Increasing the Ketone Selectivity of the Cobalt-Catalyzed Radical Chain Oxidation of Cyclohexane

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Dedicated to Professor Sir John Meurig Thomas on the occasion of his 70th birthday

Abstract: A variety of heterogeneous catalysts for the radical chain oxidation of cyclohexane has been prepared by immobilization of the well-defined cobalt acetate oligomers $[py_3Co_3(\mu_3\text{-}O)(OH)(O_2CCH_3)_5](PF_6)$ (**1**) and $[py_4Co_2(OH)_2(O_2CCH_3)_3](PF_6)$ (**2**) on carboxy-modified mesoporous silica supports **A**–**D** by carboxylate exchange. The catalytic oxidation of cyclohexane with *tert*-butyl hydroperoxide (TBHP) in the presence of these homogeneous and immobilized cobalt acetate complexes afforded the corresponding alcohol and ketone in high yield. The immobilization of **1** and **2** results in a significant increase of catalytic activity. TBHP acts as a radical initiator and as source of molecular oxygen, which is also involved in the overall oxidation process. The rate of cyclohexane conversion is limited by the diffusion of molecular oxygen, and steady-state concentrations of cyclohexanone (K, ketone) and cyclohexanol (A, alcohol) are established; these determine the maximum K:A ratio.

Keywords: carboxylate ligands · cobalt · heterogeneous catalysis · immobilization · oxidation · mesoporous materials

Introduction

The aerobic oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone (the so-called K–A oil), under mild conditions is of great industrial significance, since these two products are intermediates in the manufacture of nylon-6 and nylon-6,6.[1] The worldwide production of cyclohexanol and cyclohexanone exceeds 10^6 tonnes per year. Industrially, cyclohexane is oxidized at 398–438 K and 8–15 bar air to give an initial mixture of alcohol, ketone, and the intermediate cyclohexylhydroperoxide (CHHP), which is decomposed either directly or in a separate step to yield additional ketone and alcohol.[2] Cobalt carboxylate complexes are the most widely employed homogeneous catalysts to achieve these transformations. However, the application of these homogeneous catalysts is restricted by their generally short lifetime. The role of cobalt acetate as catalyst in the catalytic process has been studied intensely,[3] and it is now well-established that "cobalt(III) acetate" consists of various combinations of monomers, dimers, trimers, and mixed-valence trimers.[4] However, the well-defined oligomers $[py_3Co_3(\mu_3\text{-}O)(OH)(O_2CCH_3)_5](PF_6)$ (**1**) and $[py_4Co_2(OH)_2(O_2CCH_3)_3](PF_6)$ (**2**) have been isolated in high yields from cobalt acetate solutions in the presence of pyridine (py).[5]

It is equally well-established that the autoxidation of cyclohexane proceeds by free-radical pathways (Scheme 1). However, the high degree of complexity of these reactions is very challenging, and (predictive) chemical models of the overall oxidation process are evolving only slowly.[6]

Initiation by Haber–Weiss decomposition of hydroperoxides

$$ROOH + Co^{III} \longrightarrow ROO\bullet + Co^{II} + H^+ \quad (1)$$

$$ROOH + Co^{II} \longrightarrow RO\bullet + Co^{III} + OH^- \quad (2)$$

Propagation

$$ROO\bullet + c\text{-}C_6H_{12} \longrightarrow ROOH + c\text{-}C_6H_{11}^\bullet \quad (3)$$

$$RO\bullet + c\text{-}C_6H_{12} \longrightarrow ROH + c\text{-}C_6H_{11}^\bullet \quad (4)$$

$$c\text{-}C_6H_{11}^\bullet + O_2 \longrightarrow c\text{-}C_6H_{11}OO\bullet \quad (5)$$

Termination

$$ROO^\bullet + R'^\bullet \longrightarrow ROOR'^\bullet \quad (6)$$

$$2\,c\text{-}C_6H_{11}OO\bullet \longrightarrow c\text{-}C_6H_{11}OH + c\text{-}C_6H_{10}O + O_2 \quad (7)$$

R, R' = *t*Bu, *c*-C_6H_{11}

Scheme 1. Radical chain oxidation of cyclohexane.

Conversions in the industrial process have to be limited to a maximum of below 10%, to avoid overoxidation to other, unwanted products, since the desired products, cyclohexanol

