Graphical abstract

Liquid phase oxidation of cyclohexane using bimetallic Au-Pd/MgO catalysts

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This paper is dedicated to Professor Jacques Védrine on the event of his 75th birthday.

ABSTRACT: A detailed study of the selective oxidation of cyclohexane has been performed using bimetallic gold-palladium catalysts supported on magnesium oxide. Mono-metallic supported gold or palladium catalysts show limited activity for cyclohexane oxidation. However, a significantly enhanced catalytic performance is observed when supported gold-palladium alloy catalysts are used for this particular reaction. This synergy is observed for alloys spanning a wide range of gold-to-palladium molar ratios. Mechanistic studies reveal a promotion effect that occurs from alloying palladium with gold on the supported catalyst, which significantly improves the homo-cleavage of the O-O bond in cyclohexyl hydroperoxide, an important intermediate species in cyclohexane oxidation.

Keywords: gold catalysis, cyclohexane oxidation, EPR, STEM, oxidation.

1. Introduction

Aerobic oxidation of cyclohexane is of vital importance due to its use in nylon production [1]. In the present industrial production process, a facile aerobic alkane oxidation method is used, wherein materials such as cobalt naphthenate are utilised as an initiator to promote a radical autoxidation pathway [2, 3]. Nevertheless, the autoxidation is not easily controlled, which means that the conversion must typically be kept below 5% in order to achieve > 80% selectivity to the desired alcohol and ketone products [4]. Unfortunately, the development of new efficient and green catalysts is significantly hindered due to kinetic inertness of both the alkane and O₂. Furthermore, a limited understanding of both the autoxidation and the catalytic oxidation routes exists in the literature, as these reactions can be difficult to study. This often causes confusion and misinterpretation concerning the oxidation reaction which is complicated by autoxidation [5]. In order to develop new catalysts for this reaction that are capable of enhanced selectivity, more effective catalytic approaches and product analysis protocols are needed.

Gold catalysts are promising candidates for cyclohexane oxidation as they can activate molecular oxygen and enable oxidation under mild conditions [6-9]. However, a detailed study of the oxidation of cyclohexane by Hereijgers and Weckhuysen [10] pointed out inconsistencies in the literature concerning critical aspects of product analysis and mechanistic studies. They concluded that supported gold nanoparticles do not operate as a catalyst in the cyclohexane oxidation reaction, but rather as initiators which have a poor performance compared to the standard commercial cobalt naphthenate promoter [10]. On the other hand, we have recently shown that such behaviour can realistically be considered as falling somewhere in between these two extreme situations [11]. In fact, gold was found to be capable of accelerating the reaction, without the need for additional initiators, and so by definition could be considered to be a catalyst for the cyclohexane oxidation. However, the acceleration occurs by virtue of increasing the concentration of the intermediate species, which are chain carriers in the radical pathway of the reaction, and therefore promote catalytic autoxidation processes *via* a radical chain mechanism [11]. In addition, the enhancement in conversion caused by monometallic gold is limited when compared to autoxidation. This apparent dual nature of gold in cyclohexane oxidation prompted us to perform further studies in an attempt to achieve more efficient catalysts and gain deeper insights into both gold catalysis and catalytic aerobic oxidation when using gold-based alloy catalysts. In addition, a mechanistic study on promoted autoxidation is warranted due to the importance of this process in industrial nylon production, and could have a direct impact on other radical reactions, such as cobalt-mediated radical polymerization [12].

Previous studies have shown that the promising properties of Au can be manipulated by the addition of Pd to form Au-Pd bimetallic alloys as green catalysts [13-17]. Herein we report that Au-Pd nanoparticles supported on MgO can improve both conversion and product selectivity in the cyclohexane oxidation reaction as compared to the commercial cobalt naphthenate promoter. Furthermore, the improvements afforded by the MgO-supported Au-Pd particles are effective over a wide range of nominal Au : Pd compositions. Investigation of the reaction mechanism by means of electron paramagnetic resonance (EPR) spin trapping experiments on the catalytic decomposition of cyclohexyl hydroperoxide (CHHP) are used to elucidate the origin of these beneficial effects.

2. Experimental

Chemicals. HAuCl₄, PdCl₂, cyclohexane and other chemicals were purchased from Aldrich and used without further purification unless otherwise specified.

Catalyst Preparation. 1 wt% Au-Pd/MgO catalysts were prepared by using a modified sol-immobilisation method as reported previously [18]. The desired amount of HAuCl₄ and PdCl₂ were added to 800 mL water. After stirring for 15 min, 1.3 mL PVA solution (0.01 g/mL) was added and the solution was stirred for an additional 15 min. Subsequently, 3.3 mL of a freshly prepared NaBH₄ solution (0.1 M) was added to generate the Au-Pd nanoalloy particles. After reduction for 45 min, the MgO support (1.98 g) was added to immobilise the nanoparticles. After filtration and washing, the solid obtained was dried (110 °C, 16 h) before use. The relative amount of gold and palladium salts used was varied in order to obtain a systematic series of supported catalysts with different molar ratios of Au-to-Pd, ranging from 20:1 to 1:20. Mono-metallic Au- or Pd- supported catalysts were also prepared for comparative purposes, using the same total metal loading (*i.e.* 1 wt%).

