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Melián-Cabrera, Ignacio; Moulijn, Jacob A.

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6

Oxidation Tools in the Synthesis of Catalysts and Related Functional Materials

Ignacio Melián-Cabrera and Jacob A. Moulijn

6.1

Introduction

The classical design of a heterogeneous catalyst is changing from the use of conventional supports to more sophisticated high-tech structures, such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs), periodic organosilicas, and open-framework molecular sieves containing micro- and mesoporosity. These high-tech materials are in general not active themselves and require functionalization of the surface or bulk properties. Looking at recent reported work, we realized that oxidation reactions are increasingly more useful tools for functionalization, opening up opportunities to tune the catalytic performance. This chapter aims at compiling the state of the art on oxidation tools in the synthesis of catalysts and related functional materials.

6.2

Preparation Strategies Involving Chemical Oxidative Approaches

6.2.1

Calcination in Oxidative Atmospheres

Thermal treatment of a material in a gas oxidizing atmosphere is the simplest concept. This can be done in air, air diluted in N₂, dry air, or in ultrahigh purity O₂. In the laboratory practice, calcination is done in flowthrough beds, aided by fluidization, or in static box furnaces. Important aspects are the bed geometry, the removal of the generated gases, and temperature gradients.

Thermal treatments can be applied to modify the properties of a material, for example, dealumination and optimization of crystalline phases. These techniques do not require oxidants. Oxidative thermal treatments are generally employed to activate molecular sieves, by removing the organic templates employed during synthesis. This is one of the key steps when preparing porous catalysts or adsorbents. In air-atmosphere calcination, the templates are typically combusted between 400

and 700 °C. Occasionally the composite mesophases can contain up to 50 wt% of organics. The removal procedure is thus of the utmost importance.

Many studies on template thermal degradation have been reported on zeolites of industrial interest including ZSM5 [1–5], silicalite [1], and beta [6–8], as well as surfactant-templated mesostructured materials [9–13]. The latter are structurally more sensitive than molecular sieves. Their structure usually shrinks upon thermal treatment. The general practice is slow heating at 1 °C min⁻¹ (N₂/air) up to 550 °C, followed by a temperature plateau.

It is evident that dedicated studies are required for each structure to optimize the template oxidation protocol. Many structures, in particular nonsiliceous, are thermally very sensitive [14, 15]. Calcination can result in a complete breakdown due to hydrolysis, redox processes, and phase transformations. The removal of templates in those systems is critical, making the development of mild detemplation techniques necessary [16].

6.2.2

Aerosol Flame Technologies

Aerosol flame synthesis is a mature technology. A solid phase is generated by dispersing the metal precursors in a flame. The first reports are dated from the 1970s to the 1980s [17–19]. Reviews can be found in [20, 21]. Three different approaches are identified, depending on the state of precursor:

- 1) **Vapor fed aerosol flame synthesis (VAFS):** the precursor is in gas phase by using volatile metal precursors such as chlorides.
- 2) **Flame spray pyrolysis (FSP):** a liquid precursor solution is sprayed into the flame and ignites; its combustion drives the flame process.
- 3) **Flame-assisted spray pyrolysis (FASP):** this is similar to FSP, but the flame is sustained by a fuel.

These processes are very rapid and allow the preparation of inorganic supports in one step. This technique allows large-scale manufacturing of supports such as titania, fumed silica, and aluminas. Sometimes the properties of the material differ from the conventional preparation routes and make this approach unique. Multicomponent systems can be also prepared, either by multimetallic solutions or by using a two-nozzle system fed with monometallic solutions [22]. The as-prepared powder can be directly deposited onto substrates, and the process is termed *combustion chemical vapor deposition* [23].

Active heterogeneous catalysts have been obtained. Examples include titania-, vanadia-, silica-, and ceria-based catalysts. A survey of catalytic materials prepared in flames can be found in [20]. Recent advances include nanocrystalline TiO₂ [24], one-step synthesis of noble metal TiO₂ [25], Ru-doped cobalt–zirconia [26], vanadia–titania [27], Rh-Al₂O₃ for chemoselective hydrogenations [28], and alumina-supported noble metal particles via high-throughput experimentation [29].

6.2.3

Solution Combustion Synthesis

This methodology uses the heat produced from the exothermic reaction between an oxidizer, usually a metal nitrate, and a fuel possessing amino groups [30, 31]. The reactants are dissolved in water in a suitable ratio and heated until the mixture is ignited and self-propagation takes place. The main advantages are the high speed, simplicity of equipment, and easy scale-up. However, it requires ignition, relatively high temperatures, and use of specific metal precursors. Typical fuels used are urea and hydrazides due to their highly exothermic combustion [32].

Solution combustion belongs to a wider family entitled *combustion synthesis* [33], covering also solid-state processes. This approach leads to technologically interesting materials but not to many catalysts. Conversely, combustion using liquid solutions allows to prepare heterogeneous catalysts supports and multimetallic counterparts. Many applications have been reported: metal-supported $\alpha\text{Al}_2\text{O}_3$ [34], Cu/CeO₂ [35], Ag/CeO₂ [36], Pt/Pd CeO₂ [37], Ce_{1-x}Pt_xO_{2- δ} [38], HDS based CoMo [39], *in situ* methods [40], perovskite structures [41–45], Ce_{1-x}Ni_xO₂ for propane oxidative steam reforming [46], CuO/ZnO/ZrO₂/Pd for oxidative hydrogen production from methanol [47], and mesoporosity induction in MgO [48] and Al₂O₃ [49].

6.2.4

Sulfonic Acid Functionalization of Ordered Mesoporous Materials and Periodic Organosilicas

Mesoporous molecular sieves have drawn considerable attention as an alternative to zeolites. It was soon realized that additional functionalization is required. The Al-substituted formulations showed relatively low acid strengths. Research focused on the covalent attachment of HSO₃ groups to silica surfaces. This can be done by postsynthesis grafting, coating, or co-condensation of mercaptopropyl groups that are oxidized into -HSO₃. Another area of interest developed with the discovery of periodic organosilicas that required acidity incorporation too. In both cases, oxidation chemistry played an important role.

Organic modifications of the mesoporous materials were achieved by grafting on surface hydroxyl groups [50, 51] or co-condensation of siloxane and organosiloxane precursors [52–56]. Co-condensation allowed the use of alkylthiol precursors, in particular 3-mercaptopropyltrimethoxysilane (MPTMS). Stein's group reported the introduction of organosulfur groups on MCM-41 [57] that yields sulfonic acids by successive HNO₃ oxidations. The material showed acid-catalyzed behavior.

Jacob's group reported a protocol that used mild H₂O₂ oxidations and MPTMS for three approaches, namely, grafted, coated, and co-condensed MCM-41 and HMS materials [58] (Figure 6.1a). The propyl spacer was stable to the oxidation conditions while sulfonic groups were generated as evidenced by NMR spectra. These materials

Figure 6.1 (a) HSO₃-functionalization on silica MCM/HMS materials via thiol incorporation (co-condensation, grafting, or coating) and mild H₂O₂ oxidation. (Adapted with permission from [58], Copyright 1998. Royal Society of Chemistry.) (b) Model for

a phenylene periodic organosilica where the silica layers are functionalized with propylsulfonic-acid groups via HNO₃ oxidation of the thiol function. (Reprinted with permission from [68], Copyright 2002. American Chemical Society.)

proved to be active for the synthesis of 2,2-bis(5-methylfuryl)propane [58], esterification of sorbitol [58] and glycerol [59] with lauric acid, Bisphenol-A synthesis [60, 61], dehydration of xylose into furfural [62], and the esterification of high-free fatty acid soybean oil [63]. Pérez-Pariente *et al.* reported a modified MCM-41 by combining alkyl and mercaptopropyl groups [64]. H₂O₂ oxidation yielded the corresponding HSO₃ groups while the alkyl groups remained unchanged. The improved hydrophobicity of the channels benefits the esterification of fatty acids [65, 66]. Feng *et al.* [67] also applied the H₂O₂ oxidation of thiol-JLU-20 materials, obtaining a high -HSO₃ density.

In situ thiol oxidation can also be done just after the tetraethoxysilane hydrolysis. Both MPTMS and H₂O₂ are added simultaneously before aging. This was demonstrated by Stucky *et al.* [69] on SBA-15 containing HSO₃ and additional alkyl groups, followed by Mbaraka *et al.* [63], and Yang *et al.* [70], the latter including template removal. *In situ* oxidation avoids residual unreacted thiols, typically observed by postsynthetic routes.

Oxidation chemistry has also been useful for periodic organosilicas. Inagaki *et al.* reported the direct sulfonation of the phenylene group of mesoporous benzene-silica and its use as solid acid catalyst [71]. In a second protocol [68], the silica layers were functionalized while keeping the benzene sites intact (Figure 6.1b). This was done by co-condensation of 1,4-bis(triethoxy-silyl)benzene and MPTMS. Oxidation of the -SH groups was done in HNO₃ [57]. The crystal-like pore walls survived the oxidation but a decrease in BET area was observed. For the highest acidity only about 50% oxidation took place. H₂O₂ did not improve the oxidation yields [72]. Alkyl hydroperoxides were covalently functionalized onto SBA-15 by autoxidation using molecular oxygen and initiator or H₂O₂ [73]. Nonoxidative approaches have been reported as well [74–84].

