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The hydrogenation of cinnamaldehyde by supported aqueous phase (SAP) catalyst of RhCl(TPPTS)$_3$: Selectivity, kinetic and mass transfer aspects

Kamchai Nuithitikul[a,*], John Mike Winterbottom[b]

[a]*Department of Chemical Engineering, King Mongkut's Institute of Technology North Bangkok, Bangkok 10800, Thailand*
[b]*Department of Chemical Engineering, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

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Abstract

The hydrogenation of *trans*-cinnamaldehyde catalysed by a supported aqueous phase catalyst of RhCl(TPPTS)$_3$ [TPPTS: trisodium salt of tris(m-sulfophenyl)phosphine] on silica was investigated in terms of the product selectivity, reaction kinetics and mass transfer characteristics. The hydrogenation is selective at the C=C bonds in cinnamaldehyde giving hydrocinnamaldehyde as the main product. To achieve high selectivity (99.9%), it is necessary to employ a low initial concentration of cinnamaldehyde (0.076 M). The selectivity also depended on the reaction operating conditions (pressure, temperature, catalyst loading) and the water content property of the SAP catalyst. Optimum water content of the SAP catalyst giving maximum activity was obtained when the pore volume of the supports was completely filled with water. The overall order of reaction was first-order and therefore the conventional three-phase slurry model was applied to the SAP system for the mass transfer analysis. The gas–liquid mass transfer and the reaction resistances were the controlling steps of comparable significance, while liquid–solid mass transfer resistance was negligible in this system. Under similar conditions, the SAP catalyst gave a lower reaction rate than the analogous biphasic catalyst.

Keywords: Catalyst selectivity; Kinetics; Mass transfer; Multiphase reactions; SAP catalyst; TPPTS

1. Introduction

Organometallic compounds have been increasingly used to catalyse organic reactions as their activity and selectivity can be widely adjusted by a careful selection of active metals and attached organic ligands. This is particularly true for the complexes of transition metals in which partially occupied d-orbitals promote the reversible bonding to a variety of functional groups. The organometallic catalysts, in principle, work homogeneously which has a drawback due to the difficulty in the catalyst recovery. To overcome this problem, a biphasic catalyst of organometallic complexes has been developed (Dror and Manassen, 1977). Biphasic catalysts generally consist of the catalytic complex dissolved in an aqueous phase and the reactants and products are soluble in an organic phase. It has attracted much interest in recent years after successful use in industry for hydroformylation of propene (Kuntz, 1987). Another approach to immobilised homogeneous catalysis is supported aqueous phase (SAP) catalysis where an aqueous phase of a catalytic complex is supported as a thin film dispersed over the surface of a high-surface area solid. As in the biphasic system, reactants dissolve in an organic hydrophobic phase that is immiscible with an aqueous solution of a catalyst complex. The reaction takes place, depending on the mass transfer rate of reactants, either at the aqueous–organic interface or in the homogeneous aqueous solution dispersed over the support surface. An easy catalyst separation by simple filtration and a high contact area (supplied by the solid support) between the aqueous film and the reactant-containing organic solvent is achieved and can lead to a better performance than their biphasic systems (Choplin et al., 1998; Frémy et al., 1996; Li et al., 2003; Santos et al., 1998).

Arhancet et al. (1990) studied the effect of the surface area of support on the conversion in the hydroformylation reaction and found no difference in conversion if the amounts of

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[*] Corresponding author. Tel.: +66 2 9132500x8231; fax: +66 2 5870024.
E-mail address: Kamchai_Fius@yahoo.co.uk (K. Nuithitikul).

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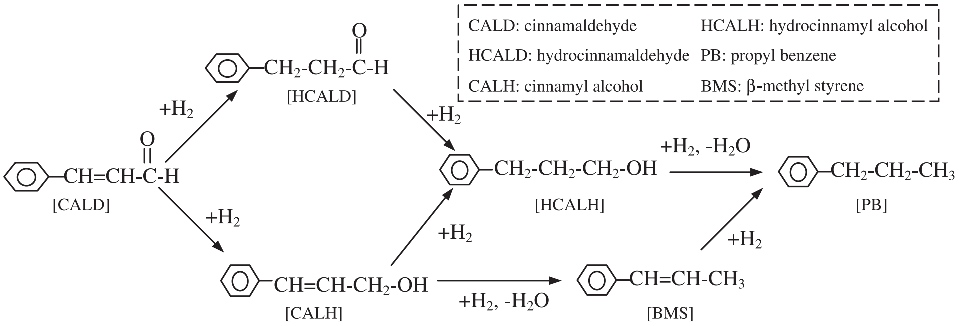