Catalyst Testing. Catalytic oxidation of cyclohexane (Alfa Aesar, 8.5 g, HPLC grade) was carried out in a glass bench reactor using 6mg of catalyst. The reaction mixture was magnetically stirred at 140°C and 3 bar O₂ for 17 h. Samples of the reaction mixture were analysed by gas chromatography (Varian 3200) with a CP-Wax 42 column. Adipic acid was converted to its corresponding ester for quantification purposes, and chlorobenzene was added as an internal standard. Furthermore, CBrCl₃ (150 mg) was used as a carbon centred radical scavenger for studying the mechanisms in these oxidation reactions. CBrCl₃ was added into the reactor prior to the catalytic oxidation under identical reaction conditions. The product distribution as a function of reaction time was monitored by studying a systematic series of reaction batches subjected to different reaction times under the same conditions of temperature and oxygen partial pressure. Re-usability testing was also performed in an identical glass reactor. Cyclohexane (8.5g) and an additional amount of 1wt% Au-Pd/MgO (6mg) were added into the batch reaction and catalytic oxidation was carried out at 140°C and 3 bar O₂ for 17 h. After reaction, the ‘used’ catalyst was washed with

cyclohexane and dried. Afterwards, the catalytic activity of the used Au-Pd/MgO catalyst was tested under the same reaction conditions (6 mg Au-Pd/MgO, 8.5 g cyclohexane, 140°C and 3 bar O₂ for 17 h). The obtained reaction mixture was analysed by gas chromatography [19-21]. Subsequent re-usability tests were carried out on the same material by following the same procedure.

EPR Experiments. X-band continuous wave (CW) EPR spectra were recorded at room temperature in deoxygenated cyclohexane using a Bruker EMX spectrometer operating at 100 kHz field modulation in an ER4119HS cavity. The typical instrument acquisition parameters were: centre field 3487 G, sweep width 100 G, sweep time 55 s, time constant 10 ms, power 5 mW, and modulation amplitude of 1 G. Quantitative spectral analyses were carried out using the WinSim software [22, 23]. The spin trapping experiments were performed using the following procedure: 5,5-dimethyl-1-pyrroline N-oxide, hereafter labelled DMPO (0.1 mL of 0.1 M solution in cyclohexane), was added to the substrate (0.1 mL of 2.5 molar % solution of CHHP in cyclohexane) in an EPR sample tube. The mixture was deoxygenated by bubbling N₂ for 1 min prior to recording the EPR spectrum in order to enhance the signal (by removing dissolved molecular oxygen which broadens the line-widths) [24]. For the reactions involving the Au/MgO, Pd/MgO and Au-Pd/MgO catalysts, de-oxygenation was carried out at room temperature, 5 min after the mixing of the catalyst with the reaction mixture. Cyclohexyl hydroperoxide, was synthesized by a Grignard reagent-oxygen reaction [23, 25]. Finally, a solution of 2.5 mol% cyclohexyl hydroperoxide in cyclohexane was obtained.

Electron Microscopy Characterisation. Samples of catalysts were prepared for TEM/STEM analysis by dry dispersing the catalyst powder onto a holey carbon TEM grid. Bright field (BF) imaging experiments were carried out on JEOL 2000FX TEM operating at 200kV. High-angle annular dark field (HAADF) imaging experiments were carried out using a 200kV JEOL 2200FS scanning transmission electron microscope equipped with a CEOS aberration corrector. This latter microscope was also equipped with a Thermo-Noran X-ray energy dispersive spectroscopy (XEDS) system for compositional analysis.

3. Results and Discussion

3.1 Morphologies and catalytic performance of bimetallic catalysts.

Our initial studies were centered on 1wt% Au-Pd/MgO catalysts prepared by sol-immobilisation. A representative bright-field (BF) electron micrograph of the as-prepared 1wt% Au-Pd/MgO material (with Au:Pd molar ratio of 1:1) is shown in Figure 1a. The mean size of the Au-Pd nanoparticles was found to be *ca.* 5.0 nm (Figure 1b). Aberration corrected STEM-HAADF imaging (Figure 1c) and XEDS analysis of individual particles (Figure 1d) in the bimetallic materials indicate that the supported particles are in fact homogenous Au-Pd random alloys. For comparison, the BF-TEM images of mono-metallic Au and Pd-catalysts are also shown in Figures 1e and f respectively. All three catalysts have rather similar mean diameters of 5.0 nm (Au-Pd), 5.3 nm (Au) and 4.2 nm (Pd), respectively, confirming that particle size is unlikely to be the main reason for any measured differences in catalytic performance.

Figure 1. TEM images of various MgO supported metallic catalysts and their corresponding particle size distributions (PSDs). (a) Representative bright field TEM image of a 1wt% Au-Pd/MgO sol-immobilized catalyst; (b) particle size distribution (PSD) derived when sampling within the 1-10 nm size range; (c) representative HAADF-STEM image of an individual nanoparticle in the 1wt% Au-Pd/MgO catalyst; and (d) its corresponding XEDS spectrum, confirming that it is a Au-Pd alloy; (e) BF image of a 1wt% Au/MgO catalyst (*left*) and its corresponding particle size distribution (*right*); (f) BF-TEM image of a 1wt% Pd/MgO catalyst (*left*) and its corresponding particle size distribution (*right*).

