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Cobalt-containing molecular sieves as catalysts for the low conversion autoxidation of pure cyclohexane. Part II. A kinetic study

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Abstract

In our preceding paper, we showed that cobalt substituted aluminophosphate molecular sieves can be successfully employed as active and truly heterogeneous autoxidation catalysts [D.L. Vanoppen, D.E. De Vos, M.J. Genet, P.G. Rouxhet, P.A. Jacobs, Angew. Chem., Int. Ed. Eng. 35 (1995) 560]. These solid catalysts show a higher selectivity for cyclohexyl hydroperoxide and an improved overall selectivity for mono-oxygenates when compared to a classic homogeneous cobalt naphthenate catalyst.

In this paper, oxygen uptake curves of the homogeneous and heterogeneous catalyzed reactions are fitted to a simplified kinetic expression. The solid catalysts exhibit a markedly different kinetic behavior when compared to the classic homogeneous catalyst. This difference in reaction kinetics may indicate a different reaction mechanism, but may be accounted for equally well by effects of sorption, competitive sorption and diffusion that are inherent to heterogenization of the cobalt ion on a microporous support.

Finally, this difference in kinetic behaviour explains the higher peroxide selectivity and overall selectivity that were observed using these heterogeneous catalysts.

Keywords: Autoxidation; Kinetics; Cyclohexanol and cyclohexanone; Heterogenization

1. Introduction

CoAPOs are aluminophosphate molecular sieves in which up to a few per cent of Al^{3+} is substituted by Co^{2+} [2–8]. CoAPO-5 has AFI-topology with 12 membered ring channels while CoAPO-11 has AEL-topology with only 10 membered ring channels. In CoAPO molecular sieves, like CoAPO-5 and CoAPO-11, it is presumed that cobalt is really substituting for aluminum and is present in tetrahedral coordination. Such samples, blue after synthesis, turn yellow or yellow-green after calcination at elevated temperatures (500°C) under oxygen. This has been understood as the oxidation of blue cobalt(II) to yellow cobalt(III) [6–8]. Others have suggested that these changes in color also might be due to a change in cobalt coordination [9]. Nevertheless, formation of oxidation products, radicals or radical cations upon reaction of calcined samples with organic substrates points to some switching between redox states [10].

While such CoAPO molecular sieves have been studied as solid acid catalysts [11–13], the incorporation of cobalt into aluminophosphate structures also opens a possible route toward heterogenization of

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cobalt autoxidation catalysis. Thus, CoAPO-5 and CoAPO-11 have been used as catalysts for the autoxidation of *p*-cresol to *p*-hydroxy-benzaldehyde in methanolic sodium hydroxide [14,15]; the autoxidation of alkanes, like cyclohexane and *n*-hexane in the presence of acetic acid [16–19] or the epoxidation of alkenes in the presence of sacrificial aldehydes [20]. However, as with other transition metals containing molecular sieves [21–24], in some cases, transition metal ions leached into solution under reaction conditions, may contribute to the catalytic activity [1,15,19].

The autoxidation of cyclohexane is an important bulk process [25–30], which is currently carried out in the presence of small amounts of dissolved cobalt salts. As oxidation products are more susceptible to oxidation than the substrate, conversion is to be kept low to obtain reasonable selectivities for mono-oxydates cyclohexanol and cyclohexanone. The homogeneous catalysts deactivate by precipitation. Besides technical advantages of catalyst heterogeneity, the catalyst activity, stability and selectivity are thus important factors to be considered in developing new heterogeneous catalysts for this process.

In our previous paper, we studied the autoxidation of cyclohexane in the presence of CoAPO-5 and CoAPO-11 molecular sieves, monitoring activity and selectivity by product formation and oxygen consumption [1]. When compared to a classic homogenous cobalt naphthenate catalyst, the most striking features of the solid catalysts were:

1. an improved stability;
2. a higher selectivity towards cyclohexyl hydroperoxide;
3. a higher overall selectivity (less side-product formation).

Site isolation resulting from incorporation of cobalt in the molecular sieve framework seemed to be critical for obtaining active and truly heterogeneous autoxidation catalysts. Up to a Co/(Co+Al) ratio of 0.01, catalytic activity increased steadily with cobalt content, while at higher loading discrepancies occurred that were attributed to cobalt leaching and/or clustering.