6.2.5

Surface Oxidation of Carbon Nanofibers Prior to Functionalization

Oxidation chemistry has been practiced widely for carbon catalyst supports. Treatments with oxidants generate oxidic groups, which can be acidic or basic. It is not only performed with gas-phase reactants, for example, air, O₂, O₃, and CO₂, at 200–500 °C but also with aqueous solutions of HNO₃, H₂SO₄, HCl, KMnO₄, and H₂O₂ usually activated by temperature. Oxidation makes the carbon surface more hydrophilic and reactive. This is important in order to improve the wetting ability, dispersing metal (nano)particles, and grafting complexes. This topic has been extensively discussed for conventional supports [85–90] but less for CNTs and CNFs. These systems are more inert and oxidation is a prerequisite before functionalization. Most of the work reported concerns CNTs and is discussed separately in Section 6.2.6.

The first studies on CNFs oxidation discussed the impact of the surface treatments on bulk ordering [91]. Investigations for catalytic purposes came later with extensive contributions by the groups in Utrecht, Geus, and de Jong. For an optimal use of CNFs as catalyst supports, their surface has to be modified. One way is by introducing oxygen-containing groups. Protocols employ oxidations with concentrated HNO₃ or a mixture with H₂SO₄ under reflux [92–94]. The graphitic layers remain unchanged while the pore volume increases [93, 94]. Toebe *et al.* showed that the most predominant effect is the opening of the inner tubes of the fibers [93]. The oxidation did not only occur at the surface but also developed 2–3 nm into the subsurface [93]. Carbonyl groups are formed, which are subsequently converted into carboxyls and carboxylic anhydrides [92].

Successful applications of the oxygen-modified CNFs are reported on immobilization of metal complexes [95], incorporation of small Rh particles [96], supported Pt and Ru CNFs by adsorption and homogeneous deposition precipitation [97, 98], Co CNFs for Fischer–Tropsch synthesis [99], and Pt CNFs for PEM fuel cells [100].

6.2.6

Purification, Opening, and Size Reduction of Carbon Nanotubes by Oxidative Treatments

Oxidation reaction is essential for processing CNTs [101–104]. It enables purification by removing metals from synthesis and amorphous carbon domains, opening the long tubes, and cutting into shorter lengths that improve the wetting and filling. Such oxidative processes involve liquid-phase treatments under reflux with concentrated HNO₃ [105], H₂SO₄ [106], a mixture of both [107], or a two-step process involving HNO₃/H₂SO₄ and H₂SO₄/H₂O₂ [108]. These treatments introduce oxygen-containing surface groups, predominantly phenolic, carboxylic, and lactonic types. These groups stabilize dispersions of CNTs at higher concentrations than are possible for pristine CNTs [109]. Application of ultrasound prior to the

acid treatment increases the number of O-groups [110] and completes the removal of wall-entrapped metallic impurities [111].

These approaches are crucial to measure the properties of the individual tubes, which are of large interest in theoretical studies [105, 112–115]. Confinement effects of metal nanoparticles within CNTs were also shown to be a promising concept in heterogeneous catalysts [116, 117]. However, several technical challenges were not solved until recently. Liquid treatments in HNO_3 mixtures remove metal catalyst impurities and amorphous carbons but at the expense of significant mass reduction of CNTs [118]. Alternative approaches include physical and gas-phase oxidations. For instance, multiwalled materials can be cut by ball milling [119, 120]. Electrical cutting in scanning tunneling [121] and atomic force microscopes [122] or electron beams [123] have been reported. Ozone treatment yields oxidation and etching of single-wall CNTs [124] too.

Recent investigations done on precise cutting of single-wall CNTs focus on (i) controlled liquid-phase oxidations after side wall damage and (ii) selective gas-phase oxidations, using metal cluster catalysts to promote an easier decomposition of the amorphous carbon domains. For instance, selective oxidation using gold particles has been reported. Clusters of about 20 nm after dispersion in carbonaceous soot containing single-wall carbon catalyze the oxidation of carbonaceous impurities at about 350 °C [125] leaving the CNTs undamaged. These results were later confirmed [126].

The first approach is carried out after purification by an uncatalyzed gas-phase oxidation. Chiang *et al.* proposed a multistep oxidation process at increasing temperatures followed by acid wash between steps [127, 128]. It is a method similar to that proposed by Dillon *et al.* [129] with the difference being the multistep procedure. At low-temperature amorphous carbon domains are removed, while the extraction of the metal residue embedded in the walls is carried out during the interstate acid washing. Such a protocol does not cut the tubes but induces sidewall damage. A second step cuts the CNTs through the damaged sites. This was achieved only by treating the purified nanotubes with 4 : 1 vol ratio of 96% H_2SO_4 –30% H_2O_2 at room temperature [130]. Low mass loss, slow etch rates, and no extra sidewall damage were found. Tran *et al.* [131] proposed a cutting method of multiwalled CNTs based on repeated brief exposure to thermally oxidative conditions.

A novel process to control the cutting of long multiwalled tubes via catalytic oxidation with reduced losses was reported by Bao *et al.* [117, 132], Figure 6.2. The material was impregnated with AgNO_3 followed by decomposition at 300 °C in Ar, creating Ag particles of 10–15 nm on the exterior surface of the tubes. Subsequent catalytic oxidation was carried out and small pits were formed around the positions where the catalyst particles were located, due to oxidative etching of carbon. Ultrasound treatment in diluted nitric acid solution offered two functions. It completes the breaking of nanotubes around the pits and removes the silver clusters at the outer surface. Controlling the oxidation conditions was fundamental to avoid severe losses. At optimal conditions weight losses are < 20 wt%.

Figure 6.2 Two-step cutting of CNTs by hydrocarbon-assisted oxidation on silver clusters, followed by HNO_3 treatment mediated by ultrasound. The length of the CNTs is controlled through the Ag loading. (Reprinted with permission from [132], Copyright 2008, The Royal Society of Chemistry.)

6.2.7

Metal-Free Catalysis by Oxygen-Containing Carbon Nanotubes

Oxidized CNTs have shown unprecedented performance in oxidative dehydrogenation of alkanes. Su and coworkers [133] showed that multiwalled CNTs containing ketonic $\text{C}=\text{O}$ groups catalyze the oxidative dehydrogenation of *n*-butane to butanes, especially butadiene. For conventional multimetal catalysts, the relatively fast alkenes oxidation limits the selectivity at higher conversion. The observed increase in selectivity comes from an inhibition of the secondary combustion. The presence of two neighboring $\text{C}=\text{O}$ pairs is required to subtract two hydrogen atoms from butane. The catalytic effect of oxygen species on carbon materials has been already reported [134–137], but only for ethylbenzene, which is easier to activate than alkanes. Su *et al.* claim three effects: (i) higher selectivity, (ii) improved stability, and (iii) low partial pressures of oxygen. Addition of phosphorus improved the selectivity further by suppressing the combustion.

The active species are generated after refluxing the pristine CNT in HNO_3 [137, 138]. Other oxidation strategies can be implemented for tuning the type and density of the oxidized catalytic functions. Resasco [139] pointed out that these results open up an avenue for tuning the density and distribution of $\text{C}=\text{O}$ pairs, in particular with controlled chiralities.

6.3

A Catalytic Oxidation Tool. Fenton Chemistry in Solid Catalyst Synthesis

6.3.1

What is the Fenton Reaction?

Fenton chemistry comprises reactions of H_2O_2 in the presence of iron species to generate reactive species such as the hydroxyl radical $\text{OH}^\bullet$. These radicals ($E^0 = 2.73 \text{ V}$) lead to a more efficient oxidation chemistry than H_2O_2 itself ($E^0 = 1.80 \text{ V}$).

The reaction was reported by Henry J. Fenton [140]. This reaction is applied in the treatment of hazardous organic wastes. A search for “Fenton reaction” in the website ISI Web of Knowledge® [141] throws up thousands of scientific papers due to the exponential growth in its use over the years. It has been reviewed in various papers [142–145]. Below, the reaction pathway in the absence of an organic compound is given:

In the absence of any oxidizable compound, the net reaction is the Fe-catalyzed decomposition of H_2O_2 (Reaction 6.8). This reaction also occurs when a target contaminant is present.

This chemistry has been investigated and implemented for wastewater mineralization by oxidizing the organic pollutants. The process is very efficient, not selective and, as a consequence, almost all carbon matter can be removed. Topical areas also include soil and aquifer treatments, sometimes in combination with a secondary biotic process [145].

6.3.2

Can We Use Fenton Chemistry in Solid Catalyst Synthesis?

