

Activated Carbon as a Mass-Transfer Additive in Aqueous Organometallic Catalysis

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Since catalysis is considered to be a foundational pillar of green chemistry, substantial efforts have been made to develop innovative catalytic processes into which respect for the environment has been integrated. The developmental objectives include designing chemical processes that reduce or eliminate the use of hazardous substances, work under milder conditions with low-energy consumption, utilize easily recyclable materials, and use more environmentally friendly solvents.

In this context, aqueous biphasic organometallic catalysis appears to be an elegant method.^[1] Indeed, the catalyst is immobilized in an aqueous phase and can be easily separated from the reaction products by simple decantation. However, the potential scope of aqueous organometallic catalysis is drastically reduced for chemical transformations involving highly hydrophobic substrates, due to severe mass-transfer limitations. To overcome this crucial problem, co-solvents,^[2] surfactants,^[3] amphiphilic phosphanes,^[4] polymers,^[5] dispersed particles,^[6] and cyclodextrins^[7] have been proposed as additives.

Unexpectedly, the possibility of using activated carbon (AC) as a mass-transfer additive in aqueous, biphasic catalytic processes has never been investigated.^[8] This is really surprising as it is known that suspended AC particles can enhance gas–liquid^[9] and liquid–liquid^[10] mass transfer. This

effect is usually explained by additional adsorptive transport mechanisms. Furthermore, carbonaceous materials satisfy most of the requirements for use in catalytic processes, including a large pore volume and surface area, stability in acidic or basic media and at high temperatures, and chemical inertness.^[11]

Herein, we report on the possibility of using AC as a mass-transfer additive in aqueous organometallic catalysis. The experiments were conducted with a commercially available AC, Nuchar WV-B (AC-WV). This appears to be a good candidate, since it has a large surface area ($1690 \text{ m}^2 \text{ g}^{-1}$), pore volume ($1.32 \text{ cm}^3 \text{ g}^{-1}$), and average pore size (3.1 nm). In fact, it exhibits a composite type I–II isotherm, consistent with a combined micro- and mesoporosity with pore sizes in the 1.5–20 nm range, as shown by the Barrett–Joyner–Halenda (BJH) pore size distribution (Figure S1 and Table S1 in the Supporting Information). Moreover, the percentage of microporosity has been determined and, interestingly, the value does not exceed 41 vol%. Indeed, typical values in the literature show that the chemically activated carbons have much higher percentages of microporosity than that measured for AC-WV^[12] and, this can lead to steric hindrance if bulky substrates containing long-chain alkyl groups are used. The Boehm titration method^[13] was also used to determine the surface chemistry of the carbonaceous material (see Table S1 in the Supporting Information). Thus, AC-WV presents a variety of species that are mainly acidic, likely due to the method of activation which utilizes phosphoric acid. However, the total number of sites is very low, that is, $39 \mu\text{mol g}^{-1}$, which is consistent with a carbon surface almost free from oxygen-containing functional groups.

To explore the effect of AC-WV on mass-transfer efficiency, the cleavage of water-insoluble allylundecylcarbonate was chosen as the model reaction (Tsuji–Trost reaction). This reaction is catalyzed, at room temperature, by a combination of palladium and the water-soluble triphenylphosphine trisulfonate trisodium salt (TPPTS) in the presence of diethylamine as an allyl scavenger.

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By comparing the conversions of the allylundecylcarbonate with and without AC over time, it is readily apparent that the reaction occurs much more slowly if the experiment is conducted without AC (Figure 1). This result confirms

