Ether synthesis from alcohol and aldehyde in the presence of hydrogen and palladium deposited on charcoal

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Abstract

The synthesis of ether from octanal and butanol was investigated on a Pd/C catalyst at 100°C under hydrogen pressure. It was shown that the acidity of the catalyst support allows conversion of the octanal mainly to dibutylketal and to traces of enolether under the equilibrium conditions. The enolether is hydrogenated to butyloctylether on the palladium particles. The reduction procedure of the Pd/C catalyst has a high influence on the rate of ether formation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Palladium on charcoal; Ketal hydrogenation; Enolether hydrogenation; Ether synthesis
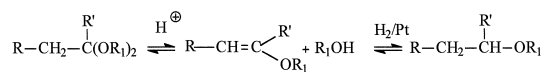
1. Introduction

In the literature, the synthesis of ethers from ketones or aldehydes and alcohols is reported in presence of hydrogen and metals from the platinum group in alcoholic acid. The hemiketal, the ketal and the enolether are suggested as possible intermediates since, in acidic solution, hydrogenation of the ketal on platinum gives the same product as that of the mixture of the carbonyl compound and the alcohol [1]. The ketal would be converted to saturated ether following Scheme 1.

On rhodium/alumina catalyst, the same mechanism is suggested for ketal hydrogenation with the enolether as reaction intermediate, the presence of which in the reaction mixture seems to be evidenced [2].

More recently, the synthesis of ethers with good yields was reported from aldehydes or ketones and alcohols using a palladium on charcoal as catalyst, without any acid addition [3]. This new method has been described for primary and secondary alcohols (Scheme 2). The reaction proceeds in the liquid phase at 100°C under a hydrogen pressure of 40 bar.

The ether thus obtained is stable under the reaction conditions, whereas in the presence of other catalysts it may be hydrogenolysed [4].

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$$R-CH_2-\overset{\overset{\displaystyle R'}{|}}{C}(OR_1)_2 \;\rightleftharpoons\; \overset{H^{\oplus}}{} \;R-CH=C\overset{\displaystyle R'}{\underset{\displaystyle OR_1}{\diagup}} + R_1OH \;\overset{H_2/Pt}{\rightleftharpoons}\; R-CH_2-\overset{\overset{\displaystyle R'}{|}}{C}H-OR_1$$

Scheme 1. Ketal hydrogenolysis [1].

The main goal of this study was to investigate the role of the Pd/C catalyst in the course of ether synthesis from octanal and butanol.

2. Experimental

2.1. Catalysts

A charcoal (L 2S from CECA, BET surface area 920 m^2/g) and a silica (from Degussa, surface area 200 m^2/g) were used as catalyst supports. The charcoal was treated for 10 h at 1000°C under hydrogen to reduce any sulphur-containing impurity. Then, it was oxidised in concentrated nitric acid at 100°C for 10 h and then washed with distilled water. The silica was treated in diluted nitric acid (1 M) for 10 h in order to eliminate alkaline impurities, then calcined in air at 500°C for 5 h. Monometallic 10 wt.% Pd/charcoal and 10 wt.% Pd/silica catalysts were prepared by impregnation of $PdCl_2$ dissolved in water. After drying overnight in air at 120°C, the catalysts were reduced at 100°C for 2 h under hydrogen flow.
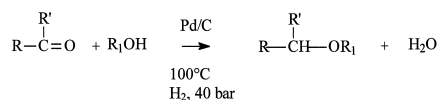
2.2. Chemicals

Octanal (Janssen, 99%), 1-butanol (Aldrich, 99.8%), acetaldehyde di-*n*-hexylketal (Lancaster, 98%), 1-hexanol (Aldrich, 98%), 2,2-dimethylpropanal (Aldrich, 99%) and 1-octanol (Aldrich, 99%) were used as received.

2.3. Experiments

The experiments were carried out in a 300 ml stirred autoclave (Autoclave Engineers) fitted with a system for liquid sampling.

