



Oxidation of heavy 1-olefins ($C_{12}^- - C_{20}^-$) with TBHP using a modified Wacker system

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ABSTRACT

The oxidation of heavy olefins ($C_{12}^- - C_{20}^-$) was carried out using a modified Wacker system with TBHP as oxidant and acetonitrile as solvent at 80 °C. This system allowed the oxidation of 1-octadecene giving rise to 90% conversion with 60% selectivity towards 2-octadecanone after 2 h while the addition of β -cyclodextrins did not increase the production of 2-octadecanone. The oxidation of an equimolar mixture of n -dodecane + 1-dodecene enhanced markedly the selectivity towards 2-dodecanone yielding 63% instead of 34% in the absence of n -paraffin after 2 h, likely due to a dilution effect of the n -dodecane which reduces the extent of the isomerization reactions. The oxidation of an equimolar mixture $C_{12}^- + C_{16}^- + C_{20}^-$ in the presence of equimolar amounts of their corresponding n -paraffins gave rise to practically complete conversion and selectivities toward 2-methylketones within 70–90% enhancing with decreasing chain length due to their higher solubility in the biphasic system. The activity of the catalyst dropped after two reaction cycles indicating its deactivation by the formation of palladium clusters. However, it was possible to obtain similar results in terms of activity and selectivity by increasing the (1-dodecene)/($PdCl_2$) ratio to 100, which is expected to increase the catalyst lifetime by decreasing the extent of palladium aggregation. In this regard, the reported system is rather promising for the oxidation of heavy 1-olefins towards methyl ketones.

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1. Introduction

Wacker reaction is a well-known palladium-catalyzed oxidation of alkenes to carbonyl compounds, wherein ketones are preferentially obtained [1,2]. This oxidation process uses air and $CuCl_2$ as cocatalyst, and has become industrially useful in the synthesis of organic chemicals since its discovery in 1959 [3]. Wacker process mechanism is dependent on reaction conditions [4,5]. The experiments indicate at least two competing mechanisms with different rate laws and product distributions dependent on (Cl^-) and ($CuCl_2$). However, conventional 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 $CuCl_2$ and HCl [6]. In addition, the low solubility of higher olefins in water has limited considerably the usage of the Wacker system for the preparation of heavy methyl ketones [7,8]. These are an important class of compounds which find wide usage as polar waxes, fragrances, cetane improvers and printer inks.

Consequently, different attempts can be found in the literature modifying the original Wacker system in order to eliminate the aforementioned drawbacks. Many of them are related to the heterogenization of the palladium catalyst system over different supports such as zeolites [9], pore glass [10], montmorillonite [11] and polymers [12,13], in order to avoid the catalyst deactivation. Likewise, a Pd nanocluster (cationic Pd_{2060}) was also heterogenized on TiO_2 for the preparation of heavy olefins [14]. Another modification was using other redox pairs instead of the $Cu(II)/Cu(I)$ pair such as *p*-benzoquinone/hydroquinone [15], $Fe(III)/Fe(II)$ [16] and heteropolyacids [6,17,18]. On the other hand, some of these systems have also been heterogenized on several supports, e.g., $H_{3+n}PVMo_{12-n}O_{40}$ on silica [18] and $Pd(OAc)_2/NPmOV$ on activated carbon [17].

The solubility of the higher alkenes can be improved by using mixtures of organic solvents and water. In order to solve this problem different organic solvents have been studied and the best results were obtained with dimethylformamide [8] or acetonitrile [19,20]. Mixtures of water and ionic liquids have also been used as solvent in Wacker oxidation of various types of terminal olefins under mild reaction conditions [21]. These biphasic systems show the key advantage of recycling both the solvent and the catalyst system, being suitable for the reuse with different types of substrates. Inverse-phase transfer catalysts such as cyclodextrins [7,22] have also been reported as efficient systems for the preparation of the

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corresponding ketones. The β -cyclodextrin is soluble in water and the well-known molecular recognition between the host cavity of cyclodextrins and organic compounds allowed for higher oxidation rate and ketone selectivity. In addition, the solvent also affects the activity of the Wacker systems. In this regard, Mitsudome et al. [23] reported the remarkable oxidation of higher 1-olefins (around 85% yields) with molecular oxygen using palladium chloride and *N,N*-dimethylacetamide as solvent, without the need for copper chloride.

In a previous work [20], a model higher 1-olefin (1-dodecene) was oxidized to 2-dodecanone and other ketones in a modified Wacker system without copper chloride and employing tert-butylhydroperoxide (TBHP) as oxidant. Acetonitrile and palladium chloride were the solvent and the catalyst of choice, respectively, due to their high selectivity towards 2-dodecanone. In addition, the most adequate operation variables were determined ($[\text{CH}_3\text{CN}]/[1\text{-dodecene}] = 10$, $[\text{TBHP}]/[1\text{-dodecene}] = 7$). In this work, the performance of the modified Wacker system in the oxidation of the heavy 1-olefins C_{12} , C_{16} , C_{18} and C_{20} is carried out. These olefins can be easily obtained in the feedstock recycling of polyethylene by thermal cracking at 350–400 °C. In addition, this Wacker oxidation would allow obtaining more valuable products than the initial 1-olefins. On the other hand, these olefins are obtained in the thermal cracking in an almost equimolar mixture with the corresponding *n*-paraffin of each fraction [24]. Owing to this, the performance of the modified Wacker system was studied under the presence of the corresponding *n*-paraffins. Henceforth, the obtained results are reported which indicate that the oxidation of the heavy olefins is feasible with this modified Wacker system and takes place with high rate for the different olefins, regardless of the molecular weight. In addition, the presence of the *n*-paraffin led to an unexpected increase in the selectivity of the corresponding 2-methyl ketone.

