DOI: 10.1002/ejoc.201501113



Palladium- and Nickel-Catalyzed Synthesis of Sodium Acrylate from Ethylene, CO₂, and Phenolate Bases: Optimization of the Catalytic System for a **Potential Process**

Simone Manzini,^[a] Núria Huguet,^[a,b] Oliver Trapp,^[a,c] and Thomas Schaub*^[a,b]

Keywords: Synthetic methods / Process development / Homogeneous catalysis / Palladium / C1 building blocks / High-pressure chemistry

The synthesis of sodium acrylate through catalytic carboxylation of ethylene with CO_2 in the presence of a base is a reaction of high interest. To develop a more efficient and sustainable method to access this valuable acrylate monomer, we optimized the system in a one-step homogeneous nickelor palladium-catalyzed reaction, without the need for stoichiometric amounts of an additional reducing agent. Suitable

nontoxic solvents such as anisole instead of the previously reported tetrahydrofuran or chlorobenzene were found to lead to acrylate formation. In combination with appropriate phenolate bases, this could allow a rational process concept for a simple catalyst recycling, product separation, and base regeneration.

Introduction

The carboxylation of ethylene with CO_2 in the presence of a base can provide an efficient and sustainable route through which to access acrylate salts, which are of high industrial importance. Sodium acrylate is produced from acrylic acid on a large scale as a monomer for use in superabsorbents.^[1] This monomer is nowadays mainly produced from propylene through a two-stage oxidation process.^[2] The direct synthesis of sodium acrylate from ethylene and CO_2 in the presence of a base could be a very attractive route that would avoid the use of propylene as feedstock. CO_2 is inexpensive and abundant and, due to the increased levels of ethane cracking, ethylene is becoming less expensive than propylene. Moreover, ethylene could also be produced from renewable sources through the dehydration of bioethanol.

The general strategies to use CO₂ as a building block for the preparation of carboxylic acids involve stoichiometric or metal-catalyzed reactions activating C-H and C-X bonds, and through hydrocarboxylation of olefins and alkynes.^[3] The carboxylation of olefins with CO₂ to access unsaturated carboxylic acids was investigated over the last decades in stoichiometric reactions^[4] based on the early re-

- Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany E-mail: thomas.schaub@basf.com
- Ruprecht-Karls-Universität [c] Organisch-Chemisches Institut, Heidelberg

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201501113.

sults of Hoberg et al.^[5] The first catalytic carboxylation of ethylene with CO₂ in the presence of NaOtBu using a nickel catalyst was described by our laboratory as a two-step process (Scheme 1, a).^[6] The first single-step catalytic system to obtain lithium acrylate was then reported in 2014 by Vogt et al.^[7] (Scheme 1, b) and towards the desired sodium acrylate in the same year by our laboratory (Scheme 1, c).^[8]



Scheme 1. Recent methodologies for the synthesis of acrylic acid salts through carboxylation of ethylene.

In the Vogt system,^[7] a nickel-phosphine catalyst is used and stoichiometric amounts of LiI, an amine base (NEt₃), and Zn are required to obtain the lithium acrylate, which is a significant drawback for a commercial application. In addition, lithium acrylate has limited commercial value because sodium acrylate is the desired product for the synthesis of superabsorbents.

[[]a] Catalysis Research Laboratory (CaRLa), Im Neuenheimer Feld 584, 69120 Heidelberg, Germany www.carla-hd.de [b] Synthesis and Homogeneous Catalysis, BASF SE,

⁶⁹¹²⁰ Heidelberg, Germany

In our system, sodium acrylate can be obtained directly when a nickel catalyst is used in combination with sodium-2-fluorophenolate as the base and Zn as an additive to achieve a TON of up to 107 (Scheme 1, c).^[8]

Even though achieving the catalytic synthesis of sodium acrylate was a significant result, before adapting this reaction to a process, the following points have to be addressed: (1) Simple separation of sodium acrylate from the reaction mixture should be integrated into the design. (2) Catalyst recycling should be possible. (3) The process should allow high conversion of the base in the carboxylation and simple base recycling as well as regeneration. (4) The formation of possible side products from the Kolbe–Schmidt reaction should be avoided. (5) The use of an additional stoichiometric reductant such as Zn should be avoided. (6) The new process should increase the TON. (7) The use of toxic solvents should be avoided.

Results and Discussion

As shown in previous work on nickel^[6,8] and palladium catalysts^[9] reported from our laboratory and by Vogt et al.,^[7] the direct synthesis of acrylic acid from CO_2 and ethylene is thermodynamically not feasible.^[6] However, the carboxylation of ethylene is made exergonic by addition of a base to generate the corresponding sodium acrylate (Scheme 2).^[6]



Scheme 2. Free energy for the synthesis of acrylic acid and for sodium acrylate.

