

# New catalysts for the aerobic selective oxidation of hydrocarbons: Mn(III)- and Co(III)-containing molecular sieves for the epoxidation of alkenes

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Co(III) or Mn(III) ions that replace some 4 atom% of Al(III) sites in microporous aluminophosphate number 36 (AIPO-36) function as catalytically active centres for the production from benzaldehyde of acylperoxy radicals: these, in turn, in dry air (30 bar) convert cyclohexene, pinene, limonene and styrene to their corresponding epoxides and diols.

Replacing stoichiometric oxidants such as  $\text{KMnO}_4$ ,  $\text{Ag}_2\text{O}$  and  $\text{CrO}_3$  by less environmentally damaging ones is self-evidently a sensible chemical strategy. Doing so catalytically, with alkylhydroperoxides or hydrogen peroxide as the oxidants, is an even better one: but best of all would be to develop<sup>1</sup> catalysts that selectively oxidise hydrocarbons using either dioxygen or air under mild conditions. In this communication we describe two related heterogeneous catalysts that efficiently epoxidise alkenes using molecular oxygen and sacrificial aldehydes, under conditions that mirror those of Mukaiyama *et al.*,<sup>2</sup> who used homogeneous (transition-metal-based) catalysts.

By extending our earlier work on the design of redox molecular sieve catalysts for the aerobic terminal oxidation of linear alkanes,<sup>3</sup> for the selective oxidation of cyclohexane<sup>4</sup> (to cyclohexanone and cyclohexanol) and for the Baeyer–Villiger oxidation of ketones to lactones,<sup>5</sup> we have achieved good conversions and selectivities for the epoxidation of cyclohexene and other alkenes using framework-substituted metal ions (M) in microporous aluminium phosphate, MAIPO-36 (M = Mn or Co), catalysts.

Details of the synthesis (and structure) of the Mn(II)- and Co(II)-containing AIPO-36 molecular sieves have been reported previously.<sup>4,6</sup> Briefly, the Mn(II) (or Co(II)) ion is introduced to the template-containing precursor gel from which small crystals of phase-pure product appear. Upon calcination in  $\text{O}_2$  at ca. 550 °C, the organic template (tripropylamine) is entirely gasified, leaving the oval-shaped cages ( $6.5 \times 7.5 \text{ \AA}$ ) of the resulting catalyst empty. X-Ray absorption spectroscopy shows<sup>7</sup> that after calcination in  $\text{O}_2$ , some 50% of the Mn(II) (or Co(II)) originally present (isomorphously substituting for Al(III)) are converted to the Mn(III) (Co(III)) oxidation state, but that all these transition-metal ions remain securely in tetrahedral co-ordination within the microporous AIPO framework.<sup>8</sup> Others<sup>9–12</sup> have also shown that Co(II) ions in framework sites may be raised to the Co(III) state without loss of structural integrity of the AIPO framework.

In a typical experiment, 0.25 g of catalyst, 35 g of the alkene and an alkene–benzaldehyde (mole) ratio of 1 : 3 are used. The reaction mixture is loaded into a stainless steel, high-pressure catalytic reactor (Cambridge Reactor Design), lined with polyether ether ketone (PEEK), and equipped with a mechanical stirrer and liquid sampling valve. Dry air is pressurised into the reaction vessel (30 bar), and the reactor heated typically for 8 h at a temperature of 323 K. The results are summarised in Table 1, and Fig. 1 shows a typical kinetic plot. Results obtained with comparable larger-pore (MAIPO-5) and smaller-pore (MAIPO-18) redox molecular sieve catalysts, the shapes of which are  $7.3 \times 7.3 \text{ \AA}$  and  $3.8 \times 3.8 \text{ \AA}$  respectively, are also tabulated. Note that conversions are consistently higher for both the MnAIPO-36 and CoAIPO-36 catalysts compared with those of their larger-pore (AIPO-5) analogues. Almost certainly, the reasons

for the superior performance of the MAIPO-36 catalyst is because a greater fraction (ca. 0.5 compared with 0.25) of the Mn (or Co) can be raised to the +3 oxidation state,<sup>7</sup> which (see below) is the root cause of catalytic activity. Significantly MgAIPO-36 is totally inactive: there is no redox ion in the framework of the micropores in this case, and hence there is no

