



Enhanced Activity and Recyclability of Palladium Complexes in the Catalytic Synthesis of Sodium Acrylate from Carbon Dioxide and Ethylene

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The Pd-catalysed synthesis of sodium acrylate from ethylene and CO₂ in the presence of alcoholate bases has been improved significantly. We used amide solvents such as *N*-cyclohexylpyrrolidone or *N,N*-dibutylformamide to achieve turnover numbers greater than 500 in one run, which is significantly higher than that of systems for this reaction reported previous-

ly. For the first time, we were able to recycle the catalyst without any additional regeneration step. With this system, it is possible to use the simple and easily recycled alcoholate base sodium isopropoxide to achieve good turnover numbers up to 200.

Introduction

Sodium acrylate is a valuable monomer for the production of polyacrylate salts, which are used as super-adsorbents or dispersants in our daily life.^[1] Sodium acrylate is nowadays produced by the two-stage oxidation of propylene towards acrylic acid followed by a reaction with NaOH.^[2] In addition to the historical routes towards acrylic acid based ethylene oxide or acetylene,^[2a] glycerol or lactic acid were also considered as bio-based alternatives to replace propylene as a feedstock.^[3] However, these feedstocks are still too expensive to be considered as economic alternatives. In contrast, the carboxylation of ethylene with CO₂ could offer a cost-competitive alternative to the propylene route. A tremendous amount of stoichiometric and catalytic carboxylation reactions that use CO₂ are known,^[4,5] but the catalytic carboxylation of ethylene into acrylic acid was reported in recently and remains relatively underdeveloped.^[6–11] Since the discovery of the first two-stage process in 2012 for the carboxylation of ethylene with CO₂ in the presence of strong bases,^[6] studies have been ongoing in

our laboratory with the aim to apply this reaction for the synthesis of sodium acrylate. After an extensive screening of several bases and ligands, the catalytic one-step synthesis of sodium acrylate using sodium-2-fluorophenolate as a base and nickel phosphine catalysts was reported by our group.^[7]

Simultaneously, the catalytic synthesis of lithium acrylate from ethylene and CO₂ was achieved by Vogt et al.,^[8] however, only low turnover numbers (TON) were achieved and no catalyst recycling was reported. In 2015, the reaction was extended to the use of Pd catalysts.^[9] We used [Pd(PPh₃)₄] (PPh₃ = triphenylphosphine) in combination with 1,2-bis(dicyclohexylphosphino)ethane (dcpe) as the catalysts to develop the first concept for a continuous process, in which the use of solid reductants such as Zn could be avoided (Scheme 1).^[10] In addition, we redesigned the continuous process with different bases and solvents to find a more suitable approach for product separation and base regeneration.

Through a deeper understanding of the base behaviour under the reaction conditions, it is now possible to use cheaper alcoholates, such as sodium *tert*-butoxide (NaOtBu), unlike in the previously reported Ni system (Scheme 1).^[11]

Despite this progress, the reaction had still some drawbacks, mainly the low TON of ~100 per run, the decrease in activity after recycling and the low space-time yield, which had to be

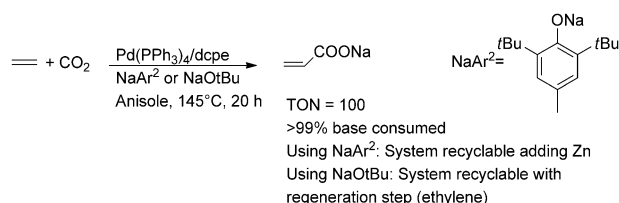
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This manuscript is part of a Special Issue on the "French Conference on Catalysis".

