



Two-step conversion of LLCN olefins to strong anti-knocking alcohol mixtures catalysed by Rh, Ru/TPPTS complexes in aqueous media



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ARTICLE INFO

Article history:

Received 16 May 2014

Received in revised form 28 June 2014

Accepted 30 July 2014

Available online 11 September 2014

Keywords:

Naphtha

Refinery process

Aqueous biphasic hydroformylation

Aqueous biphasic hydrogenation

Ruthenium

Rhodium/TPPTS

ABSTRACT

A two-step conversion of light–light cracked naphtha (LLCN) olefins to strong anti-knocking alcohol mixtures is proposed as a potential solution to the serious negative aspects from the use of gasoline ether oxygenates (MTBE, ETBE, TAME) from the refineries. Aqueous biphasic Rh/TPPTS-catalysed hydroformylation reaction of olefins present in a Greek refinery naphtha cut comprises the first part of the two-step proposed process. The second part of the proposed LLCN upgrade process is the in situ hydrogenation of the produced aldehydes to the corresponding alcohols catalysed by Ru/TPPTS complex in aqueous media. Both catalytic systems of Rh/TPPTS and Ru/TPPTS have been generated in situ by direct addition of the corresponding catalyst precursors to TPPTS in aqueous media; and they were revealed as effective catalytic systems for biphasic hydroformylation and biphasic hydrogenation of complicated mixtures, respectively. The ultimate fuel will contain more oxygen; it will have better combustion properties and higher octane numbers.

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1. Introduction

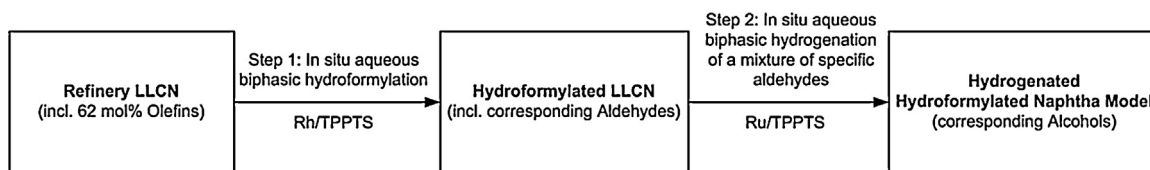
In 1973, Manassen [1] introduced the idea of biphasic catalysis by suggesting the use of two immiscible liquid phases, one holding the catalyst and the other the substrate. At the same time, Joó worked on homogeneous aqueous solutions at Debrecen, Hungary, contributing significantly on the development of aqueous biphasic catalysis [2]. Then, the initial idea of biphasic catalysis was appreciably stimulated by Kuntz's applied chemistry at Rhône-Poulenc [3,4]. Following Kuntz's experimental work and Joó's continuing research work [5,6], Cornils' group at Ruhrchemie AG managed to develop a commercial process for the oxo-synthesis of propylene to butyraldehyde in a two phase medium [7–9]. In 1984, the so-called Ruhrchemie/Rhône-Poulenc (RCH/RP) process was the first successful industrial scale-up of aqueous biphasic catalysis applied in a hydroformylation reaction, with a production capacity of 100,000 tonnes per annum in the plant of Oberhausen, Germany.

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The success of RCH/RP process lies at the use of RhH(CO)(TPPTS)₃ water-soluble catalyst, which is eventually recovered with an easy, efficient and environmentally friendly way. It was shown that the same catalytic system applied in RCH/RP process could also hydroformylate mixtures of olefins. Rh/TPPTS complexes have been reported as effective catalytic systems for the hydroformylation of C₄-alkene mixtures to C₅-aldehydes [10,11]. Furthermore, Baricelli and coworkers achieved hydroformylation of C₆-alkenes in aqueous biphasic media [12] and after few years, they mentioned the catalytic activity of RhH(CO)(TPPTS)₃ complex in the biphasic hydroformylation reaction of C₅–C₇ olefins from a naphtha cut to the corresponding aldehydes achieving up to 86% conversion of the olefins during 200 h of reaction time [13]. We have recently examined aqueous biphasic Rh/TPPTS-catalysed hydroformylation reaction of olefins present in the refinery light–light cracked naphtha (LLCN) from the Aspropyrgos refinery (Hellenic Petroleum S.A.) in Greece [14,15]. The highest conversion of 95.4% of the olefins present in the real LLCN was observed at 70 °C, 100 bar, at a short reaction time (6 h). This was the first part of the two-step conversion process of LLCN olefins to strong anti-knocking alcohol mixtures (Scheme 1).

The second part of the LLCN upgrade process is the in situ hydrogenation of the produced aldehydes of the hydroformylated



Scheme 1. Two-step conversion of LLCN olefins to strong anti-knocking alcohol mixtures catalysed by Rh, Ru/TPPTS complexes in aqueous media.

