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Involvement of Surface-Bound Radicals in the Oxidation of Toluene Using Supported Au-Pd Nanoparticles**

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The selective oxidation of hydrocarbons into useful functionalized chemicals is an important family of chemical transformations.[1–3] Consequently there is significant interest in the design of new heterogeneous catalysts for the selective oxidation of hydrocarbons (e.g., toluene) as well as for the purpose of gaining insight into the mechanism through which they operate. In industry most oxidations with O_2, the preferred terminal oxidant, involve radical pathways and the catalysis centers on the decomposition of hydroperoxides. The prime target in commercial toluene oxidation is the need to control the ratio of benzoic acid to benzaldehyde to meet market needs. To achieve this end, a detailed knowledge of the mechanism is required.[4]

In the last decade gold-based heterogeneous catalysts have been found to be effective for the selective oxidation of alcohols[5] and polyols,[6] as well as the synthesis of hydrogen peroxide[7] and the epoxidation of unsaturated hydrocarbons.[8] Most recently, we have shown that toluene can be selectively oxidized to benzyl benzoate using oxygen at 160 °C with Au-Pd alloys under solvent-free conditions.[9] Herein we report for the first time the utilization of gold-based heterogeneous catalysts for the oxidation of toluene using milder reaction conditions (80 °C) with *tert*-butyl hydroperoxide (TBHP) as the principal oxygen donor. In particular, we show for the first time that direct involvement of a surface-stabilized reactive oxygen species (ROS), having radical character and produced from TBHP, are directly involved in the surface-catalyzed reaction. Previously, studies have shown that Au surfaces are effective for the decomposition of peroxides, but it was thought that this resulted only in radicals in solution,[10] and consequently no significant surface chemistry was even taken into consideration. Our new studies definitively show that this is not the case. The fundamental issue of controlling the selectivity towards a specific product is still challenging and herein we explore the use of gold-based catalysts, synthesized by sol-immobilization, to demonstrate that this is possible for the radical initiated oxidation of toluene.

The sol-immobilization method has the advantage of controlling the mean particle size and distribution of the metal. Such materials can also be used as catalysts.[11–13] Table 1 summarizes the catalytic activity obtained with such TiO_2-supported Au-Pd catalysts for the oxidation of toluene and the corresponding blank reactions carried out in the absence of the catalyst. The Au-Pd sol and the resulting supported catalyst have been characterized by transmission electron microscopy[9] (see the Supporting Information). The nanoparticles were found to be homogeneous alloys[9] with the unsupported sol having a mean particle size of 2.9 nm and that of the corresponding supported, dried material was 3.9 nm.

Initially, reactions were conducted in the presence of air and the possible reaction of toluene with TBHP was studied. No reaction was observed under our reaction conditions. Next, the oxidation of toluene was investigated in the presence of the support, but in the absence of catalytic metal, since we have observed that with the use of an oxidant such as TBHP there can be some activity even in the absence of the metal.[8,13] However, TiO_2 is almost inactive, with small amounts of benzyl alcohol, benzaldehyde, and benzoic acid being produced. We then conducted experiments in the absence of O_2 and found that the TiO_2 was inactive. Use of a non-immobilized Au-Pd sol catalyst showed that the naked sol particles are active for this reaction in the absence of the support, as has been observed previously.[14] However, addition of the Au-Pd nanoparticles to TiO_2 increases the activity, thus showing that the metal is playing the key role in the catalysis. Reaction using the non-immobilized sol requires the addition of excess water to the reaction mixture, but this does not have an adverse effect on the overall reaction observed. The products are similar in nature to those observed when using the support alone, however much more benzoic acid is generated. Interestingly, only trace amounts of benzyl benzoate are observed, thus indicating that at 80 °C hemiacetal formation is not a preferred pathway, although we have shown this to dominate at higher temper-

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Table 1: Liquid-phase oxidation of toluene with TBHP as an oxidant at 80 °C.[a]

