

# Molecular Sieve Catalysts for the Regioselective and Shape-Selective Oxyfunctionalization of Alkanes in Air

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## ABSTRACT

Framework-substituted, molecular-sieve, aluminophosphate, microporous solids are the centerpieces of a new approach to the aerobic oxyfunctionalization of saturated hydrocarbons. The sieves, and the few percent of the Al<sup>III</sup> sites within them that are replaced by catalytically active, transition-metal ions in high oxidation states (Co<sup>III</sup>, Mn<sup>III</sup>, Fe<sup>III</sup>), are designed so as to allow free access of oxygen in to and out of the interior of these high-area solids. Certain metal-substituted, molecular sieves permit only end-on approach of linear alkanes to the active centers, thereby favoring enhanced reactivity of the terminal methyl groups. By optimizing cage dimension, with respect to that of the hydrocarbon reactant, as well as adjusting the average separation of active centers within a cage, and by choosing the sieve with the appropriate pore aperture, highly selective conversions such as *n*-hexane to hexanoic acid or adipic acid, and cyclohexane to cyclohexanol, cyclohexanone, or adipic acid, may be effected at low temperature, heterogeneously in air.

## 1. Introduction

Saturated hydrocarbons are among the most abundant of all naturally occurring organic molecules, and although they are readily oxidized to completion (burnt) at elevated temperature, they are also among the most difficult to oxyfunctionalize in a controllable manner at lower temperature. Their very name, paraffins, from the Latin *parum affinis* (slight affinity), betrays their inertness. Linear alkanes, such as *n*-hexane, resist attack by boiling nitric acid, concentrated sulfuric acid, chromic acid, or potassium permanganate. But even if suitable catalysts were found to facilitate modest reaction with these (normally)

aggressive reagents, these oxidants are not any more environmentally acceptable. Hydrogen peroxide and, better still, oxygen (air) are far superior oxidants to employ if suitable catalysts can be developed for their use.

At first sight, the prospects of achieving regiospecific oxyfunctionalization, especially at the terminal or penultimate positions of alkane chains, appear bleak, especially when it is recalled that C–H bond dissociation energies decrease from 104 to 95 to 91 kcal mol<sup>-1</sup> in proceeding from primary to secondary to tertiary carbon atoms.

However, since terminally oxidized alkanes, such as linear alcohols or acids, are extremely desirable potential feedstocks for the chemical industry, there is an exigent need for devising ways of selectively oxidizing the terminal methyl groups. In addition, there is also the intellectual (Barton) challenge posed<sup>1</sup> by the distinguished American scientist John D. Roberts, who, recognizing the immensity of the task, recently invited research groups to effect “a chemical or biochemical oxidation of *n*-hexane to adipic acid” in substantial yield.

Selectively oxyfunctionalizing alicyclic hydrocarbons such as cyclohexane and adamantane are similarly demanding tasks. Yet it was the demonstration by Barton<sup>2</sup> and his colleagues (using their so-called Gif and GoAgg systems<sup>3</sup>) that there was somewhat higher selectivity for oxidation of secondary over tertiary hydrogens in adamantane that, *inter alia*, prompted Roberts to issue the Barton challenge. Here again, practical considerations loom large, since the selective oxidation of cyclohexane into a mixture of cyclohexanol and cyclohexanone (called K-A oil) is of considerable importance in the industrial production of Nylon-6 and Nylon-6,6. Currently, K-A oil is generated from cyclohexane using homogeneous (cobalt-based) catalysts; adipic acid (AA), an important building block for a variety of commercially useful products such as polyamides (e.g., Nylon-6,6) and urethanes, is also derived from cyclohexane by nitric acid oxidation of the K-A oil.

A prodigality of papers already exists concerning the various ways in which selective oxyfunctionalization of alkanes has hitherto been attempted.<sup>4–8</sup> Cytochrome P-450 enzymes as well as non-heme, iron-based oxidases are

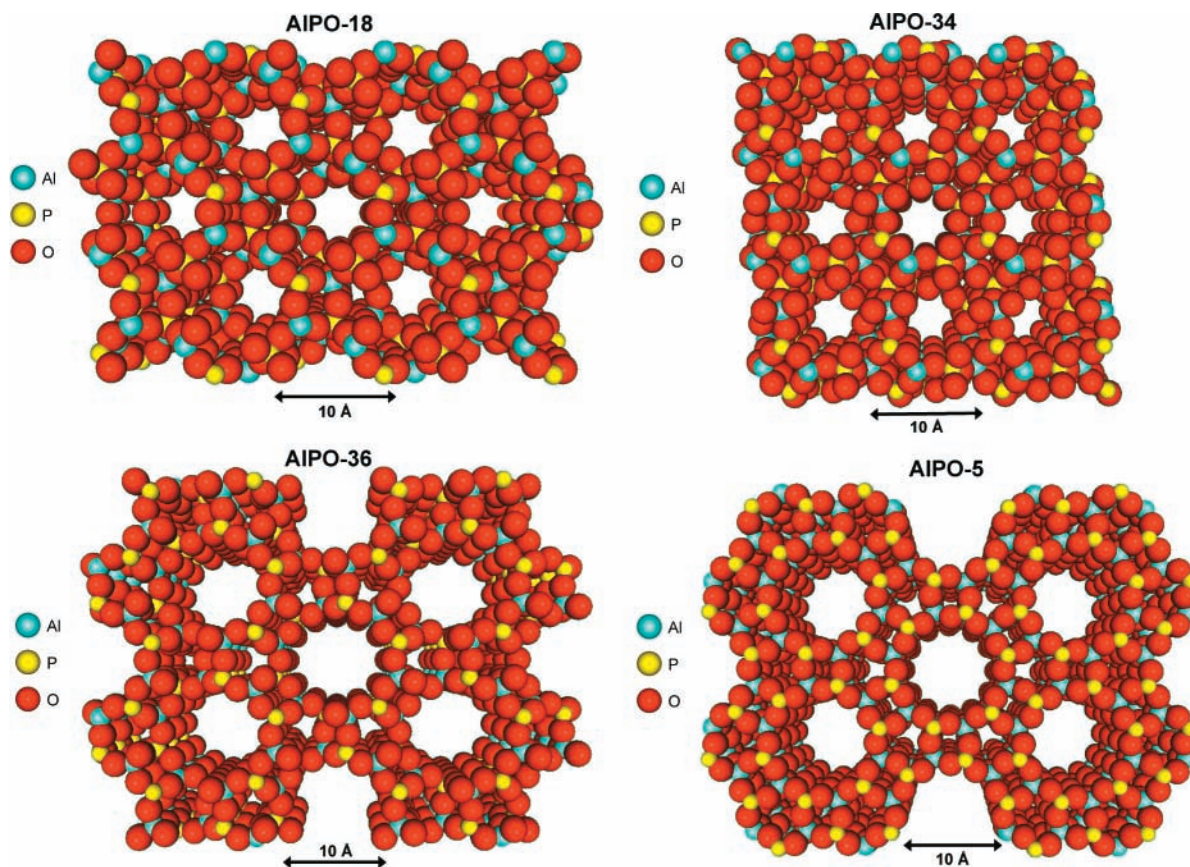
John Meurig Thomas took his initial degree at University College of Swansea, and after his Ph.D., completed in London, he taught at the University of Wales (Bangor and Aberystwyth) for 20 years. From 1978 to 1986 he was Head of the Department of Physical Chemistry, University of Cambridge, where he broadened his interests in solid-state, surface, and materials chemistry. He is Professor of Chemistry at the Royal Institution of Great Britain (of which he was Director from 1986 to 1991), where he continues his interest in developing new techniques and designing inorganic catalysts. He was knighted in 1991 for services to chemistry and the popularization of science.

