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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 a 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 a 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.

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 ($[CH_3CN]/[1\text{-dodecene}] = 10$, $[TBHP]/[1\text{-dodecene}] = 7$). 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 ($C_{42}H_{70}O_{35}\cdot xH_2O$, 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 tetrahydrofurane 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 × 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 multipoint calibration curves. Prior to the analyses, tetraline was added as internal standard to the reaction mixture previously dissolved in tetrahydrofurane. Subsequently, both the 1-olefins conversion and the selectivity towards the obtained products were determined. The conversion was defined as (mol of reacted 1-olefin) × (mol of starting 1-olefin)$^{-1}$ × 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:

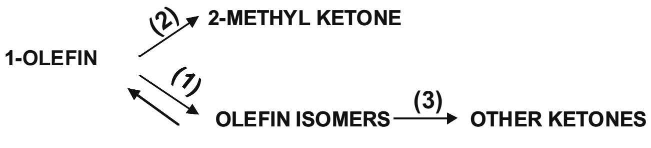
$$CH_3(CH_2)_nCH{=}CH_2 + H_2O + PdCl_2 \rightarrow CH_3(CH_2)_nCOCH_3 + Pd^0 + 2HCl \quad \text{(a)}$$

$$(CH_3)_3C{-}O{-}OH + Pd^0 + 2HCl \rightarrow PdCl_2 + (CH_3)_3COH + H_2O \quad \text{(b)}$$

However, an alternative mechanism has also proved wherein TBHP ketonizes the olefin through a peroxypalladation 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 peroxypalladium 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 peroxypalladium 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

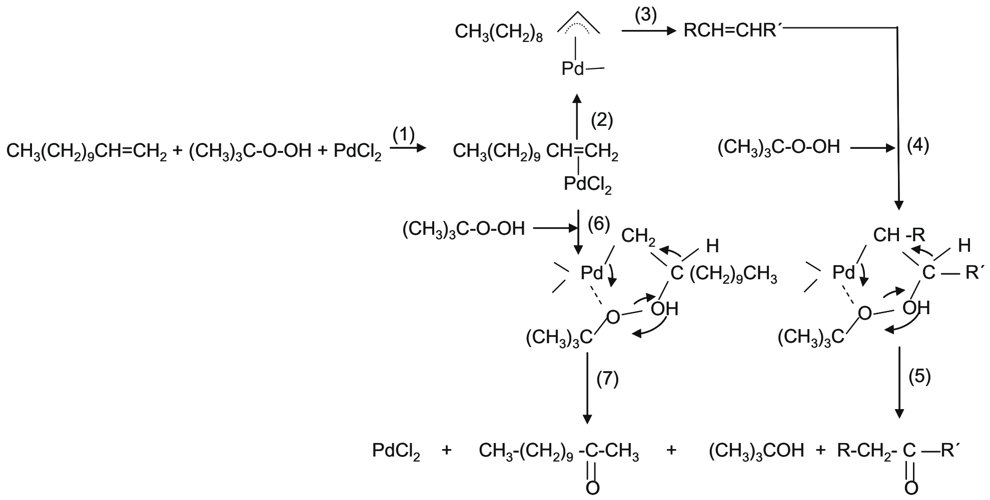


Fig. 1. Scheme of the peroxopalladation mechanism in the Wacker oxidation of 1-alkenes with TBHP. This figure was published in Applied Catalysis A: General 335(2), J. M. Escola, J.A. Botas, J. Aguado, D.P. Serrano, C. Vargas, M. Bravo, Modified Wacker Oxidation of 1-dodecene, p. 139, Copyright Elsevier, 2008.

