tions [$I \geq 2\sigma(I)$], 349 refined parameters, $R = 0.055$, $wR^2 = 0.133$, max/min residual electron density $0.35/-0.34\,e\,Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.[14] b) X-ray structure analysis of **6** ($C_{55}H_{94}N_7P_3$): $M_r = 946.28$, yellow crystals $0.25 \times 0.20 \times 0.10$ mm, $a = 10.995(2)$, $b = 15.658(3)$, $c = 17.031(3)$ Å, $\alpha = 80.33(3)$, $\beta = 88.60(3)$, $\gamma = 82.72(3)^\circ$, $V = 2867.1(9)$ Å^3, $\rho_{calcd} = 1.096\ g\,cm^{-3}$, $\mu = 12.46\ cm^{-1}$, empirical absorption correction by using ψ scan data ($0.746 \geq T \geq 0.886$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 12328 measured reflections ($+h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 11688 independent ($R_{int} = 0.016$) and 9440 observed reflections [$I \geq 2\sigma(I)$], 660 refined parameters, $R = 0.053$, $wR^2 = 0.167$, max/min residual electron density $0.43/-0.167\,e\,Å^{-3}$, disorder of the *tert*-butyl groups at C12 and C17 are described with split positions and geometric constraints, hydrogen atoms calculated and refined as riding atoms.[14]

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Designing a Heterogeneous Catalyst for the Production of Adipic Acid by Aerial Oxidation of Cyclohexane**

Markus Dugal, Gopinathan Sankar, Robert Raja, and John Meurig Thomas*

Dedicated to Professor Helmut Knözinger
on the occasion of his 65th birthday

Adipic acid (AA) is an important building block for a variety of commercially useful products such as polyamides (nylon 6.6) and urethanes.[1] Currently, it is manufactured mainly by a two-step process involving nitric acid oxidation of cylohexanone and cyclohexanol. The latter compound is generated from cyclohexane using homogeneous (cobalt-based) catalysts, often in combination with promoters and peroxides.[2–4] Alternative synthetic routes have been developed, such as the one-step oxidation of cyclohexane with either alkyl hydroperoxide as oxidant and a catalyst consisting of cobalt salts[5, 6] or dioxygen as oxidant and a cobalt acetate catalyst in acetic acid.[7] More recent industrial syntheses include the homogeneously catalysed hydrocarboxylation[8, 9] or carboalkoxylation[10] of butadiene. For the research chemist, the intellectual challenge is to devise a strategy for a one-step production of AA from hydrocarbons using an appropriately designed, heterogeneous catalyst that functions with air or dioxygen as the oxidant. Such a catalyst would allow facile separation and recycling while simultaneously avoiding the use of hazardous or corrosive reagents. Herein, we report progress towards this goal. The iron-based, framework-substituted, molecular-sieve catalyst that we describe exhibits good performance in the direct low-temperature conversion of cyclohexane to AA in air.

Based on our recent work on the selective aerial oxidation of alkanes at the terminal position[11] and, in particular, the selective aerial conversion of cyclohexane to cyclohexanol and cyclohexanone using transition metal ion substituted, microporous aluminium phosphates (MAPOs),[12, 13] we argued that it was necessary to assemble an Fe^{III}-substituted MAPO structure in which the pore aperture is significantly smaller than that of FeAlPO-5 (7.3 Å diameter). This structure creates a constrained environment for the cyclohexane oxidation (see Figure 1) and thus modifies the selectivity of the reaction. What we capitalize upon is shape-selective catalysis[14, 15] using a carefully designed microporous solid. In our previous work, we showed[16] for hydrocarbons small enough to enter into a microporous catalyst, the free radical oxidation of these materials proceeds in a highly localized manner in the restricted environment of the catalytically active sites at which the M^{III} ions are exposed on the