In the present paper, we studied the kinetics of these heterogeneous catalyzed reactions by fitting oxygen uptake to a simple kinetic expression.

2. Experimental

2.1. Catalyst preparation

CoAPO molecular sieves were prepared by hydrothermal synthesis, from gels with molar composition $2x\mathrm{Co(CH_3COO)_2{:}1P_2O_5{:}(1-}x\mathrm{)Al_2O_3{:}1.5Pr_3N{:}40H_2O}$ (CoAPO-5) or $2x\mathrm{Co(CH_3COO)_2{:}1P_2O_5{:}(1-}x\mathrm{)Al_2O_3{:}1Pr_2NH{:}40H_2O}$ (CoAPO-11) ($0<x<0.04$), in an autoclave under autogeneous pressure at 150°C for 24 h (CoAPO-5) or 175°C for 72 h (CoAPO-11). Gels were cooled during preparation. Crystallinity and cobalt incorporation were checked by X-ray diffraction and DRS. SEM-photographs showed that the CoAPO-5 samples consisted of large (3–6 μm) hexagonal prismatic crystals. CoAPO-11 samples contained mainly rosette-like aggregates (2–4 μm) of small crystals (1 μm).

2.2. Autoxidation reactions

All catalysts were calcined overnight at 500°C under oxygen flow prior to use. Autoxidation experiments were carried out in a 300 ml stainless steel Parr pressure reactor, passivated using a saturated sodium pyrophosphate solution [31,32], using 0.5 g of catalyst, 75 ml of cyclohexane and the headspace was filled with oxygen under a total pressure of 1 MPa, allowing a conversion of approximately 10%. After reaction, the catalyst was filtered off and reactor and catalysts were washed with 75 ml of acetone, to dissolve adipic acid or other precipitated products. The product mixture and the acetone were added together and analyzed by GC (CP-sil5 column, Chrompack). The following products were detected: cyclohexanol, cyclohexanone, cHHP, caprolactone, adipic, glutaric, succinic, caproic, valeric and butyric acids. Deficiency in the oxygen mass balance can be ascribed to formation of GC invisible esters. Therefore, oxygen efficiency for mono-functionalization ($E_{\mathrm{monof.}}$) calculated as (mol cHHP+mol ketone+ $0.5x$ mol alcohol)/(mmol oxygen consumed) was taken as a measure for overall selectivity for mono-oxygenates. As cHHP partially decomposed upon injection, its concentration was estimated by double analysis, before and after reducing cHHP to cyclohexanol with $\mathrm{Ph_3P}$ [33].

2.3. Kinetic analysis

The pressure drop as a function of time during the reaction was taken as a measure of oxygen consumption and fitted to the exponential expression $P(t)=C-A\exp(Bt)$ using the program Origin 2.8 (Microcal) and the obtained kinetic factors A and B were recalculated to mM (A) and s^{-1} (B).

3. Results and discussion

3.1. Development and evaluation of the kinetic model

In autoxidation reactions, free radical chain reactions primarily produce hydroperoxides, which through homolytic decomposition start off more free radical chains (Scheme 1). It is therefore hardly surprising that, unless an excess of initiator is applied, reactions are autocatalytic, with steadily increasing reaction rates. This is even more so because secondary products, resulting from termination, can contribute to an increase in reaction rate.

During this work, we observed that the evolution of the pressure in our batch reactor during autoxidation reactions can be fitted to an exponential expression:

$$P = C - A\exp(Bt). \tag{1}$$

The decrease in pressure can be taken as a measure of the consumption of oxygen during the reaction. Tables 1 and 2 show results obtained by fitting pressure curves in reactions at 130°C and 147°C, and recalculating the values to S.I. units.

