Baeyer–Villiger oxidations with a difference: molecular sieve redox catalysts for the low-temperature conversion of ketones to lactones

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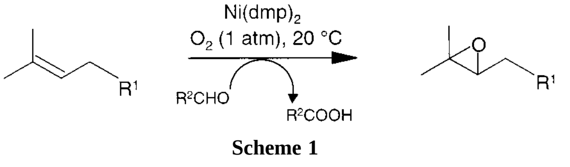
Redox molecular sieve catalysts MAlPO-36 (M = Mn or Co) convert cyclopentanone, cyclohexanone, 2-methylcyclohexanone and adamantan-2-one to their corresponding lactones with high efficiency (selectivities in excess of 90%, conversions in the range 50 to 85%), in the presence of O_2 and PhCHO as sacrificial oxidant.

In 1991 Mukaiyama and co-workers reported[1] that various aldehydes could be smoothly oxidised to their corresponding carboxylic acids by molecular oxygen in the presence of $Ni^{II}(dmp)_2$ catalysts [Hdmp = 1,3-bis(*p*-methoxyphenyl)propane-1,3-dione]. They also reported[2] an efficient method for epoxidising olefins using the same catalyst, O_2 and sacrificial aldehydes (Scheme 1).

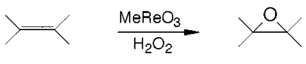
These conditions are of considerable interest in that they offer attractive alternatives to the use of environmentally less acceptable oxidants (many of which function stoichiometrically rather than catalytically) such as CrO_3, $KMnO_4$, $Pb(OAc)_4$, RuO_4 Ag_2O and $Co(acac)_3$.[3] H_2O_2 in the presence of an appropriate catalyst (*e.g.* by methyltrioxorhenium[4]) is also a good oxidant for the conversion of olefins to epoxides and cyclic ketones to lactones[5] (Scheme 2).

In pursuit of our goal to design and synthesise microporous solid catalysts for the selective aerobic oxidation of hydrocarbons, we have found that transition metal ion (framework) substituted aluminophosphates (MAlPO, where M = transition metal ions) can effectively convert alkanes[6–8] and aldehydes to their corresponding carboxylic acids. This prompted us to investigate the potential of these microporous solids for oxidation of ketones, in the presence of a sacrificial aldehyde, using air as an oxidant. Sacrificial aldehydes for the conversion of ketones to lactones (an example of Baeyer–Villiger oxidation) have been shown to be effective using various homogeneous catalysts.

Several heterogeneous catalytic systems based on hydrotalcites[9] or heteropolyoxometalates[10] have been used to effect Baeyer–Villiger oxidations. However, to the best of our knowledge, there are no reports of the use of microporous redox molecular sieves for the shape-selective conversion of ketones to lactones. Taking account of the redox properties[11] and pore dimensions of a range of metal ion substituted AlPOs, we have identified three different structures of potential catalysts that contain small amounts (up to 4 atom%) of either manganese or cobalt redox cations. The catalysts we have used are CoALPO-36, MnALPO-36, CoAlPO-5, MnAlPO-5, CoALPO-18 and MnALPO-18. The structure[12] of aluminium phosphate No. 36 (IZA structure code ATS) has well-defined, oval-shaped channels (6.5 × 7.5 Å) (Fig. 1), which, by appropriate preparative means,[7,12] 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 synthesised with specific metal ions having identical concentrations.[11] By calcining the as-prepared MAlPOs (M = Co or Mn) samples in oxygen at 550 °C, the substituted ions may be converted[12] to their +3 oxidation states, to a degree that is dependent on the structure; the trend in the concentration of the +3 state in the three structures is AlPO-18 > AlPO-36 > AlPO-5.[11] The results of Bayer–Villiger oxidation of a number of ketones to lactones, performed with these catalysts, are given in Table 1, and a typical kinetics plot for the MnAlPO-36 catalyst is shown in Fig. 2.†