Table 1 Catalytic aerobic partial oxidation of alkenes<sup>a</sup>

Substrate	Catalyst	t/h	Conv. (%)	Product selectivity (%)		
				Epoxide	Diol	Others
Cyclohexene	CoAIPO-36	8	54	69	27	4 <sup>b</sup>
	CoAIPO-5	8	47	74	15	11 <sup>b</sup>
	MnAIPO-36	8	62	77	19	5 <sup>b</sup>
	MnAIPO-5	8	44	77	13	10 <sup>b</sup>
	MgAIPO-36	8		No reaction		
$\alpha$ -(+)-Pinene	CoAIPO-36	8	54	84	—	16 <sup>c</sup>
	CoAIPO-5	8	32	55	—	46 <sup>c</sup>
	MnAIPO-36	8	59	91	—	9 <sup>c</sup>
	MnAIPO-5	8	42	66	—	34 <sup>c</sup>
(R)-(+)-Limonene	CoAIPO-36	8	46	78	—	23 <sup>d</sup>
	CoAIPO-5	8	28	39	—	61 <sup>d</sup>
	MnAIPO-36	8	51	87	—	13 <sup>d</sup>
	MnAIPO-5	8	30	51	—	49 <sup>d</sup>
Styrene	CoAIPO-36	4	46	34	59	8 <sup>e</sup>
	MnAIPO-36	4	55	27	61	12 <sup>e</sup>
	MnAIPO-5	4	32	49	60	1 <sup>e</sup>
Hex-1-ene <sup>f</sup>	CoAIPO-18	24	37	87	—	13
	MnAIPO-18	24	43	91	—	9

<sup>a</sup> Reaction conditions:  $T = 323 \text{ K}$ ; 30 bar, dry air; 35 g substrate; substrate–benzaldehyde mole ratio 1 : 3; solid catalyst 0.25 g. <sup>b</sup> Mainly cyclohex-2-en-1-ol and cyclohex-2-en-1-one. <sup>c</sup> Verbenol and verbenone. <sup>d</sup> Carveol, carvone and *trans*-carveyl acetate. <sup>e</sup> 1-Phenylethane-1,2-diol. <sup>f</sup> Hexanal was used instead of benzaldehyde.

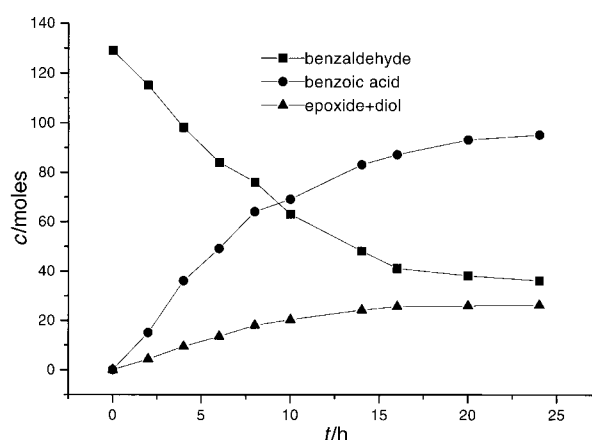
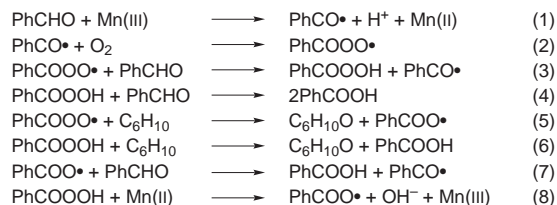


Fig. 1 Typical conversion plot for the selective oxidation of cyclohexene using CoAIPO-36 catalyst in the presence of air and benzaldehyde (conditions as in Table 1).



Scheme 1

means of initiating the free-radical reactions leading to epoxidation.

Benzaldehyde molecules may freely enter the large (*ca.* 650 m<sup>2</sup> g<sup>-1</sup>) internal surfaces of both MAIPO-36 and MAIPO-5 catalysts, thereby generating<sup>11,13</sup> first PhCO• and then the PhCOOO• radicals which, from the sequence of steps shown in Scheme 1, lead to the formation of benzoic acid and cyclohexene oxide. In this sequence, reaction (5) is known<sup>14</sup> to proceed much faster than reaction (6). This free-radical based epoxidation of cyclohexene (and the other alkenes listed in Table 1) is mechanistically quite distinct from the radical-free epoxidation of alkenes<sup>15–17</sup> using alkyl hydroperoxides and titanosilicate catalysts.

Other aldehydes may also be used as sacrificial oxidants provided they are small enough to gain access to the active sites situated at the inner surface of the molecular sieve catalyst. Benzaldehyde is itself too large to enter Mn (or Co)-AlPO-18, but hexanal is not. Although it diffuses less rapidly into the MAIPO-18 structure than benzaldehyde does in AlPO-36, it nevertheless functions efficiently in epoxidising hex-1-ene.

The experimental conditions chosen for this study—the concentration of catalytically active redox ions at the inner surface of the molecular sieve (arbitrarily set at 4 atom%), the ratio of reactants, the amount of catalyst, temperature, pressure, *etc.*—have not been optimised for maximal conversion and selectivity. There is considerable scope for achieving improvements in catalytic performance. Note also that under the reaction conditions employed here, the framework-substituted transition-metal-ions are not leached out during use. When the solid catalyst is removed by filtration and the reactants returned

into the reactor no epoxidation ensues under the conditions given in Table 1.

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