Heterogeneous Catalysis with Zeolites, Sulphides and Metals

Roel Prins*

Abstract. Zeolitic materials with sufficiently narrow pores for shape-selective reactions are developed which do not suffer from the diffusional side effects of narrow pores, such as a high *Thiele* modulus, a low effectiveness factor, and pore blocking by side reactions. The diffusional limitations are remedied by the creation of mesopores through dealumination and desilylation of the zeolites by acids and complexing agents. The removal of nitrogen from N-containing aromatics takes place *via* a complex network of hydrogenation, hydrogenolysis and N-elimination reaction steps. To investigate the catalytic sites at which these steps take place, the kinetics of the hydrodenitrogenation of model compounds such as pyridine, piperidine, quinoline, decahydroquinoline and aniline is studied at elevated temperature and pressure in plug flow reactors.

The mechanism of the formation of methanol from carbon monoxide and hydrogen at medium high pressure is studied in a plug flow reactor, as well as in a combination of a medium high pressure reactor with a surface science apparatus comprising X-ray photoelectron spectroscopy and secondary ion mass spectrometry. Experiments in plug flow equipment have shown that the methanol formation is only formed over Pd and Rh catalysts when the catalyst is doped with earth alkali metals.

1. Introduction

The main subjects of our research in heterogeneous catalysis are the (shape-selective) synthesis of intermediate chemicals, the replacement of processes which give waste problems by more ecology-friendly processes, and the catalytic removal of harmful compounds. As shown in *Sect. 2*, zeolites in their protonic form behave as strong solid acids which can replace liquid acids. The size of their well-defined micropores restricts the reactions that can take place inside the zeolite pores and may lead to selective chemistry (*Sect. 2.1*). Since zeolites can be regenerated easily, they pose considerably fewer environmental problems than liquid acids (*Sect. 2.2*). In *Sect. 2.3* a new material will be introduced which is built up of structural units similar to zeolites, but which has much larger pores. Therefore, it has great potential for application in fine chemistry.

While the introduction of heteroatoms is of great importance in the synthesis of intermediate and fine chemicals, their re-

Correspondence: Prof. Dr. R. Prins
Department of Industrial and Engineering
Chemistry
ETH-Zentrum
CH–8092 Zürich

moval is mandatory in the production of fuel fractions from oil. In *Sect. 3* the mechanism of the removal of N-atoms from N-containing molecules in oil fractions and the role of the catalyst components will be described.

As an example of our research on metal catalysts, the mechanism of the synthesis of methanol from synthesis gas will be discussed (*Sect. 4*).

2. Zeolites for the Synthesis of Intermediate Chemicals

Zeolites are crystalline aluminosilicates, built from SiO_4 and $(AlO_4)^-$ tetrahedra. Different ways of linking the tetrahedra give different zeolites with different pores and cavities inside the zeolite crystals. These pores have a diameter of, *e.g.*, 0.55 nm in the zeolite ZSM-5 and 0.74 nm in zeolite Y. Because of the limited diameter of the pores, large molecules are excluded from the interior of the zeolite and molecules which are small enough can be either selectively adsorbed or made to react inside the pores or cavities (so-called shape-selective catalysis). For every Al-atom in the zeolite lattice one unit of negative charge must be compensated by a cation or a proton. In the latter case, the zeolite has *Brønsted* acidic properties.

Acid zeolites are already widely applied in the oil industry in processes in which molecules are cracked to smaller molecules or isomerized to molecules with a high octane number and as *Friedel-Crafts* catalysts in aromatic alkylation processes such as the manufacture of ethylbenzene, *p*-xylene and cumene. In *Friedel-Crafts* acylations, the related *Fries* rearrangements and other reactions with molecules which contain heteroatoms, zeolites tend to present activity and selectivity problems because of strong adsorption of the heteroatoms on the acid sites. Nevertheless, the introduction of heteroatoms (such as N, S and O) into hydrocarbon molecules adds substantial value, and new routes for these reactions are of continuous interest to the chemical industry. In *Sect. 2.1* we will present an example of such a reaction of aniline to pyridine-type molecules over zeolite catalysts.

Zeolites, prepared according to normal recipes, contain substantial amounts of aluminium; *e.g.*, the Al/Si ratio is 0.2 in mordenite and 0.4 in zeolite Y. This means that the acid Al sites, and thus the adsorbed substrate molecules, are close together and that intermolecular coupling of the substrate molecules may occur. Such intermolecular reactions lead to blocking of the zeolite pores, to a loss in activity, and sometimes to a change in selectivity. A solution to this problem is to synthesize zeolites with low Al/Si ratios or, when this is not possible, to replace Al ions in the zeolite framework by Si ions. In this way, the effective catalytic activity may be increased, even though the number of Al ions is diminished by such a dealumination. In addition, the intrinsic activity per remaining Al ion is higher, because isolated Al ions are stronger acid sites.

When dealumination is performed by treating the zeolite with an acid, the removal of the Al ions into solution may be much quicker than the replacement by Si ions. As a result, defects will appear, and when these grow to holes and mesopores the zeolite crystals may look like the mordenite crystals presented in *Fig. 1*, obtained after a treatment in nitric acid. Although such a caries-like appearance may not be attractive, the formation of large pores can have a very positive influence on the catalytic performance of the material. In fact, the mesopores provide improved access of the substrate molecules to the catalytic sites in the micropores and faster removal of the products, as shown in the schematic drawing in *Fig. 2*. In terms of chemical engineering: by decreasing the *Thiele* modulus, the effectiveness factor of the reaction will be substantially

increased. In *Sect. 2.2* we will show how, by careful dealumination, mesoporous zeolites can be prepared which allow reactions of heteroatom-containing molecules to take place in an efficient way.