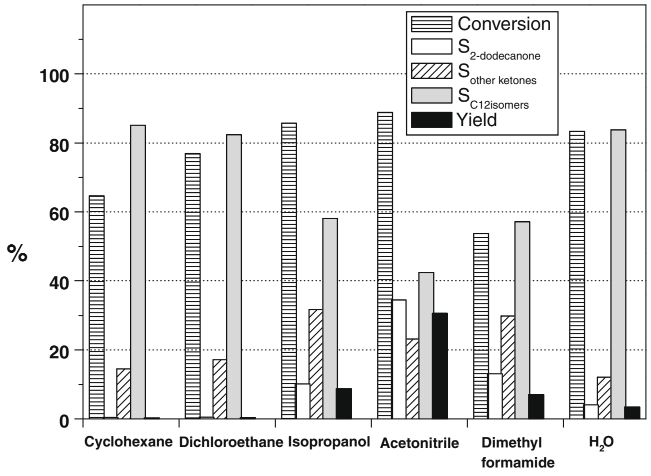


Fig. 2. Evolution of conversion, yield and selectivity in the modified Wacker oxidation of 1-dodecene using cyclohexane, dichloroethane, isopropanol, acetonitrile, dimethylformamide and water as solvents ($T = 80\,°C$, $N = 300$ rpm, time = 2 h, $[C_{12}H_{24}]/[PdCl_2] = 50$, $[solvent]/[C_{12}H_{24}] = 10$, $[TBHP]/[C_{12}H_{24}] = 6$).

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. Fig. 2 shows the results obtained in the modified Wacker oxidation of 1-dodecene at 80 °C for 2 h using different solvents: cyclohexane, dichloroethane, isopropanol, acetonitrile, dimethylformamide and water. The reactions were carried out with the suitable conditions chosen previously [20] ($N = 300$ rpm, $[C_{12}H_{24}]/[PdCl_2] = 50$, $[solvent]/[C_{12}H_{24}] = 10$, $[TBHP]/[C_{12}H_{24}] = 6$). Some of the used solvents gave rise to the formation of a monophasic system (cyclohexane, isopropanol and dimethylformamide) while the remaining solvents (acetonitrile, water and dichloroethane) render the system biphasic. The conversions were around 80% with four solvents: isopropanol, acetonitrile, water and dichloroethane. However, their respective selectivities differ meaningfully. The highest yield towards 2-dodecanone was obtained with acetonitrile as solvent (31%), with a selectivity of 35%. The yields of 2-dodecanone with the remaining solvents were far away since only isopropanol and dimethylformamide allow to get around 10%. Isomerization was above 80% with dichloroethane, water and cyclohexane while the lowest value was achieved with acetonitrile (42%). Note that dimethylformamide and isopropanol gave rise to intermediate isomerization selectivities (below 60%). In addition, both solvents also yielded considerable amounts of internal ketones (selectivity ~30%) which is noteworthy considering that they are more difficult to be oxidized [28]. No straightforward relationship could be established between the observed selectivity towards oxygenated compounds and the monophasic/biphasic nature of the used solvent. This fact suggests the occurrence of a specific interaction between acetonitrile and the catalytic species. Evidences can be found in the literature such as the variation of the reduction potential of palladium chloride depending on the chosen solvent in close Wacker systems [23].

The results obtained with acetonitrile are especially remarkable regarding that they have been obtained at 80 °C and this is a rather high temperature which is known to promote fast isomerization [20]. However, this temperature is necessary for the dissolution of heavy olefins ($>C_{12}$) into the reaction medium. Regarding the good results obtained with this solvent, it was chosen for the subsequent study with higher olefins.

