

Selective co-oligomerization of 1,3-butadiene and carbon dioxide with immobilized catalysts

Nancy Holzhey, Stephan Pitter *

Projektgruppe 'CO₂-Chemie' an der Friedrich-Schiller-Universität, Lessingstraße 12, D-07743 Jena, Germany

Abstract

Recent results on the heterogeneously catalyzed co-oligomerization of 1,3-butadiene and carbon dioxide are presented. Optimized preparation methods for the reaction of Pd(η^3 -C₃H₅)(η^5 -C₅H₅) **2** with [(i-Pr)₂P-CH₂]-polystyrene derivative **PS-P** yield palladium catalysts immobilized on polystyrene support (**PS-01**, **PS-02**, **PS-03**). Consequently, 'leaching' is reduced and catalysts may be re-used several times after a simple separation and cleaning procedure. Additionally, a similar immobilization of palladium complex units on silica is reported. The correlation of the formation of 2-[(*E*)-ethylidene]-6-heptene-5-olide **1** with process parameters such as temperature, kind of catalyst, and solvent, is presented and discussed in detail. Analytical methods (CP-MAS-NMR, XPS, SEM) were used to determine **PS-02** before and after use. XPS data indicate an initial Pd⁰ oxidation state. Used **PS-02** possesses a changed coordination sphere around the anchored palladium centres which agrees to its different catalytic behaviour. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Co-oligomerization; Carbon dioxide; Palladium catalyst

1. Introduction

A major task in the development of modern organic syntheses consists in developing economically efficient methods that meet the increasing requirements in terms of environmental compatibility. For some time now, considerable efforts have been made to develop strategies for the use of carbon dioxide in C₁ chemistry and as C₁ element for organic synthesis [1–7]. As a substitute of already established C₁ molecules such as carbon monoxide and phosgene, carbon dioxide is of particular interest, as it is available

at low costs in nearly unlimited amounts. Furthermore, its low toxicity is of considerable advantage for process control and ecological balancing of industrial processes. Due to the thermodynamic stability of carbon dioxide, however, suitable catalysts are mostly necessary for its activation for chemical synthesis.

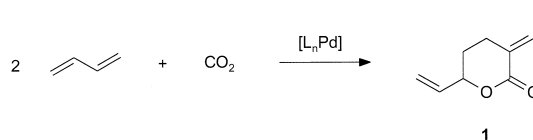
Regarding the few reactions known for the generation of new C,C bonds on the basis of CO₂, co-oligomerization with 1,3-butadiene has been in the centre of attention for some time already [8]. As products, various derivatives of carboxylic acids are obtained, which makes the technical implementation of this synthesis appear extremely interesting. Before our activities were started, co-oligomerization had only been

* Corresponding author. Tel.: +49-3641-948451; Fax: +49-3641-948452; E-mail: sp@co2.chemie.uni-jena.de

known with homogeneous catalysts of platinum metals [5,6]. Studies on separation, feedback and reprocessing of a homogeneous catalyst, which is expected to be a cost-intensive process, are in progress [9]. As the possible products are to be assigned to fine chemicals in a wider sense, their loading with the catalyst residues must be avoided. A heterogeneous catalyst of comparable activity and product selectivity seems to be ideally suited. Such catalyst should either have a high long-term stability or be suited for repeated use in batch processes with a relatively small regeneration expenditure needed.

In the past, the preparation, suitability and use of immobilized catalysts were reported rather frequently. Numerous articles on this topic document the progress achieved in the past 20 years [10–13]. In spite of the initial prognosis of them being an ‘ideal’ alternative to homogeneous catalysts, principle reservations have to be made regarding their suitability for technical use. A major drawback is the unsatisfactory long-term stability of many systems. The main reason is ‘leaching’ which is caused by the bonding between the active metal and the support being too weak. Therefore, the stability of a catalyst can only be studied when taking into account the conditions of the process planned. Generally, organic matrices exhibit a smaller chemical and mechanical stability than inorganic carrier materials and are much more dependent on the type of surrounding phase. It is also important, whether a catalyst is physisorbed on the support or fixed by chemical bonding.

Based on our activities for the development of homogeneous palladium catalysts, functionally equivalent immobilized catalysts were to be prepared. This was to be achieved by the chemical fixation of defined palladium complex units on an organic or inorganic support. Recently, we have reported about first studies on the syntheses and catalytic properties of palladium catalysts with the active metal being fixed to a functionalized polystyrene support by coor-



Scheme 1. Synthesis of **1**.

dination of phosphine functions [14]. The main product of this catalytic reaction is 2-[(*E*)-ethylidene]-6-heptene-5-olide **1** (Scheme 1).

The organic groups bound to the phosphorus atom have a strong influence on the type of the products being formed. Phenyl groups at the phosphorus functions drive catalysis towards various constitution-isomers of C_{17} carboxylic acid esters [5,6,15]. Such compounds possess a high potential for a marked consecutive chemistry, e.g., addition to the olefinic units, partial or complete hydrogenation of double bonds or reactions on the ester groups.

In the following, it shall be reported about improved methods for the preparation of immobilized catalysts on polystyrene and $(SiO_2)_y$ supports, the determination of optimized co-oligomerization process parameters for the synthesis of **1**, as well as about the characterization of catalysts in terms of stability and possible elementary stages of the catalytic cycle.

2. Experimental section

All syntheses of supported catalysts were carried out under dry argon atmosphere by standard Schlenk techniques. Solvents were distilled after purification using standard methods. Carbon dioxide (4.8) was used without modification. Butadiene (Fluka) was condensed immediately before use. Merrifield resin (Merck-Schuchardt, 5.3% Cl, cross-linked with 2% divinylbenzene) and silica 60 (Fluka, grade 0.2–0.5 mm) were pre-treated in vacuum (90°C, 48 h and 25°C, 7 days, respectively).