In a typical experiment, 100 mg of catalyst and 90 ml of solvent (1-butanol) were poured into the autoclave that was flushed first with nitrogen and second with hydrogen. The temperature was raised to 100°C under 0.1 MPa of hydrogen. Then, a mixture of substrate (3.1 ml of octanol) and of 1-butanol (10 ml) was loaded into the autoclave through a cylinder under a 4 MPa hydrogen pressure. Zero time was taken at this moment and stirring was switched on.

Liquid samples drawn from the liquid phase were analysed by VPC on a Varian 3400 chromatograph (equipped with a flame ionisation detector and a capillary column DB 1701 (J and W, 30 m, 0.25 mm i.d.) using hydrogen as carrier gas.

$$R-\overset{\overset{\displaystyle R'}{|}}{C}=O \; + R_1OH \;\underset{\underset{\displaystyle H_2,\,40\ bar}{100°C}}{\overset{Pd/C}{\longrightarrow}}\; R-\overset{\overset{\displaystyle R'}{|}}{C}H-OR_1 \; + \; H_2O$$

Scheme 2. General method for the synthesis of ethers using a 10 wt.% Pd on charcoal catalyst [3].

3. Results and discussion

Previous studies carried out by Bethmont et al. [3] led the authors to suggest the following scheme for the synthesis of butyloctylether from octanal (substrate) and 1-butanol (solvent) on a Pd/C catalyst under hydrogen:
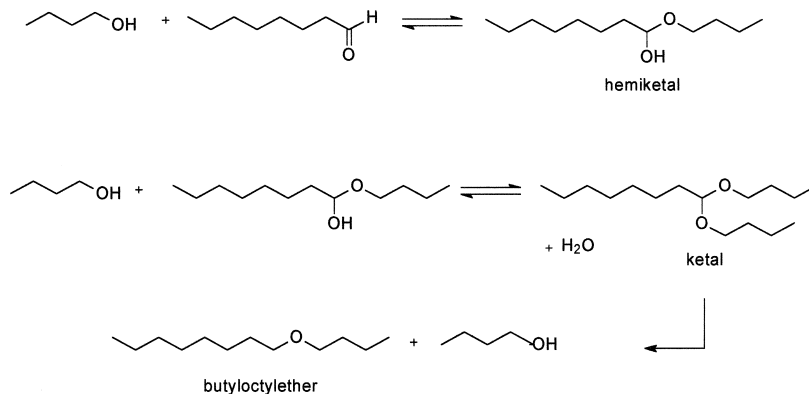
In the present study, we investigate the role of the Pd/C catalyst in the course of the two main steps of the reaction: the ketal formation and the conversion of the ketal into ether.

3.1. Ketal formation

The first step of the reaction (ketal formation) was studied at 100°C under nitrogen. When a mixture of 1-butanol and octanal was heated in the presence of the Pd/C catalyst, octanal was quickly converted into dibutyloctylketal which was the main product of the reaction, (Fig. 1). It was identified by GC-MS analysis, which revealed also the presence of a small amount (near 1–2 mol%) of the enolether (butyl-1-octenylether). This result shows that the equilibrium octanal + 1-butanol ⇔ ketal + H_2O is strongly shifted to ketal formation under the experimental conditions used in this work. Otherwise, without catalyst, the rate of ketal formation was very low (conversion < 2 mol% after 120 min reaction time). These observations point out the prominent role played by the Pd/C catalyst in the reaction under study.
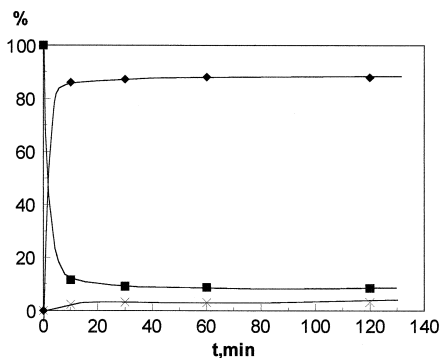
Fig. 1. Octanal conversion on the Pd/C catalyst under nitrogen: ■ octanal, ♦ ketal, × enolether.

