

Catalyst design strategies for controlling reactions in microporous and mesoporous molecular-sieves

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Received 23 January 2001; received in revised form 16 April 2001; accepted 22 June 2001

Abstract

Catalytically active transition-metal ions in high oxidation states (Co^{III}, Mn^{III}, Fe^{III}), have been designed on high-area, molecular-sieve, aluminophosphate microporous solids for the aerobic oxyfunctionalisation of a variety of saturated hydrocarbons. Certain metal-substituted molecular-sieves permit only *end-on* approach of linear alkanes to the active centres, thereby favouring enhanced reactivity *either* at one or both of the terminal methyl groups. The size and shape of the pores of the solid molecular-sieve ensure that the oxidations, which proceed by a free-radical mechanism, take place in a highly shape-selective manner in the restricted environment of the catalytically active sites. Anchored bimetallic nanoparticle catalysts display high activity for the low-temperature, selective hydrogenation of cyclic polyenes under solvent-free conditions, and chiral catalysts, derived from 1,1'-bis(diphenylphosphino)ferrocene, and anchored within mesoporous silica, display a remarkable increase in both enantioselectivity and activity, in the hydrogenation of E- α -phenyl cinnamic acid and ethyl nicotinate, when compared to an analogous homogeneous model compound. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bimetallic nanoparticles; Enantioselective hydrogenations; Molecular-sieve catalysts; Regioselective oxidation; Shape-selective oxidation

1. Introduction

Controlled partial oxidation of hydrocarbons using either dioxygen or air under rather mild conditions is of considerable interest, in that they offer attractive alternatives to the use of environmentally less acceptable oxidants, many of which function stoichiometrically rather than catalytically. Devising inorganic catalysts for the shape-selective and regiospecific oxidation of saturated hydrocarbons, with an efficiency that rivals that of natural enzymes such as cytochrome-P-450

and non-heme iron ω -hydroxylase, has proven to be extraordinarily difficult. Yet trying to do so is of considerable merit since such partial oxidation would generate a source of important feedstocks for the fine chemicals, polymer and pharmaceutical industries [1]. For example, the selective oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone (the so-called K–A oil) under mild conditions is of considerable importance in the manufacture of nylon-6 and nylon-6-6, and the regiospecific oxidation of linear paraffins generates functionalised derivatives for the production of surfactants and detergents [2,3].

Our approach to the design of effective oxidation catalysts takes advantage of two facts. First, that certain transition-metal ions, notably Co^{II} or Mn^{II},

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when they occupy a small percentage of the framework (tetrahedral) sites in a molecular-sieve, may be raised to a higher oxidation [4,5] state $\{\text{Co}^{\text{III}}$ or $\text{Mn}^{\text{III}}\}$ whilst still remaining intact in the framework, and where they can function in air as active sites in the catalytic oxidation of cyclohexane and other linear alkanes. Second, that if the appropriate molecular-sieve is chosen, only end-on entry of the linear alkanes into the cavities that contain the active sites is possible. This steric constraint predisposes the oxyfunctionalisation to be favoured at the terminal CH_3 and penultimate CH_2 groups [6].

The key features of the high-area microporous and mesoporous catalysts that we have designed are the following.

- A single-site active centre may be introduced into a well-defined chemical environment either during (especially in microporous hosts that contain within them adroitly placed potentially active centres) or after preparation of the porous material.
- The precise atomic architecture of the active centre may be determined, often under in situ conditions, prior to and during the course of the chemical transformation.
- Delicate changes to the local structure of the active centre may be effected and monitored so as to shed light on the mechanistic features, a task nowadays greatly aided by involving reliable computational procedures either of the atomistic or electronic kind [7–9].
- Permit free ingress of reactant and egress of product species that have cross-sections smaller than the diameter of the pores.
- Offer greater scope (especially in mesoporous solids) for the grafting of organometallic moieties on to the inner surfaces of the pores. This opens ready routes for the heterogenisation of homogeneous catalysts, thus capitalising on the advantages of high activity and single-site active centres of the homogeneous category, and the robustness and ease of separation that is a feature of heterogeneous catalysts.
- Open up many new strategies for shape-selective, enantioselective and regioselective conversions.

Although the main thrust of our work is to arrive at new solid inorganic catalysts by engineering appropriate active centres through the principles of solid-state

and surface chemistry, we also aim to produce those catalysts that are important in the context of clean technology. For the research chemist, the intellectual challenge is to devise a strategy for such environmentally desirable objectives as one-step processes and/or solvent-free chemical conversions [10], with air or dioxygen as the oxidant.

2. Experimental

2.1. Catalytic reactions

The oxidation and hydrogenation reactions were carried out in a high-pressure stainless steel catalytic reactor (150 ml) lined with poly ether ether ketone (PEEK). Dry air (or hydrogen) was pressurised into the reaction vessel and, using a mini robot liquid sampling valve, small aliquots of the sample were removed to study the kinetics of the reaction, without perturbing the pressure in the reactor [6].

2.2. Product analysis

The products of the oxidations were analysed (using a suitable internal standard) by gas chromatography. The acids formed were esterified [6] using $\text{BF}_3 + \text{CH}_3\text{OH}$ and analysed as methyl esters. The identity of the products was confirmed by injecting authenticated standard samples and further by LC/MS (Shimadzu QP 8000) and GC/MS (Perkin-Elmer).