2.1. *Isomerization of Aniline to 2-Methylpyridine*

Although coal tar is still an important source of aromatic N-heterocycles, rising demands have increased the interest in synthetic routes, and processes in which aldehydes and ketones are condensed with NH3 to pyridine and alkylated pyridines have been realized. For instance, pyridine is synthesized from acetaldehyde, formaldehyde and ammonia with zeolite H-ZSM-5 as the catalyst [1]. Recently, a completely new route for the preparation of alkylpyridines was patented. It was found that aniline isomerized to 2-methylpyridine [2]

and *m*-phenylenediamine to 2-amino-6-methylpyridine and 4-amino-2-methylpyridine [3] (*Scheme 1*), when the substrate was heated in the presence of a high pressure of ammonia.

The isomerization of an arylamine to an N-containing aromatic heterocycle would, in principle, open a new route from aromatic hydrocarbons, *via* nitroaromatics and arylamines, to pyridines and quinolines. We were, therefore, interested to find out the potential for this reaction and have studied the scope of the isomerization, its optimum conditions, as well as its mechanism [4]. Experiments in autoclaves demonstrated that a reasonably high temperature and ammonia pressure and an acid catalyst are required for the isomerization reaction of arylamines to methyl-aza-aromatics. Best results were obtained with acid zeolites around 600 K and 10

MPa. The only methyl-aza-aromatic products were those that seem to have been formed by an interchange of the N-atom by a C-atom from the *ortho* position of the benzene ring (*Scheme 1*).

A mechanism which can explain all results was put forward in collaboration with Prof. *D. Seebach* (Laboratory for Organic Chemistry, ETH, Zürich). It was proposed that, in order to break the aromaticity of the arylamine, ammonia should be added to the arylamine first (*Scheme 2*). This explains why a high NH3 pressure is required and why the reaction runs better with naphthylamine than with aniline. Then ring opening occurs through a reverse aldol-type reaction (*Scheme 3*), and ring closure may occur by addition of the original amino group to an imino group. Finally, the aza-aromatic is formed by elimination of NH3 (*Scheme 4*).

Zeolites with a three-dimensional pore structure, especially H-ZSM-5, showed a much higher activity than other zeolites and than non-zeolitic solid acids. We ascribe this to blocking of the pores of the latter catalysts by condensed aromatics formed in intermolecular side reactions of the highly unsaturated intermediates. The acid catalysis, in conjunction with the required high NH3 pressure, explains why a relatively high reaction temperature is needed. At low temperature, all acid sites are occupied by NH3, and only at elevated temperature will enough NH3 desorb and will acid sites become available for catalysis. Unfortunately, a high temperature also favours acid-catalyzed side reactions such as methyl shift and transmethylation. These lead to many side products and to separation problems. Our future efforts will, therefore, concentrate on less acidic catalysts, which will adsorb NH3 less strongly and do not, therefore, require high temperatures for NH3 desorption.

2.2. *Nitration of Aromatics*

For more than a century, nitroaromatics have been produced industrially by reacting aromatic molecules with a mixture of nitric acid and sulphuric acid. The sulphuric acid reacts with the nitric acid to the electrophilic species NO_2^+ and binds the water formed. High conversions can be reached in the mixed acid process (98% or more in the case of benzene), but a drawback is that, after reaction, spent sulphuric acid must be reconcentrated, which leads to corrosion problems, or neutralized, with inherent waste sulphate problems.

Nitration of aromatics in the vapour phase on acid zeolites would be an interesting alternative to the mixed acid pro-
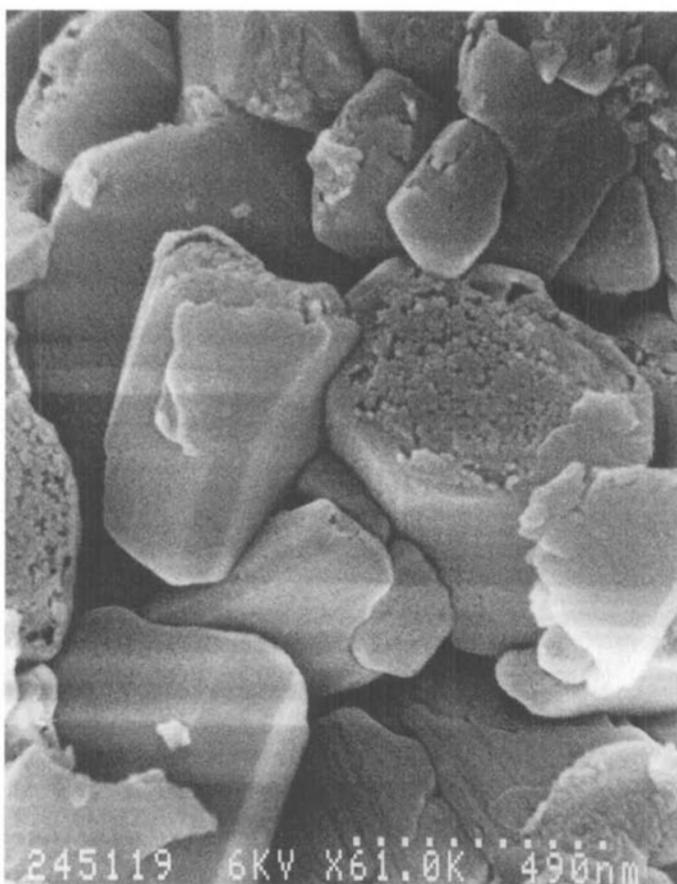
Fig. 1. *Mordenite crystals after treatment in nitric acid*