We investigated these catalysts for cyclohexane oxidation. 1wt% Au-Pd/MgO (Au:Pd molar ratio = 1:1) exhibited a conversion of 11% and a total selectivity of 95% which represents a potential improvement over the commercial cobalt naphthenate initiator (Table 1 and Figures 2a and 2b; for full by-product analysis and methodologies see supporting material, Figures S1 and S2, and Tables S1 and S2). By way of comparison, the monometallic Au/MgO and Pd/MgO counterparts display a much poorer catalytic performance, which confirms that neither Au nor Pd alone act as an effective catalyst [9, 11, 26]. Moreover, the supported Au-Pd catalyst displayed excellent stability, maintaining a 12% conversion and 98% selectivity even after being re-used multiple times (Table 2). We also tested the catalytic performance by means of GC analysis of a series of supported Au-Pd alloys having different nominal molar ratios (Figure 2b). It was found that the catalysts display a consistent catalytic performance over a wide spectrum of Au:Pd molar ratios (*i.e.* from 10:1 to 1:10). However, extremely Au-rich or Pd-rich catalysts are considerably less active, and tend towards the poorer performance exhibited by the two monometallic catalysts. The superior catalytic performance of 1wt% Au-Pd/MgO might be attributable to the modified exposed metal surface containing a mixture of Au and Pd atoms. As the enhanced activity is observed over a broad range of Au-Pd compositions, the precise Au:Pd ratio does not seem to be a crucial factor.

Table 1. Catalytic performance characteristics of cyclohexane oxidation over a variety of different catalyst materials (^a).

Catalyst	Conversion (%)	Selectivity (%)				
		A	K	CHHP	AA	Total
1wt%AuPd/MgO	11	58	37	1	0	95
Co-naphthenate	9	45	37	0	2	85
Fe(acac) ₃	7.7	35	48	0	0	82
Blank	1.1	22	19	57	0	98
MgO	1.0	40	35	20	0	95
1wt%Au/MgO	0.3	-	-	-	-	-
1wt%Pd/MgO	0	-	-	-	-	-

^[a] *Reaction conditions:* 6 mg catalyst, 8.5 g cyclohexane, 140 °C, 3 bar O₂, 17 h; Fe(acac)₃ represents Fe(III) acetylacetonate. The acronyms A, K, CHHP and AA represent cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide and adipic acid, respectively.

Figure 2. a) Comparison of various catalysts for cyclohexane oxidation, including a commercial Co promoted system (see supporting material, Table S2); b) Catalytic performance for cyclohexane oxidation using MgO supported Au-Pd as a function of the nominal Au:Pd molar ratio. The acronyms A and K represent cyclohexanol and cyclohexanone, respectively.

Table 2. Re-usability of the supported Au-Pd/MgO catalyst for cyclohexane oxidation.

Catalyst 1wt% Au- Pd/MgO	Conversion (%)	Selectivity (%)				
		A	K	CHHP	AA	Total
1 st use	11	49	37	1	6	93
2 nd use	11	49	37	1	6	93
3 rd use	10	51	36	2	5	94
4 th use	12	58	37	0	5	98

Reaction conditions: 6 mg catalyst, 8.5 g cyclohexane, 140 °C, 3 bar O₂, 17 h. The acronyms A, K, CHHP and AA represent cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide and adipic acid, respectively. To test catalyst reusability, a reaction was conducted under the same reaction conditions but using a 120 mg batch of catalyst. After reaction the catalyst was collected and washed. Following this, 6 mg the used catalyst was tested for re-usability. A similar procedure was followed for subsequent re-cycle runs.

3.2 Mechanistic studies using EPR-spin trapping.

In our previous studies, we have used the EPR-spin trapping experiment to investigate the chemical nature of autocatalysis in cyclohexane oxidation [11]. EPR spectroscopy combined with the use of cyclohexyl hydroperoxide ($C_6H_{11}OOH$; hereafter labelled CHHP) as a molecular probe has been used to definitively identify the different CHHP decomposition pathways. CHHP is a key intermediate in cyclohexane oxidation when the reaction is performed in the presence of noble metals or a cobalt salt [1]. This methodology offers a way to collect information on the mechanism of this reaction due to the large number of radical species involved [5]. In the current work, our EPR-spin trapping methodology has been extended, through both qualitative and relative quantitative studies of CHHP decomposition in the presence of cobalt naphthenate, Au/MgO, Pd/MgO and Au-Pd/MgO catalysts (summarised in Figure 3A-C, and supporting information, Figures S3-S5).