Robert Raja received his Masters degree at the Birla Institute of Technology and Science and completed his Ph.D. with Paul Ratnasamy at the National Chemical Laboratory, Pune (1997). He was Royal Commission of 1851 Exhibitor at the Davy Faraday Research Laboratory of the Royal Institution of Great Britain (1997–1999) and continues his research there and at the Department of Chemistry, Cambridge University, in joint work with Brian F. G. Johnson and John Meurig Thomas. His research interest focuses on selective oxidation processes for fine chemicals and enzyme mimics. He is the author of 25 papers and has filed 19 international patents.

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Robert Bell was born in 1964 in Bath, England. He received a B.Sc. degree in chemistry from University College London and a Ph.D. in chemistry from the University of Southampton. He currently holds the position of Leverhulme Senior Research Fellow in the Davy Faraday Research Laboratory of the Royal Institution. His research interests are centered on the application of computational chemistry methods to the study of microporous materials, with particular emphasis on adsorption processes and on structure–property relationships.



**FIGURE 1.** Three-dimensional representation of the pore structures of AIPO-18, AIPO-34, AIPO-36, and AIPO-5 (pore apertures are respectively 3.8 Å, 3.8 Å, 6.5 × 7.5 Å and 7.3 Å). In the AIPO-18 and AIPO-34 structures there are chabazitic cages (see Figure 3A) as side pockets along the 3.8 Å diameter pores. (Note: the size of the atoms in the structures corresponds to their van der Waals radii.)

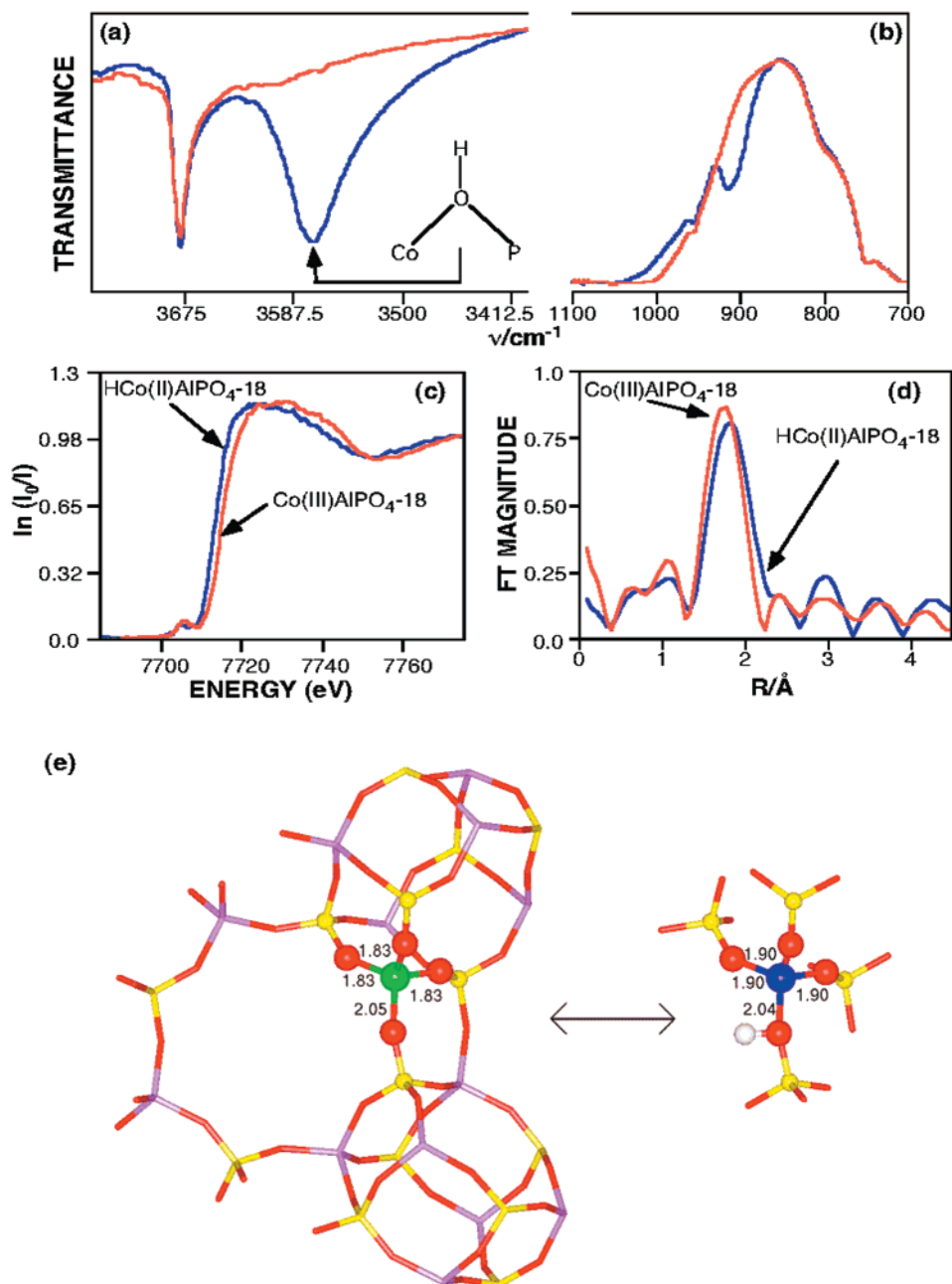
well known, and on the nonbiochemical front, it is recognized that controlled partial oxidation is easier to effect with “sacrificial” oxidants—especially in the presence of reducing agents or radical initiators—such as hydrogen peroxide,<sup>7</sup> alkyl hydroperoxides,<sup>9</sup> or iodosyl benzene<sup>10</sup> than with molecular oxygen or air. These sacrificial oxidants have been used in catalytic systems involving tailored transition-metal complexes or metal-substituted polyoxometalates either in a homogeneous state,<sup>11–14</sup> encapsulated in molecular sieves,<sup>15–17</sup> or anchored to the inner surfaces of mesoporous silica.<sup>9</sup> One recent report describes<sup>18</sup> an efficient means of producing linear alkylboranes (using a rhodium-based sandwich compound as a homogeneous catalyst) which, in turn, may be stoichiometrically converted, by H<sub>2</sub>O<sub>2</sub> for example, to linear alcohols. Another describes<sup>14</sup> an oxo-bridged diiron- or dimanganese-containing silicotungstate for the oxygenation of cyclohexane in H<sub>2</sub>O<sub>2</sub> or molecular oxygen, respectively.