Although Fenton chemistry has been solely researched in water and soil purification, it can also be an added-value tool for catalyst preparation. The next sections review this concept including the following:

- shifting the complexation equilibria for ion-exchange by oxidation of the organic chelates [146];
- one-pot synthesis of metal-exchanged zeolites [147];
- mild detemplation of micro- and mesoporous materials [148–150].

The properties of the materials were evaluated by textural and structural techniques, while the final catalysts are compared on the basis of their N_2O -decomposition under simulated industrial conditions for nitric acid plants. This reaction is known to be activated by Fe-species [151, 152].

6.3.3

Kinetics of Fenton Chemistry

Fenton kinetics is quite complex. Different oxidizing species are present but hydroxyl radicals are regarded as the unique reactive species. Hydroxyl can be produced by thermal and photochemical reactions, and destroyed by the target pollutant, reaction intermediates, and by scavenging undesired reactions. Rate law formulae involve a large number of steps. Optimal conditions can be easily obtained by semiempirical modeling by accounting for the effect of the dominating parameters. Critical parameters are iron and hydrogen peroxide concentrations, temperature, light, and pH. Experimental design and response surface methodologies have been applied [145, 153, 154].

Haber and Weiss proposed that $\text{OH}^\bullet$ is the active oxidant [155] by combining an Fe^{II} salt with H_2O_2 (Reaction 6.1). Reaction 6.2 reduces the Fe^{III} into Fe^{II} , which will generate more $\text{OH}^\bullet$. The cycle continues until H_2O_2 is consumed. Reactions 6.1 and 6.2 show that the reaction is catalytically in Fe. Reaction 6.2 is several orders of magnitude slower compared to Reaction 6.1, being the rate-determining step of the overall process [145, 156–159]. This has consequences for the oxidation state of the Fe salt. The large majority of the iron ions are present as Fe^{III} . The system will behave independently of the initial oxidation state of iron. The Fe valence is relevant when the reaction is assisted by light. $\text{OH}^\bullet$ radicals can also be produced via Reaction 6.1 by supplying stoichiometric Fe^{II} . This however generates a large Fe^{III} residue.

The discussion above refers to the classical “dark” conditions where the chemical activation is achieved thermally. Fenton requires a moderate thermal activation, resulting in a reaction temperature ranging from 25 to 90 °C. The oxidizing capacity of the Fenton reaction can be increased by UV or UV–vis light irradiation [160, 161]. The increase is interpreted by means of the photoreduction ability of Fe^{III} :

Fe^{III} complexes display ligand to metal charge transfer excitation, dissociating to give Fe^{II} and oxidized ligand [162]. The photons introduce an alternative pathway to Reaction 6.2, being the rate-determining step under dark conditions, leading to an increased $\text{OH}^\bullet$ rate. $\text{Fe}(\text{OH})^{2+}$ is the most important species (Reaction 6.9) because of its relatively high absorption coefficient and high concentration relative to other Fe^{III} species. Excitation of $\text{Fe}(\text{OH})^{2+}$ alone can be used to generate radicals without oxidant, but stoichiometric amounts of Fe^{3+} are required. Electro-Fenton methods cover electrochemical reactions that are used to generate one or both of the reagents. The most promising approach is discussed elsewhere [163].

The pH effect in Fenton reactions is due to the Fe^{III} speciation. In highly acidic solutions containing noncoordinating species, Fe^{III} exists as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. The composition as function of the pH is represented in Figure 6.3a. At increasing pH, Fe^{3+} undergoes hydrolysis forming FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, and finally FeO_x via binuclear, $\text{Fe}_2(\text{OH})_4^{2+}$, and polynuclear species. The aim of optimization is to avoid Fe precipitation, either bi-, poly-, or precipitated Fe oxides that are all inactive in

Figure 6.3 Calculated concentrations for the Fe^{III} speciation as a function of the pH in aqueous solutions taking into account the hydrolysis reactions: $\text{Fe}^{3+} + \text{H}_2\text{O} = \text{Fe(OH)}^{2+} + \text{H}^+$ ($\log K_1 = -3.05$); $\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2^+ + 2\text{H}^+$ ($\log \beta_2 = -6.31$); $2\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$ ($\log \beta_{22} =$

-2.91), where $\alpha(0) = [\text{Fe}^{3+}]/[\text{Fe}^{3+}]_{\text{TOTAL}}$; $\alpha(1) = [\text{Fe(OH)}^{2+}]/[\text{Fe}^{3+}]_{\text{TOTAL}}$; $\alpha(2) = [\text{Fe(OH)}_2^+]/[\text{Fe}^{3+}]_{\text{TOTAL}}$ and $\alpha(2,2) = [\text{Fe}_2(\text{OH})_2^{4+}]/[\text{Fe}^{3+}]_{\text{TOTAL}}$. (a) Calculation for a $[\text{Fe}^{3+}]_{\text{TOTAL}}$ of 10^{-3} M. (b) $\alpha(2,2)$ for different $[\text{Fe}^{3+}]_{\text{TOTAL}}$ ranging from 10^{-4} to 5×10^{-3} M. (Equilibria constants were taken from [164–166].)

Fenton. The maximum performance is usually observed at pH slightly below 3 because of two reasons: (i) colloids that begin to precipitate at pH above 3 via the binuclear species ($\alpha_{2,2}$) are suppressed and (ii) the concentration of Fe(OH)^{2+} (α_1) is close to its maximum. Fe(OH)^{2+} species possess a high absorption coefficient under irradiation and maximize the oxidation yield. This holds for diluted systems. When the total Fe concentration is increased, the binuclear species become dominant and precipitation is favored. Figure 6.3b clarifies this aspect by showing the $\text{Fe}_2(\text{OH})_2^{4+}$ concentration profiles for increasing Fe concentrations. In those cases, lowering the pH to about 2 is favorable.

6.4

First Concept in Catalyst Design. Shifting Complexation Equilibria for Ion-Exchange by Oxidation of the Organic Chelates

Conventional metal ion-exchange of zeolites involves aqueous solutions of soluble metal salts, usually nitrates. A disadvantage using nitrates is eutrophication of the wastewater. Metal–organic salts can be employed, but many of them form stable complexes, hindering the exchange reaction both kinetically and sterically. In some cases complexation is desired. Geus and coworkers benefited from chelation for impregnation [167, 168].

Our first example discusses the use of an oxidant to remove organic ligands in solution during ion-exchange [146]. The oxidant must be clean, strongly oxidizing, and should not generate residues on the catalyst. These properties are met by H_2O_2 . It shifts complexation equilibria efficiently and the metal cations can be

exchanged within the zeolite. The method was proven for the preparation of Fe-FER using Ferric citrate. The preparation temperature is a critical parameter. At low temperature, Fenton's kinetics is not fast enough to break down the ligands. At the highest titration temperature, the catalyst performance in N_2O decomposition dropped. This was explained by a simultaneous competitive Fe-hydrolysis process, leading to inactive FeO_x species. The optimal catalyst proved to be stable under tail gas conditions.

It was first assumed that the oxidant was H_2O_2 . However, since traces of Fe-cations are present, a Fenton's type oxidation pathway, based on OH radicals, is more likely taking place.

6.5

Second Concept in Catalyst Design. One-Pot Synthesis of Fe Zeolite Catalysts

Iron zeolites are important in environmental catalysis, covering the abatement of nitrous oxide, NO_x control, and selective oxidation of organics [169]. The preparation of Fe-exchanged zeolite catalysts consists of various steps: (i) hydrothermal zeolite synthesis using organic templates; (ii) detemplation by thermal treatment; (iii) accommodation to the desired form, usually containing NH_4 -groups; (iv) metal incorporation by wet chemistry; (v) drying; and (vi) calcination. Reducing the number of steps is challenging and can contribute to an improved and faster process.

We discuss here a combined process including detemplation and Fe incorporation by ion-exchange in the zeolite framework [147]. To achieve this, oxidants to decompose the organic template and Fe-cations for exchange are needed. Both requirements are in harmony with Fenton chemistry. The $\text{OH}^\bullet$ radicals can oxidize the template and the Fe-cations be exchanged simultaneously.

The preparation was performed on a commercial microcrystalline beta zeolite. The zeolite was treated with the Fenton's reagent and less than 0.3 wt% of carbon remained after the treatment. The porosity was fully developed as revealed by the pore-size distribution. Elemental analysis combined with TPR did confirm the high degree of Fe-exchange (98%) on the Brønsted sites.

Contacting the synthesized zeolite with the reagent leads to a ready-to-use catalyst. No further pretreatment before reaction is needed. The performance of such a novel one-pot catalyst was tested in N_2O decomposition, and was found to be even superior to the conventionally prepared counterpart. This was ascribed to the minimization of FeO_x formation.

