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Water as a catalytic switch in the oxidation of aryl alcohols by polymer incarcerated rhodium nanoparticles†

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Abstract

One of the major goals in the oxidation of organic substrates, and especially for alcohol oxidation, is the use of molecular oxygen as the oxidant under mild conditions. Here we report the synthesis and testing of Rh polymer incarcerated catalysts, using a metal so far not used for alcohol oxidation reactions, in which the catalytic activity towards aryl alcohol oxidation, for substrates like 1-phenylethanol and benzyl alcohol, is switched on by the addition of water as co-solvent in toluene. This is done by using air as oxidant at atmospheric pressure, in one of the mildest reaction conditions reported for this class of reaction. The promoting effect of water to higher conversions was observed also for rhodium over alumina supported catalysts, which were used as a benchmark allowing in all cases high conversion and selectivity to the ketone or the aldehyde within a short reaction time. The effect of water was explained as a medium capable to promote the oxidation of the alcohol to the ketone in a biphasic system assisted by phase transfer catalysis. This is particularly relevant for alcohols like 1-phenylethanol or benzyl alcohol that are not soluble in water at room temperature, and for which alternative oxidation routes are needed, as well as to switch on the catalytic activity of metal nanoparticles in a facile and green manner for the activation of molecular oxygen. Aliphatic alcohols like 1-octanol and 3-octanol were also tested, still showing Rh based catalysts as promising materials for this reaction if toluene only was used as solvent instead.

1. Introduction

The oxidation of alcohols to ketones is a very relevant oxidation reaction in the area of catalysis, with applications ranging from the manufacture of fine chemicals to mechanistic studies,[1,2] with ketones being important precursors for the drug and food industries.[3,4] On the other hand a major target both in industry and academia is the use of molecular oxygen as an oxidizing agent under mild conditions in order to achieve energy-effective and sustainable oxidation processes.[5]

In this context, a large number of catalytic systems is present in the literature for the oxidation of alcohols to ketones including: metal complexes,[6] metal oxides,[7] and supported metal nanoparticles.[8,9] Most of this recent research though is devoted to solvent-free processes.[10,11] Nevertheless, solvents can play beneficial roles in promoting the solubility of oxygen in the reaction media[12] or by promoting the reactivity of functional groups over metal or metal oxide interfaces.[13] However, these studies are mainly centred on polarity effects. In contrast, if a solvent could play a more active role for the reaction, as well as being a green solvent like water, this would be of extreme importance.

These premises, together with the aim to identify a more general trend or rule to activate alcohols under mild conditions, prompted us to investigate the use of rhodium polymer incarcerated nanoparticles (Rh-PI) for the oxidation of alcohols like: 1-phenylethanol, benzyl alcohol, 1-octanol and 3-octanol. For this, we investigated the use of a solvent/co-solvent system comprising toluene and water and the use of air as oxidant under atmospheric pressure. In fact, besides the industrial and fundamental relevance of alcohol oxidation,[14,15] the use of polymer incarcerated metal nanoparticles has received limited attention so far for alcohol oxidation despite their interesting structural properties.[16,17] These materials have the advantage of a 'soft' metal/support interaction[18,19] and therefore they are ideal for physical chemistry studies aimed to represent a catalytic system where the catalytic activity mostly originates from the metal nanoparticle only, together with a high monodispersivity.[20] Moreover, despite Rh being a metal that has been proven to be efficient for oxidative coupling reactions,[21] it is mostly used for reduction reactions,[22] and especially for the reduction of nitric oxide in automotive exhaust systems. As such, it has been so far neglected as a catalyst for alcohol oxidation, in favour of metals like Pd, Pt and Au.[23-25] Exceptions are the total electro-oxidation of ethanol to CO_2 in the presence of bimetallic electrodes comprising Rh/Pt alloys,[26] the use of porphyrin complexes,[27] and a recent theoretical study[28] for the oxidation of ethanol over Rh(111) surfaces assisted by water. These studies led us to combine the use of co-solvents mentioned above to investigate if Rh-PI nanoparticles could actually be a catalytic system for alcohol oxidation, and to explore the activity of this material against that of Rh over a standard support like alumina, or hybrid materials comprising the polymer cross linked with activated carbon.

2. Results and discussion

2.1 Catalytic tests for 1-phenylethanol oxidation in the presence of toluene as a solvent

Our investigation was initially focused on the oxidation of 1-phenylethanol to acetophenone due to its relevance in both industrial applications, as a precursor for resins, adhesives and drugs,[29] as well as in physicochemical studies,[30] as a substrate to test novel catalysts by restricting the reactivity to one CHOH group. Four different rhodium containing catalysts were prepared and investigated towards the oxidation of 1-phenylethanol to acetophenone using oxygen from air as oxidant under mild conditions.

The catalysts tested were: (i) a catalyst comprising Rh nanoparticles embedded in a polymeric matrix only[31,32] (here denoted ad Rh-PI) obtained using a styrene based copolymer (Fig. 1, experimental section and ESI, Scheme S1†) and reduction of a rhodium precursor, rhodium(II) acetate dimer $[Rh(OAc)_2]_2$ by $NaBH_4$; (ii) a catalyst obtained by in situ reduction of $[Rh(OAc)_2]_2$ by $NaBH_4$ (experimental section and ESI†) in the presence of both polymer and carbon black as support (here denoted ad Rh-PI/CB), which includes cross-linking of the polymer with activated carbon (see experimental section and ESI†); (iii) a catalyst obtained in the same way as Rh-PI/CB but using alumina as support instead (Rh-PI/Al_2O_3); and (iv) a commercial catalyst comprising Rh supported on alumina only (Rh/Al_2O_3) used as a benchmark. These catalysts form a set of materials ranging from a fully embedded metal nanoparticle with soft metal support interactions (Rh-PI) to a material presenting a metal/metal oxide interface (Rh/Al_2O_3) that could also affect the catalytic activity.[33]

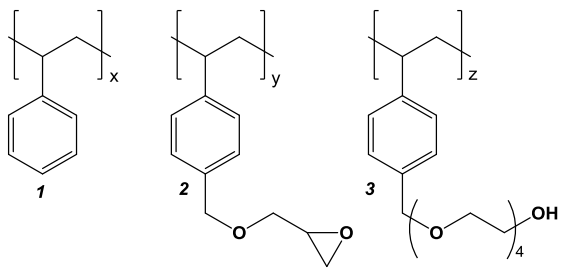


Fig. 1 Copolymer units (**1**, **2** and **3**) of the styrene based polymer used to prepare the Rh polymer incarcerated nanoparticles, Rh-PI. The metal precursor was $[Rh(OAc)_2]_2$ which was reduced by $NaBH_4$. The same polymer and precursor were used to prepare Rh-PI/CB and Rh-PI/Al_2O_3, but with the in situ reduction of the metal and crosslinking of the polymer in presence of the second support.

Catalytic tests were carried out at 100 ^oC for 4 h at atmospheric pressure of air, using toluene as a solvent and a molar metal to substrate ratio of 1:100, and their activity is reported in table 1.

Table 1 Catalytic tests for the oxidation of 1-phenylethanol in toluene by polymer incarcerated Rh nanoparticles and Rh supported on alumina. Reaction conditions: T = 100 ^{o}C, P = atmospheric pressure, molar metal-to-substrate M:S = 1:100, reaction time t = 4 h.

