Bifunctional Molecular Sieve Catalysts for the Benign Ammoximation of Cyclohexanone: One-Step, Solvent-Free Production of Oxime and ϵ-Caprolactam with a Mixture of Air and Ammonia

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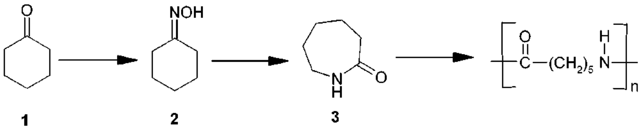
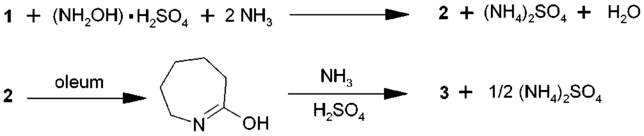
The conversion of cyclohexanone (**1**) to the oxime (**2**) and its subsequent Beckmann rearrangement to ϵ-caprolactam (**3**) are vital stepping stones in the manufacture of nylon-6[1] (Scheme 1). On an industrial scale, one popular procedure in converting **1** to **2** is to employ hydroxylamine sulfate, the sulfuric acid thus liberated being neutralized by ammonia,[2,3] with the consequential production of large quantities of (low value) ammonium sulfate.[4] The traditional industrial route for effecting the Beckmann rearrangement (**2**→**3**) is by use of a strong mineral acid such as oleum (Scheme 2).

Workers at Enichem Co. showed that the titanosilicate molecular sieve TS-1 offered an attractive, more environmentally benign route of production, a particular advantage being the use of H_2O_2 as the oxidant[5,6] in aqueous solution. Other hydrogen peroxide-based processes[7] employ organic solvents such as methanol, ethanol, or 2-propanol, and a stabilizer such as sodium EDTA so as to generate 1,1′-dihydroxydicyclohexyl peroxide. Earlier, Armor[8] had demonstrated a direct (gas phase) route to **2** and **3** from **1** using two distinct (double-bed) catalysts consisting of a variety of silicas and aluminas in the range 120−250 °C.

Scheme 1



Scheme 2



In a program directed[9−11] toward developing more benign reagents and catalysts for the laboratory-scale production of desirable commodity chemicals (such as adipic acid from either cyclohexane[12] or *n*-hexane,[13] or lactones from ketones[14]), we have investigated the effectiveness of two bifunctional transition-metal-ion (framework)-substituted aluminophosphate molecular sieve catalysts for converting **1** to **2** and **3** *in a one-step, solvent-free manner, in the liquid-phase,* using oxygen (as air) and ammonia. The catalysts are: $(\mathrm{M^{II}M^{III}})$AlPO-36, M ≡ Co, Mn; they are structurally well-defined[15] possessing pore apertures of 6.5 × 7.5 Å, and a surface area (overwhelmingly internal) of ca. 700 $m^2\ g^{-1}$. X-ray absorption spectroscopy has established[16] that of the 4 atom % of the framework $\mathrm{Al^{III}}$ isomorphously replaced by M ions, approximately 50% are in the $\mathrm{M^{II}}$ and 50% in the $\mathrm{M^{III}}$ state (Figure 1). $\mathrm{M^{II}}$ ions, since they have protons loosely bound to an adjacent framework oxygen atom, are the loci of Brönsted acid active sites. The $\mathrm{M^{III}}$ framework ions, on the other hand, are "redox" active sites, capable of activating hydrocarbons and oxygen.[17] The pore dimensions of MAlPO-36 are just large enough to permit ingress of any of the molecules **1**, **2**, or **3**. In $(\mathrm{M^{II}M^{III}})$AlPO-18, M ≡ Co, which we have also studied (see below) for the purposes of elucidating the nature of the catalysis, all of the Co ions are in the $\mathrm{Co^{III}}$ state;[16] and the pore diameter is so small that only air, H_2O_2 and ammonia (or hydroxylamine when formed[18]) may gain access to the interior surface of the sieve.

Our designed bifunctional catalysts, $\mathrm{M^{II}M^{III}}$AlPO-36, perform very well in consecutively converting **1** to **2** to **3** because: (i) hydroxylamine (NH_2OH) is readily formed in situ inside the pores from NH_3 and O_2 at the $\mathrm{M^{III}}$ active (redox) sites, (ii) the NH_2OH converts **1** to **2** both inside and outside the pores, and, likewise, at the Brönsted active sites **2** is isomerized to **3** inside the pores of the molecular sieve catalyst, and (iii) O_2 yields NH_2OH more efficiently than H_2O_2 or TBHP at the redox active sites.