Figure 3 - **A:** EPR spectra of the DMPO-spin adducts formed during the decomposition of CHHP in the presence of (a) Au-Pd/MgO, (b) Pd/MgO, (c) Au/MgO, (d) autoxidation and (e) Co-naphthenate (this final spectrum is reduced in scale by a factor of six in relation to the other plots). **B:** Experimental and simulated EPR spectra of the DMPO-spin adducts obtained in the presence of 1wt% Au-Pd/MgO: (a) experimental, (b) combined simulation, and (c-f) deconvoluted spectra of the individual spin adduct components including; (c) a di-*tert*-butyl-nitroxide derivative formed by DMPO oxidation (with $a_N=14.31$ G) [27], (d) a DMPO-O- C_6H_{11} spin adduct (with $a_N=13.37$, $a_{H(\beta)}=6.01$, $a_{H(\gamma)}=1.90$ G) [e], (e) a DMPO-OO- C_6H_{11} adduct (with $a_N=14.49$, $a_H=10.64$ G) [29], and (f) a carbon centred adduct (with $a_N=15.74$, $a_H=25.61$ G), possibly attributed to an DMPO-C(OH)R₂ adduct [30]. **C:** Experimental and simulated EPR spectra of the DMPO-spin adducts obtained in the presence of Co-naphthenate: (a) experimental, (b) combined simulation, and (c-g) deconvoluted spectra of the individual spin adduct

components including: (c) a di-*tert*-butyl-nitroxide derivative (with $a_N=14.18$ G) [31], (d) an unidentified nitroxide from DMPO (with $a_N=14.30$, $a_H=2.81$ G) possibly arising from decomposition of the DMPO itself [32], (e) a DMPO-O-C₆H₁₁ spin adduct (with $a_N=13.97$, $a_{H(\beta)}=7.01$, $a_{H(\gamma)}=2.2$ G), (f) a DMPO-OOR/OOH adduct (with $a_N=12.54$, $a_H=9.15$ G), and (g) a carbon centred adduct (with $a_N=15.67$, $a_H=25.67$ G), possibly due to the DMPO-C(OH)R₂ adduct [30].

Simulation of the EPR spectra enabled us to extract the spin Hamiltonian parameters of the spin adducts and thereby identify all of the trapped radical intermediates involved in the autoxidation of cyclohexane to cyclohexanone and cyclohexanol. These intermediates include a di-*tert*-butyl-nitroxide derivative (characterised by a coupling of $a_N=14.2$ G), a DMPO-O-C₆H₁₁ spin adduct (with $a_N=13.4$, $a_{H(\beta)}=6.01$, $a_{H(\gamma)}=1.80$ G), a DMPO-OOC₆H₁₁ adduct (with $a_N=14.2$, $a_H=10.9$ G), and a DMPO-C carbon centred adduct, possibly arising from a carbon hydroxylated species (with $a_N=15.8$, $a_H=25.7$ G) which could account for adipic acid (Figure 3 and supporting information, Figures S3-S5) [33]. We note a significant difference in the distribution of the spin adducts formed during the decomposition of CHHP in the presence of the Au-Pd based catalysts compared to Co naphthenate (in particular compare Figures 3B to 3C). The relative abundance of the various spin adducts formed with the Au-Pd based catalysts, including the di-*tert*-butyl-nitroxide derivative, DMPO-O-C₆H₁₁, DMPO-OOR/R and possibly DMPO-C(OH)R₂, are listed in Table 3. However, the relative abundance of the various spin adducts formed with the Co-naphthenate, which include a di-*tert*-butyl-nitroxide derivative, a nitroxide from DMPO decomposition by peroxides, DMPO-O-C₆H₁₁, DMPO-OOR/R adduct, and a possible DMPO-C(OH)R₂ adduct, are by comparison markedly different (Table 3). This qualitative analysis confirms that the role of Au-Pd catalyst in radical production is substantially different compared to the commercial promoter. It is important to note, that the spin trapping methodology should not be used to extract absolute concentrations. As a result the EPR-spin trapping data should only be used for relative quantitative determination of the spin adducts. In other words, it is only possible to qualitatively correlate reactivity, or lifetime, of a radical to its corresponding spin adduct. This is a consequence of various experimental factors such as: the life-time of the spin adduct, the nature of the solvent, the temperature, the pH and importantly, the efficiency of the capture reaction which is different for each radical [35,36]. For example, literature values comparing the capture of $\cdot\text{OOH}$ vs $\cdot\text{OH}$ species by DMPO in aqueous media at room temperature and pH close to neutrality, revealed kinetic constants in the range 10^1 - 10^9 M s⁻¹ respectively [37]. In other words, detection of spin adducts with similar EPR signal intensities for $\cdot\text{OOH}$ versus $\cdot\text{OH}$, actually implies that the concentration of $\cdot\text{OOH}$ is an order of magnitude higher compared to $\cdot\text{OH}$. Furthermore, for heterogeneous catalysis studies, one must also be aware that the spin traps may also abstract species weakly bound to the catalyst surface [38]. Therefore, taking all these quantitative limitations of EPR-spin trapping into account, one can nevertheless extract meaningful insights into the reaction based on the relative quantitative and qualitative assignments of the spin adducts presented in Table 3

The radicals trapped in the presence and absence of the three heterogeneous catalysts (Au/MgO, Pd/MgO and Au-Pd/MgO) are essentially similar in all sets of experiments, except for the detection of the carbon parent radical (*ca.*, 3% of spin adduct: C₆H₁₁-DMPO) in the presence of Au/MgO. However, the most remarkable difference noted between these data-sets is the increased fraction of the DMPO-alkoxyl species (C₆H₁₁-O-DMPO) versus the DMPO-peroxyl species (C₆H₁₁-OO-DMPO) when Au or Pd containing catalysts are used, compared to the pure autoxidation or blank test materials. This simple observation indicates that the MgO supported metal catalysts are capable of homo-cleavage of the O-O bond in CHHP.