Catalyst	**Conversion (%)**	**Selectivity (%)**	
		Acetophenone	Ethylbenzene
Rh-PI	< 1	100	0
Rh-PI/CB	< 1	100	0
Rh-PI/Al_2O_3	10	94	4
Rh/Al_2O_3	11	98	2

Under these reaction conditions both Al_2O_3 containing catalysts are active towards the oxidation of 1-phenylethanol in the range of 10% conversion, with acetophenone as the main product with selectivity in excess of 97% (see ESI, Figs S1-S4†). However, ethylbenzene was also identified, ca. 2-4 % selectivity. The carbon mass balance was > 98% in all cases, and no trace of benzaldehyde was detected at GC/MS level, (see ESI, Figs S5-S7†), thus showing that decarboxylation does not take place. The Rh-PI and Rh-PI/CB catalysts have a negligible activity and a set of control tests (a to f, vide infra) was carried out to confirm these results for solvent, autoxidation, support, diffusion and impurities. (a) The use of Rh/Al_2O_3 in presence of toluene only, showed that the catalyst is not able to oxidize the solvent under these reaction conditions, and therefore acetophenone is not formed by secondary reactions involving toluene. (b) A test in the absence of any catalyst for a toluene/alcohol reaction mixture led to less than 1% conversion to acetophenone, thus showing negligible autoxidation.[34] In turn, even the very small activity detected for Rh-PI and Rh-PI/CB can be ascribed to a reaction with the walls of the reactor and thus the catalysts displaying no activity. (c) A catalytic test carried out using only alumina showed little catalytic activity, ca. 1.5% but with some ethylbenzene (ca. 30% selectivity) thus suggesting that this support could promote a disproportionation pathway.[35] (d) It was also verified that at 100 ^{o}C the catalysts operate under kinetic control regime (i.e. not diffusion limited by oxygen mass transfer), by exploring a range of reaction temperatures from 80 to 120 ^{o}C. (e) Finally, GC/MS analysis of the starting materials identified trace amounts (ca. 2%) of 1-cyclohexylethanol and cyclohexyl methyl ketone for 1-phenylethanol, and o-xylene for toluene (see ESI, Figs S8-S11†), however these are not considered to affect our results. (f) Leaching tests were also carried out (see sections 2.2 and 2.4), and these also confirmed the activity is due to Rh nanoparticles.

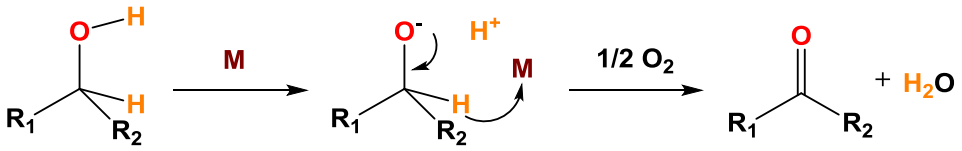
These initial set of data and control tests, would suggest that Rh-PI/Al_2O_3 and Rh/Al_2O_3 are active by virtue of a metal oxide to metal nanoparticle interface induced by alumina. Interface effects are very common in heterogeneous catalysis and can strongly promote the catalytic activity of a

reaction.[36] Conversely, as this metal oxide-to-nanoparticle interface is absent for Rh-PI and Rh-PI/CB these catalysts would not be active for the oxidation of the alcohol under these reaction conditions. Another factor that could, in principle, explain the difference in activity between these catalysts could also be the lack of swelling of the polymeric matrix for Rh-PI and Rh-PI/CB, and thus the lack of diffusion of the reactants over the Rh surface. However, these catalysts can swell well with organic solvents such as toluene, THF or DCM. In fact, PI catalysts comprising the same copolymer, although using gold as active metal were capable to oxidize alcohols[37] including 1-phenylethanol to acetophenone in the presence of toluene as a solvent, as well as aldehydes to carboxylic acids in the presence of toluene as the sole solvent.[38] Therefore, we consider toluene as an appropriate solvent to carry out the reaction also for Rh-PI and such differences in activity could then be ascribed to the presence of this particular metal.

2.2 Catalytic tests for 1-phenylethanol oxidation in the presence of toluene and water as a co-solvent, water as catalyst switch

In view of the apparent lack of activity for Rh-PI and Rh-PI/CB in toluene, we considered the possibility of catalytic tests using a reaction medium by adding water as a co-solvent, with water acting as a possible proton carrier for the oxidation reaction. It should be noted that as 1-phenylethanol and acetophenone are largely immiscible in water at room temperature, water cannot be used alone as a solvent for high alcohol concentrations, and toluene has also to be present to solubilize the substrate, the products, and to swell the nanoparticles.

The oxidation of an alcohol to a ketone is formally a sequential dehydrogenation via abstraction of two H atoms (either as charged species or radicals) from the O-H group and the C-Hα to the hydroxyl group[39] of the alcohol. Many reports suggest the presence of an alkoxide intermediate in the presence of a base[40,41] (scheme 1).



Scheme 1 One of the accepted reaction mechanisms for alcohol oxidation via alkoxide formation. In this case by considering deprotonation of the hydroxyl functional group, followed by hydrogen abstraction, as hydride, of the H in alpha to the OH group in a step mediated by the metal (changes in metal oxidation state not shown). The alkoxide can also bind to the metal.[40] An alternative mechanism involving H· radical abstraction atomic oxygen adsorbed over the catalyst surface is also possible.[37,38]

In this case, a stabilization of the transition state by a proton carrier like water should accelerate the reaction. A recent computational study on Rh[111] surfaces in the oxidation of ethanol and

glycerol,[28] showed that water could promote the dissociation of the O-H bond, which would accelerate the reaction, and slightly inhibit the dissociation of the C-H bond of the hydrogen alpha to the hydroxyl group. The net result of these two effects would be an enhanced catalytic activity promoted by water. However, it should be noted that ethanol and glycerol are fully miscible in water, unlike our substrate and products, and as such our system is necessarily biphasic. Therefore, we explored the effect of water using a water and toluene mixture with an initial 2:1 volume ratio of these two solvents. The results of these catalytic tests are reported in Table 2.

Table 2 Catalytic tests for the oxidation of 1-phenylethanol to acetophenone in water/toluene by polymer incarcerated Rh nanoparticles and Rh supported on alumina. Reaction conditions: T = 100 ^{o}C, P = atmospheric pressure, M:S = 1:100, t = 4 h. Water:toluene volume ratio 2:1. Carbon mass balance > 98%.

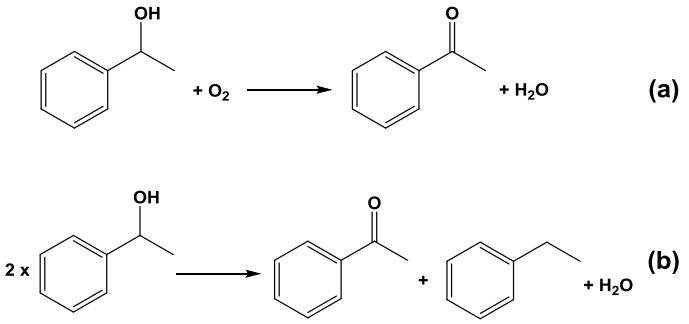
Catalyst	**Conversion (%)**	**Selectivity (%)**	
		Acetophenone	Ethylbenzene
Rh-PI	48	77	23
Rh-PI/CB	55	66	34
Rh-PI/Al_2O_3	22	86	14
Rh/Al_2O_3	36	87	13

These results are quite surprising, as under these reaction conditions water not only increased the activity of Rh-PI/Al_2O_3 or Rh/Al_2O_3 catalysts, but also switched on the activity of Rh-PI and Rh-PI/CB catalysts, turning them to materials even more active than those containing alumina, with conversions in the range of 50%. (see ESI, Figs S12-S15†). It is well known that a change in reaction medium can change the activity of a catalyst,[42] however to the best of our knowledge this is one of the most dramatic media-dependent reactivity effect observed in the area of nanoparticles. Even more importantly it is obtained by the 'simple' addition of water into the catalytic system, and under very mild reaction conditions. Moreover, this also shows that in spite of the catalysts' surface composition (vide infra, section 2.6.2), the metal surface is clearly accessible to the substrate for Rh-PI and Rh-PI/CB when water is present.

This experimental evidence prompted us to study the origin of the effect of water as a catalytic switch in the most systematic manner and extending our study to other alcohols (see section 2.7). At first we experimentally ruled out the effect of leaching, as well as assessed the role of the disproportionation pathway in this process in the first instance (vide infra). Due to the large amount of Rh^{3+} present in our catalysts, (section 2.6.2) and the known possibility of supported metal systems to be subjected to leaching effects,[43] the reaction mixtures were characterized via ICP-MS. A negligible metal leaching for all the catalysts was detected with values of < 0.1% for Rh-PI, Rh-PI/Al_2O_3 and Rh/Al_2O_3, and a metal leaching of 1.3% for Rh-PI/CB (relative amount with respect to

the total metal loading). We do not consider this amount for Rh-PI/CB to be significant with respect to the other catalysts,[44] and clearly the results of the catalytic tests in Table 2 do not correlate with the negligible amount of Rh in solution. Nevertheless, in order to rule out any possible effect induced by solubilized species even in very small amount like in our case, a control test using a soluble $RhCl_3 \cdot xH_2O$ salt was carried out. This test was also performed in toluene/water media, and used an amount of Rh equal to the total amount of Rh present in the catalyst. The test did not show any catalytic activity towards alcohol oxidation. We can conclude that the catalytic activity originates from the metal nanoparticles.

