Solvent-free aerobic epoxidation of 1-decene using supported cobalt catalysts

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ABSTRACT

In this study, active cobalt-based catalysts are reported for the solvent-free aerobic epoxidation of 1-decene as a non-noble metal, alternative to the conventionally used gold catalyst. No sacrificial reductant is applied and air is used as primary oxidant at ambient pressure. The influence of different radical initiators and the product distribution over time is investigated. Evidence for a reaction mechanism similar to the previously reported gold-catalysed aerobic epoxidation of 1-decene, is given. Furthermore, it is shown that the catalyst stability is influenced by the choice of the support.

1. Introduction

Selective oxidation is a key process for commercial applications, especially for the synthesis of chemical intermediates in the manufacturing of functionalised fine chemicals and pharmaceutics. Therefore, the oxidation of hydrocarbons to generate compounds containing oxygen is an important industrial reaction [1,2]. Conventionally, alkene epoxidation involved the addition of stoichiometric amounts of peroxides such as peracids, *tert*-butyl hydroperoxide (TBHP) or hydrogen peroxide, which are expensive and hazardous [3–6]. Taking into account, the requirements from green chemistry and atom efficiency, molecular oxygen would be the preferred oxidant. Thus, an active and selective catalytic system using molecular oxygen or air is highly desired for epoxidation reactions. Various studies using different types of heterogeneous catalysts reported that the electrophilic addition of oxygen to alkenes to form epoxides is challenging due to the presence of labile allylic H atoms, whose facile abstraction results in production of allylic products instead of epoxides [7,8]. Supported gold catalysts were previously reported as highly selective in the epoxidation of different olefins such as propene [9], cycloalkenes [7,10], as well as long chain α-olefins [8,11]. However, the application of cost-effective transition metals in epoxidation reactions would be more desirable from an economical point of view, a trend which can be observed also in many other fields of research [12–15].

Both homogeneous [16,17] and heterogeneous [18–21] cobalt-based catalysts have been reported to be active in epoxidation reactions, exhibiting high selectivity and often good yields to the epoxide. Heterogeneous cobalt catalyst, have attracted increasing interest in recent years, due to their simple separation from the product solution [22–24]. Various cobalt catalysts have been applied to the epoxidation of different alkenes, mainly in reactions with cyclic or aromatic olefins such as cyclohexene, styrene, and stilbene.

TBHP is often used as an oxidant in conjunction with cobalt catalysts in epoxidation reactions [6,22,24]. However, as previously mentioned, oxygen would be the preferred oxidant, although the activation of oxygen remains a challenge and aldehydes are used as co-reductants [16,25]. In 2004 Tang et al. reported that Co^{2+} ion exchanged zeolites are active in the epoxidation of styrene using O_2 as the oxidant, without a sacrificial reductant, in *N,N*-dimethylformamide (DMF) solvent [18]. They showed that the solvent choice is crucial and suggested that the superior activity of the cobalt catalyst in DMF is due to coordination of the solvent to the Co(II) forming the actual active site [26]. Thus, DMF became the solvent of choice in many epoxidation reactions using cobalt catalysts [20,21,23,25,27,28]. Baiker and co-workers investigated the role of DMF and other amide solvents in more detail and proposed that they react as "sacrificial solvents" [19,29]. They reported that, the solvents act as oxygen-transfer agents forming considerable amounts of by-products such as *N*-formyl-*N*-methylformamide, in the case of DMF. The authors concluded that the atom-efficiency of this reaction in the presence of DMF is poor and far from a "green" technology [19].

Therefore, there is significant scope to improve catalytic systems using supported cobalt catalyst for the alkene epoxidation under environmentally friendly reaction conditions.

With regard to the successful epoxidation of longer chain linear α-olefins there are only a few examples in the literature in which either TBHP is used as primary oxidant [22] or DMF was used as solvent [27,28]. In this work, a simple but selective supported cobalt catalysts for the epoxidation of 1-decene under solvent-free conditions using oxygen as primary oxidant at atmospheric pressure, are reported.

2. Experimental part

2.1. Catalysts preparation

All catalysts were prepared by a wet-impregnation method. The method of preparation of 2 g of the specific catalyst was as follows: Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 0.197 g, 99%, Aldrich) was dissolved in deionised water (80 °C) and mixed with the required amount of the support (1.96 g, MgO (Aldrich), TiO_2 (P25Degussa)). The mixture was stirred for 120 min and water was slowly evaporated from the mixture until it formed a paste. The resulting paste was dried in air at 110 °C for 16 h and afterwards was thoroughly ground and calcined in static air at 400 °C for 3 h (heating rate: 20 °C min^{-1}). The synthesised catalysts are referred to as 2 wt.-% Co_3O_4/support with the 2% denoting the amount of cobalt.

