Chemical Engineering and Processing 99 (2016) 107–114

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Pd-catalyzed telomerization of butadiene and methanol with direct catalyst recycling using a liquid-ionic liquid biphasic, continuous process

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ARTICLE INFO

Article history:
Received 26 February 2015
Received in revised form 12 May 2015
Accepted 4 July 2015
Available online 11 August 2015

Keywords:
Butadiene telomerization
Palladium catalyst
TPPTS
Ionic liquid
Catalyst immobilization
Loop reactor

ABSTRACT

The telomerization of 1,3-butadiene with methanol in the presence of a phosphine modified palladium catalyst was investigated in liquid-ionic liquid biphasic systems. Suitable ionic liquids were pre-selected from computational *a priori* COSMO-RS screening and tested in a batch autoclave. The Pd leaching could be suppressed significantly when the ligand TPPTS was used instead of the monosulfonated ligand TPPMS. The two most promising ionic liquids [EMMIM][NTf_2] and [BMMIM][NTf_2] were used to immobilize the Pd-TPPTS catalyst in a continuous loop reactor with integrated separation. While the monosulfonated TPPMS ligand failed to efficiently immobilize the catalyst in the ionic liquid, the TPPTS ligand resulted in very good catalyst immobilization and a constant conversion was maintained for more than 200 h time-on-stream.

1. Introduction

Telomerization is a very interesting and versatile reaction and represents the dimerization of two dienes with simultaneous addition of a nucleophile [1–3]. As the variety of possible nucleophiles is very large, a lot of synthesis routes to bulk and fine chemicals as well as pharmaceuticals are possible. Nevertheless, only two applications have been implemented so far on a larger industrial scale, both using 1,3-butadiene as feedstock. Kuraray applies the telomerization with water to form 1-octanol, an important plasticizer alcohol [4]. Dow Chemical uses telomerization with methanol as nucleophile in an elegant multi-step process to finally produce 1-octene [5]. In the latter process, the telomerization reaction is the first step of a reaction cascade yielding 1-methoxy-2,7-octadiene (1-Mode) **1** as main product with small amounts of 3-methoxy-2,7-octadiene (3-Mode) **2** and traces of 1,3,7-octatriene **3** and vinylcyclohexene **4** being formed (see Scheme 1). In a following step, 1-Mode is hydrogenated to the methyloctylether **5** which is consecutively split into 1-octene and methanol. The Dow process utilizes a phosphine modified Pd complex for the telomerization reaction which is carried out in a "once through" process where the catalyst is not recycled directly. Instead, the catalyst is carried out of the reaction system after several distillation steps via the exit stream of the byproduct 3-Mode.

For this reason, several academic and industrial research groups have investigated the immobilization of the Pd catalyst for this reaction e.g., by heterogenization or the use of macrocyclic-palladium complexes [6–11]. To the best of our knowledge, none of these attempts was followed up by an implementation in a continuously working process either in academia or industry. The multiphase approach using water as catalyst phase was the only concept that was followed up to a continuous process study by Dehn et al. [12–14]. The particular challenge of the telomerization reaction with respect to catalyst immobilization in form of a liquid–liquid biphasic reaction origins from the fact that the reactant methanol is soluble in water as well as in the organic phase and thus acts in an undesired manner as phase transfer agent.

The use of ionic liquids as catalyst immobilization phase in telomerization was reported by Magna et al. [15] already in 2003. However, this approach was only demonstrated in batch mode as a kind of proof-of-concept study. The authors claimed that the use of imidazolium based ionic liquids was only feasible if the cation was protected with a methyl group at the C_2 atom. For non-protected imidazolium cations with an acidic hydrogen bound to the imidazolium C_2, the in situ formation of Pd–carbene complexes was claimed to deactivate the catalyst for the telomerization reaction.

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http://dx.doi.org/10.1016/j.cep.2015.07.007
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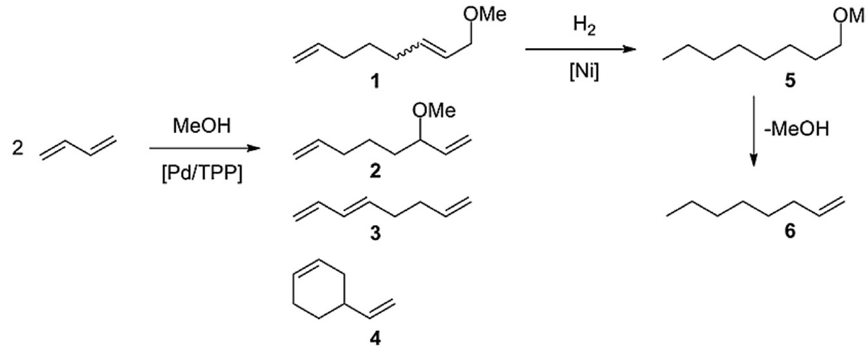

Scheme 1. Telomerization of 1,3-butadiene with methanol according to the Dow Chemical process and consecutive reactions of the major product 1-methoxy-2,7-octadiene to form the desired product 1-octene.

