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Synthesis of acrylates from olefins and CO₂ using sodium alkoxides as bases

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ABSTRACT

We have discovered a simple procedure for an industrially applicable alternative synthesis of sodium acrylate via the catalytic carboxylation of ethylene with CO₂. We identified *tert*-butoxide as suitable base in this catalytic transformation, which was excluded in previous reports, based on investigations on the stability of the corresponding carbonates. In addition, we were able to access a completely zinc-free procedure for the sodium acrylate formation by introducing a regeneration step during the catalyst recycle. Due to the basicity of the sodium *tert*-butoxide, it was also possible to carboxylate different terminal and internal olefins, which could not be achieved using the previously reported nickel system using phenolate bases.

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1. Introduction

The monomer sodium acrylate is used for the production of sodium polyacrylate. This polymer has various applications in our daily life, e.g., as superadsorbent [1]. The current production starts from propylene, followed by a gas phase heterogeneously catalyzed two-stage selective oxidation and consequent basification with sodium hydroxide [2]. This C3 feedstock is mainly based on oil via a cracking process [2b]. However, the cracking processes are optimized to produce mainly ethylene, due to the increasing ethylene demand for the production of polyethylene, which is more and more being used as substituent for polypropylene and due to the availability of cheap shale based ethane. This shift to ethane crackers is reducing the availability of propylene. Therefore, forecasts show an increasing cost of propylene, due to the reduced supply for this starting material. [3]. For these reasons, a methodology to access sodium acrylate from ethylene instead of propylene is desirable. Our laboratory has made many efforts in order to tackle this topic. After numerous developments in the metal-catalyzed carboxylation using CO₂ reported in literature, [4,5] the first two-stage process for the synthesis of sodium acrylate was discovered in 2012

[6]. Two years later, the first catalytic synthesis of acrylates from CO₂ and ethylene was achieved simultaneously by the Vogt group [7,8]. Despite the breakthrough of these catalytic systems in the scientific community, these processes were not yet efficient enough to be realized on an industrial scale. We disclosed a re-designed synthesis of this monomer suitable for continuous process concept only recently (Scheme 1) [9].

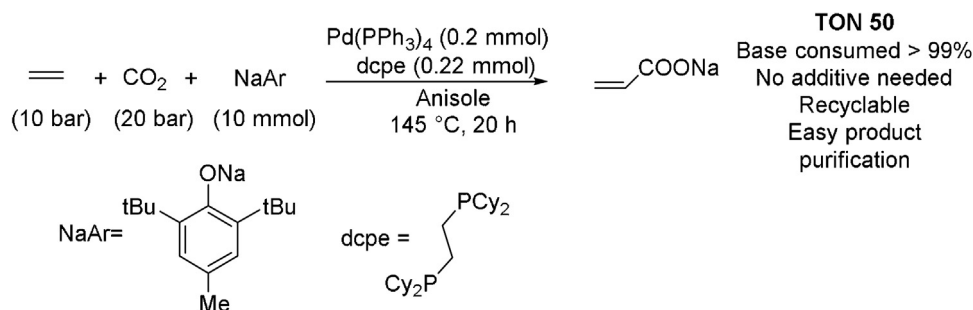
Although the simpler and easier approach was recently reported, there are still some issues that need to be addressed. In particular, use of an expensive base is still required. In addition:

- Use of a Base with a high molar mass, reducing the space time yield in the reactor.
- Amphiphilic phenolates can act as emulsifiers, which makes handling at a large scale difficult.
- High boiling phenols are difficult and energy consuming to remove from the product.
- Zinc is still needed for catalyst recycling.
- The catalyst may not be recovered in the base regeneration step.

These key issues need to be overcome to develop an appropriate process concept. Therefore we tackled these issues by investigating the possibility to use bases with a lower molecular weight and to avoid the use of zinc in the recycle step.

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Scheme 1. Pd-catalyzed synthesis of sodium acrylate using phenolates as base.