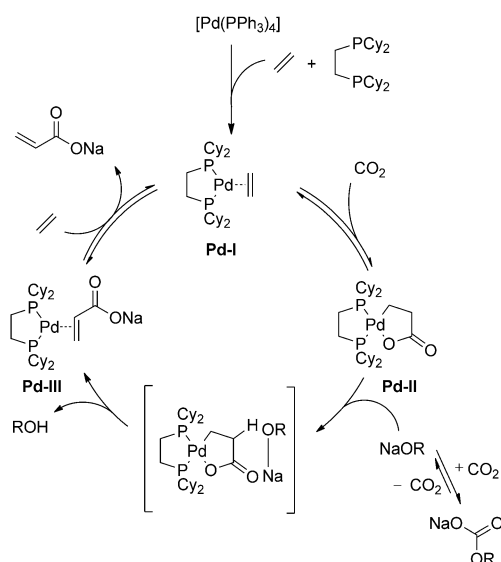


Scheme 1. Current catalyst system for the continuous synthesis of sodium acrylate from ethylene and CO₂.^[10,11]

improved before its application in an industrial-scale process. Also, to avoid the regeneration step, the activity and recyclability of the catalyst were further enhanced, the results of which are presented in this work.

Results and Discussion

The mechanism for the catalytic carboxylation of ethylene with palladium or nickel phosphine complexes has been described previously (Scheme 2).^[6,7,9,10] The metal species proposed for



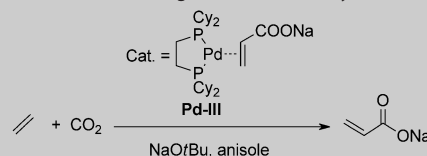
Scheme 2. Proposed mechanism for the $[Pd(PPh_3)_4]/dcpe$ -catalysed carboxylation of ethylene in the presence of an alkoxide base.

the catalytic cycle are the olefin complex I, the metallalactone II and the sodium acrylate complex III formed by the deprotonation of the lactone. According to this mechanism and if no other species were involved, the need for an additional reducing agent such as Zn or a regeneration step with ethylene to achieve any TON with the recycled catalyst phase can be questioned.^[10,11]

After the reaction, according to the mechanism presented in Scheme 2, **Pd-III** was thought to be the resting state of the catalyst as the sodium acrylate concentration is high if the ethylene pressure is released.^[9] Further insights could be found by using ^{31}P NMR spectroscopy, and **Pd-III** was observed as the main Pd species after the reaction in anisole using $[Pd(PPh_3)_4]/dcpe$ as the catalyst and NaOtBu as the base.^[12] As a result of the low concentration of the catalyst and the work-up procedure, these NMR spectroscopy investigations were treated with scepticism but provided a lead.

To investigate the activity of **Pd-III**, we synthesised this complex by the deprotonation of the acrylic acid complex reported previously with NaOtBu (Supporting Information).^[9] In contrast to the in situ generated catalyst,^[11] the sodium acrylate complex **Pd-III** showed only a very limited catalytic activity in the carboxylation of ethylene (Table 1, entry 2). This concurs with

Table 1. Effect of additives using **Pd-III** as the catalyst.



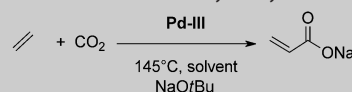
Entry ^[a]	Additive	T [°C]	TON ^[b]
1	None	145	4
2	None	100	1
3	dcpe (1 equiv.)	145	9
4	dcpe (1 equiv.)	100	3
5	dcpe (2 equiv.)	145	5
6	PPh ₃ (4 equiv.)	145	10
7	Zn (1 equiv.)	145	1
8	tBuOH (1 equiv.)	145	4
9	tBuOH (100 equiv.)	145	3

[a] Reaction conditions: 20 mmol NaOtBu, 0.2 mmol catalyst, 30 mL anisole, 10 bar ethylene, 20 bar CO₂, 8 h. The reaction was performed according to the general procedure given in the Experimental Section; [b] TON determined by using 1H NMR spectroscopy in D₂O as the solvent using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as the internal standard. A TON of 8 was observed after 8 h reaction time if we used $[Pd(PPh_3)_4]/dcpe$ as the catalyst.

the previous recycling experiments,^[10] in which hardly any activity was observed without a reactivation step. However, according to the proposed mechanism,^[9,10] **Pd-III** is part of the catalytic cycle and should, therefore, be active. To determine if other compounds in the catalytic mixture can increase the activity to the level observed with an in situ generated catalyst, we tested different additives in combination with **Pd-III** (Table 1). As it had been employed previously for catalyst regeneration Zn was also screened, as was the influence of the concentration of tBuOH.