2.2. Catalyst testing and characterisation

Epoxidation reactions were carried out in a magnetically stirred, round-bottomed glass flask reactor (50 ml volume) fitted with reflux condenser, in the temperature range of 60–90 °C for 24 h. In a typical reaction 0.1 g of catalyst was added to 10 ml of 1-decene (52.8 mmol, 94%, Aldrich) and a catalytic amount of a radical initiator, such as *tert*-butyl hydroperoxide (TBHP) (70% in water, 0.064 mmol, Aldrich), cumene hydroperoxide (CHP) (0.028 mmol, Aldrich) or azobisisobutyronitrile (AIBN) (0.036 mmol, Alfa Aesar). After the required reaction time, the mixture was cooled down to room temperature, filtered and analysed by gas chromatography (Varian Star 3800 CX) fitted with a DB-5 column and a flame ionization detector (FID). For compounds identification GC–MS was used. (Walters GCT Premier GC fitter with a HP 6890 N mass spectrometer). 1-decene conversion was determined based on the substrate concentration before and after the reaction. Mass balance for known products in all reactions was more than 88%. In addition to the products reported below, traces amount of CO and CO_2 were detected (selectivity < 1%). The standard deviations of three experiments are displayed as error bars.

An additional experiment was performed to determine the amount of 1-decene hydroperoxides intermediates as these products are not distinguished by GC analysis. A standard reaction was carried out and the reaction mixture was filtered and divided into two aliquots. The first aliquot was stirred for 1 h in air at room temperature with excess amount of triphenylphosphine (0.15 g, PPh_3, Aldrich) to trap the hydroperoxide as the corresponding aldehyde or alcohol, while the second

one was analysed directly by GC.

Surface area analysis were performed using a Micromeritics Gemini 2360 Analyser. Samples for measuring the surface area, were prepared by degassing for approx. 50 min at 120 °C in presence of He. Then, the sample was placed in a sample vessel connected to a gas inlet (liquid N_2 at −196 °C). The surface area was calculated using the Brunauer–Emmet–Teller equation.

The XRD analysis was performed using a PANalytical X'pert pro diffractometer using a Cu K α X-ray source. Typical scans were performed from 10 to 80° 2θ at 40 kV and 40 mA with a step size of 0.0167° 2θ and a scan speed of 0.0356° 2θ s^{-1}.

XPS was performed on a Kratos Axis Ultra-DLD photoelectron spectrometer, using monochromatic Al Kα radiation, at 144 W (12 mA × 12 kV) power. High resolution and survey scans were performed at pass energies of 40 and 160 eV, respectively. Magnetically confined charge compensation was used to minimize sample charging and the resulting spectra were calibrated to the C(1 s) line at 284.8 eV for adventitious carbon. All binding energies have an uncertainty of ± 0.2 eV of the reported values.

TPR analysis was carried out on a Thermo TPD/R/O 1100 series instrument equipped with a thermal conductivity detector (TCD). The catalyst (50 mg) was heated up to 800 °C (heating rate: 5 °C min^{-1}) under an atmosphere of 10% H_2/Ar (flow rate: 15 ml min^{-1}).

Infrared spectra were obtained using FT/IR-660Plus Fourier Transform infrared spectrometer (JASCO).

Inductively coupled plasma mass spectrometry (ICP-MS) was performed on an Agilent 7900 ICP-MS equipped with a micromist nebuliser. Quantification of the analysed elements was carried out by comparison with a calibration curve.

3. Results and discussion

3.1. Influence of radical initiators on 1-decene epoxidation

As molecular oxygen is a diradical in its ground state, this may lead to a contribution in radical reactions, especially in the presence of a radical initiator [8,30,31]. The radical initiator can have dual roles: to oxidise stabilisers, which are often present in the substrates [10] and to facilitate the oxidation at temperatures below the autooxidation temperature. In the case of 1-decene, this temperature was found to be 100 °C. Generally, small amounts of radical initiator will be consumed in the early stage of the reaction and further propagate the reaction under mild conditions. However, it is important to determine the effect of the initiator on the radical reaction to be able to distinguish it from the catalytic activity of the catalyst. In this study, three different radical initiators were tested, namely: *tert*-butylhydroperoxide (TBHP), cumenehydroperoxide (CHP) as hydroperoxide radical initiators and azobisisobutyronitrile (AIBN) as an azoradical initiator. These radical initiators were tested at different temperatures (60–90 °C) in the absence of a catalyst and using molecular oxygen from air as primary oxidant. Table 1 shows that no oxidation occurs in the absence of a radical initiator at temperatures between 60 and 90 °C. As expected the conversion increases with increasing temperature for all three radical

Table 1
Effect of temperature on 1-decene epoxidation using different radical initiators.