3. Results and discussion

3.1. Aerobic oxidation of cyclohexane to adipic acid

Three distinct kinds of MeAlPO molecular-sieve catalysts have been designed for the oxidation of cyclohexane: $\text{Co}^{\text{III}}(\text{Mn}^{\text{III}})\text{AlPO-36}$ [11], $\text{Fe}^{\text{III}}(\text{Co}^{\text{III}}, \text{Mn}^{\text{III}})\text{AlPO-5}$ [12], and $\text{Fe}^{\text{III}}\text{AlPO-31}$ [13]. We find that FeAlPO-5 is an exceptionally good catalyst for the selective oxidation of cyclohexane in air, the principal products being cyclohexanol, cyclohexanone and adipic acid. In line with earlier observations [6], the oxidation of cyclohexane proceeds by a free-radical mechanism. The results obtained with FeAlPO-5 are vastly superior to those obtained with

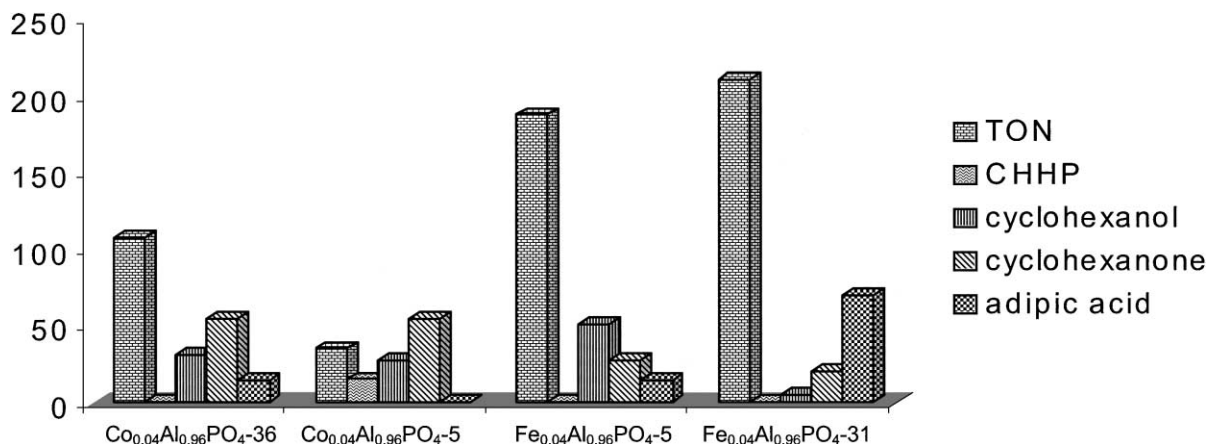


Fig. 1. Comparison of catalytic activity (TON) for the oxidation of cyclohexane, after 24 h, at 403 K, using $\text{Co}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$, $\text{Co}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-5}$, $\text{Fe}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-5}$ and $\text{Fe}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-31}$ as catalysts. Individual product distributions are also shown. Reaction conditions: cyclohexane \cong 50 g; mesitylene (internal standard) \cong 2.5 g; catalyst = 0.5 g; pressure (air) = 1.5 MPa; $T = 403$ K; $t = 24$ h; CHHP: cyclohexyl hydroperoxide; TON: moles of substrate converted per mole of metal (Co, Mn or Fe) in the catalyst.

the cobalt-substituted analogue (Fig. 1). EXAFS measurements indicate that, in CoAlPO-5 about 25% of the Co^{II} sites in the framework can be oxidised to the Co^{III} state; while in CoAlPO-36 , some 50% of the Co^{II} may be raised to a higher oxidation state by calcining in air. In FeAlPO-5 , however (pore aperture $7.3 \text{ \AA} \times 7.3 \text{ \AA}$) all the iron ions are found to be in the Fe^{III} state, in marked contrast to the above. Indeed this active site (Fe^{III} in the framework) has an immediate environment almost indistinguishable from that of Fe^{III} in FeZSM-5 in which again the Fe^{III} resides in the framework [14].

Hence we argued that if the selectivity for adipic acid was to be increased in this reaction, it was necessary to design a MeAlPO molecular-sieve catalyst in which the active sites (Fe^{III}) are the same, but the pores are significantly smaller than those of MeAlPO-5 . The framework structure of the microporous catalyst that we have prepared is the one-dimensional AlPO-31 . In view of the more puckered inner walls, compared with those of AlPO-5 , there is a smaller diameter (5.4 \AA), which introduces the kind of constrained environment that is necessary to favour production of AA. In effect, we see to take advantage of shape-selective catalysis using a carefully designed microporous solid; and product shape selectivity will apply so that only those (desired) products, with appropriate molecular dimensions, will diffuse easily out of the

pores. Larger ones (such as cyclohexanol and cyclohexanone formed from cyclohexyl hydroperoxide) formed in the course of the reaction will remain trapped inside, their diffusion outwards being retarded. There was no decrease in activity when the FeAlPO-31 catalyst was re-used, at least twice, after washing thoroughly with methanol and calcined in air at 550°C . Furthermore, XRD patterns showed the presence of microporous structure in these re-cycled catalysts and the average Fe–O distance obtained from the EXAFS data of the re-calcined catalyst is consistent with the fresh catalyst. Thus the present study clearly points out that framework substituted transition-metal ions are responsible for catalytic activity and there is a direct correlation with the amount of oxidisable metal ion, which was evaluated based on the in situ X-ray absorption spectroscopic study.

3.2. Aerial oxidation of *n*-hexane to adipic acid

Based on our successes in oxyfunctionalising only the terminal regions of linear alkanes by aerial oxidation over CoAlPO-18 and MnAlPO-18 microporous catalysts [6,15], we argued that significantly larger numbers of higher-valent (e.g. Co^{III}) framework ions need to be accommodated on the inner walls of a microporous catalyst if oxidative attack is to occur at both ends of *n*-hexane.