Some three years ago, prompted partly by the intellectual challenge of laying down the scientific foundations of clean technology, and partly because of our earlier expertise<sup>19,20</sup> in designing new molecular-sieve solids containing framework-substituted transition-metal ions in well-defined crystallographic sites, we began seeking ways of designing inorganic catalysts that would partially and regioselectively oxidize alkanes in air or oxygen at low temperature. We judged it essential for the catalyst to be

heterogeneous, as this would make separation of products from reactants easier and also facilitate recyclability of the catalyst. We also felt it desirable to utilize microporous aluminophosphates (AIPOs) since these, potentially, could be made to display many catalytic advantages. Not least among these advantages were high (internal) surfaces which could be accessible to reactant molecules of certain size and shape, and from which those products of appropriate dimension could diffuse out. Other advantages include

- the ability for small quantities of isolated transition-metal ions (M), such as Co<sup>III</sup>, Mn<sup>III</sup>, and Fe<sup>III</sup>, to be incorporated into the AIPO frameworks, thereby conferring “redox” catalytic activity at the sites of their incorporation into the resulting MAIPO, microporous solid;
- relative ease of preparation, using appropriately chosen structure-directing organic templates, of a considerable range of MAIPO structures differing in their micropore and cage characteristics (e.g., pore diameters, extent of pore intersection); and
- good thermal stability.

An added bonus was that, based on our earlier experience in designing, synthesizing, and characterizing a range of MAIPOs, detailed quantitative knowledge about the local structure of metal-ion-centered active sites in these microporous catalysts would be readily retrievable from the application of in situ techniques, such as X-ray absorption spectroscopy and FTIR.<sup>21–23a</sup>



**FIGURE 2.** Proof that when  $\text{Co}^{\text{II}}\text{AlPO}_4\text{-18}$  is converted, by calcination in oxygen, to  $\text{Co}^{\text{III}}\text{AlPO}_4\text{-18}$ , the proton is lost from the framework {as seen in the FTIR spectra of (a) and (b)}; there is a shift to increasing energy in the Co X-ray K-edge (c), and a decrease in the Co–O bond length (d). The structural details are summarized in (e).

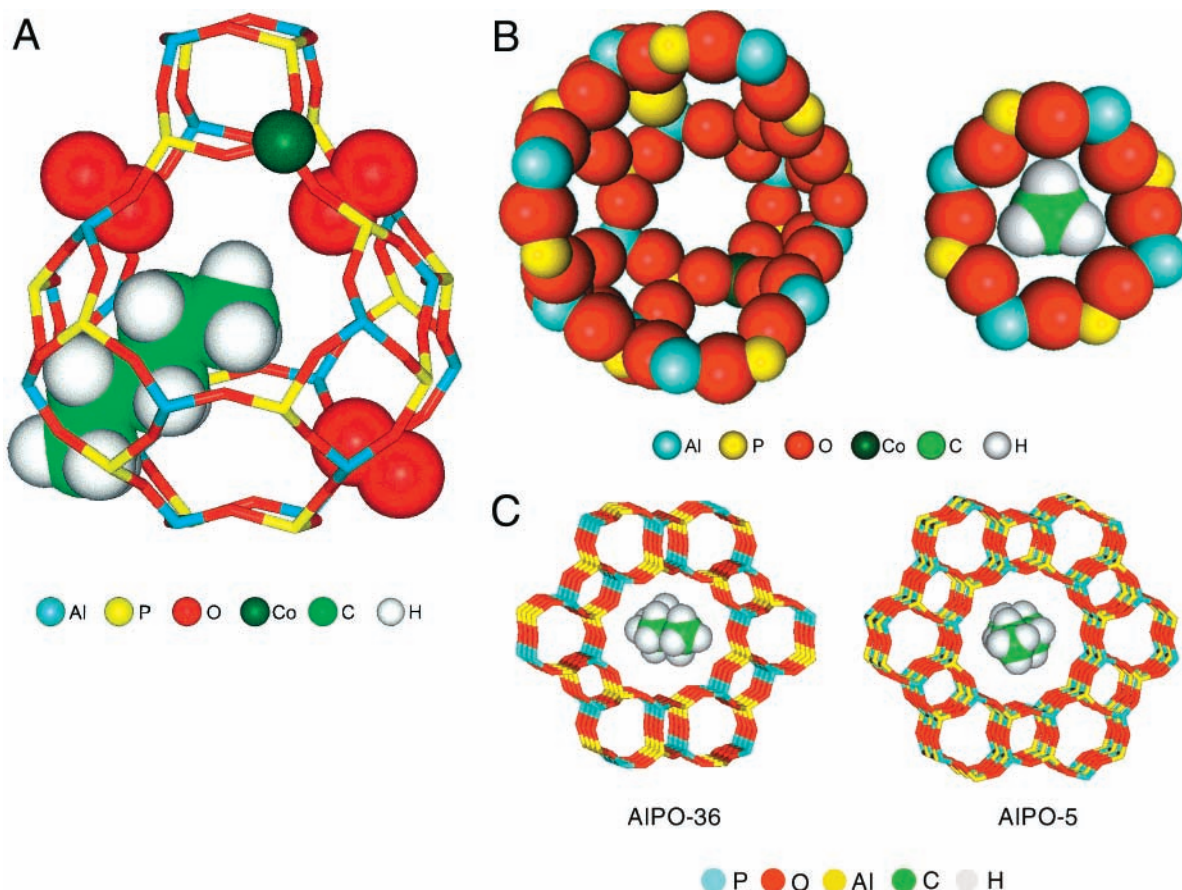
There were two other considerations that prompted us to explore the selective, oxidative power of  $\text{Mn}^{\text{III}}$  (or  $\text{Co}^{\text{III}}$ ) framework-substituted molecular-sieve catalysts, and both these arose more because of poetic suggestion rather than indisputable scientific fact. First,  $\text{Mn}^{\text{III}}$  and  $\text{Co}^{\text{III}}$  ions accommodated substitutionally in place of  $\text{Al}^{\text{III}}$  ions in the MAIPO framework possess close to tetrahedral coordination,<sup>23,24</sup> and just like four-coordinated  $\text{Ti}^{\text{IV}}$  ions in the powerful selective oxidation molecular-sieve catalyst TS-1<sup>25</sup> or the five-coordinated Mn ions in manganese superoxide dismutase,<sup>23b</sup> they are coordinatively unsaturated, a feature that facilitates redox catalytic reaction. Moreover, the occurrence of isolated  $\text{Mn}^{\text{III}}$  (or  $\text{Co}^{\text{III}}$ ) ions in the framework of the MAIPO would, in the presence of oxygen