$Pd(\eta^3-C_3H_5)(\eta^5-C_5H_5)$ **2** was prepared by literature method [16] and freshly crystallized from pentane. Synthesis of **PS-P** has been described previously [14].

NMR spectra of **3** and **4** were acquired on a Bruker AC 200 spectrometer. Chemical shifts are referenced to internal or external TMS (^1H , ^{13}C) and external 85% H_3PO_4 (^{31}P), respectively. Assignments were confirmed by ^1H , ^1H -COSY and ^1H , ^{13}C -HETCOR, ^{13}C -DEPT and selective $\{^{31}\text{P}\}$ decoupling of ^1H and ^{13}C spectra. CP-MAS-NMR spectra were recorded on a Varian Unity INOVA 400 at 298 K with ZrO_2 rotors. XPS spectra were measured on a VG ESCALAB spectrometer at 10^{-9} mbar with a Mg anode (200 W, $E_{k\alpha} = 1253.6$ eV). SEM were taken on ISI-60 microscope. EDX analyses were performed on a Kevex/Link Si (Li) detector 3212-SMS-II equipped with a W-cathode at 15 kV accelerating voltage. Quantitative analysis of **1** was performed with a Gynkotek HPLC system M480P/UV340S on a C_{18} -phase (Macherey, Nagel and Co.; ET250/4.6 Nucleosil 100-5, 18) with eluant acetonitrile/ H_2O (90/10).

2.1. Synthesis of $\text{C}_6\text{H}_5\text{-CH}_2\text{-P}(\text{i-Pr})_2$ **3**

$\text{HP}(\text{i-Pr})_2$, 2.41 g (20.37 mmol) is dissolved in 40 ml thf and 12.7 ml CH_3Li (1.6 M etheric solution) is added dropwise at -20°C . The mixture is allowed to warm up to 25°C . After 2 h this solution is added at -50°C to 2.58 g (20.37 mmol) benzylic chloride, dissolved in 30 ml thf. After stirring at 25°C for 15 h, the solvent is removed in vacuum and 75 ml hexane is added to the residue. The mixture is filtered and the volatile components are removed in vacuum. The raw product is distilled twice at $8 \cdot 10^{-6}$ mbar at $60\text{--}70^\circ\text{C}$ to result 3.25 g (77%) of colourless **3**. ^1H -NMR (CD_2Cl_2): 7.31–7.28 m (5H), 2.82 d (2H, $^2J_{\text{HP}} = 2.1$ Hz), 1.79 dsp (2H, $^2J_{\text{HP}} = 2.3$ Hz, $^2J_{\text{HH}} = 7.1$ Hz), 1.11 dd (6H, $^3J_{\text{HP}} = 11.4$ Hz, $^3J_{\text{HH}} = 7.1$ Hz), 1.09 dd (6H, $^3J_{\text{HP}} = 12.9$ Hz, $^3J_{\text{HH}} = 7.0$ Hz). ^{13}C -NMR (CD_2Cl_2): 139.9 d ($^2J_{\text{CP}} = 8$ Hz), 129.2 d ($^3J_{\text{CP}} = 7$ Hz), 128.2 s, 125.3 d ($^3J_{\text{CP}} = 2$ Hz), 30.0 d ($^1J_{\text{CP}} = 21$ Hz), 23.9 d ($^1J_{\text{CP}} = 15$ Hz), 19.8 d ($^2J_{\text{CP}} = 14$ Hz), 19.4 d ($^2J_{\text{CP}} = 11$ Hz). ^{31}P -NMR

(CD_2Cl_2): 10.7. Elemental analysis percentage found (calculated) of **3** ($\text{C}_{13}\text{H}_{21}\text{P}$, $M = 208.29$): C 75.25 (74.97), H 10.40 (10.16), P 14.51 (14.87).

2.2. Synthesis of $\text{Pd}[\text{P}(\text{i-Pr})_2(\text{CH}_2\text{-C}_6\text{H}_5)]_2$ **4**

To a solution of 0.167 g (0.785 mmol) $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$ **2** in 10 ml CH_3CN , 0.328 g (1.57 mmol) **3** dissolved in 5 ml CH_3CN is added at 25°C . After a few minutes, a yellow precipitate of $\text{Pd}_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_5)(\mu\text{-}\eta^5\text{-C}_5\text{H}_5)\text{-}[\text{P}(\text{i-Pr})_2(\text{CH}_2\text{-C}_6\text{H}_5)]_2$ is formed [17] which is dissolved by heating the mixture up to 75°C . After 5 h, the mixture is cooled down to 25°C and the solvent is removed in vacuum. An amount of 10 ml pentane is added and the mixture is filtered. Removing the volatile components in vacuum, yields 0.413 g **4** (98%) as brown viscous liquid. ^1H -NMR (C_6D_6): 7.95 d (4H, $^3J_{\text{HH}} = 7.0$ Hz), 7.27–7.06 m (8H), 2.83 s (br, 4H), 1.79 m (br, 4H), 1.16 m (br, 24H). ^{13}C -NMR (C_6D_6): 138.9 s, 131.0 s (br), 128.3 s, 126.0 s, 31.8 s (br), 25.7 t ($|^3J_{\text{CP}} + ^1J_{\text{CP}}|_{1/2} = 7$ Hz), 20.3 s (br), 20.0 s (br). ^{31}P -NMR (C_6D_6): 40.2. Elemental analysis % found (calculated) of **4** ($\text{C}_{32}\text{H}_{47}\text{P}_2\text{Pd}$, $M = 522.97$): C 60.18 (59.71), H 8.19 (8.10), P 11.42 (11.85).