3.3. Oxidation of 1-octadecene with/without β-cyclodextrins

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). This step is crucial since the solubility of this alkene is lower than that of 1-dodecene and the oxidation rate is known to decrease with increasing length of the carbon chain [8]. In addition, besides the proposed modified Wacker system, another identical system but incorporating β-cyclodextrin in a molar ratio (β-cyclodextrin)/(1-octadecene) = 1/40 was also studied in order to ascertain the effect of this phase transfer catalyst. Fig. 3 illustrates the results of conversion and selectivity obtained in the modified Wacker oxidation of 1-octadecene at 80 °C after 2 and 6 h, respectively, with or without β-cyclodextrin. Firstly, it should be mentioned that the 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, Fig. 3 shows that the presence of the β-cyclodextrin is slightly detrimental for both the conversion and the selectivity to-

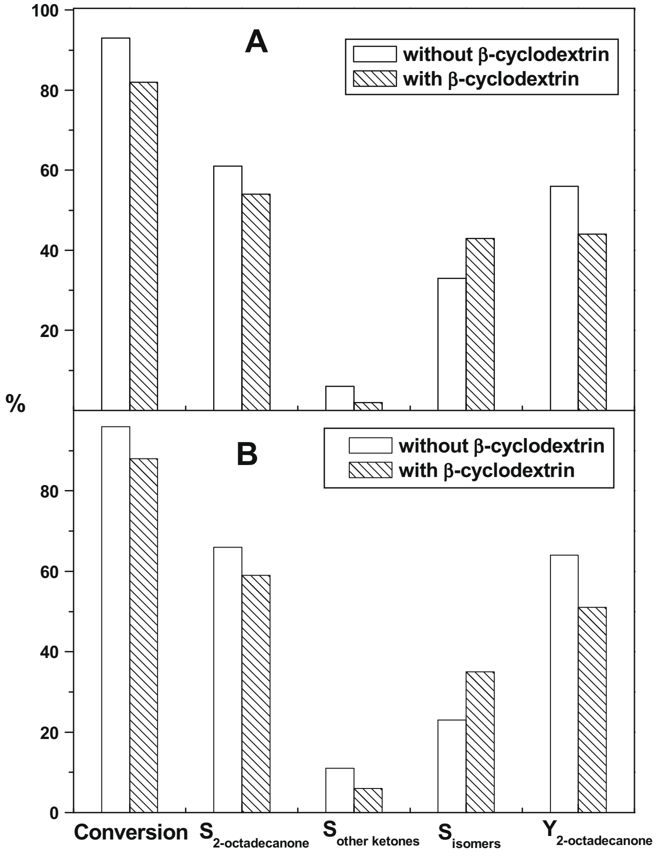


Fig. 3. Modified Wacker oxidation of 1-octadecene with and without β-cyclodextrin after 2 (A) and 6 h (B) of reaction (T = 80 °C, N = 300 rpm, $[C_{18}H_{36}]/[PdCl_2]$ = 50, $[solvent]/[C_{18}H_{36}]$ = 10, $[TBHP]/[C_{18}H_{36}]$ = 6).

wards oxygenated products (2-octadecanone + other ketones). This is in agreement with Monflier et al. results [7], wherein the occurrence of β-cyclodextrins was not useful for 1-olefins higher than C_{12}. Consequently, another way to prepare heavy ketones with higher selectivity is required.

3.4. Oxidation of 1-dodecene under the presence of n-dodecane

As it was stated in the introduction, our starting raw material for the modified Wacker oxidation was the heavy 1-olefins present in a mixture of *n*-paraffin + 1-olefin coming from the polyethylene thermal cracking at 350–400 °C. Hence, 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 in the makeup. The results obtained at 80 °C, compared to those of the oxidation of 1-dodecene without *n*-dodecane (using the same starting molar amount of 1-dodecene), are depicted in Fig. 4 and show some relevant facts. Firstly, the conversion is about 6% higher with *n*-dodecane in the mixture (95% vs. 89%). But the most striking fact comes from the selectivity data. The presence of *n*-dodecane enhances markedly the selectivity towards 2-dodecanone (63% after 2 h 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. Likewise, Fig. 4 also points out how the selectivity towards dodecene isomers is clearly lower with *n*-dodecane in the reaction medium. This unexpected result indicates that the presence of *n*-dodecane affects markedly the oxidation performance. A possible explanation of this influence stems from the variation of reduction potential of palladium chloride, in line with the work of Kaneda and co-workers [23]. However, more feasible explanation proceeds from a dilution of the concentration of 1-dodecene in the droplets when *n*-dodecane is added. This dilution effect could affect deeper the isomerization reaction than the oxidation reaction leading towards enhanced selectivities of 2-methylketone.