Moreover, the presence of the Au-Pd alloy appears to significantly promote the O-O bond dissociation, since the relative abundance of alkoxyl- to peroxy-l DMPO spin adducts doubles compared to the monometallic Au or Pd catalysts (see Table 3). Even though the rate of adduct formation may be different for alkoxyl vs peroxy radicals, this suggestion the enhanced dissociation of O-O remains valid since all Au/MgO, Pd/MgO and Au-Pd/MgO experiments were performed under identical conditions. This result implies that the Au-Pd alloy has an intrinsically stronger chemical affinity for cyclohexyl hydroperoxide, resulting in homo-cleavage of the O-O bond. In order to explain this effect, the electronic structure at the surface of the Au-Pd nanoparticles must be considered. In fact, both Au and Pd are capable of enhancing the formation of alkoxyl intermediates, compared to autoxidation, although it is only the MgO supported Au-Pd alloy that displays an enhanced conversion, *i.e.*, a higher turnover frequency. Unlike the monometallic case, alloying Au and Pd may shift the electron density from Pd to Au atoms [14, 39] whilst preserving a higher electronegativity on Au [40]. Hence, the adsorption of CHHP over an active site comprised of neighbouring Au and Pd atoms will more favourably lead to the cleavage of the O-O bond in CHHP due to the difference in induced charge between the two metal components, existing as an Au^{δ-}-Pd^{δ+} couple (Scheme 1) and this we consider gives an electronic basis for the origin of the synergistic effect that is clearly observed when Pd is added to Au (and *vice versa*) for this, and possibly other, redox reactions. This enhancement can be observed for a broad range of Au:Pd compositions, rather than just a specific composition where synergy has been observed in previous studies for other redox reactions [15-17], but clearly requires a minimum level of either metal to be present since compositions with very low amounts of Au or Pd are ineffective. As a consequence, a promoted, or in our case catalytic, decomposition of CHHP occurs (see eq. 1) thus favouring alkoxide formation at a faster rate and in turn a higher level of conversion.

Table 3. Relative quantitative and qualitative assignments of the DMPO spin adducts detected in the EPR-spin trapping experiments.

Catalyst	Nitroxide	RO·	ROO·	Carbon radicals	RO·/ROO·
Auto-oxidation	2.3	63.2	29.6	4.9	2.1
1wt% Au/MgO	5.9	82.5	5.3	6.3	15.6
1wt% Pd/MgO	5.5	82.1	6.4	6.0	12.8
1wt% Au-Pd/MgO	3.7	87.8	2.9	5.6	30.3
Co-naphthenate	44.4	8.3	8.9	2.0	0.9

Scheme 1: Specific surface substrate adsorption of CHHP in the case of a bimetallic Au-Pd catalyst (*left*) and non-specific surface substrate adsorption of CHHP in the case of a monometallic catalyst (*right*).

A similar decomposition route operates in the manganese aluminophosphate catalysts, where CHHP decomposes by adsorption on a $\text{Mn}^{\delta+}\text{-O}^{\delta-}$ moiety [41]. Despite the obvious differences between a metal nanoparticle and an aluminophosphate surface, in the latter case it was proposed that an orienting effect on the CHHP molecule was induced by the dipolar nature of the Mn and O neighbours. We postulate that an analogous effect can take place in the case of Au-Pd bimetallic nanoparticles. In fact, for the case of monometallic Au or Pd where an active site such as Au-Au or Pd-Pd will be present, the cleavage solely results from the adsorption of the hydroperoxide, but without any specific orientation of the substrate. By direct comparison, cobalt-initiated autoxidation predominantly produces peroxide species, including cyclohexyl peroxide and derivative nitroxide radicals, whereas the amount of alkoxy radicals generated is only 8.3%. This is evident from Figure 3-C, spectra (c,d), indicative of a large abundance of peroxide species that cause degradation of the spin trap [32]. Even so, the fraction of peroxy radicals detected with Co naphthenate is still significantly higher compared to the MgO supported Au-Pd catalyst. The highproduction of peroxide species was attributed to the cobalt centres favouring the attack of CHHP and the generation of ROO· in agreement with the Haber-Weiss cycle [42,43], which is preceded by cyclohexyloxy radical formation. It should also be mentioned that the peroxide species ROO· are known to be less reactive than RO· radicals [32, 34] which could lead to a slower reaction rate and lower conversion. The accepted Haber-Weiss cycle and termination reaction of the alkyl peroxide intermediate is shown below [42, 43]:

which in the case of CHHP gives the resulting net equation:

and disproportionation lead to [2, 3]:

As a consequence of these reactions, a commonly used way to estimate the radical lifetimes, affecting both the amount of the spin adducts detected and the efficiency of the oxidation reaction, is given by eq. 6 [44]:

$$\tau_c = \frac{1}{2k_{term}[X\cdot]_s} \quad (eq. 6)$$

where k_{term} is the average termination kinetic parameter and $[X\cdot]_s$ is the steady-state radical concentration. Whilst this applies to polymerization reactions, by definition it also assumes (i) a steady state radical concentration, *i.e.*, the chain carrier (which in the current system should be ROO $\cdot$) and (ii) the product formation at the termination step [45] (which in our case is represented by eq. 5). On the other hand, recent studies by Hermans and co-workers showed that a more accurate picture of the cyclohexane oxidation should not just be limited to steady state conditions, but would be better modelled by the use of quasi-steady state concentrations [46], which for ROO $\cdot$ would lead to:

$$[C_6H_{11}OO\cdot]_{qss} = \sqrt{\frac{k_{init}[C_6H_{11}OOH]}{k_{term}}} \quad (eq. 7)$$

where k_{init} and k_{term} are the rate constants of the initiation and termination reactions respectively. Equation 7 is more complex compared to a classical scheme based on the termination step and on the final [ROO $\cdot$] concentration. In fact, whereas the termination step proceeds with a very low activation barrier [2] and a pure association of two radical species, the term k_{term} is unlikely to be affected by significant traces of additives or metals. In contrast, the initiation reaction has a high activation energy (estimated to be in the range of *ca.* 170 kJ/mol), [47] therefore even a relatively small decrease of the effective barrier, in our case induced by the bimetallic species, should lead to a substantial increase in [C₆H₁₁OO $\cdot$] and hence to an increase in the hydrocarbon (R-H) oxidation rate [46]. This has obvious consequences on the effective radical lifetime which in turn affects the species actually trapped by DMPO and more importantly on the catalytic nature of the oxidation reaction (*vide infra*), with quantitative effects that are difficult to predict *a priori*.

As a consequence of these usually accepted reaction schemes, one may conclude that both alkoxyl and peroxy radicals are primary products of the Co-promoted decomposition of CHHP either *via* the Haber-Weiss cycle involving a pure radical pathway [42,43] or *via* involvement of the H⁺ or OH⁻ species [48]. Once the peroxide radical has formed, disproportionation (eq. 5) would follow and initiate the autoxidation process again (eqs. 8-11). However, our work shows that with MgO supported Au-Pd nanoparticles, a much higher abundance of alkoxyl adducts are trapped compared to the peroxy adducts. This is evident from Figure 3-B, where the experimental spectrum is dominated entirely by alkoxide species (simulated profile shown in Figure 3-B, spectrum d)) which would suggest a dominance of the initiated autoxidation (eq. 8):

However, for a complete discussion of the reactions involved, it is important to describe other aspects and parameters that are involved in the autoxidation process and which may help to clarify similarities and differences between the Co naphthenate and Au-Pd/MgO systems, as well as pure autoxidation. In fact, once the C₆H₁₁ $\cdot$ radical is formed (either at the initiation step or *via* eq. 8), this will immediately react under diffusion control with any oxygen present in solution (eq. 9) [49]:

On the other hand, pure radical combinations are not the only pathways operative in these reactions and of particular importance are those shown in eqs 10 and 11 below [2, 46]:

In this case, cobalt does not have any further direct contribution to the subsequent autoxidation after it has reacted with peroxide (eq. 1). This is particularly important in eq. 10, since recent studies [50] have shown that these reactions take place through a solvent cage and once the product from H abstraction in the α position is obtained (C₆H₁₀($\cdot$)OOH), the ketone is

formed (eq. 11) without the need for a 'standard' termination step (eq. 4). This will necessarily lead to the ketone as the product, but without the need for any additional metal centres in solution.

On the other hand, Au-Pd bimetallic catalysts are capable of an enhanced selectivity to cyclohexanol compared to Co- and Fe-salts, suggesting an easier cleavage of the O-O bond in CHHP. Consequently, even in the autoxidation reaction, the supported metallic catalysts still participate in the selective decomposition of CHHP (see Scheme 1) and lead to improved overall conversion and selectivity, by minimizing uncontrollable ring-opening reactions, which would lead to the production of acids and esters [48,50].

To further demonstrate this important aspect, we utilised a carbon-centred radical scavenger (CBrCl₃) to quench the autoxidation pathway, and thereby differentiate between the autoxidation process and the catalytic oxidation [11]. Since CBrCl₃ can quench carbon centred radicals by means of bromo-hydrocarbon formation [51], it should be noted that the use of dialkyl nitroxides for the capture of carbon centred radicals has been avoided for this particular reaction. This is because the adopted reaction conditions (*i.e.* solvent free and a reaction temperature of *ca.* 140 °C) coupled with the presence of metal centres can trigger hydrogen abstraction reactions [52] as well as oxidation of the alcohol to the ketone [53], and we wanted to minimize the presence of such parallel and undesired reaction pathways.

Therefore in the presence of an excess of CBrCl₃ (150 mg), no oxidation of cyclohexane was observed in the presence of Co-naphthenate; this confirms that the cobalt salt acts as promoter rather than a catalyst. By comparison, with Au-Pd/MgO, both oxygenation and bromination of cyclohexane took place from the outset of the reaction in the presence of CBrCl₃ (Figure 4). This confirms that the supported Au-Pd particles have a strong resistance to this radical scavenger and implies a different oxidation pathway with an enhanced CHHP decomposition compared to Co. In any case, we consider that any new reaction pathways induced by Au-Pd/MgO will not involve direct O₂ activation or adsorption. In fact, once the C₆H₁₁· radical is formed, this would react with O₂ under diffusion controlled conditions [54, 55] and the resulting C₆H₁₁-OO· radical or C₆H₁₁-OOH species will only adsorb onto the catalyst surface afterwards. This diminishes the possibility of oxidation occurring via a η_2 oxygen intermediate (*i.e.* side-on surface adsorption of molecular oxygen) as this would involve a switch in the oxidation state of the metal [56]. Furthermore, this process would be intrinsically slower than for a diffusion controlled route where O₂ reacts directly with the C₆H₁₁· radical [18].