2.3. Synthesis of **Si-01**

A mixture of 5.6 g silica and 3.9 g (16.0 mmol) (3-bromopropyl)trimethoxysilane in 100 ml toluene is stirred at 25°C for 1 h. A solution of 4.3 ml ethanol, 2 ml H_2O and 80 μl HCl is added and the mixture is refluxed for 5 h under vigorous stirring. After stirring 18 h more at 25°C , the solid is filtered off, washed three times with CH_3OH , pentane and thf and is dried in vacuum at 50°C to result 6.7 g **Si-a** (% found: C 6.40, H 1.62, Br 7.13).

At -40°C , an excess of trimethylchlorosilane is added to **Si-a**. After warming up slowly to 25°C , the mixture is refluxed for 15 h. The

solid is filtered off, washed three times with toluene, ether and thf and dried in vacuum at 50°C to result 6.9 g **Si-b** (% found: C 6.71, H 1.73, Br 6.53).

0.477 g (4.04 mmol) $P(i\text{-Pr})_2$ is dissolved in 15 ml thf and 2.5 ml CH_3Li (1.6 M etheric solution) is added dropwise at -20°C . The solution is allowed to warm up to 25°C and is added slowly to a mixture of 2.47 g **Si-b** in 10 ml thf. The reaction mixture is ultrasonic treated at 20°C for 24 h. The solid is filtered off, washed twice with thf, added to 4.04 mmol additional lithium diisopropylphosphid solution and is ultrasonic treated at 20°C for 72 h more. After reaction, the solid is filtered off, washed with thf and is dried in vacuum to result 2.76 g colourless **Si-P** (% found: C 9.26, H 2.43, Br 2.24, P 1.76).

To a mixture of 1.815 g **Si-P** ($\cong 1.031$ mmol P) and 35 ml ether, a solution of 109.6 mg (0.516 mmol) **2** in 15 ml ether is added. The reaction mixture is refluxed for 90 min. The solid is filtered off, washed five times with ether and is dried in vacuum to result 1.855 g of orange coloured **Si-01**.

2.4. Synthesis of **PS-01**

To a mixture of 6.564 g **PS-P** ($\cong 8.477$ mmol P) and 70 ml CH_3CN , 0.901 g (4.238 mmol) **2** in 35 ml CH_3CN is added. After stirring for 20 min at 25°C , the mixture is reacted for 3 h at 40°C , under decolouration of the solution. The solid is filtered off, washed five times with benzene and is dried in vacuum to result 7.125 g of tan **PS-01**.

2.5. Synthesis of **PS-02**

3.031 g **PS-P** ($\cong 3.944$ mmol P) is allowed to swell in 175 ml benzene for 30 min at 40°C . To this mixture, 0.456 g (2.146 mmol) **2** in 75 ml benzene is added slowly at 40°C . The reaction mixture is stirred for 90 min at 40°C . The solid is filtered off, washed five times with

CH_3CN and dried in vacuum to yield 3.301 g of yellow **PS-02**.

2.6. Synthesis of **PS-03**

Analogous to the synthesis of **PS-02**, 1.283 g **PS-P** ($\cong 1.669$ mmol P) and 118.3 mg (0.556 mmol) **2** are reacted to yield 1.356 g of yellow **PS-03**.

2.7. Catalytic reactions

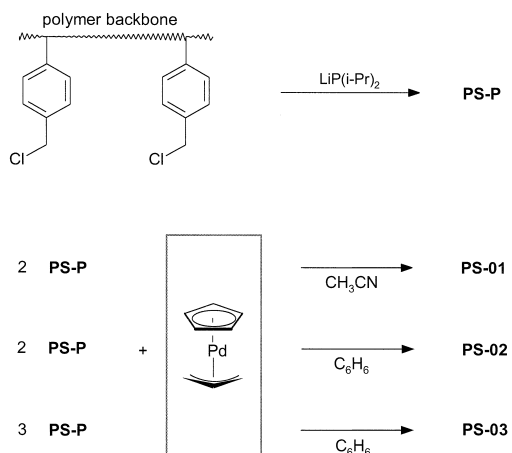
Catalyses are performed in stainless steel reactors, equipped with connections to inert gas/vacuum, carbon dioxide, temperature and pressure probe. Syntheses in a 250 ml reactor have been described [14].

Synthesis in a 175 ml Parr reactor, equipped with blade mixer: A mixture of the supported catalyst ($\cong 0.1211$ mmol Pd) and 21 ml CH_3CN is transferred to the reactor via canula. 9.5 g (0.175 mol) 1,3-butadiene is condensed into the reactor and 9.2 g (0.21 mol) carbon dioxide is inflated. The mixture is stirred at 700 min^{-1} for 18 h. Then, the reactor is cooled down to 25°C and left to expand for 30 min. The reaction mixture is filtered off, the catalyst is washed four times with thf and is dried in vacuum before it may be applied in further runs. Volatile components are removed from the filtrate in vacuum at 40°C . The raw product is weighed out and the amount of **1** is determined by HPLC.

3. Results and discussion

3.1. Syntheses of catalysts

Regarding the stability of supported catalysts, chemical immobilization was to be preferred for the planned catalysis. Under the conditions known from homogeneous catalysis with temperatures ranging between 40 and 120°C and the pressure varying between 10 and 100 bar, the synthesis principle of a homogeneous catalyst