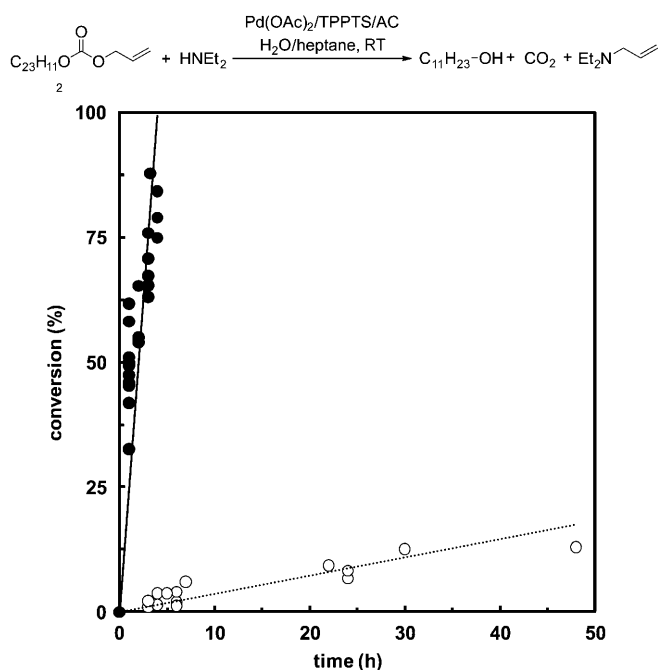


Figure 1. Conversion of allylundecylcarbonate in the Pd(TPPTS)₃-catalyzed cleavage reaction as a function of time with (●) and without (○) AC promoter. Conditions: AC-WV (5.0 mg), Pd (10.5 μmol), TPPTS (94.5 μmol), water (2.0 g), allylundecylcarbonate (0.64 mmol), diethylamine (1.28 mmol), C₁₂H₂₆ (internal standard; 0.32 mmol), heptane (1.2 g), room temperature, and stirring rate = 1250 rpm.

that the limiting step of the reaction is the mass transfer. Furthermore, AC-WV appears to be a valuable mass-transfer agent in the Tsuji–Trost reaction, since it allows much higher levels of conversion to be obtained. For instance, the conversion reaches 80% after 4 h in the presence of AC-WV, whereas it is only 2% without the promoter. Note that this beneficial effect is obtained with a low loading of AC-WV compared with that of the substrate, that is, 5 mg compared with 163 mg. It is also worth mentioning that a two-fold increase in the AC-WV loading results in a further two-fold increase in the reaction rate. Our experimental data suggest that the suspended carbon particles lead to greater mass transfer as a result of increased interfacial surface area between the aqueous and organic phases. This effect is directly proportional to the quantity of activated carbon added.

To investigate the scope and limitations of AC-WV as a mass-transfer additive, the cleavage of various allylcarbonate substrates, with alkyl chain lengths ranging from 4 to 16 carbon atoms, was performed. For comparison, all the reactions were performed without AC under biphasic conditions and the results in terms of initial relative reaction rate (ratio of the initial activity with AC-WV to that without AC-WV)

are presented in Figure 2 and Table S2 (in the Supporting Information).

Our experimental data show that, in the presence of AC-WV, the longer the alkyl chain, the greater the enhancement

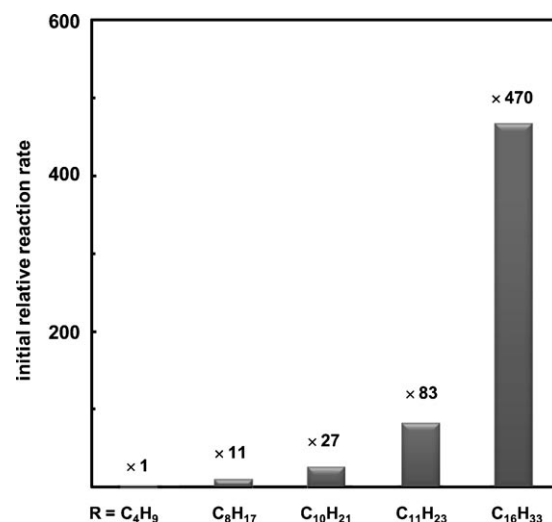


Figure 2. The effect of the addition of AC-WV on the initial relative-reaction rate in the Pd(TPPTS)₃-catalyzed cleavage reactions of various allylalkylcarbonates (R-OCO-CH₂-CH=CH₂ with R = *n*-alkyl group) and diethylamine as substrates. Conditions: AC-WV (5.0 mg), Pd (10.5 μmol), TPPTS (94.5 μmol), water (2.0 g), allylalkylcarbonate (0.64 mmol), diethylamine (1.28 mmol), C₁₂H₂₆ (internal standard; 0.32 mmol), heptane (1.2 g), room temperature, and stirring rate = 1250 rpm.

in the activity. Notably, the highest relative reaction rate is obtained with the most hydrophobic substrate (470 with R = C₁₆H₃₃), whereas no beneficial contribution is observed for the substrate containing the shortest alkyl chain (R = C₄H₉). In this last case, the solubility of the allylbutylcarbonate in water is sufficient for the reaction to progress without any limitation by mass transfer. This shows that the beneficial effect of the AC-WV carbon is strikingly connected with the solubility of the substrates in water; thus, the lower the solubility of the substrate, the more important the mass-transfer promoter contribution of the AC-WV.

Interestingly, it was found that the reaction rates were also dependent upon the amount of water used in the reaction.^[14] Thus, the highest initial reaction rates were observed if the water content was in the range 95 to 98 wt% (Figure 3).