and those alkanes whose size and shape permit access to these high-oxidation-state ions, favor the production of free radicals, which we knew<sup>4,9,26</sup> to be implicated in the selective oxidation of saturated hydrocarbons with oxygen.

## II. Two Promising MAIPO Catalysts

Earlier work by one of us (J.M.T.) had shown<sup>27</sup> that members of the family of MAIPO-18 ( $M \equiv \text{Zn}^{\text{II}}, \text{Mg}^{\text{II}}, \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}, \dots$ ) molecular sieves were powerful solid acid catalysts that shape-selectively converted methanol to light olefins, and that MAIPO-36, because of its larger pores,<sup>28</sup> allows the acid catalytic dehydration of methanol to proceed further than the olefinic stage to benzene, xylene, and beyond.





**FIGURE 3.** (A) Skeletal outline of a single chabazite cage through which molecules of dioxygen (red lobes) permeate freely. Alkanes, on the other hand, can enter the chabazite cage only by an *end-on* approach (see bottom left). (B) Views of (left) the interior of the chabazite cage in CoAIPO-18 that is lined with a  $\text{Co}^{\text{III}}$  ion, substitutionally replacing a framework  $\text{Al}^{\text{III}}$  ion; and (right) the terminal methyl group of a linear alkane (*n*-hexane) fits snugly into the aperture, the extremities of the van der Waals radii of the methyl group very nearly touch those of the oxygen atoms of the framework. (C) Representation of the *n*-hexane molecule inside the larger pore AIPO-36 and AIPO-5 structures.

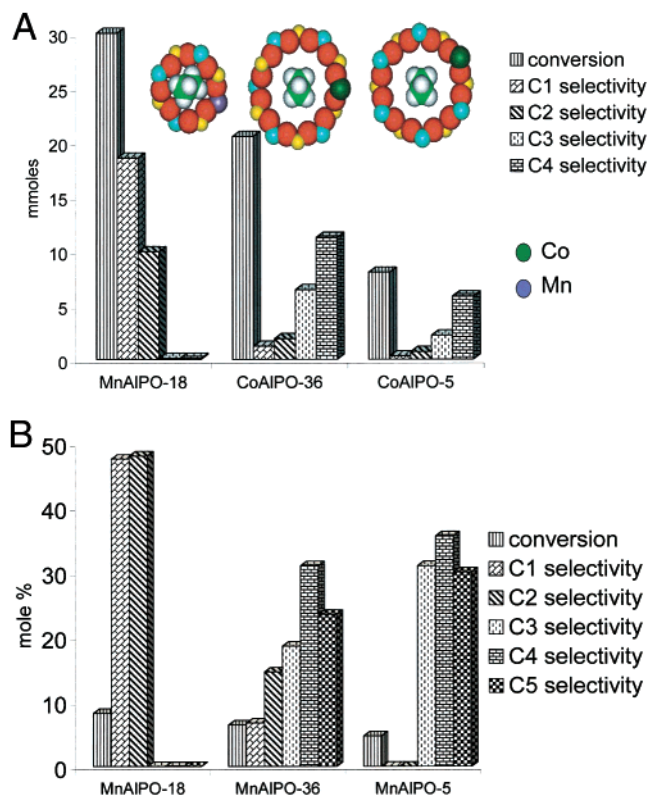
We selected AIPO-18 (idealized formula  $\text{Al}_{24}\text{P}_{24}\text{O}_{96}$ ), which has pores similar to those of the zeotypic analogue of the aluminosilicate mineral chabazite<sup>29</sup> (Figure 1). In its framework, a few percent of divalent metal ions (M) may be readily accommodated, a process that is accomplished by templated hydrothermal synthesis.<sup>30</sup> The template is driven off completely by heating in  $\text{O}_2$  to ca. 550 °C, during which process the redox ions ( $\text{Co}^{\text{II}}$  or  $\text{Mn}^{\text{II}}$ ) are raised to their next higher oxidation state ( $\text{Co}^{\text{III}}$  or  $\text{Mn}^{\text{III}}$ )<sup>24,31</sup> (Figure 2). When CoAIPO-36 and MnAIPO-36 are treated in this fashion, we find that, for reasons that are still obscure, not all the framework divalent ions can be raised to the  $\text{Co}^{\text{III}}$  (or  $\text{Mn}^{\text{III}}$ ) state (only some 45%).<sup>32</sup>

We argued<sup>24,31</sup> that oxyfunctionalization would be favored at the terminal methyl group of *n*-alkanes using  $\text{Co}^{\text{III}}$  (or  $\text{Mn}^{\text{III}}$ ) AIPO-18 catalysts because only an *end-on approach* of the alkane to the active site would be allowed, there being ready access both to the active site and to the alkane chain termini by the oxygen (Figure 3). With  $\text{Co}^{\text{III}}$  (or  $\text{Mn}^{\text{III}}$ ) AIPO-36, because of the much larger pore diameter, there is no such *end-on* restriction of entry of the alkane into the microenvironment of the active site, which is swathed in molecular oxygen.