245119 6KV X61.0K 490nm
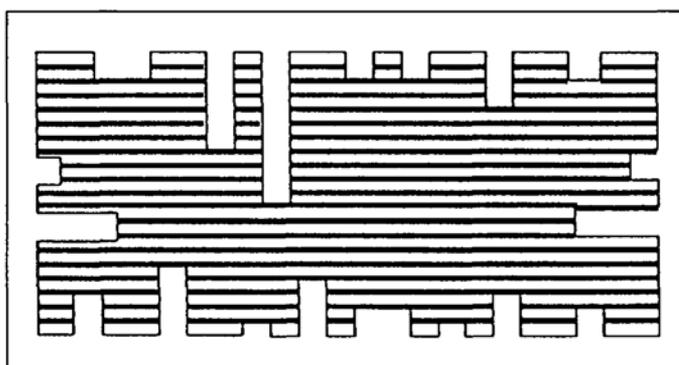
Fig. 2. *Schematic drawing of a zeolite crystal with inherent micropores and mesopores created during treatment with acid*

cess, since it avoids the use of sulphuric acid. Mordenite is a well-known high-silica zeolite which has found wide application in the oil industry. One of the most interesting features of mordenite is that it can be dealuminated by several methods without critical damage to the structure, leading to a family of highly crystalline materials with tailored acidic and textural properties. Solid-state MAS NMR showed that dealumination of mordenites by heat and acid treatments drastically reduces the aluminium content of their framework [5]. The aluminium which is removed from the zeolite framework upon thermal treatment above 873 K ends up as aluminium (hydr)oxide in the zeolite pores. This so-called extra-framework aluminium hinders the diffusion of dinitrobenzene molecules, formed as a by-product in the nitration of benzene, and results in a fast catalytic deactivation within the first hours on stream. It must be removed completely from the zeolite pores. This can be done by leaching with acid, provided that the Al has been thermally extracted from the zeolite framework at a calcination temperature below 923 K.

The influence of the calcination temperature on the catalytic performance of H-mordenite can be seen from the sequence of catalysts prepared by calcination at 773, 823, 923, 973, and 1023 K. As shown in *Fig. 3*, no significant catalytic deactivation is observed up to 823 K, owing to the relatively small amount of extra-framework Al present in the pores or at the pore mouths of the mordenite. At 923 K a small deactivation occurs and extra-framework aluminium was observed in the ^{27}Al MAS-NMR spectrum. Further increasing the calcination temperature results in a drastic decrease of the catalytic performance (*Fig. 4*) and large amounts of non-framework aluminium.

The optimum way to prepare mordenite catalysts for benzene vapour-phase nitration was a combination of several subsequent heat and acid treatments. A calcination temperature of 923 K was sufficiently high to effect a significant framework dealumination, but not too high, so that relatively small portions of extra-framework Al were formed in a less polymerized (and thus more soluble) state. These could be completely extracted by 6N HCl before a new portion of framework Al was formed by a subsequent calcination at 923 K. Materials made by a carefully chosen calcination and acid-leaching procedure were highly active and selective and retained their activity for more than 120 h on stream in the vapour-phase nitration of benzene [5].