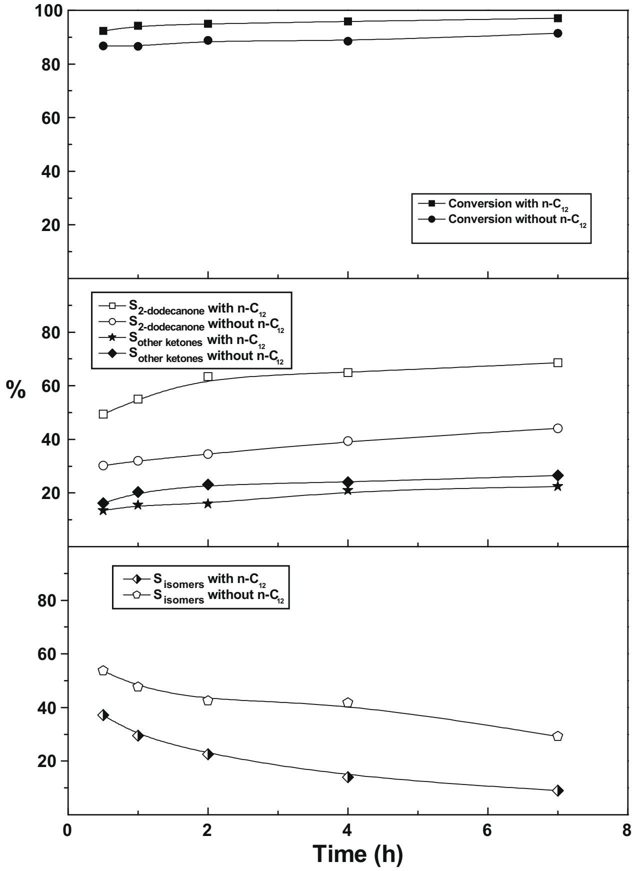


Fig. 4. Influence of the presence of *n*-dodecane in the conversion and selectivities obtained in the Wacker oxidation of 1-dodecene (T = 80 °C, $[C_{12}H_{24}]/[PdCl_2]$ = 50, $[TBHP]/[C_{12}H_{24}]$ = 6, $[CH_3CN]/[C_{12}H_{24}]$ = 10).

3.5. Oxidation of a equimolar $C_{12}^{=} + C_{16}^{=} + C_{20}^{=}$ mixture with their corresponding n-paraffins

The oxidation of equimolar mixtures of 1-dodecene, 1-hexadecene and 1-eicosene ($([C_{12}H_{24}] + [C_{16}H_{32}] + [C_{20}H_{40}])/[PdCl_2]$ = 50) with their corresponding *n*-paraffin ([1-olefin]/[*n*-paraffin] molar ratio = 1) was carried out at 80 °C in order to determine the relative rate of oxidation of the heavy 1-olefins with regard to their chain length. Fig. 5 illustrates the obtained results after 7 h of reaction. Seemingly, the conversion was similar for the three studied 1-olefins, reaching 85% after just 0.5 h of reaction, that is, the lowest time investigated. However, considerable differences can be appreciated in the selectivity among the tested 1-olefins. Hence, the selectivity towards the corresponding methyl ketones after 4 h of reaction follows the trend: $S_{2\text{-dodecanone}}$ (95%) > $S_{2\text{-hexadecanone}}$ (83%) > $S_{2\text{-eicosanone}}$ (75%), wherein the selectivity clearly decreases with the chain length of the 1-olefin. This phenomenon can be ascribed to the lower solubility of the 1-olefin with increasing molecular weight or to a competition among the alkenes for the Pd