Based on the promising results by Magna et al. [15] this contribution focuses on the development of an ionic liquid-based continuous telomerization process. Applying a computer-aided ionic liquid pre-selection as well as catalyst evaluation and recycling runs in batch mode, we demonstrate successful continuous production of 1-Mode for at least 200 h time-on-stream using a Pd–TPPTS-catalyst in a biphasic operated loop reactor. Such loop reactor has been previously successfully applied for the Ni-catalyzed, biphasic dimerization of propene and 1-butene in chloroaluminate ionic liquids [16,17].

2. Experimental

2.1. General working techniques

All experimental work was carried out under inert atmosphere. Dry and degassed methanol and hexane were used. The applied catalyst and ligand precursors were stored under inert atmosphere in a Plexiglas® Glovebox (GS GLOVEBOX Systemtechnik GmbH, Argon 4.6). For the start of reaction, a defined mass of catalyst and ligand were transferred to a Schlenk flask in the glove box and dissolved in a defined mass of methanol. All ionic liquids were dried overnight at 80 °C under high vacuum ($p < 0.1$ mbar) prior to application. All applied chemicals as well as the methanol solutions of catalyst and ligand were handled and stored using Schlenk technique.

2.2. Batch autoclave

The batch experiments were carried out in a 250 ml Hastelloy autoclave. The latter was equipped with a four-blade gas entrainment stirrer, a pressure gauge, a pressure relief valve and a heating jacket. The temperature in the vessel was measured with a thermocouple and controlled by a temperature regulator (Horst GmbH, HT MC1) connected to the heating jacket. The autoclave was connected to an argon cylinder as well as to a vacuum pump to ensure inert conditions. All experiments were carried out in the liquid phase. Different check valves were assembled to avoid back flow of the reaction mixture into the argon gas cylinder. For starting an experiment, methanol, base, catalyst and ligand solutions, hexane and ionic liquid (in case of room temperature solid ionic liquids, the latter were dissolved in methanol before) were filled in syringes and introduced to the reaction vessel via a blind plug on top of the autoclave. This mixture was heated up to reaction temperature under stirring. As soon as the reaction temperature was reached, butadiene was added to the autoclave. For this purpose, liquefied butadiene was weighed into a ballast vessel by means of an high performance liquid chromatography (HPLC) pump with cooled pump head. The ballast vessel was connected to the periphery of the autoclave and pressurized to the desired reaction pressure. As soon as the butadiene entered the autoclave by opening the respective valves, the reaction started. Samples of the upper, organic phase were taken at the end of each experiment by decanting the biphasic system. In order to ensure that no ionic liquid was transferred onto the gas chromatography (GC) column, additional hexane was added to the organic samples for further extraction. The pure organic phase was diluted with methanol and analyzed by offline GC analysis using dibutylether as external standard. At the end of reaction, stirring was stopped and the autoclave was emptied, disassembled and cleaned with ethanol. After the cleaning procedure, the autoclave was reassembled and evacuated for at least 1 h in preparation of the next experiment (Fig. 1).

2.3. Loop reactor

For the continuous experiments, a specially designed loop reactor was planned and set-up. A similar type of reactor was, e.g., successfully used and described in detail by Eichmann et al. [16,17] for the biphasic dimerization of propene and 1-butene using ionic liquid catalyst phases. The applied loop reactor concept involves continuous separation of products and catalyst phase and integrated recycling of the catalyst/reactant phase in the reactor. An interesting feature of the loop reactor is that–depending on the

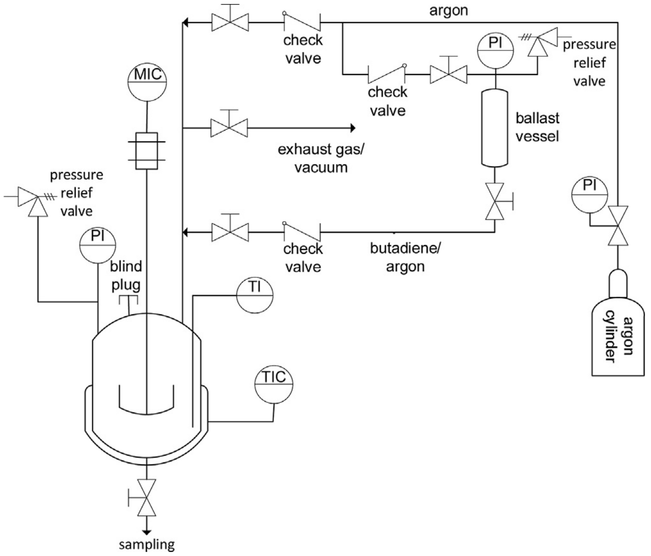

Fig. 1. Schematic flowsheet of the batch autoclave. PI = pressure indicator, TI = temperature indicator, TIC = temperature indicator and controller, MIC = stirring speed indicator and controller.