We now show that all the results given Table 1 are readily interpretable, with additional structural and shape-selective nuances, in terms of points (i−iii) above. Moreover a kinetic study (see Supporting Information) shows that NH_2OH is initially formed at a rapid rate but is then converted to **2** in the presence of cyclohexanone. Furthermore, experiments carried out in the absence of cyclohexanone proved unequivocally the formation of NH_2OH from NH_3 and O_2 at the redox ($\mathrm{Co^{III}}$) site.[19]

We note, in particular that deliberate increase of the concentration of Brönsted sites in Co(Mn)AlPO-36 (cf. G with A and H with B) significantly enhances the production of ϵ-caprolactam; no ϵ-caprolactam (**3**) is ever produced with MAlPO-18 catalysts, even when the Brönsted active center concentration is increased

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(19) NH_2OH was not formed when the reaction was carried out in NH_3 and O_2 at a $\mathrm{Co^{II}}$ active site (such as $\mathrm{Co^{II}}$AlPO-18).

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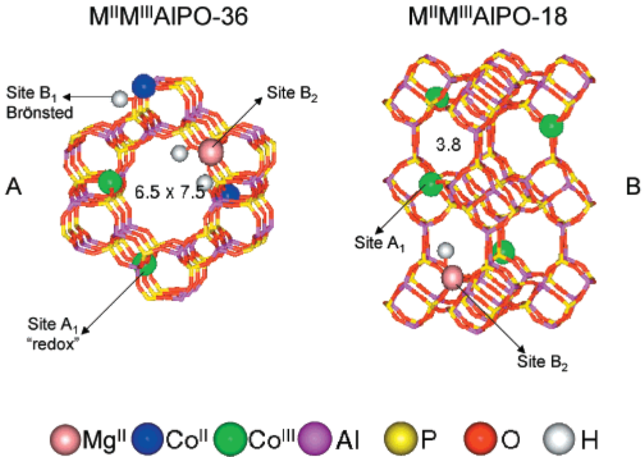

Figure 1. (A) In M^{II}M^{III}AlPO-36 (M ≡ Co, Mn), the framework M^{III} ions are the redox active centers (A$_1$), whereas M^{II} ions have associated ionizable OH bonds attached to the framework and these are the Brönsted (B$_1$) acid sites. Mg^{II} ions in the framework also have neighboring ionizable OH ions (B$_2$ sites). (B) In M^{III}AlPO-18 all the framework M^{III} ions are again redox active centers: there are no Co^{II} (or Mn^{II}) framework sites. Mg^{II} framework ions again have neighboring (B$_2$) Brönsted sites.

(cf. N and K) solely because the oxime (**2**) is too large to gain access to these centers via the 3.8 Å pore apertures; for the same reason there is no conversion at all of **1** to **2** or **3** when TBHP is used as oxidant with Co^{III}AlPO-18, as this peroxide is also too bulky to reach the redox active centers; with O_2 as oxidant, the smaller pore CoAlPO-18 (catalyst K) gives higher conversion of **1** to the oxime (**2**) than with catalysts A or B because of the higher concentration of the redox active centers in the former; we may categorically rule out the "imine" mechanism[20,21] for the formation of the oxime (**2**), according to which $C_6H_5{=}NH$ is a necessary intermediate. Since this species is also too large to enter the pores of the Co^{III}AlPO-18 (which smoothly yields **2** from **1** with a mixture of air and NH_3), the dominant mechanism entails direct conversion of **1** with NH_2OH to **2**; and Brönsted active centers alone (see catalysts I, J) are not enough to effect the conversion of **1** to **2** {and hence to **3**}. Indeed, the meagre extent of conversion (1.9% mol) is the same as is observed when no catalyst is present (cf. I and O); but when hydroxylamine hydrochloride is added to this mixture, conversion of **1** to the oxime (**2**) {only} is very high, further confirming that the hydroxylamine mechanism prevails.

Our results also demonstrate that the MAlPO catalysts that we have developed for this and other oxidations[10−14,17] function in a genuinely heterogeneous manner[22] and not seemingly so—because the active entities (e.g., Co^{III} or Mn^{III} ions in this instance) do not leach out and then simply adhere to the molecular sieve where they would operate as loosely bound homogeneous catalysts. If the Co^{III} or Mn^{III} were leached out, we would have seen appreciable conversion using TBHP with catalyst L, yet there was none. Moreover, if Mg^{II} ions were leached out, they would have catalyzed the Beckmann rearrangement of **2** to ε-caprolactam (catalyst N), but again none of the latter is formed. In a separate experiment (with reaction conditions analogous to those of H, in Table 1) the solid catalyst was filtered off from the reaction mixture (when hot) after 4 h, and the reaction was continued with the resulting filtrate for a further 16 h. No further conversion to ε-caprolactam was observed, and the filtrate analyzed by ICP/AAS analysis revealed only trace amounts of Mn and Mg (<3 ppb and <5 ppb, respectively). Finally, we took an equimolar mixture of cyclooctane[23] and cyclohexanone along with NH_3 and air over a Co^{III}Mg^{II}AlPO-18 catalyst. Unsurprisingly, there is no conversion whatsoever of the cyclooctane molecule, as it is too large to gain access into the interior of the catalyst where the vast majority of the active sites are located. The NH_3, however, gains ready access to such active sites, where NH_2OH is first produced before subsequently reacting with cyclohexanone to produce the oxime (**2**). When the active sites are deliberately leached[22] using acetic acid as a solvent, considerable oxidation of the cyclooctane now occurs (the main products being cyclooctanol, cyclooctanone, and cyclooctanoic acid), in addition to the formation of NH_2OH from NH_3. The NH_2OH, now, reacts not only with cyclohexanone to produce the corresponding oxime, but also with the cyclooctanone to give its oxime. Clearly acetic acid as a solvent results in homogeneous as well as heterogeneous catalysis.