Unfortunately, it is not possible to perform this reaction by using NaOH as the base directly because stable carbonates are formed immediately by the reaction with CO_2 .^[6,8,10,11] For this reason it is necessary to use an appropriate base that can be used to deprotonate the metallalactone intermediate, but will not irreversibly react with CO_2 under the reaction conditions (Scheme 3).^[6,8,10]

Sodium salts of substituted phenols were found to be the best compromise between reactivity and basicity (Scheme 1, c).^[8,10] Not all phenolates can be used in this transformation: di-*ortho*-substituted or *ortho*-deactivated phenols are required to avoid carboxylation in this position (Kolbe–Schmidt reaction).^[12]

To develop an economic process concept, we focused on adapting the system for use with lipophilic- and *ortho*-substituted phenols. In combination with low toxicity organic solvents with limited miscibility with water, a simple separation of the sodium acrylate from the phenol would be pos-



Scheme 3. Proposed mechanism for the nicke-catalyzed synthesis of sodium acrylate using sodium phenolates as bases.

sible when water is added after the reaction. By using a lipophilic and water-stable catalyst, the catalyst could also be separated via the organic phase (see Figure 1). The sodium phenolate in the organic mixture can then be regenerated by addition of NaOH under removal of water after separation of the product.^[13] As shown previously in mechanistic studies from our laboratory, Zn is not intrinsically necessary in the catalytic cycle and its use can, in principle, be avoided.^[6,10]



Figure 1. Process concept for the synthesis of sodium acrylate from ethylene, CO_2 , and NaOH.

In this context, it was first necessary to identify whether any of the previously reported Ni- and Pd-catalysts are compatible with di-*ortho*-substituted sodium phenolates as the base (Table 1).^[14] Table 1. Base screening for nickel and palladium catalysts.

// + CO ₂ Catalyst (0.2 mmol), Ligand (0.22 mmol), Base (20 or 30 mmol), (10 bar) (20 bar) THF, 20 h						O U ONa
Entry ^[a]	Catalyst	Ligand	T(°C)	Zn (mmol)	Base	TON ^[c]
1 ^[b,d]	Ni(COD) ₂	BenzP*	120	10	ONa F	107
2 ^[e]	PdCl ₂ (COD)	dcpe	145	10		24
3 ^[b,d]	Ni(COD) ₂	BenzP*	80	_	ONa	1
4	PdCl ₂ (COD)	dcpe	145	10	F	1
5 ^[b,d]	Ni(COD) ₂	BenzP*	80	-	ONa I	4
6	PdCl ₂ (COD)	dcpe	145	10	\bigcirc	31
7 ^[b,d]		BonzD*	80	-		4
8	Ni(COD) ₂	Denzi	145	10	ONa I	43
9		dcpe	145	10	Ŭ,	69
10	PdCl ₂ (COD)	dcpe	145	10		38

[a] Reaction conditions: base (20 mmol), catalyst (0.2 mmol), ligand (0.22 mmol), THF (30 mL), ethylene (10 bar), CO₂ (20 bar), 20 h. [b] As [a] but 30 mmol of base was added. [c] TON determined based on ¹H NMR analysis in D₂O as solvent and using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as internal standard. [d] Result from previous work in our laboratory.^[8] [e] Result from previous work in our labora-

According to the preliminary screening, di-alkyl substitution in the ortho-positions of the phenolate seems to strongly effect the activity. In case of 2,6-dimethylphenolate it was necessary to increase the temperature to 145 °C to achieve significant conversion (Table 1 entries 7-10). The [Ni(COD)₂]/BenzP* catalyst shows low activity with monoand di-alkyl-substituted phenolates at 80 °C. By increasing the temperature to 145 °C it was possible to achieve a TON of 43 by using 2,6-dimethylphenolate as the base. By changing the ligand from BenzP* [(R,R)-(+)-1,2-bis(tert-butylmethylphosphanyl)benzene] to simple dcpe (bis-1,2-dicyclohexylphosphinoethane) it is possible to increase the TON to 69 with the nickel catalyst (Table 1, entries 8 and 9). With sodium 2,6-difluorophenolate as the base, negligible catalysis was observed in both cases, probably due to the lower basicity compared to the other bases (Table 1, entries 3 and 4). Although the Ni system seems to be superior compared with Pd, several aspects of this reaction still needed to be evaluated, hence both metals were considered for further optimization.

The main drawback in the previous systems was the use of 50 equiv. Zn (relative to the catalyst) as a reductant to obtain a significant TON. The use of a solid reductant not only creates technical challenges in a continuous process, but also makes the system too expensive for an economic sodium acrylate production and produces waste. Given that Zn is not intrinsically needed for this transformation according to previous DFT calculations,^[6,10] the two catalysts were tested with catalytic amounts of Zn and without it.

In case of $[PdCl_2(COD)]/dcpe$, it was possible to reduce the amount of Zn to a tenth (from 10 to 1 mmol), whereupon the TON was reduced by only a quarter (38 vs. 29; see Table 2, entries 1–3). In the absence of Zn the activity was halved (Table 2, entries 4).

Table 2. Assessing the effect of the amount of zinc and catalyst precursor.

// (10 bar)	+ CO ₂ + ` (20 bar)	ONa (20 mmol)	Catalyst (0.2 mmol), dcpe (0.22 mmol), additive, THF, 145 °C, 20 h	O ONa
Entry ^[a]	Catalyst	Additi	ve Amount additive [mmol]	TON ^[b]
1	PdCl ₂ (COD)	Zn	10	38 ^[c]
2			1	29
3			0.5	22
4		_	_	21
5	Ni(COD) ₂	Zn	10	69 ^[c]
6			1	56
7		_	_	55
8	$Pd(OAc)_2$	_	_	11
9	[Pd(allyl)Cl] ₂	_	_	14
10	Pd(Cp)(allyl)	_	_	18
11	$Pd(dba)_2$	_	_	0
12	Pd(PPh ₃) ₄	-	_	28

[a] Reaction conditions: base (20 mmol), catalyst (0.2 mmol), dcpe (0.22 mmol), THF (30 mL), ethylene (10 bar), CO_2 (20 bar), 145 °C, 20 h. [b] TON determined based on ¹H NMR analysis in D₂O as solvent and using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as internal standard. [c] The result presented in Table 1 is given here for comparison.