Initiation:

$$In_2 \xrightarrow[k_{i,1}]{} 2In^\bullet \qquad \text{(a)}$$

$$In^\bullet + RH \longrightarrow InH + R^\bullet \qquad \text{(b)}$$

$$ROOH \xrightarrow[k_{i,2}]{} RO^\bullet + {}^\bullet OH \qquad \text{(c)}$$

$$\left|\begin{matrix} RO^\bullet \\ {}^\bullet OH \end{matrix}\right| + RH \longrightarrow \left|\begin{matrix} ROH \\ HOH \end{matrix}\right| + R^\bullet \qquad \text{(d)}$$

Propagation:

$$R^\bullet + O_2 \longrightarrow ROO^\bullet \qquad \text{(e)}$$

$$ROO^\bullet + RH \xrightarrow[k_p]{} ROOH + R^\bullet \qquad \text{(f)}$$

Termination

$$2ROO^\bullet \xrightarrow[k_t]{} NRP + O_2 \qquad \text{(g)}$$

Scheme 1. General pathways in free radical chain oxidation. NRP=non-radical products.

The general trend in the kinetic data is that addition of initiator results in an increase in the pre-exponential factor A, while addition of cobalt naphthenate results in an increase in B, accompanied by a decrease in A.

We started looking for a simplified non-steady-state solution for the general rate equations for autoxidation reactions, that would have the general form (1) and would reflect the trends observed. In Scheme 1 the rate determining steps are indicated by their rate constants k.

Table 1
Autoxidation of cyclohexane at 145°C at constant conversion (3.5%)

Reaction mixture	$t_{3.5}$ (min)[a]	S_{cHHP} (%)[b]	$E_{\mathrm{monof.}}$ (%)[c]	A (mM)[d]	B (10^{-3} s^{-1})[d]
75 ml cyclohexane	310	65±3	87±5	8.9	0.19
+100 ppb Co	140	42	59	4.0[e]	0.62[e]
+1 ppm Co	70	30	51	1.5[f]	2.5[f]
+5 ml oxidate	190	61	84	22	0.20
+10 ml oxidate	175	60	79	34	0.21

Cobalt naphthenate was added as a homogeneous catalyst. Oxidate (obtained in a blank reaction) was added as an initiator.

[a] Time needed to reach a conversion of ±3.5%.

[b] Selectivity for cyclohexyl hydroperoxide.

[c] Oxygen efficiency for monofunctionalization.

[d] Kinetic parameters A and B.

[e] Only the first 90 min of reaction were considered.

[f] Only the first 45 min of reaction were considered.

Table 2
Autoxidation of cyclohexane at 130°C in the presence of homogeneous cobalt naphthenate catalyst

[Co]	50 ppb	100 ppb	250 ppb	500 ppb	33 ppm	33 ppm
X(%)[a]	<0.005	0.34	1.55	2.45	4.6	4.9
S_{cHHP} (%)[b]	–	90	60	28	21	10
$E_{\mathrm{monof.}}$ (%)[c]	–	88	85	64	48	46
A (mM)[d]	–	–	5.1	3.5	–	–
B (10^{-3} s^{-1})[d]	–	–	0.17	0.28	–	–

[a] Conversion after 5 h of reaction.
[b] Selectivity for cyclohexyl hydroperoxide.
[c] Oxygen efficiency for monofunctionalization.
[d] Kinetic parameters A and B.

The resulting rate equations are

$$\delta[\mathrm{ROO}^\bullet]/\delta t = 2k_{i,1}[\mathrm{In}] + 2k_{i,2}[\mathrm{ROOH}] - k_t[\mathrm{ROO}^\bullet]^2 \quad (2)$$

$$\delta[\mathrm{ROOH}]/\delta t = k_\mathrm{p}[\mathrm{RH}][\mathrm{ROO}^\bullet] - k_{i,2}[\mathrm{ROOH}] \quad (3)$$

$$\delta[\mathrm{O_2}]/\delta t = -k_\mathrm{p}[\mathrm{ROO}^\bullet] + k_\mathrm{t}[\mathrm{ROO}^\bullet]^2 \quad (4)$$

When assuming (i) termination to be negligible in Eqs. (2) and (3); (ii) peroxide consumption to be negligible in Eq. (3); and (iii) $\exp\left(\sqrt{2k_{i,2}k_\mathrm{p}[\mathrm{RH}]t}\right) \gg 1$, an analytical solution of this set of different equations can be obtained:[1]

$$[\mathrm{O_2}] = [\mathrm{O_2}]_0 + \frac{1}{2}\left([\mathrm{ROOH}]_0 + \frac{k_{i,1}[\mathrm{In}]}{k_{i,2}}\right) - \frac{1}{2}\left([\mathrm{ROOH}]_0 + \frac{k_{i,1}[\mathrm{In}]}{k_{i,2}}\right)\exp\left(\left(2k_{i,2}\cdot k_\mathrm{p}[\mathrm{RH}]\right)^{1/2}t\right). \quad (5)$$

