Thermochimica Acta 499 (2010) 71–78

Contents lists available at ScienceDirect

Thermochimica Acta

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

MOF-5 based mixed-linker metal–organic frameworks: Synthesis, thermal stability and catalytic application

Wolfgang Kleist, Marek Maciejewski, Alfons Baiker*

Department of Chemistry and Applied Biosciences, Institute for Chemical and Bioengineering, ETH Zurich, Hönggerberg HCI, CH-8093 Zurich, Switzerland

ARTICLE INFO

Article history:
Received 6 August 2009
Received in revised form 3 November 2009
Accepted 8 November 2009
Available online 14 November 2009

Keywords:
CO oxidation
Coordination polymer
Metal–organic framework
Pd catalyst
PulseTA technique
TA–MS

ABSTRACT

Based on the well-known metal–organic framework material MOF-5 we developed a new route for the synthesis of highly porous mixed-linker metal–organic frameworks (MIXMOFs) where 5% and 10% of the benzene-1,4-dicarboxylate linkers have been substituted by a functionalized linker, namely 2-aminobenzene-1,4-dicarboxylate. The thermal stability of the materials decreased with increasing degree of substitution. However, all materials showed thermal stability up to at least 350 °C in oxidizing atmosphere which renders the MIXMOFs promising for catalytic applications. Choosing the optimum ratio of the two linker molecules both the number of active sites and thermal stability of the resulting catalysts could be tuned. The amino group at the functionalized linker proved to be beneficial for the immobilization of Pd species. The Pd loading achieved by equilibrium adsorption could be controlled by the number of NH_2 groups in the material. Although the thermal stability of the organic framework was affected to some extent in the presence of Pd, the Pd/MIXMOF materials could successfully be applied as catalysts in the oxidation of CO at elevated temperatures which was chosen as a test reaction.

1. Introduction

Since the first reports on porous metal–organic frameworks (MOFs, also known as porous coordination polymers) were published [1–5], this new material class has attracted enormous interest in the field of material chemistry. A large variety of bi- or multi-functional organic linkers and transition metal units have been applied as building blocks in the last years leading to numerous 2D and 3D structures [6–9]. Especially the development of high-throughput assisted preparation techniques represented an important improvement [10,11].

MOF-5, which forms a cubic network from benzene-1,4-dicarboxylate (BDC) and tetrahedral ZnO_4 units, is one of the most famous and best investigated examples for porous 3D-MOFs [12,13]. Yaghi and coworkers demonstrated successfully the synthesis of so-called "isoreticular" (=forming the same network) metal–organic frameworks (IRMOFs) by using dicarboxylates with larger organic spacers (e.g. 4,4′-biphenyl-1,1′-dicarboyxlate BPDC = IRMOF-10) or additional functional groups (like 2-amino-benzene-1,4-dicarboxylate ABDC = IRMOF-3) instead of BDC linkers [14]. Using this approach, the synthesis of materials with designed pore diameters and organic linkers bearing additional functional side-groups became feasible.

In general, these metal–organic frameworks feature microporous structures exhibiting huge specific surface areas and pore volumes, which renders them, like zeolites, interesting for various applications [15,16]. In the beginning, MOFs have been used mainly for storage of hydrogen or hydrocarbons [14,17–19], but the field of possible applications was soon extended to other important fields such as gas purification [20,21] and separation [15] or sensor techniques [22,23]. Implementation of MOFs in catalytic applications is another promising field which has recently attracted the interest of many groups (vide infra).

However, for this purpose some important requirements imposed to the framework material have to be taken into account. Most of the MOF structures that have been published in the last years suffer from undesired chemical and/or physical properties which prevent their usage under real reaction conditions. The most important among them are the insufficient thermal stability in air and the lack of tolerance towards moisture and many organic solvents. As a consequence, the stability of such framework materials under real reaction conditions has to be considered before they can be applied.

Another important aspect concerns the introduction of catalytically active sites (acid/basic groups and/or transition metals) into the framework which may also influence the thermal stability of the resulting catalyst. In principle, three different strategies have been reported in the literature up to now (see Fig. 1): in the first approach, the transition metal ions that are part of the framework structure should act as the catalytically active sites (Fig. 1A) [24–26]. The most important prerequisite here is the presence of metal centers

---

* Corresponding author. Fax: +41 44 63 21163.
E-mail address: baiker@chem.ethz.ch (A. Baiker).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.11.004

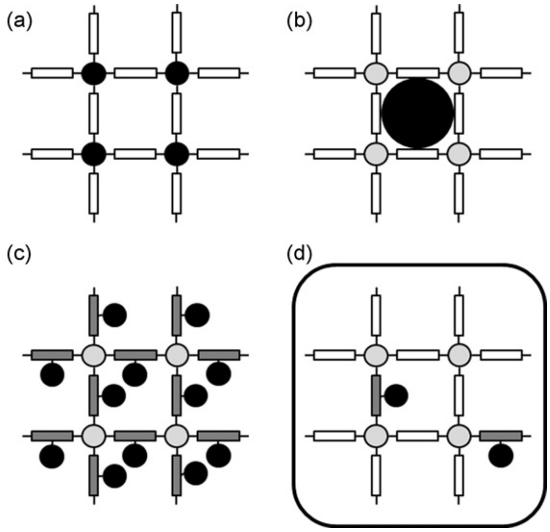


Fig. 1. Different approaches for the use of MOFs in catalysis: (A) framework metals as active centers, (B) generation of metal nanoparticles inside the pores, (C) immobilization of active metal complexes via functional side-groups of the linker molecule and (D) strategy applied in this work: synthesis of mixed-linker MOFs (MIXMOFs) where only some of the linker molecules have binding sites for noble metals. Black circles represent active metal centers and grey circles symbolize metal centers which are only used to build up the framework (no free coordination sites).

in the framework that exhibit free coordination sites. Otherwise a coordination of reactant molecules (and thus an effective catalysis) would be either impossible or cause a change in the framework structure which often leads to a destruction of the crystalline lattice.