Furthermore, the addition of water not only switched on an oxidation route of alcohol to ketone for all catalysts (scheme 2(a)), but it also led to the unexpected formation of ethylbenzene, which is a reduction product of 1-phenylethanol instead. This can be explained by disproportionation of two molecules of alcohol to give acetophenone and ethylbenzene (scheme 2(b)). Disproportionation of aryl alcohols, has been reported for palladium or gold catalysts[45] under solvent free conditions and pressure of O_2 or Ar and thus possibly suggesting the existence of both an aerobic and anaerobic disproportionation pathway for this complex reaction.[46] Though, to the best of our knowledge this parallel reaction pathway has not been reported for rhodium catalysts under mild oxidizing conditions with air.



Scheme 2 (a) direct oxidation of 1-phenylethanol to acetophenone and (b) disproportionation of two reagent molecules to acetophenone and ethylbenzene.

In view of the existence of this secondary pathway, the total amount of acetophenone would then be the consequence of two contributions: the direct oxidation route and the disproportionation route. It is possible to calculate the contribution to the formation of the ketone by these two reactions by splitting the contribution of these two routes in terms of yields (full details in ESI† and Table S1†). We observe that the amount of acetophenone obtained from the direct oxidation route is always dominant for all four catalysts and in excess of 70% with respect to the disproportionation route (Table S1), except for Rh-PI/CB where acetophenone has a nearly equal contribution from direct oxidation and disproportionation is present (ca. 50% each). Conversely (Table 2 and table S1) the two catalysts containing alumina promote the disproportionation route to a much lesser extent (2 to

3 times less, ca. 15%) than Rh-PI and Rh-PI/CB. Hydrated γ-Al_2O_3 presents a surface basicity with pK_a values in the range of 8,[45] and studies on the surface basicity of Au-Pd/TiO_2 catalysts for the disproportionation reaction of benzyl alcohol[46] also reported an inhibition of the disproportionation pathway by increased basicity of the catalyst or the reaction media. It is possible that this same parameter can affect the product distribution also in the case of Rh and Al_2O_3.

This set of catalytic data proves that water is capable to trigger a set of reactions different in nature (oxidation and disproportionation), and it also provides some ground for water to be a proton carrier for the direct oxidation route of 1-phenylethanol to acetophenone. Yet for this reaction, and to some extent also for the disproportionation reaction, we would like to emphasize that the effect of water is not as obvious as it may sound. In fact, both the polymer and the activated carbon have hydrophobic surfaces,[47] thus the presence of water was not expected to lead to a such large increase in conversion. Moreover, water is also a by-product of the oxidation reaction (see Schemes 1 and 2) and this should also discourage this high increase in conversion. These apparently counter-intuitive factors prompted us to consider the existence of a partition effect for the alcohol between the organic and the aqueous phase and how this could affect our results.

2.3 Toluene and water equilibria, partition constants

As water and toluene are not miscible, and 1-phenylethanol and acetophenone have a limited solubility in water at room temperature, 19 and 5.5 $g \cdot dm^{-3}$ respectively,[48,49] the reaction mixture is effectively a microemulsion under our reaction conditions with droplets of toluene dispersed in water.

However, the catalytic conversion is calculated by analysing the organic phase only (see experimental section and ESI†), from the amounts of 1-phenylethanol and acetophenone in toluene (ethylbenzene can be neglected in this data treatment as virtually insoluble in water). Yet despite the low solubility of 1-phenylethanol and acetophenone in water, this could potentially alter the observed conversion values in the water/toluene mixture because of a partition of the alcohol between water and toluene. That is the alcohol could solubilize in water and lead to higher conversion values than those we actually observe because of this latent partition effect.

As a consequence, and because of the lack of literature data for partition constants $K_{org,aq}$ for 1-phenylethanol and acetophenone in water/toluene mixtures, this potential artefact has been considered by experimentally determining the partition constants $K_{org,aq}$ for our reagent and product for our biphasic water/toluene system (see experimental section, ESI† and Table S2†).

For 1-phenylethanol a $K_{org,aq}$ = 43 was determined, whereas for acetophenone a $K_{org,aq}$ = 475 was obtained. With our concentrations and experimental conditions (see experimental section and SI),

the effect of the partition of acetophenone between toluene and water does not influence in any way our determinations for the catalytic conversion. For the 1-phenylethanol for example, this induces a correction factor with actual conversion values that are 1 to 2% lower (in relative terms) than if the toluene/water partition is not considered (see ESI, Table S3†). However, since the experimental error associated to our measurements is of the same order of magnitude, the two sets of data (Tables 3 and S2) can be considered experimentally identical. As such the partition does not affect our conclusions. In contrast, it validates the switch on effect of water to the Rh catalysts, and it also provides insights into the possible reaction mechanism for this reaction when water is present as a biphasic system (see next section).

Additional control tests were carried out for the aqueous phase in order to ensure that we did not neglect any reaction product and to further confirm our high carbon mass balances. This was characterised via an extraction with chloroform, (and subsequently analysed via ^{1}H-NMR in $CDCl_3$), as well as by a direct analysis via H-NMR using D_2O as a solvent (see ESI, Figs S16 and S17†), using Rh/Al_2O_3 and Rh-PI catalysts). The products in aqueous phase were the same than those in the organic phase (and present in trace amounts), thus confirming our results both qualitatively and quantitatively.

Furthermore, re-usability tests after one usage were carried out for Rh/Al_2O_3 and Rh-PI in the presence and absence of water. Both catalysts showed good re-usability with conversion and selectivity values after catalyst recovery that were within the experimental error of the activity for the fresh catalysts (Tables 1 and 2). For example the conversion of Rh/Al_2O_3 in toluene and those for Rh/Al_2O_3 and Rh-PI in water/toluene after recovery were 9%, 32% and 36% respectively (see ESI, Figs S18 and S19†).

2.3.1 Effect of water to the catalytic activity: phase transfer catalysis

As the solubility of 1-phenylethanol and acetophenone in water increases at higher temperature under reaction conditions, this could lead to multiple partition equilibria between the solvents and the catalyst surface (Fig. 2).

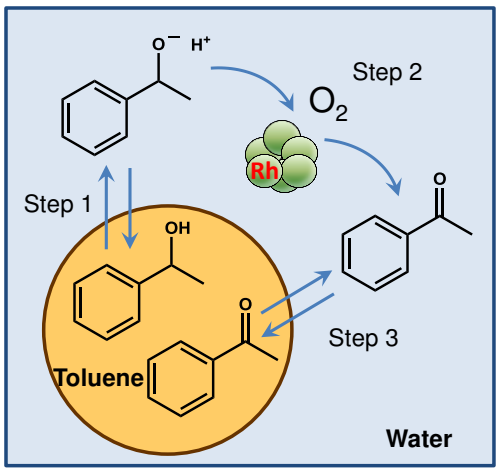


Fig. 2 Postulated phase transfer catalysis for the 'switch on' effect of water for the catalytic activity of Rh nanoparticles for the oxidation of 1-phenylethanol to acetophenone. At the start of the reaction 1-phenylethanol is in the toluene droplet. As the temperature increases the alcohol transfers to water (step 1). Then the oxidation reaction take place over Rh surface in water and acetophenone is formed (step 2). As acetophenone is largely immiscible in water, it is extracted by toluene (step 3) ensuring a high turnover frequency for the catalyst.

At the start of the reaction 1-phenylethanol is in toluene, but as the temperature increases the substrate is transferred into the aqueous phase (step 1). Water would act as a proton carrier and as such promotes the formation of an alkoxide from 1-phenylethanol when this solubilizes in water. This would be equivalent to the effect of a base to promote the oxidation of the alcohol, an effect which is well known to occur over metal nanoparticles catalysts, especially for systems comprising Au, Pd and Pt.[50] The reaction would then occur over the Rh surface with acetophenone formation (step 2). Subsequently, as acetophenone is even less soluble than the alcohol in water and with a larger $K_{org,aq}$ (vide supra), toluene would extract acetophenone from the aqueous phase thus ensuring a high turnover frequency of the catalyst (step 3). This would effectively make the water/toluene system a phase transfer catalysis, and formally a case of inverse phase transfer catalysis as the reagent is initially in the organic phase. A promoting and yet unexplained effect of water in a biphasic system similar to the one we used, has been observed for the benzyl alcohol oxidation over Au/TiO_2 catalysts[51] and for aliphatic alcohol oxidation over Pt/C catalysts[52] but by using 10 bar of oxygen to carry out the oxidation reaction. Moreover, unlike in our case, all of these catalysts were active towards alcohol oxidation even if water was not present, or by using water/dioxane mixtures, which are reciprocally miscible and as such modifying the polarity of the reaction medium.

