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Selective liquid phase oxidation of *o*-xylene with gaseous oxygen by transition metal containing polysiloxane initiator/catalyst systems

Tobias Förster [a], Stephan A. Schunk [b], Andreas Jentys [a], Johannes A. Lercher [a,*]

[a] *Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany*
[b] *hte Aktiengesellschaft, Kurpfalzring 104, D-69123 Heidelberg, Germany*

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ABSTRACT

The selective liquid phase oxidation of *o*-xylene over hydrophobic porous Co^{2+} and Mn^{3+} containing polysiloxane catalysts showed that both catalysts had higher activity than the homogeneous benchmark system Co naphthenate. The solid catalyst/initiator systems accelerate the radical initiation and the hydroperoxide decomposition. 2-Methylbenzyl hydroperoxide plays a key role in the reaction network as it is the first observed intermediate and is efficiently decomposed by the catalysts. The selectivity of the hydroperoxide decomposition can be controlled to some extent by the choice of transition metal. Co^{2+} enhances the formation of *o*-tolualdehyde, while Mn^{3+} increases the tendency to 2-methylbenzyl alcohol formation. The hydrophobic character, demonstrated by the weak adsorption of water, retards the interaction with the polar reaction products and allows their fast desorption, which in turn is a major cause for the high catalytic activity.

1. Introduction

The direct insertion of oxygen into alkanes and aromatic molecules is a promising reaction route for the synthesis of oxygenates with high atom efficiency. This makes the selective oxidation of alkanes and aromatic molecules a very attractive route for an industrial application. Examples for liquid phase oxidation reactions on industrial scale are for example the oxidation of *p*-xylene and related aromatic educts to the corresponding aldehydes and acids (especially the production of terephthalic acid from *p*-xylene [1–4]) as well as the oxidation of cyclohexane to the corresponding ketone and alcohol [5]. The resulting products are important intermediates for the production of nylon and polyethylene terephthalate (PET), respectively.

These autoxidation processes have in common that the reactions are carried out in the liquid phase using O_2 as oxidant. Both reactions proceed via a radical reaction pathway in the presence of Co and Mn compounds that act as initiators for the formation of radicals. In case of the *p*-xylene oxidation, a halogen source (i.e., HBr) is typically added to increase the activity of the system via enhancing the radical formation [6–8].

The mechanism of autoxidation reactions is described as free radical chain reaction [9], consisting of initiation, chain growth, and termination steps. The chain growth is sustained by the formation of hydroperoxides, which are thermally or catalytically decomposed over transition metal cations (e.g., Co^{2+} or Mn^{3+}) to oxygenates. This decomposition is generally described as the Haber–Weiss mechanism [10,11]. Alternatively, the hydroperoxide can also be dehydrated to an aldehyde over an acid functionality. The central roles of the transition metal species lie (i) in the generation of organic entities in the form of radicals via hydrogen abstraction and (ii) the catalytic decomposition of hydroperoxide compounds to the corresponding alcohols and aldehydes [9].

For the oxidation of cyclohexane on an industrial scale typically mixtures of cobalt and manganese naphthenates are employed. The limitations of this approach are the low conversion usually achieved and the undesired high cyclohexanol yields. The ratio of cyclohexanone to cyclohexanol is known to strongly depend on the type of transition metal cation in the catalyst [12]. Co^{2+} enhances the formation of cyclohexanone, whereas Mn^{3+} increases the selectivity toward cyclohexanol. For the commercial oxidation of *p*-xylene, mixtures of Co^{2+} and Mn^{3+} cations and Br^{-} initiators are applied as initiators in acetic acid as solvent. As acetic acid is highly corrosive, special precautions have to be taken to handle the reactant mixture on an industrial scale.

As an alternative, heterogeneous initiator and catalyst systems are available for liquid phase oxidations in the presence of oxygen that potentially combine the benefits of easy separation with the advantage of non-corrosive reaction mixtures. Several examples for the successful application of heterogeneous initiator/catalyst systems for the oxidation of alkyl substituted aromatics are described in the literature, however, in-depth insight on the prevailing reaction mechanisms is limited [13–16].

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* Corresponding author.
E-mail address: johannes.lercher@mytum.de (J.A. Lercher).

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In a notable example, Thomas et al. used heterogeneous AlPO-36 systems loaded with Co, Mn, or Fe cations for the liquid phase oxidation of *p*-xylene to *p*-toluic acid, 4-formylbenzoic acid, and terephthalic acid [13,14]. These catalysts, however, are up to date only of academic interest, because they do not reach the productivity of the industrially used Co/Mn/Br systems. MnAPO-5 was also studied by Moden et al. [17] for the decomposition of hydroperoxides during the selective oxidation reaction of cyclohexane. They were shown to act as heterogeneous catalysts by decomposing the intermediate hydroperoxide [17–19]. Ramanathan et al. developed an amorphous mesoporous cobalt-containing silicate (Co-TUD-1) as an effective catalyst for the decomposition of cyclohexyl hydroperoxide to cyclohexanol and cyclohexanone [20].

On an industrial scale, the selective oxidation of *o*-xylene to phthalic anhydride is carried out as a gas phase process using vanadia-titania catalysts [21–24]. A large number of reports on the reaction conditions, catalyst compositions, and reaction mechanism exist in the open literature for this gas phase reaction [21,23–28]. The main limitation of the process is the rather low selectivity of ca. 80–85% to phthalic anhydride at almost 100% conversion. Separating the process into two consecutive steps was presented as possible solution to increase the selectivity to 88% in the patent literature [29]. In a first step, *o*-xylene is oxidized over Co naphthenate to *o*-toluic acid, which is converted to phthalic anhydride by a subsequent partial oxidation step using a vanadia catalyst.

Recently, we described a highly promising polysiloxane-based catalysts for the selective liquid phase oxidation of one of the methyl groups of *o*-xylene under solvent-free conditions [30]. In the present contribution, we present a mechanistic study of the reaction steps involved in the liquid phase oxidation of *o*-xylene over these solid Co^{2+} and Mn^{3+} cation-containing hydrophobic initiator/catalyst systems. The formation and consumption of the radicals in the individual elementary steps of the reaction are used to determine possible the reaction pathways. A complex network of reaction steps is derived from this explaining the reactivity and selectivity to partially oxygenated products over Co^{2+} or Mn^{3+} containing initiator/catalyst systems.

2. Experimental

2.1. Catalyst synthesis

Macroscopic spherical polysiloxane bodies were synthesized by applying a sol–gel process [31,32] using a mixture of (easily hydrolysable) silane precursors and a transition metal source, which was injected into a water-filled column. The initially formed stable droplets were converted into spherical particles by polymerization of the silanes in the aqueous phase at 333 K. In order to assure a sufficient condensation rate, dibutyl tin dilaurate was added to the solution. The detailed procedure of the synthesis is described elsewhere [33]. After aging in water at room temperature for 12 h, the materials were washed with deionized water and *i*-propanol. Before their usage, the solid materials were dried by lyophilization. The diameter of the synthesized particles was in the range of 800–1200 μm.

