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Recycling in telomerization of butadiene with D-xylose: Pd(TPPTS)$_n$-KF/Al$_2$O$_3$ as an active catalyst

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A palladium-TPPTS catalyst heterogenized on KF/alumina has been shown to be effective and recyclable for the selective formation of monooctadienylxylopyranosides via the telomerization of butadiene with D-xylose. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: palladium; KF/Al$_2$O$_3$; TPPTS; telomerization; sugar; butadiene; recycling

INTRODUCTION

Over recent years we have pursued the goal of valorization of agricultural by-products based on the Pd-catalyzed telomerization of butadiene with pentoses.[1–4] Such a reaction affords biodegradable nonionic surfactants from renewable materials.[5] Although low amounts of palladium-based catalysts are generally sufficient to achieve the telomerization of butadiene with nucleophiles,[6–11] the cost of the metal necessitates the development of recyclable systems. We have previously reported the use of a 1 : 3 mixture of Pd(acac)$_2$ and (m-NaSO$_3$C$_6$H$_4$)$_3$P (TPPTS) as the catalyst for the telomerization of butadiene with pentoses; the first recycling was efficient but the conversion dropped dramatically for the second recycling.[12] This led us to direct our research toward the use of heterogeneous catalysts.[13,14] In the course of these studies, we have observed that a Pd-TPPTS catalyst heterogenized on KF/Al$_2$O$_3$ was effective and recyclable for the telomerization of butadiene with D-xylose to selectively afford monooctadienylxylopyranosides [eqn (1)]. A recent US patent[15] urges us to report our results.

EXPERIMENTAL

The catalyst, prepared as previously reported[13,16] (527 mg, 0.067 equiv. of palladium), was introduced into an autoclave (50 ml) equipped with a magnetic stir bar. After three vacuum–argon purges, the degassed solution of D-xylose (1 g) and *N*,*N*-dimethyldodecylamine (1.16 ml) in DMF (5 ml) was added under argon. The autoclave was cooled to −20 °C in a bath of acetone–liquid nitrogen. Butadiene (0.08 mol, 7 ml) condensed at −20 °C in a Schlenk tube was carefully transferred into the autoclave under argon. After heating in an oil bath at 80 °C for 1 h, the autoclave was cooled to room temperature and carefully opened under a hood (possible butadiene emanations). The catalyst was recovered by filtration. The liquid phase containing unreacted xylose and corresponding ethers was acetylated and analyzed by GC/MS as previously described.[2] The recovered catalyst was dried under vacuum (10^{-2} mmHg, 2 h at room temperature) and reused without further treatment.

DISCUSSION

With 0.067 equiv. of palladium, a stoichiometric amount of *N*,*N*-dimethyldodecylamine and an excess of butadiene, the sugar conversion attained 81% in 1 h at 80 °C with formation of 77% of the monoethers and 4% of the diethers identified as previously reported[2] (Table 1, run 1). The catalyst was recovered by filtration; its reuse under similar experimental conditions led to the slight decrease of the conversion, but the selectivity was preserved (run 2). The second and third recyclings led to similar decreases of the conversion (runs 3 and 4). However, the selectivity increased to almost 100% for the third recycling. The similarity of the conversions and yields of the third and fourth recyclings (runs 4 and 5) suggest the preservation of the catalyst activity for a number of supplementary recyclings.

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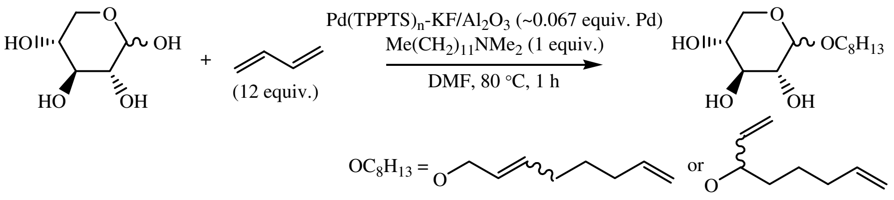

(1)

Table 1. Telomerization of butadiene with D-xylose using Pd(TPPTS)$_n$-KF/Al$_2$O$_3$ ($n = 2-3$) as the catalyst

Run[a]	Conversion of D-xylose	Yield of monoethers
1	81%	77%
2	77%	73%
3	72%	71%
4	66%	65%
5	68%	67%

[a] Experimental conditions: run 1—D-xylose (1 g), DMF (5 ml), Pd/D-xylose–Me(CH$_2$)$_{11}$NMe$_2$–butadiene ≈ 1 : 150 : 150 : 1800, 80 °C, 1 h; runs 2–5—as for run 1 except that the catalyst recovered from the preceding run was used.

Given the results collected in Table 1, a global turnover number higher than 500 was attained in five successive runs for this atom-efficient chemical process, which is in good agreement with the concept of 'atom economy'.[17,18] We have not been able to determine whether the reaction proceeds in a truly heterogeneous manner. Nevertheless, it appears that the heterogeneous support traps and stabilizes active low valence-palladium species.

In conclusion, Pd(TPPTS)$_n$-KF/Al$_2$O$_3$ is an efficient heterogeneous catalyst for the telomerization of butadiene with D-xylose. This system is easy to recover and its reuse occurs with low loss of activity.

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