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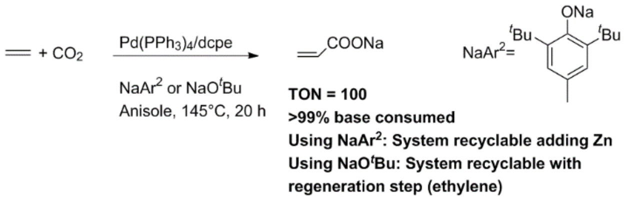
Enhanced activity and recyclability of palladium complexes in the catalytic synthesis of sodium acrylate from CO_2 and ethylene

Simone Manzini,[a] Alban Cadu,[a] Anna-Corina Schmidt,[a] Núria Huguet,[b] Oliver Trapp,[a,c] Rocco Paciello,[b] and Thomas Schaub*[a,b]

Abstract: The palladium catalysed synthesis of sodium acrylate from ethylene and CO_2 in the presence of alcoholate bases has been improved significantly. By using amide solvents like N-cyclohexyl-pyrrolidone or N,N-dibtuylformamide, we were able to achieve turn over numbers greater than 500 in one run, which is significantly higher than previous known systems for this reaction. For the first time, we were also able to recycle the catalyst without any additional regeneration step. With this system, it is also possible to use the simple and easily recycled alcoholate base NaO*i*Pr, achieving good turn over numbers: up to 200.

Introduction

Sodium acrylate is a valuable monomer for the production of polyacrylate salts, which are used as superadsorbants or dispersants in our daily life.[1] Sodium acrylate is nowadays produced via a two stage oxidation of propylene towards acrylic acid, followed by the reaction with NaOH.[2] Besides the historical routes towards acrylic acid based ethylene oxide or acetylene[2a], also glycerol or lactic acid were 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 CO_2 could offer a cost competitive approach compared to the propylene route. A tremendous amount of stoichiometric and catalytic carboxylation reactions using CO_2 is known,[4,5] but the catalytic carboxylation of ethylene into acrylic acid was just reported in the last years and remains still relatively underdeveloped.[6,7,8,9.10,11] Studies are ongoing in our laboratory, since the discovery of the first two-stage process in 2012 for the carboxylation of ethylene with CO_2 in the presence of strong bases,[6] 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 was reported by our laboratory using sodium-2-fluorophenolate as base and nickel-phosphine catalysts.[7]
Simultaneously, the catalytic synthesis of lithium acrylate from ethylene and CO_2 was achieved by *Vogt et al.*[8], however in both reports only low TON were achieved and no catalyst recycling was reported. In 2015, the reaction was extended to the use of palladium-catalysts.[9] Using $[Pd(PPh_3)_4]$ in combination with dcpe (=1,2-bis(dicyclohexylphosphino)ethane) as the catalysts, we were able to develop a first concept for a continuous process, were the use of solid reductants like Zn could be avoided (scheme 1).[10] In addition, by redesigning the continuous process with different bases and solvents, we were able to find a more suitable approach for product separation and base regeneration.



Scheme 1. Current catalyst system for the continuous approach to synthesise sodium acrylate from ethylene and CO_2.[10,11]

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, unlike in the previously reported nickel system (scheme 1).[11]
Despite these progresses, the reaction had still some drawbacks, mainly the low TON of ~ 100 per run, the drop in activity after the recycling and also the low space-time-yield, which had to be improved before its application in an industrial scale process. Also in order 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 was described previously (see scheme 2).[6,7,9,10] The metal-species proposed for