3-Aminopropyltrimethoxysilane (>97%), tetraethyl orthosilicate (>99%), 1-butanol (>99.5%), dibutyltin dilaurate (95%), cobalt (II) and manganese (III) acetylacetonate (97%), triphenyl phosphine (>98.5%), and tetradecane (>99%) used for the catalyst synthesis and the reactant *o*-xylene (>99%) were purchased from Sigma Aldrich and used without any further purification.

The concentration of the metal in the solid catalysts was determined by atomic absorption spectroscopy using a UNICAM Solaar M5 Spectrometer. For this typically 30–60 mg of the sample was dissolved in 0.5 ml of hydrofluoric acid (10%) at its boiling point (about 383 K).

2.2. Liquid phase oxidation of *o*-xylene

The liquid phase oxidation experiments were carried out in a bubble column reactor consisting of a 10-mm inner diameter glass tube loaded with reactant (*o*-xylene) and catalyst without a solvent. Prior to each reaction, the reactant was heated to the desired reaction temperature (445 K, unless stated differently) under nitrogen flow using a pressure of 2.4 bar. The gas was directed through a glass frit to form small bubbles in order to minimize the transport resistance of the gas into the liquid. The upper part of the reactor was cooled to 293 K, and the entrance gas stream was saturated at the same temperature with *o*-xylene to prevent the loss of reactant via the gas stream. The reaction was started by switching the nitrogen to a mixture of synthetic air (50%) and nitrogen. After the reactor, the gas stream was directed through a saturator filled with 0.1 M NaOH to quantify the integral amount of CO_2 formed in the reaction by back titration with hydrochloric acid.

Liquid samples were collected by using a syringe inserted from the top of the reactor. Hexachlorobenzene was used as internal standard in every reaction. To identify the concentration of products, a Shimadzu GC-2010 gas chromatograph equipped with a 30 m DB-5 column (0.25 mm inner diameter and 0.25 μm film thickness) and a FID detector was used. Tetradecane was added to each analysis as internal GC standard. To determine the concentration of the 2-methylbenzyl hydroperoxide, the procedure described by Shulpin et al. [34] was used.

2.3. Adsorption of CO or water followed by IR spectroscopy

The samples were prepared as self supporting wafers (5–10 mg cm^{-2}) and measured with a resolution of 4 cm^{-1} in transmission mode using with a Bruker IFS88 spectrometer. After activation in vacuum (10^{-6} mbar) at 723 K (heating rate 10 K min^{-1}) for one hour, the samples were cooled to 300 K and CO or water was adsorbed at partial pressure between 10^{-3} mbar and 1 mbar, respectively.

2.4. ^1H NMR spectroscopy

^1H NMR spectra of the reaction solutions were analyzed with a Bruker NMR spectrometer operating at 360 MHz, using 5-mm high-resolution liquid probes under ambient conditions. The reaction products were dissolved in $CDCl_3$.

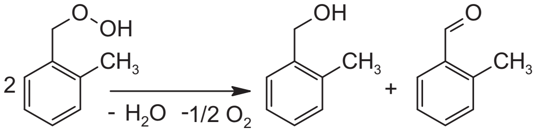
2.5. Diffuse reflectance UV/vis spectroscopy (DR UV/vis)

Diffuse reflectance UV/vis spectra of the solid catalysts were recorded with an Avantes AvaSpec-2048 spectrometer at ambient conditions using samples in powder form. For the spectra of the used catalysts, the materials were washed with acetone and dried under vacuum before the measurements.

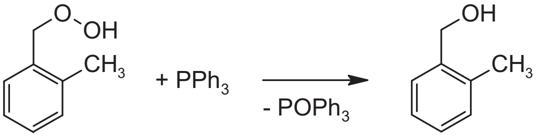
2.6. Thermal decomposition of the hydroperoxide

Hydroperoxides are formed as reaction intermediates in the initial step of the partial oxidation reaction of aromatic molecules, however, they cannot be directly detected by GC analysis as they thermally decompose into an aldehyde and an alcohol at temperatures above 473 K (see Scheme 1) [34] usually reached in the inlet system of a GC. Therefore, an indirect method was applied for the detection of 2-methylbenzyl hydroperoxide.

Using a solution containing 1 mol% 2-methylbenzyl hydroperoxide (in *o*-xylene), prepared by oxidizing *o*-xylene at 398 K with



Scheme 1. Decomposition of 2-methylbenzyl hydroperoxide to *o*-tolualdehyde and 2-methylbenzyl alcohol.



Scheme 2. Reduction of the 2-methylbenzyl hydroperoxide to 2-methylbenzyl alcohol by PPh_3.

synthetic air for 12 h, a ratio of 7:1 between *o*-tolualdehyde and 2-methylbenzyl alcohol was formed by the thermal decomposition in the GC inlet system. For the analysis of the liquid sample, a fraction of the sample was treated with triphenyl phosphine to reduce 2-methylbenzyl hydroperoxide to 2-methylbenzyl alcohol quantitatively (see Scheme 2).

A second fraction was analyzed directly by GC. Using the decomposition ratio between alcohol and aldehyde, the concentrations of alcohol, aldehyde, and hydroperoxide in the liquid samples were determined. The details of the analysis of the hydroperoxide are included in the Supplementary Material.

3. Results

3.1. Catalyst composition and properties

The chemical composition of the Co^{2+} and Mn^{3+} containing catalysts determined by AAS and elemental analysis is summarized in Table 1. Before synthesis of the catalysts, the metal compound was mixed with tetraethyl orthosilicate (TEOS) and 3-aminopropyltrimethoxysilane in a ratio of 2:1 in 10 vol.% 1-butanol and a Sn-containing reaction accelerator. The elemental composition of the catalysts was not affected by the oxidation reaction, especially the concentrations of nitrogen and transition metal remained constant. The loading of Co^{2+} was varied in the range from 0.3 to 1.9 wt.% by synthesis. The diameter of the spheres was kept constant at 800 μm for all materials. Co^{2+}-containing samples showed blue color, while the Mn^{3+} materials were brown.

3.2. Accessibility of the transition metal by CO

The accessibility of the transition metal sites in the polysiloxane network was probed by CO adsorption followed by IR spectroscopy. The IR spectra during adsorption of CO on Co-1.9 at 300 K and CO partial pressures between 10^{-3} and 1.5 mbar are shown in Fig. 1. Adsorption of CO on the Co-containing catalysts led to the formation of two bands at 2048 cm^{-1} and 2169 cm^{-1}, which are the characteristic for stretching vibrations of CO in metal carbonyl species and for CO adsorbed on Lewis acidic Co^{2+} cations [35]. The carbonyl band at 2048 cm^{-1} is more intense at low pressures and increases only slightly with the CO partial pressure, while the band at 2169 cm^{-1} (CO adsorbed on Co^{2+}) increased over the entire pressure range studied and did not reach saturation at the highest pressure applied. Therefore, its saturation coverage was calculated from fitting the coverage with a Langmuir sorption isotherm:

