

Letter

Telomerization of butadiene with water catalyzed by heterogeneous palladium catalysts

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Abstract

The telomerization of butadiene with water in the presence of heterogeneous palladium catalysts was investigated. Among various heterogeneous palladium catalysts, palladium anchored on montmorillonite showed good activity and selectivity to octadienol comparable to those of a homogeneous palladium acetate catalyst. The palladium catalyst anchored on montmorillonite could be recycled with no loss in activity and selectivity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The palladium catalyzed reaction of butadiene with water to octadienols was reported first by Atkins et al. [1]. Usually, homogeneous palladium complex catalysts have been used for the telomerization of butadiene with water [2–4]. However, in the homogeneous catalyst system, the problem of separating the homogeneously dissolved catalyst from the reaction mixture is a serious disadvantage for practical applications.

Heterogeneous catalysts appear very attractive from an industrial point of view, as they could be easily separated from the reaction products and recycled. However, heterogeneous catalysts employed for the liquid phase reaction often show leaching of palladium into the reaction medium and a reduced activity compared to the homogeneous counterparts. Recently, a swelling-type layered silicate clay, montmorillonite, has been reported to be an excellent support for immobilization of cationic transition metal complexes to conduct solution-like reactions in the solid state [5–8]. These heterogenized catalysts involving anchored palladium showed good activity in many reactions including dimerization of alkenes. In this paper, we

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wish to describe the performance of heterogeneous palladium catalysts in the telomerization of butadiene with water.

2. Experimental

Palladium catalysts supported on alumina were prepared by an incipient wetness impregnation method with γ -alumina (Strem Chemicals, BET surface area = 95 m²/g) and an organic solution containing the desired amount of palladium. Palladium acetate was used as the catalyst precursor. The prepared samples were dried in an oven at 383 K for 24 h and calcined in oxygen flow at 773 K for 2 h. Optionally, the samples were reduced in hydrogen flow at 573 K for 2 h. Palladium on activated carbon was a commercial product purchased from Aldrich.

To prepare palladium anchored on montmorillonite, a commercial Na–montmorillonite (Aldrich) was treated with a HCl solution to obtain the proton form of montmorillonite. The H–montmorillonite was refluxed with 3-aminopropylethoxysilane solution for 48 h. The silane-exchanged montmorillonite was complexed with palladium ion during the reflux with a palladium-containing solution, and then was subjected to Soxhlet extraction for 24 h. Finally, the prepared samples were dried in an oven at 383 K for 24 h.

The telomerization of butadiene with water was performed in a 100-ml stainless steel autoclave reactor (Autoclave Engineers). Typically, palladium catalyst (Pd content 0.5 mmol), triphenylphosphine (1.5 mmol), H₂O (0.5 mol), and solvent (40 ml) were introduced under nitrogen atmosphere and then 1,3-butadiene (0.25 mol) was charged. The reactor was pressurized with carbon dioxide to 200 psi at room temperature, and the contents were heated to 363 K and kept at this temperature for a desired reaction time with vigorous stirring. During the reaction, the reaction mixture was sampled and analyzed by a gas chromatograph (GC, HP 6890) with a 60 m AT-1 capillary column, and a flame ionization

detector. Products were identified by GC-mass spectroscopy (HP 5972 MSD) and NMR analysis.

3. Results and discussion

The reaction of butadiene with water using palladium acetate and triphenylphosphine as a homogeneous catalyst system gave a high TOF (turnover frequency = number of moles of butadiene reacted per mole of metal per hour) of 259 h⁻¹ at 363 K. Product distribution is as follows (selectivity in parenthesis): 2,7-octadien-1-ol (74.8%); 1,7-octadien-3-ol (7.2%); 1,3,7-octatriene (8.1%); and 1-methylene-2-vinylcyclopentane (6.6%). The distribution of products in heterogeneous catalyst systems is similar to that observed in the homogeneous catalyst system.

Typical results for the telomerization of butadiene with water over different heterogeneous catalysts are presented in Table 1. Both 5% Pd/C and 5% Pd/Al₂O₃ provided lower TOFs of 50–80 h⁻¹ compared to the homogeneous counterpart. The TOFs for heterogeneous catalysts are based on surface Pd atoms titrated by CO chemisorption at room temperature. This is justified by the finding that there is negligible dissolution of palladium metal into the reaction medium. The dispersions of palladium calculated from CO chemisorption assuming 1:1 chemisorption of CO on surface palladium atom were 49.5% for 5% Pd/C, 65.0% for 5% Pd/Al₂O₃, and 50.5% for 5% Pd/Al₂O₃ (R). The 5% Pd/C catalyst gave better activity in acetone (Run 2) than in DMF (Run 3) as a solvent. However, 5% Pd/Al₂O₃ showed higher activity in DMF (Run 7) than in acetone (Run 5). The origin of this mild solvent effect is not clear. When 5% Pd/Al₂O₃ was reduced in hydrogen, the catalytic activity was decreased (Run 6). It appears that an oxidized palladium is more active than Pd (0) in this reaction system. To investigate the occurrence of palladium leaching, heterogeneous catalysts including pal-

Table 1

Telomerization of butadiene with water over various palladium catalysts

Reaction conditions: butadiene = 0.25 mol, H₂O = 0.5 mol, Pd = 0.5 mmol, Ph₃P = 1.5 mmol, acetone = 40 ml, CO₂ = 200 psi, temperature = 363 K, time = 10 h, acetone solvent if not otherwise noted.