The encapsulation of metal nanoparticles into the pores of MOFs has been utilized as another method (Fig. 1B). Noble metals such as palladium could successfully be introduced into the MOF-5 frameworks using co-precipitation [27], solution infiltration [28] or vapor deposition [29,30] techniques. However, the specific surface area and the free pore volume decreased significantly due to filling of the pores with the metal particles. The resulting blocking of pores and channels may cause a decreased applicability of the resulting catalysts due to diffusion limitation of the reactants and products.

In the last methodology that has been used up to now for the generation of MOF-based catalysts, materials have been employed which are built up from organic linkers that feature functional side-groups (Fig. 1C). Generation of catalysts from these materials is possible by either postsynthetic modification with organic substrates [31–35] or coordination of metal ions which leads to single-site active centers [36–38]. In general, all of these functional linkers will be modified in that way, which leads to an extremely high (=stoichiometric) loading of the resulting catalysts. In the case of transition metal modified catalysts this may be seen as a severe drawback due to the high expenses when precious metal complexes are used. Additionally, in the presence of too large amounts of noble metals also the decomposition/combustion of the organic framework may be catalyzed.

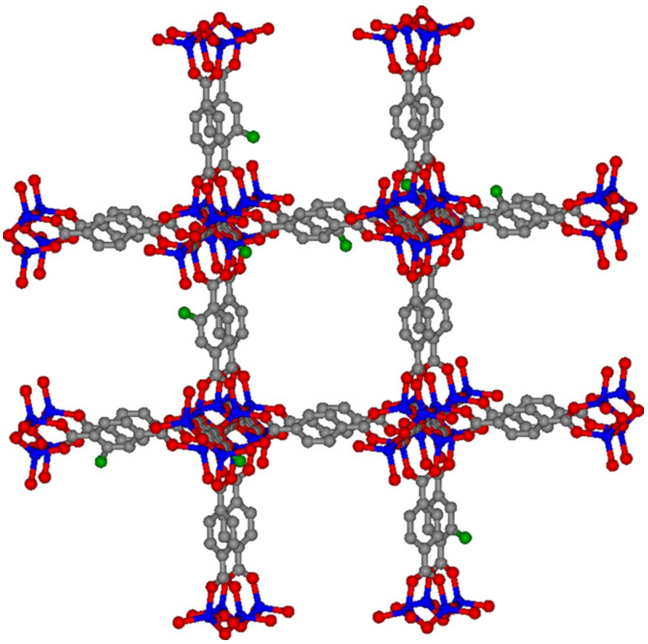
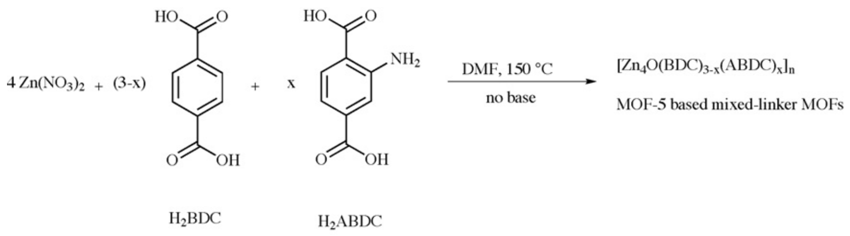


Fig. 2. Structure of Zn-based mixed-linker metal–organic frameworks (MIXMOFs) containing benzene-1,4-dicarboxylate (BDC) and 2-aminobenzene-1,4-dicarboxylate (ABDC) linkers. The two linker molecules are randomly distributed in the structure. Zn atoms are displayed in blue, O in red, C in grey and N in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In this contribution, we present an alternative approach for the synthesis of metal–organic framework based catalysts which does not suffer from these drawbacks. The general idea is the formation of so-called “mixed-linker” frameworks (“MIXMOFs”) which consist of two isoreticular linker molecules that are randomly distributed in a mixed structure (Fig. 1D) [34,39]. As one of the first examples of this class of materials, we present here a modified MOF-5 ($[Zn_4O(BDC)_3]_n$) in which some of the benzene-1,4-dicarboxylate (BDC) linkers have been substituted by a functionalized linker, namely 2-aminobenzene-1,4-dicarboxylate (ABDC, Scheme 1). The general molecular formula of the resulting materials can be described as $[Zn_4O(BDC)_{3-x}(ABDC)_x]_n$. We will prove that, due to the fact that both linker molecules have the same size and form isoreticular cubic frameworks (known as MOF-5 = IRMOF-1 and IRMOF-3, respectively), a partial substitution of BDC linkers by ABDC is possible (Fig. 2). The influence on the thermal stability of the resulting materials will be elucidated as well. This approach facilitates the synthesis of MOF-based materials with a tunable amount of active centers, which is determined by the ratio of the two linker molecules. This means that the maximum loading of the resulting catalyst can be controlled when a noble metal complex is anchored to the surface. The synthesis of Pd catalysts by equilibrium adsorption to materials, in which 5% (5%-MIXMOF, $x = 0.15$) and 10% of ABDC linkers (10%-MIXMOF, $x = 0.3$) have been



Scheme 1. Synthesis of mixed-linker metal–organic frameworks (MIXMOFs) containing benzene-1,4-dicarboxylate (BDC) and 2-aminobenzene-1,4-dicarboxylate (ABDC) linkers.

introduced, and their catalytic activity in the oxidation of carbon monoxide will also be presented.

2. Experimental procedures

2.1. General

N,*N*-dimethylformamide (DMF, >99.8%), zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$, >99.0%) and benzene-1,4-dicarboxylic acid (H_2BDC, >99.0%) were purchased from Fluka. 2-Aminobenzene-1,4-dicarboxylic acid (H_2ABDC, 99+%) was purchased from Acros Organics. All chemicals were used without further purification or drying.

2.2. Base-free synthesis of MOF-5

Benzene-1,4-dicarboxylic acid (H_2BDC, 2.492 g, 15 mmol) and $Zn(NO_3)_2·6H_2O$ (5.950 g, 20 mmol) are dissolved in 500 cm^3 of DMF at RT. The round-bottom flask (equipped with a condenser) with the solution was placed into a preheated oil bath at a reaction temperature of 150 °C for 18 h. The resulting white precipitate was filtered off after cooling down to RT and washed five times with 50 cm^3 of DMF each time. To remove physically adsorbed solvent, the resulting MOF-5 material was pretreated in vacuum at 80 °C for 5 h.