It is concluded that zeolite beta can be simultaneously detemplated and Fe-exchanged without FeO_x formation by treating the parent zeolite with a Fenton reagent. The catalyst shows good performance on N_2O decomposition. This one-pot process simplifies its preparation protocol and can be extended to other systems. Indeed, our approach was followed by Liu *et al.* [170], for preparing Fe-SBA-15 for benzylation of benzene with interesting results.

6.6

Third Concept in Catalyst Design. Fenton Detemplation. Mild Organic Template Removal in Micro- and Mesoporous Molecular Sieves

By minimizing the Fe concentration (i.e., avoiding extensive Fe-exchange), zeolites, or mesoporous compounds can be detemplated at low temperatures without the need for high-temperature calcination. This third concept refers to the low-temperature Fenton detemplation. Strictly speaking, Fenton requires thermal activation but always below 100 °C. We refer here to “quasi room temperature” as compared to the high temperatures usually applied for calcination.

6.6.1

Role of Organic Templates and Drawbacks Associated to Calcination

Most of the microporous and mesoporous compounds require the use of structure-directing molecules under hydro(solvo)thermal conditions [14, 15, 171, 172]. A serious handicap is the application of high-temperature calcination to develop their porosity. It usually results in inferior textural and acidic properties, and even full structural collapse occurs in the case of open frameworks, (proto)zeolites containing small-crystalline domains, and mesostructures. These materials can show very interesting properties if their structure could be fully maintained. A principal question is, is there any alternative to calcination? There is a manifested interest to find alternatives to calcination to show the potential of new structures.

The organic templating approach was first introduced by Barrer and Denny [173]. Since then, organic amines, quaternary-ammonium bases, metal complexes, and other compounds have been extensively used in zeolite synthesis, acting as “space fillers” with low specificity, “structure-directing agent,” or “true templates” [174]. Because such guest molecules usually interact with the frameworks through H-bonds, van der Waals’s forces, or sometimes coordination bonds, it is crucial to remove the templates properly to form structurally stable, free-pore molecular sieves.

Microcrystalline zeolites such as beta zeolite suffer from calcination. The crystallinity is decreased and the framework can be notably dealuminated by the steam generated [175]. Potential Brønsted catalytic sites are lost and heteroatoms migrate to extra-framework positions, leading to a decrease in catalytic performance. Nanocrystals and ultrafine zeolite particles display aggregation issues, difficulties in regeneration, and low thermal and hydrothermal stabilities. Therefore, calcination is sometimes not the optimal protocol to activate such systems. Application of zeolites for coatings, patterned thin-films, and membranes usually is associated with defects and cracks upon template removal.

It must be noted that sometimes calcination is beneficial to create active species. Notable examples are the Sn-beta speciation [176] and generation of extra-framework Al-Lewis sites in beta zeolite for organic transformations

[175, 177]. However, even in these cases, it might be attractive to apply a mild detemplation followed by controlled heating for optimization.

For microporous compounds with special compositions, calcination effects are even more severe. As compared with zeolites, these compounds have lower thermal stability. Strictly speaking, most of them are nonporous since removal of the occluded guest molecules by calcination usually results in collapse. This is due to strong H-bonds with the framework, coordination bonds, and sometimes the templating molecule is shared with the inorganic polyhedra. Relevant examples of low-stability microporous compounds with interesting structural features are zeolitic open-framework phosphates made of Ga [178], In [179], Zn [180], Fe [181], Ni [182], V [183], and Al [184]. SU-M [185] is a mesoporous germanium oxide with crystalline pore walls, possessing one of the largest primitive cells and the lowest framework density of any inorganic material. The channels are defined by 30-rings. Structural and thermal information show that there exists a mismatch between framework stability and template decomposition. The latter requires temperatures higher than 450 °C, while the structure is preserved only until 300 °C.

Hence, for many promising materials milder template removal strategies are needed.

6.6.2

Alternative Approaches

The first option is to improve the calcination process, usually by a two-step calcination. Other different mild template-destructive methods have been proposed. They can be divided into thermal and chemical protocols. In addition, more ambitious protocols aimed at template recovery have been proposed. The major improvements are compiled in Table 6.1.

Solvent extraction is the most important technique for recovering surfactants from mesoporous materials. However, it is not very effective when applied to microporous compounds. Davis *et al.* [186] successfully extracted borosilicate and silicate BEA structures with acetic acid while a small template fraction could be removed for the aluminosilicate.

Recent reports describe more sophisticated detemplation methods. However, they are limited to mesoporous materials for the reasons described before. We show how Fenton chemistry can fulfill various missing challenges: (i) it provides a powerful oxidation capacity at low(er) temperatures and (ii) it can work for microporous compounds as well.

6.6.3

Fenton Detemplation. Concept and Proof-of-Principle

The approach consists of a liquid-phase oxidation using $\text{OH}^\bullet$ Fenton radicals from H_2O_2 for detemplation [148–150]. The radicals oxidize the organic template into CO_2 and H_2O while the porosity of the material is developed. The proof-of-principle of this concept is discussed for two case studies.

Table 6.1 Detemplation approaches of micro- and mesoporous materials.**Strategies aiming at template recovery**

- Solvothermal approaches [186, 187]
- Use of withdrawable organic templates [188]
- Supercritical extraction in the presence of co-solvents [189]

Destructive protocols I: thermal methods

- High-temperature calcination
- Two-step calcination [187e–f, 190]
- Ammonolysis at moderate temperatures [191]
- Platinum-catalyzed template removal [192]
- Low-temperature plasma [193] and ozone treatment [194]

Destructive protocols II: chemical detemplation under relatively mild conditions

- Detemplation during the crystallization [70]
- Ozone in liquid phase [195] and UV–vis-assisted room temperature ozone [196]
- UV–vis irradiation [197]
- Digestion under microwaves [198]
- KMnO₄ combined with H₂SO₄ [199]
- Diluted hydrogen peroxide oxidation [200]
- HNO₃/H₂O₂ treatments [201]
- Fenton chemistry [148–150]

The first case study. Beta zeolite is the basis for many industrial applications due to its specific pore structure. It was successfully detemplated by controlled Fenton-oxidation. Remarkably, the template oxidation took place in the limited space of the microchannels. It was not obvious that the tiny pores in a zeolite would provide sufficient space for the process to work. The small size of the OH• compared to other oxidizing agents and its unique highly oxidizing potential must be the explanation. Characterization by low-pressure high-resolution Ar-physisorption shows an excellent Saito–Foley pore-size distribution (Figure 6.4a), comparable to reference zeolites with a pore-size development at 6.0 Å. No pore blockage due to possible impurities of remaining template was observed.

The aluminum coordination in the structure is another important aspect. The Al incorporation in a zeolite provides acidity as Brønsted sites, and these are applied as catalytic centers. When the material is air calcined, the steam generated from the template burning-off leads to a hydrolytic attack and migration of Al out of the structure. Calcination (Figure 6.4b) shows Al migration-dislodgement from the lattice as witnessed by the appearance of broad lines due to distorted tetra-, penta-, and octahedrally coordinated aluminum species around 50, 25, and 0 ppm (on the F2 axis) as well as a broadening of the line at about 55 ppm assigned to the tetrahedral framework aluminum, indicative of structural disorder. Such detrimental effects are avoided when applying OH• radicals. Fenton detemplation shows no damage at all, preserving the complete Brønsted capacity of the zeolite. Figure 6.4b

Figure 6.4 Features of beta zeolite after Fenton treatment. (a) Saito–Foley adsorption pore-size distribution from Ar-physisorption for: (O) parent zeolite containing the template (no porosity); (●) Fenton-detemplated; and (▽) commercial NH_4 -form BEA.

(b) Sheared ^{27}Al MQMAS NMR spectra obtained at 14.1 T showing the aluminum coordination for the calcined and Fenton-detemplated samples. (Data adapted from [149, 150].)

gives evidence for a total preservation of Al in the framework, showing T-site resolution (F1 projection), and no migration to extra-framework Al.

These results are promising. The challenge is to extend this methodology to other interesting structures for which calcination has proven detrimental.

The second case study. This involves all silica micro- and mesoporous SBA-15 materials. SBA-15 materials are prepared using triblock copolymers as structure-directing templates. Typically, calcined SBA-15 displays pore sizes between 50 and 90 Å and specific surface areas of 600–700 $\text{m}^2 \text{g}^{-1}$ with pore volumes of 0.8–1.2 $\text{cm}^3 \text{g}^{-1}$. Application of the Fenton concept to mesoporous materials looks simpler since mass transfer would be much less limited. However, it is not straightforward because hydrolysis can take place in the aqueous phase.

Characterization of the samples by TGA and CHN analysis shows that the template was effectively removed ($C < 0.2 \text{ wt}\%$). Small-angle X-ray scattering data of the calcined solid shows a reduction in the unit cell due to thermal shrinkage, while the values for the Fenton samples coincide with the starting precursor. Our approach therefore completely preserves the unit cell corresponding to the diameter of the micelles contained in the mesophase.