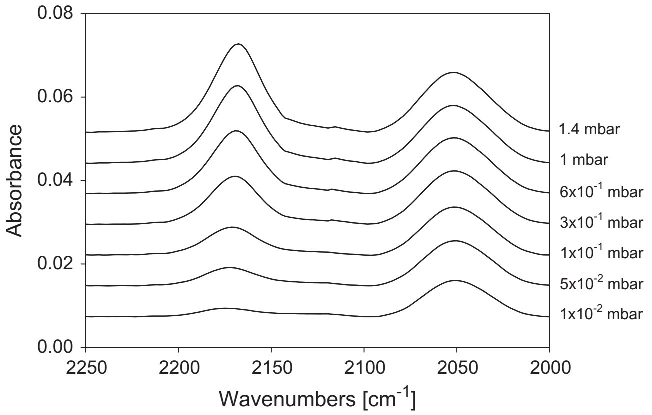


Fig. 1. Difference IR spectra of CO adsorbed on the Co-1.9 catalyst at 300 K and CO partial pressures indicated.

$$Q = Q_{sat}\frac{K \cdot p/p_0}{1 + K \cdot p/p_0}$$

With Q_{sat} the saturation coverage, K the adsorption equilibrium constant, and *p* the CO partial pressure. The value for *K* was constant at 3464 (±5%) for every catalyst sample.

The maximum CO adsorption capacity depends linearly on the Co loading (see Fig. 2), which indicates that the accessibility and the local structure of the Co^{2+} species is not affected by the metal loading. The support did not show CO adsorption at 300 K. After the oxidation reaction, the Co^{2+} catalysts showed the identical CO adsorption capacity after washing with *o*-xylene as the original samples.

The hydrophilicity of the transition metal containing polysiloxane materials was tested by adsorption of water at different partial pressures. The coverage was followed by IR spectroscopy and the intensity of the H–O–H deformation vibration band at 1630 cm^{-1} was used for quantification. After removal of the organic side groups by treatment at 873 K under air flow, the water uptake increased drastically at a given water pressure, i.e., up to a factor of three (see Fig. 3).

3.3. Catalytic activity in the oxidation of methyl-substituted aromatics

To explore the catalytic activity of Co^{2+}-containing polysiloxane spheres, a series of methyl-substituted aromatics including

Table 1
Chemical composition of the Co and Mn-containing catalysts. Note that the difference to 100% is balanced by oxygen.

Sample name	Metal concentration (wt.%)	C concentration (wt.%)	Si concentration (wt.%)	N concentration (wt.%)	H concentration (wt.%)
Co-0.3	0.3	6.7	33.6	1.1	2.7
Co-0.8	0.8	7.6	34.2	1.8	2.5
Co-1.1	1.1	8.7	33.1	2.0	2.5
Co-1.9	1.9	8.0	25.7	2.2	3.0
Mn-2.0	2.0	14.3	31.5	3.1	3.7

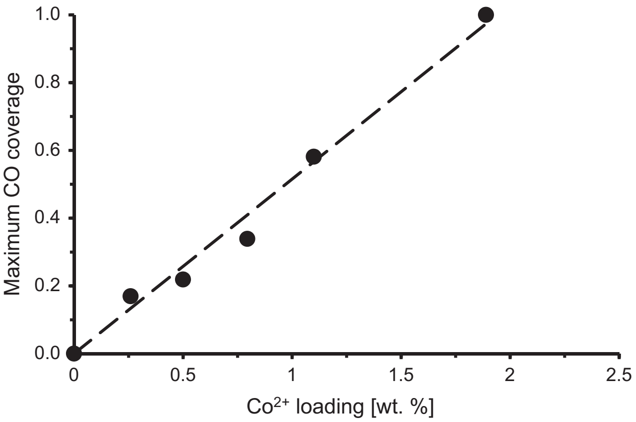


Fig. 2. CO coverage (determined from the band at 2169 cm^{-1}) as function of the Co loading. The CO coverage is shown relative to the CO adsorption of the Co-1.9 catalyst.

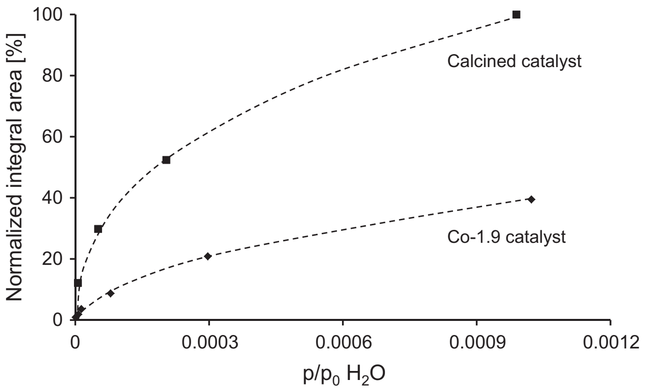


Fig. 3. Adsorption of water on the (♦) Co-1.9 catalyst compared to the corresponding (■) calcined material (without organic side groups) The adsorption of water was recorded by IR spectroscopy at 300 K using the intensity of the band at 1630 cm^{-1}.

Table 2
Conversion of various reactants with Co^{2+}-containing polysiloxane catalysts (reaction conditions: 445 K, 100 mg Co-1.9 catalyst, total pressure 2.4 bar, reaction time 180 min).

Reactant	Conversion (mol%)
Toluene	0.5
o-Xylene	16.1
1,3,5-Trimethyl benzene	6.2

toluene, *o*-xylene, and 1,3,5-trimethyl benzene (mesitylene) were tested (see Table 2). The experimental conditions were kept constant for all catalytic tests, i.e., 100 mg of the catalyst was used and the reaction temperature was 445 K.

In general, it was observed that the oxidation occurred selectively on one of the available methyl groups. In the first step, hydroperoxide was formed as an intermediate, which was further converted to the corresponding alcohol, aldehyde, and acid. The oxidation products of toluene included benzyl alcohol and benzaldehyde, while benzoic acid was observed only in very low yields under the reaction conditions applied. The reaction products of the oxidation of mesitylene were 3,5-dimethylphenyl methanol, 3,5-dimethyl benzaldehyde, and 3,5-dimethyl benzoic acid. The oxidation of *o*-xylene resulted in 2-methylbenzyl alcohol, *o*-tolualdehyde, and *o*-toluic acid. The reactivity of the substrates increased in the sequence toluene, mesitylene, and *o*-xylene, which is in good agreement with the predicted rates for the selective oxidation summarized by Partenheimer [9]. In the following, we focus, however, solely on the detailed kinetics of the selective oxidation of *o*-xylene, because of the high industrial interest in this reaction.

3.4. Selective oxidation of o-xylene

The selectivity toward oxidation products as function of the *o*-xylene conversion was independent of the transition metal loading in the catalysts. As an example, the selectivity as function of the conversion is shown in Fig. 4 for the Mn-2.0 catalyst. Initially, 2-methylbenzyl hydroperoxide, 2-methylbenzyl alcohol, and *o*-tolualdehyde were formed, whereas the selectivity toward *o*-toluic acid only increased when the conversion exceeded 4 mol%. The initial slopes indicate that 2-methylbenzyl hydroperoxide, 2-methylbenzyl alcohol, and *o*-tolualdehyde are formed as primary products, while *o*-toluic acid is a secondary product. Besides the main products, phthalide (yields of 1 mol%) and other side products such as *o*-xylene dimers, esters of *o*-toluic acid, and 2-methylbenzyl alcohol, formiates of 2-methylbenzyl alcohol, toluene, and phthalic anhydride were detected in minor concentrations (molar yields below 0.4 mol% at conversions above 20 mol%).