The addition of phosphine ligands to **Pd-III** had the highest benefit (Table 1, entries 3 and 6), and TONs similar to that of $[Pd(PPh_3)_4]/dcpe$ were achieved. The beneficial effect of addi-

Table 2. Effect of the solvent used in acrylate synthesis.



Entry ^[a]	Solvent	TON ^[b]
1	Anisole	10
2	DMAc	55
3	DMF	90
4	DBF	51
5	N-Methylpyrrolidone	55
6	NEP	60
7	CHP	152
8	N-Dodecylpyrrolidone	21

[a] Reaction conditions: The reaction was performed according to the general procedure given in the Experimental Section; [b] TON determined by using 1H NMR spectroscopy in D₂O as the solvent using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.13 mmol) as the internal standard.

tional ligands is known and can help to prevent catalyst decomposition.^[13] Further investigations to achieve the recyclability of the organic phase were still required. Additionally, the use of Zn as an additive did not lead to any conversion (Table 1, entry 7). An increase in the amount of *t*BuOH did not result in any significant increase of the TON (Table 1, entries 8 and 9). In accordance with the previous work,^[10,11] a decrease of the reaction temperature to 100 °C reduces the activity significantly (Table 2, entries 2 and 4). The activity of **Pd-III** with one additional equivalent of dcpe was probed, and the TON was also determined after 20 h. Unfortunately, only a TON of 10 could be obtained. None of the screened additives were able to increase the activity of **Pd-III** to that of [Pd(PPh₃)/dcpe] in the first run.

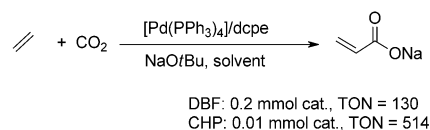
According to these observations, it seems that **Pd-III** has an intrinsically low activity in our system, which explains the low activity in the recycling of the organic catalyst phase.

One plausible reason for the lack of activity could be the agglomeration of **Pd-III** through the sodium carboxylate group in the relatively weakly coordinating solvents that were used previously. As the concentration of **Pd-III** increases during the catalysis because of the formation of sodium acrylate, this could slow the reaction over time and may explain the lack of activity if only **Pd-III** is used as the catalyst. Moreover, a higher concentration of CO₂ in the reaction solution could be beneficial to accelerate the catalytic cycle. Therefore, we investigated the influence of more coordinating solvents in which CO₂ is known to have a higher solubility: amides.^[14] For example, it is known that *N,N*-dimethylacetamide (DMAc) stabilises and activates Pd species in solution and provides a good solubility for CO₂.^[15]

To increase the CO₂ concentration within the solution, the CO₂ pressure was increased from 20 to 40 bars. With anisole, the TON was unaffected by this measure (see Table 1, entry 3 and Table 2, entry 1). In contrast, the use of amide solvents increased the activity drastically. An unprecedented TON of 152 was achieved from the combination of *N*-cyclohexylpyrrolidone (CHP) as the solvent with **Pd-III** as the catalyst and NaOtBu as the base (Table 2, entry 7). Although remarkable activities were observed, not all amide solvents are suitable for our recycling concept (the addition of water and phase separation), as DMF, DMAc and *N*-ethylpyrrolidone (NEP) have no mixing gap with water.

With the use of CHP and *N,N*-dibutylformamide (DBF) excellent to good TONs were obtained, and both solvents show limited miscibility with water. As both are, in principle, suitable for simple recycling and the process concept, further emphasis was placed on the use of these solvents in the carboxylation of ethylene. Presumably, the amides stabilise the active species, limit decomposition over time, mitigate the formation of agglomerates and favour the formation of the palladacatalyst because of the higher CO₂ concentration in solution. It is known that these amides can, in principle, act as reducing agents for Pd^{II},^[15b] although only in the presence of halides or oxygen, which are excluded from our system. It is known that CHP has a low critical hydrophobic interaction concentration with water, which disfavours the formation of catalyst clusters of **Pd-III** through the sodium acrylate ligand.^[16]

Even higher TONs could be achieved with these solvents with the in situ formation of the [Pd(PPh₃)₄]/dcpe catalyst (Scheme 3).