### III. Regioselective and Shape-Selective Oxidation of *n*-Alkanes Using $\text{Co}^{\text{III}}$ ( $\text{Mn}^{\text{III}}$ ) AIPO-18 and AIPO-36 Catalysts

In line with the expectations encapsulated in Figure 3, where we see that shape-selectivity of the *n*-alkane is crucial in the case of  $\text{M}^{\text{III}}$ AIPO-18 but not in  $\text{M}^{\text{III}}$ AIPO-36 or  $\text{M}^{\text{III}}$ AIPO-5, we observe (Figure 4) that there is a high preference for terminal (i.e.,  $\text{C}_1$ ) selectivity in the case of the former catalyst and no such selectivity with the latter two. Results for only *n*-octane and *n*-dodecane are shown, but exactly analogous ones, exhibiting similar high terminal selectivities, are seen for  $\text{C}_6$  and  $\text{C}_{10}$  *n*-alkanes also (not shown).

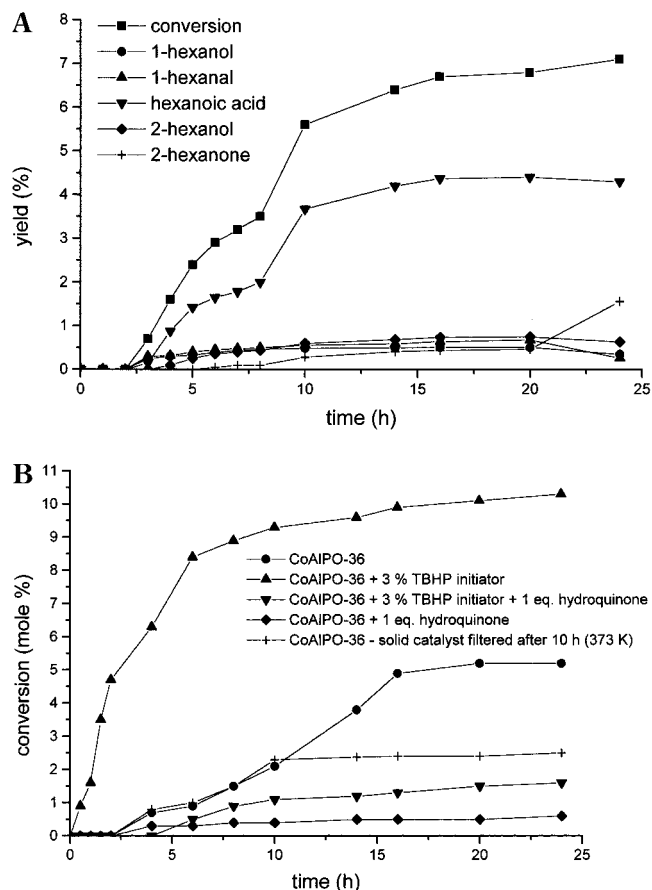
The so-called primary selectivity index (defined as the ratio of concentration of primary products to secondary/tertiary products normalized for the respective number of hydrogens in the alkane molecule) is superior for the  $\text{Co}^{\text{III}}$ AIPO-18 and  $\text{Mn}^{\text{III}}$ AIPO-18 catalysts than for all previously reported inorganic heterogeneous catalysts, even though the latter use sacrificial oxidants, not air or  $\text{O}_2$ .<sup>33</sup> It is to be noted (Figure 4A) that some 70% of the products of oxidation of *n*-octane after 24 h are the result of oxyfunctionalization of the terminal methyl group for  $\text{Co}^{\text{III}}$ -AIPO-18 (60% for  $\text{Mn}^{\text{III}}$ AIPO-18). Octanoic acid, 1-octanal,



**FIGURE 4.** (A) Performance of Co- and Mn-substituted AIPO-18, AIPO-36, and AIPO-5 catalysts in the aerial oxidation of *n*-octane after 24 h at 373 K. Because of the *end-on* approach of the *n*-octane in AIPO-18, only the C<sub>1</sub> and C<sub>2</sub> positions are preferentially oxidized, whereas the larger pore dimensions of AIPO-36 and AIPO-5 lead to oxyfunctionalization predominantly at the C<sub>3</sub> and C<sub>4</sub> positions. (B) Regioselective oxyfunctionalization of *n*-dodecane after 24 h at 373 K using MnAIPO catalysts. The regioselectivity for terminal oxidation with MnAIPO-18 far exceeds that of the other two catalysts.

and 1-octanol, in descending order, are the principal products of oxyfunctionalization.<sup>24</sup>

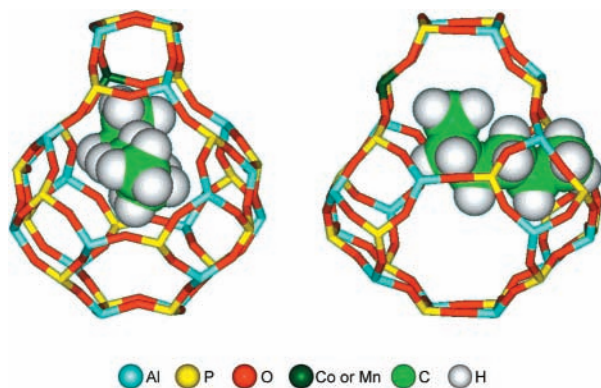
It is well known<sup>4,9,26</sup> that the aerial oxidation of alkanes by transition metal ions generally involves the participation of free radicals. We believe, for three reasons, that our regioselective oxidations, as well as the selective oxidation of cyclohexane over similar catalysts (see below), are no exceptions. Because of the small aperture of the AIPO-18 structure, it is easier to test the role of free radicals using the AIPO-36 structure, which has apertures large enough to allow alkylperoxyl radicals and radical scavengers to enter their interior surfaces. First, there is an induction period in the yield versus time plots (typified by that for *n*-hexane, using CoAIPO-36 as the catalyst, shown in Figure 5B), and this period is greatly diminished by the prior addition of traces of free radical initiators such as *tert*-butyl hydroperoxide (TBHP). Second, addition of small quantities of hydroquinone, a free radical scavenger, greatly hinders the oxidation (see curves ▼ and ◆, Figure 5B). Third, in the oxidation of cyclohexane (the peroxide of which is easier to analyze than that of *n*-alkanes) under identical conditions over a range of Co<sup>III</sup> and Mn<sup>III</sup>-AIPO catalysts, the presence of cyclohexyl hydroperoxide (which subsequently decomposes to cyclohexanol and cyclohexanone) has been directly detected.<sup>24a</sup>



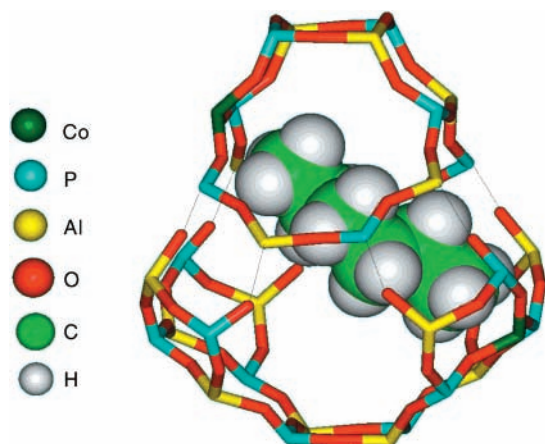
**FIGURE 5.** Kinetics of oxidation of *n*-hexane using CoAIPO-18 (0.04) (A) and CoAIPO-36 (0.04) (B) in the presence (▲) and absence (●) of free radical initiators. Addition of small amounts of free radical scavengers (▼ and ◆) completely suppresses the reaction.