In this expression, the values of the A and B factor are theoretically equal:

$$A = \frac{k_{i,1}[\mathrm{In}]}{2k_{i,2}} + \frac{1}{2}[\mathrm{ROOH}]_0 \quad (6)$$

$$B = \sqrt{2k_\mathrm{p}[\mathrm{RH}]k_{in,2}} \quad (7)$$

It should be noted that the model can be expanded with any other initiating reactions, that is of order zero in peroxide produced (and hence contributing to A) or of first-order in peroxide produced (and hence increasing B and decreasing A).

$$ROOH + M^{n+} \rightarrow RO^\bullet + \left[M^{(n+1)+}\cdot{}^{-}OH\right]$$

$$ROOH + \left[M^{(n+1)+}\cdot{}^{-}OH\right] \rightarrow ROO^\bullet + M^{n+} + H_2O$$

$$2ROOH \xrightarrow[M^{n+}/M^{(n+1)+}]{} ROO^\bullet + RO^\bullet + H_2O$$

Scheme 2. The Haber–Weiss catalytic pathway for the decomposition of hydroperoxides by transition metal ions.

These values are in good agreement with the obtained results: adding initiator $[\mathrm{ROOH}]_0$ or [In] leads to an increase in A, while adding a cobalt salt, that catalyzes homolytic peroxide decomposition (Scheme 2) and hence an increase in $k_{\mathrm{in},2}$, leads to an increase in B and a decrease in A.

However, in view of the simplifications made, extreme caution should be taken when applying this rate expression.

Firstly, the pressure curves do not only reflect oxygen uptake, but may be influenced by changing vapor pressures of reactants and products during reaction. At the low conversions used in this study, this should not result in major deviations. Furthermore, it can be checked by using numerical values that the condition $\exp\left(\sqrt{2k_{i,2}k_\mathrm{p}[\mathrm{RH}]}\cdot t\right) \gg 1$ in our reactions is fulfilled before any measurable pressure drop occurs in the reactor.

Neglecting termination presents a more serious problem. In principle this should lead to an overestimation of the reaction rate and hence to a serious deviation of the exponential behavior. Surprisingly, this was not observed: except in the case of high concentration of homogeneous catalyst (where a steady state was reached), an almost perfect fit was obtained in all reactions. On the other hand, the

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[1] A detailed mathematical description is available from the authors.

promoting effect of oxidation products, especially cyclohexanone [28], was not included in the model either. This should lead to a serious underestimation of the reaction rate. Apparently, these two effects more or less compensate one another, resulting at least in a qualitative agreement between the data and the model.

The strong points of the model are that it fits accurately to the experimental pressure curves and correctly predicts the general trends observed. Furthermore, a virtually unlimited number of data points can be recorded during reaction and used for kinetic analysis. (All the kinetic fits presented were based on over 200 data points.)

Therefore we believe that such a kinetic analysis can provide new qualitative insights in autoxidation pathways and in the effects of heterogenization on the kinetics of transition metal catalyzed autoxidations.

3.2. Relation between kinetics and selectivity

A general trend in Tables 1 and 2 is that the peroxide selectivity is lower when the reaction proceeds faster. This is not unexpected, as oxygen uptake is first-order in [ROO$^\bullet$] and termination second-order in [ROO$^\bullet$]. The faster the reaction, the higher the [ROO$^\bullet$] and hence more termination. More termination products (cyclohexanol and cyclohexanone) result in a lower selectivity for the hydroperoxide.

More surprisingly, this apparently depends on the actual kinetics as well, the decrease in peroxide selectivity being more pronounced in experiments with a high value for B and a low value for A, i.e., the cobalt naphthenate catalyzed reactions. A simple computer simulation (Fig. 1(a)) can illustrate this relationship between kinetics and selectivity by assuming exponential kinetics and numerically integrating [ROO$^\bullet$]^2.

