Synthesis of *N,N*-dimethylformamide from carbon dioxide in aqueous biphasic solvent systems

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ABSTRACT

This paper presents the homogeneous catalyzed hydrogenation of carbon dioxide to *N,N*-dimethylformamide (DMF) with an in-situ generated ruthenium catalyst based on $RuCl_3 \times H_2O$ and the phosphine ligand 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl (BISBI). Investigations showed that the complex formation of an active species requires the presence of an amine. The catalyst was recycled by immobilization in a nonpolar alcoholic solvent while the formed product was extracted in-situ into the aqueous phase. The self-assembling reaction system showed stability for 10 recycling runs without a significant loss of activity resulting in an average yield of 31% DMF at 40 bar and 140 °C without the occurrence of any byproducts. Furthermore, a combination of the developed reaction system with ternary amines enables the application of wash amine solutions as carbon dioxide carrier.

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1. Introduction

The utilization of carbon dioxide as universal C_1-building block is of high ecological and economical interest and investigated for several decades [1–6]. Especially the hydrogenation of carbon dioxide was researched in detail since it allows to broaden the product diversity due to the possible change of the carbon atom's oxidation state [7–10]. Interesting hydrogenation products are formic acid or formic acid derivatives like formamides. Especially *N,N*-dimethylformamide (DMF) can be used as intermediate, e.g. for the synthesis of isocyanates, or directly as excellent solvent [11–14]. The first synthesis of *N,N*-dimethylformamide by carbon dioxide hydrogenation was performed in 1970 by Haynes et al. with different metal complexes [15]. The hydrogenation is reported to accompany with a formate salt as intermediate (Fig. 1) [16,17]. Especially, the condensation of formic acid salts requires higher pressures or temperatures to yield formamides with better turnover numbers [18]. Nevertheless, recent developments of complex tailor-made catalysts lead to high activities at milder reaction conditions and show that even non precious metals like iron and cobalt can be applied [19,20].

The industrial formamide synthesis consists of the alcoholate catalyzed carbonylation of amines with carbon monoxide. In order to establish a competitive carbon dioxide based process, a high recycling efficiency of the more expensive hydrogenation catalyst is indispensable for a technical application. However, the long-time stability of most developed homogeneous catalyst systems has not been proven yet. Only Ding et al. recently reported a recycling concept for a homogeneous catalyst where the product DMF is vacuum distilled out of the ruthenium catalyst solution resulting in 12 batch recycling runs without a significant loss in activity but limiting this concept to low boiling products [21]. The separation of catalyst and synthesized formamide is at all a difficult task because formamides are generally excellent solvents for a broad variation of components [11].

An attractive method for a homogeneous catalyst recycling is the immobilization of the dissolved catalyst in a liquid solvent since the catalyst stays in an active environment [22]. For an efficient immobilization, the catalyst should be insoluble in the product phase while the catalyst-solvent is not soluble in the product phase. A general approach to this problem is the application of a catalyst and solvent that have a maximum polarity difference to the formed product so that a second phase is automatically formed. However, an insolubility of the substrate inside the catalytic liquid phase leads to mass transfer problems so that a compromise between reactivity and recyclability has to be made in a liquid liquid two phase system. Nevertheless, due to its efficiency this recycling concept has already found applications in industrial processes like the Ruhrchemie-Rhône-Poulenc process and the SHOP-process where the products form a separate phase [23,24]. In these applications
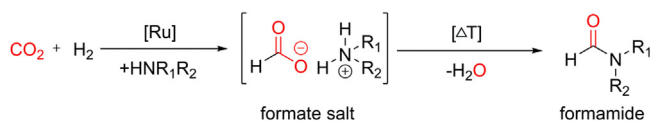
Fig. 1. Hydrogenation of carbon dioxide to formamides.

the catalysts are immobilized in polar solvents, since products like aldehydes or α-olefins are rather nonpolar.

Based on this idea we developed a liquid-liquid biphasic reaction system for the synthesis of *N,N*-dimethylformamide as model formamide product. Unlike in the industrial examples, the catalyst has to be immobilized in a nonpolar solvent as many formamides are polar aprotic solvents [11]. In order to guarantee a sufficient catalyst separation, water is used as product extraction agent since it is formed as byproduct in the condensation step anyway and has to be removed. The general application of this concept should be verified by the utilization of an in-situ generated catalyst system consisting of the polar precursor ruthenium(III)chloride hydrate and 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl (BISBI) as commercial nonpolar phosphine ligand. Desired is the formation of a catalyst complex [Ru] that stays in the organic solvent phase (step I in Fig. 2) and catalyzes the hydrogenation reaction selectively (step II, Fig. 2).