3.5. Initiation of the radical formation

Independent of the nature of the catalyst, an induction period was observed in all investigated reactions. The duration of this induction period decreased linearly with increasing Co^{2+} loading. This corresponds to the observation that the rate of 2-methylbenzyl hydroperoxide formation increased with increasing Co^{2+} concentration of the catalyst. The rate constant of 2-methylbenzyl hydroperoxide formation for catalysts with Co^{2+} loadings from 0.3 to 1.9 wt.% is compared in Fig. 5. The linear correlation of the rate constant of the 2-methylbenzyl hydroperoxide formation and the concentration of Co^{2+} in the polysiloxane strongly indicates that the transition metal cation is the active site for the radical formation and that the chemical nature of the Co^{2+} species is identical for all catalysts. Note also that the intercept with the *y*-axis suggests that also in the absence of Co^{2+} species, 2-methylbenzyl hydroperoxide is formed, however, with a much smaller rate.

3.6. Decomposition of the hydroperoxide

The effect of the transition metal catalyst on the 2-methylbenzyl hydroperoxide yield was studied by comparing different catalysts with the reaction behavior in the absence of a catalyst (see

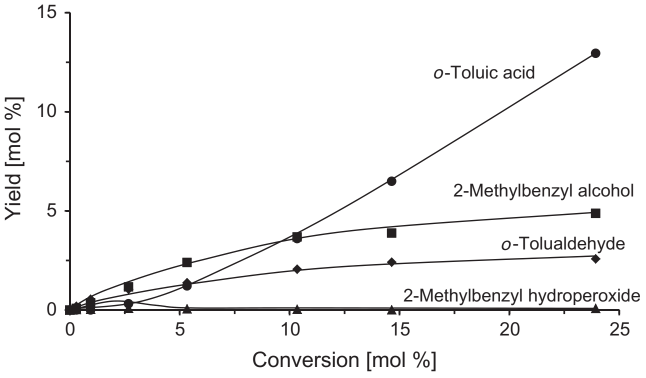


Fig. 4. Yields of *o*-tolualdehyde (♦), 2-methylbenzyl alcohol (■), 2-methylbenzyl hydroperoxide (▲), and *o*-toluic acid (●) as function of the *o*-xylene conversion (reaction conditions: 445 K, 100 mg Mn-2.0 catalyst, total pressure 2.4 bar).

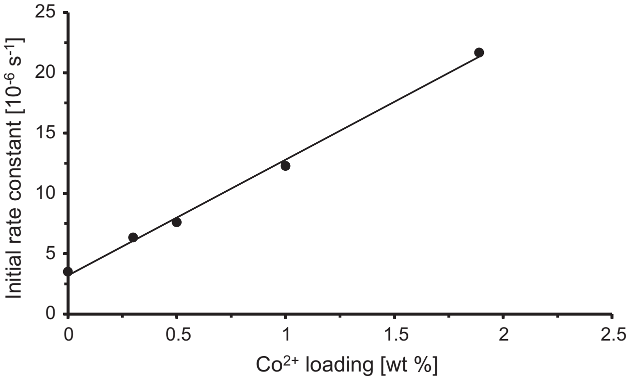


Fig. 5. Rate constants of the initial *o*-xylene oxidation rate as function of the Co^{2+} concentration of the catalyst materials (experimental conditions: 445 K, total pressure 2.4 bar).

Fig. 6). The formation of 2-methylbenzyl hydroperoxide was detected as soon as oxygen was added to the reactant gas mixture. In the absence of a catalyst, the 2-methylbenzyl hydroperoxide yield increased to 2.6 mol%, while in the presence of Co-1.9, the hydroperoxide was rapidly decomposed by the catalyst leading to a significantly lower concentration (< 0.3 mol%). In comparison, the Mn^{3+} catalyst generates a lower maximum concentration of hydroperoxide (0.08 mol% at 3.5 mol% conversion). The highest yield of 2-methylbenzyl hydroperoxide (2.6 mol%) can be considered as the maximum concentration, before the rate of decomposition to *o*-tolualdehyde and 2-methylbenzyl alcohol exceeds the formation rate in the liquid phase in the absence of a catalyst. When the support material without transition metal was tested under reaction conditions, the maximum yield of 2-methylbenzyl hydroperoxide was 0.5 mol% and the conversion was limited to 1.5 mol%. To investigate the activity of the transition metals attached to the polysiloxanes, the reaction was started without catalysts and only after the 2-methylbenzyl hydroperoxide yield reached, a constant level Co-1.9 was added. The concentration profiles of the oxidation products are shown in Fig. 7. In the initial phase, the yield of 2-methylbenzyl hydroperoxide increased to 2.4 mol% before adding the Co^{2+} catalyst. In the presence of the catalyst, the yield of 2-methylbenzyl hydroperoxide decreased rapidly and simultaneously the yields of the decomposition products *o*-tolualdehyde and 2-methylbenzyl alcohol increased almost at the same rate. Note that the *o*-toluic acid yield increased after the addition of the catalyst because of the formation of *o*-tolualdehyde from the decomposition of 2-methylbenzyl hydroperoxide.

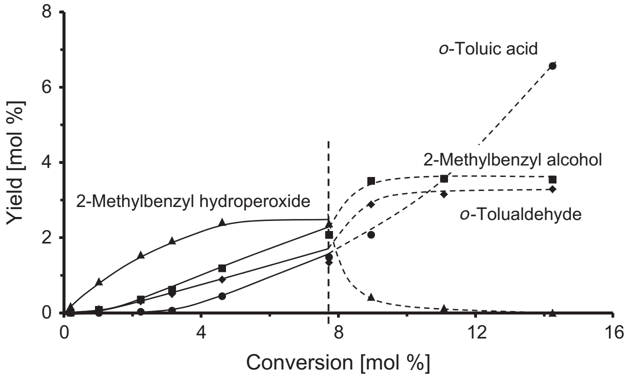


Fig. 7. Yields of *o*-tolualdehyde (♦), 2-methylbenzyl alcohol (■), 2-methylbenzyl hydroperoxide (▲), and *o*-toluic acid (●) in dependence of the *o*-xylene conversion without catalyst in the initial phase of the reaction. The Co-1.9 catalyst was added after 8 mol% conversion (vertical line) (reaction conditions: 445 K, total pressure 2.4 bar).

The ratios of *o*-tolualdehyde and 2-methylbenzyl alcohol formed over the Co^{2+} and Mn^{3+}-containing catalysts are compared in Fig. 8. This ratio can be seen as a measure for the selectivities of the 2-methylbenzyl hydroperoxide decomposition. (The absolute values for the yields of oxygenates can be seen in Fig. 4). The ratio between *o*-tolualdehyde and 2-methylbenzyl alcohol decreased from an initial value of 2.5 at low conversion to a constant level between 1 and 0.6, when Co^{2+} or Mn^{3+} were used as catalysts at higher conversion. Without catalyst, the decomposition of the 2-methylbenzyl hydroperoxide occurred only at higher concentrations and the ratio of the aldehyde and the alcohol was 0.7.