The benefits of the method are appreciated when the textural parameters are compared. Data derived from N_2 -physisorption isotherms show that Fenton detemplation leads to improved textural parameters, with BET areas around 945 $\text{m}^2 \text{g}^{-1}$ for a pore volume of 1.33 $\text{cm}^3 \text{g}^{-1}$, while calcination leads to reduced textural parameters (667 $\text{m}^2 \text{g}^{-1}$, 0.96 $\text{cm}^3 \text{g}^{-1}$). T-plot analysis, strictly speaking, is not applicable for these bi-modal materials but it gives a good estimate. It shows that the micropore volume is doubled, which corresponds to an increase in the “calculated micropore area” from about

164 to 280 m² g⁻¹. Thus, the improved porosity features come from both micro- and mesoporosity due to the absence of shrinkage in mesopores and walls. The OH density was studied by ²⁹Si MAS NMR as Q₃/Q₄ ratio, indicating an increase in the concentration of OH-bonded silanols. In addition, the walls are thicker due to the absence of wall contraction. We are pleased that our approach has been followed by several groups. Xia and Mokaya applied it for ordered mesoporous aluminosilicates [202], Xing *et al.* on MCM-56 [203], Alam and Mokaya over mesoporous silicates from layered precursors [204], and Kecht and Bein on mesoporous silica nanoparticles [205] and vanadia supported SBA-15 [206].

6.7

Concluding Remarks

Besides current development of new catalysts and related functional materials, oxidation tools have always played an important role in their synthesis, activation, and functionalization. After a separate discussion per technique we have rationalized our literature findings (Table 6.2) as five principal oxidative functions with many proven applications.

Table 6.2 Rationalization of the oxidation chemistry applied in the synthesis of heterogeneous catalysts and related functional materials.

Oxidative function	Applications
1. Controlled and selective combustion of components via thermal or chemical routes	Calcination. Thermal detemplation of organic templates in micro- and mesoporous materials. Chemical detemplation protocols. Solution combustion synthesis
2. Use of flames as external heat source to induce quick drying and calcination	One-step aerosol flame synthesis
3. Removal of amorphous domains	Purification of CNT and CNF
4. Surface oxidation generating HSO ₃ , carboxylic, ketonic, and lactone groups	Oxidation of grafted or co-condensated alkylthiol groups in ordered mesoporous materials and periodic organosilicas Functionalization of hydrophobic carbons, CNFs, and CNTs Generation of catalytically active O-species
5. Controlled cutting and opening of closed carbon systems	Direct applications of CNTs (requires 20–100 nm in length) Inner filling and impregnation of CNTs with metal nanoparticles and complexes

References

- Parker, L.M., Bibby, D.M., and Patterson, J.E. (1984) *Zeolites*, 4, 168.
- Gabelica, Z., Nagy, J.B., Bodart, P. *et al.* (1985) *Thermochim. Acta*, 93, 749.
- Tallon, J.L. and Buckley, R.G. (1987) *J. Phys. Chem.*, 91, 1469.
- Testa, F., Crea, F., Nastro, A. *et al.* (1991) *Zeolites*, 11, 705.
- Gao, X.T., Yeh, C.Y., and Angevine, P. (2004) *Microporous Mesoporous Mater.*, 70, 27.
- Páez Pariente, J., Martens, J.A., and Jacobs, P.A. (1988) *Zeolites*, 8, 46.
- Bourgeat-Lami, E., Di Renzo, F., Fajula, F., Hubert Mutin, P., and Des Courieres, T. (1992) *J. Phys. Chem.*, 96, 3807.
- Kanazirev, V. and Price, G.L. (1996) *J. Catal.*, 161, 156.
- Keene, M.T.J., Gougeon, R.D.M., Denoyel, R., Harris, R.K., Rouquerol, J., and Llewellyn, P.L. (1999) *J. Mater. Chem.*, 9, 2843.
- Kleitz, F., Schmidt, W., and Schüth, F. (2001) *Microporous Mesoporous Mater.*, 44–45, 95.
- Kleitz, F., Schmidt, W., and Schüth, F. (2003) *Microporous Mesoporous Mater.*, 65, 1.
- Berube, F. and Kaliaguine, S. (2008) *Microporous Mesoporous Mater.*, 115, 469.
- Bagshaw, S.A. and Bruce, I.J. (2008) *Microporous Mesoporous Mater.*, 109, 199.
- Schüth, F., Knaul, S.W.S., and Weitkamp, J. (2002) *Handbook of Porous Solids*, John Wiley & Sons, Inc., New York.
- Xu, R., Pang, W., Yu, J., Huo, Q., and Chen, J. (2007) *Chemistry of Zeolites and Related Porous Materials, Synthesis and Structure*, John Wiley & Sons (Asia) Pte Ltd.
- Patarin, J. (2004) *Angew. Chem. Int. Ed.*, 43, 3878.
- Formenti, M., Juillet, F., Meriaudeau, P., Teichner, S.J., and Vergnon, P. (1972) *J. Colloid Interface Sci.*, 39, 79.
- Ulrich, G.D. (1984) *Chem. Eng. News*, 62, 22.
- Kriegel, R., Töpfer, J., Preuss, N., Grimm, S., and Böer, J. (1994) *J. Mater. Sci. Lett.*, 13, 1111.
- Strobel, R., Baiker, A., and Pratsinis, S.E. (2006) *Adv. Powder Technol.*, 17, 457.
- Strobel, R. and Pratsinis, S.E. (2007) *J. Mater. Chem.*, 17, 4743.
- Strobel, R., Piacentini, M., Mädler, L., Maciejewski, M., Baiker, A., and Pratsinis, S.E. (2006) *Chem. Mater.*, 18, 2532.
- Hunt, A.T., Carter, W.B., and Cochran, J.K. Jr. (1993) *Appl. Phys. Lett.*, 63, 266.
- Balazs, N., Mogyrosi, K., Sranko, D.F. *et al.* (2008) *Appl. Catal., B Environ.*, 84, 356.
- Tiwari, V., Jiang, J., Sethi, V., and Biswas, P. (2008) *Appl. Catal., A - Gen.*, 345, 241.
- Teoh, W.Y., Setiawan, R., Madler, L. *et al.* (2008) *Chem. Mater.*, 20, 4069.
- Schimmoeller, B., Schulz, H., Ritter, A. *et al.* (2008) *J. Catal.*, 256, 74.
- van Vegten, N., Ferri, D., Maciejewski, M. *et al.* (2007) *J. Catal.*, 249, 269.
- Hannemann, S., Grunwaldt, J.D., Lienemann, P. *et al.* (2007) *Appl. Catal. A - Gen.*, 316, 226.
- Ravindranathan, P. and Patil, K.C. (1987) *Am. Ceram. Soc. Bull.*, 66, 688.
- Chick, L.A., Pederson, L.R., Maupin, G.D. *et al.* (1990) *Mater. Lett.*, 10, 6.
- Patil, K.C., Aruna, S.T., and Mimani, T. (2002) *Curr. Opin. Solid State Mater. Sci.*, 6, 507.
- Patil, K.C., Aruna, S.T., and Ekambaram, S. (1997) *Curr. Opin. Solid State Mater. Sci.*, 2, 158.
- Bera, P., Patil, K.C., Jayaram, V. *et al.* (1999) *J. Mater. Chem.*, 9, 1801.
- Bera, P., Aruna, S.T., Patil, K.C. *et al.* (1999) *J. Catal.*, 186, 36.
- Bera, P., Patil, K.C., and Hegde, M.S. (2000) *Phys. Chem. Chem. Phys.*, 2, 3715.
- Bera, P., Patil, K.C., Jayaram, V. *et al.* (2000) *J. Catal.*, 196, 293.
- Bera, P., Malwadkar, S., Gayen, A., Satyanarayana, C.V.V., Rao, B.S., and Hegde, M.S. (2004) *Catal. Lett.*, 96, 213.