Scheme 1. *Isomerization of Aniline to 2-Methylpyridine and of m-Phenylenediamine to 2-Amino-6-methylpyridine and 4-Amino-2-methylpyridine*
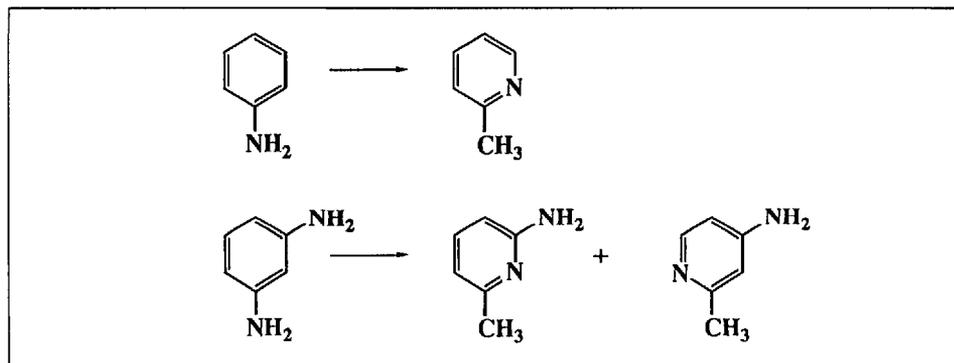
Scheme 2
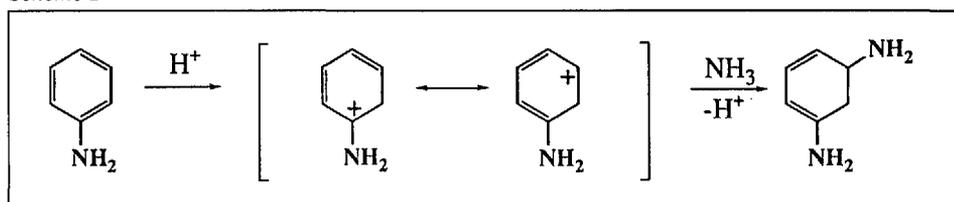
Scheme 3
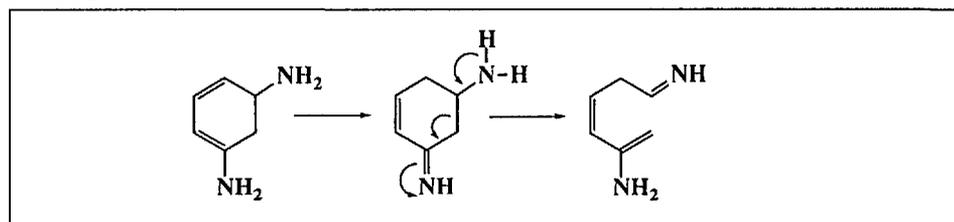
Scheme 4
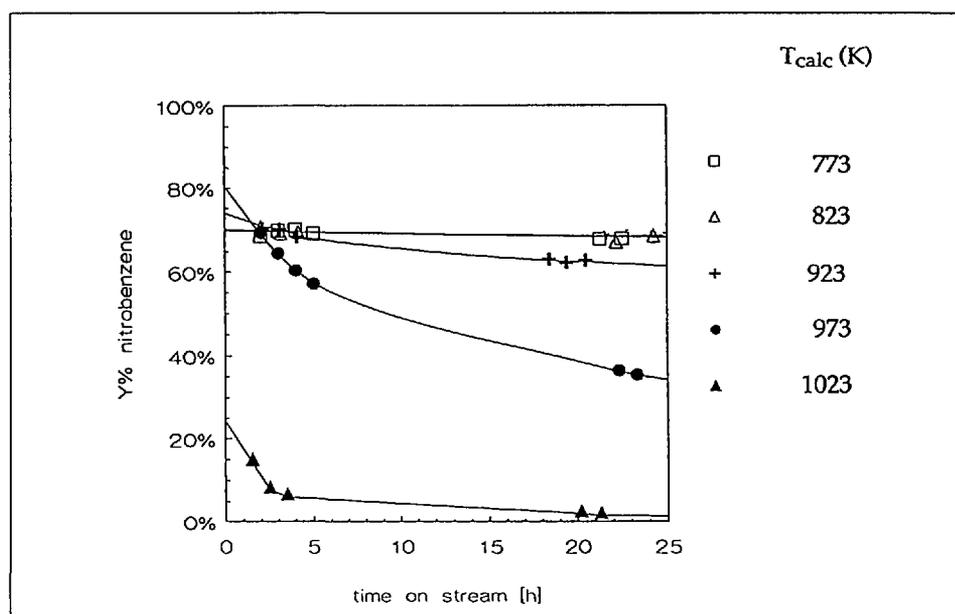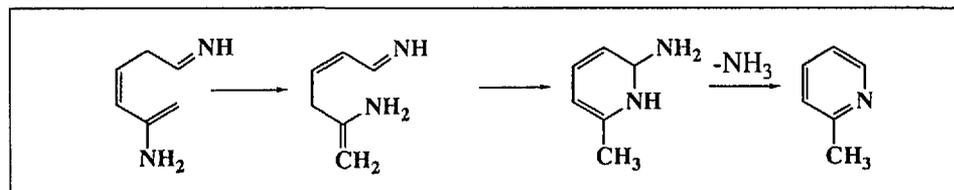
Fig. 3. *Conversion of benzene in the vapour-phase nitration with 65% HNO₃ at 443 K and atmospheric pressure with mordenite catalysts calcined between 773 and 1023 K*

2.3. *Mesoporous Solid Acids*

A limitation of zeolites is their narrow range of pore diameters which only allows (shape-selective) reactions for not too big molecules. New materials were recently discovered with a regular beehive-like arrangement of parallel pores in the range between 2 and 10 nm [6]. These MCM-41 materials are made from the same tetrahedral building units as zeolites, the difference being that a surfactant molecule like $C_nH_{2n+1}N(CH_3)_3Cl$ instead of a short-chain tetraalkylammonium salt is used as the template in the synthesis. An example of the X-ray diffraction patterns of the materials obtained with $n = 12$, 14 and 16 is shown in *Fig. 4*. The insert in *Fig. 4* demonstrates that the pore diameters calculated from the XRD results are in quite good agreement with double the length of the surfactant molecules.

If aluminium ions could be built into the MCM-41 lattice on tetrahedral positions, a solid *Brønsted* acid with wide pores could be obtained. Our group, as well as several others [7–9], are trying to do this, but have encountered several difficulties. The choice of the aluminium source and the calcination procedure needed to remove the template from the pores proved much more subtle than in zeolite synthesis. Furthermore, the acidity of Al-MCM-41 seems to be weaker than that of zeolites. Thus, 2-methoxynaphthalene could be acetylated with acetic anhydride almost equally fast over Al-MCM-41 as over zeolite Beta. As expected, because of the wider pores, acetylation took place in the 1-position with Al-MCM-41, while with zeolite Beta predominantly the linear 6-acetyl product was formed. The more difficult reaction of benzene with phthalic anhydride to an-

thraquinone and the *Fries* rearrangement of phenyl benzoate showed only low conversions with Al-MCM-41, however.

3. Hydrodenitrogenation

Hydrotreating is an important process in petroleum refining, in which S- and N-atoms are removed from molecules present in oil distillate fractions, so that less SO_2 and NO_x pollute the air when these oil fractions are burned in car engines or power plants. Furthermore, poisoning of catalysts used in the refining of oil fractions is reduced when less S- and N-containing molecules are present. Hydrotreating catalysts contain molybdenum and cobalt or nickel supported on γ-Al_2O_3, and before use the catalyst is sulphided in a mixture of H_2 and H_2S [10]. Co and Mo are used mainly in the removal of S-atoms (hydrodesulphurization), while Ni and Mo are favoured in the removal of N-atoms (hydrodenitrogenation, HDN). Extended X-ray Absorption Fine Structure (EXAFS) studies demonstrated that, in sulphided Mo/Al_2O_3, Co-Mo/Al_2O_3 and Ni-$Mo/$ Al_2O_3 catalysts, the average Mo-atom has the same environment as a Mo-atom in MoS_2 [11]. The only difference is that in the catalysts the number of Mo neighbours surrounding each Mo-atom is less than 6, the value in pure MoS_2. This indicates that the MoS_2 particles on the Al_2O_3 surface are small, with 6 to 12 Mo-atoms per MoS_2 particle.