2. Methods and materials

2.1. General considerations

All air- and moisture-sensitive manipulations were carried out using standard vacuum line-, Schlenk- and cannula techniques or in an MBraun inert argon atmosphere dry box. Solvents for air- and moisture-sensitive manipulations were dried with MBraun SPS 800 solvent purification system, degassed and stored over molecular sieves, or dried and deoxygenated using literature procedures [10]. The phenolate salts were prepared according to literature procedures [8]. The carbonates of the phenolates were prepared according to a literature procedure [11]. All other reagents were purchased from Sigma Aldrich or ABCR. Gases were purchased from Air Liquide. 60 mL capacity steel high-pressure reactors equipped with magnetic overhead stirrer purchased by Premex were used for the carboxylation reactions. ^1H , ^{31}P , and ^{13}C NMR spectra were recorded on Bruker Advance 200, 400, 500, or 600 MHz spectrometers. All ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to SiMe_4 using the ^1H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard. ^{31}P NMR was referenced to triphenylphosphine. Thermogravimetric analysis were performed under N_2 flow (20 mL/min) and with the temperature ramp of $5^\circ\text{C}/\text{min}$; temperature range from 25°C to 300°C using Mettler Toledo TGA 2(SF). The temperature decomposition analysis were performed using a 60 mL Parr reactor with external heater modified with a ATR silicon Sentinel K4 conduit probe connected to Mettler Toledo Real-time *in situ* FTIR ReactIR 45m.

2.2. Example procedure for the synthesis of sodium acrylate

Inside the glove box a 60 mL steel autoclave was charged with $\text{Pd}(\text{PPh}_3)_4$ (0.22 mmol, 0.234 g), 1,2-bis(dicyclohexylphosphino)ethane (0.20 mmol, 0.093 g) and sodium *tert*-butoxide, (20 mmol, 1.92 g) in 30 mL of anisole. The autoclave was removed from the glovebox and charged under 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 . After that, 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 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 [8].

2.3. Procedure for the recycling test with regeneration

Inside the glove box a 60 mL steel autoclave was charged with $\text{Pd}(\text{PPh}_3)_4$ (0.22 mmol, 0.234 g), 1,2-bis(dicyclohexylphosphino)ethane (0.20 mmol, 0.093 g) and sodium *tert*-butoxide, (10 mmol, 0.86 g) in 30 mL of anisole. The autoclave was removed from the glovebox and charged under 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 . After that, 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 released and introduced in the glove box. The reaction mixture was transferred into 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 favor the dissolution of sodium acrylate and let the two phases settle for 2 min. The water phase was separated and analyzed as previously described. The organic phase re-introduced in the glove box and transferred in a 60 mL steel autoclave and, outside the glovebox, pressurized with 30 bar of ethylene (if required 1 mmol Zn was previously added) and heated at 30°C for 1.5 h. After cooling at room temperature and depressurization, the autoclave was re-introduced in the glovebox, the organic mixture filtered and transferred to a third autoclave pre-charged with sodium *tert*-butoxide (10 mmol, 0.860 g). The autoclave was removed from the glove box and charged, under 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 . After that, the autoclave was heated at 145°C and left to stir for another 20 h at 800 rpm. At time elapsed the work-up and analysis are the same as described previously [9].

2.4. Procedure for substrate screening

The substrate screening was performed using a modification of the procedure for the synthesis of sodium acrylate reported above. In the case of liquid olefins, 20 mmol of them was added in the glovebox to the autoclave. When only CO_2 was added as the only gas the final pressure at room temperature is 20 bar. Butadiene was added as a 20%wt solution in toluene. Propylene was charged by stirring at 100 rpm at 12 bar for 5 min.

3. Results and discussions

As described previously, [6,8] the choice of base is crucial for obtaining sodium acrylate in the catalytic reaction. Limbach et al. pointed out in the development of the two-stage carboxylation methodology, that strong bases, such as sodium methoxide, in presence of CO_2 form stable carbonates, which are inactive under the reaction conditions. For a one-pot procedure, they found milder bases which do not form (or form less stable) carbonates but which are basic enough to promote the carboxylation [6,8].

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