Scheme 1



Scheme 2

Although the mechanistic details of the aerobic oxidation of ketones to lactones reported here still requires elucidation, preliminary studies (*cf.* ref. 6) point to the fact that the active centres in the redox catalysts are the Co^{III} (or Mn^{III}) ions that line the micropores. We know that the higher conversions are effected by the framework-substituted higher valence ions in the molecular sieve catalysts for several reasons. Firstly, divalent ion substituted AlPO-36 analogues such as Mg^{2+} (or Zn^{2+}) that are not raised to higher oxidation states upon calcination in O_2 yield conversions not significantly different from those of the Mukaiyama sacrificial oxidations with benzaldehyde alone (see Table 1, entries 5 and 7). Secondly, in a parallel experiment (Table 1, entry 6) using the smaller pore CoALPO-18 (or MnALPO-18), where all the transition-metal ions are in the +3 oxidation state,[7,11] and the diameter of micropores is 3.8 Å, no catalytic conversion of cyclohexanone to ε-caprolactone occurs when benzaldehyde is used as a sacrificial oxidant because the

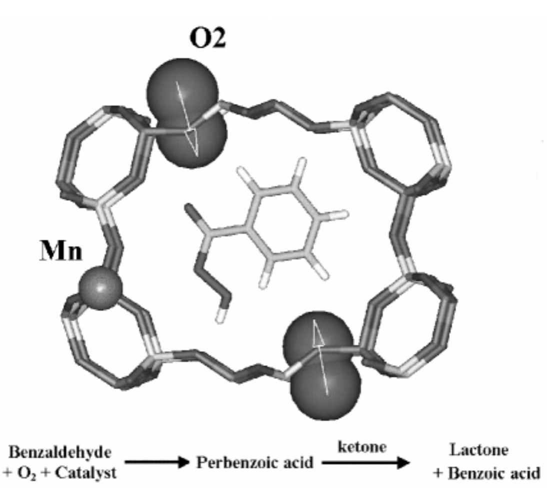


Fig. 1 Representation of the AlPO-36 catalyst, where one of the aluminium sites is occupied by manganese. The reaction scheme of the formation of the perbenzoic acid intermediate from benzaldehyde effected by Mn^{III} ions and molecular O_2 is also shown.

Table 1 Baeyer–Villiger oxidation of ketones (Mukaiyama's conditions)[a]

Entry	Substrate	Catalyst	Pore dimensions/Å	*T*/K	*t*/h	TOF[b]/h^{-1}	Conversion (%)	Lactone selectivity (%)
1	Cyclohexanone	CoALPO-36	6.5 × 7.5	323	6	250	71	98[c]
2	Cyclohexanone	CoALPO-5	7.3 × 7.3	323	6	204	60	80[c]
3	Cyclohexanone	MnALPO-36[d]	6.5 × 7.5	323	6	257	78	98[c]
4	Cyclohexanone	MnALPO-5	7.3 × 7.3	323	6	207	64	82[c]
5	Cyclohexanone	MgALPO-36	6.5 × 7.5	323	6	—[e]	20	64[c]
6	Cyclohexanone	CoALPO-18	3.8 × 3.8	323	6	—[e]	22	62[c]
7	Cyclohexanone	No Catalyst	—	323	6	—	20	65[c]
8	Cyclohexanone	CoALPO-18[f]	3.8 × 3.8	323	6	166	48	72[c]
9	Cyclopentanone	CoALPO-36	6.5 × 7.5	323	6	238	58	92[g]
10	Cyclopentanone	CoALPO-5	7.3 × 7.3	323	6	185	46	76[g]
11	Cyclopentanone	MnALPO-36	6.5 × 7.5	323	6	246	61	94[g]
12	Cyclopentanone	MnALPO-5	7.3 × 7.3	323	6	187	50	77[g]
13	Adamantan-2-one	CoALPO-36	6.5 × 7.5	353	5	220	80	99
14	Adamantan-2-one	MnALPO-36	6.5 × 7.5	353	5	224	87	99
15	2-Methylcyclohexanone	CoALPO-36	6.5 × 7.5	323	6	201	65	86
16	2-Methylcyclohexanone	MnALPO-36	6.5 × 7.5	323	6	208	72	89

