

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 $0.04\text{FeO} : 0.48\text{Al}_2\text{O}_3 : 0.5\text{P}_2\text{O}_5 : 0.8/n[\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_2]_n : 40\text{H}_2\text{O}$ (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 O₂ 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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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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important chemical feedstock, may be obtained from *n*-hexane in substantial amount using air as oxidant at low temperature and a Co^{III} framework-substituted AIPO as a catalyst.

The key features of this new class of versatile^[18] MAIPO (M = Co^{III}, Mn^{III}, Fe^{III}) microporous catalysts that we have designed and developed are the following four points. First, the size and shape of the pores of the solid molecular sieve must be carefully selected so as to ensure that alkane oxidation, which proceeds^[11] by a free-radical mechanism, takes place in an essentially shape-selective manner in the spatially restricted environment of the catalytically active sites. Second, these active sites are known^[19] (by X-ray absorption spectroscopy) to be isolated M^{III} ions exposed at the inner walls of the molecular sieve used for the particular selective oxyfunctionalization that is

being targeted. Third, the M^{III} active sites (in this case, Co^{III} ions, that have replaced a small, controlled fraction of the framework Al^{III} ions) are introduced during the synthesis and calcination of the molecular sieve catalyst (see below). Fourth, we have established^[11, 12] that the tetrahedrally coordinated Co^{III} ions in the AIPO framework function as centers for the generation of free radicals and are responsible, in concert with the constraints imposed by the shape and size of the sieve, for the preferential attack by oxygen on the terminal groups of the alkane.

To achieve oxyfunctionalization at both (methyl) ends of *n*-hexane, we argued that a sufficiently large number of framework Co^{III} ions needed to be accommodated on the inner walls of catalysts such as CoAIPO-18—which, with about 4 atom % of Al^{III} replaced by Co^{III} ions, smoothly yields the (single) terminally oxidized products hexanol, hexanal, and hexanoic acid from *n*-hexane in air or oxygen—in such a manner that two framework Co^{III} ions should be separated by about 7–8 Å from one another. In other words, it is highly plausible that there are about two (separated) Co^{III} ions in each cage of the AIPO-18 structure, preferably situated opposite one another (Figure 1).

It is not just AIPO-18 but also AIPO-34 and AIPO-44 frameworks (all of which are closely akin to the aluminosilicate mineral chabazite, of idealized formula Ca₆[Al₁₂-