Although the precise mechanism of the oxidation of the alkanes involving CoAIPO and MnAIPO catalysts and dioxygen is not clear—as is also the case of cytochrome P-450 and other enzymatic reactions—there is little doubt that catalytic autoxidation<sup>4,33</sup> dominates here. It is certain that framework-isolated Co<sup>II</sup> or Mn<sup>II</sup> ions present initially in the as-prepared sieve, when converted to the Co<sup>III</sup> or Mn<sup>III</sup> state, are vital for the catalysis. It is likely that the scope for expansion of the coordination shell of the transition-metal ion is a significant factor in facilitating reaction. Divalent ions that cannot be raised to higher states of oxidation, such as Mg<sup>II</sup>, are totally inactive as oxidation catalysts. Experiments using MgAIPO-18 and MgAIPO-36 as catalysts (for the oxidation of *n*-hexane under the conditions of Figure 5 at 373 K) showed no activity. This fact also rules out the possibility that free radicals produced solely in the gas phase play any significant role in the autoxidation. Moreover, introduction of acetonitrile (known<sup>34</sup> to coordinate Co<sup>II</sup> ions) before the admission of air completely poisons the CoAIPO-18 catalyst.

Further insight into the occurrence of the regioselectivity in the oxyfunctionalization with MAIPO-18 catalyst emerges from computer simulation<sup>35</sup> (Figure 6). This reveals the state of lowest energy adopted by the alkane inside the chabazitic cavity of the AIPO-18 framework. We



**FIGURE 6.** Energy-minimized configuration adopted by *n*-hexane at 0 K inside an AIPO-18 framework. This configuration, which was derived from a calculation<sup>35</sup> that combines Monte Carlo, molecular dynamics, and docking procedures, shows that the terminal methyl group ( $C_1$ ) is significantly closer to a tetrahedral framework site than either  $C_2$  or  $C_3$ , the respective bond distances being  $C_1 = 3.53 \text{ \AA}$ ,  $C_2 = 3.75 \text{ \AA}$  and  $C_3 = 4.03 \text{ \AA}$ .



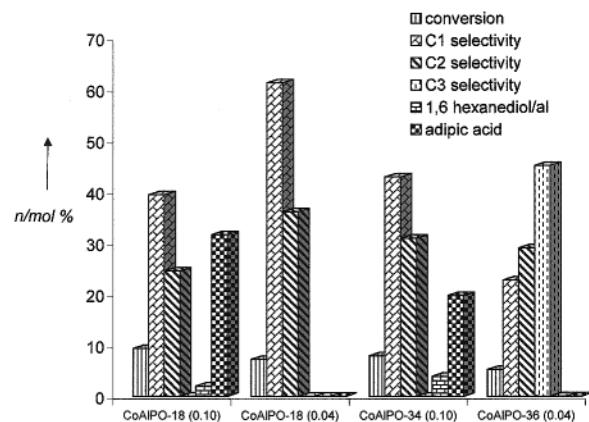
**FIGURE 7.** Expanded view of the chabazite cage showing the energy-minimized configuration of the *n*-hexane molecule and the two separated  $\text{Co}^{\text{III}}$  ions in each cage of the AIPO-18 structure. For clarity, the top half has been separated from the bottom one, the dotted lines indicating which atoms in the separated halves link up. The estimated separation distance between the van der Waals limits of these two framework ions is ca.  $7.6 \text{ \AA}$ .

see that a bound *n*-hexane, with its slightly bent end, gains ready access to the active sites, which selectively favor oxidation at the terminal carbons.

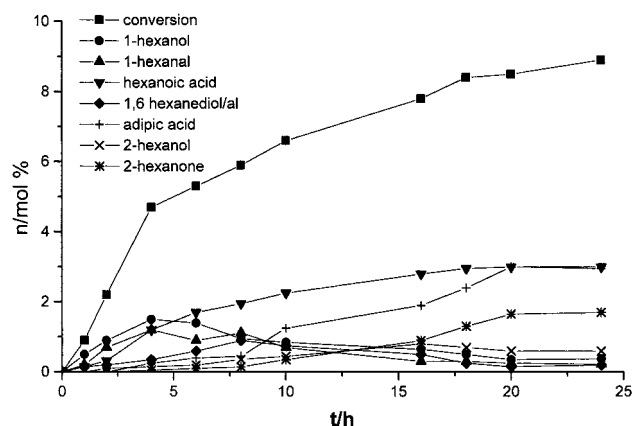
#### IV. A Molecular-Sieve Catalyst for the Aerial Oxidation of *n*-Hexane to Adipic Acid

To achieve oxyfunctionalization at both (methyl) ends of *n*-hexane, we argued that a sufficiently large number of framework  $\text{Co}^{\text{III}}$  ions need to be accommodated on the inner walls of catalysts such as CoAIPO-18 in such a manner that two  $\text{Co}^{\text{III}}$  ions should be separated by about  $7\text{--}8 \text{ \AA}$  from one another. In other words, it is desirable that there be about two (separated)  $\text{Co}^{\text{III}}$  ions in each cage of the AIPO-18 structure, preferably situated opposite one another (Figure 7).

It is not just AIPO-18 but also AIPO-34,<sup>29</sup> both of which are closely akin to the aluminosilicate mineral chabazite (idealized formula  $\{\text{Ca}_6(\text{Al}_{12}\text{Si}_{14}\text{O}_{72})\}$ ), that are suitable



**FIGURE 8.** Bar chart highlighting the contrast in catalytic performances of low and high Co/P ratios for CoAIPO-18 (i.e., 0.04 and 0.10) as catalysts for the conversion of *n*-hexane to adipic acid after 24 h at 373 K.