3.7. In situ diffuse reflectance UV/vis spectroscopy

In the UV/vis spectrum of the fresh catalyst Co-1.9, three bands at 556, 580, and 645 nm were observed, which are typical for Co^{2+} [36]. Under reaction conditions at 423 K in the presence of *o*-xylene and oxygen, the three bands assigned to Co^{2+} gradually decrease in intensity with increasing reaction time (see Fig. 9). At the same time, three new bands at 537, 565, and 599 nm were formed. Each of these newly formed bands had an absorption maximum lower than the comparable band of the original of the Co^{2+} catalyst, which indicates an interaction of the Co^{2+} site with the reactant during the reaction. The spectrum of the used Co^{2+} polysiloxane, which was washed with *o*-xylene after the reaction, is equal to that before the reaction demonstrating the reversibility

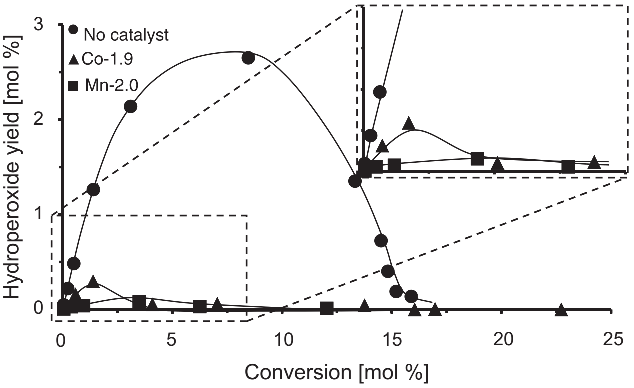


Fig. 6. 2-Methylbenzyl hydroperoxide yield as function of the *o*-xylene conversion without a catalyst (●), in the presence of the Co-1.9 (▲) and the Mn-2.0 catalyst (■) (reaction conditions: 445 K, total pressure 2.4 bar).

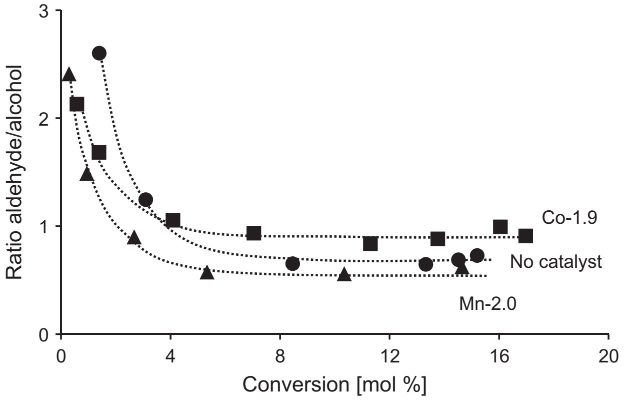


Fig. 8. Ratio between yields of *o*-tolualdehyde to 2-methylbenzyl alcohol as function of the *o*-xylene conversion for the Co-1.9 (■), Mn-2.0 (▲) catalyst and without a catalyst (●) (reaction conditions: 445 K, total pressure 2.4 bar).

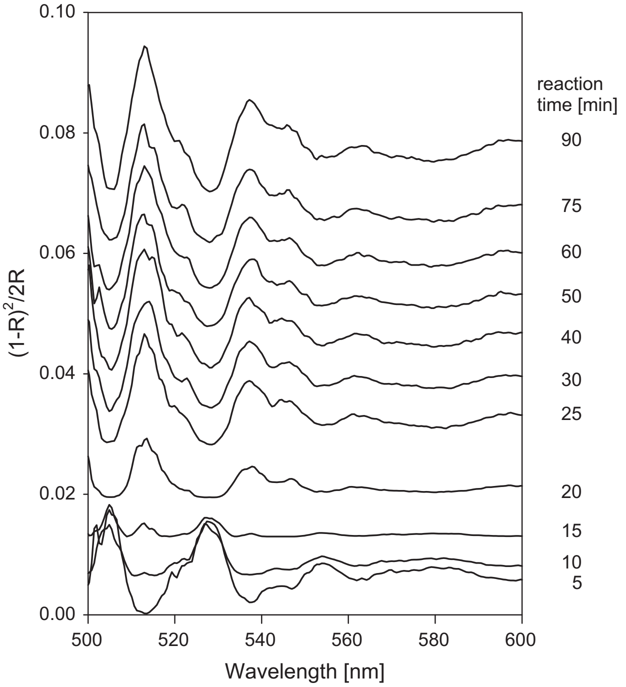


Fig. 9. DR UV/vis spectra of the Co-1.9 catalyst during the oxidation of *o*-xylene at 423 K after the time intervals indicated.

of the catalyst–substrate interactions. The IR spectra of a fresh Co catalyst and of a catalyst used in a reaction are shown in Fig. S2, All bands assigned to the polysiloxane material were present before and after the reaction demonstrating the catalyst stability.

3.8. Influence of temperature on 2-methylbenzyl hydroperoxide decomposition

The effect of the reaction temperature on the formation and decomposition of 2-methylbenzyl hydroperoxide was investigated for the Co^{2+} catalyst. The maximum yield of 2-methylbenzyl hydroperoxide and the corresponding *o*-xylene conversion at which the maximum yield has been reached are shown in Fig. 10. The maximum concentration of 2-methylbenzyl hydroperoxide in the liquid phase decreased, when the reaction temperature was increased. While the maximum hydroperoxide yield was reached at low temperatures, the hydroperoxide selectivity at its maximum yield remained approximately constant for all reaction temperatures. This indicates that the activity of the catalyst for decomposing 2-methylbenzyl hydroperoxide has a higher apparent energy of activation than the formation of the hydroperoxide.

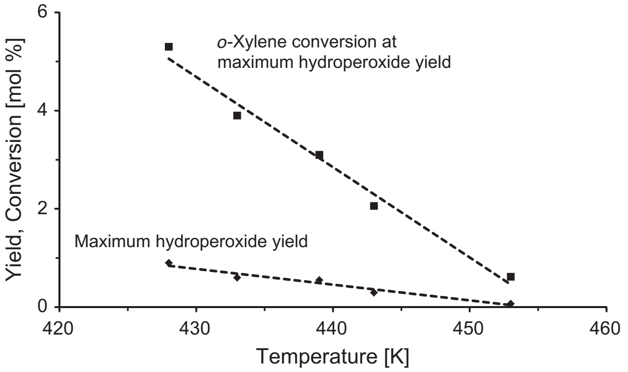


Fig. 10. Maximum yield of 2-methylbenzyl hydroperoxide (♦) and the corresponding *o*-xylene conversion at which this yield has been reached (■) (experimental conditions: 100 mg Co-1.9 catalyst, total pressure 2.4 bar).

At 445 K, the maximum 2-methylbenzyl hydroperoxide yields were reached at 2.0 mol% and 2.7 mol% conversion of *o*-xylene for Co^{2+} and Mn^{3+} catalysts, respectively, indicating that the hydroperoxide was decomposed more effectively by Co^{2+}.