Initiator	60 °C		70 °C		80 °C		90 °C	
	X (%)	$S_{Epoxide}$ (%)	X (%)	$S_{Epoxide}$ (%)	X (%)	$S_{Epoxide}$ (%)	X (%)	$S_{Epoxide}$ (%)
–	0	0	0	0	0	0	0	0
AIBN	1.3	1.4	1.6	3.7	3.4	14.2	6.4	17.2
CHP	1.3	1.3	1.2	3.1	3	4.2	5.5	13.3
TBHP	0.5	0.2	0.7	0.7	1.5	3.5	2.3	13.3

Reaction Conditions: 1-decene (53 mmol, 10 ml), TBHP (0.064 mmol, 0.01 ml), AIBN (0.036 mmol, 6 mg), CHP (0.028 mmol, 0.01 ml), atmospheric pressure, reaction time: 24 h; X = Conversion and $S_{Epoxide}$ = Epoxide selectivity.
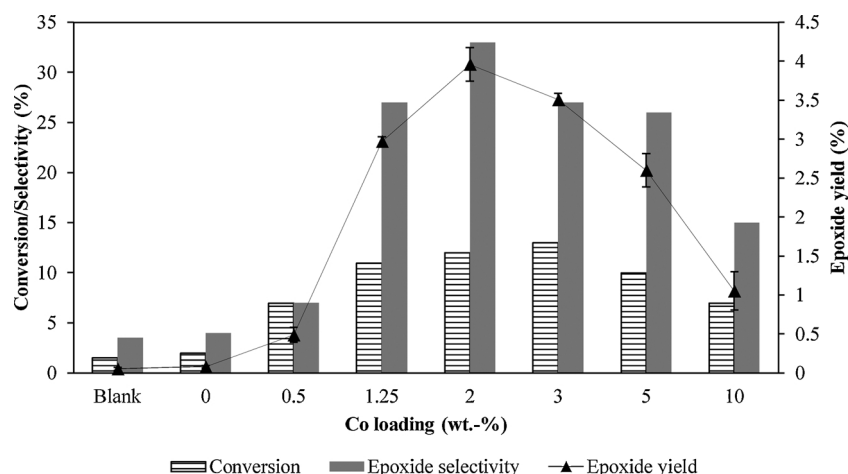
Fig. 1. Effect of cobalt loading on epoxidation of 1-decene. Reaction conditions: Co_3O_4/MgO (0.1 g), 1-decene (10 ml, 53 mmol), TBHP (0.01 ml, 0.064 mmol), 80 °C, 24 h, atmospheric pressure.

initiators. AIBN is the most active radical initiator yielding a maximum of 6.4% conversion and 17.2% selectivity towards the targeted product 1,2-epoxydecane at 90 °C, followed by CHP and TBHP with 5.5% and 2.3% conversion, respectively and a epoxide selectivity of 13.3% in both cases. Based on this data, TBHP was chosen as radical initiator for further studies at 80 °C with cobalt catalyst. At this temperature TBHP leads to lower conversion of 1-decene (1.3%) as well as to lower selectivity to the epoxide (3.5%) compared to CHP and AIBN. Therefore, the role of the investigated Co catalysts is more pronounced.

3.2. Cobalt-catalysed reactions

A 2 wt.-% Co_3O_4/MgO has been selected to study the epoxidation of 1-decene under solvent-free conditions. First, we tested the bare MgO support, which exhibited poor activity in the epoxidation reaction (2% conversion) and only 4% selectivity to the desired 1,2-epoxydecane (Fig. 1). Both values increased once Co_3O_4 was supported onto MgO. Fig. 1 shows that both, the conversion and epoxide selectivity, increase with higher cobalt loading of the catalyst, up to 2%. A further increase in cobalt loading resulted in a drop of activity and selectivity. With higher cobalt weight loadings sintering might be facilitated during the heat treatment in the catalyst preparation. This would lead to larger nanoparticles and a decrease in cobalt oxide surface area, which might be the reason for the lower acitivity and selectivity. Thus, the 2 wt.-% Co_3O_4/MgO catalyst was chosen for further investigations.