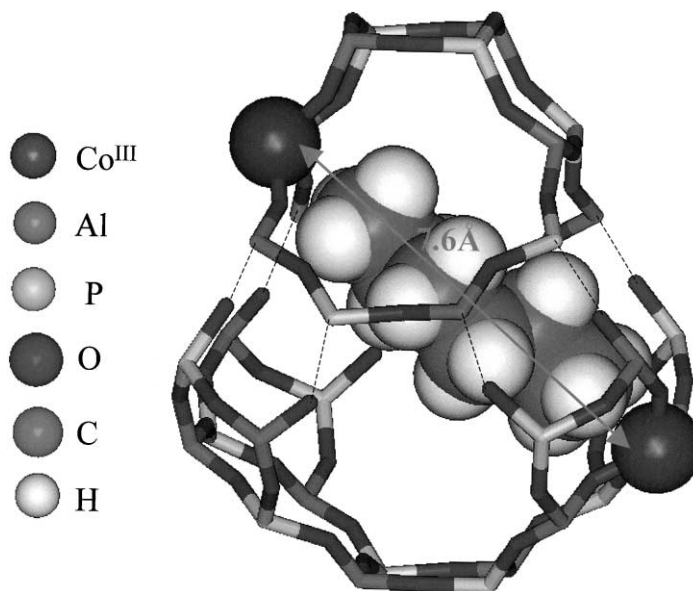


Fig. 2. Expanded view of the chabazite cage showing the energy-minimised configuration of the *n*-hexane molecule and the two separated Co^{III} ions in each cage of the AlPO-18 structure. The estimated separation distance between the van der Waals limits of these two framework ions is ca. 7.6 Å.

With the composition $\text{Co}_{0.1}\text{Al}_{0.9}\text{PO}_4$ for the CoAlPO-18 structure (i.e. with a Co/P ratio of 0.1, instead of 0.04, as above) there is a high probability for these to be two (separated) Co^{III} ions in each cage of the AlPO-18 structure, and these two ions are likely to be situated opposite one another as shown in Fig. 2. In other words, there ought to be two framework Co^{III} ions separated by ca. 7–8 Å from one another. Assuming spatially random substitution of Al^{III} by Co^{III} ions, computational estimates show that, above Co/P ratios of 0.08, there is a strong tendency for the two Co^{III} ions to be accommodated in each (chabazitic) cage of the AlPO-18 structure.

Fig. 3 summarises the results of our selective oxidation experiments, and in particular highlights the contrast in catalytic performance in regard to the production of adipic acid of low and high Co/P ratios for CoAlPO-18. It is not surprising that CoAlPO-34, with a Co/P ratio of 0.10 yields results very comparable to that of CoAlPO-18 [16] with the same Co/P ratio: their cage structures are essentially the same. But CoAlPO-36, which has a much larger pore aperture (6.5 Å × 7.5 Å), is markedly different from both CoAlPO-18 and CoAlPO-34.

Detailed kinetic studies [16] show that (with Co/P ratios of ca. 0.10) the major products during the initial stages of the reaction is 1-hexanol, but this is subsequently converted to 1-hexanal and hexanoic acid. After 5 h, 1,6-hexanediol and 1,6-hexanedial as well as traces of adipic acid appear in addition to the principal products observed earlier. It is also noteworthy that there is no decrease in the hexanoic acid selectivity, but at prolonged contact times (10–24 h) there is a steady decrease in the concentration 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. This active adipic acid-producing CoAlPO-18 catalyst, with a Co/P ratio of 0.10, is remarkably stable and there is no leaching of the cobalt ions during catalysis. It augurs well for our catalysts that such a demanding reaction may be effected with air or oxygen as oxidants.

3.3. Aerobic oxidation of *p*-xylene

Textile and synthetic fibres such as saturated polyesters (terylene) are made from terephthalic acid,

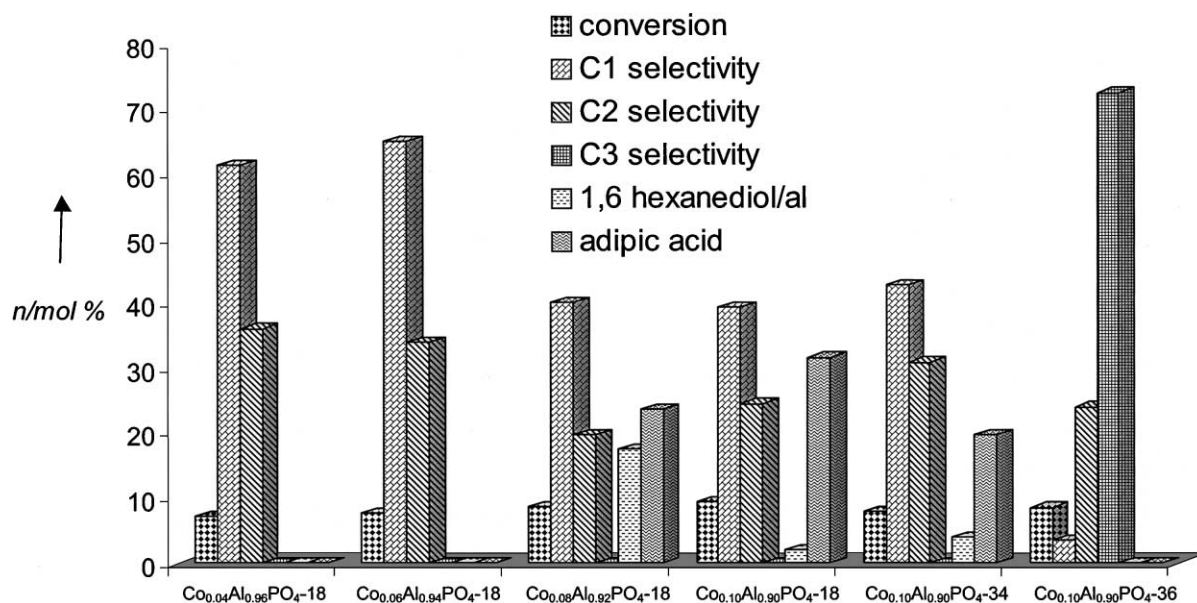


Fig. 3. Bar chart illustrating the efficacy of the cobalt-rich $\text{Co}_{0.1}\text{Al}_{0.9}\text{PO}_4\text{-18}$ and $\text{Co}_{0.1}\text{Al}_{0.9}\text{PO}_4\text{-34}$ catalysts for the conversion of *n*-hexane to adipic acid. Note that $\text{Co}_{0.1}\text{Al}_{0.9}\text{PO}_4\text{-36}$, under identical reaction conditions, does not produce any adipic acid. Reaction conditions: *n*-hexane \cong 50 g; catalyst = 0.51 g; oxidant (air) = 1.5 MPa; $T = 373$ K; $t = 24$ h; C₁ products, 1-hexanol, 1-hexanal, hexanoic acid; C₂ products, 2-hexanol, 2-hexanone; C₃ products, 3-hexanol, 3-hexanone.