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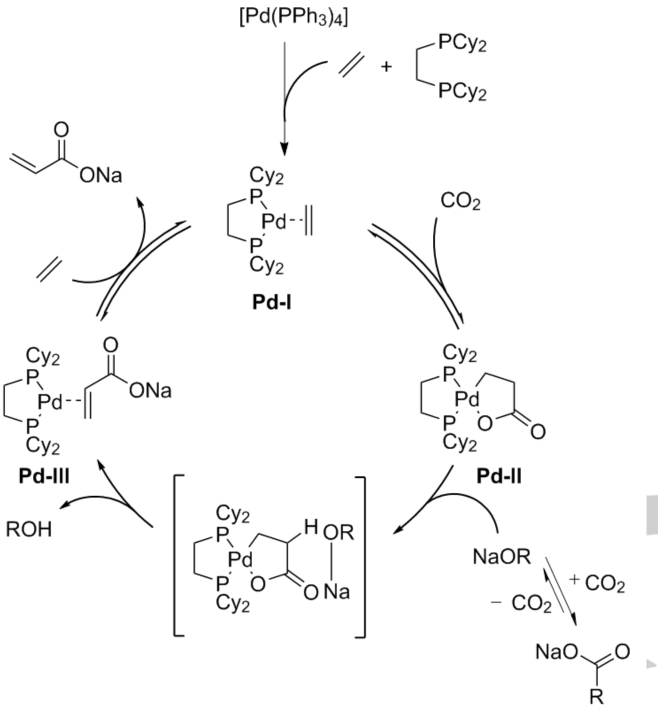
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) the catalytic cycle are the olefin-complex **I**, the metallalactone **II** and the sodium acrylate complex **III** formed by deprotonation of the lactone. According to this mechanism and if no other species were involved, the need for an additional reducing agent like Zn or a regeneration step with ethylene, in order to achieve any TON with the recycled catalyst phase can be questioned.[10,11]

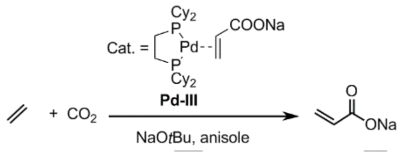


Scheme 2. Proposed mechanism for the Pd-dcpe catalyzed carboxylation of ethylene in the presence of an alkoxide-base.

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

To investigate the activity of **Pd-III**, we synthesized this complex by deprotonation with KO*t*Bu of the previously reported acrylic-acid complex (details described in the 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 (table 1, entry 2) in the carboxylation of ethylene. This concurs with the previous recycling experiments,[10] where hardly any activity was observed without a reactivation step. But according to the proposed mechanism,[9,10] **Pd-III** is part of the catalytic cycle and should therefore be active. In order 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 previously employed for catalyst regeneration Zn was also screened, as was the influence of the concentration of *t*BuOH.

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



Entry[a]	Additive	T [°C]	TON [b]
1	None	145	4
2	None	100	1
3	dcpe (1 eq.)	145	9
4	dcpe (1 eq.)	100	3
5	dcpe (2 eq.)	145	5
6	PPh_3 (4 eq.)	145	10
7	Zn (1 eq.)	145	1
8	*t*BuOH (1 eq.)	145	4
9	*t*BuOH (100 eq.)	145	3

[a] Reaction conditions: 20 mmol NaO*t*Bu, 0.2 mmol catalyst, 30 mL anisole, 10 bar ethylene, 20 bar CO_2, 8 h, Reaction performed according to the general procedure given in the experimental section; [b] TON determined via ^{1}H-NMR in D_2O as solvent using 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt (0.125 mmol) as internal standard; When using [Pd(PPh_3)$_4$]/dcpe as catalyst, also a TON of 8 was observed after 8 h reaction time.

As shown in table 2 (entries 3 and 6) the addition of phosphine-ligands to catalyst **Pd-III** had the highest benefit, with TONs similar to that of [Pd(PPh_3)$_4$]/dcpe being achieved. The beneficial effect of additional ligands is known and can help to prevent catalyst decomposition.[13] Further investigation towards achieving recyclability of the organic phase were still required. Additionally, the Zn 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] decreasing the reaction temperature to 100°C reduces the activity significantly (entries 2 and 4 in table 2). The activity of complex **Pd-III** with one additional equivalent of dcpe was probed, with the TON 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(PPh_3)/dcpe] in its first run.