3.1. *Mechanism*

Although hydrotreating has been studied intensively, and different reaction mechanisms, catalytic active sites, and functions of the catalytic components have been proposed, there are still many questions to be answered in order to better understand the reaction and the catalyst [10][12][13]. The reaction mechanism and the roles of Mo and Ni became clear from an HDN study of pyridine and piperidine [14][15]. The reaction network is shown in *Scheme 5*. Pyridine reacts very well over Mo/Al_2O_3 and Ni-Mo/Al_2O_3 catalysts, but nitrogen removal occurred to a limited extent only; most of the pyridine was just converted to piperidine (*Fig. 5, A*). A study of the reaction intermediate piperidine confirmed that, when H_2S is absent, piperidine hardly reacts to hydrocarbons (*Fig. 5, B*). When H_2S is present, however, a much higher extent of N-removal is obtained (*Figs. 5, C* and *D*). Although the total conversion of pyridine is lower than in the absence of H_2S (*cf. Fig. 5, C* with *A*), the amount of N-removal and
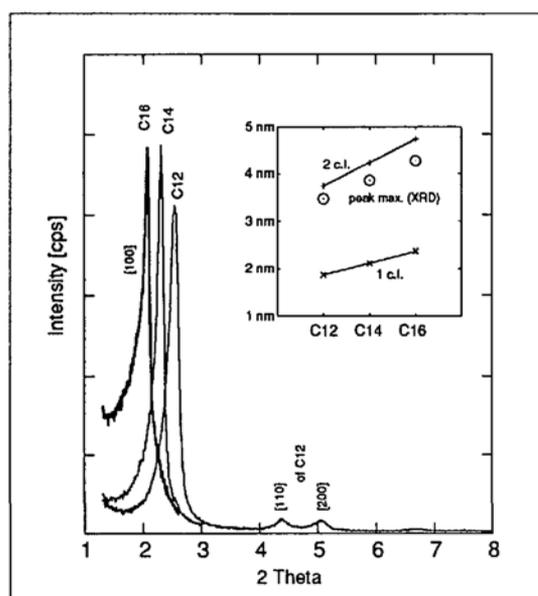
Fig. 4. *X-Ray diffraction patterns and pore diameters* (insert) *of MCM-41 synthesized from $C_nH_{2n+1}N(CH_3)_3Cl$ surfactants of different alkyl chain length* (c.l.)
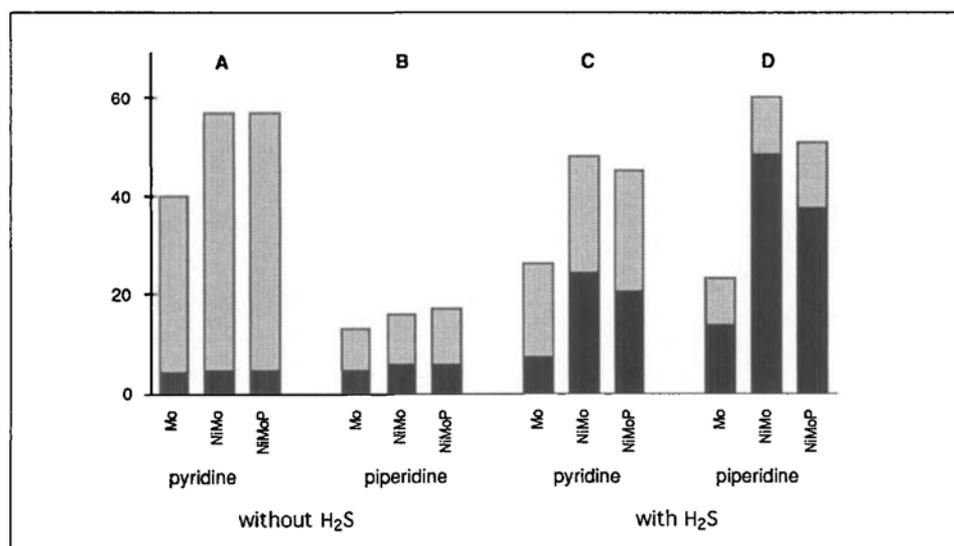
Fig. 5. *Conversions of pyridine and piperidine over sulphided Mo, NiMo and NiMo-PO_4 catalysts supported on Al_2O_3 at 593 K and 3 MPa H_2, with or without 9 kPa H_2S.* Grey: the conversions of pyridine and piperidine; black: the yields of hydrocarbons and NH_3.

hydrocarbon formation is much higher. Again, this is confirmed by the results for piperidine in the presence of H₂S (*Fig. 5, D*). When H₂S is present, piperidine smoothly converts to C_5H_{10}, C_5H_{12} and NH_3.

Hydrodenitrogenation is a compromise: on the one hand, one must saturate the aromatic N-containing rings with a catalyst which has metallic-like properties, such as a metal sulphide with a surface which is short of S-atoms. On the other hand, the resulting piperidine rings must be opened and the N-atoms must be removed by elimination reactions which are catalyzed by a surface with acid-base properties, such as a metal sulphide surface rich in sulphur.

3.2. *Role of Ni and Mo*

When comparing the Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts, it is clear that, in the presence of H₂S, the sulphided Ni-Mo/Al₂O₃ catalyst is a much better catalyst for the hydrogenation of pyridine to piperidine (*Fig. 5, C*) as well as for the N-removal reaction of piperidine to hydrocarbons (*Fig. 5, D*). This explains why, in commercial HDN catalysts, the Ni-Mo combination is preferred over Mo, but does not explain the role of the Ni-atoms. Do the Ni-atoms have a beneficial effect on the Mo surface atoms, and should they be called promoter atoms, or are the Ni-atoms, rather than the Mo-atoms, the active sites? Since pure molybdenum sulphide is much more active in hydrotreating reactions than pure nickel sulphide, Mo has, over the years, been recognised as the active component and Ni as the promoter. However, in a study of carbon-supported catalysts, it was shown that a sulphided Ni/C catalyst can be as active as a Ni-Mo/C catalyst; therefore, Ni has also been proposed as the active component [16][17]. To determine whether nickel is a promoter or a catalyst, information about the geometrical structure of Ni in the catalyst is needed.