The nickel system without Zn showed a lower decrease in the activity when compared with the system with the Pd catalyst (TON of 69 vs. 55; Table 2, entries 5–7), suggesting that the benefit of Zn is to prevent possible side reactions such as oxidations, which could lead to catalyst deactivation.

It has been found that the addition of Zn^{II} species, in particular by using $ZnCl_2$ and $Zn(OTf)_2$, has no beneficial effect on the activity (see the Supporting Information). Assuming that the role of Zn is to activate the precatalyst generating the active Pd⁰ species, we tested further Pd^{II} precursors. Without Zn, the Pd^{II} precursors were less active compared with [PdCl₂(COD)] (Table 2, entries 8–10) as expected according to previous investigations, Ni⁰ and Pd⁰ complexes are active species in the catalytic cycle,^[9] which makes them very sensitive towards traces of oxygen. It seems that the use of Zn can also reduce this sensitivity by regenerating oxidized active species.^[15]

In contrast, a TON of 28 was achieved when $[Pd(PPh_3)_4]/dcpe$ was used as catalyst, which was the highest value obtained when using Pd as catalyst without the addition of Zn (Table 2, entry 12). However, the use of a Pd⁰ precursor is not a guarantee for an active system, as shown with $[Pd(dba)_2]$, which was inactive (Table 2, entry 11).



Given that tetrahydrofuran (THF) is completely miscible with water and 2,6-dimethylphenol has a significant solubility in water, it was necessary to identify other solvents and phenols that were suitable for the concept described above. Based on the catalyst screening, we evaluated the solvent and base compatibility for [PdCl₂(COD)]/dcpe by using a catalytic amount of Zn (1 mmol) as well as for [Pd(PPh₃)₄]/ dcpe and [Ni(COD)₂]/dcpe without an additional reductant.

A convenient solvent for the process should provide: (1) A phase separation with water; (2) A high boiling point to remove water in the phenolate regeneration step by distillation; (3) Solubility for the sodium phenolates; (4) Low toxicity. A series of solvents that fulfill these requirements were identified and screened with the three catalytic systems. A representative comparison of the results is given in Table 3 (for extended solvent screening see the Supporting Information).

Table 3. Solvent screening.

// (10 bar)	ONa + CO ₂ + (20 bar)	Catalyst (0.2 mmol), dcpe (0.22 mmol), additive, THF, 145 °C, 20 h	ONa
T (a)			TONIdi
Entry	Solvent	Catalyst	ION ^[u]
1	THF	PdCl ₂ (COD)/Zn ^[b]	29 ^[e]
2		Pd(PPh ₃) ₄	28 ^[e]
3		$Ni(COD)_2$	55 ^[e]
4	anisole	PdCl ₂ (COD)/Zn ^[b]	45
5		Pd(PPh ₃) ₄	43
6		Ni(COD) ₂	44
7	anisole (wet) ^[c]	PdCl ₂ (COD)/Zn ^[b]	39
8		Pd(PPh ₃) ₄	40
9		Ni(COD) ₂	22
10	phenyl butyl ether	PdCl ₂ (COD)/Zn ^[b]	6
11		Pd(PPh ₃) ₄	0
12		Ni(COD) ₂	47
13	dibutyl glycol ether	PdCl ₂ (COD)/Zn ^[b]	1
14		$Pd(PPh_3)_4$	23
15		Ni(COD) ₂	3

[a] Reaction conditions: base (20 mmol), catalyst (0.2 mmol), dcpe (0.22 mmol), solvent (30 mL), ethylene (10 bar), CO_2 (20 bar), 145 °C, 20 h. [b] Zn (1 mmol) added. [c] Solvent saturated with water (2.9 g/L). [d] TON determined based on ¹H NMR analysis in D₂O as solvent and using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as internal standard. [e] The result presented in Table 2 is given for comparison.

According to previous results for Pd- and Ni-systems,^[6–10] the highest activity could be achieved with nonprotic, oxygen-containing solvents. In case of the Pd catalyst, the use of anisole increased the activity, raising the TON from 28 to over 40 (Table 3, entries 1, 2, 4, and 5). In the case of the Ni catalyst, the activity seems quite constant, reaching a TON of around 50 for THF, anhydrous anisole, and for butyl phenyl ether. For the other investigated solvents, only lower activities were observed. To compare the three catalysts directly, and to use a low toxicity solvent,^[16] anisole was chosen for further optimization. The stability of the catalyst towards traces of water is a very important factor for the development of a continuous system. After the product separation and base regeneration, traces of water can remain in the organic phase and could have a negative impact on the catalysis. Therefore, we tested the catalyst activity in solvents saturated with water (see the Supporting Information). Using Pd as catalyst in wet anisole (water content for water saturated anisole is 2.9 g/L),^[17] no significant drop in activity was observed, which implies that both catalysts can tolerate a certain amount of water (Table 3, entries 7 and 8). In contrast, with Ni as catalyst, the activity dropped significantly, suggesting a low water tolerance (Table 3, entry 9).

As shown in Table 4, full conversion of the base was not achieved, which could lead to leaching of the base into the aqueous phase and contamination of the final product. It was therefore necessary to adjust the amount of base to achieve higher or even full base conversion, reducing the phenolate loss into the aqueous phase. Leaching of base was also due to the solubility of the phenolate in water, which could be reduced by tuning the lipophilicity of the base. Base optimization revealed that it was possible to use half of the base loading with only a small decrease of TON (Table 4). By using 5 mmol base, TON was greatly reduced, suggesting an edge of activity at about 10 mmol of base under the used conditions.