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

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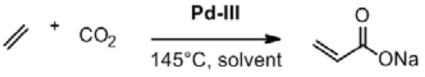
One plausible reason for the lack of activity could be the agglomeration of **Pd-III** via its sodium carboxylate group in the relatively weekly coordinating solvents which were used in the previous work. As the concentration of **Pd-III** increases during the catalysis due to the formation of sodium acrylate, this could slow down the reaction over time and may explain the lack of activity when solely **Pd-III** is used as catalyst. Also a higher concentration of CO_2 in the reaction solution could be beneficial in order to accelerate the catalytic cycle. Therefore we investigated the influence of more coordinating solvents in which CO_2 is also known to have higher solubility: amides.[14] For example it is known that N,N-Dimethylacetamide (DMAc) stabilizes and activates palladium species in solution and also provides a good solubility for CO_2.[15]

Table 2. Effect of solvent using **in** acrylate synthesis



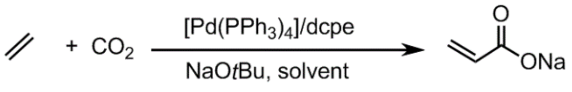
Entry[a]	Solvent	TON [b]
1	Anisole	10
2	N,N-Dimethylacetamide (DMAc)	55
3	N,N-Dimethylformamid (DMF)	90
4	N,N-Dibutylformamide (DBF)	51
5	N-Methyl-pyrrolidone (NMP)	55
6	N-Ethyl-pyrrolidone (NEP)	60
7	N-Cyclohexyl-pyrrolidone (CHP)	152
8	N-Dodecyl-pyrrolidone (NDP)	21

[a] Reaction conditions: Reaction performed according to the general procedure given in the experimental section; [b] TON determined via ^{1}H-NMR in D_2O as solvent using 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (0.13 mmol) as internal standard.

In order to increase the CO_2 concentration within the solution, the CO_2-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 CHP as solvent with **Pd-III** as catalyst and NaO*t*Bu as base (table 2, entry 7). While remarkable activities were observed, not all amide solvents are suitable for our recycling concept (addition of water and phase separation), as DMF, DMAc, NEP have no mixing gap with water.

Using CHP and DBF, excellent to good TON were obtained and both solvents show limited miscibility with water. As both are in principle suitable for a simple recycling and process concept, further emphasis was placed on the use of these solvents in the carboxylation of ethylene. Presumably the amides stabilize the active species, limit decomposition over time, mitigate the formation of agglomerates and favour the formation of the palladalactone due to the higher CO_2-concentration in solution. It is also known from literature, that these amides can in principle act as reducing agents for palladium(II)[15b], though 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 concertation with water, which disfavours the formation of catalyst clusters of **Pd-III** *via* the sodium acrylate ligand.[16]

Even higher TON could be achieved with this solvents with in situ formation of the $[Pd(PPh_3)_4]$/dcpe catalyst, as shown in scheme 3.



DBF: 0.2 mmol Cat., TON 130
CHP: 0.01 mmol Cat., TON 514

Scheme 3. Carboxylation of Ethylene in CHP and DBF using $[Pd(PPh_3)_4]$/dcpe (1 : 1.1 ratio) as catalyst. Reaction conditions: 30 mL solvent, 25 mmol NaO*t*Bu, 10 bar ethylene, 40 bar CO_2, 20 h, 145°C. Procedure given in the experimental section.

With DBF, it is possible to convert all the base and to reach a TON of 130. At lower catalyst loadings in DBF, the catalyst showed a quite slow rate of conversion reaching a TON of 80 at 0.01 mmol catalyst loading after 20 h. However, the catalyst stability and activity over time is significant improved, resulting in a TON of 215 after a reaction time of 108 h. The activity of the reaction in CHP increased enormously, reaching 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 hours (see figure 1) reaching a TON of 307 with a TOF of around 61 h^{-1}. This is a significant increase compared to the previously used solvent (anisole),[11] for which a maximum TOF of 5 h^{-1} was measured after 15 h (see supporting information).