It also appears that the initial activities remain low over a wide range of water contents, that is, below 85 wt%, and that no maximum is reached for the water concentration corresponding to total filling of the pores in the solid (10 wt% of water). It must be pointed out that the evolution of the initial activity as a function of water content is very different from that which is usually described for supported aqueous-phase catalysis (SAPC).^[8,15] Indeed, all studies concerning SAPC have demonstrated that the optimal activity is only obtained at low water concentrations, corresponding to the partial or total filling of the pores.^[16] In these cases,

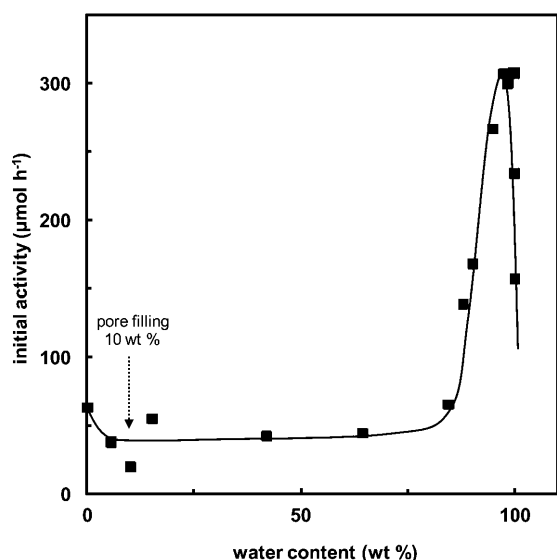


Figure 3. The effect of the amount of water on the initial reaction rate in the Pd(TPPTS)₃-catalyzed cleavage reaction of allylundecylcarbonate. Conditions: AC-WV (5.0 mg), Pd (10.5 μmol), TPPTS (94.5 μmol), allylundecylcarbonate (0.64 mmol), diethylamine (1.28 mmol), C₁₂H₂₆ (internal standard; 0.32 mmol), heptane (1.2 g), room temperature, and stirring rate = 1250 rpm.

slight deviations from this water optimum inevitably lead to decreased activities, whereas large amounts of water lead to similar activities to those found under classical biphasic conditions. In our case, the trend is completely different, since large quantities of water are required to ensure suitable conditions for catalysis. Furthermore, it can be noted that the reaction rates are maintained at their highest levels over a wide range of water/heptane volume ratios, that is, from 1:1 to 5:1 (Figure S2 in the Supporting Information), demonstrating the applicability of this method to aqueous organometallic catalysis.

By considering all of our results, we propose that the role of the carbon is to facilitate the mixing of the aqueous and organic phases and, thus, leads to a more effective interfacial area. We have also shown, by using energy-dispersive X-ray (EDX) analyses (Figure S3 in the Supporting Information), that palladium and phosphorus elements are still present after several washings of the material with water, suggesting the possibility of adsorption of the catalyst in the pores of the activated carbon. This phenomenon could also contribute to the better dispersion of the catalyst at the interface.

Finally, the reusability of the catalytic system was evaluated using allylundecylcarbonate as the substrate. Briefly, at the end of each reaction cycle the phases were separated, the clear organic (upper) phase was removed through a cannula transfer and then a new organic phase containing the allylundecylcarbonate substrate was added. As Figure 4 clearly shows, no significant loss of activity was observed after five consecutive runs and 100% conversion was achieved within 4.6 h in the fifth experiment, which corresponds to a turnover frequency (TOF) of 13 h⁻¹.

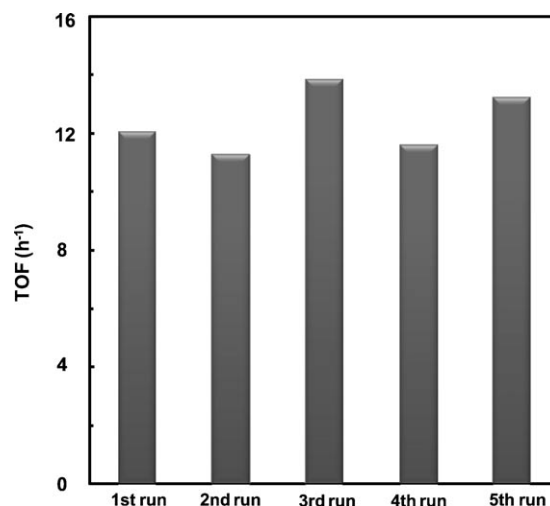


Figure 4. The reusability of the catalytic system in the Pd(TPPTS)₃-catalyzed cleavage reaction of allylundecylcarbonate. Conditions: AC-WV (5.0 mg), Pd (10.5 μmol), TPPTS (94.5 μmol), water (2.0 g), allylundecylcarbonate (0.64 mmol), diethylamine (1.28 mmol), C₁₂H₂₆ (internal standard; 0.32 mmol), heptane (1.2 g), room temperature, and stirring rate = 1250 rpm. The TOF is defined as moles of converted allylundecylcarbonate per mole of introduced palladium per hour.