Catalyst	Conversion [%] Toluene	TBHP	Selectivity [%][b] Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl benzoate	TOF $[h^{-1}]$[c]
no TBHP/no catalyst	0	–	0	0	0	0	–
no catalyst	0.5	0.4	20	76	2	2	–
no catalyst	1.1	1.0	32	58	10	0.1	–
TiO_2[d]	0.1	1.6	29	71	0	0	–
TiO_2	0.5	4.7	17	80	3	0	–
1%Au/TiO_2	3.3	7.4	15	47	38	0	54
1%Pd/TiO_2	2.0	5.8	44	46	9	0.5	32
1%Au-Pd/TiO_2[d]	4.3	13.9	21	37	42	0	71
1%Au-Pd/TiO_2	4.4	13.6	23	32	44	trace	72
1%Au-Pd/TiO_2, reuse 1	4.0	12.6	18	35	47	0.1	64
1%Au-Pd/TiO_2, reuse 2	4.0	12.4	17	34	49	0	64
1%AuPd/TiO_2, reuse 3	3.8	11.7	15	37	48	0.1	61
1%AuPd/TiO2, reuse 4	4.2	13.3	16	28	56	0.1	68
1%Au-Pd/TiO_2, reuse 5	4.0	12.8	15	36	49	0	66
Au-Pd sol[e]	2.0	1.9	30	68	2	0	33
1%Au-Pd/TiO_2[f]	5.3	23	16	32	52	0	86

[a] Reaction conditions: molar ratio toluene/TBHP = 1, 80 °C, catalyst (0.2 g), substrate/metal molar ratio = 6500, reactions carried out in the presence of air unless specified otherwise, 4 h reaction time. [b] Selectivity based on toluene conversion. [c] Turnover frequency based on total mol metal and mol toluene converted after completion of reaction. [d] Reaction carried out under a N_2 atmosphere. [e] Reaction conditions as indicated in [a], but with water (10 mL) present to ensure identical reaction conditions between non-immobilized and sol-immobilized catalysts.

atures.[9] However, in the present case water is present and this will inhibit ester formation.

Benzoic acid was formed because of the over oxidation of the benzaldehyde formed from benzyl alcohol oxidation. We confirmed this supposition by oxidizing benzyl alcohol (see Table S1 in the Supporting Information). Reactions using the supported monometallic Au and Pd catalysts illustrate that the combination of both Au and Pd causes a significant enhancement in activity as noted for other reactions.[9] As we obtained promising levels of conversion after 4 hours of reaction, we prolonged the reaction time, and higher conversions were achieved after 72 hours of reaction (Figure 1). It is clear that the oxidation of toluene continues to increase even though the conversion of TBHP has virtually ceased. This behavior is due to the involvement of benzaldehyde, that is, as long as small amounts of benzaldehyde are present in the reaction mixture the conversion of toluene continues, as confirmed by the selectivity data (Figure 1, and Table S2 in the Supporting Information). The conversion is considered to be hindered by competitive adsorption of benzoic acid[15,16] and experiments in the presence of benzoic acid confirmed this to be the case (see Table S3). Moreover, toluene conversion was accompanied by high TBHP conversion, thus indicating that the Au-Pd nanoparticles are very active in the decomposition of TBHP. These results suggest that the presence of small Au-Pd particles is active for the oxidation of toluene. Experiments in the absence of O_2 show that for all the TiO_2-supported catalysts, there is no activation of O_2 and the catalysis results from TBHP acting as the oxidant. In addition, these catalysts are reusable (Table 1) and no marked changes were observed in the conversion and selectivity even