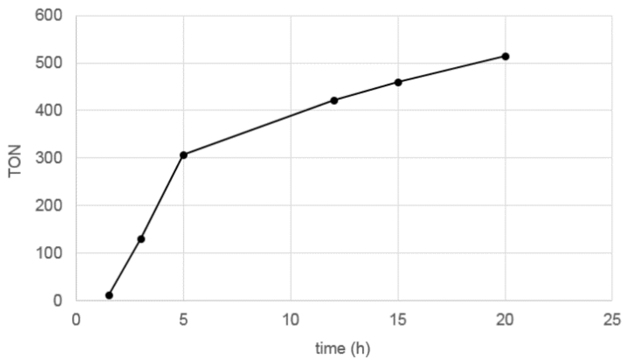
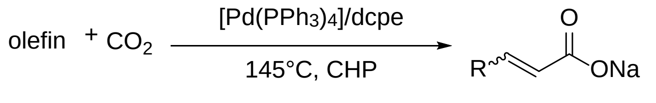


Figure 1. Carboxylation of Ethylene in CHP. Each point is an independent catalytic run, stopped after the given time. Reaction conditions: 30 mL CHP, 25 mmol NaO*t*Bu, 10 bar ethylene, 40 bar CO_2, 0.01 mmol $[Pd(PPh_3)_4]$, 0.011 mmol dcpe, 145°C. Procedure given in the experimental section.

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

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

Table 3. Carboxylation of olefins

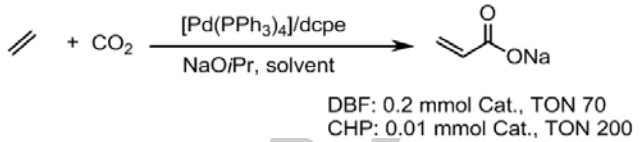


Entry[a]	Substrate	TON 1[b]
1	Ethene	152
2	Propylene	40
3	Styrene	5
4	Cyclooctadiene	5
5	Methyl acrylate	2
6	Cyclopentene	92

[a] Reaction conditions: 20 mmol NaO*t*Bu, 0.1 mmol $[Pd(PPh_3)_4]$, 0.11 mmol dpce, 30 mL CHP, 10 bar or 20 mmol of olefin, 40 bar CO_2, 20 h, Reaction performed according to the general procedure given in the experimental section; [b] TON determined via ^{1}H-NMR in D_2O as solvent using 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (0.13 mmol) as internal standard.

As sodium acrylate was the focus of this research, due to its industrial importance, optimizations were solely geared towards its synthesis. Nevertheless, we also tested some other olefins in the above described system. While high activity in the carboxylation of ethylene was achieved, other olefins led to significant lower TON being observed. The TON were typically lower than in the palladium catalysed carboxylation using anisole as the solvent, with the exception of cylcopentene.[11]

As reported previously, the choice of the base is crucial for the success of the reaction.[6,7,9,10,11] 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 CO_2,[11] cheaper and simpler bases like *tert*-butoxides were shown to be suitable for this catalytic system. Unfortunately, the regeneration of NaO*t*Bu directly from NaOH and *t*BuOH is possible but not straightforward.[18] NaO*i*Pr would be a preferable alternative, as it can be directly regenerated from NaOH and *i*PrOH.[189 Additionally, it is easier to remove and recycle owing to the lower boiling *i*PrOH compared to *t*BuOH. In contrast to the previous work when anisole was used as the solvent,[11] with the amide solvents it is also possible to use NaO*i*Pr as the base (scheme 5).



Scheme 4. Carboxylation of Ethylene in CHP and DBF using $[Pd(PPh_3)_4]$/dcpe (1:1.1 ratio) as catalyst. Reaction conditions: 30 mL solvent, 25 mmol NaO*i*Pr, 10 bar ethylene, 40 bar CO_2, 20 h, 145°C. Procedure given in the experimental section.

The achieved TON are lower than those resulting from NaO*t*Bu as base, but remain significantly higher than the TON achieved in the non-CHP systems. As it enables a simpler recycling, the use of NaO*i*Pr is interesting for a continuous carboxylation of ethylene, despite the lower TON, compared to NaO*t*Bu.

The previously reported continuous process concept is the following: the reaction is performed in a reactor containing the organic solvent, the base, the catalyst as well as ethylene and CO_2. To separate the sodium acrylate from the catalyst, water is added to a continuous stream from the reactor after depressurization. Therefore an organic solvent having a mixing gap with water is required. The alcohol which is formed in the reaction can be distilled off from the product phase and recycled with NaOH, leaving the pure sodium acrylate behind. The catalyst in the organic solvent can be recycled back into the reaction after the 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 also possible to separate from water. Under these conditions which can be applied in the process concept (phase separation above 50°C), CHP becomes an appropriate solvent.