Fig. 1. Hydrogenation reaction of cinnamaldehyde (CALD).

rhodium per unit surface area were identical. In any event, the same metal complexes in powder form that had similar surface area to their SAP catalyst and were completely insoluble in the organic phase and were not immobilised on the support were investigated. They gave a similar specific activity (based on surface rhodium) and selectivity as when they were immobilised as the SAP catalyst. These results supported the idea that in SAPC the reaction takes place at the interface. In addition, Fujita et al. (2004) reported that the hydrogenation of cinnamaldehyde (CALD) to cinnamyl alcohol (CALH) by Ru-TPPTS complexes occurred at the interface between the water film and the organic solvent, while that of hydrocinnamaldehyde (HCALD) takes place at the interface between silica, water, and toluene. However, Jáuregui-Haza et al. (2001) observed the influence of the surface characteristics of five supports in the hydroformylation of 1-octene. The results led to the conclusion that the reaction could take place, depending on the size of the pores, either at the surface of the pores or on the external surface of the particle with storage of TPPTS and catalytic complex in the filled pores. In addition, Frémy et al. (1996) noted that, depending on the solubility of the organic reactant, hydroformylation reaction could occur not only at the interface but also in the homogeneous liquid film on the support surface.

In SAP catalysis, the water content in the film is very important. When the water content increases, the activity increases, but if too much water is added to an SAP catalyst, the activity declines (Arhancet et al., 1990; Herrmann and Kohlpaintner, 1993; Frémy et al., 1996; Tóth et al., 1997; Choplin et al., 1998; Davis, 1998; Santos et al., 1998; Kalck and Dessoudeix, 1999; Jáuregui-Haza et al., 2001; Li et al., 2003). The increase in activity in the first period is due to the complex's mobility increase, resulting from increased interfacial area. However, when the water content became large, the activity decreased because of the decrease in the interfacial area (Davis, 1998). The more water filling the pore space or the thicker the water film, the less the contact between catalyst species and reactants in organic phase.

Large amounts of water caused reaction rates similar to those under classical biphasic conditions (Frémy et al., 1996). The SAP catalysts in which the amount of water exactly filled the pore volume of the supports (degree of pore filling equal to 1) were found to give maximum activity for polar organic reactants when liquid–liquid mass transfer rate was relatively high (Frémy et al., 1996; Choplin and Quignard, 1998). At levels more than filling the pores, leaching of metal could occur (Santos et al., 1998). However, for reactants having poorer solubility in water (significant liquid–liquid mass transfer resistance), the maximum activity was obtained at the degree of pore filling less than 1 (Frémy et al., 1996). In contrast to the Rh-TPPTS system, the activity of Co-TPPTS system was unaffected by the water content (Guo et al., 1991). The cause could well be because the substrate phase was homogeneous under the high-temperature conditions.

The selectivity of SAP catalysts was also affected by the water content (Arhancet et al., 1990). The selectivity reduced with an increase in the water content because the resulting greater mobility of organometallic complexes promoted decomposition reactions (Herrmann and Kohlpaintner, 1993) or side reactions. In contrast to this result, no change in selectivity was reported as a result of water content variation (Davis, 1998).

From the above studies, it can be concluded that the precise operating mode of SAP catalysts and the nature of its interaction with support are still a matter of debate. The water content in SAP catalysts should be carefully controlled in order to obtain a stable system. The amount of water should not be too low which would provide only a small film on the support and not be too high to prevent pore plugging which restricts diffusion of the reactants or prevents catalyst leaching. The optimum water content which gives the highest performance of the SAP catalyst depends on the type and properties of the supports, the water solubility of the reactants or the liquid–liquid mass transfer rate, the catalyst precursor system and also the reaction itself.

α, β-unsaturated aldehydes such as CALD have been used as the raw materials for many important applications in the fine chemical industry. Several products are generated from the hydrogenation of CALD via different reaction pathways (Fig. 1). The product (hydrocinnamaldehyde, HCALD) has been used as a food additive for flavouring and recently been reported to be an important intermediate in the preparation of pharmaceuticals used in the treatment of HIV (Lashdaf et al., 2003). CALH has been employed in perfumery manufacturing.

The small laboratory-scaled hydrogenation of CALD selectively catalysed by various metal–TPPTS complexes has been investigated less in SAP systems (Bhanage et al., 1999; Fujita et al., 2004) than in biphasic systems (Andriollo et al.,