2.3. Synthesis of mixed-linker MOFs containing 5% and 10% of ABDC linkers

Both materials were synthesized according to the procedure given for MOF-5. Instead of pure H_2BDC, a mixture of H_2BDC and H_2ABDC was used in the desired ratio: 2.367 g (14.25 mmol) of H_2BDC and 0.136 g (0.75 mmol) of H_2ABDC for the 5%-MIXMOF and 2.243 g (13.5 mmol) of H_2BDC and 0.272 g (1.5 mmol) of H_2ABDC for the 10%-MIXMOF.

2.4. Synthesis of mixed-linker MOF-based Pd catalysts

The predried MIXMOFs were calcined in air atmosphere at 250 °C for 4 h to remove the solvent from the pores of the material. Afterwards, 10%-MIXMOF (700 mg, 0.270 mmol NH_2) was suspended in 50 cm^3 of DMF. A solution of $Pd(OAc)_2$ (121 mg, 0.540 mmol = 2 equiv. based on NH_2) in 5 cm^3 of DMF was added dropwise. The resulting slurry was stirred at RT for 24 h and subsequently the solid was filtered off and washed five times with 10 cm^3 of DMF each. To remove physically adsorbed solvent, the resulting MOF-5 material was pretreated in vacuum at 80 °C for 5 h.

5%-MIXMOF was treated equally, but using 60.5 mg (0.270 mmol = 2 equiv. based on NH_2) of $Pd(OAc)_2$ in 2.5 cm^3 DMF. As a reference material, pure MOF-5 was treated in the same way using 121 mg (0.540 mmol) of $Pd(OAc)_2$.

2.5. Characterization of materials and catalysts

Powder X-ray diffraction patterns were recorded on a Siemens D5000 diffractometer equipped with a Ni filter using Cu K_α radiation. Measurements were performed in the 2Θ range from 5° to 55° with a step size of 0.01° and a step time of 2 s. Peak positions were adjusted using a copper plate as the reference (Cu (1 1 1) peak at 43.3°). High-resolution powder X-ray diffraction patterns were recorded at beamline BM01B (ESRF Grenoble) using synchrotron X-ray radiation (wavelength: 0.49896 Å).

Combined thermoanalytical (TA) and mass spectrometric (MS) experiments were carried out isothermally or non-isothermally (heating rates were generally in the range of 5–10 K min^{-1}) on a Netzsch STA 409 simultaneous thermal analyzer equipped with a gas pulse device enabling injection of a certain amount of two different pure gases or gaseous mixtures into the system. The amount of injected gas could be varied from 0.01 to 10 cm^3; primarily, volumes of 1.0 and 2.0 cm^3 were used. Gases evolved during reaction and/or injected into the system were monitored online using a Balzers QMG 420 quadrupole mass spectrometer, connected to the thermal analyzer by a heated (ca. 200 °C) stainless steel capillary. The determination of the thermal stability of the MOFs was carried out in an atmosphere of 20 vol% O_2, balance He, using a total gas flow of 50 cm^3 min^{-1}.

2.6. Oxidation of CO using Pd/MIXMOF catalysts

The catalytic oxidation of CO was performed on the thermobalance with 30 mg samples placed in quartz crucibles and cooled from 225 to 40 °C with a rate of 1 K min^{-1} in He atmosphere. At chosen temperatures the pulses of CO (2 cm^3) and oxygen (2 cm^3) were simultaneously injected into the carrier gas stream flowing through the system. The amount of CO_2 formed during CO oxidation was quantified using the PulseTA technique [40] by relating the integral intensities of the $m/z = 44$ signals formed after injection to the intensities of 1 cm^3 pulses of CO_2 injected into the system before the reaction.

3. Results and discussion

MOF-5 single crystals are in most cases synthesized under solvothermal conditions by a slow diffusion of a base into an autoclave with the reaction mixture. This is necessary to achieve a slow deprotonation of the acid groups of BDC and, thus, a slow and controlled precipitation of the solid material. This procedure is, however, not suitable when two different organic linker molecules should be randomly incorporated into the resulting lattice. According to the different acid constants of the two linker molecules, the slow addition of a base would lead to deprotonation of the more acidic linker only and, consequently, to a structure which only contains this type of linker or finally a core–shell material, where the second linker is located only in the exterior. Therefore, we used a different approach for the synthesis of a pure MOF-5 material in the absence of a base. Heating a solution of Zn nitrate and BDC in dimethylformamide (DMF) in a round-bottom flask in air atmosphere led to the precipitation of MOF-5 as a white polycrystalline powder.

A comparison of the resulting powder diffraction pattern with the theoretical one, which was simulated using the single crystal data of MOF-5 reported in the literature, proved that no other crys-

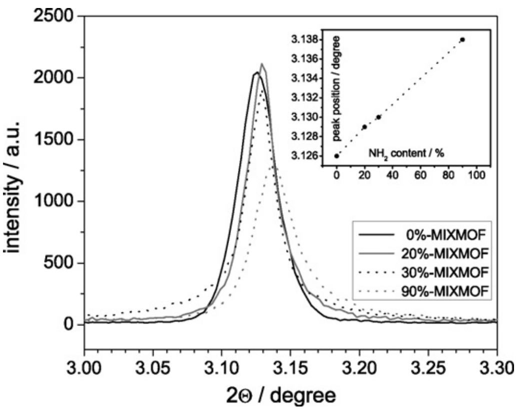


Fig. 3. Peak shift of the MIXMOF series observed using high-resolution X-ray diffraction. The formation of real MIXMOFs is proven by a linear correlation of ABDC content and peak shift according to Vegard's law.