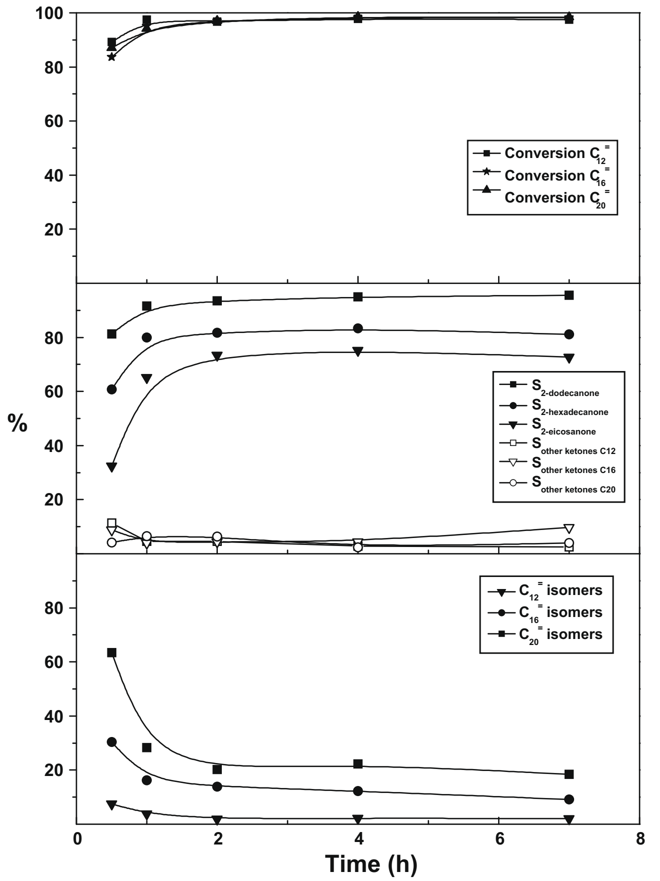


Fig. 5. Conversion and selectivity obtained in the modified Wacker oxidation of the mixture formed by 1-dodecene, 1-hexadecene and 1-eicosene with their corresponding *n*-paraffin ($T = 80$ °C, $([C_{12}H_{24}] + [C_{16}H_{32}] + [C_{20}H_{40}])/[PdCl_2] = 50$, $[TBHP]/([C_{12}H_{24}] + [C_{16}H_{32}] + [C_{20}H_{40}]) = 6$, $[CH_3CN]/([C_{12}H_{24}] + [C_{16}H_{32}] + [C_{20}H_{40}]) = 10$).

catalyst. In addition, the obtained selectivity in the mixture for 1-dodecene was higher than that with the 1-olefin alone (65%), which is likely due to the dilution effect previously indicated as its concentration is lower. The selectivity towards other ketones was similar for all the tested 1-olefins and always below 10%. In contrast, the selectivity to isomerization was enhanced with the chain length following an opposite trend to the selectivity towards 2-methyl ketone. This suggests that isomerization also occurs inside the droplet to a certain extent which is expected to affect more strongly the less soluble substrate.

3.6. Deactivation of the catalyst

Owing to the remarkable results obtained in the previous points, it was of particular interest to study the evolution of the catalytic performance after several reaction cycles to ascertain the deactivation of the catalysts. To this end, three reaction cycles were performed by adding the amount of reagents consumed after 2 h of reaction (1-dodecene and TBHP) successively to restore their initial concentration. The chosen experimental conditions were the following: $T = 40$ °C, $N = 300$ rpm, $(C_{12}H_{24})/(PdCl_2) = 50$, $(\text{solvent})/(C_{12}H_{24}) = 10$, $(TBHP)/(C_{12}H_{24}) = 6$. Fig. 6 shows the results obtained after three cycles of reaction. The conversion drops clearly in the third cycle from 65% after 2 h to 37%, which bears out the occurrence of effective catalyst deactivation. However, the selectivity towards 2-dodecanone seems to hold steady around 55% after 2 h for the three studied cycles. The decrease in activity leads towards a lower selectivity to other ketones, which drops in the 3rd cycle, likely due to the higher difficulty of these ketones to be formed in the oxidation reaction. In parallel, the amount of dodecene isomers is enhanced from the 1st to the 3rd cycle, increasing from 33% to 44% after 2 h. Therefore, the deactivation of the catalyst occurs by the aggregation of palladium into clusters and finally forming palladium black. However, this deactivation does not appear to be a continuous phenomenon as the steep decrease in conversion in the third cycle indicates. Thus, the existence of a certain critical size of these clusters is suggested which leads towards the observed decay in activity.