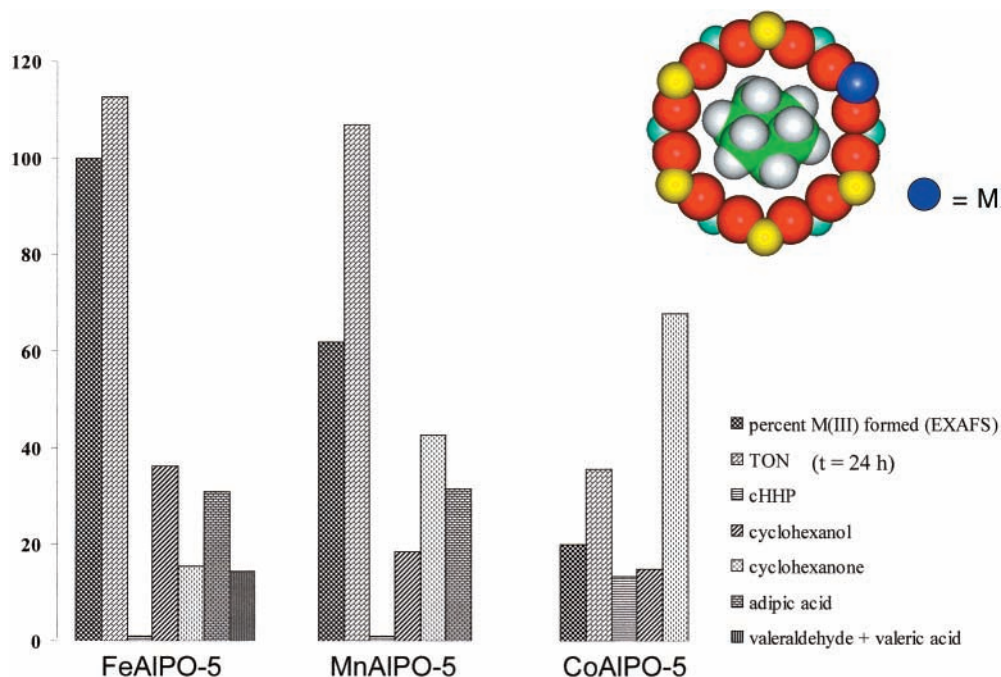
**FIGURE 9.** Kinetic plots for the oxidation of *n*-hexane, at 373 K, using the cobalt-rich CoAIPO-18 (Co/P = 0.10) catalyst.

candidates—in view of their pore dimensions and shape—for the designed catalyst. Simple computational estimates,<sup>36</sup> assuming spatially random substitution of  $\text{Al}^{\text{III}}$  by  $\text{Co}^{\text{III}}$  ions, indicate that with Co/P ratios of 0.08 and higher, there is a strong tendency for the two  $\text{Co}^{\text{III}}$  ions to be accommodated in each (chabazitic) cage.

Figure 8 summarizes the results of our selective oxidation experiments, and in particular highlights the contrast in catalytic performance—particularly in regard to production of adipic acid—of low and high Co/P ratios for CoAIPO-18 (i.e., 0.04 and 0.10 respectively). It is gratifying to note, given the essential synonymy of their framework structures, that CoAIPO-18 and CoAIPO-34, each with Co/P ratio of 0.10, exhibit broadly similar performance.

Detailed kinetic studies (Figure 9) are also informative, especially when compared with those reported earlier for CoAIPO-18 with a Co/P ratio of 0.04. With a Co/P ratio of 0.10 for both the CoAIPO-18 and CoAIPO-34 catalysts, 1-hexanol is the major product during the initial stages of the reaction, but this is subsequently converted to 1-hexanal and hexanoic acid. After 5 h, 1,6-hexanediol, 1,6-hexanediol, and traces of adipic acid appear in the reaction mixture as well as the three principal products (1-hexanol, 1-hexanal, and hexanoic acid) observed earlier.





**FIGURE 10.** Comparison of the trend in catalytic performance (turnover number {TON} after 24 h) of Fe-, Mn-, and Co-based AlPO-5 catalysts and fraction of the  $M^{III}$  ions present (estimated from EXAFS) for the oxidation of cyclohexane. Individual product selectivities (in mole %) are also shown. (Note: cHHP = cyclohexyl hydroperoxide.)

It is noteworthy that there is no decrease in hexanoic acid selectivity (Figure 9), but at prolonged contact times (10–24 h) there is a steady decrease in concentrations of both 1,6-hexanediol and 1,6-hexanedial, and a concomitant build-up in the production of adipic acid. Evidently, the production of adipic acid arises as a result of the further oxidation of the 1,6-hexanediol and 1,6-hexanedial. Further, when hexanoic acid was taken as the reactant (instead of *n*-hexane), we did not observe any conversion using CoAlPO-18 (0.10) as the catalyst. With a Co/P ratio of 0.04, the CoAlPO-18 catalyst, under identical conditions, does not produce 1,6-hexanediol or 1,6-hexanedial or any detectable adipic acid.<sup>37</sup> To verify that the above reaction is not affected by the *n*-hexane:cobalt mole ratio, we carried out two further experiments. In the first, we used 0.20 g of CoAlPO-34 (0.10), so that the number of moles of cobalt corresponds to that used in the CoAlPO-18 (0.04) experiment; and, in the second, we used 0.87 g of CoAlPO-18 (0.04), so that the cobalt concentration corresponds to that used in the present study with CoAlPO-34 (0.10). Interestingly, in the case of the former, we still observed 1,6-hexanediol, 1,6-hexanedial, and adipic acid in the reaction mixture (although the conversion was only 5.2% after 24 h), whereas in the case of the latter, we did not observe any of the above-mentioned products.

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.<sup>38</sup> The following experiments<sup>37</sup> have been carried out to rule out the possibility of leaching:

(a) In a typical experiment, the solid catalyst {CoAlPO-18 (0.10)} was filtered off from the reaction mixture (when hot) after 8 h, and the reaction was continued with the resulting filtrate for a further 16 h. No significant change

in *n*-hexane conversion or product selectivity was observed, indicating that the leached-out metal ions (if any) are not responsible for the observed activity and selectivity.

(b) The resulting filtrate (at the end of the reaction, 24 h) was independently analyzed for free or dissolved cobalt ions, and only trace amounts (<3 ppb) were detected.