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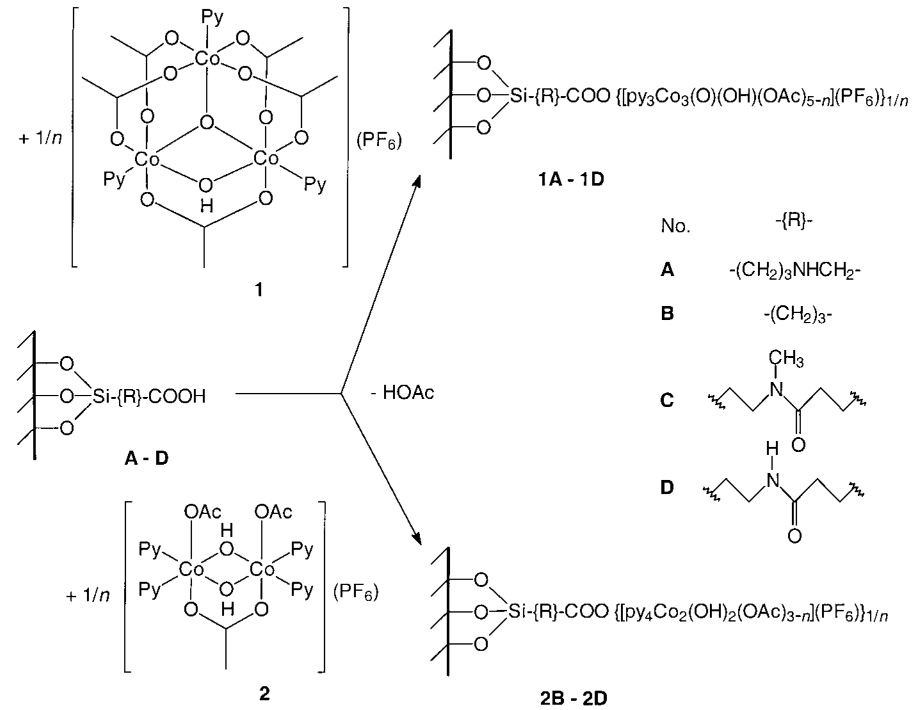
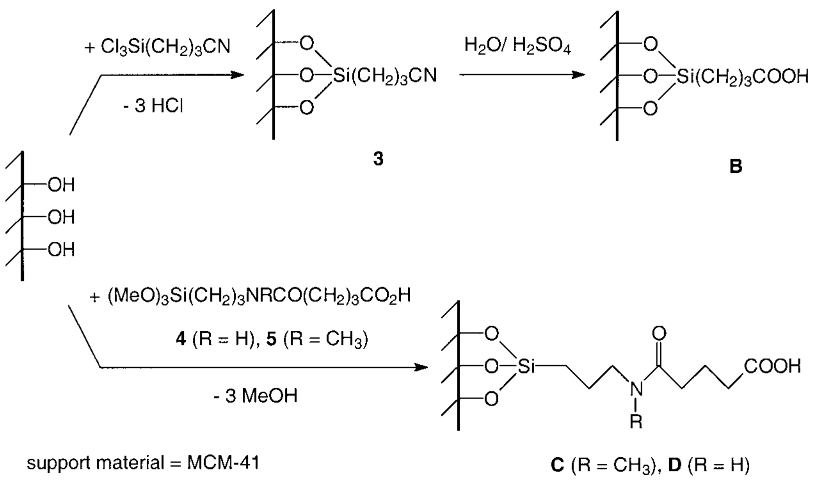
and cyclohexanone, are more readily oxidized than cyclohexane itself. Another drawback of the industrial process is the fact that the cyclohexanol produced has to be subsequently converted into the desired product cyclohexanone, which represents an additional step. Thus, an increase of the ketone:alcohol ratio (K:A), which is generally close to 1 in the industrial production, would mean a significant improvement of the overall process.



Scheme 2. Immobilization of oligonuclear cobalt acetate complexes on carboxy-functionalized MCM-41.

In a preceding study, it was demonstrated that the immobilization of the well-defined trinuclear cobalt acetate **1** inside the channels of the hexagonal mesoporous support MCM-41, which had been functionalized with carboxylic acid surface grafts, results in a durable and selective catalyst **1A** for the oxidation of cyclohexane (Scheme 2).[7] Moreover, this immobilized catalyst exhibited a high selectivity for cyclohexanone in a catalytic system which employed *tert*-butyl hydroperoxide (TBHP) as a sacrificial oxidant and no solvents other than the substrate cyclohexane. The use of **1** had been prompted by the observation that this cobalt acetate oligomer had shown promising selectivities in the catalytic oxidation of adamantane.[8] However, the catalytic behavior of the homogeneous complex **1** and of other cobalt acetate oligomers in the cyclohexane/TBHP system has not been reported so far. Therefore, we present herein the results of our study on the performance of the homogeneous cobalt acetate oligomers **1** and **2** in comparison to their respective immobilized analogues on a variety of carboxylate-modified silica supports.

In the preceding study,[7] the functionalization of the support surface was effected by derivatizing previously grafted 3-bromopropylsilane tethers with glycine. However, the low efficiency of the reaction between the amine part of the glycine and the bromoalkyl group limited the degree of glycine derivatization and, hence, the loading of the modified support with the catalyst complex. The target of the present study was to overcome this limitation by developing new, more efficient pathways of derivatizing MCM-41 with carboxylic acid grafts and, thereby, to achieve a higher loading of the support with the oligonuclear cobalt acetate complex. Moreover, we wished to study the influence of the nature of the immobilized cobalt acetate complex and to gain a deeper insight into the solvent-free cyclohexane/TBHP system in an attempt to optimize the achievable K:A ratio.



Scheme 3. Preparation of novel carboxy-functionalized MCM-41 derivatives.

Results and Discussion

Our first approach towards the synthesis of a carboxy-functionalized mesoporous support comprised the acid-catalyzed hydrolysis of 3-cyanopropyl-grafted siliceous MCM-41 (**3**), which had been obtained from a reaction of the mesopore with 3-(trichlorosilyl)butyronitrile (Scheme 3). The grafted compound **3** was converted into the carboxylate derivative **B** by treatment with aqueous sulfuric acid at 150 °C in an analogous manner to a reported procedure for functionalizing a cyanoalkyl-modified silica surface with carboxylic acid groups.[9] However, the harsh conditions of the hydrolysis step resulted in a partial collapse of the mesoporous support during the synthesis of **B**. This mesopore collapse manifested itself in a reduction of the BET surface area A_{tot} from 975 to 690 $m^2 g^{-1}$, and in a reduction of the average pore diameter D_{av} from 24 to 22 Å, as determined before and after hydrolysis, respectively. An alternative, a more gentle approach for functionalizing the mesopore surface with carboxylic acid grafts is represented by the reaction of MCM-41 with the linker **4**, which afforded the modified support **D**. Linker **4**, which itself is accessible through the ring-opening aminolysis of glutaric anhydride by 3-aminopropyltrimethoxysilane,[10] cannot be stored indefinitely because it undergoes slow polymerization as a result of carboxylic acid attack at the trialkoxysilane terminus. Therefore, it has to be freshly prepared before the immobilization step. An analogous reaction of glutaric anhydride with 3-(methylamino)propyltrimethoxysilane afforded the N-methyl derivative **5**, which in turn was grafted onto MCM-41 to give support **C**. The kinetically controlled protection of the silanol groups on the external surface of MCM-41 with an equivalent quantity of dichlorodimethylsilane[7] guaranteed the location of the subsequently introduced carboxylic acid grafts inside the mesoporous channels in all of the novel modified supports. Moreover, any residual silanol groups on the surface of the carboxy-derivatized mesoporous supports **B** and **C** were protected by reaction with excess dimethoxydimethylsilane. However, in case of derivative **D**, the residual silanol groups and the amide proton were left unprotected for an assessment of the influence of these weakly acidic sites on the course of the catalytic reaction.