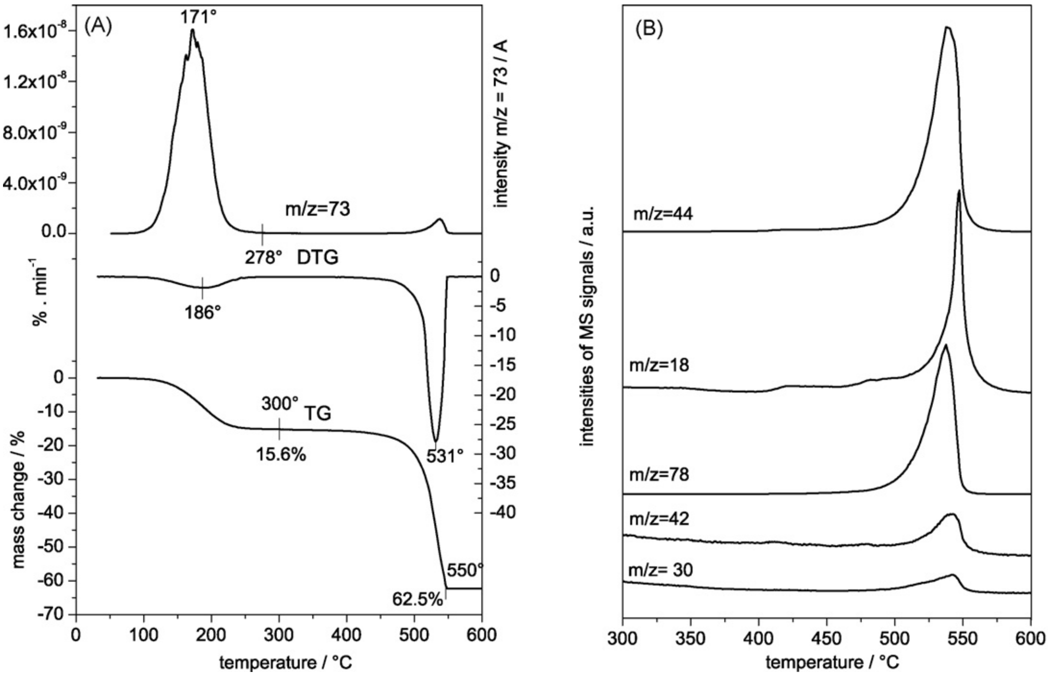


Fig. 4. Thermal decomposition of MOF-5 (0% ABDC) investigated by TA–MS: (A) TG, DTG and $m/z = 73$ (strongest mass spectrometric signal of DMF) and (B) MS signals of water ($m/z = 18$), CO_2 ($m/z = 44$), DMF ($m/z = 42$; second intense signal of DMF), NO ($m/z = 30$) and benzene ($m/z = 78$) recorded during decomposition/oxidation of the organic framework. Intensities of MS signals are expressed in arbitrary units.

talline phases were obtained in this synthesis. In the next step, we synthesized two mixed-linker MOFs (MIXMOFs) where we substituted 5% and 10%, respectively, of the BDC linkers by ABDC (in the following denoted as “5%-MIXMOF” and “10%-MIXMOF”, compare Scheme 1). In supplementary information (Fig. S1) the resulting powder diffraction patterns for a pure MOF-5 and the two MIXMOFs modified with 5% and 10% of ABDC are presented. All three materials show reflections in exactly the same positions, which are in accordance with literature data reported for MOF-5. Since both of the linker molecules have approximately the same size and the lattice constants for MOF-5 (pure BDC linkers) and IRMOF-3 (pure ABDC linkers) are very similar, it is impossible to prove the presence of real MIXMOFs (instead of a physical mixture of MOF-5 and IRMOF-3) using “normal” X-ray diffraction.

However, the application of high-resolution powder diffraction techniques (using synchrotron radiation) made this possible. While the presence of a mechanical mixture should lead to a splitting of each diffraction peak into two (one for MOF-5 and the other for IRMOF-3), a continuous peak shift should be expected (according to Vegard’s law) for real MIXMOFs. Fig. 3 visualizes the results of

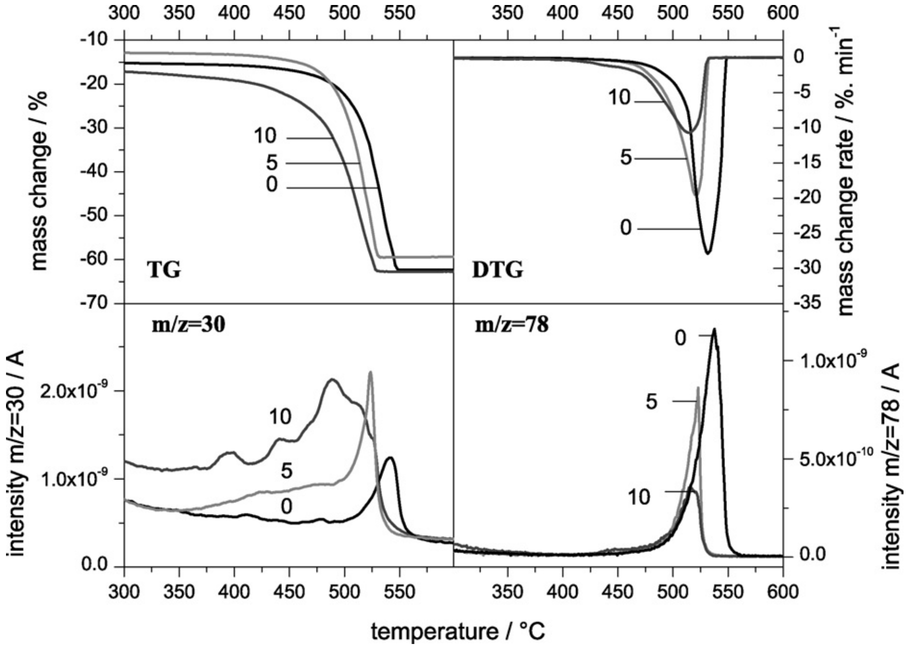


Fig. 5. TA–MS signals recorded during thermal treatment of MOF-5 (0% ABDC), 5%- and 10%-MIXMOFs in oxidizing atmosphere (20 vol% O_2 in He). Note that thermal stability is decreasing when the amount of ABDC linkers (marked on the curves) increases.

these high-resolution diffraction experiments, which show exactly the latter behavior for our series of MIXMOFs. Note that for this purpose MIXMOFs with higher ABDC content were measured in order to intensify the shift.