Table 1. Solvent-Free Ammoximation of Cyclohexanone: Performance of Various Catalysts and Oxidants[a]

						product selectivity[b] (mol %)		
I.D.	solid molecular sieve	oxidant	*t* (h)	conv mol (%)	TON[g]	oxime	ε-caprolactam	others
A	Co^{II}Co^{III}AlPO-36	O_2[c]	6	13.1	217	73.9	17.7	10.2
			20	20.2	322	54.2	21.1	24.5
B	Mn^{II}Mn^{III}AlPO-36	O_2	6	15.0	245	75.8	16.9	7.3
			20	23.6	381	57.0	20.2	22.8
C	Co^{II}Co^{III}AlPO-36	TBHP	6	9.5	167	81.7	7.9	12.0
			20	17.9	289	76.7	10.0	13.3
D	Mn^{II}Mn^{III}AlPO-36	TBHP	6	10.0	160	81.5	10.1	8.3
			20	19.0	308	65.4	18.2	15.9
E	Co^{II}Co^{III}AlPO-36	H_2O_2[d]	6	7.8	135	45.6	16.3	38.6
			20	12.9	215	36.4	14.7	55.3
F	Mn^{II}Mn^{III}AlPO-36	H_2O_2	6	8.6	140	39.8	20.8	38.4
			20	15.8	254	41.1	18.4	40.6
G	Mg^{II}Co^{III}AlPO-36	O_2	6	12.4	108	44.0	36.2	19.5
			20	21.5	212	33.9	42.9	22.7
H	Mg^{II}Mn^{III}AlPO-36	O_2	6	13.7	136	48.4	31.3	19.5
			20	23.0	262	36.2	45.2	18.0
I	Co^{II}AlPO-36	O_2	20	1.9	28	28.4	–	72.3
J	Mg^{II}Co^{II}AlPO-36	O_2	20	2.2	15	26.9	–	73.0
K	Co^{III}AlPO-18	O_2	6	21.5	367	91.7	–	8.5
			20	32.4[e]	550	86.5	–	13.7
L	Co^{III}AlPO-18	TBHP	6			no reaction		
			20					
M	Co^{III}AlPO-18	H_2O_2	6	19.7	333	65.8	–	34.0
			20	28.0[f]	477	59.3	–	41.4
N	Mg^{II}Co^{III}AlPO-18	O_2	6	19.9	274	90.4	–	9.5
			20	31.7	412	87.5	–	12.3
O	no catalyst	O_2	20	1.2	–	32.0	–	67.4
P	no catalyst + $NH_2OH{\cdot}HCl$[h]	O_2	6	32.6	–	81.5	–	19.2

[a] Cyclohexanone: oxidant (H_2O_2, TBHP) ≡ 3:1 (mol); catalyst ≡ 0.5 g; Air ≡ 3.5 MPa; cyclohexanone: NH_3 ≡ 1:3 (mol); T ≡ 328 K; cyclohexanone ≅ 50 g; mesitylene (internal standard) ≡ 2.5 g. [b] Oxime ≡ cyclohexanone oxime (**2**); others ≡ mainly high molecular weight conjugated products formed through aldol condensation of cyclohexanone plus some polycaprolactam and water. [c] The reaction mixture was colorless, indicating that very little tar is produced. [d] The reaction mixture was brownish yellow, suggesting possible formation of tar. [e] Turnover efficiencies based on moles of O_2 consumed ≅ 91%. [f] H_2O_2 efficiency ≅ 85%. [g] TON = mol of substrate converted per mol of metal (Co, Mn, or Mg) in the catalyst. [h] Cyclohexanone: $NH_2OH{\cdot}HCl$ ≡ 1:1 (mol).

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Supporting Information Available: Kinetics data showing the formation of NH_2OH from NH_3 and O_2 using Mg^{II}Mn^{III}AlPO-36 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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