which is currently produced commercially by the oxidation of *p*-xylene using aggressive reagents such as bromine, and acetic acid as solvent. Various homogeneous salts of cobalt and manganese can be used as catalysts and the bromine source is usually HBr, NaBr or tetrabromoethane. The highly corrosive bromine-acetic acid environment requires the use of titanium-lined equipment [17].

Our approach to the design of suitable catalysts for this important reaction again relies on the use of a microporous, molecular-sieve, in which the active sites are Co^{III} or Fe^{III} ions in framework sites substituting for Al^{III} ions. These catalysts operate under solvent-free conditions, requiring only benign oxidants (dioxygen or air), without the need for corrosive activators and solvents such as bromine or acetic acid. Our molecular-sieve catalysts are effective for the aerobic oxidation of *p*-xylene, the main products being toluic acid, 4-formylbenzoic acid (4-carboxybenzaldehyde) and terephthalic acid, leaving the benzene ring virtually untouched. 4-formylbenzoic acid is a troublesome impurity and because of its structural similarity to terephthalic acid,

it co-crystallises with the latter, and becomes trapped and inaccessible for completion of the oxidation. We find that AlPO-36-based catalysts, containing up to 10 at.% of transition-metal ions (Co^{III} , Mn^{III} , Fe^{III} , etc.), suppress the formation of 4-formylbenzoic acid and increase the selectivity for terephthalic acid. As in the case of Co^{III} AlPO-18, containing ca. 10 at.% of Co^{III} ions in the framework, one might envisage oxyfunctionalisation occurring simultaneously at both methyl ends of *p*-xylene, which could well be the reason for the higher selectivity of the Co^{III} AlPO-36 (0.10) catalyst for terephthalic acid (see Fig. 4), compared to Co^{III} AlPO-36 (0.04).

3.4. Bifunctional catalysts: ϵ -caprolactam from cyclohexanone

The reaction of cyclohexanone with hydroxylamine (in its sulphate or phosphate form) is the best known method for the production of cyclohexanone-oxime, and its subsequent Beckmann rearrangement to ϵ -caprolactam is an important industrially used reaction. About 90% of ϵ -caprolactam world-wide is

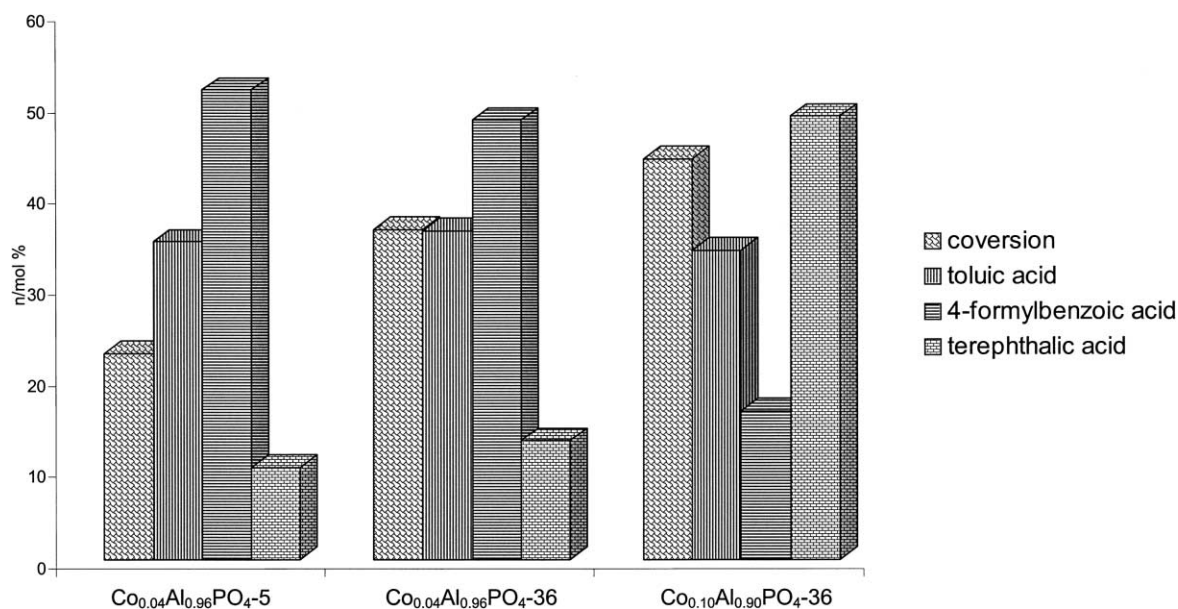


Fig. 4. Co_{0.10}Al_{0.90}PO₄-36 is a good catalyst for the aerobic oxidation of *p*-xylene to terephthalic acid. Reaction conditions: *p*-xylene \cong 50 g; mesitylene (internal standard) \cong 2.5 g; catalyst = 0.75 g; pressure (air) = 2.5 MPa; $T = 373$ K; $t = 24$ h.

produced by using the above-mentioned conventional cyclohexanone process. However, large-scale industrial processes for the production of ϵ -caprolactam (monomer for nylon-6), employing cyclohexanone as the starting material, invariably produce large quantities of ammonium sulphate as by-products, which are undesirable.