A similar partition scheme would also apply for the formation of ethylbenzene by disproportionation for steps 1 and 3. For this route step 2 would involve two alcohol molecules and the cleavage of a C-O bond, besides an O-H cleavage, to form ethylbenzene, 1-phenylethanol and water[53] (see ESI, Scheme S2†). A previous study on Pt/C catalysts[54] postulated that the formation of

organic droplets in water, could lead to micelles with the hydrophobic tail of the alcohol in toluene and the hydrophilic O-H head in water. This would promote the orientation of two molecules of alcohol needed for disproportionation, (see ESI, Fig. S20†) and possibly accelerate the reaction compared to the case in the absence of water. This effect could be operating in our case, but as shown above (Table 2 and table S1) with a strong support dependency, as in our case the presence of activated carbon support seems to promote this secondary reaction route.

In view of these results, activity tests per different water : toluene volume ratio were carried out (Table 3) by selecting Rh-PI and Rh/Al_2O_3 to represent the pair Rh-PI, Rh-PI/CB and Rh-PI/Al_2O_3, Rh/Al_2O_3 respectively, by virtue of their similarities (Table 1 and Table 2).

Table 3 Catalytic tests for the oxidation of 1-phenylethanol to acetophenone in water/toluene for different volume ratios of water. Volume V of H_2O reported in mL towards a fixed volume of toluene of 1 mL for the reactivity of polymer incarcerated Rh nanoparticles (Rh-PI) and Rh supported on alumina (Rh/Al_2O_3) catalysts. Reaction conditions: T = 100 ^oC, P = atmospheric pressure, M:S = 100, t = 4 h.

Catalyst	**Volume (mL)**	**Conversion (%)**	**Selectivity (%)**	
			Acetophenone	Ethylbenzene
Rh-PI	0	1	100	0
Rh-PI	0.5	1	100	12
Rh-PI	2	48	77	23
Rh-PI	4	46	65	35
Rh/Al_2O_3	0	9	100	0
Rh/Al_2O_3	0.5	30	88	12
Rh/Al_2O_3	2	36	87	13
Rh/Al_2O_3	4	7	60	40

By varying the amount of water, this affects both the activity (conversion) and selectivity of the catalysts. For both catalysts the larger the amount of water, the more the extent of the secondary pathway to disproportionation, and thus supporting the formation of a microemulsion in our system. This could also suggest that this role of water (microemulsion formation) might be dominant with respect to the one of water as a proton carrier. For the effect of water to the conversion, the two catalysts behave differently. For Rh-PI the larger the amount of water, the higher the conversion. For Rh/Al_2O_3 instead, a maximum is reached and then the activity decreases. We observed this trend for Rh/Al_2O_3, to be present for every substrate we tested (1-phenylethnaol, benzyl alcohol, 1-octanol and 3-octanol, see section 2.7).

To further confirm the results and trends in Table 3, additional control tests for the oxidation of 1-phenyl ethanol using Rh/Al_2O_3 and Rh-PI catalysts were carried out, but without the presence of a biphasic system, or by using D_2O. These tests made use of: (i) water only and alcohol, (ii) alcohol only with no solvent, and (iii) a D_2O/Toluene biphasic system and alcohol. In all cases the

conversions were lower than in the presence of a H_2O/toluene. In particular, conversions in presence of H_2O/alcohol or alcohol only showed conversion values in the range of 2% (see ESI, Fig S21 and S22†), thus reinforcing the need of a biphasic system to ensure high turnover, i.e. extraction of the product from the aqueous to the organic phase, and a further proof of our methodology in activating Rh nanoparticles.

The use of a D_2O/toluene (2:1 volume ratio) mixture instead, led to a conversion of ca. 5% to 7% for Rh/Al_2O_3 and Rh-PI respectively (see ESI, figure S23†). These values are lower than in H_2O/water (Table 3). Furthermore, the selectively was also significantly different than in H_2O/toluene, with a higher amount of disproportionation product (> 25%, with the remaining 75% being acetophenone). We interpreted this result as a further evidence of the existence of partition equilibria and micelles formation. In fact, at our reaction temperature the alcohol can easily exchange a proton with deuterium from D_2O to form Ph-CH(OD)-CH_3. This induces a kinetic isotope effect as a consequence of the cleavage of a O-D bond rather than a O-H bond during the oxidation process (Scheme 1) and in turn affects both conversion and selectivity.

2.4 Effect of water to the catalytic activity: water as proton carrier

In order to assess the effect and possible role of water as a proton carrier (or as a base), catalytic tests in the presence of toluene, water and NaOH were carried out (Table 4, see ESI Figs S24-S27†). NaOH was chosen as it is soluble in water but not in the organic phase. Under these reaction conditions, it is possible to observe that the selectivity to the ketone does always increase (Table 4). However, the data needs to be carefully analysed in order to extract the contribution to ketone formation from autoxidation and disproportionation. In fact, the presence of NaOH systematically decreases the selectivity to ethylbenzene, and in turn the ketone formed by disproportionation route. This would confirm that acid/base properties of the catalyst, or of the solution in this case, can indeed play a role for this secondary reaction.[45]

Table 4 Catalytic tests for the oxidation of 1-phenylethanol to acetophenone in water/toluene in the presence of NaOH, by polymer incarcerated Rh nanoparticles and Rh supported on alumina. Reaction conditions: T = 100 ^{o}C, P = atmospheric pressure, M:S = 100, t = 4 h. Water: toluene volume ratio 2:1. NaOH present with a molar ratio of 1:10 with respect to the alcohol (i.e. 1:1000 with respect to the metal centre).

Catalyst	**Conversion (%)**	**Selectivity (%)**	
		Acetophenone	Ethylbenzene
Rh-PI	43	100	0
Rh-PI/CB	27	96	4
Rh-PI/Al_2O_3	7	100	0
Rh/Al_2O_3	32	89	11

On the other hand, there are also some effects on the conversion for the catalysts, not entirely expected. For example Rh-PI is the catalyst most affected by a base leading to an enhanced conversion and selectivity towards acetophenone, thus showing a true enhanced activity as expected by a base promoted activity model. The reagent would migrate in aqueous phase, be deprotonated and give the ketone, besides suppressing disproportionation. Rh/Al_2O_3 instead seems to be affected only very little by the presence of base. For Rh-PI/CB and Rh-PI/Al_2O_3 instead, not only disproportionation is nearly suppressed, which still proves the presence of phase transfer catalysis, but the conversion decreases substantially too.

Also in this case, in order to evaluate the possibility of leaching and to exclude that homogeneous catalysis takes place, ICP-MS was carried out for these reaction mixtures. Small metal leaching of 1.0, 1.4 and 0.9% were detected for Rh-PI, Rh-PI/Al_2O_3 and Rh/Al_2O_3 respectively, and 4.2% for Rh-PI/CB. Like in the case of the absence of base we consider these values as negligible,[55] and we can conclude that the conversion values observed in the presence of a base (Table 4) are not due to the loss of active metal component.

In order to determine if the decrease in conversion is real or not, i.e. an effect observed just because no disproportionation is present, the actual yield of ketone was calculated for all catalysts (full details in ESI† and Table S4†). By treating the data in this way, it was possible to conclude that for Rh-PI there is a real enhancement in catalytic activity. In fact, the disproportionation route is suppressed, but the direct oxidation route is enhanced, with the yield of ketone from direct oxidation increasing from 26% to 43% (Tables S3 and S4). For Rh-PI/CB the loss in conversion is mostly ascribed to the suppression of the disproportionation pathway.

For Rh/Al_2O_3 no or negligible change in oxidation or disproportionation pathways was detected by comparing the data in Tables 4 and S4. However, for Rh-PI/Al_2O_3 not only the disproportionation is suppressed, but the direct oxidation route is inhibited too (yield of ketone from direct oxidation decreases from 16% to 7% in the presence and absence of base respectively). As such, this catalyst seems to contradict the hypothesis that the activity of alcohol oxidation increases with the amount of base.[56] On the other hand, a study on 1,2-propanediol oxidation by Au/Pt nanoparticles in aqueous media also showed that an increase in base amount did not necessarily lead to an increase in conversion, and if NaOH was used in excess a decrease in conversion was also observed,[57] implying that the cation could play a poisoning role by exploring different inorganic bases. Yet, this shows the richness and the complexity of these catalytic systems, and that many of the effects that we observe for these materials could be much more general and of much wider implications.

