benzene leading to the oxidation products. The reactions have been carried out in the liquid as well as in the gas phase. The catalysts contained Pd or Pt to activate oxygen and a redox metal responsible for the oxidation reaction. Redox metals used were copper,[27–32] titanium,[33] and vanadium.[34,35] Recently it has been shown that the combination of heterogeneous Pd and Pt catalysts with homogeneous catalysts accelerates the hydroxylation of benzene to phenol by oxygen and hydrogen. Using $Pt/SiO_2/V(acac)_3$ catalysts in acetic acid, a phenol selectivity of 21.8% (based on oxygen) at an oxygen conversion of 3.1% could be obtained.[36] The same study gave phenol with a selectivity of $>99\%$ at a benzene conversion of 26% by the use of $Pd/Al_2O_3/V(acac)_3$.[37] The hydroxylation of benzene using oxygen and hydrogen could also be achieved without an oxidation catalyst if Pd/Pt-containing acidic catalysts such as zeolites (BEA, MOR, FER, MFI), acidic resins such as Amberlyst or Nafion/silica composites were employed. In these studies, the last-mentioned catalyst gave relatively good results.[38,39] For example, a phenol yield of 4.2% and a phenol selectivity of 56% were obtained in a mixture of water and ethanol at a pressure of 1000 kPa.[39]

The use of a palladium membrane resulted in encouraging results for the direct hydroxylation of benzene to phenol.[43] Hydrogen penetrates through the membrane, dissociates on the palladium surface and reacts with oxygen to give active oxygen species, which attack benzene to give phenol. Phenol was formed with a selectivity of 80–90% at benzene conversions of 2–16% and with a space-time yield of 1.5 kg phenol kg_{cat}^{-1} h^{-1}. These results might indicate a first step into the direction of the practical application of oxygen and hydrogen for the hydroxylation of aromatic compounds.

There are only a few studies concerning the application of carbon monoxide as reducing agent for the oxygen activation. A phenol yield of only 2.3% (based on benzene) was obtained using a homogeneous catalyst consisting of palladium acetate und phenanthroline at 180 °C in the presence of oxygen.[40–42]

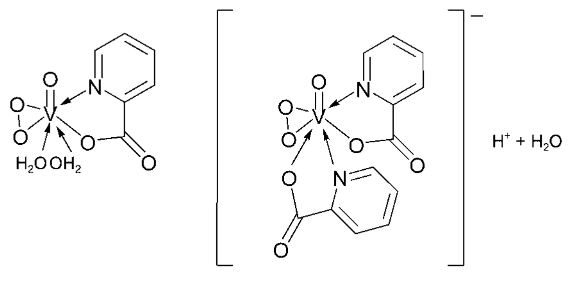
The hydroxylation of benzene with nitrous oxide in the presence of modified ZSM-5 zeolites has been investigated since the late 1980 s and opens a new way to the synthesis of phenol. The reaction proceeds with high selectivity under normal pressure at 350–400 °C. Gubelmann and Tirel achieved a phenol yield of 16% with selectivities of $>95\%$ using a Brønsted-acidic H-[Al]ZSM-5.[44] A phenol selectivity of 98% at a phenol conversion of 27% is reported by Burch and Howitt.[45] Emig et al.[46] could show that the benzene conversion rises with increasing reaction temperatures, but at the same time the phenol selectivity decreases and the deactivation of the catalyst is favoured. Total oxidation begins to occur above 400 °C. There are some contradictory views with respect to the mechanism of this reaction. While Gubelmann et al.[44] suppose that the acidity of the zeolites is responsible for the catalytic activity, Panov[47–51] take the view that a coordinatively unsaturated iron species (so-called α-sites) in the used [Fe]ZSM-5 zeolites are the active sites. The N_2O molecule decomposes at the catalyst surface with the formation of a highly reactive so-called α-oxygen, which causes the selective oxidation of benzene. Hölderich et al.[53,54] demonstrate that the phenol yield depends on the degree of dealumination of H[Al]ZSM-5 zeolites and that there is a correlation between the amount of extra-framework aluminium species and the phenol yield.

The technical realisation of the phenol production by benzene hydroxylation using nitrous oxide requires a cheap technical access to the oxidant as given, for example, by the synthesis of adipic acid. However, there have been only first tests in a pilot scale[55] but no chemical plant has been put into operation so far. One of the disadvantages of the process is that highly pure N_2O is necessary for the reaction and that the catalysts are rapidly deactivated by the deposition of coke.

In numerous studies the oxidation of benzene to phenol by hydrogen peroxide using various redox-active metals as catalysts has been described. H_2O_2-based catalytic hydroxylation can be environmentally as well as economically very favourable because H_2O is formed as the only by-product. H_2O_2 has a high content of active oxygen and is rather inexpensive compared to various organic peroxides and peracids. Hydroxylations of benzene with hydrogen peroxide in the presence of iron catalysts have been performed using both homogeneous and heterogeneous catalysts. The radical hydroxylation using Fenton's reagent has been studied repeatedly with the mechanistic aspects of the reaction being in the centre of attention.[56–58] Phenol yields of 93% (based on H_2O_2) could be obtained at very low concentrations.[59] Oxo-bridged di-iron(III) complexes such as $[Fe_2O(bipy)_4(OAc)_2]$ $[ClO_4]_4$ showed a good catalytic activity for the hydroxylation of benzene with hydrogen peroxide[60] giving a maximum phenol yield of 41%. Bianchi et al.[61] used Fe(II) complexes as catalysts and trifluoroacetic acid as co-catalyst and a phenol selectivity of 97% (based on benzene) has been reached in the two-phase system benzene in acetonitrile/H_2O at a benzene conversion of 8.6%. The phenol selectivity reached 88% (based on hydrogen peroxide) if the oxidant was charged slowly. The most effective complexing agents were derivatives of pyrazinecarboxylic acids.

Maier et al.[62] have reported on the hydroxylation of benzene with hydrogen peroxide in the presence of amorphous microporous mixed oxides. A mixed oxide containing 3% iron and 0.5% cerium turned out to be one of the most effective catalysts. Thus, a phenol selectivity of 73% at a benzene conversion of 29% has been reached using acetonitrile as solvent. However, the procedure has the drawback that a noticeable leaching of the redox-active metals has been observed.

Vanadium compounds are also applied as catalysts for the hydroxylation of benzene using hydrogen peroxide. The vanadium(V) peroxo complexes **1** and **2** (Scheme 2), prepared from H_2O_2, pyridine-2-carboxylic acid and V_2O_5, react with benzene giving a rather good phenol yield of 55 or 70% (based on the complex used).[63–65] The stoichiometric reaction is performed in acetonitrile.



1 **2**

Scheme 2. Vanadium(V) peroxo complexes.

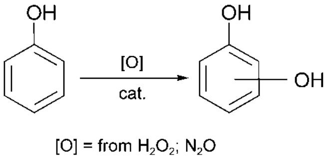
Kumar et al.[66] describe a vanadium complex from L-tyrosine and salicylaldehyde, which is bound to a polymeric support. This complex catalyzes the hydroxylation of benzene to phenol with a yield of 30%. Leaching of the vanadium could not be detected. Chen et al.[67] studied the hydroxylation of benzene to phenol with hydrogen peroxide in the presence of V-MCM-41 catalysts and the catalytic properties were compared to those of V-Y and V-BEA zeolites. It was found that V-MCM-41 [Si/V = 25] affords benzene conversions up to 18% at a maximum phenol selectivity of 40% whereas using V-BEA zeolite 16% conversion at a selectivity of 37% and using V-Y zeolite only 1% conversion at a selectivity of 3% were obtained when benzene is reacted with hydrogen peroxide in a ratio of 2:1 in acetonitrile at 60 °C. In addition, it was found that an increase of the V_2O_5 content in V-MCM-41 resulted in an increase in both the conversion from 10 to 18% and the selectivity from 30 to 40%. Phenol was found to be the only liquid product.

In 2003 Lemke, Jähnisch et al.[68] published results on the hydroxylation of benzene using hydrogen peroxide in the presence of vanadium catalysts supported on MCM-41, MCM-48, silica of the aerosil type, and microporous mixed oxides (AMM). Among the MCM-based catalysts, the highest phenol selectivity has been obtained with an MCM-41-based catalyst containing 1.1 wt % vanadium. The selectivity amounted to 67% (based on benzene). The best results have been obtained in acetonitrile with a low vanadium-containing VO_x/SiO_2 catalyst (0.14 wt % vanadium). A phenol selectivity of 81% has been observed at a benzene conversion of 10%. Phenol selectivities based on hydrogen peroxide were in the range of only 4 to 26%.

There are also numerous studies on the application of titanium-containing heterogeneous catalysts for the hydroxylation of benzene to phenol. Pinnavaia et al.[69] found that a yield of phenol of 68% at a benzene conversion of 95% is obtainable when the reaction is conducted in the presence of Ti-HMS and Ti-MCM-41 in acetone as solvent. This work was taken up in the following years by several groups but the results could not be reproduced.[70,71] The results of Pinnavaia were revised by himself in 1996.[72] Hydrogen peroxide had partly formed hydroperoxides with the acetone used as solvent so that the analytical results had been falsified.

Recently, Duan et al.[73] have estimated the dependence of the selectivity of the hydroxylation of benzene to phenol with hydrogen peroxide on the hydrophobicity of the surface of modified Al/Ti-MCM-41 materials. A benzene conversion of up to 95% was achieved with the portion of phenol in the sum of oxidation products amounting to 95%. The phenol selectivity based on reacted benzene was not given. Kumar[74,75] and Yeramian[76] investigated the oxidation of benzene to phenol with hydrogen peroxide in the presence of TS-1 catalysts. They found that the reaction proceeds more rapidly when conducted without a solvent (so-called tri-phase catalysis) as compared to the reaction in solvents such as acetonitrile, methanol or acetone because of a shorter induction period. With a molar benzene/hydrogen peroxide ratio of 1:1 a benzene conversion of 74% was found. The portion of phenol in the oxygen-containing oxidation products amounted to 86%.

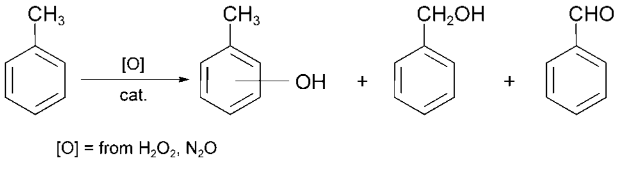
The hydroxylation of phenol to dihydroxybenzene has been studied intensively since the 1970 s (Scheme 3).



Scheme 3. Hydroxylation of phenol to dihydroxyphenol.

Strong acids such as $HClO_4$ or H_3PO_4, redox metal catalysts (Fe^{3+} and Co^{2+}) or the Ti-containing silicalite TS-1 have been employed as catalysts. The technical Enichem process using TS-1 has the advantage of being more selective and affords a higher hydroquinone/catechol ratio and less tar compared to processes using homogeneous catalysts. We have not included a detailed discussion here as Perego et al.[77] recently published a review on this subject. It should be mentioned, however, that Panov et al.[78] published results on the gas phase oxidation of phenol in the mixture with benzene one year later. They used N_2O as oxidant in the presence of Fe-containing ZSM-5 zeolites. They found that this reaction, which proceeds with comparable high selectivities, affords a higher ratio of hydroquinone/catechol and less tar as compared to the Enichem process. A further advantage of the gas phase process is that the dihydroxybenzenes are formed directly from benzene and not, as in other processes, from phenol.

