

Hydroformylation of 1-hexene in presence of sulphur and nitrogen compounds using the binuclear water soluble complex $[\text{Rh}(\text{CO})(\mu\text{-Pz})(\text{TPPTS})_2]$

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Introduction

Hydroformylation or oxo process continues to be one of the more important classes of homogeneously catalyzed reactions by transition metal complexes [1-8]. Mononuclear rhodium phosphines (Rh/PAr_3) catalysts dominate the hydroformylation industry predominantly for C3 through C6 1-alkenes, where regioselectivity towards straight chain aldehyde products is still a problem [9]. However, the use of binuclear catalyst precursors for liquid-liquid biphasic catalysis has not been exploited so far. In this sense, recently we reported the synthesis of the complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$ (TPPTS tris-meta-sulfonated-phenylphosphine and Pz = pyrazolate ligand) [10] and it showed activity for the hydroformylation of 1-hexene, styrene, allylbenzene, 2,3-dimethyl-1-butene, cyclohexene and their mixtures in the absence or presence of thiophene, where practically no change in the total conversion to aldehydes was observed. In this work, we present the results obtained during the evaluation of the liquid-liquid biphasic hydroformylation of 1-hexene in the presence of up to 2500 ppm of benzothiophene or quinoline with emphasis in the recycling properties of this complex.

Materials and Methods

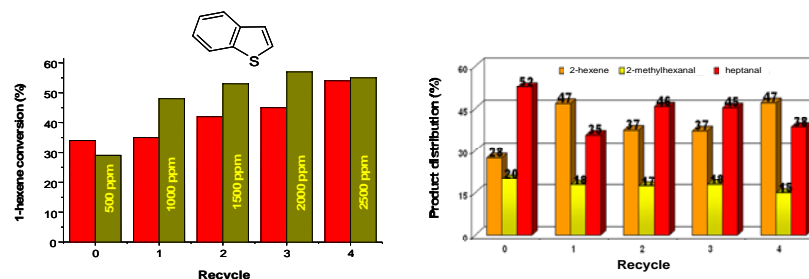
All manipulations were carried out under nitrogen atmosphere using standard Schlenck and vacuum-line techniques. Solvents were dried and distilled by known procedures and stored under inert atmosphere. The complex was synthesized according to a previous report [10]. The catalytic experiments were carried out in a glass-lined stainless steel autoclave (Parr, 100 ml). The solution of the precursor was purged three times with syngas ($\text{H}_2/\text{CO}=1/1$) and initially charged with 698.8 Kpa of the gas mixture. Then, the catalyst was incubated at 343 K for 1 hour, prior to the addition of 1-hexene in heptane and charged with the required pressure and heated to the desired temperature. The syngas pressure was varied from 1746.9 Kpa to 4981.3 Kpa. Liquid samples were removed from the reactor vessel and analyzed by GC and CG-MS techniques. The recycling experiments were carried out under anaerobic conditions, described elsewhere [10].

Results and Discussion

The biphasic hydroformylation of 1-hexene using the binuclear rhodium complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$ was carried out effectively using relative mild conditions. Initially it was

found that the pre-treatment of the complex with syn-gas produce a more active specie able to convert around 85 % of the substrate in 3 hr in comparison with the untreated complex that convert around 40 % of the 1-hexene. This result confirms that the catalyst recycling has to be done *pre-activating the catalyst precursor before any reaction*. After that, recycling experiments were carried out under aerobic or anaerobic conditions. The results show that the presence of air during the recycling of the catalyst impacts dramatically on its performance. With the best conditions, the effect of the presence of benzothiophene and quinoline in the feedstock were evaluated in 4 consecutive recycling experiments. The results obtained from the presence of up to 2500 ppm of benzothiophene are shown in Figure 1.

Figure 1. Effect of the presence of benzothiophene during the 1-hexene hydroformylation using $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$



Conditions: pre-treatment: $\text{pH}_2/\text{CO}=10$ atm, $T=343$ K, $t=1$ h. Reaction: $\text{pH}_2/\text{CO}=17$ atm, 343 K, S/C= 200/1, reaction time=3 h.

As it is presented in Figure 1, this complex is not sensible to the presence of sulphur up to 2500 ppm after 4 consecutive recycling experiments. It seems that under this conditions, it was produced a real sulphur resistant catalyst able to convert 1-hexene to oxygenated products. In the case of quinoline, the result also confirms that this catalyst precursor is also nitrogen tolerant and the interactions of quinoline with the active specie produce new complexes which display high activity towards 1-hexene hydroformylation. Further results will be present.

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