Scheme 3. Carboxylation of ethylene in CHP and DBF using [Pd(PPh₃)₄]/dcpe (1:1.1) as the catalyst. Reaction conditions: 30 mL solvent, 25 mmol NaOtBu, 10 bar ethylene, 40 bar CO₂, 20 h, 145 °C. The procedure is given in the Experimental Section.

With DBF, it is possible to convert all the base to reach a TON of 130. At lower catalyst loadings in DBF, the catalyst showed quite a slow rate of conversion to reach a TON of 80 at 0.01 mmol catalyst loading after 20 h. However, the catalyst stability and activity over time is improved significantly to result in a TON of 215 after a reaction time of 108 h. The activity of the reaction in CHP increased enormously to reach a TON of 514 in one run, which is, to best of our knowledge, the highest TON ever observed for the carboxylation of ethylene to sodium acrylate. The reaction profile for the synthesis of sodium acrylate in CHP showed the highest catalyst activity in the first 5 h (Figure 1) to reach a TON of 307 with a TOF of around 61 h⁻¹. This is a significant increase compared to the solvent used previously (anisole),^[11] for which a maximum TOF of 5 h⁻¹ was measured after 15 h (Supporting Information).

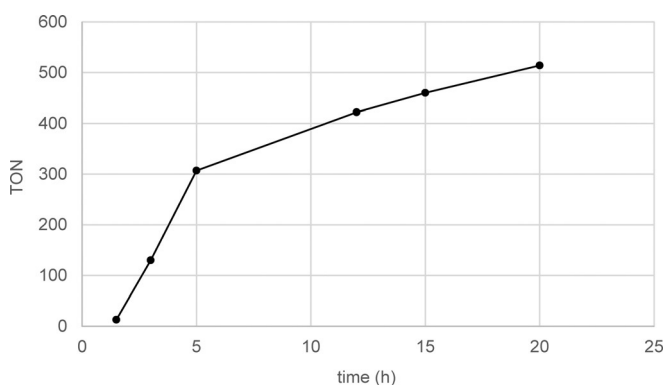


Figure 1. Carboxylation of ethylene in CHP. Each point is an independent catalytic run stopped after the given time. Reaction conditions: 30 mL CHP, 25 mmol NaOtBu, 10 bar ethylene, 40 bar CO₂, 0.01 mmol [Pd(PPh₃)₄], 0.011 mmol dcpe, 145 °C. The procedure is given in the Experimental Section.

The reaction rate is reduced over time, probably because of an alteration of the viscosity of the system from the increasing amount of sodium acrylate present in the medium.

Interestingly, Ni catalysts^[10,11] showed no catalytic activity under these reaction conditions, presumably because of the formation of inactive nickel carbonyls as the amides can act as carbonylating agents.^[17]

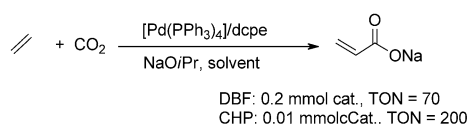
As sodium acrylate was the focus of this research because of its industrial importance, optimisation was geared solely towards its synthesis. Nevertheless, we also tested some other olefins in the proposed system (Table 3). Although a high activity in the carboxylation of ethylene was achieved, other olefins led to the observation of significantly lower TONs. Typically, the TONs were lower than that in the Pd-catalysed carboxylation using anisole as the solvent, with the exception of cyclopentene.^[11]

Table 3. Carboxylation of olefins.		
$\text{olefin} + \text{CO}_2 \xrightarrow[\text{NaOtBu}]{\text{[Pd(PPh}_3)_4]/\text{dcpe, 145}^\circ\text{C, CHP}} \text{R}-\text{CH}=\text{CH}-\text{CO}_2\text{Na}$		
Entry ^[a]	Substrate	TON 1 ^[b]
1	Ethene	152
2	Propylene	40
3	Styrene	5
4	Cyclooctadiene	5
5	Methyl acrylate	2
6	Cyclopentene	92