For the immobilization of the cobalt acetate oligomers **1** and **2** on the carboxylate-modified supports, we utilized the tendency of the bridging acetate ligands in these complexes to undergo exchange reactions with other carboxylic acids (see Scheme 2).[5b] However, an irreversible anchoring of **1** and **2** by a partial ligand exchange with surface-tethered carboxy groups requires the removal of the released acetic acid from the equilibrium. The immobilization was, thus, carried out by stirring the respective cobalt acetate complex with an excess of the carboxy-functionalized support in boiling $CHCl_3$, while the released acetic acid was trapped in the gas phase by passing the reflux through a Soxhlet thimble filled with anhydrous Na_2CO_3. Any residual, physically adsorbed cobalt acetate was subsequently removed by Soxhlet extraction of the as-prepared material with CH_2Cl_2. The application of this procedure on all possible permutations of cobalt acetate complexes and carboxy-functionalized supports afforded the series **1B–D** of immobilized trinuclear complex **1** and the series **2B–D** of immobilized dinuclear complex **2** (Scheme 2). Under identical reaction conditions, the extent of cobalt acetate incorporation, expressed by the Co content determined by X-ray fluorescence (XRF) analysis, spanned the range between 0.237 and 0.925 wt% for **2C** and **1B**, respectively. Hence, the loadings achieved by this immobilization procedure generally exceed the Co content of 0.189 wt% determined for a sample of **1A** that was prepared in accordance with the previously reported procedure.

The homogeneous cobalt acetate oligomers **1** and **2**, and all immobilized catalysts **1A–1D** and **2B–2D** were subjected to catalytic cyclohexane oxidation tests in the presence of TBHP under conditions similar to those of the original report. In agreement with the reported behavior for the catalytic system involving **1A**, cyclohexanone, after an initial phase of predominant production of cyclohexanol, represents the principle product in all systems studied. A comparison of the catalytic runs with either the homogeneous complexes **1**, **2**, or the immobilized catalyst **1B** (performed in the presence of equimolar quantities of Co), reveals some significant differences in the catalytic performance (Figure 1). Both homogeneous cobalt acetate catalysts exhibit inferior activities under the conditions applied, as indicated by the lower rate of ketone and alcohol formation relative to the immobilized counterpart **1B**. Furthermore, this reduced ability of the homogeneous catalysts to catalyze the decomposition of peroxide intermediates leads to relatively higher concentration of CHHP, which represents the main product in the reaction mixture of both **1** and **2** at runtimes under 2200 and 1200 min, respectively. The higher activity of the immobilized catalyst **1B** may be explained by the high dispersion of complex **1** on the support surface, while the low solubility of **1** and **2** in the reaction medium might prevent a complete dissolution of the homogeneous complexes under the reaction conditions employed.

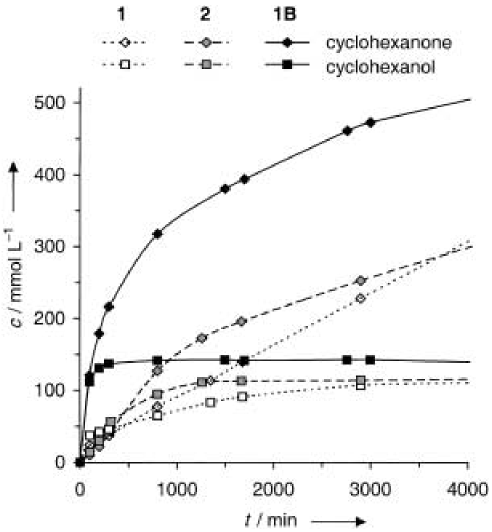


Figure 1. Comparison of the course of the catalytic oxidation of cyclohexane with TBHP in presence of cobalt acetate oligomers **1** and **2** and immobilized catalyst **1B**, respectively. A quantity of 2.6 $mmol L^{-1}$ of Co was present in all reactions.

An accurate monitoring of the TBHP concentration revealed that all catalytic systems underwent an initial phase of rapid TBHP decomposition, accompanied by vigorous evolution of molecular oxygen, which in some cases resulted in the complete consumption of TBHP and termination of the catalytic cyclohexane conversion. This initial TBHP decomposition activity decreased rapidly within the first hour. Addition of neat TBHP after that time did result in further hydroperoxide decomposition, but not at the initial rate. A simple concentration dependence of the TBHP decomposition rate must therefore be excluded, while a change in the activity pattern resulting from a structural change of the catalyst complex is a more likely explanation. Hints for such structural changes were found in an in situ EXAFS study on **1A** in the active state.[7] A modification of the experimental procedure by direct addition of half of the oxidant at the start, followed by the gradual addition of the second half during the first hour of the catalytic experiment left a sufficient concentration of TBHP at the end of the initial phase of rapid decomposition to guarantee further cyclohexane conversion.