39. Gonzalez-Cortes, S.L., Xiao, T.C., Costa, P.M.F.J., Fontal, B., and Green, M.L.H. (2004) *Appl. Catal., A - Gen.*, **270**, 209.
40. Dinka, P. and Mukasyan, A.S. (2005) *J. Phys. Chem. B*, **109**, 21627.
41. Civera, A., Pavese, M., Saracco, G. *et al.* (2003) *Catal. Today*, **83**, 199.
42. Russo, N., Fino, D., Saracco, G., and Specchia, V. (2005) *J. Catal.*, **229**, 459.
43. Biamino, S., Fino, P., Fino, D., Russo, N., and Badini, C. (2005) *Appl. Catal., B - Environ.*, **61**, 297.
44. Fino, D., Russo, N., Saracco, G., and Specchia, V. (2006) *J. Catal.*, **242**, 38.
45. Russo, N., Furfori, S., Fino, D. *et al.* (2008) *Appl. Catal., B - Environ.*, **83**, 85.
46. Pino, L., Vita, A., Cipiti, F. *et al.* (2008) *Catal. Lett.*, **122**, 121.
47. Schuyten, S., Dinka, P., Mukasyan, A.S., and Wolf, E. (2008) *Catal. Lett.*, **121**, 189.
48. Nagappa, B. and Chandrappa, G.T. (2007) *Microporous Mesoporous Mater.*, **106**, 212.
49. Pavese, M. and Biamino, S. (2009) *J. Porous Mater.*, **16**, 59.
50. Mercier, L. and Pinnavaia, T.J. (1997) *Adv. Mater.*, **9**, 500.
51. Feng, X., Fryxell, G.E., Wang, L.Q. *et al.* (1997) *Science*, **276**, 923.
52. Burkett, S.L., Sims, S.D., and Mann, S. (1996) *Chem. Commun.*, 1367.
53. Huo, Q.S., Margolese, D.I., and Stucky, G.D. (1996) *Chem. Mater.*, **8**, 1147.
54. Macquarrie, D.J. (1996) *Chem. Commun.*, 1961.
55. Lim, M.H., Blanford, C.F., and Stein, A. (1997) *J. Am. Chem. Soc.*, **119**, 4090.
56. Fowler, C.E., Burkett, S.L., and Mann, S. (1997) *Chem. Commun.*, 1769.
57. Lim, M.H., Blanford, C.F., and Stein, A. (1998) *Chem. Mater.*, **10**, 467.
58. van Rhijn, W.M., de Vos, D.E., Sels, B.F. *et al.* (1998) *Chem. Commun.*, 317.
59. Bossaert, W.D., de Vos, D.E., van Rhijn, W.M. *et al.* (1999) *J. Catal.*, **182**, 156.
60. Das, D., Lee, J.F., and Cheng, S.F. (2001) *Chem. Commun.*, 2178.
61. Das, D., Lee, J.F., and Cheng, S.F. (2004) *J. Catal.*, **223**, 152.
62. Dias, A.S., Pillinger, M., and Valente, A.A. (2005) *J. Catal.*, **229**, 414.
63. Mbaraka, I.K., Radu, D.R., Lin, V.S.Y. *et al.* (2003) *J. Catal.*, **219**, 329.
64. Diaz, I., Marquez-Alvarez, C., Mohino, F. *et al.* (2000) *J. Catal.*, **193**, 283.
65. Diaz, I., Marquez-Alvarez, C., Mohino, F. *et al.* (2000) *J. Catal.*, **193**, 295.
66. Diaz, I., Mohino, F., Perez-Pariente, J. *et al.* (2004) *Thermochim. Acta*, **413**, 201.
67. Feng, Y.F., Yang, X.Y., Di, Y. *et al.* (2006) *J. Phys. Chem. B*, **110**, 14142.
68. Yang, Q.H., Kapoor, M.P., and Inagaki, S. (2002) *J. Am. Chem. Soc.*, **124**, 9694.
69. Margolese, D., Melero, J.A., Christiansen, S.C. *et al.* (2000) *Chem. Mater.*, **12**, 2448.
70. Yang, L.M., Wang, Y.J., Luo, G.S. *et al.* (2005) *Microporous Mesoporous Mater.*, **84**, 275.
71. Inagaki, S., Guan, S., Ohsuna, T. *et al.* (2002) *Nature*, **416**, 304.
72. Hamoudi, S. and Kaliaguine, S. (2003) *Microporous Mesoporous Mater.*, **59**, 195.
73. Sasidharan, M., Kiyozumi, Y., Mal, N.K. *et al.* (2006) *Adv. Funct. Mater.*, **16**, 1853.
74. Melero, J.A., Stucky, G.D., van Grieken, R. *et al.* (2002) *J. Mater. Chem.*, **12**, 1664.
75. Melero, J.A., van Grieken, R., Morales, G. *et al.* (2004) *Catal. Commun.*, **5**, 131.
76. Melero, J.A., van Grieken, R., and Morales, G. (2006) *Chem. Rev.*, **106**, 3790.
77. Alvaro, M., Corma, A., Das, D. *et al.* (2005) *J. Catal.*, **231**, 48.
78. Alvaro, M., Corma, A., Das, D. *et al.* (2004) *Chem. Commun.*, 956.
79. Macquarrie, D.J., Tavener, S.J., and Harmer, M.A. (2005) *Chem. Commun.*, 2363.
80. Nakajima, K., Tomita, I., Hara, M. *et al.* (2005) *Adv. Mater.*, **17**, 1839.
81. Hara, M., Yoshida, T., Takagaki, A., Takata, T., Kondo, J.N., Hayashi, S., and Domen, K. (2004) *Angew. Chem. Int. Ed.*, **43**, 2955.
82. Toda, M., Takagaki, A., Okamura, M., Kondo, J.N. *et al.* (2005) *Nature*, **438**, 178.

83. Takagaki, A., Toda, M., Okamura, M., Kondo, J.N., Hayashi, S., Domen, K., and Hara, M. (2006) *Catal. Today*, **116**, 157.
84. Okamura, M., Takagaki, A., Toda, M., Kondo, J.N., Domen, K., Tatsumi, T., Hara, M., and Hayashi, S. (2006) *Chem. Mater.*, **18**, 3039.
85. (a) Boehm, H.P. (1966) *Adv. Catal.*, **16**, 179; (b) Boehm, H.P. (1994) *Carbon*, **32**, 759.
86. Vinke, P., Vandereijk, M., Verbree, M. *et al.* (1994) *Carbon*, **32**, 675.
87. Barton, S.S., Evans, M.J.B., Halliop, E. *et al.* (1997) *Carbon*, **35**, 1361.
88. Rodriguez-Reinoso, F. (1998) *Carbon*, **36**, 159.
89. Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A. *et al.* (1999) *Carbon*, **37**, 1379.
90. Boehm, H.P. (2002) *Carbon*, **40**, 145.
91. Darmstadt, H., Summchen, L., Ting, J.M. *et al.* (1997) *Carbon*, **35**, 1581.
92. Ros, T.G., van Dillen, A.J., Geus, J.W. *et al.* (2002) *Chem. Eur. J.*, **8**, 1151.
93. Toebes, M.L., van Heeswijk, E.M.P., Bitter, J.H. *et al.* (2004) *Carbon*, **42**, 307.
94. Lakshminarayanan, P.V., Toghiani, H., and Pittman, C.U. (2004) *Carbon*, **42**, 2433.
95. Ros, T.G., van Dillen, A.J., Geus, J.W. *et al.* (2002) *Chem. Eur. J.*, **8**, 2868.
96. Ros, T.G., Keller, D.E., van Dillen, A.J. *et al.* (2002) *J. Catal.*, **211**, 85.
97. Toebes, M.L., van der Lee, M.K., Tang, L.M. *et al.* (2004) *J. Phys. Chem. B.*, **108**, 11611.
98. Plomp, A.J., Vuori, H., Krause, A.O.I. *et al.* (2008) *Appl. Catal., A - Gen.*, **351**, 9.
99. Bezemer, G.L., Bitter, J.H., Kuipers, H.P.C.E., Oosterbeek, H., Holeyijn, J.E., Xu, X.D., Kapteijn, F., van Dillen, A.J., and de Jong, K.P. (2006) *J. Am. Chem. Soc.*, **128**, 3956.
100. Guha, A., Lu, W.J., Zawodzinski, T.A., and Schiraldi, D.A. (2007) *Carbon*, **45**, 1506.
101. Iijima, S. (1991) *Nature*, **354**, 56.
102. Iijima, S. and Ichihashi, T. (1993) *Nature*, **363**, 603.
103. Bethune, D.S., Kiang, C.H., Devries, M.S. *et al.* (1993) *Nature*, **363**, 605.
104. Thess, A., Lee, R., Nikolaev, P. *et al.* (1996) *Science*, **273**, 483.
105. Tsang, S.C., Chen, Y.K., Harris, P.J.F. *et al.* (1994) *Nature*, **372**, 159.
106. Hiura, H., Ebbesen, T.W., and Tanigaki, K. (1995) *Adv. Mater.*, **7**, 275.
107. Esumi, K., Ishigami, M., Nakajima, A. *et al.* (1996) *Carbon*, **34**, 279.
108. Liu, J., Rinzler, A.G., Dai, H.J. *et al.* (1998) *Science*, **280**, 1253.
109. Shaffer, M.S.P., Fan, X., and Windle, A.H. (1998) *Carbon*, **36**, 1603.
110. Lago, R.M., Tsang, S.C., Lu, K.L. *et al.* (1995) *J. Chem. Soc., Chem. Commun.*, **13**, 1355.
111. Chattopadhyay, D., Galeska, I., and Papadimitrakopoulos, F. (2002) *Carbon*, **40**, 985.
112. Laasonen, K., Andreoni, W., and Parrinello, M. (1992) *Science*, **258**, 1916.
113. Mintmire, J.W., Dunlap, B.I., and White, C.T. (1992) *Phys. Rev. Lett.*, **68**, 631.
114. Saito, R., Fujita, M., Dresselhaus, G. *et al.* (1993) *Mat. Sci. Eng., B - Solid*, **19**, 185.
115. Hamada, N., Sawada, S., and Oshiyama, A. (1992) *Phys. Rev. Lett.*, **68**, 1579.
116. Chu, A., Cook, J., Heesom, R.J.R. *et al.* (1996) *Chem. Mater.*, **8**, 2751.
117. Pan, X.L. and Bao, X.H. (2008) *Chem. Commun.*, **47**, 6271.
118. Hu, H., Zhao, B., Itkis, M.E. *et al.* (2003) *J. Phys. Chem. B*, **107**, 13838.
119. Jia, Z.J., Wang, Z.Y., Liang, J. *et al.* (1999) *Carbon*, **37**, 903.
120. Pierard, N., Fonseca, A., Konya, Z. *et al.* (2001) *Chem. Phys. Lett.*, **335**, 1.
121. Rubio, A., Apell, S.P., Venema, L.C. *et al.* (2000) *Eur. Phys. J. B*, **17**, 301.
122. Park, J.Y., Yaish, Y., Brink, M. *et al.* (2002) *Appl. Phys. Lett.*, **80**, 4446.
123. Banhart, F., Li, J.X., and Terrones, M. (2005) *Small*, **1**, 953.
124. Mawhinney, D.B., Naumenko, V., Kuznetsova, A. *et al.* (2000) *J. Am. Chem. Soc.*, **122**, 2383.
125. Mizoguti, E., Nihey, F., Yudasaka, M. *et al.* (2000) *Chem. Phys. Lett.*, **321**, 297.