2. Experimental

2.1. Materials

All applied solvents and the dimethylamine solution (40 wt.% in water) were purchased from Acros Organics in standard purity. Ruthenium(III)chloride monohydrate (99.9% on metal basis, 38–40 wt.% ruthenium) and BISBI (99%) were purchased from ABCR. All chemicals were used as delivered without any further purification.

2.2. Catalytic experiments and sampling

At first, the desired amount of ruthenium precursor and ligand were weighted on a precision scale and transferred into the reaction vessel. The solvent and subsequently the aqueous amine-solution were added directly into the autoclave with a precision of 0.01 g. Afterwards, the reactor was sealed and the gas phase was flushed with argon. The reactor was pressurized with the desired hydrogen and carbon dioxide pressures and the reaction was started by heating to the desired temperature. In case of a perturbation experiment, two hours of preforming duration were performed, before the actual reaction was started with all components.

After the desired reaction time the reactor was cooled to ambient temperature and degassed, if not other stated. Subsequently, the biphasic reaction mixture was split in a tempered separating funnel and each phase was weighted and analyzed. In the case of a recycling experiment, the organic phase was returned to the reactor without any sampling of this phase.

Two different reactor types were used which were made out of stainless steel 316 L. The first reactor type contained a volume of 22 mL and is stirred via a magnetic bar while the second reactor, purchased from Parr Instrument GmbH, held a total volume of 300 mL and was stirred via a magnetically coupled stirrer motor. Both reactor types were electrically heated with a temperature deviation below 2 K.

2.3. Analysis

The amount of synthesized DMF was measured gas chromatographically (Agilent 6890) by a thermal conductivity detector. The GC was equipped with an Innowax column (30 m, 250 μm, 0.25 μm) and dimethyl sulfoxide was used as internal standard. The turn-over-number (TON_i) of carbon dioxide to a component i and the degree of extraction were calculated with the following Eqs. (1) and (2).

$$TON_i = \frac{n_i}{n_{ruthenium}} \tag{1}$$

$$E_i(\%) = \frac{n_{i,aqueousphase}}{n_{i,total}} \tag{2}$$

The measurement of formic acid was performed by HPLC (Hitachi Lachrom Elite) with an UV/Vis detector at 207 nm. Acidic water (pH 2.2 adjusted by H_3PO_4) and acetonitrile at a volume ratio of 98:2 were used as mobile phase with a total flow rate of 1.5 mL/min over a Zorbax XDB-C8 stationary phase (150 mm, 4.6 mm, 5 μm) with propionic acid as internal standard. The column temperature was set to 413 K. The amount of ruthenium and phosphorous compounds were measured with ICP-AES (Iris Intrepid from Thermo Elemental) and according standard solutions as reference. The leaching of a catalyst component was calculated via Eq. (3).

$$Ru\text{-}Loss(\%) = \frac{n_{Ru,aqueousphase}}{n_{Ru,applied}} \tag{3}$$

3. Results and discussion

3.1. Design of a biphasic solvent system

In homogeneous catalysis, the first step for the development of an efficient catalyst immobilization in a biphasic solvent system is the identification of suitable solvents. The investigated polar substrate dimethylamine (DMA) is already applied as 40 wt.% aqueous solution so that a suitable nonpolar solvent for the catalyst immobilization is necessary. In order to balance out a sufficient solubility of the substrate dimethylamine in the catalytic phase and a good recyclability of the ruthenium catalyst, several nonpolar solvents with different water solubility were investigated in the ruthenium catalyzed hydrogenation reaction (Table 1).

The screening revealed that very water insoluble compounds, as aliphatic hydrocarbons are not suitable as catalyst solvents because they do not dissolve the substrate and additionally lead to a precipitation of ruthenium. A minimal water solubility increases the yield of DMF significantly. Especially alcohols form a stable catalytic phase with the highest activities. A reason for the higher activity might be that the alcohol acts as reducing agent for the ruthenium(III)chloride hydrate to form an active ruthenium(II) species. General procedures for ex-situ syntheses of ruthenium complexes with $RuCl_3$ x H_2O utilize alcohols like ethanol as reducing agent whereby the corresponding aldehydes are formed [25,26]. Traces of aldehydes were not observed since the ruthenium species is highly active for the aldehyde reduction to alcohols (see Supporting info for details).

A higher water solubility of benzyl alcohol does not benefit the reaction anymore and leads to an unsatisfactory product distribution where 79 wt.% of the formed DMF stays in the catalytic phase. In conclusion, benzyl alcohol does not fulfill the separation between catalyst and product anymore even though the catalyst leaching is with 3 wt.% of ruthenium minimal. That is why 2-ethylhexan-1-ol delivers the best combination of reactivity, extraction efficiency and catalyst leaching.

3.2. Investigation of the in-situ catalyst complex formation

Further investigations with 2-ethylhexan-1-ol (EH) as solvent were made regarding the in-situ generated catalyst system in