As previously reported, 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 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, water removal from the organic phase is required prior to recycling: a simple evaporation of water from the high boiling catalyst-containing DBF- or CHP-phase was sufficient (see modified process concept in Figure 2).

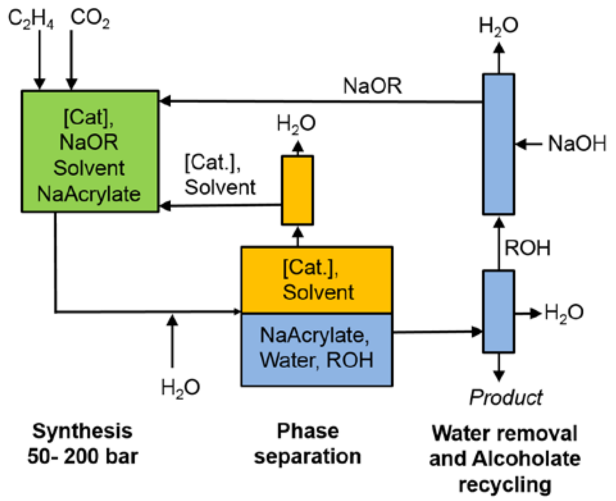


Figure 2. Modified process concept for the palladium catalysed synthesis of sodium acrylate from ethylene and CO_2 using amide solvents.

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

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

Entry[a]	Base (mmol)	Catalys-Loading (mmol)	Solvent	TON 1[b]	TON 2[b]
1	NaO*t*Bu (25 +25)	0.2	DBF	135	100
2	NaO*i*Pr (15 + 15))	0.2	DBF	30	100
3	NaO*t*Bu (15 + 15)	0.1	CHP	78	90
4	NaO*i*Pr (15 + 15)	0.1	CHP	30	100

[a] Reaction conditions: Catalyst: $[Pd(PPh_3)_4]$/dcpe,30 mL solvent, 10 bar ethylene, 40 bar CO_2 145°C, 20 h, Reaction and recycling performed according to the procedure given in the experimental section; [b] TON determined via ^{1}H-NMR in D_2O as solvent using 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (0.125 mmol) as internal standard.

With CHP as 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, like Et_2O was necessary at room temperature (which can be avoided when the phase separation is carried out above 50°C).

Conclusions

By using amides as solvents, the catalyst activity was increased and a facilitated recycling was enabled. TON of over 500 were achieved in one run, which is about 5 times higher than the best hitherto published systems. Due to the amide solvents, the additional regeneration step is no longer necessary in order recycle the catalytic solution in the synthesis step, and therefore allows a more straightforward process concept. Also, NaO*i*Pr can now 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 CO_2. 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 carried out using standard vacuum line, Schlenk and cannula techniques or in an MBraun inert argon atmosphere glove box. Solvents for air- and moisture-sensitive manipulations were dried with and MBraun SPS 800 solvent purification system, degassed and stored over molecular sieves, or dried and deoxygenated using standard literature procedures. [Pd(Cp)(allyl)] and the palladium complexes Pd-IIIa have been synthesised according to literature procedures.[9] Synthesis and characterization 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. 60 mL capacity steel reactors equipped with a magnetic overhead stirred purchased from Premex were used for the carboxylation reactions under pressure. ^{1}H, ^{31}P and ^{13}C-NMR spectra were recorded on Bruker Advance 200, 400, 500 or 600 spectrometers. All ^{1}H and ^{13}C-NMR chemical shifts are reported in ppm relative to $SiMe_4$ using the ^{1}H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard. ^{31}P-NMR was referenced to PPh_3.