2.5 Kinetic studies of 1-phenylethanol oxidation in presence and absence of water

In view of these data, the catalysts Rh/Al_2O_3 and Rh-PI were selected to represent the pair containing alumina and the pair non-containing alumina and their temporal profiles investigated in terms of conversion (Fig. 3) and selectivity (Fig. S28) both for a reaction mixture containing only toluene and for a reaction mixture containing water: toluene with a volume ratio of 2:1. This was to allow a comparison also in terms of initial rates, as well as to rule out deactivation of initially highly active catalysts, or deactivation of initially active catalysts. The catalysts were investigated for reaction times from 0 to 24 h (Fig. 3).

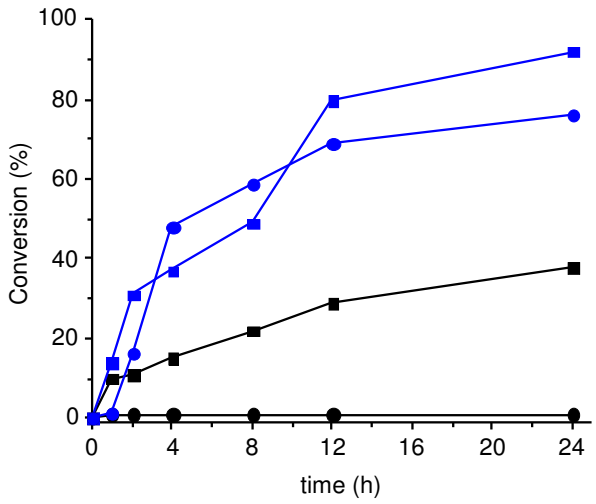


Fig. 3 Temporal profile for the conversion of 1-phenylethanol to acetophenone by (•) Rh-PI and (■) Rh/Al_2O_3 in toluene, and by (•) Rh-PI and (■) Rh/Al_2O_3 in a water: toluene mixture with a 2:1 volume. Reaction conditions: T = 100 ^oC, P = atmospheric pressure, reaction time from 0 to 24 h.

If toluene only is used as a solvent, Rh-PI is not active even for a long reaction time, whereas Rh/Al_2O_3 can reach an activity of about 30% after 24 h. When water is added to the system a switch on effect is observed for both catalysts. They are capable to retain activity and they are both able to reach alcohol conversion in the range of 80% within 24 h. If the final activity (conversion) is considered as a term of comparison water can accelerate the activity of Rh/Al_2O_3 by ca. 2.5 times, and that of Rh-PI by about 100 times.

Regarding the selectivity, the behaviour of these two catalysts is nearly identical (see ESI Fig. S28), with a selectivity to the ketone of nearly 100% at the initial stage of the reaction and then a steady value of about 80% to the ketone for Rh/Al_2O_3 and ca. 70% for Rh-PI. The catalysts appear to be stable under our reaction conditions and therefore a viable alternative to other precious metals for this kind of oxidation reaction.

2.6 Characterization of the catalysts

In order to identify possible structure-activity correlations, and to identify a trend for the various catalysts we tested, as well as means to enhance the catalytic activity, the catalysts were systematically evaluated by using XRPD, XPS and TEM, in order to gather information about the presence of rhodium oxide species, different exposed fraction or particle size.

2.6.1 XRPD and bulk structure of the catalysts

XRPD patterns were collected for all of the four catalysts (Fig. 4) to gather information on the catalyst bulk structure. These patterns did not show any unusual feature that could explain such differences in catalytic activity, but the obvious presence of Al_2O_3 for two of them. Rh/Al_2O_3 and Rh/Al_2O_3 present only peaks for γ-alumina,[58] whereas Rh-PI and Rh-PI/CB show a typical featureless background as expected for polymer or carbon based matrices.

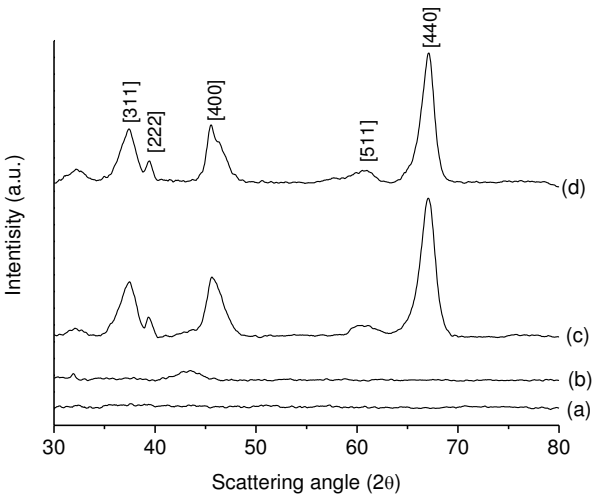


Fig. 4 XRD patterns of: (a) Rh-PI, (b) Rh-PI/CB, (c) Rh-PI/Al_2O_3 and (d) Rh/Al_2O_3. No Rh or Rh_2O_3 are detected in these XRD patterns. Facets typical for γ-Al_2O_3 were detected for samples (c) and (d) and the corresponding Miller indices are reported in pattern (d).

Diffraction peaks for the Rh facets [111], [002] and [022] are expected at 41.07^o, 47.79^o and 69.89^o 2θ respectively,[59] however no reflections for Rh metal were detected. This suggests either: (i) a particle size of below 4-5 nm, (ii) a thin layered metal structure or (iii) highly dispersed metal species even at 5% loading.[60] Rh_2O_3 is not detected in these samples, although its presence for the Al_2O_3 catalysts could be possible.[61] Diffraction peaks for Rh_2O_3 facets [112], [220] and [312] are expected at 34.49^o, 48.80^o and 62.07^o 2θ respectively.[62] However, as these reflections are not detected either, the same considerations as done for Rh metal can be applied.

2.6.2 XPS of the catalysts, surface composition and Rh oxidation state

The catalysts were characterized by using X-ray photoelectron spectroscopy to highlight differences in catalyst surface composition or oxidation state of Rh that could explain the trend reported in Table 1 including the presence or absence of alumina. However, we underline that while this is reasonably straight forward for the alumina containing catalysts because of their high Rh exposed fraction (> 2 at%, see ESI Table S5†), this same determination for Rh-PI Rh-PI/CB is extremely challenging due to the weakness of the resulting Rh signal and the embedding of Rh into the carbon polymer matrix. Bearing this in mind, Rh-PI/Al_2O_3 and Rh/Al_2O_3 presented an amount of surface of Rh^{3+} of 46% and 65% respectively, consistent with Rh_2O_3[63] (binding energies centred at Rh $3d_{5/2}$ = 308.6 eV and Rh $3d_{3/2}$ = 313.3 eV, (Fig. 5). This does not contradict XRD data, as XPS is a surface technique, and further suggests the presence of a metal oxide interface that could bind rhodium in oxidized form, with Rh/Al_2O_3 having an amount of Rh^{3+} greater than Rh-PI/Al_2O_3.

