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Gold-catalyzed oxidation of substituted phenols by hydrogen peroxide

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1. Introduction

Oxygen-containing molecules like alcohols, aldehydes, ketones, epoxides and carboxylic acids are important molecules in the production of polymers and fine chemicals. They are generally obtained by oxidation of organic substrates with inorganic oxidizing agents like chromium and manganese oxides or nitric acid. As a result, in addition to corrosion problems, the reaction is not very selective and leads to a large amount of undesirable and polluting compounds. Nowadays, environmentally unacceptable oxidation methods are being progressively replaced by cleaner methods, in particular heterogeneous catalytic methods. Therefore, the discovery of new efficient catalysts for the selective oxidation of hydrocarbons with clean oxidizing agents has become extremely important in chemistry research.

Quinones represent a very important class of molecules used to produce drugs, fragrances and vitamins [1]. Recently, heterogeneous catalytic routes have been reported to produce quinones from the corresponding phenols in the liquid phase, using tert-butyl hydroperoxide (TBHP), hydrogen peroxide (H₂O₂) or molecular oxygen as oxidants [2]. The most efficient catalysts consist in heteropolyacids [3], immobilized metal complexes like iron phthalocyanines [4-8] and transition metal containing molecular sieves [9-15]. These catalysts give excellent yields in the oxidation of 2,3,6-trimethyl phenol (TMP) to the corresponding trimethyl-1,4-benzoquinone (TMBQ), an important intermediate

ABSTRACT

Gold nanoparticles deposited on inorganic supports are efficient catalysts for the oxidation of various substituted phenols (2,6-di-tert-butyl phenol and 2,3,6-trimethyl phenol) with aqueous hydrogen peroxide. By contrast to more conventional catalysts such as Ti-containing mesoporous silicas, which convert phenols to the corresponding benzoquinones, gold nanoparticles are very selective to biaryl compounds (3,3',5,5'-tetra-tert-butyl diphenoquinone and 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol, respectively). Products yields and selectivities depend on the solvent used, the best results being obtained in methanol with yields >98%. Au offers the possibility to completely change the selectivity in the oxidation of substituted phenols and opens interesting perspectives in the clean synthesis of biaryl compounds for pharmaceutical applications.

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in the preparation of vitamin E. In 1996, Pinnavaia and co-workers already mentioned the activity of Ti-HMS samples in the oxidation of di-tert-butyl phenol (DTBP) with hydrogen peroxide to the corresponding 2,6-di-tert-butyl benzoquinone (DTBQ) [16]. Later, the excellent performance of Ti-MCM-41 samples was confirmed in the oxidation of TMP and various functionalized phenols by H₂O₂. High substrate conversions are obtained when the reaction is performed in acetonitrile or acetone, with high quinone selectivity and very low amount of by-products [15].

Recently, supported gold catalysts have been found to be particularly effective in the oxidation of a large variety of substrates like alcohols, alkenes, amines, ..., using molecular oxygen [17–23] or hydrogen peroxide [24–30]. Up to date, reports on the use of Au for the oxidation of substituted phenols are scarce. Kholdeeva et al. have shown that 2-methyl-1-naphthol was oxidized to 2-methyl-1,4-naphthaquinone with molecular oxygen over Au/C and Au/TiO₂ catalysts, but yields were not as good as those obtained on Ti-MCM-41 and iron phthalocyanines. Actually, the authors suggested that gold could favor over-oxidation of the substrate, thus decreasing the selectivity in the target product [8].

The present work examines the performance of gold nanoparticles in the oxidation of substituted phenols using hydrogen peroxide as oxygen donor. The activity of Au catalysts in the hydroxylation of 2,6-di-tert-butyl phenol (DTBP) and 2,3,6-trimethyl phenol (TMP) was systematically compared with that of more conventional Ti-containing mesoporous silica.

2. Experimental

The Au/TiO₂ catalyst (1.4 wt.% Au) was a gold reference catalyst (Sample No 84A) supplied by the World Gold Council (the

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Table 1

Oxidation of di-tert-butyl phenol (DTBP) over Ti-HMS and Au/TiO2 catalysts.