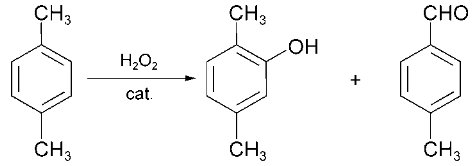
A literature survey reveals that there are only a few studies on the ring hydroxylation of other substituted aromatic compounds. Toluene was hydroxylated with hydrogen peroxide in the presence of vanadium catalysts (Scheme 4).



Scheme 4. Hydroxylation of toluene with H_2O_2.

If VS-2 was used as catalyst the oxidation took place not only at the ring but also at the side chain with a product distribution of 20% 2-methyl-, 20% 4-methylphenol and 52% benzaldehyde.[79] In addition, vanadium(V)-substituted polyoxometallates are suited for this reaction.[80] If $K_7[P_2W_{15}Mo_2VO_{62}]$ was employed as catalyst 53% 2-methylphenol and 20% benzaldehyde were found as the main products whereas using $(Bu_4N)_4K[PW_{10}V_2O_{40}]$ 76% benzaldehyde was produced. The vanadium(V) peroxo complex **1** (Scheme 2) has also been employed in the toluene oxidation. A product distribution of 32% 2-methyl-, 27% 3-methyl-, 9% 4-methylphenol, 4% benzyl alcohol, and 28% benzaldehyde was found. Ring-hydroxylated compounds as the sole products were found for the oxidation of toluene with hydrogen peroxide in the presence of TS-1 catalysts.[81] 56% 4-methyl- and 41% 2-methylphenol were formed as main products. Klemm et al.[82] studied the oxidation of toluene with N_2O on two different H[Al]ZSM-5 zeolites with an Si/Al ratio of about 25 and different crystal sizes. A toluene conversion of about 25% with selectivity to cresol of about 40% was observed.

The reaction of xylene with hydrogen peroxide in the presence of TS-1 as catalyst[83] is shown in Scheme 5.



Scheme 5. Hydroxylation of xylene with H_2O_2.

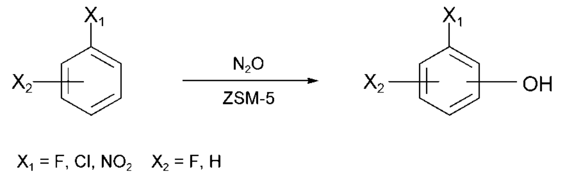
Dimethylphenol is formed at a xylene conversion of 2.5%. The best results for the hydroxylation of *p*-xylene with hydrogen peroxide could be achieved when employing Cu-containing montmorillonites as catalysts.[84] Dimethylphenol and *p*-methylbenzaldehyde were formed with a product distribution of 53% and 43% at a conversion of 24%. The reaction was performed in acetonitrile as solvent with the addition of hydrogen peroxide in small portions.

In addition, there are also a few reports on the ring hydroxylation of electron-poor aromatic compounds. Fluoro- and chloroaromatics can be hydroxylated using N_2O over ZSM-5 catalysts[53,85–87] (Scheme 6).

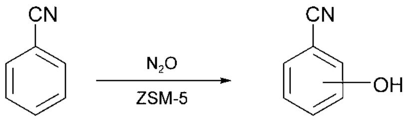
Thus, Hölderich found[53] that chlorobenzene reacts with N_2O giving a chlorophenol selectivity of 58% at a conversion of 23%. The distribution of the *ortho*- and *meta*-isomers is 28:72.

The hydroxylation of benzonitrile with N_2O is of particular interest as the products are important intermediates for the production of plant-protecting compounds which were until now produced by a multi-step procedure (Scheme 7).

This hydroxylation was first published by Hölderich et al.[53] and systematically examined by Ehrich, Jäh-



Scheme 6. Ring hydroxylation of halo-substituted aromatic compounds.



Scheme 7. Hydroxylation of benzonitrile with N_2O.

nisch et al.[88] ZSM-5 zeolites are excellent catalysts for this reaction affording a hydroxybenzonitrile selectivity of 58% at a benzonitrile conversion of 15%. The 3 isomers of hydroxybenzonitrile have been found in *ortho*:*meta*:*para* ratio of 1:6:3. The catalyst activity can be increased by decreasing the Si/Al ratio of the ZSM-5 zeolites. They found that the catalyst activity can be increased by the addition of iron. However, this higher activity is linked with an extreme loss of selectivity caused by stronger total oxidation and a more rapid deactivation of the catalyst.

3 Acetoxylation of Methyl Substituted Aromatic Compounds

Benzylic alcohol and benzyl acetate, the products obtained from the acetoxylation of toluene, are used as fragrances, in the food industry, as solvents and as intermediates for further synthetic steps. The synthesis by direct oxidation is possible by the so-called acetoxylation, which is defined as the conversion of vinyl-, allyl-, or benzyl compounds (with activated CH-groups) in presence of carboxylic acid and O_2 to their corresponding esters in a single step (Scheme 8).

$$R\text{-}CH_3 \xrightarrow[1/2\ O_2\ /\ cat]{AcOH} R\text{-}CH_2OAc + H_2O$$

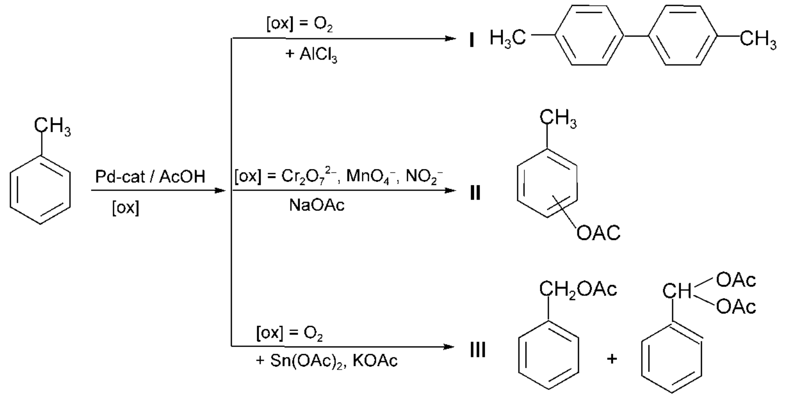
Scheme 8. Direct acetoxylation of aromatic compounds to their corresponding esters.

Over the past two decades the Pd-catalysed oxidation of α-olefins and alkyl aromatic hydrocarbons has become an increasingly attractive field and, in some instances, the only effective route for the selective synthesis of vinylic, allylic, benzylic alcohols and esters. Thus, in the selective oxidation of toluene other well known catalytic systems give rise to the formation of benzaldehyde/benzoic acid as the major oxidation products.[89–91]

Depending on the reaction conditions, the Pd-catalysed oxidation of toluene can be directed to the formation of bitolyls,[92,93] tolyl acetates, benzyl acetate or benzylidene diacetate (Scheme 9).

The formation of acetyltoluene by acylation (**II**) was firstly reported by Davidson and Triggs,[94] the formation of only bitolyls (**I**) was observed by Helden and Verberg[95] using $PdCl_2$ as catalyst. For the synthesis of benzyl acetates in general palladium acetate catalysts are used. Bryant et al. studied this reaction using a $Pd(OAc)_2$-$Sn(OAc)_2$-charcoal mixture or 5% Pd on charcoal-$Sn(OAc)_2$ as catalysts.[96] A number of reactions using methylbenzenes were studied using this catalyst system. The main product resulted from oxidation of the methyl group to the benzyl ester function, but in the case of oxygen in appreciable amounts the consecutive oxidation of this group to further acylated products was also found (**III**).

In an earlier study, Bushweller investigated the influence of the electronic factor and found that electron-donating groups favoured the acetoxylation reaction.[97] Thus, *p*-methoxytoluene gave a 46% yield of *p*-methoxy-



Scheme 9. Influence of reaction conditions and catalysts on toluene oxidation.

benzyl acetate while *p*-nitrotoluene gave only 2% yield and *p*-chlorotoluene gave 25% of the corresponding ester.

Benazzi et al.[89] have studied the palladium-catalysed benzylic acetoxylation of toluene and reported that the acetoxylation to benzyl acetate was a purely heterogeneously catalysed reaction, which occurred on supported metallic palladium particles. The catalyst system applied was composed of $Pd(OAc)_2$, $Sn(octoate)_2$, KOAc and Norit PKDA 1–3 charcoal with a Pd:Sn:K molar ratio of 1:5:10. The addition of Sn^{2+}, K^+ and charcoal led to an increased rate of $Pd(OAc)_2$ decomposition to metallic palladium. The addition of tin(II) is believed to lower the activation energy of the reaction by over 25% and may also serve as a reducing agent in the initial stages of Pd(0) particle formation. The addition of various acetate counterions had little effect on the catalytic activity (except K^+ or Rb^+). The mentioned system with Pd:Sn:K = 1:5:10 was found to be the most effective one. After 180 min activation the toluene was completely converted at 100 °C and 1.2 bar O_2 resulting in the following product selectivities: 77% benzyl acetate, 20.5% benzylidene diacetate and 2.5% benzaldehyde. In a further study Benazzi et al.[98] have reported that the acetoxylation of toluene to benzyl acetate is highly influenced by the particle size of the palladium. The reaction rate is the highest with 30–35 Å particle size corresponding to a 0.33% dispersion. As mentioned earlier, the effect of tin is to reduce Pd^{2+} to Pd(0) under *in situ* conditions in the formed catalyst system.

Augustine et al.[99] also used Pd-Sn catalysts (on silica) and found that, on the one hand, the porosity of the support (optimum average pore diameter near to 20–30 Å) and, on the other hand, the preparation conditions, particularly the pH value for the formation of the Sn component, are of decisive influence.[100] The optimised system requires a pH level of 4.2–4.7 in the tin precipitation step and a Pd:Sn ratio of 0.5. They conclude that the toluene acetoxylation rate over a bimetallic $PdSn_2$ complex depends on the state of Sn coverage of the silica support prior to the immobilization of the Pd.

Benazzi et al.[89,98] discussed the Pd(0) species as the catalytically active one and, therefore, the Pd particle size plays an important role. The influence of the Sn(II) may assist by an electron transfer in the formation of Sn(IV) and Pd(O). The optimum particle size of about 30–35 Å leads to the conclusion that several surface Pd atoms may be introduced in the catalytic process. Thus, the reaction cannot be explained as a simple insertion of Pd into a benzylic C–H bond or the formation of a η^3-benzylic-Pd complex. More probably, the aromatic system is primarily chemisorbed as a π complex on the Pd surface, then the benzylic H will be abstracted and the benzyl acetate is formed by nucleophilic attack on the CH_x group. The chemisorption of the aromatic system on the surface is strongly influenced by steric effects, which may hamper, for instance, the formation of diacetates. The nucleophilic attack on the CH_x group may be supported by an oxidative addition of C–H on the Pd surface forming $PdH + Pdx\text{-}\pi\text{-}C_6H_5CH_2\text{-}Pd$ or by a concerted nucleophilic substitution by the acetate supported by formation of PdH^+-benzyl acetate. The restoration of the surface by oxidation of the PdH species is realised by the oxygen in the reaction mixture forming at least water.