Table 1
Octanal conversion under nitrogen on Pd/C (a) and pre-treated charcoal (b)

Time (min)	Octanal (%)		Ketal (%)		Enolether (%)	
	a	b	a	b	a	b
0	100.0	100.0	0.0	0.0	0.0	0.0
10	11.5	15.0	86.1	82.1	2.3	2.9
30	9.1	10.0	87.3	87.0	3.2	3.0
60	8.7	9.5	88.1	87.5	3.1	3.0
120	8.5	9.0	88.0	88.1	3.2	2.9

The same experiment was carried out on the pre-treated activated carbon that was used for the preparation of the Pd/C catalyst. The results reported in Table 1 show similar rates for ketal formation on the Pd/C catalyst and on the pre-treated activated carbon. Thus, the carbon support is responsible for the ketal formation on the Pd/C catalyst. On the other hand, the same experiment performed in the presence of the unpretreated activated carbon did not led to ketal formation with a significant rate. This result means that the acid treatment is a requisite in order to promote the activity of the CECA L2S carbon for ketal formation from octanal and 1-butanol.

The nitric acid treatment of the carbon support is known to generate acidity as it creates carboxylic groups at the carbon surface. This effect is borne out by the pH values taken by the slurries made of water and of the different catalysts (Table 2). Indeed, the pretreated carbon in water led to an acidic pH (3.9), while with the unpretreated carbon, it remained near neutrality. Otherwise we observe that the pretreated carbon and the Pd/C catalyst led to comparable pH when slurried in water, which is in accordance with the observed acid catalysis for ketal formation. Finally, chemical analysis of the activated carbon showed a large increase of the oxygen content after the nitric acid treatment, in accordance with the formation of carboxylic groups on the carbon surface.

In conclusion, these different experiments showed that the acidic sites on the carbon surface are responsible for the activity of the Pd/C catalyst in the ketal formation from octanal and 1-butanol.

3.2. Ether synthesis

The reaction procedure was the same as that used for ketal formation, but nitrogen was replaced by hydrogen (0.1 MPa) before the heating of the reactor. Thus, the Pd/C catalyst was reduced during heating prior to the introduction of the substrate (octanal) and hydrogen (4.0 MPa) into the autoclave.

The curves reported in Fig. 2 show that the reaction carried out under hydrogen leads to the formation of butyloctylether, whereas this product was not observed under nitrogen. Moreover, the ketal concentration goes through a maximum for a 10-min reaction time, then decreases as the ether is formed. This trend shows that the dibutyloctylketal really is an intermediate of the butyloctylether

Table 2
Values of pH taken by slurries made of water and catalysts

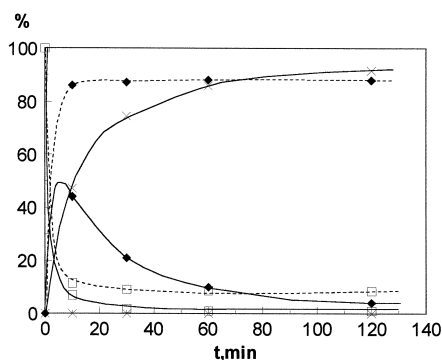| Catalyst	pH
Charcoal pretreated in HNO_3	3.9
Unpretreated charcoal	7.6
Pd/C catalyst	3.8
Pd/SiO_2	6.8

Fig. 2. Octanal conversion on the Pd/C catalyst under nitrogen: dotted lines, and under hydrogen: full lines,: □ octanal, ◆ ketal, × ether.

synthesis from octanal and butanol. Moreover, the low octanol concentration detected after a 2 h reaction time states as previously mentioned [3] the low efficiency of palladium for the aldehydic carbonyl reduction.