It is generally accepted that achieving high selectivity to the epoxide in aerobic epoxidation reactions under solvent-free conditions remains a challenge. Thus, even in the present case, when a good epoxide selectivity of 33% at 12% conversion is observed using a 2 wt.-% Co_3O_4/MgO catalyst, numerous by-products were detected and quantified. The full list of products formed during a 24 h reaction and their selectivities is presented in Table S1 (supporting information). In order to understand the detailed reaction profile of 1-decene epoxidation over the 2 wt.-% Co_3O_4/MgO catalyst, time online studies have been carried out over the period of 96 h (Fig. 2). As expected, the conversion of 1-decene increases with increasing reaction time from 1% at 4 h to 36% at 96 h. It can be seen that allylic products such as 1-decen-3-one, 1-decen-3-ol, 2-decenal, 2-decen-1-ol are the predominant products at the beginning of the reaction. With progressing reaction time the selectivities to these products decrease, while the epoxide selectivity increases to a maximum of 35% after 48 h. Further increase in the reaction time resulted in a steady decrease in the epoxide selectivity to a value of 28% after 96 h, which is believed to be a result of epoxide ring opening leading to the formation of 1,2-decane diol. This is caused by the reaction between the epoxide and *in-situ* formed water, which may come from the

breakdown of the hydroperoxy intermediate to form the allylic ketone and water. Once water is formed, the epoxide is easily hydrolysed to the diol. The presences of hydroperoxy species was demonstrated earlier when using a supported gold catalyst [8].

Leaching of the active component is a major problem facing heterogeneous catalysts especially in the liquid phase reactions. Co_3O_4/MgO catalysts exhibited high activity in the epoxidation reactions, but the ICP AES analysis showed that the materials were indeed leaching active components into the reaction mixture. In the case of the 2 wt.-% Co_3O_4/MgO catalyst, ICP analysis showed cobalt leaching on the level of 45 ppm in the reaction effluent, corresponding to approximately 23% of metal present in the fresh catalyst. This significant leaching might be due to the fact that various alcohols and acids are formed during the reaction, causing leaching of the active components in liquid phase oxidations due to their strong complexing and solvolytic properties [32]. One option to reduce the loss of the active species is to increase the metal-support interaction. Among many supports, TiO_2 is known to be an appropriate material for oxidation reactions and has a good interaction with metals if used as a support [33]. Therefore, further studies were conducted using TiO_2 as support. From Fig. 3 it can be seen that the change from MgO to TiO_2 resulted in higher activity (4% conversion of 1-decene and 17% selectivity to 1,2-epoxydecane) when the bare support was tested in the epoxidation reaction. In the presence of 2 wt.-% Co_3O_4/TiO_2 catalysts, the conversion of 1-decene and the epoxide selectivity is enhanced to 14% and 34%, respectively. The 2 wt.-% Co_3O_4/TiO_2 catalyst shows no superior activity and selectivity in comparison to the MgO-supported material, but it is more stable. When TiO_2 was used as support, the quantity of cobalt leached from the catalyst decreased to 12 ppm, accounting for 6% of cobalt loading and therefore, making it a more appropriate catalyst for the epoxidation of 1-decene.

Since the more stable 2 wt.-% Co_3O_4/TiO_2 catalyst is still very active and selective it can be assumed that the cobalt in solution is not the main active species in the epoxidation reaction. However, to confirm this assumption a hot filtration experiment was performed. In Table 2 the results of a standard epoxidation of 1-decene after 8 h and 24 h are compared to the results of the hot filtration test where the reaction was stopped after 8 h and the catalyst was filtered off before the reaction was continued for another 16 h. As no significant increase in the conversion was observed after the catalyst was removed from the reaction solution, the main catalytic route can be considered to be heterogeneous. The slight increase in epoxide selectivity from 10 to 15% might be ascribed to previously formed decene hydroperoxide (not detectable *via* GC, this will be discussed in more detail below), an intermediate, converting into alkoxy radicals which recombine with 1-
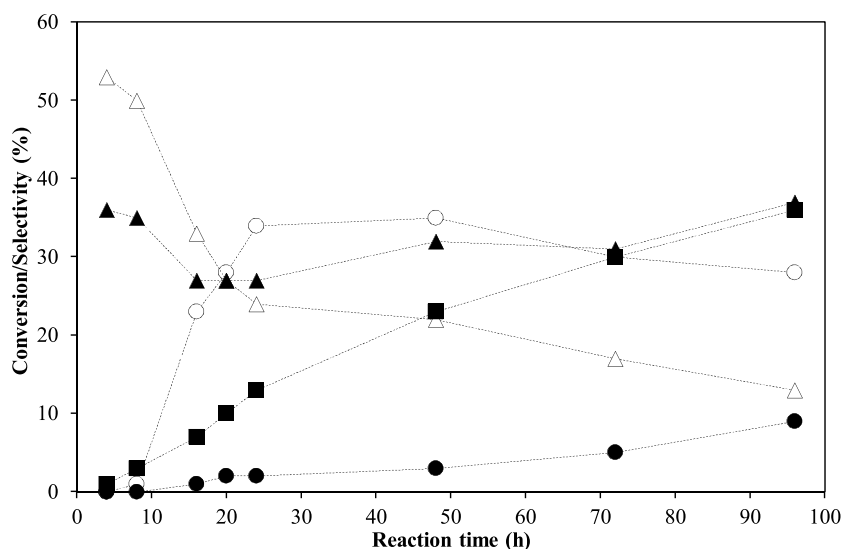
Fig. 2. Effect of reaction time on conversion and selectivity. Legend: conversion: ■, Epoxide selectivity: ○, Allylic products selectivity: △, Others selectivity: ▲, Diol selectivity: ●. Allylic products = Σ (1-decen-3-one, 1-decen-3-ol, 2-decenal, 2-decen-1-ol). Others products = Σ ($C_7 + C_8 + C_9$ acids, $C_8 + C_9$ aldehyde, $C_7 + C_8$ alcohol, 3-Nonanone, 2-decenoic acid). Reaction conditions: 2 wt.-% Co_3O_4/MgO (0.1 g), 1-decene (10 ml, 53 mmol), TBHP (0.01 ml, 0.064 mmol), 80 °C, 24 h, atmospheric pressure.