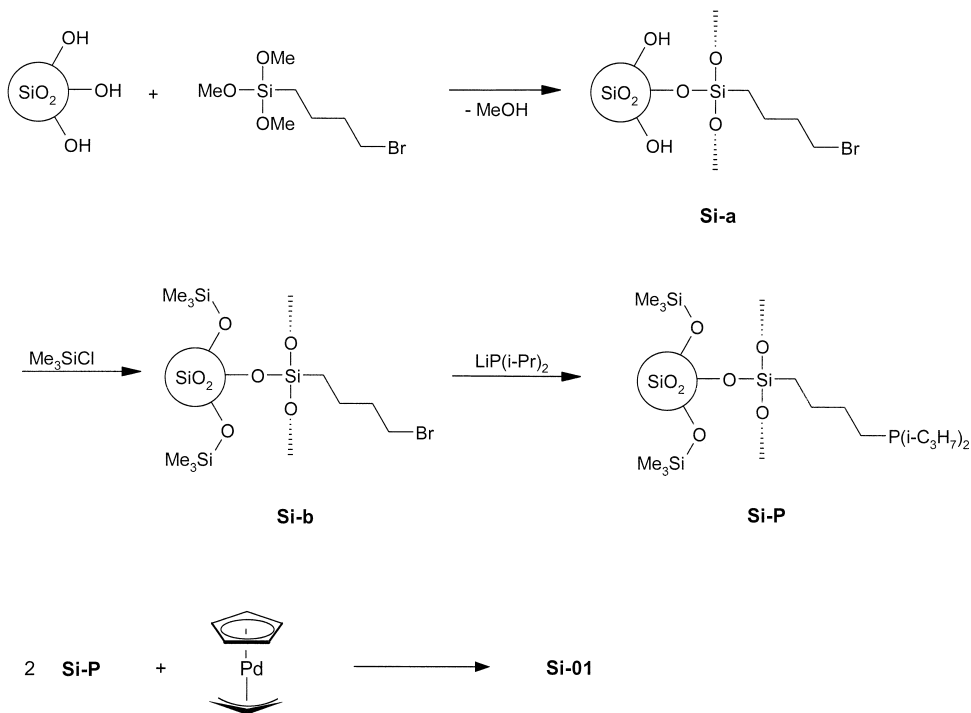


Scheme 2. Synthesis of catalysts supported on polystyrene.

was to be transferred to the immobilization on an organic support. The Merrifield polymer, which is known from peptide synthesis and available at low costs, is commonly applied for the synthesis of immobilized catalysts [18]. In two steps (Scheme 2), the desired catalysts **PS-**

01, **PS-02**, and **PS-03** are obtained. Palladium fixation takes place by coordinative bonding to the phosphino groups of **PS-P**.

As far as mononuclear palladium(0) complexes are concerned, the general types $\text{Pd}(\text{PR}_3)_2$ (**A**), $\text{Pd}(\text{PR}_3)_3$ (**B**) and $\text{Pd}(\text{PR}_3)_4$ (**C**) are known from the transformation of $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$ **2** with phosphines. Binuclear species $\text{Pd}_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_5)(\mu\text{-}\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)_2$ (**D**) have been described as isolable intermediates [19,20]. Here, syntheses have been performed using **2** as palladium precursor and one, two and three equivalents of the organic support, relative to the phosphorus content determined by elementary analysis. While a red-coloured solution of **2** is discoloured after a short time already by transformation under Pd/P stoichiometries of 1:2 and 1:3, fixation of the palladium on the support is incomplete in the case of a 1:1 stoichiometry. Hence, there is no evidence for complex species on the support being similar to complex type **D**.

Scheme 3. Synthesis of **Si-01**.

Due to the preliminary discussed differences regarding the support of immobilized catalysts (see Section 1), an analogous catalyst synthesis was performed on an inorganic support, yielding **Si-01**. The successive formation of functionalized side chains on commercially available silica (Scheme 3) has the advantage to introduce the phosphine group in the last step only. The silylation of free hydroxyl groups is necessary to avoid hydrolysis of the applied phosphide. Unfortunately, the conversion of the alkyl bromide derivative is incomplete, independent from the time of reaction. The macroscopic properties of silica are maintained during all stages of the reaction shown in Scheme 3.

3.2. Catalytic co-oligomerization

The co-oligomerization experiments were performed taking into account the following features:

- activity related to the conversion of 1,3-butadiene
- selectivity in the formation of **1**
- influence of the reaction temperature
- influence of the reaction medium
- reusability of immobilized catalysts.

For the performance of the experiments, it was therefore necessary to select reaction parameters, at which the substrate conversion is incomplete. The results of the experiments are

Table 1
Overview of catalytic syntheses; $t = 18$ h (refer to Section 2)

Catalyst	T [°C]	Solvent	Run	Conversion BTD [%]	Selectivity (1) [%]	TON (1)
PS-01	40	CH ₃ CN	–	2	48	8
PS-01	45	CH ₃ CN	–	4	55	13
PS-01	50	CH ₃ CN	–	6	56	22
PS-01	55	CH ₃ CN	–	7	58	28
PS-01	60	CH ₃ CN	–	11	61	46
PS-01	65	CH ₃ CN	–	14	61	57
PS-01	70	CH ₃ CN	–	17	57	65
PS-01	75	CH ₃ CN	–	20	51	69
PS-01	80	CH ₃ CN	–	22	45	65
PS-01	85	CH ₃ CN	–	22	38	55
PS-01	90	CH ₃ CN	–	25	25	40
PS-02	70	CH ₃ CN	–	38	33	82
PS-02	70	thf	–	24	18	28
PS-02	70	thf/CH ₃ CN (1:1)	–	42	27	74
PS-02	70	C ₆ H ₆	–	24	17	26
PS-02	70	C ₆ H ₆ /CH ₃ CN (1:1)	–	43	27	74
PS-02	70	C ₆ H ₅ N	–	56	16	56
PS-02	70	C ₆ H ₅ N/CH ₃ CN (1:1)	–	55	27	95
Si-01	70	CH ₃ CN	–	6	49	19
Si-01	80	CH ₃ CN	–	10	48	31
PS-02	70	CH ₃ CN	1	35	40	92
PS-02	70	CH ₃ CN	2	15	69	71
PS-02	70	CH ₃ CN	3	12	68	56
PS-02	70	CH ₃ CN	4	11	68	50
PS-02	70	CH ₃ CN	5	11	68	50
PS-03	70	CH ₃ CN	1	48	23	71
PS-03	70	CH ₃ CN	2	27	57	105
PS-03	70	CH ₃ CN	3	17	66	77
PS-03	70	CH ₃ CN	4	13	68	61
PS-03	70	CH ₃ CN	5	11	69	52
4	70	CH ₃ CN	–	37	90	239

BTB: 1,3-butadiene.