Catalyst	Oxidant	Solvent ^a	6 h			24 h		
			DTBP conv. (%)	Product yield (%)		DTBP conv. (%)	Product yield (%)	
				DTBQ	DPQ		DTBQ	DPQ
Ti-	TBHP	AC=0	3	2	1	9	6	3
HMS		MeCN	1	1	0	3	3	0
		MeOH	0	0	0	5	4	1
	H_2O_2	AC=O	51	45	6	69	70	9
		MeCN	40	33	7	58	62	6
		MeOH	59	53	6	87	71	36
Au/TiO ₂	TBHP	AC=0	3	3	0	9	4	5
		MeCN	5	3	2	11	6	5
		MeOH	7	7	0	11	8	3
		MCH	2	0	2	5	2	3
	H_2O_2	AC=0	24	20	4	27	22	5
		MeCN	13	10	3	21	11	10
		MeOH	90	0	100	91	0	100

^a AC=O: acetone, MeCN: acetonitrile, MeOH: methanol, MCH: methylcyclohexane.

mean diameter of the gold particles, determined by TEM, was 3.7 ± 1.5 nm; the TiO₂ support is P25).

Au/Al₂O₃ was prepared by direct anionic exchange [31] using HAuCl₄·3H₂O as gold precursor. Typically, 0.0808 g HAuCl₄·3H₂O is dissolved in 1 L H₂O and 2 g γ -Al₂O₃ are added to the solution under stirring. The temperature is increased to 70 °C and stirring is maintained at this temperature for 1 h. The solid is then filtered, washed with a NH₄OH solution (7 × 10⁻² mol L⁻¹), dried overnight at 100 °C and calcined in air at 300 °C for 4 h. Characterization of the sample gave a S_{BET} of 189 m²/g, Au content of 1.38 wt.% and a mean particle size of ca. 2.3 ± 0.8 nm [32].

P25, purchased from Degussa, is a mixed-phase titanium oxide containing 80% anatase and 20% rutile with a BET surface area close to $50 \text{ m}^2/\text{g}$.

A sample of Ti-containing mesoporous silica Ti-HMS was prepared according to a published procedure [33]. Primary amines were removed from the mesopores by ethanol extraction, followed by calcination in air at 550 °C. The BET surface area and mean pore diameter of the solid were 879 m²/g and 3.6 nm, respectively. Moreover, the Ti content in the dry solid was 1.87 wt.%. The UV-vis spectrum of the calcined dried sample showed a maximum around 230 nm without any signal above 320 nm, suggesting highly dispersed Ti species in the silica network [34,35].

Phenol hydroxylation was performed in a round-bottomed flask equipped with condenser and magnetic stirrer. In a typical experiment, 5×10^{-3} mol phenol was dispersed in 20 mL solvent. Then an amount of catalyst corresponding to 2×10^{-6} mol Au was added and the mixture was heated at 60 °C under stirring. For Ti-HMS, experimental conditions were adapted from literature data and reactions were performed with 200 mg catalyst [16]. After stabilization of the temperature, an amount of H₂O₂ (35 wt.% solution in water, Aldrich) corresponding to an oxidant/phenol molar ratio of 1 was added in one lot. For comparison, experiments were also carried out using *tert*-butyl hydroperoxide (TBHP, 70 wt.% in water, Alfa Aesar). Then, samples were periodically taken and analyzed by gas chromatography using a 30 m × 0.32 mm × 0.25 µm Varian capillary column filled with CP-WAX 52 CB.

For reactions performed under argon atmosphere, the solvent, phenol and catalyst were preliminary mixed and stirred overnight at 60 °C under Ar bubbling. Then, hydrogen peroxide was added in one lot and the reaction was continuously performed under Ar.

Biaryl compounds (3,3'-5,5'-tetra-*tert*-butyl-4'4'-diphenoquinone and 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol) were identified by comparing their NMR spectra with those of pure compounds. These solids were separated from catalytic batches by filtration, dissolved in methyl alcohol-d (99.5+ atom % D, Aldrich) and spectra were recorded on a Bruker Avance 250 spectrometer.