decene to yield 1,2-epoxydecane as proposed earlier in the mechanism for the epoxidation of 1-decene [8].

3.3. Catalysts reusability

Given that the stability of the supported Co_3O_4 catalyst was enhanced by changing the support to TiO_2, a more detailed study of catalyst reusability could be performed. The results of 1-decene epoxidation over a fresh and used 2 wt.-% Co_3O_4/TiO_2 catalysts are summarized in Fig. 4. As mentioned above, when a fresh 2 wt.-% Co_3O_4/ TiO_2 catalyst was used the conversion reached 14% with an epoxide selectivity of 34%. However, reusing the catalyst without a washing step (dried over night at 110 °C) resulted in a large decrease in conversion as well as epoxide selectivity to 7 and 19%, respectively. The decrease in activity may be ascribed to loss of the active metal or alternatively adsorption of products on the catalyst surface blocking active sites. IR analysis of the used catalyst confirmed presence of additional species with strong stretching modes visible in the region of 2900–2970 cm^{-1}, which can be assigned to C−H stretching (SI-Fig. S1) from adsorbed reaction products. When the catalyst was washed with acetone before being dried and reused, the decrease in conversion and selectivity was less pronounced (*cf.* Fig. 4), suggesting that some of the adsorbed products were removed from the catalyst surface. This is in

Table 2
Comparison of conversion (X) and epoxide selectivity ($S_{Epoxide}$) of a standard epoxidation reaction of 1-decene with a hot filtration (HF) test.
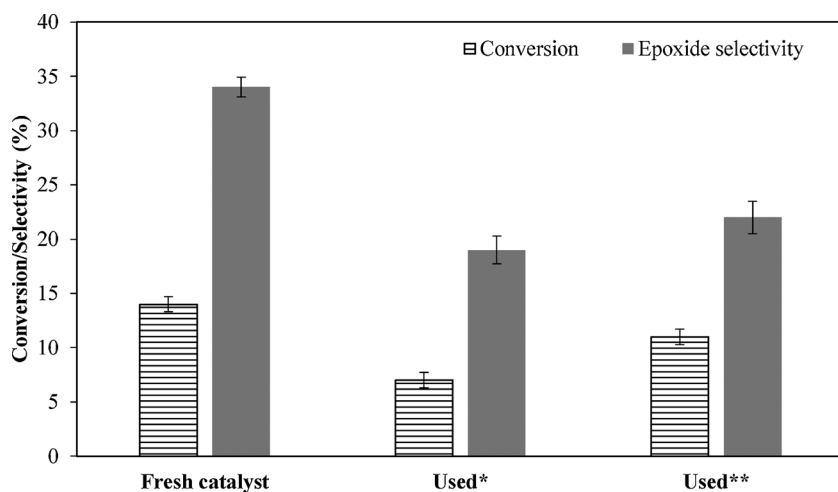
Reaction time (h)	X (%)	$S_{Epoxide}$ (%)
8	3.4	10
24	14	34
HF*	4	15