Fig. 5 summarises the results of our ammoximation experiments using, cyclohexanone in the presence of ammonia and air (H₂O₂ or *tert*-butyl-hydroperoxide (TBHP) can also be used as oxidants), and MnAlPO-5 or Mn(Co)AlPO-36 as catalysts, to produce the corresponding cyclohexanone-oxime and ϵ -caprolactam. The ketone (cyclohexanone) is first oxidised in the presence of the 'redox' (Co^{III}, Mn^{III}) ions and ammonia to the oxime (cyclohexanone-oxime). The Brønsted acid sites in the molecular-sieves catalyse the subsequent Beckmann rearrangement of cyclohexanone-oxime to ϵ -caprolactam. Interestingly, the (deliberate) introduction of acid centres (in the form of Mg^{II} or Zn^{II}, during synthesis, and typified by CoMAPO-36 in Fig. 5) further enhanced the selectivity for ϵ -caprolactam, thereby bringing out the bifunctional ability possessed by our catalysts.

3.5. Baeyer–villiger oxidation of alkenes and ketones

Here we describe two related heterogeneous catalysts that efficiently convert cyclic ketones to lactones or epoxidise alkenes using molecular oxygen and a sacrificial aldehyde, under conditions that mirror those of Yamada et al. [18], who used homogeneous (transition-metal-based) catalysts. These conditions are of considerable interest in that they offer attractive alternatives to the use of environmentally less acceptable oxidants (many of which function stoichiometrically rather than catalytically) such as CrO₃, KMnO₄, Pb(OAc)₄, RuO₄ and Ag₂O.

The catalysts we have used are CoAlPO-36, MnAlPO-36, CoAlPO-5, MnAlPO-5, CoALPO-18 and MnALPO-18 (Table 1). The structure of aluminium phosphate No. 36 (ATS) has well-defined, oval-shaped channels, which, by appropriate preparative means, may be lined with a substantial number of either cobalt or manganese ions framework-substituted in place of Al^{III} ions. Similarly, two other types of materials, AlPO-5 (AFI) and AlPO-18 (AEI) with pore dimensions of 7.3 and 3.8 Å, respectively, were

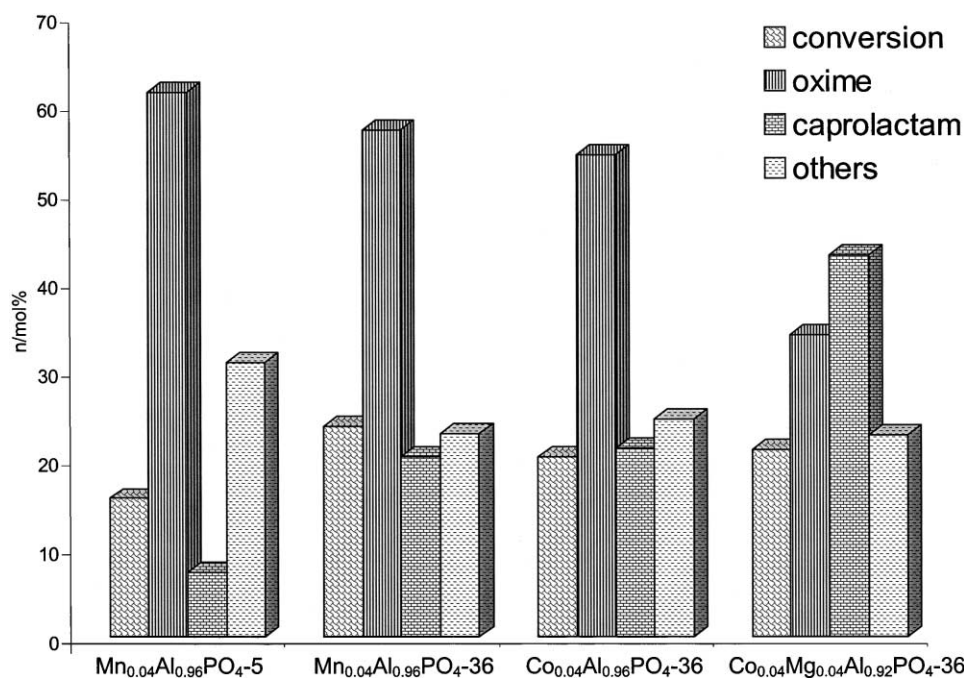


Fig. 5. The relative performances of various AIPO-catalysts in the conversion of cyclohexanone to its corresponding oxime and ϵ -caprolactam using air as oxidant. Introduction of Brønsted acid active sites ($\text{Co}_{0.04}\text{Mg}_{0.04}\text{Al}_{0.92}\text{PO}_4\text{-36}$) increases the selectivity for ϵ -caprolactam. Reaction conditions: cyclohexanone: $\text{NH}_3 \equiv 1:3$ mol; catalyst $\equiv 0.5$ g; air $\equiv 3.5$ MPa; $T \equiv 328$ K; cyclohexanone $\cong 50$ g; mesitylene (internal standard) $\equiv 2.5$ g; $t = 20$ h; oxime \equiv cyclohexanone-oxime.

Table 1
Baeyer–villiger oxidation of alkenes and ketones^a

Substrate	Catalyst	t (h)	Conversion (mol%)	TOF (h^{-1})	Product selectivity (mol%)		
					Lactone	Epoxide	Diol
Cyclohexanone	$\text{Co}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$	6	71	250	98	–	–
Cyclohexanone	$\text{Mn}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$	6	78	257	98	–	–
Cyclohexanone	$\text{Mn}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-5}$	6	64	207	82	–	–
2-Adamantanone	$\text{Co}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$	5	80	220	99	–	–
2-Adamantanone	$\text{Mn}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$	5	87	224	99	–	–
Cyclohexene	$\text{Co}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$	8	54	184	–	69	27
Cyclohexene	$\text{Mn}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$	8	62	203	–	77	19
Cyclohexene	$\text{Mn}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-5}$	8	44	136	–	77	13
α -(+)-Pinene	$\text{Co}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$	8	54	111	–	84	–
α -(+)-Pinene	$\text{Mn}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-36}$	8	59	127	–	91	–
α -(+)-Pinene	$\text{Mn}_{0.04}\text{Al}_{0.96}\text{PO}_4\text{-5}$	8	42	78	–	66	–

^a Reaction conditions: substrate (ketone) $\cong 20$ g; substrate (alkene) $\cong 35$ g; catalyst $\cong 0.25$ g; substrate benzaldehyde = 1:3 mol; O_2 (air) = 30 bar; $T = 323$ K; mesitylene (internal standard) = 2.5 g; TOF: turnover frequency, moles of ketone converted, per hour, per mole of cobalt (or manganese) in the catalyst.

synthesised with specific metal ions having identical concentrations.