Thereafter we studied the effect of the reduction process of the Pd/C catalyst on its activity for the ketal conversion. The Pd/C catalyst was either (i) directly introduced into the autoclave and reduced under hydrogen at 100°C after immersion into the butanol (in situ reduction) or (ii) pre-reduced under hydrogen at 100°C in the gas phase and transferred into the autoclave without exposure to air (ex situ reduction). The curves reported in Fig. 3 show that the activity of the Pd/C catalyst for ether formation strongly depends on the activation procedure, since the ex situ reduction led to a far less active catalyst. On the other hand, the ketal formation was not affected by the reduction mode of the Pd/C catalyst. Indeed, the equilibrium octanal + butanol ⇌ dibutyloctylketal + water was strongly shifted to ketal formation after a 10-min reaction time whatever the experimental reduction conditions of the Pd/C catalyst.

Two hypotheses can be put forward to explain the different behaviour of the Pd/C catalyst for the ether synthesis: the first one is that the in situ reduction of the catalyst produced water which remained in the reaction mixture and may modify the activity of the metal particles for the hydrogenolysis of the ketal to ether. On the contrary, this water was eliminated in the course of the ex situ reduction and so was not present in the autoclave. The second hypothesis is that the structure of
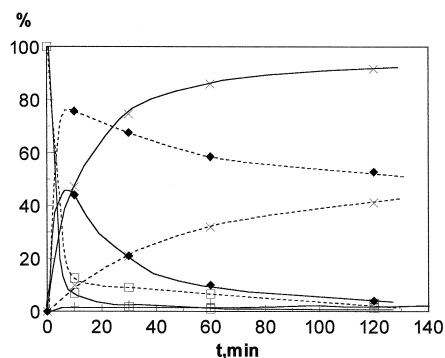

Fig. 3. Octanal conversion under hydrogen on the Pd/C catalyst reduced ex situ: dotted lines, and in situ: full lines.: □ octanal, ◆ ketal, × ether.

Table 3
Octanal conversion under hydrogen on ex situ reduced Pd/C: without addition of water (a) and with addition of water (b)

Time (min)	Octanal (%)		Ketal (%)		Ether (%)		Octanol (%)	
	a	b	a	b	a	b	a	b
0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
10	12.6	13.0	75.6	74.8	9.9	10.2	1.8	2.0
30	9.1	10.8	67.6	66.9	20.9	18.7	2.4	3.6
60	6.6	8.3	58.5	57.0	31.9	30.9	2.9	3.8
120	3.1	5.9	52.8	48.0	41.1	42.1	3.0	4.0

the catalyst and particularly the average metal particle size depend on the activation process, leading to different catalytic properties.

The effect of water was studied by adding water (0.1 ml) to the substract (octanal) before its introduction on the ex situ reduced catalyst. The values reported in Table 3 point out that water did not promote the activity of the pre-reduced catalyst for ether synthesis. In order to check the second hypothesis, the Pd/C catalysts were observed by transmission electronic microscopy (TEM) after the test reaction. The TEM micrographs have revealed that the average size of the metal particles was affected by the reduction process. Indeed, the in situ reduction led to larger palladium particles. The average sizes calculated from the histograms of metal size distributions were 19.0 nm and 11.0 nm for the in situ and the ex situ reduced catalysts, respectively. (Table 4). Likewise, the DRX characterization of the used catalysts allowed to calculate the mean diameter of metal particles from the diffraction line width using the Debye–Sherrer equation. After ex situ reduction, the average diameter was near 10 nm while it was 18.0 nm after in situ reduction (Table 4). These different values show that the average metal particle size is affected by the reduction process and that probably it is the main reason for the different activities observed on the Pd/C catalyst after ex situ and in situ reductions. Thus, this ether synthesis would be a metal structure sensitive reaction which would occur preferentially on the large palladium particles.