The decomposition of large amounts of TBHP under formation of molecular oxygen does not represent an unproductive loss of the oxidant. Volumetric monitoring of the released gas revealed that the amount of dioxygen reaches a maximum shortly after the end of the initial TBHP decomposition phase after ≈150 min. Subsequently, it is consumed again in the course of the catalytic cyclohexane oxidation. The formation, as well as consumption, of dioxygen is indicative of a catalytic system that proceeds via free-radical chains, which originate from a Haber–Weiss hydroperoxide decomposition cycle[11] (Scheme 1, Eqs. (1) and (2)) and partially terminate in Russell recombination steps[12] (Scheme 1, Eq. (7)). This underlying mechanism also explains the formation of the detected monooxygenated products CHHP, cyclohexanol, cyclohexanone, and of the coupling products *tert*-butylcyclohexylperether (TBCP) and *tert*-butyl peroxide (TBP), while the detected adipic acid (AA) represents the principal product of overoxidation.[2, 3] The typical variation of the concentrations of these compounds during the course of the catalytic reaction, exemplified by a reaction that employed catalyst **1B**, is represented in Figure 2.

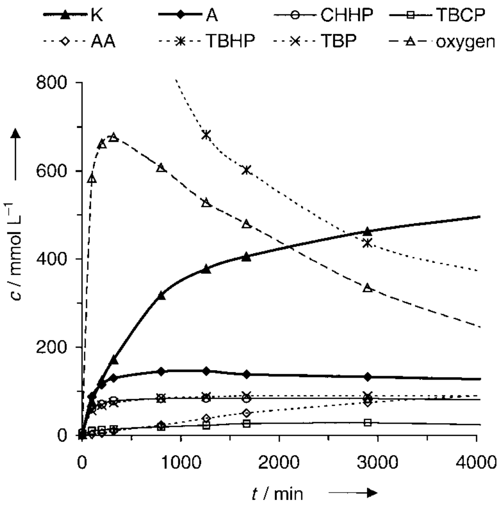


Figure 2. Course of the oxidation of cyclohexane with TBHP in the presence of immobilized catalyst **1B**. The amount of released molecular oxygen is given with respect to the liquid volume of the reaction mixture to facilitate comparison.

The initially high rate of cyclohexanol formation decreases in all systems investigated until the cyclohexanol concentration reaches a steady-state level of 160 ± 5 mmol L^{-1}. The steady-state nature of this limiting concentration has been confirmed in a separate experiment by the addition of excess cyclohexanol to a catalytic run involving catalyst **1B**. Consequently, the system responded by a relaxation of the elevated alcohol concentration towards the original steady-state value (Figure 3 a), thereby indicating the consumption of cyclohexanol in subsequent oxidation steps. The CHHP and TBP concentrations adopt similar steady-states in all catalytic systems within the first 500 min of the catalytic reaction. The cyclohexanone concentration increases steadily in all systems during the course of the reaction, thereby resulting in a continuous rise of the K:A ratio with increasing runtime, until the cyclohexanone concentration approaches a steady-state level near 500 mmol L^{-1}. Yet, this steady-state of cyclohexanone concentration is never fully established under the applied standard conditions since the near-complete consumption of the oxidants TBHP and molecular oxygen at extended reaction times results in a general decrease in the rate of reaction.

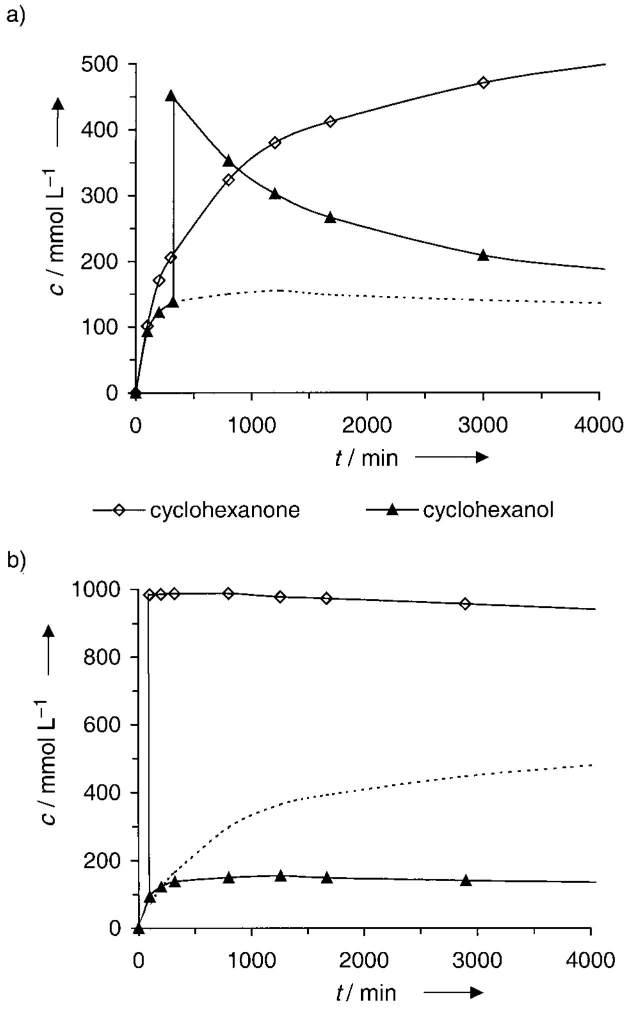
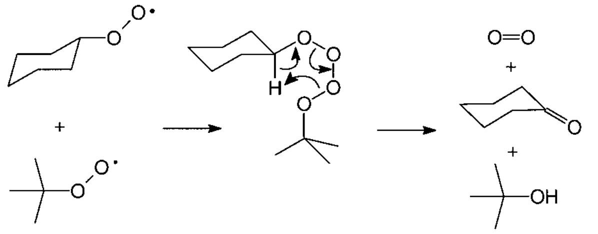


Figure 3. a) Response of the catalytic system with catalyst **1B** to the addition of an excess of cyclohexanol at $t = 300$ min. b) Response of the same system to the addition of an excess of cyclohexanone at $t = 100$ min. Dashed lines represent the behavior of the undisturbed system.