Run	Catalyst	C ₄ H ₆ conversion (%)	Selectivity (%)					TOF (h ⁻¹)	
			2,7- Octadien- 1-ol	1,7- Octadien- 3-ol	1,3,7- Octatriene	1-Methylene 2-vinyl cyclopentane	4-Vinyl cyclohexene		High molecular weight
1 ^a	Pd(II)(CH ₃ CO ₂) ₂	77.6	74.8	7.2	8.1	6.6	0	3.3	259
2	5% Pd/C	82.2	74.5	9.3	9.5	2.1	1.4	3.3	83
3 ^b	5% Pd/C	31.2	56.9	4.7	19.2	4.8	3.8	10.6	32
4 ^c	5% Pd/C	8.9	49.1	6.4	13.5	0	0	31.1	10
5 ^d	5% Pd/Al ₂ O ₃	71.3	71.9	11.9	4.8	1.5	2.2	7.7	55
6 ^e	5% Pd/Al ₂ O ₃ (R)	45.7	66.3	14.6	5.4	1.6	3.0	8.9	46
7 ^f	5% Pd/Al ₂ O ₃	83.5	65.1	8.2	5.4	0.9	0.9	19.6	65
8 ^g	5% Pd/Al ₂ O ₃	80.2	60.3	8.0	3.9	0.7	1.5	25.6	62
9 ^h	Montmorillonite Si(CH ₂) ₃ NH ₂ Pd	70.8	77.3	7.8	6.7	3.5	1.0	3.6	216

^aReaction time = 1.5 h.^bDMF instead of acetone.^cDMF instead of acetone. Solid catalyst was recycled from run 3.^dCatalyst was calcined in oxygen at 873 K for 2 h before reaction.^eCatalyst was reduced in H₂ at 573 K for 2 h before reaction.^fDMF instead of acetone. Catalyst was calcined in oxygen at 873 K for 2 h before reaction.^gDMF instead of acetone. Catalyst was calcined in oxygen at 873 K for 2 h before reaction. Solid catalyst was recycled after the catalyst from run 7 was calcined in oxygen at 873 K for 2 h.^hPd = 0.082 mmol.

ladium anchored on montmorillonite were filtered from the reaction solution after the reaction and palladium contents of the liquid phase were analyzed by atomic absorption spectroscopy. In all cases, palladium in solution was less than 1% of total Pd in catalysts. This indicates that these heterogeneous catalysts for the telomerization of butadiene with water do not release palladium into the reaction medium to a significant extent. However, when 5% Pd/C was separated from the liquid products and recycled (Run 4) under the same conditions as for the fresh catalysts (Run 3), a low activity was observed. It appears that the catalyst has been deactivated by high-molecular-weight carbon products. Thus, when deactivated 5% Pd/Al₂O₃ catalyst was treated under oxygen flow at 573 K for 2 h, the same activity (Run 8) as the fresh catalyst (Run 7) was obtained. Furthermore, Fig. 1 shows CO₂ evolution in temperature-programmed oxidation (TPO) of 5%

Pd/Al₂O₃ used in Run 7. The TPO was carried out for 0.1 g of the catalyst in 1% O₂/He flow (2.2 μmol/s) with a heating rate of 10 K/min.

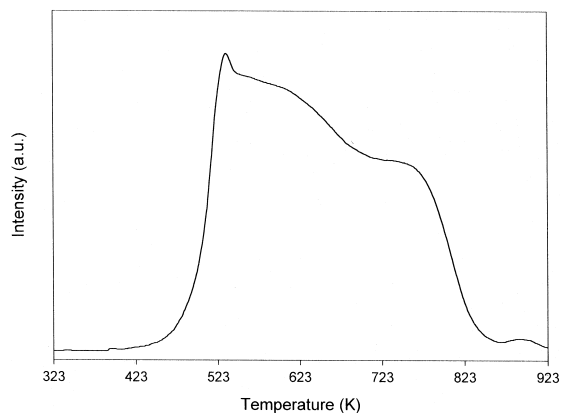


Fig. 1. CO₂ evolution in TPO of 5% Pd/Al₂O₃ used at 363 K for the telomerization of butadiene with water (Run 7 of Table 1). The flow rate of 1% O₂/He = 2.2 μmol/min, heating rate = 10 K/min, catalyst = 0.1 g.