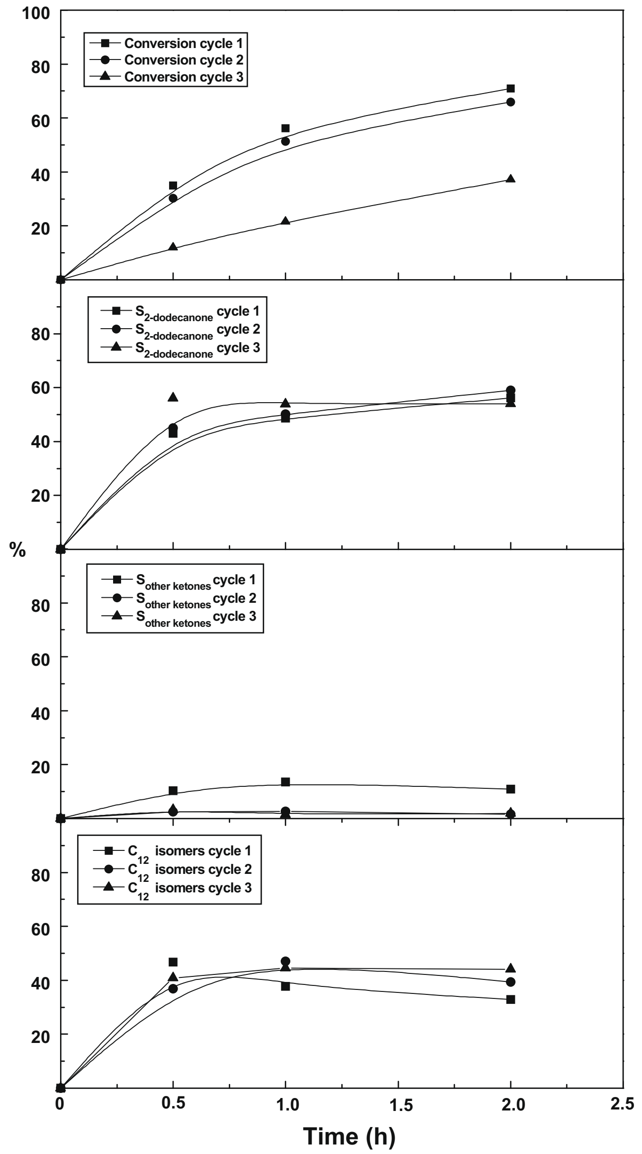


Fig. 6. Study of the catalyst deactivation in the 1-dodecene-modified Wacker oxidation ($T = 40$ °C, $N = 300$ rpm, $[C_{12}H_{24}]/[PdCl_2] = 50$, $[CH_3CN]/[C_{12}H_{24}] = 10$, $[TBHP]/[C_{12}H_{24}] = 6$).