The TOFs for the Co and Mn polysiloxane catalysts were 4.0 min^{-1} and 3.5 min^{-1}, respectively, which is twice as high as the TOF of the benchmark system Co naphthenate (TOF = 2.0 min^{-1}). With the benchmark catalyst, the yield of *o*-tolualdehyde was the highest tested (5 mol% *o*-xylene conversion; see Table 3). The yield of 2-methylbenzyl alcohol was the highest with Mn^{3+}-based catalysts, while in the case of Co^{2+} based catalysts, the selectivities toward *o*-tolualdehyde and 2-methylbenzyl alcohol were nearly equal (2.0 and 1.8 mol%, respectively). When Co naphthenate was used, 1 mol% of the ester of *o*-toluic acid and 2-methylbenzyl alcohol was formed. Note that the yield of 2-methylbenzyl hydroperoxide was very low (<0.1 mol%) at conversions of 5 mol%, as it is apparently decomposed to a large extent. As additional product, phthalide was formed over all catalysts used, which also balances the sum of yields to 5 mol%.

3.9. Stability of the catalyst–initiator system

In order to demonstrate that the transition metal was not leached during the reaction, the Co^{2+}-containing catalyst was used under the typical reaction conditions at 445 K until 2-methylbenzyl hydroperoxide was decomposed, i.e., at 7 mol% conversion (Fig. 11). After reaching this point, the catalyst was removed from the liquid phase by filtration at 353 K and the solution was returned into the reactor for further reaction at 445 K. The concentration of 2-methylbenzyl hydroperoxide increased again after the catalyst was removed from the reaction mixture, while the concentration of *o*-tolualdehyde and 2-methylbenzyl alcohol only increased very slowly until the maximum hydroperoxide concentration of 0.7 mol% was reached. At this concentration, the decomposition rate of the hydroperoxide in the liquid phase became larger than the formation rate, similar to the reaction carried out without catalyst (see Fig. 11). In consequence, the concentrations of the alcohol and aldehyde started to increase more rapidly. Interestingly, the formation of the acid was not affected by the removal of the catalysts, which indicates that the formation of *o*-toluic acid from *o*-tolualdehyde does not require the presence of the catalyst. The concentration of 2-methylbenzyl hydroperoxide was lower than the concentration when reacting pure *o*-xylene, which is attributed to the presence of oxygenates, inhibiting the formation of new radicals. Additionally, the reaction was carried out without catalyst using the reactant/product composition corresponding to a conversion of 7 mol% (see Fig. 11). The concentration profiles of the reaction products were equal to the reaction, in which the catalyst was removed at a conversion of 7 mol%, confirming the evidence for the absence of Co^{2+} in the solution after physical removal of the catalyst.

To test further whether or not Co^{2+} is leached into the liquid phase, the chemical composition of the reaction mixture after the

Table 3
Yields (in mol%) of main oxygenates with different catalyst systems (experimental conditions: 445 K, total pressure 2.4 bar, 5 mol% conversion).

Compound	Co naphthenate	Co-1.9	Mn-2.0
o-Tolualdehyde	2.3	2.0	1.4
2-Methylbenzyl alcohol	0.2	1.8	2.4
o-Toluic acid	0.8	1.1	1.1

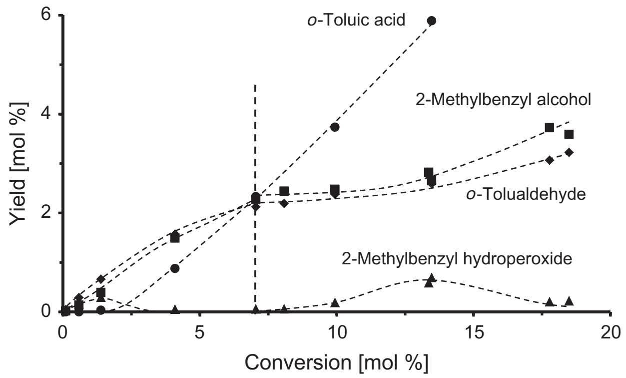


Fig. 11. Yields of oxygenates, i.e., *o*-tolualdehyde (♦), 2-methylbenzyl alcohol (■), 2-methylbenzyl hydroperoxide (▲), and *o*-toluic acid (●) as function of the *o*-xylene conversion (reaction conditions: 445 K, 100 mg Co-1.9 catalyst, total pressure 2.4 bar). The Co catalyst was removed from the reaction mixture when the concentration of 2-methylbenzyl hydroperoxide was below 0.03 mol% (at conversion of 7 mol%), which is indicated by the vertical line.

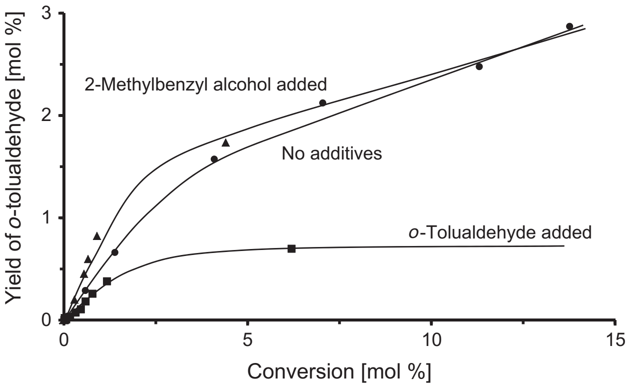


Fig. 12. Yields of *o*-tolualdehyde after adding 1.8 mol% 2-methylbenzyl alcohol (▲) or 1.6 mol% *o*-tolualdehyde (■) to the reactant and for the reaction of *o*-xylene (●) (reaction conditions: 445 K, 100 mg Co-1.9 catalyst, total pressure 2.4 bar).

oxidation reaction (20 mol% conversion) was determined by atomic absorption spectroscopy, showing no detectable concentration of Co^{2+} in the solution (concentration below 0.01 mg l^{-1}). Also, the treatment of the Co^{2+} catalyst in a solution of 20 mol% *o*-toluic acid in *o*-xylene under reaction conditions did not give any evidence for leached Co cations or other Co-containing species. To test the reusability, the catalyst was washed and dried after a reaction to remove reactant and oxygenates potentially present at the active centers/surface and reused showing the same activity as a fresh catalyst. This is in accordance with its unchanged chemical composition before and after the reaction and with the observation that no transition metal leaching occurred.

3.10. Reaction network of the selective oxidation of o-xylene

The analysis of the reaction products (see Fig. 4) indicates that the primary reaction product 2-methylbenzyl hydroperoxide is decomposed to *o*-tolualdehyde and 2-methylbenzyl alcohol, but it cannot be deduced whether or not the alcohol is further oxidized to aldehyde and what is the precursor for *o*-toluic acid. To follow the change in the yield of *o*-tolualdehyde in the presence of a defined starting concentration of its assumed precursor, 2-methylbenzyl alcohol was added prior to the reaction start. The same procedure was performed to understand the formation of *o*-toluic acid. In this case, *o*-tolualdehyde was added to the reactant. The yield of *o*-tolualdehyde after adding 2-methylbenzyl alcohol or *o*-tolualdehyde is illustrated in Fig. 12.