Reaction conditions: 2 wt.-% Co_3O_4/TiO_2 (0.1 g), 1-decene (10 ml, 53 mmol), TBHP (0.01 ml, 0.064 mmol), 80 °C, atmospheric pressure. *HF: reaction was stopped after 8 h and the catalyst was filtered off before the reaction was continued for another 16 h.

agreement with the IR analysis of this sample, where the characteristic bands reduced in size compared to the unwashed sample (SI-Fig. S1). Another possible explanation for the decreased activity in the recycle experiment might be the change in the cobalt oxide structure during the reaction as observed by XPS analysis. After use, the characteristic photoemission lineshape for CoO is observed, instead of that for the Co_3O_4 spinel. This change in structure, combined with the decrease in activity of the catalyst, suggests that the cobalt spinel structure is beneficial for an enhanced epoxidation catalyst.
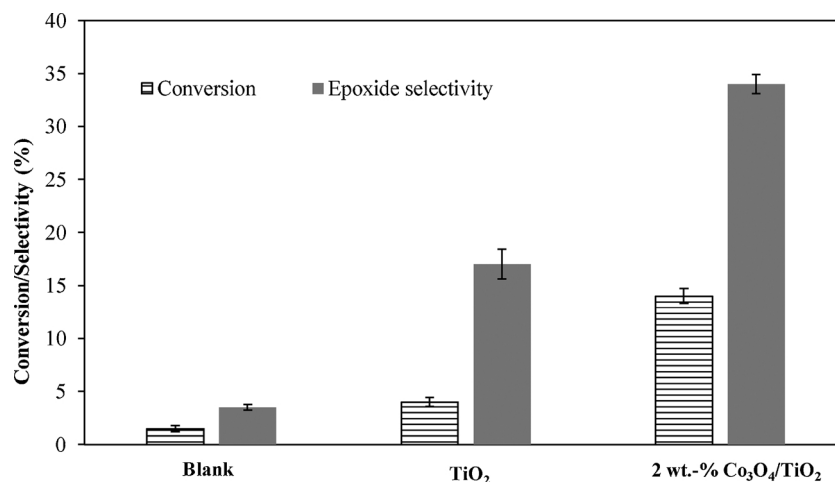
Fig. 3. Effect of TiO_2 and 2 wt.-% Co_3O_4/TiO_2 on 1-decene epoxidation. Reaction conditions: Catalyst (0.1 g), 1-decene (10 ml, 53 mmol), TBHP (0.01 ml, 0.064 mmol), 80 °C, 24 h, atmospheric pressure.

Fig. 4. Catalyst reusability study for epoxidation of 1-decene. Reaction conditions: 2 wt.-% Co_3O_4/TiO_2 (0.1 g), 1-decene (10 ml, 53 mmol), TBHP (0.01 ml, 0.064 mmol), 80 °C, 24 h, atmospheric pressure. Used*: Used without washing, dried in static air at 110 °C for 16 h. Used**: Used and afterwards washed with acetone, dried in static air at 110 °C for 16 h.

3.4. Mechanism for cobalt-catalysed aerobic epoxidation of 1-decene

As seen in Table 3 the absence of radical initiator resulted in negligible conversion after the 24 h reaction. This observation is in agreement with a previous study reported by Gupta et al. [8] and suggests a free radical mechanism. Another experiment to confirm the radical mechanism for 1-decene epoxidation involves the reaction in the presence of a radical scavenger, which should circumvent the radical chain reaction. The results displayed in Table 3 show that when adding 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the epoxidation of 1-decene, no conversion can be observed. Thus, BHT reacted as radical scavenger and terminated the reaction, which demonstrates that radical chemistry is highly involved in the present reaction mechanism and oxygen from air seems to be activated *via* a free-radical species.

Previously, a reaction mechanism was proposed for the epoxidation of 1-decene using a supported gold catalyst by our research group [8]. It was shown that decene hydroperoxide is an intermediate in the epoxidation reaction, which most likely produces the epoxide and the allylic products. This intermediate cannot be easily identified by using gas chromatography, as it decomposes in the injector inlet due to the high temperatures [34]. However, it is possible to reduce the hydroperoxide to corresponding products such as the aldehyde and alcohol. Triphenylphosphine is frequently used to scavenge thermally unstable peroxides in GC analysis [8,11,29,34]. Hence, the difference between concentration of aldehyde and alcohol before and after triphenylphosphine reduction gives an estimated amount of hydroperoxide present in the reaction mixture. A standard reaction was performed for 24 h at 80 °C in presence of TBHP and 2 wt.-% Co_3O_4/TiO_2 catalysts. After filtration, the reaction mixture was divided into two aliquots, then PPh_3 was added to one of them and stirred for 1 h at room temperature. Reaction mixtures before and after PPh_3 treatment were analysed by GC. The change in colour from transparent to yellow solution suggested conversion of the hydroperoxide into the corresponding allylic products