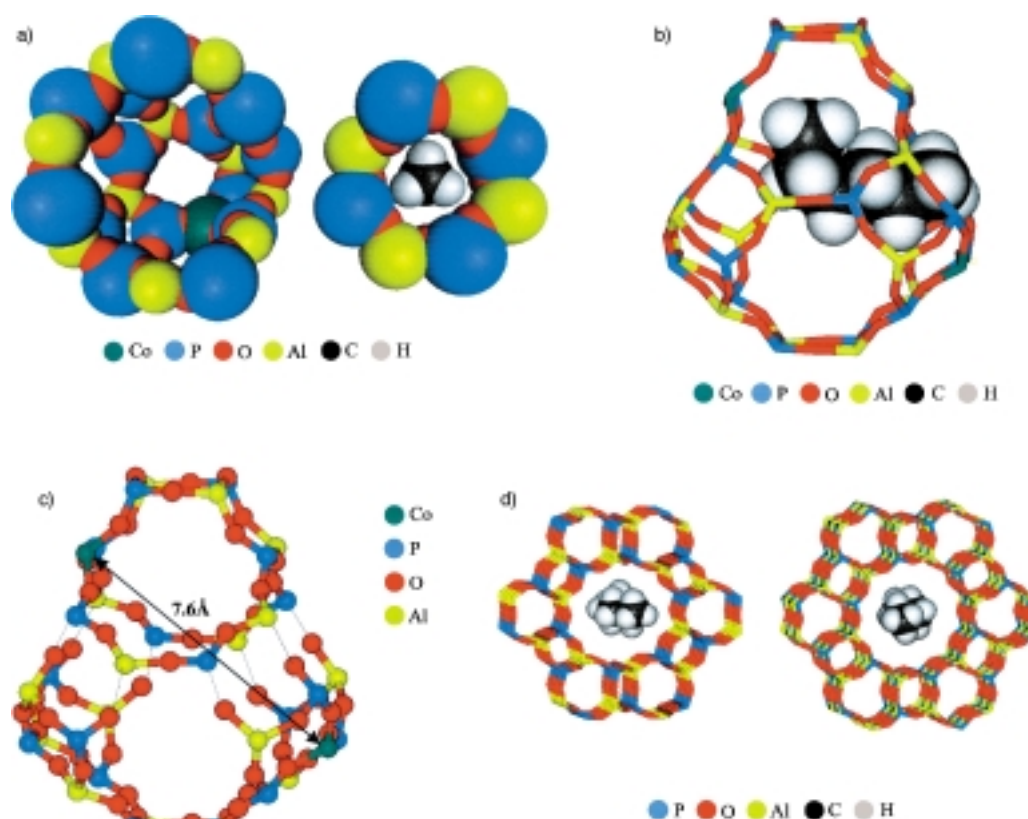


Figure 1. a) Views of (left) interior of the cage in the Co^{III}AIPO-18 catalyst and (right) of the aperture of the cage, which shows a terminal methyl group of an *n*-hexane molecule. b) The energy-minimized configuration (see ref. [11]) of an *n*-hexane molecule at 0 K inside an AIPO-18 framework. Two Co^{III} ions have been placed at the opposite vertices of the cage, at positions compatible (see text) with the composition Co_{0.1}Al_{0.9}PO₄. We estimate the separation distance between the van der Waals limits of these two framework ions to be about 7.6 Å. c) Expanded view of a cage in the CoAIPO-18 catalyst. For clarity, the top half has been separated from the bottom, the dotted lines indicating which atoms in the separated halves connect. d) The structures of the AIPO-36 (left) and AIPO-5 (right) catalysts.

Si₂₄O₇₂]) that are candidates—in view of their pore dimensions and shape—for the designed catalyst. Experiments showed that AIPO-44 structures are not thermally stable;^[20] they were not, therefore, considered further by us in this context. AIPO-34, although difficult to prepare in a phase-pure form with Co:P ratios less than 0.1, are, however, viable candidate catalysts along with AIPO-18 and are prepared through the agency of structure-directing (template) quaternized organic bases according to procedures described elsewhere.^[21, 22] (A new template, trimethyl azabicyclooctane, was found to be effective for the preparation of CoAIPO-34 with Co:P ratios of about unity.^[23])

It is not, unfortunately, readily possible by direct electron microscopic^[24] or other techniques to determine the precise distribution of the Co^{III} ions in the AIPO framework, as the transition metal cation is not ordered within the structure. Simple computational estimates,^[25] which assume spatially random substitution of Al^{III} by Co^{III} ions, indicate that with Co:P ratios of 0.08 and higher there is a strong tendency for two Co^{III} ions to be accommodated in each (chabazitic) cage.

Table 1 and Figure 2 summarize the results of our selective oxidation experiments and specifically highlight the contrast in catalytic performance—particularly in regard to production of adipic acid—of low and high Co:P ratios for CoAIPO-18 (namely, 0.04 and 0.10, respectively). It is gratifying to note,

Table 1. Aerial oxidation of *n*-hexane: comparison of catalysts^[a]