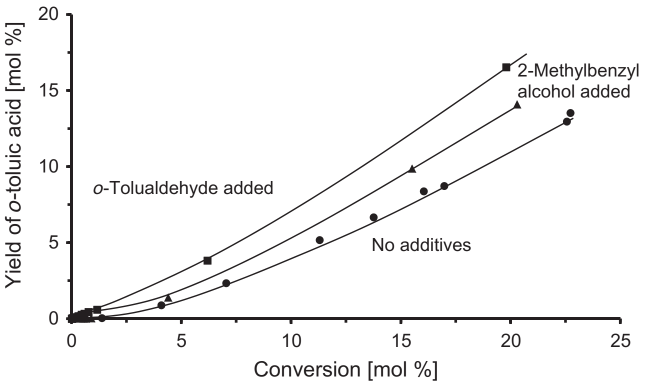


Fig. 13. Yields of *o*-toluic acid after adding 1.8 mol% 2-methylbenzyl alcohol (▲) or 1.6 mol% *o*-tolualdehyde (■) to the reactant and for the reaction of *o*-xylene (●) (reaction conditions: 445 K, 100 mg Co-1.9 catalyst, total pressure 2.4 bar).

At low conversion levels, the yield of *o*-tolualdehyde increased after adding 2-methylbenzyl alcohol, while at higher conversion levels, the addition of 2-methlybenzyl alcohol did not change the yield of *o*-tolualdehyde compared to the oxidation of *o*-xylene. This confirms that *o*-tolualdehyde is a consecutive product of 2-methylbenzyl alcohol. In contrast, the addition of *o*-tolualdehyde to the reactant significantly lowered its formation in the reaction.

Adding 2-methylbenzyl alcohol or *o*-tolualdehyde to the reactant had a positive effect on the yield of *o*-toluic acid (see Fig. 13) and, in general, increased the induction period, which implies that the formation of radicals is retarded, when oxygenates (i.e., aldehydes or alcohols) are present. After adding the intermediate products, not only the selectivity toward the consecutive products, but also the rate of *o*-toluic acid formation increased in the sequence *o*-xylene, 2-methlybenzyl alcohol addition, *o*-tolualdehyde addition.

4. Discussion

Overall, the intermediates and products and their formation rates strongly indicate that the selective oxidation of *o*-xylene over Co^{2+} and Mn^{3+}-containing catalysts proceeds primarily via radical reaction pathways. The observed selectivity toward oxidation of only one methyl group are governed by the differences between the rate of the initial CH activation and the further oxidation as well as by the –*I* effect of the oxygen-containing functional group at the aromatic nucleus. The formation and decomposition of 2-methylbenzyl hydroperoxide are concluded to be the initial steps in the oxidation of *o*-xylene followed by a series of radical reactions leading to *o*-tolualdehyde, 2-methylbenzyl alcohol, and *o*-toluic acid. To compare the formation and consumption of the radicals by the individual reactions along the reaction route, the most feasible reactions occurring in a radical-based oxidation of *o*-xylene are summarized in Scheme S1 in the supporting information. The reactions include the routes to all main products observed, i.e., 2-methylbenzyl hydroperoxide, *o*-tolualdehyde, 2-methylbenzyl alcohol, and *o*-toluic acid.

The formation of 2-methylbenzyl alcohol can proceed via five possible pathways (all reactions described in the following are summarized in Scheme S1 in the supporting information). Four of these routes proceed via the formation of 2-methylbenzyl hydroperoxide (reactions 1.0, 1.2, or 1.3 in combination with 2.0 and 3.0) followed by its thermal or catalytic decomposition (reactions 5.0 and 6.1, 5.1 and 6.1, 4.0 and 6.1, or 3.0 and 6.0).

Alternatively, 2-methylbenzyl alcohol can be formed from a benzylic radical by the recombination with an OH-radical (reaction 6.2), which originates from the decomposition of hydroperoxide.

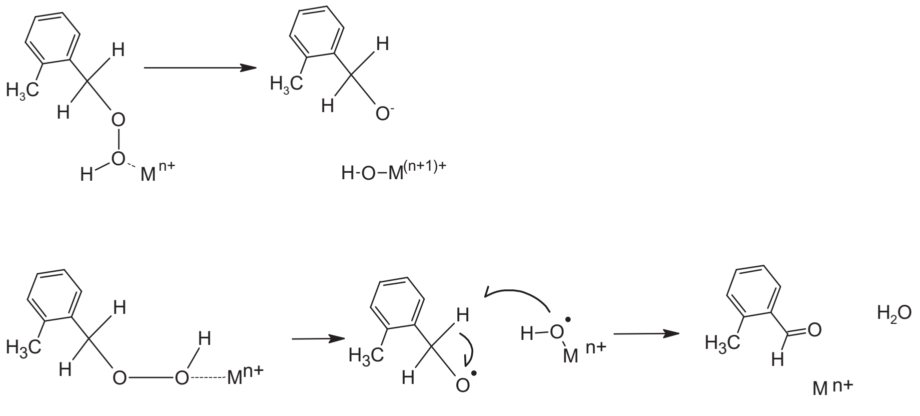
For the formation of *o*-tolualdehyde, three pathways are feasible. One is the direct route starting from *o*-xylene, which proceeds via the dehydration of 2-methylbenzyl hydroperoxide (reaction 7.0). Alternatively, *o*-tolualdehyde can be formed from 2-methylbenzyl alcohol as a consecutive product (reactions 7.1, 7.2) or via 2-methylbenzyl alcohol by the reaction with an alkoxy radical delivering a hydrogen atom to a carbon-based radical (reaction 7.2). The latter step is consuming radicals to a high degree and, therefore, the formation of *o*-tolualdehyde via this pathway is highly radical annihilating. A certain initial radical concentration of it is necessary to allow propagation of the radical chain. When the *o*-tolualdehyde concentration, however, exceeds a certain threshold limit, the chain propagation is strongly retarded, because its formation is highly radical consuming.

Comparing the oxidation of *o*-tolualdehyde and 2-methylbenzyl alcohol (reactions 7.1, 7.2 and 8.0, 9.0, 8.1, 9.0 followed by 10.0, 11.0, 11.1, and 12.0), it appears unlikely that the oxidation of 2-methylbenzyl alcohol significantly contributes to the formation of *o*-toluic acid. No direct route from 2-methylbenzyl alcohol to *o*-toluic acid is feasible, because only one step oxidation reactions are observed in radical-based mechanisms. This conclusion is supported further by the increase in the selectivity toward *o*-toluic acid, when *o*-tolualdehyde was added into the reactant. *o*-Toluic acid was formed with a higher rate, independently whether 2-methylbenzyl alcohol or *o*-tolualdehyde was added, although the acceleration is more pronounced, when *o*-tolualdehyde was added. In this context, it should be emphasized that the presence of aldehydes in radical-based shifts the reaction pathways into the direction of peracids, which subsequently react to the corresponding acid. Consequently, the formation of peracidic species, described in reaction steps 9.0, 10.0, 11.*x*, and 12.0, is enhanced by higher concentrations of *o*-tolualdehyde (which is the case at high conversion levels or when it is directly added to the reactant). The initial addition of aldehyde induces the reduction in the reaction rate, because it forms stable oxygen-based radicals, which do not support the radical chain propagation. Thermodynamic limitations for the lowering of the reaction rate can be excluded, because the equilibrium between the aldehyde and the acid is not being reached under these conditions (higher *o*-tolualdehyde concentrations are observed). Note that also the conversion between the alcohol and the aldehyde is not catalyzed, as this would enhance the rate of 2-methylbenzyl alcohol formation.