[a] Reaction conditions: 20 mmol NaOtBu, 0.1 mmol [Pd(PPh₃)₄], 0.11 mmol dcpe, 30 mL CHP, 10 bar or 20 mmol of olefin, 40 bar CO₂, 20 h. The reaction was performed according to the general procedure given in the Experimental Section; [b] TON determined by using ¹H NMR spectroscopy in D₂O as the solvent using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.13 mmol) as the internal standard.

As reported previously, the choice of the base is crucial for the success of the reaction.^[6,7,9–11] In earlier work, a compromise between activity and continuous process compatibility was found in substituted phenolates.^[10] From an intensive study of the base behaviour in the presence of CO₂,^[11] cheaper and simpler bases such as *tert*-butoxides were shown to be suitable for this catalytic system. Unfortunately, the regeneration of NaOtBu directly from NaOH and *t*BuOH is possible but not straightforward.^[18] Sodium *isopropoxide* (NaOiPr) would be a preferable alternative as it can be regenerated directly from NaOH and *i*PrOH.^[19] Additionally, it is easier to remove and recycle because of the lower boiling point of *i*PrOH than *t*BuOH. In contrast to the previous work in which anisole was used as the solvent,^[11] with the amide solvents it is also possible to use NaOiPr as the base (Scheme 4).

The achieved TONs are lower than those if NaOtBu was used as the base but remain significantly higher than the TONs achieved in the non-CHP systems. As it enables a simpler recy-



Scheme 4. Carboxylation of ethylene in CHP and DBF using [Pd(PPh₃)₄]/dcpe (1:1.1) as the catalyst. Reaction conditions: 30 mL solvent, 25 mmol NaOiPr, 10 bar ethylene, 40 bar CO₂, 20 h, 145 °C. The procedure is given in the Experimental Section.

cling, the use of NaOiPr is interesting for the continuous carboxylation of ethylene, despite the lower TON than that with the use of NaOtBu.

The continuous process concept reported previously is as follows: the reaction is performed in a reactor that contains the organic solvent, the base, the catalyst, ethylene and CO₂. To separate the sodium acrylate from the catalyst, water is added to a continuous stream from the reactor after de-pressurisation. Therefore, an organic solvent that has a mixing gap with water is required. The alcohol formed in the reaction can be distilled off from the product phase and recycled with NaOH to leave the pure sodium acrylate behind. The catalyst in the organic solvent can be recycled back into the reaction after phase separation.

DBF has a mixing gap with water and can, therefore, be used in this concept. At room temperature, CHP has no mixing gap with pure water but at higher temperatures (above 50 °C) and in the presence of electrolytes in the aqueous phase (in this case sodium acrylate), it is possible to separate it from water. Under these conditions, which can be applied in the process concept (phase separation above 50 °C), CHP becomes an appropriate solvent.

As reported previously, the catalyst is stable towards traces of water under the reaction conditions.^[10,11] However, Zn or ethylene were required in the previous systems to obtain an active catalyst through recycling. As the water content in wet DBF and CHP is higher than that in anisole, it was necessary to test the catalytic system in water-saturated DBF and CHP. Regrettably, the catalyst lost its activity under these conditions. Therefore, the removal of water from the organic phase is required before recycling: the simple evaporation of water from the high-boiling, catalyst-containing DBF or CHP phase was sufficient (see modified process concept in Figure 2).

In a first experiment, the catalyst phase was dried at 50 °C in vacuo for 2 h before recycling. This permitted the reuse of the catalyst in the amide solvent without a significant decrease in activity or a regeneration step (using Zn or ethylene). This concept works for any combination of DBF or CHP as the solvent and NaOtBu or NaOiPr as the base (Table 4).