126. Zhang, M., Yudasaka, M., Nihey, F. *et al.* (2000) *Chem. Phys. Lett.*, **328**, 350.
127. Chiang, I.W., Brinson, B.E., Smalley, R.E. *et al.* (2001) *J. Phys. Chem. B.*, **105**, 1157.
128. Chiang, I.W., Brinson, B.E., Huang, A.Y. *et al.* (2001) *J. Phys. Chem. B.*, **105**, 8297.
129. Dillon, A.C., Jones, K.M., Bekkedahl, T.A. *et al.* (1997) *Nature*, **386**, 377.
130. Ziegler, K.J., Gu, Z.N., Peng, H.Q. *et al.* (2005) *J. Am. Chem. Soc.*, **127**, 1541.
131. Tran, M.Q., Tridech, C., Alfrey, A. *et al.* (2007) *Carbon*, **45**, 2341.
132. Wang, C.F., Guo, S.J., Pan, X.L. *et al.* (2008) *J. Mater. Chem.*, **18**, 5782.
133. Zhang, J., Liu, X., Blume, R., Zhang, A.H., Schlögl, R., and Su, D.S. (2008) *Science*, **322**, 73.
134. Pereira, M.F.R., Orfao, J.J.M., and Figueiredo, J.L. (1999) *Appl. Catal., A - Gen.*, **184**, 153.
135. Fiedorow, R., Przystajko, W., and Sopa, M. (1981) *J. Catal.*, **68**, 33.
136. Mestl, G., Maksimova, N.I., Keller, N. *et al.* (2001) *Angew. Chem. Int. Ed.*, **40**, 2066.
137. Zhang, J., Su, D.S., Zhang, A.H. *et al.* (2007) *Angew. Chem. Int. Ed.*, **46**, 7319.
138. Supporting material available on Science Online ref. 133.
139. Resasco, D.E. (2008) *Nat. Nanotechnol.*, **3**, 708.
140. Fenton, H.J.H. (1894) *J. Chem. Soc.*, **65**, 899.
141. ISI Web of Knowledge®. Thomson Reuters. URL: www.isiknowledge.com/
142. (a) Tarr, M.A. (2003) *Chemical Degradation Methods for Wastes and Pollutants*, In Environmental, Science and Pollution Control Series, vol. 26, Marcel Dekker, Inc., p. 165; (b) Burkitt, M.J. (2003) *Prog. React. Kinet. Mechanism*, **28**, 75.
143. Neyens, E. and Baeyens, J. (2003) *J. Hazard. Mater.*, **98**, 33.
144. Parsons, S. (2004) *Advanced Oxidation Processes for Water and Wastewater Treatment*, IWA Publishing, London.
145. Pignatello, J.J., Oliveros, E., and MacKay, A. (2006) *Crit. Rev. Env. Sci. Technol.*, **36**, 1.
146. Melián-Cabrera, I., Kapteijn, F., and Moulijn, J.A. (2005) *Chem. Commun.*, (12), 1525.
147. Melián-Cabrera, I., Kapteijn, F., and Moulijn, J.A. (2005) *Chem. Commun.*, (16), 2178.
148. Melián-Cabrera, I., Kapteijn, F., and Moulijn, J.A. (2006) EP1690831 A1.
149. Melián-Cabrera, I., Kapteijn, F., and Moulijn, J.A. (2005) *Chem. Commun.*, (16), 2744.
150. Melián-Cabrera, I., Osman, A.H., van Eck, E.R.H., Kentgens, A.P.M., Polushkin, E., Kapteijn, F., and Moulijn, J.A. (2007) *Stud. Surf. Sci. Catal.*, **170**, 648.
151. Pérez-Ramírez, J. (2002) "Catalyzed N₂O Activation, Promising (new) Catalyst for Abatement and utilization", PhD Thesis dissertation, TU-Delft, The Netherlands.
152. Pérez-Ramírez, J., Kapteijn, F., Schoffel, K. *et al.* (2003) *Appl. Catal., B-Environ.*, **44**, 117.
153. Oliveros, E., Goeb, S., Bossmann, S.H., Braun, A.M., Nascimento, C.A.O., and Guardani, R. (2000) Waste water treatment by the photochemical enhanced Fenton reaction: Modeling and optimization using experimental design and artificial neural networks, in *Sustainable Energy and Environmental Technology, Proceedings of the Third Asia Pacific Conference* (eds X. Hu and P.L. Yue), World Scientific, Singapore, p. 577.
154. Oliveros, E., Legrini, O., Braun, A.M. *et al.* (1997) *Water Sci. Technol.*, **35**, 223.
155. Haber, F. and Weiss, J. (1934) *Proc. R. Soc. A.*, **134**, 332.
156. Buxton, G.V., Greenstock, C.L. *et al.* (1988) *J. Phys. Chem. Ref. Data*, **17**, 513.
157. Walling, C. and Goosen, A. (1973) *J. Am. Chem. Soc.*, **95**, 2987.
158. De Laat, J. and Gallard, H. (1999) *Environ. Sci. Technol.*, **33**, 2726.
159. Rossetti, G.H., Albizzati, E.D., and Alfano, O.M. (2002) *Ind. Eng. Chem. Res.*, **41**, 1436.
160. Pignatello, J.J. (1992) *Environ. Sci. Technol.*, **26**, 944.