Figure 4. Product formation as a function of reaction time in the presence of CBrCl₃ using the Au-Pd/MgO catalyst. A = cyclohexanol, K = cyclohexanone, and BCH = represent cyclohexanol, cyclohexanone, and bromocyclohexane.

Oxygen could in principle still play a role if hydride intermediates are present, as in the case of β -elimination of alcohols [22]. In that case, it would be involved in the regeneration of the active metal site *via* formation of non-alkyl hydroperoxide intermediates. However, our spin trapping experiments do not provide any evidence for pure hydroperoxide intermediates. Only alkyl peroxide species were detected, thus supporting the notion of adsorption of ROO· or ROOH substrates onto the catalyst surface.

Nevertheless, the enhanced CHHP decomposition still leads to species that are also detected in the presence of Co (ROO· and RO·) and therefore this is still an autoxidation pathway. However, our data would suggest that Co naphthenate operates by promoting autoxidation via the intermediacy of peroxy species, whereas supported Au-Pd nanoparticle operate by enhancing the amount of alkoxy species produced.

3. Conclusions

For the selective oxidation of cyclohexane, it is possible to classify the Au-Pd nanoparticles both as a catalyst and as an initiator, since the bimetallic material remains persistently active during the whole oxidation process for peroxide decomposition. The presence of Au-Pd nanoparticles clearly has a significant positive influence on the overall catalytic performance in cyclohexane oxidation, and in particular, inhibits production of unwanted by-products. We show that the free radical chain pathway can be manipulated by selectively decomposing the peroxide intermediate to improve the overall catalytic performance and productivity. Our data suggest a cooperative effect between Au and Pd that could induce an orienting effect of the CHHP intermediate moiety.

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References

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- [1] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. da Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinacé, E. L. Pires, *Appl. Catal. A: Gen.* **211** (2001) 1-17.
 - [2] I. Hermans, T. L. Nguyen, P. A. Jacobs, J. Peeters, *Chem. Phys. Chem.* **6** (2005) 637-645.
 - [3] I. Hermans, P. A. Jacobs, J. Peeters, *Chem. Eur. J.* **12** (2006) 4229-4240.
 - [4] U. Schuchardt, W. Al. Carvalho, E. V. Spinacé, *Synlett.* **10** (1993) 713-718.
 - [5] J. Kim, R. G. Harrison, C. Kim, L. Que, *J. Am. Chem. Soc.* **118** (1996) 4373-4379.
 - [6] T. Ishida, M. Haruta, *Angew. Chem. Int. Ed.* **46** (2007) 7154-7156.
 - [7] Y. J. Xu, P. Landon, D. Enache, A. F. Carley, M. W. Roberts, G. J. Hutchings, *Catal. Lett.* **101** (2005) 175-179.
 - [8] G. Lu, R. Zhao, G. Qian, Y. Qi, X. Wang, J. Suo, *Catal. Lett.* **97** (2004) 115.
 - [9] L. X. Xu, C. H. He, M. Q. Zhu, S. Fang, *Catal. Lett.* **114** (2007) 202-205.
 - [10] B. P. C. Hereijgers, B. M. Weckhuysen, *J. Catal.* **270** (2010) 16-25.
 - [11] M. Conte, X. Liu, D. M. Murphy, K. Whiston, G. J. Hutchings, *Phys. Chem. Chem. Phys.* **47** (2012) 16279-16285.
 - [12] R. K. Biyani, R. V. Subramanian, R. Mahalingam, *J. Appl. Pol. Sci.* **25** (1980) 1257-1260.
 - [13] J. K. Edwards, G. J. Hutchings, *Angew. Chem. Int. Ed.* **47** (2008) 9192-9198.
 - [14] J. Pritchard, L. Kesavan, M. Piccinini, Q. He, R. Tiruvalam, N. Dimitratos, J.-A. Lopez-Sanchez, A. F. Carley, J. K. Edwards, C. J. Kiely, G. J. Hutchings, *Langmuir* **26** (2010) 16568-16577.
 - [15] R. Su, L. Kesavan, M. M. Jensen, R. Tiruvalam, Q. He, N. Dimitratos, S. Wendt, M. Glasius, C. J. Kiely, G. J. Hutchings, F. Besenbacher, *Chem. Commun.* **50** (2014) 12612-12614.
 - [16] G. J. Hutchings, *Catal. Today* **238** (2014) 69-73.
 - [17] E. Nowicka, J. P. Hofmann, S. F. Parker, M. Sankar, G. M. Lari, S. A. Kondrat, D. W. Knight, D. Bethell, B. M. Weckhuysen, G. J. Hutchings, *Phys. Chem. Chem. Phys.*, **15** (2013) 12147-12155.
 - [18] B. A. Steinhoff, S. S. Stahl, *Org. Lett.* **4** (2002) 4179-4181.
 - [19] L. Zhou, J. Xu, H. Miao, F. Wang, X. Li, *Appl. Catal. A: Gen.* **292** (2005) 223-228.
 - [20] S. B. Turnipseed, A. J. Allentoff, J. A. Thompson, *Anal. Biochem.* **213** (1993) 218-225.
 - [21] R. Raja, P. Ratnasamy, *Catal. Lett.* **48** (1997), 1-10.
 - [22] Simulations were carried out using WinSim software: <http://www.niehs.nih.gov/research/resources/software/tox-pharm/tools/index.cfm>.
 - [23] M. Conte, K. Wilson, V. Chechik, *Org. Biomol. Chem.* **7** (2009) 1361-1367.