TON: turn over number.

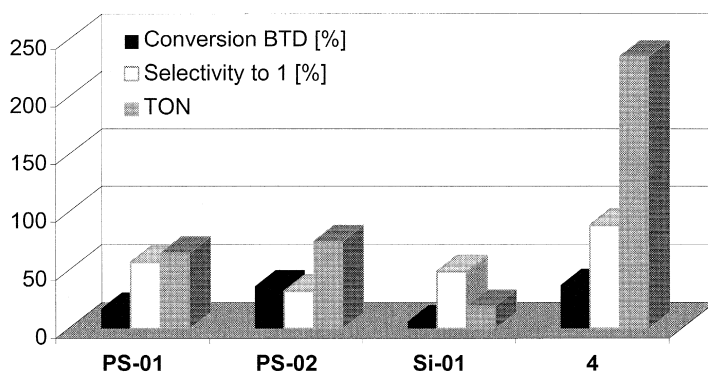


Fig. 1. Catalytic synthesis of **1** from co-oligomerization of 1,3-butadiene (BTD) and CO₂ (TON: turn over number).

represented in Table 1 and Figs. 1–4. Under the given conditions, all tested catalysts exhibit an activity in the transformation to co-oligomerization products (Fig. 1).¹ It is known that comparable homogeneous catalysts coordinated by phosphino groups with bulky, electron-pushing substituents preferably catalyze the formation of **1**. If immobilized catalysts with diisopropylphosphino groups are used instead, **1** also is a major product. For direct comparison of the efficiency of homogeneous and heterogeneous catalysis, Pd[C₆H₅–CH₂–P(*i*-Pr)₂]₂ **4** was prepared and used as a catalyst. This complex was to have a similar coordination geometry at the active metal centre than the catalysts **PS-01** and **PS-02** immobilized on a polystyrene support (see also Section 3.3).

PS-01 is found to show a similar activity in butadiene conversion. However, **4** reaches a higher selectivity in the formation of **1**. In many other catalytic reactions, immobilized catalysts exhibit an activity which is much more smaller than that of the respective homogeneous ones by a factor of 2–5 [21].

The swelling capacity of polystyrene is supposed to be the reason for the insignificant limitation of the reaction velocity by diffusion processes in the polymeric resin. Under the

same conditions, the activity of **Si-01** immobilized on a (SiO₂)_x support is smaller. Here, the conversion velocity is reduced, probably by partial poisoning of the catalyst from the residual halogen content.

Comparison of several individual experiments performed at various reaction temperatures with **PS-02** as catalyst shows that favourable operating conditions of the reactor are encountered in the interval of 65°C to 85°C (Fig. 2). It is possible to increase the conversion to co-oligomers by a further temperature increase, however, growing formation of by- and consecutive products will then lead to a significant reduction of selectivity to **1**. A temperature decrease will also result in a reduction of selectivity.

The dependence of homogeneous co-oligomerization on the surrounding reaction medium was recognized very early [22]. For an efficient activation, palladium phosphine catalysts require a weak donor ligand. The use of acetonitrile as solvent turned out to be necessary. Recently, it was demonstrated that a similar activation of homogeneous catalysts for co-oligomerization is achieved when using hemilabile phosphine ligands with a nitrile function and that the reaction takes place successfully in a number of other solvents [23]. Furthermore, the swelling capacity of polystyrene is strongly influenced by the surrounding liquid phase. The activity of **PS-02** was therefore investigated in various liquid phases. As expected, the best results are achieved when acetonitrile is a major

¹ Turn over number: formation of mol (product) per mol (active metal).

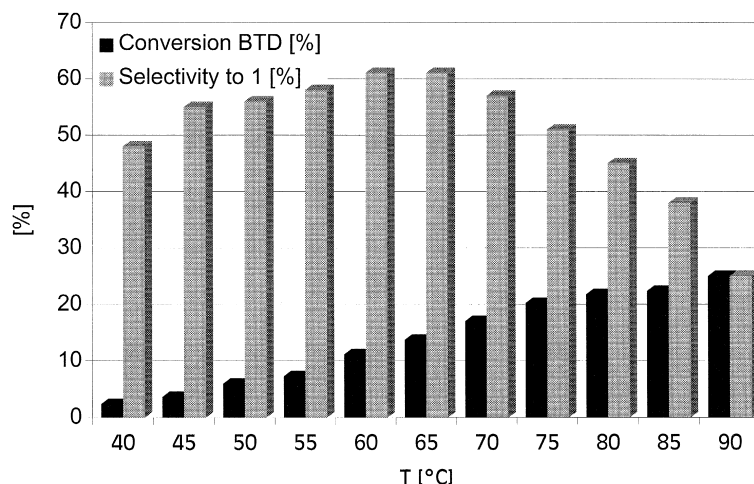
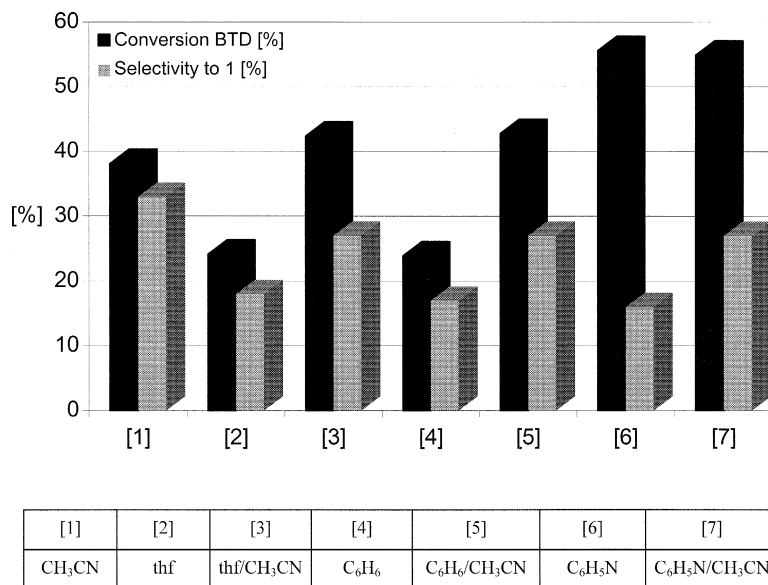