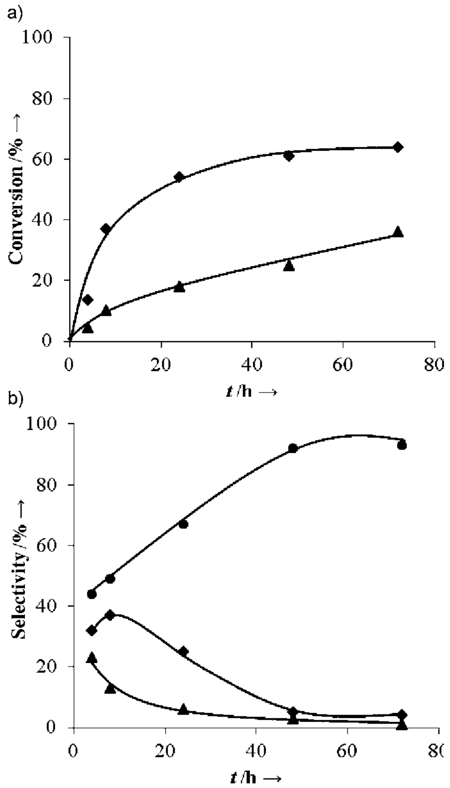

Figure 1. Time-on-line data for the reaction of toluene. a) Conversion of toluene (▲) and TBHP (◆). b) Selectivities to benzaldehyde (◆), benzyl alcohol (▲) and benzoic acid (●). Reaction conditions as in Table 1.

after five reuses. The catalysts were also effective for the oxidation of ethyl benzene (see Table S4).

It is well known that metal nanoparticles can efficiently decompose oxidants such as H_2O_2 and TBHP.[10] Recently, it has been reported that supported gold catalysts can produce extremely high rates of decomposition of peroxides such as hydrogen peroxide to form $^{\bullet}$OH and $^{\bullet}$OOH radicals. In addition, the efficient conversion of alcohols using TBHP has been demonstrated.[17,18] Furthermore, decomposition of the these peroxides can produce reactive oxygen species (ROS) or radicals, such as $^{\bullet}$OH and *t*BuO$^{\bullet}$, in addition to decomposition products such as H_2O, O_2, and *tert*-butyl alcohol. However, the activity of the surface-bound (metal and/or support) ROS with the organic substrates has not previously been considered in any detail and it is not clear if the peroxide species formed can be adsorbed on the catalyst surface. However, it has been recently shown that surface species, derived from azobis(isobutyronitrile) (AIBN), can be formed on gold catalysts and these can promote oxygen activation via peroxo radical species.[19–21]

To elucidate details of the reaction mechanism and especially the role of TBHP, on both the Au-Pd nanoparticles and the support, we performed a series of additional experiments (Table 2, and see Table S5 in the Supporting Information). In the first experiment (Table 2, entry 1), the oxidation of toluene in the absence of catalyst using TBHP showed low conversion. Whereas, the oxidation of toluene in the presence of catalyst and TBHP showed high activity as expected, thus highlighting the importance of the catalyst (Table 2, entry 2). In the case of entry 3 in Table 2, TBHP was decomposed over the catalyst with subsequent addition of toluene, without removal of the catalyst, and low conversion was observed. For entry 4 in Table 2, TBHP was decomposed over the catalyst and the catalyst was removed by filtration, dried overnight (110 °C), and then reacted with toluene. In the case of entry 5 in Table 2, the same procedure was followed with the exception that the catalyst was not dried and toluene was added after the decomposition of TBHP. Low levels of toluene conversion were observed for the examples in entries 4 and 5. For entries 6 and 7 in Table 2, the complete decomposition of TBHP in either the presence or absence of catalyst, and the subsequent addition of toluene, did not produce any products. The low levels of conversion observed using a 'pre-TBHP-activated' catalyst indicate that residual surface-stabilized ROS/organic surface radicals can lead to the conversion of toluene. Furthermore, after the complete decomposition of TBHP in the presence of the catalyst, and filtration to remove the catalyst, the addition of toluene to the remaining solution gave no appreciable conversion. This again highlights the importance of surface-based ROS/organic surface radicals, and demonstrates that the solution-based ROS are short lived, and do not survive long enough to induce toluene oxidation. The surface acts to provide a platform to stabilize the ROS, thereby extending their lifetime and facilitating oxidation. To confirm this important finding an additional experiment was conducted (Table 2, entry 8) wherein the methodology used in entry 4 was employed using a catalyst having the same total mass, but containing half the concentration of metals, that is, 0.25 % Au-0.25 % Pd/TiO_2. Hence the amount of metal present is halved but the surface area of TiO_2 remains unchanged. The observation that the toluene conversion was approximately halved, within experimental error (± 0.005 %), clearly shows that the surface-based ROS are associated with the Au-Pd nanoparticles and not solely the bare TiO_2 support.