Catalyst (Co:P ratio)	Time [h]	Conversion [%]	Product selectivity (mole %) ^[b]								
			A	B	C	D	E	F	G	H	others
CoAlPO-18 (0.10)	8	5.9	15.8	19.0	32.8	7.3	14.7	6.2	2.5	–	2.3
	24	9.3	4.0	2.4	33.0	31.6	1.9	6.3	18.2	–	2.8
	24 ^[c]	9.5	3.1	2.3	35.2	33.6	–	4.5	19.7	–	2.5
CoAlPO-18 (0.04)	8	3.5	13.1	24.3	57.1	–	–	3.5	2.1	–	–
	24	7.2	4.5	3.3	53.5	–	–	13.9	22.2	–	4.4
CoAlPO-34 (0.10)	8	6.3	20.5	16.0	26.7	4.0	17.3	8.2	6.2	–	1.5
	24	7.9	7.3	6.2	29.4	19.7	3.9	7.5	23.4	–	2.6
CoAlPO-36 (0.04)	8	3.1	9.9	2.0	2.5	–	–	18.3	12.5	49.6	4.7
	24	5.2	8.7	3.8	10.2	–	–	9.2	19.8	45.1	3.2

[a] Reaction conditions: *n*-hexane \approx 50 g; catalyst = 0.51 g; oxidant (air) = 1.5 MPa; $T = 373$ K. [b] Products: A = 1-hexanol; B = 1-hexanal; C = hexanoic acid; D = adipic acid; E = 1,6-hexanediol and 1,6-hexanedial; F = 2-hexanol; G = 2-hexanone; H = 3-hexanol and 3-hexanone; others = traces of fragmentation products such as succinic and glutaric acids. [c] The italicized numbers denote results obtained from a duplicate experiment, in which the same catalyst was washed thoroughly with methanol and recalined at 550 °C before use.

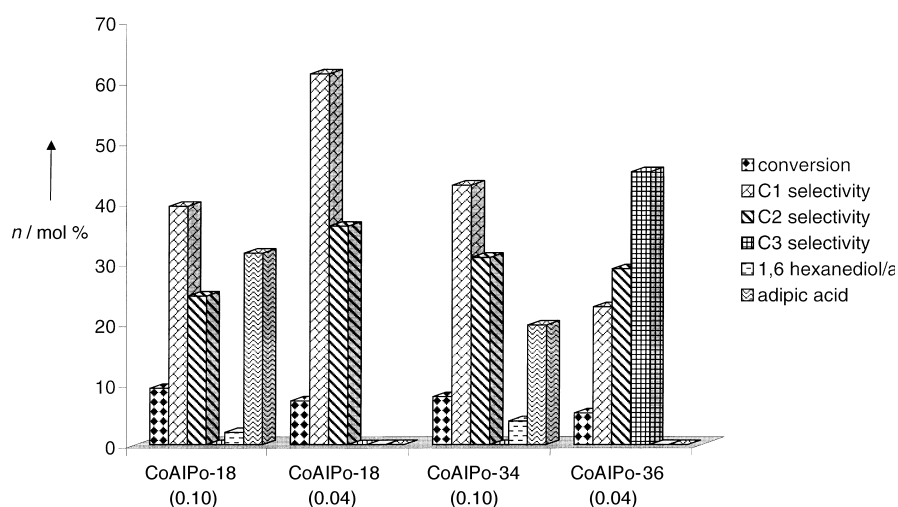


Figure 2. Bar chart to illustrate the efficacy of the cobalt-enriched CoAPO-18 (Co:P=0.10) as a catalyst for the conversion of *n*-hexane to adipic acid. The values in parentheses refer to the Co:P ratio.

given the essential synonymy of their framework structures, that CoAlPO-18 and CoAlPO-34 (each with Co:P ratios of 0.10) exhibit broadly similar performances. On the other hand, CoAlPO-36 is markedly different, and this is to be expected, because of its larger pore structure and shape (Figure 1 d).