2. Experimental section

2.1. Chemicals

The chemicals used in the present research were as follows: 1-dodecene (95 wt.%, Aldrich), *n*-dodecane (99%, Aldrich), 1-hexadecene (99 wt.%, Aldrich), *n*-hexadecane (99%, Aldrich), 1-octadecene (90 wt.%, Aldrich), *n*-octadecane (99%, Aldrich), 1-eicosene (90 wt.%, Aldrich), *n*-eicosane (Aldrich, 97%), tert-butylhydroperoxide (TBHP, 70 wt.% aqueous solution, Aldrich), acetonitrile (99.5 wt.%, Scharlau) and palladium (II) chloride (99 wt.%, Fluka). Additionally, other used chemicals were cyclohexane (99.5 wt.%, Aldrich), dichloroethane (99.8 wt.%, Aldrich), 2-propanol (99.5 wt.%, Aldrich), *N,N*-dimethylformamide (99.8 wt.%, Aldrich) and β -cyclodextrin ($\text{C}_{42}\text{H}_{70}\text{O}_{35} \cdot x\text{H}_2\text{O}$, Aldrich).

2.2. Experimental installation and oxidation reactions

The catalytic experiments were carried out in a stirred glass batch reactor equipped with a reflux column and propeller stirrer. The reaction temperature was controlled by a thermostatic bath where the reactor was placed. In a typical experiment, 5.0 g of the 1-dodecene was loaded inside the reactor with 11.6 g of acetonitrile. Later, 21.6 g of TBHP and 0.1 g of palladium (II) chloride were also loaded and the reaction started. The mixture was stirred at 300 rpm at the reaction temperature (80 °C) during 7 h. In the case of using 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. After finishing the reaction and in order to homogenize the medium, 179.0 g of tetrahydrofuran was added to the mixture for the subsequent analysis of the obtained products by gas chromatography.

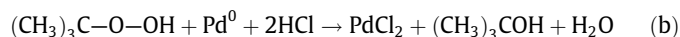
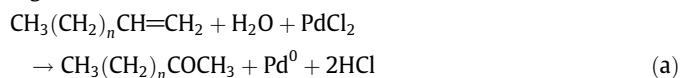
2.3. Analysis of the reaction products

The reactions were run for 7 h, with the samples being taken at regular intervals and analyzed with a Varian 3900 gas chromatograph provided with a CP8907 methylsilicone column of 15 m length \times 0.25 μm width, using a flame ionization detector (FID). Identification of the different reaction products was performed by using commercial standards. Product distribution and overall mass balances (closure was >98%) were determined using appropriate reactant and product response factors, derived from multi-point calibration curves. Prior to the analyses, tetraline was added as internal standard to the reaction mixture previously dissolved in tetrahydrofuran. Subsequently, both the 1-olefins conversion and the selectivity towards the obtained products were determined. The conversion was defined as $(\text{mol of reacted 1-olefin}) \times (\text{mol of starting 1-olefin})^{-1} \times 100$. The selectivity was divided into the three obtained product groups: 2-ketone ($S_{2\text{-ketone}}$), other ketones ($S_{\text{other ketones}}$) and alkene isomers (S_{isomers}).

3. Results and discussion

3.1. Mechanisms in the modified Wacker TBHP oxidation

Wacker oxidation using TBHP may proceed according to two different mechanisms. Firstly, the water from the TBHP reagent (70 wt.% aqueous solution) can act as oxygen source for the olefin oxidation according to the conventional hydroxypalladation mechanism of the Wacker–Schmitt oxidation [25] leading to the following scheme of reactions:



However, an alternative mechanism has also proved wherein TBHP ketonizes the olefin through a peroxy-palladation step, according to Mimoun et al. [26] and Cornell and Sigman [27]. In a previous work [20], we proposed the scheme of reactions shown in Fig. 1 for the oxidation of 1-dodecene. The first step comprises the complexation of the reacting olefin to the palladium (II) complex (step 1). Subsequently, the complex proceeds giving rise to a π -allylpalladium species (step 2) which drives to the formation of the different dodecene isomers (step 3). Tert-butyl hydroperoxide is incorporated inside the palladium complex of the dodecene isomers forming a five-membered pseudocyclic peroxy-palladium complex (step 4). Afterwards, 1,2-hydride shift takes place and the release of both tert-butanol and the desired product (other ketone) occurs (step 5). In step 6, the peroxy-palladium complex is formed with 1-dodecene instead of the dodecene isomers, releasing the desired product 2-dodecanone (step 7).

3.2. Effect of the used solvent

The reactions taking place in the studied Wacker system, according to the previous research, are the following ones:



Oxidation is a slow reaction (pathway 2) which competes with the fast isomerization of 1-olefin (pathway 1). However, isomerization

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