3. Results

Supported gold nanoparticles are traditionally used to oxidize organic molecules with molecular oxygen [20-23]. Even in the case of epoxidation reactions performed with TBHP, Lignier et al. clearly showed that the latter is a radical initiator, oxygen from the air being the primary oxidant [36,37]; yields of epoxide one order of magnitude higher than the initial amount of TBHP present could be obtained and increasing TBHP initial concentration essentially increased the epoxide production rate. Moreover, the nature of the solvent was of prime importance, the best results being achieved with alkylbenzenes [38] or methyl-substituted cyclohexanes [39]. Indeed, it has been postulated that activation of molecular oxygen was carried out by a substituted cyclohexyl radical, produced by abstraction of one the tertiary atoms of the solvent molecule by tert-butyl hydroperoxy radicals. As shown in Table 1, attempts to convert 2,6-di-tert-butyl phenol with TBHP were not successful, even when the reaction was performed in methylcyclohexane. For a TBHP/DTBP ratio of one. the DTBP conversion does not exceed 11% in methanol and acetonitrile and is even lower in methylcyclohexane. Hydrogen peroxide is by far a better oxidant than TBHP in the reaction. However, conversions and selectivities strongly depend on the nature of the solvent and are very different from a catalyst to another. As already reported, Ti-HMS converts DTBP to the corresponding benzoquinone (DTBQ) [9,16]. The selectivity in DTBQ is good but a second product, identified by NMR as 3,3'-5,5'-tetra-tert-butyl-4'4'-diphenoquinone (DPQ) was also obtained as secondary product (Scheme 1). A higher conversion is obtained in methanol, but this solvent favors the formation of the biaryl compound.

In all three solvents, the use of Au nanoparticles as catalyst increases the selectivity to DPQ, the C–C coupling product of phenoxy radicals. Methanol appears to be the best solvent, with conversions far beyond those obtained in acetone or acetonitrile. Indeed, after 6 h, the conversion is almost complete (90%) in MeOH whilst it is only 24 and 13% in acetone and acetonitrile, respec-



Scheme 1. Main products of the oxidation of 2,6-di-*tert*-butyl phenol by hydrogen peroxide.



Scheme 2. Two different pathways for the oxidation of 2,6-di-*tert*-butyl phenol by H_2O_2 over Ti-HMS and Au/TiO₂.

tively. MeOH was already an excellent solvent when using Ti-HMS but the difference with other solvents was not so clear, particularly when compared with acetone. Furthermore, the gold catalyst is 100% selective in DPQ when the reaction is performed in methanol. By contrast to acetone or acetonitrile, in which both DTBQ and DPQ are formed, and by contrast with the titanium catalyst, quinone has never been observed and the biaryl compound is the only product formed all along the reaction.

Catalytic data in the hydroxylation of 2,6-di-*tert*-butyl phenol strongly suggest that the main reaction mechanisms with H_2O_2 are different over Ti-HMS and Au/TiO₂. Whatever the catalyst used, methanol as solvent enhances the production of the biaryl compound, but this compound becomes the sole product of reaction in the case of gold. In other words, gold nanoparticles inhibit the formation of the benzoquinone (Scheme 2).

In order to confirm the difference, the two catalysts have been tested in the hydroxylation of a second substrate, i.e. 2,3,6trimethyl phenol (TMP) (Scheme 3).

Previous results showed that the H_2O_2/TiO_2-SiO_2 system is very active and also very selective in the corresponding quinone (2,3,6-trimethyl benzoquinone or TMBQ) [40].

Scheme 3. Main products of the oxidation of 2,3,6-trimethylphenol by hydrogen peroxide.

Phthalocyanines grafted on silica generally give moderate yields with TBHP as oxidant, but can be very selective in the biaryl compound with molecular oxygen, in the presence of a sacrificial aldehyde [5,41]. Catalytic data reported in Table 2 confirm that both Ti-HMS and Au/TiO₂ are poorly active with TBHP, whatever the solvent used. By contrast, both catalysts are active with hydrogen peroxide, and their behaviors are quite similar to those previously observed with DTBP (Table 1). Over Ti-HMS, the conversion is almost complete after 6 h, which indicates that TMP is certainly easier to oxidize than DTBP. Moreover, reaction rates and final product selectivities do not significantly depend on the nature of the solvent. The major product formed is TMBQ, in agreement with the reaction mechanism reported in the literature [13]. Quinone selectivities are very high, most likely because fast reaction rates limit the formation of coupling products.

