

Powerful Redox Molecular Sieve Catalysts for the Selective Oxidation of Cyclohexane in Air

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Received September 29, 1999

Apart from its intrinsic importance in the chemistry of C–H activation,^{1–4} the selective oxidation of cyclohexane to yield cyclohexanol and cyclohexanone is the center-piece of the commercial production of Nylon.⁵ We have recently explored framework-substituted aluminum phosphate (AIPO) molecular sieves as catalysts for the aerobic selective oxidation of linear and cyclic alkanes, alkenes, and ketones,^{6–10} and have found that AIPO-36 (pore aperture $6.5 \times 7.5 \text{ \AA}$) in which a few percent of the Al^{III} ions have been replaced by Co^{III} (or Mn^{III}) is a good catalyst for cyclohexane oxidation, and that Co^{III} (or Mn^{III}) substituted AIPO-18 (pore aperture 3.8 \AA) for the regioselective, terminal oxidation of linear alkanes predominantly to yield the corresponding *n*-alkanoic acids.⁷

A key factor⁷ in achieving the highest catalytic performance of a MAIPO sieve is for the transition metal ions (M) to be in a high oxidation state while still remaining an integral part of the AIPO framework. It so happens that the extent to which M ions originally present in the II oxidation state can be raised to their III state is dependent, for a given ion, on the structure of the AIPO in which it is incorporated substitutionally. This fraction of M^{III} ions is evaluated^{7,11} from X-ray absorption spectroscopy. In the MAIPO-18 structure all the Co^{II} ions, but less than 20% of the Co^{II} ions in MAIPO-5 (up to ca. 4 atom % of the Al^{III} which they replace), may be raised to the III state upon calcination

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(12) We observed cyclohexyl hydroperoxide (cHHP) in the reaction mixture when CoAlPO-5 was used as the catalyst, and in the early stages of the reaction (3 h) with MnAlPO-5 . FeAlPO-5 was more reactive than CoAlPO-5 and MnAlPO-5 , and hence cHHP was not detected in the reaction mixture.

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(14) To illustrate this point we took an equimolar mixture of *n*-hexane and cyclohexane and subjected it to a catalytic test over MnAlPO-18 (or CoAlPO-18). There was, unsurprisingly, absolutely no conversion of the cyclohexane molecule, as it is too large to access the active, framework tetrahedral sites in the AIPO-18 structure. The conversion of *n*-hexane, however, was as expected quite substantial, there being good selectivity (66%) for terminally functionalized⁷ products. However, when the same reactant mixture was dissolved in acetic acid, the MnAlPO-18 catalyst now gives rise to considerable oxidation of both cyclohexane (conversion = 8.7%) and *n*-hexane (conversion = 5.2%), C_2 and C_3 alcohols and ketones being main products (selectivity = 91%). Clearly acetic acid as a solvent results in homogeneous as well as heterogeneous catalysis.