Komatsu et al.[101] reported very recently the gas phase oxidative acetoxylation over intermetallic palladium-containing compounds (e.g., Pd_5Ge, Pd_2Ge, PdZn, Pd_5Ga_2 and others) with crystallite diameters below 7 nm. Nevertheless, the highest selectivity for benzyl acetate (36%) was obtained at a toluene conversion of nearly 20% resulting in a yield of *ca.* 7%.

New results from our group[102] showed that the gas phase acetoxylation of toluene to benzyl acetate in a single step can be carried out at a toluene conversion of about 60% with a benzyl acetate selectivity over 80%. The performance of the catalysts is strongly influenced by various factors such as Pd loading, Pd particle size, type of promoter and the nature of the support of different Pd/Sb-catalysts. The titania (anatase) supported system is observed to exhibit superior performance compared to all other supports.

4 Synthesis of Aldehydes by Side-Chain Oxidation

The side-chain oxidation of alkyl (methyl) aromatic compounds to aldehydes, without reflecting the aromatic nucleus needs at least a nucleophilic type of oxidation

Table 1. Selective oxidation of methoxytoluene over V-containing catalysts.

Catalyst	T [°C]	X [%] (*p*-methoxytoluene)	Y [%] (aldehydes)	Refs.
V_2O_5-CaO-MgO	400	30	16	[118]
V_2O_5-K_2O/Cs_2O	360	60	40	[122]
VPO-CuO-K_2SO_4	452	75	48	[117]
V_2O_5–TiO_2	430	83	63	[111]
V_2O_5–Ga_2O_3-TiO_2	400	72	65	[120,121]
VPO-CuO-K_2SO_4	460	–	≤72.5	[116]

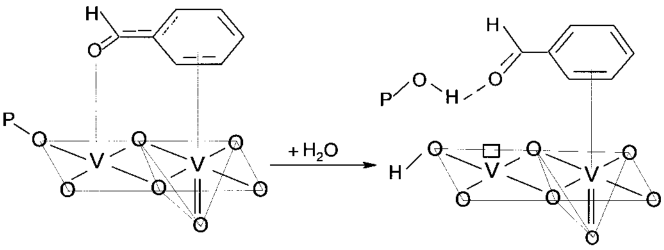
X = conversion; Y = yield.

(O-incorporation in the side-chain). The selective synthesis of aromatic aldehydes is complicated because the aldehydes themselves are easily oxidized to acids and further to total oxidation products. Thus, benzaldehyde can be produced only at low toluene conversion (10–20%) per pass at short residence time (<1 sec) with only 40–60% selectivity.[103] Therefore, substantial reports on the commercialisation of the oxidation of toluene and substituted toluenes are rather rare in the literature. Some examples for side-chain oxidation are given below in Table 1. Commonly applied catalyst systems are, e.g., V_2O_5-H_2SO_4,[104,105] novel ultrafine complex Mo-based oxide particles,[106] V_2O_5-TiO_2 oxide phases doped with Te or K_2SO_4,[107] V-containing micro- and mesoporous materials,[108] and Fe-Mo substituted deboronated borosilicates.[109]

Preferentially, Japanese groups reported on the role of the acid-base properties of vanadium oxide-based catalysts, which contain also other metal oxides (K, Rb, Cs, Ti, Ag) for the partial oxidation of dimethylbenzene to methylbenzaldehyde and other substituted toluenes.[110–112] Summarizing the results, they stated that activity is strongly dependent on the amount and strength of acid sites, and the selectivity of the formed benzaldehydes should be closely related to the basic properties of the catalyst. This means that the toluene molecule needs a strong enough chemisorption in the first step on coordinatively unsaturated sites (Lewis centres) and finally the rather basic aldehydes molecule must be rapidly desorbed from basic surface regions.

These results can be supported by our own studies on the oxidation of toluene to benzaldehyde on oxovanadium diphosphates (VPP), which have a rather acidic surface.[113] These compounds contain vanadyl octahedras as construction units, which possess Lewis sites that are responsible for the toluene chemisorption in the form of a π complex. Furthermore, under the reaction conditions (H_2O is formed by partial as well as total oxidation) the formation/addition of water can hydrolyse the existing V–O–V and/or V–O–P bonds resulting in the generation of surface OH groups. These newly formed OH groups are responsible as Brønsted sites for the strengthening of the chemisorptive interaction of the surface benzaldehyde species in addition to the initially formed surface π-complex on co-ordinately unsaturated sites. The reason is the generation of hydrogen bonding between the aldehyde carbonyl group and neighbouring OH groups[114] as shown in Scheme 10 and demonstrated by FTIR spectra in Fig. 1.

Spectra a) (after air-toluene exposure) and b) (additionally water vapour was dosed) reveal a similar appearance, i.e., the admixture of water vapour does not significantly change the product distribution as well as the acidic properties of the $(VO)_2P_2O_7$ surface (Fig. 1). This indicates that the water formed during the reaction is able to generate a sufficient amount of surface Brønsted OH groups. The comparison of c) benzaldehyde chemisorption on untreated catalyst (*ca.* 1705 cm^{-1}) and d) benzaldehyde on water vapour treated catalyst surface (*ca.* 1680 cm^{-1}) reveals that there is a shift of a band by 25 cm^{-1} to lower wave numbers on the water vapour treated catalyst. This fact shows that a very strong adsorption of benzaldehyde is taking place on the water vapour pre-treated catalyst compared to its untreated counterpart. A similar observation can also be made after the addition of pyridine to the feed mixture. Bearing in mind that the pyridine will not get oxidised under the reaction conditions for the partial oxidation of toluene, the pyridine molecule is able to block the *in situ* generated Brønsted acid sites resulting in suppression of the hydrogen bonding (Scheme 10) and hence a speed-up of the process of desorption of aldehyde species from the catalyst surface. This aspect is clearly depicted in Scheme 11 and the FTIR supporting evidence is presented in Fig. 2.



Scheme 10. Generation of H-bonding between aldehyde species and neighbouring OH groups under real working conditions.

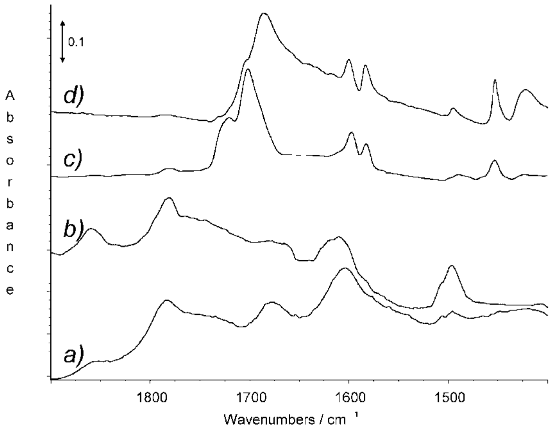
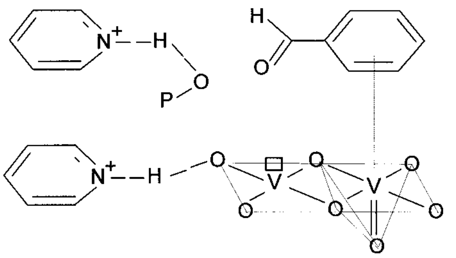


Figure 1. FTIR spectra of adsorbates on $(VO)_2P_2O_7$ catalyst after *a)* air-toluene flow, *b)* air-toluene flow after water vapour treatment, *c)* air-benzaldehyde flow and *d)* air-benzaldehyde flow after water vapour treatment.

It is evident from Fig. 2 that the FTIR spectra a) and b) reveal the picture of adsorbed aldehydes and formed cyclic anhydrides (benzaldehyde 1678 cm^{-1}, cyclic anhydride 1852 cm^{-1}, 1783 cm^{-1}) which can be estimated as intermediates for total oxidation. However, it is surprising to note spectrum c) (recorded after addition of



Scheme 11. Influence of pyridine addition on the desorption of the products.

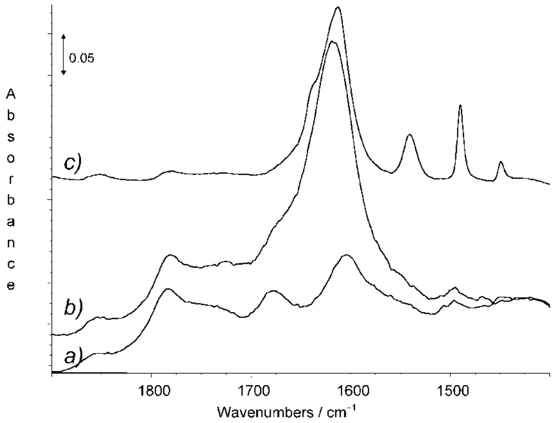


Figure 2. FTIR spectra of adsorbates after *a)* air-toluene flow, *b)* air-toluene-water vapour flow and *c)* air-toluene-4% aqueous pyridine vapour flow.

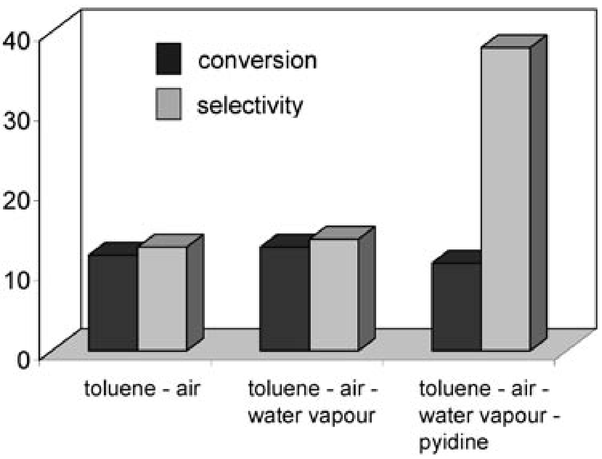


Figure 3. Comparison of benzaldehyde selectivity on VPP in the oxidation of toluene under comparable conditions, feeding toluene-air, toluene-air-water vapour and toluene-air-water vapour-pyridine (4% aqueous solution).

4% pyridine into the air/toluene stream), which shows mainly the bands corresponding to pyridine adsorbates, but no traces of aldehydes and only low intensities of cyclic anhydrides. This observation gives an indication that the addition of pyridine in the reactant feed mixture favours the fast desorption of aldehyde species from the catalyst surface. These findings in the spectra are also supported by the catalytic tests, which resulted in three-fold higher aldehyde selectivity with the addition of an appropriate amount of pyridine to the reactant feed mixture, as illustrated in Fig. 3.

In the same direction, the addition of alkali metal salts to vanadium-containing catalysts as described in[104,105] leads to an easier desorption of the desired aldehydes by surface basification. Such catalysts were also used in our earlier studies, which showed a significant increase in catalytic activity and aldehydes selectivity[115] (toluene conversion 17%, benzaldehyde selectivity 40% at 643 K).