In order to investigate the mechanism of ether formation from the ketal we studied the conversion of a commercial ketal (acetaldehyde di-n-hexylketal) over in situ reduced Pd/C and Pd/SiO$_2$

Table 4
Average particle diameters of Pd catalysts deduced from electronic microscopy (Me$^-$) and X-ray diffraction (DRX)

Catalyst	$\bar{d}$ (nm); (Me$^-$)	$\bar{d}$ (nm); (DRX)
In situ reduced Pd/C	19.0	18.0
Ex situ reduced Pd/C	11.0	10.5
Pd/SiO$_2$	17.0	16.0

Table 5
Acetaldehyde di-n-hexylketal conversion under hydrogen on in situ reduced Pd/C (a) and Pd/SiO$_2$ (b)

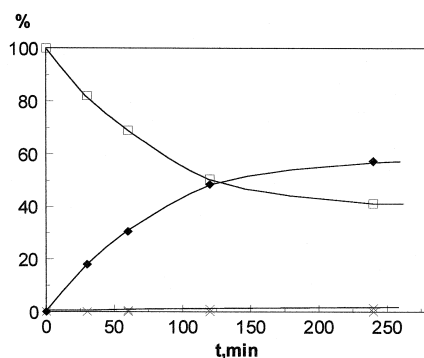| Time (min)	Acetaldehyde di-n-hexylketal (%)		Ethylhexylether (%)	
	a	b	a	b
0	100.0	100.0	0.0	0.0
10	39.7	99.8	60.3	0.2
30	8.0	99.7	92.0	0.3
60	1.0	99.5	99.0	0.5
120	0.9	99.5	99.1	0.5

Fig. 4. Pivaldehyde conversion on the Pd/C catalyst.: □ pivaldehyde, ◆ ketal, × ether.

catalysts. These two catalysts have comparable metal particle sizes (Table 4) but different support acidities since the pH of a mixture of water and Pt/SiO_2 remains neutral. The results of the reaction of the ketal over the Pd/C and Pd/SiO_2 catalysts are shown in Table 5.

In accordance with the results reported in the first part of this paper, the ketal was quickly converted to ether over the in situ reduced Pd/C catalyst. On the other hand, the rate of ether formation was very low in the presence of the in situ reduced Pd/SiO_2 catalyst. These results indicate that the formation of ether does not occur by direct hydrogenolysis of a C–O bond of the ketal on the metal function and that the acid function of the support plays a key role for ether formation from the ketal. Indeed, the protonation of the ketal allows the formation of the enolether (Scheme 1) followed by the hydrogenation to the ether on palladium particles. In order to bear out such a scheme, we studied the reaction between pivaldehyde (2,2-dimethylpropanal) and 1-octanol over the in situ reduced Pd/C catalyst at 100°C under hydrogen. This aldehyde was chosen because it does not allow the formation of enolether as intermediate product since it has no hydrogen in α position of the carbonyl function. The curves reported in Fig. 4 show that the pivaldehyde is converted to the ketal but the rate of ether formation is very low. This result shows clearly that the formation of ether would occur via the hydrogenation of the corresponding enolether on the metal function. The low ether formation from pivaldehyde could only result from the slow hydrogenation of the protonated intermediate species A shown in Scheme 3.
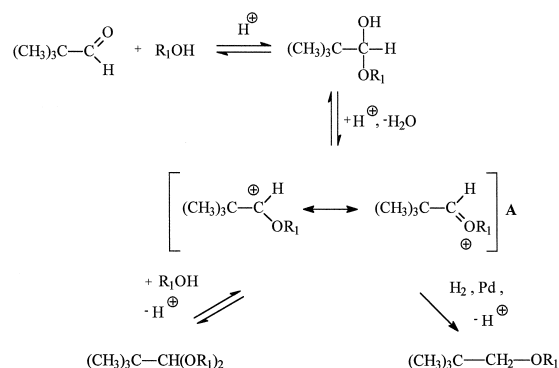
Scheme 3.

4. Conclusion

The results reported in this paper show that the support acidity of a Pd/C catalyst is responsible for the formation of the ketal and of the enolether from octanal and butanol. The enolether is hydrogenated to the ether on the palladium crystallites, the large particles being more active than the small ones.

Acknowledgements

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