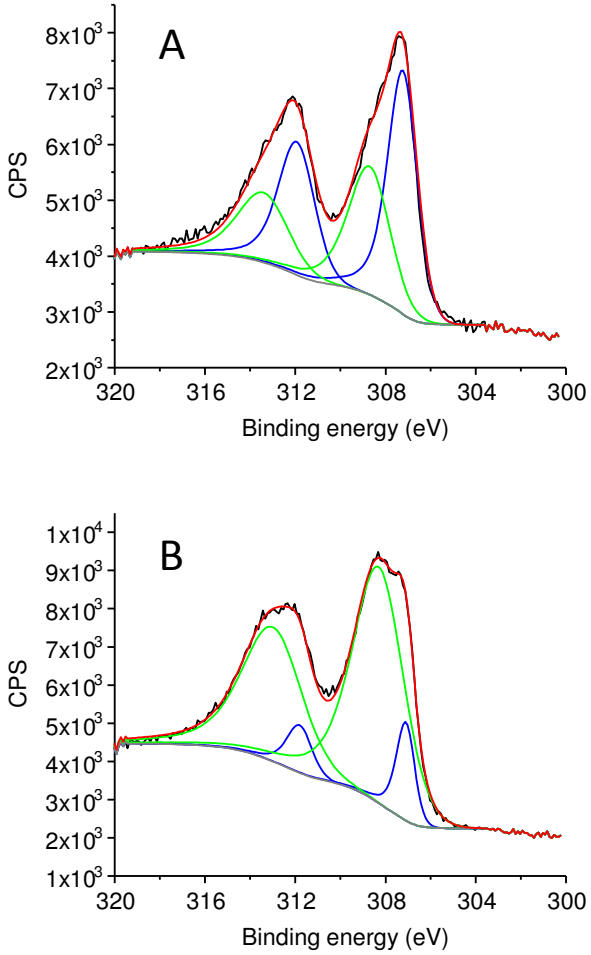


Fig. 5 XPS spectra for (A) Rh-PI/Al_2O_3 and (B) Rh/Al_2O_3. The samples comprises both Rh^0 (centred at Rh $3d_{5/2}$ = 307.2 eV and Rh $3d_{3/2}$ = 311.9 eV) and Rh^{3+} (centred at Rh $3d_{5/2}$ = 308.6 eV and Rh $3d_{3/2}$ = 313.3 eV). The percentage of Rh^{3+} for these catalysts was 46% and 65% for Rh-PI/Al_2O_3 and Rh/Al_2O_3 respectively. Colour code: (black lines) experimental data and baseline, (red line) simulated spectra, (blue line) Rh^0 components and (green line) Rh^{3+} components.

However, this relatively large variation in Rh^{3+} content between these two catalysts does not appear to play a driving role for our reaction if toluene is used as a solvent (Table 1). It may affect the conversion when water is present though as Rh/Al_2O_3 is more active than Rh-PI/Al_2O_3 (Table 2).

2.6.3 Transmission electron microscopy and Rh particle size

Besides the nature of the support and oxidation state, a known parameter affecting the catalytic activity of metal nanoparticle is the particle size,[64] and the few studies carried out for rhodium so far, show a very strong dependence on the activity from this parameter. For example if rhodium is used for CO insertion on ethane[65] or CO oxidation[66] the catalytic activity is centred on a narrow range of particle size distribution between 2 and 3 nm only. Therefore, we determined this parameter for our catalysts. Representative TEM images for each catalyst, together with their particle size distribution are shown in Figs 6A-D.

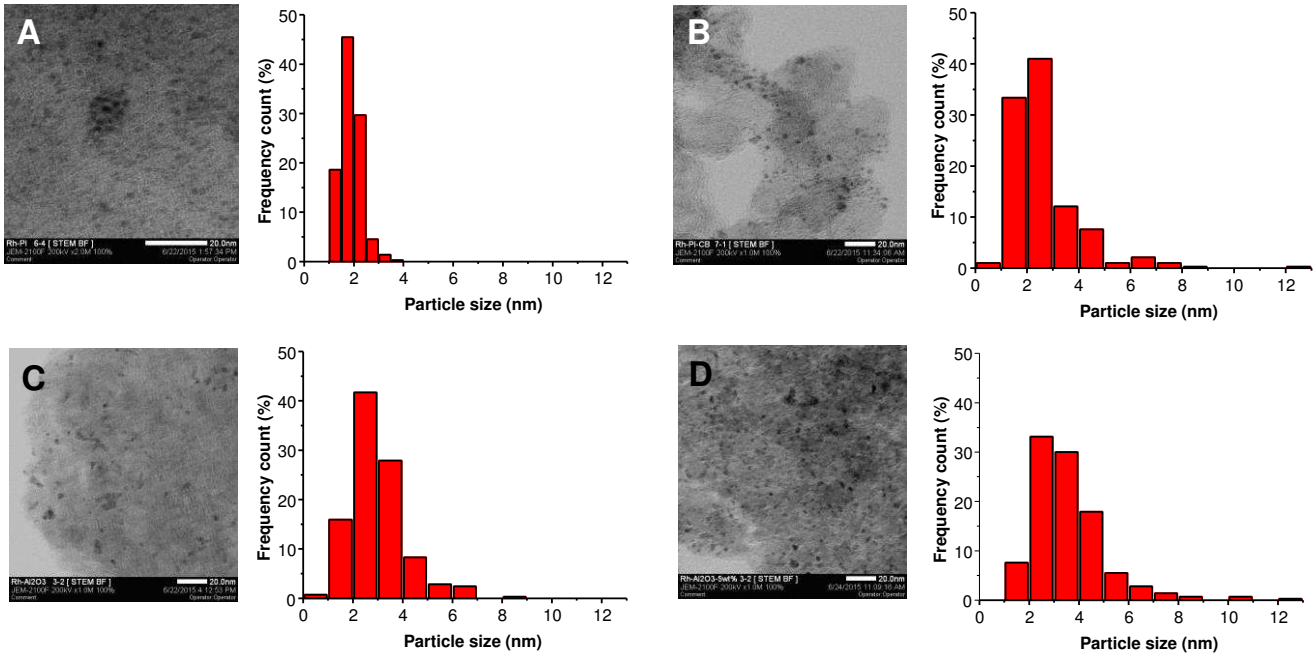


Fig. 6 Transmission electron microscopy and particle size distribution of Rh nanoparticles for: (A) Rh-PI catalyst, average particles size $\bar{d}$ = 1.9 ± 0.4 nm; (B) Rh-PI/CB, $\bar{d}$ = 2.6 ± 1.3 nm; (C) Rh-PI/Al_2O_3, $\bar{d}$ = 3.0 ± 1.1 nm and (D) Rh/Al_2O_3, $\bar{d}$ = 3.6 ± 1.5 nm. The frequency count for the particle size was obtained from a set of 300 particles for each catalyst.

From these data it is evident that the particle size distribution, for Rh-PI is markedly and statistically different from all the other catalysts, as assessed by applying an analysis of variance ANOVA test[67] (see ESI, Tables S6 and S7†). This is also the catalyst that shows the higher selectivity to acetophenone and the one for which the conversion is increased by the addition of a base. Rh-PI has an average particles size $\bar{d}$ of 1.9 nm but with a very low polydispersivity, and a standard deviation of just 0.4 nm, compared to standard deviation values in the range of 1.3 nm for

the support containing materials. For Rh-PI/CB and Rh-PI/Al_2O_3 there are interesting similarities. As long as a support is introduced together with the polymer, an increase in both particle size and dispersion is observed, with values of $\bar{d}$ equal to 2.6 ± 1.3 and 3.0 ± 1.1 nm respectively. The commercial Rh/Al_2O_3 sample presents the larger particle size and dispersion, in relative terms, with $\bar{d}$ = 3.6 ± 1.5 nm, and it appears to be the material least affected by the addition of a base in water.

It is beyond the scope of this work to carry out a systematic preparation and investigation of Rh nanoparticles of different size. However, future studies could include the preparation of large Rh clusters to identify whether the same particle size dependence observed for CO oxidation[66] could also be applicable to alcohol oxidation both in terms of conversion and selectivity though the direct oxidation route, as the particles around 3 nm appear to be among the most active for this reaction pathway in the presence of water, and this could be the structural element that discriminates these materials.

2.7 Catalytic tests for benzyl alcohol, 1-octanol and 3-octanol oxidation

In order to assess if the catalytic behaviour that we observe for our materials is more general and not restricted to 1-phenylethanol, we extended our catalytic tests in presence and absence of water to the substrates: benzyl alcohol, 1-octanol and 3-octanol with expected oxidation products being benzaldehyde, octanal and 3-octanone respectively. The selection of these alcohols as substrates is due to both their relevance towards their oxidation products, such as food and drug sectors[68,69] as well as to highlight differences and similarities in aryl and aliphatic alcohols either primary or not. These substrates were compared at 'standard' reaction conditions like those in Table 3, and assessing the effect of water using different water to toluene ratios. 1-phenylethanol is also reported for comparison Fig. 7A-D (and ESI Fig. S29† for the selectivities), and these substrates showed a nearly complete selectivity to the expected ketone or aldehyde (see ESI, Figs S30-S35†).