[a] Reaction conditions: substrate = *ca.* 20 g; catalyst = *ca.* 0.15 g; substrate:benzaldehyde = 1:3 (mol/mol); O_2 (air) = 30 bar. [b] TOF = turnover frequency = moles of ketone converted per hour per mole of metal (Co, Mn) in the catalyst. [c] ε-Caprolactone. [d] After the reaction the catalyst was filtered off, washed thoroughly with MeOH and calcined at 550 °C for 12 h. It was then re-used twice without significant loss in catalytic activity. The reaction mixture (after 6 h) was also analysed by ICP (and atomic absorption spectroscopy) and only trace amounts (< 2 ppb) of metal were detected. In a separate experiment, the solid catalyst (entry 3) was filtered off from the reaction mixture (at 323 K) after 2 h (conversion = 29%) and the reaction was continued for a further 4 h (conversion after 6 h = 33%) with the resulting filtrate [which also had trace amounts (< 2 ppb) of metal]. No substantial increase in conversion was observed, clearly showing that the reactions are heterogeneously catalysed. [e] The TOF have not been calculated in these cases, as the conversions obtained here are non-catalytic. [f] Hexanal was used instead of benzaldehyde. [g] δ-Valerolactone.

latter is too large to gain access to the active site. (In addition, this clearly rules out the possibility of autoxidation by surface or transition metal impurities.) Further, to substantiate that the autoxidation of the aldehyde is shape-selective, we used the straight-chain hexanal, which is small enough to enter the 3.8 Å cages of the CoALPO-18 catalyst, as a sacrificial oxidant. The Baeyer–Villiger conversion of cyclohexanone to ε-caprolactone (Table 1, entry 8) freely ensues, because the hexanal gains ready access to the framework active sites and forms the peroxy acid. Thus, large-pore CoALPO-36 (or MnALPO-36) and CoAlPO-5 (or MnAlPO-5) catalysts offer easy access to bulky sacrificial oxidants (such as bezaldehyde), and oxidise a number of ketones, including adamantan-2-one, to their corresponding lactones with very high selectivity.

The implications are clear: the aldehyde is first converted by O_2 at the active sites to the corresponding peroxy acid inside the micropores, and this peroxy acid, in the manner first outlined by Criegee[5,13]—involving its initial nucleophilic attack at the carbonyl carbon—leads to the production of the lactone. In addition, as in our study of the selective oxidation of cyclohexane,[7] there appears to be a clear trend in the dependence of catalytic activity on the combination of the pore-dimension of the molecular sieve and the framework-substituted ion: the ATS structure shows higher conversion and selectivity compared to AFI, and Mn^{II} containing catalysts are slightly more active than their Co^{III} analogues. This agrees well with our estimation of the fraction of the metal ions that undergoes redox reaction.[11]

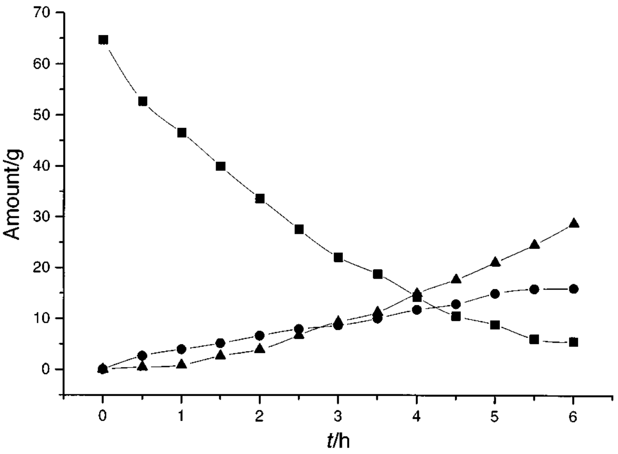


Fig. 2 Typical kinetics plot for the oxidation of cyclohexanone using MnAlPO-36, in the presence of air and benzaldehyde: (■) benzaldehyde, (●) caprolactone and (▲) benzoic acid. When the amount of aldehyde is decreased (cyclohexanone : benzaldehyde = 1 : 1), the rate of formation of the lactone decreases. We believe that the ketones compete with the aldehyde for access to the interiors of the micropores, thereby inhibiting the oxidation of the aldehyde to the peroxy acid.

In summary, a heterogeneous redox molecular sieve catalyst first of all converts the sacrificial aldehyde involved in the Mukaiyama reaction shape-selectively (inside the micropores of the catalyst) into the active peroxy acid. This peroxy acid then converts the cyclic ketone to the lactone (outside the catalyst).

Notes and references

† *Catalytic reactions.* The reactions were carried out in a high-pressure stainless steel catalytic reactor employing the conditions mentioned in Table 1. For other details see refs. 7 and 8.

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