Detailed kinetic studies (Figure 3) are also informative, especially when compared with those reported earlier^[11] for CoAlPO-18 with a Co:P ratio of 0.04. With a Co:P ratio of 0.1 for both the CoAlPO-18 and CoAlPO-34 catalysts, hexanol is the major product during the initial stages of the reaction but this is subsequently converted to hexanal and hexanoic acid. After 5 h, 1,6-hexanediol, 1,6-hexanedial, and traces of adipic acid appear in the reaction mixture as well as the three principal products (hexanol, hexanal, and hexanoic acid) observed earlier.^[11]

It is noteworthy, that there is no decrease in hexanoic acid selectivity (Figure 3) but, that at prolonged contact times (10–24 h), there is a steady decrease in the concentrations of both 1,6-hexanediol and 1,6-hexanedial and a concomitant increase in the production of adipic acid. Evidently, the production of adipic acid arises as a result of the further oxidation of 1,6-hexanediol and 1,6-hexanedial. Further, when

hexanoic acid was taken as the substrate (instead of *n*-hexane), using CoAlPO-18 (Co:P=0.10) as the catalyst we did not observe any conversion. With a Co:P ratio of 0.04, the CoAlPO-18 catalyst, under identical conditions, produces neither 1,6-hexanediol, 1,6-hexanedial, nor any detectable adipic acid.^[26]

The active, adipic acid-producing CoAlPO-18 catalyst, with its Co:P ratio of 0.10, is remarkably stable and we did not observe any leaching of the cobalt ions during the catalysis.^[27] Even upon removal of the template molecule by gentle calcination in oxygen, in order to produce empty cages, the X-ray absorption and diffraction data, collected by in situ measurements as previously described,^[10, 20] leave no doubt about the retention of structural integrity whilst the oxidation state of Co^{II} ions in the as-prepared solid increases to Co^{III} (Figure 4). This behavior mirrors exactly that of CoAlPO-18, which has a Co:P ratio of 0.04.^[28]

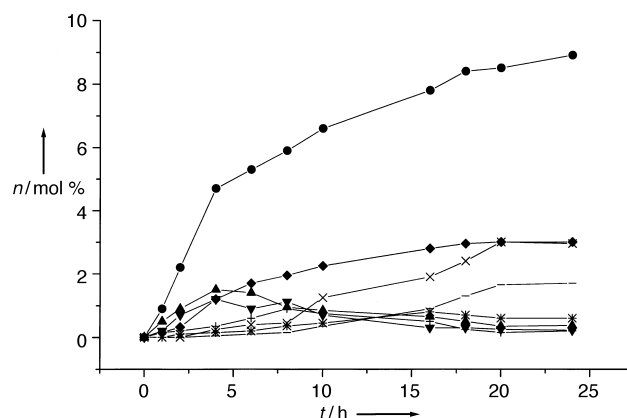


Figure 3. Kinetic plots showing the overall conversion of *n*-hexane and the appearance of various products with the CoAlPO-18 catalyst (Co:P=0.10): ● = conversion; ▲ = 1-hexanol; ▼ = 1-hexanal; ◆ = hexanoic acid; + = 1,6-hexanediol and 1,6-hexanedial; × = adipic acid; * = 2-hexanone; – = 2-hexanone.