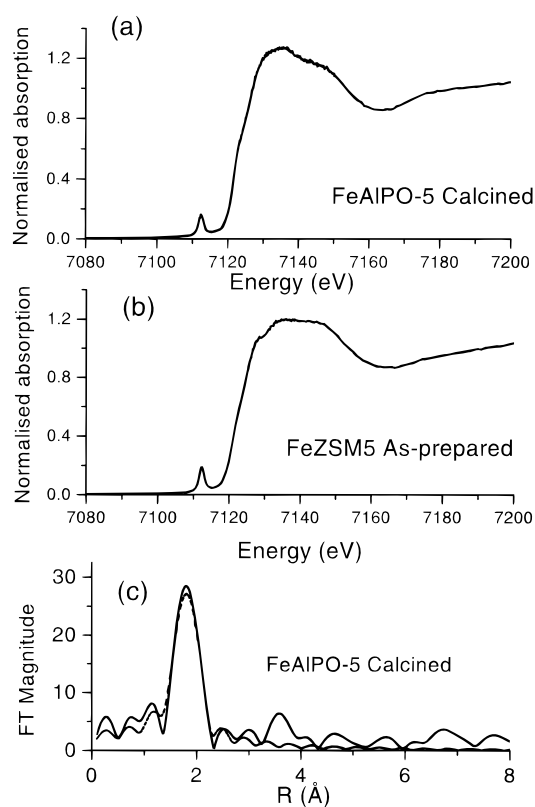


Figure 1. (a) Fe K-edge XANES of calcined FeAlPO-5 (tetraethylammonium hydroxide was used as the templating agent). Note that the edge position and in particular the pre-edge feature is similar to that of framework-substituted FeZSM-5 catalyst [in part b]. Fourier transforms [in part c] of the Fe K-edge EXAFS of calcined FeAlPO-5 . The solid line is the experimental and dashed curve the computed data generated using EXCURV98. Structural data for the oxygen shell yields an average Fe–O distance of $1.86 \pm 0.02 \text{ \AA}$, which is similar to that of FePO_4 ¹⁵ and Fe^{III} containing ZSM-5¹⁶ wherein the Fe^{III} is present in tetrahedral coordination.

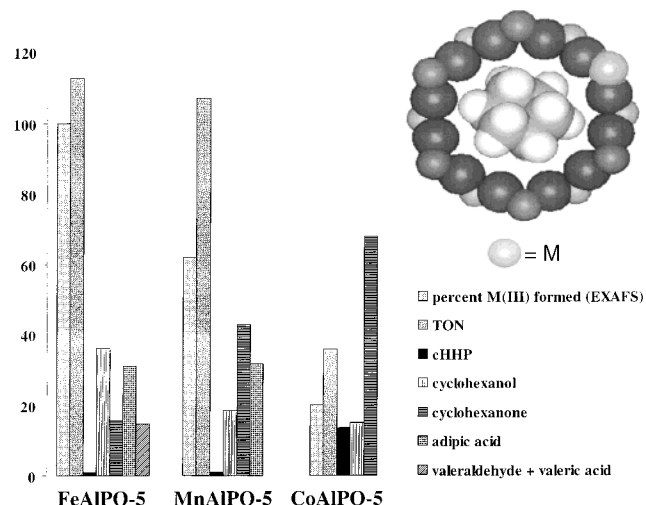


Figure 2. Comparison of the fraction of $\text{M}(\text{III})$ ions present (estimated from EXAFS) in the calcined FeAlPO-5 , MnAlPO-5 , and CoAlPO-5 and their catalytic activity (TON) for the oxidation of cyclohexane after 24 h at 403 K. Individual product distributions are also shown.

in O_2 or air at ca. $550 \text{ }^\circ\text{C}$. However, the pore dimension of the MAIPO-18 is too small to permit ingress of cyclohexane to the

Table 1. Oxidation of Cyclohexane^a in Dry Air (1.5 MPa)

catalyst	time, h	TON ^f	conv, mol %	product distribution, mol %						
				cHHP ^b	-ol	-one	aa	vald	vacid	others
FeAlPO-5	8	45	2.5		41.1	17.9	26.2	13.5	-	1.9
	24	113	6.6		36.2	15.5	31.0	9.2	5.4	2.7
FeAlPO-5 ^e	8	205	11.7		30.5	28.9	28.0	6.3	1.7	4.8
	24	346	19.8		21.7	32.5	32.3	5.0	3.4	5.4
FeAlPO-5 ^d	8	7	0.4	23.1	77.0					
	24	16	0.9		100					
MnAlPO-5	8	47	2.7		36.9	56.0	5.9			1.2 ^c
	24	107	6.2		18.5	42.8	31.5			7.9 ^c
MnAlPO-5 ^e	8	170	9.6		26.7	59.8	9.0			4.6 ^c
	24	292	16.5		19.5	43.1	29.3			8.4 ^c
MnAlPO-5 ^d	24				no reaction					
CoAlPO-5	8	29	1.6	44.1	35.0	21.7				
	24	36	2.0	13.5	15.0	67.8				3.4
CoAlPO-5 ^e	8	106	5.8	14.2	36.5	41.2	4.4			3.5
	24	221	12.2	-	31.9	55.7	8.5			4.3
CoAlPO-5 ^d	24				no reaction					