Table 4. Base loading screening for the $PdCl_2(COD)/dcpe/Zn$ system.

ONa // + CO ₂ +		Pd(COD)Cl ₂ (0.2 mi dcpe (0.22 mmol Zn (1 mmol) Anisole, 145 °C, 2	nol),), 20 h	
Entry ^[a]	Base [mmol]	TON ^[b]	Base conv. [%] ^[c]	Base in D ₂ O [%] ^[d]
1	20	45 ^[e]	45	29
2	10	39	78	16
3	5	14	56	10

[a] Reaction conditions: Pd (0.2 mmol), ligand (0.22 mmol), Zn (1 mmol), solvent (30 mL), ethylene (10 bar), CO₂ (20 bar), 145 °C, 20 h. [b] TON determined based on ¹H NMR analysis in D₂O as solvent and using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as internal standard. [c] Base conversion determined based on product formation and the amount of base added at t = 0. [d] Base loss into the water phase determined after filtration and evaporation, the solid residue was dissolved in D₂O and the same internal standard was used for the TON determination. [e] The result presented in Table 3 is given for comparison.

Although reduced base loss can be achieved by lowering the base load (Table 4), the values remained too high, and more lipophilic substituted sodium phenolates needed to be identified to reduce its solubility in water (Table 5).

The three catalysts showed a different behavior with highly substituted phenolates. [PdCl₂(COD)]/dcpe/Zn showed the highest sensitivity towards base modifications. Increasing the steric hindrance in the *ortho*-positions reduced the activity greatly. For example, when the steric hindrance was increased from methyl, over isopropyl, to *tert*butyl substituents in both *ortho*-position, the TON dropped Table 5. Base screening for the palladium system.^[a,c]

Entry	Catalyst	Zn (equiv.)	Base	TON	Base conv. (%) ^[d]	Base in D ₂ O ^[e]
1	PdCl ₂ (COD)	1		39 ^[f]	78	
2	Pd(PPh ₃) ₄	-	ONa	40	80	16% ^[f]
3	Ni(COD) ₂	-		44	88	
4	PdCl ₂ (COD)	1		24 ^[b]	24 ^[b]	
5	Pd(PPh ₃) ₄	-	ONa J	35	60	3.2%
6	Ni(COD) ₂	-	\checkmark	46	92	
7	PdCl ₂ (COD)	1		4 ^[b]	4 ^[b]	
8	Pd(PPh ₃) ₄	-	ONa Cona	20	40	n.d.
9	Ni(COD) ₂	-		17	34	
10	PdCl ₂ (COD)	1		7 ^[b]	7 ^[b]	
11	Pd(PPh ₃) ₄	-	ONa	50	>99	<0.6%
12	Ni(COD) ₂	-	Ť	33	66	
13	Pd(PPh ₃) ₄	-	UNa K	20	40	
14	Ni(COD) ₂	-	Ţ,	2	4	n.a.
15	PdCl ₂ (COD	1		3 ^[b]	3 ^[c]	
16	Pd(PPh ₃) ₄	-	- VNa	27	54	<0.6%
17	Ni(COD) ₂	-	\checkmark	0	0	

[a] Reaction conditions: base (10 mmol), catalyst (0.2 mmol), dcpe (0.22 mmol), anisole (30 mL), ethylene (10 bar), CO₂ (20 bar), 145 °C, 20 h. [b] As [a] but with 20 mmol base added. [c] TON determined based on ¹H NMR analysis in D₂O as solvent and using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as internal standard. [d] Base conversion determined based on product formation and on the amount of base added at t = 0; n.d.: not determined. [e] Base loss into the water phase determined after filtration and evaporation, the solid residue was dissolved in D₂O and using the same internal standard for the TON determination; The lower limit of the analysis is defined by the assumption that the sensitivity of the NMR analysis is ca. 1 mg phenol in 0.5 mL of solvent; n.d. = not determined. All the base loss values reported are referred to the reaction with Pd(PPh₃)₄. [f] The result presented in Table 4 is given for comparison.

from 78 to a minimum of 4 (Table 5, entries 1, 4 and 7). The presence of *para*-substituents was also detrimental for the activity of this catalyst (Table 5, entries 10 and 15; see also the Supporting Information). Within the same line as using $[PdCl_2(COD)]/dcpe/Zn$, $[Ni(COD)_2]/dcpe$ showed only a reduced activity with phenolates bearing *tert*-butyl substituents in the *ortho*-positions (Table 5, entries 9, 12,15,17). In contrast, no significant effect of the steric bulk

of the substituents was observed with [Pd(PPh₃)₄]/dcpe as the catalyst, and this system exhibited good TON and complete base conversion even with the highly lipophilic NaBHT base (sodium 2,6-di-*tert*-butyl-4-methylphenolate) (Table 5, entry 11).

Regarding the properties of the base required in this process concept and the observed activity, we investigated further the scope of the $[Pd(PPh_3)_4]/dcpe$ catalyst system in the presence of NaBHT as base. To confirm that anisole remained the optimal solvent, a solvent screening was undertaken with this new combination of base (NaBHT) and catalyst (Table 6). The results, given in Table 6, confirmed that anisole was also the solvent of choice for our concept.

Table 6. Solvent screening with NaBHT as base.