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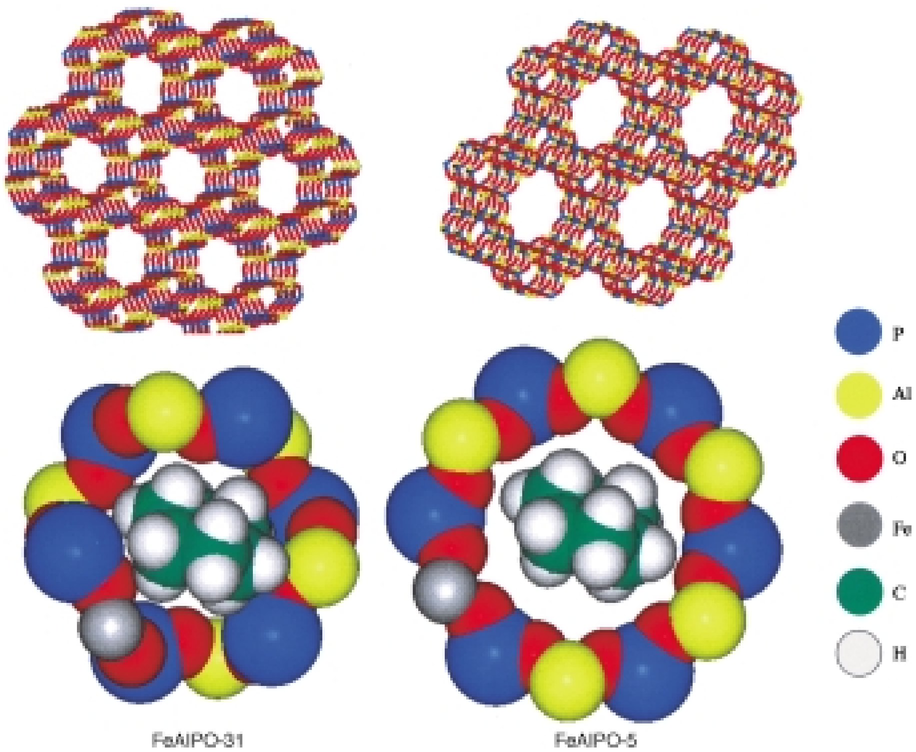


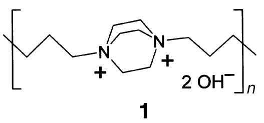
Figure 1. Above: A side view of the microporous AlPO-31 and AlPO-5 structures, which show the one-dimensional channels. Below: Representation of the cyclohexane molecule in the differently sized pore openings of FeAlPO-31 (5.4 Å) and FeAlPO-5 (7.3 Å).

inner walls of the micropores (M = Co, Mn, Fe). In effect, we have here "product shape selectivity"—only those products with appropriate molecular dimensions may diffuse easily out of the pores, whereas larger ones formed in the course of the reaction are trapped inside (on account of their significantly retarded diffusion). Qualitatively, we may envisage the free radical and molecular intermediates (cyclohexanol, cyclohexanone formed from cyclohexyl hydroperoxide[13] or 2-hydroxycylohexanone and 1,2-cyclohexanedione) to be held in the vicinity of the active site until oxidation proceeds further to yield the more mobile (and desired) linear products.

For the present purposes, the framework structure of the microporous catalyst that we have targeted is the one-dimensional channel system, AlPO-31[17] (Figure 1). Because of the more puckered inner walls, compared with AlPO-5,[13, 17] there is a smaller pore of diameter 5.4 Å, which introduces the very kind of constrained environment that is required here.

As with the oxidation of *n*-alkanes at the terminal position over Co^{III}- or Mn^{III}-substituted AlPO-18 catalysts[11] and the conversion of cyclohexane to cyclohexanol over an Fe^{III}AlPO-5 catalyst,[13] framework-isolated, transition metal ions in their M^{III} oxidation states are vital for the catalysis. We therefore devised a facile means of preparing Fe^{III}AlPO-31 microporous samples, in which up to about four atom per cent of the Al^{III} framework ions are replaced by Fe^{III}, and where all these active sites are accessible to cyclohexane at the inner surfaces of the micropores.

Building on our prior experience with quaternized template cations (such as for the synthesis of DAF-1[18]) and the work of Wright et al.,[19] who used several types of polymeric-template ammonium salts to produce various solid acid Mg-substituted aluminophosphates (which include AlPO-5, AlPO-31, and STA-1), we selected the polymeric-template ammonium salt **1**, which strongly favors the production of MAPO-31.[20] This template



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salt was prepared through a Menshutkin-type reaction from 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1,6-dibromohexane, then followed by ion exchange of the bromide counterion against hydroxide. Employing an optimized modification of the reported literature procedures[18, 22] (see the Experimental Section), the required template was obtained in high yield and purity.