Therefore, to investigate the nature of the aforementioned surface-based ROS, CW-EPR spectra were recorded for the Au-Pd/TiO_2 sample in the presence and absence of TBHP. The solid-state EPR spectra of the dried samples after the appropriate treatment are shown in Figure 2 (see the

Table 2: The oxidation of toluene with TBHP.[a]

Entry	Reaction conditions	*t* [h]	Conv. [%]	Selectivity [%]			
				Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl benzoate
1	Solution of toluene and TBHP reacted in the absence of catalyst.	7	0.53	14.9	76.2	8.9	0
2	Solution of toluene and TBHP in the presence of 0.5%Au-0.5%Pd/TiO_2.[b]	8	10.0	12.8	37.2	49.4	0.6
3	Step 1: complete decomposition of TBHP in the absence of toluene and presence of 0.5%Au-0.5%Pd/TiO_2; Step 2: addition of toluene and reaction started.[c]	7	0.13	8.1	67.8	24.1	0
4	Step 1: complete decomposition of TBHP in the absence of toluene and presence of 0.5%Au-0.5%Pd/TiO_2; Step 2 recovery of catalyst by filtration; Step 3 catalyst dried; Step 4: addition of toluene to the dried catalyst and reaction started.[c]	7	0.06	3.2	96.8	0	0
5	Step 1: complete decomposition of TBHP in the absence of toluene and presence of 0.5%Au-0.5%Pd/TiO_2; Step 2: recovery of catalyst by filtration; Step 3: addition of toluene to the catalyst and reaction started.[c]	7	0.06	29.5	61.0	9.5	0
6	Step 1: complete decomposition of TBHP in the absence of toluene and presence of 0.5%Au-0.5%Pd/TiO_2; Step 2: removal of catalyst by filtration; Step 3: addition of toluene in the absence of catalyst and reaction started.	7	0	0	0	0	0
7	Step 1: complete decomposition of TBHP in the absence of toluene and catalyst; Step 2: addition of toluene in the absence of catalyst and reaction started.	7	0	0	0	0	0
8	Step 1: complete decomposition of TBHP in the absence of toluene and presence of 0.25%Au-0.25%Pd/TiO_2; Step 2 recovery of catalyst by filtration; Step 3: catalyst dried; Step 4:addition of toluene to the dried catalyst and reaction started.[d]	7	0.02	9.3	90.7	0	0

[a] Reaction conditions: toluene = 94.1 mmol, ratio toluene (mol)/ TBHP (mol) = 1:1, 80 °C, [b] Substrate/metal = 6500, [c] Substrate/metal = 1300, [d] Substrate/metal = 2600.

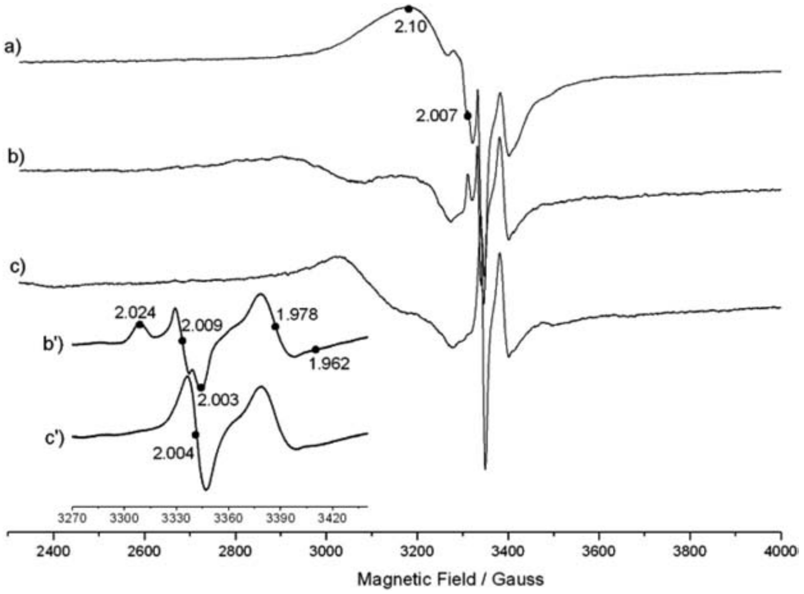

Figure 2. X-band CW-EPR spectra (140 K) of a) Au-Pd/TiO_2, b) Au-Pd/TiO_2 after treatment with TBHP, and c) Au-Pd/TiO_2 after treatment with TBHP + toluene. The expanded views of the center field regions of b) and c) are shown in the inset and labeled b′ and c′, respectively.