[a] Reaction conditions: base (10 mmol), Pd (0.1 mmol), ligand (0.11 mmol), solvent (30 mL), ethylene (10 bar), CO_2 (20 bar), 145 °C, 20 h. [b] TON determined based on ¹H NMR analysis in D₂O as solvent and using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as internal standard. [c] The result presented in Table 5 is given for comparison.

Another crucial point for the development of an appropriate process concept is metal leaching into the aqueous phase. For simple catalyst separation and suitable product quality (no heavy metals in the sodium acrylate), the catalyst should be soluble in the organic phase and insoluble in the product phase after the addition of water to the reaction mixture. Given that the solubility of the catalyst is influenced by the lipophilicity of the ligand, ligand screening at low catalyst loading was carried out with the optimized system (Table 7).

As shown in Table 7, chelating and alkyl-substituted phosphine ligands are necessary to obtain catalytically active Pd species (Table 7, entries 1 and 2), which is consistent with our previous results.^[10] The bite angle seems to play an important role in the activity. Ligands bearing spacers that are longer than C₃ or shorter than C₂ are not suitable for this transformation (Table 7, entries 3 and 5– 10). σ -Donating ligands such as alkyl-substituted phosphine are also crucial for this transformation because no catalytic activity could be observed by using aryl-substituted phosphines such as dppe (Table 7, entries 11 and 12). In accordance to the results given in Table 6, dcpe is the ligand of choice for the proposed process concept. By using [Pd(PPh₃)₄]/dcpe, the catalyst loading could be reduced to Table 7. Ligand screening.

// + CO ₂ + (10 bar) (20 bar)	tBu tBu	Pd(PPh ₃) ₄ (0.01 mmol), <u>ligand (0.011 mmol),</u> Anisole, 145 °C, 20 h	ONa
	(10 mmol)		

	(To minol)		
Entry ^[a]	Ligand	TON ^[c]	Pd leaching (ppm)
1 ^[b]	none	0	n.d. ^[d]
2	PCy ₃	0	<1
3	Cy ₂ P PCy ₂	0	13
4		106	1
5	Cy ₂ P PCy ₂	50 ^[b,e]	10 ^[b]
6	Cy ₂ PPCy ₂	22	<1
7	Cy2P PCy2	9	<1
8	Fe PCy ₂	5	1
9	Cy ₂ P-Cy ₂	0	2
10		0	<1
11	PCy ₂	7	2
12	Ph ₂ P PPh ₂	0	<1
13		0	<1
14	$(BF_4)_2^{2^2}$	36	25
15	(C ₁₄ H ₂₉) ₂ P P(C ₁₄ H ₂	22	<1
16	PtBu ₂ PtBu ₂	17	14
17	PiPr ₂ PiPr ₂	40	22
18	Et ₂ PPEt ₂	0	27
19	Me ₂ PPMe ₂	0	49

[a] Reaction conditions: base (10 mmol), catalyst (0.01 mmol), ligand (0.011 mmol), anisole (30 mL), ethylene (10 bar), CO_2 (20 bar), 145 °C, 20 h. [b] As [a] but catalyst (0.2 mmol), ligand (0.22 mmol). [c] TON determined based on ¹H NMR analysis in D₂O as solvent and using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as internal standard. [d] n.d.: not determined. [e] The result presented in Table 5 is given for comparison.



0.01 mmol, whereby a TON of 106 was achieved. This is comparable with the previous reported nickel system^[8] for which 50 equiv. Zn was required. The reason for this increase in activity is probably due to the lower concentration of sodium acrylate and phenol in the reaction medium because sodium acrylate has a low solubility in anisole. At higher product concentrations, the reaction mixture became heterogeneous, which affects the final TON. Limitations in our laboratory set up (60 mL steel autoclave equipped with mechanical stirrer) meant that it was not possible to increase the rate of stirring above 1000 rpm, which led to problems in mixing the reaction medium when it became heterogeneous. This effect has also been observed in the case of highly sterically congested bases (see Table 5, entries 13–18).

Regarding the leaching of palladium at low catalyst loadings and using dcpe as ligand, only 1 ppm palladium was found in the aqueous phase, which is a good compromise for a useful activity and simple catalyst separation.

An efficient process concept for the synthesis of sodium acrylate through ethylene carboxylation also requires catalyst recycling, especially at the low TON observed in single runs. To address this point, we performed the following recycle test: The reaction was set up in an autoclave as described in the experimental section. After the reaction time, the autoclave was cooled to room temperature and depressurized. As the Pd⁰- and Ni⁰-phosphine complexes are presumably highly oxygen-sensitive, we carried out the recycling procedure under an argon atmosphere. The workup and recycle procedure were (Figure 2): (1) The autoclave was transferred and opened inside an argon atmosphere glove box. (2) The reaction mixture was transferred to a Schlenk flask and taken out of the glove box. (3) By using Schlenk techniques, 30 mL of degassed deuterated water were added to the reaction mixture. (4) After mixing and phase separation, the two fractions were separated by syringe suction of the water phase. (5) The Schlenk flask containing the organic phase was reintroduced into the glove box and the organic phase was transferred to an autoclave that was precharged with a fresh amount of base (and Zn if needed). Recycling of catalyst in the three systems considered in this publication was assessed, and the results are given in Table 8.