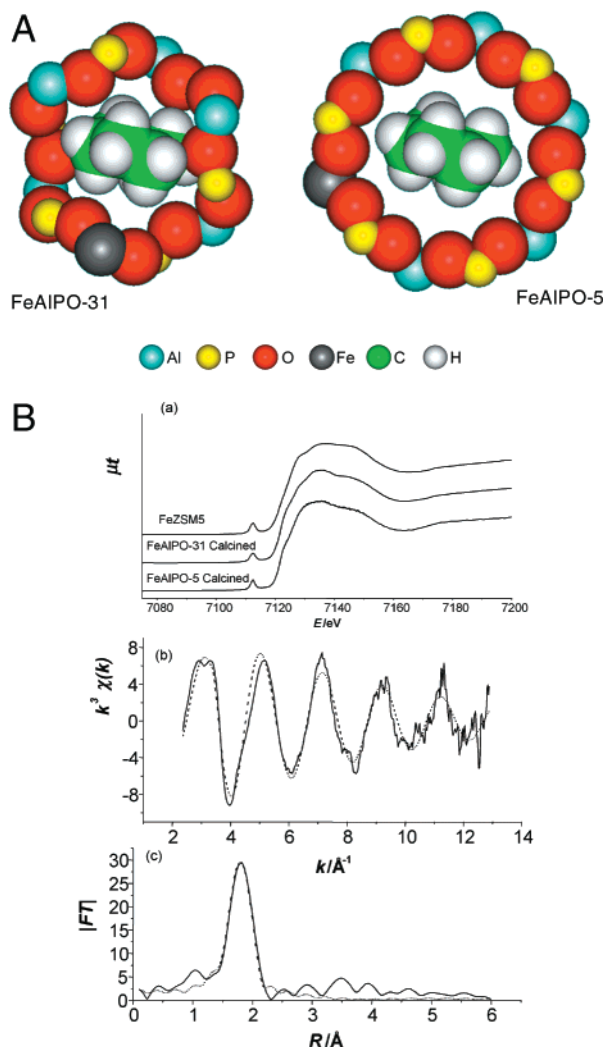
(c) When an equimolar mixture of *n*-hexane and cyclohexane was subjected to a catalytic test over CoAlPO-18 (0.10), there was, unsurprisingly, absolutely no conversion of the cyclohexane molecule, as it is too large to access the active, framework  $Co^{III}$  sites in the AlPO-18 structure, while the conversion of *n*-hexane remained unaffected. If hexanoic acid or adipic acid were leaching out any cobalt from the framework, then the cyclohexane molecule would have been oxidized to cyclohexanol and cyclohexanone. Even upon removal of the template molecule (*N,N*-diisopropyl ethylamine), by gentle calcination in oxygen so as to produce empty cages, the X-ray absorption and diffractometric data, collected by in situ measurements as previously described,<sup>23</sup> leave no doubt about the retention of structural integrity while the oxidation state of  $Co^{II}$  ions in the as-prepared solid increases to  $Co^{III}$ . This behavior mirrors exactly that of CoAlPO-18, which has a Co/P ratio of 0.04.<sup>22</sup>

## V. Shape-Selective Oxidation of Cyclohexane to Cyclohexanol, Cyclohexanone, and Adipic Acid

In designing appropriate molecular-sieve (MAIPO) catalysts for these conversions, it is necessary to optimize the dimensions of the pores (with respect to the size and shape of the reactants and desirable products) and also





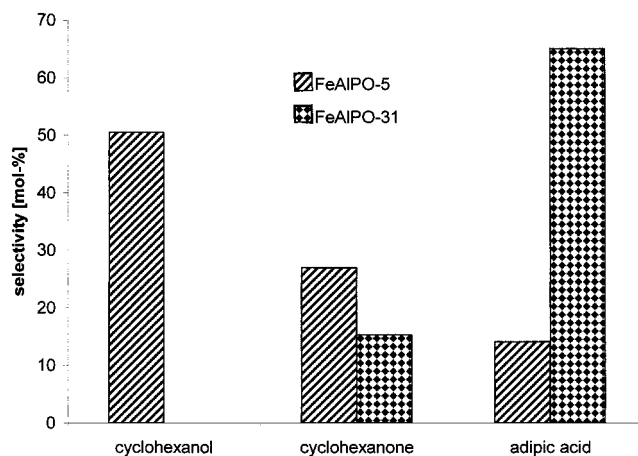


**FIGURE 12.** (A) Representation of the cyclohexane molecule in the differently sized pore openings of FeAlPO-31 (5.4 Å) and FeAlPO-5 (7.3 Å). The more puckered inner walls of the former introduce a constrained environment for the cyclohexane molecule as compared to the latter. (B) XANES spectra of as-synthesized FeZSM-5, calcined FeAlPO-31, and FeAlPO-5 (a). Note the similarities in pre-edge intensities. (b) EXAFS and (c) associated Fourier transform of calcined FeAlPO-31. (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 respectively  $3.85 \pm 0.4$ ,  $1.85 \pm 0.02$ , and  $0.0045 \text{ \AA}$ . The decrease in the Fe–O bond distance from 1.94 to 1.85 Å upon calcination coupled with the similarity of the intense pre-edge feature leaves no doubt that the substituted iron ions are present in the III+ state and in a tetrahedral geometry.

sample were removed to study the kinetics of the reaction, without perturbing the pressure in the reactor.<sup>24,40</sup>

**B. Product Analysis.** The products of the oxidations were analyzed (using a suitable internal standard)<sup>41</sup> by gas chromatography. The acids formed were esterified<sup>24</sup> using  $\text{BF}_3 + \text{CH}_3\text{OH}$  and analyzed as methyl esters. The identity of the products was confirmed by injecting authenticated standard samples and further by LCMS (QP 8000, Shimadzu) and GC/MS (Perkin Elmer).

**C. X-ray Absorption Studies.** Mn and Co K-edge X-ray absorption spectra (XAS) were recorded in situ at Station



**FIGURE 13.** Bar chart comparing the product selectivities (at similar levels of conversion) in the aerial oxidation of cyclohexane, after 24 h, at 373 K, with FeAlPO-31 and FeAlPO-5.

8.1 of the Daresbury Synchrotron radiation source.<sup>24</sup> In addition, time-resolved in situ-combined XRD/XAS data for FeAlPO-5<sup>40</sup> and FeAlPO-31<sup>41</sup> were recorded at Station 9.3, which is also equipped with ion chambers and a fluorescence detector. XRD data were recorded below the Mn K-edge at a wavelength of 1.9375 Å for 180 s during the course of calcining the catalyst in oxygen. XAS data were analyzed using the EXCALIB, EXBROOK, and EXCURV97 suite of programs.

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