FeAlPO-31 was obtained from a hydrothermal synthesis (see the Experimental Section) in a phase-pure form (Figure 2). The diffraction pattern of the calcined sample, recorded in situ,[23] is essentially identical to that of the as-prepared material, which demonstrates structural stability upon removal of the template. A helpful feature of the in situ combined XRD/XAS study[23] is that, although the diffraction pattern (hence the framework structure) remains the same, there is a significant increase of the pre-edge feature and a decrease in Fe–O distance from 1.94 to 1.85 Å upon calcination. The similarity of the intense pre-edge feature and the Fe–O distance with the corresponding values in either $FePO_4$ or Fe-substituted ZSM-5 shows that the substituted iron ions are present in the Fe^{III} state and with a tetrahedral geometry.

Comparisons of the catalytic performance of FeAlPO-31 and of FeAlPO-5 are summarized in Figure 3 and in Table 1. In addition to a higher turnover number (TON) for FeAlPO-31 compared to FeAlPO-5, there are significant differences in the product selectivities: With FeAlPO-5 as the catalyst, cyclohexanol and cyclohexanone were the major products,[13] whereas FeAlPO-31 predominantly produces adipic acid and comparatively small amounts of other oxidation and fragmentation products. At higher temperatures with FeAlPO-31 there is no significant change in the overall conversion but the formation of tar and other fragmentation products (succinic and glutaric acids) increases. The structure of the catalysts, as we conclude from identical XRD patterns recorded before and after the catalytic reaction, remains unchanged under the chosen reaction conditions. (Further ICP analysis of the reaction mixture gave no indication of any leaching of iron out of the framework.)

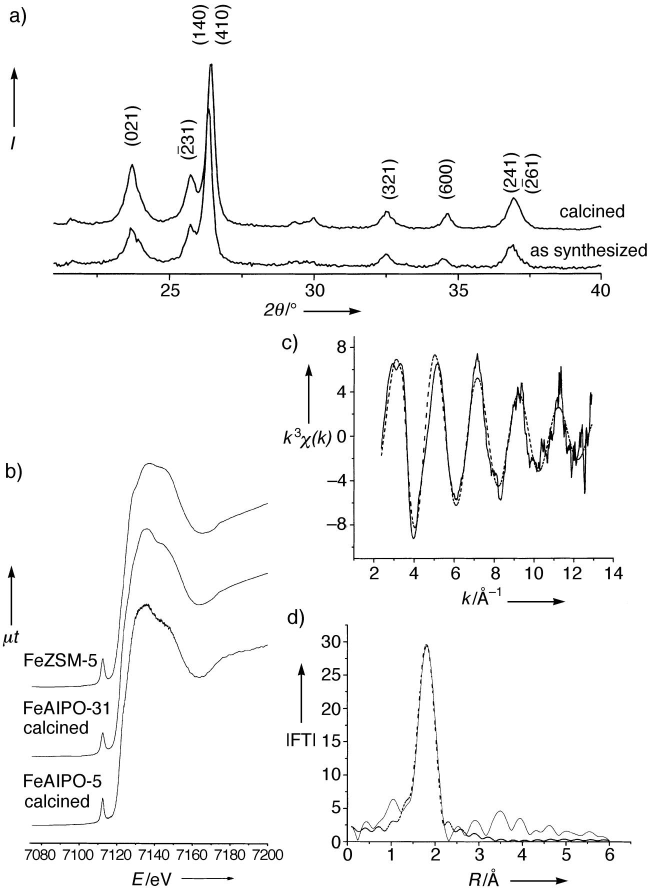

Figure 2. a) XRD patterns of FeAlPO-31 before and after calcination in O_2 at 550 °C recorded by employing the in situ, combined XRD/XAS technique. b) XANES spectra of as-synthesized FeZSM-5[13] and of calcined FeAlPO-31 and FeAlPO-5.[13] Note the similarities in the pre-edge intensities. c) EXAFS and d) the associated Fourier transform of calcined FeAlPO-31. The solid and the dashed curves represent the experimental and calculated data, respectively. The EXAFS derived Fe–O coordination number, bond distance, and Debye–Waller factor are 3.85 ± 0.4, 1.85 ± 0.02 Å, and 0.0045 Å^2, respectively. In (a), only a small range of $2\theta = 22-40°$ is displayed for clarity. Note that it is not possible to record XRD data below about 11°, since there is a dead space associated with the INEL detector and hence this detector should be positioned in such a way that transmitted intensity (I_t) for EXAFS measurement is not affected.