of the aliquot containing PPh_3. After analysis there was an increase in the selectivity to the 2-decenal from 3.4% to 6.2% and 2-decen-1-ol from 6.7% to 8.9%. Therefore, it can be reasoned that hydroperoxides are intermediates of the 1-decene epoxidation when a cobalt-based catalyst is applied. Thus, the reaction most likely follows the same reaction mechanism as previously suggested for gold catalysts [8]. The reaction is initiated by a radical initiator to form an allylic radical. Then a hydroperoxide intermediate is formed from this allylic radical and oxygen before it reacts on the catalysts' surface yielding an enyloxy radical, which then reacts with another 1-decene molecule to produce the epoxide and another allylic radical (Scheme 1).

3.5. Catalyst characterization

XRD analysis of the supports and corresponding cobalt catalysts were carried out in order to understand the catalyst's structure (Figs. S2 and S3). Comparing the MgO and 2% Co_3O_4/MgO diffraction pattern (Fig. S2) no significant change can be observed, thus, only the support is detected in the 2% Co_3O_4/MgO sample. This can be ascribed to small crystallite size which can't be detected by XRD. A similar observation has been found in a previous study where authors could not detect cobalt oxide in loadings as high as 10% Co_3O_4/TiO_2 by XRD [35]. However, in the 2 wt.-% Co_3O_4/TiO_2 sample the reflections for the Co_3O_4 spinel can be observed in addition to the support as displayed in Fig. S3.

The results of XPS analysis of both fresh and used Co catalysts are given in Table S2. Co supported on TiO_2 exhibits a Co(2p3/2) binding energy of 779.1 eV and a lineshape characteristic of that for the spinel oxide [36]. For the used catalyst, the cobalt is found to have a binding energy of 780.5 eV, characteristic of Co^{2+} in CoO [37]. Clearly, there is a large difference in the Co concentration between fresh and used samples, with the latter exhibiting an amount *ca.* 65% of that of the fresh material, which could indicate loss of cobalt or sintering. The first effect has been demonstrated from ICP analysis and so can partially account for loss of signal seen in XPS. Although the leaching could be significantly reduced when TiO_2 was applied as support material, it was not prevented completely. However, it should be considered that XPS shows a 65% reduction in Co surface species compared to the 6% loss from ICP. It is therefore likely that in addition to leaching, product inhibition and also particle sintering account for loss of Co XPS signal. For the MgO supported cobalt samples, the Co signal is very weak for the fresh catalyst, but the binding energy ascertained from the peak maxima is in agreement with that of the nature of the cobalt found on the TiO_2-supported samples. The used catalyst, however, shows no cobalt, which again would indicate leeching, as previously demonstrated by ICP.

The H_2-TPR profiles of the 2 wt.-% Co_3O_4/TiO_2 catalysts and pure

Table 3
Effect of radical scavenger on epoxidation of 1-decene.

Catalyst	Radical initiator	Radical scavenger	Conversion (%)	Epoxide selectivity (%)
2 wt.-% Co_3O_4/MgO	–	–	1	0
–	TBHP	–	1.5	3.5
2 wt.-% Co_3O_4/MgO	TBHP	–	12	33
2 wt.-% Co_3O_4/MgO	TBHP	BHT	0	0

