A manganese-containing molecular sieve catalyst designed for the terminal oxidation of dodecane in air

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Mn^{III} ions that replace a few percent of the framework Al^{III} sites in a microporous aluminophosphate—number 18, with a pore aperture of 3.8 Å—function as catalytically active centres for the selective oxidation of dodecane preferentially at C_1 and C_2.

The activation and functionalisation of alkanes are notoriously difficult to execute and control—far more so than the processes involved in their complete oxidation (combustion).[1] Taking cues from the general field of redox metallo-enzymes[2–4] that catalyse shape- and regio-selectively the oxidation of hydrocarbons, but also from framework-substituted, transition-metal-ion-incorporated microporous aluminium phosphates (AlPOs),[5–7] we have designed a heterogeneous catalyst that selectively converts dodecane in air, without the need for stoichiometric donors such as alkyl hydroperoxides or H_2O_2.

The catalyst consists of so-called AlPO-18,[8] in which a small fraction, typically 4 atom%, of the Al^{III} ions has been isomorphously replaced, during synthesis,[9] by Mn^{II} ions. Separate experiments, involving combined *in situ* X-ray absorption spectroscopy and X-ray diffractometry[10,11] plus *ex situ* scanning transmission electron microscopy, have established that, in O_2 or dry air, at temperatures up to *ca*. 550 °C, the Mn^{II} ions (like those of isomorphously substituted Co^{II}) are all converted to the +3 oxidation state while remaining tetrahedrally coordinated (*i.e.* coordinatively unsaturated) without loss of structural integrity of the AlPO host or exsolution from it of its embedded transition-metal ions. EXAFS and other analyses show that the individual Mn^{III} active sites are spatially well separated throughout the three-dimensional internal surface of the catalyst. Whereas all these active centres are accessible to small molecules, because of the structural characteristics of AlPO-18 (see Fig. 1) only those situated at the mouths of the pores that emerge at exterior surfaces are accessible to the extremities of the linear dodecane.

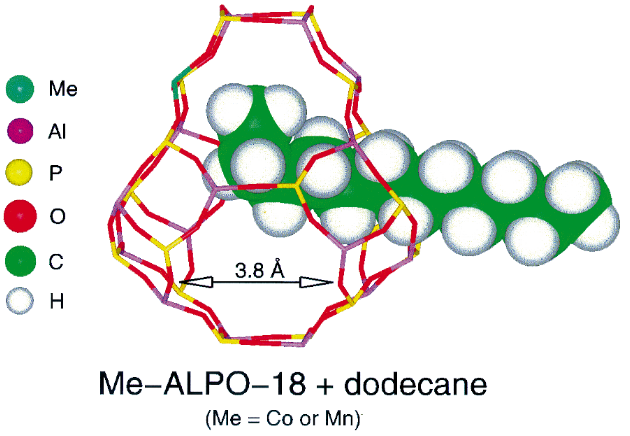

Fig. 1 Energy-minimised configuration adopted by *n*-dodecane at 0 K inside an AlPO-18 framework. The terminal methyl group (C_1) and C_2 of the dodecane are significantly closer to a tetrahedral framework site containing the metal ion (manganese, in this case) than either C_3, C_4 or C_5, implying that the Mn^{III} ions in the framework of the AlPO-18 cage, along with intracage O_2, exert a greater influence on the C_1 and C_2 than on other carbons on the dodecane backbone.

The details of the synthesis of Mn^{II}-containing AlPO-18 are exactly the same as for that of other MeAlPO-18 (Me = Co, Zn, Mg, Mn, *etc*.) catalysts.[6] Briefly, the Mn^{II} ion is introduced to the template-containing precursor gel from which small crystals of phase pure product appear. Upon gentle calcination in O_2, the template (*N*,*N*-diisopropylethylamine) is entirely gasified, leaving the cages of the resulting catalyst empty. In a typical experiment, 0.5 g of catalyst was added to 50 g of dodecane in a stainless steel high pressure catalytic reactor (Cambridge Reactor Design) lined with PEEK (poly ether ether ketone), and equipped with a mechanical stirrer and liquid sampling valve. Removal of samples for analyses during the course of the reaction is possible without perturbing the pressure in the reactor. Dry air was pressurised into the reaction vessel (1.5 MPa) and the reactor was heated to the desired temperature (373 K). Samples were periodically removed, analysed by gas chromatography (GC; Varian 3400 CX} equipped with a BPX5 column (25 m × 0.32 mm) and a flame ionisation detector (FID), and the total conversion and product distribution (estimated in moles and normalised with respect to the GC response factor) were determined as a function of time (using 1,2-dichlorobenzene as internal standard). The acids formed were esterified and analysed as methyl esters.[12] The identity of the products was confirmed by injecting authenticated standard samples. The mass balance was calculated for each run and the estimated error in the analysis arising from handling or sampling loss is less than 6.0 mol%.

Exactly analogous experiments were carried out with another manganese-containing AlPO, MnAlPO-36[13] in which the pore diameter is appreciably larger (6.5 Å × 7.5 Å), thereby permitting much greater access to the dodecane. Fig. 2 and Table 1 summarise the results. It is obvious that the small pore aperture of MnAlPO-18 (and of CoAlPO-18) results in

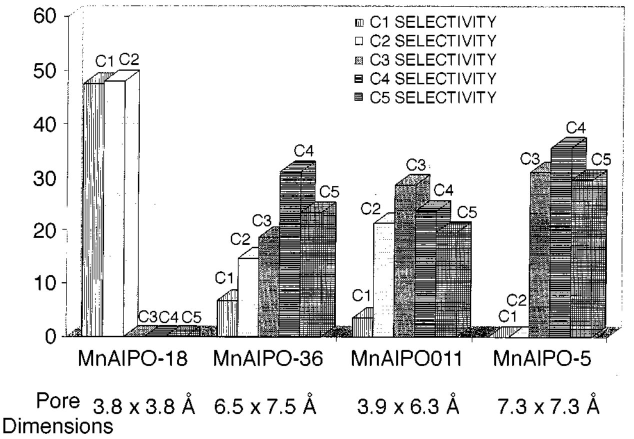

Fig. 2 Bar chart summarising the various degrees of regio-selectivity in the oxidation of dodecane over four microporous MnAlPO catalysts. The regioselectivity for terminal oxidation with MnAlPO-18 far exceeds that of any of the other three.