The reason for this relationship is obvious from Fig. 1(b). In the first case, high A and moderate B, the reaction takes off smoothly and during the whole of the reaction moderate rates are observed. Hence [ROO$^\bullet$] is moderate during the whole of the reaction, and not too much termination occurs. In the second case, with a high value for B and low A, the reaction rate is very low at the beginning and the rate (and hence ROO$^\bullet$ concentration) at the end of the reaction is very high and hence more termination takes place. It should be noted that this effect results directly from the fact that propagation is first-order in [ROO$^\bullet$] and termination second-order. The validity of this reasoning depends only on the kinetics of oxygen uptake being exponential and is independent of the accuracy of our kinetic model. The results in Fig. 2 are in good agreement with the predictions in Fig. 1(a).

Tables 1 and 2 show a second general trend: the lower the peroxide selectivity, the lower the overall selectivity for mono-oxygenates. This well-known behavior results directly from the fact that cyclohexanone, formed during termination, is much more

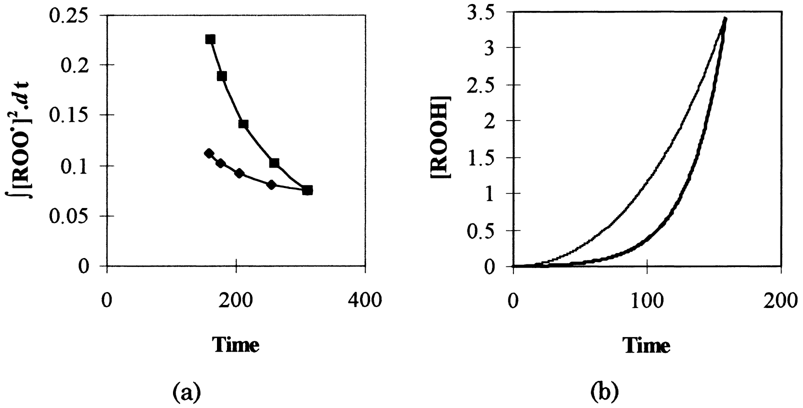

Fig. 1. Computational simulations obtained by numerical integration: (a) value obtained for numerical integration of [ROO$^\bullet$]^2·dt as a function of time needed to reach a value of 3.4 for [ROOH]. The upper curve (■) results from systematically increasing $k_{i,2}$, while the lower curve (◆) results from increasing $k_{i,1}$·[In]. (b) Evolution of [ROOH] formation. The upper curve results from using a high value for $k_{i,1}$·[In], the lower from using a high value for $k_{i,2}$.

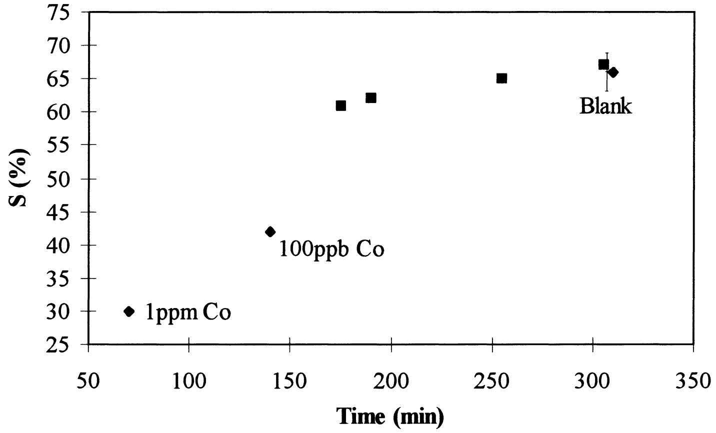

Fig. 2. Autoxidation of cyclohexane at 145°C in the presence of increasing amounts of initiator (■) or cobalt naphthenate (◆). Peroxide selectivity as a function of time required for reaching a conversion of 3.5%.

susceptible to further oxidation than cyclohexane or cyclohexyl hydroperoxide [28].

3.3. *Kinetics of autoxidation catalyzed by CoAPO-5 and CoAPO-11*

Up to a Co/(Co+Al) ratio of 0.01, in the case of CoAPO-5, factors *A* and *B* increase simultaneously with cobalt content (Fig. 3). Using CoAPO-11, the factor *A* increases with cobalt content, the *B* factor remains constant.