Reactions performed over Au/TiO₂ produce exclusively biaryl compounds. Once more, a comparison of conversions at 6 h clearly shows the particular properties of methanol as compared to acetone and acetonitrile. Conversions at 6 h do not exceed 30 and 40% in acetonitrile and acetone, respectively, but reach 92% in MeOH. The reaction in methanol is very selective and leads to a unique product, which precipitates as a gray powder and was identified as 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol (HMBP) by NMR. It is interesting to note that the diphenoquinone, which results from the over-oxidation of the biphenol and was the only compound found with DTBP, is not observed with TMP. The difference between DTBP and TMP has been explained by a sterical hindrance of the 3 substituting groups to further oxidation [13]. In acetone and acetonitrile, the reaction is less selective and a second product is detected by GC. This product, which selectivity did not exceed 10%, could not

Table 2

Oxidation of 2,3,6-trimethyl phenol (TMP) over Ti-HMS and Au/TiO₂ catalysts.

Catalyst	Oxidant	Solvent ^a	TMP conv. (%) after 6 h	Product yield (Product yield (%)			
				TMBQ	HMBP	Others ^b		
Ti-	TBHP	AC=0	2	2	0	-		
HMS		MeCN	-	-	-	-		
		MeOH	3	2	1	-		
	H_2O_2	AC=0	86	74	6	6		
		MeCN	98	85	10	3		
		MeOH	97	87	10	-		
Au/TiO ₂	TBHP	AC=O	-	-	-	-		
		MeCN	-	-	-	-		
		MeOH	5	2	2	1		
	H_2O_2	AC=0	41		37	4		
		MeCN	30	-	27	3		
		MeOH	96	-	94	-		
		MeOH ^c	97	-	97	-		
No	H_2O_2	MeOH	3	-	-	-		
TiO ₂	H_2O_2	MeOH	6	4	2	-		
Au/Al_2O_3	H_2O_2	MeOH	92	-	92	-		

^a AC=O: acetone, MeCN: acetonitrile, MeOH: methanol.

^b This product was assumed to be a phenoxyphenol (PP). The yield was estimated by the difference between the conversion and the amount of known products (TMBQ+HMBP).

^c Reaction performed under argon atmosphere.



Scheme 4. Reaction pathway for the oxidation of 2,3,6-trimethylphenol by H₂O₂ over Au/TiO₂.

be isolated and completely identified. However, based on previous studies on the oxidation of TMP with H_2O_2 , the unidentified product could be tentatively assigned to a phenoxyphenol (PP). This compound, which results from the C–O coupling between phenoxy radicals, was previously observed in the oxidation of TMP with H_2O_2 in acetonitrile [11]. TMBQ is never detected as a primary product by chromatography, even at the level of traces, confirming the difference between Ti and Au in the reaction.

In order to confirm the role of catalysts in the conversion of substituted phenols, additional experiments have been performed. First, a reaction was carried out in methanol with TMP as substrate in the absence of any catalyst. After 6 h, the conversion was only 3% and it reached 8% after 24 h (Table 2). In a second experiment, 30 mg of P25, which is the titania support for the commercial Au/TiO₂ catalyst, were added to the reaction mixture. Indeed, the activity of Ti-HMS suggested that TiO₂ could also be active in the reaction. Even after 24 h, the conversion did not exceed 10%, far below that obtained in the presence of Au nanoparticles, and both TMBQ and HMBP are formed (Table 2). Third, the same reaction was performed using Au/Al₂O₃ as catalyst. Comparison with Au/TiO₂ is straightforward because the two catalysts possess very similar Au content and particle sizes. This catalyst was as active as Au/TiO₂ and HMBP was once more the only product formed (Table 2). All these experiments clearly demonstrate the primary role of gold nanoparticles in the catalytic process, as recently shown in the radical oxidation of bulky alkenes [42]. They also show that bulk TiO₂ is inactive and that the nature of the support has no influence on the intrinsic activity of Au particles in the present reaction.

