

HYDROFORMYLATION OF OCT-1-ENE BY SUPPORTED AQUEOUS PHASE CATALYSIS: INFLUENCE OF CATALYTIC COMPLEX AND PREPARATION METHOD OF THE SUPPORTS

U. J. JÁUREGUI-HAZA*

Centro de Química Farmacéutica, Apdo. 16042, C. Habana, Cuba. E-mail: ulises@caf.co.cu

A. M. WILHELM, H. DELMAS

Ecole Nationale Supérieure d'Ingénieurs de Génie Chimique, 18 chemin de la Loge, 31078 Toulouse, France

Keywords: Supported Aqueous-Phase Catalysis (SAPC), hydroformylation, oct-1-ene, silica, rhodium

Abstract

Four silica samples were evaluated as supports in the hydroformylation of oct-1-ene by Supported Aqueous Phase Catalysis (SAPC) using $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ and $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ as catalysts. Adsorption studies of the $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ complex from aqueous solutions on the supports were carried out at 25 °C. The isotherms obtained were correlated by several models, among which the Fowler-Guggenheim/Jovanovic-Freundlich equation was found to be the most satisfactory. The influence of the nature of catalytic complex and of the methods for supporting the catalyst on the silica conversion was also studied.

1. Introduction

The recent development of Supported Aqueous Phase Catalysis (SAPC) opened the way to hydroformylate very hydrophobic alkenes such as octene, dicyclopentadiene or oleyl alcohol with water-soluble catalysts (Arhancet *et al.*, 1989). But SAPC is still used with empirical rules, because the mechanisms governing the interactions between complex, water and solid surface are not well elucidated. For this reason, it is necessary to study in depth the adsorption of water soluble ligands and catalytic complexes onto inorganic supports, as an important step in the preparation of catalyst-support complex and the understanding of these catalytic properties. Recently, the adsorption of aqueous solutions of benzenesulfonic acid, 3, 3', 3''-phosphinidynetris-, trisodium salt (TPPTS), the most used hydrosoluble ligand in biphasic catalysis, and di (μ -tertiobutylthiolato) dicarbonyl, *bis* (benzenesulfonic acid, 3, 3', 3''-phosphinidyne-tris-, trisodium salt) dirhodium ($[\text{Rh}(\mu\text{-}^t\text{Bu})(\text{CO})(\text{TPPTS})_2]$ or **C1**, M.W. = 1577.04) on different silica supports was reported (Jáuregui-Haza *et al.*, 2001a). Although **C1** and di (1,5 cyclo-octadiene) dichloro dirhodium, benzenesulfonic acid, 3, 3', 3''-phosphinidyne-tris-, trisodium salt ($[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}_2$ or **C2**, M.W. = 1629.93) had been used for hydroformylating oct-1-ene by biphasic catalysis or SAPC (Chaudhari *et al.*, 1995; Deshpande *et al.*, 1996; Kalck *et al.*, 1998; Jáuregui-Haza *et al.*, 2001b), it was necessary to obtain the adsorption isotherms for this second complex and to compare the performances of these two supported catalysts in the same operating conditions.

On the other hand, several methods have been used for preparing the SAP catalysts. According to the preparation procedure, the methods can be classified into two groups : i) indirect method, when the support is first impregnated with the hydrosoluble catalytic complex, then dried and rehydrated before use (Arhancet *et al.*, 1989, 1990, 1991a; Choplin *et al.*, 1998; Guo *et al.*, 1991; Horvath, 1990) ; ii) direct method : the support, catalytic complex and water are mixed at the same time in the reaction system (Arhancet *et al.*, 1991b; Kalck *et al.*, 1998). In general, the best conversions of hydroformylation of alkenes by SAPC have been obtained when the SAP catalyst was prepared by indirect method.

This paper deals with the hydroformylation of oct-1-ene by SAPC using **C1** and **C2** and four silica samples as supports. Adsorption studies of the **C2** from aqueous solutions on the supports were carried out at 25 °C; the influence of the method of preparation of the supported catalyst was also investigated. Finally, the catalytic performances of this catalyst were evaluated and compared to those of **C1**.

2. Experimental section

TPPTS was supplied by Rhône-Poulenc. The complex **C1** was synthesized as reported before (Kalck *et al.*, 1988). The other chemicals and solvents were purchased from Aldrich and SDS, and used without further purification. All the reactions and adsorption experiments were carried out under an inert atmosphere (Argon or Nitrogen).

Four supports were used to prepare SAP catalysts: the Sipernat silica samples DS22 and DS50 (from Degussa) and two SDS silica samples (S60 and S200). Their BET

*Author to whom correspondence should be addressed