The increase in *A* is quite unexpected and may point to a shift in mechanism with respect to the homogeneous case. The direct electron transfer between Co^{III} and organic substrates in strongly acidic solution [34–36]; and even alkanes (in the presence of acetic acid) [19] or alkenes [10] in CoAPOs has been reported. However, we were unable to find convincing evidence for such a reaction with cyclohexane, without an additional acid present. Moreover, it should be clear that the peroxides present during reaction are far better electron donors (acceptors) than cyclohexane (oxygen).

On the other hand, the kinetic behavior can be rationalized equally well by factors that are inherent to the heterogenization of cobalt ions on a microporous support. As stated earlier, the increase in A may result from any initiation process that is not proportional to the peroxide concentration during reaction. Effects of sorption, competitive sorption and diffusion may lead to a situation where the actual rate of homolytic peroxide decomposition is no longer first-order in peroxide concentration, even if the mechanism is unchanged. Such effects may be

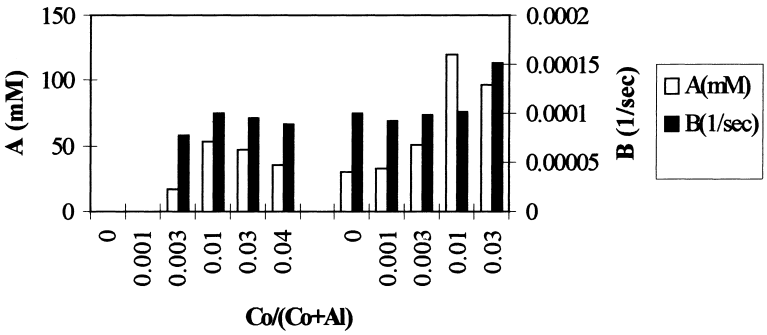

Fig. 3. Autoxidation of cyclohexane in the presence of CoAPO-5 or CoAPO-11 with varying Co/(Co+Al). 130°C, 5 h, 1 MPa O_2 initial pressure. Kinetic parameters A and B obtained by fitting the experimental pressure curves to $P(t)=C-A\exp(B(t-t_0))$.

expected when converting a non-polar substrate into hydrophylic products over a hydrophylic, microporous catalyst.

We observe that whatever the case, it is clear that this change in kinetic behavior with respect to homogeneous catalysis readily explains the higher peroxide selectivity and overall selectivity for mono-oxygenates.

At high cobalt loadings the kinetic parameters confirm the differences between AFI and AEL type catalysts reported earlier [1]. At a Co/(Co+Al) ratio of 0.03, A suddenly decreases and B increases in the case of CoAPO-11, while using CoAPO-5, A and B start to decrease simultaneously. These sudden changes are accompanied by substantial leaching of cobalt into solution. The changes observed for CoAPO-11 are therefore consistent with a significant homogeneous contribution to the catalysis, while in the case of CoAPO-5 free cobalt seems to lead to inhibition of the reaction. We observed a similar difference between the behavior of cobalt-exchanged Y and ZSM-5 type zeolites, the former resulting in inhibition, the latter showing typical kinetic features of homogeneous cobalt catalysis.

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References

[1] D.L. Vanoppen, D.E. De Vos, M.J. Genet, P.G. Rouxhet, P.A. Jacobs, Angew. Chem., Int. Ed. Eng. 35 (1995) 560.

[2] S.T. Wilson, E.M. Flanigen, US Patent 4 567 029 (1986).

[3] E.M. Flannigen, B.M. Lok, R.L. Patton, S.T. Wilson, in: Y. Murakami, A. Iijima, J.W. Ward, Proceedings of the Seventh International Zeolite Conference, Tokyo, 1986, Kodansha-Elsevier, Tokyo, 1986, p. 103.

[4] L.E. Iton, I. Choi, J.A. Desjardins, V.A. Maroni, Zeolites 9 (1989) 535.

[5] R.A. Schoonheydt, R. de Vos, J. Pelgrims, H. Leeman, Stud. Surf. Sci. Catal. 49 (1989) 559.

[6] S. Ernst, L. Puppe, J. Weitkamp, in: P.A. Jacobs, R.A. van Santen (Eds.), Zeolites: Facts, Figures, Future, Elsevier, Amsterdam, 1988, pp. 447–458.