Supporting Information). The background EPR spectrum of the untreated sample (Figure 2a) contains signals arising from bulk Ti^{3+} centers ($g_{\perp} = 1.978$, $g_{\parallel} \approx 1.962$)[22] and Pd^+ ions ($g_1 \approx 2.80$, $g_2 = 2.13$, $g_3 = 2.080$).[23] Owing to the broad profile of the axially symmetric Ti^{3+} signal, it is not possible to assign these centers specifically to the anatase or rutile component of the P25. Nevertheless formation of Ti^{3+} centers in P25 by gentle annealing is not uncommon.[24] The Pd^+ signal suggests that small amounts of Pd oxide or isolated Pd centers exist on the catalyst. After treatment with TBHP, the EPR spectrum changes markedly (Figure 2b). The majority of the Pd^+ signal disappears, the bulk Ti^{3+} remains visible, and a new signal, assigned to the superoxide radicals (O_2^-), is observed. The measured g values of $g_1 = 2.003$, $g_2 = 2.004$, and $g_3 = 2.024$, and line width are consistent with a nonvacancy $Ti^{4+}..O_2^-$ coordinated site for a 'side-on' ionically bonded conformation.[25] This species is considered to be derived directly (from TBHP decomposition) or indirectly (by reduced Ti^{3+} centers reacting with molecular oxygen) from TBHP, as it is not present when THBP is absent; for example, direct exposure of the Au-Pd/TiO_2 catalyst to oxygen does not generate this signal in the absence of TBHP. There was no evidence of either a hydroperoxy ($HO_2^{\bullet}$) species or the other oxygen-centered radical (peroxy), which have been previously identified on P25.[26]

When the sample was subsequently treated with TBHP/toluene (Figure 2c), the superoxide signal disappeared completely and a new inhomogeneously broadened symmetric signal with $g = 2.004$ was formed. Coupled with the relatively large linewidth, one may conclude that the radical responsible for this signal is surface based. Surface O_2^- radicals can oxidize various organic substrates over TiO_2 (P25), although oxidation by other surface ROS such as acyl or organoperoxyl radicals is more facile.[27] Whilst the former ionic species (O_2^-) are stable on TiO_2, the latter species are more difficult to detect directly on the oxide support,[27] let alone on a metal particle where spin polarization would considerably broaden any signal, hence they may be formed but are not observed in the current experiments. Nevertheless these EPR results at least demonstrate the role of surface O_2^- radicals in the oxidation of toluene. This role is clearly evidenced by the fact that when we recovered and dried the catalysts after TBHP addition (Figure 1b) the O_2^- signal remained. After subsequent toluene addition, the O_2^- signal disappeared, thus proving the reaction of toluene with this surface-bound radical species. However, we cannot preclude the possible role of other unobserved surface ROS.

The reactions we are observing between toluene and TBHP can therefore be rationalized on the basis of free radical chemistry, although many of the radicals concerned should be regarded as surface-bound ROS. It is possible that a number of potential pathways exist for the formation of the primary product, that is, benzyl alcohol, involving free radical formation and termination. However, based on our detailed experimentation, we consider that these products arise from interactions of a surface-bound ROS which behaves chemically like radicals. Therefore it is clear from our results that for Au-Pd/TiO_2 the bifunctional role of Au-Pd sites and Ti^{4+} centers on the surface of titania facilitates the activation of toluene and affects the product distribution.

In summary, we have successfully utilized Au-Pd nanoparticles supported on TiO_2 as catalysts for the selective oxidation of toluene under mild reaction conditions using a sol-immobilization methodology for catalyst synthesis. We have shown for the first time that surface-bound oxygen-centred radicals play a role in activating toluene. At present we have not been fully able to delineate the contributions to the overall oxidation reaction by the surface-bound radicals, but the mere observation of this new pathway will aid and inform future catalyst design.

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