Due to the following reason no single crystals of the MIXMOFs could be obtained: growing of single crystals generally requires the slow addition or diffusion of a base into the reaction solution for a slow deprotonation of the dicarboxylic acid and thus a very slow and controlled precipitation of the metal–organic framework. In the case of the MIXMOFs such a slow addition of a base would lead to a selective deprotonation of one of the linker molecules (namely the one with the lower pK_a value). Consequently, a pure MOF-5 or IRMOF-3 would be expected instead of a MIXMOF with random distribution of the two linker molecules.

Another crucial requirement for successful use in catalysis is a sufficient stability of the materials under conditions that are typically applied in catalytic reactions. To elucidate the thermal stability of pure MOF-5, a combined TG/MS study was performed in oxygen containing atmosphere (20% O_2 in He). Fig. 4 summarizes the most important findings of this study. Although the material was predried in vacuum for 4 h, a significant amount (15.6 wt%) of DMF solvent ($m/z = 73$) was still present inside the pores. These solvent molecules could only be removed by heating to temperatures of ≈280 °C. Together with DMF also traces of water evolved from the pores of the material. After the calibration of the MS traces of water and DMF by the differential and pinhole methods described by Eigenmann et al. [41] we found that the amount of evolved water between room temperature and 300 °C was in the range of 0.8–0.9 wt%. TG, DTG and MS traces show that the sample was thermally stable even in oxidizing atmosphere (20 vol% O_2) in the temperature range 300–450 °C. The decomposition/combustion of the organic framework begun at ca. 470 °C and was manifested by the increasing intensity of the MS signal $m/z = 78$ which is characteristic for the benzene ring being the product of the cracking of the organic framework. The main gaseous products were water ($m/z = 18$) and CO_2 ($m/z = 44$) resulting from the framework combustion. Note that small amounts of DMF ($m/z = 73$ and $m/z = 42$), which could not be removed by heating, were still present in the material when the decomposition started. The observed weak signal of NO ($m/z = 30$) also resulted from the combustion of the residual DMF. The presented results indicate a surprisingly high thermal stability of the material and the necessity of the heat treatment for the removal of the DMF which was still present in the pores (despite the former vacuum drying).

In the next step we compared the thermal stability of pure MOF-5 and the two mixed-linker materials 5%- and 10%-MIXMOF (Fig. 5). TG and DTG curves show that the thermal stability of the materials decreased with increasing amount of the second linker (ABDC). However, no destruction of the framework was observed below temperatures of 350 °C for all three materials. The temperatures of the end of the decomposition under applied conditions (heating rate of 10 K min^{-1}, 20 vol% O_2) and maxima of DTG curves depicting the maximal rate of the decomposition/combustion change from 533, 522 and 516 °C (TG) and 533, 522 and 518 °C (DTG) for MOF-5,

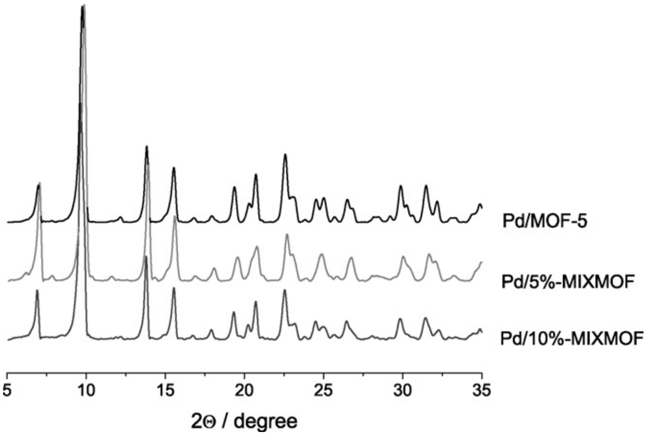


Fig. 6. X-ray powder diffraction patterns of Pd-modified MOF-5 (0% ABDC), 5%- and 10%-MIXMOFs.

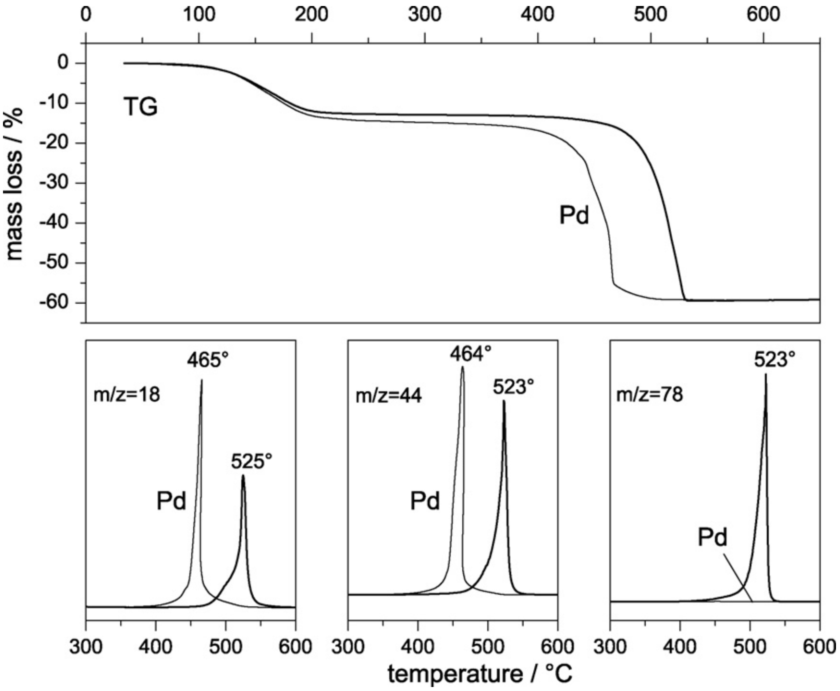


Fig. 7. Influence of Pd content on the thermal stability/oxidation of 5%-MIXMOF investigated by TA–MS. Both samples contain 5% of the ABDC linker, the TA and MS traces for the sample without Pd are displayed in black lines, the Pd containing sample in grey.

Table 1
Quantification of the amount of NH_2 in MOF-5 (0% ABDC), 5%- and 10%-MIXMOF expressed as integral intensities of mass spectrometric signals from NO (m/z = 30) formed during oxidation of nitrogen containing species.