Benzaldehyde molecules may freely enter the large internal surfaces of these catalysts, and in the presence of O_2 , generate first $PhCO^\bullet$ and then the $PhCOO^\bullet$ radicals inside the micropores. This peroxy acid is then involved in a nucleophilic attack at the substrate, leading to the production of epoxides and lactones [19]. In addition, there appears to be a clear trend in the catalytic activity and on the combination of the type of molecular-sieve and the cations; the ATS structure shows higher conversion and selectivity compared to AFL, and manganese containing solids are slightly more active than the cobalt ones.

3.6. Encapsulated bimetallic nanocatalysts for solvent-free reactions

The chemical conversions upon which we here focus consist of the hydrogenation of 1-hexene, 1-dodecene, naphthalene and cyclic polyenes: 1,5,9-cyclododecatriene, 1,5-cyclooctadiene and 2,5-norbornadiene. The monoenes of all three polyenes are used extensively as intermediates in the synthesis of dicarboxylic aliphatic acids, ketones, cyclic alcohols, lactones, and other intermediates. The selective hydrogenation of 1,5,9-cyclododecatriene to cyclododecane and cyclododecene is industrially important in the synthesis of valuable organic and polymer intermediates such as 12-lauro lactam and

dodecanedioic acid, which are important monomers for nylon-12, nylon-612, copolyamides, polyesters and coating applications.

The catalytic performance of the Pd_6Ru_6 [20], Cu_4Ru_{12} [21] and Ru_6Sn [22] clusters (Fig. 6) in alkene and cyclic polyene hydrogenation is given in Table 2. Kinetic studies of 1-hexene at 20 bar (H_2) and $373^\circ C$ using the Cu_4Ru_{12} catalyst, shows an induction time of 60 min and an overall turnover frequency of $25,700 \text{ mol}[\text{hex}]\text{mol}[\text{Cu}_4\text{Ru}_{12}]^{-1} \text{ h}^{-1}$. The induction period may arise due to several factors, for example, in situ activation of the catalyst particles by further reduction in hydrogen, diffusion of hydrogen into the mesoporous structure, diffusion-induced lag of product emerging from the mesopores or effusion of $PPNCl$. The kinetics also reveal that the Pd_6Ru_6 catalysts showed a higher selectivity for *n*-hexane (or *n*-dodecane) than Cu_4Ru_{12} . It is also noteworthy that the Pd_6Ru_6 catalyst is more active than Cu_4Ru_{12} for the hydrogenation of 1-hexene (≈ 2 times) and 1-dodecene (≈ 2.5 times). For comparison, monometallic Ru_6 and Pd clusters were encapsulated in mesoporous silica, and both were tested for the hydrogenation of 1-hexene employing the same reaction conditions. It is clear from Table 2 that the bimetallic catalysts are far superior in performance than their monometallic analogues and more importantly yield a higher selectivity for hydrogenated products, suggesting a possible synergism between the two bimetallic nanoparticles. Surveys by electron-stimulated energy

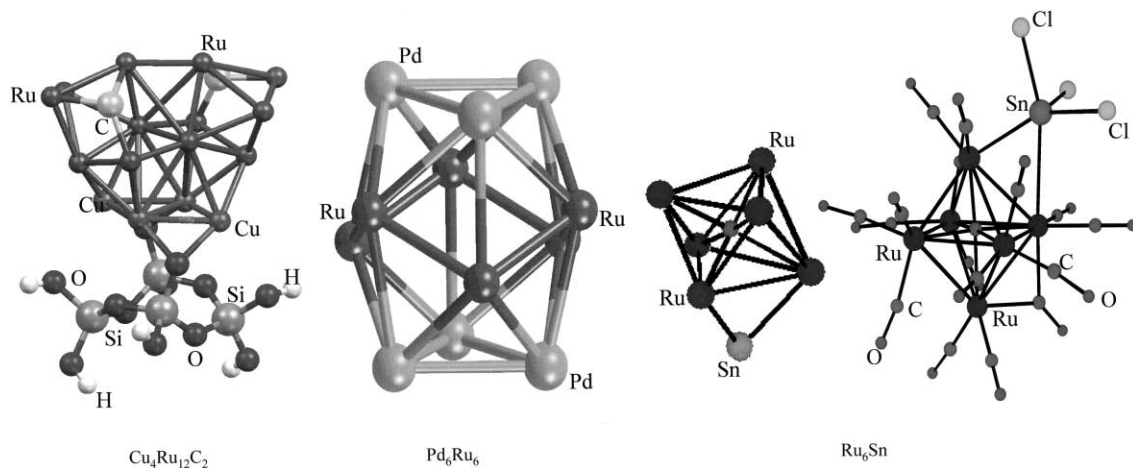


Fig. 6. Schematic diagrams of the Cu_4Ru_{12} , Pd_6Ru_6 and Ru_6Sn clusters.