The synthesis of substituted benzaldehydes is particularly of interest because the compounds are important as organic intermediates and fine chemicals.

Because the first step of the catalytic cycle is the chemisorption of the aromatic system forming a π complex on the surface, the electron density of the aromatic nucleus plays a role, and this should be influenced by the kind of substituent.

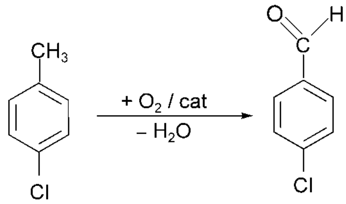
The comparison of the selective oxidation of the *p*-methoxy- and the *p*-chlorotoluene underlines this statement. Because *p*-methoxybenzaldehyde is an important compound in the production chain for pharmaceuticals and cosmetics. One can find the first results of industrial efforts on the gas phase operation beginning in the 1970s in Japan (Tanabe Seiyaka Co.[116,117]). The partial oxidation was carried out over V-P-Cu-O catalysts doped with K-sulphate and the yields of methoxybenzaldehyde were reported up to *ca.* 70%. Other research groups also reported on the role of acid-base properties of vanadium oxide systems that are already discussed in connection with the benzaldehyde formation above.[110–112]

Recently, Reddy et al.[118,119] reported the formation of *p-me*thoxybenzaldehyde over vanadium oxides on basic supports, but the yields over V_2O_5 on CaO-MgO are rather poor (10–15%). To achieve both high conversion and high aldehyde selectivity, on the one hand, the acid-base properties and, on the other hand, the redox activities of the catalysts are very important. With vanadium oxide on special binary oxides (e.g., Ga_2O_3-TiO_2; 1:5) Reddy et al.[120,121] obtained high *p-me*thoxybenzaldehyde yields of about 65%. The Table 1 gives information about the different catalytic performances reported recently.

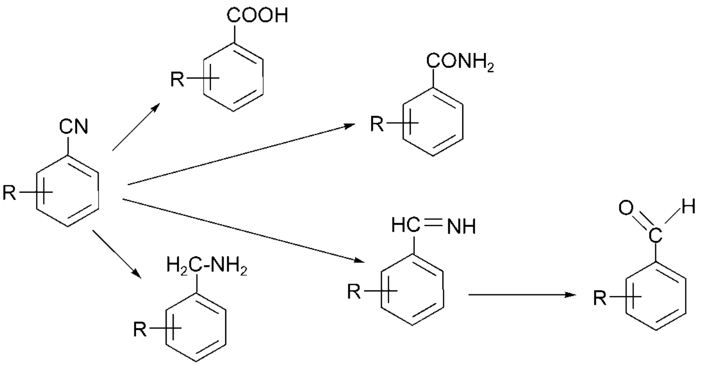
Because the performance of the catalysts depends on different factors such as catalyst composition, method of preparation, reaction conditions, etc., the reproducibility is sometimes also limited.

Reports on the selective oxidation of *p*-chlorotoluene to the corresponding aldehyde are rather limited (Scheme 12).

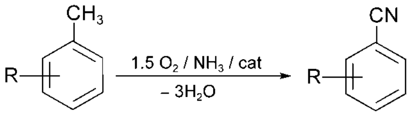
Chopra et al.[123] reported that the selective oxidation of *p*-chlorotoluene can be carried out over Bi-Mo-O sys-



Scheme 12. Oxidation of *p*-chlorotoluene to its corresponding aldehyde.



Scheme 13. Substituted aromatic nitriles as intermediates for aromatic acids, amides, imines, aldehydes and amines.



Scheme 14. Ammoxidation of various methyl aromatics to their corresponding nitriles.

tems achieving selectivities up to nearly 90% at a conversion level of 92% at 450 °C. However, these results could not be reproduced in other investigations. At the Hoechst Company a V-Cs-Fe-O-catalyst (doped with different transition metals) exhibited a *p*-chlorobenzaldehyde selectivity of about 20% at a conversion of nearly 70% at *ca.* 427 °C.[124]

The substantial difference between the chloro- and the methoxy-substituted aromatic compounds is the different influence of the substituent on the electron density of the aromatic nucleus resulting in the different strength of the chemisorption on the catalyst surface. This should result in a higher selectivity at higher conversion in the case of the selective oxidation of compounds with electron-withdrawing effects. Investigations about this consideration were taken up by the group of Ueshima.[111,112] In this study the ionisation potential of the reactant and the reactivity of the selective oxidation was compared by Dadyburjor et al.[125] These investigations resulted in the conclusion that the rate-determining step is the chemisorption step, that means the electron transfer from the aromatic component to the Lewis sorption site of the catalyst.[111] To stabilise the product selectivity, the formed aldehydes on the surface must be desorbed very quickly, before deeper oxidation can take place. This will be supported by weak chemisorption of the reactant molecule.

From the results of the selective oxidation of differently substituted toluenes it can be derived that, besides the redox properties of the catalyst, a well-balanced relation in the strength and distribution of acid (Lewis) and basic sites of the surface is also very important. This opens the way for a broad range of catalyst variations for the development of an optimum system.

5 Ammoxidation of Aromatic Side-Chains

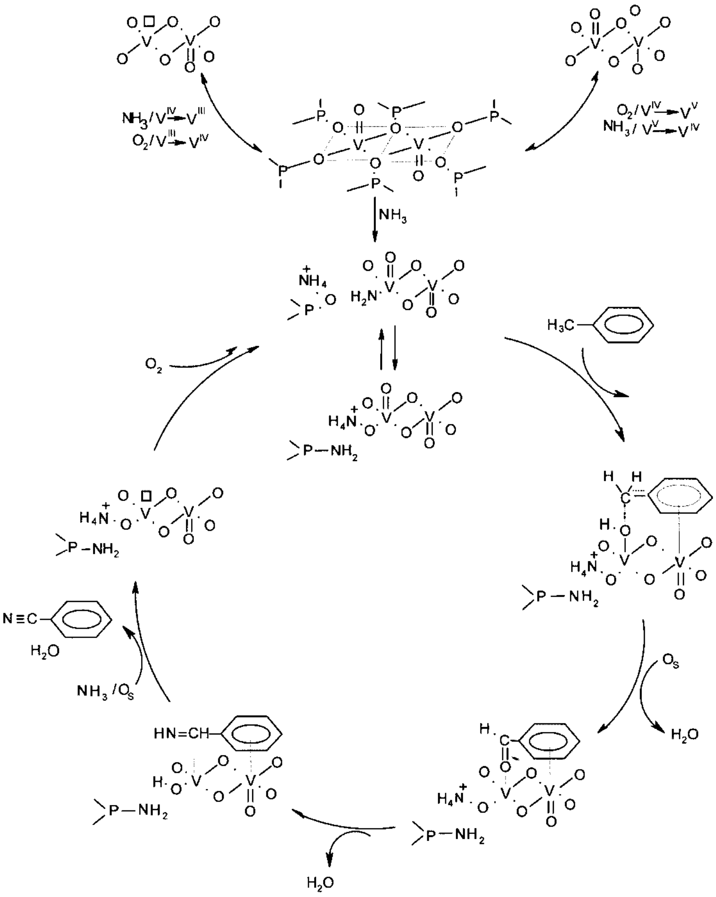
Aromatic nitriles are relatively stable under oxidation conditions even at higher temperatures compared to oxy products. Therefore these compounds, which can be easily synthesised from toluenes by ammoxidation, are used as intermediates for different subsequent hydrogenation or reduction steps (Scheme 13).

Compared with the selective oxidation of toluenes, which normally give lower yields of aldehydes, the ammoxidation results in distinctly higher yields of the desired nitrile product. Therefore, the ammoxidation reaction, which is briefly shown in Scheme 14, will be reported in more detail in this section.

This will cover different factors of influence on the reaction as well as steric and electronic effects of various substituents, also in combination with acid-base properties of catalyst surfaces. These investigations resulted in the conclusion that the catalytic activity and selectivity is primarily influenced by the electronic nature and the position of the substituent due to changes in the accessibility of the side-chain CH group as well as the possible stabilisation for reaction intermediates chemisorbed on the catalyst surface.

It is generally accepted that the reaction proceeds by chemisorption of the aromatic molecule on the catalyst surface through the formation of a π complex with a Lewis site of the catalyst, furthermore H abstraction of a benzylic H-atom to form a methylene-like species with parallel formation of water, then partial oxidation, N-insertion and subsequent rearrangements of the chemisorbed activated surface species and desorption of the so formed benzonitrile, followed by oxidative reconstruction of the catalyst surface. Particularly for adjacent surface VO groups as realised for $(VO)_2P_2O_7$ catalysts,[126] all the reaction steps can be formulated as shown in the following reaction scheme (Scheme 15).

Literature reports indicate[127,128] that the reactivity of the alkylbenzene in the ammoxidation reaction increases with increase in size of the alkyl groups in the side-chain.[129] The rate of ammoxidation of alkylbenzenes mainly depends on the chemical nature, size and structure of substituent, but for this aspect only few reports



Scheme 15. Reaction pathway for the formation of benzonitrile over a $(VO)_2P_2O_7$ catalyst, including toluene chemisorption, partial oxidation, N-insertion, nitrile desorption and catalyst reoxidation steps.

are available.[130] A critical analysis of both the open and the patent literature clearly reveals that the most active and selective catalysts that are generally used for different ammoxidations, particularly for methylaromatics/heteroaromatics, are based on V-Ti-O,[131,132] V-Mo-O,[133] V-Sb-O,[134] V-Zr-O,[135–137], bulk V-P-O[138,139] furthermore multi-component catalysts like KNiCoFeBiPMoOx on silica,[140] AgAIBOx,[141] VMoCrPdOx,[142] SbV-TiOx with additives[143], perovskii systems such as $YBaCu_3H_6$,[144] CeOx on TiO_2[145] and so on. Nowadays, zeolite-supported catalysts are also used,[146] e.g., V-Cu-H-ZSM-5,[147] Cu-Na-ZSM-5,[148] or Cu-Na-mordenite.[149] In addition, metal fluorides such as CeF_3, AlF_3 and MgF_2 have also been used in recent times as effective supports for vanadia catalysts for ammoxidation reactions.[150–152]

Selectivity determining factors are, on the one hand, the catalyst structure and texture and, on the other hand, also the substrate structure and the reaction mechanism. In general the redox mechanism with Mars-van-Krevelen kinetics is necessary and the catalytic systems (transition metal oxides) with easily changing the valence state (e.g., V, Mo) are preferred.

The common mechanistic features of alkylaromatics in the selective ammoxidation reactions are given in the earlier part of this review. Such a general mechanism was also proposed by Andersson and Lundin[153] for the ammoxidation of 3-methylpyridine. Depending on the catalyst, there are slight differences in some mechanistic steps, particularly in the discussion about the ammonia insertion and in the structure of the N-containing intermediate.