[PdCl₂(COD)]/dcpe in the presence of Zn could be recycled via the organic phase, and a TON of 15 was achieved for the second run. In the case of [Pd(PPh₃)₄]/dcpe and [Ni(COD)₂]/dcpe, recycling of the catalyst was not possible without the addition of Zn in the second cycle. This drop of activity in the second cycle is mainly due to the limitation of the recycle procedure applied. As showed in Figure 2, the recycling is not performed in a sealed system. A series of different equipment, techniques, materials (autoclave, Schlenk flasks, syringes, septa) has to be used to perform the recycling, increasing the probability of contamination with oxygen, and resulting in rapid deactivation of the catalyst. To overcome this limitation in the laboratory, the addition of a reductant such as Zn can prevent the formation of these deactivated species by reducing the oxidized spe-



Figure 2. Flow chart of the recycling methodology with additional amount of fresh base.

Table 8. Recycle test with a fresh amount of base.^{[a], [d]}

Entry	Catalyst	Base [mmol]	Zn [mmol]	TON 1	TON 2
1 ^[b] 2 ^[c] 3 ^[c] 4 ^[b] 5 ^[b]	PdCl ₂ (COD) Pd(PPh ₃) ₄ Pd(PPh ₃) ₄ Ni(COD) ₂ Ni(COD) ₂	$20 + 20 \\ 10 + 10 \\ 10 + 10 \\ 10 + 10 \\ 10 + 10 \\ 10 + 10$	$ \begin{array}{r} 1 + 1 \\ 0 + 0 \\ 0 + 1 \\ 0 + 0 \\ 0 + 0 \end{array} $	55 50 50 44 44	15 1 18 0 10

[a] Reaction conditions: Pd (0.1 mmol), ligand (0.11 mmol), anisole (30 mL), ethylene (10 bar), CO₂ (20 bar), 145 °C, 20 h. [b] 2,6-Dimethylphenolate was used as base. [c] NaBHT was used as base. [d] TON determined based on ¹H NMR analysis in D₂O as solvent and using 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (0.125 mmol) as internal standard.

cies. Further investigations on the development of an appropriate recycling protocol are under investigation.

Conclusions

We were able to further improve the catalytic carboxylation of ethylene with CO_2 for the synthesis of sodium acrylate by considering a sustainable process concept. However, further improvements are needed. At this stage, the catalysis is not completely additive free, especially after the system has been recycled. The reaction should also be tested in a closed oxygen-free set-up, ideally in a continuous mode. Despite the obtained TON of 106 with the $[Pd(PPh_3)_4]/$ dcpe catalyst system, showing the possibility to access the same TON as reported with the nickel system in the presence of 50 equiv. Zn, this TON is still low. It is necessary to optimize further the catalyst system to achieve a higher TON through efficient catalyst recycling. Despite these critical points, which are under investigation in our laboratory, we have achieved a big step in the development of a process concept to apply this interesting route for the production of valuable sodium acrylate.

Experimental Section

General Considerations: All air- and moisture-sensitive manipulations were carried out either by using standard vacuum line, Schlenk, and cannula techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified argon. Solvents for air- and moisture-sensitive manipulations were dried with an MBraun SPS 800 solvent purification system, degassed, and stored over molecular sieves, or dried and deoxygenated by using reported procedures. $[(\mu^5-Cp)Pd(\mu^3-allyl)]$ and the phenolate salts were prepared according to reported procedures.^[8,10,18] All other reagents were purchased from Sigma-Aldrich or ABCR. Gases were purchased from Air Liquide. Steel high-pressure reactors (60 mL capacity) equipped with magnetic overhead stirrer purchased by Premex were used for the carboxylation reactions. ¹H, ³¹P, and ¹³C NMR spectra were recorded with Bruker Advance 200, 400, 500, or 600 MHz 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 signals were referenced to triphenylphosphine. Elemental analysis and mass spectra were recorded by the analytical service of the chemistry department of the University of Heidelberg. ICP-MS analysis to determine the trace metal content in the product phase were performed by the analytical department of BASF SE.

Typical Procedure for the Synthesis of Sodium Acrylate: Inside a glovebox, a 60 mL steel autoclave was charged with (COD)PdCl₂ 1,2-bis(dicyclohexylphosphanyl)ethane (0.22 mmol, 0.057 g), (0.20 mmol, 0.093 g), sodium 2,6-dimethylphenoxolate (20 mmol, 2.860 g), and Zn (1 mmol, 0.065 g). The solid mixture was dissolved in anisole (30 mL). The autoclave was removed from the glovebox and charged while stirring at 800 rpm with 10 bar of ethylene and 20 bar of CO₂ (total pressure 30 bar) for 15 min each at 25 °C. The autoclave was then heated at 145 °C and stirred for 20 h at 800 rpm. The autoclave was cooled to 20 °C, the pressure was released and the reaction mixture was transferred to 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, 0.0216 g) was added and additional D₂O (10 mL) was added to the glass bottle. To favor phase separation, Et₂O (40 mL) was added to the mixture. An aliquot of the aqueous phase was collected, centrifuged and analyzed by ¹H NMR spectroscopy. The TON was determined by ¹H NMR analysis (200 MHz, 70 scans) according to a reported procedure.^[8]

Typical Procedure for the Zinc-Free Synthesis of Sodium Acrylate: Inside a glove box, a 60 mL steel autoclave was charged with $Pd(PPh_3)_4$ (0.22 mmol, 0.234 g), 1,2-bis(dicyclohexylphosphanyl)ethane (0.20 mmol, 0.093 g), and sodium 2,6-dimethylphenoxolate (20 mmol, 2.860 g) in anisole (30 mL). The autoclave was removed from the glovebox and charged while stirring at 800 rpm with 10 bar of ethylene and 20 bar of CO_2 (total pressure 30 bar) for 15 min each at 25 °C. The autoclave was then heated at 145 °C and stirred for 20 h at 800 rpm. 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 favor phase separation, Et₂O (40 mL) was added to the mixture. An aliquot of the aqueous phase was collected, centrifuged, and analyzed by ¹H NMR (200 MHz, 70 scans) analysis according to a reported procedure.^[8]