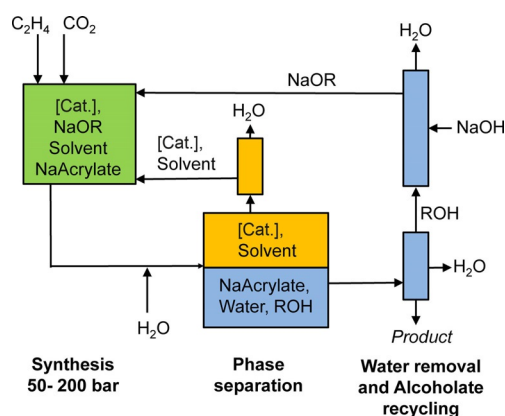
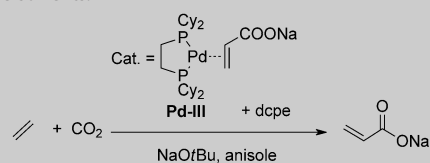


Figure 2. Modified process concept for the Pd-catalysed synthesis of sodium acrylate from ethylene and CO₂ using amide solvents and NaOiPr.

Table 4. Catalyst recycling solvents in the carboxylation of ethylene using amide solvents.

Entry ^[a]	Base [mmol]	Catalyst loading [mmol]	Solvent	TON 1 ^[b]	TON 2 ^[b]
1	NaOtBu (25+25)	0.2	DBF	135	100
2	NaO <i>i</i> Pr (15+15)	0.2	DBF	30	100
3	NaOtBu (15+15)	0.1	CHP	78	90
4	NaO <i>i</i> Pr (15+15)	0.1	CHP	30	100

[a] Reaction conditions: Catalyst: [Pd(PPh₃)₄]/dcpe, 30 mL solvent, 10 bar ethylene, 40 bar CO₂ 145 °C, 20 h. The reaction and recycling were performed according to the procedure given in the Experimental Section; [b] TON determined by using ¹H NMR spectroscopy in D₂O as the solvent using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as the internal standard.

With CHP as the solvent, the formed sodium acrylate was not an effective electrolyte with regard to favouring phase separation at room temperature. Hence an additional amount of a more lipophilic solvent, such as Et₂O, was necessary at room temperature (which can be avoided if the phase separation is performed above 50 °C).

Conclusions

We used amides as solvents to increase the catalyst activity and to facilitate recycling. Turnover numbers of over 500 were achieved in one run, which is approximately five times higher than the best hitherto published systems. As a result of the use of the amide solvents, the additional regeneration step is no longer necessary to recycle the catalytic solution in the synthesis step, and therefore, a more straightforward process concept is realised. Additionally, sodium *isopropoxide* can be used as a simple and easily recycled alcoholate base, which reduces the complexity of a potential process for the synthesis of sodium acrylate from ethylene and CO₂. With this system in hand, we believe that a significant step towards the application of this system in a real process has been made. Therefore, we will focus our future work on the development of a continuous synthesis set-up for the proof-of-concept of this approach.

Experimental Section

General: All air- and moisture-sensitive manipulations were performed using standard vacuum line, Schlenk and cannula techniques or by using an MBraun Ar-atmosphere glovebox. Solvents for air- and moisture-sensitive manipulations were dried by using an MBraun SPS 800 solvent purification system, degassed and stored over molecular sieves or dried and deoxygenated using standard literature procedures. Cyclopentadienyl allyl palladium ([Pd(Cp)(allyl)]) and **Pd-IIIa** were synthesised according to literature procedures.^[9] The synthesis and characterisation of **Pd-III** is given in the Supporting Information. All other reagents were purchased

from Sigma–Aldrich or ABCR and used as received. Gases were purchased from Air Liquide. Steel reactors (60 mL capacity) equipped with a magnetic overhead stirrer purchased from Premex were used for the carboxylation reactions under pressure. ¹H, ³¹P and ¹³C NMR spectra were recorded by using Bruker Advance 200, 400, 500 or 600 spectrometers. All ¹H and ¹³C NMR chemical shifts are reported in ppm relative to SiMe₄ using the ¹H (residual) and ¹³C chemical shifts of the solvent as a secondary standard. ³¹P NMR spectra were referenced to PPh₃.