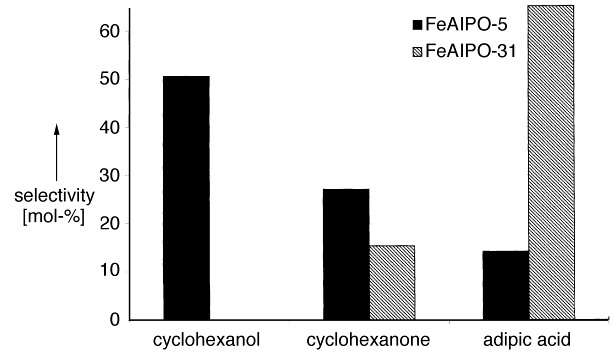

Figure 3. Bar chart comparing the product selectivities (given in mol-%) after 24 h in the aerial oxidation of cyclohexane ($T = 373$ K) with FeAlPO-31 and FeAlPO-5 as catalysts. Only major products are shown.

The remarkable fact that the selectivity pattern of FeAlPO-31 is so completely different from that of FeAlPO-5, even though the structure of their active sites is identical, is explicable only in terms of the difference in pore dimensions of the two AlPO hosts for the isolated sites. The cyclohexane molecule is much more confined in case of the FeAlPO-31 than in FeAlPO-5. Owing to this constraint, the diffusion of cyclohexane and the cyclic intermediates in the oxidation reaction within the FeAlPO-31 channel system is severely limited and therefore further oxidation of the cyclic intermediates to linear products as adipic acid is facilitated.

Although many features of this new catalyst (FeAlPO-31) rival those of commercial catalysts used in the production of AA, our principal aim in this work was not to develop a new industrial procedure but rather to adopt a design approach for the development of many other new catalysts for converting organic molecules to useful products under mild and environmentally benign conditions. We believe that there is scope to extend the free radical, shape selective catalysis described herein to other systems.

Experimental Section

Synthesis of **1**: DABCO (98%, Aldrich, 22.9 g, 0.2 mol) was dissolved in toluene (500 mL) and 1,6-dibromohexane (96%, Aldrich, 50.7 g, 0.2 mol) was added slowly under vigorous stirring. The mixture was heated to 105 °C (oil bath temperature) for 3 h upon which a voluminous white precipitate formed. After cooling, the bromide salt of the template[19, 21] was collected by filtration, washed with toluene (3 × 150 mL) and pentane (3 × 150 mL) and dried in vacuo (60.3 g white, hygroscopic powder, 82% yield). Ion exchange was accomplished by stirring a solution of the bromide salt in deionized water (0.45 g mL^{-1}) with an excess amount of a strongly basic ion-exchange resin (Dowex SBR, Aldrich, 150 g resin per 100 g solution)

Table 1. Comparison of the catalytic behavior of FeAlPO-31 and FeAlPO-5 in the aerial oxidation of cyclohexane.[a]

Catalyst	t	T [h]	Conversion [K]	TON[b] [mol-%][c]	Product selectivities [mol-%][c, d] A	B	C	D	E	F	G	H
FeAlPO-31	8	373	2.5	78	6.3	31.0	55.3	1.9	3.2	–	–	2.5
FeAlPO-31	24	373	6.6	211	–	15.3	65.0	5.9	7.7	–	–	6.0(I)
FeAlPO-31	8	403	3.9	121	–	12.5	53.7	14.2	10.0	–	–	9.8(I)
FeAlPO-31	24	403	7.7	239	–	6.8	31.3	24.7	11.3	–	–	26.0(I)
FeAlPO-5	8	373	1.7	20	83.0	6.5	9.2	–	–	–	–	1.5
FeAlPO-5	24	373	5.3	62	50.5	27.0	14.1	–	–	6.3	–	1.8
FeAlPO-5	8	403	2.5	45	41.1	17.9	26.2	–	–	13.	–	1.9
FeAlPO-5	24	403	6.6	113	36.2	15.5	31.0	–	–	9.2	5.4	2.7