The combination of the reaction of *o*-tolualdehyde and the lower formation rate due to the high degree of radical annihilation leads to a relative increase in the selectivity to 2-methylbenzyl alcohol. In consequence, the ratio of *o*-tolualdehyde to 2-methylbenzyl alcohol decreases with increasing conversion on all catalysts. Thus, the Co^{2+} and Mn^{3+} polysiloxanes act as initiator for the formation of radical species and catalyze the decomposition of 2-methylbenzyl hydroperoxide to *o*-tolualdehyde and 2-methylbenzyl alcohol. The linear correlation of the Co^{2+} loading and the hydroperoxide formation rate implies that the active site for the initiation reaction is the Co^{2+}or Mn^{3+} cation. As IR spectra of adsorbed CO document the direct proportionality of the intensity of the CO stretching band and the Co^{2+} concentration, we conclude that either all Co^{2+} cations are accessible or that at least the fraction of accessible cations remains constant as the concentration increases. The interaction of *o*-xylene with Co^{2+} is well documented in the UV/vis spectra. Under reaction conditions, the three characteristic Co^{2+} bands shifted to lower wavelengths upon contact of the sample with *o*-xylene and oxygen indicating that the interaction with the reactants decreases the electron density on Co^{2+}. The interaction of the substrate and the Co^{2+} cations is concluded to be reversible, as the spectra of the catalyst before and after the oxidation reaction are identical.

The transition metal polysiloxanes also catalyze the decomposition of intermediately formed hydroperoxides. The selectivity to the decomposition products, defined as the ratio of *o*-tolualdehyde and 2-methylbenzyl alcohol, depends on the type of transition metal in the catalyst. The ratio of *o*-tolualdehyde and 2-methylbenzyl alcohol starts at values of about 2.5 independent of the catalyst system used. This indicates that the formation of the aldehyde occurs intrinsically with a higher rate. However, its formation is highly radical consuming and, thus, the aldehyde formation is favored at low conversions when the overall radical concentration is high. Note that also a direct pathway from *o*-xylene without the hydroperoxide intermediate may exist. One possibility is a direct reaction channel proceeding via $ArCH^{\bullet}COOH$ radicals as described by Hermans et al. [37].

The decomposition of the initially formed 2-methylbenzyl hydroperoxide in the main reaction pathway on transition metals to *o*-tolualdehyde and 2-methylbenzyl alcohol can be described by an adsorption of the hydroperoxide to the transition metal center. The decomposition reaction (see Scheme 3) proceeds via the cleavage of the O–O bond assisted by the transition metal. When 2-methylbenzyl hydroperoxide is bound to a transition metal cation, the O–O bond is weakened and tends to decompose resulting in *o*-tolualdehyde or 2-methylbenzyl alcohol. The specificity of the metal cation is remarkable. Mn^{3+} increases the selectivity toward 2-methylbenzyl alcohol, whereas Co^{2+} favors the formation of *o*-tolualdehyde (see also Refs. [7,12]). As soon as the conversion exceeds 4 mol%, however, a constant ratio depending on the type of transition metal is observed, i.e., 1 for Co^{2+} and 0.6 for Mn^{3+}. In



Scheme 3. Suggested pathways for the transition metal catalyzed decomposition of 2-methylbenzyl hydroperoxide to *o*-tolualdehyde and 2-methylbenzyl alcohol.

presence of Mn^{3+}, the O–O bond is preferably cleaved heterolytically (see Scheme 3 upper route) resulting in an alkoxide intermediate, which is subsequently transformed to 2-methylbenzyl alcohol. The higher selectivity of Co^{2+} toward *o*-tolualdehyde attributed to Co^{2+} favoring homolytic bond scission (see Scheme 3 lower route). This is supported by the observation that in the case of Co^{2+} a higher maximum concentration of 2-methylbenzyl hydroperoxide is produced during the reaction compared to Mn^{3+} (2-methylbenzyl hydroperoxide yield 0.3 vs. 0.08 mol%, see Fig. 6). Note that the observation of hydroperoxide can directly be related to the presence of radicals in the reaction solution, as it can only be formed via a radical pathway.

The qualitative and quantitative stability of the initiator/catalyst materials are unequivocally proven by the combination of assessing the concentrations of metal cations (i.e., the constant elemental composition of the polysiloxanes and the absence of Co^{2+} in the liquid phase after reaction) as well as by spectroscopic characterization of their interaction with probe molecules and reactants. In this respect, note that the CO concentration on used catalysts was identical to that on the fresh materials provided that the accessibility of the transition metal cations was assured. UV/vis spectroscopy in turn gives evidence that the Co species after reaction are identical to those before the reaction indicating no change in the overall oxidation state.

It is interesting to note that the activity normalized to the concentration of the transition metal cations (turnover frequency, TOF) of the discussed initiator/catalyst system is drastically higher than that of the benchmark system Co naphthenate system. Apparently, the more hydrophobic environment of the solid support destabilizes the more polar products, helping so to reduce (not to complete eliminate) this interaction. It should be also kept in mind that the hydrophobic environment will decrease the concentration (not the activity) of the polar reaction participants, by minimizing the interactions and reduce so the apparent residence time of the products in the pores.

5. Conclusions

The novel hydrophobic Co^{2+} and Mn^{3+} cation-containing polysiloxanes act as efficient catalysts and initiator systems in the selective oxidation of methyl-substituted aromatics under solvent-free conditions, accelerating the initiation of the radical chain and efficiently decomposing the intermediately formed hydroperoxide. The activity of both anchored transition metals, Co^{2+} and Mn^{3+}, was superior to the benchmark system Co naphthenate, as the hydrophobicity of the polysiloxane material facilitates the desorption of the polar reaction products and reduces their concentration in the pores. The decomposition of the hydroperoxide (formed as primary intermediate) depends on the type of transition metal with Co^{2+} enhancing the formation of *o*-tolualdehyde and Mn^{3+} increasing the selectivity toward 2-methylbenzyl alcohol. The difference in selectivity is attributed to the different decomposition pathways. Heterolytic O–O bond cleavage in the hydroperoxide leads to the alcohol, the homolytic scission to the aldehyde. The heterogeneous polysiloxane materials show high stability under reaction conditions. Leaching of transition metal was not observed and the accessibility of active species was not affected by the oxidation reaction. This indicates that polysiloxane-based catalysts systems are interesting alternatives for radical oxidation catalysis. The possibility to subtly tailor the polarity of the pore walls and the potential to include specific bonding sites into these walls open up a highly flexible strategy for catalyst design.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.06.019.

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