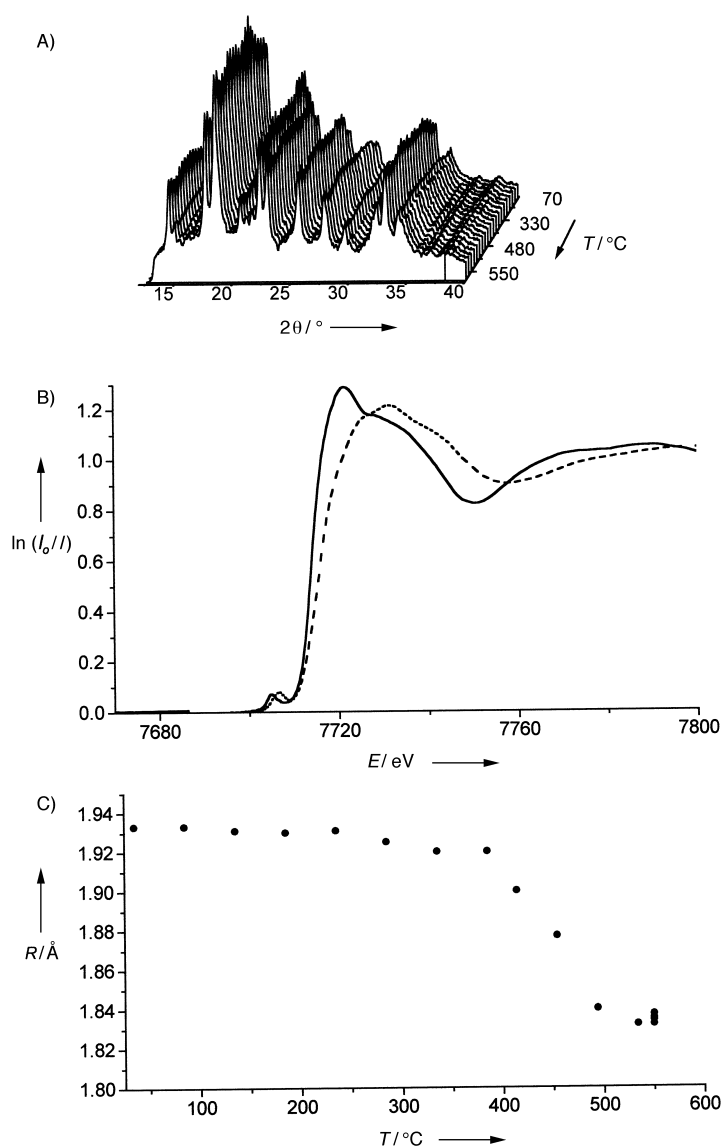


Figure 4. Combined time-resolved X-ray diffraction (XRD) patterns and X-ray near-edge absorption (XANES) spectra^[20,28] of the progressively calcined CoAlPO-18 show, when the organic template (*N,N*-diisopropylethylamine) is driven off, the framework structure of the microporous catalyst does not collapse and the Co^{II} ions, present in the as-prepared material, are oxidized to Co^{III} at around 550 $^\circ\text{C}$. A) Stacked XRD diffractograms; B) XANES spectra (compare with ref. [28]); C) the progressive decrease of the mean Co-O bond distance (R ; derived from extended X-ray absorption fine structure (EXAFS) analysis) as the template molecule is removed by calcination.

To our knowledge, this is the first report that describes the formation of substantial amounts of adipic acid directly from *n*-hexane, a process hitherto considered so demanding as to become the quintessence of J. D. Roberts', the famous American chemist, Barton challenge.^[15]

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- [27] The following experiments have been carried out to rule out the possibility of leaching. 1) In a typical experiment (see Table 1), the solid catalyst (CoAlPO-18; Co:P=0.10) was filtered from the hot reaction mixture after 8 h and the reaction continued with the resulting filtrate for a further 16 h. No significant change in *n*-hexane conversion or the product selectivity was observed, which indicated that the leached metal ions (if any) are not responsible for the observed activity and selectivity. 2) The resulting filtrate (at the end of the reaction, 24 h) was analyzed independently by ICP and AAS for free or dissolved cobalt ions; only trace amounts (<3 ppb) were detected. 3) When an equimolar mixture of *n*-hexane and cyclohexane was subjected to a catalytic test over CoAlPO-18 (Co:P=0.10), there was, unsurprisingly, absolutely no conversion of the cyclohexane molecule, as it is too large to access the active Co^{III} framework sites in the AlPO-18 structure, while the conversion of *n*-hexane remained unaffected. If hexanoic acid or adipic acid leached cobalt from the framework, the cyclohexane molecule would have also been oxidized to cyclohexanol and cyclohexanone. See ref. [12] for further details.
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