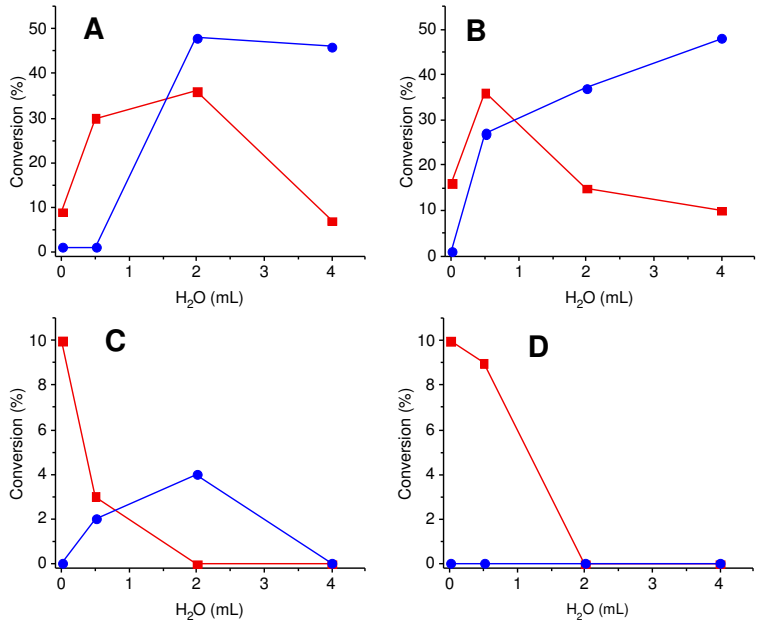


Fig. 7 Conversion by varying the amount of water for the oxidation of: (A) 1-phenylethanol, (B) benzyl alcohol,* (C) 1-octanol and (D) 3-octanol, by using (•) Rh-PI and (■) Rh/Al_2O_3 catalysts. Reaction conditions: T = 100 ^oC, P = atmospheric pressure, M:S = 100, t = 4 h. (*) for this substrate a possible disproportionation products would be toluene, which is also the solvent of this reaction, as such selectivity's values are referred to benzaldehyde and benzoic acid only (see ESI†).

If benzyl alcohol is used as substrate the catalysts are capable to replicate an activity similar to that of 1-phenylethanol, thus showing that our implications are more general and not restricted to a particular substrate only. That is, water can switch on the activity of Rh-PI entirely from a non-active catalyst to a very active material when water is present. Rh/Al_2O_3 is also activated by the presence of water but for a different (smaller) water to toluene ratio if compared to 1-phenylethanol (less than 1:1 rather than 2:1).

The results by using aliphatic alcohols are rather surprising. Aliphatic alcohols are known to be more difficult to oxidize than aryl species,[70] and in fact conversion values in the presence of pure toluene are a bit lower than in presence of aryl species a substrates. However, if water is introduced in large excess, it does not promote the catalytic activity and the conversion actually follows an opposite trend with respect to aryl alcohols. This would suggest that of the two proposed effects of water: (i) being a partition medium and (ii) being a proton carrier, it is the partition effect that dominates. In fact, if this was due to water as a base it should affect all of the substrates in the same manner and by increasing their activity. Furthermore, long chain aliphatic alcohols are less soluble than short aryl alcohols in water and this could further corroborate our model of activity as a result of a phase transfer catalysis.

Also in this case control tests by the extraction of the aqueous phase were carried out (see ESI, Figs S36 and S37†) also confirming our results both qualitatively and quantitatively. In addition, control

tests for the oxidation of these alcohols using Rh/Al_2O_3 and Rh-PI in the presence of: H_2O, no solvent, and D_2O/toluene, were also carried out in analogy to what was done for 1-phenylethanol (see section 2.3). As for 1-phenylethanol, the catalysts' activity using water only as a solvent was lower than in the biphasic system as well as for the tests in presence of alcohols without any solvent (ca. 2% or less), thus showing the need of an organic phase to extract the products. Interestingly though, this activity in water roughly correlates with the solubility of the alcohols, with benzyl alcohol being the most active (in relative terms, up to ca. 7% conversion if Rh-PI was used) and the 3-octanol being the least active (< 1% conversion). (see ESI, Figs S38 and S39†)
Analogies to the reactivity trend of 1-phenylethanol in presence of D_2O/toluene were also observed for these alcohols, i.e. an activity that is lower than in H_2O/toluene due to the presence of a strong kinetic isotope effect that we ascribed to the deuteration of the OH group of the alcohol by proton/deuterium exchange with D_2O. In the case of benzyl alcohol though the activity in D_2O/toluene (conversion ca. 21%), although lower than in H_2O/toluene, was still significantly higher than in the presence of toluene only (see ESI, Figs S40 and S41†). We think this result correlates to the (relatively) higher solubility of benzyl alcohol in water compared to all the other substrates that we tested and yet further supporting our results.

An additional factor, to explain our results and the difference between aryl and aliphatic alcohols, in a perspective of micelle formation, could also be that aryl alcohols usually present a lower critical micelle concentration than aliphatic species[71] and this could help to explain their higher reactivity under our conditions and the presence of relatively larger amounts of disproportionation product in our biphasic system. For the specific case of Rh/Al_2O_3 though, a large excess of water could promote the formation of β-$Al(OH)_3$.[72] Although this process is known to occur over a scale of weeks or even months, the formation of this species could inhibit the reaction. Alternatively, as these alcohols are not miscible with water, if a large amount of water is present, hampering diffusion effects could be operating (as suggested by tests using water only, vide supra). In any case, these experimental observations, on the effect of water either on the catalyst or the reaction mixture, could have much wider implications. For instance, besides the oxidation of an alcohol to a ketone, also the oxidation of a hydrocarbon to an alcohol is a process that necessarily generates water and which could fall in one of the categories above, with water either promoting or discouraging the further oxidation of the alcohol within the reaction media, if water is not removed from the reaction system. The latter is a frequent case in many batch to batch studies, and thus it would allow to tune or to affect, either in a positive or in a negative way the activity of a given catalyst.

3. Conclusions

Rh polymer incarcerated nanoparticles were proven to be an efficient catalytic system for the oxidation of aryl alcohols like 1-phenylethanol and benzyl alcohol. Remarkably, the activity was found to be dependent on the reaction media to its extreme, from inactive catalysts in toluene, to active catalysts if water was introduced as a co-solvent. At the same time water was proven to enhance the activity of Rh if this metal was supported on alumina. Our data ascribe the effect of water to the presence of a phase transfer catalysis where water extracts the alcohol from toluene to react in aqueous media at high temperature, and then toluene extracts the ketone from water to complete the catalytic cycle, and ensures high turnover frequency for the catalyst. Interestingly, water also enhanced a disproportionation pathway of 1-phenylethanol to acetophenone and ethylbenzene, with a strong dependency from the support used, the highest for carbon the lowest for alumina. However, this parallel pathway could be inhibited by the addition of a base and turns a material like Rh-PI to a highly active and selective catalyst at the same time. A similar reactivity trend was observed if benzyl alcohol was used as a substrate, however an actual maximum for the activity was identified for a smaller water to toluene ratio compared to those detected in case of 1-phenylethanol. If aliphatic alcohols like 1-octanol or 3-octanol were used as a substrate, Rh/Al_2O_3 was still capable to oxidize them, and with reasonably good yields considering their aliphatic nature and reaction conditions. However, for these substrates, water was having a detrimental effect towards the catalysts' activity. This opposite effect of water for these substrates could be due to the lower solubility of these alcohols in aqueous media, and in turn hampering the partition effect of the substrate in the biphasic system.

In view of all these factors, we consider this study to have vast general implications beyond those observed for the specific alcohols and metal that we tested, as it can shed light for a deeper understanding of this important class of oxidation reactions. Moreover as water is ever-present in any partial oxidation reaction, kinetics data could be affected by its presence if this product is not removed by the reaction mixture during the course of the reactions. Finally our study also showed that it was possible to turn Rh nanoparticles, currently mostly used for reduction reactions, into active species for oxidation reactions instead, and in this case it could be competitive with nanoparticles comprising Au, Pd and Pt when aryl alcohols were used as substrate.

4. Experimental

4.1 Rh-PI Nanoparticles catalysts preparation

Styrene based copolymer[31] (full details in ESI†) (800.0 mg) and $NaBH_4$ (10.1 mg) were dissolved in diglyme (13 mL) at room temperature. To this solution was slowly added rhodium(II) acetate dimer (31.1 mg) with 5 mL of THF.