Procedure for the Recycling Test with (COD)PdCl₂/Zn/dcpe: Inside a glove box a 60 mL steel autoclave was charged with (COD)PdCl₂ 0.057 g), 1,2-bis(dicyclohexylphosphanyl)ethane (0.22 mmol. (0.20 mmol, 0.093 g), sodium 2,6-dimethylphenoxolate (20 mmol, 2.860 g), and Zn (1 mmol, 0.065 g), and the solid mixture was dissolved in anisole (30 mL). The autoclave was removed from the glove box and charged, while stirring at 800 rpm, with 10 bar of ethylene and 20 bar of CO₂ (total pressure 30 bar) for 15 min each at 25 °C. The autoclave was heated at 145 °C and stirred for 20 h at 800 rpm. The autoclave was cooled to 20 °C and, after releasing the pressure, was introduced into the glove box. The reaction mixture was transferred to a 100 mL Schlenk flask equipped with a magnetic bar and, outside the glove box, degassed water (30 mL) was added by using a syringe. The mixture was stirred for 10 min at room temperature to promote dissolution of sodium acrylate and the two phase were allowed to settle for 2 min. The water phase was separated and analyzed as described previously. The organic phase was reintroduced into the glove box and transferred to a 60 mL steel autoclave previously charged with sodium 2,6-dimethylphenoxolate (20 mmol, 2.860 g) and Zn (1 mmol, 0.065 g). The autoclave was then removed from the glove box and charged, while stirring at 800 rpm, with 10 bar of ethylene and 20 bar of CO₂ (total pressure 30 bar) for 15 min each at 25 °C. The autoclave was then heated at 145 °C and stirred for another 20 h at 800 rpm. At time elapsed the work-up and analysis were the same as described previously.

General Procedure for the Determination of Base Residual in the Water Phase: From the water phase, after the work up, an aliquot of was collected and filtered through a Millipore 0.5 μ m microfilter. The clear solution was evaporated under vacuum. The residual solid was redissolved in D₂O (0.5 mL) and analyzed by ¹H NMR spectroscopy, integrating the residual base peaks of the base considered with the 3 CH₃ peak of the 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt used as standard in the determination of the sodium acrylate content. The lower limit of the analysis was defined by the assumption of the sensitivity of the NMR spectrometer beiong approximately 1 mg phenol in 0.5 mL of solvent.

General Procedure for the Determination of Pd Leaching in the Water Phase: From the water phase, after the work up, an aliquot was collected and filtered twice through a Millipore 0.5 μ m micro-filter. The Pd content was determined by ICP-MS analysis (measurements carried out by the certified central analytics laboratories of BASF SE in Ludwigshafen).