[a] Conditions: cyclohexane ≅ 50 g, catalyst 0.75 g, pressure (air) 1.5 MPa. [b] TON = moles of substrate converted per mol of metal (Fe) in the used amount of catalyst, as determined by elemental analysis (FeAlPO-31: Fe = 1.43 wt-% Fe; FeAlPO-5: 3.77 wt-% Fe). [c] Determined by GC against mesitylene (≅ 2.5 g) as internal standard. [d] Overall yield; product abbreviations: A: cyclohexanol; B: cyclohexanone; C: adipic acid; D: succinic acid; E: glutaric acid; F: valeraldehyde; G: valeric acid; H: probably CO_2, CO, water, and traces of lower olefins in the gas phase; I: tar.

for 3 h. The solution of the hydroxide form of the template **1** obtained after filtration was used directly in the aluminophosphate synthesis.

Synthesis of FeAlPO-31: To a solution of phosphoric acid (85%, Aldrich) in water, aluminium hydroxide hydrate (Aldrich) and an aqueous solution of iron(II) acetate (Aldrich) was added, and the mixture was stirred until homogeneous. To this, an aqueous solution of **1** was added slowly with vigorous stirring to obtain a gel with the empirical composition $0.04\,FeO:0.48\,Al_2O_3:0.5\,P_2O_5:0.8/n\,[C_{12}H_{26}N_2O_2]_n : 40\,H_2O$ (pH 7–8). The gel was sealed in a Teflon-lined stainless steel autoclave and heated at 195°C under autogeneous pressure for 48 h. The solid product was isolated by filtration, washed with deionized water, and dried in air (90°C). The as-prepared product was calcined first in nitrogen and then in dry oxygen at 550°C for 1 h and 10 h, respectively.

In situ XRD/XAS measurements:[20] The combined XRD/XAS measurements were performed at station 9.3 of the Daresbury synchrotron radiation source, which operates at 2 GeV with a typical current 130–250 mA. The station is equipped with a Si(220) double-crystal monochromator and ion chambers for measuring incident (I_0) and transmitted (I_t) beam intensities. For the in situ experiment, 25 mg of FeAlPO-31 was calcined in an situ cell at 550°C in an O_2 flow. The XRD/XAS measurements were performed during the course of increasing the temperature (5 $K\,min^{-1}$) and at the final temperature. The XRD patterns were collected at the wavelength of 1.8088 Å, below the Fe–K edge. Each XRD pattern was measured for 180 s and each XAS spectrum for 380 s associated with a dead time of 40 s, to give a total cycle time of 10 min. The data were analysed using the suite of programs EXCALIB, EXBROOK, and EXCURV98, available at Daresbury laboratory.

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Designing a Molecular Sieve Catalyst for the Aerial Oxidation of *n*-Hexane to Adipic Acid**

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John Meurig Thomas*

Dedicated to Professor H. W. Roesky
on the occasion of his 65th birthday

Linear alkanes are so notoriously difficult to oxidize that their very name—paraffins, from the Latin *parum affinis* (slight affinity)—emphasizes their inertness. *n*-Hexane, for example, is not attacked by boiling nitric acid, concentrated sulphuric acid, potassium permanganate, or chromic acid. It is widely acknowledged that the controlled oxyfunctionalization of alkanes is one of the major challenges of modern catalysis;[1–4] particularly desirable products are those that are oxidized at the terminal position (hexanoic acid, for example), since these serve as feedstocks for the chemical and pharmaceutical industries.

A decade ago, following the discovery[5, 6] of molecular sieve titanosilicates such as TS-1, it was reported[7, 8] that *n*-hexane yielded a mixture of four products when hydrogen peroxide was used as the oxidant for the selective oxidation catalyzed by TS-1: 2-hexanol (17%), 3-hexanol (39%), 2-hexanone (34%), and 3-hexanone (10%). In a series of recent papers[9–13] we have reported how aluminophosphate (AlPO) molecular sieves, which contain an appropriate, framework-substituted transition-metal ion, M, in a high oxidation state, serve as effective catalysts for the selective oxidation of alkanes (especially at the terminal position). Molecular sieve catalysts are potentially more powerful for regioselective oxidation and are demonstrably capable of going beyond what may be achieved by Gif reagents developed by Barton et al.[14] for the rather high oxidative selectivity for secondary over tertiary positions in saturated hydrocarbons.[15–17] Here, we report how adipic acid, an

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