Fig. 2. Catalytic synthesis of **1** from co-oligomerization of 1,3-butadiene (BTD) and CO₂ (catalyst: **PS-02**).

constituent of the liquid phase (Fig. 3). However, catalyst activity is less dependent on it than in homogeneous catalysis. If conversion takes place in benzene instead of acetonitrile, the TON is reduced from 57 to 18 only. The maximum TON of 95 is reached in mixtures of pyridine and acetonitrile.

The stability and lifetime of a catalyst are of crucial importance for a heterogeneously cat-

alyzed reaction becoming an efficient technical process. **PS-02** was applied in five successive batch syntheses. Upon the completion of each reaction, the catalyst is filtered, scrubbed and dried, before it is used again under identical conditions. A significant decrease in the activity was observed in the second run. After repeated use, a constant activity of 12% butadiene conversion is reached. The selectivity to **1** increases



[1]	[2]	[3]	[4]	[5]	[6]	[7]
CH ₃ CN	thf	thf/CH ₃ CN	C ₆ H ₆	C ₆ H ₆ /CH ₃ CN	C ₆ H ₅ N	C ₆ H ₅ N/CH ₃ CN

Fig. 3. Catalytic synthesis of **1** from co-oligomerization of 1,3-butadiene (BTD) and CO₂ utilizing different liquid phases (catalyst: **PS-02**).

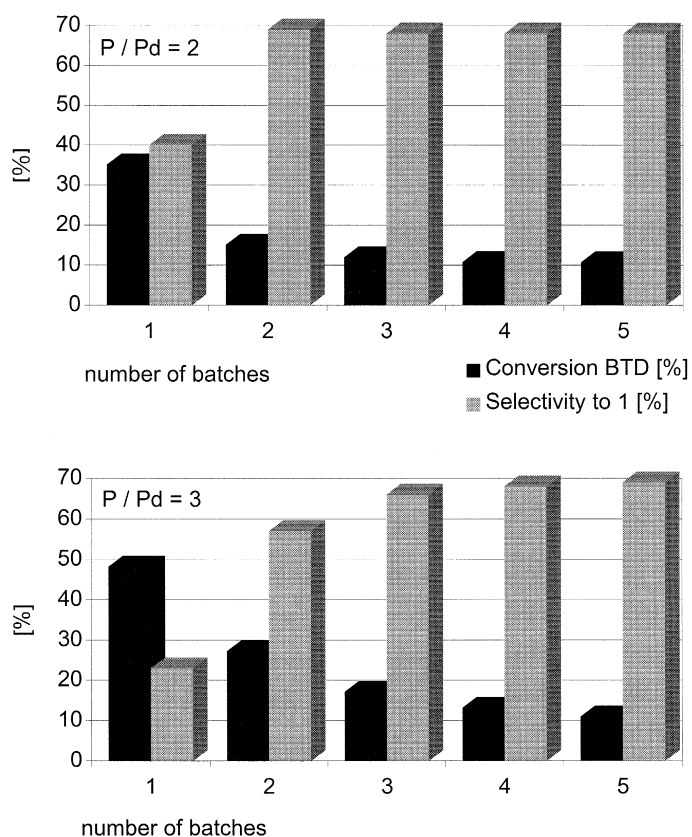
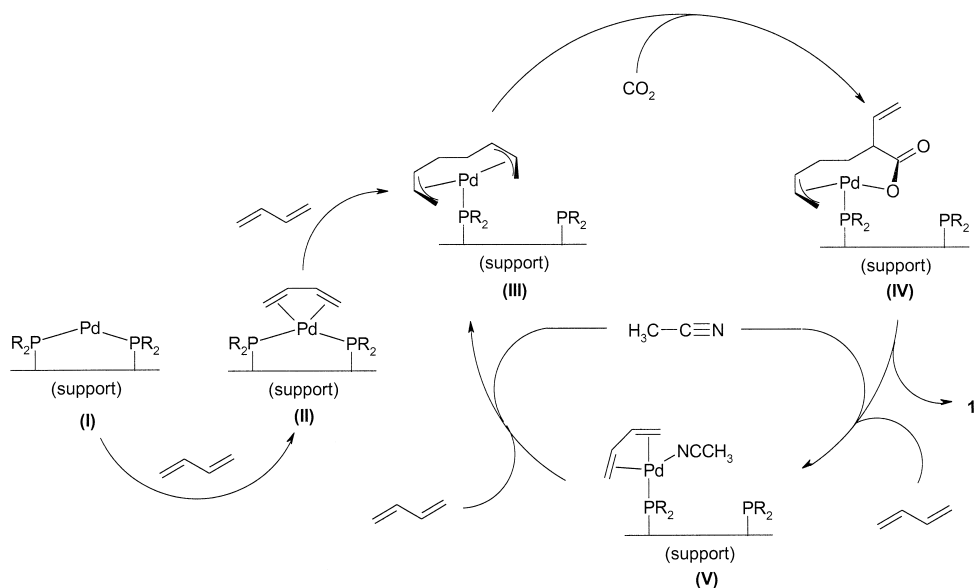


Fig. 4. Catalytic synthesis of **1** from co-oligomerization of 1,3-butadiene (BTD) and CO₂ with **PS-02** (top) and **PS-03** (bottom).