LLCN to the corresponding alcohols catalysed by Ru/TPPTS complex in aqueous media (Scheme 1). Ru/TPPTS complexes have been reported as effective catalytic systems for the hydrogenation of aldehydes. Fache et al. [16] examined Ru/TPPTS-catalysed hydrogenation reaction of propionaldehyde in aqueous media. Then, Gosselin et al. [17] first reported the catalytic system $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/\text{TPPTS}$ for the hydrogenation of 3-methyl-2-butenal in aqueous two-phase system (water–toluene). Moreover, the hydrogenations of 3-phenyl-2-propenal [18–21], 2-butenal [18,19] and fructose [22] catalysed by Ru/TPPTS complexes have been reported successfully. Also, Tilloy et al. [23] investigated the Ru/TPPTS-catalysed hydrogenation of various aldehydes in the presence of cosolvents or cyclodextrins. Our research group studied for the first time the aqueous biphasic hydrogenation of a hydroformylated naphtha model (mixture of 2-methylvaleraldehyde, 2-ethylbutyraldehyde, hexanal, heptaldehyde, 2-phenylpropionaldehyde and hydrocinnamaldehyde) catalysed by Ru/TPPTS complex, which was generated in situ by direct addition of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ catalyst precursor to TPPTS (TPPTS = $\text{P}[\text{m-C}_6\text{H}_4\text{SO}_3\text{Na}]_3$, trisodium salt of m-trisulfonated triphenyl phosphine) [24,25]. The upgraded LLCN could potentially replace the harmful gasoline ether oxygenates (MTBE, ETBE, TAME) from the refinery blended gasoline pool [14,15,24,25].

In the current research work, a comprehensive overview of the two-step conversion of LLCN olefins to strong anti-knocking alcohol mixtures catalysed by Rh, Ru/TPPTS complexes in aqueous media take place. In addition, the salt effect in aqueous biphasic hydrogenation of a hydroformylated naphtha model is examined along with the influence of the reaction time in biphasic hydrogenation of aldehydes present in a real refinery hydroformylated naphtha cut.

2. Experimental details

2.1. Materials and instrumentation

LLCN was granted by Aspropyrgos refinery (Hellenic Petroleum S.A.). $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and TPPTS were purchased from Alfa Aesar and used as catalyst precursor and ligand for hydroformylation reactions, respectively. 2-Ethylbutyraldehyde, heptaldehyde, 2-phenylpropionaldehyde and hydrocinnamaldehyde were obtained from Aldrich. Hexanal was obtained from Merck and 2-methylvaleraldehyde was purchased from Alfa Aesar. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from Aldrich and used as catalyst precursor for hydrogenation reactions. Toluene extra pure and NaCl were obtained from Merck. Syn-gas ($\text{CO}/\text{H}_2 = 1/1$), H_2 , N_2 , Ar, Zero Air, and He 5.0N were purchased from Aeroscopio Hellas and Axarlis. CO/H_2 (1/1) and hydrogen 5.0N were used in the hydroformylation and hydrogenation reactions, respectively, without further purification. Na_2SO_4 was used for drying and was obtained from Panreac.

All the reactions were performed in 100 mL Autoclave Engineers batch reactor which was equipped with a low carbon stainless steel vessel (316 LSS), an electromagnetic agitation system, a cooling–heating system, a central control unit (URC) and a sampling valve. The substrate and the products were analysed using a Perkin Elmer 8700 gas chromatograph (GC) with a flame ionisation

detector (FID) and an Agilent 6890N/5973N GC/MS system both of them employing a Petrocol DH 150 capillary column (150 m length, 0.25 mm diameter, 1.0 μm film). Column temperature was kept initially constant at 40 °C for 5 min. Then it was raised at 200 °C at a rate of 2 °C min^{-1} and remained there for 45 min. Helium (99.999%) was used as a carrier gas with a flow rate 20 cm^3/s at 175 °C and 65 psig. In order to clean the column from various remaining redundant compounds the oven temperature was kept at 230 °C for 180 min (the temperature of both the injector and detector was 280 °C) prior to the analysis.

2.2. Analytical method

The methods of gas chromatography with FID and mass spectroscopy were used for qualitative analysis of the LLCN, of the hydroformylated and of the hydrogenated products. In the quantitative analysis of the substrates and of the products, it was important to correct the areas of the reported peaks of the GC, due to the existence of organic compounds in various homologous series. Owing to the complexity of the substrate and the lack of literature as far as it concerns the characterisation of complicated organic mixtures, the response factors (f_i) have been calculated by applying Ongkiehong's equations [26,27] and taking into consideration the theoretical approaches of the response in a FID [28–30] for both the reactants and the products of the reactions (Scheme 2).

2.3. Two-step conversion of LLCN olefins to alcohol mixtures

The hydroformylation and hydrogenation reactions as well as the analysis of the products were carried out at the Petroleum & Natural Gas Chemistry & Technology and the Chemical Process Simulations Laboratories of the Department of Petroleum & Mechanical Engineering, of Eastern Macedonia and Thrace Institute of Technology. All manipulations and reactions were performed under argon or nitrogen atmosphere using standard Schlenk techniques [31].

In the beginning of the experimental procedure for both catalytic reactions (hydroformylation, hydrogenation), deoxygenation of distilled demineralised water was carried out via an ultrasonic cleaning bath under high vacuum for 3 h prior to use. Zero time of the reaction was taken when the temperature inside the autoclave reached the preferred value. At the end of every run the autoclave vessel was rapidly cooled in ice and salt, the stirring was stopped and the reactor was vented before opening

$$\begin{aligned} \text{Equation applying to olefins: } f_i &= \frac{M_i}{(\sum n_i \times 12)} \\ \text{Equation applying to aldehydes: } f_i &= \frac{M_i}{((\sum n_i - 1) + 0.3) \times 12} \\ \text{Equation applying to alcohols: } f_i &= \frac{M_i}{((\sum n_i - 1) + 0.5) \times 12} \end{aligned}$$

Scheme 2. The response factors (f_i) equations for olefins, aldehydes and alcohols, respectively based upon Ongkiehong's results. M_i : molecular weight of a compound i , $\sum n_i$: the amount of carbon atoms of a compound i .

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