Murakami and Niwa[154,155] studied the toluene ammoxidation over V_2O_5/Al_2O_3 catalysts and suggested that the reaction proceeds *via* the reaction of ammonium ions with benzoate ions, which are detected as surface species by IR spectroscopy. Cavalli et al.[156a,157] proposed benzylamine and benzaldehyde species as reaction intermediates from their kinetic data in the ammoxidation of toluene over V_2O_5-TiO_2, which was in agreement with other results from this group reported by Busca et al.[158] A kinetic study by Otamiri and Andersson[159] suggests that vanadium imido (V=NH) or hydroxylamino (V-NH-OH) species may play a role as nitrogen insertion sites on the catalyst surface, consecutive reaction of which transform adsorbed toluene to an amine species (R-CH_2-NH_2) and subsequently to an imine (R-CH=NH) surface species followed by generation of the nitrile as the final desorbed product.

A further mechanistic scheme for the toluene ammoxidation over V_2O_5-TiO_2 catalysts suggested by Sanati and Andersson[160] includes $(C_6H_5)CH(NH_2)O$- and $(C_6H_5)CH(NH_2(CO\text{-})_2$ species as reaction intermediates. Amido groups, besides protonated and coordinated ammonia, in connection with the ammonia adsorption are also reported by Ramis et al.[161] Based on the results of pulse flow experiments Azimov et al.[162] postulated vanadium imido species (V=NH) and benzylamine surface species. Detailed mechanistic features about the ammoxidation of toluenes were derived from studies with vanadium phosphate catalysts. The mechanism of formation of surface intermediates of vanadyl diphosphate, $(VO)_2P_2O_7$ from feed components of the toluene ammoxidation was investigated by *in situ* FTIR spectroscopy and other methods.[163] This investigation underlined the preferred role of a benzaldehyde-like species, whereas the reaction pathway *via* benzamide or benzylamine intermediates seems to be not so probable. From this study a reaction pathway could be derived as shown in Scheme 15.

Adsorbed ammonia can exist in three different kinds of nitrogen-containing surface species such as protonated cation (NH_4^+), co-ordinately adsorbed NH_3 and $-NH_2$ groups. All these species may act as N-insertion species, and the concentration of these species increases by the interaction of ammonia with the catalyst surface at elevated temperatures.[164] In the catalytic reaction steps, the molecular geometry of the $(VO)_2P_2O_7$ catalyst may play a role (edge sharing VO_6 octahedra of the pyrophosphate): the coordinatively unsaturated part

(Lewis site) of the VO_6 dimer could chemisorb the aromatic ring *via* π complex formation and the partial oxidation can occur on the other site according to V...V distance of the vanadyl groups of about 3.4 Å[165] and the C−C ring and $C-CH_3$ distances of the toluene molecule of 1.4 Å and 1.52 Å,[166] respectively. The distance of the π complex centre to the methyl group carbon amounts to *ca.* 3 Å. The schematic view of the toluene chemisorption on the VO_6 octahedra units (100) is outlined elsewhere.[167]

The ammonia for the N-insertion should be chemisorbed and activated under the reaction conditions[158,168,169] but does not directly originate from the gas phase which was demonstrated by pulse experiments over ^{14}N-containing $(NH_4)_2(VO)_3P_2O_7$-catalyst using ^{15}N-containing ammonia ($^{15}NH_3$) gas in the reactant feed mixture.[170] In the ammoxidation, the role of ammonia involve different ways such as i) source for N-insertion, ii) partial reduction of the surface for enhancement of the selectivity[164,167] or iii) site blocking of weakly bound oxygen to decrease total oxidation.[156a,157,171]

Another important point to be considered in almost all ammoxidation reactions is NH_3 oxidation. There is always a competition between NH_3 oxidation and ammoxidation on the catalyst surface. Furthermore, the contact of ammonia with the catalyst surface, particularly at high temperatures, causes a partial reduction of the oxide surface due to the occurrence of NH_3 oxidation to N_2. Therefore, control of the rate of unselective oxidation of ammonia to N_2 (NO_x) has been reported[156] to be an important factor in determining the selectivity of the nitrile product, because this side reaction limits the availability of the surface ammonia species that are necessary for nitrile synthesis. Additionally, NH_3 oxidation not only leads to the consumption of extra NH_3 but also leads to the emission of undesired toxic compounds (i.e., NO_x). It is known from the literature[156] that ammonia oxidation is a faster reaction when compared to ammoxidation; addition of ammonia modifies the surface oxidation characteristics of the catalyst and decreases ammoxidation activity, especially at higher NH_3 concentrations in the feed gas. Nevertheless, it is also very difficult to completely avoid ammonia oxidation; it can only be minimised to the maximum possible extent.

5.1 Ammoxidation of Substituted Toluenes

The ammoxidation of substituted toluenes such as 1,2-, 1,3- or 1,4-methyl-substituted toluenes can result in mono- or dinitriles.[172,173] The ammoxidation of *o*-xylene gives *o*-tolunitrile, *o*-phthalodinitrile[174] and even phthalimide,[175,176] *m*-xylene is converted to *m*-tolunitrile and isophthalodinitrile,[177–179] and *p*-xylene is ammoxidised to either *p*-tolunitrile or terephthalodinitrile.[140] There are also a few reports on shape-selective ammoxidations, one such example is the ammoxidation of *m*- and *p*-xylenes over Cu-containing ZSM-5 zeolites to their corresponding mono- and dinitriles.[147,148] Besides dialkyl-substitutions, higher methylated benzene (e.g., mesitylene) can also be ammoxidised, however, with increase in the number of methyl groups the number of products will also increase (e.g., for mesitylene, nitrile formation result, from the ammoxidation of one, two and three methyl groups.[180,181] Furthermore, ammoxidations of substituted methylaromatics like α-methylstyrene to atroponitrile,[96,182] β-methylstyrene or allylbenzene to cinnamonitrile[183] are also reported in the literature.

5.2 Ammoxidation of Halogen-Substituted Toluenes

The activity and the nitrile selectivity of the ammoxidations of substituted toluenes, on the one hand, depend strongly on the position of the substituent, effecting a more hindered accessibility of the methyl group in the order $p < m < o$. A second substituent of the similar type could further strengthen the steric hindrance. On the other hand, electron-withdrawing substituents influence the strength of the chemisorption and the stabilisation of reaction intermediates, thus enhancing the nitrile yield whereas electron-donating substituents cause an increased total oxidation.

Therefore, halogen-substituted toluenes are easily converted into nitriles. The specific examples for this type are fluoro-, chloro-, bromo- and iodo-substituted toluenes.[184–187] The conversion rate of *p*-halotoluenes is found to be nearly independent of the nature of the halogen substituent, but the selectivity decreases in the sequence $p\text{-Cl} > p\text{-Br} >> p\text{-I}$ (over VPO-catalysts[184,186]). Nevertheless, the ammoxidation of the isomeric chlorotoluenes reveals changed conversions ($p >> o > m$) and selectivities ($p > o > m$) depending on the position of the substituent.[184,186,187]

Furthermore, the reaction of dichloro-substituted toluenes is much more influenced by the geometric position of the substituents, a closer proximity of the substituents to the methyl group results in lower conversions and nitrile selectivities (2,6-di-Cl < 2,5di-Cl < 2,3-di-Cl < 2,4-di-Cl < 3,4-di-Cl).[187,188] The 2,6-dichlorobenzonitrile, the ammoxidation product of 2,6-dichlorotoluene, is of particular industrial importance for the production of herbicides, pesticides and for preparing special kinds of engineering plastics with high thermal resistance. Therefore there have also been some attempts to reach acceptable yields of this compound.[189–191] Additionally, halogen-substituted xylenes can also be ammoxidised to their corresponding nitriles, e.g., 3,4,5,6-tetrachlorophthalodinitrile is formed from the corresponding chloro-substituted xylene in 45% yield.[192] Some recent patent applications for the ammoxidation of halo-toluenes are also cited here.[193–199]

5.3 Ammoxidation of Hydroxy- and Alkoxy-Substituted Toluenes

The ammoxidation of toluenes substituted with electron-donating groups is rather less selective. Nevertheless, under carefully chosen conditions (choice of the catalyst, feed composition, reaction conditions) sufficient yields of nitriles can be achieved. Particularly, the ammoxidation of hydroxytoluenes (cresols) is difficult. However, a direct synthesis of *p*-hydroxybenzonitrile is possible using bismuth-molybdenum oxide, iron-antimony oxide or uranium-antimony oxide catalysts[200] that are normally used for the ammoxidation of propylene. Unfortunately, the catalysts are rapidly deactivated by coke formation. Better results are described for these reactions by the use of boron phosphates[201,202] with highly diluted feed gas (cresol: $NH_3 : air : N_2 = 1 : 10 : 40 : 120$). Landau et al. [203] obtained 63% *p*-hydroxybenzonitrile, over silica supported B-P catalyst, which, however is deactivated by the deposition of polymeric residues, but can be regenerated in a mixture of air, N_2 and steam.

In contrast to the chemisorption mode of alkylaromatics (flat chemisorption by π-complex formation with the possibility of methyl group activation), the cresols are chemisorbed perpendicularly at the surface (formation of a phenoxide ion) hampering the activation of the methyl group.[204] Further examples for the cresol ammoxidation are given in references.[205–207].

For this type of ammoxidations the OH group can be protected by methylation to change the mode of chemisorption. Thus, the ammoxidation of *p*-methoxytoluene can be carried out over V/Ti oxides in 65% yield.[200,208] Due to differences in the reactivity mixtures of *m*- and *p*-methoxytoluenes, they can be ammoxidised under reactive separation to *p*-methoxybenzonitrile and unreacted *m*-methoxytoluene.[208]

The higher electron density of the aromatic nucleus given by the electron-donating substituent leads to a stronger adsorption during the reaction cycle and hampers the faster desorption of products resulting in more unselective consecutive/secondary reactions.[167] Further reports on the ammoxidation of *p*-methoxytoluene are given by Zheng et al. over VPO/SiO_2 catalysts[209] and Cavani et al. over V-Ti-O catalysts.[210]

The ammoxidation of methoxy- and isomeric phenoxytoluenes is described by Ivanov using V/Sb/Cr/O catalysts.[211] The formation of phenoxybenzonitrile with 58% selectivity at 85% conversion over a multi-component catalyst at 420 °C is also described elsewhere.[212]

Other protective groups for the OH function (e.g., acylation) seem to be not much preferred due to the easy decomposition of the acyl group under thereaction conditions. For example, acetoxy-*o*-xylene cannot be ammoxidised to its corresponding nitriles or acetoxyphthalic acid derivatives.[213] On the other hand, 9,10-bis-(acetoxymethyl)anthracene was converted to 10-(acetoxymethyl)anthracene-9-carbonitrile in 64% yield.[214]

6 Conclusions

On the whole, it can be stated that the hydroxylation of aromatic compounds with various oxidants and catalysts can be conducted with relatively high conversions and selectivities, which would certainly be of interest from a practical point of view. So far, N_2O and hydrogen peroxides have yielded the best results. However, in many published results the selectivity of the product formation based on the educts is not given but only the product distribution in the mixture of all oxidation products. Therefore, comparisons of the published results are difficult. Other unsolved problems are the leaching of the redox metals in heterogeneous catalysts and the low selectivity of the hydroxylated aromatic compounds based on oxidants such as hydrogen peroxide.