The structure of the Co- and Ni-atoms in hydrotreating catalysts was determined with the aid of inverse *Mössbauer* [18], EXAFS [11][19][20] and IR [21] spectroscopy. In the sulphidic form, nickel may be present in three forms, as Ni₃S₂ crystallites on the support surface, as Ni ions adsorbed on the surface of MoS₂ crystallites (the so-called Ni-Mo-S phase), and in octahedral sites in the γ-Al₂O₃ lattice. By combining *Mössbauer* and catalytic activity studies, *Topsøe et al.* established that the promoter effect of Co and Ni is related to the Co- or Ni-atoms in the Co-Mo-S and Ni-Mo-S phase respectively [22]. Although the *Mössbauer* [18] and

Scheme 5. *HDN Reaction Network of Pyridine and Piperidine*
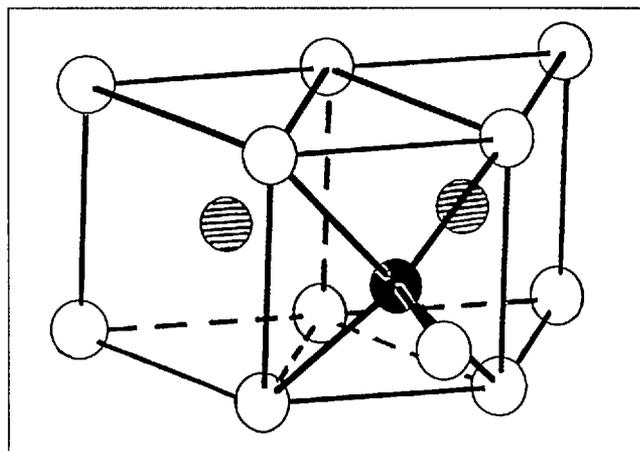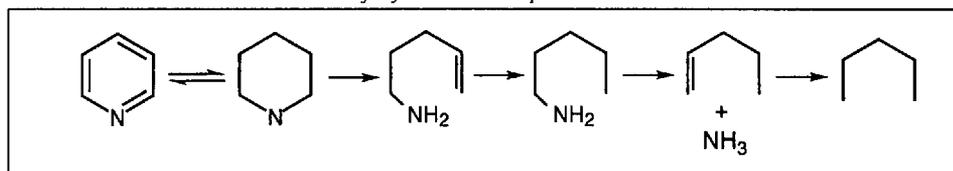
Fig. 6. *Structure of the Ni-atoms in a sulphided NiMo/Al₂O₃ catalyst* (Ni black, Mo hatched, S white)

IR studies [21] suggested that the Co- and Ni-atoms are located at the edges of the MoS₂ crystallites, the exact location could not be determined. X-Ray diffraction or electron diffraction cannot determine the location either, because of the lack of long range order in small MoS₂ crystallites.

Since in EXAFS spectroscopy only short range order is required, the EXAFS technique is well suited for solving the local structure of the Ni-atoms. In order to do this, however, the problem of the three forms in which the Ni-atoms can occur had to be solved. EXAFS is a bulk technique; if all three forms of nickel would be present in a sulphided Ni-Mo/Al₂O₃ catalyst (Ni-Mo-S, Ni₃S₂ and Ni in Al₂O₃), a summation of three spectra would be observed, from which it would be extremely difficult to extract the information on the local Ni structure in the Ni-Mo-S phase. We have solved this problem, first, by using carbon instead of Al₂O₃ as a support to avoid the dissolution of Ni-atoms into the support and, second, by using a recipe for catalyst preparation which exclusively leads to the Ni-Mo-S phase [20].

The EXAFS investigations showed that the Ni-atoms are surrounded by five S-atoms at 0.222 nm and by one to two Mo-atoms at *ca.* 0.28 nm [20] (*Fig. 6*), and proved that the Ni-atoms are linked to the MoS₂ edges. There was no significant difference between the EXAFS parameters of the carbon- and alumina-supported Ni-Mo catalysts. EXAFS measurements demonstrated that, in the Ni-Mo catalysts, all Mo-atoms are completely surrounded by six S-atoms, while in Mo-only cata-

lysts the Mo-atoms have a lower coordination number [11]. This shows that the Ni-atoms and the S-atoms, which because of stoichiometry come along with the Ni-atoms, fully cover the Mo-atoms in the Ni-Mo catalysts. Since fully covered Mo-atoms have no free ligand positions available for substrate molecules, the HDN reactions cannot take place at the Mo-atoms in the Ni-Mo/Al₂O₃ catalysts. Therefore, the real catalytic sites in the Ni-Mo/Al₂O₃ catalysts are the Ni-atoms. The MoS₂ crystallites function as a secondary support for these Ni-atoms, the MoS₂ crystallites being supported in turn by the Al₂O₃ support.

3.3. *Role of Phosphate*

Modern HDN catalysts often contain phosphate in addition to Ni and Mo. Although phosphate is primarily used to enhance the solubility of molybdate in water, and thus to simplify the catalyst preparation, it has also been claimed that phosphate improves the catalytic activity of the ultimate, sulphided catalyst. In model studies with quinoline, we confirmed that a phosphate-containing Ni-Mo/Al₂O₃ catalyst has a higher HDN activity [23]. Because of the complexity of the reaction network (*Scheme 6*), however, no clue to the role of phosphate could be obtained. By turning our attention to the simpler molecules decahydroquinoline (DHQ) and *ortho*-propylaniline (OPA), which are intermediates in the reaction network of quinoline (*Scheme 6*), we are now in the process of unravelling the role of phosphate in HDN catalysis.