^a Cyclohexane \cong 50 g, mesitylene (internal standard) \cong 2.5 g; catalyst = 0.5 g; pressure (air) = 1.5 MPa; temperature = 403 K. ^b cHHP = cyclohexyl hydroperoxide; -ol = cyclohexanol; -one = cyclohexanone; aa = adipic acid; vald = valeraldehyde; vacid = valeric acid; others = probably CO₂, CO, water, and traces of lower olefins in the gas phase. ^c Mainly glutaric + traces of succinic acid. ^d Reactions carried out in the presence of air and small amounts (3 wt % of cyclohexane) of hydroquinone (free-radical scavenger). ^e Reactions carried out using air and a free-radical initiator, TBHP (3 wt % of cyclohexane). ^fTON = moles of substrate converted per mole of metal (Co, Mn, or Fe) in the catalyst.

active sites of this catalyst.⁸ In the calcined MAIPO-5 catalysts, where the diameter (7.3 Å) of the pores is much larger than in MAIPO-18, all the iron ions are present in the III state (Figure 1), and for manganese- and cobalt-containing catalysts ca. 60 and 20% respectively may be raised to their corresponding III states. MAIPO-5 catalysts are readily crystallized from their precursor gels and are also thermally robust.

We find that FeAlPO-5 is an exceptionally good catalyst (Table 1 and Figure 2) for the selective oxidation of cyclohexane in air. In line with earlier observations,^{7,9} the oxidation of cyclohexane proceeds by a free-radical mechanism. This is evidenced by (i)

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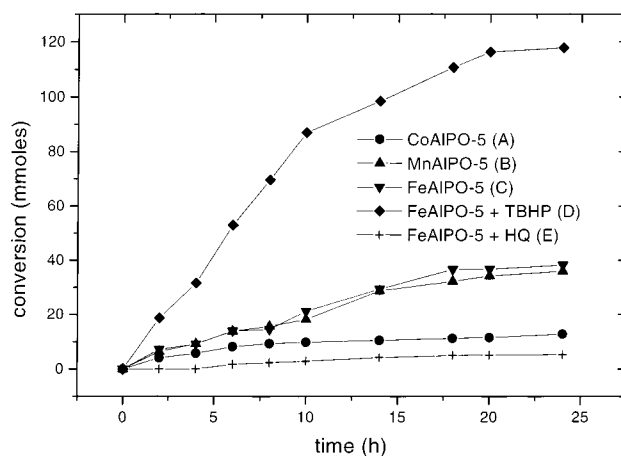


Figure 3. Comparative kinetic plots for the oxidation of cyclohexane using CoAlPO-5 (A), MnAlPO-5 (B), FeAlPO-5 (C), FeAlPO-5 in the presence of a free radical initiator {*tert*-butyl hydroperoxide} (D), and FeAlPO-5 in the presence of a free radical scavenger {hydroquinone} (E).

the fact that the addition of a free-radical initiator (TBHP) greatly increases both the rate and degree of conversion of cyclohexane while still retaining a high preference for the three desired products (cyclohexanol, cyclohexanone, and adipic acid), (ii) the fact that the addition of a free-radical scavenger (hydroquinone) essentially stops the reaction and profoundly affects the product distribution (see Figure 3), and (iii) the presence of cyclohexyl hydroperoxide (cHHP)¹² during the initial stages of the reaction, which subsequently decomposes to cyclohexanol and cyclohexanone.

We have found that the widely held¹³ view that MAIPO sieves (M \equiv Mg, Zn, Co, Mn, etc.) are unpromising as catalysts because of the propensity for the M ions to leach out of the structure during use is exaggerated. If aggressive solvents such as acetic acid are avoided, MAIPO sieves exhibit good, sustained catalytic performance.¹⁴

Acknowledgment. We thank the EPSRC (UK) for a rolling grant to J.M.T. and The Royal Commission for the Exhibition of 1851 for a research fellowship to R.R. We dedicate this to Dr. K. U. Ingold on the occasion of his 70th birthday.

JA9935052