An artificial increase in the cyclohexanone concentration well above its steady-state level by addition of a surplus of cyclohexanone at the beginning of the catalytic reaction resulted in a decrease from this elevated level because of the increased efficiency of substrate-dependent overoxidation processes (Figure 3b). However, the rate of this decrease towards the steady-state level is significantly lower than the respective rate for cyclohexanol. This difference in rates of oxidation is one of the causes of the increasing K:A ratio in the catalytic system studied. An additional contribution to the predominance of cyclohexanone over cyclohexanol in the TBHP-promoted oxidation of cyclohexane derives from the lack of an α-proton in tBuOO$^\bullet$, which will favor the decay under formation of cyclohexanone in a mixed Russell termination between this radical and c-$C_6H_{11}OO^\bullet$ (Scheme 4).



Scheme 4. Mixed Russell termination step between tBuOO$^\bullet$ and c-$C_6H_{11}OO^\bullet$.

The independence of the steady-state concentrations of cyclohexanol and cyclohexanone on the catalyst concentration was also revealed in a series of experiments that used the catalyst **1B** at various concentrations (Figure 4). The existence of steady-state concentrations of both cyclohexanol and cyclohexanone limits the theoretically achievable K:A ratio in the system under consideration. Moreover, this limiting K:A value can be approached only at the price of a decreased selectivity for monooxygenated products, since allowing the system to proceed to a conversion of >15% results in a considerable degree of overoxidation under predominant formation of adipic acid (Table 1). Trace amounts of 6-hydroxycaproic, glutaric, succinic, and valeric acids were also detected in the reaction mixture as a result of further overoxidation processes. The gradually increasing concentration of carboxylic acids in the reaction mixture may also explain the observed leaching of the cobalt acetate complexes from the supports at extended reaction times (Table 1), since these acids are able to replace the carboxylate tethers of the immobilized complexes, thereby reversing the original immobilization procedure.

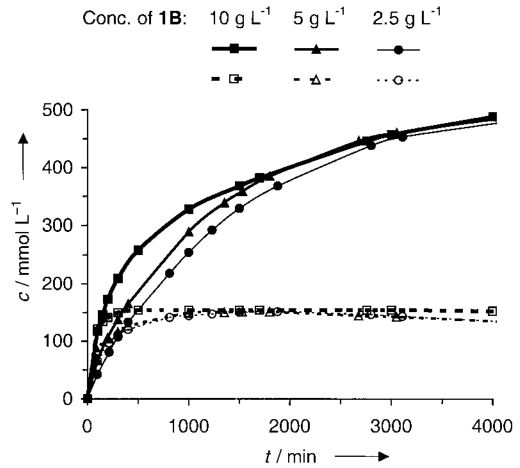


Figure 4. Time-dependence of the concentrations of cyclohexanone (solid lines) and cyclohexanol (dashed lines) in the course of the catalytic oxidation of cyclohexane in presence of different amounts of immobilized catalyst **1B**.

The initial rate of the catalytic cyclohexane conversion that used the immobilized catalysts **1A**–**1D** and **2B**–**2D**, expressed in terms of the respective cyclohexane conversion at a runtime of 100 min[13] and under consideration of blank effects, exhibits a linear dependence with respect to cobalt loading (Figure 5). An influence of the nature of the various immobilized cobalt acetate complexes, supports, or tethers on the course of the catalytic reaction was not noticed, even at this early stage. Moreover, even the early correlation with the Co concentration will be obscured when the catalytic system evolves towards its equilibrium state. Therefore, any comparison of the catalytic performance after the early stage of the catalysis in terms of turnover numbers is meaningless.

Table 1. Oxidation of cyclohexane with TBHP catalyzed by cobaltic acetate oligomers.[a]

		$t = 100$ min					$t = 4000$ min								
Cat no.	[Co] [mM]	[K] [mM]	[A] [mM]	[CHHP] [mM]	[TBCP] [mM]	Conv.[b] [mol%]	[K] [mM]	[A] [mM]	[CHHP] [mM]	[TBCP] [mM]	[AA] [mM]	K/A	S_{mono}[c] [%]	Conv.[b] [%]	Leach.[d] [%]
–[e]	0	12	18	52	1	1.51	49	36	159	4	3	1.36	98.81	4.55	–
1	2.59	24	38	72	5	2.65	316	111	137	14	62	2.85	90.31	12.21	–
2	2.6	10	14	70	1	1.81	301	104	171	15	53	2.89	91.77	12.32	–
1A	0.32	24	37	74	3	2.47	474	136	108	29	111	3.49	87.06	15.13	0.08
1B	1.58	147	131	44	17	6.25	497	128	80	23	108	3.89	87.08	15.42	0.98
1C	1.15	141	121	47	15	5.86	468	144	39	42	101	3.24	87.28	14.36	2.07
1D	1.25	124	123	49	13	5.59	445	121	85	33	113	3.69	85.82	14.41	0.90
2B	0.60	57	92	54	9	3.82	509	142	64	35	128	3.58	85.42	15.82	3.06
2C	1.06	107	116	51	14	5.20	532	150	60	34	119	3.56	86.70	16.15	2.87
2D	0.82	62	94	65	9	4.22	545	140	54	39	121	3.89	86.54	16.48	2.60