Table 1 Oxidation of dodecane^a in air: comparison of catalysts

		Product^b distribution/mmol											
Catalyst	Conv./mmol	C_1-ol	C_1-al	Lauric acid	C_2-ol	C_2-one	C_3-ol	C_3-one	C_4-ol	C_4-one	C_5-ol	C_5-one	Others^c
Mn-ALPO-18 (0.04)	16.08	1.27	4.71	1.65	4.47	3.25	—	—	—	—	—	—	0.73
Mn-ALPO-36 (0.04)	15.20	0.47	—	0.55	0.95	1.27	1.37	1.45	2.63	2.07	1.65	1.89	0.90
Mn-ALPO-5 (0.04)	13.75	—	—	—	—	—	2.28	1.97	2.07	2.83	1.59	2.46	0.55
Mn-ALPO-11 (0.04)	6.82	0.24	—	—	0.91	0.53	0.75	1.19	0.58	1.03	0.43	0.91	0.25

^{a} Dodecane = 49.7 g; catalyst = 0.5 g; air = 1.5 MPa; temp. = 373 K; time = 24 h. ^{b} C_1-ol = dodecan-1-ol; C_1-al = dodecanal; C_2-ol = dodecan-2-ol; C_2-one = dodecan-2-one; C_3-ol = dodecan-3-ol; C_3-one = dodecan-3-one; C_4-ol = dodecan-4-ol; C_4-one = dodecan-4-one; C_5-ol = dodecan-5-ol; C_5-one = dodecan-5-one. ^{c} Others = mainly CO_2, CO, water and lower olefins/hydrocarbons in the gas phase.

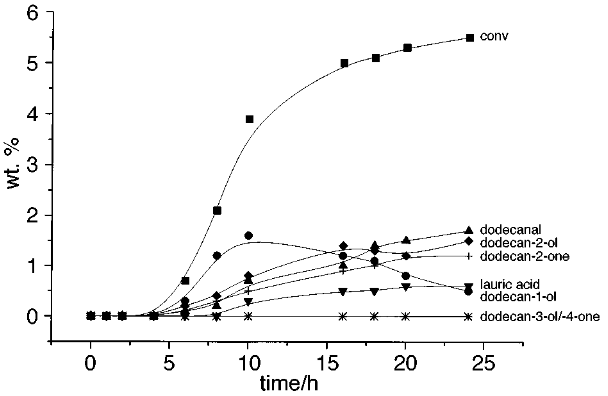

Fig. 3 Typical kinetic plots for the oxidation of dodecane over MnAlPO-18 catalyst under the conditions given in Table 1

oxidation of the dodecane (total conversion = 5.5 wt.%) only at C_1 and C_2, whereas in MnAlPO-36 (possessing essentially the same concentration of the active site) (total conversion = 5.2 wt.%) the oxyfunctionalization occurs at essentially all the carbon atoms of the dodecane backbone, and more predominantly at the C_4 and C_5 positions. The kinetics of oxidation of dodecane using MnAlPO-18 was studied in detail (Fig. 3), and after an initial period of induction (4 h), dodecan-1-ol and dodecan-2-ol were formed simultaneously, and were subsequently oxidised to dodecanal, lauric acid and dodecan-2-one at prolonged contact times. In an identical experiment, the solid catalyst was filtered off (when hot) after 8 h (conversion = 2.4 wt.%) and the reaction was continued for a further 16 h. But, no further conversion was observed, showing that the Mn^{III} ions in the framework of the molecular sieve are solely responsible for the catalysis. (The reaction mixture was independently analysed by ICP analysis and no detectable quantities of Mn or Co were observed.) MnAlPO-18 and CoAlPO-18 (and possibly other transition-metal ion substituted AlPO-18) are therefore good candidates for suitable catalysts in the production of functionalised hydrocarbons required as surfactants and detergents. We know from parallel work[14] that a CoAlPO-18 (total conversion = 7.1 wt.%) catalyst preferentially activates the terminal and secondary methyl groups of *n*-hexane.

We believe that the key to the catalytic activity is the coordinatively unsaturated Mn^{III} ion. Just as with the tetrahedrally coordinated Ti^{IV} ions in TS-1,[15] metallocene derived Ti ↑ MCM-41[16,17] and especially the Co^{III} ions in CoAlPO-18,[14] expansion of the coordination shell in the transition state is likely to be facile. Moreover, after the departure of the products, the retention of the isolated Mn^{III} ions in the framework of the microporous host favours the regeneration of the catalyst's activity. Its selectivity, however, is solely due to the pore size dimensions that govern access of the hydrocarbon. It should be mentioned that, after the reaction, the catalyst (MnAlPO-18) was washed thoroughly with methanol and activated at 550 °C for 12 h in the presence of dry air. It was then recycled twice without significant loss in catalytic activity (conv. = 15.65 mmol) and selectivity (C_1 = 48% and C_2 = 47.6%).

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