As shown in *Fig. 5*, phosphate decreases the conversion of piperidine as well as the further reaction to pentene over the NiMo(P)/Al$_2$O$_3$ catalysts, indicating that phosphate diminishes the C–N bond cleavage activity. Phosphate was found to have a similar negative effect on the HDN of DHQ, a key intermediate in the HDN of quinoline [15] (*Scheme 6*). This seems to be in contradiction to the positive influence of phosphate observed in the HDN of quinoline, since the C–N bond opening in DHQ is supposed to be the most difficult reaction step in the reaction network of quinoline.

In contrast to its negative effect in the HDN of piperidine and DHQ, phosphate exhibited a strong positive effect on the HDN of OPA [24]. Since OPA is also an intermediate in the HDN of quinoline, this suggests that the promotional effect of phosphorus observed in the model study with quinoline might be due to a rate enhancement of the reaction of OPA to hydrocarbons. Although the concentration of aniline-type compounds in oil fractions is usually quite low, their concentration in the reaction effluent can be substantial due to the inhibiting effect of other N-containing compounds on their conversion [25] [26]. Therefore, it can be expect-

ed that in industrial HDN processes phosphorus may exhibit a promotion effect on NiMoP/Al$_2$O$_3$ catalysts under hydrotreating conditions, when there is an accumulation of aniline-type compounds.

Why the presence of phosphate in the Ni-Mo catalyst has a negative influence on the elimination reactions of piperidine and DHQ to hydrocarbons and a positive effect on the hydrogenation of aniline is still unclear. If phosphate itself were responsible for the catalytic effects, one would expect it to influence the elimination reactions, but certainly not the hydrogenation reaction. A phosphate on Al$_2$O$_3$ catalyst, however, showed no catalytic activity for either reaction. The influence of phosphate must, therefore, arise from its effect on Ni and/or Mo. A model which we are presently pursuing is that H-atoms, which are formed on the sulphided Ni-Mo phase, diffuse to the phosphate and reduce part of it to PH$_3$ molecules. These may undergo an exchange reaction with S-atoms of the Ni-Mo sulphide and create phosphide anions at the catalyst surface. As a consequence of this doping, the electronic properties of the Ni-atoms, and thus their catalytic properties, would be altered.

4. Effect of Basic Metal Oxides on the CO Hydrogenation to Methanol

A wide variety of products, such as methane, ethane and higher hydrocarbons, methanol, ethanol and other oxygenated compounds, can be formed by the hydrogenation of CO. The product distribution is affected by the choice of the active metal, catalyst support, promoter, catalyst pretreatment and reaction conditions. Even after intensive catalytic and surface science studies, the elementary steps in the catalytic conversion of synthesis gas are not completely clear. The mechanism for the formation of hydrocarbons and oxygenated compounds (by dissociative adsorption of H$_2$ and CO on the metal catalyst surface and further reaction of the formed surface CH$_x$ fragments to hydrocarbons or to higher oxygenated compounds through CO insertion) is well accepted [27], but that for the formation of methanol is still under debate (*Scheme 7*). Methanol is a bulk chemical with a worldwide production of 22 Mio. t in 1991 and 11% growth per year over the last five years, due to the strongly increasing demand for methyl *tert*-butyl ether (an octane number booster, needed because of the phasing out of tetraethyllead and benzene from gasoline).

It has been demonstrated that basic metal oxides promote the hydrogenation of CO to methanol. Thus, it is understandable that the industrially most widely used catalyst consists of Cu crystallites supported on ZnO. Some authors have proposed that basic additives may stabilize metal cations in the metal catalyst. CO may then insert into a metal cation hydride bond and the resulting formyl species is hydrogenated on the metal surface to methanol (*Scheme 7, A*) [28]. A different model suggests that the formation of methanol starts on the support rather than on the metal [29][30]. CO is thought to react with an OH group on the basic oxide to formate, which can subsequently be hydrogenated to methanol either by H-atoms which diffuse from the metal particles to the basic metal oxide surface or on the metal surface after migration of the formate from the basic oxide to the metal (*Scheme 7, B*).

To explain the role of basic promoters, we have studied the effect of several alkali and earth-alkali metal oxides on the formation of methanol from synthesis gas over Pd and Rh catalysts supported on SiO$_2$ [31]. The silica was synthesized in a very pure form, with impurities below the ppb level, to avoid eventual contamination effects. Pd was chosen because it can hardly dissociate CO, while Rh can adsorb