Standard procedure for the synthesis of sodium acrylate: Inside a glovebox, a 60 mL steel autoclave was charged with the catalyst, the base and the solvent. The autoclave was removed from the glovebox and charged under stirring at 800 rpm with the given pressure of ethylene and CO₂ for 15 min each at 25 °C. After that, the autoclave was heated to the given temperature and left to stir at 800 rpm for the given reaction time. After the reaction, the autoclave was cooled to 20 °C, the pressure was released, and the reaction mixture was transferred into a 100 mL glass bottle. The autoclave vessel was rinsed with D₂O (15 mL) to wash the autoclave. To this mixture, 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.13 mmol, 0.022 g) was added, and additional D₂O (10 mL) was added to the glass bottle. To favour the phase separation, Et₂O (40 mL) was added to the mixture. An aliquot of the aqueous phase was collected, centrifuged and analysed by using ¹H NMR spectroscopy. The TON was determined by ¹H NMR spectroscopy (200 MHz, 70 scans) according to a procedure reported previously.^[6,7,10]

Standard procedure for the synthesis of other acrylates: Inside the glovebox, a 60 mL steel autoclave was charged with the olefin (20 mmol), [Pd(PPh₃)₄] (0.1 mmol), dcpe (0.11 mmol), NaOtBu (20 mmol) and CHP (30 mL). The autoclave was removed from the glovebox and charged under stirring at 800 rpm with 40 bars CO₂ for 15 min at 25 °C. The autoclave was heated to the given temperature and left to stir at 800 rpm for the given reaction time. After the reaction, the autoclave was cooled to 20 °C, the pressure was released, and the reaction mixture was transferred into a 100 mL glass bottle. The autoclave vessel was rinsed with D₂O (15 mL) to wash the autoclave. 3-(Trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.13 mmol, 0.022 g) and D₂O (10 mL) were added to the glass bottle. To favour the phase separation, Et₂O (40 mL) was added to the mixture. An aliquot of the aqueous phase was collected, centrifuged and analysed by using ¹H NMR spectroscopy. The TON was determined by using ¹H NMR spectroscopy (200 MHz, 70 scans) according to a procedure reported previously.^[6,7,10]

Procedure for the catalyst recycling: Inside the glovebox, a 60 mL steel autoclave was charged with [Pd(PPh₃)₄], 1,2-bis(dicyclohexylphosphino)ethane, the base and the solvent (30 mL). The autoclave was removed from the glovebox and charged under stirring at 800 rpm with 10 bar of ethylene and 40 bar of CO₂ (total pressure 50 bar) for 15 min each at 25 °C. The autoclave was heated at 145 °C and left to stir for 20 h at 800 rpm. The autoclave was cooled to 20 °C, the pressure was released and it was taken back into the glovebox. The reaction mixture was transferred into a 100 mL Schlenk flask equipped with a magnetic stirrer bar and, outside the glovebox, degassed water (30 mL) was added with a syringe. The mixture was stirred for 10 min at RT to favour the dissolution of sodium acrylate, and the two phases were left to settle for 2 min. In the case of CHP, Et₂O (30 mL) was added to achieve the proper phase separation at RT. The water phase was separated and analysed as described previously. The organic phase was dried under vacuum at 50 °C for 2 h and reintroduced into the glovebox and transferred into a third autoclave pre-charged with the given

amount of the base. Then, the autoclave was removed from the glovebox and charged with 10 bar of ethylene and 40 bar of CO₂ (total pressure 50 bar) for 15 min each at 25 °C under stirring at 800 rpm. The autoclave was heated to 145 °C and stirred for another 20 h at 800 rpm. After the reaction, the work-up and analysis are the same as described previously.^[6,7,10]

Acknowledgements

CaRLa (Catalysis Research Laboratory) is co-financed by the Ruprecht-Karls-University Heidelberg (Heidelberg University) and BASF SE.

Keywords: amides • carboxylation • homogeneous catalysis • palladium • solvent effects

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Manuscript received: September 14, 2016

Version of record online: December 28, 2016