Standard procedure for the synthesis of sodium acrylate: Inside the glove box 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 CO_2 for 15 min each at 25 °C. After that, the autoclave was heated to the given temperature and left to stir with 800 rpm for the given reaction time. After the reaction, the autoclave was cooled to 20 °C, the pressure released and the reaction mixture was transferred into a 100 mL glass bottle. The autoclave vessel was rinsed with 15 mL D_2O to wash the autoclave. To this mixture, 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (0.13 mmol, 0.022 g) was added and additional 10 mL of D_2O were added to the glass bottle. In order to favor the phase separation, 40 mL of Et_2O were added to the mixture. An aliquot of the aqueous phase was collected, centrifuged and analyzed by ^{1}H NMR. The TON was determined by ^{1}H NMR (200 MHz, 70 scans) according to the previous reported procedure.[6,7,10]

Standard procedure for the synthesis of other acrylates: Inside the glove box a 60 mL steel autoclave was charged with the olefin (20mmol), $[Pd(PPh_3)_4]$ (0.1 mmol), dcpe (0.11mmol), NaO*t*Bu (20 mmol) and CHP (30mL). The autoclave was removed from the glovebox and charged under stirring at 800 rpm with 40 bars CO_2 for 15 min at 25 °C. After that, the autoclave was heated to the given temperature and left to stir with 800 rpm for the given reaction time. After the reaction, the autoclave was cooled to 20 °C, the pressure released and the reaction mixture was transferred into a 100 mL glass bottle. The autoclave vessel was rinsed with 15 mL D_2O to wash the autoclave. To this mixture, 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (0.13 mmol, 0.022 g) was added and additional 10 mL of D_2O were added to the glass bottle. In order to favor the phase separation, 40 mL of Et_2O were added to the mixture. An aliquot of the aqueous phase was collected, centrifuged and analyzed by ^1H NMR. The TON was determined by ^1H NMR (200 MHz, 70 scans) according to the previous reported procedure.[6,7,10]

Procedure for the catalyst recycling according to table 7.
Inside the glove box a 60 mL steel autoclave was charged with $[Pd(PPh_3)_4]$, 1,2-bis(dicyclohexylphosphino)ethane, the bas and 30 mL of the Solvent. The autoclave was removed from the glovebox and charged under stirring at 800 rpm with 10 bar of ethylene and 40 bar of CO_2 (total pressure 50 bar) for 15 min each at 25 °C. After that, the autoclave was heated at 145°C and left to stir for 20 hours at 800 rpm. The autoclave was cooled to 20 °C, the pressure released and introduced in the glove box. The reaction mixture was transferred in to a 100 ml Schlenk flask equipped with a magnetic bar and, outside the glove box 30 mL of degassed water were added through syringe. The mixture was stirred for 10 min at room temperature in order to favour the dissolution of sodium acrylate and let the two phases settle for 2 minutes. In the case of CHP, Et_2O (30 mL) has to be added for a proper phase separation at room temperature. The water phase was separated and analysed as previously described. The organic phase was dried under vacuum at 50°C for two hour and re-introduced in the glove box and transferred to a third autoclave pre-charged with the given amount of the base. Then, the autoclave was removed from the glove box and charged, under stirring at 800 rpm, with 10 bar of ethylene and 40 bar of CO_2 (total pressure 50 bar) for 15 min each at 25 °C. After that, the autoclave was heated at 145°C and left to stir for another 20 hours at 800 rpm. After the reaction, the work-up and analysis are the same as described previously.[6,7,10]

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Keywords: CO_2 • sodium acrylate • palladium • catalysis • recycling

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2001, 2327-2336. We also run a NMR-experiment with [Ni(COD)$_2$], dcpe and DMF at 140°C, whereby the corresponding complex [(dcpe)Ni(CO)$_2$] was formed. See ESI for experimental details.

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Entry for the Table of Contents

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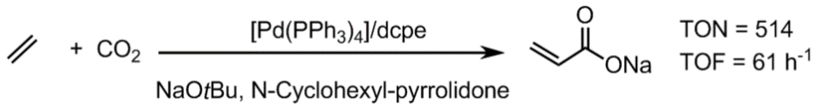

The palladium catalysed synthesis of sodium acrylate from ethylene and CO_2 in the presence of alcoholate bases could be improved significantly by the use of amide solvents.

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Page No. – Page No.

Enhanced activity and recyclability of palladium complexes in the catalytic synthesis of sodium acrylate from CO_2 and ethylene

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