[a] General conditions: 6 mL of a mixture of cyclohexane (5.58 mol L^{-1}), TBHP (3.14 mol L^{-1}) and chlorobenzene (0.44 mol L^{-1}), amount of catalyst as indicated in text, 343 K. [b] Conversion of cyclohexane.[13] [c] Selectivity for monooxygenated products after 4000 min, calculated as 100([mono])/([mono] + [AA]), where [mono] = [K] + [A] + [CHHP] + [TBCP]. [d] amount of Co in solution after 4000 min, referred to total amount of Co. [e] Blank reaction in absence of immobilized catalyst. K = cyclohexanone, A = cyclohexanol, CHHP = cyclohexyl hydroperoxide, TBCP = *tert*-butylcyclohexylperether, AA = adipic acid.

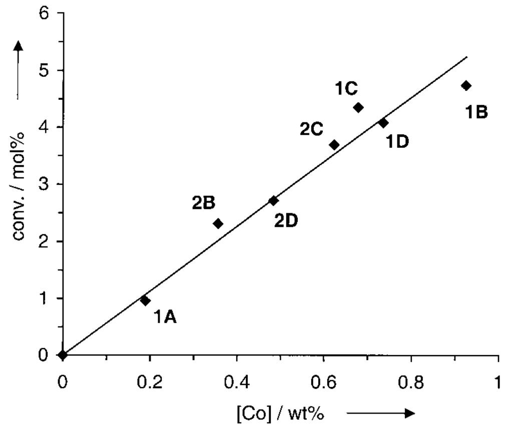


Figure 5. Correlation of the cyclohexane conversion at $t = 100$ min with the Co loading of the immobilized catalyst employed, **1A–1D** and **2B–2D**, respectively.

The observation of TBHP- and catalyst-independent steady-state concentrations for cyclohexanol and cyclohexanone indicates a mass-transfer limitation in molecular oxygen of the radical chain oxidation. Hence, radical chains that were initiated by the immobilized cobalt acetate complexes inside the mesopores of **1A–1D** and **2B–2D** must escape from the porous space into the bulk solution during the course of the reaction. Consequently, cyclohexane conversion is increasingly governed by freely evolving radical chains, and any effect of confinement control by the mesoporous host becomes negligible. The observed mass-transfer limitation underlines the significance of the molecular oxygen released from the TBHP decomposition for the product formation within the radical chain (Scheme 1, Eq. (5)). The influence of molecular oxygen on the course of the radical chain oxidation of cyclohexane by TBHP has also been observed in a different catalytic system.[14]

In contrast, the role of the second potential oxidant TBHP in the system under consideration is that of a radical initiator (Scheme 1, Eqs. (1) and (2)) rather than that of a direct oxygen-transferring agent towards the substrate (apart from being the source of the released molecular oxygen), because its contribution to product formation is not rate-determining. However, TBHP plays an important role in the subsequent oxidation of cyclohexanol to cyclohexanone, and hence in the increase of the K:A ratio.[15]

Conclusion

The catalytic cyclohexane oxidation that employs cobalt acetate complexes as catalysts and TBHP as the oxidant is a typical radical chain-oxidation process. The moderate catalytic activity of the oligomeric catalyst complexes **1** and **2** is significantly increased by their immobilization on carboxy-modified mesoporous silica supports. In the early phase of the catalytic reaction involving the immobilized catalysts **1A–1D** and **2B–2D**, the principal parameter determining the system reactivity is the respective Co loading. A substantial effect of confinement on the selectivity of the radical chain oxidation is not observed. This is consistent with a rapid escape of radical chains from their origin (at the catalyst inside the mesopores) into the bulk solution. An analysis of the already intricate catalytic system is further complicated by the fact that molecular oxygen (which originates from an initial phase of rapid TBHP decomposition in presence of the catalyst) is present as a second terminal oxidant in large quantities. After the initial stage, the catalytic system is governed by mass-transfer limitation in molecular oxygen, which obscures any differences that arise from nature or concentration of the immobilized cobalt acetate catalysts. The achievable K:A ratio in this catalytic system is limited by the appearance of catalyst-independent steady-state concentrations of both cyclohexanol and cyclohexanone.

Experimental Section

General remarks: All reactions involving alkoxysilanes or chlorosilanes were carried out under nitrogen with standard Schlenk techniques. Siliceous MCM-41,[16] complexes **1** and **2**,[5] and the immobilized catalyst **1A**[7] were prepared according to published procedures. 3-(Methylamino)-propyltrimethoxysilane was acquired from Fluka, while all other chemicals were purchased from Aldrich. All stoichiometric calculations involving support surfaces are based on an average surface silanol density of 7.8×10^{-6} mol SiOH m^{-2}.[17] ^{1}H and ^{13}C liquid-state NMR spectra were recorded on a Varian Unity Inova spectrometer and referenced against internal TMS. ^{13}C MAS NMR spectra were acquired on a Varian VXR400S spectrometer. XRD data were obtained from a Philips PW1840 diffractometer operating with $Cu_{K\alpha}$ radiation. XRF analyses were carried out on a Philips PW1480 instrument. IR spectra were recorded on a Perkin–Elmer Spectrum 1000FT-IR spectrometer. GC analyses were carried out on an Agilent6890 gas chromatograph equipped with a split inlet (200 °C, split ratio 10.0), a Chrompack Sil5CB capillary column (50 m × 0.53 mm; constant flow of N_2 4.0 mL min^{-1}; temperature program: isothermal at 45 °C for 33 min, followed by heating to 300 °C with a rate of 20 °C min^{-1}, final time 15 min at 300 °C) and a FID detector (set to 325 °C); retention times (min): cyclohexane 8.83, TBHP 10.97, TBP 15.23, methyl valeriate 23.44, chlorobenzene 26.58, cyclohexanone 33.59, cyclohexanol 34.18, dimethyl succinate 39.02, CHHP 39.48, TBCP 40.21, dimethyl glutarate 40.47, dimethyl adipate 41.49. Cobalt concentrations in the filtrates of the catalytic experiments were determined by AAS analysis on a Perkin–Elmer4100ZL spectrometer. BET surface areas A_{tot}, BJH pore volumes V_{tot}, and average pore diameters D_{av} were determined by nitrogen adsorption analysis at 77 K on a Quantachrome Autosorp-6B instrument.