[7] C. Montes, M.E. Davis, B. Murray, M. Narayana, J. Phys. Chem. 94 (1990) 6425.

[8] B. Kraushaar-Czarnetzki, W.G.M. Hoogervorst, R.R. Andréa, C.A. Emeis, W.H.J. Stork, J. Chem. Soc., Faraday. Trans. 87 (1991) 891.

[9] H. Berndt, A. Martin, Y. Zhang, Micropor. Mater. 6 (1996) 1–12.

[10] Y.-J. Lee, H. Chon, J. Chem. Soc., Faraday Trans. 92 (1996) 3453–3457.

[11] N.J. Tapp, N.B. Milestone, J. Chem. Soc. Chem. Commun., 1985, p. 1801.

[12] J. Chen, J.M. Thomas, J. Chem. Soc. Chem. Commun., 1994, p. 603.

[13] J.M. Thomas, Angew. Chem. 106 (1994) 936.

[14] J. Dakka, R.A. Sheldon, Netherl. Pat. NL A 9200968 (1992).

[15] M.P.J. Peeters, M. Busio, P. Leijten, Appl. Catal. A 118 (1994) 51–62.

[16] B. Kraushaar-Czarnetzki, W.G.M. Hoogervorst, Eur. Pat. Appl. 0519569A2 (1992).

[17] S-S. Lin, H-S. Weng, Appl. Catal. A 105 (1993) 289.

[18] S-S. Lin, H-S. Weng, Appl. Catal. A 118 (1994) 21–31.

[19] B. Kraushaar-Czarnetzki, W.G.M. Hoogervorst, W.H.J. Stork, Stud. Surf. Sci. Catal. 84 (1994) 1869.

[20] H.F.W.J. van Breukelen, M.E. Gerritsen, V.M. Ummels, J.S. Broens, J.H.C. van Hooff, Stud. Surf. Sci. Catal. 105 (1996) 1029–1036.

[21] P.R. Hari Prasad Rao, A.A. Belhekar, S.G. Hedge, A.V. Ramaswamy, P. Ratnasamy, J. Catal. 141 (1993) 595–603.

[22] B.I. Whittington, J.R. Anderson, J. Phys. Chem. 97 (1993) 1032–1041.

[23] H.E.B. Lempers, R.A. Sheldon, Stud. Surf. Sci. Catal. 105 (1996) 1061–1068.

[24] M.J. Haanepen, A.M. Elemans-Mehring, J.H.C. van Hooff, Appl. Catal. A 152 (1997) 203–219.

[25] R.A. Sheldon, J.K. Kochi, Metal-catalysed Oxidations of Organic Compounds, Academic Press, New York, 1981.

[26] G. Franz, R.A. Sheldon, in: Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim vol. A18, 1986, pp. 261–311.

[27] J.E. Lyons, Appl. Ind. Catal. 3 (1984) 131–214.

[28] C.A. Tolman, J.D. Druliner, M.J. Nappa, N. Herron, in: C.L. Hill (Ed.), Activation and Functionalization of Alkanes, Wiley, New York, 1989, pp. 303–360.

[29] M.T. Musser, in: Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, vol. A8, 1986, pp. 217–226.

[30] T. Mill, D.G. Hendry, in: C.H. Bamford, C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, vol. 16: Liquid-Phase Oxidation, Elsevier, Amsterdam, 1980, pp. 1–88.

[31] K. Tanaka, J. Imamura, Chem. Lett., 1974, p. 1347.

[32] U. Schuchardt, W.A. Carvalho, E.V. Spinacé, Synlett, 1993, p. 713.

[33] G.B. Shul'pin, D. Attanasio, L. Suber, J. Catal. 142 (1993) 147.

[34] J. Hanotier, M. Hanotier-Bridoux, J. Mol. Catal. 12 (1981) 133–147.

[35] E.I. Heilba, R.M. Dessau, W.J. Koehl, J. Am. Chem. Soc. 91 (1969) 6830–6837.

[36] J. Hanotier, Ph. Camerman, M. Hanotier-Bridoux, P. de Radzitzky, Low-temperature oxidation of *n*-alkenes by cobaltic acetate activated by strong acids, J. Chem. Soc., Perkin II, (1972) 2247–2252.