

A MODIFIED WACKER SYSTEM FOR THE OXIDATION OF HEAVY 1-OLEFINS

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Abstract

Heavy olefins were oxidated using a modified Wacker system with TBHP as oxidant and acetonitrile as solvent. The oxidation of both pure heavy olefins (C₁₂-C₂₀) and equimolecular mixtures of them with or without their corresponding n-paraffins, were carried out with the addition of β-cyclodextrins in some cases. In the oxidation of 1-octadecene a value of 90 % of conversion was achieved and the selectivity towards the product of interest, 2-octadecanone, after 2h of reaction time was of 60 %. The addition of β-cyclodextrins did not increase the production of 2-octadecanone. Nevertheless, the selectivity towards the ketone in the oxidation of an equimolecular mixture of n-dodecane + 1-dodecene was a 29 % higher than the achieved in the absence of the n-paraffin, likely due to a dilution effect of the n-dodecane which reduces the extent of the isomerization reactions. Moreover, the oxidation of an equimolecular mixture C⁼₁₂+C⁼₁₆+C⁼₂₀ in the presence of equimolecular amounts of their corresponding n-paraffins gave rise to practically complete conversion and selectivities towards 2-methylketones within 70-90 % enhancing with decreasing chain length due to their higher solubility in the biphasic system. Finally the catalyst was not active after two reaction cycles by the palladium clusters formation. However increasing the 1-dodecene/PdCl₂ ratio to 100 comparable catalytic results were obtained, being expected to increase the catalyst lifetime by decreasing the extent of palladium aggregation.

Keywords: heavy olefins, Wacker oxidation, acetonitrile, palladium chloride, tert-butylhydroperoxide

1. Introduction

Wacker oxidation of alkenes to ketones is a conventional industrial process for the synthesis of organic chemicals catalysed by palladium. In this reaction air is typically used as oxidant and CuCl₂ as cocatalyst [1]. However, Wacker oxidation involves several disadvantages such as the appearance of palladium black leading towards the deactivation of the palladium catalysts, the formation of unwanted chlorinated by-products and the occurrence of a corrosive reaction medium due to the use of CuCl₂ and HCl. In addition, in the case of heavy olefins which are important as their application in polar waxes, fragrances, cetane improvers or printer inks, the usage of the Wacker system is limited due to their low solubility in water. Consequently, different attempts can be found in literature modifying the original Wacker system in order to eliminate the aforementioned drawbacks. Many of them are related to the heterogeneization of the palladium catalyst system over different supports such as zeolites, pore glass, montmorillonite [2] or polymers, in order to avoid the catalyst deactivation. In addition, mixtures of water and ionic liquids have been also reported as solvents in Wacker oxidation as well as inverse phase transfer catalysts such as cyclodextrins, to improve the solubility of the higher alkenes. β-cyclodextrins are soluble in water and well known molecular recognition between the host cavity of cyclodextrins and organic compounds allowed for higher

oxidation rate and ketone selectivity. In a previous work [3], the most adequate operation variables were determined for a model higher 1-olefin (1-dodecene) oxidized to 2-dodecanone and other ketones in a modified Wacker system without copper chloride and employing tert-butylhydroperoxide (TBHP) as oxidant, acetonitrile as solvent and palladium chloride as catalyst ([CH₃CN] / [1-dodecene] = 10, [TBHP] / [1-dodecene] = 7). In the present work, the performance of the modified Wacker system in the oxidation of the heavy 1-olefins C₁₂, C₁₆, C₁₈ and C₂₀ is carried out. These olefins can be easily obtained in the feedstock recycling of polyethylene by thermal cracking at 350–400 °C in an almost equimolar mixture with the corresponding n-paraffin of each fraction [4]. Owing to this, the performance of the modified Wacker system was studied under the presence of the corresponding n-paraffins, finding an increase in the selectivity of the corresponding 2-methylketones.

2. Materials and Methods

In a typical experiment, 5.0 g of the 1-dodecene was loaded inside a stirred glass batch reactor equipped with a reflux column and propeller stirrer, with 11.6 g of acetonitrile. After, 21.6 g of TBHP and 0.1 g of palladium (II) chloride were also loaded and the reaction started. The reaction temperature was controlled by a thermostatic bath, where the reactor was placed. The mixture was stirred at 300 rpm at the reaction temperature (80 °C) during 7 h. In reactions with β-

cyclodextrin, this was added with a molar ratio of [1-olefin] / [β -cyclodextrin] = 40. If the experiment was carried out in the presence of the corresponding n-alkane, the mixture loaded was [1-alkene] / [n-alkane] molar ratio = 1. Finally, 179.0 g of tetrahydrofuran were added to the mixture in order to homogenize the medium and for the subsequent analysis of the obtained products by gas chromatography using a Varian 3900GC provided with a CP8907 methylsilicone column of 15 m length x 0,25 μ m width, using a flame ionization detector (FID).