161. Sun, Y. and Pignatello, J.J. (1993) *Environ. Sci. Technol.*, **27**, 304.
162. Sima, J. and Mikanova, J. (1997) *Coord. Chem. Rev.*, **160**, 161.
163. Qiang, Z., Chang, J.H., and Huang, C.P. (2003) *Water Res.*, **37**, 1308.
164. Baes, C.F. and Mesmer, R.E. (1976) *The Hydrolysis of Cations*, Wiley Interscience, New York.
165. Flynn, C.M. Jr. (1984) *Chem. Rev.*, **84**, 31.
166. Gallard, H., De Laat, J., and Legube, B. (1999) *Water Res.*, **33**, 2929.
167. van den Brink, P.J. *et al.* (1991) *Stud. Surf. Sci. Catal.*, **63**, 527.
168. van Dillen, A.J. *et al.* (2003) *J. Catal.*, **216**, 257.
169. Weckhuysen, B.M. (2005) Proceedings of the International Workshop on Microporous and Mesoporous Materials as Catalytic Hosts for Fe, Cu and Co, Scheveningen, The Netherlands.
170. Liu, Y.M. *et al.* (2008) *J. Phys. Chem. C*, **112**, 16575.
171. Cejka, J., van Bakkum, H., Corma, A., and Schueth, F. (eds) (2007) *Introduction to Zeolite Science and Practice*, 3rd revised edn, Studies in Surface Science and Catalysis, vol. 168, Elsevier, Amsterdam.
172. Reviews: (a) Corma, A. (1995) *Chem. Rev.*, **95**, 559; (b) Corma, A. (2003) *J. Catal.*, **216**, 298; (c) Corma, A. (1997) *Chem. Rev.*, **97**, 2373; (d) Davis, M.E. (2002) *Nature*, **417**, 813; (e) Marcilly, C. (2001) *Stud. Surf. Sci. Catal.*, **135**, 37; (f) Davis, M.E. (1993) *Acc. Chem. Res.*, **26**, 111; (g) Yu, J.H. and Xu, R.R. (2003) *Acc. Chem. Res.*, **36**, 481; (h) van Donk, S., Janssen, A.H., Bitter, J.H., and de Jong, K.P. (2003) *Catal. Rev.-Sci. Technol.*, **45**, 297; (i) Cundy, C.S. and Cox, P.A. (2005) *Microporous Mesoporous Mater.*, **82**, 1.
173. Barrer, R.M. and Denny, P.J. (1961) *J. Chem. Soc.*, 971.
174. (a) Davis, M.E. and Lobo, R.F. (1992) *Chem. Mater.*, **4**, 389; (b) Lobo, R.F., Zones, S.I., and Davis, M.E. (1995) *J. Inclusion Phenom. Mol.*, **21**, 47.
175. (a) Cambor, M.A. and Pérez-Pariente, J. (1991) *Zeolites*, **11**, 202; (b) Cambor, M., Corma, A., and Valencia, S. (1998) *Microporous Mesoporous Mater.*, **25**, 59; (c) Müller, M., Harvey, G., and Prins, R. (2000) *Microporous Mesoporous Mater.*, **34**, 135; (d) van Bokhoven, J.A., Koningsberger, D.C., Kunkeler, P., van Bakkum, H., and Kentgens, A.P.M. (2000) *J. Am. Chem. Soc.*, **122**, 12842; (e) Beers, A.E.W., van Bokhoven, J.A., de Lathouder, K.M. *et al.* (2003) *J. Catal.*, **218**, 239.
176. (a) Corma, A., Nemeth, L.T., Renz, M., and Valencia, S. (2001) *Nature*, **412**, 423; (b) Boronat, M., Concepción, P., Corma, A., Renz, M., and Valencia, S. (2005) *J. Catal.*, **234**, 111.
177. (a) Corma, A. and García, H. (1997) *Catal. Today*, **38**, 257; (b) Sheldon, R.A. and van Bakkum, H. (2001) *Fine Chemicals Through Heterogeneous Catalysis*, Wiley-VCH Verlag GmbH, Weinheim; (c) Corma, A. and García, H. (2003) *Chem. Rev.*, **103**, 4307.
178. (a) Sasse, C., Loiseau, T., Taulelle, F., and Férey, G. (2000) *Chem. Commun.*, 943; (b) Sasse, C., Marrot, J., Loiseau, T., and Férey, G. (2002) *Chem. Mater.*, **14**, 1340; (c) Beitone, L., Marrot, J., Loiseau, T., Férey, G., Henry, M., Huguenard, C., Gansmuller, A., and Taulelle, F. (2003) *J. Am. Chem. Soc.*, **125**, 1912; (d) Walton, R.I., Millange, F., Loiseau, T., O'Hare, D., and Férey, G. (2000) *Angew. Chem. Int. Ed.*, **39**, 4552; (e) Chippindale, A.M., Peacock, K.H., and Cowley, A.R. (1999) *J. Solid State Chem.*, **145**, 379.
179. (a) Dhingra, S.S. and Haushalter, R.C. (1993) *J. Chem. Soc., Chem. Commun.*, 1665; (b) Williams, I.D., Yu, J., Du, H., Chen, J., and Pang, W. (1998) *Chem. Mater.*, **10**, 773; (c) Thirumurugan, A. and Natarajan, S. (2003) *Dalton Trans.*, 3387.
180. (a) Yang, G. and Sevov, S.C. (1999) *J. Am. Chem. Soc.*, **121**, 8389; (b) Rodgers, J.A. and Harrison, W.T.A. (2000) *J. Mater. Chem.*, **10**, 2853; (c) Neeraj, S., Natarajan, S., and Rao, C.N.R. (1999) *Chem. Commun.*, 165.
181. (a) Moore, P.B. and Shen, J. (1983) *Nature*, **306**, 356; (b) Choudhury, A., Natarajan, S., and Rao, C.N.R. (1999) *Chem. Commun.*, 1305.

182. Guillou, N., Gao, Q., Forster, P.M., Chang, J., Nogués, M., Park, S.E., Férey, G., and Cheetham, A.K. (2001) *Angew. Chem. Int. Ed.*, **40**, 2831.
183. Soghomonian, V., Chen, Q., Haushalter, R.C. *et al.* (1993) *Science*, **259**, 1596.
184. Davis, M.E., Saldarriag, C., Montes, C., Garces, J., and Zhao, X. (1998) *Nature*, **331**, 698.
185. Zou, X., Conradsson, T., Klingstedt, M. *et al.* (2005) *Nature*, **437**, 716.
186. Jones, C.W., Tsuji, K., Takewaki, T., Beck, L.W., and Davis, M.E. (2001) *Microporous Mesoporous Mater.*, **48**, 57.
187. (a) Hitz, S. and Prins, R. (1997) *J. Catal.*, **168**, 194; (b) Jones, C.W., Tsuji, K., and Davis, M.E. (1998) *Nature*, **393**, 52; (c) Takewaki, T., Beck, L.W., and Davis, M.E. (1999) *Top. Catal.*, **9**, 35; (d) Jones, C.W., Tsuji, K., Takewaki, T., Beck, L.W., and Davis, M.E. (2001) *Microporous Mesoporous Mater.*, **48**, 57; (e) Yang, C.M., Zibrowius, B., Schmidt, W., and Schüth, F. (2003) *Chem. Mater.*, **15**, 3739; (f) Yang, C.M., Zibrowius, B., Schmidt, W., and Schüth, F. (2004) *Chem. Mater.*, **16**, 2918; (g) Whitehurst, D.D. (1992) US Patent 5,143,879.
188. (a) Lee, H., Zones, S.I., and Davis, M.E. (2003) *Nature*, **425**, 385; (b) Lee, H., Zones, S.I., and Davis, M.E. (2004) *Recent Advances in the Science and Technology of Zeolites and Related Materials, Parts A-C*, Elsevier Science BV, Amsterdam.
189. (a) Kawi, S. and Lai, M.W. (1998) *Chem. Commun.*, 1407; (b) van Grieken, R., Calleja, G., Stucky, G.D., Melero, J.A., Garcia, R.A., and Iglesias, J. (2003) *Langmuir*, **19**, 3966.
190. Aguado, J., Escola, J.M. *et al.* (2005) *Microporous Mesoporous Mater.*, **83**, 181.
191. Kresnawahjuesa, O., Olson, D.H. *et al.* (2002) *Microporous Mesoporous Mater.*, **51**, 175.
192. Krawiec, P., Kockrick, E., Simon, P. *et al.* (2006) *Chem. Mater.*, **18**, 2663.
193. (a) Maesen, T.L.M. *et al.* (1987) *J. Chem. Soc., Chem. Commun.*, **17**, 1284; (b) Maesen, T.L.M. *et al.* (1989) *Appl. Catal.*, **A**, **48**, 373; (c) Maesen, T.L.M. *et al.* (1990) *J. Chem. Soc., Chem. Faraday Trans.*, **86**, 3967.
194. (a) Keene, M.T.J. *et al.* (1998) *Chem. Commun.*, 2203; (b) Heng, S., Pui Sze Lau, P. *et al.* (2004) *J. Membr. Sci.*, **243**, 69; (c) Motuzas, J. *et al.* (2007) *Microporous Mesoporous Mater.*, **99**, 197; (d) Kuhn, J. *et al.* (2009) *Microporous Mesoporous Mater.*, **120**, 12; (e) Kuhn, J. *et al.* (2009) *Microporous Mesoporous Mater.*, **120**, 35.
195. Buchel, G., Denoyel, R., and Llewellyn, P.L. (2001) *J. Rouquerol, J. Mater. Chem.*, **11**, 589.
196. Li, Q., Amweg, M.L., Yee, C.K., Navrotsky, A., and Parikh, A.N. (2005) *Microporous Mesoporous Mater.*, **87**, 45.
197. Parikh, A.N., Navrotsky, A., Li, Q., Yee, C.K. *et al.* (2004) *Microporous Mesoporous Mater.*, **76**, 17.
198. Tian, B., Liu, X., Yu, C., Gao, F., Luo, Q., Xie, S. *et al.* (2002) *Chem. Commun.*, 1186.
199. Lu, A.H., Li, W.C., Schmidt, W., and Schüth, F. (2006) *J. Mater. Chem.*, **16**, 3396.
200. Xiao, L., Li, J., Jin, H., and Xu, R. (2006) *Microporous Mesoporous Mater.*, **96**, 413.
201. Masuda, T. *et al.* (2003) *Sep. Purif. Technol.*, **32**, 181.
202. Xia, Y.D. and Mokaya, R. (2006) *J. Phys. Chem. B*, **110**, 9122.
203. Xing, H.J., Zhang, Y., Jia, M.J. *et al.* (2008) *Catal. Commun.*, **9**, 234.
204. Alam, N. and Mokaya, R. (2008) *J. Mater. Chem.*, **18**, 1383.
205. Kecht, J. and Bein, T. (2008) *Microporous Mesoporous Mater.*, **116**, 123.
206. Xu, J., Chen, M., Liu, Y.M. *et al.* (2009) *Microporous Mesoporous Mater.*, **118**, 354.