3.7. Influence of the (1-dodecene)/($PdCl_2$) ratio

Finally, the effect of this molar ratio is investigated in order to find out the most adequate ratio to get the better balance in terms of activity and cost of the catalysts. In addition, it is interesting to determine if the catalyst can work with higher ratio since this is expected to decrease the extent of the catalyst deactivation by aggregation into clusters to form palladium black, enhancing its

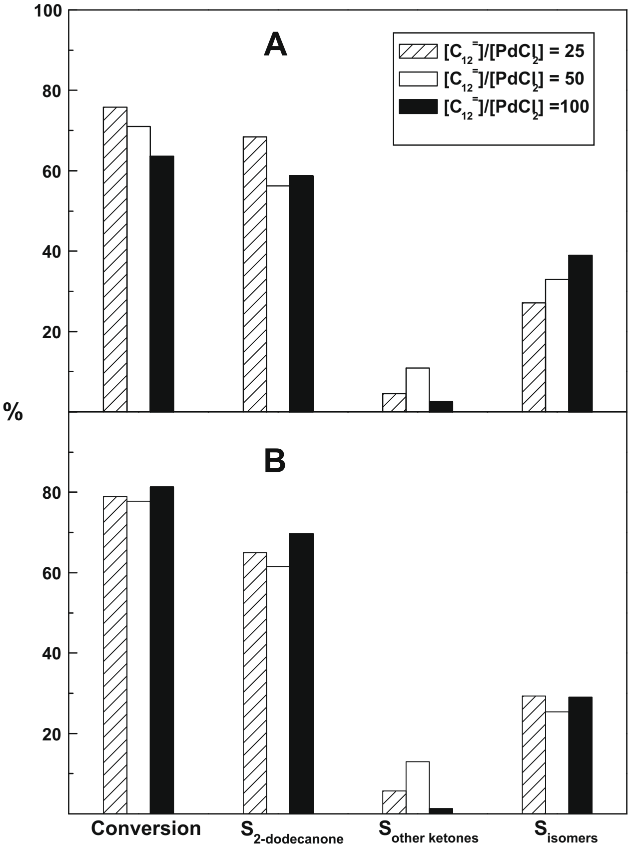


Fig. 7. Evolution of 1-dodecene conversion and selectivity in the modified Wacker oxidation using different ($C_{12}H_{24}$)/($PdCl_2$) molar ratios after 2 (A) and 4 h (B) (T = 40 °C, N = 300 rpm, [$C_{12}H_{24}$]/[$PdCl_2$] = 100, 50 and 25, [CH_3CN]/[$C_{12}H_{24}$] = 10, [TBHP]/[$C_{12}H_{24}$] = 6).

lifetime. Three (1-dodecene)/($PdCl_2$) molar ratios (25, 50, 100) were investigated with the following reaction conditions: T = 40 °C, N = 300 rpm, ($C_{12}H_{24}$)/($PdCl_2$) = 100, 50 and 25, (CH_3CN)/($C_{12}H_{24}$) = 10, (TBHP)/($C_{12}H_{24}$) = 6 and t = 2 and 4 h. Fig. 7 illustrates the obtained results after 2 h (A) and 4 h (B). It can be clearly observed that after 2 h, the conversion varies within 60–70% while after 4 h, the conversions are rather similar (80%) for the three studied ratios. The selectivity towards 2-dodecanone was higher after 2 h for a (1-dodecene)/($PdCl_2$) = 25 (68%) while the selectivity for the three studied ratios was similar (65%) after 4 h. In addition, the selectivity towards other ketones was higher for a (1-dodecene)/($PdCl_2$) = 50 (10%) but was negligible for a (1-dodecene)/($PdCl_2$) = 100 (<2%). Considering these results as a whole, it seems that the usage of a (1-dodecene)/($PdCl_2$) ratio of 100 seems enough for getting reasonable selectivity towards 2-dodecanone. In addition, higher ratio (lower amount of catalyst by raw material) is expected to increase the catalyst lifetime by reducing its agglomeration into clusters.

4. Conclusions

The reported modified Wacker system with TBHP as oxidant and acetonitrile as solvent has been proved useful in the oxidation of the heavy 1-olefins within the C_{12}–C_{20} range at 80 °C. 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 isomerization reaction. On the other hand, the oxidation of a 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 towards 2-methylketones within 70–90%, enhancing with decreasing chain length. This is related to the higher solubility of lower molecular weight compounds.

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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