To sum up, we have described a simple and environmentally friendly strategy for enhancing the overall Tsuji–Trost reaction rate, based on the combined use of a water-soluble palladium complex and AC as a mass-transfer promoter. Simultaneous to the activity enhancement, this method allows the separation of the products from the catalytic suspension and catalyst recyclability with no detectable loss of activity. Moreover, it has been shown that the mechanism cannot be ascribed to a SAPC-type mechanism. From these observations, the AC-WV solid appears to be an adequate mass-transfer additive for use in aqueous biphasic organometallic catalysis that makes the extraction of the organic substrate from the organic phase easier through nonpolar/nonpolar interactions with the carbon support. We assume that the relatively hydrophobic cavities of AC-WV act as nanometer-sized pockets that enable the confinement of the reactants and the water-soluble catalyst. Further experiments to confirm the aforementioned hypothesis and to extend the range of use of porous carbon materials in aqueous organometallic catalysis are currently under way.

Experimental Section

Chemicals: The activated carbon, denoted as AC-WV, was supplied by MeadWestvaco Corporation, Covington, USA. It was produced from wood and activated by a phosphorus acid. The trisodium salt of triphenylphosphine trisulfonate (TPPTS: P(*m*-C₆H₄SO₃Na)₃) was synthesized according to the method reported by Gärtner et al.^[17] The purity of the TPPTS was carefully controlled by ¹H, ¹³C, and ³¹P{¹H} NMR analyses and MALDI-TOF mass spectrometry. ³¹P{¹H} NMR spectroscopy indicated that the product contained a mixture of phosphane (ca. 98%) and its oxide (ca. 2%). Double distilled water was used in all experiments. All

other reagents were purchased from Aldrich Chemicals or Acros Organics in their highest purity and used without further purification.

Porosity: The nitrogen adsorption/desorption isotherm was obtained at -196°C by using a Nova 2200 apparatus from the Quantachrome Corporation, after having degassed the sample overnight at 100°C . The specific area was calculated from the Brunauer–Emmett–Teller (BET) equation using P/P_0 values between 2.5×10^{-3} and 1.7×10^{-2} and the pore size distribution was obtained from the desorption branch using the BJH method. The total pore volume was estimated at $P/P_0 = 0.95$ while the micropore volume was determined by the Dubinin–Radushkevich method. The average pore size was estimated from the ratio of the total pore volume to the BET surface area by using Gurvich's rule and assuming that pores are of cylindrical geometry.

Catalytic experiments (general procedure): The cleavage of allylundecylcarbonate was chosen as the model reaction and performed as follows: water-soluble TPPTS ($94.5 \mu\text{mol}$, 9 equiv) and $\text{Pd}(\text{OAc})_2$ ($10.5 \mu\text{mol}$) were dissolved in water (2.0 g), in a Schlenk tube and stirred for 4 h, at room temperature, under a nitrogen atmosphere. The yellow solution obtained was transferred by cannula into another Schlenk tube containing the activated carbon (5 mg) and the resulting catalytic suspension was stirred at room temperature for 17 h. Then, allylundecylcarbonate (0.64 mmol), diethylamine (1.28 mmol), and dodecane (0.32 mmol; used as an internal standard) were dissolved in heptane (1.2 g) and transferred into the catalytic suspension. The biphasic medium was stirred at room temperature and the reaction was monitored by analyzing aliquots of the reaction mixture (organic phase) with a Shimadzu GC-17 A gas chromatograph equipped with a methyl silicone capillary column ($30 \text{ m} \times 0.32 \text{ mm}$) and a flame ionization detector. The stirring rate was adjusted (1250 rpm), so that external mass-transfer limitations were eliminated (Figure S4 in the Supporting Information).

Catalytic experiments (reusability): The catalytic experiments for reusability were carried out as follows: the catalytic solution prepared as previously described with TPPTS ($94.5 \mu\text{mol}$), $\text{Pd}(\text{OAc})_2$ ($10.5 \mu\text{mol}$), and water (2 g) was added to AC-WV (5 mg) in a Schlenk tube, under a nitrogen atmosphere. The mixture was kept at room temperature for 17 h. In another Schlenk tube, allylundecylcarbonate (0.64 mmol), diethylamine (1.28 mmol), and dodecane (0.32 mmol) were dissolved in heptane (1.2 g) and the solution was transferred by cannula into the previously described one. The resulting mixture was stirred at room temperature until total conversion had occurred. After decantation, the organic phase was removed by cannula and the recovered aqueous phase was reloaded with allylundecylcarbonate, diethylamine, dodecane, and heptane as described above.

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Keywords: activated carbon • mass transfer • palladium • phase-transfer catalysis • water chemistry

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