3. Results and Discussion

3.1. Oxidation of 1-octadecene with/without β -cyclodextrins. According to the previous research, the reactions taking place in the studied Wacker system are presented in scheme 1.



Scheme 1. Reactions in studied Wacker system

Oxidation is a slow reaction (pathway 2) which competes with the fast isomerization of 1-olefin (pathway 1). However, isomerization is also a reversible reaction which leads towards the starting 1-olefin as it is consumed in the oxidation reaction. The relative extent of these reactions might be related either to the biphasic nature of the system or to the occurrence of a specific interaction with the solvent, being acetonitrile the one with best results was achieved. Once the reported modified Wacker system was proved to be suitable for the oxidation of 1-dodecene, it was applied to the oxidation of a higher olefin (1-octadecene). In addition, besides the proposed modified Wacker system, another identical one but incorporating β -cyclodextrin ([β -cyclodextrin] / [1-octadecene] = 1 / 40) were also studied in order to study the effect of this phase transfer catalyst. Conversion and selectivity results obtained in the modified Wacker oxidation after 2 and 6 h respectively with or without β -cyclodextrin are shown in Figure 1.

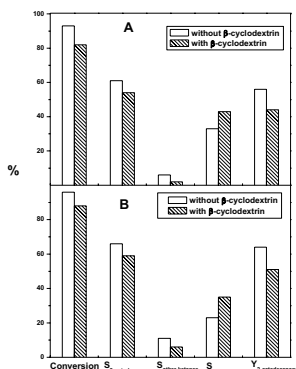


Figure 1. Modified Wacker oxidation of 1-octadecene with and without β -cyclodextrin after 2 (A) and 6 h (B) of reaction (T = 80 °C, N = 300 rpm, [C₁₈H₃₆] / [PdCl₂] = 50, [solvent] / [C₁₈H₃₆] = 10, [TBHP] / [C₁₈H₃₆] = 6).

Wacker system without β -cyclodextrin leads to conversions around 90% after 2 and 6 h, with a selectivity towards 2-octadecanone above 60% for both times (61 and 66%, respectively). In addition, the selectivity towards other ketones was around 6-10%. These are remarkable results considering the high molecular weight of 1-octadecene. In addition, at it is shown in Figure 1 the presence of the β -cyclodextrin is slightly detrimental for both the conversion and the selectivity towards oxygenated products (2-octadecanone + other ketones). Consequently, another way to prepare heavy ketones with higher selectivity is required.

3.2. Oxidation of 1-dodecene under the presence of n-dodecane. The performance of the modified Wacker system in the oxidation of a model equimolar mixture of n-dodecane + 1-dodecene at 80°C was initially studied in order to ascertain the influence of the presence of the n-paraffin. The results obtained were compared to those of the oxidation of 1-dodecene without n-dodecane. Firstly, the conversion is about 6% higher with n-dodecane in the mixture (95% vs. 89%). In terms of selectivity, the presence of n-dodecane enhances markedly the selectivity towards 2-dodecanone (63% after 2h instead of 34% with no n-dodecane present). In addition, the selectivity towards other ketones remains similar in both cases (around 20%). Thus, the total amount of oxygenates after 2 h with n-dodecane adds up to 85 % while in its absence accounts for only 60%. Consequently, the presence of n-dodecane increases meaningfully the selectivity towards oxygenates, mostly 2-dodecanone.

4. Conclusions

The reported modified Wacker system with TBHP as oxidant and acetonitrile as solvent has been proved useful in the oxidation at 80°C of the heavy 1-olefins. Initially, the system allowed the oxidation of 1-octadecene with complete conversion and selectivity close to 60% towards 2-octadecanone after 2 h of reaction. In addition, the presence of β -cyclodextrins in the reaction medium was not effective in improving the conversion and selectivity towards 2-octadecanone. In contrast, the addition of an equimolar amount of n-dodecane to the reaction medium allowed to increase the selectivity towards 2-dodecanone from 34 to 63% after 2 h of reaction, which was ascribed to a dilution effect of the n-paraffin, leading to a lower extent of the isomerisation reaction.

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