Despite high activity of Au-based catalysts, phenol conversions are never complete, even after 48 h, when reactions are performed with H_2O_2 /phenol = 1. Actually, the conversion reaches a maximum (80–90%) after approx. 10 h and then it remains constant. After one day, the reaction immediately restarts upon addition of 0.5 mL H_2O_2 , and the phenol conversion is complete within 3 h. Clearly, the reaction does not stop because of catalyst deactivation, but because active oxygen species are not available anymore. By contrast to previous observations, molecular oxygen from the air does not seem to take part in the reaction. A reaction performed under argon atmosphere confirmed that neither the reaction rate nor the selectivity in biaryl compounds was significantly affected by the absence of air. This suggests that oxygen species involved in the process essentially result from the decomposition of H_2O_2 over gold particles (Table 2 and Fig. 1), as will be discussed later.

4. Mechanism

As previously reported in the literature, gold nanoparticles catalyze the decomposition of alkyl hydroperoxides to alkoxy radicals, which can further react with the peroxide to form alkylperoxy radicals [39]. These species can carry out hydrogen abstraction from a tertiary C–H bond at 80 °C, triggering a low temperature oxidation mechanism involving molecular oxygen [43]. Hydrogen peroxide has proven unsuccessful in initiating such a reaction [39]. We can thus assume that Au will not simply cleave the H₂O₂ peroxide bond, but will form Au-H₂O₂ adducts (Scheme 4), as previously proposed [44]. These Au-hydroperoxide species will then react with DTBP or TMP to form phenoxy radicals, like those produced by reaction with Ti-OOH species [45]. The subsequent formation of quinone (Route 1) then relies on an intermediate complex involving Ti peroxo species and phenoxy radicals [13]. However, by contrast to Ti-OOH species, which are very stable and can be easily characterized in solution (deep yellow color), Au-H₂O₂ intermediates are



Fig. 1. . 2,3,6-Trimethylphenol conversion in methanol over Au/TiO₂ under air (\bigcirc) and argon (\bullet) atmospheres.



Fig. 2. 2,3,6-Trimethylphenol conversion over Ti-HMS () and Au/TiO $_2$ () in MeOH (a) and MeCN (b).

certainly unstable under reaction conditions and rapidly dissociate to regenerate the reduced gold nanoparticle. The unstability of the Au–peroxo species may explain why phenoxy radicals are not oxidized to quinone but simply recombine to form the biaryl compound (Route 2).

More information about the gold-catalyzed process has been obtained from the evolution of 2,3,6-trimethyl phenol conversion with time. In methanol, the TMP conversion profile vs. time obtained over Au/TiO₂ is almost identical to that observed over Ti-HMS materials: the apparent initial reaction rate is identical on both catalysts, suggesting that the rate-limiting step is independent of the catalyst nature; the reaction rate then decreases with increasing TMP conversion (Fig. 2a). By contrast, in acetone or acetonitrile, the initial reaction rates observed over Au/TiO₂ are low and TMP conversions vary almost linearly with time, whilst conversion profiles are basically unchanged over Ti-HMS (Fig. 2b). Additional experiments performed with various TMP and Au/TiO₂ concentrations gave similar linear profiles and quite close reaction rates, indicating thermodynamic (as opposed to kinetic) control of the reaction. This is attributed to the complexing nature of the C=O and especially C=N functions of the solvents towards gold. Cyanides are actually widely used to extract gold from ores and propionitrile has led to Au leaching from Au/TiO₂, as previously described [32]. Although no gold leaching is observed under these conditions, it is likely that acetone and acetonitrile solvent molecules complex gold particles, thereby limiting their accessibility, as recently described with 2,2'-azo-bis-isobutyronitrile [43]. On the other hand, Ti sites are not affected by these functions.

5. Conclusions

The H_2O_2 -Au system has proven to be particularly effective in the mild oxidation of substituted phenols in the liquid phase. However, the product distribution is different from that obtained using Ti-containing silica catalysts: whilst Ti is very selective to the corresponding benzoquinones, Au directs the reaction to C-C coupling products. This has been explained by the low stability of Au-H₂O₂ adducts as compared to Ti-OOH species, thus favoring the formation of phenoxy radicals and free-radical coupling reactions, and inhibiting the catalytic formation of benzoquinone. The reaction rate and product selectivities depend on the nature of the solvent but yields in biaryl compounds higher than 90% have been obtained in methanol. Gold is thus complementary to Ti-silicas and could be a promising catalyst for the clean synthesis of biaryl compounds (low temperature, no by-products, green oxidants).

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