Preparation of carboxylic acid-grafted supports

[MCM-41]-(CH$_2$)$_3$CN (3): MCM-41 (25 g, $A_{tot} = 1025$ m^{2}g^{-1}, 200 mmol-SiOH) was dehydrated for 3 h at 200 °C in vacuo and subsequently suspended in dry hexane (70 mL). Dichlorodimethylsilane (0.69 g, 5.36 mmol) was added dropwise at 20 °C to protect the external surface. The mixture was stirred for 12 h, then 3-cyanopropyltrichlorosilane (2.43 g, 12 mmol, 0.2 equiv) was added dropwise, and stirring was continued for additional 12 h. All volatiles were removed in vacuo and the remaining solid was suspended in toluene (100 mL). Dimethoxydimethylsilane (8.4 g, 70 mmol) was added to protect the residual silanol groups, and the resulting mixture was heated under reflux for 20 h. The product was collected by filtration, washed with acetone and ether and dried in vacuo at 80 °C for 12 h. Yield 25.5 g; XRD: $2\Theta = 2.48°$; BET: $A_{tot} = 973$ m^{2}g^{-1}, $V_{tot} = 0.873$ cm^{3}g^{-1}, $D_{av} = 24$ Å; IR (KBr): $\tilde{\nu}_{CN} = 2259$ cm^{-1}; ^{13}C CP-MAS NMR (100 MHz): $\delta = 0.0$ (SiCH$_3$), 10.7 (CH$_2$), 19.1 (2 × CH$_2$), 48.8 (residual OCH$_3$), 111.3 ppm (CN).

[MCM-41]-(CH$_2$)$_3$COOH (B): Compound **3** (5 g) was suspended in a mixture of H_2O and H_2SO_4 (40 mL, 1:1 (v/v)) and heated to 150 °C for 1 h. The solid was collected by filtration and washed with water until the filtrate gave a neutral reaction. Subsequent washing with methanol and ether followed by drying in vacuo at 80 °C overnight afforded 4.94 g of **B**. XRD: $2\Theta = 2.54°$; BET: $A_{tot} = 690$ m^{2}g^{-1}, $V_{tot} = 0.612$ cm^{3}g^{-1}, $D_{av} = 21$ Å; IR

(KBr): $\tilde{\nu}_{CO} = 1733\ cm^{-1}$; ^{13}C CP-MAS NMR (100 MHz): $\delta = 0.0$ ($SiCH_3$), 11.66 (CH_2), 18.10 (CH_2), 35.71 (CH_2), 177.32 ppm (CO).

$(H_3CO)_3Si(CH_2)_3NHCO(CH_2)_3COOH$ (4): Glutaric anhydride (0.384 g, 3.37 mmol) in dry THF (20 mL) was added dropwise to a solution of 3-aminopropyltrimethoxysilane (0.556 g, 3.12 mmol) in THF (30 mL). After the mixture had been stirred for 12 h at 20 °C, the solvent was removed in vacuo. Compound **4** was isolated as a colorless oil in quantitative yield. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 0.65$ (m, 2H; $SiCH_2$), 1.63 (m, 2H; CH_2), 1.96 (m, 2H; CH_2), 2.28 (m, 2H; CH_2), 2.41 (m, 2H; CH_2), 3.24 (m, 2H; CH_2), 3.57 (s, 9H; OCH_3), 6.25+6.44 (1H; NH), 11.21 ppm (s, 1H; COOH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 6.5$, 20.9, 22.6, 33.2, 35.4, 42.0 (CH_2), 50.6 (OCH_3), 172.9 (C(=O)N), 176.9 ppm (COOH); IR (CH_2Cl_2): $\tilde{\nu} = 1713$ (COOH), 1670 (amide I), 1522 (amide II) cm^{-1}.

$(H_3CO)_3Si(CH_2)_3N(CH_3)CO(CH_2)_3COOH$ (5): Compound **5** was prepared in quantitative yield in an analogous manner to the synthesis of **4** from 3-(methylamino)propyltrimethoxysilane (0.929 g, 4.8 mmol) and glutaric anhydride (0.547 g, 4.8 mmol). ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 0.59$ (m, 2H; $SiCH_2$), 1.65 (m, 2H; CH_2), 1.95 (m, 2H; CH_2), 2.38–2.52 (m, 4H; $2CH_2$), 2.92+3.00 (2s, 3H; NCH_3), 3.31 (m, 2H; NCH_2), 3.57 (s, 9H; OCH_3), 11.58 ppm (s, 1H; COOH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 6.3$, 20.2, 21.7, 31.9+32.5, 33.4, 51.3+52.2 (CH_2), 34.7+35.4 (NCH_3), 50.6 (OCH_3), 172.6+172.7 (C(=O)N), 177.0 ppm (COOH); IR (CH_2Cl_2): $\tilde{\nu} = 1715$ (COOH), 1651 (amide) cm^{-1}.