-
- [24] C. Walling, S. A. Buckler, *J. Am. Chem. Soc.* **77** (1955) 6032-6038.
- [25] G. J. Hutchings, *Dalton Trans.* (2008) 5523-5536.
- [26] J. Long, H. Liu, S. Wu, S. Liao, Y. Li, *ACS Catal.* **3** (2013) 647-654.
- [27] E. G. Janzen, B. J. Blackburn, *J. Am. Chem. Soc.* **91** (1969) 4481-4490.
- [28] S. L. Baum, I. G. M. Anderson, R. R. Baker, D. M. Murphy, C. C. Rowlands, *Anal. Chim. Acta.* **481** (2003) 1-13.
- [29] M. J. Davies, T. F. Slater, *Biochem. J.* **240** (1986) 789-795.
- [30] E. G. Janzen, J.-P. Liu, *J. Magn. Reson.* **9** (1973) 510-512.
- [31] M. Conte, H. Miyamura, S. Kobayashi, V. Chechik, *Chem. Commun.* **45** (2010) 145-147.
- [32] M. Conte, K. Wilson, V. Chechik, *Rev. Sci. Instrum.* **81** (2010) 104102-104108.
- [33] E. J. Silke, W. J. Pitz, C. K. Westbrook, M. Ribaucour, *J. Phys. Chem. A* **111**, 2007, 3761-3775.
- [34] M. Conte, V. Chechik, *Chem. Commun.* **46** (2010) 3991-3993.
- [35] P. Ionita, M. Conte, B. C. Gilbert, V. Chechik, *Org. Biomol. Chem.* **5** (2007) 3504-3509.
- [36] P. Ionita, B. C. Gilbert, A. C. Whitwood, *Perkin Trans. 2* (2000) 2436-2440.
- [37] E. Finkelstein, G. M. Rosen, E. J. Rauckman, *J. Am. Chem. Soc.* **102** (1980) 4994-4999.
- [38] M. Conte, H. Miyamura, S. Kobayashi, V. Chechik, *J. Am. Chem. Soc.* **131** (2009) 7189-7196 9.
- [39] Z. Li, F. Gao, Y. Wang, F. Calaza, L. Burkholder, W. T. Tysoe, *Surf. Sci.* **601** (2007) 1898-1908.
- [40] M. Conte, A. F. Carley, G. Attard, A. A. Herzog, C. J. Kiely, G. J. Hutchings, *J. Catal.* **257** (2008) 190-198.
- [41] B. Modén, B.-Z. Zhan, J. Dakka, J. G. Santiesteban, E. Iglesia, *J. Catal.* **239** (2006) 390-401.
- [42] J. Weinstein, B. H. J. Bielski, *J. Am. Chem. Soc.* **101** (1979) 58-62.
- [43] S. Tanase, E. Bouwman, J. Reedijk, *Appl. Catal. A: Gen.* **259** (2004) 101-107.
- [44] S. K. Reddy, N. B. Cramer, Christopher N. Bowman, *Macromolecules* **39** (2006) 3673-3680.
- [45] G. Odian, *Principles of Polymerization*, 3rd Ed.; John Wiley & Sons: New York, (1991).
- [46] I. Hermans, J. Peeters, P. A. Jacobs, *ChemPhysChem.* **7** (2006) 1142-1148.
- [47] C. A. Tolman, J. D. Druliner, M. J. Nappa, N. Herron, in: *Activation and Functionalization of Alkanes* (Ed.: C. L. Hill), Wiley, New York, (1989).
- [48] B. P. C. Hereijgers, B. M. Weckhuysen, *J. Catal.* **270** (2010) 16-25.
- [49] M. S. Stark, *J. Am. Chem. Soc.* **122** (2000) 4162-4170.
- [50] I. Hermans, P. Jacobs, J. Peeters, *Chem. Eur. J.* **13** (2007) 754 - 761.
- [51] S. V. Dvinskikh, A. V. Yurkovskaya, H.-M. Vieth, *J. Phys. Chem.* **100** (1996) 8125-8130.
- [52] C. Berti, M. J. Perkins, *J. Chem. Soc. Chem. Comm.* (1979) 1167-1168.
- [53] A. Dhakshinamoorthy, M. Alvaro, Hermenegildo García, *ACS Catal.* **1** (2011) 48-53.
- [54] N. A. Porter, *J. Org. Chem.* **78** (2013) 3511-3524.
- [55] J. M. Keith, W. A. Goddard III, *Organometallics* **31** (2012) 545-552.
- [56] F. Acke, I. Panas, *J. Phys. Chem. B* **102** (1998) 5158-5164.

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