Scheme 6. *HDN Reaction Network of Quinoline*
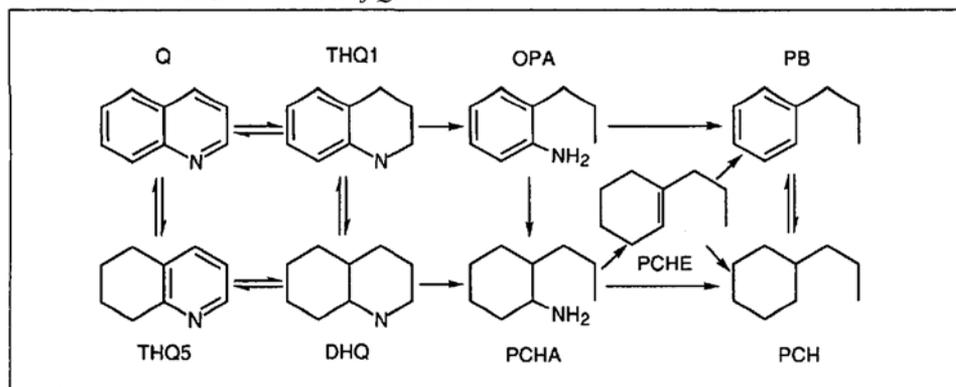
Scheme 7. *Possible Reaction Pathways for Methanol Formation and Schematic Description of the Catalytic Sites*
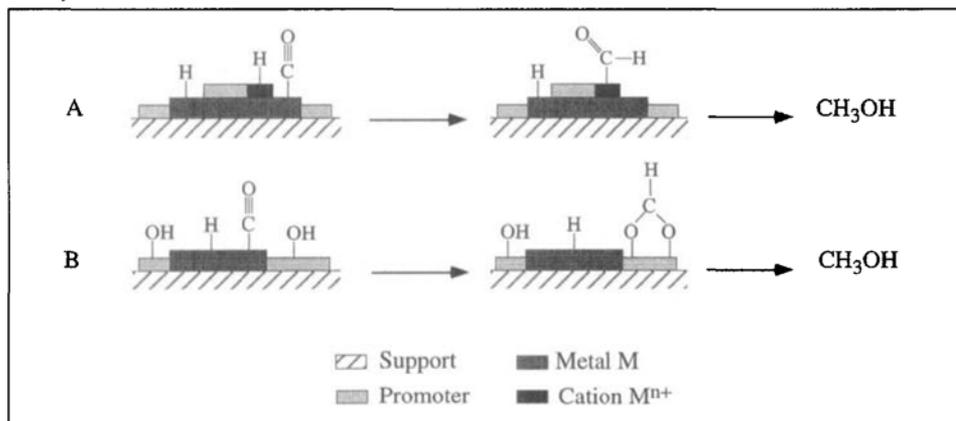
CO associatively as well as dissociatively. Thus, one may expect that the Pd catalyst synthesizes almost exclusively methanol, while the Rh catalyst might produce substantial amounts of hydrocarbons and higher oxygenated products.

The conversion of CO to methane, C_{2+}, C_{1oxo} and C_{2oxo} compounds on Rh and Pd catalysts as a function of time is presented in *Fig. 7*. The total activity of Pd/SiO_2 catalysts was almost two orders of magnitude smaller than that of Rh/SiO_2, and the product distribution was limited to small amounts of methane, C_2–C_3 hydrocarbons and C_{1oxo} products (methanol and dimethyl ether). Rh/SiO_2 on the other hand produced substantial amounts of hydrocarbons and C_{2oxo} products (mainly acetaldehyde) (*Fig. 7, A*). Both catalysts had an equally low methanol activity, indicating that Pd catalysts supported on an impurity-free SiO_2 are not particularly efficient in the production of methanol, despite a predominantly non-dissociative CO adsorption. Doping of the Pd/SiO_2 and Rh/SiO_2 catalysts with Ca resulted in a strong decrease in hydrocarbons formation, due to the suppression of the CO dissociation, and in a dramatic increase in the methanol production (*Fig. 8*), confirming the promoting effect of basic oxide species, close to or on the metal particles, in the methanol formation. The fact that the methanol production is independent of the metal (*Fig. 8*) suggests that insertion of CO into an OH group on the basic oxide is rate limiting (*Scheme 7, B*).

The intentional doping with other alkaline earth oxides also led to a strong suppression of methane and C_{2+} formation and a strong promotion of methanol production. This is in accordance with the assumption that the formation of methanol occurs through formate intermediates. Indeed, methylformate used to be produced industrially by reacting CO and methanol over sodium hydroxide. However, proof has to come from a surface science experiment. Such a combined high-pressure UHV experiment, in which the catalytic activity of a Pd single crystal doped with CaO is measured at 3 MPa and its surface composition is studied before and afterwards under UHV conditions with XPS and SIMS, is in progress.

Fig. 7. *Product activities in the CO hydrogenation over* A) Rh/SiO_2 *and* B) Pd/SiO_2 ◇ CH_4, △ C_{2+}, ● C_{1oxo}, ○ C_{2oxo}
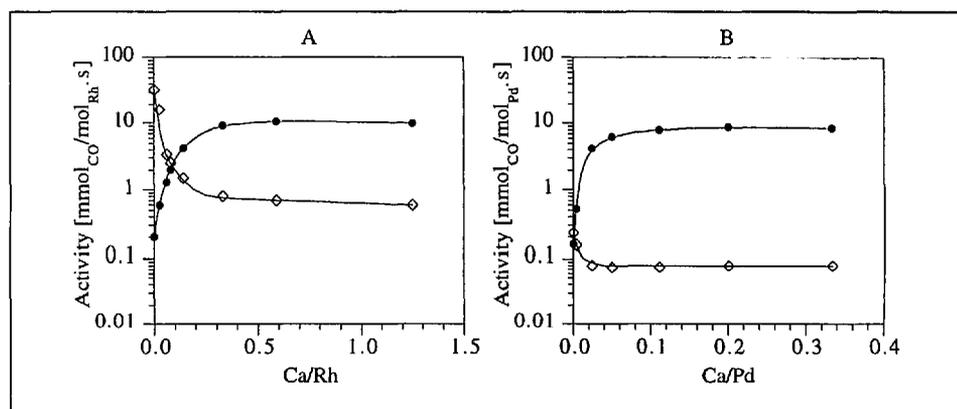
Fig. 8. *Effect of the addition of Ca to* A) Rh/SiO_2 *and* B) Pd/SiO_2 *catalysts* ◇ C_{1+} *hydrocarbons*, ● C_{1oxo}

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