[MCM-41]-$(CH_2)_3NHCO(CH_2)_3COOH$ (D): After dehydration for 3 h at 200 °C in vacuo, MCM-41 (5 g, $A_{tot} = 1025\ m^2 g^{-1}$, 40 mmol SiOH) was suspended in hexane (50 mL), and the external surface was protected by addition of dichlorodimethylsilane (0.138 g, 1.07 mmol). After the mixture had been left to stir for 12 h at 20 °C, all volatiles were removed in vacuo. A solution of freshly prepared **4** (0.863 g, 2.94 mmol) in THF (30 mL) was added, and the resulting suspension was stirred at 20 °C for 44 h. The title compound was isolated by filtration and washed with CH_2Cl_2. Drying in vacuo at 80 °C overnight afforded 5.293 g of **D**; 112 mg of nonadsorbed **4** was recovered from the filtrates. ^{13}C CP-MAS NMR (100 MHz): $\delta = -0.3$ ($SiCH_3$), 18–49 (br, CH_2), 172.0 (C(=O)N), 174.0 ppm (COOH); IR (KBr): $\tilde{\nu} = 1725$ (COOH), 1650 (amide I), 1558 (amide II) cm^{-1}.

[MCM-41]-$(CH_2)_3N(CH_3)CO(CH_2)_3COOH$ (C): MCM-41 (15 g, $A_{tot} = 1025\ m^2 g^{-1}$, 120 mmol SiOH) was dehydrated for 3 h at 200 °C in vacuo, and the external surface was protected by addition of dichlorodimethylsilane (0.414 g, 3.22 mmol) in hexane (100 mL). After the slurry had been stirred for 12 h at 20 °C, all volatiles were removed in vacuo. The residue was suspended in THF (100 mL), and **5** (0.934 g, 3 mmol, freshly prepared in THF (20 mL)) was added under stirring at 20 °C. Stirring was continued for 12 h, and the mixture was subsequently heated under reflux for 6 h. Dimethoxydimethylsilane (6.2 mL, 45 mmol) was added dropwise, and heating under reflux was continued for additional 12 h. Filtration, washing with CH_2Cl_2, and drying in vacuo overnight at 80 °C afforded 15.33 g of **C**. ^{13}C CP-MAS NMR (100 MHz): $\delta = -3.5$ ($SiCH_3$), 20–55 (br, $CH_3 + CH_2$), 173.0 (C(=O)N), 177.1 ppm (COOH); IR (KBr) : $\tilde{\nu} = 1731$ (COOH), 1636 (amide) cm^{-1}.

General procedure for the immobilization of cobalt acetate clusters on carboxylic acid grafted supports: The amounts of cobalt(III) acetate oligomer and modified support that are stated below were suspended in $CHCl_3$ (30 mL), and the resulting slurry was heated under reflux for 24 h in a flask which was equipped with a Soxhlet extractor that contained a thimble filled with anhydrous Na_2CO_3 (0.5 g) that was used to trap any acetic acid released. The product was collected by filtration, extracted with CH_2Cl_2 in a Soxhlet device for 20 h, and finally dried in vacuo at 80 °C for 24 h.

1B: From **1** (0.2 g, 0.226 mmol) and **B** (2.0 g). Yield 2.128 g. XRF: [Co] 0.925 wt %.

1C: From **1** (0.2 g, 0.226 mmol) and **C** (2.0 g). Yield 2.064 g. XRF: [Co] 0.678 wt %.

1D: From **1** (0.1 g, 0.113 mmol) and **D** (2.0 g). Yield 2.074 g. XRF: [Co] 0.735 wt %.

2B: From **2** (0.1 g, 0.137 mmol) and **B** (2.0 g). Yield 2.012 g. XRF: [Co] 0.356 wt %.

2C: From **2** (0.1 g, 0.137 mmol) and **C** (2.0 g). Yield 1.993 g. XRF: [Co] 0.623 wt %.

2D: From **2** (0.2 g, 0.274 mmol) and **D** (2.0 g). Yield 1.983 g. XRF: [Co] 0.484 wt %.

Catalytic investigations: In all catalytic experiments, a stock solution of TBHP in cyclohexane was used which had been prepared by extraction of commercial TBHP (Aldrich, 70 % in water) into an equal volume of cyclohexane. Phase separation was promoted by saturation of the aqueous layer with solid NaCl. The organic layer was dried over $MgSO_4$, filtered and stored at 4 °C.

Homogeneous catalytic experiments were carried out with finely powdered **1** (4.6 mg, 5.19 μmol) or **2** (6.1 mg, 7.8 μmol). A 60-mg quantity of dry catalyst was used in all catalytic experiments that used immobilized cobaltic acetate oligomers.

The respective catalyst was added to 3 mL of a mixture consisting of cyclohexane ($5.58\ mol L^{-1}$), TBHP ($3.14\ mol L^{-1}$), and chlorobenzene ($0.44\ mol\ L^{-1}$) as internal standard in a 10-mL reactor fitted with a reflux condenser and a magnetic stirring bar. The mixture was rapidly heated to 70 °C by immersion in a thermostated bath. An additional 3 mL of the reagent mixture was added in 0.5 mL portions at intervals of 10 min. The course of the reaction was monitored by GC analysis of liquid samples, beginning after the evolution of molecular oxygen had mostly ceased at 100 min.[13] The production and consumption of molecular oxygen was monitored volumetrically with an attached gas burette. The concentration of carboxylic acid side products was determined by GC analysis from separate samples after conversion into the respective methyl esters.[18] The extent of Co leaching was determined by AAS analysis of the filtered reaction mixture after the end of the catalytic experiment.

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