The ammoxidation of methylaromatic compounds is a convenient route to produce many nitriles required for further syntheses of side-chain functionalised products. This method is versatile and can be carried out very easily due to the stability and undamaged desorption of the formed nitriles under severe gas phase conditions. This research should certainly open the way for further, broader application of the ammoxidation as a normal tool of the organic chemist.

The formation of side-chain alcohols (*via* acetoxylation) or aldehydes (by direct gas phase oxidation) is rather limited due to some selectivity limitations. This field is still under development and will be opened step by step for organic synthesis in the near future.

The direct oxidation of the aromatic nucleus is a real challenge and a useful reaction for the production of commodities (phenol, diphenols) as well as substituted phenols for further syntheses of valuable chemicals. Up to now, the application of this reaction for organic synthesis is also rather limited. Nevertheless, the approaches with alternative oxidants are promising.

References

[1] a) B. Lücke, A. Martin, *The Future Role of Aromatics in Refining and Petrochemistry*, (Proc.of the DGMK-Conference on Petrochemistry, Erlangen, Germany, **1999**, p. 139; b) J. Haber, in: *Perspectives in Catalysis*, IUPAC, (Eds.: J. M. Thomas, K. I. Zamarev), Oxford, Blackwell Scientific Publications, **1992**, p. 371.

[2] P. Arpentinier, F. Cavani, F. Trifiro, *The Technology of Catalytic Oxidations*, Editions Technip, Paris, **2001**.

[3] G. Centi, F. Cavani, F. Trifiro, in: *Selective Oxidation by Heterogeneous Catalysis*, (Eds.: M. V. Twigg, M. S. Spencer), Kluwer Academic/Plenum Publ., New York, **2001**.

[4] A. Bielanski, J. Haber, *Catal. Rev. Sci. Eng.* **1979**,*19*, 1.

[5] J. Bielanski, J. Haber, *Oxygen in Catalysis*, Marcel Dekker, New York, **1991**.

[6] C. Friedel, J. M. Crafts, *Ann. Chim.* (Paris) **1888**, 14, 935.

[7] IG Farben, *German Patent* DE 501467, **1927**.

[8] Socony-vacuum oil Co.; *U. S. Patent* 2,456,597, **1948**; *Chem. Abstr*. **1949**, 1805.

[9] H. Yamanaka, R. Hamada, H. Nibuta, S. Nishiyama, S. Tsuruya, *J. Mol. Catal. A: Chemical* **2002**, *178*, 89.

[10] I. Yamanaka, M. Katagiri, S. Takenaka, K. Otsuka, *Stud. Surf. Sci. Catal.* **2000**, *130*, 809.

[11] S. Ito, A. Kunai, H. Okada, K. Sasaki, *J. Org. Chem.* **1988**, *53*, 296.

[12] L. C. Passoni, A. T. Cruz, R. Buffon, U. Schuchardt, *J. Mol. Catal. A: Chemical* **1997**, *120*, 117.

[13] S. Goto, Y.-J. Seo, Y. Mukai, T. Tagawa, *J. Mol. Catal. A: Chemical* **1997**, *120*, 149.

[14] U. Schuchardt, A. T. Cruz, C. H. Collins, L. C. Passoni, *Stud. Surf. Sci. Catal.* **1994**, *82*, 551.

[15] *Chem. Eng. News* **1993**, 23.

[16] B. Cornils, W. A. Herrmann, *J. Catal.* **2003**, *216*, 23.

[17] S. Udenfriend, C. T. Clark, J. Axelrod, B. B. Brodie, *J. Biol. Chem.* **1954**, *208*, 731.

[18] P. R. Grinstead, *J. Am. Chem. Soc.* **1960**, *82*, 3472.

[19] M. B. Dearden, C. R. E. Jefcoate, J. R. Lindsay, *Adv. Chem. Ser.* **1968**, *70*, 260.

[20] J. R. Lindsay, B. A. J. Shaw, D. M. Foulkes, A. M. Jeffrey, D. M. Jerina, *J. Chem. Soc. Perkin Trans.* 2 **1977**, 1583.

[21] S. Ito, K. Ueno, A. Mitarai, K. Sasaki, *J. Chem. Soc. Perkin Trans. 2* **1993**, 255.

[22] T. Ohtani, S. Nishiyama, S. Tsuruya, M. Masai, *J. Catal.***1995**, *155*, 158.

[23] J. Okamura, S. Nishiyama, S. Tsuruya, M. Masai, *J. Mol. Catal. A: Chemical* **1998**, *135*, 133.

[24] T. Miyahara, H. Kanzaki, R. Hamada, S. Kuroiwa, S. Nishiyama, S. Tsuruya, *J. Mol. Catal. A: Chemical* **2001**, *176*, 141.

[25] E. Battistel, R. Tassinari, M. Fornaroli, L. Bonoldi, *J. Mol. Catal. A: Chemical* **2003**, *202*, 107.

[26] Y. Masumoto, R. Hamada, K. Yokota, S. Nishiyama, S. Tsuruya, *J. Mol. Catal. A: Chemical* **2002**, *184*, 215.

[27] A. Kunai, T. Kitano, Y. Kuroda, J. Li-Fen, K. Sasaki, *Catal. Lett.* **1990**, *4*, 139.

[28] T. Kitano, T. Nakai, M. Nitta, M. Mori, S. Ito, K. Sasaki, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2850.

[29] T. Kitano, Y. Kuroda, M. Mori, S. Ito, K. Sasaki, M. Nitta, *J. Chem. Soc. Perkin Trans. 2* **1993**, 981.

[30] T. Kitano, Y. Kuroda, A. Itoh, J. Li-Fen, A. Kunai, K. Sasaki, *J. Chem. Soc. Perkin Trans. 2* **1990**, 1991.

[31] Y. Kuroda, M. Mori, A. Itoh, T. Kitano, F. Yamaguchi, K. Sasaki. M. Nitta, *J. Mol. Catal. A* **1992**, *73*, 237.

[32] A. Kunai, T. Wani, Y. Uehara, F. Iwasaki, Y. Kuroda, S. Ito, K. Sasaki, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2613.

[33] T. Tatsumi, K. Yuasa, H. Tominaga, *J. Chem. Soc. Chem. Commun.* **1992**, 1446.

[34] T. Miyake, M. Hamada, Y. Sasaki, M. Oguri, *Appl. Catal. A: General* **1995**, *131*, 33.

[35] H. Ehrich, H. Berndt, M.-M. Pohl, K. Jähnisch. M. Baerns, *Appl. Catal. A: General* **2002**, *230*, 271.

[36] T. Miyake, M. Hamada, H. Niwa, M. Nishizuka, M. Oguri, *J. Mol. Catal. A: Chemical* **2002**, *178*, 199.

[37] J. E. Remias, T. A. Pavlovsky, A. Sen, *J. Mol. Catal. A: Chemical* **2003**, *203*, 179.

[38] W. Laufer, W. F. Hölderich, *J. Chem. Soc. Chem. Commun.* ***2002***, 1684.

[39] W. Laufer, J. P. M. Niederer, W. F. Hölderich, *Adv. Synth. Catal.* ***2002***, *344*, 1084.

[40] T. Jintoku, H. Taniguchi, Y. Fujimara, *Chem. Lett*. **1987**, 1865.

[41] T. Jintoku, K. Takak, Y. Fujimara, Y. Fuchita, K. Hiraki, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 438.

[42] T. Jintoku, K. Nishimura, K. Takaki, *Chem. Lett*. **1990**, 1687.

[43] S. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba, F. Mizukami, *Science* **2002**, *295*, 105.

[44] M. Gubelmann, P. Tirel, (Rhone-Poulenc Chimie), *EP 0341165*, **1988**.

[45] R. Burch, C. Howitt, *Appl. Catal. A: General* **1993**, *103*, 135.

[46] M. Häfele, A. Reitzmann, D. Roppelt, G. Emig, *Appl. Catal. A: General* **1997**, *150*, 153.

[47] G. I. Panov, A. S. Kharitonov, V. I. Sobelev, *Appl. Catal. A: General*, **1993**, *98*, 1.

[48] G. I. Panov, V. I. Sobolev, K. A. Dubkov, A. S. Kharitonov, *Stud. Surf. Sci. Catal.* **1996**, *101*, 493.

[49] G. I. Panov, A. K. Uriarte, M. A. Rodkin, V. I. Sobolev, *Catal. Today* **1998**, *41*, 365.

[50] D. P. Ivanov, V. I. Sobolev, G. I. Panov, *Appl. Catal. A.: General* **2003**, *241*, 113.

[51] K. A. Dubkov, N. S. Ovanesyan, A. A. Shteinman, E. V. Starokon, G. I. Panov, *J. Catal.* **2002**, *207*, 341.

[52] M. Häfele, A. Reitzmann, D. Roppelt, G. Emig, *Erdöl, Erdgas, Kohle* **1996**, *112*, 512.

[53] J. L. Motz, H. Heinichen, W. F. Hölderich, *J. Mol. Catal. A: Chemical* **1998**, *136*, 175.

[54] W. F. Hölderich, *Appl. Catal. A: General* **2000**, *194–195*, 487.

[55] A. K. Uriarte, M. A. Rodkin, M. J. Gross, A. S. Kharitonov, G. I. Panov, *Stud. Surf. Sci. Catal.* **1997**, *110*, 857.

[56] S. Ito, A. Mitarai, K. Hikino, M. Hirama, K. Sasaki, *J. Org. Chem.* **1992**, *57*, 6937.

[57] T. Kurat, Y. Watanabe, M. Katoh, Y. Sawaki, *J. Am. Chem. Soc.* **1988**, *110*, 7472.

[58] A. Kunai, S. Hata, S. Ito, K. Sasaki, *J. Am. Chem. Soc.* **1986**, *108*, 6012.

[59] E. A. Karakhanov, C. J. Narin, T. J. Filippova, A. G. Dedov, *Dolk. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1387.

[60] S. Menage, J. M. Vincent, C. Lambeaut, M. Fontecave, *J. Chem. Soc. Dalton Trans.* **1994**, 2081.

[61] D. Bianchi, R. Bortolo, R. Tassinari, M. Ricci, R. Vignola, *Angew. Chem.* **2000**, *112*, 4491.

[62] M. Stöckmann, F. Konietzni, J. U. Notheis, J. Voss, W. Keune, W. F. Maier, *Appl. Catal. A: General* **2001**, *208*, 343.

[63] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, R. Weiss, *J. Am. Chem. Soc.* **1983**, *105*, 3101.

[64] M. Bonchio, V. Conte, F. Di Furia, G. Modena, *J. Org. Chem.* **1989**, *54*, 4368.

[65] M. Bonchio, V. Conte, F. Di Furia, G. Modena, S. Moro, *J. Org. Chem.* **1994**, *59*, 6262.

[66] S. K. Das, A. Kumar Jr., S. Nandrajog, A. Kumar, *Tetrahedron Lett.* **1995**, *36*, 7909.

[67] Y.-W. Chen, Y.-H. Lu, *Ind. Eng. Chem. Res.* **1999**, *38*, 1893.