Table 2
Hydrogenation of olefins and cyclic polyenes: comparison of catalysts^a

Catalyst	Substrate	<i>t</i> (h)	<i>T</i> (K)	Conversion (mol%)	TOF (h ⁻¹)	Product distribution (mol%)		
						A	B	C
Pd ₆ Ru ₆ /MCM-41	1-Hexene	4	373	99	4954	68	22	9
Cu ₄ Ru ₁₂ /MCM-41	1-Hexene	4	373	56	2805	51	30	19
Ru ₆ /MCM-41	1-Hexene	4	373	13	115	14	42	45
Pd/MCM-41	1-Hexene	4	373	6	24	6	45	48
No catalyst	1-Hexene	24	373	7	–	–	32	67
Pd ₆ Ru ₆ /MCM-41	1-Dodecene	4	373	88	2202	63	29	7
Cu ₄ Ru ₁₂ /MCM-41	1-Dodecene	4	373	35	877	54	32	13
Pd ₆ Ru ₆ /MCM-41	Naphthalene	8	373	19	50	86	4	9
Cu ₄ Ru ₁₂ /MCM-41	Naphthalene	8	373	–	–	–	–	–
Ru ₆ Sn/MCM-41	1,5-Cyclooctadiene	8	353	11.7	1980	100	–	–
Cu ₄ Ru ₁₂ /MCM-41	1,5-Cyclooctadiene	8	353	11.5	690	70.4	29.2	–
Ag ₄ Ru ₁₂ /MCM-41	1,5-Cyclooctadiene	8	353	9.0	465	57.3	42.5	–
Pd ₆ Ru ₆ /MCM-41	1,5-Cyclooctadiene	8	353	36.9	2012	15.7	84.5	–
Ru ₆ /MCM-41	1,5-Cyclooctadiene	24	353	2.5	141	–	36.2	–
Pd/MCM-41	1,5-Cyclooctadiene	24	353	7.3	212	–	100	–
Ru ₆ Sn/MCM-41	1,5,9-Cyclododecatriene	8	373	17.2	1940	17.2	82.4	–
Pd ₆ Ru ₆ /MCM-41	1,5,9-Cyclododecatriene	8	373	64.9	5350	–	11.7	88.5
Ru ₆ Sn/MCM-41	2,5-Norbornadiene	8	333	51.4	10210	88.6	11.3	–
Pd ₆ Ru ₆ /MCM-41	2,5-Norbornadiene	8	333	76.4	11176	24.7	75.1	–

^a Reaction conditions: substrate ≈ 50 g; catalyst = 25 mg; H₂ (pressure) = 30 bar; products: for 1-hexene, A = *n*-hexane; B = *cis*-2-hexene; C = *trans*-2-hexene; for 1-dodecene, A = *n*-dodecane; B = *cis*-2-dodecene; C = *trans*-2-dodecene; for naphthalene, A = *cis*-decalin; B = *trans*-decalin; C = others; for 1,5-cyclooctadiene, A = cyclooctene; B = cyclooctane; for 1,5,9-cyclododecatriene, A = 1,9-cyclododecadiene; B = cyclododecene; C = cyclododecane; for 2,5-norbornadiene, A = norbornene; B = norbornane; TOF = [(mol_{substr})(mol_{cluster})⁻¹ h⁻¹].

dispersive X-ray emission of the Pd–Ru nanocatalyst particles after their use in four consecutive test runs showed that there was no segregation of the two components of the bimetallic catalyst. Moreover, annular dark field (*Z*-contrast) high-resolution microscopy showed that there was no evidence of coalescence or sintering of the nanoparticles during catalytic use.

The marked dependence of temperature upon selectivity in the catalytic hydrogenation of 1,5,9-cyclododecatriene is shown in Fig. 7, from which we note that, even as low as 80 °C, this solvent-free, hydrogenation to cyclododecene is 70% selective and well in excess of 90% at 100 °C. This particular selective hydrogenation falls off in efficiency with further increase in temperature, and conversion to the fully hydrogenated cyclododecane is progressively favoured. It is noteworthy that conversion to the cyclododecadiene on the other hand is favoured at the lowest test temperature (80 °C). By contrast, the Pd₆Ru₆ catalyst, displays

very little selectivity for the 1,5-cyclododecadiene or cyclododecene, even at temperatures as low as 40 °C. By comparison with three other bimetallic catalysts (Cu₄Ru₁₂, Ag₄Ru₁₂ and Pd₆Ru₆), we note that the Ru₆Sn bimetallic catalyst displays the best performance, so far as selective hydrogenation of one of the two double bonds in the hydrogenation of 1,5-cyclooctadiene is concerned (Table 2).

Both the Ru₆Sn and Pd₆Ru₆ anchored bimetallic nanoparticle catalysts have been re-used six to seven times for the hydrogenation of 1,5-cyclooctadiene and 1,5,9-cyclododecatriene, without appreciable loss in catalytic activity or selectivity. Further scope for fine-tuning both the conversion and selectivity is obtained by varying the contact times, for a range of polyenes (Table 2). It is particularly interesting that, in the case of 2,5-norbornadiene, the conditions (and catalyst) may be so chosen as to produce a high yield of either norbornene or norbornane. Considerable scope