Acknowledgments

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



- M. Frank, Superabsorbents, in: Ullmann's Encyclopaedia of Industrial Chemistry, vol. 35, Wiley-VCH, Weinheim, Germany, 2003, p. 213–232.
- [2] T. Ohara, T. Sato, N. Shimizu, G. Prescher, H. Schwind, O. Weiberg, K. Marten, H. Greim, *Acrylic Acid and Derivates*, in: *Ullmann's Encyclopaedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany, **2011**, p. 1–18.
- [3] For reviews and highlights on the use of CO_2 for carboxylation reactions, see: a) B. Yu, Z. F. Diao, C. X. Guo, J. CO2 Util. 2013, 1, 60-68; b) M. Aresta, A. DiBenedetto, Dalton Trans. 2007, 2975-2992; c) S. Pulla, C. M. Felton, P. Ramidi, Y. Gartia, N. Ali, U. B. Nasini, A. Ghosh, J. CO2 Util. 2013, 2, 49-57; J. Takaya, N. Iwasawa, C-1 Building Blocks in Organic Synthesis, in: Science of Synthesis 2014, 46, 263-288; d) A.W. Kleij, ChemCatChem 2013, 5, 113-115; e) X. Cai, B. Xie, Synthesis 2013, 45, 3305-3324; f) T. Moragas, A. Correa, R. Martin, Chem. Eur. J. 2014, 20, 8242-8258; g) M. T. Johnson, O. F. Wendt, J. Organomet. Chem. 2014, 751, 213-220; h) L. Yang, H. Huang, Chem. Rev. 2015, 115, 3468-3517; i) T. E. Müller W. Leitner, Beilstein J. Org. Chem. 2015, 11, 675-677; j) M. Peters, T. Mueller, W. Leitner, Tce 2009, 813, 46-47; k) M. Limbach, Advances in Organometallic Chemistry, vol. 63, Burlington, Academic Press, 2015, p. 175-202.
- [4] a) R. Alvarez, E. Carmona, D. J. Cole-Hamilton, A. Galindo, E. Gutierrez-Puebla, A. Monge, M. L. Poveda, C. Ruiz, J. Am. Chem. Soc. 1985, 107, 5529–5531; b) A. Galindo, A. Pastor, P. Pérez, E. Carmona, Organometallics 1993, 12, 4443–4451; c) R. Fischer, J. Langer, A. Malassa, D. Walther, H. Görls, G. Vaughan, Chem. Commun. 2006, 2510–2512; d) D. Jin, P. G. Williard, N. Hazari, W. H. Bernskoetter, Chem. Eur. J. 2014, 20, 3205–3211; e) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, Angew. Chem. Int. Ed. 2011, 50, 8510–8537; Angew. Chem. 2011, 123, 8662–8690; f) P. Braunstein, D. Matt, D. Nobel, Chem. Rev. 1988, 88, 747–764; g) Y. Tsuji, T. Fujihara, Chem. Commun. 2012, 48, 9956–9964; h) K. Ukai, M. Aoki, J. Takaya, N. Iwasawa, J. Am. Chem. Soc. 2006, 128, 8706–8707.
- [5] a) H. Hoberg, D. Schaefer, J. Organomet. Chem. 1982, 236, C28-C30; b) H. Hoberg, D. Schaefer, B. W. Oster, J. Organomet. Chem. 1984, 266, 313-320; c) H. Hoberg, D. Schaefer, J. Organomet. Chem. 1983, 251, C51-C53; d) H. Hoberg, K. Jenni, C. Krüger, E. Raabe, Angew. Chem. Int. Ed. Engl. 1986, 25, 810-811; Angew. Chem. 1986, 98, 819-820; e) H. Hoberg, Y. Peres, A. Milchereit, J. Organomet. Chem. 1986, 307, C41-C43; f) H. Hoberg, Y. Peres, A. Milchereit, J. Organomet. Chem. 1986, 307, C38-C40; g) H. Hoberg, K. Jenni, J. Organomet. Chem. 1987, 322, 193-201; h) H. Hoberg, S. Gross, A. Milchereit, Angew. Chem. Int. Ed. Engl. 1987, 26, 571-572; Angew. Chem. 1987, 99, 567-569; i) H. Hoberg, Y. Peres, C. Krüger, Y. H. Tsay, Angew. Chem. Int. Ed. Engl. 1987, 26, 771-773; Angew. Chem. 1987, 99, 799-800; j) H. Hoberg, Y. Peres, A. Milchereit, S. Gross, J. Organomet. Chem. 1988, 345, C17-C19; k) H. Hoberg, D. Bärhausen, J. Organomet. Chem. 1989, 379, C7-C11; l) H. Hoberg, A. Ballesteros, A. Sigan, J. Organomet. Chem. 1991, 403, C19-C22; m) H. Hoberg, A. Ballesteros, A. Sigan, C. Jegat, A. Milchereit, Synthesis 1991, 395-398; n) H. Hoberg, A. Ballesteros, A. Sigan, C. Jégat, D. Bärhausen, A. Milchereit, J. Organomet. Chem. 1991, 407, C23-C29.
- [6] M. L. Lejkowski, R. Lindner, T. Kageyama, G. É. Bódizs, P. N. Plessow, I. B. Müller, A. Schäfer, F. Rominger, P. Hofmann, C. Futter, S. A. Schunk, M. Limbach, *Chem. Eur. J.* 2012, 18, 14017–14025.
- [7] C. Hendriksen, E. A. Pidko, G. Yang, B. Schäffner, D. Vogt, *Chem. Eur. J.* 2014, 20, 12037–12040.
- [8] N. Huguet, I. Jevtovikj, A. Gordillo, M. L. Lejkowski, R. Lindner, M. Bru, A. Y. Khalimon, F. Rominger, S. A. Schunk, P. Hofmann, M. Limbach, *Chem. Eur. J.* 2014, 20, 16858–16862.

FULL PAPER

- [9] S. C. E. Stieber, N. Huguet, T. Kageyama, I. Jevtovikj, P. Ariyananda, A. Gordillo, S. A. Schunk, F. Rominger, P. Hofman, M. Limbach, *Chem. Commun.* 2015, *51*, 10907–10909.
- [10] a) P. N. Plessow, A. Schäfer, M. Limbach, P. Hofmann, Organometallics 2014, 33, 3657–3668; b), P. N. Plessow, L. Weigel, R. Lindner, A. Schäfer, F. Rominger, M. Limbach, P. Hofmann, Organometallics 2013, 32, 3327–3338.
- [11] The calculation of the sodium carbonate formation energy is based on the following publication: R. Berg, C. E. Vanderzee, *J. Chem. Thermodyn.* **1978**, *10*, 1113–1136.
- [12] S. Walendy, G. Francio, M. Hoelscher, W. Leitner, *Experiments in Green and Sustainable Chemistry* 2009, 275–277.
- [13] a) A. A. Volod'kin, G. E. Zaikov, *Russ. Chem. Bull.* 2002, 51, 2189–2195; b) A. A. Volod'kin, G. E. Zaikov, *Russ. Chem. Bull.* 2006, 55, 2220–2225.

- [14] The results in Table 1, entries 1, 3, 5, and 7 are reported in ref.^[8] The result presented in Table 1, entry 2 is reported in ref.^[9]
- [15] a) A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, 2nd ed., 2001; b) W. M. Haynes, *CRC Handbook of Chemistry and Physics*, 93rd ed., 2012.
- [16] R. K. Henderson, C. Jiménez-González, D. J. C. Constable, S. R. Alston, G. G. A. Inglis, G. Fisher, J. Sherwood, S. P. Binks, A. D. Curzons, *Green Chem.* 2011, 13, 854–862.
- [17] The water content was determined in our laboratory by Karl-Fischer titration.
- [18] Y. Tatsuno, T. Yoshida, S. Otsuka, *Inorg. Synth.* 1979, 19, 220. Received: August 27, 2015 Published Online: October 8, 2015