[68] K. Lemke, H. Ehrich, U. Lohse, H. Berndt, K. Jähnisch, *Appl. Catal. A: General* **2003**, *243*, 41.

[69] P. T. Tanev, M. Chibwe, T. J. Pinnavaia, *Nature* **1994**, *368*, 321.

[70] A. Keshavaraja, V. Ramaswamy, H. S. Soni, A. V. Ramaswamy, P. Ratnasamy, *J. Catal.* **1995**, *157*, 501.

[71] A. V. Ramaswamy, S. Sivasanker, P. Ratnasamy, *Microp. Mater.* **1994**, *2*, 451.

[72] W. Zhang, J. Wang, P. T. Tanev, T. J. Pinnavaia, *J. Chem. Soc. Chem. Commun.* **1996**, 979.

[73] H. Jing, Z. Guo, H. Ma, D. G. Evans, X. Duan, *J. Catal.* **2002**, *212*, 22.

[74] A. Bhaumik, P. Mukherjee, R. Kumar, *J. Catal.* **1998**, *178*, 101.

[75] R. Kumar, P. Mukherjee, A. Bhaumik, *Catal. Today.* **1999**, *49*, 185.

[76] J. F. Bengoa, N. G. Gallegos, S. G. Marchetti, A. M. Alvarez, M. V. Cagnoli, A. A. Yeramian, *Microp. Mesop. Mater.* **1998**, *24*, 163.

[77] C. Perego, A. Carati, P. Ingallina, M. A. Mantegazza, G. Bellussi, *Appl. Catal. A: General* **2001**, *221*, 63.

[78] D. P. Ivanov, V. I. Sobolev, L. V. Pirutko, G. I. Panov, *Adv. Synth. Catal.* **2002**, *344*, 986.

[79] A. V. Ramaswamy, S. Sivasanker, *Cat. Lett.* **1993**, *22*, 239.

[80] K. Nomiya, K. Hashino, Y.Nemoto, M. Watanabe, *J. Mol. Catal. A: General* **2001**, *176*, 79.

[81] R. Kumar, A. Bhaumik, *Microp. Mesop. Mater.* **1998**, *21*, 497.

[82] B. Vogel, C. Schneider, E. Klemm, *Catal. Lett.* **2002**, *79*, 107.

[83] C. B. Khouw, C. B. Dartt, J. A. Labinger, M. E. Davis, *J. Catal.* **1994**, *149*, 195.

[84] K. Bahranowski, M. Gasior, A. Kielski, J. Podobinski, E. M. Serwicka, L. A. Vartikian, K. Wodnicka, *Clay Miner.* **1999**, *43*, 79.

[85] M. Gubelmann, P. Tirel, (Rhone-Poulenc-Chimie), *EP 341 113*, **1989**.

[86] M. Gubelmann, J. Popa, P. Tirel, (Rhone-Poulenc-Chimie); *EP 406 050*, **1990**.

[87] L. M. Kustov, A. L. Tarasov, V. I. Bogdan, A. A. Tyrlov, J. W. Fulmer, *Catal. Today* **2000**, *61*, 123.

[88] H. Ehrich, W. Schwieger, K. Jähnisch, *Appl. Catal. A (Gen.)* **2004**, submitted.

[89] E. Benazzi, C. J. Cameron, *J. Mol. Catal. A* **1991**, *69*, 299.

[90] M. Constatini, L. Krumenacker, *Stud. Surf. Sci. Catal.* **1980**, *4*, 158.

[91] B. Grzybowska, M. Czerwenka, J. Sloczynski, *Catal. Today* **1987**, *1*, 157.

[92] L. M. Stock, K.Tse, L. J. Vorvick, S. A. Walstrum, *J. Org. Chem.* **1981**, *46*, 1757.

[93] M. O. Unger, R. A. Fouty, *J. Org. Chem.* **1969**, *34*, 18.

[94] J. M. Davidson, C. Triggs, *J. Chem. Soc. (A)* **1968**,1331.

[95] R. van Helden, G. Verberg, *Recl. Trav. Chim. Pay Bas* **1965**, 84.

[96] D. R. Bryant, J. E. McKeon, B. C. Ream, *J. Org. Chem.* **1968**, *33*, 4123.

[97] C. H. Bushweller, *Tetrahedron Lett.* **1968**, 6123.

[98] E. Benazzi, H. Mimoun, C. J. Cameron, *J. Catal.* **1993**, *140*, 311.

[99] S. K. Tanielyan, R. L. Augustine, *J. Mol. Catal.* **1994**, *87*, 311.

[100] S. K. Tanielyan, R. L.Augustine, *J. Mol. Catal.* **1994**, *90*, 267.

[101] T. Komatsu, K. Inabe, T. Uezono, A. Onda, T. Yashima, *Appl. Catal .A* **2003**, *251*, 315.

[102] A. Benhmid, K. V. Narayana, A. Martin, B. Lücke, personal communication, **2003**.

[103] F. Brühne, E. Wright in: *Ullmann's Encylopedia of Technical Chemistry*, (benzaldehyde entry), 6th Edition, Electronic Release, Wiley-VCH, Weinheim, **1998**.

[104] A. Kaszanyi, M. Antol, M. Hronec, G. Delahay, D. Ballivet-Thatchenko, *Collect. Czech. Chem. Commun.* **1995**, *60*, 505.

[105] M. Ponzi, C. Duschatzky, A. Carrascull, E. Pozzi, *Appl. Catal. A* **1998**, *169* 373.

[106] Y. Fan, W. Kuang, W. Zhang, Yi Chen, *Stud. Surf. Sci. Catal.* **1997**, *110*, 903.

[107] A. Aguilar Elguizabal, V. Cortes Correbbaran, *Catal. Today* **1996**, *32*, 265.

[108] G. Centi, F. Fazzini, L. Canesson, A. Tuel, *Stud. Surf. Sci. Catal* **1997**, *110*, 893.

[109] J. S. Yoo, *Appl. Catal. A* **1996**, *143*, 29.

[110] N. Shimizu, N. Saito, M. Ueshima, *Stud. Surf. Sci. Catal.* **1988**, *44*, 131.

[111] M. Ueshima, N. Saito, N. Shimizu, *Stud. Surf. Sci. Catal.* **1994**, *90*, 59.

[112] M. Ueshima, N. Saito, *Chem. Lett.* **1992**, 1341.

[113] A. Martin, U. Bentrup, A. Brückner, B. Lücke, *Catal. Lett.* **1999**, *59*, 61.

[114] A. Martin, U. Bentrup, B. Lücke, A. Brückner, *J. Chem. Soc. Chem. Commun.* **1999**, 1169.

[115] A. Martin, B. Lücke, in: *Catalysis of Organic Reactions*, (Ed.: M. E. Ford), Marcel Dekker, New York. Basel, **2000**, p. 346.

[116] Tanabe Seiyaku Co., *US Patent 4,054,607*, **1977**.

[117] H. Seko, Y. Tokuda, M. Matsuoka, *Nippon Kagaku Kaishi* **1979**, 558.

[118] B. M. Reddy, M. V. Kumar, K. J. Ratnam, *Res. Chem. Intermed* **1998**, *24*, 919.

[119] B. M. Reddy, M. V. Kumar, K. J. Ratnam, *Appl. Catal. A* **1999**, *181*, 77.

[120] B. M. Reddy, I. Ganesh, B. Chowdary, *Chem. Lett.* **1997**,1145.

[121] B. M. Reddy, I. Ganesh, B. Chowdary, *Catal. Today* **1999**, *49*, 115.

[122] A. Martin, B. Lücke, personal communication.

[123] M. B. Chopra, V. Ramakrishna, *Indian Chem. J.* **1974**, *72*, 38; *Chem. Abstr.* **1974**, *80*, 119931.

[124] Hoechst AG, *European Patent* 0723949, **1996**.

[125] D. B. Dadyburjor, S. Jewur, E. Ruckenstein, *Catal. Rev. Sci. Eng.* **1979**, *19*, 293.

[126] Y. Zhang, A. Martin, H. Berndt, B. Lücke, M. Meisel, *J. Mol. Catal. A* **1997**, *110*, 919.

[127] K. J. Aredshidze, G. O. Shikadze, C. J. Naskidashvili, *Izv. Akad. Nauk, Gruz. SSR* **1974**, *76*, 89.

[128] A. D. Kagerlitzki, B. V. Suvorov, S. R. Rafikov, A. S. Kosronim, *Zh. Prikl. Khim.* **1963**, *36*,1848.

[129] I. M. Chmyr, N. R. Bukeiklavo, B. V. Suvorov, *Izv. Akad. Nauk. Kaz. SSR, Ser. Khim.* **1983**, *36*, 43.

[130] A. Martin, B. Lücke, *Catal. Today* **2000**, *57*, 61.

[131] a) P. Cavalli, F. Cavani, I. Manenti, F. Trifiro, *Catal. Today* **1987**, *1*, 245; b) M. Sanati, A. Andersson, *J. Mol. Catal.* **1990**, *59*, 233.

[132] a) K. V. Narayana, A. Venugopal, K. S. Rama Rao, V. Venkat Rao, S. Khaja Masthan, P. Kanta Rao, *Appl. Catal. A* **1997**, *150*, 269; b) K. V. Narayana, A. Venugopal, K. S. Rama Rao, S. Khaja Masthan V. Venkat Rao, P. Kanta Rao, *Appl. Catal. A* **1997**, *167*, 11.

[133] W. S. Chen, H. B. Chiany, M. D. Lee, *J. Chin. Chem. Eng.* **1994**, *25*, 45.

[134] A. Andersson, S. L. T. Andersson, G. Centi, R. K. Grasselli, M. Sanati, F. Trifiro, *Appl. Catal. A* **1994**, *43*, 43.

[135] M. Sanati, A. Andersson, L. R. Wallenberg, B. Rebenstorf, *Appl. Catal. A* **1993**, *106*, 51.

[136] L. Makedonski, V. Nikolov, N. Nikolov, U. Blaskov, *React. Kinet. Catal. Lett.* **1999**, *66*, 237.

[137] K. V. R. Chary, G. Kishan, K. V. Narayana, T. Bhaskar, *J. Chem. Res. S* **1998**, 314.

[138] M. B. Reddy, M. V. Kumar, B. Manohar, *Chem. Ind. Series.* Vol. 62 (Eds.: M. G. Scaros, M. C. Prunier), Marcel Dekker, New York, **1995**, p. 487.

[139] A. Martin, G.-U. Wolf, U. Steinicke, B. Lücke, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2227.

[140] Standard Oil of Ohio, *German Patent DE 2314151*, **1973**; *Chem. Abstr.* **1974**, *80*, 3281e.

[141] Amoco Co., *US Patent 4,766,102*, **1980**; *Chem. Abstr.* **1990**, *112*, 12538a.

[142] Hodogaga Chem. Co., *Japan Patent 0344362*, **1991**; *Chem. Abstr.* **1991**, *114*, 246976 h.

[143] Degussa AG, *European Patent 726092*, **1996**; *Chem. Abstr.* **1996**, *125*, 225060n.