The CO₂ evolution was observed between 473 and 873 K.

Palladium anchored on montmorillonite showed high catalytic activity and selectivity to telomer, and it was very stable under this reaction condition. The observed TOF (216 h⁻¹) for the anchored catalyst (Run 9) was almost the same as that for homogeneous Pd(CH₃CO₂)₂ catalyst (Run 1). The TOF was based on total palladium contained in the catalyst like the homogeneous catalyst because palladium is present as a molecular species in this catalyst. This also indicates that there is no mass-transfer limitation of reactants between liquid phase and palladium located in the interlayer space of the clay. The effects of different silane ligands and palladium precursors on palladium–montmorillonite are shown in Table 2. Among various palladium precursors, palladium acetate (Run 9) gave more active catalyst than chlorine-contain-

ing palladium precursors (Runs 11–13). In a homogeneous catalytic system, palladium chloride also showed lower activity than palladium acetate under the same reaction conditions (Run 10). Chloride ions appear to block free coordination sites at palladium and inhibit palladium from coordinating with phosphine [9]. Palladium–montmorillonite showed a higher activity in DMF (Run 15) than in acetone (Run 9) as was also observed for 5% Pd/Al₂O₃. To check if the catalytic system was really heterogeneous, the liquid product solution was separated from palladium–montmorillonite, and recycled by charging a fresh batch of butadiene. The recycled solution had no activity. Also, when Pd–montmorillonite was separated from the liquid products and reused as catalyst under the same conditions as for the fresh catalyst (Run 14), the same activity and selectivity of the original experiment (Run 9) was reproduced. This sug-

Table 2

Telomerization of butadiene with water over various palladium–montmorillonite catalysts

Reaction conditions: butadiene = 0.25 mol, H₂O = 0.5 mol, Pd = 0.5mmol, Ph₃P = 1.5 mmol, acetone = 40 ml, CO₂ = 200 psi, temperature = 363 K, time = 20 h, acetone solvent if not otherwise noted.

Run	Catalyst	Pd content (wt.%)	C ₄ H ₆ conversion (%)	Selectivity (%)						TOF (h ⁻¹)
				2,7-Octadien-1-ol	1,7-Octadien-3-ol	1,3,7-Octatriene	1-Methylene-2-vinylcyclopentane	4-Vinylcyclohexene	High molecular weight	
1 ^a	Pd(II)(CH ₃ CO ₂) ₂	–	77.6	74.8	7.2	8.1	6.6	0	3.3	259
10 ^b	Pd(II)Cl ₂	–	3.0	0	0	19.3	0	22.8	58.0	10
11	Montmorillonite Si(CH ₂) ₃ NHC ₂ H ₄ NH ₂ PdCl ₂	4.86	11.0	40.9	13.8	7.6	0	7.2	30.6	3
12	Montmorillonite Si(CH ₂) ₃ NH ₂ PdCl ₂	4.76	3.2	16.3	10.2	3.6	12.5	32.1	25.3	1
13	Montmorillonite Si(CH ₂) ₃ NH ₂ Pd(NO ₂)Cl	5.15	60.3	71.1	7.9	9.0	2.9	3.8	5.4	15
9 ^c	Montmorillonite Si(CH ₂) ₃ NH ₂ Pd	0.87	70.8	77.3	7.8	6.7	3.5	1.0	3.6	216
14 ^d	Montmorillonite Si(CH ₂) ₃ NH ₂ Pd	0.87	69.5	69.8	12.8	4.9	1.3	2.6	8.6	212
15 ^e	Montmorillonite Si(CH ₂) ₃ NH ₂ Pd	0.87	91.0	76.8	8.5	5.8	2.1	0.7	6.1	277

^aReaction time = 1.5 h.

^bReaction time = 1.5 h.

^cPd = 0.082mmol and reaction time = 10 h.

^dPd = 0.082mmol and reaction time = 10 h. Solid catalyst was recycled from run 9.

^ePd = 0.082mmol and reaction time = 10 h. DMF instead of acetone.

gests that most palladium complexes were not released from the support during the reaction and the catalyst recovered by filtration could be recycled.

4. Conclusions

Heterogeneous palladium catalysts were employed for the telomerization of butadiene with water. In the presence of triphenylphosphine, palladium anchored on montmorillonite showed good activity and selectivity. Among various palladium precursors that were used for immobilizing palladium in montmorillonite, $\text{Pd}(\text{CH}_3\text{COO})_2$ was the most effective. Recycle experiments allow one to conclude that the palladium is anchored to the montmorillonite in a stable form and works as a heterogenized catalyst without an appreciable leaching of metal species into the reaction medium.

Acknowledgements

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