Scheme 4. Possible mechanism of the heterogeneously catalyzed co-oligomerization.

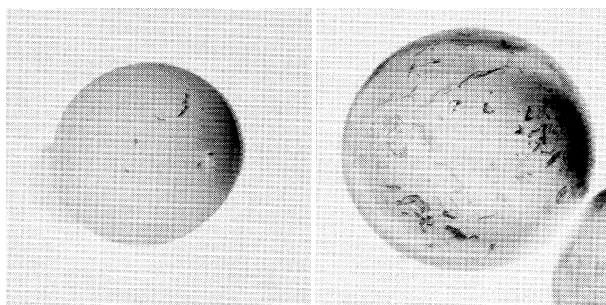


Fig. 5. SEM of **PS-02** particles; unused (left), used (right); horizontal scale: 530 μm .

from 40% to 68% and remains constant after the third run. ‘Leaching’ does not occur: The palladium content of the reaction products is found to be within the detection limit (ICP-MS) such that the palladium discharge from the catalyst is $<0.2\%$. It is suspected that the catalyst property is changed by a change in the coordination sphere of the fixed palladium atoms (see also Section 3.3).

For long-term stability, it is of minor importance whether the Pd/P ratio amounts to 1:2 or 1:3. Although in the beginning, the activity of **PS-03** is higher with the selectivity in the formation of **1** being smaller, the values determined for repeated use are the same than those for **PS-02**. It may therefore be concluded that finally, there is a similar distribution of palladium complex units on the support.

3.3. Reaction mechanism and characterization of catalysts

Regarding the properties of immobilized catalysts, at first, one has to consider that a broad range of molecular weight distribution is given for the catalysts. Also, the geometry of the anchored metal complex units depends on the distribution of the phosphine groups bonded to the support. At least, a reaction mechanism should be discussed with respect to any complex species formed during catalysis. In order to distinguish between intrinsic properties and changes caused by use in catalysis, the characterization of catalysts has been performed with **PS-02** before and after use.

As the product distribution is similar to homogeneous catalysis, the key steps of the catalytic cycle are expected to be the same (Scheme 4). The 14e palladium species **I** successively coordinates two butadiene molecules, forming a bis(allyl) species **III** under cleavage of one phosphine donor function. Carbon dioxide is inserted to result the carboxylato complex **IV**. From **IV**, **1** is formed by reductive elimination. The palladium is coordinating the next butadiene molecule and may further be stabilized in **V** by coordination of a nitrile molecule from the liquid phase.

Fig. 5 shows that **PS-02** particles retain the appearance of polystyrene. As expected from the catalysis conditions (70°C, 25 bar), the used

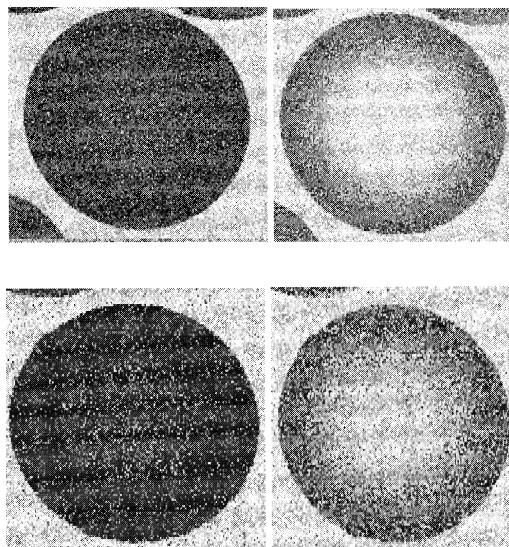


Fig. 6. EDX mapping of **PS-02** particles; P (left), Pd (right); unused (top), used (bottom); horizontal scale: 530 μm .

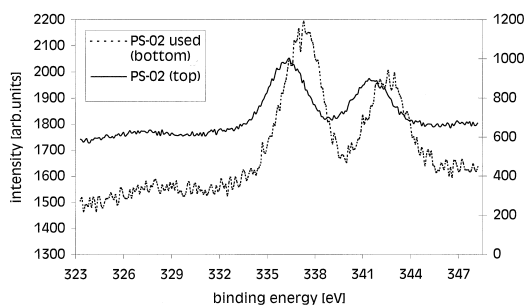


Fig. 7. XPS spectra of **PS-02**; region of the palladium 3d level.

PS-02 catalyst has undergone some changes in the surface appearance. The elemental distribution of phosphorus and palladium from EDX analysis in a single representative particle is given in Fig. 6. Interestingly, palladium remains in the outer particle sphere only, which covers around 90% of the spherical volume. After use, the amount inside the inner sphere has become significantly higher. This is a hint for the temporary opening of bonds between palladium and phosphorus.

Information concerning the oxidation state of palladium is obtained by XPS analysis (Fig. 7). Before use, **PS-02** shows two signals for the $3d^{5/2}$ and $3d^{3/2}$ levels at 336.5 and 341.8 eV, respectively. The value for **PS-02** is associated with Pd(0) and is in agreement to the supposed partial structure of **I** (Scheme 4). Having been used, both 3d signals shift 1.1 eV (± 0.2 eV) to higher energies, indicating a change in the coordinations sphere of the palladium atoms. These values are below typical values for Pd(II), for

example $\text{PdCl}_2[\text{P}(i\text{-Pr})_2(\text{CH}_2)_6\text{CN}]_2$ ($3d^{5/2}$: 338.2 eV) [24].