Material	Integral intensity of m/z = 30 (NO) [a.u.]
MOF-5 (0% ABDC)	0.05
5%-MIXMOF	0.19
10%-MIXMOF	0.30

5%- and 10%-MIXMOF, respectively. In the DTG curves we observe one maximum for each of the three materials which is shifted to lower temperatures with increasing ABDC content. This is another clear indication for the successful synthesis of MIXMOFs in which both linkers are randomly distributed in the lattice. If a physical mixture of MOF-5 and IRMOF-3 would be obtained in the synthesis, we would expect the presence of two DTG maxima (one for MOF-5, the other for IRMOF-3) with different intensities. This has been proven by the results from a corresponding control experiment, which are presented in the supplementary information (Fig. S2). Based on these findings, we claim the formation of a true MIXMOF structure (like presented in Fig. 2) with a random distribution of BDC and ABDC linker molecules. The increasing amount of ABDC which is present in the structure can nicely be visualized using the evaluation of the MS signals for m/z = 30 (NO) and 78 (benzene) during combustion of the materials. Oxidation of the NH_2 groups at the aromatic ring at these temperatures causes the formation of NO and according to the increasing amount of ABDC linkers, the integral intensity of this signal is also increasing from MOF-5 to 10%-MIXMOF. In addition, a decrease of the integral intensity of the benzene fragment (m/z = 78) is observed in the series. This fact might be explained by the formation of aniline fragments (not monitored) instead of benzene during the decomposition of ABDC.

A quantitative determination of the amount of the NH_2 groups (from the ABDC linkers) by elemental analysis was not possible due to the presence of significant (unknown) amounts of DMF as an additional nitrogen source. Therefore we evaluated the NH_2 content using the integral intensity of the MS signal of NO (Table 1) for the three materials. The presented results show a linear increase of the evolved NO, but it is necessary to keep in mind that some minor amount of NO also evolved from the unmodified MOF-5 (which does not contain amino groups) due to the combustion of the residual amounts of DMF which is present in the MOF structure even at such high temperatures.

In the first part of this paper we have shown that it is possible to modify a MOF-5 material by exchanging a certain amount of its BDC linkers by ABDC. Although the thermal stability of the materials decreases with increasing NH_2 content, all three materials are thermally stable up to at least 350 °C in an atmosphere containing 20 vol% O_2. Therefore the materials seem to withstand the conditions normally encountered in catalytic reactions.

In the second part we focus on Pd catalysts based on MOF-5, 5%- and 10%-MIXMOF. The MOF materials were suspended in DMF and treated with a solution of $Pd(OAc)_2$. The solutions contained a molar amount of Pd which was twice as high as the molar amount of amino groups in the two MIXMOFs (=two equivalents of Pd based on NH_2). In the case of the pure MOF-5 the same amount as in 10%-MIXMOF was used. After an equilibration time of 24 h, the materials were thoroughly washed with DMF to remove Pd species which were only weakly physisorbed on the surface. The Pd content of the resulting catalysts was determined by AAS after drying at 80 °C in vacuum. While only 0.19 wt% was found in the pure MOF-5 (without NH_2 groups), the amount of Pd in the two MIXMOFs was significantly higher (0.52 for 5%-MIXMOF and 1.76 wt% for 10%-MIXMOF, respectively, see Table 2). These results clearly indicate a strong interaction between the NH_2 groups in the ABDC linkers which hampers the elution of Pd species from the pores.

Table 2
Pd loading of MIXMOF catalysts.

Material	Pd loading [wt%]
MOF-5 (0% ABDC)	0.19
5%-MIXMOF	0.52
10%-MIXMOF	1.76

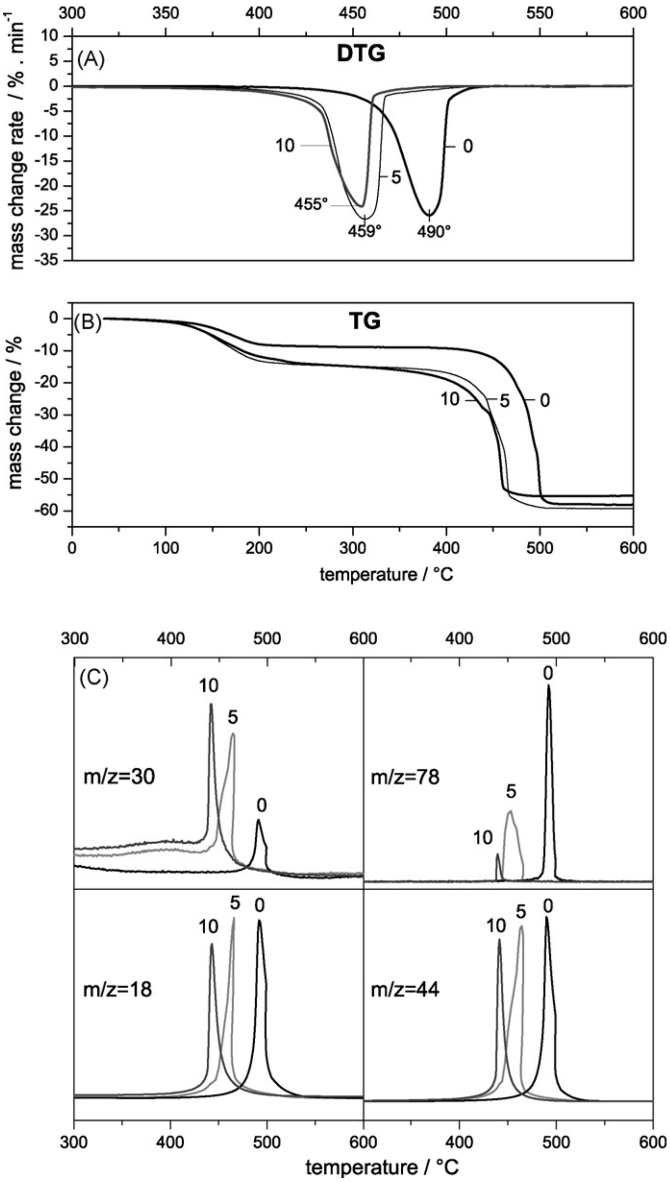


Fig. 8. Thermal decomposition of Pd containing MOF-5 (0% ABDC) and 5%- and 10%-MIXMOFs (percentages of ABDC linkers are marked on the curves) investigated by TA–MS: (A) DTG and (B) TG signals. (C) mass spectrometric signals of water (m/z = 18), CO_2 (m/z = 44), NO (m/z = 30) and benzene (m/z = 78) recorded during decomposition/oxidation of the organic framework. Note the significant influence of the Pd presence on the stability of the samples and catalytic oxidation of the benzene.