[144] J. C. Otamiri, S. L. T. Andersson, A. Andersson, *Appl. Catal. A* **1990**, *65*, 159.

[145] P. Kanta Rao, K. S. Rama Rao, S. K. Masthan, K. V. Narayana, T. Rajiah, V. V. Rao, *Appl. Catal. A* **1997**, *163*, 123.

[146] F. Cavani, F. Trifiro, P. Jiru, K. Habersberger, Z. Tvaruzkova, *Zeolites* **1988**, *8*, 12.

[147] a) K. Beschmann, S. Fuchs, T. Hahn, *Chem.-Ing. Techn.* **1998**, *70*, 1436; b) K. Beschmann, L. Riekert, *Chem.-Ing. Techn.* **1993**, *70*, 1251.

[148] S. H. Kim, H. Chon, *Appl. Catal. A* **1992**, *85*, 47.

[149] J. Fu, I. Ferino, R. Monaci, E. Rombi, V. Salinas L. Fornib, *Appl. Catal. A* **1997**, *154*, 241.

[150] K. V. Narayana, S. Khaja Masthan, V. Venkat Rao, P. Kanta Rao, *J. Chem. Res. S* **1997**, 328.

[151] K. V. Narayana, S. Khaja Masthan, V. Venkat Rao, B. David Raju, P. Kanta Rao, *Catal. Commun.* **2002**, *3*, 173.

[152] K. V. Narayana, S. Khaja Masthan, V. Venkat Rao, B. David Raju, P. Kanta Rao, *Catal. Lett.* **2002**, *48*, 27.

[153] A. Andersson, S. T. Lundin, *J. Catal.* **1979**, *58*, 383.

[154] J. Y. Murakami, M. Niwa, T. Hattori, S. Osawa, S. Igushi, H. Ando, *J. Catal.* **1977**, *49*, 83.

[155] M. Niwa, H. Ando, H. Murakami, *J. Catal.* **1977**, *49*, 92.

[156] a) P. Cavalli, F. Cavani, F. Manenti, F. Trifiro, *Ind. Eng. Chem. Res.* **1987**, *26*, 639; b) G. Centi, F. Marchi, S. Perathoner, *Appl. Catal. A* **1997**, *149*, 225.

[157] P. Cavalli, F. Cavani, I. Manenti, F. Trifiro, M. El-Sawi, *Ind. Eng. Chem. Res.* **1987**, *26*, 804.

[158] G. Busca, F. Cavani, F. Trifiro, *J. Catal.* **1987**, *106*, 471.

[159] J. Otamiri, A. Andersson, *Catal. Today* **1988**, *3*, 211 and 223.

[160] M. Sanati, A. Andersson, *J. Mol. Catal. A* **1993**, *81*, 51.

[161] G. Ramis, G. Busca, F. Bregani, P. Forzatti, *Appl. Catal. A* **1990**, *64*, 259.

[162] A. B. Azimov, V. P. Vislovskii, E. A. Mamedov, R. G. Rizaev, *J. Catal.* **1991**, *127*, 354.

[163] Y. Zhang, A. Martin, H. Berndt, B. Lücke, M. Meisel, *J. Mol. Catal. A* **1997**, *118*, 205.

[164] H. Berndt, K. Büker, A. Martin, A. Brückner, B. Lücke, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 725.

[165] M. R. Thompson, A. C. Hess, J. B. Nicholas, J. C. White, J. Anchell, J. R. Ebner, *Stud. Surf. Sci. Catal.* **1994**, *82*, 167.

[166] *Handbook of Chemistry and Physics*, 75th edn., CRL Press, Boca Raton, **1995**.

[167] A. Martin, A. Brückner, Y. Zhang, B. Lücke, *Stud. Surf. Sci. Catal.* **1997**, *108*, 377.

[168] Yu. V. Belokpytov, K. M. Kholyavenko, S. V. Gerei, *J. Catal.* **1979**, *60*, 1.

[169] M. Takagi-Kavai, M. Soma, T. Onishi, K. Tamaru, *Can. J. Chem.* **1980**, *58*, 2132.

[170] A. Martin, Y. Zhang, H.-W. Zanthoff, M. Meisel, M. Baerns, *Appl. Catal. A* **1996**, *139*, L11.

[171] R. K. Grasselli, *J. Chem. Ed.* **1986**, *63*, 216.

[172] R. G. Rizayev, E. A. Mamedov, V. P. Vislovskii, V. E. Sheimin, *Appl. Catal. A* **1992**, *83*, 103.

[173] M. C. Sze, A. P. Gelbein, *Hydrocarbon Processing*, **1979**, *55*, 103.

[174] L. L. Saurambaeva, I. S. Kolodina, D. Kh. Sembaev, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* **1991**, *4*, 80.

[175] Inst. Chem., Akad. Sciences, Kazhak. SSR, *SU Patent 169998*, **1991**; *Chem. Abstr.* **1992**, *116*, 235437a.

[176] BASF, *European Patent 0767165*, **1997**; *Chem. Abstr.* **1997**, *126*, 293193k.

[177] Standard Oil of Ohio, *US Patent 5,183,793*, **1993**; *Chem. Abstr.* **1993**, *118*, 194026n.

[178] T. Romotowski, J. Komorek, J. Stock, *Pol. J. Chem.* **1998**, *72*, 2450.

[179] T. Romotowski, J. Komorek, V. Tershik, *Pol. J. Chem.* **1998**, *72*, 2564.

[180] A. S. Zulhasheva, N. R. Bukeikhanov, B. V. Suvorov, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* **1986**, *1*, 56.

[181] T. Ono, Y. Nakagava, Y. Kubokawa, *Bull. Chem. Soc. Jpn*. **1981**, *54*, 343.

[182] R. K. Grasselli, J. D. Burrington, D. D. Suresh, M. S. Friedrich, M. A. Hazle, *J. Catal.* **1981**, *68*, 109.

[183] R. K. Grasselli, J. D. Burrington, D. D. Suresh, M. S. Friedrich, M. A. Hazle, *J. Catal.* **1981**, *41*, 317.

[184] A. Martin, B. Lücke, *Catal. Today.* **1996**, *32*, 279.

[185] A. Martin, B. Lücke, *Chem. Ind. Series,* Marcel Dekker, New York, **2001**, Vol. 82, 337.

[186] A. Martin, B. Lücke, *Chem. Ind. Series,* Marcel Dekker, New York, **1996**, Vol. *68*, 451.

[187] A. Martin, B. Lücke, G.-U. Wolf, M. Meisel, *Chem.-Ing. Tech.* **1994**, *66*, 948.

[188] A. Martin, B. Lücke, G.-U. Wolf, M. Meisel, *Catal. Lett.* **1995**, *33*, 349.

[189] K. Omoto, A. Imai, T. Hanada, H. Mito, Hodogaya Chem. Corp., *Japan. Pat. 0344362*, **1991**; *Chem. Abstr.* **1991**, *114*, 246976k.

[190] Q. Zheng, H. Huang, Q. Han, C. Xu, G. Chen, Y. Chen, *Wukan Daxue Xuebao, Ziran Kexueban* **1998**, 44, 167; *Chem. Abstr.* **1998**, *129*, 291385u.

[191] Nitto Kagaku Kogyo K. K., *German Patent 746883*, **1998**; *Chem. Abstr.* **1998**, *128*, 32131z.

[192] A. A. Shapalov, D. Kh. Sembaev, *Izv. Minist. Nauki-Akad. Nauk Resp. Kaz. Ser. Chim.* **1996**, *2*, 89.

[193] X. H. Diao, Y. L. Yang, W. Y. Wang, W. Y. Li, J. B. Zhang, *Hebei Keji Daxue Xuebao* **2000**, *21*, 84; *Chem. Abstr.* **2001**, *134*, 224265.

[194] C. Huang, Y. Zheng, G. Xie, C. Xu, Y. Chen, *Huxue Shiji* **2000**, *22*, 182.

[195] *Chinese Patent CN 1230464 A*, **1999**; *Chem. Abstr.* **2000**, *133*, 49564.

[196] J. H. Chen, *Jingai Huagong* **1999**, *16*, 6; *Chem. Abstr.* **2000**, *132*, 295324.

[197] C. Huang Q. Zhen, G. Xie, C. Xu, Q. Han, Y. Chen, *Cuihua Xuebo* **1999**, *20*, 679; *Chem. Abstr.* **2000**, *132*, 109720.

[198] *Chinese Patent CN 1168378 A*, **1997**; *Chem. Abstr.* **2000**; *132*, 65726.

[199] C. Huang, Q. Zheng, G. Y. Xie, C. W. Xu, G. Q. Chen, Y. Y. Chen, *Wuhan Daxue Xuebao, Ziran Kexueban* **1999**, *45*, 177; *Chem. Abstr.* **1999**, *131*, 214066.

[200] A. Martin, *Ph. D. Thesis*, Berlin, Germany, **1986**.

[201] B. V. Suvorov, V. K. Promonenkov, N. R. Bukeikhonov, L. V. Lee, B. T. Jusupov, T. A. Khodareva, R. K. Abdukhasubetova, *USSR Author Cert.* 1047505, **1985**.

[202] B. V. Suvorov, K. V. Topchieya, N. R. Butikhonov, A.-A. Kubasov, C. V. Lee, L. E. Kitayev, A. S. Zulkasheva, L. N. Saiko, *USSR Author Cert.* 1132967, **1985**.

[203] M. V. Landau, M. L. Kaliya, M. Hershkowitz, *Appl. Catal. A*. **2001**, *208*, 21.

[204] H. Miyata, T. Ohno, F. Hatayama, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 3505.

[205] N. R. Bukeikhanov, B. V. Suvorov, L. V. Li, T. A. Hodoreva, paper presented at VINITI (Russ.), **1984**, p.7487.

[206] *German Patent DE 2421491*, **1974**.

[207] A. Martin, H. Seeboth, H. Wolf, B. Lücke, *DDR-Patent 232693*, **1984**.

[208] A. Martin, J. French, H. Seeboth, B. Lücke, E. Fischer, *J. Prakt. Chem.* **1990**, *332*, 551.

[209] Q. Zheng, G. Y. Xie, C. Huang, C. W. Xu, Y. Y. Chen, *Fenzi Cuihua* **1999**, 13, 464; *Chem. Abstr.* **2000**, *132*, 196077.

[210] F. Cavani, G. Centi, F. Trifiro, *La Chimica and L'Industria.* **1992**, *74*, 182.

[211] E. V. Ivanov, I. A. Stepanova, E. M. Guseinov, B. V. Suvorov, *Neftekhimiya* **1990**, *30*, 63.

[212] Sumitomo Chem.Co., Koei Chem. Co., *Japan Patent 07145521*, **1993**; *Chem. Abstr.* **1995**, *123*, 339406a.

[213] A. A. Shapovalov, D. Kh. Sembaev, *Izv. Nauk Resp. Kaz. SSR, Ser. Khim.* **1992**, *3*, 80.

[214] B. V. Suvorov, L. A. Krichevkii, A. K. Amirkhanova, *Izv. Akad. Nauk, Kaz. SSR, Ser. Khim.* **1991**, *1*, 74.