^{31}P CP-MAS-NMR spectra of **PS-02** before and after use are given in Fig. 8. Resonances are broad, characteristic for polymers. Unused, **PS-02** shows one signal at +50 ppm with several side bands. This shift is near to the shift of the homogeneous catalyst **4** but away from resonances of comparable phosphines (0–10 ppm). After use, a new signal is detected at +37 ppm with no side bands visible. Obviously, a new palladium complex species has been formed on the support, corresponding to the results of the catalytic reactions and the XPS analysis. The preliminary ^{13}C -NMR analysis of used **PS-02** shows a broad resonance at 173 ppm assigned to be a coordinating carboxylato group.

It is assumed that **I** is the initially prepared immobilized catalyst; after butadiene activation **I** is not involved in the catalytic cycle anymore, according to Scheme 4. In the catalyst remaining after use, **I** is slowly displaced by a yet unknown palladium species which might be a carboxylato complex species. This transformation of **I** is assumed to be the reason of the decreasing activity and the increasing selectivity.

As advantage of catalysts supported on functionalized polystyrene, the good selectivity in the formation of **1** has to be marked. Regarding the possible upscaling of this process, the negligible leaching of palladium is technically advantageous. For the near future, it is planned to test immobilized catalysts in a fixed-bed process.

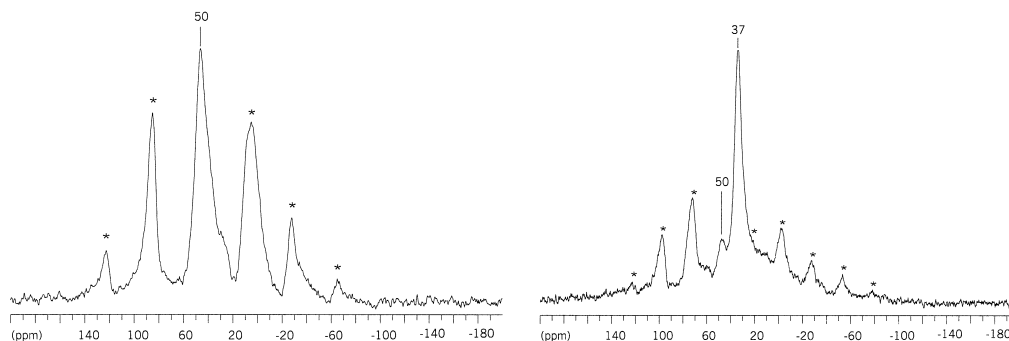


Fig. 8. ^{31}P CP-MAS-NMR spectra of **PS-02**; unused (left, $\nu = 6$ kHz), used (right, $\nu = 4$ kHz); *: rotational side bands.

Acknowledgements

We like to thank Dr. F. Gaßner (Forschungszentrum Karlsruhe, Germany) for the measurement of the CP-MAS-NMR spectra. Dr. H. Klewe-Nebenius (Forschungszentrum Karlsruhe, Germany) performed the XPS analysis. We are grateful to Dr. B. Tesche and Mr. H. Bongard (Max-Planck-Institut für Kohlenforschung, Mülheim, Germany) for electron microscopy and EDX analyses. Dr. G. Kaiser (Max-Planck-Institut für Metallforschung, Stuttgart, Germany) and Dr. M. Lohse (Umweltforschungszentrum Magdeburg, Germany) determined the palladium contents. This work was financially supported by the Max-Planck-Gesellschaft.

References

- [1] W. Leitner, *Coord. Chem. Rev.* 153 (1996) 257.
- [2] D. Walther, *Nach. Chem. Technol. Lab.* 40 (1992) 37.
- [3] A. Behr, *Angew. Chem.* 100 (1988) 681.
- [4] A. Behr, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 661.
- [5] P. Braunstein, D. Matt, D. Nobel, *Chem. Rev.* 88 (1988) 747.
- [6] A. Behr, *Carbon Dioxide Activation by Metal Complexes*, Verlag Chemie, Weinheim, 1988.
- [7] D. Walther, *Coord. Chem. Rev.* 79 (1987) 135.
- [8] Y. Sasaki, Y. Inoue, *J. Chem. Soc. Chem. Commun.* (1976), p. 605.
- [9] A. Behr, *Chem. Ing. Tech.* 70 (1998) 685.
- [10] P. Panster, S. Wieland, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 2, Verlag Chemie Weinheim, 1996, p. 605.
- [11] D.C. Bailey, S.H. Langer, *Chem. Rev.* 81 (1981) 109.
- [12] R.H. Grubbs, *CHEMTECH*, 1977, p. 512.
- [13] J.C. Bailar Jr., *Catal.-Rev. Sci. Eng.* 10 (1974) 17.
- [14] N. Holzhey, S. Pitter, E. Dinjus, *J. Organomet. Chem.* 541 (1997) 243.
- [15] A. Musco, R. Santi, G. Chiusoli, *Ger. Offen. DE 28 38 610 A1*, 1979.
- [16] Y. Tatsuno, T. Yoshida, S. Otsuka, *Inorg. Synth.* 19 (1979) 220.
- [17] S. Pitter, N. Holzhey, unpublished results, 1998.
- [18] R.H. Grubbs, L.C. Kroll, *J. Am. Chem. Soc.* 93 (1971) 3062.
- [19] H. Werner, D. Tune, G. Parker, C. Krüger, D.J. Brauer, *Angew. Chem.* 87 (1975) 205.
- [20] A. Kühn, H. Werner, *Chem. Ber.* 113 (1980) 2308.
- [21] D.D. Whitehurst, *CHEMTECH*, 1980, p. 44.
- [22] A. Behr, R. He, K.-D. Juszak, C. Krüger, Y.H. Tsay, *Chem. Ber.* 119 (1986) 991.
- [23] S. Pitter, E. Dinjus, *J. Mol. Catal. A* 125 (1997) 39.
- [24] S. Pitter, H. Klewe-Nebenius, unpublished results, 1998.