Reaction conditions: 2 wt.-% Co_3O_4/MgO (0.1 g), 1-decene (10 ml, 53 mmol), TBHP (0.01 ml, 0.064 mmol), 80 °C, 24 h, atmospheric pressure. BHT: 2,6-di-*tert*-butyl-4-methylphenol.
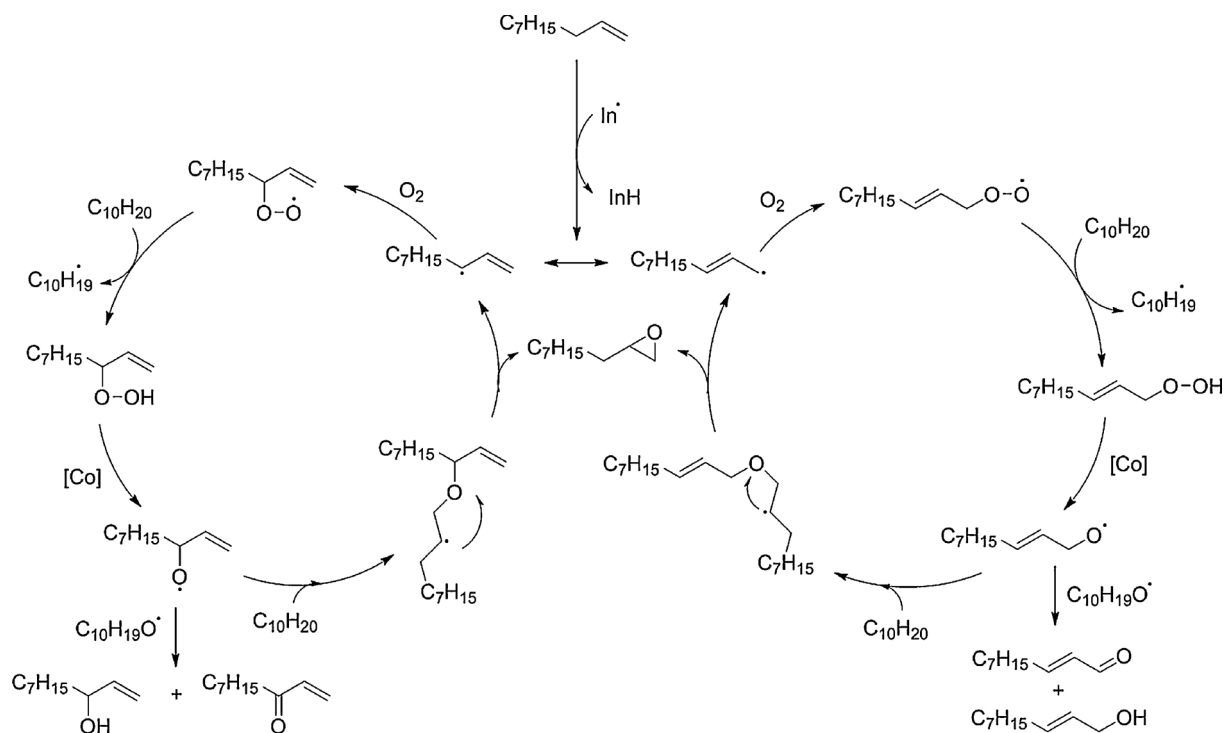
Scheme 1. Proposed mechanism analogue to the previously proposed mechanism for gold catalysts [8].

Co_3O_4 (Sigma, 99.5%) are displayed in Figure S4. The results show that the reduction peaks of the 2 wt.-% Co_3O_4/TiO_2 exhibit two hydrogen consumption peaks attributed to a two-step reduction, which is in agreement with the reduction of unsupported Co_3O_4. The first reduction peak is observed at ~345 °C and mainly results from the reduction of Co_3O_4 to CoO. The second peak of the reduction of 2 wt.-% Co_3O_4/TiO_2 at 475 °C is attributed to the reduction of CoO to metallic Co. This is in agreement with previous studies reported for Co_3O_4/TiO_2 [38,39]. The higher temperature reduction of CoO to Co in the TiO_2 supported sample relative to unsupported Co_3O_4 is indicative of a strong metal-support interaction.

The surface areas of different supported cobalt catalysts are listed in Table S3. There is a small reduction in the surface area of the 2 wt.-% Co_3O_4/support catalysts compared to the fresh supports, which may indicate the incorporation of Co_3O_4 into the pores of the support. Furthermore, there is a further slight decrease in the surface area of the used 2 wt.-% Co_3O_4/TiO_2, which may be a result of adsorption of products on the surface. However, the changes in surface areas are so small in both cases that it is at the error limit of the nitrogen physisorption method.

4. Conclusions

It was shown that supported Co catalysts are active in the solvent-free epoxidation of 1-decene using oxygen from air as primary oxidant at 80 °C. The combination of small amounts of TBHP as radical initiator and supported cobalt catalysts resulted in high conversion in epoxidation of 1-decene and epoxide selectivity under the applied conditions. Leaching of the supported Co_3O_4 catalyst was observed but was significantly decreased by changing the support from MgO to TiO_2, due to a stronger metal support interaction between Co oxides and the TiO_2. A hot filtration experiment underlined the heterogeneous nature of the Co_3O_4/TiO_2 catalyst. Yet, recyclability still remains a challenge, most likely due to the loss of active species, adsorption of products on the surface, as suggested by IR analysis, or the change in cobalt oxide structure from Co_3O_4 to CoO as observed by XPS. Furthermore, the involvement of free radicals in the reaction mechanism in the liquid phase epoxidation of 1-decene was verified and evidence for a mechanism with allylic hydroperoxide intermediates involved in the formation of the epoxide, was given.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2018.09.005.

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