The mixture was stirred for 3 h at room temperature, and diethylether (30 mL) was slowly added to the mixture at room temperature. Polymer coacervates enveloped the metal dispersed in the medium. The catalyst capsules were then washed with diethylether several times and dried at room temperature. Next, the catalyst capsules were heated at 150 °C for 5 h without solvent to prepare the wine red solid. The solid thus prepared was washed with dichloromethane and water, crushed, and dried to result in a black powder. This powder was heated at 150 °C for 5 h without solvent to afford Rh-PI.

4.1.1 Rh-PI/CB and Rh-PI/Al_2O_3 catalyst preparation

The catalyst was prepared as in [31,73] and references therein. Copolymer (full details in ESI†) (100.0 mg), activated carbon ketjen black EC300J (100.0 mg) and $NaBH_4$ (10.6 mg, 0.28 mmol) were combined in diglyme (8 mL) at room temperature, to this solution was slowly added rhodium(II) acetate dimer (8.8 mg, 0.02 mmol) with 5 mL of THF. The mixture was stirred overnight at room temperature and diethyl ether (50 mL) was slowly added to the mixture at room temperature. After the catalysts, which were black powders, were filtered and crashed, they were washed with diethyl ether several times and dried at room temperature. Next, the catalysts were heated at 150 °C for 5 h without solvent and were stirred in 1:1 ratio of THF/water co-solvent overnight. The catalysts were filtered, washed with dichloromethane and THF and dried to afford black powder. This powder was heated at 170 °C for 5 h without solvent to afford Rh-PI/CB. Rh-PI/CB (10-20 mg) was heated in mixture of sulfuric acid and nitric acid at 200 °C, the mixture was cooled to room temperature and aqua regia was added. The amount of Rh in the resulting solution was measured by ICP analysis to determine the loading of Rh.

The same procedure was applied for the preparation of Rh-PI/Al_2O_3 but substituting the carbon black with Al_2O_3.

4.1.2 Commercial Rh/Al_2O_3

The catalyst was purchased from Sigma-Aldrich and used as received, Rh content 5% wt.

4.2 Catalytic tests

The catalyst (50 mg) was dispersed in toluene (Fluka, 0.75 mL) and 1-phenylethanol (Sigma-Aldrich) adjusting the amount of alcohol to a molar metal to substrate ratio of 1:100 for each catalyst with respect to the total amount of rhodium. The reaction mixture was heated under reflux at 100 ^{o}C for 4 hours with a magnetic stirrer operating at 700 rpm at atmospheric pressure. The tests in presence of toluene and water were carried out under identical conditions to those in toluene but the addition of deionized water (1.5 mL). Deionized water was obtained using a Elgastat Option 3B

unit with a conductivity of 1 MΩ cm^{-1} at neutral pH. Additional specifications are: organics < 0.001 AU at 254 nm, TOC < 50 ppb, bacteria < 1 cfu mL^{-1}. The tests in presence of toluene, water and NaOH (Fluka) were carried out by preparing NaOH in aqueous solutions, using a 1-phenylethanol to NaOH molar ratio of 10:1 (that is with a molar Rh metal to NaOH ratio of 1:1000), for each catalyst.

4.2.1 NMR

Analysis of the reaction mixture to determine product selectivity and conversion was obtained via ^{1}H-NMR using a Bruker Avance IIIHD 400 spectrometer operating at 400 MHz. NMR spectra were collected using $CDCl_3$ as solvent. Chemical shifts were reported in parts per million (ppm) from tetramethylsilane using the methyl group of toluene resonance as the internal standard (toluene CH_3, s, δ: 2.36 ppm) for ^{1}H NMR.[74]

Analysis of the aqueous phase in biphasic experiments, for the identification of residues, was also carried oud by extraction using $CDCl_3$ or by direct analysis using D_2O. In the latter case, the signal of undeuterated water H_2O at 4.79 ppm in D_2O was taken as internal standard.

4.2.2 GC/MS

Gas chromatography mass spectrometry analysis was additional used for the characterization of the reaction mixtures and analysis of traces. Two chromatographic methods were used. In the first method GC/MS was carried out using a Perkin Elmer Turbomass GC-MS, equipped with a Phenomenex Zebron ZB-5MS column 30 m × 0.25 mm, 0.25 μm film thickness. The carrier gas was helium at 1 mL min^{-1}, the injection volume 1.0 μL, injector temperature was 250 ^oC the temperature programme was 60 to 260 ^oC using a ramp at 10 ^oC min^{-1} then hold for 10 minutes. A second method for fine resolution of the reaction mixture and identification of impurities, made use of a Agilent Technologies 7200Q-ToF GC-MS, equipped with a Phenomenex Zebron ZB-5MS column 30 m × 0.25 mm, 0.25 μm film thickness. The carrier gas was helium at 1 mL min^{-1}, the injection volume 1.0 μL, injector temperature was 250 ^oC the temperature programme was 40 ^oC held for 5 minutes then heated to 240 ^oC at 5 ^oC min^{-1}.

4.2.3 Partition control tests

Partition constants $K_{org,aq}$ for 1-phenylethanol and acetophenone were determined via ^{1}H-NMR by calibration on seven toluene/water mixtures with a volume ratio ranging from 1:1 to 1:10 for the two solvents using octane as internal standard (a species soluble in toluene only). By comparing the ^{1}H-NMR signal of 1-phenylethanol and acetophenone in organic phase to the one of octane it was

then possible to determine the amount of these species in organic phase and in turn in aqueous phase (full details in ESI†).

4.2.4 Re-usability tests

Catalysts were recovered by carrying out an initial test with 70 mg of catalyst (and scaling up all the amounts of reagents accordingly). The catalyst was then recovered via centrifugation, washed with acetone (50 mL), and dried at 70 ^{o}C for 16 h. 50 mg of the dried powder were then used for a re-usability test.

4.2.5 ICP-MS

Inductively coupled plasma was used for reaction mixture characterization. The reaction mixture was analysed via ICP-MS using a Agilent 7500CE instrument which was calibrated up to 10ppb using standards prepared by dilution from a stock 1000 ppm Rh standard with 1% nitric acid. The Rh signal (mass 103) was measured for samples and standards along with Ru (mass 101) which was added online as an internal standard. The samples were acidified with one drop of concentrated nitric acid (14M), then diluted the samples 10-fold with 1% nitric acid. The Rh concentrations in the samples were calculated against a calibration graph.

4.3 Catalysts characterization

4.3.1 XRPD

X-ray powder diffraction (XRPD) patterns were acquired using a Bruker D8 Advance equipped with a LynxEye detector. The instrument was operating at 40 kV and 40 mA selecting the CuK_{α} radiation as X-ray source. The samples were analysed in the range 30 ^{o} to 80° 2θ for a scan time of 20 min.

4.3.2 XPS

X-ray photoelectron spectroscopy was performed with a Kratos Axis Nova spectrometer using a monochromatised AlK_{α} X-ray source (225 W) with an analyser pass energy of 160 eV for survey scans and 20 eV for detailed elemental scans. Three positions per sample were analysed using charge neutralization. Binding energies are referenced to the C1s binding energy of carbon, taken to be 284.8 eV.[44] The Rh^{3+} and Rh^{0} amounts are reported as a percentage of the total Rh amount.

4.3.3 Electron microscopy

STEM/EDS images were obtained using a JEOL JEM-2100F instrument operated at 200 kV. All STEM specimens were prepared by placing a drop of the solution on carbon-coated Cu grids and allowed to dry in air (without staining).

4.3.4 ICP

ICP for catalysts characterization for metal content. An amount of catalyst between 10-20 mg was heated in a mixture of sulfuric acid and nitric acid at 200 °C, the mixture was cooled to room temperature and aqua regia was added. The amount of Rh in the resulting solution was measured by ICP analysis to determine the loading of Rh. ICP analysis was performed on Shimadzu ICPS-7510 apparatus.

Conflict of Interest

There are no conflicts to declare, and the authors declare no competing financial interests.

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Statement of Contributions

J.O.W., D.S., C.A.B., P.K.S., and M.C. performed the catalytic tests, NMR, XRD and GC/MS. H.M., T.Y., and S. K., synthesised the catalysts, performed the polymer characterization and TEM. Y.R., performed data analysis, XRD, and statistics, M.B.S., N.S., and P.J.C. performed XPS analysis. M.C. wrote the paper.

† **Electronic supplementary information (ESI) available:** ^{1}H-NMR spectra, GC/MS chromatograms and fragmentation patterns, XPS spectra. Details of styrene based copolymer synthesis, products characterization, partition constants, particle size distribution. Schemes S1 to S3, Figs S1 to S41, and Tables S1 to S7.

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