Powder X-ray diffraction patterns of the three Pd catalysts showed that the structure of the three frameworks remained unchanged after the immobilization of Pd (Fig. 6). As expected, no additional signals of large crystalline Pd particles could be observed.

In order to check the influence of Pd on the thermal stability of the materials under oxidizing conditions, we compared the behaviour of pure 5%-MIXMOF and the resulting Pd catalyst. The TA–MS results presented in Fig. 7 indicate a significant impact of

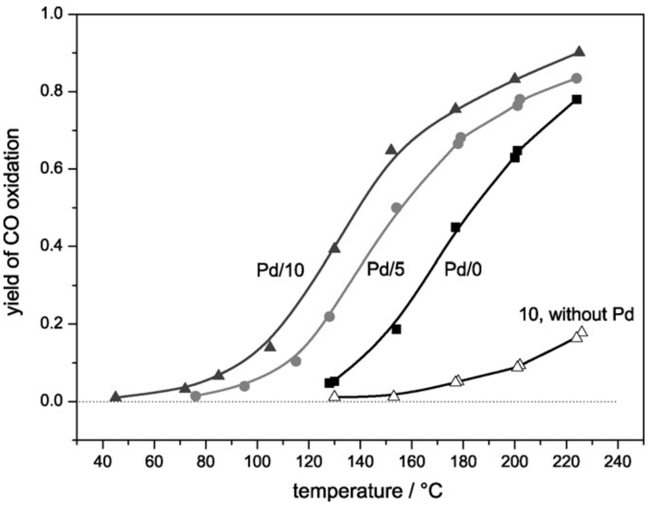


Fig. 9. Yield of the CO oxidation (CO:O_2 ratio 1:1) for the Pd containing MOF-5 (0% ABDC), 5%- and 10%-MIXMOFs as a function of the amount of the ABDC linkers (marked on the curves) and the temperature. The activity of pure Pd-free 10%-MIXMOF (pure 10%-MIXMOF without Pd) is displayed as reference.

the presence of Pd in the MIXMOF on the decomposition/oxidation process. In the presence of Pd the thermal stability decreased by ca. 60 °C (TG traces), also the maxima of the MS signals depicting the formation of the total combustion products water and CO_2 were shifted by ca. 60 °C. The absence of benzene fragments ($m/z = 78$) in the gaseous products of the decomposition/combustion process of the sample containing Pd indicates the strong catalytic activity of Pd in the combustion of the organic framework.

A comparison of the thermal stability of the three Pd catalysts that were obtained from MOF-5, 5%- and 10%-MIXMOF is given in Fig. 8. As already pointed out, an increasing number of ABDC linkers (i.e. NH_2 groups) leads to an increase of the Pd content in these catalysts. Since the combustion/decomposition of the framework is favoured in the presence of the noble metal, an additional decrease in thermal stability could be expected for the materials with higher Pd loading. The results presented in Fig. 8A and B (DTG and TG) indicate that the difference between the traces of the TA signals of 5%- and 10%-MIXMOF (459 and 455 °C, DTG maxima) is not as significant as between the MIXMOFs and the unmodified MOF-5 (455, 459 and 490 °C, respectively). However, the mass spectrometric signals presented in Fig. 8C, clearly indicate how an increasing amount of ABDC linkers in Pd containing samples shifts the decomposition/oxidation process towards lower temperatures.

The oxidation of CO (ratio CO/oxygen = 1:1) was chosen as a test reaction to check the applicability of the as-prepared Pd catalysts for oxidation reactions in the gas phase. The yield of the CO oxidation as a function of the reaction temperature was determined for Pd/MOF-5, Pd/5%- and Pd/10%-MIXMOF, respectively (Fig. 9). As a reference Pd-free 10%-MIXMOF was used. The activity was determined in the range 225–45 °C starting from the higher temperature to avoid the adsorption of formed CO_2 on the samples. During the cooling ramp with a rate of 1 K min^{-1}, four 1 cm^3 pulses in the order O_2–CO–O_2–CO were injected during 30 s into the carrier gas (He) at chosen temperatures. For the quantification of the formed CO_2 its integral intensities of MS signal ($m/z = 44$) were compared with the integral intensity obtained during injection of 1 cm^3 of CO_2 into the empty thermoanalyzer before the experiment.

The results shown in Fig. 9 indicate a significant increase of the catalytic activity in CO oxidation for the samples containing more ABDC and consequently more Pd. At a temperature of 150 °C the yield of CO oxidation amounted to 19%, 50% and 65% for the Pd catalysts Pd/MOF-5, Pd/5%- and 10%-MIXMOF, respectively. The Pd-free 10%-MIXMOF shows only a CO conversion of 1% at this temperature. This means that very small amounts of Pd (0.19 wt% in Pd/MOF-5) are sufficient to catalyze effectively the oxidation of CO. As a consequence, the resulting Pd catalysts seem to be promising candidates also for other gas phase oxidation reactions in the temperature range up to 350 °C.

4. Conclusions

Mixed-linker metal–organic frameworks (MIXMOFs) could successfully be synthesized using a mixture of the two isoreticular linker molecules benzene-1,4-dicarboxylate (BDC) and 2-aminobenzene-1,4-dicarboxylate (ABDC). The ratio of the two linker molecules determines as well the number of active sites (i.e. amino groups) as the thermal stability of the materials which decreases with increasing amino content. Nevertheless, the MIXMOFs exhibit thermal stability in oxidizing atmosphere up to 350 °C. The optimum of thermal stability as well as the number of active centers can be tuned for a certain application by choosing the optimum ratio of the two linker molecules. The presence of amino groups is also beneficial for the synthesis of Pd/MIXMOF catalysts which can be obtained by equilibrium adsorption. The interaction between the amino groups and the Pd leads to highly dispersed Pd species which do not form particles which are big enough to block pores or channels of the microporous MOF structure. Although the presence of Pd inside the pores of the material affects the thermal stability to some extent, the Pd/MIXMOF catalysts can be used as effective catalysts in the oxidation of CO at elevated temperatures. Based on the results of these first catalytic tests, Pd/MIXMOF materials seem to be promising catalysts also for other gas phase oxidation reactions in the temperature range up to 350 °C.