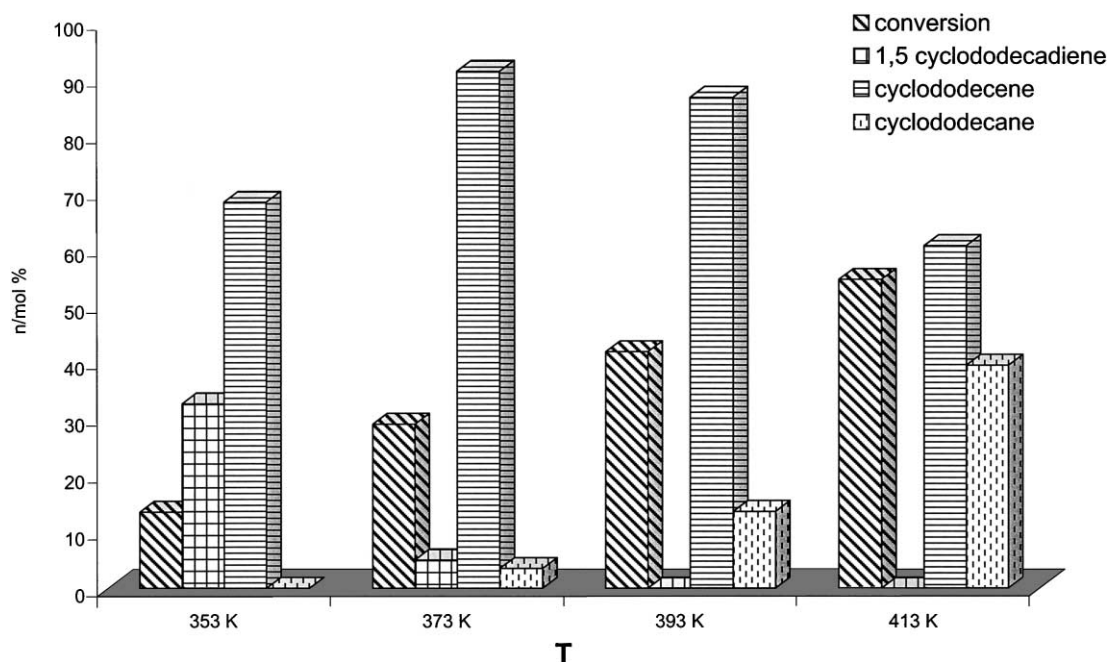


Fig. 7. The effect of temperature on the selectivity in the hydrogenation of 1,5,9-cyclododecatriene using the Ru_6Sn catalyst. Reaction conditions: 1,5,9-cyclododecatriene \approx 50 g; catalyst = 25 mg; H_2 (pressure) = 30 bar; t = 24 h.

clearly exists, using the principles that we have outlined here, and previously, to develop other, solvent-free systems for the selective conversion of organic compounds.

3.7. Enantioselective hydrogenations using constrained chiral catalysts

It is acknowledged that, in view of their biological activity, the enantioselective synthesis of chiral saturated ring systems involving piperidine or cyclohexane is of considerable practical interest. Previously, efforts to hydrogenate enantioselectively an aromatic ring such as that in ethyl nicotinate have resulted in values of enantiomeric excess (e.e.) that are less than 6% [23]. However, very recently, a two-step process, involving initial hydrogenation in high yield to the comparatively stable 1,4,5,6-tetrahydronicotinate, followed by subsequent hydrogenation in the presence of a dihydrocinchonidine modified noble metal catalyst, yielded quite high e.e. of the nipecotinate [24].

Our approach in the synthesis of the heterogeneous catalyst was to design a homogeneous,

metal-containing ferrocenyl precursor, which possessed a functionality capable of reacting directly with a silica surface. This precursor could be characterised in detail using solution spectroscopic techniques, and then anchored to the surface of the mesoporous silica support in a one-step reaction. The synthetic strategy involved the reaction between (*S*)-1-[(*R*)-1,2'-bis(diphenylphosphino)-ferrocenyl]-ethylacetate and 3(methylamino)propyltrimethoxysilane to form a silane functionalised ferrocenyl ligand, the incorporation of palladium dichloride to which forms the target ferrocenyl precursor. The ferrocenyl precursor was then reacted with the mesoporous silane MCM-41, the outer walls of which were previously deactivated via treatment with $[\text{Ph}_2\text{SiCl}_2]$, a method which we have already shown to be applicable in this situation. The anchored catalyst was characterised using ^{13}C and ^{31}P MAS NMR spectroscopy [25].

The two catalysts were tested in the one-step hydrogenation of ethyl nicotinate and *E*- α -phenyl cinnamic acid (Table 3). The catalysis was performed under mild conditions (20 bar H_2 , 40 °C) and in both cases proceeded with the formation of the desired products.

Table 3

Enantioselective hydrogenation of E- α -phenyl cinnamic acid and ethyl nicotinate^a

Dppf-ferrocenyl-diamine-Pd-catalyst	Substrate	T (h)	Conversion (mol%)	Product distribution (mol%)		e.e. (%)
				A	B	
Homogeneous	E- α -phenyl cinnamic acid	48	23.6	83.5	16.8	–
		72	38.3	76.2	23.1	–
Tethered-silica	E- α -phenyl cinnamic acid	48	19.8	44.1	55.3	36.1
		72	26.0	38.4	62.0	27.2
MCM-41-confined	E- α -phenyl cinnamic acid	48	62.0	100	–	90.7
		72	90.5	100	–	96.5
Homogeneous	Ethyl nicotinate	72	15.9	27.3	72.5	–
		120	27.2	4.8	95	–
Tethered-silica	Ethyl nicotinate	72	12.6	16.9	83	2
		120	19.2	–	100	2
MCM-41-confined	Ethyl nicotinate	48	35.5	5.2	94.5	17
		72	53.7	–	100	20

^a Substrate = 5 g; catalyst = 250 mg; H₂ (pressure) = 20 bar; solvent \equiv methanol; THF = 1:9; T = 40 °C; products: for E- α -phenyl cinnamic acid, A = 1,2-diphenyl propionic acid; B = 2,2/3,3-diphenyl propionic acid; for ethyl nicotinate, A = 1,4,5,6-tetrahydro nicotinate; B = ethyl nipecotinate.

However, analysis of the products revealed that the MCM-41 anchored species catalysed the reaction with a higher e.e., whilst the use of the homogeneous silsesquioxane complex resulted in a racemic product. This remarkable change in stereo-selectivity demonstrates the profound importance of confinement in the catalysis. These results show the considerable potential that this type of catalyst offers, and how, by careful design of an active centre, a heterogeneous catalyst may be engineered, the performance of which is far superior to its free, homogeneous analogue.

Acknowledgements

We thank EPSRC (for a rolling Grant to J.M.T.), The Commissioners of the Royal Commission of 1851 for an Exhibition (to R.R.), and our colleagues, especially Prof. B.F.G. Johnson, Drs. Sankar, Bell, Hermans, and Raynor for their valuable stimuli.

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