Acknowledgments

The authors thank the Swiss-Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble for providing beamtime and Wouter van Beek for supporting the high-resolution XRD measurements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.11.004.

References

[1] E.A. Tomic, J. Appl. Polym. Sci. 9 (1965) 3745–3752.
[2] O.M. Yaghi, G. Li, H. Li, Nature 378 (1995) 703–706.
[3] O.M. Yaghi, H. Li, J. Am. Chem. Soc. 117 (1995) 10401–10402.
[4] S. Kawata, S. Kitagawa, H. Machida, T. Nakamoto, M. Kondo, M. Katada, K. Kikuchi, I. Ikemoto, Inorg. Chim. Acta 229 (1995) 211–219.
[5] M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Honda, S. Kitagawa, Dalton Trans. (1994) 2771–2775.
[6] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705–714.
[7] A.K. Cheetham, C.N.R. Rao, R.K. Feller, Chem. Commun. (2006) 4780–4795.
[8] S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334–2375.
[9] G. Férey, Chem. Soc. Rev. 37 (2008) 191–214.
[10] S. Bauer, C. Serre, T. Devic, P. Horcajada, J. Marrot, G. Férey, N. Stock, Inorg. Chem. 47 (2008) 7568–7576.
[11] E. Biemmi, S. Christian, N. Stock, T. Bein, Micropor. Mesopor. Mater. 117 (2009) 111–117.
[12] H. Li, M. Eddaoudi, T.L. Groy, O.M. Yaghi, J. Am. Chem. Soc. 120 (1998) 8571–8572.
[13] H. Li, C.E. Davis, T.L. Groy, D.G. Kelley, O.M. Yaghi, J. Am. Chem. Soc. 120 (1998) 2186–2187.
[14] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Science 295 (2002) 469–472.
[15] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastré, J. Mater. Chem. 16 (2006) 626–636.

[16] U. Müller, M.M. Schubert, O.M. Yaghi, in: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Wiley–VCH, Weinheim, Germany, 2008, pp. 247–262.
[17] T. Dueren, L. Sarkisov, O.M. Yaghi, R.Q. Snurr, Langmuir 20 (2004) 2683–2689.
[18] J.L.C. Rowsell, O.M. Yaghi, Angew. Chem. Int. Ed. 44 (2005) 4670–4679.
[19] H. Frost, T. Düren, R.Q. Snurr, J. Phys. Chem. B 110 (2006) 9565–9570.
[20] K. Schlichte, T. Kratzke, S. Kaskel, Micropor. Mesopor. Mater. 73 (2004) 81–88.
[21] S.S.Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, Science 283 (1999) 1148–1150.
[22] E. Biemmi, C. Scherb, T. Bein, J. Am. Chem. Soc. 129 (2007) 8054–8055.
[23] W.J. Rieter, K.M.L. Taylor, W. Lin, J. Am. Chem. Soc. 129 (2007) 9852–9853.
[24] L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P.A. Jacobs, D.E. De Vos, Chem. Eur. J. 12 (2006) 7353–7363.
[25] F.X. Llabres i Xamena, A. Abad, A. Corma, H. Garcia, J. Catal. 250 (2007) 294–298.
[26] A.D. Burrows, C.G. Frost, M.F. Mahon, M. Winsper, C. Richardson, J.P. Attfield, J.A. Rodgers, Dalton Trans. (2008) 6788–6795.
[27] S. Opelt, S. Türk, E. Dietzsch, A. Henschel, S. Kaskel, E. Klemm, Catal. Commun. 9 (2008) 1286–1290.
[28] M. Sabo, A. Henschel, H. Fröde, E. Klemm, S. Kaskel, J. Mater. Chem. 17 (2007) 3827–3832.
[29] S. Hermes, M.-K. Schröter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R.W. Fischer, R.A. Fischer, Angew. Chem. Int. Ed. 44 (2005) 6237–6241.
[30] S. Hermes, F. Schröder, S. Amirjalayer, R. Schmid, R.A. Fischer, J. Mater. Chem. 16 (2006) 2464–2472.
[31] Z. Wang, S.M. Cohen, J. Am. Chem. Soc. 129 (2007) 12368–12369.
[32] K.K. Tanabe, Z. Wang, S.M. Cohen, J. Am. Chem. Soc. 130 (2008) 8508–8517.
[33] Z. Wang, S.M. Cohen, Angew. Chem. Int. Ed. 47 (2008) 4699–4702.
[34] A.D. Burrows, C.G. Frost, M.F. Mahon, C. Richardson, Angew. Chem. Int. Ed. 47 (2008) 8482–8486.
[35] T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey, N. Stock, Inorg. Chem. 48 (2009) 3057–3064.
[36] S.-H. Cho, B. Ma, S.T. Nguyen, J.T. Hupp, T.E. Albrecht-Schmitt, Chem. Commun. (2006) 2563–2565.
[37] K.C. Szeto, K.P. Lillerud, M. Tilset, M. Bjørgen, C. Prestipino, A. Zecchina, C. Lamberti, S. Bordiga, J. Phys. Chem. B 110 (2006) 21509–21520.
[38] K.C. Szeto, C. Prestipino, C. Lamberti, A. Zecchina, S. Bordiga, M. Bjørgen, M. Tilset, K.P. Lillerud, Chem. Mater. 19 (2007) 211–220.
[39] W. Kleist, F. Jutz, M. Maciejewski, A. Baiker, Eur. J. Inorg. Chem. (2009) 3552–3561.
[40] M. Maciejewski, C.A. Müller, R. Tschan, W.D. Emmerich, A. Baiker, Thermochim. Acta 295 (1997) 167–182.
[41] F. Eigenmann, M. Maciejewski, A. Baiker, Thermochim. Acta 440 (2006) 81–92.